



Doctoral thesis

**Sustainable electrochemical energy storage
systems working in aqueous medium with
high-voltage and long-term cyclability**

Amelia Aleksandra KLIMEK

Supervisor: prof. dr hab. Elżbieta FRĄCKOWIAK

Supervisor: dr hab. (HDR) Camélia MATEI GHIMBEU

Université de Haute-Alsace
Institut de Science des
Matériaux de Mulhouse

Poznań University of Technology
Institute of Chemistry and
Technical Electrochemistry

Poznań, 2026

**„Do not go where the path may lead,
go instead where there is no path
and leave a trail”**

~ Ralph Waldo Emerson

Table of contents

Abstract	7
Streszczenie	9
Résumé	12
Funding	15
Abbreviations	16
1 Introduction	18
1.1 Motivation	18
1.2 Outline and objectives of the thesis	23
2 Electrochemical capacitors (ECs)	26
2.1 Principle of ECs operation and properties	26
2.2 Mechanisms of energy storage in ECs	29
2.1.1 Electrical double layer models	29
2.1.2 Pseudocapacitance	31
3 Electrolytes used for ECs	39
3.1 General overview on EC electrolytes	39
3.2 Aqueous electrolytes	44
3.2.1 Acids, bases	44
3.2.2 Neutral salts	45
3.2.3 Water-in-salt	45
3.3 Gel electrolytes	47
3.4 Redox-active electrolytes	48

4 Electrode materials used for ECs	56
4.1 Characteristics of carbons utilized as EC electrodes	56
4.2 Textural/structural effects on the performance of carbon-based electrochemical capacitors	61
5 Characterization techniques	72
6 Electrochemical capacitor in aqueous electrolyte with long lifespan improved by hydrogen bond donor addition	79
7 Effect of a buffer/iodide electrolyte on the performance of electrochemical capacitors	99
8 Lignin as a precursor of a gel electrolyte and salt templated carbon for sustainable electrochemical capacitors	114
9 Impact of disorder, porosity, and surface chemistry of salt templated carbons on capacitance	133
10 Insights of N-carbon quantum dots effect on charge storage in supercapacitors	154
11 General conclusions	198
12 Wnioski końcowe	203
13 Conclusion générale	209
14 Doctoral thesis summary	215
15 Podsumowanie pracy doktorskiej	222
16 Ecole Doctorale résumé	230
17 Scientific achievements	238
Copyrights	245
Declaration of co-authors	248
Acknowledgements	265

Abstract

The shift toward renewable energy necessitates efficient and sustainable energy storage solutions. Electrochemical capacitors (ECs) provide high power density and fast charging/discharging rates, hence, they could be considered for the periodic energy accumulation from sun, or wind. Nevertheless, the low energy density and environmental concerns limit ECs widespread applications. This PhD thesis addresses key challenges of aqueous ECs: narrow operating voltage, low specific capacitance, short lifespan, and safety through the modification of neutral salt electrolytes and the tailoring of the carbon electrode's texture/structure, considering the environmental friendliness.

The *chapter 1* relates to the motivation and objectives of the thesis. The *chapters (2-5)* provide an in-depth overview of EC fundamentals, including charge storage mechanisms (electrical double layer and pseudocapacitance), as well as a detailed discussion on electrolytes (aqueous, non-aqueous, and solid-like). Furthermore, various carbon-based electrode materials are specified, with particular emphasis on adjusting porosity, surface chemistry, and structural disorder through activation and templating. Advanced physicochemical and electrochemical characterization techniques, with main importance to the thesis, are also discussed.

The experimental part of the thesis is organized into five respective *chapters* composed of four peer-reviewed articles (6-9) and one manuscript (10). EC performance depends on both electrolyte and electrodes, with persistent bottlenecks. Electrolyte issues such as low voltage, corrosive properties, short lifespan and safety remain critical, leading to further investigation of these limitations in this thesis. *Chapter 6* describes the development of a neutral salt aqueous electrolyte modified with a hydrogen bond donor additive. The improvement in EC lifespan (> 350 floating hours) and anti-corrosive characteristics of stainless-steel current collectors (ten-fold decrease of corrosion current) was demonstrated after 2M urea additive to 1M Li₂SO₄. *Chapter 7* presents novel aqueous electrolytes composed of different pH buffer solutions combined with redox-active iodide species. It was shown that extended ECs operating voltage range (1.5 V), enhanced capacitance (149 F g⁻¹), and sustained long-term stability (310 floating hours) are due to the acetate buffer-controlled pH stabilization and pseudocapacitance

from iodine/iodide redox pair. *Chapter 8* reveals a sustainable approach utilizing waste-derived lignosulfonate (LS) for the preparation of gel electrolytes and tailored carbon electrodes. Importantly, LS gel acted as both electrolyte and separator, preventing leakage, thus improving the EC safety. The LS-based EC achieved a stable operating voltage (1.6 V), reduced self-discharge (loss of ~30% of the initial voltage), and long lifespan (170 floating hours). This strategy of LS utilization could reduce CO₂ emissions by 32-49%, highlighting its strong capability for more sustainable ECs.

Limitations of EC performance also arise from the texture/structure of carbon electrodes (e.g., low specific surface area and electric conductivity). Moreover, the impact of other features, e.g., structural disorder, active sites and surface functional groups is not clearly identified. In this thesis, strategies such as salt templating and heteroatom functionalization were explored, providing the insights into the effect of texture/structure/surface chemistry on EC performance. *Chapter 9* demonstrates a systematic study of salt templated carbons synthesized using mixtures of alkali metal salts. The fundamental relationships between the structure, porosity, surface chemistry of salt templated carbon electrodes and EC capacitance, retention, lifespan were investigated. Notably, it was revealed that carbons with increased disorder (high I_{D1}/I_G Raman ratio and active surface area), high porosity, are likely to display enhanced capacitance, but shorter lifespan. *Chapter 10* introduces an original study on synthesis and detailed physicochemical/electrochemical characterization of nitrogen-doped carbon quantum dots (N-CQDs). They were prepared by hydrothermal carbonization of citric acid and various amines. The N-CQDs exhibited particle size of ~6 nm, blue fluorescence under UV light and significant functional groups. It was found that the surface chemistry (O-, N-groups), quantum effects (nanoscale size/modification of electron density), and electrolyte ionic conductivity are at the origin of the improvement of the capacitance (146 F g⁻¹) and lifespan (200 floating hours).

The obtained results summarized in *chapters 11-13* highlight that design, modification, and deeper understanding of the aqueous electrolytes and porous carbon electrodes lead to the substantial improvement in EC performance, operating voltage window, in turn energy density and lifespan. It is especially important for advancing the sustainable and safer electrochemical capacitors but also other energy storage devices.

Streszczenie

Przejsie na odnawialne źródła energii wymaga wydajnych i zrównoważonych rozwiązań w zakresie magazynowania energii. Kondensatory elektrochemiczne (*ang. electrochemical capacitors - ECs*) charakteryzują się wysoką gęstością mocy oraz szybkim ładowaniem/wyładowaniem, dzięki czemu można je rozważać jako rozwiązanie do okresowego gromadzenia energii słonecznej i wiatrowej. Niemniej jednak niska gęstość energii oraz obawy dotyczące negatywnego wpływu na środowisko ograniczają szerokie zastosowanie ECs. Niniejsza praca doktorska dotyczy kluczowych wyzwań związanych z ECs na bazie wodnych elektrolitów: wąskim zakresem napięcia, niską pojemnością właściwą oraz krótką żywotnością poprzez modyfikację elektrolitów na bazie neutralnych soli oraz kontrolę tekstury/struktury elektrod węglowych, z uwzględnieniem aspektów ekologicznych.

Rozdział 1 dotyczy motywacji i celów pracy doktorskiej. W *rozdziałach 2-5* przedstawiono dogłębny przegląd podstawowych zagadnień dotyczących ECs, w tym mechanizmów magazynowania ładunku (podwójna warstwa elektryczna i pseudopojemność), a także szczegółowe omówienie elektrolitów (wodnych, niewodnych i stałych). Ponadto przeanalizowano różne materiały elektrodowe na bazie węgla, ze szczególnym uwzględnieniem kontroli porowatości, powierzchniowych grup funkcyjnych oraz nieuporządkowania strukturalnego poprzez aktywację lub użycie matryc. Omówiono również zaawansowane metody charakteryzacji fizykochemicznej i elektrochemicznej, które mają kluczowe znaczenie dla niniejszej pracy.

Część eksperymentalna pracy podzielona jest na pięć *rozdziałów*, obejmujących cztery recenzowane artykuły (6-9) oraz jeden manuskrypt (10). Działanie ECs zależy zarówno od elektrolitu, jak i od elektrod, przy czym w obu przypadkach występują pewne ograniczenia. Problemy związane z elektrolitem, takie jak niskie napięcie, właściwości korozyjne, krótka żywotność i bezpieczeństwo, pozostają kwestiami kluczowymi, co jest tematem niniejszej pracy doktorskiej. W *rozdziale 6* opisano opracowanie wodnego elektrolitu na bazie neutralnej soli, zmodyfikowanego dodatkiem donora wiązań wodorowych. Wykazano poprawę stabilności ECs (> 350 godzin stałonapięciowej polaryzacji) oraz właściwości antykorozyjnych w stosunku do kolektorów prądowych ze

stali nierdzewnej (dziesięciokrotny spadek prądu korozji) po dodaniu 2M mocznika do 1M Li_2SO_4 . *Rozdział 7* przedstawia badania dotyczące nowatorskich roztworów buforowych o różnym pH w połączeniu z jonami jodkowymi wykazującymi aktywność redoks. Udowodniono, że rozszerzony zakres stabilnego napięcia ECs (1.5 V), zwiększona pojemność (149 F g^{-1}) oraz długa żywotność (310 godzin stałonapięciowej polaryzacji) wynikają ze stabilizacji pH przez bufor octanowy oraz pseudopojemności pary redoks jod/jodek. *Rozdział 8* dotyczy zrównoważonego podejścia wykorzystującego lignosulfonian (LS) pochodzący z odpadów drzewnych do przygotowania elektrolitów żelowych oraz elektrod węglowych otrzymanych metodą matrycy solnej. Co istotne, LS żel pełnił rolę zarówno elektrolitu, jak i separatora, zapobiegając wyciekom, a tym samym zwiększając bezpieczeństwo EC. LS-EC osiągnął stabilne napięcie (1.6 V), zmniejszone samowyladowanie (utrata ~30% napięcia początkowego) oraz długą żywotność (170 godzin stałonapięciowej polaryzacji). Zaproponowana strategia efektywnego wykorzystania LS jako komponentów EC zmniejszyła emisję CO_2 o 32-49%, podkreślając duże perspektywy w zakresie rozwoju zrównoważonych ECs.

Ograniczenie wydajności ECs wynika również z tekstury/struktury elektrod węglowych (np. małej powierzchni właściwej i przewodnictwa elektrycznego). Ponadto nie określono jednoznacznie wpływu innych cech, takich jak nieuporządkowanie strukturalne, centra aktywne czy obecności grup funkcyjnych. W niniejszej pracy zbadano takie strategie jak użycie matryc solnych i domieszkowanie heteroatomami, co pozwoliło ocenić wpływ właściwości teksturalno-strukturalnych oraz obecności grup funkcyjnych na działanie ECs. *Rozdział 9* przedstawia badania nad węglami zsyntezowanymi przy użyciu matrycy solnej, wykorzystując mieszaniny soli metali alkalicznych. Zbadano podstawowe zależności między strukturą, porowatością oraz powierzchniowymi grupami funkcyjnymi węgla a pojemnością, retencją i żywotnością ECs. Wykazano, że węgle o zwiększonym stopniu nieuporządkowania (wysoka wartość I_{D1}/I_G i duża powierzchnia aktywna) oraz rozwiniętej porowatości wykazują zwiększoną pojemność, ale krótszą żywotność. *Rozdział 10* przedstawia oryginalne badania dotyczące syntezy i szczegółowej charakterystyki fizykochemicznej/elektrochemicznej węglowych kropek kwantowych domieszkowanych azotem (*ang. nitrogen doped carbon quantum dots - N-CQDs*) przy użyciu hydrotermalnej karbonizacji kwasu cytrynowego oraz wybranych amin. N-CQDs wykazywały wielkość cząstek ~ 6 nm, niebieską fluorescencję pod wpływem światła UV i znaczącą ilość grup funkcyjnych. Stwierdzono, że powierzchniowe grupy funkcyjne (O-, N-), efekty kwantowe (wielkość w nanoskali/modyfikacja gęstości elektronowej) oraz przewodnictwo jonowe elektrolitu

spowodowały poprawę pojemności (146 F g^{-1}) i żywotności (200 godzin stałonapięciowej polaryzacji) ECs.

Wyniki przedstawione w *rozdziałach 11-13* wskazują, że projektowanie, modyfikacja oraz głębsze zrozumienie elektrolitów wodnych i porowatych elektrod węglowych prowadzą do znacznej poprawy parametrów ECs, w tym gęstości energii, napięcia i żywotności. Ma to szczególne znaczenie dla rozwoju zrównoważonych i bezpieczniejszych kondensatorów elektrochemicznych, a także innych urządzeń do magazynowania energii.

Résumé

La transition vers les énergies renouvelables requière des solutions de stockage d'énergie efficaces et durables. Les condensateurs électrochimiques (CE) offrent une densité de puissance élevée et des vitesses de charge/décharge rapides, ce qui leur permet d'être envisagés pour l'accumulation périodique d'énergie solaire ou éolienne. Néanmoins, leur faible densité d'énergie et les préoccupations environnementales limitent leurs applications à grande échelle. Cette thèse de doctorat aborde les principaux défis liés aux CE aqueux, que sont leur plage de tension de fonctionnement étroite, leur faible capacité spécifique et leur durée de vie courte. Ceci est réalisé grâce à la modification des électrolytes aqueux à base de sels neutres et à l'adaptation de la texture/structure des électrodes en carbone, tout en tenant compte du respect de l'environnement.

Le chapitre 1 traite de la motivation et des objectifs de la dissertation. Les *chapitres 2 à 5* offrent un aperçu approfondi des principes fondamentaux concernant les condensateurs électrochimiques, notamment de leurs mécanismes de stockage de charge (double couche électrique et pseudocapacité), ainsi qu'une présentation détaillée des électrolytes (aqueux, non aqueux et de type solide). En outre, divers matériaux d'électrodes à base de carbone sont examinés, en mettant particulièrement l'accent sur le contrôle de la porosité, de la chimie de surface et du désordre structural par le biais de méthodes d'activation et de templating. Les méthodes avancées de caractérisation physico-chimique et électrochimique, revêtant une importance majeure pour la thèse, sont également abordées.

La partie expérimentale de la thèse s'articule en cinq *chapitres* distincts, comprenant quatre articles évalués par des pairs (6-9) et un manuscrit soumis pour publication (10). Les performances des CE sont limitées de manière récurrente par les propriétés de l'électrolyte et des électrodes. Les problèmes liés à l'électrolyte, tels que la faible tension, les propriétés corrosives, la durée de vie et la sécurité relativement faibles restent critiques, et de ce fait justifient l'étude plus approfondie de ces limitations conduite dans cette thèse. Le *chapitre 6* décrit la mise au point d'un électrolyte aqueux à base de sel neutre modifié par un additif donneur de liaisons hydrogène. Une

amélioration de la durée de vie du CE (> 350 heures à tension maximale) et des caractéristiques anticorrosives vis-à-vis des collecteurs de courant en acier inoxydable (courant de corrosion diminué d'un ordre de grandeur) est démontrée après l'ajout d'urée 2M à Li_2SO_4 1M. Le *chapitre 7* présente la conception de nouveaux électrolytes aqueux obtenus par addition d'espèces iodures à activité redox à différentes solutions tampons de pH. Il est démontré que l'extension de la tension maximale des CE (1.5 V), l'augmentation de leur capacité (149 F g^{-1}), ainsi que l'amélioration de leur stabilité à long terme (310 heures à tension maximale) sont dues à la stabilisation du pH contrôlée par le tampon acétate et à la pseudocapacité provenant de la paire redox iode/iodure. Le *chapitre 8* présente une approche durable utilisant le lignosulfonate (LS) issu de déchets pour la préparation d'électrolytes gélifiés et d'électrodes de carbone sur mesure. Il est important de noter que le gel de LS joue à la fois le rôle d'électrolyte et de séparateur, empêchant ainsi les fuites et améliorant de ce fait la sécurité du CE. Le condensateur électrochimique à base d'électrolyte LS gélifié démontre une tension de fonctionnement stable (1.6 V), une autodécharge réduite (perte d'environ 30 % de la tension initiale) et une longue durée de vie (170 heures à tension maximale). Cette approche permettrait de réduire les émissions de CO_2 à 32-49 %, soulignant son fort potentiel pour les condensateurs électrochimiques à électrolyte gélifié plus durables.

Les performances des CE sont également limitées par la texture/structure des électrodes de carbone (par exemple, une faible surface spécifique et une faible conductivité électrique). De plus, l'impact d'autres caractéristiques, comme le désordre structural, les sites actifs et la présence de groupes fonctionnels de surface, n'est pas clairement identifié. Dans cette thèse, des stratégies telles que le templating par des sels fondus et la fonctionnalisation par des hétéroatomes ont été explorées, permettant de mieux comprendre l'effet de la texture/structure/chimie de surface sur les performances des CE. Le *chapitre 9* présente une étude systématique de carbones synthétisés par templating à partir de mélanges de sels de métaux alcalins. Les relations fondamentales entre la structure, la porosité et la chimie de surface des électrodes en carbone, et la capacité, la rétention et la durée de vie des CE sont étudiées. Il est notamment révélé que les carbones présentant un degré de désordre accru (rapport Raman $I_{\text{D1}}/I_{\text{G}}$ et surface active élevés) et une porosité importante sont susceptibles de fournir une capacité améliorée, mais une durée de vie plus courte. Le *chapitre 10* présente une étude originale sur la synthèse et la caractérisation physico-chimique et électrochimique détaillée de points quantiques de carbone (carbon quantum dots – en anglais) dopés à l'azote (N-CQDs). Ces N-CQDs sont préparés par carbonisation hydrothermale d'acide citrique et de diverses amines. Les N-CQDs se présentent sous forme de particules

d'environ 6 nm, avec une fluorescence bleue et des groupes fonctionnels en abondance. Il a été constaté que la chimie de surface (groupes O-, N-), les effets quantiques (taille nanométrique/modification de la densité électronique) et la conductivité ionique de l'électrolyte sont à l'origine de l'amélioration de la capacité (146 F g^{-1}) et de la durée de vie (200 heures à tension maximale).

Les résultats obtenus montrent que la conception, la modification et une meilleure compréhension des électrolytes aqueux et des électrodes en carbone poreux permettent d'améliorer substantiellement les performances et la tension maximale des condensateurs électrochimiques, et par voie de conséquence leur densité d'énergie et leur durée de vie. Ceci est particulièrement important pour le développement de condensateurs électrochimiques durables et plus sûrs, mais aussi d'autres dispositifs de stockage d'énergie.

Funding

The research presented in this thesis was supported by:



French Government Scholarship France Excellence within the framework of the 2023 - 2025 granted by the **French Embassy in Poland**.



北海道大学
HOKKAIDO UNIVERSITY



POZNAN UNIVERSITY OF TECHNOLOGY

INPUTDoc Project 'Towards Internationalization of Poznań University of Technology Doctoral School' (2022 - 2024) within the STER Programme, co-financed by **Polish National Agency for Academic Exchange (NAWA)**.



NATIONAL SCIENCE CENTRE
POLAND

National Science Centre in Poland within the **Preludium 23**, grant number 2024/53/N/ST5/02202 "Carbon materials decorated by quantum dots – synthesis, characterization", principal investigator: MSc. Eng. Amelia Klimek.

National Science Centre in Poland within the **OPUS 16**, grant number 2018/31/B/ST4/01852 "Study of electrode/electrolyte interface of high stability and quick charge response", principal investigator: Prof. dr hab. Elżbieta Frąckowiak.

Abbreviations

AC	activated carbon
ASA	active surface area
BET	Brunauer-Emmett-Teller
C	capacitance
CB	carbon black
CNOs	carbon nano-onions
CNTs	carbon nanotubes
CNFs	carbon nanofibers
CQDs	carbon quantum dots
CV	cyclic voltammetry
DFT	density functional theory
DES	deep eutectic solvent
E	energy
EC	electrochemical capacitor
EDL	electrical double layer
EDX	energy-dispersive X-ray spectroscopy
EIS	electrochemical impedance spectroscopy
ESR	equivalent series resistance
FTIR	Fourier transform infrared spectroscopy
GCD	galvanostatic charge/discharge
GCMS	gas chromatography mass spectrometry
GE	gel electrolyte
HBD	hydrogen bond donor
HTC	hydrothermal treatment
I_D/I_G	degree of disorder
IL	ionic liquid
Li-ion	lithium-ion battery

NMR nuclear magnetic resonance
NiO(OH)-Cd nickel-cadmium battery
NiO(OH)-MH nickel-metal hydride battery
P power
SEM scanning electron microscopy
SSA specific surface area
SPE solid-state polymer electrolyte
TC templated carbon
TEM transmission electron microscopy
TGA thermogravimetric analysis
TPD-MS temperature programmed desorption coupled with mass spectrometry
U voltage
WIS water-in-salt
XRD X-ray diffraction
XPS X-ray photoelectron spectroscopy

Introduction

1.1 Motivation

Every stage of the fossil fuel life cycle – extraction, processing, transportation, and burning/conversion to petrochemical products releases greenhouse gases. These gases (e.g., CO₂, CH₄, N₂O) contribute to global warming and pollutants detrimental to people's and other living organisms' health, while also resulting in extensive environmental damages¹. It is reported, that extraction and burning of oil, gas, and coal account for nearly 90% of CO₂ emissions and about 79% of overall greenhouse gas emissions². Importantly, these gas releases are accelerating climate change, leading to ocean acidification, and triggering a series of unprecedented climate disasters (e.g., hurricanes, heat waves, flooding)³. Therefore, the society is forced to limit the use of fossil fuels, and implement a rapid, reliable transition to clean, renewable energy.

Renewable energy sources are perfect solution to support transformation of fossil-fuel based energy in the coming decades. These sources, coming from the sun, wind, tides, are cost-effective and unlimited⁴. Diverse methods transform renewable sources to electrical energy, e.g., solar cells utilize the photovoltaic effect to convert solar energy, while wind turbines convert kinetic energy from the wind⁵. However, renewable sources are highly dependent on unstable weather conditions and/or geographic localization, with the periods of shortage and surplus⁶. That is why, energy storage systems and their further development is extremely important to align the green energy supply with the demand.

There are several types of energy storage devices which are currently utilized, e.g., secondary (rechargeable) batteries, capacitors. Among them, secondary batteries, including lead-acid, NiO(OH)-Cd, NiO(OH)-MH, and Li-ion batteries represent the most

effective and versatile solution for storing and releasing energy⁷. They are available in a range of the shapes and sizes, which enhances their utility for the grid energy storage and other applications such as powering portable devices, and electric/hybrid vehicles. Nonetheless, the functioning mechanism based on reversible redox reactions presents certain constraints, such as limited discharge rates, diminished lifespan, and kinetics limitations leading to low power⁸. Importantly, the significant accumulation of chemical energy in a compact form can result in dangerous incidents, including fires, explosions, and environmental pollution especially with Li-ion batteries that employ organic solvents⁹. Consequently, it is crucial to investigate alternative energy storage systems, to address some, if not all of these drawbacks, thereby promoting safer, more efficient, and adaptable devices.

Electrochemical capacitors (ECs) stand out to their straightforward design and the electrostatic energy storage mechanism leading to the release of high amount of energy within very short time¹⁰. The high surface area of the carbon electrodes submerged in an electrolyte solution causes in the storage of much more energy, surpassing those of traditional electrolytic capacitors¹¹. The features of ECs including high-power density (10-30 kW kg⁻¹)¹²⁻¹⁴, quick charge/discharge (seconds)^{13,15}, and long lifespan (> 1 000 000 cycles)¹³ enable their application in regenerative braking, start/stop systems in electric/hybrid vehicles, emergency aircraft doors, wearable electronics, power buffers, and more recently the Internet of Things¹⁶⁻¹⁸.

However, the ECs components at an industrial scale frequently do not meet ecological requirements. Predominantly used organic electrolyte 1M tetraethylammonium tetrafluoroborate in acetonitrile (1M TEABF₄/ACN) allows to reach elevated voltages (≥ 2.5 V)^{14,15}, which enhance significantly the energetic performance. Nonetheless, use of organic electrolytes, particularly ACN solvent pose environmental concerns (toxicity) and safety risks (flammability)¹⁹. Furthermore, organic electrolytes strongly absorb moisture, which deteriorate their performance requiring the storage and assembly of the EC in the inert atmosphere that generate additional costs.

On the other hand, traditional aqueous electrolytes including H₂SO₄ and KOH had been utilized to mitigate some of the previously mentioned drawbacks of organic medium, i.e., environmental benign and cost-effectiveness. Nevertheless, given that the stable operating voltage falls below 1 V^{14,20}, and due to the corrosion-accelerating properties, these electrolytes do not present a compelling option for ECs. Hence, to overcome a narrow functioning voltage issue, neutral salt electrolytes i.e., 1M Li₂SO₄, 1M Na₂SO₄,

1M LiNO₃ had been proposed²¹. Even though, the operating voltage of 1.5-1.6 V^{14,22} increased the stored energy, the occurring corrosion processes, that shorten lifespan and other limitations are still present.

Typically, carbon-based electrodes with high specific surface area and developed porosity are utilized in ECs²³. Such a carbon coming from carbonization of natural materials or synthetic precursors is further activated using gases (e.g., CO₂, steam) or chemicals, (e.g., KOH, H₃PO₄). Generally, chemical activation is better for producing activated carbon with higher specific surface area than steam activation, but requires use of hazardous chemicals²⁴. Nevertheless, during the physical/chemical activation processes it is difficult to precisely control the porosity (micropores and mesopores) of carbon to match the size of ions of the selected EC electrolyte as well as the structural disorder and surface functional groups²⁵.

Consequently, further development in the ECs field should be oriented towards the modification of the neutral salt aqueous electrolytes and tailoring of the texture/structure of the carbon electrode material, considering sustainable aspect^{26,27}. It is of high importance to investigate the mechanism of electrical double layer formation and related parameters. These improvements should enable the preparation of a system that can compete in the performance characteristics with benchmark organic-based ECs.

References

- 1 Wolf, S.; Bullard, R.; Buonocore, J. J.; Donley, N.; Farrelly, T.; Fleming, J.; González, D. J. X.; Oreskes, N.; Ripple, W.; Saha, R.; Willis, M. D. Scientists' Warning on Fossil Fuels. *Oxford Open Climate Change* **2025**, *5* (1) kgaf011. <https://doi.org/10.1093/oxfclm/kgaf011>
- 2 United Nations, Causes and Effects of Climate Change. United Nations. <https://www.un.org/en/climatechange/science/causes-effects-climate-change> (accessed **2026-05-07**)
- 3 Ripple, W.J., Wolf, C., Gregg, J.W., Rockstorm, J., Mann, M.E., Oreskes, N., Lenton, T.M., Rahmstorf, S., Newsome, T.M., Xu, C., Svenning, J.C., Pereira, C.C., Law, B.E., Crowther, T.W., The 2024 state of the climate report: Perilous times on planet Earth. *BioScience* **2024**, *74* (12), 812-824. <https://doi.org/10.1093/biosci/biae087>
- 4 Panwar, N. L.; Kaushik, S. C.; Kothari, S. Role of Renewable Energy Sources in Environmental Protection: A Review. *Renewable and Sustainable Energy Reviews* **2011**, *15* (3), 1513–1524. <https://doi.org/10.1016/j.rser.2010.11.037>
- 5 Ang, T.Z.; Salem, M.; Kamarol, M.; Das, H. S.; Nazari, M. A.; Prabakaran, N. A Comprehensive Study of Renewable Energy Sources: Classifications, Challenges and Suggestions. *Energy Strategy Reviews* **2022**, *43*, 100939. <https://doi.org/10.1016/j.esr.2022.100939>
- 6 Zhao, J.; Li, F.; Zhang, Q. Impacts of Renewable Energy Resources on the Weather Vulnerability of Power Systems. *Nature Energy* **2024**, *9* (11), 1407–1414. <https://doi.org/10.1038/s41560-024-01652-1>
- 7 Vasant Kumar, R.; Sarakonsri, T. A Review of Materials and Chemistry for Secondary Batteries. In *Rechargeable Ion Batteries: Materials, Design and Applications of Li-Ion Cells and Beyond*; John Wiley & Sons, Ltd, **2022**; pp 49–81. <https://doi.org/10.1002/9783527836703.ch3>
- 8 Simon, P.; Gogotsi, Y.; Dunn, B. Where Do Batteries End and Supercapacitors Begin? *Science* **2014**, *343* (6176), 1210–1211. <https://doi.org/10.1126/science.1249625>
- 9 Takada, K. Progress and Prospective of Solid-State Lithium Batteries. *Acta Materialia* **2013**, *61* (3), 759–770. <https://doi.org/10.1016/j.actamat.2012.10.034>
- 10 Conway, B. E. *Electrochemical Supercapacitors*; Springer US: Boston, MA, **1999**. <https://doi.org/10.1007/978-1-4757-3058-6>
- 11 Miller, J. R.; Simon, P. Electrochemical Capacitors for Energy Management. *Science* **2008**, *321* (5889), 651–652. <https://doi.org/10.1126/science.1158736>
- 12 Zhang, D.; Yang, B.; She, W.; Gao, S.; Wang, J.; Wang, Y.; Wang, K.; Li, H.; Han, L. Simultaneously Achieving High Energy and Power Density for Ultrafast-Charging Supercapacitor Built by a Semi-Graphitic Hierarchical Porous Carbon Nanosheet and a High-Voltage Alkaline Aqueous Electrolyte. *Journal of Power Sources* **2021**, *506*, 230103. <https://doi.org/10.1016/j.jpowsour.2021.230103>
- 13 Skeleton, Supercapacitors data sheet (accessed: **2026-05-07**) <https://www.skeletontech.com/En/Skelcap-Supercapacitors>
- 14 Azmi, S.; Klimek, A.; Frackowiak, E. Why Electrochemical Capacitor Electrolytes Should Not Be Ignored? *Electrochimica Acta* **2023**, *452*, 142347. <https://doi.org/10.1016/j.electacta.2023.142347>
- 15 Burke, A. F.; Zhao, J. Past, Present and Future of Electrochemical Capacitors: Technologies, Performance and Applications. *Journal of Energy Storage* **2021**, *35*, 102310. <https://doi.org/10.1016/j.est.2021.102310>
- 16 Burke, A.; Liu, Z.; Zhao, H. Present and future applications of supercapacitors in electric and hybrid vehicles. *IEEE Conference Publication*, **2014** <https://ieeexplore.ieee.org/document/7056094> (accessed 2026-05-07)

- 17 Dubal, D. P.; Chodankar, N. R.; Kim, D.-H.; Gomez-Romero, P. Towards Flexible Solid-State Supercapacitors for Smart and Wearable Electronics. *Chemical Society Reviews* **2018**, 47 (6), 2065–2129. <https://doi.org/10.1039/C7CS00505A>
- 18 Yang, P.; Mai, W. Flexible Solid-State Electrochemical Supercapacitors. *Nano Energy* **2014**, 8, 274–290. <https://doi.org/10.1016/j.nanoen.2014.05.022>
- 19 Wang, Z.; Richter, S. M.; Rozema, M. J.; Schellinger, A.; Smith, K.; Napolitano, J. G. Potential Safety Hazards Associated with Using Acetonitrile and a Strong Aqueous Base. *Organic Process Research & Development* **2017**, 21 (10), 1501–1508. <https://doi.org/10.1021/acs.oprd.7b00158>
- 20 Ruiz, V.; Santamaría, R.; Granda, M.; Blanco, C. Long-Term Cycling of Carbon-Based Supercapacitors in Aqueous Media. *Electrochimica Acta* **2009**, 54 (19), 4481–4486. <https://doi.org/10.1016/j.electacta.2009.03.024>
- 21 Fic, K.; Płatek, A.; Piwek, J.; Menzel, J.; Ślesiński, A.; Bujewska, P.; Galek, P.; Frackowiak, E. Revisited Insights into Charge Storage Mechanisms in Electrochemical Capacitors with Li₂SO₄-Based Electrolyte. *Energy Storage Materials* **2019**, 22, 1–14. <https://doi.org/10.1016/j.ensm.2019.08.005>
- 22 Slesinski, A.; Sroka, S.; Fic, K.; Frackowiak, E.; Menzel, J. Operando Monitoring of Local pH Value Changes at the Carbon Electrode Surface in Neutral Sulfate-Based Aqueous Electrochemical Capacitors. *ACS Applied Materials & Interfaces* **2022**, 14 (33), 37782–37792. <https://doi.org/10.1021/acsami.2c09920>
- 23 Beguin, F.; Frackowiak, E.; *Carbons for Electrochemical Energy Storage and Conversion Systems*; CRC Press: Boca Raton, **2009**. <https://doi.org/10.1201/9781420055405>
- 24 Shahcheragh, S. K.; Bagheri Mohagheghi, M. M.; Shirpay, A. Effect of Physical and Chemical Activation Methods on the Structure, Optical Absorbance, Band Gap and Urbach Energy of Porous Activated Carbon. *SN Applied Sciences* **2023**, 5 (12), 313. <https://doi.org/10.1007/s42452-023-05559-6>
- 25 Díez, N.; Fuertes, A. B.; Sevilla, M. Molten Salt Strategies towards Carbon Materials for Energy Storage and Conversion. *Energy Storage Materials* **2021**, 38, 50–69. <https://doi.org/10.1016/j.ensm.2021.02.048>
- 26 Nita, C.; Bensafia, M.; Vaulot, C.; Delmotte, L.; Matei Ghimbeu, C. Insights on the Synthesis Mechanism of Green Phenolic Resin Derived Porous Carbons via a Salt-Soft Templating Approach. *Carbon* **2016**, 109, 227–238. <https://doi.org/10.1016/j.carbon.2016.08.011>
- 27 Pohlmann, S; Metrics and Methods for Moving from Research to Innovation in Energy Storage. *Nature Communications* **2022**, 13 (1), 1538. <https://doi.org/10.1038/s41467-022-29257-w>

1.2 Outline and objectives of the thesis

In the light of the aforementioned challenges, this PhD thesis aims to improve the performance of electrochemical capacitors considering sustainable aspect. According to the formula: $E = \frac{1}{2} C U^2$, energy (E) is a function of capacitance (C) and voltage (U) of the electrochemical capacitor. Therefore, there are two ways of improving the energy storage, i.e., increase of the capacitance, which is directly related to the electrode materials and/or enhancement of the stable operating voltage, linked to the utilized electrolyte. Consequently, the following several hypotheses (H1-H5) are proposed:

H1 New formulation of electrolyte with hydrogen bond donor extends EC functioning voltage and limits corrosion.

H2 The modification of neutral aqueous electrolyte by redox active species boosts capacitance values.

H3 Lignosulfonate can serve as sustainable material for electrolyte and electrode.

H4 Salt template approach is ideal for tailoring texture/structure of electrode material.

H5 Porous carbon functionalized by nitrogen-based carbon quantum dots enhances the EC performance.

In this PhD thesis, I present the research results in the form of four original peer-reviewed articles (P1-P4) and additional manuscript (5.), which is not yet peer-reviewed (under revision):

- P1 Sara Azmi, **Amelia Klimek**, Elzbieta Frackowiak*
"Electrochemical capacitor in aqueous electrolyte with long lifespan improved by hydrogen bond donor addition",
Materials Today 68 (2023) 34-50
<https://doi.org/10.1016/j.mattod.2023.06.018>
IF: 21.1, MNI_{SW}: 200
- P2 **Amelia Klimek**, Maciej Tobis, Elzbieta Frackowiak*
"Effect of a buffer/iodide electrolyte on the performance of electrochemical capacitors",
Green Chemistry 26 (2024) 6684-6695
<https://doi.org/10.1039/D4GC01748J>
IF: 9.2, MNI_{SW}: 200
- P3 **Amelia Klimek**, Lina Amro, Nutthira Pakkang, Camelia Matei Ghimbeu, Elzbieta Frackowiak*, Shiori Suzuki*
"Lignin as precursor of gel electrolyte and salt templated carbon for sustainable

electrochemical capacitor”

Green Chemistry 28 (2026) 4225-4242

<https://doi.org/10.1039/D5GC05533D>

IF: 9.2, MNiSW: 200

- P4 **Amelia Klimek**, Benedicte Rety, Camelia Matei Ghimbeu*, Elzbieta Frackowiak*
“Impact of disorder, porosity and surface chemistry of salt templated carbons on capacitance”
Advanced Science 12 (2025) e05032
<https://doi.org/10.1002/advs.202505032>
IF: 14.3, MNiSW: 200
5. **Amelia Klimek**, Emmanuel Salomon, Samar Hajjar-Garreau, Elzbieta Frackowiak*, Camelia Matei Ghimbeu*
“Insights of N-carbon quantum dots effect on charge storage in supercapacitors”
under revision, (2026)

The chapters, which contain complete versions of the peer-reviewed articles (*Chapters 6-9*), and the manuscript under revision (*Chapter 10*) are introduced by the theoretical overview of electrochemical capacitors, including EC functioning mechanism, electrolytes, electrode materials, and characterization techniques (*Chapters 2-5*).

Chapter 2 introduces electrochemical capacitors, discussing the principle of their operation, explaining electrical double layer models and pseudocapacitance phenomena.

Chapter 3 addresses the physicochemical and electrochemical characteristics of electrolytes used for ECs, including aqueous electrolytes (acids/bases, neutral salts, and water-in-salt), non-aqueous electrolytes (organic, ionic liquids), deep eutectic solvents, redox-active electrolytes and solid-like electrolytes.

Chapter 4 focuses on the electrode materials used for ECs emphasizing different carbon materials including activated carbon, templated carbon, carbon nano-onions, carbon nanofibers, carbon nanotubes, graphene, carbon black, and carbon quantum dots. Importantly, the attention is given to the tailoring of the carbon’s texture/structure through the activation (physical, chemical) and templating (hard- soft-, salt-). The chapter is summarized by the discussion about the recently reported textural/structural effects on the EC performance.

Chapter 5 presents the techniques used for the characterization of carbon materials (X-ray diffraction, X-ray photoelectron spectroscopy, transmission electron microscopy, temperature programmed desorption coupled with mass spectrometry including active surface area estimation, gas adsorption/desorption) and electrochemical capacitors

(cyclic voltammetry, galvanostatic charge/discharge, electrochemical impedance spectroscopy).

The PhD thesis attempts to address important challenges in electrochemical capacitors by the following objectives:

Chapter 6 (P1) - developing neutral salt aqueous electrolyte with hydrogen bond donor additive, thereby significantly improving the cycle life and anti-corrosive properties of ECs.

Chapter 7 (P2) - inventing advanced aqueous electrolyte composed of buffer solutions with different pH and redox active pair additive, reaching high voltage and energy density as well as long lifespan of ECs.

Chapter 8 (P3) - developing gel electrolyte with high solution uptake and salt templated carbon with tailored texture/structure utilizing a waste-derived biopolymer, offering more sustainable, safer and high-performance EC.

Chapter 9 (P4) - synthesizing and characterizing a series of soft-salt templated carbons utilizing double alkali metals mixtures, thus providing universal relationships between the structure/texture of carbons and electrochemical properties of aqueous ECs.

Chapter 10 (5.) - synthesizing carbon quantum dots abundant in nitrogen and oxygen functional groups and understanding their role in the enhancement of capacitive performance as well as EC lifespan.

The implementation of the proposed objectives should facilitate the mitigation of existing constraints and enhance the ECs performance, considering the environmental impact. It is essential for addressing the evolving energy storage requirements of a modern society.

The final chapters present a summary of the key findings presented in the PhD thesis and perspectives (*Chapters 11-16*), followed by an overview of my academic journey and accomplishments (*Chapter 17*).

Electrochemical capacitor

2.1 Principle of ECs operation and properties

Electrochemical capacitor (EC) is composed of two electrodes, usually made of porous carbon soaked in electrolyte solution¹. The electrodes are separated by a non-conductive membrane, to prevent short-circuiting, but allowing the free movement of the ions. The scheme presenting a symmetric, charged electrochemical capacitor is shown in **Figure 1**.

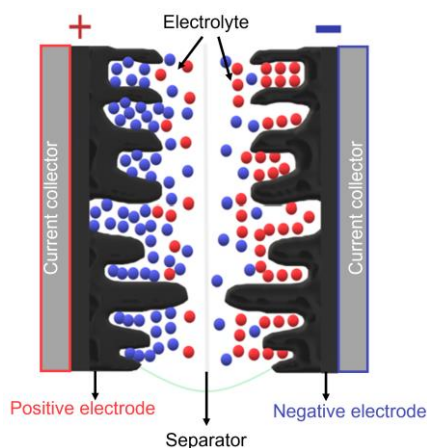


Figure 1. Scheme presenting a symmetric, charged electrochemical capacitor.

The applied potential difference induces the electrostatic adsorption of the ions at the electrode/electrolyte interface. The term capacitance (C_{ele}) indicates the quantity of charge (Q) stored at a specified operating voltage (U), according to the **Equation 1**².

$$C_{\text{ele}} = \frac{Q}{U} \quad \left[\frac{\text{A} \cdot \text{s}}{\text{V}} \right] = [\text{F}] \quad \text{Equation 1}$$

When charged, the EC functions as two capacitors with capacitances of positive electrode (C_+) and negative electrode (C_-) connected in series. Then, the capacitance of the full cell (C_{cell}) is defined by the **Equation 2**^{3,4}:

$$\frac{1}{C_{\text{cell}}} = \frac{1}{C_+} + \frac{1}{C_-} \quad \text{Equation 2}$$

$$C_{\text{cell}} = \frac{C_+ \cdot C_-}{C_+ + C_-} \quad [\text{F}]$$

Importantly, even though the symmetric EC is considered, the electrodes often exhibit differences in the capacitance values due to various sizes of the ions in the electrolyte. Consequently, the electrode with the smaller capacitance determines the overall capacitance of the device^{4,5}.

On the other hand, when the impact of the electrode material is considered, the gravimetric (specific) capacitance of one electrode (C_s) is generally presented. In the case of symmetric EC, and assuming that the both electrodes share the same characteristics, i.e., type of the material, mass, thickness, volume, and specific surface area, the **Equation 3** is applicable⁶:

$$C_s = \frac{2 \cdot C}{0.5 \cdot m_a} \quad [\text{F} \cdot \text{g}^{-1}] \quad \text{Equation 3}$$

where the C (in F) stands to the capacitance of the cell referred to the total mass, while m_a (in g) is the mass of active material present in both electrodes. It means that the capacitance of single electrode (C_s) is 4 times higher than the full device capacitance (C).

Then, to emphasize the practical utilization of EC, and to compare its performance metrics with other energy storage devices, the term energy (E) and power (P) are commonly employed. The energy stands for the amount of the stored charge, while the power describes how fast the energy is released. They both can be related to the mass of the device, known as gravimetric (specific) energy (E_s in Wh kg^{-1}) and power (P_s in W kg^{-1}). The specific energy, E_s is influenced by the capacitance (C in F) of the device, the operating voltage (U in V), and the mass of the device (m in kg), as shown below (**Equation 4**)⁴:

$$E_s = \frac{C \cdot U^2}{2 \cdot m} \quad [\text{Wh} \cdot \text{kg}^{-1}] \quad \text{Equation 4}$$

The specific power, P_S , as defined using **Equation 5**, depends on EC operating voltage (U in V) which is divided by the equivalent series resistance (R_{ESR} in Ohms), and the mass of the device (m in kg)⁴. The R_{ESR} also called as internal resistance is associated with the resistance of the bulk electrolyte, the electrode, and the contact between the electrode and the current collector^{4,7}. Also, there is another way to express the specific power, where the specific energy (E_S in Wh kg⁻¹) is divided by the discharge time (t in h) according to the **Equation 6**⁸.

$$P_S = \frac{U^2}{4 \cdot R_{ESR} \cdot m} \quad [W \cdot kg^{-1}] \quad \text{Equation 5}$$

$$P_S = \frac{E_S}{t} \quad [W \cdot kg^{-1}] \quad \text{Equation 6}$$

Interestingly, it is common in academia to normalize the energy and power values to the active masses of the electrodes (or total masses) what limits evaluations alongside other commercial energy storage devices⁹. The Ragone plot is used for graphical presentation of the device's specific energy and the specific power (**Figure 2**).

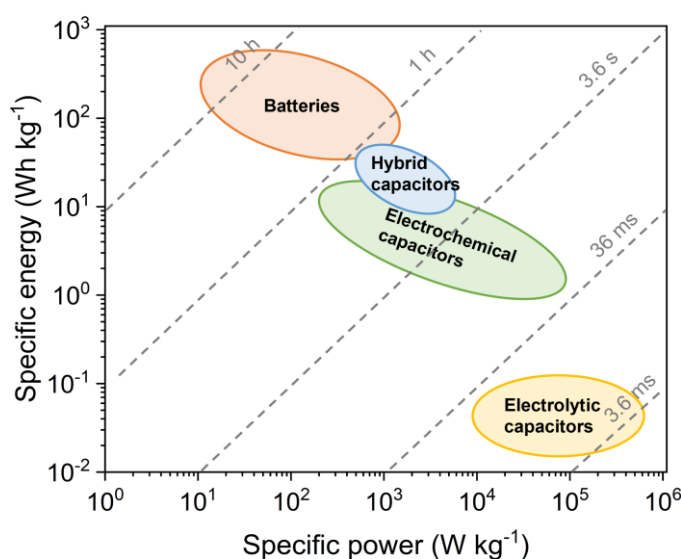


Figure 2 Ragone plot comparing different energy storage systems. Data extracted from the reference¹⁰.

The diagonal dashed lines visible in the Ragone plot stand for the specific energy/specific power ratio⁹, referred to the time constant (τ), which is expressed as the capacitance of the cell (C) multiplied by the equivalent resistance series (R_{ESR}) (**Equation 7**).

$$\tau = R_{ESR} \cdot C \quad [s] \quad \text{Equation 7}$$

It is clear that the ECs outperform the electrolytic capacitors in the terms of specific energy. On the other hand, ECs lack the specific energy compared to the batteries. It is

connected to the limitation of the functioning mechanism based on the electrostatic attraction of the ions. Hybrid capacitors with battery-like anode and EC-based positive electrode are filling the gap between the performance of ECs and batteries. Nevertheless, they face complex material processing and manufacturing.

2.2 Mechanisms of energy storage in ECs

2.2.2 Electrical double layer models

The electrical double layer (EDL) refers to the reversible electrostatic accumulation of ions on the surface of the electrodes⁴. Over past two centuries, a multitude of EDL layer formation models have been established to comprehend and interpret various interfacial processes and improve a variety of electrochemical processes, i.e., electrocatalysis, electrochemical energy storage, ion transport through biological membranes, and corrosion¹¹. The Helmholtz model proposed in 1853 defines the charge separation at the electrolyte/electrode interface, under polarization. In this scenario, ions with opposite charges diffuse through the electrolyte resulting in the formation of a few nanometers layer within a plane that is parallel to the electrode surface, thereby maintaining neutral charge (**Figure 3 a**). This phenomenon is defined as the EDL formation. The potential profile φ_e drops linearly with the increase of the distance from positively charged electrode surface to the center of negatively charged ions. Capacitance indicates the electrode ability to accumulate charge. In this context, the capacitance of simplified EDL Helmholtz model (C_H) (without consideration of electrolytic solution effects) is defined by **Equation 8**^{4,9,12}:

$$C_H = \frac{\epsilon_0 \cdot \epsilon_r \cdot S}{d} \quad [F] \quad \text{Equation 8}$$

where, the ϵ_0 is the vacuum permittivity ($\epsilon_0 = 8.854 \cdot 10^{-12} \text{ F m}^{-1}$), ϵ_r stand for dielectric constant of electrolyte (different for each electrolyte), S is the accessible surface area of the electrode (m^2), and d is a distance from positively charged electrode surface to the center of negatively charged ions (m). Typically, the double layer capacitance expressed per area varies within the range of several tens $\mu\text{F cm}^{-2}$ ¹². The EDL Helmholtz model, which assumes the accumulation of negative ions in a single layer along the electrode surface, has several drawbacks. The model does not consider the occurring interactions beyond the compact layer, i.e., the diffusion of ions in the solution, dipole moment of the solvent and the interaction with electrode⁴.

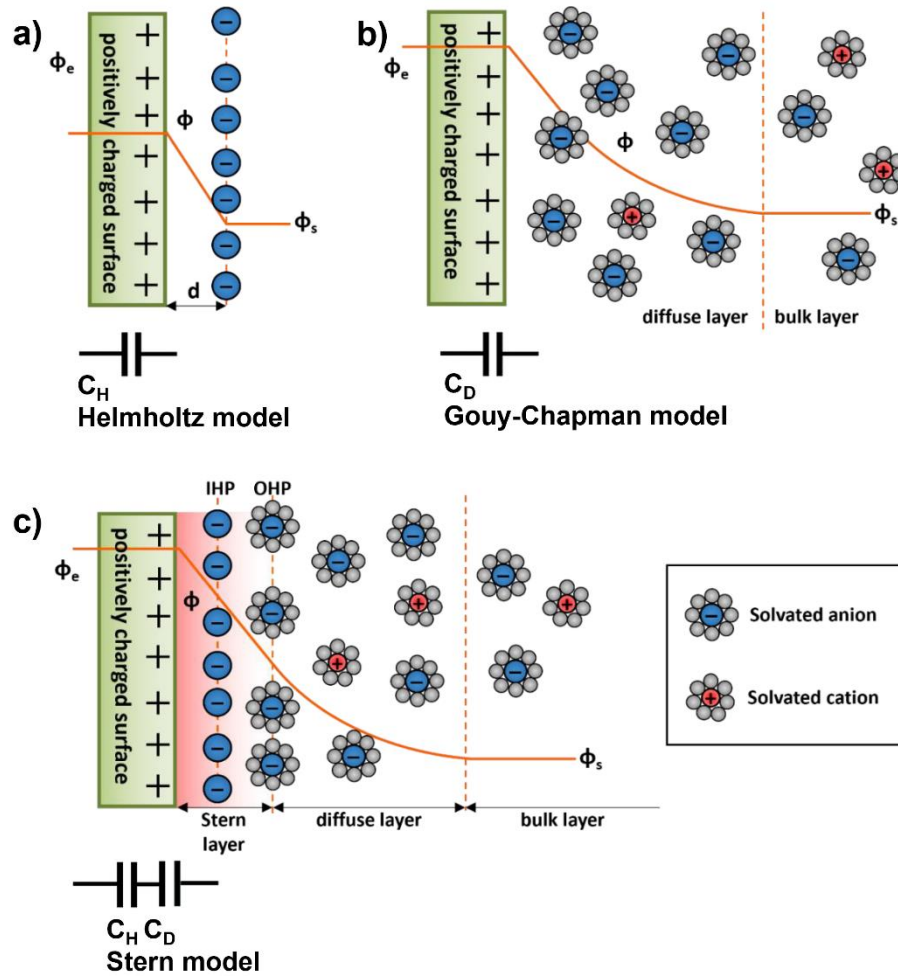


Figure 3 Schematic presentation of electrical double layer models on the surface of positively charged electrode in electrolytic solution: **a)** Helmholtz model, **b)** Gouy-Chapman model, **c)** Stern model. The electrical potential ϕ diminishes as it moves from the electrode (ϕ_e) to the bulk electrolyte (ϕ_s). The lower insets illustrate the simplified equivalent circuits. Adapted from the reference⁴.

Then, Gouy and Chapman introduced a diffuse model, where the double layer is not as compact as in Helmholtz rigid layer but exhibits a variable thickness, allowing ions to move freely^{13,14} (**Figure 3 b**). They took into account thermal fluctuation, which refers to the random thermal motion of ions in the electrolyte near a charged electrode surface (Poisson-Boltzmann differential equation). The capacitance of double layer noted by the Gouy-Chapman (C_D) is defined using **Equation 9**¹²:

$$C_D = \frac{\epsilon_0 \cdot \epsilon_r}{\lambda_D} \cosh \left(\frac{z \cdot F \cdot \phi}{2 \cdot R \cdot T} \right) \quad [\text{F m}^{-2}] \quad \text{Equation 9}$$

where the ϕ is the applied electrical potential to the electrode (V), F is the Faraday constant (96485 C mol^{-1}), z is ionic charge number (valence), R is the ideal gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$), T is the temperature (K). The average thickness of the diffuse layer (λ_D) is given by the **Equation 10**¹²:

$$\lambda_D = \sqrt{\frac{\epsilon_0 \cdot \epsilon_r \cdot R \cdot T}{2 \cdot F^2 \cdot C_0}} \quad [\text{m}] \quad \text{Equation 10}$$

where C_0 is the concentration in the bulk electrolyte (mol m^{-3}). Nevertheless, the Gouy-Chapman model defines ions as point charges, that do not interact with other particles, neglecting the electrolyte effect in the higher concentrations (i.e., layering effects, ion pairing formation, ion crowding) and assuming that the solvent has uniform dielectric permittivity¹⁵. Thus, in this model, the electrode potential diminishes exponentially from the electrode surface to the fluid bulk⁴.

The imperfections of Helmholtz and Gouy-Chapman double layer models were solved by the concept introduced by Stern¹⁶. The closest ions to the electrode are adsorbed on the electrode surface, establishing a compact layer, followed by a diffuse layer extended into the bulk electrolyte, as shown in **Figure 3 c**). Consequently, the capacitance of the compact Helmholtz layer and diffuse Gouy-Chapman layer functions as two capacitors in series, and the final EDL capacitance is given by the **Equation 11**⁴:

$$\frac{1}{C_{\text{EDL}}} = \frac{1}{C_{\text{H}}} + \frac{1}{C_{\text{D}}} \quad \left[\frac{1}{\text{F}}\right] \quad \text{Equation 11}$$

where C_{EDL} is the electrical double layer capacitance, C_{H} stands for the Helmholtz layer capacitance, and C_{D} is the capacitance of Gouy-Chapman diffuse layer. The Stern model becomes up to date to explain the mechanism of the EDL formation¹⁷. Interestingly, there are several factors that influence the EDL behavior at a planar electrode surface including the electrical field applied across the electrode, the type of ions in the electrolyte and the solvent, chemical affinity between the adsorbed ions and the electrode surface¹⁸.

2.2.2 Pseudocapacitance

The charge storage mechanism in ECs extends beyond the EDL formation through the electrostatic ion's adsorption, to include the charge transfer (faradaic reactions) between the electrode and electrolyte¹⁹. These reactions correspond to the electron flow (e^-) between oxidized (Ox) and reduced (Red) form of the materials as shown in **Equation 12**²⁰. Notably, the faradaic reactions are restricted by the thermodynamic kinetics of the processes²¹.



The correlation between voltage and charge is not completely linear, as for EDL-based ECs; hence, the capacitance does not stay constant with enhancing potential, referred to as pseudocapacitance². Pseudocapacitive effects increase the EC capacitance compared with those based on EDL formation by 10-100 times²². *Conway* proposed classification into three different phenomena of pseudocapacitance based on the adsorption, redox and intercalation processes, as shown in **Figure 4**^{2,19}. The adsorption pseudocapacitance occurs when electrosorbed ions form a monolayer on the electrode surface (**Figure 4 a**). This process is typical for adsorption of hydrogen on noble metal (e.g., Pt, Pd, Rh, Au) surface²³.

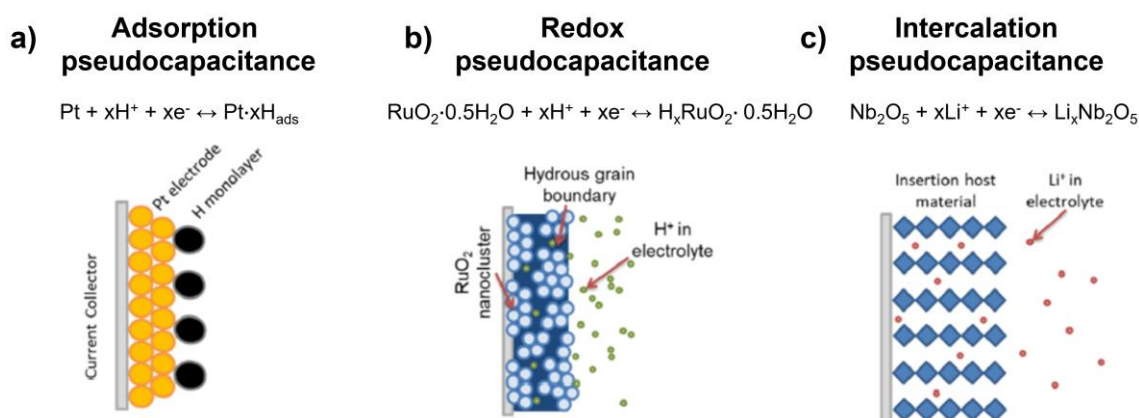
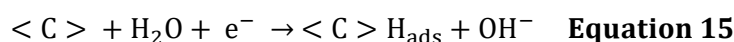


Figure 4 Scheme presenting three different types of pseudocapacitance: **a)** adsorption pseudocapacitance, **b)** redox pseudocapacitance, **c)** intercalation pseudocapacitance. Adapted from reference²⁴.

Interestingly, the hydrogen electrosorption stands out as particularly significant in aqueous-based ECs, that utilize porous carbon electrodes²⁵. The hydrogen generated through the electrochemical breakdown of the electrolyte is electrosorbed by the microporous texture of the negative electrode, described by the **Equations 13-15**. Upon reversal polarization, the electrosorbed hydrogen is oxidized, resulting in the formation of water alongside the OH⁻ ions in the electrolyte^{26,27}.



Redox pseudocapacitance refers to the process when ions participate in a reaction with the electrode material (**Figure 4 b**)²⁰. It can be realized when the electroactive particles of transition metals oxides, e.g., RuO₂²⁸, MnO₂²⁹, TiO₂³⁰ are utilized. For example, RuO₂ in acidic medium was deeply investigated, and it was found that the charge storage is limited just to the electrode surface^{31,32}. Moreover, the crystalline form of RuO₂ plays

important role, especially bounded structural water, that enables Ru^{4+} redox activity, RuO_2 metal-like electric conductivity, and fast proton transfer during charge storage^{33,34}.

Another way of providing redox capacitance can be realized through the use of carbons enriched in heteroatoms, e.g., oxygen, nitrogen, sulphur, phosphorus^{4,35,36}. The adjustment of the type, concentration, and distribution of dopant leads to the enhancement of electrical conductivity, wettability, and the availability of redox-active sites, combining EDL capacitance with fast faradaic pseudocapacitance³⁷.

Oxygen doping was found to especially improve the EC capacitance and wettability of the porous carbon materials^{38,39}. Several types of O-functional groups were distinguished (i.e., carbonyl, carboxyl, quinone, ether) and their impact on EC performance was studied⁴⁰. Moreover, it was found that depending on the pH of the EC electrolyte, the O-functionalities can interact specifically with the electrolyte, thus result in differences of EC performance⁴⁰. For example, the pyrolysis of sodium alginate resulted in a carbon with high amount of oxygen ~15 at.%. The role of pseudocapacitance was validated using CV, evidenced by the reversible redox peaks. The elevated capacitance ($\sim 200 \text{ F g}^{-1}$) of carbon derived from sodium alginate was associated with charge transfer reactions involving the quinone, phenol and ether functional groups in 1M H_2SO_4 ⁴¹. Notably, the impact of individual oxygen groups was rarely studied in the literature. Also, high O-groups content can be detrimental to the capacitance since it reduces electronic conductivity, and to cycle life, favoring degradation.

Nitrogen functionalities exhibit higher electrochemical stability than oxygen functional groups⁴². N element is predominantly utilized owing to its comparable atomic radius to carbon (facilitating integration with the carbon framework), lower band gap compared with carbon (resulting in an elevated electron transfer rate and enhanced conductivity), and the presence of lone pair electrons (which improve the hydrophilicity and wettability)⁴². *Frackowiak et al.* synthesized N-doped porous carbon using steam activation of N-polymers and showed that an optimal nitrogen content of up to 7 wt.% yields high electrochemical capacitance ($\sim 200 \text{ F g}^{-1}$)⁴³. *Lukaszewicz et al.* proved that N-doped carbons obtained from chitosan, gelatin, and green algae ($\sim 7 \text{ wt.}\%$ of N) exhibited high capacitance ($\sim 230 \text{ F g}^{-1}$). Furthermore, it was found that even though quaternary-N and pyrrolic-N groups enhance EC performance due to their positive charge and improved electron transfer at elevated current loads, the primary functional group influencing the effective charge storage is quaternary-N⁴⁴.

Moreover, in contrast to single heteroatom doping, multiple doping presents a versatile synthesis strategy that can further modify the characteristics of material. Nitrogen doping

typically enhances the electrical conductivity of carbon materials, while sulphur, owing to its larger atomic size, provides polarizable electron pairs and hence greater chemical reactivity⁴⁵. For instance, natural polymers were used to produce N/S-oxidized carbons through the co-carbonization of sulfonated lignin and chitosan, resulting in hierarchical structure enriched with SO_x and N functionalities. These electrodes provided capacitance of ~400 F g⁻¹ and energy densities close to ~10 Wh kg⁻¹, in addition to outstanding cycle life and flexibility in quasi-solid-state ECs⁴⁶.

Importantly, excessive incorporation of heteroatom-containing functional groups leads to carbon pore blockage, hence, diminishes their electrical conductivity as well as accelerates the electrolyte decomposition³⁹. Consequently, the judicious regulation of the amount/type of heteroatom-functionalities should be strictly controlled for the desired EC performance.

Intercalation pseudocapacitance happens when the insertion of the ions into the electrode surface (and sub-surface layers) is accompanied by charge transfer reactions but no crystallographic phase alteration is observed (**Figure 4 c**)²⁴. For instance, nanosized crystallites of Nb₂O₅ operating in non-aqueous medium displayed intercalation pseudocapacitance through the insertion of lithium ions and the redox activity of the Nb⁵⁺/Nb⁴⁺^{47,48}. On the other hand, the intercalation pseudocapacitance was not reported for the bulk-like Nb₂O₅⁴⁸. Interestingly, there are several factors that impact pseudocapacitance type, resulting in the differences in electrochemical behavior, e.g., interaction of ions with the electrode, nanostructuring of electrode, thin films. Also, a notable increase of the literature regarding the charge storage in electrode materials is observed, often described as pseudocapacitive, despite their actual battery-like characteristics^{49,50}. For that purpose, the terms intrinsic and extrinsic pseudocapacitance have been introduced²⁴. The intrinsic pseudocapacitance focuses on the material's own crystal structure (e.g., RuO₂·0.5H₂O⁵¹, MnO₂⁵²), while extrinsic pseudocapacitance refers to the tailoring the texture/structure of the material (e.g., nanostructured V₂O₅⁵³, LiCoO₂⁵⁴, Nb₂O₅⁴⁸, MoS₂⁵⁵, MXene Ti₂C⁵⁶).

Concluding, the pseudocapacitive materials are interesting for the improvement of the ECs metrics. Moreover, by exploiting the compositional and structural versatility of the electrode materials, there is a possibility to further extend the range of materials available for advanced energy storage devices.

References

- 1 Holze, R. in Supercapacitors – Materials, Systems, and Applications. *J Solid State Electrochem* **2015**, *19* (4), 1253–1253. <https://doi.org/10.1007/s10008-014-2718-2>
- 2 Conway, B. E. *Electrochemical Supercapacitors*; Springer US: Boston, MA, **1999**. <https://doi.org/10.1007/978-1-4757-3058-6>
- 3 Kötz, R.; Carlen, M. Principles and Applications of Electrochemical Capacitors. *Electrochimica Acta* **2000**, *45* (15), 2483–2498. [https://doi.org/10.1016/S0013-4686\(00\)00354-6](https://doi.org/10.1016/S0013-4686(00)00354-6)
- 4 Béguin, F.; Presser, V.; Balducci, A.; Frackowiak, E. Carbons and Electrolytes for Advanced Supercapacitors. *Advanced Materials* **2014**, *26* (14), 2219–2251. <https://doi.org/10.1002/adma.201304137>
- 5 Yang, N.; Yu, S.; Zhang, W.; Cheng, H.M.; Simon, P.; Jiang, X. Electrochemical Capacitors with Confined Redox Electrolytes and Porous Electrodes. *Advanced Materials* **2022**, *34* (34), 2202380. <https://doi.org/10.1002/adma.202202380>
- 6 Laheäär, A.; Przygocki, P.; Abbas, Q.; Béguin, F. Appropriate Methods for Evaluating the Efficiency and Capacitive Behavior of Different Types of Supercapacitors. *Electrochemistry Communications* **2015**, *60*, 21–25. <https://doi.org/10.1016/j.elecom.2015.07.022>
- 7 Mei, B.A.; Munteshari, O.; Lau, J.; Dunn, B.; Pilon, L. Physical Interpretations of Nyquist Plots for EDLC Electrodes and Devices. *The Journal of Physical Chemistry C* **2018**, *122* (1), 194–206. <https://doi.org/10.1021/acs.jpcc.7b10582>
- 8 Gittins, J. W.; Chen, Y.; Arnold, S.; Augustyn, V.; Balducci, A.; Brousse, T.; Frackowiak, E.; Gómez-Romero, P.; Kanwade, A.; Köps, L.; Jha, P. K.; Lyu, D.; Meo, M.; Pandey, D.; Pang, L.; Presser, V.; Rapisarda, M.; Rueda-García, D.; Saeed, S.; Shirage, P. M.; Ślesieński, A.; Soavi, F.; Thomas, J.; Titirici, M.-M.; Wang, H.; Xu, Z.; Yu, A.; Zhang, M.; Forse, A. C. Interlaboratory Study Assessing the Analysis of Supercapacitor Electrochemistry Data. *Journal of Power Sources* **2023**, *585*, 233637. <https://doi.org/10.1016/j.jpowsour.2023.233637>
- 9 Simon, P.; Gogotsi, Y. Perspectives for Electrochemical Capacitors and Related Devices. *Nature Materials* **2020**, *19* (11), 1151–1163. <https://doi.org/10.1038/s41563-020-0747-z>
- 10 Burke, A. F.; Zhao, J. Past, Present and Future of Electrochemical Capacitors: Technologies, Performance and Applications. *Journal of Energy Storage* **2021**, *35*, 102310. <https://doi.org/10.1016/j.est.2021.102310>
- 11 Favaro, M.; Jeong, B.; Ross, P. N.; Yano, J.; Hussain, Z.; Liu, Z.; Crumlin, E. J. Unravelling the Electrochemical Double Layer by Direct Probing of the Solid/Liquid Interface. *Nature Communications* **2016**, *7* (1), 12695. <https://doi.org/10.1038/ncomms12695>
- 12 Shao, H.; Wu, Y.C.; Lin, Z.; Taberna, P.L.; Simon, P. Nanoporous Carbon for Electrochemical Capacitive Energy Storage. *Chemical Society Reviews* **2020**, *49* (10), 3005–3039. <https://doi.org/10.1039/D0CS00059K>
- 13 Oldham, K. B. A Gouy–Chapman–Stern Model of the Double Layer at a (Metal)/(Ionic Liquid) Interface. *Journal of Electroanalytical Chemistry* **2008**, *613* (2), 131–138. <https://doi.org/10.1016/j.jelechem.2007.10.017>
- 14 Chapman, D.L.; A contribution to the theory of electrocapillarity. *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science* **1913**, *148*, 475–481. <https://doi.org/10.1080/14786440408634187>
- 15 Torrie, G. M.; Valleau, J. P. Electrical Double Layers. 4. Limitations of the Gouy-Chapman Theory. *The Journal of Physical Chemistry*. **1982**, *86* (16), 3251–3257. <https://doi.org/10.1021/j100213a035>

- 16 Stern, O. Zur Theorie Der Elektrolytischen Doppelschicht. *Zeitschrift für Elektrochemie und angewandte physikalische Chemie* **1924**, 30 (21–22), 508–516. <https://doi.org/10.1002/bbpc.192400182>
- 17 Lebègue, E. Allen J. Bard, Larry. R. Faulkner, Henry S. White: *Electrochemical Methods: Fundamentals and Applications*, 3rd Edition, Wiley. *Transition Metal Chemistry* **2023**, 48 (6), 433–436. <https://doi.org/10.1007/s11243-023-00555-6>
- 18 Zhang, L. L.; Zhao, X. S. Carbon-Based Materials as Supercapacitor Electrodes. *Chemical Society Reviews* **2009**, 38 (9), 2520–2531. <https://doi.org/10.1039/B813846J>
- 19 B. E. Conway. Transition from “Supercapacitor” to “Battery” Behavior in Electrochemical Energy Storage **1991** *Journal of the Electrochemical Society* 138 1539. <https://doi.org/10.1149/1.2085829>
- 20 Panchu, S. J.; Raju, K.; Swart, H. C. Emerging Two-Dimensional Intercalation Pseudocapacitive Electrodes for Supercapacitors. *ChemElectroChem* **2024**, 11 (15), e202300810. <https://doi.org/10.1002/celec.202300810>
- 21 Augustyn, V.; Simon, P.; Dunn, B. Pseudocapacitive Oxide Materials for High-Rate Electrochemical Energy Storage. *Energy Environmental Science* **2014**, 7 (5), 1597–1614. <https://doi.org/10.1039/C3EE44164D>
- 22 Frackowiak, E.; Béguin, F. Carbon Materials for the Electrochemical Storage of Energy in Capacitors. *Carbon* **2001**, 39 (6), 937–950. [https://doi.org/10.1016/S0008-6223\(00\)00183-4](https://doi.org/10.1016/S0008-6223(00)00183-4)
- 23 Łukaszewski, M.; Hubkowska, K.; Czerwiński, A. Electrochemical Absorption and Oxidation of Hydrogen on Palladium Alloys with Platinum, Gold and Rhodium. *Physical Chemistry Chemical Physics* **2010**, 12 (43), 14567–14572. <https://doi.org/10.1039/C0CP00542H>
- 24 Fleischmann, S.; Mitchell, J. B.; Wang, R.; Zhan, C.; Jiang, D.; Presser, V.; Augustyn, V. Pseudocapacitance: From Fundamental Understanding to High Power Energy Storage Materials. *Chemical Reviews* **2020**, 120 (14), 6738–6782. <https://doi.org/10.1021/acs.chemrev.0c00170>
- 25 Demarconnay, L.; Raymundo-Piñero, E.; Béguin, F. A Symmetric Carbon/Carbon Supercapacitor Operating at 1.6 V by Using a Neutral Aqueous Solution. *Electrochemistry Communications* **2010**, 12 (10), 1275–1278. <https://doi.org/10.1016/j.elecom.2010.06.036>
- 26 Slesinski, A.; Sroka, S.; Fic, K.; Frackowiak, E.; Menzel, J. Operando Monitoring of Local pH Value Changes at the Carbon Electrode Surface in Neutral Sulfate-Based Aqueous Electrochemical Capacitors. *ACS Applied Materials & Interfaces* **2022**, 14 (33), 37782–37792. <https://doi.org/10.1021/acsami.2c09920>
- 27 Vix-Guterl, C.; Frackowiak, E.; Jurewicz, K.; Friebe, M.; Parmentier, J.; Béguin, F. Electrochemical Energy Storage in Ordered Porous Carbon Materials. *Carbon* **2005**, 43 (6), 1293–1302. <https://doi.org/10.1016/j.carbon.2004.12.028>
- 28 Sugimoto, W.; Kizaki, T.; Yokoshima, K.; Murakami, Y.; Takasu, Y. Evaluation of the Pseudocapacitance in RuO₂ with a RuO₂/GC Thin Film Electrode. *Electrochimica Acta* **2004**, 49 (2), 313–320. <https://doi.org/10.1016/j.electacta.2003.08.013>
- 29 Patel, M. N.; Wang, X.; Slanac, D. A.; Ferrer, D. A.; Dai, S.; Johnston, K. P.; Stevenson, K. J. High Pseudocapacitance of MnO₂ Nanoparticles in Graphitic Disordered Mesoporous Carbon at High Scan Rates. *Journal of Materials Chemistry* **2012**, 22 (7), 3160–3169. <https://doi.org/10.1039/C1JM14513D>
- 30 Que, L.-F.; Yu, F.-D.; Wang, Z.-B.; Gu, D.-M. Pseudocapacitance of TiO₂-x/CNT Anodes for High-Performance Quasi-Solid-State Li-Ion and Na-Ion Capacitors. *Small* **2018**, 14 (17), 1704508. <https://doi.org/10.1002/sml.201704508>
- 31 Yan, W.; Dong, T.; Zhang, W.; Zheng, W. Clarifying the Origin of Pseudocapacitance from a Perspective of RuO₂. *Communications Chemistry* **2026**. <https://doi.org/10.1038/s42004-026-01964-1>

- 32 Conway, B. E.; Birss, V.; Wojtowicz, J. The Role and Utilization of Pseudocapacitance for Energy Storage by Supercapacitors. *Journal of Power Sources* **1997**, *66* (1), 1–14. [https://doi.org/10.1016/S0378-7753\(96\)02474-3](https://doi.org/10.1016/S0378-7753(96)02474-3)
- 33 Zheng, J. P.; Cygan, P. J.; Jow, T. R. Hydrous Ruthenium Oxide as an Electrode Material for Electrochemical Capacitors. *Journal of the Electrochemical Society* **1995**, *142* (8), 2699. <https://doi.org/10.1149/1.2050077>
- 34 Long, J. W.; Swider, K. E.; Merzbacher, C. I.; Rolison, D.R.; Voltammetric Characterization of Ruthenium Oxide-Based Aerogels and Other RuO₂ Solids: The Nature of Capacitance in Nanostructured Materials. *Langmuir*. **1999**, *15*, (3) <https://doi.org/10.1021/la980785a>
- 35 Vignesh, G.; Devendran, P.; Nallamuthu, N.; Sudhahar, S.; Kumar, P. S.; Kumar, M. K. Effects of Nitrogen, Sulphur, and Temperature Treatments on the Spectral, Structural, and Electrochemical Characteristics of Graphene Oxide for Energy Storage Applications. *Carbon Trends* **2023**, *11*, 100262. <https://doi.org/10.1016/j.cartre.2023.100262>
- 36 Abbas, Q.; Raza, R.; Shabbir, I.; Olabi, A. G. Heteroatom Doped High Porosity Carbon Nanomaterials as Electrodes for Energy Storage in Electrochemical Capacitors: A Review. *Journal of Science: Advanced Materials and Devices* **2019**, *4* (3), 341–352. <https://doi.org/10.1016/j.jsamd.2019.07.007>
- 37 Wang, X.; Sun, G.; Routh, P.; Kim, D.-H.; Huang, W.; Chen, P. Heteroatom-Doped Graphene Materials: Syntheses, Properties and Applications. *Chemical Society Reviews* **2014**, *43* (20), 7067–7098. <https://doi.org/10.1039/C4CS00141A>
- 38 Zhong, R.; Zhang, H.; Zhang, Y.; Yue, P.; Wu, X. KMnO₄-Assisted Synthesis of Hierarchical Porous Carbon with Ultrahigh Capacitance for Supercapacitor. *Journal of Energy Storage* **2022**, *51*, 104346. <https://doi.org/10.1016/j.est.2022.104346>
- 39 Wang, J.; Huo, T.; Zhao, Y.; Lu, R.; Wu, X. Recent Advances in Heteroatoms-Doped Porous Carbon Electrode Materials for Supercapacitors: A Review. *Journal of Energy Storage* **2025**, *110*, 115216. <https://doi.org/10.1016/j.est.2024.115216>
- 40 Réty, B.; Yiin, H.Y.; Matei Ghimbeu, C. Quantification of Activated Carbon Functional Groups and Active Surface Area by TPD-MS and Their Impact on Supercapacitor Performance. *Energy Storage Materials* **2024**, 103963. <https://doi.org/10.1016/j.ensm.2024.103963>
- 41 Raymundo-Piñero, E.; Kierzek, K.; Machnikowski, J.; Béguin, F. Relationship between the Nanoporous Texture of Activated Carbons and Their Capacitance Properties in Different Electrolytes. *Carbon* **2006**, *44* (12), 2498–2507. <https://doi.org/10.1016/j.carbon.2006.05.022>
- 42 Ghosh, S.; Barg, S.; Jeong, S. M.; Ostrikov, K. (Ken). Heteroatom-Doped and Oxygen-Functionalized Nanocarbons for High-Performance Supercapacitors. *Advanced Energy Materials* **2020**, *10* (32), 2001239. <https://doi.org/10.1002/aenm.202001239>
- 43 Lota, G.; Grzyb, B.; Machnikowska, H.; Machnikowski, J.; Frackowiak, E. Effect of Nitrogen in Carbon Electrode on the Supercapacitor Performance. *Chemical Physics Letters* **2005**, *404* (1), 53–58. <https://doi.org/10.1016/j.cplett.2005.01.074>
- 44 Ilnicka, A.; Skorupska, M.; Szkoda, M.; Zarach, Z.; Kamedulski, P.; Zielinski, W.; Lukaszewicz, J. P. Combined Effect of Nitrogen-Doped Functional Groups and Porosity of Porous Carbons on Electrochemical Performance of Supercapacitors. *Scientific Reports* **2021**, *11* (1), 18387. <https://doi.org/10.1038/s41598-021-97932-x>
- 45 Wang, T.; Wang, L.X.; Wu, D.L.; Xia, W.; Jia, D.Z. Interaction between Nitrogen and Sulfur in Co-Doped Graphene and Synergetic Effect in Supercapacitor. *Scientific Reports* **2015**, *5* (1), 9591. <https://doi.org/10.1038/srep09591>
- 46 Abbas, S. C.; Hua, Z.; Deng, Q.; Ahommed, M. S.; Guo, J.; Huang, H.; Ma, X.; Cao, S.; Ni, Y. Natural Polymers as Sustainable Precursors for Scalable Production of N/SO_x Doped Carbon Material Enabling High-Performance Supercapacitors. *EcoMat* **2024**, *6* (2), e12434. <https://doi.org/10.1002/eom2.12434>

- 47 Augustyn, V.; Come, J.; Lowe, M. A.; Kim, J. W.; Taberna, P. L.; Tolbert, S. H.; Abruna, H.D.; Simon, P.; Dunn, B. High-rate electrochemical energy storage through Li⁺ intercalation pseudocapacitance. *Nature Materials*. **2013**, *12*, 518-522 <https://doi.org/10.1038/nmat3601>
- 48 Come, J.; Augustyn, V.; Kim, J. W.; Rozier, P.; Taberna, P.-L.; Gogotsi, P.; Long, J. W.; Dunn, B.; Simon, P. Electrochemical Kinetics of Nanostructured Nb₂O₅ Electrodes. *Journal of the Electrochemical Society* **2014**, *161* (5), A718. <https://doi.org/10.1149/2.040405jes>
- 49 Gogotsi, Y.; Simon, P. True Performance Metrics in Electrochemical Energy Storage. *Science* **2011**, *334* (6058), 917–918. <https://doi.org/10.1126/science.1213003>
- 50 Brousse, T.; Bélanger, D.; Long, J. W. To Be or Not To Be Pseudocapacitive? *J. Electrochem. Soc.* **2015**, *162* (5), A5185. <https://doi.org/10.1149/2.0201505jes>
- 51 Zhan, C.; Jiang, D. Understanding the Pseudocapacitance of RuO₂ from Joint Density Functional Theory. *Journal of Physics: Condensed Matter* **2016**, *28* (46), 464004. <https://doi.org/10.1088/0953-8984/28/46/464004>
- 52 Guo, W.; Yu, C.; Li, S.; Wang, Z.; Yu, J.; Huang, H.; Qiu, J. Strategies and Insights towards the Intrinsic Capacitive Properties of MnO₂ for Supercapacitors: Challenges and Perspectives. *Nano Energy* **2019**, *57*, 459–472. <https://doi.org/10.1016/j.nanoen.2018.12.015>
- 53 Jain, A.; Manippady, S. R.; Tang, R.; Nishihara, H.; Sobczak, K.; Matejka, V.; Michalska, M. Vanadium Oxide Nanorods as an Electrode Material for Solid State Supercapacitor. *Scientific Reports* **2022**, *12*, (1), 21024. <https://doi.org/10.1038/s41598-022-25707-z>
- 54 Okubo, M.; Hosono, E.; Kim, J.; Enomoto, M.; Kojima, N.; Kudo, T.; Zhou H., Honma I. Nanosize Effect on High-Rate Li-Ion Intercalation in LiCoO₂ Electrode. *Journal of the American Chemical Society*. **2007** *129*, (23), 7444-7452 <https://doi.org/10.1021/ja0681927>
- 55 Tobis, M.; Elmanzalawy, M.; Choi, J.; Frąckowiak, E.; Fleischmann, S. Controlling Structure and Morphology of MoS₂ via Sulfur Precursor for Optimized Pseudocapacitive Lithium Intercalation Hosts. *Batteries & Supercaps* **2024**, *7* (11), e202400277. <https://doi.org/10.1002/batt.202400277>
- 56 Wang, X.; Kajiyama, S.; Iinuma, H.; Hosono, E.; Oro, S.; Moriguchi, I.; Okubo, M.; Yamada, A. Pseudocapacitance of MXene nanosheets for high-power sodium-ion hybrid capacitors, *Nature Communications*. **2015**, *6*, 6544. <https://doi.org/10.1038/ncomms7544>

Electrolytes used for ECs

3.1 General overview on EC electrolytes

The electrolyte is recognized as a crucial component in the advancement of electrochemical capacitors. It significantly affects the EC characteristics such as equivalent series resistance, lifespan, energy/power density as shown in **Figure 5**^{1,2}. The most important electrolyte properties include the ionic conductivity (to maximize power density, **Equation 4**), the electrochemical stability window (for high energy density, **Equation 5-6**), and the diameter of the solvated ions (to match the porosity of the electrode material)³.

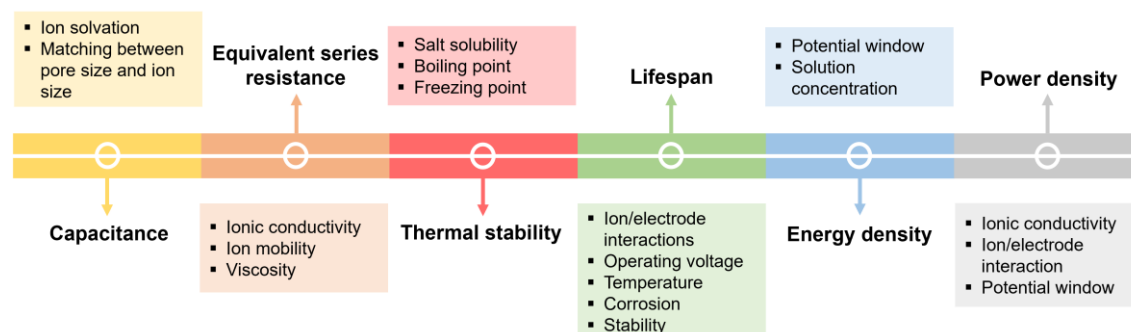


Figure 5 The effect of electrolyte characteristics on the EC performance. Adapted from reference¹.

Several types of electrolytes are currently employed in ECs, e.g., aqueous, organic, redox-active, gel polymers⁴. The classification of EC electrolytes is shown in **Figure 6**. Liquid electrolytes are divided into three subgroups: aqueous electrolytes (acids/bases, neutral salts, water-in-salt (WIS)), deep eutectic solvents (DES) and non-aqueous electrolytes (organic, ionic liquids (IL) and its mixtures). Solid state electrolytes are classified into gel polymer electrolytes (GE), dry solid-state polymer electrolytes (SPE),

and inorganic electrolytes. Additionally, redox-active electrolytes can be distinguished. EC electrolytes possess different characteristics, as summarized in **Table 1**.

Currently, the benchmark EC electrolyte is the organic salt tetraethylammonium tetrafluoroborate (TEABF₄) in acetonitrile (ACN) as a solvent⁵. It enables the EC to reach wide electrochemical stability window 2.5-3.0 V (high energy and power density), long lifespan, exceeding 1 000 000 cycles and wide temperature tolerance (-40 to 65°C)⁵⁻⁷. It makes the organic-based ECs perfect for the standard EC applications, i.e., grid management systems, automotive, but also for medical devices, robotics, or aerospace⁸⁻¹⁰. Nevertheless, organic electrolytes are highly moisture sensitive, the EC cell must be assembled under inert atmosphere requiring the rigorous drying of all the components (i.e., electrodes, separator), which substantially increase the manufacturing cost. Another disadvantage is their low ionic conductivity and high viscosity. Moreover, organic electrolytes (mainly solvents) are hazardous, flammable, volatile which make them problematic for the processing and recycling as well as the overall device safety.

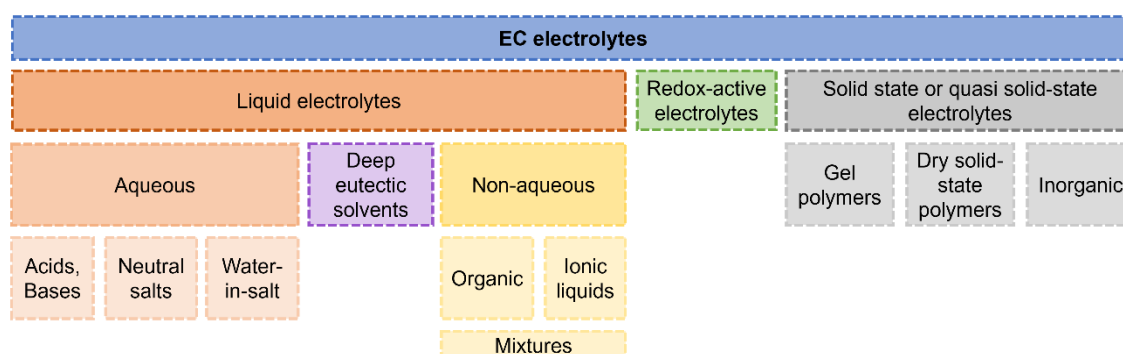


Figure 6 Classification of EC electrolytes.

Ionic liquids gain interest due to the possibility of expanding the electrochemical stability window, even above 3.5 V, which is much higher than for other types of the EC electrolytes¹¹. ILs do not contain any solvent and they are liquid in the room temperature. Various ILs can be applied in ECs, composed of cations, e.g., imidazolium, pyrrolidinium coupled with anions such as bis(trifluoromethanesulfonyl) imide or bis(fluorosulfonyl) imide¹². Notably, ILs are characterized by high electrochemical and thermal stability, alongside being non-flammable and non-volatile^{13,14}. ILs are more sustainable than certain organic-based electrolytes, but it is contingent upon their precise composition, as some ILs present issues about toxicity and recycling. On the other hand, ILs have some disadvantages. Their ionic conductivity is merely a few mS cm⁻¹ (compared with other electrolytes), hence, their enhanced viscosities impede the mobility of ions within the electrolyte¹³. Moreover, ILs are highly sensitive to traces of water, so they require a

Table 1 Summary of the liquid electrolytes characteristics: acids/bases, neutral salts, water-in-salt, deep eutectic solvents, organic, and ionic liquids.

Liquid Electrolyte	Acids, bases	Neutral salts	Water-in-salt	Deep eutectic solvents	Organic	Ionic liquids
Ionic conductivity at RT (mS cm ⁻¹)	~ 1000 ¹	~ 100 ¹⁵	~ 10-60 ¹	~ 1 ¹⁶	~ 20-60 ^{1,17}	~ 10 ¹
Viscosity (cP)	~0.7 ¹⁸	~0.9 ¹⁹	~7.5-28 ²⁰	~1750 ¹⁶	~1.5-66 ²¹	~41-219 ¹⁷
Voltage (V)	0.8-1.0 ^{1,22}	1.5-1.6 ¹⁵	2.0-3.0 ^{23,24}	1.7-2.2 ^{16,25}	2.5-2.8 ¹	>3.5 ^{12,26}
Capacitance (F g ⁻¹)	112-150 ^{27,28}	123 ²⁷	100 ²³	96 ¹⁶	110 ²⁹	140 ³⁰
Lifespan (floating hours)	15 ²⁷	120 ²⁷	170 ²⁰	200 ^{16,27}	1500 ⁶	200-500 ³¹
Assembly	Air	Air	Air	Air	Inert	Inert
Safety	High	High	High	High	Low	High
Price	Low	Low	Moderate	Moderate	High	Very high
Example	1M KOH, 1M H ₂ SO ₄	1M Li ₂ SO ₄ , 1M Na ₂ SO ₄	20m LiTFSI, <11m KOAc	Urea-choline chloride (2:1)	1M TEABF ₄ in ACN	[EMI] [TFSI], [EMIM] [BF ₄]

moisture free atmosphere during the cell preparation, increasing the cost. Notably, ILs are very expensive in terms of the synthesis and further purification, which limits their widespread application as EC electrolyte.

Aqueous electrolytes have been proposed to address the main issues of the organic medium. These electrolytes are characterized mainly by high ionic conductivity, low viscosity, environmental friendliness, safety, and cost-effectiveness¹. The EC cell can be assembled in the air atmosphere, further reducing the device cost. Nevertheless, the electrochemical stability window of EC operating in aqueous medium is very narrow (0.8-1.2 V) as it depends on the thermodynamic potential of water decomposition³².

Among aqueous electrolytes, the acids (e.g., H₂SO₄) and bases (e.g., KOH) offer very high ionic conductivity (even up to 1000 mS cm⁻¹)¹, which is at least one order of magnitude higher than that of non-aqueous electrolytes³³. It results in very high-power density of EC, but in turn much lower energy density. Unfortunately, acids and bases are highly corrosive, what diminishes the EC lifespan.

Neutral salt electrolytes such as 1M Li₂SO₄, 1M Na₂SO₄ have been widely studied due to the possibility of the electrochemical stability window extension up to 1.5-1.6 V¹⁵. Local

changes of pH (alkalization) in the bulk of porous carbon electrode during negative polarization are related to reversible H storage as well as to voltage range extension. Therefore, ECs based on neutral salt electrolytes can deliver much more energy than EC employing the acids/bases³⁴. Importantly, neutral salts are much safer and less corrosive than the acids/bases. Regardless the advancements with neutral salt aqueous electrolytes, the operating voltage and lifespan remains unsatisfactory to compete with ECs utilizing non-aqueous electrolytes.

Then, highly concentrated aqueous neutral salts solutions called “water-in-salt” have been introduced³⁵. Several WIS electrolytes, e.g., 20m (molal) lithium bis(trifluoromethanesulfonyl) imide (LiTFSI)³⁶, 17m sodium perchlorate (NaClO₄)³⁷ were tested to improve the EC metrics. The ultra-high concentration reduced the water activity by strongly coordinating water molecules to ions and disrupting the hydrogen-bond network, thereby extending the electrochemical stability window (2-3 V)^{1,4}. The operating voltage of EC, when WIS electrolyte is applied exceeds that of acid/bases and neutral salt electrolytes, moreover can compete with benchmark organic electrolytes⁴. The ionic conductivity and viscosity are much lower than these observed for other aqueous electrolytes, but generally improved when compared to non-aqueous electrolytes. Despite the significant enhancement in the voltage window, the economic and environmental issues that impede practical application of WIS remain unaddressed. Preparation of WIS electrolytes requires substantial amount of the salt, which increases the total price of the device³⁸. Furthermore, the salt should have a high solubility, what narrows down the selection of the possible salts for WIS electrolyte preparation. Moreover, some salts, e.g., LiTFSI has limited large scale-availability, while NaClO₄ raise environmental concerns³⁸.

Lately, a new type of EC liquid electrolyte has been investigated, i.e., deep eutectic solvents¹⁶. DES are mixtures composed of minimum two constituents, hydrogen bond donor (HBD), and hydrogen bond acceptor (HBA), in a specified molar ratio, exhibiting a reduced melting point to that of the individual components³⁹. Various compounds can be considered as HBD (e.g., urea, glycerol, ethylene glycol) and HBA (e.g., choline chloride, tetramethylammonium chloride)⁴⁰. DES are characterized by the similar characteristics to that of ILs, but being more sustainable and cost-effective^{1,39}. For instance, reline (mixture of choline chloride and urea in a molar ratio 1:2) was proposed as EC electrolyte¹⁶. The operating voltage was extended up to 2.2 V, as the result of negligible presence of water¹⁶. The reline-based EC had improved energetic metrics referring to those of ILs and neutral salt electrolytes^{1,16}. Notably, EC cell assembly does not require inert atmosphere, contrary to ILs^{16,41}. Also, the anti-corrosive character of reline towards

stainless-steel current collectors was proven²⁷. Nevertheless, the reported power density is relatively low, due to the very low ionic conductivity of DES ($\sim 1 \text{ mS cm}^{-1}$) and very high viscosity ($\sim 1000 \text{ cP}$)¹⁶. To solve that problem, small quantity of water was added to DES (1 wt.%), slightly improving the ionic conductivity and viscosity^{16,27}.

Solid-state electrolytes attracted the main interest due to the growing demand for flexible electric devices, e.g., wearable electronics, portable devices, and microelectronics^{2,42}. The greatest advantage of these electrolytes is the limited leakage out of the device (solid or quasi-solid form), what significantly improves safety compared to other types of electrolytes^{43,44}. Importantly, solid-state electrolytes can serve as well as a separator, which is preventing short circuiting of electrodes and simplifying the EC manufacturing⁴⁵. Thus far, the predominant type of solid-state electrolytes used in ECs have been gel electrolytes, with less research devoted to dry solid-state electrolytes (e.g., poly(ethylene oxide)-PEO/LiCl) and inorganic materials (e.g., $\text{Li}_2\text{S-P}_2\text{S}_5$)². Typically, GE are composed of polymeric matrix (e.g., poly(vinyl alcohol) – PVA, PEO) and the aqueous electrolyte (e.g., KOH, Na_2SO_4) or a conducting salt dissolved in the solvent⁴⁶. On the other hand, SPEs are fully composed of polymers, and salts, thus do not require any solvents (e.g., PEO/LiCl)⁴⁴. Generally, GEs are characterized by the low ionic conductivity, in the range of $0.01\text{-}10 \text{ mS cm}^{-1}$ ^{47,48}. In contrast, GE provides higher ionic conductivity than SPE due to the presence of liquid phase, and it is a main reason for its broader application as EC electrolyte^{47,49}. It should be emphasized that GE contribute to the reduced leakage current and self-discharge of the ECs⁵⁰. On the other hand, GE may suffer from the narrow operating voltage, especially if the water is used as a solvent⁴⁶. Another concern of GEs is their mechanical strength, which depends on the utilized polymeric matrix and the solvent, limiting the contact surface area with the porous electrode material. It impacts the EC metrics, especially ESR, rate performance, and capacitance². Furthermore, GEs widely utilize synthetic polymers, which lack in terms of environmental friendliness, and the use of biopolymers is still not widespread.

Redox-active electrolytes have been proposed as the EC electrolytes due to the additional pseudocapacitance contribution from the redox species at the electrode/electrolyte interface². Among possible redox active pairs, iodides are the most environmentally friendly and cost-effective. Moreover, the iodides present good solubility, high ionic conductivity and rich variety of oxidation states. For instance, the enormously high capacitance of the positive electrode ($\sim 1800 \text{ F g}^{-1}$) was reported, when 1M KI (iodide/iodine) served as EC electrolyte⁵¹. Nevertheless, the capacitance of the full device is restricted by the electrode with lower capacitance (**Equation 2**), thus, finally

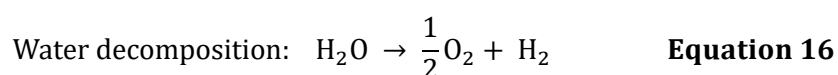
was significantly reduced. However, the improvement of the total EC capacitance is still substantial, i.e., two-fold higher than those reported for acid-based EC⁵¹. It has to be considered that the redox reactions occur upon the selected pH. It is important for iodides, especially when added to another electrolytic solution⁵². The shift of the pH into the more alkaline pH causes the formation of insoluble polyiodides, that block the porosity of the positive electrode, thus, worsen the EC performance⁵².

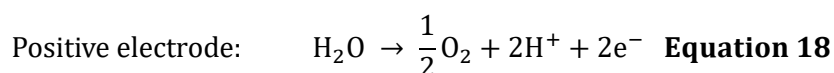
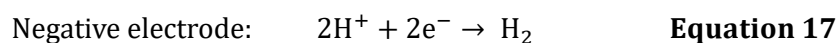
Noteworthy, there is no ideal EC electrolyte. Each type of the electrolyte possesses distinct advantages and disadvantages; thus, selection must be tailored to the specific application and the electrode material utilized. Considering, the scope of this thesis, i.e., sustainability, cost-effectiveness, safety as well as the physicochemical parameters that influence the energetic metric and lifespan of EC, the main importance is given to the aqueous electrolytes (acids/bases, neutral salts, water-in-salt), redox-active electrolytes, and gel electrolytes, which are in-detail characterized below.

3.2 Aqueous electrolytes

3.2.1 Acids, bases

The initial aqueous electrolytes utilized for the ECs are based on the acid (e.g., H₂SO₄) or alkali (e.g., KOH)⁵³ solutions. These electrolytes are characterized by the high ionic conductivity as well as low viscosity among all EC electrolytes, as summarized in **Table 1**. These characteristics are ideal for the high-power ECs³. Also, they are inexpensive, the device can be assembled in the air atmosphere, and they do not require toxic solvents, contrary to the organic electrolytes⁵⁴. For instance, high capacitance was reported for the carbon-based ECs operating in 1M H₂SO₄ (150 F g⁻¹) and 1M KOH (112 F g⁻¹)²⁸. The enhanced capacitance in acidic medium is associated with the reversible reactions of the surface functional groups of carbon electrodes with the hydrogen protons⁵⁵. Nevertheless, their operating voltage is narrow, limited to the thermodynamical decomposition of water (~1.23 V), which in practice is even lower ~0.8-1.0 V⁵⁶. At the negative electrode, hydrogen is generated by the hydrogen evolution reaction, while at the positive electrode, water is decomposed into oxygen *via* the oxygen evolution reaction, as defined by **Equations 16-18**²:





These reactions cause the aging of the electrodes, and consequently they shorten the EC's cycle life. Another issue of the acids and bases is their strong corrosiveness towards the stainless-steel collectors, mainly accelerated by the water splitting²⁷. Importantly, corrosion of the EC current collectors has been identified as the one of critical reasons for the reduced lifespan⁵⁷. That is why, usually the current collectors made of noble metals, (e.g., gold) are utilized with acidic electrolyte.

3.2.2 Neutral salts

To overcome the issues of highly corrosive character of acids/bases, as well as the narrow electrochemical stability window, electrolytes with neutral pH have been investigated³. Among them, 1M Li_2SO_4 ^{15,58}, 1M Na_2SO_4 ⁵⁹, 1M LiNO_3 ⁶⁰ have drawn particular attention. The carbon-based EC voltage values were extended up to 1.5-1.6 V due to the application of neutral salt electrolyte^{15,34}. Importantly, the hydrogen storage within the microporous texture of the carbon electrode enabled neutral salt-based ECs to function beyond the thermodynamic potential of water splitting. The local increase of the pH at the electrode/electrolyte surface is explained by the generation of OH^- during the hydrogen electrosorption (**Equation 15**). It induces a modification of the Nernst potential for hydrogen evolution, thereby altering the hydrogen evolution overpotential³⁴. Even though, neutral salt electrolytes particularly improved the operating voltage, safety, and EC lifespan (from ~15 floating hours for 1M KOH to 120 floating hours for the 1M Li_2SO_4), the corrosion of the stainless-steel current collector was still problematic²⁷. Therefore, the further development of neutral salt electrolytes should be oriented towards the effective protection of the positive electrode against oxidation¹⁵.

3.2.3 Water-in-salt

Recently, novel high-concentration aqueous salt solutions, referred to as water-in-salt have been introduced. Such electrolytes are restricted by the mass ($m_{\text{salt}}/m_{\text{water}}$)

and/or volume ($V_{\text{salt}}/V_{\text{water}}$) ratio above 1⁶¹. Notably, WIS electrolytes outperform acids/bases and neutral salt electrolytes in the terms of the operating voltage. WIS electrolytes enable the extension of electrochemical stability window up to 3 V, which is comparable with organic electrolytes²⁴. It is possible due to extremely high-concentrated solutions, where the binding of water molecules is diminished *via* the breaking of hydrogen bonds¹. It results in suppression of hydrogen evolution and electrode oxidation⁶². The first reported WIS electrolyte was 20m LiTFSI⁶², thus, further it was the most investigated electrolyte using advanced physicochemical and electrochemical techniques. For instance, Raman spectroscopy was utilized for the investigation of various concentrations of LiTFSI ranging from 1 to 21m³⁵. It was observed that the stretching modes of water were decreased and a peak referred to the hydration of Li⁺ ions was growing with the increase of the solution concentration. This suggests that water molecules are primarily engaged in the solvation of Li⁺ cations, while the quantity of unbound water molecules is reduced³⁵.

Furthermore, it was proved by the thermogravimetric analysis that the diminished sorption of water on the positive carbon electrode origin from the low hydration degree of Li⁺ cations. Consequently, the TFSI⁻ anions are adsorbed and stored within the porosity of positive electrode, resulting in a shift of the oxygen evolution potential³⁶. Through the molecular dynamics (MD) it was reported that the fraction of free water molecules decreases by nearly 50% (from 5 to 21m LiTFSI), emphasizing the role of water in the solvation of Li⁺ cations when the solution concentration rises⁶².

Even though, the improvement in the electrochemical stability window was achieved for the LiTFSI systems, some of the economic and environmental concerns are still unresolved³⁸. Importantly, the type and the amount of the salt needed for the formulation of the WIS solution should be considered. For instance, preparation of the 1 L of the 20m LiTFSI requires approximately 5 times more lithium in comparison to the 1m LiTFSI³⁸. Additionally, lithium is the one of the rarest elements in the Earth's crust. Therefore, a diverse range of other WIS electrolytes has been examined and utilized in ECs, e.g., 8m NaTFSI⁶³, 17m NaClO₄³⁷, 11-27m KOAc^{64,65}.

3.3 Gel electrolytes

Gel electrolytes are currently the most thoroughly investigated electrolytes owing to their elevated ionic conductivity (compared to other solid-state electrolytes) and enhanced safety (preventing the leakage out of the device). Also, GEs offer possibility to operate simultaneously as EC electrolyte and separator. GEs contain the polymer host and an aqueous electrolyte or a conductive salt dissolved in a solvent. Notably, the gels that incorporate water are called as hydrogels⁶⁶. The polymer works as a matrix that can shrink/swell by the solvent, with ions being transported in the solvent rather than within the polymer phase². GEs, while predominantly liquid, exhibit solid-like behavior owing to a continuous three-dimensional network extending through the liquid⁶⁷. There are two ways of the preparation of GEs, through the physical and the chemical crosslinking. The physical crosslinking involves the connection of the polymeric chains through the electrostatic links, hydrogen bonds, or chain entanglements. On the contrary, chemical crosslinking requires formation of covalent bonds⁶⁸. Importantly, the properties of GEs depend on the structure of the polymeric network that constitutes the gel, the interactions between the polymeric network/solvent, and the type of the salt. Typically, salt supplies free ions that contribute to the increase of ionic conductivity, while the solvent facilitates ion solvation as well as further enhances the ionic conductivity. The polymeric matrix provides the mechanical stability by increasing the electrolyte's viscosity. Therefore, it is highly recommended to utilize the aqueous medium with the high mobility of the ions, and the high ionic conductivity even though the electrochemical stability window is narrow⁶⁹.

Various polymers can be used in GE, including poly(ethylene oxide), poly(vinyl chloride) (PVC), poly(acrylic acid), poly(vinylidene fluoride), poly(methyl methacrylate)^{4,70}. Currently, PVA is the most used polymer due to its facile preparation, mechanical strength, chemical stability, hydrophilicity, and possibility to form transparent films⁴. For instance, GE, which also served as separator was prepared using PVA and Na₂SO₄. The carbon-based EC based on the PVA-Na₂SO₄ GE reached 1.8 V operating window outperforming the liquid Na₂SO₄⁷¹. Another GE composed of PVA, Li₂SO₄ and IL (1-butyl-3-methylimidazolium trifluoromethanesulfonate) exhibited high ionic conductivity (~13 mS cm⁻¹), outstanding mechanical and thermal stability. The electrochemical stability window was increased up to 2 V, and the capacitance of carbon-based EC reached 117 F g⁻¹⁷².

Nevertheless, the synthetic polymers (i.e., PVA) lack in terms of environmental friendliness. That is why, a wide group of biopolymers, e.g., cellulose, lignin, chitin, alginate, agar and its derivatives (e.g., carboxymethylcellulose, lignosulfonate, chitosan) are explored for the preparation of GE^{73,74}. *Zallouz et al.* proposed a flexible supercapacitor employing hydrogel (chitosan/KOH), that reached high ionic conductivity (10 mS cm⁻¹) and elevated mechanical integrity⁷⁵. Nevertheless, the operating voltage was limited up to 0.8 V⁷⁵. *Muddasar et al.* proposed hydrogel composed of lignin/PEGDGE/KOH⁷⁶. The high swelling capacity and flexibility confirmed by stable capacitance under bending and twisting was reported⁷⁶. On the other hand, the hydrogel was characterized by low ionic conductivity and voltage limitation (1.0 V)⁷⁶. Another work was reported on the supercapacitor based on lithium alginate/lithium acetate (LiOAc) as a gel electrolyte⁷⁷. The high operating voltage (1.8 V), and improved flame-retardant characteristics (oxygen index of 35%) were noted⁷⁷. Nonetheless, the reduced mechanical strength at high salt concentration was observed⁷⁷.

3.4 Redox-active electrolytes

The improvement of the EC characteristics can be achieved not only through the pseudocapacitive electrode materials (**Chapter 2.2.2**), but also due to the use of redox-active electrolytes³. The presence of redox species boosts of the EC performance⁴⁶. Importantly, the tailoring of the texture/structure of electrode material has to be taken into account, since the redox reactions are occurring at the electrode/electrolyte interface³.

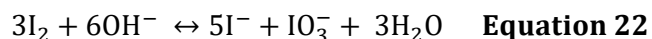
Several redox pairs were considered e.g., iodine/iodide⁷⁸, bromine/bromide⁷⁹, quinone/hydroquinone⁸⁰, thiocyanogen/thiocyanate⁸¹ for EC application. Among them, aqueous solutions with I₂/2I⁻ have recently surpassed others in application⁸². For instance, it was proved that carbon-based EC operating in 1M KI exhibited almost doubled capacitance, compared with the system operating in 1M H₂SO₄⁵¹. The main reaction that occurs on the positive electrode can be described using **Equation 19**⁵¹:



To further advance the use of redox activity of iodide/iodine, *Menzel et al.* tested different molar concentrations of NaI⁸³. The increase of iodide concentration impacted the potential range of the positive electrode, leading to the enhancement of the capacitance

from 198 F g⁻¹ (0.25M NaI) to 272 F g⁻¹ (2M NaI)⁸³. *Kruner et al.* investigated the EC with higher concentration of KI (6M) and porous carbon electrodes⁸⁴. It was found that the redox active electrolyte combined with highly porous carbon enhanced the capacitance to 493 F g⁻¹, comparing to 127 F g⁻¹ reached in 1M Na₂SO₄⁸⁴. Consequently, the ECs operating with aqueous iodides solutions present superior capacitance, but a narrow operating voltage (0.8 - 1.2 V)⁸².

Recently, it has been recommended to utilize bi-functional aqueous electrolytes developed by combining redox pair (to achieve high capacitance) with supportive neutral salt electrolyte (to extend electrochemical stability window)^{63,85,86}. For instance, the additive of 0.5M KI to 1M Li₂SO₄ resulted in high overpotential of hydrogen evolution at the negative electrode, thus 1.6 V could be achieved⁸⁶. At the same time, the two-fold increased capacitance was maintained for the neutral salt electrolyte with redox pair additive (similarly to the EC operating in KI solution)⁸². Even though, the iodide/iodine redox pair enhances significantly the capacitance, the EC lifespan is still problematic. It was found that polyiodide solid-state deposits (i.e., I₃⁻, I₅⁻) block the access to the microporosity of the positive electrode, according to the **Equations 20-22**^{87,88}.



Importantly, the potential of redox reactions is influenced by the pH and the concentration of the solution⁸⁸. According to the *Pourbaix* diagram of iodide species, a higher pH shifts the redox activity from iodine (I₂) to polyiodides (I₃⁻, I₅⁻), and iodate (IO₃⁻). Moreover, the further salt precipitation results from the limited solubility of iodate⁵². The EC lifespan can be improved either by keeping the pH values below 8 which eliminates solid state iodate formation⁵².

References

- 1 Azmi, S.; Klimek, A.; Frackowiak, E. Why Electrochemical Capacitor Electrolytes Should Not Be Ignored? *Electrochimica Acta* **2023**, 452, 142347. <https://doi.org/10.1016/j.electacta.2023.142347>
- 2 Zhong, C.; Deng, Y.; Hu, W.; Qiao, J.; Zhang, L.; Zhang, J. A Review of Electrolyte Materials and Compositions for Electrochemical Supercapacitors. *Chemical Society Reviews*. **2015**, 44 (21), 7484–7539. <https://doi.org/10.1039/C5CS00303B>

- 3 Béguin, F.; Presser, V.; Balducci, A.; Frackowiak, E. Carbons and Electrolytes for Advanced Supercapacitors. *Advanced Materials* **2014**, *26* (14), 2219–2251. <https://doi.org/10.1002/adma.201304137>
- 4 Lu, J.; Zhang, J.; Wang, X.; Zhang, J.; Tian, Z.; Zhu, E.; Yang, L.; Guan, X.; Ren, H.; Wu, J.; Li, X.; Wang, G. A Review of Advanced Electrolytes for Supercapacitors. *Journal of Energy Storage* **2024**, *103*, 114338. <https://doi.org/10.1016/j.est.2024.114338>
- 5 Patil, I. M.; Burton, T.; Ladam, A.; Fantini, S.; Balducci, A. Electrochemical Performance of Electrochemical Double Layer Capacitors Containing Pyrrolidinium and Ammonium Fluorosulfonyl Imide in Acetonitrile-Based Electrolytes. *Electrochimica Acta* **2025**, *525*, 146133. <https://doi.org/10.1016/j.electacta.2025.146133>
- 6 Skeleton, Supercapacitors data sheet (accessed: **2026-05-07**) <https://www.skeletontech.com/En/Skelcap-Supercapacitors>
- 7 Azaïs, P.; Duclaux, L.; Florian, P.; Massiot, D.; Lillo-Rodenas, M.-A.; Linares-Solano, A.; Peres, J.-P.; Jehoulet, C.; Béguin, F. Causes of Supercapacitors Ageing in Organic Electrolyte. *Journal of Power Sources* **2007**, *171* (2), 1046–1053. <https://doi.org/10.1016/j.jpowsour.2007.07.001>
- 8 Simon, P.; Gogotsi, Y. Perspectives for Electrochemical Capacitors and Related Devices. *Nature Materials*. **2020**, *19* (11), 1151–1163. <https://doi.org/10.1038/s41563-020-0747-z>
- 9 Acharjee, A.; Saha, B. Organic Electrolytes in Electrochemical Supercapacitors: Applications and Developments. *Journal of Molecular Liquids* **2024**, *400*, 124487. <https://doi.org/10.1016/j.molliq.2024.124487>
- 10 Miller, J. R. Market and Applications of Electrochemical Capacitors. In *Supercapacitors*; John Wiley & Sons, Ltd, **2013**; pp 509–526. <https://doi.org/10.1002/9783527646661.ch14>
- 11 Wang, Y.; Xue, K.; Zhang, X.; Zhang, X.; Ma, P.; Yang, B.; Xu, S.; Lang, J. High-Voltage Electrochemical Double Layer Capacitors Enabled by Polymeric Ionic Liquid. *Electrochimica Acta* **2023**, *441*, 141829. <https://doi.org/10.1016/j.electacta.2023.141829>
- 12 Wang, G.; Zhang, L.; Zhang, J. A Review of Electrode Materials for Electrochemical Supercapacitors. *Chemical Society Reviews*. **2012**, *41* (2), 797–828. <https://doi.org/10.1039/C1CS15060J>
- 13 Kwon, H.-N.; Jang, S.-J.; Kang, Y. C.; Roh, K. C. The Effect of ILs as Co-Salts in Electrolytes for High Voltage Supercapacitors. *Sci Rep* **2019**, *9* (1), 1180. <https://doi.org/10.1038/s41598-018-37322-y>
- 14 Soavi, F.; Mastragostino, M.; Supercapacitors | Ionic Liquids Electrolytes. *Encyclopedia of Electrochemical Power Sources (Second Edition)*. **2009**, 445–455. <https://doi.org/10.1016/B978-0-323-96022-9.00367-4>
- 15 Fic, K.; Płatek, A.; Piwek, J.; Menzel, J.; Ślesiński, A.; Bujewska, P.; Galek, P.; Frackowiak, E. Revisited Insights into Charge Storage Mechanisms in Electrochemical Capacitors with Li₂SO₄-Based Electrolyte. *Energy Storage Materials* **2019**, *22*, 1–14. <https://doi.org/10.1016/j.ensm.2019.08.005>
- 16 Azmi, S.; Koudahi, M. F.; Frackowiak, E. Reline Deep Eutectic Solvent as a Green Electrolyte for Electrochemical Energy Storage Applications. *Energy Environmental Science* **2022**. <https://doi.org/10.1039/D1EE02920G>
- 17 Galek, P.; Slesinski, A.; Fic, K.; Menzel, J. Peculiar Role of the Electrolyte Viscosity in the Electrochemical Capacitor Performance. *Journal of Materials Chemistry A* **2021**, *9* (13), 8644–8654. <https://doi.org/10.1039/D0TA11230E>
- 18 Srinivasan, M. K.; Prasad, B. Viscosity and Density of Aqueous Solutions of Sulphuric Acid at 35° C. *Transactions of the Faraday Society*. **1939**, *35* (0), 374–378. <https://doi.org/10.1039/TF9393500374>

- 19 Abdulagatov, I. M.; Zeinalova, A.; Azizov, N. D. Viscosity of Aqueous Na₂SO₄ Solutions at Temperatures from 298 to 573 K and at Pressures up to 40 MPa. *Fluid Phase Equilibria* **2005**, 227 (1), 57–70. <https://doi.org/10.1016/j.fluid.2004.10.028>
- 20 Klimek, A.; Amro, L.; Pakkang, N.; Matei Ghimbeu, C.; Frackowiak, E.; Suzuki, S. Lignin as a Precursor of a Gel Electrolyte and Salt Templated Carbon for Sustainable Electrochemical Capacitors. *Green Chemistry* **2026**, 28 (9), 4225–4242. <https://doi.org/10.1039/D5GC05533D>
- 21 Shan, Y.; Yuan, X.; Zhang, J.; Fu, Z.; Huang, M.; Liang, Z. Establishing Viscosity-Involved Formula of Mass Transfer Coefficient for Aqueous Organic Redox Flow Battery. *Chemical Engineering Science* **2025**, 318, 122164. <https://doi.org/10.1016/j.ces.2025.122164>
- 22 González, A.; Goikolea, E.; Barrena, J. A.; Mysyk, R. Review on Supercapacitors: Technologies and Materials. *Renewable and Sustainable Energy Reviews* **2016**, 58, 1189–1206. <https://doi.org/10.1016/j.rser.2015.12.249>
- 23 Zallouz, S.; Dentzer, L.; Matei Ghimbeu, C. Carbon Capacitors Operating at 1.8 V Based on Concentrated Aqueous Electrolytes: Impacts of the Electrolyte Concentration and Carbon Properties. *ACS Applied Energy Materials* **2024**, 7 (4), 1448–1460. <https://doi.org/10.1021/acsaem.3c02593>
- 24 Gomez Vazquez, D.; Ingenmey, J.; Trapp, K.; Ciliak, D.; Salanne, M.; Lukatskaya, M. R. Extended Stability Window in Water-in-Salt Electrolytes: Understanding the Origins. *Journal of American Chemical Society* **2025**, 147 (39), 35953–35961. <https://doi.org/10.1021/jacs.5c12989>
- 25 Parejo-Tovar, A.; Béguin, F. The NaClO₄-Water Eutectic Electrolyte for Environmentally Friendly Electrical Double-Layer Capacitors Operating at Low Temperature. *Energy Storage Materials* **2024**, 69, 103387. <https://doi.org/10.1016/j.ensm.2024.103387>
- 26 Venâncio, R.; da Silva, D. A. C.; Borges, L. O.; Silva, I. A.; Da Silva, L. M.; Doubek, G.; Siqueira, L. J. A.; Zanin, H. High Performance of Supercapacitors Containing an Ionic Liquid Electrolyte by Means of Electrochemical and Computational Studies. *Electrochimica Acta* **2025**, 535, 146569. <https://doi.org/10.1016/j.electacta.2025.146569>
- 27 Azmi, S.; Klimek, A.; Frackowiak, E. Anticorrosive Performance of Green Deep Eutectic Solvent for Electrochemical Capacitor. *Chemical Engineering Journal* **2022**, 444, 136594. <https://doi.org/10.1016/j.cej.2022.136594>
- 28 Taer, E.; Febriyanti, F.; Apriwandi; Taslim, R.; Agustino; Sinta Mustika, W. Investigation of H₂SO₄ and KOH Aqueous Electrolytes on the Electrochemical Performance of Activated Carbon Derived from Areca Catechu Husk. *Journal of Physics: Conference Series* **2021**, 1940 (1), 012033. <https://doi.org/10.1088/1742-6596/1940/1/012033>
- 29 Bichat, M. P.; Raymundo-Piñero, E.; Béguin, F. High Voltage Supercapacitor Built with Seaweed Carbons in Neutral Aqueous Electrolyte. *Carbon* **2010**, 48 (15), 4351–4361. <https://doi.org/10.1016/j.carbon.2010.07.049>
- 30 Rennie, A. J. R.; Martins, V. L.; Torresi, R. M.; Hall, P. J. Ionic Liquids Containing Sulfonium Cations as Electrolytes for Electrochemical Double Layer Capacitors. *Journal of Physical Chemistry C* **2015**, 119 (42), 23865–23874. <https://doi.org/10.1021/acs.jpcc.5b08241>
- 31 Dagousset, L.; Pognon, G.; Nguyen, G. T. M.; Vidal, F.; Jus, S.; Aubert, P.-H. Electrochemical Characterisations and Ageing of Ionic Liquid/ γ -Butyrolactone Mixtures as Electrolytes for Supercapacitor Applications over a Wide Temperature Range. *Journal of Power Sources* **2017**, 359, 242–249. <https://doi.org/10.1016/j.jpowsour.2017.05.068>
- 32 Saha, M.; Kumar, A.; Kanaoujiya, R.; Behera, K.; Trivedi, S. A Comprehensive Review of Novel Emerging Electrolytes for Supercapacitors: Aqueous and Organic

- Electrolytes Versus Ionic Liquid-Based Electrolytes. *Energy Fuels* **2024**, *38* (10), 8528–8552. <https://doi.org/10.1021/acs.energyfuels.4c00685>
- 33 Galiński, M.; Lewandowski, A.; Stępnia, I. Ionic Liquids as Electrolytes. *Electrochimica Acta* **2006**, *51* (26), 5567–5580. <https://doi.org/10.1016/j.electacta.2006.03.016>
 - 34 Slesinski, A.; Sroka, S.; Fic, K.; Frackowiak, E.; Menzel, J. Operando Monitoring of Local pH Value Changes at the Carbon Electrode Surface in Neutral Sulfate-Based Aqueous Electrochemical Capacitors. *ACS Applied Materials & Interfaces* **2022**, *14* (33), 37782–37792. <https://doi.org/10.1021/acsami.2c09920>
 - 35 Yamada, Y.; Usui, K.; Sodeyama, K.; Ko, S.; Tateyama, Y.; Yamada, A. Hydrate-Melt Electrolytes for High-Energy-Density Aqueous Batteries. *Nat Energy* **2016**, *1* (10), 16129. <https://doi.org/10.1038/nenergy.2016.129>
 - 36 Pamet , E.; Beguin, F. Effect of Salt Concentration in Aqueous LiTFSI Electrolytes on the Performance of Carbon-Based Electrochemical Capacitors. *Electrochimica Acta* **2021**, *389*, 138687. <https://doi.org/10.1016/j.electacta.2021.138687>
 - 37 Gharouel, S.; B guin, F. Revisiting the Performance of Electrical Double-Layer Capacitors Implementing a Sodium Perchlorate Water-in-Salt Electrolyte. *Electrochimica Acta* **2023**, *450*, 142212. <https://doi.org/10.1016/j.electacta.2023.142212>
 - 38 Lukatskaya, M. R.; Feldblyum, J. I.; Mackanic, D. G.; Lissel, F.; Michels, D. L.; Cui, Y.; Bao, Z. Concentrated Mixed Cation Acetate “Water-in-Salt” Solutions as Green and Low-Cost High Voltage Electrolytes for Aqueous Batteries. *Energy Environmental Science* **2018**, *11* (10), 2876–2883. <https://doi.org/10.1039/C8EE00833G>
 - 39 Abbott, A. P.; Capper, G.; Davies, D. L.; Rasheed, R. K.; Tambyrajah, V. Novel Solvent Properties of Choline Chloride/Urea Mixtures. *Chem. Commun.* **2003**, No. 1, 70–71. <https://doi.org/10.1039/B210714G>
 - 40 Smith, E. L.; Abbott, A. P.; Ryder, K. S. Deep Eutectic Solvents (DESs) and Their Applications. *Chemical Reviews* **2014**, *114* (21), 11060–11082. <https://doi.org/10.1021/cr300162p>
 - 41 Juli o, D.; Xavier, M.; Mascarenhas, X. Deep Eutectic Solvents: Viable Sustainable Electrolytes for Supercapacitors. *Materials Today Energy* **2024**, *42*, 101432. <https://doi.org/10.1016/j.mtener.2023.101432>
 - 42 Bhat, V. S.; Shivanna, J. M.; Shetty, A.; Molahalli, V.; Krishnan, S. G.; Sahoo, S.; Pai, R. K.; Aminabhavi, T. M.; Hegde, G. Flexible Supercapacitors and Solid-State Electrolytes: A Perspective on the Key to Flexibility. *Energy Fuels* **2025**, *39* (35), 16737–16767. <https://doi.org/10.1021/acs.energyfuels.5c00973>
 - 43 Taniki, R.; Matsumoto, K.; Nohira, T.; Hagiwara, R. All Solid-State Electrochemical Capacitors Using *N,N*-Dimethylpyrrolidinium Fluorohydrogenate as Ionic Plastic Crystal Electrolyte. *Journal of Power Sources* **2014**, *245*, 758–763. <https://doi.org/10.1016/j.jpowsour.2013.07.020>
 - 44 Jrad, E. B. H.; Soavi, F.; Dridi, C. Development and Performances Analysis of Eco-Friendly Pullulan/ Polyvinyl Alcohol Composites Based All-Solid-State Supercapacitors. *Journal of Materials Chemistry A* **2026**. <https://doi.org/10.1039/D5TA07754K>
 - 45 Hu, Y.; Li, P.; Lai, G.; Lu, B.; Wang, H.; Cheng, H.; Wu, M.; Liu, F.; Dang, Z.-M.; Qu, L. Separator with High Ionic Conductivity Enables Electrochemical Capacitors to Line-Filter at High Power. *Nature Communications* **2025**, *16* (1), 2772. <https://doi.org/10.1038/s41467-025-58064-2>
 - 46 Pal, B.; Yang, S.; Ramesh, S.; Thangadurai, V.; Jose, R. Electrolyte Selection for Supercapacitive Devices: A Critical Review. *Nanoscale Advances* **2019**, *1* (10), 3807–3835. <https://doi.org/10.1039/C9NA00374F>
 - 47  atoszy ska, A. A.;  ukowska, G. Z.; Rutkowska, I. A.; Taberna, P.L.; Simon, P.; Kulesza, P. J.; Wieczorek, W. Non-Aqueous Gel Polymer Electrolyte with Phosphoric

- Acid Ester and Its Application for Quasi Solid-State Supercapacitors. *Journal of Power Sources* **2015**, *274*, 1147–1154. <https://doi.org/10.1016/j.jpowsour.2014.10.094>
- 48 Yu, H.; Wu, J.; Fan, L.; Xu, K.; Zhong, X.; Lin, Y.; Lin, J. Improvement of the Performance for Quasi-Solid-State Supercapacitor by Using PVA–KOH–KI Polymer Gel Electrolyte. *Electrochimica Acta* **2011**, *56* (20), 6881–6886. <https://doi.org/10.1016/j.electacta.2011.06.039>
 - 49 Verma, M. L.; Minakshi, M.; Singh, N. K. Synthesis and Characterization of Solid Polymer Electrolyte Based on Activated Carbon for Solid State Capacitor. *Electrochimica Acta* **2014**, *137*, 497–503. <https://doi.org/10.1016/j.electacta.2014.06.039>
 - 50 Gong, K.; Lee, H.; Choi, Y.; Jung, G.; Keum, K.; Kim, J. W.; Ha, J. S. A Flexible Supercapacitor with High Energy Density and Wide Range of Temperature Tolerance Using a High-Concentration Aqueous Gel Electrolyte. *Electrochimica Acta* **2024**, *475*, 143585. <https://doi.org/10.1016/j.electacta.2023.143585>
 - 51 Lota, G.; Frackowiak, E. Striking Capacitance of Carbon/Iodide Interface. *Electrochemistry Communications* **2009**, *11* (1), 87–90. <https://doi.org/10.1016/j.elecom.2008.10.026>
 - 52 Platek-Mielczarek, A.; Frackowiak, E.; Fic, K. Specific Carbon/Iodide Interactions in Electrochemical Capacitors Monitored by EQCM Technique. *Energy & Environmental Science* **2021**, *14* (4), 2381–2393. <https://doi.org/10.1039/D0EE03867A>
 - 53 Frackowiak, E.; Abbas, Q.; Béguin, F. Carbon/Carbon Supercapacitors. *Journal of Energy Chemistry* **2013**, *22* (2), 226–240. [https://doi.org/10.1016/S2095-4956\(13\)60028-5](https://doi.org/10.1016/S2095-4956(13)60028-5)
 - 54 Chapter Electrical Double-Layer Capacitors and Pseudocapacitors. In *Carbons for Electrochemical Energy Storage and Conversion Systems*; Beguin, F., Frackowiak, E., Eds.; CRC Press, **2009**
 - 55 Réty, B.; Yiin, H.Y.; Matei Ghimbeu, C. Quantification of Activated Carbon Functional Groups and Active Surface Area by TPD-MS and Their Impact on Supercapacitor Performance. *Energy Storage Materials* **2024**, 103963. <https://doi.org/10.1016/j.ensm.2024.103963>
 - 56 Ruiz, V.; Santamaría, R.; Granda, M.; Blanco, C. Long-Term Cycling of Carbon-Based Supercapacitors in Aqueous Media. *Electrochimica Acta* **2009**, *54* (19), 4481–4486. <https://doi.org/10.1016/j.electacta.2009.03.024>
 - 57 Wojciechowski, J.; Kolanowski, Ł.; Graś, M.; Szubert, K.; Bund, A.; Fic, K.; Lota, G. Anti-Corrosive Siloxane Coatings for Improved Long-Term Performance of Supercapacitors with an Aqueous Electrolyte. *Electrochimica Acta* **2021**, *372*, 137840. <https://doi.org/10.1016/j.electacta.2021.137840>
 - 58 Ratajczak, P.; Jurewicz, K.; Skowron, P.; Abbas, Q.; Béguin, F. Effect of Accelerated Ageing on the Performance of High Voltage Carbon/Carbon Electrochemical Capacitors in Salt Aqueous Electrolyte. *Electrochimica Acta* **2014**, *130*, 344–350. <https://doi.org/10.1016/j.electacta.2014.02.140>
 - 59 Demarconnay, L.; Raymundo-Piñero, E.; Béguin, F. A Symmetric Carbon/Carbon Supercapacitor Operating at 1.6 V by Using a Neutral Aqueous Solution. *Electrochemistry Communications* **2010**, *12* (10), 1275–1278. <https://doi.org/10.1016/j.elecom.2010.06.036>
 - 60 Piwek, J.; Platek, A.; Frackowiak, E.; Fic, K. Mechanisms of the Performance Fading of Carbon-Based Electrochemical Capacitors Operating in a LiNO₃ Electrolyte. *Journal of Power Sources* **2019**, *438*, 227029. <https://doi.org/10.1016/j.jpowsour.2019.227029>
 - 61 Park, J.; Lee, J.; Kim, W. Water-in-Salt Electrolyte Enables Ultrafast Supercapacitors for AC Line Filtering. *ACS Energy Letters*. **2021**, *6*, (2), 769–777. <https://doi.org/10.1021/acsenrgylett.0c02442>

- 62 Suo, L.; Borodin, O.; Gao, T.; Olguin, M.; Ho, J.; Fan, X.; Luo, C.; Wang, C.; Xu., K. "Water-in-salt" electrolyte enables high-voltage aqueous lithium-ion chemistries. *Science*. **2015**, 350, (6263), 938-943. <https://doi.org/10.1126/science.aab1595>
- 63 Reber, D.; Kühnel, R.S.; Battaglia, C. High-Voltage Aqueous Supercapacitors Based on NaTFSI. *Sustainable Energy & Fuels* **2017**, 1 (10), 2155–2161. <https://doi.org/10.1039/C7SE00423K>
- 64 Thareja, S.; Kumar, A. "Water-In-Salt" Electrolyte-Based High-Voltage (2.7 V) Sustainable Symmetric Supercapacitor with Superb Electrochemical Performance—An Analysis of the Role of Electrolytic Ions in Extending the Cell Voltage. *ACS Sustainable Chemistry & Engineering* **2021**, 9 (5), 2338–2347. <https://doi.org/10.1021/acssuschemeng.0c08604>
- 65 Liao, H.; Zhong, L.; Zeng, H.; Xiao, Y.; Cheng, B.; Lei, S. A Dual-Acetate Synchronous Catalysis-Activation Strategy towards Regulable Porous Graphitic Carbon for High-Energy Supercapacitor with Acetate Water-in-Salt Electrolyte. *Carbon* **2023**, 213, 118305. <https://doi.org/10.1016/j.carbon.2023.118305>
- 66 Gajewski, P.; Béguin, F. Hydrogel–Polymer Electrolyte for Electrochemical Capacitors with High Volumetric Energy and Life Span. *ChemSusChem* **2020**, 13 (7), 1876–1881. <https://doi.org/10.1002/cssc.201903077>
- 67 Almdal, K.; Dyre, J.; Hvidt, S.; Kramer, O. What Is a 'Gel'? *Makromolekulare Chemie. Macromolecular Symposia* **1993**, 76 (1), 49–51. <https://doi.org/10.1002/masy.19930760107>
- 68 Xue, X.; Hu, Y.; Wang, S.; Chen, X.; Jiang, Y.; Su, J. Fabrication of Physical and Chemical Crosslinked Hydrogels for Bone Tissue Engineering. *Bioactive Materials* **2022**, 12, 327–339. <https://doi.org/10.1016/j.bioactmat.2021.10.029>
- 69 Alipoori, S.; Mazinani, S.; Aboutalebi, S. H.; Sharif, F. Review of PVA-Based Gel Polymer Electrolytes in Flexible Solid-State Supercapacitors: Opportunities and Challenges. *Journal of Energy Storage* **2020**, 27, 101072. <https://doi.org/10.1016/j.est.2019.101072>
- 70 Azimi, M.; Subramanian, A.; Fan, J.; Soavi, F.; Cicoira, F. Electrical and Mechanical Stability of Flexible, Organic Electrolyte-Gated Transistors Based on Ionogel and Hydrogels. *Journal of Materials Chemistry C* **2023**, 11 (14), 4623–4633. <https://doi.org/10.1039/D3TC00410D>
- 71 Batisse, N.; Raymundo-Piñero, E. A Self-Standing Hydrogel Neutral Electrolyte for High Voltage and Safe Flexible Supercapacitors. *Journal of Power Sources* **2017**, 348, 168–174. <https://doi.org/10.1016/j.jpowsour.2017.03.005>
- 72 Shuaibu, A. D.; Shah, S. S.; Alzahrani, A. S.; Aziz, Md. A. Development and Assessment of an Innovative Gel Electrolyte Using Polyvinyl Alcohol, Lithium Sulfate, and 1-Butyl-3-Methylimidazolium Trifluoromethanesulfonate for Advanced Supercapacitor Performance. *Journal of Energy Storage* **2024**, 92, 112040. <https://doi.org/10.1016/j.est.2024.112040>
- 73 Ding, J.; Yang, Y.; Poisson, J.; He, Y.; Zhang, H.; Zhang, Y.; Bao, Y.; Chen, S.; Chen, Y. M.; Zhang, K. Recent Advances in Biopolymer-Based Hydrogel Electrolytes for Flexible Supercapacitors. *ACS Energy Letters* **2024**, 1803–1825. <https://doi.org/10.1021/acsenenergylett.3c02567>
- 74 Yang, W.; Yang, W.; Zeng, J.; Chen, Y.; Huang, Y.; Liu, J.; Gan, J.; Li, T.; Zhang, H.; Zhong, L.; Peng, X. Biopolymer-based Gel Electrolytes for Electrochemical Energy Storage: Advances and Prospects. *Progress in Materials Science* **2024**, 144, 101264. <https://doi.org/10.1016/j.pmatsci.2024.101264>
- 75 Zallouz, S.; Meins, J.M. L.; Matei Ghimbeu, C. Alkaline Hydrogel Electrolyte from Biosourced Chitosan to Enhance the Rate Capability and Energy Density of Carbon-Based Supercapacitors. *Energy Advances* **2022**, 1 (12), 1051–1064. <https://doi.org/10.1039/D2YA00250G>

- 76 Muddasar, M.; Beaucamp, A.; Culebras, M.; Collins, M. N. High Performance All Lignin Derived Supercapacitors for Energy Storage Applications. *Materials Today Sustainability* **2024**, *26*, 100767. <https://doi.org/10.1016/j.mtsust.2024.100767>
- 77 Ye, T.; Li, D.; Liu, H.; She, X.; Xia, Y.; Zhang, S.; Zhang, H.; Yang, D. Seaweed Biomass-Derived Flame-Retardant Gel Electrolyte Membrane for Safe Solid-State Supercapacitors. *Macromolecules* **2018**, *51* (22), 9360–9367. <https://doi.org/10.1021/acs.macromol.8b01955>
- 78 Taer, E.; Putri, A.; Farma, R.; Awitdrus; Taslim, R.; Apriwandi; Agustino; Yusra, D. A. The Effect of Potassium Iodide (KI) Addition to Aqueous-Based Electrolyte (Sulfuric Acid/H₂SO₄) for Increase the Performance of Supercapacitor Cells. *Materials Today: Proceedings* **2021**, *44*, 3241–3244. <https://doi.org/10.1016/j.matpr.2020.11.447>
- 79 Fic, K.; Morimoto, S.; Frackowiak, E.; Ishikawa, M. Redox Activity of Bromides in Carbon-Based Electrochemical Capacitors. *Batteries & Supercaps* **2020**, *3* (10), 1080–1090. <https://doi.org/10.1002/batt.202000061>
- 80 Tiwari, B.; Joshi, A.; Munjal, M.; Kaur, G.; Sharma, R. K.; Singh, G. Synergistic Combination of N/P Dual-Doped Activated Carbon with Redox-Active Electrolyte for High Performance Supercapacitors. *Journal of Physics and Chemistry of Solids* **2022**, *161*, 110449. <https://doi.org/10.1016/j.jpcs.2021.110449>
- 81 Gorska, B.; Bujewska, P.; Fic, K. Thiocyanates as Attractive Redox-Active Electrolytes for High-Energy and Environmentally-Friendly Electrochemical Capacitors. *Physical Chemistry Chemical Physics* **2017**, *19* (11), 7923–7935. <https://doi.org/10.1039/C7CP00722A>
- 82 Gorska, B.; Frackowiak, E.; Beguin, F. Redox Active Electrolytes in Carbon/Carbon Electrochemical Capacitors. *Current Opinion in Electrochemistry* **2018**, *9*, 95–105. <https://doi.org/10.1016/j.coelec.2018.05.006>
- 83 Menzel, J.; Fic, K.; Meller, M.; Frackowiak, E. The Effect of Halide Ion Concentration on Capacitor Performance. *Journal of Applied Electrochemistry* **2014**, *44* (4), 439–445. <https://doi.org/10.1007/s10800-013-0657-8>
- 84 Krüner, B.; Lee, J.; Jäckel, N.; Tolosa, A.; Presser, V. Sub-Micrometer Novolac-Derived Carbon Beads for High Performance Supercapacitors and Redox Electrolyte Energy Storage. *ACS Applied Materials & Interfaces* **2016**, *8* (14), 9104–9115. <https://doi.org/10.1021/acsami.6b00669>
- 85 Abbas, Q.; Babuchowska, P.; Frackowiak, E.; Béguin, F. Sustainable AC/AC Hybrid Electrochemical Capacitors in Aqueous Electrolyte Approaching the Performance of Organic Systems. *Journal of Power Sources* **2016**, *326*, 652–659. <https://doi.org/10.1016/j.jpowsour.2016.03.094>
- 86 Przygocki, P.; Abbas, Q.; Béguin, F. Capacitance Enhancement of Hybrid Electrochemical Capacitor with Asymmetric Carbon Electrodes Configuration in Neutral Aqueous Electrolyte. *Electrochimica Acta* **2018**, *269*, 640–648. <https://doi.org/10.1016/j.electacta.2018.03.016>
- 87 Meller, M.; Menzel, J.; Fic, K.; Gastol, D.; Frackowiak, E. Electrochemical Capacitors as Attractive Power Sources. *Solid State Ionics* **2014**, *265*, 61–67. <https://doi.org/10.1016/j.ssi.2014.07.014>
- 88 Platek, A.; Piwek, J.; Fic, K.; Frackowiak, E. Ageing Mechanisms in Electrochemical Capacitors with Aqueous Redox-Active Electrolytes. *Electrochimica Acta* **2019**, *311*, 211–220. <https://doi.org/10.1016/j.electacta.2019.04.117>

Electrode materials used for ECs

4.1 Characteristics of carbons utilized as EC electrodes

Electrodes are fundamental constituents of electrochemical capacitors, ensuring high capacitance, suitable balance between the energy/power density output, as well as long lifespan¹. The ideal EC electrode material should be characterized by the high specific surface area (SSA) with tailored porosity and structural disorder, good electric

Ideal electrode material	High specific surface area	Increases the interface between electrode and electrolyte, enabling more charge accumulation
	High electrical conductivity	- Facilitates effective charge transfer - Minimize internal resistance - Enables fast charge/discharge
	Tailored porous texture	- Provides efficient pathways for ion diffusion - Balances micro- and mesopores ratio for desired performance - Supports high power density and rapid charge/discharge
	Tailored surface chemistry	- Improves wettability and ion accessibility - Provides faradaic reactions, increasing overall capacitance
	Tailored structural disorder	- Introduces defects that create additional active sites - Enhances adsorption and/or redox activity
	Corrosion resistance	Ensures long-term stability in aggressive electrolytes
	Processing and compatibility in composites	- High mechanical stability - Facile integration with additives (i.e., conductive additives, binder) and current collectors
	Low production cost	- Cost-effective and abundant precursors - Efficient, scalable manufacturing - High quality

Figure 7 The characteristics of ideal EC electrode material.

conductivity, corrosion resistance, low production cost, and facile processing in composites, as shown in **Figure 7**². Also, the compatibility of electrode material and electrolyte, namely matching of pore size with ion size or surface chemistry with active redox species should be considered.

Carbon materials are among the most abundantly available and diverse materials³. Particularly, carbon materials classified into the family with $sp^2+\pi$ hybridization present a variety of structures and textures as shown in transmission electron microscopy (TEM) images (**Figure 8**)⁴. Typical carbon materials utilized in ECs include e.g., activated carbons (ACs), templated carbons (TCs), graphene, carbon black (CB), carbon nanofibers (CNFs), carbon nano-onions (CNOs), carbon nanotubes (CNTs), graphite, and very recently carbon quantum dots (CQDs). Interestingly, carbon materials can be additionally doped with heteroatoms (i.e., O, N, S, and P), which may provide pseudocapacitance.

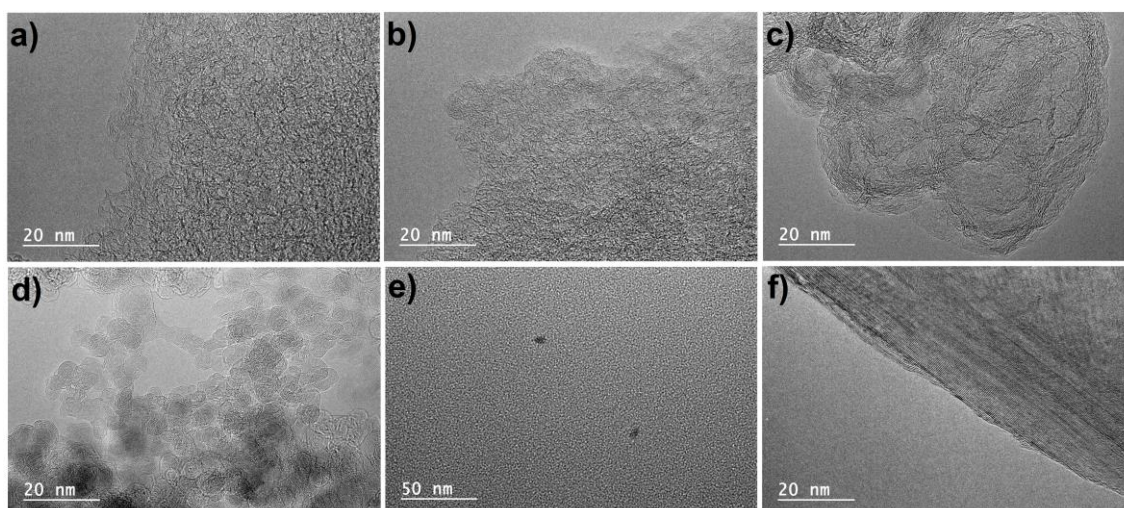


Figure 8 TEM images of carbons with different texture/structure used as EC electrode materials: **a)** activated carbon, **b)** activated carbon nanofibers, **c)** carbon black, **d)** carbon nano-onions, **e)** carbon quantum dots, **f)** graphite.

Activated carbon belongs to the family of three-dimensional carbon materials and consist of disoriented arrangement of Csp^2 sheets that are interconnected in a random manner⁵, as shown in **Figure 8 a)**. The connection between these fragments creates slits and tunnels within the structure⁵. Currently, AC is the most commonly utilized electrode material for ECs, in both academia and industry, owing to its high SSA ($\sim 3000 \text{ m}^2 \text{ g}^{-1}$), porous texture, and moderate manufacturing cost⁶⁻⁸. ACs can be obtained from high temperature pre-carbonization of natural (i.e., coconut shells³, lignin⁹) or synthetic (i.e., resins¹⁰, coal¹¹) carbon rich precursors followed by the activation to create new pores to increase the surface area and tailor textural features³. Two types of activation routes can

be distinguished, i.e., physical and chemical¹². Physical activation employs heat-treatment of pre-carbonized precursor at high-temperatures (700-950°C) in the presence of the oxidizing gases like steam or CO₂^{13,14}. On the other hand, chemical activation involves chemical reagents, e.g., NaOH¹⁵, KOH¹⁶, ZnCl₂¹⁷, H₃PO₄¹⁸ and lower temperature range 400-700°C¹³. Unlike chemical activation, physical activation is viewed as more sustainable since it does not involve highly corrosive chemicals, and eliminates the time-consuming washing processes¹⁹. On the contrary, chemical activation is generally preferred due to lower temperature, and better activation effects^{12,20}. The AC-based ECs have a capacitance of ~100 F g⁻¹, when the SSA of AC is around 1500 m² g⁻¹²¹. Importantly, the main constraint of ACs is the lack of the precise control of the carbon's texture and structure. It is especially important for the design of the ECs with desired metrics.

Template-assisted carbonization enables precise tuning of the carbon's texture, especially development of surface area, tuning of porosity as well as the tailoring of the structure²². It is possible through the variety of available templating agents. Based on the employed templating agent, a hard-, soft- and salt-templating can be distinguished.

Hard templating requires use of e.g., zeolite²³, silica²⁴, metal oxides²⁵ as templates. Typically, hard templates are utilized for the preparation of ordered, mesoporous carbons. Silica and metal oxides cannot exceed ~1000 m² g⁻¹, without further activation. On the other hand, zeolite templated carbons reach high SSA up to ~4000 m² g⁻¹, due to the presence of micropores (30-70%) inside the mesopores walls^{23,26}. Unfortunately, hard templating requires application of hazardous chemicals (e.g., HF or highly concentrated NaOH) for the removal of the template, raising the environmental concerns²⁶.

On the other hand, simpler and more sustainable templating approach have been established using phase-separated block co-polymers or organic micelles as soft templates²⁷. The process involves the formation of nanostructures *via* the self-assembly of organic molecules at molecular level through hydrogen bonding, hydrophobic/hydrophilic interactions, ion pairing²⁸. Nevertheless, soft templated carbons exhibit a particular SSA that typically does not surpass 1000 m² g⁻¹²². The self-assembly of surfactant micelles leads to abundant mesopores formation upon thermal decomposition, but it cannot facilitate the formation of high SSA, which is more linked with the decomposition of carbon precursor (generally a phenolic resin)^{22,29}.

Interestingly, combining soft and salt templating lead to the material's enhanced textural characteristics, including a well-balanced micro- and mesopores volume, elevated SSA

(even up to $\sim 2600 \text{ m}^2 \text{ g}^{-1}$), and adjustable pore size and shape²². The salt template facilitates the development of micropores, through the melting of the salt and strong cation's interaction with the carbon matrix^{22,29}. Various inorganic salts can be utilized as salt templates, including alkali metal chlorides^{22,29}, acetates³⁰, carbonates³¹. For instance, *Nita et al.* synthesized a soft-salt templated carbon utilizing triblock co-polymer (Pluronic F127) as soft template, phloroglucinol and glyoxylic acid to form a phenolic resin network as well as alkali metal salts (i.e., NaCl, KCl, LiCl) as salt template²⁹. Moreover, the impact of several synthesis parameters including the ratio of reagents, type of salt template, type/volume of the solvent, pH, time, temperature on the carbon texture/structure formation was investigated²⁹. Control of graphitization can be achieved due to the increase in cation- π binding energy to the carbon core, although a decrease of SSA occurs²⁹. Importantly, the salt template can be easily removed by simple water washing (avoiding the carbon etching) and further recovered in $>80\%$ after synthesis, contrary to hard templating^{22,31}. Additionally, utilizing environmentally benign precursors and solvents, facilitates a one-step carbonization and activation, unlike other approaches, where carbonization and activation are consisting of two- or three-steps²². Moreover, the overall C-yield of soft-salt templating synthesis is higher ($\sim 30\%$) than for conventional pyrolysis of coconut shells combined with CO_2 activation ($\sim 25\%$)³².

Graphene is a two-dimensional monolayer planar sheet consisting of sp^2 -bonded carbon atoms³³. Notably, the discovery of the graphene, awarded by the 2010 Nobel Prize revolutionized the electronics and energy sectors³⁴. First graphene layer was isolated from several-layered graphite by tape and this basic technique further evolved into micromechanical cleavage³⁴. Unfortunately, manufacturing of a high-quality graphene is frequently challenging (re-stacking of the Csp^2 layers), expensive, and time-consuming³⁵. The carbon structural defects may be introduced during processing, impacting the unique characteristics of the graphene. Graphene is characterized by stable physical structure, high theoretical SSA ($\sim 2600 \text{ m}^2 \text{ g}^{-1}$ - but difficult to achieve experimentally), outstanding thermal and electrical conductivity^{33,34}. It makes graphene a promising material for use as electrodes in ECs³³. Nevertheless, graphene is used especially in composites with pseudocapacitive materials (i.e., metal oxides) to enhance their electric conductivity³⁶.

Carbon nanotubes are one-dimensional (1D) structures, consisting of graphene sheets rolled into hollow tubes³⁷. Typically, synthesis of CNTs encompasses arc discharge, laser ablation or chemical vapor deposition³⁸. Also, based on the preparation technique employed, it is possible to obtain either single-layer or multi-walled CNTs³⁸. Nevertheless,

the rigorous control over the number of the layers presents significant challenges. Frequently, CNTs are contaminated by metals (Co, Fe, Ni), graphitized carbon, and amorphous carbon, which reduce their purity even up to 75%^{38,39}. Typically, acids and the thermal oxidation treatments are utilized to remove the impurities, and amorphous carbon fraction, respectively. The SSA of CNTs range from ~300 to 1300 m² g⁻¹⁴⁰. The good electrical conductivity and high mesoporosity of CNTs allows quick charging of EDL layer, perfect for high-power demand. Nevertheless, relatively low SSA, but high external surface area results in moderate capacitance, below 50 F g⁻¹, that limits their widespread applications^{41,42}. Interestingly, more often CNTs serve as an excellent supportive material, for the enhancement of the electric conductivity and mechanical properties⁴¹.

Another 1D material - carbon nanofibers are characterized by their nanometer-scale diameter and no hollow core, including numerous edge sites on their outer wall⁴³. The most common method utilized for the preparation of CNFs is electrospinning⁴⁴. Nevertheless, there are several parameters which are hard to be precisely controlled during the electrospinning, such as temperature and humidity⁴⁴. CNFs are perfect for wearable devices, as they provide flexibility. Also, there is no need of the binder, which simplifies the electrodes processing. Importantly, similarly to CNTs, they provide high electric conductivity, but limited SSA, that is why they mainly serve as a support for other materials⁴⁴.

Carbon black is graphitic material which presents a very small spherical and nanometric particles (~10-20 nm) that are connected⁴⁵, as shown in **Figure 8 c**). Commonly, it is produced through the controlled thermal decomposition (i.e., partial combustion) of carbon rich feeds⁴⁵. The SSA of CB is low to moderate and range from ~30 to 600 m² g⁻¹^{46,47}. Thus, CB is often used as heat-resistant additive as well as to increase the electric conductivity of EC electrodes⁴⁸.

Carbon nano-onions are composed of the aggregation of a few tens' nanometers in size (< 10 nm) carbon particles⁴⁹. As it can be observed from TEM image (**Figure 8 d**), CNO particles display a spherical shape characterized by concentrically arranged layers of graphitic (sp²) planes⁵⁰. Commonly, CNOs are synthesized using ultrapure nanodiamond particles which are graphitized at high temperature (≥ 1500°C) in the inert gas atmosphere^{49,50}. The SSA of CNOs range from ~300 to 800 m² g⁻¹, which is notably lower than SSA reported for activated carbon^{49,51}. Nevertheless, they are characterized by the interparticle and intercluster pores, that affects total pore volume⁵¹. CNOs have completely accessible surface for ion adsorption, given by the absence of porous

network within particles, what makes them perfect for the investigation of property-capacitance relationships^{50,52}. The CNOs demonstrated a promising EC performance, achieving a capacitance of up to 126 F g⁻¹ in 1M KNO₃⁵³. On the other hand, the non-porous, ion-accessible outer shells of CNOs impose constraints on the EC energy density, necessitating a large SSA⁵³.

Carbon quantum dots present a novel category of zero-dimensional materials made of nanosized carbon particles (≤ 10 nm)⁵⁴. CQDs with a Csp² or Csp²/sp³ core and plentiful functional groups in the shell, demonstrate potential to improve the performance of ECs⁵⁵. They can be synthesized through two approaches: bottom-up and top-up⁵⁶. The bottom-up strategy involves hydrothermal/solvothermal treatment, microwave treatment or pyrolysis of organic molecules (e.g., carbohydrates, amines) or polymer precursors⁵⁶. On the other hand, top-down approach focusses on low-dimensioning the larger carbon cluster structures into carbon nanoparticles using laser ablation, arc discharge, or ultrasonication⁵⁶. Nevertheless, the yield of the CQDs synthesis is low, reaching up to 10%⁵⁷. That is why, CQDs are mainly used as the electrode additive, depending on the desired EC metrics⁵⁸. Ideally, the CQDs additive increases ion transport, provides beneficial quantum effects (nanoscale size) and pseudocapacitance (surface chemistry), thus improve the EC metrics^{59,60}. For instance, graphene CQDs made of Csp² enhance the conductivity, while the CQDs with mixed hybridization made through the low-temperature hydrothermal treatment provide substantial pseudocapacitance⁶⁰. Nevertheless, the synthesis of CQDs with uniform sizes and controllable functionalities as well as their physicochemical and electrochemical characterization is still challenging.

4.2 Textural/structural effects on the performance of carbon-based electrochemical capacitors

Multiple parameters influence the capacitive performance of carbon-based EC electrodes, as mentioned in **Figure 7**. Nevertheless, the most pertinent factors are associated with the porous texture (SSA, pore volume, pore size distribution) and structure (defects, surface functionalities)⁶¹.

A high SSA is inherently required for the formation of EDL layer (**Equation 8**), ensuring high capacitance. Importantly, carbon with a pore size smaller than that of the ions will be unable of charge storage². The International Union of Pure and Applied Chemistry

(IUPAC) categorized porous materials, including carbon, into three classes based on the pore diameter⁶². Microporous materials are characterized as pores with less than 2 nm, and ultramicroporous materials denote sub-nanometer pores smaller than 0.7 nm⁶². Mesoporous materials possess dimensions ranging from 2 to 50 nm, while pores above 50 nm in diameter are categorized as macroporous materials⁶². The microporous materials are the most suitable for the ion adsorption process. On the other hand, mesoporous materials create pathways for efficient ion transport and charge propagation allowing high-rate capability. Therefore, preparation of the carbon electrodes with balanced micro/mesopores ratio is crucial.

As firstly demonstrated by *Kötz et al.*, the specific capacitance of 10 commercial carbons showed a linearity with increasing SSA_{BET} (SSA evaluated using Brunauer-Emmett-Teller equation), but not higher than $1200 \text{ m}^2 \text{ g}^{-1}$ ⁶³. Above that value, there was observed a plateau⁶³. This behavior was related to the space constriction for the charge accommodation inside the pore walls⁶³. Carbons, as semiconductors, exhibited low charge-carrier density, and the space-charge capacitance was more constrained in those with higher surface area^{63,64}.

Then, *Taberna et al.* demonstrated “anomalous” enhancement of the capacitance normalized to SSA_{BET} for a specifically designed microporous carbide-derived carbons (with pore width < 1 nm), when the pore dimensions were approximate to those of the desolvated ion size⁶⁵. The results were attributed to the partial or complete desolvation of the electrolyte ions upon entering the sub-nanometer pores⁶⁵. The sieving effect resulted in a reduced distance between the ion center and the electrode surface, hence improving the capacitance⁶⁵.

After the publication of the “anomalous” increase of the capacitance in the range of sub-nanometer pores⁶⁵, several researchers tried to verify described findings. *Beguin et al.* found that the capacitance was almost proportional to SSA of series of carbons with progressively modified textural properties by heat treatment (500-1000°C), followed by the KOH activation⁶⁶. Moreover, the analysis of the electrochemical performance in aqueous and organic electrolyte revealed that an adequate pore size is a mandatory requirement to benefit from high surface area, otherwise, the SSA cannot be fully accessible to the ions⁶⁶. The anomalous increase of the capacitance in the sub-nanometer pores was not confirmed, but it was found that the pore size of 0.7 nm (aqueous electrolyte), and 0.8 nm (organic electrolyte) are optimal for the efficient EDL formation⁶⁶.

Centeno et al. utilized 42 microporous carbons for the in-detail analysis of the relationship between the carbon's porosity and capacitance⁶⁷. For that purpose, the SSA evaluated using BET equation (S_{BET}) was compared with SSA estimated with other methods (i.e., Dubinin-Radushkevich equation, density functional theory (DFT), phenol immersion enthalpy, the Kaneko's comparison plot on N_2 adsorption isotherms at -196°C), denoted as S_{av} . A good agreement was found in the values of SSA obtained through each method for carbons with pore widths between 0.66 nm and 1.65 nm. Importantly, the analysis indicated that S_{BET} and S_{av} exhibit a correlation with capacitance exclusively for pores of ~ 0.9 nm in width⁶⁷.

Lately, *Centeno et al.* employed carbons with narrow micropore size distributions and confirmed that the surface normalized capacitance does not rely on the micropore size⁶⁸. Indeed, there was observed an "anomalous" increase of C/S_{BET} for the pores with diameter smaller than 0.9 nm, attributed to the SSA underestimation by BET equation⁶⁸.

Interestingly, the term accessible specific surface area was proposed as a link between the textural properties and storage behavior²¹. It should be emphasized that the SSA commonly determined just by the physisorption of the N_2 molecules, may not access all the pores, therefore, CO_2 sorption is used as a complementary technique to estimate the volume of ultramicropores (≤ 0.7 nm). These narrow pores are extremely important for ECs operating in aqueous medium since desolvated and solvated ions are much smaller than organic/ILs ions.

For instance, *Fic et al.* reported a linear correlation between the SSA_{BET} , SSA_{DFT} , volume of micropores, and volume of ultramicropores with the capacitance. No limitation of capacitance with the increase of SSA (up to $\sim 2600 \text{ m}^2 \text{ g}^{-1}$) or average pore size (0.7 to 1.0 nm) was noticed, either anomalous increase of capacitance. In the employed series of templated carbons with precisely tailored texture/structure, a fully accessible SSA was involved in charge storage²².

Considering the previous articles, the authors focused mainly on the porosity while ignoring other important parameters, i.e., degree of disorder ($I_{\text{D}}/I_{\text{G}}$) and surface chemistry. Depending on the carbons, some of them may have very high SSA, but limited conductivity (high $I_{\text{D}}/I_{\text{G}}$) which leads to the lower capacitance. An important work which considers the impact of the carbon disorder was performed using nuclear magnetic resonance (NMR)⁶⁹. It was revealed that more disordered carbons, with less graphene-like domains show higher capacitance due to the more efficient ion storage in their nanopores⁶⁹. Later, the same research group employed commonly available Raman

spectroscopy and found that the carbons with smaller I_D/I_G intensity ratios exhibit higher capacitance⁷⁰. Precisely, lower I_D/I_G ratio is associated with the higher presence of graphitic carbon structure (C_{sp^2})⁷¹, thus resulting in lower capacitance, which is contradictory to the conclusions noted in the NMR study. Moreover, the degree of disorder was calculated based on the intensities of D and G bands, rather than the area, which remains questionable for the porous carbons⁷¹.

Interestingly, *Vix-Guterl et al.* used unique approach called active surface area (ASA), which provides the exact area of the defects caused by dislocations, stacking faults, surface functionalities in the CNOs⁵². The linear correlation between the capacitance (aqueous, organic medium) and the ASA was reported⁵².

Another work provides an understanding of surface functional groups effect on the capacitance⁷². Bio-char-based carbons rich in quinone, phenol, and ether groups (detected by the X-ray photoelectron spectroscopy (XPS)) improved the EC capacitance, resulting in additional pseudocapacitance⁷². Furthermore, *Sudoh et al.* reported a linear correlation between the capacitance in aqueous medium and the amount of quinone functional group (distinguished by the XPS)⁷³.

Notably, recently published work provides comprehensive information on the role of the oxygen surface functionalities on the EC performance in three different pH aqueous electrolytes⁷⁴. For that purpose, a temperature programmed desorption coupled with mass spectrometry (TPD-MS) and ASA approach of several carbons was utilized. It was highlighted that only a certain O-functional groups (carboxylic, phenol-ether, carbonyl-quinone) are linearly correlated to the capacitance⁷⁴.

The effect of the selected O-functional group on the capacitance may vary across the conditions of studies performed⁷⁴. The variations may be attributed to the distinct types of carbon materials (i.e., ACs, TCs, CNOs) as well as the characterization techniques (i.e., XPS, TPD-MS). Furthermore, while quinones serve as electron acceptors that provide additional pseudocapacitance, it is essential to identify an optimal quantity of these surface groups. Their behavior is also likely influenced by pH of the employed electrolyte (i.e., electrolyte rich in protons support the redox activity of the functional group)⁷⁴.

Concluding, several factors should be considered along with the specific surface area, pore size distribution and matching of the size/kind of ions used, as they influence the capacitance in porous carbons. Local graphitization (degree of disorder), which allows

electrons to flow even through high porosity, as well as the surface chemistry providing the additional redox activity cannot be neglected.

The impact of the electrode material physicochemical properties is most often evaluated in terms of capacitance, while their effect on other critical parameters – such as capacitance retention, and lifespan remains not well explored. Moreover, commonly a few selectively picked textural/structural properties (e.g., SSA and/or surface chemistry) are considered, not giving a total overview on the structure-performance relationships.

Additionally, the physicochemical characterization of carbon materials is typically performed on pristine powders, whereas electrochemical measurements are carried out on the electrodes, what may contribute to the differences in EC performance. The factor that makes a difference between the pristine porous carbon and electrode is a polymeric binder (and in some cases a conductive carbon additive). Typically, for the manufacturing of carbon electrodes for aqueous-based ECs, polytetrafluoroethylene (PTFE) (5 wt.%) and conductive carbon black (5 wt.%) are utilized⁷⁵. There are already reported some particular experimental data on the impact of the carbon electrode additives. *Beguin et al.* reported that electrodes with PTFE binder are less microporous than the pristine carbon powder. Importantly, the change of the porosity caused by the binder may depend on the physicochemical characteristics of the carbon material and nature of the electrolyte used for EC testing⁷⁶. *Frackowiak et al.* investigated the pristine activated carbon and the electrode containing 90 wt.% of active mass. The SSA was reasonably lower for the electrodes ($1833 \text{ m}^2 \text{ g}^{-1}$) than for pristine material ($2136 \text{ m}^2 \text{ g}^{-1}$)⁷⁷. *Platek et al.* confirmed that a formation of self-standing electrodes does not destroy the pristine salt templated carbons features. The presence of polymeric binder (10 wt.%) only filled a portion of the pores indicated by a decreased SSA_{BET} , V_{micro} (e.g., for KCl-templated carbon from $1673 \text{ m}^2 \text{ g}^{-1}$ to $1353 \text{ m}^2 \text{ g}^{-1}$ and $0.61 \text{ cm}^3 \text{ g}^{-1}$ to $0.51 \text{ cm}^3 \text{ g}^{-1}$, respectively). The authors mentioned that those parameters were changed to the same extent due to the comparable amount of the binder and conductive carbon additive during electrode manufacturing²². *Fic et al.* focused also on the comparison of the structural disorder of pristine salt templated carbons and electrodes studied by Raman spectroscopy. Negligible differences of degree of disorder were noted for electrodes, due to the incorporation of a binder and conductive carbon²². More recently, *Forse et al.* restarted the investigation on the effect of a polymeric binder on EC performance, initially published by the *Beguin et al.* and did not find any novel reason of the binder action other than clogging of the carbon porosity⁷⁸. Concluding, similar behavior, i.e., a decrease in porosity and slight changes in the structural disorder of carbons are expected to occur

due to the manufacturing of the electrodes from other carbons, resulting in slight differences in EC performance.

References

- 1 Mirzaeian, M.; Abbas, Q.; Ogwu, A.; Hall, P.; Goldin, M.; Mirzaeian, M.; Jirandehi, H. F. Electrode and Electrolyte Materials for Electrochemical Capacitors. *International Journal of Hydrogen Energy* **2017**, *42* (40), 25565–25587. <https://doi.org/10.1016/j.ijhydene.2017.04.241>
- 2 Béguin, F.; Presser, V.; Balducci, A.; Frackowiak, E. Carbons and Electrolytes for Advanced Supercapacitors. *Advanced Materials* **2014**, *26* (14), 2219–2251. <https://doi.org/10.1002/adma.201304137>
- 3 Fic, K.; Platek, A.; Piwek, J.; Frackowiak, E. Sustainable Materials for Electrochemical Capacitors. *Materials Today* **2018**, *21* (4), 437–454. <https://doi.org/10.1016/j.mattod.2018.03.005>
- 4 Inagaki, M.; Kang, F.; *Materials Science and Engineering of Carbon: Fundamentals*, **2014**. <https://doi.org/10.1016/C2013-0-13699-9>
- 5 Ergun, S.; Tiensuu, V. Tetrahedral Structures in Amorphous Carbons. *Acta Crystallographica* **1959**, *12* (12), 1050–1051. <https://doi.org/10.1107/S0365110X59002936>
- 6 Simon, P.; Gogotsi, Y. Materials for Electrochemical Capacitors. *Nature Materials* **2008**, *7* (11), 845–854. <https://doi.org/10.1038/nmat2297>
- 7 Zhu, Y.; Murali, S.; Stoller, M.D.; Ganesh, K.J.; Cai, W.; Ferreira, P.J.; Pirkle, A.; Wallace, R.M.; Cychosz, K.; Ruoff, R.S. Carbon-Based Supercapacitors Produced by Activation of Graphene. *Science*. **2011**, *332*, (6037), 1537–1541. <https://doi.org/10.1126/science.1200770>
- 8 Wei, L.; Sevilla, M.; Fuertes, A. B.; Mokaya, R.; Yushin, G. Hydrothermal Carbonization of Abundant Renewable Natural Organic Chemicals for High-Performance Supercapacitor Electrodes. *Advanced Energy Materials* **2011**, *1* (3), 356–361. <https://doi.org/10.1002/aenm.201100019>
- 9 Bergna, D.; Varila, T.; Romar, H.; Lassi, U. Activated Carbon from Hydrolysis Lignin: Effect of Activation Method on Carbon Properties. *Biomass and Bioenergy* **2022**, *159*, 106387. <https://doi.org/10.1016/j.biombioe.2022.106387>
- 10 Lei, C.; Amini, N.; Markoulidis, F.; Wilson, P.; Tennison, S.; Lekakou, C. Activated Carbon from Phenolic Resin with Controlled Mesoporosity for an Electric Double-Layer Capacitor (EDLC). *Journal of Materials Chemistry A* **2013**, *1* (19), 6037–6042. <https://doi.org/10.1039/C3TA01638B>
- 11 Spencer, W.; Senanayake, G.; Altarawneh, M.; Ibane, D.; Nikoloski, A. N. Review of the Effects of Coal Properties and Activation Parameters on Activated Carbon Production and Quality. *Minerals Engineering* **2024**, *212*, 108712. <https://doi.org/10.1016/j.mineng.2024.108712>
- 12 Pandolfo, A. G.; Hollenkamp, A. F. Carbon Properties and Their Role in Supercapacitors. *Journal of Power Sources* **2006**, *157* (1), 11–27. <https://doi.org/10.1016/j.jpowsour.2006.02.065>
- 13 Gao, Y.; Yue, Q.; Gao, B.; Li, A. Insight into Activated Carbon from Different Kinds of Chemical Activating Agents: A Review. *Science of The Total Environment* **2020**, *746*, 141094. <https://doi.org/10.1016/j.scitotenv.2020.141094>
- 14 Muthmann, J.; Bläker, C.; Pasel, C.; Luckas, M.; Schledorn, C.; Bathen, D. Characterization of Structural and Chemical Modifications during the Steam

- Activation of Activated Carbons. *Microporous and Mesoporous Materials* **2020**, 309, 110549. <https://doi.org/10.1016/j.micromeso.2020.110549>
- 15 Cazetta, A. L.; Vargas, A. M. M.; Nogami, E. M.; Kunita, M. H.; Guilherme, M. R.; Martins, A. C.; Silva, T. L.; Moraes, J. C. G.; Almeida, V. C. NaOH-Activated Carbon of High Surface Area Produced from Coconut Shell: Kinetics and Equilibrium Studies from the Methylene Blue Adsorption. *Chemical Engineering Journal* **2011**, 174 (1), 117–125. <https://doi.org/10.1016/j.cej.2011.08.058>
 - 16 Kierzek, K.; Frackowiak, E.; Lota, G.; Gryglewicz, G.; Machnikowski, J. Electrochemical Capacitors Based on Highly Porous Carbons Prepared by KOH Activation. *Electrochimica Acta* **2004**, 49 (4), 515–523. <https://doi.org/10.1016/j.electacta.2003.08.026>
 - 17 Chang, B.; Wang, Y.; Pei, K.; Yang, S.; Dong, X. ZnCl₂-Activated Porous Carbon Spheres with High Surface Area and Superior Mesoporous Structure as an Efficient Supercapacitor Electrode. *RSC Advances* **2014**, 4 (76), 40546–40552. <https://doi.org/10.1039/C4RA06418F>
 - 18 Bhatti, A. H.; Waris, M.; Kazmi, W. W.; Kang, K.-H.; Bhatti, U. H. Acid-Treated Activated Carbon as Simple and Inexpensive Catalyst to Accelerate CO₂ Desorption from Aqueous Amine Solution. *Carbon Capture Science & Technology* **2023**, 8, 100131. <https://doi.org/10.1016/j.ccst.2023.100131>
 - 19 Gao, Y.; Yue, Q.; Gao, B.; Li, A. Insight into Activated Carbon from Different Kinds of Chemical Activating Agents: A Review. *Science of The Total Environment* **2020**, 746, 141094. <https://doi.org/10.1016/j.scitotenv.2020.141094>
 - 20 Hsiao, C.-H.; Gupta, S.; Lee, C.-Y.; Tai, N.-H. Effects of Physical and Chemical Activations on the Performance of Biochar Applied in Supercapacitors. *Applied Surface Science* **2023**, 610, 155560. <https://doi.org/10.1016/j.apsusc.2022.155560>
 - 21 Lobato, B.; Suárez, L.; Guardia, L.; Centeno, T. A. Capacitance and Surface of Carbons in Supercapacitors. *Carbon* **2017**, 122, 434–445. <https://doi.org/10.1016/j.carbon.2017.06.083>
 - 22 Platek-Mielczarek, A.; Nita, C.; Matei Ghimbeu, C.; Frackowiak, E.; Fic, K. Link between Alkali Metals in Salt Templates and in Electrolytes for Improved Carbon-Based Electrochemical Capacitors. *ACS Applied Materials & Interfaces* **2021**, 13 (2), 2584–2599. <https://doi.org/10.1021/acsami.0c18627>
 - 23 Nishihara, H.; Kyotani, T. Zeolite-templated carbons – three-dimensional microporous graphene frameworks. *Chemical Communications*. **2018**, 54, 5648–5673. <https://doi.org/10.1039/C8CC01932K>
 - 24 Leyva-García, S.; Lozano-Castelló, D.; Morallón, E.; Cazorla-Amorós, D. Silica-Templated Ordered Mesoporous Carbon Thin Films as Electrodes for Micro-Capacitors. *Journal of Materials Chemistry A* **2016**, 4 (12), 4570–4579. <https://doi.org/10.1039/C5TA10552H>
 - 25 Singh, G.; Kunjumon, J.; Kaur, H.; Singh, N.; Franklin, G.; Tiwari, A. P.; Van Zweiten, L.; Kennedy, J.; Vinu, A. Nanoarchitectonics of Porous Carbons Templated by Inorganic Metal Oxides and Alkali Metal Salts for Energy and Environmental Applications. *Advanced Science*. **2026** e17776. <https://doi.org/10.1002/advs.202517776>
 - 26 Nishihara, H.; Kyotani, T. Templated Nanocarbons for Energy Storage. *Advanced Materials* **2012**, 24 (33), 4473–4498. <https://doi.org/10.1002/adma.201201715>
 - 27 Tanaka, S.; Nishiyama, N.; Egashira, Y.; Ueyama, K. Synthesis of Ordered Mesoporous Carbons with Channel Structure from an Organic–Organic Nanocomposite. *Chemical Communications*. **2005**, 16, 2125–2127. <https://doi.org/10.1039/B501259G>
 - 28 Liang, C.; Li, Z.; Dai, S. Mesoporous Carbon Materials: Synthesis and Modification. *Angewandte Chemie International Edition*. **2008**, 47 (20), 3696–3717. <https://doi.org/10.1002/anie.200702046>

- 29 Nita, C.; Bensafia, M.; Vaulot, C.; Delmotte, L.; Matei Ghimbeu, C. Insights on the Synthesis Mechanism of Green Phenolic Resin Derived Porous Carbons *via* a Salt-Soft Templating Approach. *Carbon* **2016**, *109*, 227–238. <https://doi.org/10.1016/j.carbon.2016.08.011>
- 30 Dai, J.; Tian, S.; Jiang, Y.; Chang, Z.; Xie, A.; Zhang, R.; Yan, Y. Facile Synthesis of Porous Carbon Sheets from Potassium Acetate *via in-Situ* Template and Self-Activation for Highly Efficient Chloramphenicol Removal. *Journal of Alloys and Compounds* **2018**, *732*, 222–232. <https://doi.org/10.1016/j.jallcom.2017.10.237>
- 31 Zhao, H.; Qu, J.; Li, X.; Zhao, Z.; Chen, X.; Xie, H.; Yin, H. Carbonate Materials Synthesis Using Molten Salt Templates. *Journal of Materials Science* **2022**, *57* (16), 7778–7790. <https://doi.org/10.1007/s10853-022-07152-5>
- 32 Decaux, C.; Matei Ghimbeu, C.; Dahbi, M.; Anouti, M.; Lemordant, D.; Béguin, F.; Vix-Guterl, C.; Raymundo-Piñero, E. Influence of Electrolyte Ion–Solvent Interactions on the Performances of Supercapacitors Porous Carbon Electrodes. *Journal of Power Sources* **2014**, *263*, 130–140. <https://doi.org/10.1016/j.jpowsour.2014.04.024>
- 33 Yin, X.T.; You, E.M.; Zhou, R.Y.; Zhu, L.H.; Wang, W.W.; Li, K.X.; Wu, D.Y.; Gu, Y.; Li, J.F.; Mao, B.W.; Yan, J.W. Unraveling the Energy Storage Mechanism in Graphene-Based Nonaqueous Electrochemical Capacitors by Gap-Enhanced Raman Spectroscopy. *Nature Communications* **2024**, *15* (1), 5624. <https://doi.org/10.1038/s41467-024-49973-9>
- 34 Mbayachi, V. B.; Ndayiragije, E.; Sammani, T.; Taj, S.; Mbuta, E. R.; Khan, A. Ullah. Graphene Synthesis, Characterization and Its Applications: A Review. *Results in Chemistry* **2021**, *3*, 100163. <https://doi.org/10.1016/j.rechem.2021.100163>
- 35 Chowdhury, S.; Balasubramanian, R. Three-Dimensional Graphene-Based Macrostructures for Sustainable Energy Applications and Climate Change Mitigation. *Progress in Materials Science* **2017**, *90*, 224–275. <https://doi.org/10.1016/j.pmatsci.2017.07.001>
- 36 Wang, B.; Ruan, T.; Chen, Y.; Jin, F.; Peng, L.; Zhou, Y.; Wang, D.; Dou, S. Graphene-Based Composites for Electrochemical Energy Storage. *Energy Storage Materials* **2020**, *24*, 22–51. <https://doi.org/10.1016/j.ensm.2019.08.004>
- 37 Zhang, Y.; Wu, H.; Cheng, L.; Zheng, L.; Yuan, W. Carbon Nanotubes for Electrochemical Capacitors. In *Industrial Applications of Carbon Nanotubes*; Elsevier, **2017**; pp 277–321. <https://doi.org/10.1016/B978-0-323-41481-4.00010-1>
- 38 Gacem, A.; Modi, S.; Yadav, V. K.; Islam, S.; Patel, A.; Dawane, V.; Jameel, M.; Inwati, G. K.; Piplode, S.; Solanki, V. S.; Basnet, A. Recent Advances in Methods for Synthesis of Carbon Nanotubes and Carbon Nanocomposite and Their Emerging Applications: A Descriptive Review. *Journal of Nanomaterials* **2022**, *2022* (1), 7238602. <https://doi.org/10.1155/2022/7238602>
- 39 Ribeiro, H.; Schnitzler, M. C.; da Silva, W. M.; Santos, A. P. Purification of Carbon Nanotubes Produced by the Electric Arc-Discharge Method. *Surfaces and Interfaces* **2021**, *26*, 101389. <https://doi.org/10.1016/j.surfin.2021.101389>
- 40 Peigney, A.; Laurent, Ch.; Flahaut, E.; Bacsá, R. R.; Rousset, A. Specific Surface Area of Carbon Nanotubes and Bundles of Carbon Nanotubes. *Carbon* **2001**, *39* (4), 507–514. [https://doi.org/10.1016/S0008-6223\(00\)00155-X](https://doi.org/10.1016/S0008-6223(00)00155-X)
- 41 Lota, G.; Fic, K.; Frackowiak, E. Carbon Nanotubes and Their Composites in Electrochemical Applications. *Energy Environmental Science* **2011**, *4* (5), 1592–1605. <https://doi.org/10.1039/C0EE00470G>
- 42 Peigney, A.; Laurent, Ch.; Flahaut, E.; Bacsá, R. R.; Rousset, A. Specific Surface Area of Carbon Nanotubes and Bundles of Carbon Nanotubes. *Carbon* **2001**, *39* (4), 507–514. [https://doi.org/10.1016/S0008-6223\(00\)00155-X](https://doi.org/10.1016/S0008-6223(00)00155-X)
- 43 Kim, S.-U.; Lee, K.-H. Carbon Nanofiber Composites for the Electrodes of Electrochemical Capacitors. *Chemical Physics Letters* **2004**, *400* (1), 253–257. <https://doi.org/10.1016/j.cplett.2004.10.124>

- 44 Peng, Y.; Zhang, X.; Sun, R.; Zhang, X.; Ge, C.; Liu, Y. Review of Electro-Spun Carbon Nanofiber Electrode Materials for Electrochemical Capacitors. *Journal of Materials Chemistry A* **2024**, *12* (47), 32566–32592. <https://doi.org/10.1039/D4TA06221C>
- 45 Khodabakhshi, S.; Fulvio, P. F.; Andreoli, E. Carbon Black Reborn: Structure and Chemistry for Renewable Energy Harnessing. *Carbon* **2020**, *162*, 604–649. <https://doi.org/10.1016/j.carbon.2020.02.058>
- 46 Al-Hartomy, O. A.; Al-Solamy, F.; Al-Ghamdi, A.; Dishovsky, N.; Ivanov, M.; Mihaylov, M.; El-Tantawy, F. Influence of Carbon Black Structure and Specific Surface Area on the Mechanical and Dielectric Properties of Filled Rubber Composites. *International Journal of Polymer Science* **2011**, *2011* (1), 521985. <https://doi.org/10.1155/2011/521985>
- 47 Williams, J. H.; Gbadosi, M.; Greytak, A. B.; Myrick, M. L. Measuring the Surface Area of Carbon Black Using BET Isotherms: An Experiment in Physical Chemistry. *Journal of Chemical Education* **2023**, *100* (12), 4838–4844. <https://doi.org/10.1021/acs.jchemed.3c00764>
- 48 Yang, K.; Cho, K.; Kim, S. Effect of Carbon Black Addition on Thermal Stability and Capacitive Performances of Supercapacitors. *Scientific Reports* **2018**, *8* (1), 11989. <https://doi.org/10.1038/s41598-018-30507-5>
- 49 Zeiger, M.; Jäckel, N.; Mochalin, V. N.; Presser, V. Review: Carbon Onions for Electrochemical Energy Storage. *Journal of Materials Chemistry A* **2016**, *4* (9), 3172–3196. <https://doi.org/10.1039/C5TA08295A>
- 50 Sakulaue, P.; Réty, B.; Ishii, T.; Ghimbeu, C. M.; Nueangnoraj, K. Unveiling the Influence of Graphitic Nanocarbon Structures, Defects, and Surface Functional Groups on Supercapacitive Performance in LiTFSI Electrolyte. *Batteries & Supercaps* **2026**, *9* (2), e202500932. <https://doi.org/10.1002/batt.202500932>
- 51 Zeiger, M.; Jäckel, N.; Aslan, M.; Weingarth, D.; Presser, V. Understanding Structure and Porosity of Nanodiamond-Derived Carbon Onions. *Carbon* **2015**, *84*, 584–598. <https://doi.org/10.1016/j.carbon.2014.12.050>
- 52 Moussa, G.; Matei Ghimbeu, C.; Taberna, P.L.; Simon, P.; Vix-Guterl, C. Relationship between the Carbon Nano-Onions (CNOs) Surface Chemistry/Defects and Their Capacitance in Aqueous and Organic Electrolytes. *Carbon* **2016**, *105*, 628–637. <https://doi.org/10.1016/j.carbon.2016.05.010>
- 53 Gao, Y.; Zhou, Y. S.; Qian, M.; He, X. N.; Redepenning, J.; Goodman, P.; Li, H. M.; Jiang, L.; Lu, Y. F. Chemical Activation of Carbon Nano-Onions for High-Rate Supercapacitor Electrodes. *Carbon* **2013**, *51*, 52–58. <https://doi.org/10.1016/j.carbon.2012.08.009>
- 54 Wang, Y.; Hu, A. Carbon Quantum Dots: Synthesis, Properties and Applications. *Journal of Materials Chemistry C* **2014**, *2* (34), 6921–6939. <https://doi.org/10.1039/C4TC00988F>
- 55 Arora, G.; Sabran, N. S.; Ng, C. Y.; Low, F. W.; Jun, H. K. Applications of Carbon Quantum Dots in Electrochemical Energy Storage Devices. *Heliyon* **2024**, *10* (15), e35543. <https://doi.org/10.1016/j.heliyon.2024.e35543>
- 56 Kumar, P.; Dua, S.; Kaur, R.; Kumar, M.; Bhatt, G. A Review on Advancements in Carbon Quantum Dots and Their Application in Photovoltaics. *RSC Advances* **2022**, *12* (8), 4714–4759. <https://doi.org/10.1039/D1RA08452F>
- 57 Solomon Jones, S.; Sahatiya, P.; Badhulika, S. One Step, High Yield Synthesis of Amphiphilic Carbon Quantum Dots Derived from Chia Seeds: A Solvatochromic Study. *New Journal of Chemistry* **2017**, *41* (21), 13130–13139. <https://doi.org/10.1039/C7NJ03513F>
- 58 Hoang, V. C.; Dave, K.; Gomes, V. G. Carbon Quantum Dot-Based Composites for Energy Storage and Electrocatalysis: Mechanism, Applications and Future Prospects. *Nano Energy* **2019**, *66*, 104093. <https://doi.org/10.1016/j.nanoen.2019.104093>

- 59 Alva, M. S.; Nazareth, R. A.; Sudhakar, Y. N.; Desai, N. Carbon Quantum Dot Incorporated Xanthan Gum Based Gel Polymer Electrolytes for High Performance Supercapacitors. *Scientific Reports* **2025**, *15* (1), 18227. <https://doi.org/10.1038/s41598-025-02341-z>
- 60 Yu, Y.; Ma, T.; Huang, H. Semiconducting Quantum Dots for Energy Conversion and Storage. *Advanced Functional Materials* **2023**, *33* (16), 2213770. <https://doi.org/10.1002/adfm.202213770>
- 61 R. Holze, F. Béguin, E. Frąckowiak (eds): Supercapacitors – Materials, Systems, and Applications. *Journal of Solid State Electrochemistry* **2015**, *19* (4), 1253–1253. <https://doi.org/10.1007/s10008-014-2718-2>
- 62 Thommes, M.; Kaneko, K.; Neimark, A. V.; Olivier, J. P.; Rodriguez-Reinoso, F.; Rouquerol, J.; Sing, K. S. W. Physisorption of Gases, with Special Reference to the Evaluation of Surface Area and Pore Size Distribution (IUPAC Technical Report). *Pure and Applied Chemistry* **2015**, *87* (9–10), 1051–1069. <https://doi.org/10.1515/pac-2014-1117>
- 63 Barbieri, O.; Hahn, M.; Herzog, A.; Kötz, R. Capacitance Limits of High Surface Area Activated Carbons for Double Layer Capacitors. *Carbon* **2005**, *43* (6), 1303–1310. <https://doi.org/10.1016/j.carbon.2005.01.001>
- 64 Lazzari, M.; Soavi, F.; Mastragostino, M. Mesoporous Carbon Design for Ionic Liquid-Based, Double-Layer Supercapacitors. *Fuel Cells* **2010**, *10* (5), 840–847. <https://doi.org/10.1002/fuce.200900198>
- 65 Chmiola, J.; Yushin, G.; Gogotsi, Y.; Portet, C.; Simon, P.; Taberna, P. L. Anomalous Increase in Carbon Capacitance at Pore Sizes Less Than 1 Nanometer. *Science* **2006**, *313* (5794), 1760–1763. <https://doi.org/10.1126/science.1132195>
- 66 Raymundo-Piñero, E.; Kierzek, K.; Machnikowski, J.; Béguin, F. Relationship between the Nanoporous Texture of Activated Carbons and Their Capacitance Properties in Different Electrolytes. *Carbon* **2006**, *44* (12), 2498–2507. <https://doi.org/10.1016/j.carbon.2006.05.022>
- 67 Stoeckli, F.; Centeno, T. A. Optimization of the Characterization of Porous Carbons for Supercapacitors. *Journal of Materials Chemistry A* **2013**, *1* (23), 6865–6873. <https://doi.org/10.1039/C3TA10906B>
- 68 García-Gómez, A.; Moreno-Fernández, G.; Lobato, B.; A. Centeno, T. Constant Capacitance in Nanopores of Carbon Monoliths. *Physical Chemistry Chemical Physics* **2015**, *17* (24), 15687–15690. <https://doi.org/10.1039/C5CP01904D>
- 69 Liu, X.; Lyu, D.; Merlet, C.; Leesmith, M. J. A.; Hua, X.; Xu, Z.; Grey, C. P.; Forse, A. C. Structural Disorder Determines Capacitance in Nanoporous Carbons. *Science* **2024**, *384* (6693), 321–325. <https://doi.org/10.1126/science.adn6242>
- 70 Liu, X.; Choi, J.; Xu, Z.; Grey, C. P.; Fleischmann, S.; Forse, A. C. Raman Spectroscopy Measurements Support Disorder-Driven Capacitance in Nanoporous Carbons. *Journal of the American Chemical Society* **2024**, *146* (45), 30748–30752. <https://doi.org/10.1021/jacs.4c10214>
- 71 Sadezky, A.; Muckenhuber, H.; Grothe, H.; Niessner, R.; Pöschl, U. Raman Microspectroscopy of Soot and Related Carbonaceous Materials: Spectral Analysis and Structural Information. *Carbon* **2005**, *43* (8), 1731–1742. <https://doi.org/10.1016/j.carbon.2005.02.018>
- 72 Pinero-Raymundo, E.; Leroux, F.; Beguin, F. A High-Performance Carbon for Supercapacitors Obtained by Carbonization of a Seaweed Biopolymer. *Advanced Materials* **2006**, *18* (14), 1877–1882. <https://doi.org/10.1002/adma.200501905>
- 73 Okajima, K.; Ohta, K.; Sudoh, M. Capacitance Behavior of Activated Carbon Fibers with Oxygen-Plasma Treatment. *Electrochimica Acta* **2005**, *50* (11), 2227–2231. <https://doi.org/10.1016/j.electacta.2004.10.005>
- 74 Réty, B.; Yiin, H.Y.; Matei Ghimbeu, C. Quantification of Activated Carbon Functional Groups and Active Surface Area by TPD-MS and Their Impact on Supercapacitor

- Performance. *Energy Storage Materials* **2024**, 103963. <https://doi.org/10.1016/j.ensm.2024.103963>
- 75 Salleh, N. A.; Kheawhom, S.; Ashrina A Hamid, N.; Rahiman, W.; Mohamad, A. A. Electrode Polymer Binders for Supercapacitor Applications: A Review. *Journal of Materials Research and Technology* **2023**, 23, 3470–3491. <https://doi.org/10.1016/j.jmrt.2023.02.013>
- 76 Abbas, Q.; Pajak, D.; Frackowiak, E.; Béguin, F. Effect of Binder on the Performance of Carbon/Carbon Symmetric Capacitors in Salt Aqueous Electrolyte. *Electrochimica Acta* **2014**, 140, 132–138. <https://doi.org/10.1016/j.electacta.2014.04.096>
- 77 Piwek, J.; Platek, A.; Fic, K.; Frackowiak, E. Carbon-Based Electrochemical Capacitors with Acetate Aqueous Electrolytes. *Electrochimica Acta* **2016**, 215, 179–186. <https://doi.org/10.1016/j.electacta.2016.08.061>
- 78 Im, J.; Liu, X.; O’Keefe, C. A.; Grey, C. P.; Forse, A.C. Pore-Intrusion of Polymeric Binder in Supercapacitor Electrodes Decreases Capacitance. *Nanoscale* **2026**. <https://doi.org/10.1039/D5NR05282C>

Characterization techniques

Several techniques served for the characterization of the carbon-based electrode materials and electrochemical capacitors as shown in **Figure 9**. Combination of various, complementary techniques resulted in better understanding of the texture/structure/surface chemistry of carbons that impact the EC performance. Below, selected characterization techniques with the main importance for this thesis were briefly described.

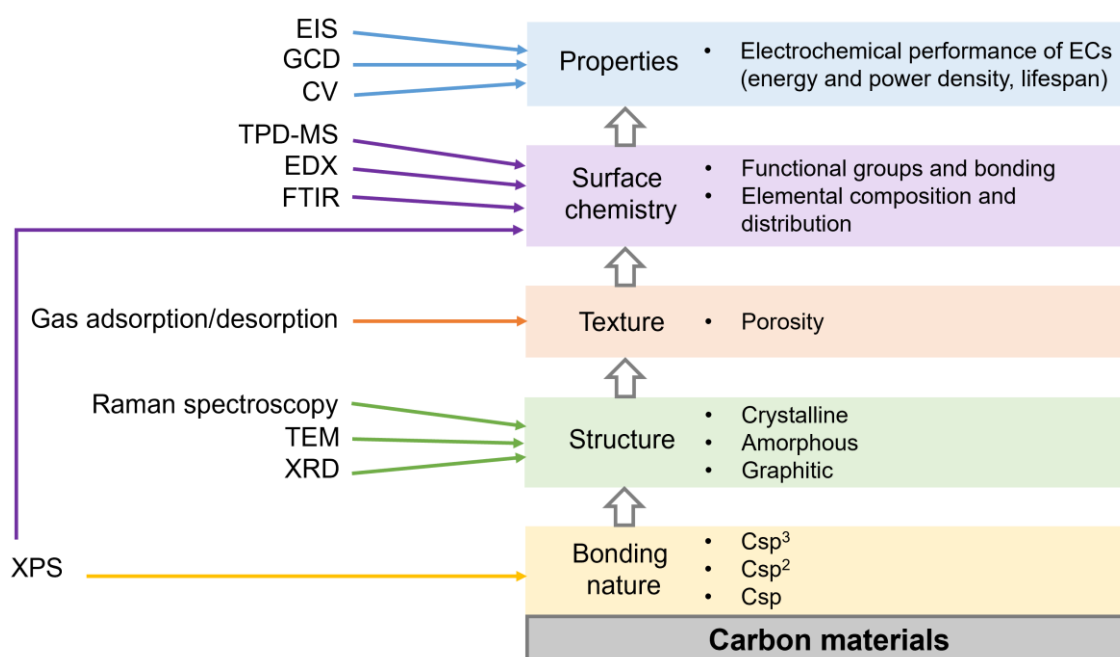


Figure 9 Several techniques employed for characterization of carbon materials (XPS, XRD, TEM, Raman spectroscopy, gas adsorption/desorption, FTIR, EDX, TPD-MS) and electrochemical capacitors (CV, GCD, EIS).

Three main techniques were used for the analysis of the carbon structure, i.e., X-ray diffraction (XRD), transmission electron microscopy (TEM), and Raman spectroscopy. XRD serves for phase identification, microstructural characterization, and structure determination of the powder material. The phenomenon of diffraction arises from the

diffusion of electromagnetic radiation through the solid and structured material¹. According to the Bragg's law, it yields data on interlayer spacing (d_{002}), crystallite size (via Scherrer formula), and the degree of graphitization². Importantly, disordered carbons exhibit a minimal absorption coefficient for X-rays, which causes the diffraction profile to move to a lower angle and broaden considerably¹.

TEM (high-resolution) offers imaging of carbon materials surface at the nanoscale, providing the information on the surface morphology (e.g., the number of graphene layers, and presence of the defects, nanoparticle size), microstructure, and homogeneity³. The mechanism of TEM is based on the interaction between a beam of high-energy accelerated electrons and the atoms of the sample³. Additionally, it serves also to see the mesopores/macropores and eventual impurities; when linked with energy dispersive X-ray spectroscopy (EDX), chemical composition/dopants can be also determined.

Raman spectroscopy is widely used to characterize the local structure of the carbon materials. It employs an incident laser beam that interacts only with the π electrons of sp^2 -hybridized carbon networks⁴. Importantly, the information from Raman spectra is limited to that from thin surface of about 30-60 nm as well as the diameter of the incident laser beam on the sample ($1\ \mu\text{m}$)¹. Therefore, it is highly recommended to collect several Raman spectra across the sample⁵. Typically, two primary bands are noted in the Raman spectra of porous carbons. The first-order graphite band (G) placed around $1590\ \text{cm}^{-1}$ is associated with in-plane vibrations of sp^2 -hybridized carbon atoms^{6,7}. The disorder-induced band (D) observed at $1340\ \text{cm}^{-1}$ corresponds to ring breathing modes primarily driven by disorder (structural defects)⁴. The ratio between the area of D and G bands, described as degree of disorder (I_D/I_G) provides direct information on the carbon structure⁶. The higher I_D/I_G , the higher disorder of the carbon material. Interestingly, the deconvolution of the Raman spectra can further support the interpretation of the results. For instance, the deconvolution into four peaks reveal presence of two additional bands D_2 ($\sim 1180\ \text{cm}^{-1}$) and D_3 ($\sim 1500\ \text{cm}^{-1}$)⁶. The D_2 band, observed as a shoulder of D band is associated with the presence of polyene-like structure, while D_3 band corresponds to the amorphous carbon fraction comprising of e.g., functional groups⁶.

Another characterization technique - X-ray photoelectron spectroscopy (XPS) provides information on the material bonding states, and texture. XPS serves for the analysis of the material's surface up to 10 nm in-depth¹. The XPS spectrum is generated by exposing the material to monoenergetic X-rays, resulting in the emission of photoelectrons. The

energy emitted by the photoelectrons is quantified, followed by the identification, state, and quantity of the element being investigated. Notably, the deconvoluted high-resolution XPS spectra provide information on quantitative surface composition and chemical bonding states (hybrid orbitals employed by carbon atoms, and bonding states of carbon atoms with heteroatoms)¹.

Gas adsorption/desorption is a very useful technique that serves for the material texture analysis. Gas adsorption/desorption isotherm measurements are frequently utilized on porous carbon materials to acquire quantitative data regarding the accessible pores for adsorptive gases, e.g., N₂ (77K), CO₂ (273K)¹. An adsorption isotherm refers to the correlation between the quantity of gas adsorbed and the relative pressure (p/p_0) at a constant temperature. Several types of isotherms were proposed by the IUPAC, through the analysis of the curve shape⁸. For instance, the isotherm denoted as type I corresponds to the highly microporous material, as it strongly adsorbs gas molecules at low p/p_0 (< 0.1), leading to a saturation of adsorption capacity at p/p_0 (< 0.2). Furthermore, depending if the material displays narrow micropores (< 1 nm) or wider micropores and possibly narrow mesopores (< 2.5 nm), an isotherm of type I(a) or I(b) can be distinguished, respectively. In mesoporous materials, characterized by the pore sizes of 2-50 nm, the initial phases of adsorption include the formation of monolayers and multilayers on the pore walls, succeeded by capillary condensation at elevated pressures, resulting in the type IV isotherm, commonly linked to distinct hysteresis loop⁸.

Importantly, the textural characterization of the carbon materials involves essential metrics such SSA, pore volume, and pore size distribution, which are derived often from nitrogen adsorption/desorption measurement⁹. The predominant method for assessing the SSA is the BET equation, which points that the initial layer of adsorbed gas molecules constitutes a complete monolayer prior to the adsorption of further layers. Nonetheless, in microporous carbons, pore filling frequently coincides with the formation of monolayer and multilayer, confounding the interpretation¹⁰. That is why, it is highly recommended to use very low range of p/p_0 (0.01 to 0.05) while using BET equation for porous materials⁵. Recently, another method using two-dimensional-non-local density functional theory (2D-NLDFT) was proposed for the evaluation of cumulative surface area, average pore size, and pore volume¹¹. Traditional model (NLDFT) considered idealized, smooth pore geometries, which is far from the real texture of the tailored carbons. Then, the proposed improvement of the model took into account surface roughness, and heterogeneity (2D-NLDFT)¹¹. Nevertheless, the predominant method for assessing SSA is still the BET equation, because of its ease of use, as well as the comparison with many other studies.

Temperature programmed desorption coupled with mass spectrometry (TPD-MS) is commonly used to analyze the materials functional groups (especially O-groups like carbonyl, carboxyl, hydroxide, quinone, phenol, ether, anhydride)¹². TPD-MS involves the desorption of the functional groups within the increasing temperature up to 950°C followed by quantification of the releasing gases (typically CO, CO₂, H₂, and H₂O) through the mass spectrometry¹². Importantly, the whole bulk of the material is analyzed contrary to the XPS, where only few top material layers are considered. By understanding the temperatures and nature of generated gases associated with various oxygenated surface groups, it is possible to deconvolute the TPD-MS desorption profiles and precisely quantify these functional groups^{12–14}.

Additionally, TPD-MS can give information on the extent of defects and active sites by quantifying the active surface area (ASA)¹³. The ASA is established *via* the chemisorption of O₂ on a carbon devoid of functional groups (desorbed during the thermal treatment of 1st TPD-MS), subsequently followed by the quantification of the resulting oxygenated species (2nd TPD-MS)¹⁵. The assessment of ASA necessitates a specific equipment configuration and calculation, with only a few research studies reporting such values¹⁶. The ASA is a structural parameter linked with defects in the basal and edge planes of carbon (e.g., topological defects, structural defects, dopants). On the other hand, the defects that exist in the graphene basal planes, are evidenced by Raman spectroscopy. Thus, ASA estimation and Raman spectroscopy serve as complementary techniques, since they do not provide information on exactly the same type of defects.

Electrochemical characterization techniques are essential for ascertaining properties of ECs, including capacitance, operating voltage, internal resistance, and power/energy density. For that purpose, several methods such as cyclic voltammetry (CV), galvanostatic charge/discharge (GCD), and electrochemical impedance spectroscopy (EIS) are utilized. These techniques rely on precise measurements of essential parameters – voltage, current, and time – to derive important cell properties.

CV involves linear sweeping the potential of the working electrode between two voltage limits, while measuring the resulting current¹⁷. It leads to a cyclic voltammogram, where current is a function of applied potential, which elucidates charge storage mechanism (capacitive or faradaic), reaction kinetics, and electrode stability of the system¹⁸. For an ideal EC, a rectangular shape of CV curve should be observed, emphasizing the EDL operating mechanism, whereas the presence of redox peaks indicates pseudocapacitive contribution¹⁹.

In GCD, the cell is charged with a constant current until it reaches a maximum voltage, and then subsequently discharged with a constant current of identical magnitude, but opposite direction to the charging current, until it attains a minimum voltage²⁰. Commonly, the voltage is recorded as a function of time during the testing. The ideal EC behavior should be observed as a symmetrical triangle, with the energetic efficiency that is equal between the charging and discharging¹⁹. Nonetheless, in practical situations, deviations from ideal GCD curve frequently arise. GCD is very often used for the calculation of the capacitance, as the integral serve for precise acquiring of the area under the discharge and charge curve²¹. Moreover, GCD can be employed to analyze the EC lifespan through cycling (repeating GCD until end-of-life is reached) or floating (protocol consisting of three GCD followed by the 2h voltage hold, repeated until end-of-life is achieved)²².

EIS in potentiostatic mode is characterized by a small amplitude sinusoidal voltage (± 5 -10 mV) superimposed on a constant voltage setpoint. The resultant (sinusoidal) current response is observed as a function of frequency, generally in a broad range (kHz to mHz) to elucidate processes occurring at various time scales²³. EIS results, including impedance magnitude, phase angle, and frequency, can be depicted in diverse graphical styles to examine the electrochemical behavior of the system^{23,24}. One possibility is Nyquist plot, where $\text{Re}(Z)$ is plotted on the X-axis and the $-\text{Im}(Z)$ on the y-axis. Every point on the Nyquist plot represents the impedance at a particular frequency, with high-frequency data generally situated near the origin and low-frequency data spreading further along the plot²⁵. The shape of the Nyquist plot provides valuable insights into the electrochemical processes of the system through the analysis of the parameters of importance, e.g., electrode resistance, internal resistance, charge transfer resistance, and diffuse layer resistance^{25,26}.

References

- 1 Inagaki, M.; Kang, F.; *Materials Science and Engineering of Carbon: Fundamentals*, **2014**. <https://doi.org/10.1016/C2013-0-13699-9>
- 2 Putman, K. J.; Rowles, M. R.; Marks, N. A.; de Tomas, C.; Martin, J. W.; Suarez-Martinez, I. Defining Graphenic Crystallites in Disordered Carbon: Moving beyond the Platelet Model. *Carbon* **2023**, *209*, 117965. <https://doi.org/10.1016/j.carbon.2023.03.040>
- 3 Pawlyta, M. Transmission Electron Microscope Studies on Carbon Nanostructured Materials. *Archives of Materials Science and Engineering*, **2013**, Vol. 63, Iss. 2, p. 58-67
- 4 Ferrari, A. C.; Robertson, J. Interpretation of Raman Spectra of Disordered and Amorphous Carbon. *Physical Review B* **2000**, *61* (20), 14095–14107. <https://doi.org/10.1103/PhysRevB.61.14095>
- 5 Platek-Mielczarek, A.; Nita, C.; Matei Ghimbeu, C.; Frackowiak, E.; Fic, K. Link between Alkali Metals in Salt Templates and in Electrolytes for Improved Carbon-Based Electrochemical Capacitors. *ACS Applied Materials & Interfaces* **2021**, *13* (2), 2584–2599. <https://doi.org/10.1021/acsami.0c18627>
- 6 Sadezky, A.; Muckenhuber, H.; Grothe, H.; Niessner, R.; Pöschl, U. Raman Microspectroscopy of Soot and Related Carbonaceous Materials: Spectral Analysis and Structural Information. *Carbon* **2005**, *43* (8), 1731–1742. <https://doi.org/10.1016/j.carbon.2005.02.018>
- 7 Pawlyta, M.; Rouzaud, J.N.; Duber, S. Raman Microspectroscopy Characterization of Carbon Blacks: Spectral Analysis and Structural Information. *Carbon* **2015**, *84*, 479–490. <https://doi.org/10.1016/j.carbon.2014.12.030>
- 8 Thommes, M.; Kaneko, K.; Neimark, A. V.; Olivier, J. P.; Rodriguez-Reinoso, F.; Rouquerol, J.; Sing, K. S. W. Physisorption of Gases, with Special Reference to the Evaluation of Surface Area and Pore Size Distribution (IUPAC Technical Report). *Pure and Applied Chemistry* **2015**, *87* (9–10), 1051–1069. <https://doi.org/10.1515/pac-2014-1117>
- 9 Sing, K. S. W. Reporting Physisorption Data for Gas/Solid Systems with Special Reference to the Determination of Surface Area and Porosity (Recommendations 1984). *Pure and Applied Chemistry*. **1985**, *57* (4), 603–619. <https://doi.org/10.1351/pac198557040603>
- 10 Bardestani, R.; Patience, G. S.; Kaliaguine, S. Experimental Methods in Chemical Engineering: Specific Surface Area and Pore Size Distribution Measurements—BET, BJH, and DFT. *The Canadian Journal of Chemical Engineering* **2019**, *97* (11), 2781–2791. <https://doi.org/10.1002/cjce.23632>
- 11 Jagiello, J.; Olivier, J. P. 2D-NLDFT Adsorption Models for Carbon Slit-Shaped Pores with Surface Energetical Heterogeneity and Geometrical Corrugation. *Carbon* **2013**, *55*, 70–80. <https://doi.org/10.1016/j.carbon.2012.12.011>
- 12 Rocha, R. P.; Pereira, M. F. R.; Figueiredo, J. L. Characterisation of the Surface Chemistry of Carbon Materials by Temperature-Programmed Desorption: An Assessment. *Catalysis Today* **2023**, *418*, 114136. <https://doi.org/10.1016/j.cattod.2023.114136>
- 13 Réty, B.; Yiin, H.Y.; Matei Ghimbeu, C. Quantification of Activated Carbon Functional Groups and Active Surface Area by TPD-MS and Their Impact on Supercapacitor Performance. *Energy Storage Materials* **2024**, 103963. <https://doi.org/10.1016/j.ensm.2024.103963>
- 14 Ishii, T. Molecular-Level Understanding of Carbon Materials by Temperature-Programmed Desorption. *Carbon Reports* **2023**, *2* (2), 78–90. <https://doi.org/10.7209/carbon.020203>

- 15 Beda, A.; Vaulot, C.; Rabuel, F.; Morcrette, M.; Ghimbeu, C. M. The Role of Specific and Active Surface Areas in Optimizing Hard Carbon Irreversible Capacity Loss in Sodium Ion Batteries. *Energy Advances* **2022**, *1* (4), 185–190. <https://doi.org/10.1039/D2YA00004K>
- 16 Moussa, G.; Matei Ghimbeu, C.; Taberna, P.-L.; Simon, P.; Vix-Guterl, C. Relationship between the Carbon Nano-Onions (CNOs) Surface Chemistry/Defects and Their Capacitance in Aqueous and Organic Electrolytes. *Carbon* **2016**, *105*, 628–637. <https://doi.org/10.1016/j.carbon.2016.05.010>
- 17 Elgrishi, N.; Rountree, K.J.; McCarthy, B.D.; Rountree, E.S.; Eisenhart, T.T.; Dempsey, J.L.; A Practical Beginner's Guide to Cyclic Voltammetry, *Journal of Chemical Education*. **2018**, *95*, (2), 197–206. <https://doi.org/10.1021/acs.jchemed.7b00361>
- 18 Conway, B. E. *Electrochemical Supercapacitors*; Springer US: Boston, MA, **1999**. <https://doi.org/10.1007/978-1-4757-3058-6>
- 19 Béguin, F.; Presser, V.; Balducci, A.; Frackowiak, E. Carbons and Electrolytes for Advanced Supercapacitors. *Advanced Materials* **2014**, *26* (14), 2219–2251. <https://doi.org/10.1002/adma.201304137>
- 20 Misra, A. Concepts of Electrochemical Processes. In *Supercapacitors: Concepts and advances*; IOP Publishing, **2025**. <https://doi.org/10.1088/978-0-7503-5944-3ch3>
- 21 Gittins, J. W.; Chen, Y.; Arnold, S.; Augustyn, V.; Balducci, A.; Brousse, T.; Frackowiak, E.; Gómez-Romero, P.; Kanwade, A.; Köps, L.; Jha, P. K.; Lyu, D.; Meo, M.; Pandey, D.; Pang, L.; Presser, V.; Rapisarda, M.; Rueda-García, D.; Saeed, S.; Shirage, P. M.; Ślesieński, A.; Soavi, F.; Thomas, J.; Titirici, M.-M.; Wang, H.; Xu, Z.; Yu, A.; Zhang, M.; Forse, A. C. Interlaboratory Study Assessing the Analysis of Supercapacitor Electrochemistry Data. *Journal of Power Sources* **2023**, *585*, 233637. <https://doi.org/10.1016/j.jpowsour.2023.233637>
- 22 Platek, A.; Piwek, J.; Fic, K.; Frackowiak, E. Ageing Mechanisms in Electrochemical Capacitors with Aqueous Redox-Active Electrolytes. *Electrochimica Acta* **2019**, *311*, 211–220. <https://doi.org/10.1016/j.electacta.2019.04.117>
- 23 Holze, R. F. Béguin, E. Frackowiak (Eds): Supercapacitors – Materials, Systems, and Applications. *Journal of Solid State Electrochemistry* **2015**, *19* (4), 1253–1253. <https://doi.org/10.1007/s10008-014-2718-2>
- 24 Zhang, J.; Zhao, X. S. On the Configuration of Supercapacitors for Maximizing Electrochemical Performance. *ChemSusChem* **2012**, *5* (5), 818–841. <https://doi.org/10.1002/cssc.201100571>
- 25 Mei, B.A.; Munteshari, O.; Lau, J.; Dunn, B.; Pilon, L. Physical Interpretations of Nyquist Plots for EDLC Electrodes and Devices. *The Journal of Physical Chemistry C* **2018**, *122* (1), 194–206. <https://doi.org/10.1021/acs.jpcc.7b10582>
- 26 Parejo-Tovar, A.; Béguin, F. The NaClO₄-Water Eutectic Electrolyte for Environmentally Friendly Electrical Double-Layer Capacitors Operating at Low Temperature. *Energy Storage Materials* **2024**, *69*, 103387. <https://doi.org/10.1016/j.ensm.2024.103387>

Electrochemical capacitor in aqueous electrolyte with long lifespan improved by hydrogen bond donor addition

<https://doi.org/10.1016/j.mattod.2023.06.018>

In electrochemical capacitors utilizing neutral salt aqueous electrolytes, the corrosion of the stainless-steel current collectors poses a major challenge, impacting the lifespan, efficiency, and the capacitance. In the study presented in this chapter, for the first time the effect of the hydrogen bond donor (HBD) additive to 1M Li_2SO_4 electrolyte is investigated, resulting in a green, low-cost EC. Importantly, urea effectively inhibits the corrosion of stainless steel and enhance the EC lifespan due to specific interaction of urea-water- Li_2SO_4 in the hydrogen bonded network, as shown in **Figure 10**.

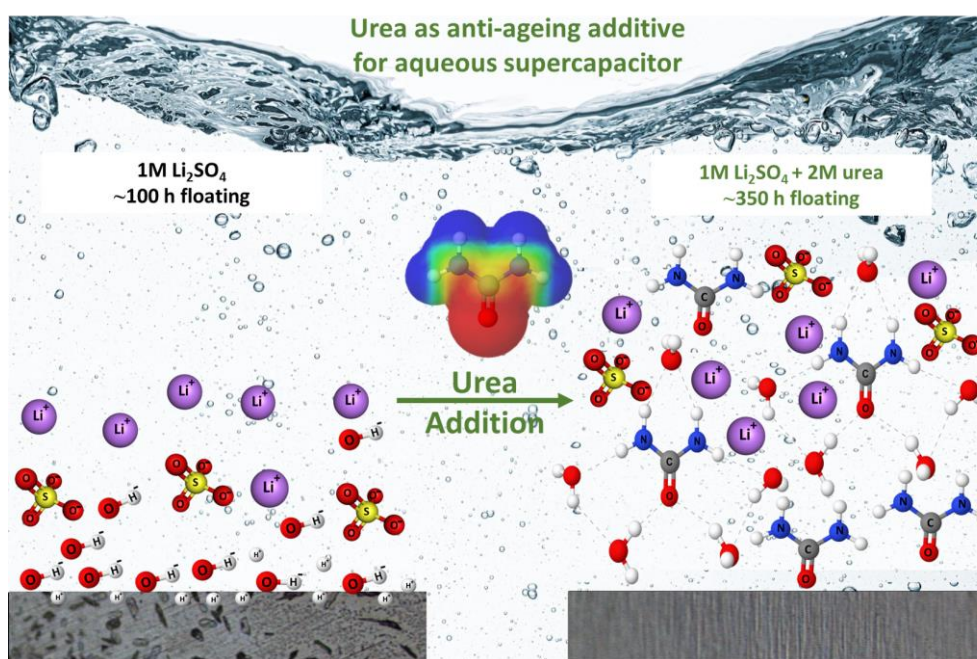


Figure 10 Graphical presentation of anti-corrosive and anti-ageing effect on EC due to the formation of hydrogen bond network after adding urea to 1M Li_2SO_4 .

The new EC electrolyte was composed of 1M Li₂SO₄ and urea additive in different concentrations (0.5, 1, 2M). Several physicochemical (pH, conductivity measurement, FTIR, TEM, SEM, N₂ sorption, Raman spectroscopy, GCMS) and electrochemical (CV, GCD, EIS, linear polarization, cyclic potentiodynamic polarization) techniques were employed for in-detail characterization.

Physicochemical characterization of the electrolyte revealed that the urea additive did not impact significantly the ionic conductivity and pH of the 1M Li₂SO₄. The ionic conductivity slightly decreased from 77 mS cm⁻¹ to 65 mS cm⁻¹, when 2M of urea was added. The pH shifted slightly into more alkaline, due to weak base character of urea. The FTIR spectra of the electrolyte with and without urea additive overlapped, except the band associated with C-N stretching vibration. Notably, the urea could be easily incorporated into a 1M Li₂SO₄ solution without being split into ions.

Electrochemical corrosion analyses demonstrated that urea markedly suppresses stainless-steel degradation. Specifically, the corrosion current decreased substantially (from 6.60 μA to 0.55 μA) and the corrosion potential shifted toward more cathodic value with the increasing urea concentration (up to 2M), confirming its strong inhibiting effect. Moreover, Raman spectra of stainless-steel discs after corrosion testing further revealed that the urea prevents the development of pitting corrosion products, i.e., Fe₂O₃, and promotes the formation of a passivation layer composed of FeOOH.

A symmetric cell containing porous carbon electrodes and 1M Li₂SO₄ electrolyte, with/without urea was subjected to the EC electrochemical testing. Several types of porous carbons were considered (YP50F, YP80F, BP2000, Kynol 507-20). Among them, BP2000 was selected as the most appropriate due to its high mesoporosity, that supports high-rate capability of EC. The CV voltage extension emphasized that there is no significant deviation from the ideal rectangular CV shape when the urea is added. Moreover, the GCD served for the calculation of coulombic efficiency (95%) and energetic efficiency (80%), thus 1.6 V was set as a stability limit. The capacitance value of ~100 F g⁻¹ was similar for the electrolytes with different urea concentrations, as well as the pure 1M Li₂SO₄. Therefore, the urea additive is not detrimental to the electrochemical stability and capacitive performance of the device.

The lifespan of the EC was evaluated using two protocols – cycling and floating. Two parameters of importance were tracked – capacitance retention and equivalent series resistance retention until at least one of the end-of-life criteria was achieved. High cycling stability of the EC with urea additive (< 60 000 cycles) was observed, comparing with 1M Li₂SO₄ (47 000 cycles). Additionally, floating which is a less time consuming and more

harsh protocol emphasized more clearly the benefit of the urea additive. The additive of 0.5M urea delayed the drop in the relative capacitance for up to 206 floating hours. Importantly, further increasing the concentration of the added urea to 1M Li_2SO_4 , resulted in nearly three times EC lifespan improvement (350 floating hours with 2M urea).

Then, two advanced techniques were utilized to understand the origin of the lifespan improvement as well as the anticorrosive character of carbon-based EC operating with/without 2M urea additive to 1M Li_2SO_4 . Raman spectroscopy in *operando* mode served for the evaluation of the physicochemical changes at the electrode/electrolyte interface during the cycling. Notably, the degree of disorder remained constant in the case of the urea additive, while increased when 1M Li_2SO_4 was utilized. It emphasizes the accelerated degradation of the electrode material due to the formation of defects, when 1M Li_2SO_4 was employed as electrolyte. Moreover, the changes of the water peak were observed for the urea-based electrolyte, while it remained stable in the 1M Li_2SO_4 . The band around 3500 cm^{-1} , ascribed as stretching of OH group was not present in the solution with urea additive. On the other hand, the OH related band was well visible for EC operating in 1M Li_2SO_4 . Then, *operando* gas chromatography-mass spectrometry (GCMS) allowed the analysis of the gas evolution from electrolyte/electrode interface during the EC lifespan evaluation by floating. Lower CO_2 evolution was observed for 1M Li_2SO_4 with 2M urea additive than for pure 1M Li_2SO_4 based EC. In conclusion, the *operando* testing indicated that urea has an ability to reduce the activity of the water (formation of hydrogen bond network), thus, preventing the structural degradation of the electrode.

Importantly, the density functional theory (DFT) calculation served for the estimation of the interactions that occur between water, urea, and Li_2SO_4 molecules. A formation of a strong hydrogen bond network was confirmed, where urea interacts strongly with surrounding water molecules, and participates in the restructuring of the solvation shells of Li^+ and SO_4^{2-} ions. Furthermore, the hydrogen bond network reduces the fraction of free water molecules and modifies the ion-solvent interaction, thereby suppressing water activity.

Concluding, the incorporation of the urea as a hydrogen bond donor additive to 1M Li_2SO_4 electrolyte efficiently mitigated corrosion of stainless-steel current collectors, and limited ageing processes. At the same time, the high ionic conductivity and capacitive characteristics of 1M Li_2SO_4 based EC was preserved. This study offers a facile, cost-effective, and environmentally benign approach to the development of durable, high-performance aqueous electrochemical capacitors.



Electrochemical capacitor in aqueous electrolyte with long lifespan improved by hydrogen bond donor addition

Sara Azmi*, Amelia Klimek, Elzbieta Frackowiak*

Institute of Chemistry and Technical Electrochemistry, Poznan University of Technology, Berdychowo 4, Poznan 60-965, Poland

In the electrochemical capacitors (ECs) operating with aqueous electrolytes, corrosion of the current collector is one of critical issues that affects the cycling life, efficiency, and capacitance of the devices. So far, there are no stable metal current collectors in the water-based electrolyte because of its corrosive nature, even if the pH is close to neutral. Here, urea ($\text{CH}_4\text{N}_2\text{O}$) is used as an anticorrosive, green additive to 1 M lithium sulfate electrolyte for low-cost electrochemical capacitors based on carbon BP2000 electrodes. In this work, the corrosion study of stainless steel in the presence of such amide demonstrates an effective corrosion-inhibiting character owing to the urea interaction with water in the hydrogen-bonded network. Chemical stability of current collectors owing to a significant 10-fold decrease of the corrosion current and shift of the corrosion potential into negative side has been achieved when 2 M urea, i.e., hydrogen-bond donor (HBD) is added to electrolyte. Furthermore, the addition of this organic compound improves the capacitive performance of the system and prevents the fading of the device with no influence on the electrolyte conductivity. During the floating test of EC at 1.6 V operating in 1 M Li_2SO_4 with 2 M urea, the capacitance and resistance values keep the end-of-life criteria for over 350 h. Moreover, the galvanostatic investigation of such EC (at 1 A/g) displays performance of more than 60 000 cycles. Furthermore, operando experiments proved that carbon-based electrodes behave differently in lithium sulfate with urea and without additive owing to the formation of strong hydrogen bond network. The molecular structure of electrolyte has been estimated by DFT calculations. Overall, by using lithium sulfate and urea as an electrolytic system, the EC current collector has not only superior corrosion resistance against the aqueous electrolyte but also a high anti-ageing character at 1.6 V, which is favorable to improve the EC electrochemical performance. The use of urea as a stable, cheap electrolyte additive provides an innovative technique to enhance the performance of low-cost aqueous based supercapacitors.

Keywords: Electrochemical capacitor; Hydrogen bond donor; Lithium sulphate; Urea; Neutral electrolyte

Introduction

The use of electricity in the total world energy consumption is growing rapidly, and this trend is expected to increase in the

future. The challenge of the 21st century consists of harnessing new and clean energy on a worldwide level, as we need to drastically reduce our dependence on fossil fuels, a source of greenhouse gas emissions. Within this context, several alternative solutions are being considered. In particular, further progress must be made in the implementation of renewable energy. Consequently, electricity storage should enable a significant increase

* Corresponding authors.

E-mail addresses: Azmi, S. (sara.azmi.sa@gmail.com), Frackowiak, E. (elzbieta.frackowiak@put.poznan.pl).

in the market for renewable energy production in power grids. In fact, the charge storage has always been a major weakness of the energy cycle [1]. Several energy storage systems are available. Among them, battery technology delivers long operation time (10 h) and high energy. However, its lower power density and poor cyclability limit the battery application in several sectors [2]. The electrochemical capacitor (EC), also known as the supercapacitor (SC), is one of the emerging alternatives that bridge the gap between batteries and conventional capacitors due to its high power, safety, and long cycle life [3]. ECs are generating considerable interest in terms of their application in aerospace [4], defense application [5], implantable electronic medical devices, and electromobilities [6]. Generally, ECs store a charge by an electrostatic process, however, faradaic reactions can as well take place at the electrode/electrolyte interface [7]. Traditionally, the porous carbon allotropes are the preferred choice as the EC electrodes because of their high surface area and electrical conductivity [8]. Activated carbon [9], graphene [10], nanotubes [11], and carbide-derived carbon [12,13] are the most widely applied carbon electrodes for the ECs. To date, additional materials based on MXenes [14–16], transition metals dichalcogenides and oxides [17–19], layered double hydroxides [20,21] have also been used as electrodes for the ECs. The EC characteristics (power density, cyclability, and energy density) are strongly affected by the electrolytes [22]. Several electrolytes have been developed for the ECs, such as organic [12], ionic liquids [23,24], deep eutectic solvents [10,25], and aqueous [26,27] electrolytes. In the EC manufacturing, several parameters are taken into consideration, including the assembling and raw material costs, eco-friendliness, and long-term performance [28]. In this regard, the aqueous electrolyte-based EC offers a great opportunity to develop safe, eco-friendly, and cheap ECs with competitive characteristics [29]. Commonly, the ECs based on aqueous electrolytes such as alkaline KOH or acidic H_2SO_4 display a narrow cell voltage range (0–1 V) limited by water splitting [30,31]. Neutral electrolytes including Na_2SO_4 and LiNO_3 have proven higher operating cell voltages (1.5–2 V) depending on the type of the current collector due to the high overpotential for hydrogen evolution at the negative electrode [32] but also hydrogen electrosorption.

Lithium sulfate (Li_2SO_4) is among the best neutral electrolytes offering high solubility and good capacitive performance for the device [33]. However, the ECs operating with Li_2SO_4 using stainless steel current collectors suffer from a low lifetime resulting from the corrosion products due to the current collector degradation. Béguin *et al.* studied the ageing of symmetric carbon-based EC operating in Li_2SO_4 [34]. They confirmed the effect of the stainless steel current collector corrosion products on blocking the carbon pores and thus reducing the device performance. Indeed, the use of an inhibitor of the stainless steel's surface will provide a solution for the ageing of ECs operating in aqueous electrolyte. Several technologies including coatings [35], additives [33], and cathodic protection [36] were reported on the protection of the stainless steel current collector surface from corrosion. Urea ($\text{CH}_4\text{N}_2\text{O}$) is already known as a remarkable low-cost amide and eco-friendly chemical compound used in several fields (agriculture, cosmetics) for different purposes [37–39]. For instance, 32 wt% aq. solution of urea (AdBlue) serves effi-

ciently against NO_x emission from the car exhaust systems. Urea has been used as an anticorrosive agent for very aggressive chlorides. Most often the corrosion inhibitor contains such elements as nitrogen, oxygen, sulfur and phosphorus. The combination of two elements supplies even better anticorrosive effect. Hence, hydrogen bond donor such as urea with oxygen and nitrogen in its composition [40–44] can contribute to preventing the EC corrosion caused by the aqueous electrolyte. To the best of our knowledge, there are no studies which report the use of urea as an additive for corrosion inhibition in EC application. Besides the interest in improving ECs performance through current collector protection [45], the ageing and the electrochemical stability have been considered as aspects of high importance [46]. Cycling is the most important property of SCs to analyze the long-term operation of the system. Since such a test requires a long period, an alternative floating methodology with shorter investigation time can be applied to prove the lifetime, stability and ageing of the device [34]. In this work, the principal objective is the application of urea as an additive into the salt aqueous electrolyte to improve the performance of SCs with the stainless steel current collectors. The characteristics of the devices as well as their stability were investigated in 1 M Li_2SO_4 electrolyte with and without urea addition at different concentrations (0.5, 1, and 2 M). Within the eco-friendly, cheap and efficient strategy, this work reports, for the first time, the attractive anti-corrosion properties of the urea as an electrolyte additive to carbon-based ECs with the stainless steel current collectors. Urea as a hydrogen bond donor due to strong interaction with water plays an important multifunctional role in preventing the EC ageing.

Experimental section

Materials

The current collector based on a stainless steel 316L (SS316L) sheet (thickness of 0.01 mm) was obtained from Materialise, Belgium. Black Pearl 2000 (BP 2000) powder was supplied by Cabot®, USA. Kuraray YP50F, YP80F and Kynol ACC 507–20 were utilized for comparison. All chemicals in this study were used without additional purification, urea (ACS reagent, $\geq 99\%$) and lithium sulfate (Li_2SO_4 , $\geq 98\%$) were provided from Sigma Aldrich.

EC electrode preparation

Black Pearl 2000 (BP2000) carbon was used as the electrode material for ECs. The electrode material based on powdered BP2000 was prepared from a paste comprising 85% of BP2000, 10 wt% of poly(tetrafluoroethylene) (PTFE) binder (60% suspension in water) and 5% of C65 conductive carbon black mixed with isopropanol as a solvent. Additional activated carbon materials were used for a comparison study. The YP50F and YP80F electrodes were prepared from a paste containing 90% of active carbon material with 5% PTFE and 5% C65. The mass of the electrode varied from ca. 5 to ca. 13 mg. The components were combined in a mortar and a homogenous paste was obtained. Then, the dough was press-rolled to a thickness of 200 μm , using the calendaring machine. Electrode with the biggest mass (12.7 mg) has a thickness of 400 μm . Self-standing electrodes from activated carbon cloth Kynol® 507–20 have been tested. Finally, electrodes with a diameter of 10 mm were cut and dried for 24 h at 60 °C.

Electrochemical characterization

At the beginning, the electrochemical characterization was used to define the corrosion properties of the stainless steel 316L in 1 M Li_2SO_4 and its mixtures with urea at different concentrations (0.5, 1, and 2 M). For this purpose, the stainless steel discs with a diameter of 10 mm were cut and utilized as working and counter electrodes in the three-electrode Swagelok® cells. Before the electrochemical investigations, the electrodes were cleaned ultrasonically in acetone and distilled water for 15 min, then, dried in a dryer. The electrochemical behavior of the samples was studied using a multichannel potentiostat/galvanostat (VMP3, Biologic, France). The electrochemical procedure was initiated by measurement of the open circuit potential (OCP) for 180 min, followed by linear polarization (LP). From the extrapolation of polarization curves Tafel plots were crossed out. Next, the cyclic potentiodynamic polarization (CPP) analysis was conducted at 20 mV min^{-1} . The working electrode was polarized cathodically versus OCP and then anodically until a current value of $100 \mu\text{A}$ was obtained.

For study of the electrochemical capacitor performance, BP2000-based electrodes were assembled and tested using 1 M Li_2SO_4 and its mixtures with urea in different concentrations. For this purpose, a two-electrode PTFE based Swagelok® cell with a stainless-steel current collector was used for building symmetrical cells. Cyclic voltammetry (CV) at sweep rates of $1\text{--}100 \text{ mV s}^{-1}$, galvanostatic charge–discharge (GCD) at $0.1\text{--}10 \text{ A g}^{-1}$ current density, as well as electrochemical impedance spectroscopy from 100 kHz to 1 MHz frequency range (at 0 V), have been utilized. Capacitance values were expressed per one electrode. The EC performance stability was investigated by a long-term ageing procedure called floating using three GCD cycles at cell maximum voltage (U_{max}), followed by a voltage holding at U_{max} (1.6 V) for 2 h. After each voltage holding, CV and EIS measurements were recorded. Galvanostatic cycling was carried out at 1 A g^{-1} .

Physicochemical characterization

All the used carbon materials were characterized by Brunauer–Emmett–Teller (BET) isotherm analysis (77 K) with N_2 as the adsorbate (ASAP 2460, Micromeritics, USA) to evaluate the surface area and porosity of the samples. Further morphology investigation was performed using the Scanning Electron Microscopy (SEM) and the Transmission Electron Microscopy (TEM) analysis. The electrical conductivity and the pH of the urea-based electrolytes were investigated using the conductivity meter and the pH meter (Mettler Toledo®, Switzerland). The absorption spectra of the electrolytes were recorded utilizing a PerkinElmer FTIR spectrophotometer with a resolution of 4 cm^{-1} . To assess the structural corrosion properties of the stainless steel 316L discs, Raman spectroscopy analysis was carried out for the identification of the corrosion phases using Thermo Scientific DXR-2 Raman Microscope with a laser emitting at $\lambda = 532 \text{ nm}$ and a power of 5 mW . The estimation of the mass fraction of nitrogen was performed in Thermo Scientific FlashSmart equipment.

Operando characterizations

Raman spectra were recorded with a ThermoFisher® DXR-2 Raman microscope equipped with a 532 nm laser. A three-

electrode electrochemical cell with a BP2000 pellet electrode, Pt wire as the counter electrode and Ag/AgCl as a reference was used. The electrochemical data from cyclic voltammetry (scan rate of 1 mV s^{-1}) in the potential range from -0.86 V to 0.73 V vs NHE were collected every 60 mV . An adequate distance between the working electrode (WE) and the counter electrode (CE) was maintained to avoid any impact of oxygen evolution (at the CE) on measurements. The evolution of gas during capacitor operation was conducted in PAT-Cell-Gas (El-Cell) in an online mode using gas chromatography-coupled with mass spectrometry (GC-MS, Bruker). The monitored mass $m/z = 44$ signal assigned to carbon dioxide was recorded.

Modeling

Geometric optimization of electrolyte molecular structure was calculated using the Density functional theory (DFT), which allows for an approximate solution of the Schrödinger equation for a multiple-particle system (calculation method ab initio). Accurate representation of molecular structure was considered by selecting the specific basis function 6-311G++(d, p), which is appropriate to account for the asymmetry of molecular orbitals. Moreover, the d-type functions with valence p orbitals together with the diffuse functions indicated by the + sign allow for more precisely characterization of the distant parts of the atomic orbitals, which are remotely located from the atomic nuclei. Commercial Gaussian software was used in the calculation.

Based on the results of the modelling, the estimated electron density field (expressed in atomic units e/a_0^3) was used for the calculation of the Laplacian, defined as the divergence of the gradient, according to the following equation and allows to construct the relief map of the molecules:

$$\Delta\rho = \nabla^2\rho = \nabla \cdot \nabla\rho \quad (1)$$

As the electron density is a continuous function in the space of the simulated molecule, the calculation of the Laplacian according to eq. (1) is allowed. The calculation was applied to three-dimensional volumetric data of the electron density using the Paraview 5.11.0 tool, which allows the user to redefine field variables and apply the necessary operators to them. The final profile of the Laplacian is obtained by a three-dimensional scalar field represented on the slice located at water and lithium atoms. The slice contains ten profiles for Laplacian range between -0.01 and 0.01 .

Results and discussion

Electrode characterizations

In electrochemical capacitor, the specific surface area and pore distribution of the electrode materials as well as heteroatom doping [47] are critical for the device performance. For this purpose, the nitrogen adsorption/desorption isotherm and pore size distribution of BP2000 were studied and the results are presented in Fig. S1 (a). By analyzing the isotherm, the presence of a hysteresis loop of adsorption and desorption process at higher relative pressures confirms the presence of mesopores. It can be clearly seen that the BP2000 carbon electrode is composed of micropores but also mesopores between 2 and 50 nm distributed in different sizes. Morphological features of BP2000 were analyzed by

TABLE 1
pH and conductivity (mS cm^{-1}) of 1 M Li_2SO_4 and its mixture with urea ($\text{CH}_4\text{N}_2\text{O}$) at various concentrations at $T = 25^\circ\text{C}$.

Sample	pH	Conductivity (mS cm^{-1})
1 M Li_2SO_4	6.74	76.9
1 M Li_2SO_4 + 0.5 M $\text{CH}_4\text{N}_2\text{O}$	7.05	69.8
1 M Li_2SO_4 + 1 M $\text{CH}_4\text{N}_2\text{O}$	7.23	67.9
1 M Li_2SO_4 + 2 M $\text{CH}_4\text{N}_2\text{O}$	7.57	65.4

SEM and TEM. Fig. S1(b) shows SEM images of BP2000. The BP2000 demonstrates a microstructure with particle cluster structure. Furthermore, TEM images (Fig. S1(c,d)) indicate a spiral lattice fringes with a uniform size distribution.

Electrolyte characterization

Lithium sulfate (1 M) with urea addition was used as an electrolytic solution. Urea (NH_2)—CO—(NH_2) is a planar compound rich in N and O, it can provide a lone pair of electrons acting as adsorptive sites on the metal surface. It is a hydrogen bond donor (HBD), hence, in aqueous electrolyte various intermolecular bonds, i.e., urea-water, urea-urea, water-water interactions play a crucial role at electrode/electrolyte interface, in turn, in the corrosion inhibition process. Urea can easily replace water molecules in the ion solvated shell without its breaking structure or solution segregation, especially in lower concentration. At room temperature, urea molecules, which have covalent internal bonds, are easily incorporated into a water medium without being split into ions [48]. Instead, a large number of associations of hydrogen bonds between water molecules and urea molecules is provided because of the strong propensity for urea and water to

form hydrogen bonds with each other [48]. In this work, various concentrations of urea were added to the lithium sulfate electrolyte to provide detailed insight for using it as an anticorrosion and anti-ageing additive. For the high efficiency of corrosion inhibition, a moderate urea concentration has been selected (0.5–2 M) taking into account that above 0.4 mass fraction of urea the physicochemical properties of solution such as conductivity, viscosity, surface tension gradually aggravate. Initially, the conductivity and pH of all urea concentrations were measured and the results are shown in Table 1. It can be noticed that the addition of different concentrations of urea (0.5, 1 and 2 M) did not influence the electrolyte conductivity. It only shifts from 76.9 mS cm^{-1} for 1 M Li_2SO_4 to 65.4 mS cm^{-1} after adding 2 M urea.

The obtained results for the pH study at different concentrations showed a negligible difference of the pH value. This is attributed to the weak base character of urea with an equilibrium constant of $(1.5 \cdot 10^{-14})$ [49]. Furthermore, it was reported by Bull *et al.* that urea decreases the activity of the proton throughout the entire pH range and if the urea concentration is high, hence, pH increases [50]. Therefore, adding urea to lithium sulfate does not significantly affect the pH. The conductivity of the electrolyte at these concentrations slightly decreases. Moreover, the properties of 1 M Li_2SO_4 with and without urea addition (0.5, 1, 2 M) were investigated using infrared spectroscopy (IR) and the results are shown in Fig. 1. It can be noted that the characteristic spectra of the studied electrolytes overlap with the water IR spectrum with its three fundamental molecular vibrations. As can be seen from the figure, the IR spectrum of water is dominated by the intense first two absorption bands around 3657 and 2756 cm^{-1} related to the symmetric and asymmetric O–H stretching, respectively. The third water molecular vibration around 1647 cm^{-1} is originated from the H–O–H bending mode

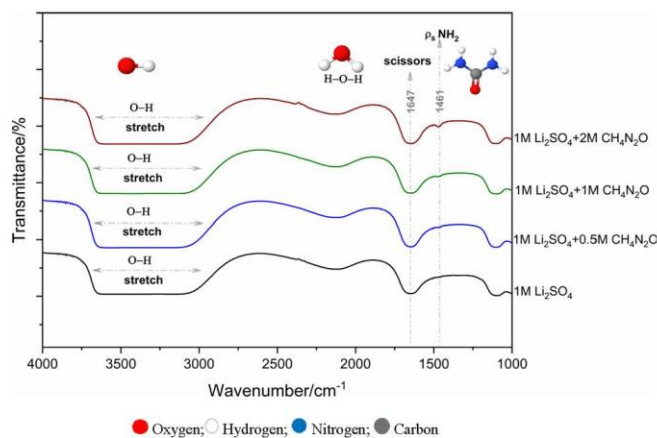


FIG. 1

IR spectra for 1 M Li_2SO_4 , 1 M Li_2SO_4 + 0.5 M urea, 1 M Li_2SO_4 + 1 M urea and 1 M Li_2SO_4 + 2 M urea. ● Oxygen; ○ Hydrogen; ● Nitrogen; ● Carbon.

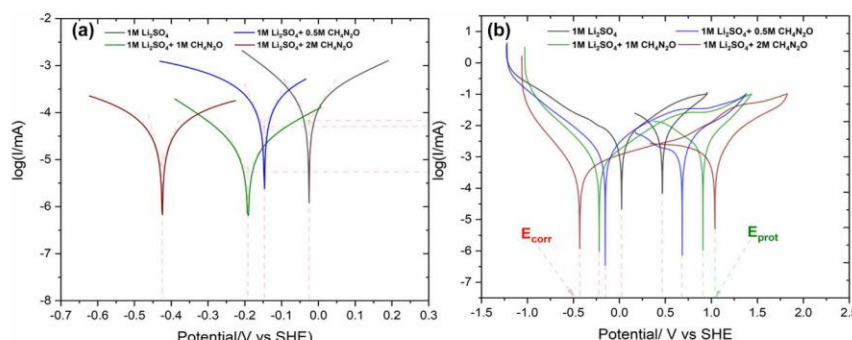


FIG. 2

(a) Tafel plot and (b) Cyclic potentiodynamic polarization curves of stainless steel 316L disc electrodes in 1 M Li_2SO_4 and its urea mixtures (0.5, 1 and 2 M).

(scissoring). After the addition of urea, the IR spectroscopy indicates a new peak around 1461 cm^{-1} characteristic of C-N stretching vibration. Overall, adding urea to the lithium sulfate solution does not decompose the electrolyte. Besides, the energy of urea decomposition in aqueous neutral medium is high (135 kJ/mol).

Current collector corrosion

During the EC cycling, the current collector may suffer corrosion which affects directly the performance of the device [51]. Several studies reported the effectiveness of urea as a significant corrosion inhibitor of metals and alloys [41–43]. In this work, the corrosion inhibition of the stainless steel disc electrodes by urea was studied using the Tafel plots and the cyclic potentiodynamic polarization (Fig. 2(a–b)). Fig. 2(a) shows the polarization curves of stainless steel in various solutions of 1 M Li_2SO_4 with different concentration of urea from 0 to 2 M. From the plots, it can be observed that the addition of urea leads to a shift of the plots towards more cathodic values which confirm the inhibition effect of urea. The corrosion potential (E_{corr}) and the corrosion current (I_{corr}) are obtained using Tafel extrapolation method and the results are shown in Table 2. The E_{corr} of 1 M Li_2SO_4 shifts from -25 mV vs SHE to -146 mV vs SHE after adding 0.5 M of urea. By increasing the urea concentration, the E_{corr} moves gradually towards a more cathodic value. This demonstrates the corrosion inhibition of urea on the stainless steel current collectors. The value of I_{corr} for the 1 M Li_2SO_4 was $6.60\text{ }\mu\text{A}$. When urea was added, the I_{corr} was reduced to $5\text{ }\mu\text{A}$ due to the corrosion protection of urea. Upon increasing the urea concentration, I_{corr} values decreased to $0.55\text{ }\mu\text{A}$, which is one of the most important parameters in demonstrating the corrosion inhibition efficiency of urea [43].

Furthermore, the anticorrosive properties of the studied solutions towards the stainless steel discs have been tested using the cyclic potentiodynamic polarization and the results are shown in Fig. 2(b). Initially, the stainless steel electrode polarization started from the negative values vs OCP passing through the region of active corrosion and then polarized in the direction

TABLE 2

Corrosion parameters for stainless steel 316L discs in 1 M Li_2SO_4 and its mixture with urea ($\text{CH}_4\text{N}_2\text{O}$) at various concentrations at $T = 25^\circ\text{C}$.

Sample	E_{corr} (mV vs SHE)	I_{corr} (μA)	E_{prot} (mV vs SHE)
1 M Li_2SO_4	–25	6.60	477
1 M $\text{Li}_2\text{SO}_4 + 0.5\text{ M}$ $\text{CH}_4\text{N}_2\text{O}$	–146	5.00	692
1 M $\text{Li}_2\text{SO}_4 + 1\text{ M}$ $\text{CH}_4\text{N}_2\text{O}$	–192	0.63	914
1 M $\text{Li}_2\text{SO}_4 + 2\text{ M}$ $\text{CH}_4\text{N}_2\text{O}$	–423	0.55	1045

of the positive values over the passivation region until the current density reached $100\text{ }\mu\text{A}$. The obtained plot can be divided into active region displaying a remarkable drop in current defined as the corrosion potential E_{corr} , and passive regions where the scan direction moves towards a negative potential leading to a passive drop which presents the protection potential E_{prot} .

Raman spectroscopy measurements were performed to analyze the corrosion products of the corroded stainless steel discs in 1 M Li_2SO_4 and its urea mixtures and the results are shown in Fig. 3(a). The spectra are plotted from 200 cm^{-1} to 1500 cm^{-1} wavenumbers. Before corrosion, the Raman spectra (Fig. S2) do not display any corrosion phase peaks. After the corrosion of the sample in 1 M Li_2SO_4 , the graph shows the presence of a sharp peak of metal oxide (hematite $\alpha\text{-Fe}_2\text{O}_3$) at 1008 cm^{-1} which is the product of the stainless steel corrosion process. Additional small peaks around 720 cm^{-1} can be associated with the presence of magnetite ($\gamma\text{-Fe}_2\text{O}_3$), which is the product of pitting corrosion. Raman spectroscopic measurements were also carried out after urea addition to 1 M Li_2SO_4 and the spectrum shows a peak that corresponds to the FeOOH phase (940 cm^{-1}) resulting from the slight increase of pH, but the surface of stainless steel does not have a metal oxide phase (Fig. S3). Moreover, the inhibition effect of urea towards the stainless steel corrosion is clearly noticed by comparing the Raman spectra before and

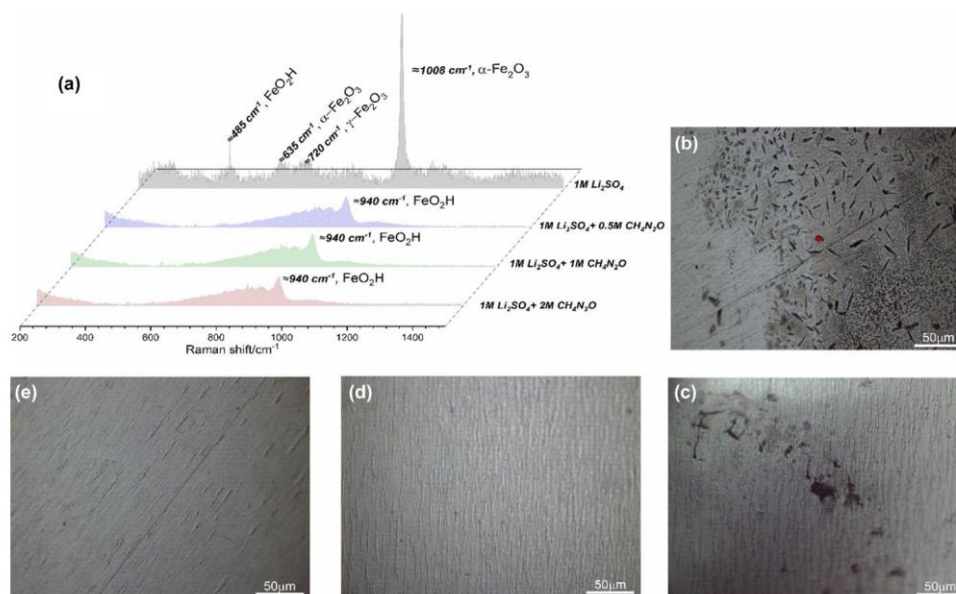


FIG. 3

(a) Raman spectroscopy analysis of the stainless steel 316L disc electrodes after corrosion test in 1 M Li_2SO_4 and its urea mixtures (0.5, 1 and 2 M) electrolytes; Micrographic images of 316L samples tested in: (b) 1 M Li_2SO_4 (c) 1 M Li_2SO_4 + 0.5 M $\text{CH}_4\text{N}_2\text{O}$, (d) 1 M Li_2SO_4 + 1 M $\text{CH}_4\text{N}_2\text{O}$, (e) 1 M Li_2SO_4 + 2 M $\text{CH}_4\text{N}_2\text{O}$.

after its addition. Furthermore, Fig. 3(b-e) presents images of the stainless steel corroded in 1 M Li_2SO_4 with and without urea addition. Before the corrosion study, stainless steel (Fig. S2) displays a smooth surface with several parallel stripes resulting from the mechanical rolling operations. After being corroded in 1 M Li_2SO_4 (Fig. 3(b)), a significant change and defects can be noticed on the stainless steel surface due to the corrosion tendency of the solution. Interestingly, the sample tested in 1 M Li_2SO_4 + 0.5 M $\text{CH}_4\text{N}_2\text{O}$ electrolyte (Fig. 3(c)) shows some decrease in the corrosion effect on the surface, however, some inhomogeneity is visible with traces of corrosion (5 μA corrosion current). Remarkably, by increasing the concentration of urea from 1 M to 2 M (Fig. 3(d-e)), the surface shows the same morphology with no corrosion products on the surface except for some parallel traces resulting from the sample manufacturing. This indicates the highest corrosion resistance of the urea on stainless steel when added to 1 M Li_2SO_4 . It can be concluded that by increasing the urea concentration, the corrosion effect of stainless steel decreases. Overall, the Raman results match well with the electrochemical corrosion investigations and confirm the remarkable inhibition effect of the urea in preventing stainless steel corrosion. Hence, urea is an effective additive that will boost the application of aqueous electrolyte for EC usage by preventing the current collectors corrosion and thus offering a longer lifespan.

Electrochemical capacitor study

Various concentrations of urea (0.5, 1 and 2 M) in the supporting electrolyte 1 M of Li_2SO_4 were examined to provide detailed insight into the effectiveness of using the organic compound (amide) as an attractive anti-ageing additive. For this purpose, a symmetrical two-electrode system assembled using BP2000 electrodes was subjected to electrochemical tests at room temperature. In the initial stage, the maximum operating voltage and the capacitive performance of ECs in 1 M Li_2SO_4 and its urea mixture electrolytes were evaluated by CV analysis and the results are shown in Fig. 4(a-d).

The extended voltage of a device operating in aqueous solution can improve the energy density of the system. From the CV curves recorded at 5 mV s^{-1} , it can be seen that by extending the voltage window from 1 V to 1.6 V, no significant deviation from the initial rectangular shape of CV was observed for the four samples. Higher vertex voltages result in a deviation from the ideal capacitive behavior. Fig. S4(a) presents GCD profiles recorded at 0.5 A g^{-1} for different voltage limitations ranging from 0.8 V to 2.0 V and Fig. S4(b) the coulombic and energetic efficiencies corresponding to each voltage limit. At all the capacitor voltages, the coulombic efficiency calculated from the discharging time is above 95% referring to the ideal capacitive behaviour of the system. However, the coulombic efficiency cal-

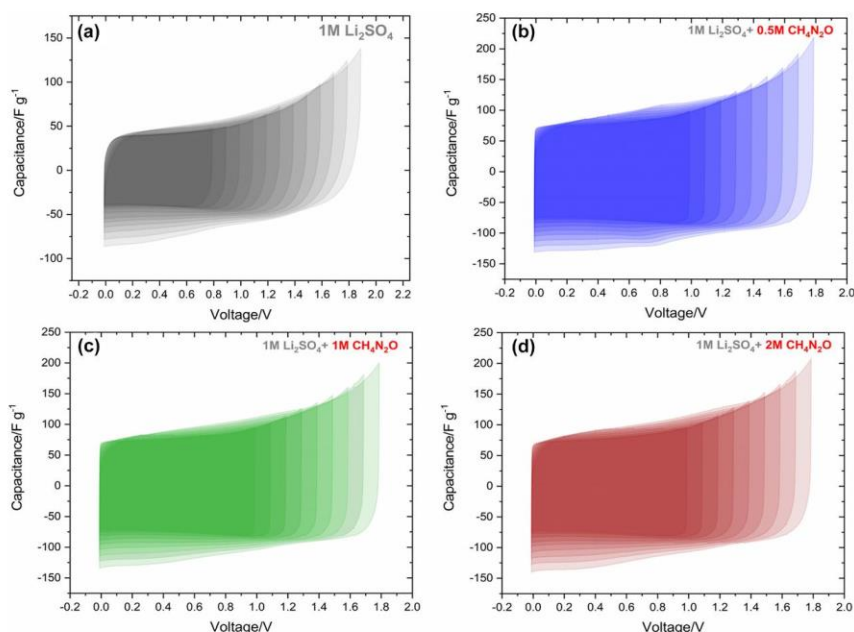


FIG. 4

CV curves at 5 mV s^{-1} of BP2000 electrochemical capacitor for: (a) $1 \text{ M Li}_2\text{SO}_4$, (b) $1 \text{ M Li}_2\text{SO}_4 + 0.5 \text{ M CH}_4\text{N}_2\text{O}$, (c) $1 \text{ M Li}_2\text{SO}_4 + 1 \text{ M CH}_4\text{N}_2\text{O}$, (d) $1 \text{ M Li}_2\text{SO}_4 + 2 \text{ M CH}_4\text{N}_2\text{O}$ for various voltage extensions.

calculations do not take in consideration the total charge loss. A calculation of the energetic efficiency is needed in order to confirm the electrochemical stability of the system. Up to 1.3 V , the energetic efficiency calculated from the discharge curve integration displayed a value of 90%. Between 1.3 V and 1.6 V , the energetic efficiency reached 80%. Above 1.6 V , it fell to 72% and the GCD profiles showed a distortion from a linear discharge curve. Overall, 1.6 V range indicates a safe voltage for the device with a good coulombic (95%) and energetic efficiency (80%). Thus, 1.6 V has been selected as the maximum operational voltage window for the devices. Additionally, it can be concluded that the urea addition to $1 \text{ M Li}_2\text{SO}_4$ did not influence the electrochemical stability of the device. Furthermore, the capacitive performance of the studied samples shows approximately the same values at different urea concentrations ($\sim 100 \text{ F g}^{-1}$). Supplementary results from two-electrode measurements are presented in Fig. S4(c, d). As seen from the cyclic voltammetry (Fig. S4(c)) and the galvanostatic charging/discharging (Fig. S4(d)), all ECs performed similarly from a qualitative and quantitative point of view. Addition of urea maintains the rectangular-like shape of the cyclic voltammograms and the typical triangular shape of GCD curves, suggesting a good surface area access and satisfactory conductivity of the electrode materials. The GCD curves recorded at 1 A g^{-1} almost overlap each other for the samples with and without urea.

The addition of urea slightly improves the performance of the electrochemical capacitors. The influence of the concentration on the charge propagation was studied by electrochemical impedance spectroscopy and the results are shown in Fig. 5(a, b). The Nyquist plot of the ECs operation in $1 \text{ M Li}_2\text{SO}_4$ electrolyte with and without urea addition (Fig. 5(a)) displays more or less comparable equivalent series resistance (ESR) values ranging from 1.07Ω (for the ECs operating in pure $1 \text{ M Li}_2\text{SO}_4$ and $1 \text{ M Li}_2\text{SO}_4 + 0.5 \text{ M CH}_4\text{N}_2\text{O}$) to 0.77Ω (for ECs operating in $1 \text{ M Li}_2\text{SO}_4 + 1 \text{ M CH}_4\text{N}_2\text{O}$). At high frequency regions, the plots show a semicircle followed by a straight line at the low frequency region. The capacitance vs. frequency graphs are presented in Fig. 5(b) for various urea concentrations. By comparing the characteristics, a well-defined plateau can be seen at all concentrations in the low frequency region, revealing the pure capacitive behavior of the system. Furthermore, the charge capability is slightly increased after the urea addition, leading to a better migration of ions in the porosity. Moreover, adding urea causes the inhibition of the corrosion process [52]. The lifetime stability of the device with urea-based aqueous electrolytes was studied using the GCD cycle technique Fig. 5(c) and floating Fig. 5(d). Before urea addition, the EC operating in $1 \text{ M Li}_2\text{SO}_4$ presents a good long-term stability for the first 10 000 cycles and it fades after 47 000 cycles. The cyclability of the three samples with urea

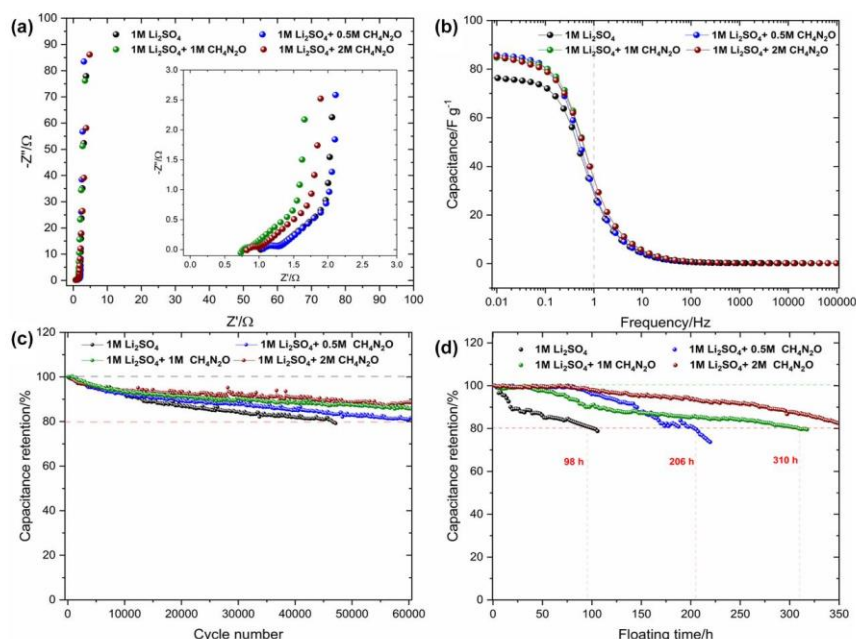


FIG. 5

(a) Nyquist plot and (b) Capacitance vs. frequency plots obtained from BP2000 based ECs operating in 1 M Li_2SO_4 and its urea mixture (0.5, 1 and 2 M). Capacitance retention of BP2000 based ECs tests operating in 1 M Li_2SO_4 and its urea mixtures (0.5, 1, and 2 M) during (c) cycling (1 A/g) and (d) floating (at 1.6 V).

addition confirms the high stability of the device for more than 60 000 cycles. None of these ECs reached the 20% of loss which is the main characteristic of the end-of-life [53,54]. By adding 2 M of urea to the 1 M Li_2SO_4 electrolyte, the EC displays excellent cycling stability with 91% of the initial capacitance after 60 000 charging/discharging cycles.

The GCD curves of the samples with and without urea addition before and after cycling are shown in Fig. 6. By comparing the four GCD profiles, the EC operating without urea addition presents a remarkable distortion from its initial linear discharge curve. Interestingly, after adding urea, the EC shows better stability and neglected loss especially after addition of 1 M and 2 M urea to 1 M Li_2SO_4 electrolyte. It is therefore interesting to determine the limit of such EC performance. For this purpose, a less time-consuming alternative is needed. The voltage holding test, so-called floating, that is used industrially to compare the lifetime of devices, was applied to prove the lifetime stability of the device operating in the urea-based electrolytes. Each system was charged up to a maximum voltage (1.6 V) with a current density of 1 A g^{-1} followed by a voltage hold at 1.6 V for 2 h. Between each voltage hold, EIS and CV spectra were recorded. Every 2 h, the values of capacitance were determined from gal-

vanostatic cycles. Fig. 5(d) illustrates the results of the floating tests. During the first 10 h, the capacitance gradually decreased for the 1 M Li_2SO_4 electrolytic system until it reached 20% capacitance loss after 98 h. The addition of 0.5 M $\text{CH}_4\text{N}_2\text{O}$ to 1 M Li_2SO_4 delays the drop in capacitance for up to 200 h, which is considerably more than twice the capacitance of the system without urea. By increasing the concentration of the added urea to 1 M, the system's capacitance retention maintains stable during the first 50 h and then it slightly decreases after a total floating time of 310 h, which is more than 3 times higher than for pure Li_2SO_4 .

While increasing the urea concentration to 2 M, the capacitance retention of the system remains stable for the first 100 h, then it gradually decreases without reaching 20% of loss for up to 350 h. Fig. S5 displays the Nyquist plots of the ECs operating in 1 M Li_2SO_4 and with different concentrations of urea before and after floating tests. Without the addition of urea, the capacitor resistance (ESR and EDR) before and after 98 h of floating (Fig. S5(a)) increased twofold, which reveals the device end-of-life due to the accumulation of the stainless steel corrosion products between the carbon electrode and the current collector but also aggravated performance of electrodes. The capacitance

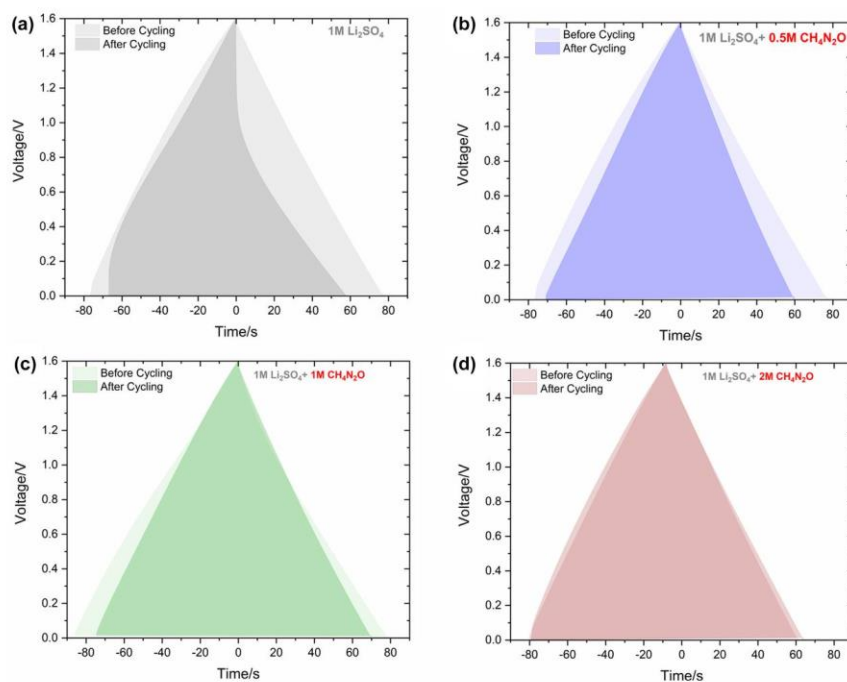


FIG. 6

Galvanostatic charge/discharge profiles before and after cycling tests at 1 A/g for ECs operating in (a) 1 M Li_2SO_4 , (b) 1 M Li_2SO_4 + 0.5 M $\text{CH}_4\text{N}_2\text{O}$, (c) 1 M Li_2SO_4 + 1 M $\text{CH}_4\text{N}_2\text{O}$, (d) 1 M Li_2SO_4 + 2 M $\text{CH}_4\text{N}_2\text{O}$.

decreased from 76 F g^{-1} to 58 F g^{-1} per one electrode as shown in the capacitance vs frequency graphs (Fig. S5b and Fig. S6). After adding urea, the Nyquist diagrams of the devices before and after floating (Fig. S5(b-d)) also showed some resistance increase. However, the enlargement of the semicircle after urea addition could be attributed to the stainless steel corrosion inhibition and the beneficial surface passivation by FeOOH. In the case of 1 M Li_2SO_4 + 2 M $\text{CH}_4\text{N}_2\text{O}$ electrolyte, the EC displays high floating time (350 h), which confirms the inhibition character of urea towards stainless steel corrosion. Interestingly, the elemental analysis of electrodes after floating pointed out c.a. 2 wt% of nitrogen. It is well-known that nitrogen doping of carbon electrodes improves electrochemical performance owing to conductivity and wettability increase as well pseudocapacitive effects. Fig. S5(a) presents the effect of floating on Nyquist plots of EC in lithium sulfate. The corrosion of the stainless steel in Li_2SO_4 after floating causes worse charge propagation (Fig. S6) leading to lower capacitive performance of the EC. Fig. S6 also shows a comparison of the capacitor's performance based on electrolyte with urea after floating where definitively a better charge propagation is observed. Fitting of EIS data for selected electrochemical capacitors before and after floating for 1 M Li_2SO_4 and 1 M

Li_2SO_4 + 2 M urea was realized and shown in Fig. S7. Taking into account complex phenomena it is difficult to find an ideal fitting (especially at the very low frequency 1–10 mHz). However, an equivalent circuit with three time constants seems to be the most adapted in our case. The sum of three time constants from modeling is equal to time constant from $C = f(\text{Hz})$ dependence. The cyclic voltammograms recorded before and after floating in the studied electrolytes are shown in Fig. S8. The CV recorded for EC operating in 1 M Li_2SO_4 before and after prolonged floating for 98 h at 1.6 V (Fig. S8 (a)) reveals a remarkable drop of capacitance at voltage higher than 1 V. This behavior is related to the side reactions connected with a partial oxidation of positive electrode, formation of solid state deposit (e.g. Li_2CO_3) as effect of carbon corrosion with CO and CO_2 release porosity at high voltage [53]. Finally, higher evolution of CO_2 has also been confirmed by our operando GC-MS experiments for pure lithium sulfate electrolyte. In the case of 0.5 M urea addition, the cyclic voltammogram presents a capacitive current drop at 1.2 V with better charge propagation and longer lifespan compared to the electrolytic system without urea addition. Surprisingly, by increasing the urea concentration of the system, a possible reversible hydrogen electrosorption/desorption process occurs after

prolonged floating at 1.6 V with a nondestructive character for the electrodes for up to 310 h in the case of 1 M Li_2SO_4 + 1 M $\text{CH}_4\text{N}_2\text{O}$ and up to 350 h for the devices operating in 1 M Li_2SO_4 + 2 M $\text{CH}_4\text{N}_2\text{O}$. This behavior is attributed also to the high adsorption of urea molecules especially at the electrode/electrolyte interface blocking free water molecules as well as to the generation of new functionalities, e.g., quinone/hydroquinone on the AC surface during floating giving pseudocapacitive effects.

Generally, organic molecules which contain polar groups with nitrogen, oxygen and sulfur atoms in a conjugated structure have a tendency to form a stronger coordination bond especially for compounds with both O and N atoms together [54]. Urea ($\text{H}_2\text{N}-\text{CO}-\text{NH}_2$) does not dissociate into ions in aqueous solutions with pH ranging from 4 to 8 at ambient temperature. However, by increasing the temperature, the urea decomposes at all pH values. Moreover, urea molecules can be hydrolyzed to bicarbonate and ammonia, but this does not happen under neutral pH, except in the presence of the enzyme (urease) which is able to catalyze this reaction. Several studies reported the water-urea mixture interactions owing to the importance of this H-bonding in biological application mainly to denature proteins [55,56] and for hydrogen production [57,58]. Traditionally, hydrogen bonds have a significant influence on aqueous solutions. In each solution, there are two types of atoms competing to form the H-bonding network: the hydrogen bond donors and acceptors. In the urea water system, the carbonyl and oxygen atoms of water are competing as hydrogen bond acceptors. While, the water and the amide hydrogen atoms in urea compete as donors of forming hydrogen bonds. These two hydrogen bonding interactions create the strong hydrogen bonding networks in the urea-water mixtures [59]. Several simulation and modeling investigations have been reported on the structure and hydrogen bonding in urea-water system [48,55,56,59]. The behavior of the hydrogen bonds donor and acceptors in both

water rich and poor regions at different urea concentrations was evaluated. The authors reported that the carbonyl oxygen atoms of urea increase with the urea concentration and form clusters that are accepting one proton of water in water poor region and two protons in the water rich region which makes the carbonyl oxygen a good proton acceptor [59]. The amide proton from urea is not dominating the water rich region at low concentrations. By increasing the urea content, the fraction of the amide hydrogen bonds increases which leads to its association with the water oxygen atoms. Their findings highlight the presence of two type of H-bonding networks: the first network is formed between the oxygen atoms of water with the N—H of urea. The second network is a self-aggregation of urea that is forming a H bonding network by itself and this happened when the urea molecules are dominants. Overall, the urea water mixture leads to a H bonding network creation and this bonding network depends on the urea molecule present in the solution. At lower quantities, the oxygen atoms of water prefer its own hydrogen atom as acceptors. At fully urea domination mixture, the structure of the water cluster is broken down, and the urea self-associate clusters become dominant. This can explain the outstanding behavior of urea in extending the cycle life of the aqueous based ECs that is mainly due to the interaction of this organic molecule with water. The dissolution process of urea molecules includes the additional energy to break the attractive forces between the molecules in the solid structure and the release of energy as molecules form new attractive forces with water molecules around them (Fig. 7) [60]. In fact, urea molecules have internal covalent bonds and will not decompose easily into ions in water medium electrolytes. Instead, there will be a numerous number of associations of hydrogen bonds between water molecules and urea molecules [60–64]. In the solvation shell around urea, the water is more strongly bound to urea than to bulk water (Fig. 7). Overall, the urea has the ability to fit in the water structure without breaking it.

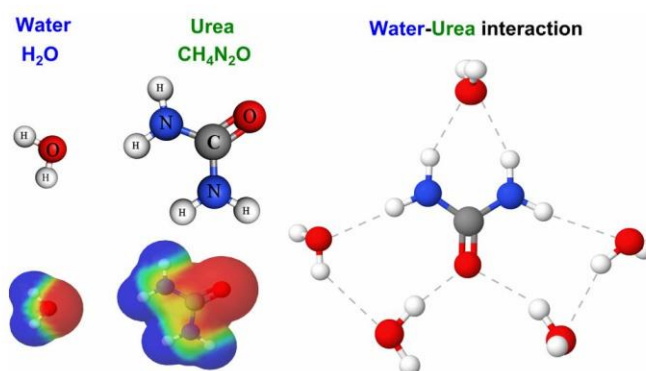


FIG. 7

Molecular presentation of water and urea molecules including the possible hydrogen bond interactions.

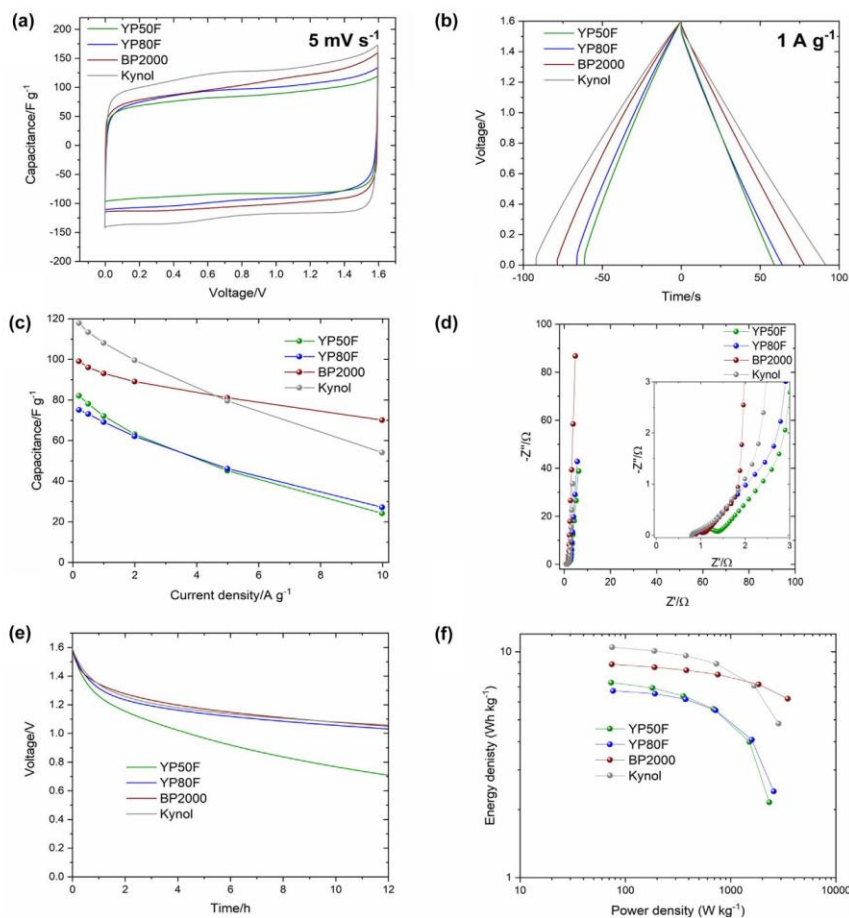


FIG. 8

Electrochemical performances of electrochemical capacitors with different carbon materials in 1 M Li₂SO₄ + 2 M urea. (a) Cyclic voltammograms recorded at 5 mV s⁻¹, (b) Galvanostatic charge/discharge curves at 1 A/g (c) Specific capacitance at different current densities, (d) Nyquist plots, (e) Self-discharge profiles of the different carbons, (f) Ragone plots.

It is noteworthy that energy of intermolecular forces such as van der Waals and H-bonding ranges from a few kJ mol⁻¹ to 10–100 kJ mol⁻¹, respectively. It has been proved by molecular simulation studies that energy of water-urea bonding is equal to ca. 50 kJ mol⁻¹. Although a single urea molecule has a planar structure, urea-water configuration is rather distorted because of two strong hydrogen bonds. Such new arrangement of electrode/electrolyte interface with the smaller participation of free water molecules plays important role for EC performance. For

this reason, the urea addition to the water medium system leads to an improvement of the anticorrosive properties of this organic molecule towards stainless steel. This is due to the ability of urea (HBD) to link with water by the hydrogen bond network without breaking the tetrahedral structure of the water and thus reducing the corrosive effects in the electrolyte. It should be also taken into account that the smaller fraction of free solvent (water) contributes to the oxidative stability of the current collector and the carbon electrode. This phenomenon is well observed in high-

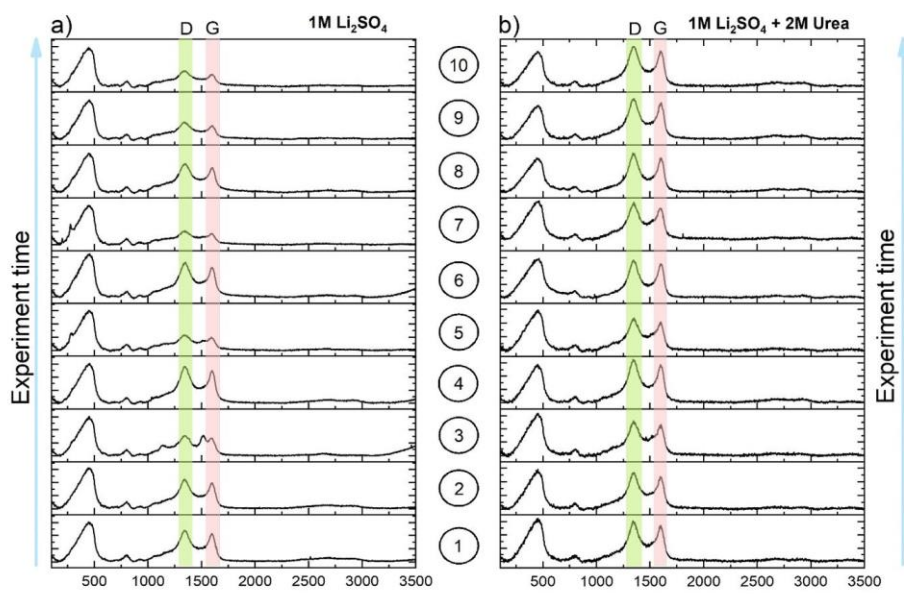


FIG. 9 Raman spectra of the G and D band position of BP2000 based electrochemical capacitor operating in (a) 1 M Li_2SO_4 and (b) 1 M Li_2SO_4 + 2 M urea. Selected potentials for the Raman profiles are indicated by marked points.

concentration electrolytes so called “water in salt”. Overall, the performance of the EC operating in Li_2SO_4 -urea electrolytic system, with high urea concentration (1–2 M) displays a remarkable capacitive and anti-ageing performance. Furthermore, the presence of urea at the electrode surface leads to a corrosion inhibition because of its association with water molecules offering a long-term stability of the device.

The beneficial effect of urea was also checked in a larger scale device, i.e., pouch cell. The pouch cell has been assembled using two symmetrical BP2000 electrodes (4 cm^2). The assembled cell was sealed except for the top side, then the electrolyte was filled in and sealed. By comparing the electrochemical performances of the pouch cell operating in 1 M Li_2SO_4 with and without 2 M urea addition (Fig. S9), the same conclusion as from the Swagelok cell can be noticed. The system with urea improves its overall capacitive Fig. S9(a–c) and energetic performance Fig. S9 (d). The results shown in Fig. S10 display a comparison of the different electrochemical profiles obtained using the Swagelok cell and the pouch cell set-up. The CV profiles at low scan rates (Fig. S10 (a)) show almost a perfect rectangular shape for both systems with lower capacitance for the pouch cell strongly affected by the not optimized assembly. By increasing the scan rate to 100 mV s^{-1} (Fig. S10(b)), the CV of the Swagelok cell retained the rectangular pattern. However, the pouch cell CV showed a distorted profile demonstrating the higher internal cell resistance. The GCD patterns for the two set-ups recorded at 1 A

g^{-1} are shown in Fig. S10(c). Both GCD profiles showed an ideal triangular shape with a very low ohmic drop. By integrating the discharge curve of the GCD, the Swagelok cell has the largest specific capacitance 93 F g^{-1} while one of the pouch cells is 62 F g^{-1} . When increasing the current density (Fig. S10(d)), the capacitance decreased progressively to 81 F g^{-1} for the Swagelok cell and to 41 F g^{-1} for the pouch cell. The Nyquist comparison plot of both constructions operating in 1 M Li_2SO_4 + 2 M urea is shown in Fig. S11 (a). At high frequency regions, the plots show a semicircle followed by a straight line at the low frequency region. The two systems present different ESR, i.e., 0.55Ω for the pouch cell and 1.07Ω for the Swagelok cell. It is also worth noticing that the Nyquist plots present different bending in the middle to low frequency region which can be attributed to the pore diffusion resistance as can be seen from the frequency vs capacitance Bode plot Fig. S11(b). The self-discharge profile of the fabricated systems was investigated to highlight the voltage drops and the results are shown in Fig. S11(c) where the cell was charged up to 1.6 V at 1 A g^{-1} . After discharging, the pouch cell voltage fell from 1.6 V to 1.15 V while the Swagelok voltage decreased to 1.05 V after 12 h. Energy to power features of both devices is represented in Fig. S11(d). The Swagelok cell reveals an energy density of 8.8 Wh kg^{-1} at 0.5 A g^{-1} and a power density of 3516 W kg^{-1} at 10 A g^{-1} . On the other hand, the pouch cell displays a lower energy density of 5.8 Wh kg^{-1} at 0.5 A g^{-1} and a power density of 2714 W kg^{-1} at 10 A g^{-1} . In this comparison,

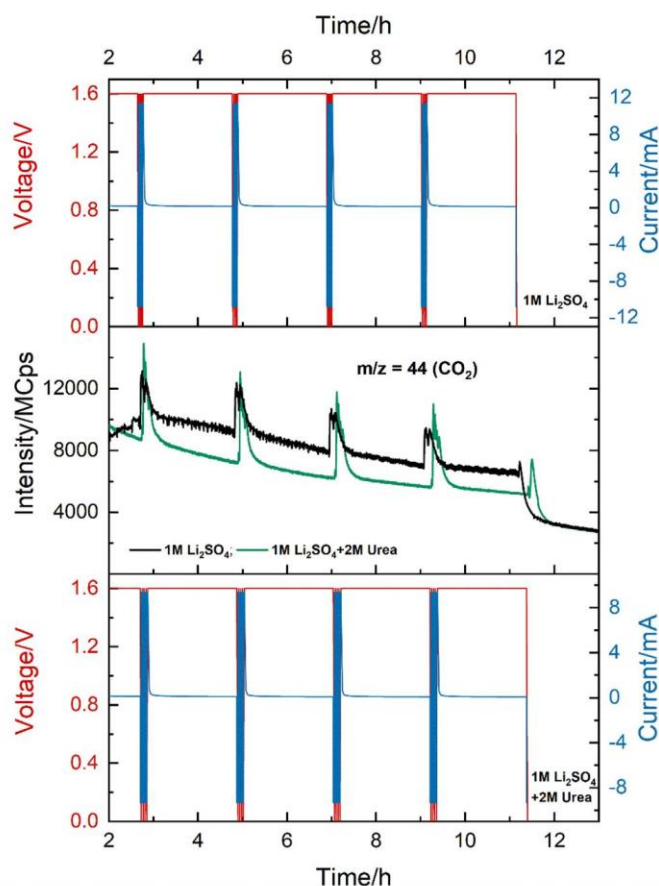


FIG. 10

The first and last row show the electrochemical data (three galvanostatic charge/discharge cycles and 2h floating at 1.6V), while the row in the middle displays the CO₂ evolution (black curve concerns Li₂SO₄, green shows Li₂SO₄ with 2M urea).

the differences in the two systems electrochemical profiles can be discarded since similar electrolyte and electrode components were used in both systems. The differences should be mainly attributed to electrical and interfacial resistance contributions, which arise as a consequence of the differences in the cell assembly process and electrode size.

Electrode mass loading is an important device parameter for supercapacitors. Generally, most electrode materials show good performances at a rather low mass loading. In this study, the effect of the carbon mass loading has been studied for the BP2000 carbon-based ECs operating in 1 M Li₂SO₄ + 2 M urea. Two-electrode Swagelok cell was used to assemble two symmetric EC with different carbon mass loadings, namely 5.5 and 12.7 mg.

The full electrochemical characterization has been performed and the results are shown in Fig. S12. To understand the effect of the mass loading on the ion transport of the ECs with different mass loadings, the EIS analysis has been performed and the obtained Nyquist and Bode plots are presented in Fig. S12(a, b). At the low-frequency region, the nearly vertical curves of the Nyquist plot indicate the ideal capacitive behaviour of the two devices. In the middle and low-frequency region, a straight line can be noticed with a slope which is characteristic of the ion transport in the pores. In high frequency regions, the semi-circle is caused by charge transfer resistance. The above EIS features displayed the lowest ESR for the low carbon mass loading EC (5.5 mg) compared to the EC with 12.7 mg mass loading. Fur-

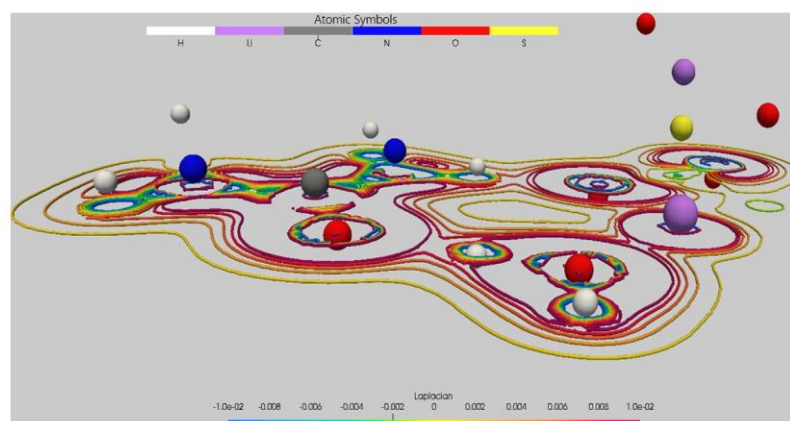


FIG. 11

Relief map of Laplacian of electron density for Urea–Li₂SO₄–Water system, in [e/a_0^3].

thermore, the different bending in the middle frequency region is caused by the different ion transport processes in both systems. In the low mass loading system, more open and direct pores are available which increase the accessible active sites and consequently a better ion transport process. Unlike high loading mass EC, which offers access to the long deep pores of the system leading to slower ion transport and thus a decrease in the capacitive performances of the EC as seen from Fig. S12(b). The CV curves in Fig. S12(c) exhibit an ideal capacitive behaviour of the two systems with a rectangular CV profile. However, by increasing the carbon mass loading the system faces a fading of the capacitance which is due to the pore access that is getting less available for high carbon loading samples. The same behaviour can be seen from the GCD curves Fig. S12(d), by integrating the discharge slope of the GCD profiles at 1 A g⁻¹, the EC delivered 93 F g⁻¹ for the 5.5 mg carbon and 74 F g⁻¹ for 12.7 mg loading. By increasing the current density Fig. S12(e), the specific capacitance of the low mass loading EC decreased progressively to 70 F g⁻¹ at 10 A g⁻¹. While the specific capacitance of the high mass loading EC fades to 21 F g⁻¹ at 10 A g⁻¹ which influences the energy and power densities of the system as can be noticed on the Ragone plot (Fig. S12(f)).

Additionally, electrochemical performance of urea-based electrolyte has been tested for different carbon materials (YP50F, YP80F, BP2000 and Kynol 507–20 characterized in Fig. S13 and Table S1) in two electrode cell configurations using 1 M Li₂SO₄ + 2 M urea electrolyte. The CV results recorded at 5 mV s⁻¹ for different carbon electrodes are shown in Fig. 8(a). By comparing the four CV voltammograms at a low scan rate, the tested electrodes present a purely capacitive behaviour with an ideally rectangular CV shape. The GCD profiles of the different samples at 1 A g⁻¹ (Fig. 8(b)) show a practically symmetric triangular shape which proves a capacitive behaviour. The speci-

fic capacitance calculated by integrating the discharge slope at 1 A g⁻¹ showed a maximum value for the Kynol electrode (108 F g⁻¹) followed by the BP2000 (93 F g⁻¹), YP50F (72 F g⁻¹) and YP80F (69 F g⁻¹). These differences are due to the different porous networks of the tested carbons that influence directly the ion diffusion and transport processes in the electrode. At high current densities (Fig. 8(c)), charging and discharging rates are too fast for the ion diffusion which is limiting the access to the total electrode and thus results in lower capacitance.

The results of the EIS measurements of the different carbon-based EC operating in 1 M Li₂SO₄ + 2 M urea are presented in Fig. 8(d). For the four samples, the Nyquist plots show semicircles at high frequencies followed by a slope of the straight line in the low frequencies region. The more perpendicular characteristics, the better capacitive properties. The BP2000, Kynol and YP50F ESR present the same value of around 0.8 Ω with some slight deviation for the YP80F. While the YP50F shows higher ESR with a wider semicircle and bigger diffusion resistance. These differences are related to the overall sizes of the solvated ions and big urea molecules. Less mesoporous carbon-based supercapacitor displays limited electrolyte ion penetration through the pores, which is illustrated by the wider semicircle. The voltage losses due to self-discharge were evaluated for different carbon-based EC operating in 1 M Li₂SO₄ + 2 M urea electrolyte and the results are shown in Fig. 8(e). Before the measurements the EC cells were charged at 1 A g⁻¹ until 1.6 V then the OCV was monitored for 12 h. The cells with BP2000, YP80F and Kynol exhibited slower OCV decays with the same trend and the voltage dropped to 1.15 V. However, a severe drop can be noticed for the cell based on the microporous YP50F. The differences in the specific capacitance at different current regimes for the tested carbons influenced the energy and power densities as can be seen in Fig. 8(f). Among all carbons, the BP2000 is the one with the

higher rate capability which is due to its mesoporous characteristic ($V_{\text{meso}} = 1.90 \text{ cm}^3 \text{ g}^{-1}$) compared to the other carbons.

Operando studies

In order to identify the phenomena occurring in the BP2000 carbon electrodes with and without urea addition, Raman spectroscopy is one of the most powerful techniques for characterizing structure–property relation [65]. For that purpose, operando Raman spectroscopy was performed using three-electrode electrochemical cell where the working electrode was polarized from -0.8 V to $+0.8 \text{ V}$ vs NHE. Fig. 9 exhibits the Raman spectra registered under polarization of BP2000 electrodes operating in $1 \text{ M Li}_2\text{SO}_4$ electrolyte without (a) and with (b) 2 M urea addition. The purpose of this study is to elucidate mechanism of charging/discharging phenomena of electrode and to highlight the major physicochemical changes occurring at the electrode/electrolyte interface while cycling. Three main peaks are identified from the Raman signals, i.e., the first is a sharp peak around 480 cm^{-1} related to electrolyte contribution such as the librational modes of water molecules, the vibrational intramolecular mode associated with the covalent bonding of the sulfur and oxygen atoms of the sulfate anion as well as stretching vibration of hydrated Li^+ [72–74] followed by the two first order peaks of sp^2 carbon around 1350 cm^{-1} and 1585 cm^{-1} assigned to the D and G bands, respectively [66]. From all the Raman peaks obtained, it is observed that significant changes of the water peak intensity take place in the urea-based electrolyte while it remains stable in the $1 \text{ M Li}_2\text{SO}_4$ electrolyte. Since the intensity of Raman scattered light depends on the concentration of the Raman-active molecules, the difference in the Raman spectra for the water peak can confirm the different behavior of the water in presence of urea under polarization which can evidence changes occurring in the structure of the electrical double-layer for each electrolyte. An important feature regarding the Raman spectra obtained for sp^2 carbon is the possibility to evaluate the defects concentration by analysis of the shift and intensity ratio of the different peaks [66]. Fig. S14 shows the Raman plots in the form of the so-called ‘heat map’ graphs recorded in operando mode with intervals of 2 min during polarization of carbon electrodes tested in $1 \text{ M Li}_2\text{SO}_4$ with and without urea addition. By analyzing the Raman signals for the two samples, the D and G peak intensities are changing remarkably in the case of the Li_2SO_4 compared to the sample studied in the $1 \text{ M Li}_2\text{SO}_4 + 2 \text{ M}$ urea. Furthermore, a split of the G-band leading to the formation of the G-band doublet can be noticed for the sample without urea which is responsible for the higher hydrogen sorption ($\text{C} < \text{H} >$ formation in the range of 1500 cm^{-1}) and the creation of defects [67]. From the deconvolution of the Raman signals, I_D/I_G intensity ratio gives an indication of the carbon structural defects while cycling. In the case of urea based electrolyte, the I_D/I_G ratio remains fairly constant during experiment (1.13 vs 1.12). On the other hand, the I_D/I_G ratio of the carbon tested without urea increased from 1.13 to 1.34 meaning there is some degradation of the material during polarization. Thus, the carbon structure is more affected in the case of $1 \text{ M Li}_2\text{SO}_4$ compared to the one tested after adding urea. What is more, Raman spectra for pure lithium sulfate solution indicate clearly stretching O–H signal at $3400\text{--}3500 \text{ cm}^{-1}$ whereas it is not present for solution with urea

additive where water molecules are less mobile. Overall, the operando Raman investigations of BP2000 carbon evidenced the benefit of urea addition in preventing the structural degradation of the electrode owing to the H bonding network with water.

Further investigations were performed in order to confirm the effectiveness of urea in promoting the EC lifespan. The operando gas chromatography–mass spectrometry (GC–MS) is a pertinent technique which allows performing electrochemical measurements while probing and analyzing the liquid electrolyte in real-time [68]. For that purpose, the operando GC–MS was conducted to study the gases during capacitor operation and to prove the non-decomposition of the urea while cycling. The CO_2 pattern is a fingerprint of the presence of the water decomposition reaction [68] on the positive electrode. Fig. 10 shows the cell current response as well as the CO_2 mass signal intensities during three galvanostatic charge/discharge cycles and 2 h floating of symmetric BP2000 carbon based EC operating in $1 \text{ M Li}_2\text{SO}_4$ with and without 2 M urea at the voltage window from 0 to 1.6 V .

The CO_2 signal for the two electrolytes appearing at $m/z = 44$ presents different evolution profiles. It is clearly seen that the CO_2 evolution is definitely higher for pure lithium sulphate especially during harsh floating mode (at 1.6 V). During three galvanostatic cycles CO_2 evolution is quite comparable. Overall, the urea addition to $1 \text{ M Li}_2\text{SO}_4$ influence the storage mechanism of carbon based EC by changing the water behaviour in the aqueous electrolyte (less free water molecules).

In silico modeling

DFT calculations allowed to estimate the hydrogen bonding network that occurs in the water–urea system. According to the observations made by Hammami *et al.* [69], the carbon–oxygen double bond in urea is the most sensitive to hydration. Hydrogen bond formation in the system under consideration manifests itself by weakening the carbon–oxygen bonds as a result of changes in the intramolecular structure of urea. This effect is observed by changing the length of the bonds in the urea molecule before and after hydration, as presented in Table 3. In addition, the intermolecular bond lengths do not change in the analysed systems. The distances between the donor and acceptor, and thus the hydrogen bond lengths $\text{X} \cdots \text{X}$ and $\text{X} \cdots \text{H}$ (where $\text{X} = \text{N}, \text{O}$) are, independently of the system, respectively $\text{O}_w \cdots \text{N}_u$ $3.702 \text{ \AA}$, $\text{O}_w \cdots \text{O}_u$ $1.461 \text{ \AA}$, $\text{H}_w \cdots \text{N}_u$ $2.925 \text{ \AA}$, and $\text{H}_w \cdots \text{O}_u$ $1.461 \text{ \AA}$.

Thus, it could be concluded that the addition of lithium sulphate does not alter the length of the bonds, which demonstrates the stability of the urea–water complex formed. Moreover, natural bond orbital analysis proves that strong hydrogen bonds exist in aqueous solutions of urea [70]. At the same time, changes in the

TABLE 3

Comparison between the calculated bond lengths in pure urea and urea–water complex.

Bond Length, in $\text{\AA}$	Urea	Urea–Water	Urea– Li_2SO_4 –Water
$\text{C}=\text{O}$	1.196	1.245	1.245
$\text{C}-\text{N1}$	1.366	1.353	1.353
$\text{C}-\text{N2}$	1.366	1.366	1.366

water molecule itself can be observed in systems containing urea. The intramolecular O–H bond lengths of water molecule remain unaffected in the system with urea or urea-Li₂SO₄, while the H–O–H angle changes from 104.45° to 107.53°. When analyzing the presence of lithium salt in the system, the interaction of Li₂SO₄ with water is also important. As in [70], the presence of water changes the length of the Li–S bond from 2.32 Å to 2.41 Å, indicating an interaction between the two molecules. Increasing the amount of water molecules in the system generates a further elongation of the bond considered. It is also worth noting that water molecules prefer the proximity of lithium ions to that of a sulphate anion. This indicates that the interaction between Li and H₂O is stronger than the OH...O(SO₄²⁻) hydrogen bond and the H₂O...H₂O hydrogen bond. Therefore, the beneficial presence of hydrogen bond network in aqueous lithium salt solution with urea was confirmed. The strong interactions in system Urea–Li₂SO₄–Water are also evidenced by the determined total energy of the system. The energies for all considered systems are equal to –714.37 au, –301.81 au, and –1016.24 au, for Li₂SO₄, Urea – Water, and Urea – Li₂SO₄ – Water, respectively, resulting in a total energy of bonding in 3-component mixtures –160.19 kJ/mol.

In addition, the confirmation of the interaction between molecules in Urea–Li₂SO₄–Water, is presented in Fig. 11 in the form of the Laplacian of electron density. This plot shows the spatial changes in the shell structure of the atoms in the molecule by showing the profiles of charge concentration and charge depletion [71]. The uniform sphere of charge concentration present in the valence shell of a free atom is distorted by chemical bonding to form local maxima and minima. The high values of the Laplacian correspond to electron shells of nucleophilic character, whereas the low values correspond to electrophilic character. The zero value profile contour (yellow) is defined as the reactive surface enveloping the space of highest electronic charge.

Conclusions

For the first time, this work introduces the use of urea (hydrogen bond donor) as a green anti-corrosive and anti-ageing additive to 1 M lithium sulfate electrolyte for a long-lifespan electrochemical capacitor. In the presence of urea, the corrosion of stainless steel provoked by aqueous medium is avoided. Additive of urea also affects electrode performance and contributes to stable electrolyte voltage by blocking to some extent 'free' water. A significant improvement of the electrochemical capacitor cycle life at voltages up to 1.6 V has been achieved when 2 M of urea is added to 1 M Li₂SO₄. Such EC demonstrates more than 60 000 cycles during galvanostatic tests (1 A g⁻¹) and >350 h at constant polarization (floating). Moreover, some nitrogen doping (1–2 wt%) of carbon electrodes after floating have been confirmed, what improves the EC metrics. The electrochemical corrosion investigations on the stainless steel discs in Li₂SO₄ + CH₄N₂O prove remarkably the urea inhibition properties towards averting the stainless steel corrosion. Shifting of the corrosion potential into more negative values and reduction of the corrosion current are beneficial effects of urea addition. The difference between corrosion and protection potentials increases from ca. 500 mV for pure lithium sulfate to ca. 1500 mV for 2 M urea addition.

As a consequence, adding of 2 M urea to 1 M Li₂SO₄ results in 10-fold decrease of the corrosion current, preventing the pitting corrosion of the stainless steel collector when the capacitor is polarized up to 1.6 V. Raman spectra have shown formation of thin protective layer of FeOOH on stainless steel discs after corrosion tests but only for electrolytes with urea addition. The urea addition is beneficial for different carbons and mass loadings ECs which make its real application possible. The excellent protective properties of urea can be attributed to its ability to substitute for water in the hydrogen bond network, very well in geometric terms, without breaking the tetrahedral structure of water. Such unique hydrogen bond network of urea based electrolytic medium, in turn, a lack of free water molecules at the interface is at the origin of corrosion protection and better long-term cycling. Hence, urea is a cheap, green additive for supercapacitors using salt aqueous electrolytes and low-cost stainless steel collectors. In addition to the anticorrosive properties of urea, operando characterizations confirm further effect of urea on the EC electrode such as a diminished evolution of carbon dioxide. By adding urea to 1 M Li₂SO₄ electrolyte, the electrode degradation is protected while cycling by reducing the appearance of the carbon structural defects. Undoubtedly, the beneficial effect of urea is linked with strong hydrogen bond network demonstrated by modeling where the total energy of Urea–Li₂SO₄–Water system is equal to 160 kJ mol⁻¹. This study describes an entirely new approach for improving the aqueous electrolyte application for a long-term electrochemical capacitor by taking advantage of the corrosion inhibition by this amide. Our findings can be used in the development of non-corrosive, highly stable, and cheap electrochemical capacitors.

CRediT authorship contribution statement

Sara Azmi: Conceptualization, Methodology, Validation, Investigation, Writing – original draft. **Amelia Klimek:** Methodology, Validation, Investigation. **Elzbieta Frackowiak:** Conceptualization, Validation, Writing – review & editing, Resources, Supervision.

Data availability

Data will be made available on request.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work was supported by the National Science Centre, Poland (project no. 2018/31/B/ST4/01852) and partially by project no. 0911/SBAD/2201. The authors would like to acknowledge Dr Katarzyna Staszak and Dr Maciej Staszak for modeling.

Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.mattod.2023.06.018>.

References

- [1] H. Abdi, B. Mohammadi-ivatloo, S. Javadi, A.R. Khodaei, E. Dehnavi, in: G.B. Gharehpetian, S.M. Mousavi Agah (Eds.) *Distributed Generation Systems*, Butterworth-Heinemann, 2017, pp. 333–368.
- [2] P. Simon, Y. Gogotsi, *Nat. Mater.* 19 (2020) 1151–1163.
- [3] C.S. Rout, D.J. Late, in: C.S. Rout, D.J. Late (Eds.) *Fundamentals and Supercapacitors Applications of 2D Materials*, Elsevier, 2021, pp. 1–10.
- [4] H. Ç nar, I. Kandemir, *Aerospace*. 8 (2021) 85.
- [5] L.H.W.S. Rezende, F.S. Semaan, L.E.P. Borges, R.P. Pereira, in: à. Rocha, C.H. Fajardo-Toro, J.M.R. Springer (Eds.) *Developments and advances in defense and security*, Singapore, 2022, pp. 241–248.
- [6] G. Abbate, E. Saraceno, A. Damasco, Supercapacitor for future energy storage, in: J.A. Stagner, D.S.-K. Ting (Eds.), *Sustaining Resources for Tomorrow*, Springer International Publishing, Cham, 2020, pp. 205–243.
- [7] E. Frackowiak, F. Béguin, *Carbon* 39 (2001) 937–950.
- [8] K. Fic et al., *Mater. Today* 21 (2018) 937–1454.
- [9] F. Barzegar et al., *AIP Adv.* 5 (2015) 097171.
- [10] S. Azmi, M.F. Koudahi, E. Frackowiak, *Energy Environ. Sci.* 15 (2022) 1156–1171.
- [11] G. Lota, K. Fic, E. Frackowiak, *Energy Environ. Sci.* 4 (2011) 1592–1605.
- [12] M. Arulepp et al., *J. Power Sources*. 162 (2006) 1460–1466.
- [13] J. Chmiola et al., *Science* 313 (2006) 1760–1763.
- [14] S. Venkateshulu, A.N. Grace, *Appl. Mater. Today*. 18 (2020) 100509.
- [15] Z. Ling et al., *Proc. Natl. Acad. Sci. USA* 47 (2014) 16676–16681.
- [16] Q. Zhu et al., *Energy Storage Mater.* 35 (2021) 630–660.
- [17] M. Tobis, S. Sroka, E. Frackowiak, *Front. Energy Res.* 9 (2021) 647878.
- [18] W.A. Haider et al., *ACS Cent. Sci.* 6 (2020) 1901–1915.
- [19] T. Brezesinski et al., *J. Sol-Gel Sci. Technol.* 57 (2011) 330–335.
- [20] A.K. Das et al., *Chem. Eng. J.* 417 (2021) 128019.
- [21] A. Malak-Polaczyk, C. Vix-Guterl, E. Frackowiak, *Energy Fuels*. 24 (2010) 3346–3351.
- [22] K. Nasrin et al., *Energy Fuels* 35 (2021) 6465–6482.
- [23] E.P. Yambou, B. Gorska, F. Béguin, *ChemSusChem*. 14 (2021) 1196–1208.
- [24] S. Wong et al., *Appl. Mater. Today*. 18 (2020) 100522.
- [25] S. Amara et al., *J. Chem. Phys.* 154 (2021) 164708.
- [26] B. Gorska, E. Frackowiak, F. Béguin, *Curr. Opin. Electrochem.* 9 (2018) 95–105.
- [27] B. Pal et al., *Nanoscale Adv.* 1 (2019) 3807–3835.
- [28] J.R. Miller, P. Simon, *Science*. 321 (2008) 651–652.
- [29] B. Dyatkin et al., *ChemSusChem*. 6 (2013) 2269–2280.
- [30] C. Li et al., *Adv. Sci.* 6 (2019) 1801665.
- [31] K. Fic et al., *Electrochim. Acta*. 206 (2016) 496–503.
- [32] A. Slesinski et al., *ACS Appl. Mater. Interfaces*. 14 (2022) 37782–37792.
- [33] Q. Abbas, P. Ratajczak, F. Béguin, *Faraday Discuss.* 172 (2014) 199–214.
- [34] P. Ratajczak, K. Jurewicz, F. Béguin, *J. Appl. Electrochem.* 44 (2014) 475–480.
- [35] J. Wojciechowski et al., *Electrochim. Acta*. 372 (2021) 137840.
- [36] E. McCafferty, in: E. McCafferty (Eds.) *Introduction to corrosion science*, Springer, New York, 2010, pp. 263–313.
- [37] J.G. Driver et al., *Front. Energy Res.* 7 (2019) 88.
- [38] J. Piquero-Casals et al., *Dermatol. Ther.* 11 (2021) 1905–1915.
- [39] C.O. Dimkpa et al., *Environ. Sci. Adv.* 1 (2022) 47–58.
- [40] M. Manivannan, S. Rajendran, *Int. J. Eng. Sci. Technol.* 3 (2011) 8048–8060.
- [41] H.-D. Chang et al., *J. Mol. Liq.* 359 (2022) 119344.
- [42] A.S. Abdullah, *Eng. Sci. Technol. Int. J.* 5 (2015) 368–371.
- [43] R.J. Marathe et al., *RSC Adv.* 5 (2015) 15539–15546.
- [44] A.S. Mahdi, *Int. J. Adv. Research Eng. Tech.* 5 (2014) 30–39.
- [45] A. Oz et al., *J. Power Sources*. 355 (2017) 74–82.
- [46] M. He et al., *Energy Env. Sci.* 9 (2016) 623–633.
- [47] A. Bianco et al., *Carbon*. 161 (2020) 373–391.
- [48] A.K. Soper, E.W. Castner, A. Luzar, *Biophys. Chem.* 105 (2003) 649–666.
- [49] E.H. Archibald, in: *The Electrical Conductivity and Ionization Constants of Organic Compounds by Heyward Scudder*, D Van Nostrand Co, Science, New York, 1914, p. 29.
- [50] H.B. Bull et al., *Arch. Biochem. Biophys.* 104 (1964) 297–304.
- [51] S. Azmi, A. Klimek, E. Frackowiak, *Chem. Eng. J.* 444 (2022) 136594.
- [52] Z. Moghadam, M. Shabani-Nooshabadi, M. Behpour, *J. Mol. Liq.* 242 (2017) 971–978.
- [53] P. Ratajczak et al., *Electrochim. Acta*. 130 (2014) 344–350.
- [54] D. Weingarth, A. Foelske-Schmitz, R. Kötz, *J. Power Sources*. 225 (2013) 84–88.
- [55] J. Menzel et al., *Energy Storage Mater.* 49 (2022) 518–528.
- [56] S. Deng, X. Li, X. Xie, *Corros. Sci.* 80 (2014) 276–289.
- [57] M.C. Stumpe, H. Grubmüller, *J. Phys. Chem. B*. 111 (2007) 6220–6228.
- [58] F. Hammami, N. Issaoui, S. Nasr, *Comput. Theor. Chem.* 1199 (2021) 113218.
- [59] B.K. Boggs, R.L. King, G.G. Botte, *Chem. Commun.* 32 (2009) 4859–4861.
- [60] B. Zhu, Z. Liang, R. Zou, *Small*. 16 (2020) 1906133.
- [61] R. Zhang, G. Zhao, W. Wu, *Chin. J. Chem. Phys.* 22 (2009) 511–516.
- [62] D. Bandyopadhyay et al., *J. Phys. Chem. B*. 118 (2014) 11757–11768.
- [63] P.-O. Åstrand, A. Wallqvist, G. Karlström, *J. Chim. Phys. Phys.-Chim. Biol.* 88 (1991) 2457–2464.
- [64] N. Panyachariwat, H. Steckel, *J. Cosmet. Sci.* 65 (2014) 187–195.
- [65] W.G. Nunes et al., *J. Energy Storage*. 28 (2020) 101249.
- [66] G. Socrates, *Infrared and Raman characteristics group frequencies: tables and charts*, 3rd edition., Wiley, 2001.
- [67] S. Varghese, K. Hariharan, Influence of quenching on the structural and conduction characteristics of lithium sulfate, *Ionics* 24 (2018) 2591–2599.
- [68] F. Rull, Raman spectroscopic study of the ion association of lithium sulfate aqueous solutions, *Zeitschrift für Naturforschung A* 50 (1995) 292–300.
- [69] A.C. Ferrari, D.M. Basko, *Nat. Nanotechnol.* 8 (2013) 235–246.
- [70] S. Leyva-García et al., *Carbon*. 69 (2014) 401–408.
- [71] A. Slesinski et al., *ACS Appl. Mater. Interfaces*. 14 (2022) 37782–37792.
- [72] F. Hammami, H. Ghalla, S. Nasr, *Theor. Chem. J.* 1070 (2015) 40–47.
- [73] G. Feng et al., *Phys. Chem. Chem. Phys.* 17 (2015) 5624–5631.
- [74] M.T. Carroll, C. Chang, R.F.W. Bader, *Mol. Phys.* 63 (2006) 387–405.

Effect of a buffer/iodide electrolyte on the performance of electrochemical capacitors

<https://doi.org/10.1039/D4GC01748J>

Aqueous electrolytes employed in ECs face several drawbacks like narrow operating voltage and relatively low capacitance. Indeed, there is a possibility to improve the capacitive performance two-fold through the iodide/iodine redox pair. Nevertheless, the EC operating voltage still do not exceed 1.2 V (water splitting). To solve that problem several buffer solutions with pH up to 7 were utilized to stabilize the iodide/iodine redox pair formed during EC operation. Proposed electrolyte allowed to reach 1.5 V stable voltage, high capacitance as well as enhanced EC lifespan (**Figure 11**).

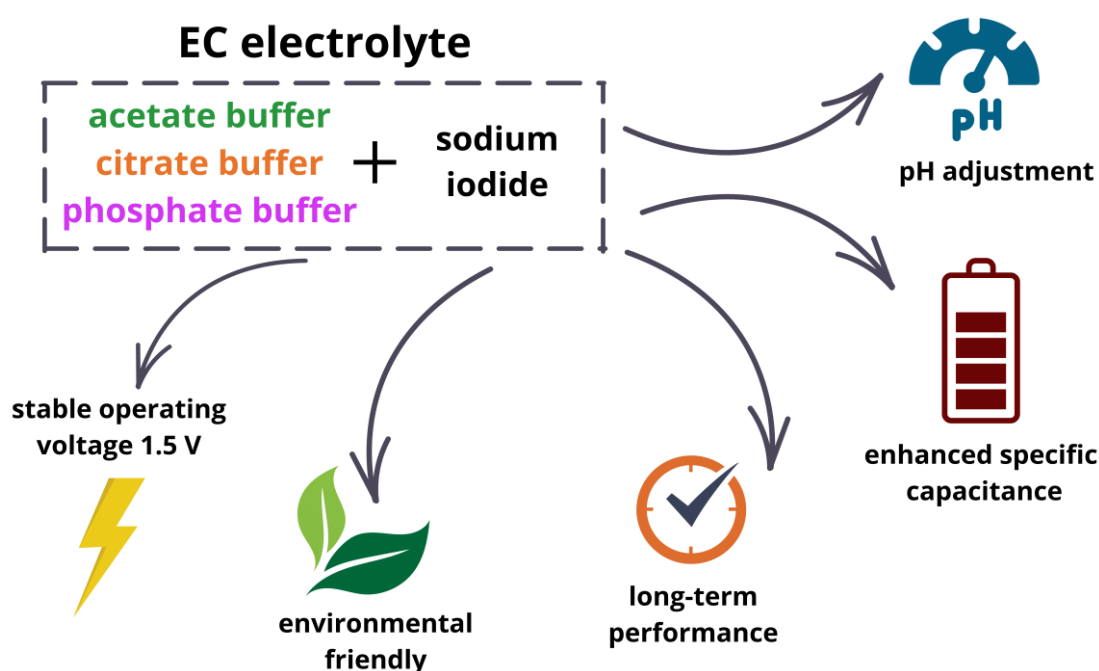


Figure 11 Graphical presentation of the novel buffer-iodide/iodine EC electrolyte with its advantages.

A new EC aqueous electrolyte was composed of NaI as a source of iodide/iodine redox pair and different buffer solutions – acetate (AcB), citrate (CB), and phosphate (PhB). Various physicochemical (pH and conductivity measurement, FTIR, Raman spectroscopy, XPS, XRD, SEM, N₂ sorption) and electrochemical (CV, GCD, EIS) techniques were employed for the material and device characterization.

The additive of NaI in several concentrations (0.2 - 2M) significantly increased the buffers ionic conductivity, while causing only negligible changes in pH, indicating that the buffer solutions retained their chemical stabilizing function even after iodide addition.

The stability of carbon-based ECs operating in buffer/iodide electrolytes was evaluated using the GCD voltage extension from 0.8 to 1.8 V. The voltage extensions for the buffers with/without the iodide additive demonstrated that all ECs exhibited enhanced stability with the redox pair, evidenced by a nearly perfect triangular shape of charge/discharge curve. Moreover, the potential of positive and negative electrodes was monitored, consequently, a limit of 1.5 V was set as the EC stable operating voltage. Three electrode study revealed the capacitive behavior of the negative electrode and a broad, pronounced redox peak of positive electrode correlated with faradaic reaction of iodides. Notably, the specific capacitance was increased substantially when the 0.2M NaI was added: from 91 to 149 F g⁻¹ (AcB), from 7 to 101 F g⁻¹ (CB), from 22 to 132 F g⁻¹ (PhB).

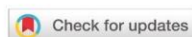
The long-term behavior of the EC was tested by the floating at 1.5 V. It revealed that the combination of the buffering action and iodide redox chemistry can markedly improve the EC lifespan, although the effect depends strongly on the pH of the buffer, carbon texture, and the concentration of added NaI. In the AcB with 0.2M NaI, the YP50F based EC sustained 310 floating hours, compared with only 100 floating hours for AcB without iodide. Even more strikingly, the CB with the same iodide concentration enabled exceptional 1006 floating hours, whereas a CB reached only 30 floating hours. It suggests that a slightly acidic buffered environment (~5) is favorable for maintaining reversible long-term iodide redox activity, while limiting the detrimental side reactions. In contrast, the PhB buffer showed less benefit from iodide additive, due to near-neutral pH, that approaches the boundary of the efficient I⁻/I₂ reaction.

The investigation of the several concentrations of NaI additive (0.2, 0.5, 1, 2M) to AcB revealed that even if high iodide concentration supplied a high capacitance at the beginning, it did not guarantee a long lifespan and gradually formed polyiodides could easily block the available porosity of the carbon. The EC lifespan was better, with the decrease in the NaI concentration, from 34 floating hours for 2M NaI to 310 floating hours for 0.2 M NaI additive.

Then, the effect of the carbon electrode structure on the EC lifespan was investigated. Among several carbons with different structural/textural characteristics (YP50F, BP2000, YP80F, Kynol, salt-templated carbon), it was found that the highly microporous carbon YP50F provided the most favorable balance between capacitance enhancement and long-term lifespan.

Additionally, *post-mortem* analysis of the carbon electrodes after EC lifespan testing was performed. XRD did not reveal formation of any solid-state deposits, which could block the porosity and deteriorate the EC performance. Furthermore, the XPS showed that the positive electrode underwent greater oxidation than the negative electrode. Nevertheless, the oxidation was less severe in the buffer/iodide system than in buffer alone. The signals associated with iodide-containing species on the carbon surface suggest partial grafting or persistent interfacial interaction of iodine species with the electrode. These findings imply that buffer-controlled pH stabilization not only supports reversible redox activity but also mitigates surface degradation and suppresses the formation of iodates and/or polyiodides.

In conclusion, the study introduces buffer/iodide electrolytes as a promising and sustainable EC electrolyte. Through the combination of the buffer's pH stabilization and pseudocapacitance from iodine/iodide redox pair, the proposed electrolyte enables simultaneous improvement of the capacitance, operating voltage, and lifespan.

Cite this: *Green Chem.*, 2024, **26**, 6684

Effect of a buffer/iodide electrolyte on the performance of electrochemical capacitors†

Amelia Klimek,  Maciej Tobis  and Elzbieta Frackowiak  *

One of the major problems affecting the energetic characteristics and cycle life of electrochemical capacitors (ECs) utilizing aqueous electrolytes is the narrow operating voltage range, which is limited by the thermodynamic stability of water (1.23 V). An improvement in the EC energy can be realized by a capacitance and/or voltage increase. For that purpose, cost-effective and environmentally friendly iodides have been added to aqueous electrolytes to improve the redox activity. Moreover, buffer agents (acetate, citrate, and phosphate) that are well known for adjusting the pH of an electrolyte have been applied, which enabled ECs to reach a stable operating voltage of 1.5 V. After adding iodide to the buffer system, the conductivity increased notably, whereas the pH values remained nearly the same. Galvanostatic charge/discharge test (0.5 A g^{-1}) for ECs operating in buffer electrolytes containing 0.2 mol L^{-1} NaI showed that this additive noticeably increased the specific capacitance values from 91 to 149 F g^{-1} for acetate buffer, from 7 to 101 F g^{-1} for citrate buffer, and from 22 to 132 F g^{-1} for phosphate buffer. The long-time performance of the ECs was investigated through accelerated potentiostatic floating. The electrochemical performance was studied using various activated carbons. During the floating aging test, the YP50F-based EC working in acetate buffer with 0.2 mol L^{-1} NaI displayed the best long-term performance (310 h) compared to YP80F and BP2000 carbons, which exhibited 212 h and 126 h, respectively. The highly microporous YP50F carbon in the acetate buffer/iodide electrolyte revealed the best wettability. Interestingly, the citrate buffer/iodide EC system with YP50F demonstrated an extremely long floating performance (1006 h). Thus, this study presents a new strategy for improving the energetic metrics and cycling performance of carbon-based ECs operating in buffer electrolytes with an iodide redox pair.

Received 9th April 2024,
Accepted 22nd April 2024
DOI: 10.1039/d4gc01748j
rsc.li/greenchem

1. Introduction

The worldwide utilization of electrical energy is increasing rapidly owing to population growth and technological advancements. Currently, fossil fuels (e.g., oil, coal, and natural gas) continue to be the base of global power systems, accounting for 64% of the world's electricity supply.¹ The main benefit of petroleum-based fuels is their incredible effectiveness. However, their major disadvantages are their limited resources in the earth's crust and the emission of CO_2 during their combustion, which contributes to the greenhouse effect. Consequently, natural and self-replenishing renewable energy sources are attracting increasing attention. However, these are often dependent on unstable weather conditions, such as the sun or wind. Additionally, the real-time operation of the power

grid presents an engineering problem since power is produced and consumed simultaneously, with generation fluctuating to maintain system balance.^{1–3} To overcome this issue, various electrochemical storage systems, including batteries, redox flow batteries, and electrochemical capacitors (ECs), have been proposed. Batteries offer high energy density and a significant operating time; however, their use in several industries is limited by their low power density and poor cyclability. ECs, also known as supercapacitors, can overcome the drawbacks of batteries as they exhibit higher power densities, safety, green profile, and extended cycle life.⁴ Consequently, ECs are widely used in various sectors, such as transportation,⁵ aerospace,⁶ medical devices,⁷ construction, and building management.⁸ ECs store energy through the formation of an electrical double-layer (EDL) at the electrode/electrolyte interface. Nonetheless, there is a possibility to increase the amount of stored energy thanks to fast faradaic reactions coming from e.g., redox-active species.⁹ There are several materials, such as graphene oxide,¹⁰ activated carbon,¹¹ carbide derived carbon,¹² COF,¹³ MOF,¹⁴ MXenes,¹⁵ and carbon nanotubes,¹⁶ that can be utilized as electrode materials for ECs. Furthermore,

Institute of Chemistry and Technical Electrochemistry, Poznan University of Technology, Berdychowo 4, Poznan 60-965, Poland.
E-mail: elzbieta.frackowiak@put.poznan.pl
† Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d4gc01748j>

the application of newly discovered quantum dots is attracting more and more interest.¹⁷ Among the various carbon forms, activated carbon is the best due to its high surface area, low resistance, cost-effectiveness, high conductivity, chemical stability, and versatility.¹⁸ Electrolytes affect the characteristics of ECs, mostly the operating voltage window.¹⁹ Typically, aqueous media,^{20,21} organic media,²² ionic liquids,²³ and deep eutectic solvents^{24,25} can be utilized as EC electrolytes. An ideal EC electrolyte should be characterized by several parameters, such as cost-effectiveness, environmental friendliness, good conductivity, and wide operating voltage range, which should allow the EC to reach high energetic characteristics and long-term cycle life. In this sense, the aqueous-based electrochemical capacitor presents an excellent system, competitive to the organic one, that is also safe, green, and affordable.²⁶ Among the first water-based electrolytes utilized in ECs were KOH and H₂SO₄. However, such electrolytes cannot be considered for commercial application due to their narrow voltage window (ca. 0.8 V), limited by the thermodynamic stability of water²⁷ and corrosive character. Consequently, neutral solutions, such as sulfates (Li₂SO₄) and nitrates (LiNO₃), have been proposed, which can offer a higher voltage window up to 1.5 V by utilizing stainless steel current collectors. These neutral electrolytes enabled overcoming water splitting issues due to the electrosorption of hydrogen at the negative electrode.^{28,29} Another approach is the use of buffer solutions as electrolytes in ECs. To date, there are a few papers that have reported the application of buffer solutions in ECs, but mainly as an additive to the neutral electrolyte.^{30,31}

A weak or medium-strong acid/base and the equivalent salt are called buffers. When acids (H⁺ ions) or bases (OH⁻ ions) are introduced, a solution that functions as a buffer system resists to maintain the solution pH.³² That is why buffers are mostly used for various experiments involving chemical/biological reactions,³³ calibration, and standardization to keep a stable pH environment.³⁴ Moreover, Salis *et al.* discovered an additional function of buffers in biological systems, in which buffers could compete for the adsorption at the charged surfaces with strong electrolytes, thus modulating the Hofmeister effect.³⁵ Regarding the application of buffers in energy-storage systems, Chien *et al.* discussed hydrogen adsorption/desorption in asymmetric activated carbon-based SCs, and proved that the additive of a buffer agent (NaH₂PO₄) into the neutral electrolyte (Na₂SO₄) could stabilize the local pH value at the electrode/electrolyte interface as weakly acidic, neutral, or weakly basic pH. They also showed it significantly increased the proton supply and the rate of hydrogen adsorption at the electrode/electrolyte interface, leading to a higher pseudocapacitive effect, in addition to changing the potential for hydrogen evolution.³⁰ Vindt *et al.* studied the effect of phosphate buffer (K₂HPO₄ + KH₂PO₄) in a neutral electrolyte (KNO₃) for carbon-based supercapacitors. The study confirmed that the wider operating voltage window of the EC based on the neutral electrolyte was mainly due to local pH changes at the electrode surface. Nevertheless, the buffer capacity, rather than the electrolyte's pH value, determined how strong the

effect was. By studying the impact of a buffer to neutral electrolytes, they demonstrated that a 56% higher storage capacity could be achieved by controlling the buffer capacity of the electrolyte.³¹ In both cases, the experiments were done mostly using three-electrode cells utilizing mainly cyclic voltammetry.^{30,31} Sodium acetate electrolytes, buffered by acetic acid, were used to alter the pH of the solution, and in turn to boost the pseudocapacitive behavior of supercapacitors utilizing MXenes as an electrode material.³⁶ and a molten-salt (MS) synthesis procedure of MXenes was proposed with the creation of -O and -Cl surface groups. The formation of such groups enabled a better compatibility with the acetate-based electrolytes. The authors reported achieving a high energy density (37 W h kg⁻¹) for an asymmetric supercapacitor based on MS-MXene as a negative electrode and MnO₂ as a positive electrode in 1 M sodium acetate (buffered at pH = 5). Moreover, the suppression of hydrogen evolution was observed.³⁶ Sugimoto *et al.* selected acetic acid-lithium acetate (AcOH-AcOLi) buffered solutions in various volume ratios as an electrolyte to study the origin and mechanism of the pseudocapacitance of ruthenium-based oxides in electrochemical capacitors.³⁷ The highest capacitance (1038 F g⁻¹) was obtained for RuO₂ nanosheet electrodes in 5 M AcOH-AcOLi (pH 5.4). They found that the pseudocapacitive behavior declined with lowering the pH when the volume ratio of AcOH-AcOLi was changed. While the extremely high capacitance values are promising; however, the use of ruthenium oxide in energy-storage devices is limited due to its high cost and toxicity.³⁷ Acetate salts (not necessarily in the form of a buffer) are becoming more popular today as aqueous electrolytes for high energy ECs due to their eco-friendliness, price, and high solubility in water. Piwek *et al.* studied carbon-based electrochemical capacitor operating in acetate-based salts, and reported that acetates (Li⁺, Na⁺, and Mg²⁺) at molar concentrations ranging from 0.1 to 2 mol L⁻¹ with moderate conductivity values could have an impact on the maximum operating voltage and enable the EC voltage to be increased. An EC based on commercial YP50F carbon in 0.5 M CH₃COONa reached 77 F g⁻¹ at 1.5 V (0.5 A g⁻¹). The aging of the same system was investigated by the floating method and displayed good capacitance retention after 130 h.³⁸ Potassium acetate due to its extremely high solubility in water was tested at various concentrations (20–60 wt%) by Matei Ghimbeu *et al.* An increase in the voltage window (1.8 V) and significantly improved capacitance (130 F g⁻¹ at 1 A g⁻¹) were achieved for a carbon-based EC operating in 40 wt% KOAc.³⁹ Despite enabling the significant extension of the operating voltage in neutral electrolytes, overcoming the thermodynamic stability of water, the systems lacked energy. An increase in capacitance and thus energy density of ECs could be achieved by the addition of redox-active species. Lota *et al.* reported a novel EC operating in 1 mol L⁻¹ potassium iodide for carbon-based ECs, which enabled double the capacitance values compared to ECs operating in 1 mol L⁻¹ H₂SO₄. The outstanding performance of the electrolyte only for the positive electrode was associated with the good conductivity and quick faradaic reac-

tions of the iodide. It is noteworthy that iodides are the most eco-friendly compared to the rest of the halides (*e.g.*, bromides, fluorides).^{40,41} When utilizing an iodide as an electrolyte, it is crucial to refer to the Pourbaix diagram, which shows the stability regions of various redox species.⁴² Importantly, in the region of water stability and pH up to 7, the redox reaction (1) is favorable. Despite the reversible $I_2/2I^-$ reaction, other processes (2)–(5) can take place:⁴³



A novel approach of this work is the application of the redox-active sodium iodide (NaI) as an additive into buffer solutions as an electrolyte to enhance the energy and cyclic performance of carbon-based electrochemical capacitors with stainless steel current collectors. The characteristics of the ECs were studied in acetate buffer (AcB), citrate buffer (CB), and phosphate buffer (PhB) without and with sodium iodide at different concentrations (0.2, 0.5, 1, 2 mol L⁻¹). The effect of various porosity commercially available activated carbons (YP50F, BP2000, YP80F) on the selected electrolytes was also taken into account. Furthermore, two additional activated carbons (Kynol, C-ST) with a high volume of micropores and larger specific surface area than YP50F were also tested. The present work reports a promising strategy to improve the performance of aqueous-based electrochemical capacitors.

2. Experimental section

2.1. Materials

Two of the buffer solutions, *i.e.*, acetic acid/sodium acetate (pH 5.12) and potassium dihydrogen phosphate/sodium hydroxide (pH 7), were provided by Fluka Analytical and used as received. Citrate buffer was prepared by mixing citric acid monohydrate and sodium hydroxide (from POCH) to obtain pH ~4. Sodium iodide ACS reagent was supplied by Sigma-Aldrich and was used for the preparation of 0.2, 0.5, 1, and 2 mol L⁻¹ additives for the buffer solutions. Three commercially available activated carbons were utilized as the electrode material: Black Pearl 2000 (BP2000) provided by Cabot® (USA), and YP50F and YP80F supplied by Kuraray (Japan). Additionally, carbon cloth Kynol-5092-20 was provided by Kynol company and was used as received. Moreover, highly microporous carbon was tested. This carbon (C-ST) was prepared by a salt-templated method reported elsewhere.⁴⁴ Whatman GF/A (260 µm) glass fiber served as the separator. Moreover, PTFE (60% suspension in water), provided by Sigma-Aldrich, and C65 carbon black (C-ENERGY™ Super C65), from Imerys, were used during the electrode preparation.

2.2. EC electrode preparation

The powdered activated carbons (YP50F, YP80F, C-ST) were used as the electrode materials for ECs. The electrode material consisted of 90 wt% of the selected carbon, 5 wt% of PTFE as a binder, and 5 wt% of C65 to improve the conductivity. In the case of BP2000 activated carbon, the electrode contained 85 wt% active material, 10 wt% PTFE, and 5 wt% C65. The mentioned components were mixed in the mortar, with the addition of a solvent (isopropanol) to obtain a homogenous dough-like paste. Then, the paste was press-rolled to form a thin 200 µm film in a calendaring machine. In the last step, the film was cut into disk electrodes with a diameter of 10 mm and dried for 24 h at 60 °C. Kynol electrodes were prepared by cutting carbon cloth into self-standing disks with 10 mm diameter.

2.3. Electrochemical characterization

The prepared electrodes were placed in symmetric two PTFE-based Swagelok® systems with stainless steel 316L current collectors. Before assembly of the device, the electrodes and separators were soaked in the selected electrolytes. The Hg/Hg₂SO₄ reference electrode (0.640 V vs. SHE) was used to monitor the potential of each electrode during the electrochemical measurements. The study of the electrochemical performance of the ECs was performed using a multi-channel potentiostat/galvanostat (VMP3, Biologic®). Cyclic voltammetry (CV) at sweep rates of 1–500 mV s⁻¹, galvanostatic charge/discharge (GCD) tests at current densities of 0.1–2 A g⁻¹, and electrochemical impedance spectroscopy (EIS) in the frequency range of 100 kHz to 1 mHz were performed for electrochemical characterization of the ECs. All the presented capacitance values of the ECs were calculated per active mass of one electrode. The long-term stability tests of the ECs were performed by the so-called floating test. The floating procedure consists of three galvanostatic charges/discharges (1 A g⁻¹) at a maximum operating voltage (U_{max}) followed by holding the voltage at U_{max} for 2 h. The CV and EIS spectra were recorded after each voltage hold.

2.4. Physicochemical characterization

The surface area and porosity of the selected activated carbons were evaluated using Brunauer–Emmett–Teller (BET) isotherm analysis at 77 K (ASAP 2460, Micromeritics®). The pore-size distribution of the electrode materials was estimated based on the 2D non-local density functional theory (2D NLDFT). Scanning electron microscopy (SEM) observation was used to further investigate the morphology of the carbons. A conductivity meter and pH meter (both manufactured by Mettler Toledo®, Switzerland) were applied to measure the conductivity and pH of the prepared electrolytes at ambient temperature. An optical contact angle (OCA 15Pro) system equipped with a goniometer (DataPhysics®, Germany) was utilized for the wettability analysis. The SCA 20 module software, which enables the measurement of the static contact angle on a flat surface by automatically recognizing baselines and tangents,

was used for liquid droplet analysis. The injection sample volume was 8 μL and the speed was 2 $\mu\text{L s}^{-1}$. A PerkinElmer FTIR spectrophotometer was used to record the electrolyte absorption spectra (resolution of 4 cm^{-1}). A Thermo Scientific DXR-Raman microscope with a laser emitting at 532 nm and power of 5 mW was used to record the spectra in order to explain the solvent effect between the electrolytes. Powder X-ray diffraction (XRD) patterns of the different carbon materials were obtained using a Bruker D8 Advanced diffractometer operating in the Bragg-Brentano geometry with a Cu $K\alpha$ radiation source ($\lambda = 1.5406 \text{ \AA}$). The surface chemistry of the electrode materials was investigated by X-ray photoelectron spectroscopy (XPS) on a PHI VersaProbe Scanning XPS system (Al $K\alpha = 1486.6 \text{ eV}$) with 0.5 eV resolution and 100 μm analysis spot scanned over the area of 1600 μm^2 .

3. Results and discussion

3.1. Electrode materials characterization

Various features of electrode materials, such as specific surface area and pore-size distribution, are important for the performance of electrochemical capacitors. Moreover, to achieve a high power and high capacitance of ECs, the ion size of the electrolyte must be smaller than the pore size of the electrode material.^{18,44,45} Nitrogen adsorption/desorption isotherms and the pore-size distribution of YP50F, BP2000, and YP80F activated carbons were examined for that purpose, and the findings are shown in Fig. 1a and b. The isotherms for YP50F and YP80F activated carbons demonstrated the typical, microporous characters. However, the visible hysteresis loop at high relative pressures (0.5–0.9 P/P_0) suggested the presence of a small amount of mesopores, as confirmed by the volume of

mesopores equal to 0.01 $\text{cm}^3 \text{ g}^{-1}$ for YP50F and 0.24 $\text{cm}^3 \text{ g}^{-1}$ for YP80F (Table 1). The textural properties of the additionally tested microporous carbons (Kynol 5092-20 and C-ST) are presented in Table S1.†

Upon examining the adsorption/desorption isotherm and pore-size distribution for BP2000, it was evident that the carbon had both micropores (0.5 $\text{cm}^3 \text{ g}^{-1}$) and mesopores (1.77 $\text{cm}^3 \text{ g}^{-1}$). Small mesopores are essential for ECs because they act as pathways for ions that are typically solvated. It is important to match the size of ions with the pores of carbons. The diameters of the selected solvated ions, namely Na^+ , I^- , HPO_4^{2-} , CH_3COO^- , and $\text{C}_3\text{H}_4(\text{OH})(\text{COO})_3^{3-}$ (Fig. 1b), were located in the region of micropores (<2 nm).^{46–49} The exact values of the solvated cations diameters are presented in the ESI (Table S2†). The highest specific surface area was found for Kuraray YP80F (2018 $\text{m}^2 \text{ g}^{-1}$), whereas YP50F and BP2000 showed lower values of 1693 and 1513 $\text{m}^2 \text{ g}^{-1}$, respectively. The SEM image of BP2000 carbon in Fig. S1a† displayed a particle cluster structure. The SEM images of YP50F and YP80F shown in Fig. S1b and c† indicated the typical texture of activated carbons.

3.2. Electrolyte characterization

The electrolytic conductivity and pH of acetate, citrate, and phosphate buffers with/without 0.2 mol L^{-1} NaI were measured, and the results are collected in Table 2. Overall, adding sodium iodide in various concentrations (0.2, 0.5, 1, 2 mol L^{-1}) increased the conductivity of all the selected buffers (Table S3†). The conductivity values for acetate buffer ranged from 63.3 to 72.2 mS cm^{-1} after adding 0.2 mol L^{-1} NaI. For the citrate buffer, the conductivity value changed from 3.0 to 16.5 mS cm^{-1} after adding 0.2 mol L^{-1} NaI. In the case of

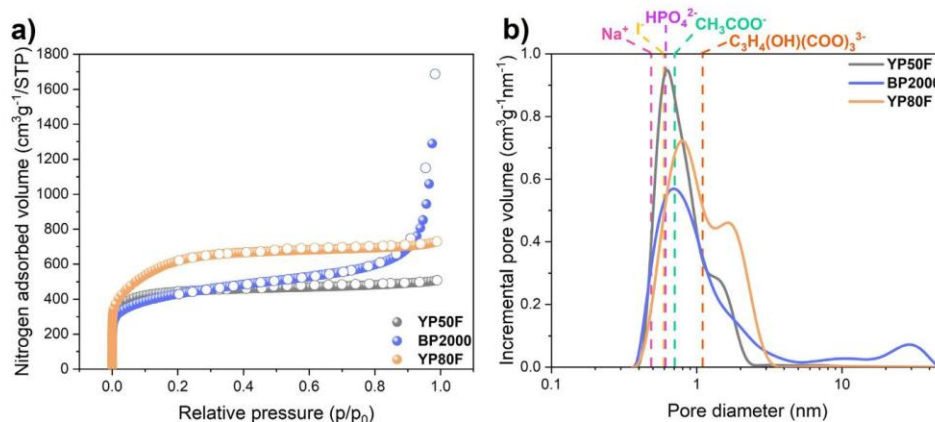


Fig. 1 (a) Nitrogen adsorption/desorption isotherms at 77 K; (b) pore-size distributions of YP50F, BP2000, YP80F activated carbons and pore diameters of selected solvated ions.

Table 1 Specific surface area and pore volume of the micro/mesopores of YP50F, BP2000, and YP80F activated carbons

	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	V_{micro} ($\text{cm}^3 \text{g}^{-1}$)	V_{meso} ($\text{cm}^3 \text{g}^{-1}$)
YP50F	1693	0.64	0.01
BP2000	1513	0.50	1.77
YP80F	2018	0.78	0.24

Table 2 Conductivity (mS cm^{-1}) and pH values of sodium iodide (0.2 mol L^{-1}) and acetate buffer (AcB), citrate buffer (CB), and phosphate buffer (PhB) with/without the addition of sodium iodide (0.2 mol L^{-1})

Electrolyte	Conductivity (mS cm^{-1})	pH
AcB	63.3	5.08
AcB + 0.2 mol L^{-1} NaI	72.2	5.05
CB	3.0	3.74
CB + 0.2 mol L^{-1} NaI	16.5	3.58
PhB	6.9	7.18
PhB + 0.2 mol L^{-1} NaI	25.5	6.98

phosphate buffer, the conductivity ranged from 6.9 to 25.5 mS cm^{-1} after adding iodide. The pH values were recorded for acetate buffer (5.08), citrate buffer (3.74) and phosphate buffer (7.18) at ambient temperature. It was noted that the pH changed negligibly after the addition of selected NaI concentrations ($0.2, 0.5, 1, 2 \text{ mol L}^{-1}$) into the buffers.

These results perfectly show that one of the crucial buffer features is the ability to neutralize small amounts of H^+ or OH^- ions when they are added to solution. When the buffering capacity is surpassed, the rate of pH change rapidly increases.⁵⁰ The buffer agents were able to keep nearly the same pH after adding selected quantities of sodium iodide. FTIR and Raman spectroscopies are complementary techniques that allow evaluating the vibrational and stretching movements of different species in electrolytes. In this case, these techniques could be helpful to analyze the influence of the iodides presence on the buffer molecules stretching and vibrational modes. Here, FTIR analysis (Fig. S2a†) revealed some common features within the electrolytes, *i.e.*, the water signature associated with the O–H stretching mode with a peak centered at 3583 cm^{-1} , the presence of CO_2 diluted in each electrolyte with peak centered at 2440 cm^{-1} , and the presence of the C–H stretching mode associated with the peak positioned at *ca.* 600 cm^{-1} . After the addition of 0.2 mol L^{-1} NaI to the buffer solutions, we found that the O–H stretching mode associated with the water signature positioned at 3583 cm^{-1} became significantly more pronounced for the citrate and phosphate buffers, while for acetate buffer it remained the same. Signal transmittance originating from the C–H positioned at *ca.* 600 cm^{-1} was significantly improved after the addition of iodides to each buffer solution due to the pronounced signal of iodides in the same frequency range of *ca.* 600 cm^{-1} . The Raman studies (Fig. S2b†) showed no influence from the addition of iodides on the Raman spectra. No red- or blue-shifts of the peaks were observed. The changes in the FTIR and Raman spectra were not significant. Hence, no

clear conclusions regarding the solvent effect between the buffer, iodides, and water ions could be drawn.

3.3. Electrochemical capacitor study

The conductivity studies showed that the addition of the smallest NaI concentration (0.2 mol L^{-1}) to the buffer solution significantly improved the conductivity. Owing to this, the electrochemical investigation focused mainly on the mentioned concentration. The electrochemical investigation started with the assembly of a two-electrode system utilizing YP50F electrodes, with a large specific surface area and high volume of micropores. The maximum operating voltage window of the AcB, CB, and PhB buffers with and without 0.2 mol L^{-1} NaI was extended from 0.8 V to 1.8 V during the GCD technique at a 0.5 A g^{-1} current density, and the results are shown in Fig. 2a, c, e (with iodides) and Fig. S3a, c, e† (without iodides). The energetic and coulombic efficiencies were calculated from GCD curves and are shown in Fig. 2b, d, f and Fig. S3b, d, f†. The coulombic efficiency, which is determined by the discharging time, was greater than 96% (at 1.5 V), indicating the best possible capacitive behavior of each EC. The energetic efficiency, calculated by integration of the discharge curve, showed values ranging from 62% for AcB + 0.2 mol L^{-1} NaI, to 74% for CB + 0.2 mol L^{-1} and 81% for PhB + 0.2 mol L^{-1} based ECs. The GCD curves revealed a deviation above 1.5 V that was more visible in the case of AcB + 0.2 mol L^{-1} NaI as well as the significant energetic efficiency drop to less than 50%. ECs based on acetate and phosphate buffers alone revealed energetic efficiencies (at 1.5 V) of 65% and 52%, respectively. Regarding the system based on citrate buffer, the energetic efficiency was significantly lower ($\sim 30\%$), which means that more energy was supplied during charging than recovered while discharging. The voltage extensions for the buffers with and without the iodide additive showed that all the systems were more stable with the redox pair, by showing a nearly perfect triangular shape of charge/discharge curves. Therefore, a 1.5 V limit was set as the maximum stable operating voltage for all the systems. Fig. S4† presents the voltammograms at 5 mV s^{-1} for YP50F carbon-based EC operating in AcB and AcB + $0.2, 0.5, 1, 2 \text{ mol L}^{-1}$ NaI. The CV curve for AcB demonstrated a perfect rectangular shape associated with pure electrostatic attraction, which plays a crucial role in charge storage. The shape of the curves for the EC operating in AcB with NaI additives showed a deviation from a rectangular shape, as well as the rise of the specific capacitance, which was caused by the $\text{I}_2/2\text{I}^-$ redox activity. We also performed electrochemical studies of the voltage extension in AcB electrolyte with and without the addition of iodides by the CV method (Fig. S5†). By monitoring the electrochemical behavior of each electrode, *i.e.*, positive and negative separately (Fig. S5b†), we could observe almost square-shaped CVs resembling the behavior in standard aqueous neutral electrolytes, *e.g.*, $1 \text{ mol L}^{-1} \text{Li}_2\text{SO}_4$.^{51,52} Both electrodes had the same potential window (*i.e.*, 0.75 V) with comparable capacitance, indicating the charge-storage mechanism was based on the adsorption of ions through the formation of an electrical double-layer

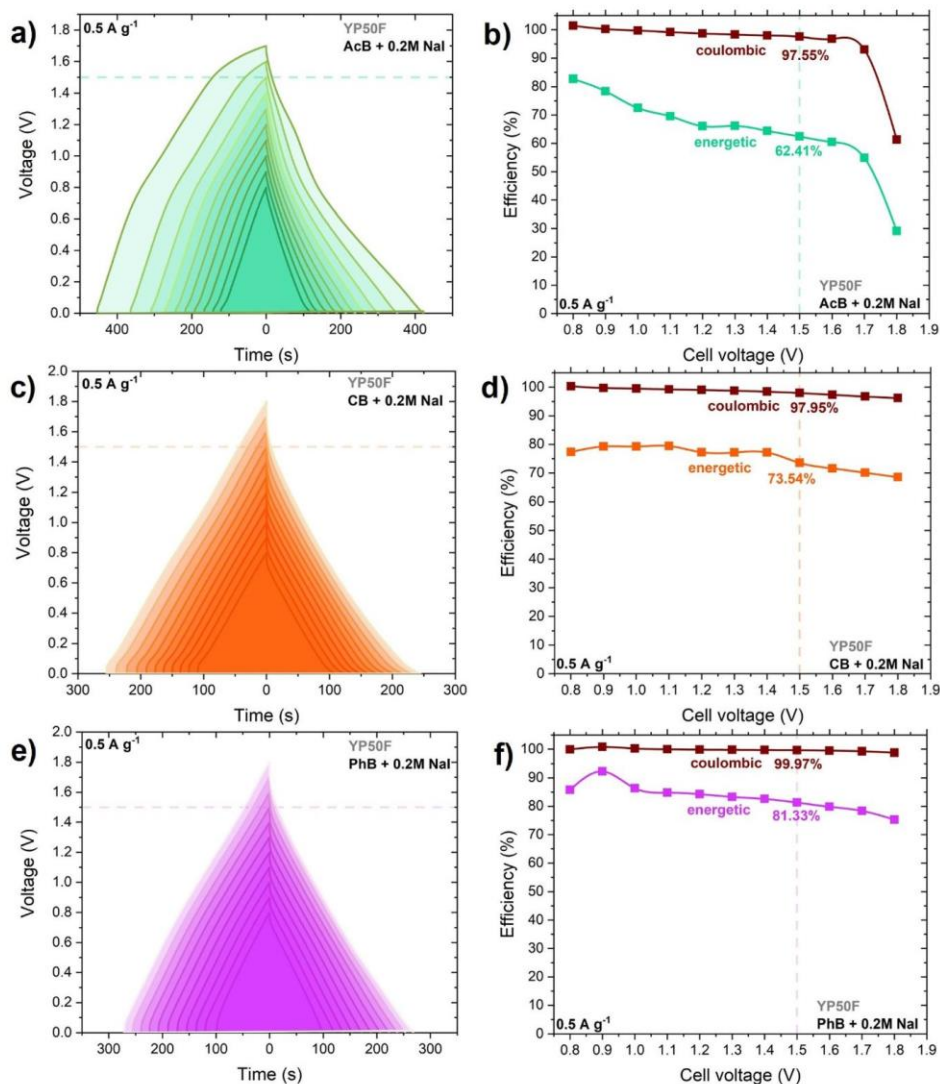


Fig. 2 Galvanostatic charge/discharge voltage extension at 0.5 A g⁻¹ for ECs operating in (a) acetate buffer + 0.2 mol L⁻¹ NaI, (c) citrate buffer + 0.2 mol L⁻¹ NaI, and (e) phosphate buffer + 0.2 mol L⁻¹ NaI for various voltages. Energetic and coulombic efficiency calculated from the GCD curves for ECs operating in (b) acetate buffer + 0.2 mol L⁻¹ NaI, (d) citrate buffer + 0.2 mol L⁻¹ NaI, and (f) phosphate buffer + 0.2 mol L⁻¹ NaI.

(Fig. S5c†). After the addition of iodides to the system (AcB + 0.2 mol L⁻¹ NaI), the CV shape of the two-electrode cell showed small current humps, and it deviated from the ideal

shape of the capacitor, indicating the strong redox activity of the iodides (Fig. S5d†). Typically, the positive electrode showed a broad and pronounced redox peak correlated with the fara-

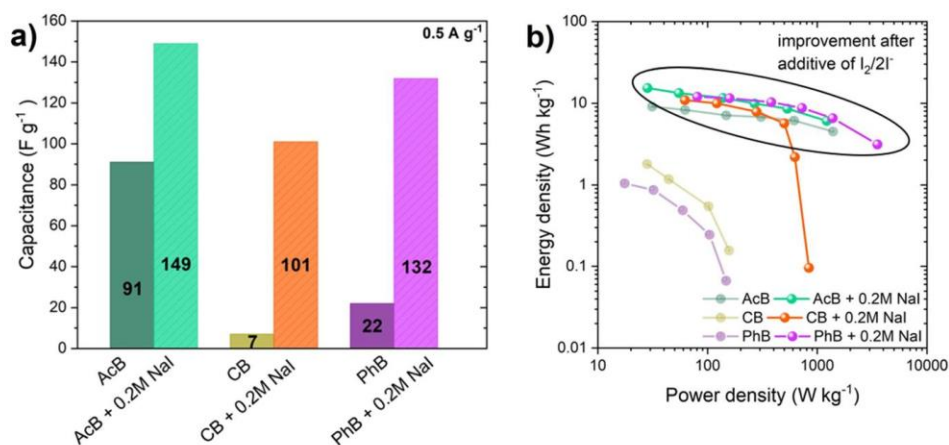


Fig. 3 (a) Specific capacitance values at 0.5 A g⁻¹ and (b) Ragone plots for ECs operating in acetate buffer, citrate buffer, and phosphate buffer with/without 0.2 mol L⁻¹ NaI additive.

daic reaction of iodides (Fig. S5e†). In comparison to the pristine buffer solution, the positive electrode in iodide showed a higher capacitance, which resulted in the unbalanced separation of charge in the system, and led to an extended potential window of the negative electrode (0.85 V) (Fig. S5f†), consequently improving the specific capacitance of the system at a high voltage window of 1.5 V. This mechanism for the iodide reaction was comparable to the other works reported on the use of iodides in electrochemical capacitors employing reactions presented by eqn (1)–(3).⁵³ Fig. 3a visualizes the specific capacitance values calculated from the GCD at 0.5 A g⁻¹ for AcB, CB, and PhB with/without 0.2 mol L⁻¹ NaI. The additive of the iodide/iodine redox pair enhanced the specific capacitance values for each EC, by 40% in the case of AcB, 93% for CB, and 83% for PhB. The influence of 0.2 mol L⁻¹ NaI additive on the energy and power metrics of the buffer-based ECs could be noticed in the Ragone plot as well (Fig. 3b).

Along with the importance of increasing the energetic characteristics of ECs, the electrochemical stability and long-time performance are also considered to be crucial factors. One of the most popular and commonly used techniques for that purpose is galvanostatic cycling. However, such a technique requires a lot of time. Therefore, a less time-consuming alternative technique (floating) was used. Floating consists of three GCD cycles with a voltage hold for 2 h at U_{max} . The criterion end-of-life is a 20% loss of initial capacitance or 200% increase in the initial resistance.⁵⁴ Before and after the floating tests, cyclic voltammetry at 5 mV s⁻¹ and electrochemical impedance spectroscopy analysis were carried out to assess the impact of the accelerated aging of ECs. The results of the floating for the different commercial carbon-based ECs

(YP50F, BP2000, and YP80F) operating in AcB with 0.2 mol L⁻¹ NaI and YP50F-based EC working in AcB (without iodide) are shown in Fig. S6a†. The highest long-term performance for the ECs with an iodide/iodine pair was noted for YP50F carbon (310 h) followed by 212 h for the YP80F-based EC and 126 h for the BP2000-based EC. This study revealed that carbon with a higher micropore volume presents a longer floating time than typical mesoporous ones. Presumably, the reversible I₂/2I⁻ redox pair was well confined inside the micropores. Moreover, the contact angle measurements confirmed the best wettability was for YP50F. Poor wettability leads to a low utilization of the surface area, resulting in a low specific capacitance. The contact angle of 65° was measured for BP2000 carbon with acetate buffer/iodide, followed by 64° for YP80F carbon and 60° for YP50F carbon. Several concentrations of NaI additive (0.2, 0.5, 1, 2 mol L⁻¹) to AcB electrolyte were applied for the YP50F-based EC during the floating test (Fig. S7a†). The floating time of such systems was the best for 0.2 mol L⁻¹ of NaI additive (310 h), whereas for pure AcB, it was equal to 100 h only. The worst floating (34 h) was recorded for the 2 mol L⁻¹ NaI additive. These findings provide clear proof that the concentration of iodide additive must be carefully selected for a long lifespan of ECs. Even if a high iodide concentration supplies a high capacitance at the beginning, it does not guarantee a long cycling life, and gradually, the formed polyiodides can easily block the available surface of the carbon. The Nyquist plots before and after 100 h floating for the AcB system and 310 h floating for the AcB + 0.2 mol L⁻¹ NaI system are shown in Fig. S7b† and Fig. 4b, respectively.

The equivalent series resistance increased twofold in both cases, indicating the EC's end-of-life would be mainly due to

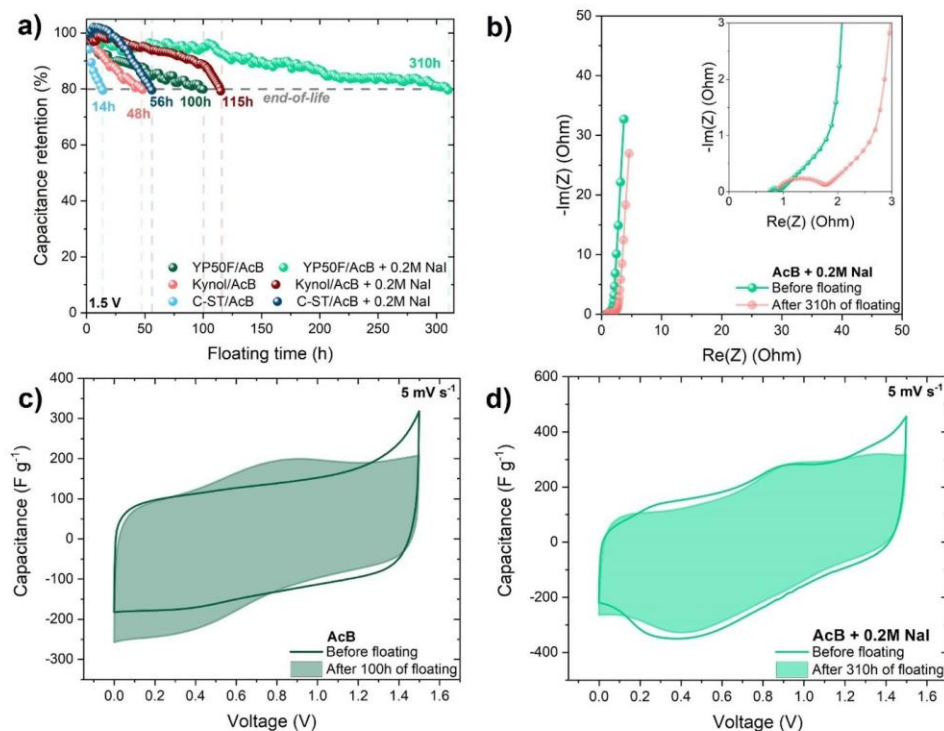


Fig. 4 (a) Capacitance retention of different microporous carbons (YP50F, Kynol, and C-ST) based ECs operating in acetate buffer with and without 0.2 mol L⁻¹ NaI additive during the floating test (at 1.5 V). (b) Nyquist plots obtained from YP50F-based ECs operating in acetate buffer + 0.2 mol L⁻¹ NaI before and after 310 h floating test. Cyclic voltammogram at 5 mV s⁻¹ recorded for (c) acetate buffer before and after 100 h floating test; (d) acetate buffer + 0.2 mol L⁻¹ NaI before and after 310 h floating test.

the deterioration of the electrode performance (parasitic reactions) and the presence of stainless steel corrosion products. Cyclic voltammetry (5 mV s⁻¹) was applied in order to compare the impacts of accelerated aging for pure AcB and that with iodide additive (Fig. 4c and d). The cyclic voltammograms recorded for ECs with NaI additive after prolonged floating time exhibited almost the same charge propagation. However, they exhibited a noticeably more resistant character. Such ECs subjected to prolonged polarization at $U_{\max} = 1.5$ V were exposed to the occurrence of parasitic processes. The peaks associated with the redox activity could be attributed to the side reactions of the new functional groups on the carbon electrode surface, e.g., quinone-hydroquinone.

The electrochemical measurements proved that microporous carbon YP50F was the best choice in terms of energy density as well as long-term performance compared to the available mesoporous carbons (YP80F, BP2000). That is why, to extend the provided studies, other types of highly microporous

carbons with larger specific surface areas (Kynol, C-ST) were investigated. The galvanostatic charge/discharge technique was applied for comparison of the electrochemical performance of ECs operating in acetate buffer with and without 0.2 mol L⁻¹ NaI additive (Fig. S8a and b†). The development of the specific surface area to 2640 m² g⁻¹ as well as the micropore volume to 0.97 cm³ g⁻¹ in the case of the salt-templated carbon (C-ST) enabled a significant increase in capacitance values for the EC operating in AcB + 0.2 mol L⁻¹ NaI to reach 244 F g⁻¹. In the case of the system based on carbon cloth (Kynol), there was also a visible increase in the capacitance value compared to the EC based on YP50F operating in acetate buffer with/without iodide additive. Both additionally tested carbons had a larger S_{BET} than YP50F, which affects the electrochemical performance of ECs. Furthermore, the long-term performance of Kynol and C-ST microporous carbons operating in acetate buffer with and without I₂/2I⁻ additive were analyzed (Fig. 4a). The investigation revealed that the

YP50F-based EC operating in acetate buffer + 0.2 mol L⁻¹ NaI, despite its lower specific surface area, showed the best long-term performance (310 h of floating), followed by 115 h of floating for the Kynol- and 56 h of floating for the C-ST-based ECs. In the ESI,† the cyclic voltammograms, Nyquist plots, and galvanostatic charge/discharge curves before and after the floating tests are provided for the YP50F-, Kynol-, and C-ST-based ECs operating in acetate buffer with/without 0.2 mol L⁻¹ NaI additive (Fig. S9–S11†).

After the floating tests, the electrodes were also analyzed by X-ray diffraction measurements (XRD) to study the structures of the samples and/or residues of the electrolyte components (Fig. S12†). Pristine YP50F showed broad and low intensity peaks characteristic for activated carbon positioned at *ca.* 22° and 43°, corresponding to the (002) and (100) planes of graphite structure (JCPDS 00-056-0159). Iodides underwent redox reactions on the positive electrode, effectively improving the reachable capacitance of the system, as we have shown in our manuscript. In standard aqueous electrolytes, the aging process of the electrodes included oxidation of the carbon surface eventually leading to a change of the pH at the electrode/electrolyte interface. However, the systems operating in the buffer with the iodide solutions were able to withstand such changes. Taking into account the redox activity of iodides at the positive electrode, we decided to study only (+) electrodes after floating tests operating in AcB and AcB + 0.2 mol L⁻¹ NaI electrolytes (Fig. S12†). It occurred that both electrodes showed broad peaks at comparable positions to the pristine YP50F. The sharp peak at *ca.* 18° corresponded to the presence of the PTFE in the electrode material. There was no presence of additional peaks, which was proof that the long-term electrochemical operation had no effect on the formation of solid-state residues, which could cause porosity blockage and deterioration of the electrochemical performance of the system.

To further study the surface chemistry of cycled electrodes, we utilized the X-ray photoelectron spectroscopy (XPS) technique. Table S4 and Fig. S13† present the surface concentrations of chemical bonds, derived from fitting the XPS data for the pristine electrode (YP50F) and electrodes (positive and negative) cycled in buffer solutions without and with the addition of sodium iodides. After the floating tests, we observed a decrease in C=C sp² bonding and an increase in C-C sp³ bonding in the C 1s spectrum (Fig. S13a†) on the surface of both electrodes in comparison to the pristine YP50F electrode. This indicates that the electrochemical tests in AcB buffer electrolyte affected the surface chemistry of the electrode material, as reflected by the altered content of oxygen groups. In the case of the positive electrode, a much higher decrease in C=C sp² bonding was observed (from 56.9% to 41.4%) compared to the negative electrode (from 56.9% to 51.6%), suggesting that the positive electrode was more affected by electrochemical parasitic processes. We also observed a variation in the oxygen content in the O 1s region (Fig. S13b†). On the positive electrode, the signals from the oxygen functionalities increased, *i.e.*, in the C 1s spectrum, the signal from O-C=O at 288.9 eV increased from 3.2% to 3.8%, and in the O 1s spectrum, the signal from (C-O, -OH) at 533.8 eV increased from 2.2% to 4.9%. The content of other oxygen functionalities, such as (C-O-C, C-OH) at 286.3 eV or (-COOH) at 290.3 eV slightly decreased from 7% to 6.3% and from 2.7% to 2.2%, respectively. This suggests that after the floating tests, not all the functional groups were contributing to the increase in the oxygen content. Interestingly, we observed a comparable pattern in the case of the negative electrode (see Table S4† for details), but the changes were not as pronounced as in the case of the positive electrode.

We also investigated the surface composition of electrodes after floating in AcB + 0.2 mol L⁻¹ NaI electrolyte. Interestingly, the results revealed a much higher content of

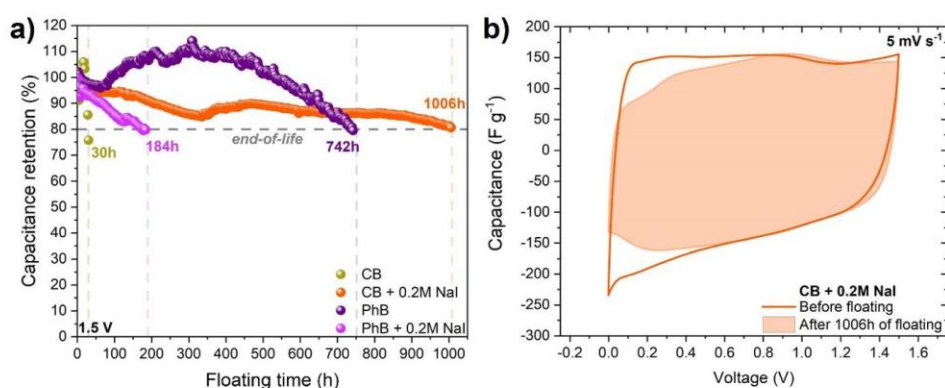


Fig. 5 (a) Capacitance retention of YP50F-based ECs operating in citrate buffer and phosphate buffer with/without 0.2 mol L⁻¹ NaI additive during floating test (at 1.5 V). Cyclic voltammograms for ECs operating in (b) citrate buffer + 0.2 mol L⁻¹ NaI before and after 1006 h floating test.

C=C sp² bonding in comparison to the electrodes aged in AcB alone (from 56.9% to 51.2% for the negative electrode and 47.0% for the positive electrode), which could indicate that the iodides were not as oxidative as the AcB electrolyte alone. We observed a similar trend in terms of the positive electrode being more prone to oxidation, but overall, the surface of the electrodes was less oxidized than when cycled in pure AcB.

Additionally, we observed signals at 618.4 and 620.6 eV in the I 3d_{5/2} spectrum (Fig. S13c†), corresponding to the presence of NaI and CH-I bonds. These provide evidence that the iodides were partly grafted on the carbon surface after the prolonged electrochemical tests. At the same time, we did not observe the presence of insolubilities in the water iodates, which suggests that the buffer solution restricted changes in the pH, preventing the electrochemical formation of side products.

Finally, the influence of 0.2 mol L⁻¹ NaI additive to the citrate and phosphate buffers on the ECs was tested with the floating method, as shown in Fig. 5. Surprisingly, the pure CB-based system reached only 30 h of floating. The addition of 0.2 mol L⁻¹ NaI into the CB-based EC significantly improved the floating time (1006 h), suggesting that the slightly acidic citrate buffer is suitable for reversible long-term iodide redox activity.

Regarding phosphate buffer-based ECs, it could be seen that some fluctuations, especially around 300 h, and a capacitance retention value above 100% took place. Such behavior was associated with not enough time for electrode soaking in the electrolyte before the experiment. The high contact angle of 70° and slower wettability time could affect the performance. Finally, the system was able to reach the end-of-life criterion after 742 h. Unexpectedly, the 0.2 mol L⁻¹ NaI additive to the phosphate-based EC did not improve the long-term performance, with a 184 h floating time. Such a performance could be influenced by the pH value, which was 7.18, and according to the Pourbaix diagram, it seemed to be a limit for the efficient working of the I₂/2I⁻ redox pair.

4. Conclusions

The iodide/buffer electrolyte as an environmentally friendly and cost-effective composition was introduced for the first time for the energy enhancement of carbon-based electrochemical capacitors. The buffer environment, *i.e.*, acetate, citrate, and phosphate, with stable pH, enabled extending the operating voltage of ECs up to 1.5 V. Such a result is meaningful, since it is well-known that a stable operating voltage for iodides-based ECs is limited to 1.2 V. A noteworthy improvement of the electrochemical capacitor cycle life at a voltage of 1.5 V was achieved when 0.2 mol L⁻¹ NaI was added to acetate buffer and citrate buffer. During the aging test (at 1.5 V) such ECs exhibited 310 h and 1006 h prolonged floating times, respectively. These results are substantial when compared to ECs operating in pure acetate (100 h) and citrate (30 h). Moreover, the contact angle measurements of selected acti-

vated carbons with different porosities and acetate buffer + 0.2 mol L⁻¹ NaI revealed that highly microporous Kuraray YP50F carbon had the best wettability, as confirmed by the smallest contact angle of 60°. As a consequence, the microporous carbon-based EC operating in AcB + 0.2 mol L⁻¹ NaI showed the best long-term performance (310 h) during the accelerated aging test compared to YP80F (212 h) and BP2000 (126 h) activated carbons. The galvanostatic charge/discharge carried out on ECs working in buffer electrolytes with 0.2 mol L⁻¹ NaI proved that such additive could significantly increase the specific capacitance values, from 91 to 149 F g⁻¹ for acetate buffer, from 7 to 101 F g⁻¹ for citrate buffer, and from 22 to 132 F g⁻¹ for phosphate buffer. The work evidenced that the use of a buffer as an electrolyte with iodide additive significantly improved the EC performance. The beneficial effect of the stabilized pH of such buffer-based electrolytes relies on a limited oxidation of the positive electrode. This was especially pronounced in the buffer/iodide-based electrolytes. After electrochemical floating, the covalent bonding between carbon and iodide was proven by XPS. Stabilization of the pH at the electrode/electrolyte interface prevented the formation of insoluble products. Our experiments showed negligible solvent effects for buffer/iodide-based electrolytes. Such sustainable system buffer/iodide-based electrolytes could be practically utilized. To sum up, our demonstrated buffer/iodide electrolyte-based EC is a cheap, green, and reliable approach, with significant promise for future widespread application.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

This work was supported by project no. 0911/SBAD/2401.

References

- 1 BP Statistical Review of World Energy (2022).
- 2 P. A. Owusu and S. Asumadu-Sarkodie, A review of renewable energy sources, sustainability issues and climate change mitigation, *Cogent Eng.*, 2016, **3**, 1167990.
- 3 G. Palmer, Renewables rise above fossil fuels, *Nat. Energy*, 2019, **4**, 538–539.
- 4 P. Simon, Y. Gogotsi and B. Dunn, Where do batteries end and supercapacitors begin?, *Science*, 2014, **343**, 1210–1211.
- 5 A. Burke, Z. Liu and H. Zhao, Present and future applications of supercapacitors in electric and hybrid vehicles, *IEEE-IEVC*, 2014, 1–8.
- 6 T. Shimizu and C. Underwood, Super-capacitor energy storage for micro-satellites: feasibility and potential mission applications, *Acta Astronaut.*, 2013, **85**, 138–154.
- 7 Y. Su, N. Li, L. Wang, R. Lin, Y. Zheng, G. Rong and M. Sawan, Stretchable transparent supercapacitors for

- wearable and implantable medical devices, *Adv. Mater. Technol.*, 2022, **7**, 2100608.
- 8 A. Muzaffar, M. B. Ahamed, K. Deshmukh and J. Thirumalai, A review on recent advances in hybrid supercapacitors: design, fabrication and applications, *Renewable Sustainable Energy Rev.*, 2019, **101**, 123–145.
 - 9 S. Yamazaki, T. Ito, M. Yamagata and M. Ishikawa, Non-aqueous electrochemical capacitor utilizing electrolytic redox reactions of bromide species in ionic liquid, *Electrochim. Acta*, 2012, **86**, 294–297.
 - 10 L. Yang, L. Zhang, X. Jiao, Y. Qiu and W. Xu, The electrochemical performance of reduced graphene oxide prepared from different types of natural graphites, *RSC Adv.*, 2021, **7**, 4042–4052.
 - 11 I. Piñeiro-Prado, D. Salinas-Torres, R. Ruiz-Rosas, E. Morallón and D. Cazorla-Amorós, Design of activated carbon/activated carbon asymmetric capacitors, *Front. Mater.*, 2016, **3**, 16.
 - 12 J. Chmiola, G. Yushin, R. K. Dash, E. N. Hoffman, J. E. Fischer, M. W. Barsoum and Y. Gogotsi, Double-layer capacitance of carbide derived carbons in sulfuric acid, *Electrochem. Solid-State Lett.*, 2005, **8**, A357.
 - 13 A. Halder, M. Ghosh, M. A. Khayum, S. Bera, M. Addicoat, S. H. Sasmal, S. Karak, S. Kurungot and R. Banerjee, Interlayer hydrogen-bonded covalent organic frameworks as high-performance supercapacitors, *J. Am. Chem. Soc.*, 2018, **35**, 10941–10945.
 - 14 H. Furukawa, K. E. Cordova, M. O'Keeffe and O. M. Yaghi, The chemistry and applications of metal-organic frameworks, *Science*, 2013, **341**, 1230444.
 - 15 B. Anasori, M. R. Lukatskaya and Y. Gogotsi, 2D metal carbides and nitrides (MXenes) for energy storage, *Nat. Rev. Mater.*, 2017, **2**, 1–17.
 - 16 C. Niu, E. K. Sichel, R. Hoch, D. Moy and H. Tennent, High power electrochemical capacitors based on carbon nanotube electrodes, *Appl. Phys. Lett.*, 1997, **70**, 1480–1482.
 - 17 M. Fu, W. Chen, Y. Lei, H. Yu, Y. Lin and M. Terrones, Biomimetic construction of ferrite quantum dot/graphene heterostructure for enhancing ion/charge transfer in supercapacitors, *Adv. Mater.*, 2023, **35**, 2300940.
 - 18 K. Zou, P. Cai, B. Wang, C. Liu, J. Li, T. Qiu, G. Zou, H. Hou and X. Ji, Insights into enhanced capacitive behavior of carbon cathode for lithium ion capacitors: the coupling of pore size and graphitization engineering, *Nano-Micro Lett.*, 2020, **12**, 121.
 - 19 A. Balducci, Electrolytes for high voltage electrochemical double layer capacitors: a perspective article, *J. Power Sources*, 2016, **326**, 534–540.
 - 20 V. Khomenko, E. Raymundo-Piñero, E. Frackowiak and F. Béguin, High-voltage asymmetric supercapacitors operating in aqueous electrolyte, *J. Appl. Phys. A*, 2006, **82**, 567–573.
 - 21 L. Suo, O. Borodin, T. Gao, M. Olguin, J. Ho, X. Fan, C. Luo, C. Wang and K. Xu, Water-in-salt electrolyte enables high-voltage aqueous lithium-ion chemistries, *Science*, 2015, **350**, 938–943.
 - 22 S. E. M. Pourhosseini, A. Bothe, A. Balducci, F. Béguin and P. Ratajczak, Strategy to assess the carbon electrode modifications associated with the high voltage ageing of electrochemical capacitors in organic electrolyte, *Energy Storage Mater.*, 2021, **38**, 17–29.
 - 23 A. Balducci, U. Bardi, S. Caporali, M. Mastragostino and F. Soavi, Ionic liquids for hybrid supercapacitors, *Electrochem. Commun.*, 2004, **6**, 566–570.
 - 24 W. Zaidi, A. Boisset, J. Jacquemin, L. Timperman and M. Anouti, Deep eutectic solvents based on N-methylacetamide and a lithium salt as electrolytes at elevated temperature for activated carbon-based supercapacitors, *J. Phys. Chem. C*, 2014, **118**, 4033–4042.
 - 25 S. Azmi, A. Klimek and E. Frackowiak, Anticorrosive performance of green deep eutectic solvent for electrochemical capacitor, *Chem. Eng. J.*, 2022, **444**, 136594.
 - 26 S. Azmi, A. Klimek and E. Frackowiak, Why electrochemical capacitor electrolytes should not be ignored?, *Electrochim. Acta*, 2023, **452**, 142347.
 - 27 C. Li, W. Wu, P. Wang, W. Zhou, J. Wang, Y. Chen, L. Fu, Y. Zhu, Y. Wu and W. Huang, Fabricating an aqueous symmetric supercapacitor with a stable high working voltage of 2 V by using an alkaline-acidic electrolyte, *Adv. Sci.*, 2019, **6**, 1801665.
 - 28 K. Fic, G. Lota, M. Meller and E. Frackowiak, Novel insight into neutral medium as electrolyte for high-voltage supercapacitors, *Energy Environ. Sci.*, 2012, **2**, 5842–5850.
 - 29 A. Slesinski, S. Sroka, K. Fic, E. Frackowiak and J. Menzel, Operando monitoring of local pH value changes at the carbon electrode surface in neutral sulfate-based aqueous electrochemical capacitors, *ACS Appl. Mater. Interfaces*, 2022, **33**, 37782–37792.
 - 30 C. H. Chien, T.-H. Wu, M. Rajkumar and C.-C. Hu, Effects of buffer agents on hydrogen adsorption and desorption at/within activated carbon for the negative electrode of aqueous asymmetric supercapacitors, *Electrochim. Acta*, 2016, **205**, 1–7.
 - 31 S. T. Vindt and E. M. Skou, The buffer effect in neutral electrolyte supercapacitors, *Appl. Phys. A*, 2016, **122**, 64.
 - 32 E. Proksch, Buffering capacity, *Curr. Probl. Dermatol.*, 2018, **54**, 11–18.
 - 33 H. Hashiba, L.-C. Weng, Y. Chen, H. K. Sato, S. Yotsushashi, C. Xiang and A. Z. Weber, Effects of electrolyte buffer capacity on surface reactant species and the reaction rate of CO₂ in electrochemical CO₂ reduction, *J. Phys. Chem. C*, 2018, **7**, 3719–3726.
 - 34 R. A. Durst, *Standard reference materials: standardization of pH measurements*, U.S. Department of Commerce, Rogers C. B. Morton, 1975.
 - 35 A. Salis and M. Monduzzi, Not only pH. Specific buffer effects in biological systems, *Curr. Opin. Colloid Interface*, 2016, **23**, 1–9.
 - 36 B. Wang, Q. Fan, L. Xu, J. Liu, C. Dai, M. Tang, K. Liang, P. L. Taberna, Y. Liu, P. Simon and Z. Lin, Activating pseudocapacitive charge storage of molten-salt-synthesized

- MXenes in mild aqueous electrolytes, *ACS Appl. Energy Mater.*, 2023, DOI: [10.1021/acsaelm.3c02376](https://doi.org/10.1021/acsaelm.3c02376).
- 37 S. Makino, T. Ban and W. Sugimoto, Towards implantable bio-supercapacitors: pseudocapacitance of ruthenium oxide nanoparticles and nanosheets in acids, buffered solutions, and bioelectrolytes, *J. Electrochem. Soc.*, 2015, **162**, A5001.
 - 38 J. Piwek, A. Platek, K. Fic and E. Frackowiak, Carbon-based electrochemical capacitors with acetate aqueous electrolytes, *Electrochim. Acta*, 2016, **215**, 179–186.
 - 39 S. Zallouz, L. Dentzer and C. Matei Ghimbeu, Carbon capacitors operating at 1.8 V based on concentrated aqueous electrolytes: impacts of the electrolyte concentration and carbon properties, *ACS Appl. Energy Mater.*, 2024, **7**, 1448–1460.
 - 40 G. Lota and E. Frackowiak, Striking capacitance of carbon/iodide interface, *Electrochem. Commun.*, 2009, **11**, 87–90.
 - 41 S. E. Chun, B. Evanko, X. Wang, D. Vonlanthen, X. Ji, G. D. Stucky and S. W. Boettcher, Design of aqueous redox-enhanced electrochemical capacitors with high specific energies and slow self-discharge, *Nat. Commun.*, 2015, **6**, 7818.
 - 42 A. Platek-Mielczarek, E. Frackowiak and K. Fic, Specific carbon/iodide interactions in electrochemical capacitors monitored by EQCM technique, *Energy Environ. Sci.*, 2021, **4**, 2381–2393.
 - 43 A. Platek, J. Piwek, K. Fic and E. Frackowiak, Ageing mechanisms in electrochemical capacitors with aqueous redox-active electrolytes, *Electrochim. Acta*, 2019, **311**, 211–220.
 - 44 A. Platek-Mielczarek, C. Nita, C. Matei Ghimbeu, E. Frackowiak and K. Fic, Link between alkali metals in salt templates and in electrolytes for improved carbon-based electrochemical capacitors, *ACS Appl. Mater. Interfaces*, 2021, **13**, 2584–2599.
 - 45 B. Yan, J. Zheng, L. Feng, Q. Zhang, C. Zhang, Y. Ding, J. Han, S. Jiang and S. He, Pore engineering: structure-capacitance correlations for biomass-derived porous carbon materials, *Mater. Des.*, 2023, **229**, 111904.
 - 46 I. Persson, Hydrated metal ions in aqueous solution: how regular are their structures?, *Pure Appl. Chem.*, 2010, **82**, 1901–1917.
 - 47 B. Tansel, Significance of thermodynamic and physical characteristics on permeation of ions during membrane separation: hydrated radius, hydration free energy and viscous effects, *Sep. Purif. Technol.*, 2012, **86**, 119–126.
 - 48 M. V. Fedotova and S. E. Kruchinin, Hydration of acetic acid and acetate ion in water studied by 1D-RISM theory, *J. Mol. Liq.*, 2011, **164**, 201–206.
 - 49 D. Moreno, Y. Bootwala, W.-Y. Tsai, Q. Gao, F. Shen, N. Balke, K. B. Hatzell and M. C. Hatzell, In situ electrochemical dilatometry of phosphate anion electrosorption, *Environ. Sci. Technol.*, 2018, **5**, 745–749.
 - 50 V. Chiriac and G. Balea, Buffer index and buffer capacity for a simple buffer solution, *J. Chem. Educ.*, 1997, **8**, 937.
 - 51 K. Fic, A. Platek, J. Piwek, J. Menzel, A. Slesinski, P. Bujewska, P. Galek and E. Frackowiak, Revisited insights into charge storage mechanisms in electrochemical capacitors with Li₂SO₄-based electrolyte, *Energy Storage Mater.*, 2019, **22**, 1–14.
 - 52 J. Menzel, A. Slesinski, P. Galek, P. Bujewska, A. Kachmar, E. Frackowiak, A. Washio, H. Yamamoto, M. Ishikawa and K. Fic, Operando monitoring of activated carbon electrodes operating with aqueous electrolytes, *Energy Storage Mater.*, 2022, **49**, 518–528.
 - 53 G. Lota, K. Fic and E. Frackowiak, Alkali metal iodide/carbon interface as a source of pseudocapacitance, *Electrochem. Commun.*, 2011, **13**, 38–41.
 - 54 P. Ratajczak, K. Jurewicz, P. Skowron, Q. Abbas and F. Béguin, Effect of accelerated ageing on the performance of high voltage carbon/carbon electrochemical capacitors in salt aqueous electrolyte, *Electrochim. Acta*, 2014, **130**, 344–350.

Lignin as precursor of gel electrolyte and salt templated carbon for sustainable electrochemical capacitor

<https://doi.org/10.1039/D5GC05533D>

The study presented in this chapter provides comprehensive and sustainable strategy for the development of ECs using liginosulfonate (LS), a waste-derived technical lignin, as a multifunctional precursor for all key EC components, including the electrolyte, separator, and electrodes, as shown in **Figure 12**. This work addresses critical environmental and performance limitation of ECs (e.g., safety, narrow operating voltage).

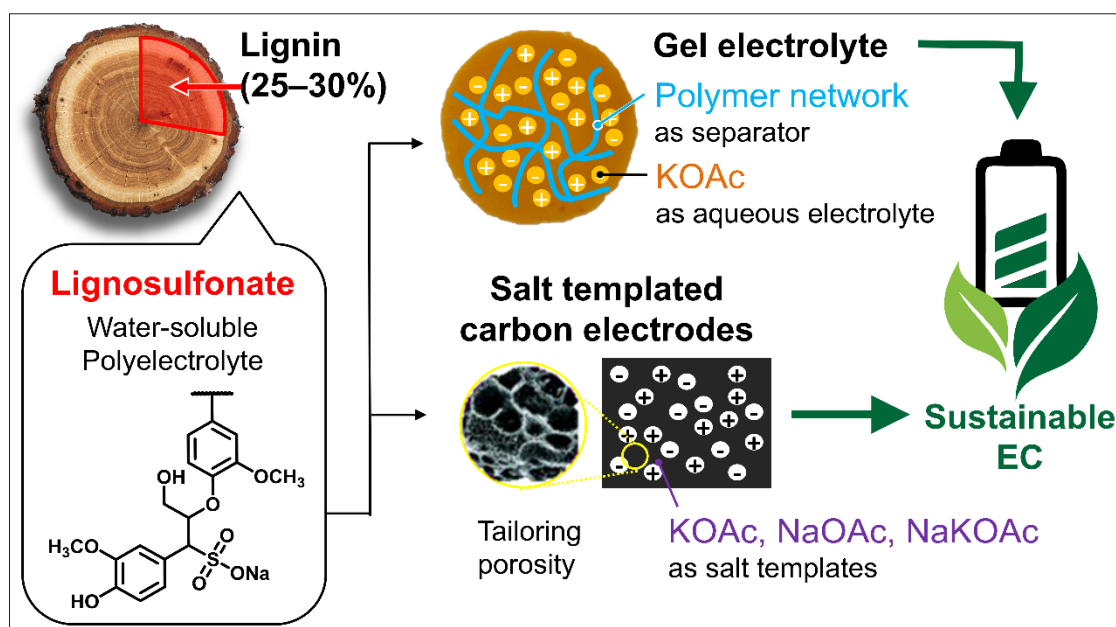


Figure 12 Novel and environmentally friendly strategy for effective utilization of a waste-derived technical lignin from wood, as a renewable precursor of EC electrolyte, electrodes, and separator.

Hence, the innovation in this research relies on the development of LS-based gels with expected high aqueous electrolyte uptake capacity in combination with water-in-salt electrolytes. As well, LS can be used as a carbon precursor to produce tailored electrode materials *via* salt templating approach. In both cases, acetate salts (NaOAc, KOAc, LiOAc, and its mixtures) served for the preparation of LS gel electrolyte and LS salt template carbons.

For that purpose, thin films of gels were prepared *via* chemical crosslinking of LS and a crosslinker PEGDGE (poly(ethylene glycol) diglycidyl ether) with PEO (poly (ethylene oxide)) repeating units of 22. The LS gel structure observed using Cryo SEM exhibited a porous, three-dimensional network capable of incorporation aqueous acetate solution. The LS-based gel electrolyte was optimized using acetate solutions varying the cations used (Li^+ , Na^+ , K^+), and concentrations (1 - 24m) through the systematic investigation of the solution uptake ability and change of swelling degree. It was proved that both: solution uptake and swelling degree decrease with increase of acetate salts concentration, due to higher osmotic pressure and viscosity, which limit solvent diffusion into the polymer network. Among the tested gels, KOAc-based gels exhibited the most stable performance, maintaining relatively high solution uptake even at elevated concentrations, attributed to the lower hydration energy and higher mobility of K^+ ions. It facilitated more effective combination of the KOAc solution with the LS gel matrix. The ionic conductivity of the LS-KOAc reached the highest value of ($\sim 10 \text{ mS cm}^{-1}$) for the LS-1m KOAc due to the greater solution uptake. Nevertheless, LS-5 m KOAc gel provided the best compromise between the ionic conductivity, reduced free water content, and mechanical stability, making it the most suitable for further EC testing.

The modification in texture/structure of LS carbons was achieved through the salt templating route. Notably, acetate salts (NaOAc, KOAc, NaKOAc) served as both structural templates and self-activating agents. Formation of microporosity was possible due to the effect of the salt template (diameter of ions), nevertheless, at the same time, some graphitic domains were formed, influenced by the cation's affinity towards carbon core and the cations size. The LS carbons exhibited predominantly microporous texture with SSA ranging from $881 \text{ m}^2 \text{ g}^{-1}$ (NaOAc) to $1754 \text{ m}^2 \text{ g}^{-1}$ (KOAc) and differences in degrees of structural disorder ($I_{D1}/I_G = 1.37 - 3.00$). KOAc template promoted higher microporosity due to weaker cation- π interactions, while NaOAc induced greater graphitization and reduced surface area. In mixed NaKOAc template, a synergistic effect of both salts enhanced carbon-salt interactions, and led to partial graphitization with increased mesoporosity.

Electrochemical testing of ECs composed of LS-5m KOAc gel electrolyte and LS-salt templated carbons demonstrated nearly ideal EDL behavior with rectangular CV profiles and triangular GCD curves up to 1.6 V. Capacitance values ranged from 46 to 82 F g⁻¹ depending on the carbon texture, with the highest capacitance observed for highly disordered and porous LS-KOAc carbon. A strong linear correlation between capacitance and accessible SSA as well as micropore volume ($R^2 \sim 0.95$) confirmed that charge storage is dominated by ion adsorption in micropores. In contrast, excessive graphitization of LS-NaOAc, LS-NaKOAc carbons reduced capacitance due to decreased SSA.

The LS gel electrolyte played a critical role in the improvement of EC safety and stability. Compared to diluted liquid electrolytes, the LS gel electrolyte significantly reduced self-discharge and leakage current of EC, maintaining higher voltage over extended periods. Additionally, gel acted as both electrolyte and separator, eliminating the need for synthetic membranes and minimizing the risk of electrolyte leakage. The assembled ECs achieved improved lifespan (up to 170 floating hours for LS-NaKOAc) and reduced self-discharge compared to commonly used glass fiber separator (by ~10%). Further analysis of structure - performance relationships revealed that not only textural parameters (SSA, pore size distribution) but also structural disorder and surface chemistry critically influence electrochemical performance. In particular, a higher degree of disorder correlated with increased capacitance as defect-rich structure provided more electroactive sites and facilitated ion adsorption. On the other hand, higher disorder resulted in reduced EC lifespan, decreasing the conductivity as well as promoted electrode degradation. High microporosity enhanced capacitance, while mesopores contributed primarily to ion transport and rate capability.

Importantly, the environmental impact of the LS-based EC was evaluated in comparison to existing literature. The present approach employed renewable LS as carbon source with yield comparable to conventional methods, resulting in similar energy requirements, while significantly improving sustainability. This strategy allowed CO₂ emission reduction of 32-49%, demonstrating its strong potential for the development of more environmentally friendly electrochemical capacitors. Concluding, this study proved that LS can be effectively utilized as high-performance, sustainable EC components. The combination of bio-derived gel electrolyte with tailored porous carbon provided a viable pathway toward environmentally benign ECs, combining safety, and competitive electrochemical performance over conventional designs.

Cite this: *Green Chem.*, 2026, **28**, 4225

Lignin as a precursor of a gel electrolyte and salt templated carbon for sustainable electrochemical capacitors

 Amelia Klimek,^{a,b,c,d} Lina Amro,^a Nutthira Pakkang,^{d,e}
 Camélia Matei Ghimbeu,^{b,c,f} Elzbieta Frackowiak^{b,*a} and Shiori Suzuki^{b,*d}

Electrochemical capacitors (ECs) belong to attractive high-power devices; however, their key components often do not meet ecological requirements. Herein, we propose a sustainable EC based on a gel electrolyte and porous carbon, both of which are made from lignosulfonate (LS), a waste-derived technical lignin from wood. First, the uptake ability of the LS-based gel electrolyte was systematically investigated using several concentrations (1–24 m) of aqueous acetate salt solutions containing different cations (Li, Na, and K). An optimized aqueous electrolyte, 5 m KOAc, was selected due to the high ionic conductivity and ion mobility. Next, LS was converted into porous carbons through an environmentally friendly salt templating approach using NaOAc and KOAc, which enabled precise control of the carbon structure and texture. The resulting carbons exhibited predominantly microporous characteristics with specific surface areas ranging from 881 to 1754 m² g⁻¹. Raman spectroscopy analysis revealed various degrees of structural disorder (I_{D1}/I_G ranged from 1.37 to 3.00). Finally, ECs were assembled with the LS-based gel electrolyte and salt templated carbons. They achieved a stable operating voltage (1.6 V), reduced self-discharge (loss of ~30% of initial voltage), and a long lifespan (170 h of floating), which is competitive with reference aqueous ECs (loss of ~40% of initial voltage and 120 h of floating). Importantly, the LS gel plays a two-in-one role as an electrolyte and a separator. The lack of electrolyte leakage also ensures safety of the device. To sum up, our study proved that water-soluble LS waste can be transformed into components of green energy storage systems.

 Received 17th October 2025,
 Accepted 29th January 2026
 DOI: 10.1039/d5gc05533d
 rsc.li/greenchem

Green foundation

1. This work proposes a novel and eco-friendly strategy for effective utilization of lignosulfonate (LS), a waste-derived technical lignin from wood, as a renewable precursor for electrochemical capacitor (EC) components (electrolyte, electrodes, and separator). ECs based on optimized LS-derived components offer a more sustainable, safe and high-performance alternative to conventional aqueous ECs.
2. LS serves as a green precursor for preparing gel electrolytes with high uptake ability, which can reduce the risks of leakage and corrosion processes, thus increasing safety. Thanks to its versatile properties, it also simultaneously serves as a separator, avoiding the use of synthetic membranes. Moreover, this biopolymer was a source of a carbon material prepared through a salt templating approach, which enabled tailoring the carbon structure/texture.
3. In the future, the main feature of the LS-gel electrolyte, i.e., flexibility, could be tested in real devices, expanding its application in wearable electronics.

1 Introduction

Utilization of renewable sources highly depends on unstable weather conditions,¹ necessitating the assistance of energy storage devices, such as electrochemical capacitors (ECs),² to store energy when available. High-power density, quick charge/discharge, and long lifespan are the key features of ECs, which are mainly used in the automotive and electronic sectors.^{3,4} The growing commercial application of ECs inevitably brings to light important considerations of sustainability as well as further improvement of energy metrics.⁵ The term “sustainable” ideally should be applied to a system where every single component is environmentally friendly and can be safely dis-

^aInstitute of Chemistry and Technical Electrochemistry, Poznan University of Technology, Berdychowo 4, Poznan 60-965, Poland.
E-mail: elzbieta.frackowiak@put.poznan.pl

^bInstitut de Science des Matériaux de Mulhouse, Université de Haute-Alsace, F-68100 Mulhouse, France

^cUniversité de Strasbourg, F-67081 Strasbourg, France

^dResearch Faculty of Agriculture, Hokkaido University, Kita 9, Nishi 9, Kita-ku, Sapporo 060-8589, Japan. E-mail: suzuki-s@agr.hokudai.ac.jp

^eDepartment of International Collaborative Program in Sustainable Materials and Technology for Industries between Nagoya University and Chulalongkorn University, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan

^fRéseau sur le Stockage Electrochimique de l'Energie (RS2E), 80039 Amiens Cedex, France



posed of or incinerated after use.⁵ For meeting the sustainability criteria, the design of ECs should be focused on the modification of the electrolyte and the tailoring of the texture/structure of the electrode material.

The current benchmark for the supercapacitor field is organic-based ECs whose characteristics are summarized in Table S1. These ECs exhibit a wide voltage range (2.5–3.0 V),^{6,7} reduced self-discharge,⁸ and a long lifespan (1500 h of floating).⁷ However, they use flammable, harmful electrolytes (*e.g.*, (C₂H₅)₄NBF₄ in acetonitrile) and require inert conditions (Ar or N₂ atmosphere with O₂ and H₂O < 1 ppm) as well as rigorous and time/energy-consuming drying of electrodes.⁹ As a greener alternative, neutral-aqueous-based ECs are proposed. Such ECs are characterized by a stable operating voltage up to 1.6 V,¹⁰ a loss of initial voltage by ~40% (self-discharge)¹¹ and a lifetime up to 120 h of floating.¹² Certainly, organic-based ECs outperform aqueous-based ECs but lack in terms of environmental friendliness. Hence, a lot of research is focused on eco-friendly gel-type electrolytes to increase sustainability. Therefore, the use of commercially available technical lignin, a byproduct of wood pulping, has attracted attention. Lignosulfonate (LS) is one of the traditional technical lignins, produced in the sulfite pulping process,¹³ and its market is expected to grow from 1.68 billion USD in 2025 to 2.34 billion USD by 2034.¹⁴ Water solubility is a beneficial characteristic of LS due to the presence of sulfonate groups, which enables facile preparation of energy storage materials as well as contributes to better ionic conductivity.¹⁵

Gel electrolytes (GEs) are promising functional separators that enhance the charge mobility of ECs and prevent leakage by retaining liquid electrolytes within the polymer network structure, thereby improving safety.¹⁶ Among GEs, hydrogels containing aqueous liquid electrolytes are notably advantageous due to their stability and non-inflammability in contrast to organogels.¹⁷ Furthermore, GEs contribute to reduced leakage current and self-discharge as well as the flexibility of the device,^{18,19} although the gel form decreases ionic conductivity and mobility.²⁰ The main advantages and disadvantages of GEs are summarized in Table S2. Interestingly, the demand for GEs is steadily increasing; recent market analysis forecasts that its global market will grow substantially by 2035 (up to 4.63 billion USD), driven by demand for flexible, safe, and sustainable energy storage devices²¹ as shown in Fig. S1.

The existing aqueous GEs for ECs remain nascent and predominantly rely on petroleum-based synthetic polymers, *e.g.*, poly(vinyl alcohol)²² and poly(methyl methacrylate),²³ although a few alternatives using natural polymers were reported.²⁴ In the context of life cycle assessment (LCA), climate change potential (CPP) and cumulative energy demand (CED) are crucial indicators to evaluate the sustainability of materials.²⁵ Table S3 summarizes the examples of polymers used in GEs and their CPP and CED values. Biomass-based polymers exhibit the lowest CPP,^{26,27} followed by biopolymers^{26,28–30} and petrochemical-based polymers.²⁵ The classification is not always clear, since biomass is a complex material combining cellulose, hemicellulose, lignin, and other

inorganic compounds.³¹ Biopolymers, including LS, combine low CCP, which originates from the fact that lignin stores CO₂ during tree growth, and its processing requires fewer fossil inputs.²⁶ The relatively low CED values of LS arise from the fact that the processing involves only mild conditions (neutralization, purification, or fractionation), unlike the highly energy-intensive production of biomass or petrochemical polymers.^{32,33}

In most reported works, aqueous GEs are combined with typical electrolytes, such as H₂SO₄,³⁴ KOH,³⁵ and NaCl,⁵ exhibiting high water uptake ability, moderate ionic conductivity (~10^{−3} S cm^{−1})³⁶ and a gravimetric capacitance ranging from 40 F g^{−1} to 129 F g^{−1}.^{37,38} Nevertheless, the performance of such aqueous GE-based ECs is limited to only 0.8 V–1.0 V, dominantly because of water splitting.³⁹ Only a few GEs are combined with a neutral aqueous electrolyte, which can operate up to 1.6 V.⁴⁰ Nevertheless, gel characteristics, such as solution uptake and swelling degree, are neglected.^{37,40}

In addition to the electrolyte, an equally important component of ECs is the electrode material, whose texture/structure plays a vital role in charge storage.⁴ A relatively new approach, called salt templating, is more effective for tailoring the carbon characteristics (*i.e.*, specific surface area, pore size distribution, and degree of structural disorder) *via* selecting the salts and their interaction with carbon cores.^{41,42} The C yield of the synthesis salt templated carbon is slightly higher (30%)⁴³ compared to conventional carbonization combined with CO₂ activation (20–25%).^{44,45} Moreover, the environmental friendliness and cost efficiency of the total process are enhanced owing to the use of inorganic salts as templates and water for the removal of templates (>80% of the salt can be recovered after the synthesis).⁴³ Using a biopolymer as a precursor, a certain amount of residual ash in the final carbon originates from naturally occurring inorganic elements in the precursor.⁴⁶ Water washing is not enough to remove such elements; therefore, acidic washing is recommended.

Herein, we synthesized and optimized an EC utilizing water-soluble LS as an original precursor for the main EC components: electrolyte, separator, and electrodes, which is a milestone for the further development of sustainable ECs. For the first time, an LS-based gel electrolyte with optimized solution uptake of acetate salts with different cations (Li, Na, and K) and at several concentrations (1–24 m) was used. Moreover, LS served as a precursor for the preparation of carbon electrodes through the salt templating approach. The resultant EC based on the LS-derived gel electrolyte and salt templated carbon improved the EC energetic metrics. Nonetheless, employing an LS gel obviates the necessity for a separator, hence improving safety and environmental impact.

2 Experimental

2.1 Materials

Purified lignosulfonate (LS) was kindly supplied by Nippon Paper Industries Co. Ltd, purity: 92%, sulfonate content: 6.6%,



relative molar mass: 33 600 Da, and used without further purification. Poly(ethylene glycol) diglycidyl ether (PEGDGE, repeating unit of PEO = 22) (Denacol EX-861) was provided by Nagase ChemteX Corp. Even though PEG (polyethylene glycol) is currently produced from bioethanol, the epoxidation processing (PEGDGE) is still challenging in terms of eco-friendliness. Lithium acetate (LiOAc), sodium acetate (NaOAc), and potassium acetate (KOAc) ($\geq 99\%$) were purchased from Sigma-Aldrich, while potassium hydroxide (KOH, $\geq 85\%$) was obtained from POCH. The commercially available carbon YP80F (Kuraray) was used as a reference carbon. The binder PTFE (60 wt% solution in H_2O) was provided by Sigma-Aldrich, while conductive carbon black (C65) was provided by Imerys. A glass fiber GF-A separator was purchased from Whatman.

2.2 Preparation of the LS-derived GE (LSGE)

LS (3 g) and PEGDGE (1.2 g) were dissolved in distilled water (5.4 mL) at RT (25 °C). The ratio between LS and PEGDGE was 1 : 0.4 (w/w). The schematic illustration of the preparation of the LS-derived GE is shown in Fig. 1. The molar ratio of epoxy groups in PEGDGE to total hydroxy groups in LS was determined *via* ^{31}P NMR and was consistently maintained at 0.17 $\text{mmol}_{\text{epoxy}}/\text{mmol}_{\text{OH total-LS}}$ (Tables S4 and S5). After stirring for 24 h, 10 M KOH (0.6 mL) was added dropwise to the solution and stirred for 5 min. The resultant mixture was degassed using a centrifuge (15 min, 8000 rpm) and then transferred in between two glass plates with 200 μm thick PTFE strips as a frame. After standing at RT for 24 h, the gel thin film was peeled off the glass plates and repeatedly washed with distilled water (minimum 3 times every 24 h). The water present in the gel structure was exchanged into the selected acetate aqueous solution (LiOAc, NaOAc, and KOAc) by changing the solution into a fresh one 3 times every 24 h to yield LSGE. Each product was labelled indicating the acetate solution used and its molar concentration (1–24 mol $(\text{kg H}_2\text{O})^{-1}$); e.g., LS-5 m KOAc.

2.3 Preparation of LS-based salt templated carbon (CLS)

LS (50 g) as a carbon precursor was dissolved in distilled water (250 mL) and stirred overnight at RT. The selected acetate salt (NaOAc or KOAc) (25 g) was then added to the solution and further stirred overnight at RT. The scheme of the LS-based salt templated carbon preparation is shown in Fig. 1. Additionally, a mixture of two acetate salts, NaOAc (25 g) and KOAc (25 g), was used as well. The resultant mixture was dried in an oven at 80 °C for a minimum of 5 days. The LS and template salt mixture was then carbonized at 900 °C for 1 h in N_2 flow (heating degree 3 °C min^{-1}) to obtain salt templated carbon. A slow heating rate resulted in rather slow generation of volatile compounds, and hence, less disturbance of the molecular orientation in the material.⁴⁷ The salt was removed by washing with distilled water. Furthermore, the obtained material was washed with 0.1 M HCl (500 mL) solution to remove ash, and then distilled water, to maintain a pH of 7. To reduce the harmful impact of acidic washing, HCl was diluted and wastewater treatment, including neutralization of HCl to NaCl, was realized. Finally, the purified carbon was dried at 80 °C overnight and subsequently ground in a mortar. The prepared carbons were labeled to distinguish the salt used, *i.e.*, CLS-NaOAc, CLS-KOAc, and CLS-NaKOAc. The C yield of the synthesis of the LS salt templated carbons ranged from 16% for CLS-KOAc, 24% for CLS-NaKOAc to 20% for CLS-NaOAc in line with other works and commercial carbons. The C yield depends on the salt type, *e.g.*, KOAc leads to lower yields than NaOAc because potassium promotes gasification. Additionally, one LS-derived carbon was prepared without using a salt template. In that particular case, the steam activation process was performed during 1 h hold at 900 °C by introducing steam at a rate of 10 mL h^{-1} . The steam activated carbon was labelled as CLS-SA.

2.4 Physicochemical characterization

A conductivity meter and a pH meter (Mettler Toledo) were used to measure the conductivity and pH of the prepared elec-

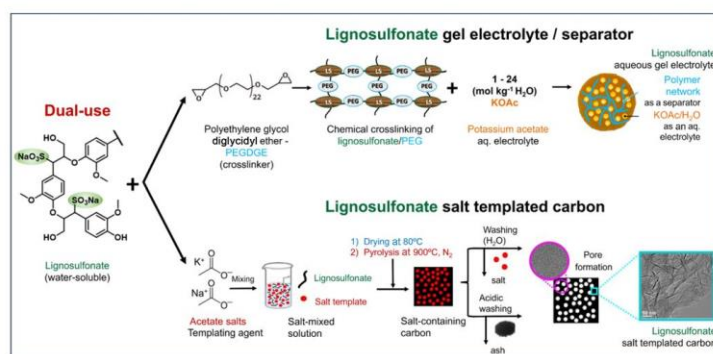


Fig. 1 Schematic illustration of the preparation of an LS-based gel electrolyte and salt templated carbon.

trolytes at RT. The viscosity of the electrolytes was measured using a Brookfield DV2T viscometer at RT. A PerkinElmer FTIR spectrophotometer was used to record the electrolyte absorption spectra (resolution of 4 cm^{-1}). Solution uptake of the LSGEs was calculated according to the mass change measured by weighing the gel film before and after exchange of water into the selected acetate solution. The swelling degree of LSGEs was determined based on the diameter variation before and after the acetate solution exchange. Electrochemical impedance spectroscopy (EIS) was used for conductivity measurement of the LSGEs. High resolution transmission electron microscopy (HRTEM) observation was performed using a JEOL ARM-200F operating at 200 kV to investigate the morphology of the carbons. Raman spectra were acquired using a laser with $\lambda = 532\text{ nm}$ and a power of 3 mW (Thermo Scientific DXR-Raman microscope). The average Raman spectra were deconvoluted into four peaks utilizing the Lorentzian fitting function.⁴⁸ The I_{D1}/I_G ratio was determined using peak integrated areas. Nitrogen sorption measurements were conducted using Micromeritics ASAP 2460 apparatus at 77 K on LS-carbons prior to degassing at 300 °C for 24 h. The specific surface area (SSA) was determined using DFT and BET models based on the linear relationship of relative pressures from 0.01 to 0.05. The pore size distribution was obtained using a 2D-NLDFT heterogeneous surface model for carbon materials (SAIEUS, Micromeritics). The slit pores and adsorption branch were considered. Elemental analysis (Thermo Scientific FlashSmart Elemental Analyser, USA) was performed to measure the wt% content of C, H, N, S and O in the carbons.

2.5 Electrochemical characterization

Electrodes were prepared by mixing 90 wt% of the selected LS-derived carbon or commercial carbon, 5 wt% of PTFE as a binder, and 5 wt% of carbon black (C65) to improve the conductivity. These components were combined in a mortar using isopropanol to achieve a uniform paste. Then, the paste was subsequently press-rolled to obtain a thin film of 200 μm in a calendaring machine. The film was cut into disc electrodes with 10 mm diameter (mass loading: $\sim 10\text{ mg}$) and then dried in an oven at 80 °C for 24 h. The LSGE was cut into 12 mm discs (thickness: $\sim 200\text{ }\mu\text{m}$). The prepared LS-electrodes and GE were placed in symmetric PTFE-based Swagelok systems with stainless steel 316L current collectors. For three electrode measurements, a Hg|Hg₂SO₄ system was used as the reference electrode. The electrochemical performance of LS-based ECs was investigated using a multi-channel potentiostat/galvanostat (VMP3, Biologic). Cyclic voltammetry (CV) was conducted at scanning rates of 1–200 mV s^{−1}, along with galvanostatic charge/discharge (GCD) (0.1–5 A g^{−1}) and EIS (100 kHz–1 mHz). All capacitance values of ECs were calculated per active mass of one electrode utilizing formulas from ref. 49. The lifespan of ECs was determined using the floating procedure,⁴³ which involves three GCDs (1 A g^{−1}) at the maximum working voltage (1.6 V), followed by a 2 h voltage hold at 1.6 V. Furthermore, the self-discharge technique was employed, followed by a 2 h voltage hold at 1.6 V and the subsequent recording

of the open circuit voltage (OCV) over 12 h. During the 2 h voltage hold at 1.6 V, the leakage current was tracked.

3 Results and discussion

3.1 Physicochemical properties of LSGE

A LS-derived hydrogel was synthesized *via* chemical crosslinking of hydroxy groups in LS with a diepoxy-terminated crosslinking agent (PEGDGE) in the presence of an alkali (KOH) to promote efficient reaction,^{37,50,51} as shown in Fig. 1.

The 3D microstructure of the LS gel without dehydration was observed using cryogenic-temperature scanning electron microscopy (Cryo SEM).⁵² This technique enables the observation of the fully hydrated state, and the inside structure of the gel, while eliminating drying artifacts.⁵³ Cryo SEM images of our LS show interconnecting hydrogel networks and a macroporous structure with an average pore size of $\sim 11\text{ }\mu\text{m}$. (Fig. S2a–c). An important mechanical property of hydrogels is compressibility with stress. The LS hydrogel shows an elongation at break value of 13.4% (Fig. S3). Furthermore, compression tests show that the LS gel exhibits a compression modulus (E_{mod}) of $65.9 \pm 15.3\text{ kPa}$. Classical hydrogels, being soft polymeric networks, frequently break down under light compression due to the diminished mobility of chain entanglements and inadequate stress distribution indicated by the E_{mod} of 39–86 kPa.⁵⁴ Interestingly, such an LS hydrogel was directly subjected to exchange water for the selected acetate aqueous solutions to prevent significant deformation of the polymer network structure caused by drying.⁵⁵

To quantitatively evaluate the gel uptake capacity and swelling behaviour of LSGEs under different conditions, lithium, sodium, and potassium acetate salts were tested at concentrations of 1, 3, and 5 m. This was conducted to systematically investigate the effects of cation type (Li⁺, Na⁺, and K⁺) and electrolyte concentration on the GE properties. The swelling is seen as effective if the liquid electrolyte is retained within the crosslinked polymer network and results in elevated ionic conductivity values, while simultaneously maintaining the mechanical strength.⁵⁶

The solution uptake and swelling degree changes over the selected electrolytes and concentrations are shown in Fig. 2a. The gel's interconnected porous structure⁵⁷ allowed the uptake of acetate solutions, ranging from 0.65 to 0.15 for LiOAc and NaOAc, and from 0.50 to 0.30 for KOAc. However, the solution uptake was decreased with an increase in acetate concentration, regardless of the type of electrolyte. The same tendency was observed for the swelling degree change. Typically, the solution uptake and swelling degree of gels are facilitated by strong affinity between the polymer network and the solvent, as well as the flexibility of the polymer network, yet it can be impeded by the elevated external osmotic pressure resulting from the addition of the salt.¹⁷ The differences in the investigated abilities between the selected cations were less pronounced for KOAc-based GEs, making this solution the most promising.



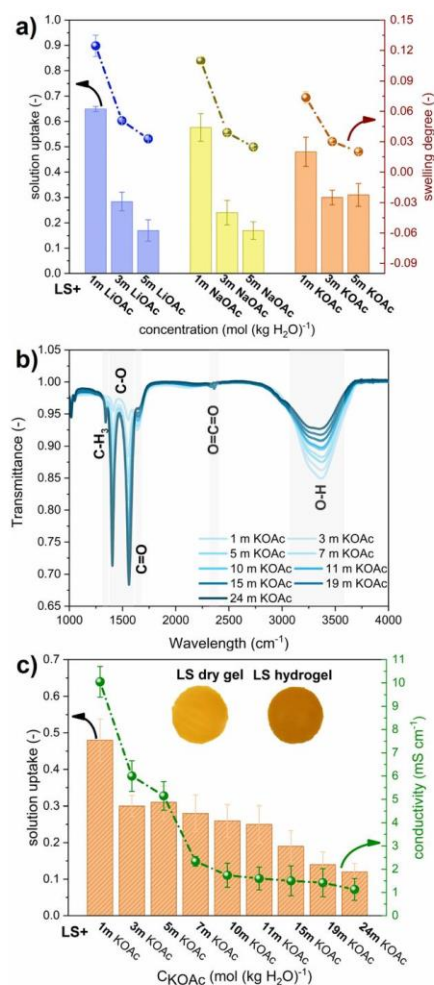


Fig. 2 (a) Solution uptake and swelling degree curve of LSGEs in LiOAc, NaOAc, and KOAc liquid electrolytes at different concentrations (1, 3, and 5 m), (b) FTIR spectra of KOAc at different concentrations (1–24 m), and (c) solution uptake and conductivity of LSGEs in KOAc at different concentrations (1–24 m).

As shown in Fig. S4, the viscosity of LiOAc, NaOAc, and KOAc aqueous solutions increased with higher concentrations. The solution pH was typically alkaline, ranging from 9 to 10 for used acetates, and rather stable within the tested concentrations (Fig. S4). The alkaline condition promotes deprotonation of acidic groups, leading to greater electrostatic repulsion and higher osmotic pressure, thus resulting in higher solution

uptake and swelling degree of gels than in acidic medium.⁵⁸ Both the solution uptake and swelling degree decreased with increasing alkali acetate concentration, reflecting osmotic pressure reduction and polymer–ion interactions. Notably, the LSGEs in KOAc solution exhibited a smaller performance loss compared to those in LiOAc and NaOAc. This trend can be rationalized by the weaker hydration energy of K^+ ions, which enhances their ability to penetrate and strongly coordinate within the lignosulfonate network.⁵⁹

On the other hand, ionic conductivity was increased up to 5 m only in the case of KOAc, while the increase was visible up to 3 m for LiOAc and NaOAc (Fig. S4). In fact, K^+ has the highest ion mobility, and the lowest hydration enthalpy compared to Li^+ and Na^+ (Table S6), impacting the kinetics of water exchange into the selected acetate. Although high concentrations can reduce the osmotic driving force into the polymeric network, higher ionic conductivity is proportional to ion mobility. Therefore, the solution uptake was increased, confirmed by a nearly equal solution uptake and swelling degree change of 3 m and 5 m KOAc by the gel matrix, even though the viscosity was higher.

The extended study including solution uptake and conductivity of GEs was performed in a wide range of KOAc concentrations (1–24 m), as shown in Table S7, due to the exceptionally high solubility of this salt (256 g per 100 mL at RT).⁶⁰ As shown in Fig. S5, the ionic conductivity reached a maximum of 150 mS cm^{-1} at 5 m and then decreased to 40 mS cm^{-1} at 24 m. The pH was strongly alkaline, increasing from 8 to 11 with higher concentrations. The viscosity was increased in the same manner as the pH, ranging from 0.5 to 28 mPa s^{-1} . The FT-IR spectra of KOAc solutions (Fig. 2b) show characteristic bands for KOAc, *i.e.*, $-CH_3$, $-C-O$, $-C=O$, and $-OH$.⁶¹ Moreover, the effect of the change in the concentration was noticeable by the higher intensity/area of the OH band corresponding to the lower KOAc concentrations, containing an increased amount of free water molecules. In the case of $<10 \text{ m}$ KOAc, the OH band was less broad/intense, due to the formation of a hydrogen bonding network.⁶² The GEs with the highest acetate solution uptake was LS-1 m KOAc and showed a high ionic conductivity of 10 mS cm^{-1} at RT (Fig. 2c). The solution uptake and conductivity were decreased with the increase in KOAc concentration (up to 24 m). In general, concentrated aqueous electrolytes higher than 10 m, defined as water-in-salt, are not easily incorporated within the gel network due to the very high viscosity. Among the tested GEs, LS-1 m KOAc exhibited the highest solution uptake, swelling degree and ionic conductivity and could be considered as the most promising. However, the significant amount of existing water in the GE would deteriorate the operating voltage of the EC. Therefore, LS-5 m KOAc with satisfactory characteristics and reduced water content was selected for further electrochemical studies.

3.2 Electrochemical performance of LSGE-based ECs (with commercial carbon-based electrodes)

A stable operating voltage, alongside ionic conductivity, is a crucial parameter for EC electrolytes.⁴ To investigate the



electrochemical performance of LSGE, an EC was assembled with electrodes based on commercial porous carbon (YP80F). HRTEM images of this carbon are presented in Fig. S6. These images show a better developed microstructure with short graphene layers that are stacked together in two or three layers. Some isolated (closed) mesopores are seen as well. Moreover, carbon is highly microporous ($0.78 \text{ cm}^3 \text{ g}^{-1}$), with an SSA_{BET} of $2018 \text{ m}^2 \text{ g}^{-1}$. The isotherm of YP80F is of type I (b), implying also the presence of small mesopores (2–3 nm) corresponding to the mesopore volume ($0.24 \text{ cm}^3 \text{ g}^{-1}$), as shown in Fig. S7 and Table S8. The Raman spectra of YP80F after deconvolution (Fig. S8) proves high disorder of the material, with an $I_{\text{D1}}/I_{\text{G}}$ value of 2.50. The stable operating voltage of LS-5 m KOAc was determined by the voltage extension method. It is important that hydrated ion sizes match the average size of micropores of YP80F, assuring effective formation of the electrical double layer (EDL). The triangular shape of GCD curves (Fig. 3a) indicative of EDL performance was noticeable up to 1.6 V. At elevated voltages, the curves exhibited non-linear behavior, including higher ohmic drop, indicating the occurrence of faradaic processes, specifically electrolyte breakdown. To evaluate the electrolyte instability during GCD, the energetic efficiency, a ratio between the integrated values of discharge and charge energy, was assessed.⁶³ As shown in Fig. 3b, the energetic efficiency remained at 80–85% up to 1.6 V, while it decreased rapidly over 1.7 V. This result suggests that the value of 1.6 V is a stable operating voltage for the LS-5 m KOAc electrolyte. Then, it was further validated by tracking the potential of positive and negative electrodes individually in a three-electrode setup. As shown in Fig. 3c, the positive electrode (E^+) consistently operates beneath the limit of water decomposition, indicated by the oxygen evolution potential, OEP (dashed line). At higher potentials, deterioration of electrodes (carbon oxidation)¹⁰ could take place. In contrast, the negative electrode (E^-) consistently functions beneath the water splitting limit, shown as the hydrogen evolution potential (dashed line). Hydrogen, which is a product of electrolyte decomposition, is electrosorbed by the porous electrode itself.⁶⁴ Nonetheless, the GCD curves remained triangular with very high energetic efficiency (Fig. 3a and b), and the positive electrode operated below the OEP (Fig. 3c). Hence, 1.6 V was selected as a stable operating voltage suitable for further advanced electrochemical investigation.

3.3 Physicochemical characterization of LS-derived carbons

LS-derived carbons (LS-carbon) were prepared by the salt templating approach (Fig. 1), whereas one LS-carbon (CLS-SA) was synthesized by simple carbonization followed by steam activation. In the template method, LS acted as a carbon source, and three different inorganic salts, namely NaOAc and KOAc, and a mixture of both (NaKOAc), were used as templates. Formation of microporosity is possible due to the effect of the salt template (diameter of ions); nevertheless, at the same time, some graphitic domains are formed, influenced by the cation's affinity towards the carbon core⁴² (Table S6).

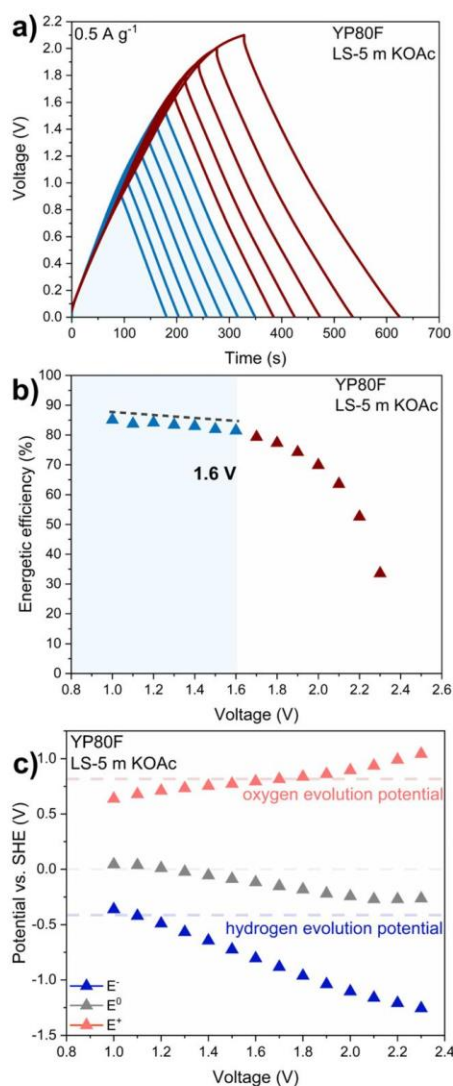


Fig. 3 Preliminary electrochemical performance of YP80F carbon-based ECs operating in the LS-5 m KOAc GE: (a) galvanostatic charge/discharge voltage extension, (b) energetic efficiency vs. voltage, and (c) potential of the electrodes (E_0 , E^+ and E^-) vs. operating voltage.

The morphology of the synthesized LS-carbons was observed by HRTEM (Fig. 4a–f and Fig. S9a–f). CLS-SA had a noticeable mixture of dense and mesoporous structures



(Fig. 4a). CLS-NaOAc presented visible graphite domains in addition to more disordered ones while CLS-KOAc showed a disordered structure with no visible porosity or graphitic domains (Fig. 4b and c). In contrast, CLS-NaKOAc presented short stacked graphene layers (2–3 nm, Fig. 4d and e) with obvious mesopores, and long graphitic domains where graphene is stacked in 3–9 layers (Fig. 4f). Carbon's graphitic domains evolve beyond 600 °C, at temperatures higher than the melting points of the salts (325 °C for NaOAc and 292 °C for KOAc), and continue to grow as the temperature rises. This process is significantly influenced by the salt type and its quantity. In this particular case, the mixture of two acetates

(NaKOAc) yields the highest level of graphitization, which might be due to its substantial cation- π interactions with the carbon network.⁴³

To quantitatively analyze the composition of the carbons utilized in this study, elemental analysis with direct estimation of oxygen was used and the results are presented in Table S9. The highest wt% of the carbon (~95 wt%) as well as the lowest contribution of other elements, including O (~2 wt%), was reported for commercial carbon. In contrast, the LS-carbons present lower wt% of carbon (~85 wt%); however, the negligible presence of N and S was noted as well. The highest amount of O was observed for CLS-KOAc (7.5 wt%), followed

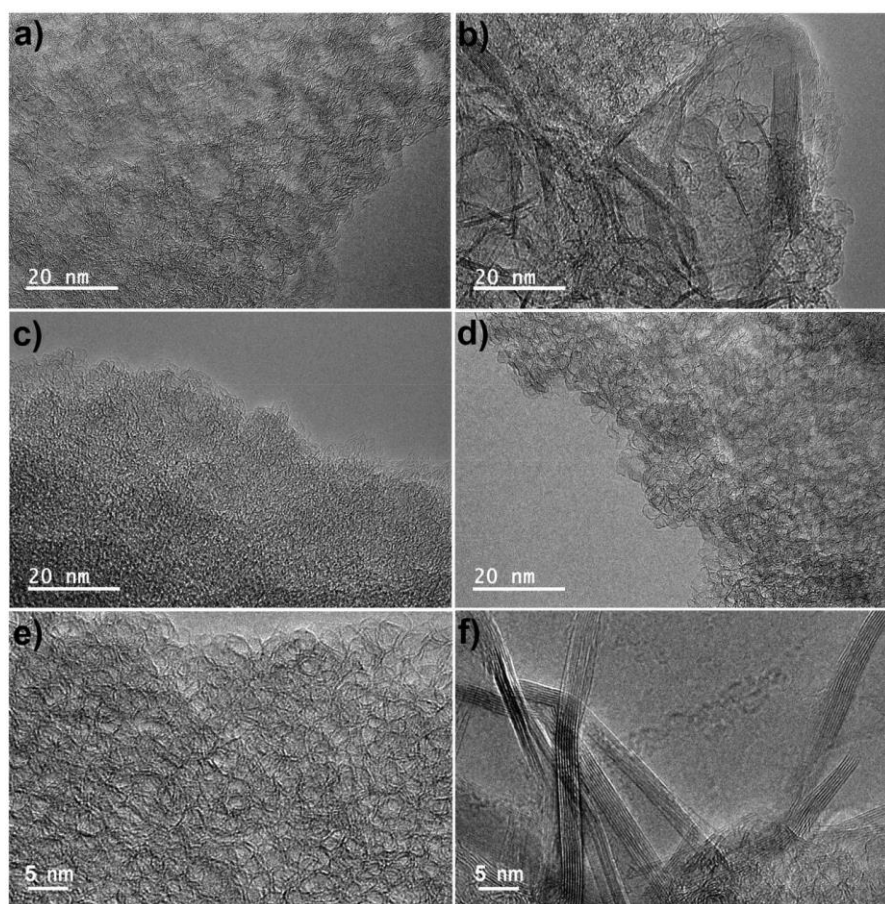


Fig. 4 HRTEM images of LS-carbons: (a) CLS-SA, (b) CLS-NaOAc, (c) CLS-KOAc, and (d–f) CLS-NaKOAc.

by CLS-NaOAc (6.7 wt%), CLS-SA (6 wt%), and CLS-NaKOAc (5 wt%).

The microstructure of LS-carbons was investigated using Raman spectroscopy (Fig. 5). Two principal bands were observed: the disordered-induced band (D) at $\sim 1350\text{ cm}^{-1}$ and the first order graphite band (G) at $\sim 1580\text{ cm}^{-1}$.⁶⁵ Additionally, a band in the range of $2500\text{--}2800\text{ cm}^{-1}$ denoted as the overtone of the D band (2D) is related to the more ordered structures.⁶⁶ As shown in Fig. 5, LS-carbons exhibited well-pronounced D and G bands, but their broadness and height differed. In the cases of CLS-SA, CLS-NaOAc, and CLS-KOAc, the D band was broader than the G band. On the other hand, the G band was intense and narrow only for CLS-NaKOAc, associated with the presence of a 2D band. The ratio of the integrated areas of D and G bands ($I_{\text{D1}}/I_{\text{G}}$) reflects the disorder level of porous carbon materials.^{43,48} The $I_{\text{D1}}/I_{\text{G}}$ value of CLS-KOAc was 3.00, the highest among LS-carbons, indicating the highest disorder. This value was followed by 2.81 for CLS-NaOAc, 2.61 for CLS-SA, and 1.37 for CLS-NaKOAc. The Raman spectra indicate that LS-carbons have different degrees of disorder, highly disordered for CLS-KOAc, CLS-NaOAc, and CLS-SA, whereas a more ordered structure was observed for CLS-NaKOAc carbon. These results are in agreement with HRTEM analyses.

To investigate the detailed contribution of each band, the deconvolution of D and G bands with a Lorentzian fitting function was performed (Fig. S10). The deconvolution of four

peaks revealed two additional peaks, a D₂ band related to a polyene-like structure at the layer edges (associated with the presence of an elevated amount of surface functionalities), and a D₃ band typical of amorphous carbon fractions and functionalities.^{43,48} The contribution of the D₂ band (area) was the highest for CLS-NaKOAc, followed by CLS-NaOAc, CLS-SA, and CLS-KOAc. Therefore, CLS-NaKOAc with the lowest degree of disorder shows the highest contribution of surface functionalities at the layer edges in contrast to CLS-KOAc with the highest degree of disorder. The D₃ band area changed in the order from the highest for CLS-KOAc, followed by CLS-NaOAc, CLS-SA, and CLS-NaKOAc. Consequently, the amorphous phase (corresponding to the area of the D₃ band) is the most influential for carbon with the high degree of disorder (CLS-KOAc, CLS-NaOAc, and CLS-SA). These findings based on Raman spectroscopy are supported by the HRTEM observations of LS-carbons (Fig. 4a–d, and Fig. S9), where only CLS-NaKOAc displayed numerous graphitic zones. Porous carbons consist primarily of turbostratic arrangements of graphene-like sheets – aromatic carbon layers that are randomly stacked and twisted, lacking the long-range order found in graphite. These layers form a largely sp² hybridized carbon network with defects (topological) and edge sites. The defects in carbon can be defined as vacancies, dislocations, paramagnetic sites, and radicals, as well as surface functional groups. Defects cause uneven distribution of delocalized electrons in the carbon matrix. In disordered carbon, the distance between the graphene domains (d_{002}) is much higher than for graphitic carbons ($\sim 0.400\text{ nm}$ for very disordered carbon vs. 0.335 nm for graphite).⁶⁷ However, it cannot be precisely calculated in the case of salt templated carbons due to the absence of a well-defined d_{002} XRD peak.⁴³ Therefore, the Tuninstra-Koenig relation can be applied on Raman results to calculate La (the size (height) of stacked graphene layers),^{65,68} as summarized in Table S10. It is clearly seen that La ranges from 5.58 nm for CLS-KOAc to 12.33 nm for CLS-NaKOAc. Therefore, the graphitic domains formed during carbon preparation are increasing with the cation- π binding energy.⁶⁹ It is expected that the crystalline structure of CLS-NaKOAc enhances electron mobility, but more ordered and higher stacked graphitic domains with a reduced distance between the graphene layers are contributing to lower porosity.

The texture of LS-carbons was analyzed by nitrogen sorption at 77 K . Fig. 6a shows the sorption characteristics of all carbons (CLS-NaOAc, CLS-KOAc, CLS-NaKOAc, and CLS-SA). The isotherms are of type I (a) for CLS-KOAc and CLS-NaOAc, indicating their high microporosity and pores with a narrow pore size distribution ($<1.0\text{ nm}$).⁴² Regarding CLS-NaKOAc, the isotherm deviates from the perfect type I (a) isotherm, and the shape can be classified as type I (b) isotherm according to the IUPAC.⁷⁰ This is specific for materials with a broader pore size, namely larger micropores and/or narrow mesopores. Indeed, the pore size distribution shows in addition the main peak centered at $\sim 0.5\text{ nm}$, and the appearance of a small peak at $\sim 2\text{--}3\text{ nm}$ (Fig. 6b). Differently, CLS-SA presents isotherms of type I at low p/p_0 (<0.2) and of type IV at elevated relative pres-

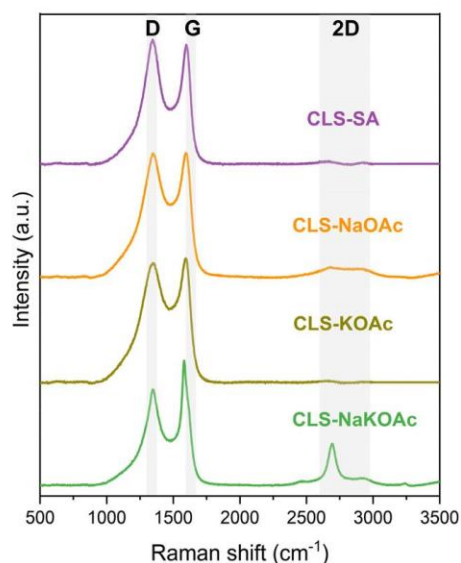


Fig. 5 Raman spectra of all LS-carbons.



ures with an H2 hysteresis loop, characteristic of the presence of both micro- and mesopores. The micropore peak is the narrowest and its maximum is placed at ~ 1 nm, while the mesopore peak is very broad and ranged between 2 and 8 nm (Fig. 6b). The latter two materials present the highest fraction of mesopores ($0.38 \text{ cm}^3 \text{ g}^{-1}$ for CLS-SA and $0.18 \text{ cm}^3 \text{ g}^{-1}$ for CLS-NaKOAc, compared to $0.05 \text{ cm}^3 \text{ g}^{-1}$ for the other materials, Table S11). Therefore, CLS-SA can be considered as a micro/mesoporous material, CLS-NaOAc is mainly microporous with a minute fraction of small mesopores, while the other materials are rather purely microporous.

The values of S_{BET} of all LS-carbons ranged from $881 \text{ m}^2 \text{ g}^{-1}$ (CLS-NaOAc) to $1754 \text{ m}^2 \text{ g}^{-1}$ (CLS-KOAc) as summarized in Tables 1 and S11. Interestingly, Matei Ghimbeu *et al.* reported that templated carbons synthesized using NaCl and KCl had similar S_{BET} .⁴² In the case of LS-carbons, the use of NaOAc and KOAc as templates resulted in a significant difference in S_{BET} (Tables 1 and S11) since acetate salts can act as both structural templates and self-activating agents. Also, such a trend can be explained by differences in cation- π binding energy, cation size, and partial graphitization, reducing S_{BET} . Worth mentioning is the fact that the textural and structural characterization was per-

formed on pristine LS-carbons, while for EC testing, LS-carbon based electrodes were used. For the electrodes, the values of S_{BET} and the degree of disorder are slightly lower, equivalent with the wt% of the binder/conductive carbon additive utilized.^{69,71}

The C values of BET indicate the energy of interaction between the N_2 and the surface of the carbon. Moreover, it is linked to the difference in adsorption energy between the first N_2 adsorbed layer and subsequent layers.⁷² The C values of 150–200 are associated with micropore filling (strong interaction of the N_2 molecules and carbon surface at low pressures).⁷⁰ High C values for LS-carbons (from 454 to 839) and for YP80F (332) as shown in Tables S11 and S8 suggest the strongest carbon- N_2 interactions and that the first adsorbed layer is almost complete before the subsequent layers begin to form. Worth mentioning is that the C values increase with the increase in oxygen content and total amount of heteroatoms (Fig. S11); therefore, functional groups (especially O-ones) enhance the interaction of N_2 with the carbon surface. The carbons poor in O and rich in C exhibit lower interactions (*i.e.*, YP80F).

Interestingly, the porosity formation mechanisms are different in the case of CLS-SA and salt templated carbons

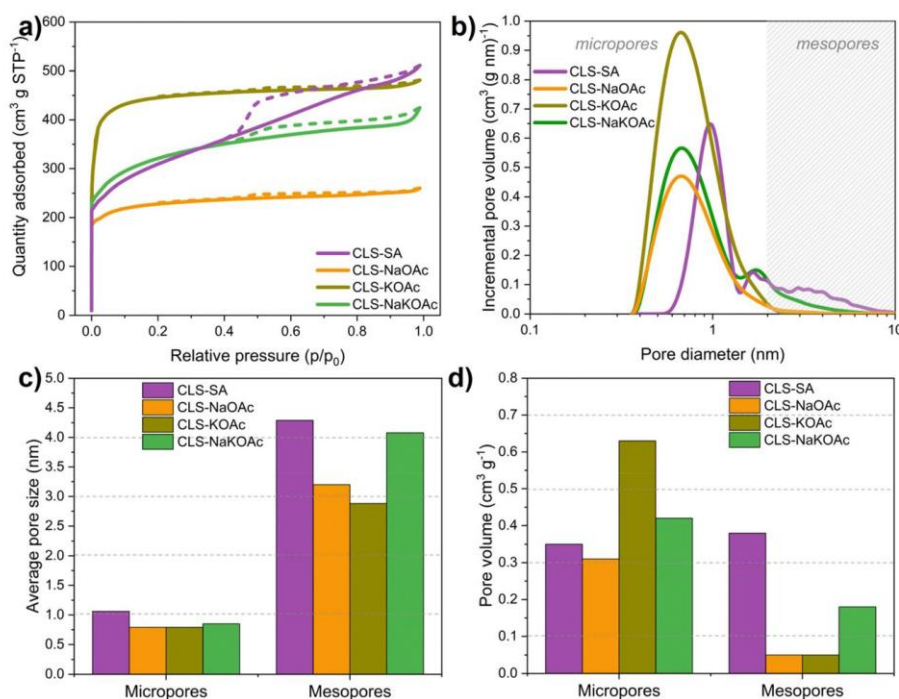


Fig. 6 (a) Nitrogen sorption isotherms at 77 K, (b) pore size distribution, (c) average pore size, and (d) pore volume of LS-carbons.

Table 1 Summary of the physicochemical parameters of LS carbons (S_{BET} , V_{micro} , V_{meso} , L_0 , L_{micro} , O (wt%), $I_{\text{D1}}/I_{\text{G}}$, and La) and the electrochemical performance of LSCE-based ECs (gravimetric capacitance at 0.5 A g⁻¹ and floating time)

Carbon	S_{BET} , m ² g ⁻¹	V_{micro} , cm ³ g ⁻¹	V_{meso} , cm ³ g ⁻¹	L_0 , nm	O, wt%	$I_{\text{D1}}/I_{\text{G}}$, a.u.	La, nm	Capacitance@0.5 A g ⁻¹ , F g ⁻¹	Floating time, h
CLS-SA	1079	0.35	0.38	1.06	6.0	2.61	6.42	63	58
CLS-NaOAc	881	0.31	0.05	0.79	6.7	2.81	5.96	46	102
CLS-KOAc	1754	0.63	0.05	0.79	7.5	3.00	5.58	82	160
CLS-NaKOAc	1169	0.42	0.18	0.85	5.0	1.37	12.33	52	170

(CLS-KOAc, CLS-NaOAc, and CLS-NaKOAc); therefore, a further discussion is provided. The pore size distribution was determined using two-dimensional nonlocal density functional theory (2D-NLDFT). The advantage of this model is that it eliminates the typical artifacts of the standard homogeneous slit pore model.⁷³ Fig. 6b illustrates the pore size distribution of LS-carbons, highlighting two regions: up to 2 nm (micropores) and from 2 to 10 nm (mesopores). Micropores are the most helpful in the formation of an EDL, whereas mesopores facilitate the paths for electrolyte ions to access micropores,⁷⁴ thereby improving the rate capability.⁷⁵ The bar plots in Fig. 6c and d show the average pore size and pore volume of LS-carbons, respectively. The average size of micropores (L_0 , L_{micro}) of LS-carbons did not exceed 1.06 nm, and the size was appropriate for matching the solvated K⁺ and OAc⁻ ions (0.66 and 0.71 nm, respectively), justifying the selection of these carbons for electrochemical capacitor application.

The volume of micropores (V_{micro}) and the volume of mesopores (V_{meso}) are nearly equal for steam activated carbon (CLS-SA). The average size of micropores (L_0 , L_{micro}) of 1.06 nm and the average size of mesopores (L_0 , L_{meso}) of 4.29 nm are shown in Fig. 6c. Similar values were reported for the steam activated carbon from the cellulose fibers as the precursor ($S_{\text{BET}} = 1018 \text{ m}^2 \text{ g}^{-1}$, $V_{\text{micro}} = 0.39 \text{ cm}^3 \text{ g}^{-1}$).⁷⁶ Steam molecules are responsible for a pore-opening process at the surface, thus leading to an increase in surface area. The process of steam activation may lead to the expansion of the pre-existing micropores and the formation of new micropores as steam molecules interact with the carbon matrix.^{76,77} Nonetheless, the steam activation process has the tendency to enlarge pores beyond 2 nm, resulting in the formation of mesopores, confirmed by the highest V_{meso} and L_0 , L_{meso} for CLS-SA among all LS-carbons.

The formation of the texture/structure of the LS salt templated carbons is affected mainly by the interactions of cations with the carbon matrix,⁴² the amount of the salt template,⁷⁸ the melting point of the salt template⁶⁹ and the temperature of the synthesis.^{42,78} This was mainly observed when using metal chloride salts. In our case, alkali metal acetates were utilized and we investigated the impact of the different cations in the salt and their quantity on the carbon's texture/structure. Unlike chloride salts, where the salt serves primarily as a template to generate porosity and the cation mainly promotes graphitization, the acetate salts can act as both structural templates and self-activating agents.⁷⁹ First, physical templating with acetate salt leads to the development of void spaces and graphitization during carbonization, in a similar manner to

chloride salts. During pyrolysis, the molten potassium acetate and the *in situ* formed K₂CO₃/K species can diffuse into the carbon matrix resulting in pore formation and sheet-like morphologies.^{80,81} At higher temperatures, chemical activation is induced by acetate salt decomposition *via* the formation of secondary products (e.g., CO₂, K₂O, and K) that react with the carbon framework to widen existing pores or to create new ones. KOAc decomposes at ~440 °C into K₂CO₃, and then into CO₂ and K₂O at ~800 °C. The generated CO₂ etches the carbon framework (activation) to create micropores and mesopores. NaOAc behaves similarly to KOAc with the formation of Na₂CO₃ and CO₂.⁷⁹ As for the LS salt templated carbons, the micropore volume (V_{micro}) was the highest for CLS-KOAc (0.63 cm³ g⁻¹) and the lowest for CLS-NaOAc (0.31 cm³ g⁻¹). This increase in the micropore fraction is explained by the higher atomic mass/cation size of the alkali metal (K > Na) in the template, in agreement with the results observed on metal chloride salts.^{42,69} In contrast, the mesopore volume (V_{meso}) was the same for both carbons (0.05 cm³ g⁻¹). It proves that the cation type did not influence the mesoporosity but has a significant effect on the microporosity. The binding energy of a cation to the aromatic domains directly impacts the porosity of the carbon; a higher binding energy (Na⁺) causes stronger interactions that induce the carbon aromatic sheets to form stacks, thus lowering S_{BET} and V_{micro} , contrary to the cation with a lower binding energy (K⁺).⁶⁹ On the other hand, there is no difference between the L_0 , L_{micro} of CLS-NaOAc and CLS-KOAc, since the difference in cation sizes is not significant. However, such a difference is more pronounced considering L_0 , L_{meso} , where the smaller mesopores are reported for CLS-KOAc (2.88 nm) contrary to CLS-NaOAc (3.20 nm).

The quantity of the template salt is influential, and increasing the salt amount in the synthesis can increase the carbon porosity,⁷⁹ resulting in higher S_{BET} and V_{micro} .⁷⁸ In the cases of CLS-KOAc and CLS-NaOAc, the weight ratio between the carbon precursor and salt was 2 : 1 (w/w), whereas for CLS-NaKOAc, this ratio was 1 : 1 (w/w); hence, the salt quantity was twice higher. Therefore, a significant difference in textural properties between these LS-salt-templated carbons should be observed; however, such results were not observed in this study.

To have a fair comparison of the carbon precursor : salt template ratio effect using the same salt mixture (NaKOAc), a sample with a lower amount of salt (2 : 1, w/w) was prepared. The SSA was lower (752 m² g⁻¹ vs. 1169 m² g⁻¹) and graphitization was less developed ($I_{\text{D1}}/I_{\text{G}} = 1.80$ vs. $I_{\text{D1}}/I_{\text{G}} = 1.37$). The V_{micro} of CLS-NaKOAc (0.42 cm³ g⁻¹) is placed in between



those of CLS-KOAc and CLS-NaOAc. Such a tendency was not observed for V_{meso} , which was the highest reported value ($0.18 \text{ cm}^3 \text{ g}^{-1}$) among the LS salt templated carbons. The development of mesopores when using NaKOAc is induced by a synergetic effect of both salts. A mixture of salts presents a lower melting point than individual salts, enhancing the interaction with the carbon framework and promoting porosity. Excessive etching of the carbon network leads to a decrease of microporosity, micropore widening and the formation of extensive mesopores.^{43,75}

Another mechanism that explains the decrease in the micropores and the development of mesopores for CLS-NaKOAc relies on the synergetic effects of NaOAc and KOAc salts, which leads to graphitization of the structure (Fig. 4d, $I_{\text{D1}}/I_{\text{G}} = 1.37$). This is different from CLS-KOAc and CLS-NaOAc, where graphitization does not occur (Fig. 4b and c, $I_{\text{D1}}/I_{\text{G}} \sim 3$). The graphitization of CLS-NaKOAc proceeds first by pore closure (lower SSA), approaching the graphene layers and stacking them together (higher La). The short graphene layers stacked in only 2–3 layers are arranged in a concentric

manner and form mesopores (Fig. 4e), while the long and highly stacked graphene layers (Fig. 4f) contribute to the decrease of microporosity and S_{BET} . The graphitization of CLS-NaKOAc can be linked to the salt's interaction with the carbon. The mixed salt presents a lower melting point, strongly interacting with the carbon, leading to graphitization and mesopore formation. This was observed when LiCl was used as a salt template at a pyrolysis temperature (900°C) exceeding its melting point ($\sim 600^\circ\text{C}$).⁴² Overall, the results allow us to conclude that both the increase of the salt amount and the low melting point of the salt mixture develop the textural properties (micro- and mesopores) and the graphitization level (Table S12).

3.4 Electrochemical performance of green LS-based ECs

Sustainable, LS-based ECs were assembled with LSGE (LS-5 m KOAc) and LS-carbon electrodes to assess the electrochemical performance of the device. The CV and GCD curves of LS-based ECs (Fig. 7a and b) exhibited rectangular and triangular

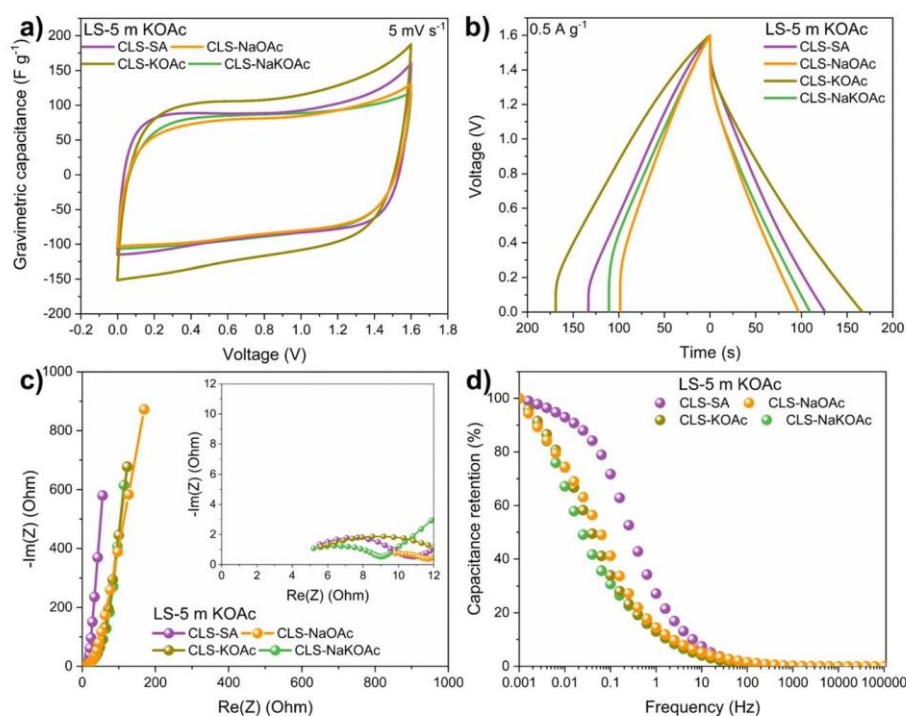


Fig. 7 Electrochemical performance of LS-carbon-based ECs operating in an LS-5 m KOAc GE at 1.6 V: (a) cyclic voltammetry, (b) galvanostatic charge/discharge, (c) Nyquist plot, and (d) capacitance retention vs. frequency.



profiles, respectively, within the 1.6 V range, signifying a nearly ideal EDL formation. The gravimetric capacitance was calculated from the integrated area of the galvanostatic discharge curve according to the previous report.⁶³

The summary of the physicochemical and electrochemical parameters of LS carbons is shown in Table 1. The gravimetric capacitance at 0.5 A g⁻¹ ranged from 46 F g⁻¹ to 82 F g⁻¹ LS-based ECs (Fig. 7b and Table S13). The highest SSA and I_{D1}/I_G of CLS-KOAc (Table 1) led to the highest capacitance of the EC. In contrast, the smallest SSA of CLS-NaOAc caused the lowest capacitance among LS-based ECs, although the degree of disorder was relatively high. Therefore, the SSA of the carbon material appears to be the most impacting factor for the capacitive performance of ECs.

The charge propagation of LS-based ECs was investigated using EIS. The Nyquist plots (Fig. 7c) were typical of ECs based on activated carbon electrodes.⁸² The minor semicircle observed in the high-frequency region is ascribed to the charge transfer impedance related to faradaic reactions. The curve exhibiting a slope in the medium frequency range is generally linked to the diffusion of the electrolyte into the porosity of the electrode material. Finally, the low-frequency region is attained when the entire surface of the electrodes becomes saturated with ions from the electrolyte, resulting in capacitance that is independent of frequency; the recorded value approaches a parallel alignment with the imaginary axis, related to the cell's capacitive behavior.^{82,83} The equivalent series resistance (ESR) was determined from the intercept with the real axis at high frequency,⁸⁴ and was nearly similar (~5 Ohm) for CLS-KOAc, CLS-NaKOAc, and CLS-SA-based ECs (Fig. 7c). A slightly higher ESR (~9 Ohm) was observed for CLS-NaOAc-based ECs, which could be affected by the cell assembly.⁸⁵ Capacitance retention as a function of frequency (Fig. 7d) illustrates better performance in the low frequency range, impacted by the highest mesopore volume for CLS-SA, contrary to the other templated carbons with a higher micropore volume that slows down ion diffusion. Additionally, capacitance retention vs. frequency dependence allows the estimation of important EC parameters such as the time constant. The time constants acquired for CLS-based capacitors are placed from 3 s (CLS-SA) to 20 s (CLS-NaKOAc). However, a definitely better value (0.6 s) was obtained for an EC with an LS-gel electrolyte and commercial YP80F carbon (Fig. S12). This means that charge propagation is determined by the electrode and by the gel electrolyte.

The size of ions plays a crucial role in EDL formation. The diameter of the desolvated ions changes from 0.23 nm for K⁺ (0.66 nm when solvated) to 0.15 nm for CH₃COO⁻ (0.71 nm when solvated).^{10,86} All ions, even when completely solvated, are supposed to be accommodated within the majority of the pores of the utilized LS-derived carbons (L_{0_micro} = 0.85–1.06 nm), consequently contributing to the formation of the electrode/electrolyte interface.⁵ Insights into the molecular-scale mechanism of charge storage in the EC with the gel electrolyte can be monitored by tracking the behavior of positive and negative electrodes operating in the LS-5 m KOAc GE

and carbon (YP80F) (Fig. 3a–c). The formation of a double layer at the interface between the carbon electrode and LS-5 m KOAc GE is evidenced by the nearly perfect, triangular shape of the GCD curve (distinct absence of redox humps up to 1.6 V). Moreover, an energetic efficiency of 82% was noted, confirming good conductivity and low resistance of the system (Fig. 3b). Above 1.6 V, the shape started to deteriorate from the perfect triangular shape. This directly indicates the occurrence of faradaic processes, such as carbon oxidation, current collector corrosion and gradual electrolyte breakdown.¹⁰ The noted faradaic contribution can also be linked to the charge transfer processes taking place among the functional groups found in lignosulfonate, especially with cationic species such as Na⁺ and K⁺. Lignosulfonate contains hydroxyl (–OH), carboxyl (–COOH), and sulfonate (=SO₃²⁻) functional groups, thereby improving the wettability of the carbon electrode surface. This improvement affects faradaic reactions and supports ion adsorption.²⁰ Various studies have documented interactions between these functional groups and cations, including K⁺ ions derived from the acetate electrolyte.^{20,86–88}

Interestingly, information on the charge storage mechanism can also be obtained from the most reliable technique, *i.e.*, galvanostatic charge–discharge. The GCD technique was employed to observe the electrochemical performance of LS-carbons in LS-GE-based EC systems (Fig. 7b). The shape of the GCD curve slightly deteriorates from a perfect triangle. Furthermore, lower energetic efficiencies were noted (CLS-SA: 63%, CLS-NaOAc: 46%, CLS-KOAc: 65%, and CLS-NaKOAc: 52%). The noticeable differences in the energetic efficiency values for ECs based on LS-carbons and LS-GE can be attributed to the presence of defects and heteroatoms. To quantitatively analyze the composition of the carbons utilized in this study, elemental analysis with direct estimation of oxygen was used and the results are presented in Table S9. The highest wt% of carbon (~95 wt%) as well as the lowest contribution of other elements, including O (~2 wt%), was measured for commercial carbon. In contrast, LS-carbons present a relatively high wt% of carbon (~85 wt%), negligible presence of N and S but a noticeable amount of O (~6 wt%). Therefore, a slight deviation in the GCD shape at 1.6 V and lower values of energetic efficiency (contrary to EC-LS-GE-YP80F) can be explained especially by the presence of oxygen functionalities, which reduce the stability of the electrolyte. Carbon rich in oxygen supplies additional charge (*e.g.*, pseudocapacitance from C=O ↔ C–OH)⁸⁹ but redox reactions are sluggish/diffusion dependent; hence, EC time constants are higher, and energetic efficiency and power density are lower. In conclusion, the mechanism of charge storage is not purely based on the electrostatic attraction of the ions and subsequent adsorption in the pores; the faradaic reactions related to the presence of oxygen also contribute.

Fig. 8a presents a Ragone plot for LS-based ECs. The energy density reached about ~10 Wh kg⁻¹ across a broad power range, indicating high-power characteristics of the device. Additionally, a reference EC based on a 0.5 M CH₃COONa liquid electrolyte was added to the Ragone plot and presents



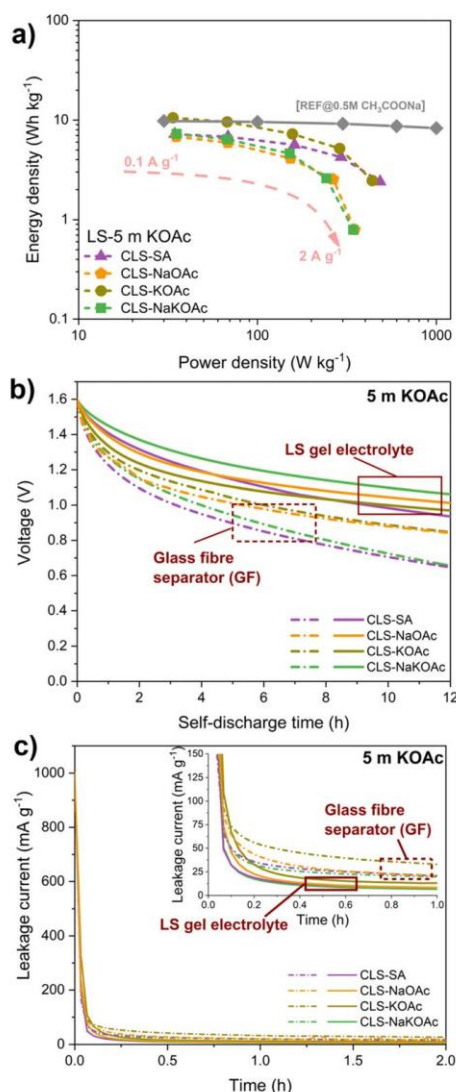


Fig. 8 Electrochemical performance of LS-carbon-based ECs operating in an LS-5 m KOAc (LSGE) or glass fibre separator (GF) with a 5 m KOAc liquid electrolyte at 1.6 V: (a) Ragone plot, (b) self-discharge, and (c) leakage current.

comparable energy metrics with LSGE-based ECs at low current densities. Another important metric of ECs is self-discharge. The spontaneous voltage decline between electrodes

under open circuit conditions is referred to as self-discharge.⁹⁰ The primary disadvantage of ECs is the relatively rapid self-discharge, due to the charge redistribution in variably shaped pores with liquid electrolytes characterized by high mobility of ions.⁹¹ Rapid self-discharge also reflects leakage current and faradaic reactions.⁹⁰ One possible solution to this issue is the use of GEs instead of liquid electrolytes.⁴⁰ For this purpose, ECs based on a commonly used glass-fibre separator (GF) and liquid electrolyte (5 m KOAc) were compared to those based on an LSGE (LS-5 m KOAc). As shown in Fig. 8b, the solid-state form of the LSGE considerably influenced the self-discharge of ECs, maintaining a higher voltage (~ 1 V) for a longer duration compared to the reference system using liquid electrolytes (~ 0.7 V). Moreover, the self-discharge profiles (Fig. 8b) indicate a diffusion-controlled mechanism, linked to the redistribution of ions within the micropores.¹¹ Furthermore, the leakage current of LSGE-based ECs decreased in contrast to liquid electrolyte-based ECs (Fig. 8c). This measurement was performed by a 2 h hold of the maximum operating voltage of the system. Under such harsh conditions, the breakdown of the liquid electrolytes occurs faster than for GEs, and generates gases, *i.e.*, CO and CO₂, which shifts the equilibrium of the system, resulting in an increase of the leakage current.¹¹

To provide more insights into the operating mechanism, the relationship between the LS-carbon texture/structure and the electrochemical performance was investigated. A strong linear correlation between carbon properties and electrochemical performance ($R^2 > 0.86$ and $R^2 > 0.78$) was observed (Fig. S13a and b), demonstrating that higher S_{BET} and V_{micro} substantially improve gravimetric capacitance. This results from the enhanced accommodation of the electrolyte ions, thereby promoting an EDL capacitive storage mechanism. A similar relationship was already very well investigated and reported elsewhere.^{43,75}

The structural defects of carbon arise from *e.g.*, stacking faults, dislocations, multiple vacancies, and edge sites associated with the presence of oxygen surface functionalities.⁹² Interestingly, a high coefficient of determination is noted (0.98) when the band D₃ after Raman deconvolution is taken into account (Fig. S13c). Band D₃ originates from the amorphous carbon fraction, comprising functional groups.^{43,48} This confirms that Raman spectroscopy and elemental analysis are complementary techniques to provide information on carbon defects.

Linearity is not observed when analyzing the correlation of $I_{\text{D1}}/I_{\text{G}}$ with gravimetric capacitance. Typically, such a correlation was observed elsewhere.^{43,75,93} This difference may arise from the fact that the synthesized LS carbons are heterogeneous, mainly disordered but with local graphitic domains, as shown in HRTEM images. Also, the relationship of the total oxygen content and gravimetric capacitance deviates from linearity with $R^2 = 0.36$. In our case, the gel electrolyte was utilized, which differs from the conventional aqueous electrolytes and the capacitance values reported for such systems. Both the gel electrolyte and the carbons were synthesized using lignosulfonate (waste from paper production), which has slightly reduced purity.



The next important parameter of ECs is its durability (lifespan). The maximum stable operating voltage (1.6 V) of the LS-5 m KOAc-based EC was set during potentiostatic floating, which is the most credible method for determining the lifespan.⁹⁴ Fig. 9 and Fig. S14 show the plots of relative capacitance and relative resistance vs. floating time. End-of-life is achieved when 20% decrease in the initial capacitance and/or 100% increase in the initial resistance is recorded.⁹⁵ Nevertheless, end-of-life is impacted by the desired application of ECs as well; therefore, achieving just one criterion is satisfactory.⁹⁶ As shown in Fig. 9, end-of-life, limited by the initial capacitance decrease, ranged from 58 h (CLS-KOAc-based EC) to 170 h (CLS-NaKOAc-based EC). On the other hand, end-of-life, determined by a relative resistance increase, was reached only for the CLS-NaKOAc-based EC. The degradation of the systems could be ascribed to the decomposition of carbon surface functional groups, water splitting (HER and OER), and carbon corrosion.⁹⁷ The most disordered CLS-KOAc ($I_{D1}/I_G = 3.00$) presenting the highest S_{BET} value ($1754 \text{ m}^2 \text{ g}^{-1}$) demonstrated the shortest floating time, in contrast to the most ordered CLS-NaKOAc ($I_{D1}/I_G = 1.37$) presenting a lower S_{BET} value ($1169 \text{ m}^2 \text{ g}^{-1}$). Worth mentioning is that the CLS-NaKOAc-based EC showed a rather similar floating time to the CLS-NaOAc-based EC (170 h vs. 160 h), although CLS-NaOAc presented a high degree of disorder (2.81) and a low S_{BET} value ($881 \text{ m}^2 \text{ g}^{-1}$).

Importantly, the differences in the end-of-life of ECs depend on the texture and structure of LS-carbons used for electrodes.⁴³ A higher degree of disorder links with the defect density and reflects the presence of oxygenated functional groups, enhancing wettability and pseudocapacitive contribution. On the other hand, disorder may introduce more electrochemically active sites, resulting in acceleration of parasitic reactions and structural degradation, shortening the lifespan of the device.

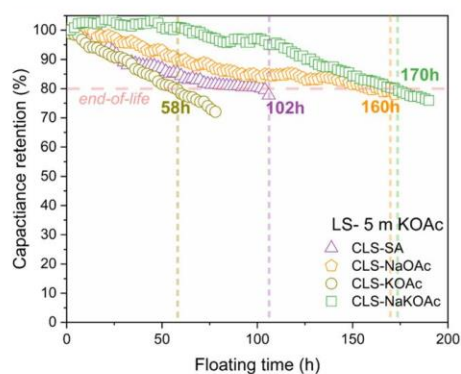


Fig. 9 Relative capacitance vs. floating time of LS-carbon-based ECs operating in an LS-5 m KOAc gel electrolyte at 1.6 V.

It is expected that the more ordered structure of CLS-NaKOAc enhances the electron mobility, thus improving the conductivity, resulting in a better lifespan.^{43,69} However, more ordered and higher stacked graphitic domains with a reduced distance between the graphene layers and smaller SSAs contribute to a decrease in capacitance. Similarly, a high surface area arising from extensive microporosity increases charge storage but can hinder ion transport, trap solvated ions, and compromise mechanical integrity during long-term performance. In contrast, mesopores create stable ion diffusion paths, which helps to maintain long-term performance,⁹⁶ particularly important in gel-based systems where mobility is more limited than in liquid electrolytes. As reported herein, CLS-KOAc, which is the most disordered and porous (the highest I_{D1}/I_G , S_{BET} and V_{micro}), improved the gravimetric capacitance of such a system but shortened its lifetime significantly. In contrast, LS-carbons with higher graphitic order display excellent structural stability but reduced capacitance due to limited accessible surface area and microporosity.

Therefore, optimal design requires moderate disorder of carbons with a hierarchical pore structure that combines micropores for capacitance and mesopores for ion transport. A gel electrolyte should have good conductivity and mechanical stability. This balance is key to simultaneously achieving high capacitance, energy efficiency, and long cycling stability.

Table S14 displays a summary of aqueous-gel based EC metrics. The idea of a lignin-based EC has already been proposed.^{19,37} Park *et al.* reported an EC with an alkali lignin/PEGDGE-based GE containing 3.3 M KOH. Additionally, the authors prepared electrode carbon from alkali lignin/polyacrylonitrile with a relatively high S_{BET} value ($1176 \text{ m}^2 \text{ g}^{-1}$).³⁷ The gravimetric capacitance of the assembled EC was reported to be 129 F g^{-1} (0.5 A g^{-1} , 1 V); however, expensive gold current collectors were required.³⁷ On the other hand, Collins *et al.* reported an EC with an organosolv lignin/PEGDGE-based GE containing 6 M KOH and electrodes prepared through carbonization of a gel.¹⁹ The gravimetric capacitance was 41 F g^{-1} (0.5 A g^{-1} , 1 V), but this work lacks details on carbon characterization, e.g., S_{BET} .¹⁹

As a brief summary, these ECs use KOH-based non-practical aqueous electrolytes, and therefore, a higher voltage above 1.23 V cannot be applied, limiting their energy metrics, which are more affected by voltage than capacitance values ($E \sim U^2$). An in-depth comparison with these reported ECs is so difficult because different electrode materials and electrolytes were utilized as summarized in Table S14. Herein, the main strategy is to optimize the LSGE by using an aqueous acetate electrolyte with stable dielectric properties, which enables the EC to operate at a higher voltage of 1.6 V. Moreover, the salt templating approach was employed to reach the well-developed porosity of carbon as an electrode material. Owing to the optimization of EC lignosulfonate-based components, it was possible to reach both the high energetic metrics and long lifespan of LS-based ECs. It is worth underlining that our ECs were tested by floating at 1.6 V, which is harsh but very reliable for lifespan determination. Using cyclic voltammetry for long-term



testing²⁰ is not recommended, and hence galvanostatic cycling is adapted according to the international standards; however, floating is trustworthy especially in industries.

Additionally, in Table S14, we summarized the performance of ECs based on bio-derived gel electrolytes, which gives the idea of the capacitance values and lifespan of such systems. In particular, our LS-based EC outperforms the reported systems in terms of stable operating voltage and the majority of the capacitance values reported.^{19,20,24,38} High capacitance values found in the literature could also be questionable, and the authors use a very small mass of electrode and/or often do not show the calculation procedure clearly.^{20,38,98} The low conductivity of the gel type electrolyte is generally at the origin of moderate capacitance values.

Moreover, to further underline the green aspect of our work, we benchmarked our synthesis route against published LCAs for fossil- and lignin-based carbons. Conventional coal/oil-derived carbons exhibit a cradle-to-gate global warming potential of approximately 2.4 kg CO₂-eq per kg product.⁹⁹ In contrast, lignin-derived materials produced *via* similar slow-pyrolysis with subsequent heat treatment steps can achieve net-negative or near-neutral footprints, on the order of −0.23 kg CO₂ per kg product, with typical climate-change savings of 20–80% relative to fossil analogues.¹⁰⁰ Because our process uses a standard slow-pyrolysis heating rate (3 °C min^{−1}) followed by high-temperature, its energy demand is expected to be comparable to conventional carbon production, while the use of biogenic lignin and the potential for long-term carbon storage imply a substantially more favorable climate performance than coal-based carbons. Lignin, as a renewable material, participates in CO₂ removal from air through photosynthesis.¹⁰¹ Regarding the environmental impact, CO₂ reduction by replacing fossil fuels with lignosulfonate-based EC components was estimated to range from 32% to 49%, as shown in Fig. S15. Compared with other references, our process is very promising for the further enhancement of environmental sustainability, ensuring good energy metrics of ECs.

4 Conclusions

For the first time, a gel electrolyte and porous carbon as the main components of ECs were synthesized from LS and optimized to enhance the sustainability of aqueous ECs with high performance. LS, a commercially available technical lignin, was selected as the dual precursor due to its environmental friendliness, high carbon content and water solubility. Moreover, the gel was composed of 72% LS, which is significantly better compared to other reported gels, making perfect use of the waste biopolymer.

The LS-based gel electrolyte was optimized using different liquid electrolytes through systematic investigation of its solution uptake ability, and 5 m KOAc was selected owing to the highest ion mobility for further application in ECs. The LS-carbon, prepared *via* a green salt templating approach,

enabled precise control of the carbon structure and texture by selecting different template salts (NaOAc, KOAc, and their mixture NaKOAc). The amount and type of salt dictated the characteristics of carbon materials: (i) dominance of micropores, with a small fraction of mesopores for single salts (CLS-NaOAc and CLS-KOAc), (ii) high SSA ranging from 881 to 1754 m² g^{−1}, and (iii) various degrees of disorder (I_{D1}/I_G of 3.00–1.37), from highly disordered carbons (single salts) to ordered graphitized carbon (double salts).

The resultant EC assembled with an LS-based gel electrolyte and LS-carbons demonstrated a stable operating voltage of 1.6 V, a significant reduction in self-discharge (~30% loss of initial voltage), and a substantial lifespan of 170 h of floating. Hence, the performance of our LS-based EC is competitive with reference aqueous-based ECs. Moreover, the gel structure effectively inhibited electrolyte leakage, thereby enhancing the safety of the device. Nevertheless, using such a gel electrolyte eliminates the need for a separator, reducing the cost and environmental impact of the EC.

In summary, the valorization of water-soluble LS by its application as a precursor of the gel electrolyte and electrode material is an effective approach to reduce our dependence on non-renewable sources. It has been proven that LS waste can be transformed into valuable components of energy storage systems.

Author contributions

A. Klimek: conceptualization, data curation, formal analysis, investigation, methodology, visualization, writing – original draft, and writing – review & editing; L. Amro: investigation and writing – review & editing; N. Pakkang: investigation; C. Matei Ghimbeu: supervision, validation, and writing – review & editing; E. Frackowiak: conceptualization, funding acquisition, project administration, supervision, validation, and writing – review & editing; and S. Suzuki: conceptualization, funding acquisition, project administration, supervision, validation, and writing – review & editing.

Conflicts of interest

There are no conflicts of interest to declare.

Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information is available. See DOI: <https://doi.org/10.1039/d5gc05533d>.



Acknowledgements

This research was supported by a French Government Scholarship France Excellence, Polish National Agency for Academic Exchange (NAWA) under the STER programme "Towards Internationalization of Poznan University of Technology Doctoral School (2022-2024)", the Ministry of Higher Education of Poland (Project 0911/SBAD/2501), the Japan Science and Technology Agency (JST) ALCA-Next (grant number: JPMJAN23C3), Co-Creation Core for Soft Materials Aspiring Research & Translation (C3-SMART), Japan Society for the Promotion of Science (JSPS) J-PEAKS and KAKENHI (grant number: 23H03828). The authors would like to acknowledge L. Vidal for the HRTEM analysis.

References

- 1 S. Wolf, R. Bullard, J. J. Buonocore, N. Donley, T. Farrelly, J. Fleming, D. J. X. Gonzalez, N. Oreskes, W. Ripple, R. Saha and M. D. Willis, *Oxf. Open Clim. Change*, 2025, 5, 1–26.
- 2 G. Notton, M. L. Nivet, C. Voyant, C. Paoli, C. Darras, F. Motte and A. Fouilloy, *Renewable Sustainable Energy Rev.*, 2018, 87, 96–105.
- 3 M. Zhou, A. Gallegos, K. Liu, S. Dai and J. Wu, *Carbon*, 2020, 157, 147–152.
- 4 F. Béguin, V. Presser, A. Balducci and E. Frackowiak, *Adv. Mater.*, 2014, 26, 2219–2251.
- 5 B. Dyatkin, V. Presser, M. Heon, M. R. Lukatskaya, M. Beidaghi and Y. Gogotsi, *ChemSusChem*, 2013, 6, 2269–2280.
- 6 K. Dissanayake and D. Kularatna-Abeywardana, *J. Energy Storage*, 2024, 96, 112563.
- 7 SkelCap, supercapacitor, Skeleton Technologies GmbH, preliminary data sheet, 2024.
- 8 J. Kowal, E. Avaroglu, F. Chamekh, A. Šenfelds, T. Thien, D. Wijaya and D. U. Sauer, *J. Power Sources*, 2011, 196, 573–579.
- 9 S. Azmi, A. Klimek and E. Frackowiak, *Electrochim. Acta*, 2023, 452, 142347.
- 10 K. Fic, A. Platek, J. Piwek, J. Menzel, A. Ślesieński, P. Bujewska, P. Galek and E. Frackowiak, *Energy Storage Mater.*, 2019, 22, 1–14.
- 11 P. Galek, A. Ślesieński, K. Fic and J. Menzel, *J. Mater. Chem. A*, 2021, 9, 8644–8654.
- 12 M. Antonietti, N. Fechner and T. P. Feller, *Chem. Mater.*, 2014, 26, 196–210.
- 13 A. Anukam, J. Berghel, G. Henrikson, S. Frodeson and M. Ståhl, *Renewable Sustainable Energy Rev.*, 2021, 148, 111249.
- 14 C. Jaiswal, Lignosulfonate Market Size, Share & Industry Report 2024, Market Research Future, September 2025, <https://www.marketresearchfuture.com/reports/lignosulfonate-market-26116>.
- 15 J. Li, P. Yu, S. Zhang, Z. Wen, Y. Wen, W. Zhou, X. Dong, Y. Liu and Y. Liang, *J. Colloid Interface Sci.*, 2021, 600, 586–593.
- 16 Y. K. Han, J. Y. Cheon, T. Kim, S. B. Lee, Y. D. Kim and B. M. Jung, *RSC Adv.*, 2020, 10, 18945–18952.
- 17 F. Honda, S. Taira, S. Suzuki, K. Shikina, K. Shigetomi and Y. Uraki, *Holzforchung*, 2023, 77, 776–783.
- 18 K. Gong, H. Lee, Y. Choi, G. Jung, K. Keum, J. W. Kim and J. S. Ha, *Electrochim. Acta*, 2024, 475, 143585.
- 19 M. Muddasar, A. Beaucamp, M. Culebras and M. N. Collins, *Mater. Today Sustain.*, 2024, 26, 100767.
- 20 G. Landi, L. La Notte, V. Granata, G. Avallone, C. Barone, G. Carapella, S. Pagano, A. L. Palma, P. Sdringola and G. Puglisi, *ChemElectroChem*, 2023, 10, e202300443.
- 21 Research Nester "Gel polymer electrolyte market" – size, emerging trends & forecast to 2035.
- 22 G. Wang, X. Lu, Y. Ling, T. Zhai, H. Wang, Y. Tong and Y. Li, *ACS Nano*, 2012, 6, 10296–10302.
- 23 P. Yang, P. Zhang, C. Shi, L. Chen, J. Dai and J. Zhao, *J. Membr. Sci.*, 2015, 474, 148–155.
- 24 S. Zallouz, J. M. L. Meins and C. Matei Ghimbeu, *Energy Adv.*, 2022, 1, 1051–1064.
- 25 X. Hu, A. K. J. An and S. S. Chopra, *ACS Sustainable Chem. Eng.*, 2022, 10, 5708–5718.
- 26 J. Huang, S. Wang, J. Chen, C. Chen and E. Lizundia, *Adv. Mater.*, 2025, 37, 2416733.
- 27 F. Vollrath, R. Carter, G. K. Rajesh, G. Thalwitz and M. F. Astudillo "Life cycle analysis of cumulative energy demand on sericulture in Karnataka, India" BISERICA 2013 6th BACSA International Conference: Building Value Chains in Sericulture.
- 28 M. Lettner, P. Solt, B. Rößiger, D. Pufky-Heinrich, A. S. Jäskeläinen, P. Schwarzbauer and F. Hesser, *Sustainability*, 2018, 10, 2745.
- 29 Borregaard USA, Inc., Environmental product declaration: sodium lignin biopolymer D powder, NEPD-5614-4920-EN, The Norwegian EPD Foundation, 2023.
- 30 T. Hammar, D. Peñaloza, A.-C. Hanning, N. Haatanen and J. Pakkasmaa, *J. Cleaner Prod.*, 2023, 426, 139189.
- 31 J. Ding, Y. Yang, J. Poisson, Y. He, H. Zhang, Y. Zhang, Y. Bao, S. Chen, Y. M. Chen and K. Zhang, *ACS Energy Lett.*, 2024, 9, 1803–1825.
- 32 A. Larrabide, I. Rey and E. Lizundia, *Adv. Energy Sustain. Res.*, 2022, 3, 2200079.
- 33 A. Dér, N. Dilger, A. Kaluza, C. Creighton, S. Kara, R. Varley, C. Herrmann and S. Thiede, *J. Cleaner Prod.*, 2021, 303, 127105.
- 34 G. Ma, M. Dong, K. Sun, E. Feng, H. Peng and Z. Lei, *J. Mater. Chem. A*, 2015, 3, 4035–4041.
- 35 K. Subramani, N. Sudhan, R. Divya and M. Sathish, *RSC Adv.*, 2017, 7, 6648–6659.
- 36 N. A. Choudhury, S. Sampath and A. K. Shukla, *Energy Environ. Sci.*, 2008, 2, 55–67.
- 37 J. H. Park, H. H. Rana, J. Y. Lee and H. S. Park, *J. Mater. Chem. A*, 2019, 7, 16962–16968.

Impact of disorder, porosity, and surface chemistry of salt templated carbons on capacitance

<https://doi.org/10.1002/advs.202505032>

In this chapter, the fundamental relationships between the structural disorder, porosity and surface chemistry of templated carbons on the capacitance, retention and lifespan of aqueous-based ECs are investigated, as shown in **Figure 13**. Notably, salt templated carbons with higher structural disorder (higher I_{D1}/I_G ratio) exhibit enhanced capacitance across a wide range of current densities, although EC performance is also strongly affected by specific surface area, microporosity/mesoporosity, and surface functionalities.

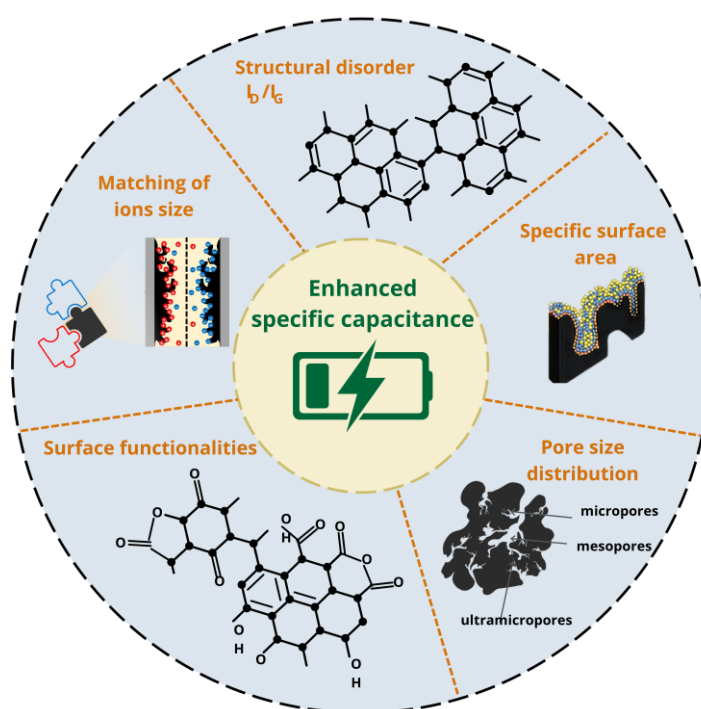


Figure 13 The parameters of importance considered for the enhanced ECs performance.

Key challenge of enhancing EC capacitance, can be realized by optimal design of electrodes. The soft-salt templating approach has garnered interest due to its simplicity, environmental friendliness, and cost-effectiveness. The synthesis relies on the use of green phenolic-resin (carbon source), the soft template (mesoporosity creating agent), and the salt template (microporosity and graphitic structure mediator). Numerous property-capacitance relationships have been reported, concerning various carbons, electrolytes, and testing conditions, complicating the extrapolation of a general trend.

In this study, a series of porous carbons was synthesized *via* a sustainable soft-salt templating approach. The mixtures of alkali metal chlorides in their eutectic ratio (CsCl/KCl, CsCl/NaCl, CsCl/LiCl, NaCl/KCl, LiCl/KCl, LiCl/NaCl) were utilized as salt templates. The interactions of the salt template, namely its cation binding energy to the carbon core as well as the cation size resulted in differences of texture/structure/surface chemistry between the carbons. Prepared carbons were characterized physicochemically (XRD, TEM, Raman spectroscopy, TPD-MS, ASA, N₂/CO₂ sorption), and electrochemically (CV, GCD, EIS) leading to several linear property-performance relationships.

TEM images indicated generally disordered structure for all salt templated carbons, with the highest disorder observed in CsCl-templated carbons, while the presence of LiCl as template (LiCl/NaCl-T and LiCl/KCl-T) promoted the formation of larger and more extended graphitic domains.

XRD analysis revealed that salt templated carbons exhibited broad and poorly defined diffraction peaks corresponding to the hexagonal graphite planes, confirming their predominant disordered structure with randomly stacked graphene layers. Interestingly both peaks (002, 100) were higher for LiCl/NaCl-T and LiCl-KCl-T indicating more stacked and larger graphene domains than for CsCl-templated carbons.

The average Raman spectra for all carbons showed that wider D bands are associated with the use of CsCl-template, while more narrow D bands are linked to the LiCl-templated carbons. Additionally, the 2D band was noticed in more ordered materials and particularly observed for LiCl-based carbons. Quantitative analysis using the I_{D1}/I_G ratio (based on peak areas) revealed the differences of structure among the carbons. Four-peak deconvolution provided a more detailed description of defect type. For instance, CsCl-T exhibited the highest disorder degree (I_{D1}/I_G=2.36), while LiCl/NaCl-T was the most ordered (I_{D1}/I_G=1.66).

Surface chemistry analysis through the TPD-MS demonstrated the presence of different type and amount of oxygen functional groups within carbons. CsCl-based carbons exhibited higher CO, and CO₂ evolution, indicating high incorporation of oxygen functionalities. Notably, the carbons were especially abundant in carbonyl/quinone, carboxylic, and phenol/ether groups. Furthermore, TPD-MS enabled quantification of ASA, associated with edge sites and structural defects. The estimation of ASA is very rare, and requires a special equipment set-up, with only a few groups in the world reporting such a value. The ASA ranged from 37 m² g⁻¹ for the most disordered CsCl-T to 18 m² g⁻¹ for the more ordered LiCl/NaCl-T. Importantly, ASA showed a clear relationship with the I_{D1}/I_G.

N₂ sorption indicated that salt templated carbons were mostly microporous (type I/IV isotherms) with high specific surface areas (1453 - 2640 m² g⁻¹) and presence of a small fraction of mesopores. CsCl-templated carbons exhibited the highest micropore volume (up to 0.97 cm³ g⁻¹), while LiCl-based carbons showed reduced microporosity, but increased mesoporosity due to enhanced graphitization. Overall, the prepared carbon series is characterized by various textural, structural, and surface chemistry properties that allow to establish property-performance relationships.

Electrochemical testing in 1M Li₂SO₄ electrolyte revealed that all salt templated carbons exhibited typical EDL behavior with near-ideal rectangular CV curves, and triangular GCD profiles. The maximum gravimetric capacitance reached 244 F g⁻¹ (CsCl/KCl-T) at an operating voltage of 1.6 V. The salt templated carbons showed a good rate capability, corresponding to the ~51% retention from 0.2 to 20 A g⁻¹. Furthermore, the long-term lifespan of salt templated carbons was observed especially for more ordered LiCl/KCl-T (288 floating hours at 1.6 V).

The physicochemical properties of salt templated carbons were correlated with the capacitance, rate capability, and stability. It was revealed that the salt templated carbons with increased disorder, characterized by the greater I_{D1}/I_G Raman ratio, are likely to display enhanced capacitance, confirmed as well by the ASA approach across different current densities. Importantly, the high coefficient of determination (R²) ~0.91 - 0.94 was reported, reflecting that defects in carbon's structure promote capacitive performance.

Another factor of importance is surface chemistry. Overall, total CO, CO₂ evolution profiles correlated with capacitance, but with low linearity due to the complex and competing roles of surface functionalities. Only particular oxygen functional groups were beneficial for the EC operating in 1M Li₂SO₄. The phenol/ether and carboxyl groups were

found as the most influential on the capacitance ($R^2 \sim 0.56 - 0.71$), while carbonyl/quinone and other groups showed weak or no clear correlation.

SSA, volume of micropores, volume of ultramicropores exhibited strong linear correlations with capacitance (R^2 up to ~ 0.96), confirming that charge storage was primarily governed by accessible surface within micropores. In contrast, the volume of mesopores showed a weaker or inverse relationship with capacitance, acting mainly as ion transport pathways rather than charge storage sites.

Concluding, various parameters impact the performance of salt templated carbons-based ECs, i.e., degree of disorder, specific surface area, pore size distribution, matching of size/kind of ions used and surface functional groups. None of these should be ignored. For example, increased disorder of carbon, characterized by accessible microporosity that aligns with the solvated ions of the electrolyte, together with some mesoporosity (facilitating fast kinetics), and a balanced surface functional groups, result in improved capacitance, but reduced lifespan. In contrast, the highly ordered material with a high concentration of graphitic domains exhibits an extended lifespan, but decreased capacitance. Although highly disorder carbon supply increase of capacitance, defects contribute to a reduced lifespan.

These findings provide a valuable guidance on how we can significantly improve and optimize the design of novel materials with controlled features for sustainable energy storage systems.

Impact of Disorder, Porosity, and Surface Chemistry of Salt Templated Carbons on Capacitance

Amelia Klimek, Bénédicte Réty, Camélia Matei Ghimbeu,* and Elzbieta Frackowiak*

The necessity of tailoring the structure/texture of carbons to improve the performance of aqueous-based electrical double-layer capacitors (EDLCs) is emphasized. A green soft-salt templating approach allowed the preparation of a series of porous carbons for this target. The EDLCs operating in 1M Li_2SO_4 demonstrated a maximum capacitance of 244 F g^{-1} at 1.6 V (CsCl/KCl-T), long-term cycle life (288 h for LiCl/KCl-T), and a specific energy exceeding 10 Wh kg^{-1} . The physicochemical properties of carbons have been correlated with capacitance, retention, and stability. The investigation by Raman spectroscopy revealed that carbons with the increased disorder, thus, higher I_D/I_G ratio, are in accord with enhanced capacitance. Active surface area (ASA) values, related to carbon defects, perfectly supported the Raman findings. Surface functionality, i.e., the phenol/ether and carboxyl groups are found to affect capacitance. The carbons showed a predominance of micropores, with a specific surface area (SSA) ranging from 2640 to $1453 \text{ m}^2 \text{ g}^{-1}$. In sum, I_D/I_G , SSA, ASA, and volume of micropores are in linear proportion with capacitance at various regimes. However, the most ordered and less porous materials provided better lifespan performance. Therefore, a good compromise is required to satisfy both high capacitance and the long cycle life of EDLCs.

1. Introduction

Electrical double-layer capacitors (EDLCs) are widely identified as high-power energy storage devices with outstanding long-term cycle life. Such characteristics are possible by the reversible electrostatic accumulation of ions at the electrode/electrolyte interface.^[1] According to the formula $E = 0.5CU^2$, energy density (E) can be increased by enhancing the capacitance (C) and working voltage (U) of the EDLC. Therefore, there is a great interest in developing novel electrolytes and electrode materials that notably affect the final performance of the device.^[2] Ideal EDLC electrolytes should be environmentally friendly, cost-effective,

exhibit high ionic conductivity, and low viscosity, as well as offer wide stable operating voltage.^[3,4] The most attractive neutral electrolytes, e.g., Na_2SO_4 , Li_2SO_4 , K_2SO_4 , have been used for the voltage extension.^[5,6] It was proven by *operando* studies that 1.6 V is the practical maximum operating voltage of EDLC in 1M Li_2SO_4 , and it is possible due to the electrosorption of hydrogen in the negative electrode.^[7]

Optimal electrode material for EDLC should be characterized by high specific surface area (SSA) and good electrical conductivity.^[8] Activated carbon is the most promising electrode material for EDLCs because of reasonable electrical conductivity, chemical/thermal stability, variety of morphologies, tunable porous texture, and cost-effectiveness.^[9–11] In addition to the extension of the voltage which is directly linked to the used electrolyte, as well as the increase of electrode surface area, there is another option to enhance the energy density of the EDLC.^[12] The importance

of tailoring carbon texture/structure has already been mentioned.^[13,14] It is possible by the application of the soft-salt templating method.^[15] The incorporation of a soft template creates mesoporosity, while the salt template is responsible for microporosity. Both templates are removed from the carbon structure, the soft template is thermally decomposed during the annealing and the salt template is washed out with water directly after synthesis, with the possibility of recovery for further utilization.^[16] This is an advantage over the traditional hard template route, where the template cannot be recovered, and its removal requires dangerous and hazardous HF acid.^[17] Moreover, compared to CO_2 activation methods using biomass

A. Klimek, E. Frackowiak
Poznan University of Technology
Institute of Chemistry and Technical Electrochemistry
Berdychowo 4, Poznan 60-965, Poland
E-mail: elzbieta.frackowiak@put.poznan.pl

A. Klimek, B. Réty, C. Matei Ghimbeu
Université de Haute-Alsace
Institut de Science des Matériaux de Mulhouse
Mulhouse F-68100, France
E-mail: camelia.ghimbeu@uha.fr

The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/advs.202505032>

© 2025 The Author(s). Advanced Science published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

DOI: 10.1002/advs.202505032

A. Klimek, B. Réty, C. Matei Ghimbeu
Université de Strasbourg
Strasbourg F-67081, France
C. Matei Ghimbeu
Réseau sur le Stockage Electrochimique de l'Energie (RS2E)
Amiens Cedex 80039, France

precursors^[18] (e.g., coconut shells), the soft-salt templating methods using phenolic resin^[19] as a carbon source present higher carbon yield and lower gas emissions.^[20]

Nita *et al.*^[15] proposed three salt templates, i.e., KCl, NaCl, and LiCl, to obtain porous carbons. The microporosity varied with the used salt in the order KCl > NaCl > LiCl, while mesoporosity was in the opposite direction. Furthermore, the authors reported structural changes of the prepared templated carbons from more disordered (KCl) to more graphitic (NaCl, LiCl) concluded by the analysis of transmission electron microscopy (TEM) images and Raman spectra. Then, Platek *et al.*^[21] advanced the works on salt-templated carbons for EDLCs by matching the salt template cations (Li, Na, K, Rb, Cs chlorides) with the electrolyte (Li, Na, K, Rb, Cs hydroxides). It has been shown that EDLCs based on the synthesized carbons provide improved capacitance retention when the cation employed during synthesis is coupled to the cation present in the electrolyte.^[21]

Many works focused on the correlation between capacitance and the specific surface area/pore size distribution of carbon-based materials.^[22–24] In most cases, the higher the SSA, the higher the capacitance is observed. However, the lack of linearity is often noticed, especially for carbons with extraordinarily developed specific surface area, which is considered to be undesirable for EDLCs.^[25] Another important factor that directly affects capacitance is pore size distribution. As a rule of thumb, the closed pores do not participate in charge accumulation, and the pores smaller than the ion's size (or equal) do not participate in the formation of EDL. However, a partial desolvation of ions should not be completely excluded, particularly at strong polarization. Till now, some contrasting results have been reported on capacitance vs. pore size dependence, especially for pores ca. 1 nm. Chmiola *et al.*^[26,27] claimed that normalized capacitance of carbide-derived carbon in organic electrolytes exhibits anomalous values for accessible pore sizes less than 1 nm. Jäckel *et al.*^[28] revisited this issue by studies in organic and ionic liquid media considering the desolvation of ions especially under higher polarization. Yet, Béguin *et al.*^[29] found that EDL is efficiently formed when the optimal size is assured as ≈ 0.7 nm for aqueous medium and ≈ 0.8 nm for organic medium. Interestingly, Centeno *et al.*^[30] studied 28 porous carbons and found that capacitance in the organic medium is relatively constant between 0.7 and 15 nm.

Some research has already reported on the dependence of capacitance and structural ordering of the electrode material. At first, Vix-Guterl *et al.*^[31] showed that the higher the presence of structural defects in the bulk of electrode material, the higher the capacitance, in both organic and aqueous media. Moreover, Forse *et al.*^[32] demonstrated that structural disordering of the carbon network, rather than pore size distribution in carbon materials, determines capacitance. Organic electrolyte (1M TEABF₄ in ACN) and nuclear magnetic resonance technique were employed to show that the degree of disorder in the graphene-like sheets correlates with capacitance.^[32] Another factor that affects the capacitance of EDLCs is the presence of surface functional groups (i.e., oxygen-containing) on carbons.^[33–35]

Nevertheless, there is still a lack of understanding of how the characteristics of carbon materials impact their electrochemical EDLC performance. Although some property-capacitance correlations have been already reported, these relate to different carbons, electrolytes, and cycling conditions, which make it difficult

to extrapolate a general trend. Moreover, research work, that gathers all the physicochemical properties of a series of porous carbons with electrochemical performance (capacitance, retention, and stability) in an aqueous electrolyte, is missing. In this paper, special attention was devoted to the correlation of carbon disorder, defects, porosity and surface chemistry with the capacitance of aqueous-based EDLC. Our findings can significantly improve and optimize the design of novel materials with controlled features for sustainable energy storage systems, such as EDLCs.

2. Results and Discussion

2.1. Structural Properties of Salt Templated Carbons

The synthesis is based on the use of a phenolic-resin which acts as a carbon source, the soft template that generates the mesoporosity, and the salt template that creates microporosity and in some cases mesoporosity, required for ion adsorption and diffusion. Moreover, at the same time, some graphitic domains are formed (depending on the cation's binding energy to the carbon core), providing good conductivity, in addition to a high specific surface area. These property modifications are possible due to the flexibility of the synthesis, involving an extensive range of synthesis parameters to be modified (e.g., pH, type and ratio of salt/soft template, temperature).^[15] In particular, the influence of different eutectic salt mixtures was investigated in this work. The synthesis appears advantageous due to the cost-effectiveness and environmental friendliness of salt templates (e.g., alkali metal chlorides), which can be recovered in >80% after the synthesis (86% when the CsCl template was used) by simple washing with hot water.^[21] Moreover, in the case of soft-salt templating, the C-yield is higher ($\approx 30\%$) than for conventional routes (carbonization combined with CO₂ activation $\approx 25\%$).^[19]

The local nanostructure of carbons was observed using the TEM technique, which also makes it possible to prove that the materials contain graphitic domains.^[36] TEM images (Figure 1a–d; Figure S1a–d, Supporting Information) for a series of carbons indicate a generally disordered structure, which is beneficial for the formation of the EDL. The more disordered zones are observed mostly for carbons synthesized with cesium chloride as a salt template: CsCl-T, CsCl/NaCl-T, CsCl/KCl-T (Figure S1a, b, Supporting Information; Figure 1a). The TEM images for NaCl/KCl-T, and CsCl/LiCl-T illustrate the existence of small, narrow graphitic domains, however, predominantly exhibit a disordered structure (Figure 1b; Figure S1c, Supporting Information). The LiCl/NaCl-T and LiCl/KCl-T carbons (Figure 1c; Figure S1d, Supporting Information) display extensive graphitic domains consisting of overlapping several flat graphene-like sheets. These domains are much longer and wider (Figure 1d) than for the NaCl/KCl-T carbon. Evolution of graphitic domains of carbon occurs above 600 °C, i.e., at temperatures above the melting point of all salts, and further develops with temperature increase.^[15] This process is also strongly affected by the type of salt, with LiCl providing the highest degree of graphitization due to its high cation- π interactions with the carbon matrix (Table S2, Supporting Information).^[21] Therefore, the thermodynamic properties of template alkali cations affect carbon structure formation.

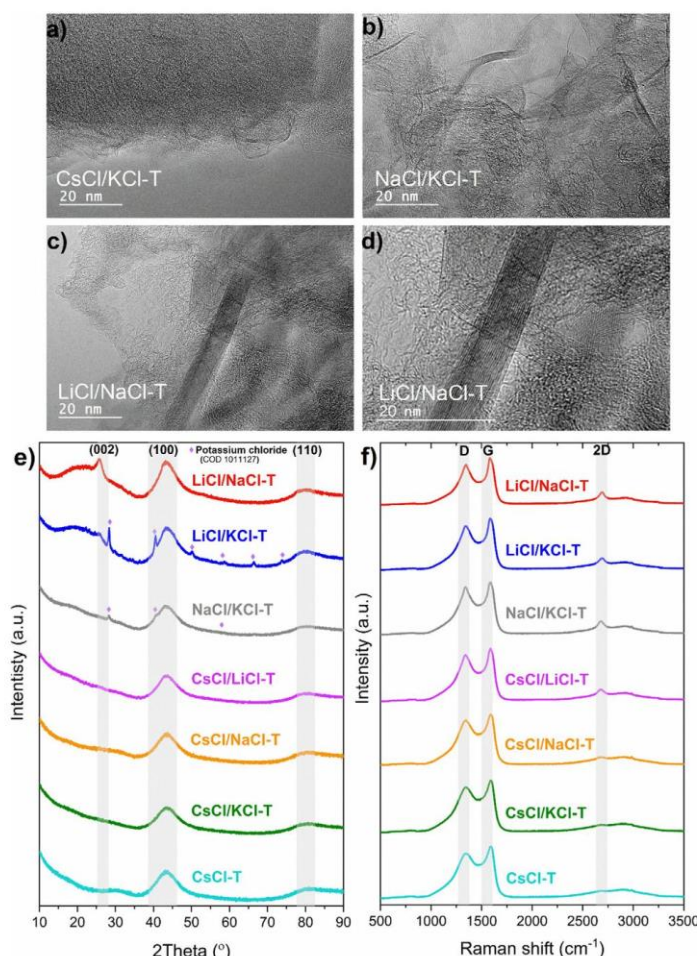


Figure 1. TEM images of salt templated carbons: a) CsCl/KCl-T, b) NaCl/KCl-T, c) LiCl/NaCl-T, d) magnification of graphitic zone of LiCl/NaCl-T; e) X-ray diffraction patterns, f) Raman spectra of all salt templated carbons. T indicates template.

XRD is primarily used to characterize crystalline structures like graphite, but disordered carbons can also yield some structural information mainly because of the presence of randomly stacked graphene layers.^[37] XRD patterns for salt-templated carbons (Figure 1e) show poorly defined diffraction peaks at 2 theta values of 26°, 43°, and 78°, which are associated with the hexagonal graphite (Crystallography Open Database (COD) - 9011577) diffraction planes (002), (100), and (110), respectively.^[21] For most materials, the (002) peak is hardly visible or very broad,

which aligns well with the results for other disordered-like carbon materials.^[38] A small, sharp peak at $\approx 26^\circ$ (002) suggests the presence of a graphite phase which is noticeable mainly on LiCl/NaCl-T, in accordance with TEM images, showing extensive graphitized regions.

Furthermore, for all carbons, it is evident that the (100) peak, which is linked with the graphene lateral size (length), is definitely more intense than the (002) peak, and that intensity varies in the manner described below: LiCl/KCl-T carbon is followed by

LiCl/NaCl-T, NaCl/KCl-T, CsCl/LiCl-T, CsCl/KCl-T, CsCl/NaCl-T, CsCl-T. The order is related to the cation binding energy toward carbon rings.

Additionally, in the case of NaCl/KCl-T and LiCl/KCl-T carbons, there are visible diffraction peaks corresponding to the potassium chloride (COD 1011127) in the carbon structure. Some small quantities of KCl could not be washed out easily due to very strong carbon/alkali ion interactions, which also generate graphitic domains. Moreover, potassium as a cation is more easily incorporated than sodium because of its weaker solvation energy, which favors more interaction of potassium with the aromatic moieties.^[21] It is also worth mentioning that herein HCl was not used (which would have removed all the KCl) as shown in other works, but only hot water, in order to limit environmental problems.^[39]

A reliable and effective method for investigation of structural disorder in carbon-based materials is Raman spectroscopy; consequently, it supplies crucial additional insights to TEM and XRD studies. Raman spectroscopy involves an incident laser beam that only interacts with the π electrons of sp^2 -hybridised carbon networks. Thus, the acquired Raman spectrum does not provide direct information concerning sp^3 -hybridised carbon atoms.^[40] Generally, two main bands are observed in Raman spectra of disordered carbons.^[40] The first-order graphite band (G) located at 1580–1590 cm^{-1} corresponds to the in-plane vibrations of sp^2 -hybridised carbon atoms, rather than those in hexagonal rings. The disorder-induced band (D) placed at 1330–1350 cm^{-1} is linked to ring breathing modes activated mainly in the presence of disorder; thus, it is directly correlated with the existence of six fold aromatic rings and exhibit intensity for materials with structural defects.^[40–42] It is important to note that the peak intensity changes from zone to zone, as supplied in the Raman mapping of 11 different points over the salt-templated carbons (Figure S2a–g, Supporting Information), which indicated that the local structure is heterogeneous, especially for materials containing a mixture of disordered and graphitic domains. The average Raman spectra for all carbons (Figure 1f) show that wider D bands are associated with the utilization of the cesium chloride template, while more narrow D bands are linked to the lithium chloride template. Additionally, an overtone of the D band (called as well as the 2D band or second-order G' band) located at 2500–2800 cm^{-1} is related to ordered materials.^[43] The 2D band is mainly observed for CsCl/LiCl-T, NaCl/KCl-T, LiCl/NaCl-T, and LiCl/KCl-T carbons. In conclusion, the salt-templated carbon structure integrates both disordered and graphitic domains (as evidenced by TEM images and XRD); thus, a well-defined D-band correlates with the larger presence of structural defects, while the graphitic domains are associated with an intense G-band and the presence of 2D band. The ratio of integrated areas or intensities of disordered and ordered bands (I_D/I_G) is widely used to evaluate the degree of disorder.^[44] However, it is essential to note that, when calculating the I_D/I_G ratio of disordered carbons correctly, the integrated area of the D and G bands provides a more accurate result than their intensity.^[45–47] Following the D and G band intensities (i.e., the heights of D and G peaks) can give misleading information for porous carbons which present a disordered structure.^[21,45] Sadezky *et al.*^[42] used the peak areas for reliable calculation of I_D/I_G of different industrial carbon black materials. The pioneering work of Ferrari *et al.*^[40] mentioned that in the case

of amorphous/disordered carbon, it is misleading to use only the I_D/I_G ratio calculated based on the peak intensities (i.e., heights). The widening of the D peak is associated with a distribution of clusters that have different orders and dimensions. Hence, the information on the less distorted aromatic rings (six rings) is reflected in the maximum intensity rather than the width, which is contingent upon the disorder. Ring orders other than six, typically diminish the peak height and increase its width. Therefore, when dealing with disordered materials, it is important to consider the peak width as well as its area. Additionally, the procedure of the deconvolution of the peaks might affect the I_D/I_G ratio.

First, spectral parameters of salt-templated carbons were determined based on the two peaks deconvolution utilizing the Lorentzian fitting function (Figure S3a, b, Supporting Information), and the values are summarized in Table S3 (Supporting Information). The I_D/I_G ratios determined by the integrated area of D and G bands indicate that among all salt-templated carbons, a clear trend is observed; the LiCl/NaCl-T carbon has the most ordered structure with the lowest I_D/I_G area (2.01), while CsCl-T carbon presents the most disordered structure (I_D/I_G area = 2.41). A similar trend is observed when compared with I_D/I_G calculated from the intensities of D and G bands.

The full width at half maximum (FWHM) of the D band facilitates as well the qualitative analysis of the structural disorder of the carbon materials.^[40] The FWHM of the D band supports the tendency of the I_D/I_G ratios, with a wider D band associated with the most disordered salt-templated carbon (CsCl-T). The two peaks deconvolution is very facile to realize and at the same time provides meaningful spectral information.

However, some authors have reported that the implementation of the four-peak analysis yields a piece of more precise information than the two-peak analysis for carbons exhibiting different levels of disorder.^[42,48] Therefore, a four-peak deconvolution using the Lorentzian fitting function was also performed (Figure S3c,d, Supporting Information) and spectral parameters are gathered in Table S4 (Supporting Information). Interestingly, more insightful details related to the structural defects (D_1 band) can be concluded, associated with the presence of additional D_2 and D_3 bands after the deconvolution. The D_2 and D_3 bands are rather challenging to observe as they are inside the D and G regions, and for highly defective materials, the D and G bands exhibit broadness, resulting in the D_2 band visibility only as a shoulder in the overall spectrum.^[49] Sadezky *et al.*^[42] mentioned that the D_1 band ($\approx 1350\text{ cm}^{-1}$) displays a shoulder at $\approx 1180\text{ cm}^{-1}$, denoted as the D_2 band, which provides evidence for the existence of sp^2 - sp^3 bonds or C–C and C=C stretching vibrations of polyene-like structure. Some other authors claim that the origin of the D_2 band comes exactly from transpolyacetylene segments at grain boundaries and surfaces^[50] or sp^2 -based transpolyacetylene-like chains at layer edges.^[51] According to Merlen *et al.*^[49] the D_2 band (sometimes called TPA for trans-polyacetylene) has been applied to fit the Raman spectra of disordered materials like amorphous carbons with some local order (sp^2 aromatic domains). The elevated intensity $\approx 1500\text{ cm}^{-1}$, between D_1 and G bands can be indicated as the D_3 , which comes from the amorphous carbon fraction, comprising organic molecules, fragments, or functional groups.^[42] Beyssac *et al.*^[52] reported that the D_3 band is present only as a very wide band in poorly crystallized carbonaceous materials and attributed the band to defects outside the plane

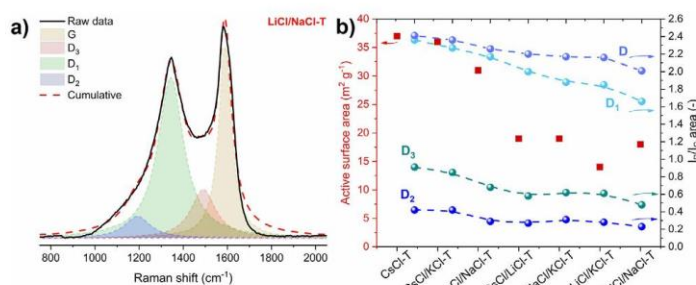


Figure 2. a) Raman spectrum of the most graphitic-like salt templated carbon LiCl/NaCl deconvoluted into four peaks using Lorentzian fitting function, b) graphical representation of the dependence of active surface area and the degree of disorder (I_{D_1}/I_G area (two peaks fitting), I_{D_1}/I_G area, I_{D_2}/I_G area (four peaks fitting)) for salt templated carbons.

of aromatic layers like tetrahedral carbons. An example of such detailed peak deconvolution of Raman spectra for LiCl/NaCl-T carbon is presented in **Figure 2a**. Visually, the intensity and peak area after four peaks deconvolution (Figure S3c, d, Supporting Information) of both D₂ and D₃ bands vary from the highest for CsCl-T (more disordered) carbon to the lowest for LiCl/NaCl-T (more ordered) carbon. Moreover, four-peak fitting is more accurate, since the cumulative curve matches better the raw data, than simple two-peak fitting as shown in Figure S3a, b (Supporting Information). Taking into account, the fitted peak areas, the highest value of D₁, D₂, and D₃ peak areas as well as the maximum I_{D_1}/I_G , I_{D_2}/I_G , and I_{D_3}/I_G area ratios are noted for CsCl-T carbon, while the lowest values of these spectral parameters correspond to LiCl/NaCl-T carbon. FWHM of the D₁, and D₂ bands and the ratio of FWHM of D₁, and D₂ bands (respectively) related to the area of the G band support the tendency observed for spectral parameters mentioned already. A slightly weaker tendency is visible for the FWHM of the D₃ band and the FWHM of the D₃ band related to the area of the G band. The spectral parameters after four peaks deconvolution are summarized in Tables S4 and S5 (Supporting Information). Despite several advantages of Raman spectroscopy, comprehensive information can be obtained from temperature programmed desorption coupled with mass spectrometry (TPD-MS) and active surface area (ASA) estimation.

TPD-MS can successfully quantify the extent of defects and active sites by quantifying the active surface area, ASA.^[53] The ASA is associated with various defects found not necessarily only at the carbon edges, including stacking faults, single/multiple vacancies, and dislocations. The existence of these active sites is crucial, as they have the ability to engage with other species in the electrolyte, and even improve the capacitance.^[31] The ASA is established through the chemisorption of O₂ on a salt-templated carbon which is exempt from functional groups (removed during the 1st heating step of TPD-MS), followed by the quantification of the oxygenated complexes that are formed. The evaluation of this parameter requires a particular equipment configuration and calculation method that is relatively rarely described in the existing literature,^[54] with only a limited number of studies documenting such values. In particular, most studies were done on graphitic

or more ordered hard carbon materials,^[55] and information on activated carbons is missing. Only recently a protocol has been developed for accurate determination of ASA for porous activated carbons.^[56] The reported active surface area values vary from 37 m² g⁻¹ for CsCl-T to 18 m² g⁻¹ for LiCl/NaCl-T, as summarized in **Table 1**. Figure 2b illustrates the correlation of active surface area vs. I_{D_1}/I_G area ratios. Such a dependence was not reported before. It can be concluded that the highest active surface area, and the highest disorder degree of the salt-templated carbons, highlight the contribution of the D₃ band which is associated with the presence of functional groups. Nevertheless, O-groups are bonded on some edge defects, while there are topological defects in the graphene basal planes as well.

2.2. Carbon Surface Chemistry

To further understand the material surface chemistry, TPD-MS was used to determine the oxygen functional groups that exist within the salt-templated carbon structure.^[57] TPD-MS is often a more judicious choice over X-ray photoelectron spectroscopy (XPS) for analyzing carbon materials. It offers the possibility to analyze the surface chemistry in the bulk of carbon materials (in contrast to XPS, where only a top few nanometers of the material are analyzed). TPD-MS is performed by heating to 900°C the materials, and the O-functional groups undergo decomposition, resulting in the release of CO, CO₂, H₂O, and H₂ at the temperatures that align with their thermal stability (Figure 3a,b; Figure S4, Supporting Information). The main released gases during heating up the salt-templated carbons are CO₂ and CO. The quantity of functional groups when examining salt-templated carbons is also of significant interest. In general, CO₂ is emitted due to the presence of mainly acidic groups, specifically carboxyl, anhydride, and/or lactones, whereas CO is obtained from the decomposition of groups such as phenol, ether, carbonyl, and quinone.^[58,59] One main peak is visible in the CO₂ desorption curve (Figure 3a) for all carbons in the temperature range of 150–400°C with a maximum intensity at 250°C. The occurrence of CO₂ groups primarily originates from the breakdown of carboxyl groups at 250°C, however, within the

Table 1. Textural properties determined by nitrogen adsorption (SSA, V_{micro} , $L_{0\text{micro}}$, V_{meso} , $L_{0\text{meso}}$, V_{total}), disorder degree obtained by Raman spectroscopy (I_{D1}/I_G area), quantities of gases released (CO_2 , CO) during TPD-MS, and ASA of salt templated carbons.

Material	SSA [m^2/g]	V_{micro} [cm^3/g]	$L_{0\text{micro}}$ [nm]	V_{meso} [cm^3/g]	$L_{0\text{meso}}$ [nm]	V_{total} [cm^3/g]	I_{D1}/I_G [-]	CO_2 [mmol/g]	CO [mmol/g]	ASA [m^2/g]
CsCl-T	2640	0.97	0.91	0.16	4.49	1.13	2.36	0.78	1.30	37
CsCl/KCl-T	2446	0.92	0.86	0.15	4.70	1.07	2.27	0.73	1.37	36
CsCl/NaCl-T	2456	0.92	0.87	0.15	5.27	1.07	2.17	0.74	1.40	31
CsCl/LiCl-T	2202	0.83	0.85	0.12	4.52	0.95	2.00	0.62	1.06	19
NaCl/KCl-T	1949	0.72	0.77	0.24	5.89	0.96	1.88	0.64	1.03	19
LiCl/KCl-T	1600	0.61	0.73	0.10	5.57	0.71	1.85	0.58	1.05	14
LiCl/NaCl-T	1453	0.52	0.75	0.42	8.45	0.94	1.66	0.77	1.26	18

temperature rise, the CO_2 peak exhibits shoulder $\approx 550^\circ\text{C}$, which is more pronounced for LiCl/KCl-T, and CsCl-T and results from carboxylic anhydrides and lactones, according to the deconvolution presented in the Figure S5 (Supporting Information). The CO desorption rate profiles exhibit one principal peak, with a maximum at 799°C for CsCl-T, CsCl/NaCl-T, CsCl/KCl-T, NaCl/KCl-T and with a maximum at 862°C for CsCl/LiCl-T, LiCl/NaCl-T, LiCl/KCl-T (Figure 3b). This CO peak can be deconvoluted and quantified into more stable oxygen groups (Figure S5, Supporting Information), which occur at high temperatures such as carbonyl/quinone ($800\text{--}850^\circ\text{C}$), phenol/ether ($400\text{--}800^\circ\text{C}$), and anhydride ($500\text{--}800^\circ\text{C}$). It can be noted that this shift of the CO peak for the latter materials is accompanied by a change in its shape, which becomes narrower, indicating the presence of more stable O-groups, such as carbonyl/quinone. The total quantities of released gases during TPD and the exact amounts of oxygen functional groups were determined by the integration and deconvolution of the TPD-MS peak area, respectively (Figures S4 and S5a–d, Supporting Information), and presented as a column plot for better visibility (Figure 3c). For all materials, carbonyl/quinone is the most predominant group, followed by carboxyl and phenol/ether. Anhydride and lactone are present in lesser amounts. Therefore, the basic groups are more abundant than acidic groups on the surface of the materials, while (NaCl/KCl-T, CsCl/LiCl-T, LiCl/NaCl-T, and LiCl/KCl-T) present less O-functional groups compared to CsCl-based materials. Interestingly, Figure 3d shows that total gas quantities (CO_2 , CO), correlates with ASA increase. A high active surface allows more O-groups to bond on the surface, which might be beneficial for pseudo-capacitive reactions.

Additionally, besides the desorption of CO_2 groups, water, and hydrogen are also desorbed in small quantities (Figure S4, Supporting Information). The origin of the water is dual, comprising physisorbed water (low temperatures) and water generated in situ by the side reactions of oxygen functional groups during heating.^[60] A small amount of hydrogen is released at elevated temperatures, attributed to the breaking of C–H bonds and carbon arrangements.

2.3. Textural Properties of Salt Templated Carbons

Textural properties of salt-templated carbons were determined by the sorption of nitrogen at 77K, and the sorption of carbon

dioxide at 273K. Nitrogen sorption is the most commonly used method to investigate parameters such as specific surface area and pore size distribution, which are important for the performance of EDLCs. Moreover, to achieve high power and high capacitance of EDLCs, the ion size of the electrolyte must be smaller than (or equal to) the pore size of the electrode material. Nitrogen sorption isotherms of salt-templated carbons are shown in Figure 4a, and according to the IUPAC classification, are of type I/IV, indicating mostly microporous materials with a fraction of mesopores.

The substantial increase in the quantity of adsorbed nitrogen at low relative pressures is linked to the micropores resulting from the degradation of phenolic resin (carbon precursor) and the templating effect of salt. The observed hysteresis loop at elevated relative pressures refers to the self-organization of resin/soft-template within the macromolecular framework and the subsequent decomposition of the template, resulting in mesoporosity creation. The formation of micelles and mesoporosity probably also was affected by the salt template, explaining the different hysteresis shapes/sizes. The values of specific surface areas are summarised in Table 1 and range from $2640\text{ m}^2\text{ g}^{-1}$ for CsCl-T to $1453\text{ m}^2\text{ g}^{-1}$ for LiCl/NaCl-T.

Figure 4b shows the pore size distribution of salt-templated carbons, with the indication of two regions up to 2 nm (micropores) and 2–10 nm (mesopores). Micropores appear as the most interesting ones in the charge storage mechanism (EDL formation), while mesopores create pathways for electrolyte ions to reach the micropores.^[61] The $L_{0\text{micro}}$ of all carbons does not exceed 0.91 nm (the most disordered CsCl-T), while the lowest value 0.73 nm is reached by the more ordered LiCl/KCl-T. The $L_{0\text{meso}}$ changes in the opposite direction, with the larger average size (up to 8.45 nm) for the most ordered materials and the smaller average size (up to 4.49 nm) for the more disordered materials. Figure 4c displays a column plot with the repartition of the volume of micropores and mesopores within the total pore volume. The highest micropore volume is observed for the most disordered carbon, CsCl-T ($0.97\text{ cm}^3\text{ g}^{-1}$), and this volume changes only slightly when CsCl is combined with other salts, which emphasizes the strong effect of CsCl on pore formation: CsCl/KCl-T ($0.92\text{ cm}^3\text{ g}^{-1}$), CsCl/NaCl-T ($0.92\text{ cm}^3\text{ g}^{-1}$), and CsCl/LiCl-T ($0.83\text{ cm}^3\text{ g}^{-1}$). When mixtures of Li, Na, and/or K chlorides are used, in the absence of CsCl, the micropore volume decreases, as a result of the predominant effects of these salts for graphitization of materials: NaCl/KCl-T ($0.72\text{ cm}^3\text{ g}^{-1}$), LiCl/KCl-T

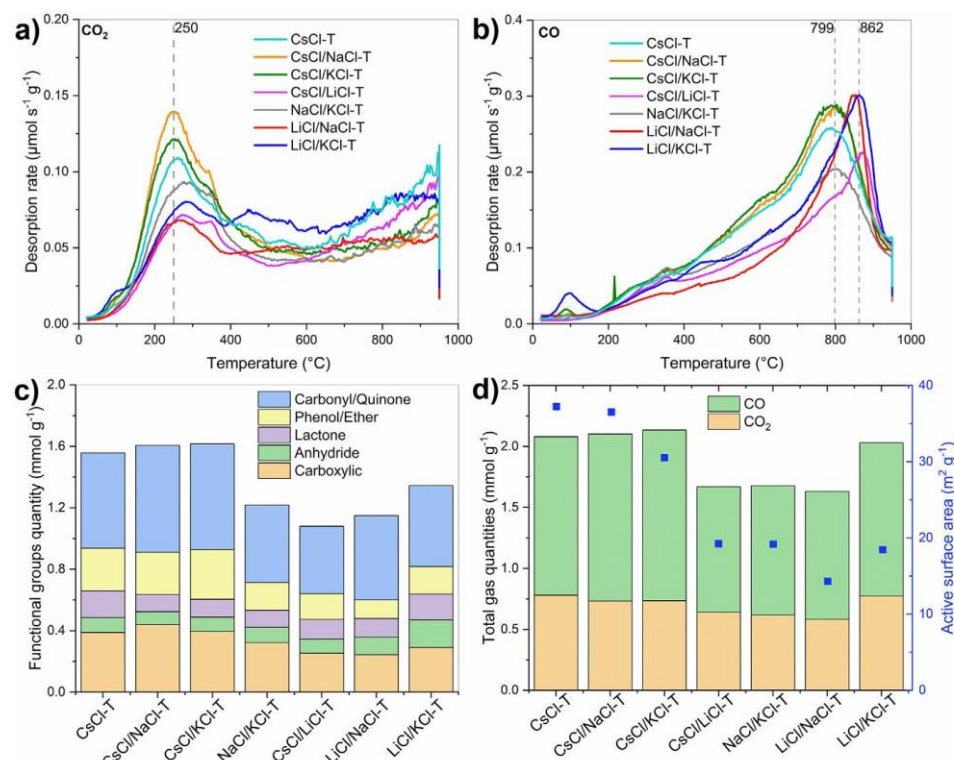


Figure 3. TPD-MS gas desorption profiles of salt-templated carbon materials for a) CO_2 , b) CO . Amounts of c) oxygen functional groups released determined by the deconvolution of the TPD-MS peaks area, d) total gas quantities (CO , CO_2) and active surface area for salt templated carbon materials.

($0.61 \text{ cm}^3 \text{ g}^{-1}$), LiCl/NaCl ($0.52 \text{ cm}^3 \text{ g}^{-1}$). In addition, for the latter materials, the maximum volume of mesopores (0.42 and $0.24 \text{ cm}^3 \text{ g}^{-1}$ for $\text{LiCl}/\text{NaCl-T}$ and $\text{NaCl}/\text{KCl-T}$, respectively) is achieved and can be attributed to the voids between stacked graphene-like layers. The decomposition of soft-template and the carbon-cation interactions resulted in the formation of such graphitic domains and mesopores. Additionally, lithium and sodium cations have the highest hydration enthalpies among all used cations; therefore, the biggest hydrated ion diameter influenced the formation of micelles and enhanced the ratio of mesopores (Table S2, Supporting Information). All parameters (SSA , V_{micro} , $L_{0 \text{ micro}}$, V_{meso} , $L_{0 \text{ meso}}$) based on nitrogen sorption data are summarised in Table 1. Then, for further investigation of the microporosity of salt-templated carbons, sorption of carbon dioxide at 273 K was used (Figure 4d; Table S6, Supporting Information). The CO_2 molecule can access the ultramicropores ($< 0.7 \text{ nm}$) due to its size and better diffusion, which is favored by the higher analysis temperature (273 K) than for N_2 sorption (77 K). The volume of ultramicropores calculated with CO_2 sorption data

exhibited lower values compared to those assessed through N_2 sorption, with the lowest volume for the most ordered carbon ($\text{LiCl}/\text{NaCl-T}$) and the highest for the most disordered carbons (CsCl-T , $\text{CsCl}/\text{KCl-T}$). However, it is noteworthy that $\approx 50\text{--}60\%$ of the specific surface area is placed in the ultramicropores region. It means that the pore confinement in the range from 0.3 to 0.7 nm plays an important role in the charge accumulation. The findings on the synthesized salt-templated carbon texture indicated that alkali cation sizes affect micropore volume and average diameter – larger cation sizes correspond to increased micropore volume and average diameter of micropores, consistent with the SSA values.

2.4. Electrochemical Investigation of Salt Templated Carbons

The electrochemical investigation started with the construction of two-electrode EDLCs employing electrodes prepared from salt-templated carbons, $1 \text{ M Li}_2\text{SO}_4$ as the electrolyte, and glass fiber

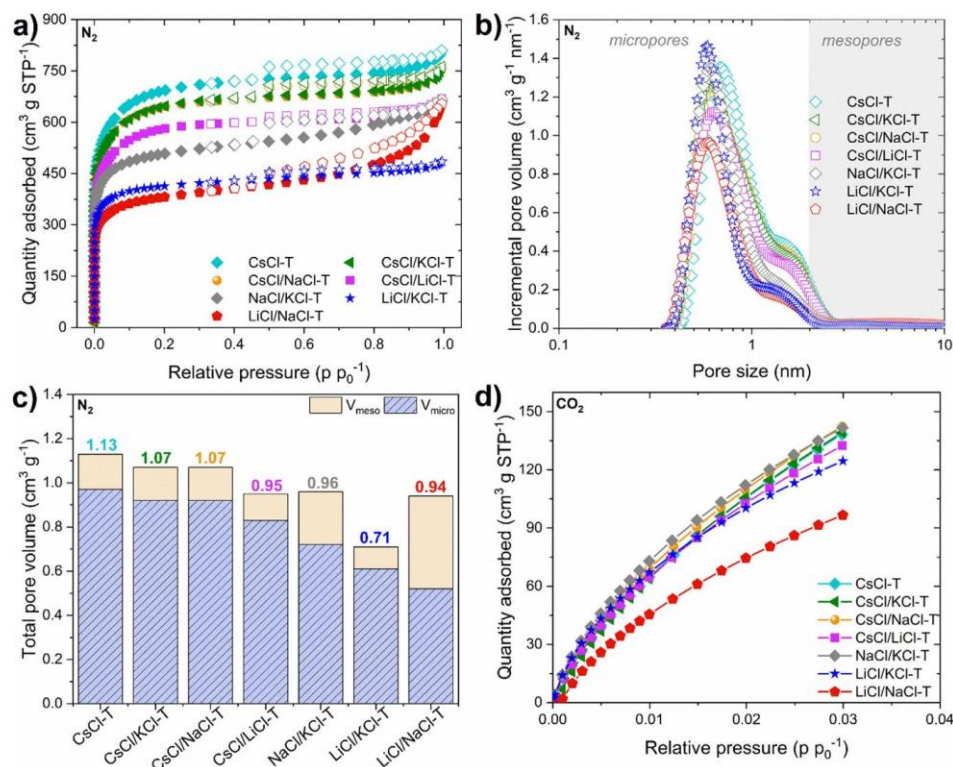


Figure 4. a) Nitrogen adsorption/desorption isotherms at 77K, b) pore size distribution for nitrogen adsorption using 2D-NLDFT heterogeneous surface model from SAIEUS software, c) total pore volume and repartition of pore volumes (micro and meso) determined from nitrogen adsorption, d) carbon dioxide adsorption isotherms at 273K of salt templated carbons.

as a separator. The maximum stable operating voltage of the system was set as 1.6 V according to previous studies on the stability of 1M Li_2SO_4 as an electrolyte.^[7,62] The voltammograms of all the systems are presented in Figure 5a (5 mV s^{-1}) and Figure S6a,b (Supporting Information) ($100, 200 \text{ mV s}^{-1}$). The CV curves at 5 mV s^{-1} displayed an ideal, rectangular shape, indicating pure electrostatic attraction of ions. Therefore, the charge storage mechanism is based on the formation of an electrical double layer. The characteristic shape of CV curves suggests optimal accessibility of ions to pores and adequate conductivity of the electrode materials. However, the voltammograms at elevated scanning rates, i.e., $100, 200 \text{ mV s}^{-1}$, show a slight deviation from the typical rectangular shape with a decrease in capacitance (Figure 5b; Figure S6a,b, Supporting Information).

As demonstrated by the galvanostatic charge/discharge curves at 1 A g^{-1} , all EDLCs based on salt-templated carbons exhibited an ideal triangular shape (Figure 5c). The capacitance values calculated by integrating area under the discharge curve at 1 A g^{-1}

range from 197 F g^{-1} for CsCl-T, to 100 F g^{-1} for LiCl/NaCl-T-based EDLCs. Salt-templated carbons present higher capacitance values than typically used commercially available carbons, as shown in Table S7 (Supporting Information).

The energetic efficiency during galvanostatic charging/discharging was calculated by dividing the integrated values of discharge and charge energy, then multiplying by 100 to express the final value as a percentage, following the approach outlined in ref.[63]. The energetic efficiency at 1 A g^{-1} ranges from 84% for CsCl-T to 70% for NaCl/KCl-T-based EDLCs. At extremely high current regime (10 A g^{-1}), when the electrode material is requested for rapid charge/discharge ($\approx 12 \text{ s}$), deviation from an ideal triangular shape of GCD is observed, with a decrease in initial capacitance of almost half, i.e., from 185 F g^{-1} at 0.2 A g^{-1} to 95 F g^{-1} at 20 A g^{-1} (capacitance retention 51%) for CsCl/NaCl-T based EDLC (Figure S7a,b, Supporting Information). However, if a system works well at high current densities ($> 10 \text{ A g}^{-1}$) it indicates that such EDLC

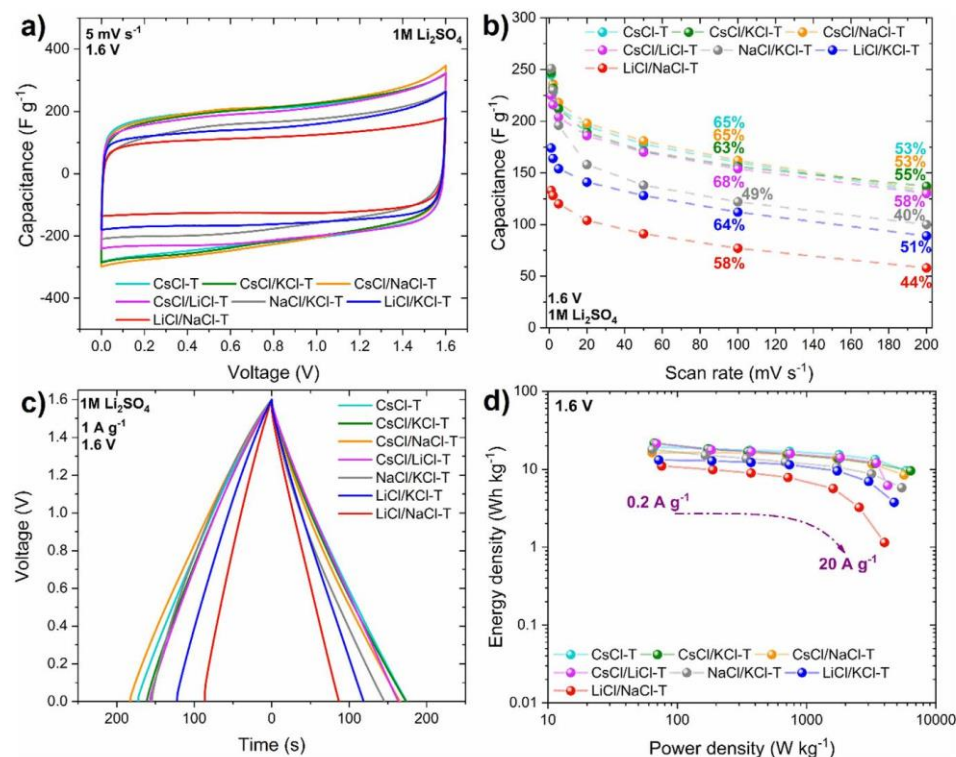


Figure 5. Electrochemical performance of salt-templated carbons-based EDLCs operating in 1M Li₂SO₄ at 1.6 V: a) cyclic voltammetry at 5 mV s⁻¹, b) gravimetric capacitance (F g⁻¹) vs. scan rate (mV s⁻¹), c) galvanostatic charge/discharge at 1 A g⁻¹, d) Ragone plot.

is characterized by quite good electrochemical performance with fast kinetics and good charge propagation desired for high-power applications. The effect of the beneficial properties of salt-templated carbons on the energy and power metrics of EDLC is evident in the Ragone plot (Figure 5d). Specific energy higher than 10 Wh kg⁻¹ is observed in the wide power range.

Charge propagation of capacitor materials was examined using electrochemical impedance spectroscopy, and results are presented in Figure S7c,d (Supporting Information). The Nyquist plot (Figure S7c, Supporting Information) reveals relatively similar equivalent series resistance values, ranging from 0.49 Ω for CsCl/KCl-T to 0.61 Ω for LiCl/KCl-T based EDLCs. These values do not provide a trend, the resistance of the system can be impacted by the cell assembly.^[64] In the high-frequency zone, the graphs exhibit a semicircle, followed by a linear segment in the low-frequency region. Capacitance retention as a function of frequency (Figure S7d, Supporting Information) illustrates a clear plateau in the low frequencies, indicating a purely capacitive charge. Moreover, the charge capability is slightly increased

in the case of EDLCs based on carbons utilizing cesium cation as a salt template, resulting in improved ion mobility inside the porosity.

Volumetric capacitance is a crucial parameter, especially from the industrial point of view, where compact and miniaturized devices including wearable electronics require reduced space. Figure S8 (Supporting Information) shows the volumetric capacitance vs. current density for salt-templated carbons-based EDLCs operating in 1M Li₂SO₄ up to 1.6 V.

The values range from 77 F cm⁻³ for the most porous carbons (based on the cesium salt template) to 49 F cm⁻³ for more ordered carbons (based on the lithium salt template) at 1 A g⁻¹. A trend is consistent for both the gravimetric and volumetric capacitances of salt-templated carbons. Self-discharge is an unavoidable issue for EDLCs that refers to the loss of voltage and finally stored energy.^[65] This voltage drop occurs when EDLC remains at open circuit condition for 12 h after charging.^[66] The main causes of self-discharge are charge redistribution in pores,^[67] faradaic reactions,^[68] and so-called ohmic leakage.^[69]

Galek et al.^[70] reported that the voltage dropped from 1.6 to 0.97 V (39% loss of the voltage) for EDLC based on commercial carbon YP80F electrodes and 1M Li₂SO₄ as the electrolyte. In comparison, the EDLCs based on salt-templated carbons and the same electrolyte show slightly reduced loss of the voltage ranging from 29% for LiCl/NaCl-T to 36% for CsCl-T, LiCl/NaCl-T, and LiCl/KCl-T (Figure S9, Supporting Information). When the electrochemical behavior of positive and negative electrodes of EDLCs based on selected carbons (CsCl-T and LiCl/NaCl-T) is studied individually at relatively low current density and scan rate, nearly square-shaped cyclic voltammograms, and ideal triangular-shaped galvanostatic charge/discharge curves are observed for LiCl/NaCl-T based EDLC (Figure S10c,d, Supporting Information). It is analogous to characteristics obtained in the same electrolyte (1M Li₂SO₄).^[71] Contrarily, there is a visible deviation from ideal CV and GCD curves for CsCl-T-based EDLC (Figure S10a,b, Supporting Information). In the case of the most disordered carbon (CsCl-T), the decomposition of the electrolyte (1M Li₂SO₄) is more significant due to the presence of a higher amount of oxygenated functionalities and a more defective structure. The decomposition of the electrolyte also takes place in LiCl/NaCl-T-based EDLCs, however, it is less evident due to the lower amount of surface functionalities. Also, the shape of CV is more resistive for CsCl-T carbon-based EDLC owing to higher disorder, i.e., less conductivity of the material. In addition to the importance of enhancing the energetic performance of EDLCs, the electrochemical stability, and long-term performance are also recognized as critical factors. Galvanostatic cycling stands out as a widely predictable and frequently employed method for achieving that objective. Nonetheless, this technique demands a substantial amount of time. Herein, a less time-demanding voltage holding test, commonly referred to as floating, and widely employed in the industry, is used to demonstrate the lifespan stability of EDLCs based on selected salt-templated carbons and 1M Li₂SO₄ as an electrolyte.^[72]

Each EDLC was charged to a maximum voltage of 1.6 V (1 A g⁻¹), subsequently maintaining a voltage hold at 1.6 V for 2 h. During each voltage hold, additionally, CV and EIS were recorded. Capacitance and equivalent series resistance (ESR) values were assessed every 2 h until at least one of the end-of-life criteria was reached. Three carbons with differences in properties and performance were selected for long-time performance testing, i.e., the most porous/less graphitic (the highest capacitance) CsCl-T, the more graphitic/less porous (lower capacitance) LiCl/KCl-T and intermediate porosity-graphitization and performance NaCl/KCl-T. As can be seen in Figure 6a, the plot of relative capacitance vs. aging time at 1.6 V shows that a 20% decrease of initial capacitance was reached after 30 h for CsCl-T, 40 h for NaCl/KCl-T, and 288 h for LiCl/KCl-T based EDLCs. The second end-of-life criterion, i.e., a 100% increase of relative resistance, was reached only in the case of LiCl/KCl-T-based EDLC, after 288 h. Other systems based on CsCl-T and NaCl/KCl-T reached a 150% and 120% increase in relative resistance, respectively (Figure 6b). Interestingly, from the industrial point of view, the term end-of-life is extended by the device application.^[73] End-of-life based on capacitance retention is more crucial in the case of prolonged pulses, while end-of-life caused by resistance retention is more important for brief, high-power pulses.^[72] Therefore, the differences in reaching end-of-life criteria by the EDLCs based on

salt-templated carbons may extend the variety of possible applications.

The wettability of electrode materials by the electrolyte is crucial for efficient EDL formation, significantly impacting the performance of the device. Good wettability increases the ion-accessible surface area, facilitates ion diffusion within the porosity and promotes ion mobility.^[74] Therefore, insufficient wettability results in underutilization of surface area, which in turn leads to diminished gravimetric capacitance and retention at fast regimes. The contact angle value measured for CsCl-T is the lowest one, i.e., 111°, indicating a more hydrophilic surface compared to 127° for NaCl/KCl-T and 131° for LiCl/KCl-T (Figure 6c). Indeed, the highest amount of O-containing functional groups for CsCl-T improves the wettability of the material and can slightly improve electrochemical performance by providing more pseudocapacitance.^[75]

The voltammograms and galvanostatic charge/discharge curves for EDLCs before and after prolonged floating (Figure 6d–f; Figure S11a–c, Supporting Information) show a significant decrease in capacitance at voltages exceeding 0.8 V. EDLCs polarised at $U_{max} = 1.6$ V are susceptible to the parasitic reactions. The humps (visible especially for LiCl/KCl-T, Figure 6f) are linked to the redox activity of O-groups and pH variation of the electrode/electrolyte interface.^[76] Partial oxidation of the positive electrode may occur due to the prolonged floating time due to the carbon corrosion involving side reactions accompanied by the emission of CO and CO₂. It results in the production of solid-state deposits (Li₂CO₃) due to the reaction of electrolyte with CO₂ by-products of carbon corrosion, which gradually blocks the porosity at elevated voltage.^[77,78] Figure 6g–i illustrates the impact of accelerated aging on the Nyquist plots of EDLCs based on selected carbons. The slight increase in resistance is visible for CsCl-T (ESR +50%) and for NaCl/KCl-T (ESR +20%) based EDLCs. A noticeable, two-fold increase of resistance is obvious for the LiCl/KCl-T-based system, which reached two end-of-life criteria after the longest time (288 h). Concluding, the aging of the systems operating in such electrolytes is primarily attributed to the decline in electrode performance due to the formation of new surface functionalities,^[7] collapse of porosity,^[78] pH modification in both electrode/electrolyte interfaces^[7] and possible accumulation of corrosion products originating from the electrode material and/or stainless steel current collectors.^[62] The EDLC based on CsCl-T salt templated carbon reached its end-of-life after only 30 h. The CsCl-T is the most disordered material of all, and its enhanced porosity and O-functionalities are susceptible to adverse structural alternations during ion transport. In contrast, the more graphitic-like and less porous materials exhibit superior long-term performance (LiCl/KCl-T). Obviously, there is a trade-off to be found between the high capacitance values and the lifespan of EDLC.

2.5. Correlation of Salt Templated Carbons Properties with Gravimetric Capacitance

In-depth textural/structural characterization of synthesized salt templated carbons combined with the electrochemical performance of aqueous-based EDLC, allowed significant insights to be gained. Such advanced physicochemical and electrochemical

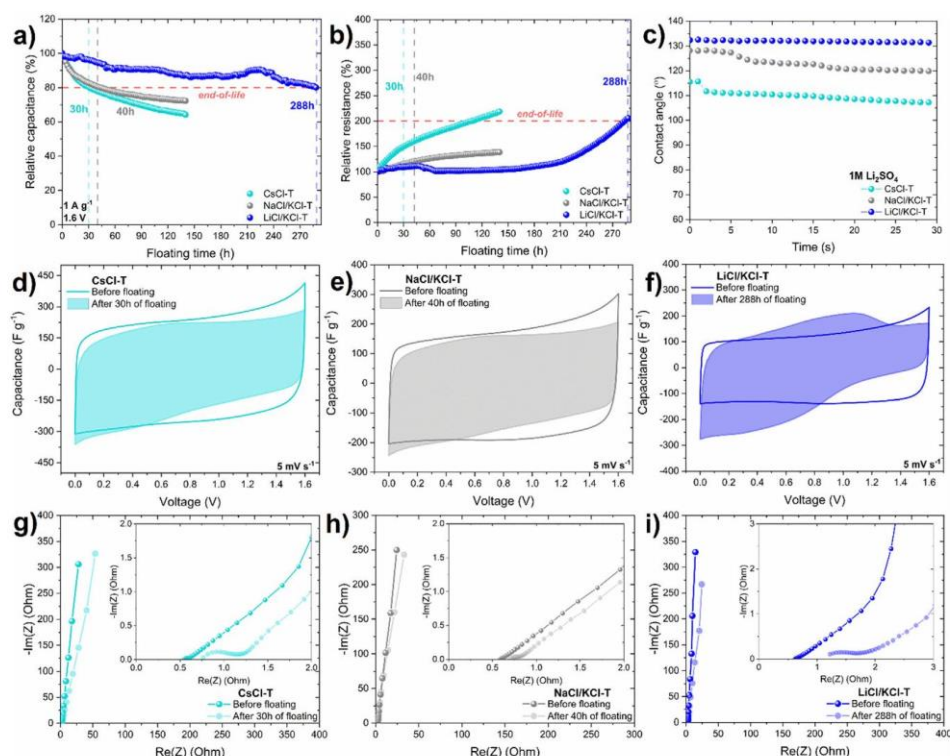


Figure 6. Electrochemical performance of selected salt templated carbons-based EDLCs operating in 1M Li_2SO_4 at 1.6 V, 1 A g^{-1} : a) relative capacitance (%) vs. floating time (h), b) relative resistance (%) vs. floating time (h), c) Contact angle measurements for selected salt templated carbon materials in 1M Li_2SO_4 , d–f) cyclic voltammogram at 5 mV s^{-1} before and after the floating test, g–i) Nyquist plot at 0 V before and after the floating test.

characterization by various and complementary techniques is required to prove that the correlations that were found are reliable and consistent. Moreover, many researchers, while correlating their structural and/or textural findings with gravimetric capacitance, neglect the role of the current density applied and show results in accordance with one selected regime. Figure S12a–c (Supporting Information) presents the correlations of Raman spectral parameters obtained with two peaks fitting (I_D/I_G , FWHM D) and gravimetric capacitance for salt-templated-based EDLCs operating in 1M Li_2SO_4 . The general tendency of higher capacitance values with higher disorder of the materials is observed in each case with good coefficients of determination (R^2). A small deviation from linearity ($R^2 = 0.82$) is shown for capacitance vs. FWHM of the D band, probably caused by the slight inaccuracy of the two peaks fitting procedure. For comparison, the spectral parameters after four peaks fitting and gravimetric capacitance are shown in Figures 7a, S13, and Table S8 (Supporting Information). The findings from the two peaks fitting are confirmed, i.e.,

the more disordered carbons (higher I_{D1}/I_G ratio, higher FWHM D_1) tend to have higher gravimetric capacitances. As more detailed, the spectral parameters after four peaks deconvolution by the Lorentzian fitting function are employed for further analysis and correlations with gravimetric capacitances. Figure 7a,b and Figure S14a–e (Supporting Information) depict the correlation of degree of disorder (I_{D1}/I_G area) with the gravimetric capacitance of carbons operating in 1M Li_2SO_4 at different current densities (0.2 – 20 A g^{-1}). Gravimetric capacitance clearly increases with the higher disorder of the salt-templated carbons (higher I_{D1}/I_G area ratio) as summarized in Table 1, and Table S8 (Supporting Information) with satisfactory R^2 (e.g., 0.91 at 1 A g^{-1} , 0.95 at 20 A g^{-1}). It is clear that, the higher the disorder and amount of defects, the higher the capacitance. The defects in the form of topological and edge sites cause uneven distribution of delocalized electrons in the carbon matrix. Edge-oriented sites are more favorable for the electrostatic attraction of ions.^[79] Additionally, in disordered carbon, the distance between the graphene domains

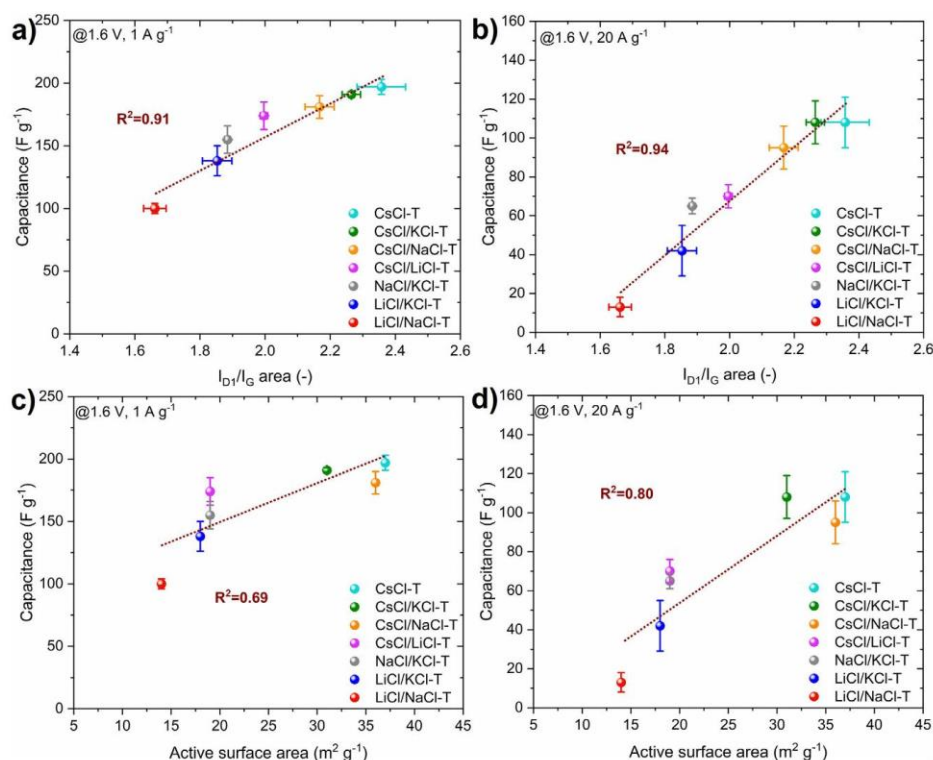


Figure 7. Correlation of gravimetric capacitance and I_D/I_G ratio at different current densities a) 1 A g⁻¹, b) 20 A g⁻¹ of salt templated carbons. Correlation of gravimetric capacitance and active surface area at different current densities c) 1 A g⁻¹, d) 20 A g⁻¹ of salt-templated carbons.

(d_{002}) is much higher than for graphitic carbons (≈ 0.400 nm for very disordered carbon vs. 0.335 nm for graphite).^[80] However, it cannot be precisely calculated in the case of salt-templated carbons due to the absence of a well-defined 002 XRD peak. The larger interlayer spacing in the CsCl-T carbon (as suggested by the extremely broad and low intense 002 XRD peak) allows better ion transport, compared to the LiCl/NaCl-T carbon. The latter presents a more intense, broad 002 XRD peak – linked to the disordered carbon with few stacked graphenes and in addition, a sharp 002 XRD peak – associated with graphite, thus smaller d_{002} distance results in more difficult ion diffusion/adsorption. As the d_{002} from XRD cannot be determined for salt-templated carbons, the Tunstall and Koenig relation can be applied to Raman results to calculate L_a (the size (height) of stacked graphene layers),^[40,81] as summarized in Table S9 (Supporting Information). It is clearly seen that L_a ranges from 7.98 nm for the CsCl-T to 9.56 nm for the LiCl/NaCl-T templated carbon. Therefore, the graphitic domains are increasing with the cation- π binding energy, in line with the TEM results. It is expected that the crystalline structure

of the LiCl/NaCl-T enhances the electron mobility, but more ordered and higher stacked graphitic domains with reduced distance between the graphene layers are contributing to the capacitance decrease (along with SSA decrease). Hence, it is perfectly supporting our correlation of the I_D/I_G ratio vs. capacitance.

In Figure 7c,d, the ASA and gravimetric capacitance correlate with R^2 0.69 (1 A g⁻¹) and 0.80 (20 A g⁻¹) which is in accordance with the Raman findings. It is worth mentioning that the correlation is the most linear at the highest current density applied (20 A g⁻¹), where the activity of surface functionalities is excluded. There is a better correlation with the I_D/I_G than for the ASA vs. capacitance. To explain that behavior, the differences between Raman spectroscopy and ASA estimation must be clarified. Raman spectroscopy is a local technique that analyses ≈ 300 nm of the surface, contrary to the TPD-MS (ASA estimation), where the entire material is analyzed. Moreover, Raman spectroscopy has several advantages, but it has been noted that this type of analysis cannot quantify the exact area occupied by the defects or quantify functional groups present in the

carbon. The ASA is associated with various defects found both on the basal planes and at the carbon edges, including stacking faults, single/multiple vacancies, and dislocations. Nevertheless, during ASA estimation, oxygen functionalities are bonded rather on some edge defects, while there are defects in the graphene basal planes as well (monitored by Raman spectroscopy). Thus, by Raman spectroscopy and ASA, we are not analyzing exactly the same type of defects. Both ASA and Raman spectroscopy are complementary techniques, with slight differences as explained above, therefore, some variations in the correlations with electrochemical performance are possible. Interestingly, a similar dependence of gravimetric capacitance and degree of disorder was proven by NMR studies on activated carbon^[32] and TPD-MS on graphitic nanocarbon.^[31] Moreover, the correlation of gravimetric capacitance vs. I_{D1}/I_G area ratio and FWHM of the D_1 band (respectively) support the recent findings of *Forse et al.*^[48] The discrepancy is observed in the case of the I_D/I_G ratio calculated from peak intensities in the reported work,^[48] which should not be considered as appropriate procedure for disordered carbons. Our investigation of I_D/I_G area ratio vs. gravimetric capacitance has been conducted using an aqueous electrolyte, contrary to the findings of other groups^[48] where the organic electrolyte was applied. In both cases, for aqueous and organic electrolytes, the carbon functional groups may influence the total charge of the carbon.^[82] Certainly, in the aqueous electrolytes, the protonation or deprotonation of certain oxygen-containing groups (e.g., carboxylic, phenolic, carbonyl, quinone) is contingent upon local pH changes. Furthermore, the presence of oxygen surface functionalities, which are often polar, enhances the hydrophilicity of the material.^[83] Such affinity to water can be attributed to the hydrogen bonds formed between water molecules and the surface oxygen atoms.^[84] On the other hand, heteroatoms such as oxygen create active sites for the electrolyte decomposition,^[85] diminishing the conductivity of carbon and, in turn, charge propagation.

Ultimately, it is important to admit that numerous additional variables may influence capacitance, other than simply the local ordering of carbons. Therefore, elemental analysis was used to estimate the % of oxygen, and TPD-MS was used to analyze and quantify the oxygen functionalities that impact the performance of EDLCs. The oxygen content in salt-templated carbons verified by elemental analysis ranges from 2.1% (LiCl/KCl-T) to 3.5% (CsCl/NaCl-T), which can be considered as small amounts (Table S10, Supporting Information). Owing to the careful analysis of TPD-MS results, the amount of CO and CO₂ released by the surface group materials can be correlated with the gravimetric capacitance (Figure 8a). Linear dependence is observed; with a higher quantity of released gases, the gravimetric capacitance is increasing. Elevated amounts of CO and CO₂ are associated with more disordered salt-templated carbons and are linking other findings from Raman spectroscopy and active surface area studies. It can be seen that the R^2 is small (< 0.4). This may be related to the presence of several functional groups on the carbon surface, which have different interactions with the electrolyte, impacting the capacitance in diverse ways.

Indeed, if the exact quantities of surface functionalities determined after deconvolution of TPD-MS peaks are correlated with the gravimetric capacitance at 1 A g⁻¹ (Figure 8b,c), good linear dependence is observed for gravimetric capacitance vs. quantity

of phenol/ether and carboxylic functional groups, with higher R^2 (0.71 and 0.56, respectively), while lack of linearity is observed for carbonyl/quinone, anhydride, and lactone functional groups.

Moreover, it is important to mention that the possible redox activity of surface functional groups is excluded at elevated current densities (i.e., 20 A g⁻¹) due to the insufficient time for redox reactions, therefore, such correlations are slightly inconsistent with gravimetric capacitances recorded at 1 A g⁻¹. Another factor is that not all the defects have a favorable effect on capacitance improvement. In the case of salt-templated carbons, a better correlation of ASA coming from the contribution of phenol/ether and carboxyl groups vs. capacitance was found in our previous work.^[36] Contrary, carbonyl/quinone, anhydride, and lactone-derived ASA did not show high R^2 . The specific surface area and pore size distribution (total volume and average diameter) of the materials are the other factors that influence the gravimetric capacitance as well as the degree of disorder. Figure 8d and Figure S15a (Supporting Information) illustrate the correlation for specific surface area (N₂ sorption at 77K) of salt-templated carbons and gravimetric capacitance of EDLC based on these carbons at 1 and 20 A g⁻¹, respectively. It is evident that gravimetric capacitance rises with the increase of specific surface area, presenting a high coefficient of determination factors, i.e., $R^2 = 0.93$ for 1 A g⁻¹ and $R^2 = 0.95$ for 20 A g⁻¹ current densities. The EDL develops at the carbon/electrolyte interface, according to the formula $C = \epsilon \epsilon_0 S/d$. Consequently, a substantial surface area is inherently required for charge storage. The correlation of SSA vs. capacitance is in accordance with *Platek et al.*^[21] emphasizing that in both cases the materials prepared by the soft-salt templating method, but with different salts, lead to similar results. However, non-linear dependence has also been reported. As mentioned by *Kötz et al.*^[25] the specific capacitance of selected commercial carbons does not show linearity with increasing the SSA over the entire range of values. Specifically, it exhibits a plateau for the values of SSA higher than 1200 m² g⁻¹. This behavior is related to the space constriction for the charge accommodation inside the pore walls (>1200 m² g⁻¹; the pore walls can no longer accommodate the same amount of the charge at a given electrode potential). It is worth mentioning that the authors used organic electrolytes, which present larger molecular size contrary to our studies focused on aqueous electrolytes. In addition, there is no information about the degree of disorder and surface functionalities of the selected carbons, which surely impacts the performance of EDLCs. The gravimetric capacitance in aqueous electrolyte was found as almost proportional to SSA in a series of carbons with progressively modified textural properties by heat treatment at different temperatures, followed by KOH activation.^[29] Moreover, the analysis of electrochemical performance in various electrolytes revealed that adequate pore size is a mandatory requirement to benefit from the high surface area, otherwise, the SSA cannot be fully accessible to the ions. *Lobato et al.* utilized a variety of carbons and found that standard textural characterization by gas adsorption may be very limited in evaluating their actual porosity involved in charge storage.^[23] Selecting the proper approach for gas sorption is crucial to finding the real SSA and pore size distribution. Nevertheless, SSA from the isotherm sorption will never reflect the electrochemically available surface area.

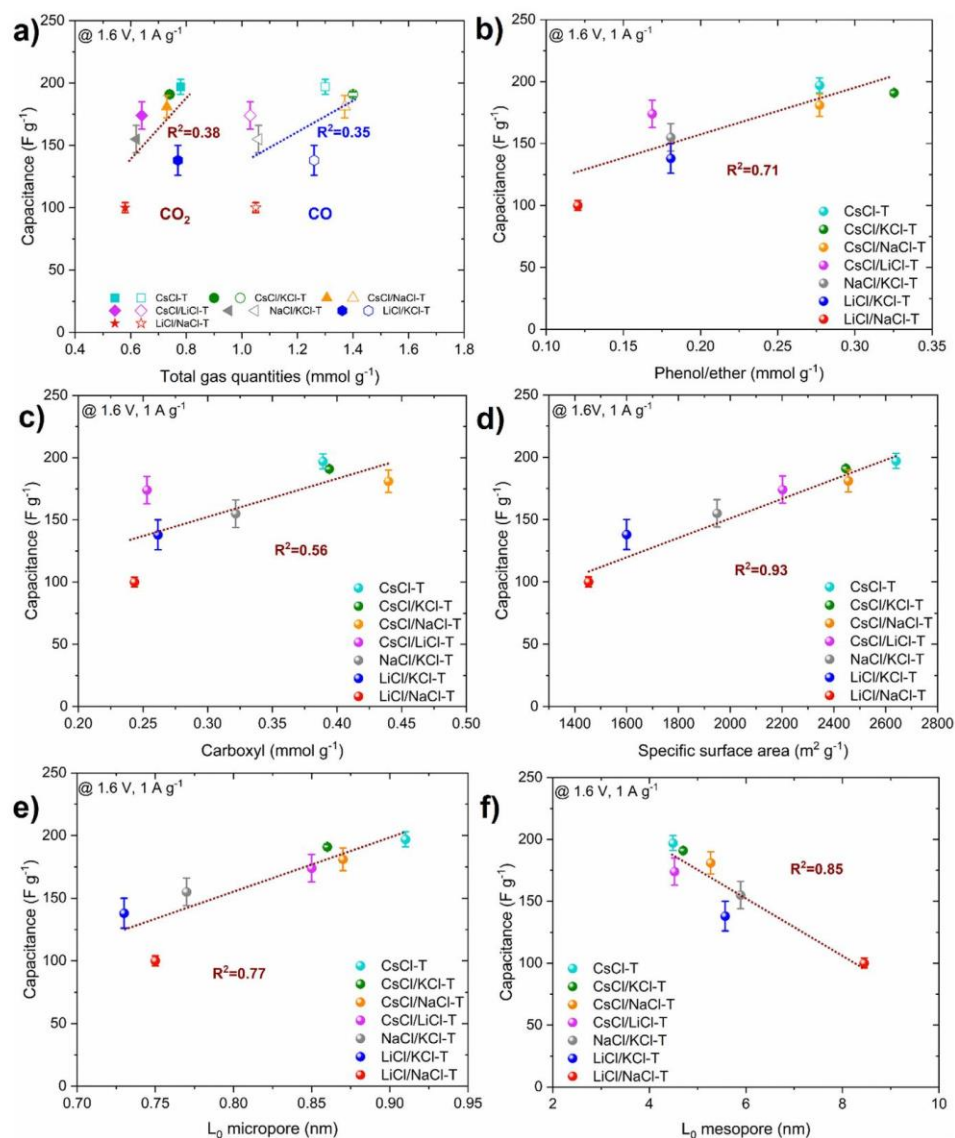


Figure 8. Correlation of gravimetric capacitance ($1\ A\ g^{-1}$, $1.6\ V$) and a) total CO_2 and CO quantities, the quantity of O-functional groups: b) phenol/ether, c) carboxyl, d) specific surface area determined from nitrogen sorption at $77\ K$, e) the average diameter of micropore, f) the average diameter of mesopore of salt templated carbons.

Interestingly, the effective specific surface area (ESSA) is proposed as a link between the textural properties of carbon and storage behavior.^[86] The term ESSA is known also as an accessible specific surface area. It should be emphasized that the SSA determined by the physisorption of the standard N_2 molecule may not access all the pores (small micropores, called ultramicropores), therefore, CO_2 sorption is used as a complementary technique to estimate the volume of ultramicropores (<0.7 nm). These narrow pores are extremely important for EDLCs operating in aqueous medium since desolvated and solvated ions are much smaller than organic/ionic liquid ions. In our series of carbons, a fully accessible specific surface area is involved in charge storage, thus a linear correlation between surface area and capacitance is reported. Therefore, tailoring carbon materials by the so-called matching of the average diameter of micropores with solvated ion dimensions cannot be neglected. Additionally, small mesopores are advantageous for effective dynamic charge propagation and must be taken into account as well.

In Figure 8e,f the average diameter of micropores and mesopores is plotted vs. the gravimetric capacitance at 1 A g^{-1} . A linear dependence is visible in both cases with $R^2 = 0.77$ ($L_{0 \text{ micro}}$) and $R^2 = 0.85$ ($L_{0 \text{ meso}}$). A slight deviation from the linear trend is observed for $L_{0 \text{ micro}}$ vs. gravimetric capacitance for LiCl/NaCl-T carbon. The lowest volume of micropores among all carbons for LiCl/NaCl-T may be caused by the highest ordering of the structure. The capacitance increases linearly with $L_{0 \text{ micro}}$, whereas diminishes in the case of higher mesopores. This illustrates that the gravimetric capacitance increases with the increase of micropore size up to 1 nm (the studied range), while for the mesopores, the smaller pores ($\approx 4 \text{ nm}$) are more efficient than the larger pores ($5\text{--}8 \text{ nm}$). Therefore, the correlation reported herein does not support the anomalous increase of capacitance for pores below 1 nm .^[26] The correlation of capacitance retention vs. $L_{0 \text{ micro}}$ (Figure S15b, Supporting Information) and $L_{0 \text{ meso}}$ (Figure S15c, Supporting Information) shows good linear dependence with R^2 coefficients of 0.73 and 0.75 , respectively. Another factor of importance is the total volume of pores, Figure S15d–f (Supporting Information) shows the correlation of gravimetric capacitance (1 A g^{-1} , 1.6 V) and $V_{\text{ultramicro}}$ ($d < 0.7 \text{ nm}$), V_{micro} ($d < 2.0 \text{ nm}$), and V_{meso} ($d > 2.0 \text{ nm}$), respectively. Despite the discrepancy in volume of the smallest pores measured by distinct adsorbates (N_2 and CO_2), the trend in gravimetric capacitance is the same, i.e., with the highest volume of ultramicropores (Figure S15d, Supporting Information) and micropores (Figure S15e, Supporting Information) the capacitance is increasing with R^2 0.92 and 0.96 , respectively. On the other hand, the relationship of V_{meso} and gravimetric capacitance (Figure S15f, Supporting Information) is the opposite, a smaller volume of mesopores matches with higher capacitances, however, the R^2 is not as high (0.52) as in the case of microporous volume. Additionally, capacitance retention at a high current regime (20 A g^{-1}) vs. V_{micro} (Figure S16a, Supporting Information), and V_{meso} (Figure S16b, Supporting Information) were plotted, respectively and the relationship is similar to the correlations with gravimetric capacitance at 1 A g^{-1} (1.6 V). It clearly shows that mesopores, especially bigger ones, are useless for efficient charge storage.

3. Conclusions

This extensive research offers substantial insights into the importance of tailoring the structure and texture of carbons for enhanced performance of aqueous-based EDLCs. For that purpose, several physicochemical and electrochemical techniques were employed. The optimized salt templating synthesis allowed the preparation of porous carbons with different characteristics. Utilization of alkali metal chloride salts in their eutectic ratio enabled strict control of their melting points, thus ensuring the proper formation of local carbon structure and porosity. The electrochemical investigation of EDLCs based on such a prepared series of carbons and $1 \text{ M Li}_2\text{SO}_4$ revealed good performance, with the highest capacitance of 244 F g^{-1} at 0.2 A g^{-1} (CsCl/KCl-T) and specific energy over 10 Wh kg^{-1} observed in the wide power range at 1.6 V . The longest floating time was reported for LiCl/KCl-T (288 h), while the shortest was for CsCl-T (30 h)-based EDLCs. These results emphasized that the most disordered material, highly microporous, with O-functionalities, is prone to faster degradation. Controversially, the material that is more graphitic, and less microporous, thus with a lower amount of surface functionalities has enhanced long-term performance.

The investigation of Raman spectra of salt-templated carbons has been instrumental in elucidating the local ordering of a series of prepared carbons. Interestingly, the linear dependence of the degree of disorder and gravimetric capacitance of $1 \text{ M Li}_2\text{SO}_4$ -based EDLCs has been found. It was revealed that salt-templated carbons displaying higher disorder, namely those with a higher I_D/I_G ratio, exhibited an increase of gravimetric capacitances at a wide range of current densities. Such findings were supported additionally by the active surface area determination. ASA related to the area occupied by the carbon structural defects presented quite a good correlation with gravimetric capacitances.

Another factor of importance is related to the porosity of salt-templated carbons, i.e., specific surface area and pore size distribution (volume and average diameter of micropores and mesopores). The salt-templated carbons were highly microporous with a specific surface area ranging from $2640 \text{ m}^2 \text{ g}^{-1}$ for CsCl-T to $1453 \text{ m}^2 \text{ g}^{-1}$ for LiCl/NaCl-T. The presence of the mesopores for more ordered carbons (LiCl templated) was also noted since they influence the ion transport. Importantly, a substantial specific surface area is inherently required for the formation of an electrical double layer, thus storing energy in the EDLC. However, the matching of the solvated ion size with the pore size (which has to be bigger or equal to the ion dimension) is the real factor that contributes to the enhanced performance of the EDLC.

Due to the possible interactions of the aqueous medium, which was utilized as an electrolyte for EDLCs with the carbon, the type and quantity of surface functionalities were investigated in detail, to prove the reliability of the provided correlations. Temperature-programmed desorption coupled with mass spectrometry (TPD-MS) allows for monitoring of CO and CO_2 evolution and their deconvolution was matched with temperatures of decomposition of specific oxygen functional groups. The quantity of phenol/ether and carboxyl was substantial, thus showing linear dependence with gravimetric capacitance.

In conclusion, several parameters impact the performance of carbon-based EDLCs, i.e., degree of disorder, specific surface

area, pore size distribution, matching of size/kind of ions used, and surface functional groups. None of these should be ignored. In particular, the role of such parameters must be considered during the selection of the electrode material to achieve the desired EDLC performance. For instance, more disordered carbon, with accessible microporosity matching the solvated ions of the selected electrolyte, but also the presence of some mesoporosity (fast kinetics) and balanced surface functionalities content lead to enhanced gravimetric capacitance but a shorter cycle life. Contrarily, the ordered carbon material with an elevated amount of graphitic domains presents a long-cycling life. In brief, even if highly disordered carbons supply enhanced capacitance, yet, defects are responsible for lifespan shortage.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This research was supported by a French Government Scholarship France Excellence and the Ministry of Higher Education of Poland (Project 0911/SBAD/2501). We acknowledge the ANR-10-LABX-76-01, STORE-EX for supporting this work. Special thanks to L. Vidal for providing TEM images and fruitful discussions, J.M. Le Meins for performing XRD diffraction measurements, and C. Vaultot for assistance in performing N_2/CO_2 sorption experiments.

Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

A.K. performed conceptualization, data curation, formal analysis, investigation, methodology, visualization, and software, and wrote the original manuscript. B.R. performed data curation, visualization, and software. C.M.G.: performed conceptualization, funding acquisition, project administration, supervision, and validation, wrote, reviewed, and edited the final manuscript. E.F. performed conceptualization, funding acquisition, project administration, supervision, and validation, and wrote, reviewed, and edited the final manuscript.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords

active surface area, disordered carbons, electrical double-layer capacitors, microporosity, salt-templated carbons

Received: March 19, 2025
Revised: April 17, 2025
Published online: May 30, 2025

- [1] F. Béguin, V. Presser, A. Balducci, E. Frackowiak, *Adv. Mater.* **2014**, *26*, 2219.
- [2] P. Simon, Y. Gogotsi, *Nat. Mater.* **2020**, *19*, 1151.
- [3] A. Klimek, M. Tobis, E. Frackowiak, *Green Chem.* **2024**, *26*, 6684.
- [4] A. Balducci, *J. of Power Sources* **2016**, *326*, 534.
- [5] T. Lin, I. W. Chen, F. Liu, C. Yang, H. Bi, F. Xu, F. Huang, *Science* **2015**, *350*, 1508.
- [6] L. Demarconnay, E. Raymundo-Piñero, F. Béguin, *Electrochem. Commun.* **2010**, *12*, 1275.
- [7] M. He, K. Fic, E. Frackowiak, P. Novák, E. J. Berg, *Energy Environ. Sci.* **2016**, *9*, 623.
- [8] P. Ratajczak, M. E. Suss, F. Kaasik, F. Béguin, *Energy Storage Mater.* **2019**, *16*, 126.
- [9] E. Frackowiak, F. Béguin, *Carbon* **2001**, *39*, 937.
- [10] A. G. Pandolfo, A. F. Hollenkamp, *J. of Power Sources* **2006**, *157*, 11.
- [11] K. Fic, G. Lota, M. Meller, E. Frackowiak, *Energy Environ. Sci.* **2012**, *5*, 5842.
- [12] S. Pohlmann, *Nat. Commun.* **2022**, *13*, 1538.
- [13] L. Borchardt, M. Oschatz, S. Kaskel, *Mater. Horiz.* **2014**, *1*, 157.
- [14] H. Nishihara, T. Kyotani, *Adv. Mater.* **2012**, *24*, 4473.
- [15] C. Nita, M. Bensafia, C. Vaultot, L. Delmotte, C. Matei Ghimbeu, *Carbon* **2016**, *109*, 227.
- [16] A. Platek, C. Nita, C. Matei Ghimbeu, E. Frackowiak, K. Fic, *Electrochim. Acta* **2020**, *338*, 135788.
- [17] J. Lee, S. Han, T. Hyeon, *J. Mater. Chem.* **2004**, *14*, 478.
- [18] C. Nita, B. Zhang, J. Dentzer, C. Matei Ghimbeu, *J. Energy Chem.* **2021**, *58*, 207.
- [19] C. Decaux, C. Matei Ghimbeu, M. Dahbi, M. Anouti, D. Lemordant, F. Béguin, C. Vix-Guterl, E. Raymundo-Piñero, *J. of Power Sources* **2014**, *263*, 130.
- [20] J. Krishna Mishra, C. S. P. Rao, P. S. C. Bose, N. N. Nath, G. R. Rao, *Defence Science Journal* **2021**, *71*, 289.
- [21] A. Platek-Mielczarek, C. Nita, C. Matei Ghimbeu, E. Frackowiak, K. Fic, *ACS Appl. Mater. Interfaces* **2021**, *13*, 2584.
- [22] R. Heimböckel, F. Hoffmann, M. Fröba, *Phys. Chem. Chem. Phys.* **2019**, *21*, 3122.
- [23] B. Lobato, L. Suárez, L. Guardia, T. A. Centeno, *Carbon* **2017**, *122*, 434.
- [24] E. Taer, A. Agustino, R. Farma, R. Taslim, Awitdrus, M. P., A. Ira, S. D. Yardi, Y. P. Sari, H. Yusra, S. Nurjanah, S. D. Hartati, Z. Aini, R. N. Setiadi, *J. Phys.: Conf. Ser.* **2018**, *1116*, 032040.
- [25] O. Barbieri, M. Hahn, A. Herzog, R. Kötz, *Carbon* **2005**, *43*, 1303.
- [26] J. Chmiola, G. Yushin, Y. Gogotsi, C. Portet, P. Simon, P. L. Taberna, *Science* **2006**, *313*, 1760.
- [27] C. Largeot, C. Portet, J. Chmiola, P.-L. Taberna, Y. Gogotsi, P. Simon, *J. Am. Chem. Soc.* **2008**, *130*, 2730.
- [28] N. Jäckel, P. Simon, Y. Gogotsi, V. Presser, *ACS Energy Lett.* **2016**, *1*, 1262.
- [29] E. Raymundo-Piñero, K. Kierzek, J. Machnikowski, F. Béguin, *Carbon* **2006**, *44*, 2498.
- [30] T. A. Centeno, O. Sereida, F. Stoeckli, *Phys. Chem. Chem. Phys.* **2011**, *13*, 12403.
- [31] G. Moussa, C. Matei Ghimbeu, P.-L. Taberna, P. Simon, *Carbon* **2016**, *105*, 628.
- [32] X. Liu, D. Lyu, C. Merlet, M. J. A. Leesmith, X. Hua, Z. Xu, C. P. Grey, A. C. Forse, *Science* **2024**, *384*, 321.
- [33] J. E. Zuliani, S. Tong, C. Q. Jia, D. W. Kirk, *J. of Power Sources* **2018**, *395*, 271.
- [34] H. Oda, A. Yamashita, S. Minoura, M. Okamoto, T. Morimoto, *J. of Power Sources* **2006**, *158*, 1510.
- [35] T. A. Centeno, M. Hahn, J. A. Fernández, R. Kötz, F. Stoeckli, *Electrochem. Commun.* **2007**, *9*, 1242.

- [36] S. Bonnamy, A. Oberlin, in *Materials Science and Engineering of Carbon*, (Eds.: M. Inagaki, F. Kang), Butterworth-Heinemann, Oxford, UK **2016**, pp. 45–70.
- [37] N. Iwashita, in *Materials Science and Engineering of Carbon* (Eds.: M. Inagaki, F. Kang), Butterworth-Heinemann, Oxford, UK, **2016**, pp. 7–25.
- [38] E. R. Buiel, A. E. George, J. R. Dahn, *Carbon* **1999**, 37, 1399.
- [39] V. Pusarapu, R. N. Sarma, P. Ochonma, G. Gadikota, *Nature* **2024**, 2, 1.
- [40] A. C. Ferrari, J. Robertson, *Phys. Rev. B* **2000**, 61, 14095.
- [41] P. Lespade, R. Al-Jishi, M. S. Dresselhaus, *Carbon* **1982**, 20, 427.
- [42] A. Sadezky, H. Muckenhuber, H. Grothe, R. Niessner, U. Pöschl, *Carbon* **2005**, 43, 1731.
- [43] Z. Li, L. Deng, I. A. Kinloch, R. J. Young, *Prog. in Mater. Sci.* **2023**, 135, 101089.
- [44] M. A. Pimenta, G. Dresselhaus, M. S. Dresselhaus, L. G. Cançado, A. Jorio, R. Saito, *Phys. Chem. Chem. Phys.* **2007**, 9, 1276.
- [45] L. G. Cançado, A. Jorio, E. H. M. Ferreira, F. Stavale, C. A. Achete, R. B. Capaz, M. V. O. Moutinho, A. Lombardo, T. S. Kulmala, A. C. Ferrari, *Nano Lett.* **2011**, 11, 3190.
- [46] D. M. Basko, S. Piscanec, A. C. Ferrari, *Phys. Rev. B* **2009**, 80, 165413.
- [47] E. H. Martins Ferreira, M. V. O. Moutinho, F. Stavale, M. M. Lucchese, R. B. Capaz, C. A. Achete, A. Jorio, *Phys. Rev. B* **2010**, 82, 125429.
- [48] X. Liu, J. Choi, Z. Xu, C. P. Grey, S. Fleischmann, A. C. Forse, *J. Am. Chem. Soc.* **2024**, 45, 30748.
- [49] A. Merlen, J. G. Buijnsters, C. Pardanaud, *Coatings* **2017**, 7, 153.
- [50] A. C. Ferrari, J. Robertson, *Phys. Rev. B* **2001**, 63, 121405.
- [51] C. Hu, S. Sedghi, A. Silvestre Alberio, G. G. Andersson, A. Sharma, P. Pendleton, F. Rodríguez Reinoso, K. Kaneko, M. J. Biggs, *Carbon* **2015**, 85, 147.
- [52] O. Beyssac, B. Goffé, J.-P. Petit, E. Froigneux, M. Moreau, J.-N. Rouzaud, *Spectrochim. Acta, Part A* **2003**, 59, 2267.
- [53] C. del Mar Saavedra Rios, A. Beda, L. Simonin, C. Matei Ghimbeu, in *Na-ion batteries* (Eds.: L. Monconduit, L. Croguennec), Wiley **2021**, pp. 101–146, <https://doi.org/10.1002/9781119818069.ch3>.
- [54] A. Beda, C. Vaulot, F. Rabuel, M. Morcrette, C. Matei Ghimbeu, *Energy Adv.* **2022**, 1, 185.
- [55] C. Matei Ghimbeu, A. Beda, B. Rety, H. E. Marouazi, A. Vizintin, B. Tratinik, L. Simonin, J. Michel, J. Abou Rjeily, R. Dominko, *Adv. Energy Mater.* **2024**, 14, 2303833.
- [56] B. Réty, H. Y. Yiin, C. Matei Ghimbeu, *Energy Storage Mater.* **2025**, 74, 103963.
- [57] C. Qiu, L. Jiang, Y. Gao, L. Sheng, *Mater. Des.* **2023**, 230, 111952.
- [58] J. L. Figueiredo, M. F. R. Pereira, M. M. A. Freitas, J. J. M. Órfão, *Carbon* **1999**, 37, 1379.
- [59] C. Matei Ghimbeu, R. Gadiou, J. Dentzer, D. Schwartz, C. Vix-Guterl, *Langmuir* **2010**, 26, 18824.
- [60] C. Matei Ghimbeu, B. Zhang, A. Martinez de Yuso, B. Réty, J.-M. Tarascon, *Carbon* **2019**, 153, 634.
- [61] L. M. Da Silva, R. Cesar, C. M. R. Moreira, J. H. M. Santos, L. G. De Souza, B. M. Pires, R. Vicentini, W. Nunes, H. Zanin, *Energy Storage Mater.* **2020**, 27, 555.
- [62] S. Azmi, A. Klimek, E. Frackowiak, *Mater. Today* **2023**, 68, 34.
- [63] J. W. Gittins, Y. Chen, S. Arnold, V. Augustyn, A. Balducci, T. Brousse, E. Frackowiak, P. Gómez-Romero, A. Kanwade, L. Köps, P. K. Jha, D. Lyu, M. Meo, D. Pandey, L. Pang, V. Presser, M. Rapisarda, D. Rueda-García, S. Saeed, P. M. Shirage, A. Ślesięński, F. Soavi, J. Thomas, M. M. Titirici, H. Wang, Z. Xu, A. Yu, M. Zhang, A. C. Forse, *J. of Power Sources* **2023**, 585, 233637.
- [64] K. B. Li, D. W. Shi, Z. Y. Cai, G. L. Zhang, Q. A. Huang, D. Liu, C. P. Yang, *Electrochim. Acta* **2015**, 174, 596.
- [65] W. Gu, G. Yushin, *WIREs Energy and Environment* **2014**, 3, 424.
- [66] J. Menzel, E. Frackowiak, K. Fic, *Electrochim. Acta* **2020**, 332, 135435.
- [67] J. Niu, B. E. Conway, W. G. Pell, *J. of Power Sources* **2004**, 135, 332.
- [68] H. A. Andreas, *J. Electrochem. Soc.* **2015**, 162, A5047.
- [69] B. E. Conway, W. G. Pell, T. C. Liu, *J. of Power Sources* **1997**, 65, 53.
- [70] P. Galek, A. Slesinski, K. Fic, J. Menzel, *J. Mater. Chem. A* **2021**, 9, 8644.
- [71] J. Menzel, A. Slesinski, P. Galek, P. Bujewska, A. Kachmar, E. Frackowiak, A. Washio, H. Yamamoto, M. Ishikawa, K. Fic, *Energy Storage Mater.* **2022**, 49, 518.
- [72] E. Pamete, L. Kops, F. A. Kreth, S. Pohlmann, A. Varzi, T. Brousse, A. Balducci, V. Presser, *Adv. Energy Mater.* **2023**, 28, 2301008.
- [73] H. Gualous, R. Gallay, M. Al Sakka, A. Oukaour, B. Tala-Ighil, B. Boudart, *Microelectron. Reliab.* **2012**, 52, 2477.
- [74] J. Zhao, H. Lai, Z. Lyu, Y. Jiang, K. Xie, X. Wang, Q. Wu, L. Yang, Z. Jin, Y. Ma, J. Liu, Z. Hu, *Adv. Mater.* **2015**, 27, 3541.
- [75] J. Li, Y. Gao, K. Han, J. Qi, M. Li, Z. Teng, *Sci. Rep.* **2019**, 9, 17270.
- [76] A. Slesinski, S. Sroka, K. Fic, E. Frackowiak, J. Menzel, *ACS Appl. Mater. Interfaces* **2022**, 14, 37782.
- [77] J. Piwek, A. Platek, E. Frackowiak, K. Fic, *J. of Power Sources* **2019**, 438, 227029.
- [78] M. Zhu, C. J. Weber, Y. Yang, M. Konuma, U. Starke, K. Kern, A. M. Bittner, *Carbon* **2008**, 46, 1829.
- [79] B. E. Conway, *Electrochemical Supercapacitors*, Springer, Boston, MA, USA **1999**.
- [80] S. Biniak, M. Pakula, A. Świątkowski, M. Bystrzejewski, S. Błazewicz, *J. Mater. Res.* **2010**, 25, 1617.
- [81] L. Larbi, B. Larhib, A. Beda, L. Madec, L. Monconduit, C. Matei Ghimbeu, *ACS Appl. Energy Mater.* **2023**, 6, 5274.
- [82] D. Lyu, K. Märker, Y. Zhou, E. W. Zhao, A. B. Gunnarsdóttir, S. P. Niblett, A. C. Forse, C. P. Grey, *J. Am. Chem. Soc.* **2024**, 146, 9897.
- [83] B. Petrovic, M. Gorbounov, S. M. Soltani, *Micropor. and Mesopor. Mat.* **2021**, 312, 110751.
- [84] D. Saha, M. J. Kienbaum, *Micropor. and Mesopor. Mat.* **2019**, 287, 29.
- [85] T. J. Bandoz, C. O. Ania, in *Interface Science and Technology*, (Ed.: T. J. Bandoz), Elsevier, Amsterdam, North Holland, Netherlands **2006**, pp. 159–229.
- [86] X. Zhang, C. Yu, Y. Xie, J. Yu, Y. Liu, Y. Yang, J. Wang, S. Lan, S. Hou, K. Liu, J. Qiu, *J. Mater. Chem. A* **2024**, 12, 12054.

Insights of N-carbon quantum dots effect on charge storage in supercapacitors

Carbon quantum dots (CQDs) with Csp²/Csp³ core and plentiful functional groups in the shell show promise for improving the EC performance, as shown in **Figure 14**. Nonetheless, application and understanding their real effect on the EC performance remain nascent. In this chapter, a straightforward strategy to enhance the electrochemical performance of porous carbon cloth electrodes for ECs by integrating N-doped carbon quantum dots (CQDs) is reported. Especially, critical role of CQDs properties that affect the EC characteristics was unrevealed.

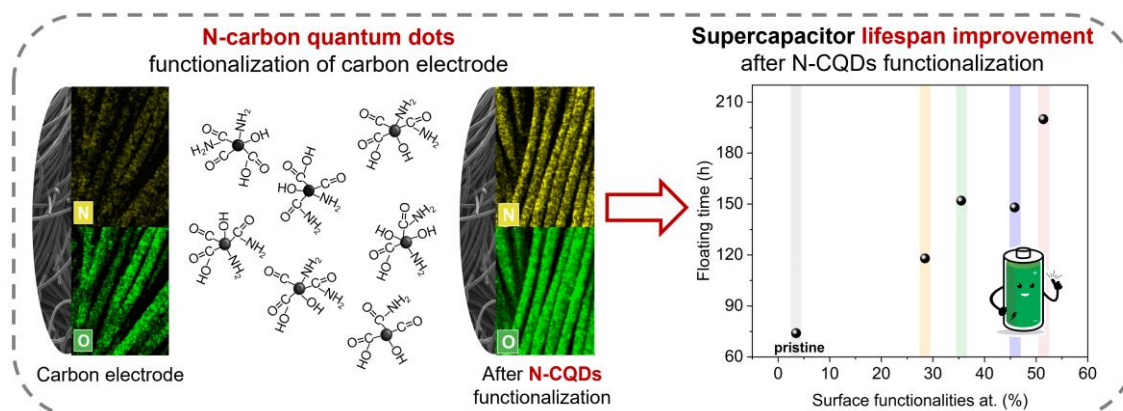


Figure 14 The beneficial effect of the electrode functionalization by carbon quantum dots abundant in oxygen and nitrogen functional groups on the EC lifespan.

An adjusted bottom-up approach was utilized to obtain CQDs with different disorder degree, functional groups content and fluorescence properties. For that purpose, various pairs of citric acid and amines (EDA (ethylenediamine), HMTA (hexamethylenetetramine), TEDA (1,4-diazabicyclo[2.2.2]-octane), oPDA (o-phenylenediamine)) were utilized to

prepare aqueous solutions of CQDs by hydrothermal carbonization (HTC). In-detail purification employing centrifugation, dialysis, and filtration was implemented to remove the unreacted products and larger particles. Importantly, several techniques were used for physicochemical (FTIR, UV, fluorescence spectroscopy, TEM, SEM-EDX, XPS, N₂ sorption) and electrochemical (CV, GCD, EIS) characterization. Such comprehensive characterization lacks in the literature, making the understanding of the role of CQDs properties on electrochemical performance difficult to assess.

The N-CQDs with a size of approximately 6 nm exhibited blue light emission at $\lambda=365$ nm, which was attributed to the recombination of electron-hole pairs located within the Csp². Additionally, polydispersity index (PDI) values confirmed excellent monodispersity of EDA-, HMTA-, TEDA-CQDs, and severe polydispersity of oPDA-CQDs.

As-synthesized N-CQDs possessed a high abundance of hydrophilic groups, with oxygen content reaching up to 23 at.% and nitrogen content up to 20 at.%. It was revealed that EDA- and oPDA-CQDs had the highest abundance of N-groups, specifically C-N (EDA-CQDs) and -NH₂ (oPDA-CQDs), whereas TEDA- and HMTA-CQDs were characterized by a predominance of O-groups. The variations in the quantity and nature of surface groups stem from the structural differences of the chosen amines.

Absorption spectra revealed characteristic π - π^* and n - π^* transitions, with variations in peak position and width linked to differences in particle size distribution, heteroatom content, and structural defects. TEDA-CQDs displayed the narrowest size distribution and sharpest absorption peak, while oPDA-CQDs showed broader distributions and more defect-related features. All samples exhibited excitation-dependent photoluminescence, though the degree of spectral shift and emission bandwidth varied, indicating differences in homogeneity and electronic structure. While both quantum confinement and surface states influence emission, no single factor fully explains the observed fluorescence intensity, highlighting the complex interplay between particle size, surface chemistry, and defect states in governing N-CQDs optical properties.

A facile impregnation of Kynol porous carbon cloth with N-CQDs was performed, and the even distribution of C, N, and O elements within the carbon matrix was validated through the chemical mapping. Notably, Kynol carbon cloth impregnated with N-CQDs served as electrodes that were directly employed in aqueous based ECs (1M Li₂SO₄).

Thermogravimetric analysis (TGA) revealed that the stability limitation of the N-CQDs was 200°C. Above that temperature, the substantial decomposition of oxygen/nitrogen functionalities was occurring, irreversibly altering the structure of N-CQDs. Also, the

weight loss investigated during TGA was related to the total amount of N-CQDs on the Kynol surface, which was higher for EDA-CQDs and oPDA-CQDs (~25 wt.%), whereas lower for the HMTA-CQDs and TEDA-CQDs (~13 wt.%). Moreover, XPS study of surface state of Kynol and Kynol impregnated with EDA-CQDs proved that ~30% of the EDA-CQDs were present on the Kynol surface, confirming the TGA findings.

The N-CQDs improved the EC capacitance, reaching 146 F g^{-1} (Kynol-TEDA-CQDs) in contrast to 116 F g^{-1} (Kynol), especially in the small current regimes, where the kinetics of the redox reactions from N-CQDs was not hindered. In order to explain the mechanism of EC operation, Dunn's method was employed. The diffusive contribution varied from 26% for Kynol-EDA-CQDs to 14% for Kynol-HMTA-CQDs, in contrast to 8% for pristine Kynol at small scanning rate (1 mV s^{-1}). This contribution was much reduced to 3-8% for Kynol-N-CQDs and to 2% for Kynol, when the higher scanning rate was considered. Therefore, EC operating mechanism remained mainly capacitive, nevertheless the diffusive contribution played a significant role.

Importantly, the EC lifespan was markedly enhanced during prolonged floating after the N-CQDs impregnation of Kynol. For instance, the end-of-life criteria after reaching 20% decrease in EC relative capacitance was achieved at 74 floating hours for Kynol, whereas at 200 floating hours for Kynol-TEDA-CQDs based ECs.

Through linear correlations, it was identified that CQDs possessing high amount of surface groups and low content of $\text{Csp}^2/\text{Csp}^3$ core, were at the origin of better capacitive and long-term performance. These functional groups improved the wettability of the carbon surface, provided additional redox-active sites and electron rich zones, that facilitated pseudo-capacitance, charge transfer within the porous network and protective barrier against degradation. Additionally, the analysis of the photoluminescence emission through the fluorescence spectroscopy before/and after electrochemical testing proved that the N-CQDs were partially released to the electrolyte solution. It led to the enhanced electrolyte ionic conductivity, contributing to the EC performance improvement as well.

This work provides insightful understanding to the current knowledge of N-CQDs effect on the EC performance. Particularly, the surface chemistry (O-, N-groups), quantum effects (nanoscale size/modification of electron density), and electrolyte ionic conductivity are at the origin of the improvement of capacitance and lifespan. Importantly, these findings offer a strong basis for the subsequent design of electrode/electrolyte interface utilizing N-CQDs for electrochemical capacitors.

Insights of N-Carbon Quantum Dots Effect on Charge Storage in Supercapacitors

Amelia Klimek^{1,2,3}, Emmanuel Salomon⁴, Samar Hajjar-Garreau^{2,3},
Elzbieta Frackowiak^{*1}, Camélia Matei Ghimbeu^{*2,3,5}

¹Institute of Chemistry and Technical Electrochemistry, Poznan University of Technology,
Berdychowo 4, 61-131 Poznan, Poland

²Institut de Science des Matériaux de Mulhouse (IS2M), Université de Haute-Alsace,
F-68100 Mulhouse, France

³Université de Strasbourg, F-67081 Strasbourg, France

⁴Laboratoire d'Innovation Moléculaire et Applications (LIMA), Université de Haute-Alsace,
Université de Strasbourg, CNRS, LIMA UMR 7042, F-68100 Mulhouse, France

⁵Réseau sur le Stockage Electrochimique de l'Energie (RS2E), 80039 Amiens Cedex, France

*Corresponding authors

elzbieta.frackowiak@put.poznan.pl, camelia.ghimbeu@uha.fr

Abstract

Carbon quantum dots (CQDs) combining Csp^2 core and plentiful functional groups shell, exhibit possibility to enhance electrochemical capacitors (ECs) performance. However, their application and their impact on the ECs is still in infancy. Herein, a hydrothermal synthesis of N-CQDs utilizing citric acid and various amines (EDA, HMTA, TEDA, oPDA) is developed. The characterization of N-CQDs revealed that structural differences of amines impacted the amount (26–38 at.%) and the type of surface functional groups (O-, N-). N-CQDs with size of ~ 6 nm showed blue emission ($\lambda = 365$ nm). Porous Kynol carbon cloth electrodes were impregnated with N-CQDs solutions. The N-CQDs improved the capacitance (146 F g^{-1} for Kynol-TEDA-CQDs vs. 116 F g^{-1} for Kynol), especially in the small current regimes. The diffusive contribution was increased up to 26% (Kynol-EDA-CQDs) vs. 8% (Kynol). Importantly, N-CQDs enhanced significantly the EC lifespan tested by the floating (200 h, Kynol-TEDA-CQDs) compared to Kynol (74 h). The incorporation of heteroatoms resulted in redox species and electron-rich regions on electrode surface, promoting ion adsorption from the aqueous electrolyte (1M Li_2SO_4). Notably, the N-CQDs which are rich in functionalities and present a disordered structure (low Csp^2 , Csp^3) proved to be the most promising to improve the capacitance lifespan.

Keywords: carbon quantum dots, N-CQDs, surface functionalities, electrochemical capacitor, aqueous electrolyte, floating, lifespan

1. Introduction

The immediate need to address the energy demand and to reduce inevitable emission of pollutants from fossil fuels has compelled the scientific community and industries to select renewable energy sources[1]. However, renewable sources highly depend on unstable weather conditions, necessitate the assistance of energy storage devices, such as electrochemical capacitors (ECs), to store energy when available[2]. The high-power density, quick charge/discharge, and long lifespan are the key features of ECs[3]. However, their energy density must be enhanced, if they need to efficiently power smartphones, flexible/wearable electronics as well as hybrid/electric vehicles[4]. Thus, the further improvement of the main EC components (electrolytes, electrode materials) is indispensable.

Aqueous electrolytes are interesting due to their eco-friendliness, high ionic conductivity and low cost[5]. Among them, the neutral electrolytes offer stable operating cell voltage up to 1.6 V, surpassing the thermodynamical potential of water splitting due to the high overpotential for hydrogen evolution at the negative electrode, but also hydrogen electrosorption[6,7]. Interestingly, lithium sulphate (Li_2SO_4) is defined as the best neutral electrolyte with high solubility (26 g/100 mL at RT)[8], good capacitive ($\sim 100 \text{ F g}^{-1}$) and long-term performance ($\sim 100 \text{ h}$) for EC[9].

The charge storage mechanism of ECs is based on the formation of an electrical double layer (EDL) at the charged electrodes, utilizing the expanded specific surface area (SSA) commonly offered by carbon materials[10]. Variety of carbon materials including activated carbons, carbon-derived carbides, and templated carbons have been developed to achieve high SSAs up to $3000 \text{ m}^2 \text{ g}^{-1}$, with pore sizes in the sub-nanometer range[11]. Furthermore, their structure/texture has been tailored to align closely with the diameters of electrolyte ions, thereby enhancing the charge storage[12,13]. Nevertheless, processing the electrodes out of these materials requires a polymeric binder, which is diminishing the SSA by $\sim 10\%$ and clogging some available porosity[14]. To solve that problem, binder-free carbon cloth (i.e., Kynol 5092-20) has been proposed due to its high microporosity, narrow pore size distribution (PSD) and facile processing, which do not require any additives during electrodes manufacturing[7].

Typically, ECs accumulate charge through EDL mechanism, however, faradaic reactions may also take place at the interface between the electrode and electrolyte[15]. This

additional redox activity enhances the performance of ECs, especially at the small current regimes[13]. Several heteroatoms, i.e., O, N, S are utilized for doping and functionalization of carbon materials[16]. Among them, nitrogen is the most commonly used due to the similar radius with carbon (facile integration with carbon skeleton), low band gap compared to carbon (higher electron transfer rate and improved conductivity), and lone pair electrons (enhancement of the hydrophilicity and wettability)[16–18]. For instance, *Lota et al.* obtained N-doped porous carbons by steam activation of N-polymers and proved that up to 7 wt.% of N appears to be the optimum for obtaining high EC capacitance ($\sim 200 \text{ F g}^{-1}$)[19].

Recently, a new concept compared to the classical doping/functionalization of carbon has been introduced. The approach is focused on the implementation of the faradaic reactions to the EC through the carbon quantum dots (CQDs) additive[20]. CQDs are a new class of zero-dimensional functional nanomaterials that attracted attention thanks of their properties, i.e., non-toxicity, outstanding photoluminescence, and cost-effectiveness[21,22]. CQDs have a core-shell structure, in which the core can be either amorphous (sp^2/sp^3) or graphitic (sp^2). The shell of CQDs is typically amorphous, with significant number of oxygen-containing functionalities (i.e., -OH, -COOH, C=O) that strengthen their hydrophilicity. Additionally, a variety of modification methods can be used to further tune their physicochemical properties, like the presence of O-, N-, S-, P- dopants during hydrothermal carbonization (HTC)[23]. It makes them perfect for biomedicine, optoelectronics, catalysis, sensors and more recently for energy storage applications[24]. Ideally, the additive of CQDs enhances ion transport and provide additional pseudocapacitive behavior, thus improving the energy storage systems performance[25]. Some works report on the outstanding EC performance enhancement due to use of the CQDs. *Qing et al.* synthesized graphene quantum dots (GQDs) through the HTC, followed by the pre-carbonization at 500°C [26]. Then, quantum dots were combined with KOH and treated at 800°C [26]. Activated carbon with embedded GQDs possessed high SSA ($2829 \text{ m}^2 \text{ g}^{-1}$) and when applied as EC electrodes, a capacitance of 388 F g^{-1} , as well as an outstanding rate performance (4% capacitance fading from 50 to 100 A g^{-1}) and cycle stability (no capacitance fading after 10,000 cycles) was achieved[26]. *Wei et al.* proposed lignin derived hierarchical porous carbon with embedded CQDs synthesized by HTC followed by salt template-assisted carbonization (800°C) and additional activation[27]. This material reached superior EC capacitance of $\sim 460 \text{ F g}^{-1}$ ($1 \text{ M H}_2\text{SO}_4$ electrolyte) and excellent cycling stability with high capacitance retention after 10,000 cycles[27]. *Yu et al.* prepared 3D carbon composite

using steam activated lignin-based carbon which was decorated with N-CQDs[28]. The capacitance of the EC was improved to reach $\sim 302 \text{ F g}^{-1}$ with coulombic efficiency around 100% after 3,000 cycles for such modified carbon[28]. *Xie et al.* designed a CQDs modified polypyrrole/titania nanotube hybrid and the capacitance of the EC based on this material was enhanced to $\sim 850 \text{ F g}^{-1}$ [29]. The capacitance retention was slightly increased by $\sim 10\%$ after 2,000 cycles[29]. *Xiong et al.* reported on the CQDs-hydrogel derived carbon obtained by calcination process at 800°C as a novel negative electrode material for hybrid ECs[30]. The EC capacitance based on the prepared material ranged from 440 to 510 F g^{-1} in different electrolytes (acidic, neutral, alkaline)[30]. The rate capability of $\sim 80\%$ at the $1\text{-}30 \text{ A g}^{-1}$ current densities and the cycling capacity retention of 100% after 10,000 cycles was shown[30].

Even though, the authors reported on the unique properties of CQDs and their research advances in ECs, an in-depth understanding on the role of CQDs additive for electrode materials and electrolytes is needed. Preparing CQDs with uniform sizes and controllable surface functionalities is still challenging. Particularly, the attention should be given to the proper purification, including centrifugation, filtration, and dialysis as well as the physicochemical characterization, i.e., transmission electron microscopy (TEM), particle size distribution and photoluminescence (PL) emission, which is often neglected. The difficultness arises from the integration of the CQDs additive with the electrode material. To the best of our knowledge, the as-synthesized CQDs (without any modification) are not yet tested in ECs and their real impact on the device is not described. In the reported works, CQDs were firstly synthesized (often ignoring the purification[26–28] as well as in-detail physicochemical characterization[26–29]) and further treated at high temperature up to 800°C [26–30]. The structure/texture of CQDs is significantly modified through the thermal treatment due to the decomposition of some surface functional groups. Therefore, the real effect of the CQDs on the EC performance in the mentioned works is questionable. The improvement of EC performance ascribed as coming from the CQDs additive could origin from the activation process of the carbon (KOH[26], steam[28], salt-templating[27]). Also, the electrochemical testing is frequently performed in the highly corrosive electrolytes (i.e., KOH[26,30], H_2SO_4 [27–30]). These electrolytes are far from the practical applications and the stability of CQDs in such media is not described. Additionally, results obtained from three-electrode setup[26–30] deviate significantly from two-electrode capacitive response which resembles true EC performance.

Herein, the hydrothermal synthesis of N-CQDs was optimized and the detailed physicochemical characterization is provided. Importantly, carbon cloth electrode material was simply impregnated with the N-CQDs and investigated both physiochemically and electrochemically. Considering all above-mentioned issues, herein we report on the real impact of N-CQDs on the EC performance. In fact, contrary to outstanding results found in the literature, we reveal slight improvement of capacitance values especially at small current regimes. However, a significant enhancement of EC lifespan after impregnation of carbon cloth electrode by N-CQDs is demonstrated, and the reasons behind this behavior were elucidated. This research provides valuable insights into the understanding of the N-CQDs effect for electrochemical capacitors.

2. Results and Discussion

Synthesis route of N-CQDs from citric acid and selected amines (EDA/HMTA/TEDA/oPDA) is shown in **Fig. 1** and described in-detail in the Materials and Methods section in the supplementary information (SI). During the hydrothermal carbonization treatment, the polymerization of citric acid and amine occurs, followed by various changes of the chemical structure including nucleation, and growth of the carbonized nanoparticles (detachment of small molecules through the dehydration)[31–33]. Importantly, the N-CQDs were purified utilizing centrifugation, dialysis, and filtration to remove reaction residues and to stabilize them.

TEM analysis served for investigation of morphology and particle size distribution of N-CQDs (**Fig. 2 a-d**, **Fig. S1**). The N-CQDs displayed a spherical shape. Moreover, a narrow particle size distribution of 5.4 - 6.2 nm (inset graph of **Fig. 2 a-d**) was observed. This is in agreement with a definition of CQDs, as nanoparticles with size below 10 nm[32]. Moreover, TEM images show a high particle density, especially for HMTA-CQDs followed by EDA-, TEDA- and oPDA-CQDs. Additionally, a polydispersity index (PDI) was calculated to comment on the dispersion of the particles. The low PDI values for EDA- (0.10), HMTA- (0.05), and TEDA-CQDs (0.07) confirm their excellent monodispersity. In contrast, higher PDI (0.25) observed for oPDA-CQDs indicates severe polydispersity.

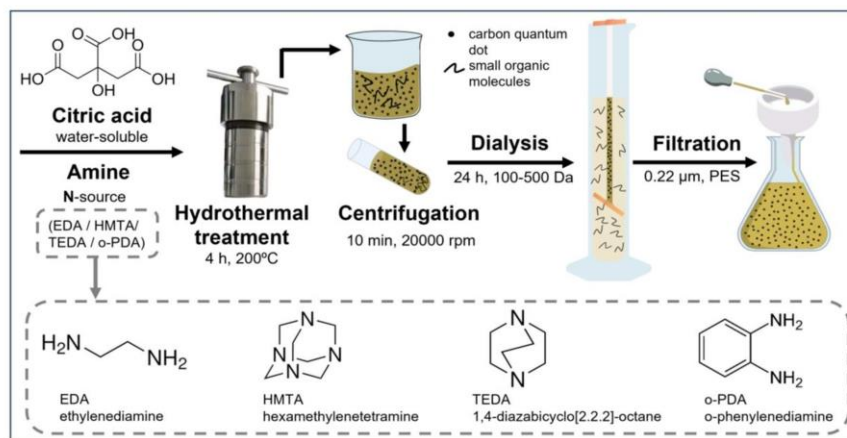


Fig. 1 Schematic illustration of N-CQDs synthesis.

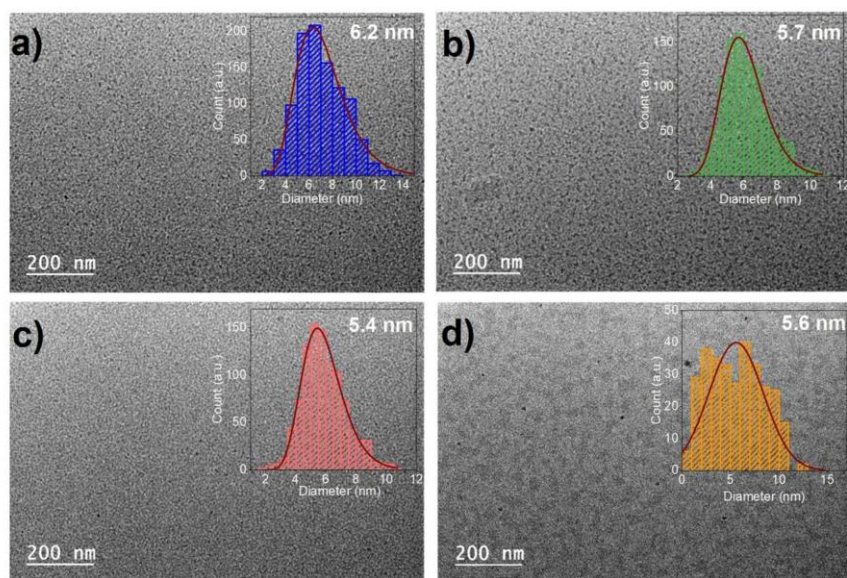


Fig. 2 TEM images (inset graph is the particle size distribution of the corresponding N-CQDs) of: **a)** EDA-CQDs, **b)** HMTA-CQDs, **c)** TEDA-CQDs, **d)** oPDA-CQDs.

The synthesized N-CQDs were studied through Fourier transform infrared spectroscopy (FTIR) to determine the nature of the functionalization (**Fig. 3 a**). The FTIR spectra indicated that all N-CQDs possess hydrophilic groups on their surface, including O-H and N-H (broad peak at $\sim 2963\text{-}3688\text{ cm}^{-1}$), thereby confirming their excellent dispersion in water[34]. Furthermore, the vibrations of the CO_2 (2349 cm^{-1}), N-H/C=C/C=N (1650 cm^{-1}), and C-H/C=C ($670\text{-}900\text{ cm}^{-1}$)[34] were consistently observed in every sample.

In order to gain a more profound insight into the surface functionalities of N-CQDs and to investigate their elemental composition, X-ray photoelectron spectroscopy (XPS) was used. **Fig. 3 b**) illustrates the results of the XPS-wide scan, highlighting the presence of carbon, oxygen, and nitrogen on the surface of N-CQDs. The atomic composition of N-CQDs varies between 62 to 73.9 at.% for carbon, 11.4 to 23 at.% for oxygen, and 10.7 to 20.1 at.% for nitrogen. Interestingly, the highest nitrogen content was reported for EDA-CQDs (~ 20 at.%), followed by the oPDA, HMTA-, and TEDA-CQDs. Regarding O content, the highest amount was observed for TEDA-CQDs (23.02 at.%), while the lowest for oPDA-CQDs (11.42 at.%). Therefore, the highest amount of O-, N-functional groups and the lowest amount of carbon were noticed for EDA-CQDs, while oPDA-CQDs showed the opposite behavior. **Fig. 3 c-f**) shows the deconvoluted components of C 1s spectra, which generally comprise C-C/C-H, C-O/C-N, C=O/O-C-N denoted for all N-CQDs, and additionally O=C-O for oPDA-CQDs. The bar plot in **Fig. 3 g**) illustrates surface chemical composition derived from the C 1s XPS spectra.

It is obvious that N-CQDs are composed mainly of carbon but also have plenty of various functional groups. The individual XPS spectra of O 1s revealed that three types of functional groups can be distinguished, C-O/O-C-N, C-O, O=C=O as shown in **Fig. 3 h**) and **Fig. S2 a-d**). Deconvolution of the N 1s spectra yields 2 peaks, corresponding to the amide group (C-N) and amine group (N-H) as shown in **Fig. S2 e-h**). The exact amounts of amide and amine groups were quantified to elucidate their impact on the N-CQDs physicochemical properties (**Fig. 3 i**). Amide group is generated through the polymerization and de-hydrolysis process between carboxyl and amine groups[34,35] (dominant for EDA-, HMTA-, TEDA-CQDs). On the other hand, amine group is major type for the oPDA-CQDs. The differences in the type of surface functionalities arise from the chemical structure of the utilized amines (**Fig. 1**). XPS results align with FTIR analysis, confirming the existence of O- and N- groups on the surface of N-CQDs.

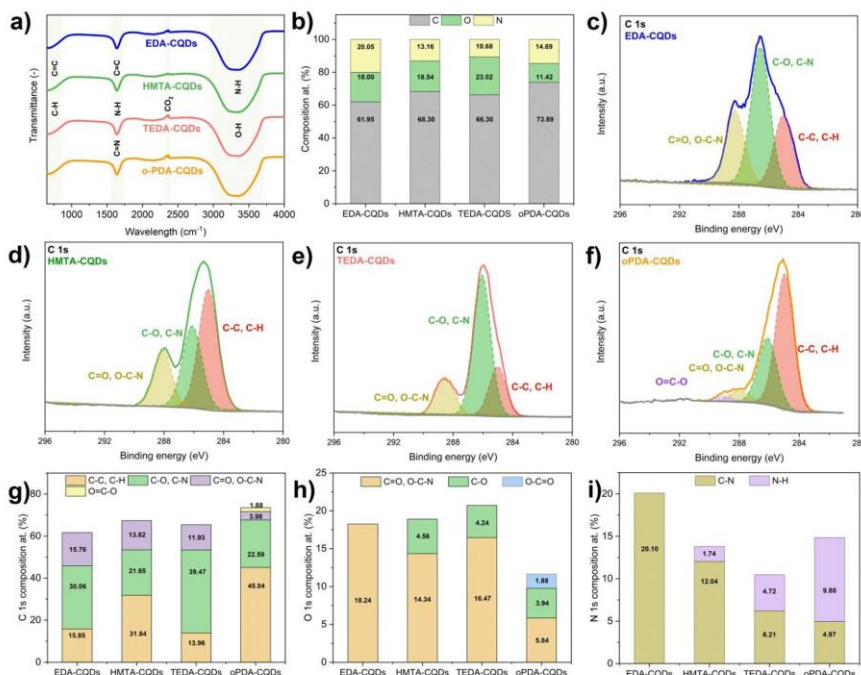


Fig. 3 a) FTIR spectra, b) surface chemical composition from XPS analysis of N-CQDs. XPS spectra deconvolution (C 1s) of: c) EDA-CQDs, d) HMTA-CQDs, e) TEDA-CQDs, f) oPDA-CQDs. Composition of: g) functional groups derived from C 1s XPS spectra, h) O-functional groups derived from the O 1s XPS spectra, i) N-functional groups derived from the N 1s XPS spectra.

Optical photographs of N-CQDs are visible in **Fig. S3**. The colors of N-CQDs varied from yellowish (EDA-CQDs), brownish (HMTA-CQDs) to no-color (TEDA-, oPDA-CQDs) under the daylight (**Fig. S3 a**). The blue PL (photoluminescence) color of the N-CQDs was observed under the UV light of 365 nm (inset **Fig. 4** and **Fig. S3 b**). The detailed optical properties of N-CQDs were investigated through absorption spectra analysis. The absorption peaks are placed at ~280 nm, ~350 nm, and ~370 nm depending on the N-CQDs sample (**Fig. 4** (dash line)). The ~280 nm peak indicates π - π^* electron transition associated with graphitic core (C=C/C-C) found within sp^2 domains in sp^3 network, while the ~350 nm band corresponds to the n - π^* (C=O) transitions and C-N/C=N bonds[31,36,37]. The π - π^* transition is well visible for TEDA-CQDs, and the n - π^* for EDA-, HMTA-, and oPDA-CQDs. Additionally, a shoulder around 370 nm observed for HMTA- and oPDA-CQDs is originated from low-energy surface

centers, typically related to the nanoparticle functionalization[37,38] and/or structural defects[39].

The discrepancies in absorption bands and its broadness emphasize the differences in the electronic structure and chemical environment of N-CQDs[40]. Furthermore, the absorption peak can be influenced by the particle size distribution, dispersion of the particles, surface chemistry and/or surface states. TEDA-CQDs present the narrowest particle size distribution (inset graph in **Fig. 4 c**), followed by slightly larger broadness of particle size distribution peak for EDA- and HMTA-CQDs (inset graph in **Fig. 4 b-c**). The highest broadness of the particle size distribution peak is observed for oPDA-CQDs (inset graph in **Fig. 4 d**). It explains the narrowest absorption peak for TEDA-CQDs (the smallest average size), and larger for EDA-, HMTA-, and oPDA-CQDs. Moreover, EDA-CQDs present also the highest amount of heteroatoms (> 38 wt.%, XPS analysis), which even better explains the larger absorption peak. oPDA-CQDs present much broader particle size distribution and the highest PDI, than other N-CQDs, and furthermore have the smallest quantity of heteroatoms. This material presents two clear absorption peaks which emphasize presence of more structural defects.

The PL emission spectra of N-CQDs were recorded across several excitation wavelengths as illustrated in **Fig. 4** (solid line). PL emission reported for each N-CQDs exhibited excitation-dependent PL, which is advantageous for e.g., bio-imaging[41], LED lightning[42]. RFU (relative fluorescence unit) intensity of CQDs mainly depends on their emissive electronic structure and how efficiently excitons recombine radiatively, which in practice is governed by surface chemistry, defect states, and quantum yield. The peaks of PL emission were shifted with the application of various excitation wavelengths, and each type of N-CQDs demonstrated optimal excitation wavelength. Precisely, for the EDA-CQDs, and oPDA-CQDs the red shift of PL emission spectra with the excitation is not significant, while for HMTA-CQDs, and TEDA-CQDs, the shift is well visible. For the latter two materials, the full width at half maximum (FWHM) of the peaks is much broader. Interestingly, the FWHM of the PL emission spectra gives valuable information regarding the homogeneity of the N-CQDs[40].

The red shift of PL spectra for TEDA- and HMTA- CQDs correlates to their lower PDI (the highest homogeneity) and the narrowest particle size distribution evidenced by TEM data. The PL emission results align with earlier findings that reported the excitation dependent emission phenomenon of CQDs[43]. For comparison, PL emission spectra of N-CQDs under

UV excitation at 360 nm are shown in **Fig. S4**. The highest RFU intensity at ~ 450 nm was noted for oPDA-CQDs followed closely by EDA-, HMTA-, and TEDA-CQDs with a negligible shift in the wavelength. Nonetheless, the underlying mechanism governing excitation-dependent properties remain unclear[36,44]. A widely recognized and currently accurate mechanism for the explanation of the excitation-dependent PL of the CQDs is the quantum confinement effect often referred to as the size effect[45]. Typically, nanoparticles with wide size distribution results in a variety of energy gaps, thus differences in emission wavelengths. Consequently, the reported PL emission can be attributed to the radiative recombination of electron-hole pairs located within the sp^2 carbon nanostructures[36,46]. However, the quantum confinement effect is not the most predominant mechanism. Smaller particles induce higher RFU signal, which is contradictory for oPDA-CQDs with bigger average particle size than HMTA- and TEDA-CQDs. Possibly, the higher concentration of oPDA-CQDs (16 mg mL^{-1}) contributes to the higher signal. The density and nature of surface states – functional groups (i.e., carboxyl, hydroxyl, amine) control the number of radiative, thus the RFU intensity.

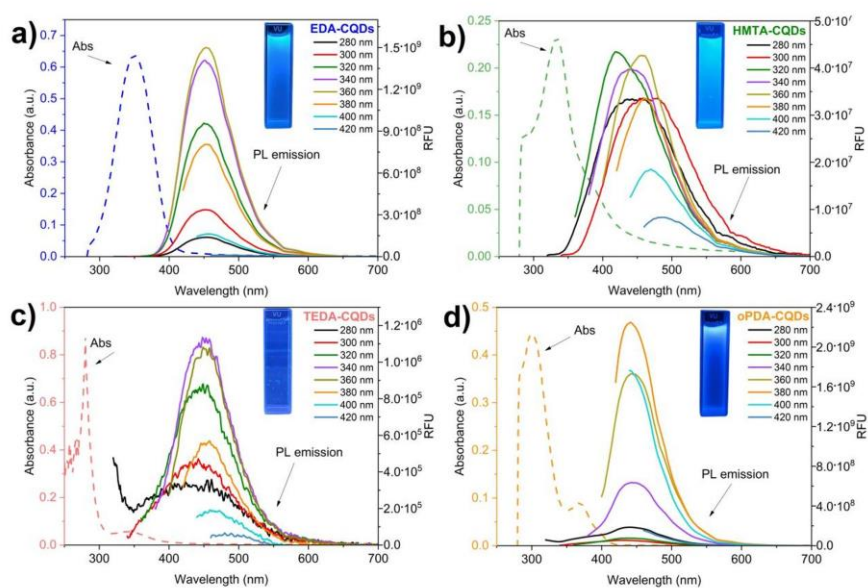


Fig. 4 The absorbance spectra and PL emission spectra using different excitation wavelengths (inset optical photo for the corresponding N-CQDs exposed to UV light 365 nm) of N-CQDs: **a)** EDA-CQDs, **b)** HMTA-CQDs, **c)** TEDA-CQDs, **d)** oPDA-CQDs.

EDA-CQDs has the highest amount of functional groups, while oPDA- CQDs the lowest amount and both materials present similar RFU intensity (10^9). EDA-CQDs has the same high amount of functional groups as TEDA-CQDs, but the RFU intensity is very different. Therefore, even if the surface groups impact RFU, it is difficult to see a clear trend based only on the quantities. On the other hand, the type of N-groups is different among the materials: EDA-CQDs rich in amide, while oPDA-CQDs rich in amine.

In order to utilize the as-synthesized N-CQDs in ECs, simple impregnation of Kynol carbon cloth was performed using aqueous N-CQDs solutions. EDA-CQDs with the highest N-content were selected for the in-detailed physicochemical and electrochemical characterization of impregnated Kynol cloth. Notably, during the impregnation process, the yellowish color of EDA-CQDs solution changed to colorless after 24 hours, as shown in **Fig. S5**. It can be a proof that the majority of the EDA-CQDs were sorbed by the Kynol electrode.

Thermal stability of Kynol and Kynol-EDA-CQDs was assessed *via* thermogravimetric analysis (TGA) in the air (**Fig. 5 a**) and inert atmosphere (N_2) (**Fig. S6 a**). TGA curve (air) of Kynol-EDA-CQDs revealed four distinct stages in the thermal decomposition: the first stage ($\sim 120^\circ C$) due to the physisorbed water loss and second stage ($\sim 200^\circ C$) related to the chemisorbed water removal[47,48]. The third stage ($200-540^\circ C$), shows noticeable and continuous weight loss (~ 24 wt.%) and can be assigned as decomposition of the abundant oxygen[48], nitrogen functionalities and combustion of CQDs[49]. It is in line with the EDA-CQDs amount, considering the XPS analysis. The last stage ($\geq 700^\circ C$) observed for both materials (Kynol-EDA-CQDs and Kynol, respectively) corresponded to the oxidative decomposition of Kynol support material with release of gases, e.g., CO, CO_2 [47,49].

Additionally, TGA curves (air) of other Kynol-N-CQDs are shown in **Fig. S6 b-d**). The thermal decomposition stages look similarly to the as described for Kynol-EDA-CQDs, starting with the weight loss associated with loss of the sorbed water ($\sim 120^\circ C$), followed by the removal of oxygen/nitrogen functionalities ($200-540^\circ C$), and total decomposition of Kynol support material ($\geq 700^\circ C$). Interestingly, the weight loss associated with the decomposition of the surface functionalities is higher for EDA-CQDs (~ 24 wt.%) and oPDA-CQDs (~ 25 wt.%), whereas lower for the HMTA-CQDs and TEDA-CQDs (~ 13 wt.%). Also, the weight loss can be related to the total amount of N-CQDs adsorbed on the Kynol surface. The differences may come from the type/amount of functionalities (not the same for each N-CQDs), with the higher amount of N-groups for EDA-, oPDA-CQDs, and O-groups for HMTA-, TEDA-CQDs.

Importantly, amines selected for the synthesis of N-CQDs could interact differently with the carbon structure. Aromatic oPDA tend to stronger structural integration with graphitic core, whereas aliphatic amine (EDA) more commonly generate surface amino functionalities as well as yield slight graphitic N. More complex amines (TEDA, HMTA) exhibit the weakest covalent incorporation.

On the other hand, some similarities in the thermal decomposition were noticed in the TGA curve (N₂) of Kynol-EDA-CQDs compared (**Fig. S6 a**) to TGA curve (air) (**Fig. 5 a**). The first and second stages corresponded to the removal of the sorbed water and the third stage (~13 wt.%) was assigned to the oxygen/nitrogen surface functionalities loss[48,49]. The last stage (850°C) corresponded to the further decomposition of oxygen (phenol, quinone)[48] and nitrogen (i.e., C-N) functionalities[49], with a relatively small mass loss (~4 wt.%). No important change of the weight was observed in the TGA curve (N₂) of Kynol. At overall, these quantities are very low in N₂ compared to air. Possibly, air environment led to formation of more O-groups in the surface of CQDs. Concluding, the mass changes observed till 200°C were not significant for Kynol-EDA-CQDs, hence the decomposition of functional groups was negligible. Therefore, 200°C can be set as thermal stability limit for Kynol-EDA-CQDs.

Scanning electron microscopy (SEM) images of the Kynol indicated the carbon fibers of approximately 12 µm diameter that formed interwoven bundles in a repeating pattern (**Fig. 5 b**). The presence and distribution of heteroatoms in the pristine Kynol and Kynol-EDA-CQDs were further examined using elemental mapping through SEM/EDX (SEM/energy dispersive X-ray spectroscopy) technique. Elemental mapping investigation demonstrated that C, and O are uniformly distributed within the Kynol and Kynol-EDA-CQDs, with a more prevalent presence of O on the latter material (**Fig. 5 c-d**). The N distribution, is strongly visible for Kynol-EDA-CQDs, confirming successful N-CQDs incorporation in pristine Kynol electrode.

In-detailed surface state of Kynol and Kynol-EDA-CQDs was further studied by XPS. The at.% of C, N, O elements were evaluated from the wide scan shown in **Fig. 5 e**). The O content increased after the impregnation of pristine Kynol by EDA-CQDs from ~3 at.% to ~6 at.% (**Fig. S6 e**), in line with EDX observations. Importantly, there was noted significant amount of N (~8 at.%) after the impregnation, supporting the EDX observations. After the deconvolution of the C 1s spectra, a slight decrease in the sp²-hybridized graphitic carbon and notable increase of the sp³ fraction for Kynol is illustrated in **Fig. 5 f-g**). Taking into account the sp²-hybridized carbon in both materials, it can be concluded that ~30 at.% of the EDA-

CQDs are present on the surface of Kynol electrode. Although, higher quantity of Csp^2 is helpful for improving the electronic conductivity, the Csp^3 fraction is responsible for the pseudocapacitance[47]. The O 1s deconvoluted spectra showed more rich oxygen functionalities of impregnated Kynol-EDA-CQDs electrode, than for pristine Kynol (**Fig. S6 f-g**). Importantly, through the analysis of N 1s spectra, the C-N group is present in the impregnated Kynol electrode, similarly to the as-synthesized EDA-CQDs (**Fig. S6 h**).

To elucidate the relationship between physicochemical properties and electrochemical characteristics of Kynol and Kynol-EDA-CQDs, their texture was analyzed using N_2 sorption at 77K. The isotherms illustrated in the **Fig. 5 h**) can be classified as a type I isotherm according to the IUPAC classification, which is representative for highly microporous materials[50].

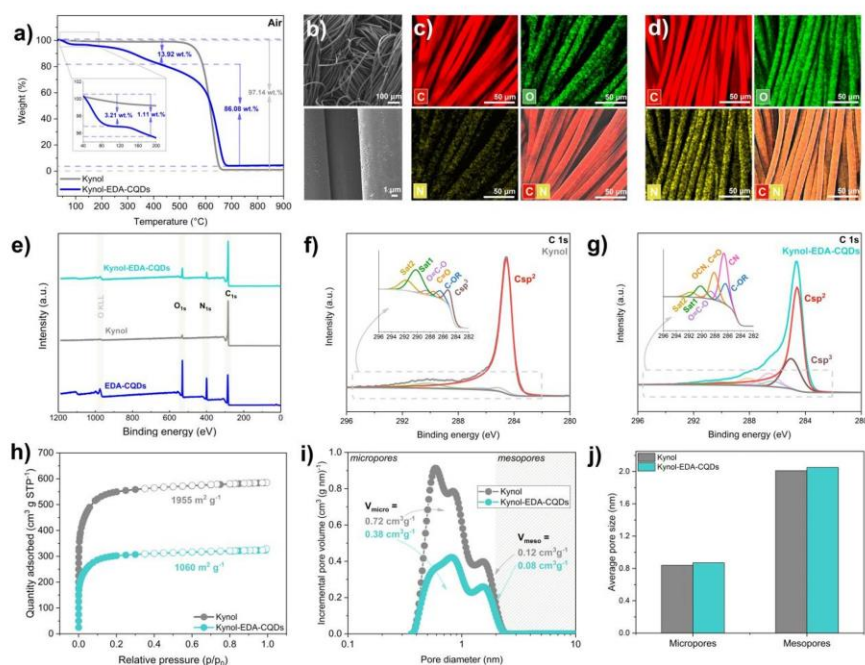


Fig. 5 a) TGA curves (air) of Kynol and Kynol-EDA-CQDs; **b)** SEM images of Kynol; **c)** Elemental mapping images of: **c)** Kynol, **d)** Kynol-EDA-CQDs; **e)** Survey XPS spectra of EDA-CQDs, Kynol, and Kynol-EDA-CQDs; XPS spectra deconvolution (C 1s) of: **f)** Kynol, **g)** Kynol-EDA-CQDs; **h)** Nitrogen sorption of Kynol and Kynol-EDA-CQDs at 77K, **i)** Pore size distribution, **j)** Average pore size of Kynol and Kynol-EDA-CQDs.

Negligible hysteresis loop indicates the presence of the mesopores[50]. The Brunauer-Emmett-Teller specific surface area (S_{BET}) ranges from the 1955 $\text{m}^2 \text{g}^{-1}$ for Kynol to 1060 $\text{m}^2 \text{g}^{-1}$ for consistent pore size distribution comprising a predominant portion of micropores ($< 2 \text{ nm}$). However, very small mesopores (2 - 3 nm) are noticed as well. Importantly, the volume of micropores (V_{micro}) and mesopores (V_{meso}) lower after the impregnation process of pristine Kynol. A more predominant decrease of pore below 1.0 nm is seen, indicating preferential confinement of N-CQDs in narrow pores. The average size of micropores ($L_0 \text{ micro}$) and mesopores ($L_0 \text{ meso}$) did not change notably after the impregnation as illustrated in **Fig. 5 j**).

The influence of the as-synthesized N-CQDs on the electrochemical performance of aqueous based ECs remains poorly investigated. To obtain deeper understanding of this matter several electrochemical techniques, i.e., cyclic voltammetry (CV), galvanostatic charge/discharge (GCD), and electrochemical impedance spectroscopy (EIS) were utilized. Firstly, a two-electrode ECs using N-CQDs impregnated Kynol electrodes, GF-A separator and 1M Li_2SO_4 as the electrolyte were assembled. The maximum stable operating voltage of the EC was set as 1.6 V based on the prior research about the stability of 1M Li_2SO_4 [51].

Fig. 6 a) displays CV curves at scan rate of 5 mV s^{-1} . The gravimetric capacitance values are definitely higher for Kynol-N-CQDs-based ECs than EC with pure Kynol. The typical rectangular shape characteristic of CV[52] is observed for the Kynol-based EC. Slight deviation from this shape is visible for Kynol N-CQDs-based ECs. Additionally, a small redox peak for Kynol-EDA-CQDs is observed around 1.0 V. To get further insights into this faradaic phenomenon, a positive and negative electrode were studied separately at very small scan rate and compared to pristine Kynol-based EC (**Fig. S7 a-b**). The CV profiles of Kynol-EDA-CQDs displayed apparent deviation from ideal rectangular (CV) shape as shown in **Fig. S7 b**). In the case of Kynol-based EC, CV characteristics of negative electrode are very close to perfect rectangular and triangular shapes, however, the positive electrode slightly deviates from such a characteristic. Slight shift of potentials for both electrodes and irreversible oxidation peak at $\sim 0.1 \text{ V}$ was remarked for Kynol-EDA-CQDs. Some reversible electrosorption of hydrogen in the negative electrodes during EC charging process cannot be excluded[53]. At low scanning rates, the kinetics of the redox reactions at both electrodes is well demonstrated. The highest amount of O- and N- functionalities present in Kynol-EDA-CQDs result in pseudocapacitive phenomena, but also the acceleration of the electrolyte decomposition, contrary to the pure EDL behavior for Kynol. Although, O-, N-groups enhance pseudocapacitance *via* reversible proton-coupled electron transfer, they decrease the HER (hydrogen evolution reaction)

overpotential at negative potential. The N-CQDs groups (-OH, -COOH, amines) act as active sites or proton adsorption, lowering HER energy barrier. Moreover, they can contribute to local pH change and H adsorption, promoting H₂ release[54,55]. Interestingly, CV results can be shown as capacitance of the electrode material normalized to the accessible surface area[56] if we assume that all N-CQDs are strongly bonded to the Kynol surface. As illustrated in **Fig. S7**, the value of normalized capacitance is higher for EDA-CQDs (0.16 F m⁻²) compared to Kynol-based ECs (0.06 F m⁻²).

The GCD curves at 0.1 A g⁻¹ reveal that ECs utilizing Kynol-N-CQDs deviate from perfect triangular shape, comparing with Kynol which presents rather right-angled triangular shape, as illustrated in **Fig. 6 b**). The gravimetric capacitance determined through the integration of the area under the discharge curve vary from 146 F g⁻¹ for Kynol-TEDA-CQDs electrodes to 116 F g⁻¹ for Kynol-based ECs electrodes, as summarized in **Tab. 1**. The gravimetric capacitance values vs. current densities are presented in **Fig. 6 c**). Interestingly, all types of Kynol-N-CQDs outperforms Kynol-based ECs, but only in small current regime (0.1 A g⁻¹). On the other hand, a clear capacitance fade in higher current regimes (> 1 A g⁻¹) can be observed, with the exception for Kynol-TEDA-CQDs-based EC. The capacitance ranged from 146 F g⁻¹ (0.1 A g⁻¹) to 85 F g⁻¹ (5 A g⁻¹) for TEDA-CQDs compared with 116 F g⁻¹ (0.1 A g⁻¹) to 75 F g⁻¹ (5 A g⁻¹) for pure Kynol-based ECs.

The charge propagation of the Kynol-N-CQDs was investigated through EIS, with results illustrated in **Fig. 6 d-e**). Nyquist plot of the typical activated carbon electrodes presents small semi-circle in the high-frequency region followed by the sloppy curve in the medium range of frequency and the signal almost parallel to imaginary axis at low frequency[57] what can be observed as well for the Kynol-N-CQDs (**Fig. 6 d**). Further, the Nyquist plots were used to extract the parameters of importance, including the electrode resistance (R_e), the internal resistance (R_i), charge transfer resistance (R_{ct}) and the diffuse layer resistance (R_{diff}) as summarized in **Tab. S2**, according to the methodology reported in[57,58]. The R_i encompasses the contributions from the bulk electrolyte resistance, the R_e and the R_{ct} . Meanwhile, the R_{ct} indicates the contact resistance between the electrode and the current collectors, but also charge transfer of redox reactions. The R_{diff} arises from the transport of ions at the interface between electrode/electrolyte, as well as the formation of EDL. It is noteworthy that the resistance values can be influenced by the cell assembly[59]. The analysis of different types of resistances revealed that Kynol-EDA-, HMTA-, TEDA-CQDs present rather similar values with noticeable

deviation for Kynol-oPDA-CQDs as summarized in **Tab. S2**. Although oPDA-CQDs present the highest quantity of carbon in their structure, and the lowest amount of heteroatoms, the concentration of these CQDs is the highest (16 mg/L), which is almost double than for other N-CQDs. The higher concentration emphasizes higher content of O and increased pore blockage, resulting in the higher resistance and the lower capacitance. Interestingly, the resistance values (R_e , R_i , R_{diff}) are smaller for the Kynol-EDA-CQDs when compared to Kynol and other N-CQDs. Notably, the Kynol-EDA-CQDs is characterized by the highest number of N-functionalities. The capacitance retention as a function of frequency (**Fig. 6 e**) reveals a distinct plateau in the lower frequency range, signifying a mostly capacitive charge behavior. Furthermore, the operating frequency at which capacitance is 50% of the maximum value and relaxation time constant (τ_0) are crucial quantitative indicators of how fast the materials

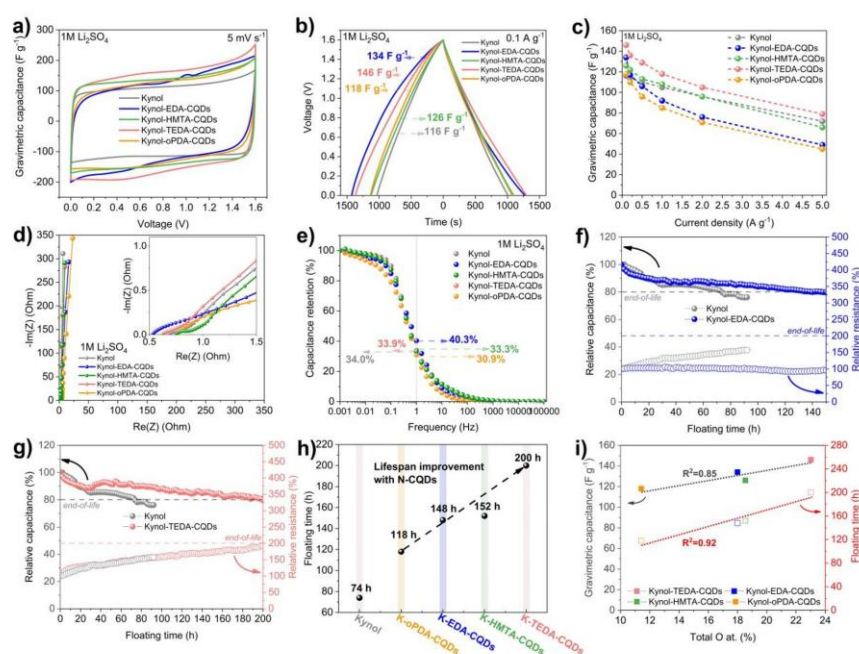


Fig. 6 Electrochemical performance of Kynol-CQDs based ECs operating in 1M Li_2SO_4 : **a**) CV, **b**) GCD, **c**) Gravimetric capacitance vs. current density, **d**) Nyquist plot, **e**) Capacitance retention vs. frequency (two-electrode cell); relative capacitance and resistance vs. floating time of Kynol and **f**) Kynol-EDA-CQDs, **g**) Kynol-TEDA-CQDs, **h**) Summary plot of floating time after reaching 20% decrease in initial capacitance **i**) Gravimetric capacitance and floating time presented as a function of total oxygen content derived from the XPS survey spectra.

undergo charging/discharging[60]. The time constants range from 1.5 s (Kynol-EDA-CQDs) to 2.2 s (Kynol-oPDA-CQDs). Notably, the time constant for Kynol-EDA-CQDs is better than for the Kynol (2.0 s).

To investigate the lifespan of ECs-based on Kynol electrodes with N-CQDs, a voltage-hold test (so-called floating) was used. Floating is less time-consuming alternative to the commonly known galvanostatic cycling, which is one of the most reliable protocols to investigate the EC ageing[57,61]. The plot of relative capacitance (C/C_0) and relative resistance (R/R_0) of Kynol and Kynol-N-CQDs based-ECs is shown in **Fig. 6 f-g**) and **Fig. S9 a-b**). The end-of-life considering the 20% decrease in relative capacitance of the EC is reached at 74 h for Kynol and at 148 h for Kynol-EDA-CQDs, 152 h for Kynol-HMTA-CQDs, 200 h for Kynol-TEDA-CQDs, 118 h for oPDA-CQDs, and summarized in **Fig. 6 h**). Thus, the N-CQDs incorporation provided remarkable improvement in stability of the ECs. The second criteria of end-of-life evaluation related to the 100% increase in the resistance was achieved just for Kynol-TEDA-CQDs after 200 h. Notably, the resistance is almost unchanged after 148 h of floating for Kynol-EDA-CQDs, contrary to the Kynol, where the 58% increase in time is observed.

Typically, the floating time of activated carbon-based ECs operating in 1M Li_2SO_4 declines when subjected to voltage above 1.5 V, resulting in capacitance fade, resistance increase and gas evolution, attributed to the electrochemical oxidation of the positive electrode and H_2 generation at the negative electrode after approximately 100 h[9,62]. Also, it was proved that the carbon defects, especially O-functionalities and enhanced porosity accelerate the ageing[13]. Nevertheless, in our case the opposite result was observed, the EC based on Kynol functionalized by N-CQDs reached significantly longer lifespan compared to pristine Kynol. Nitrogen doping plays impactful role in the ageing by enhancement of the electrical conductivity, increase of material's stability and decrease in the electrolyte decomposition rate[63].

Additionally, the ionic conductivity and pH of the N-CQDs aqueous solutions were measured and the results are summarized in **Tab. S3**. The pH of all N-CQDs solutions is neutral (~ 7), while the ionic conductivity ranges from $52.3 \mu\text{S cm}^{-1}$ for oPDA-CQDs to $317.4 \mu\text{S cm}^{-1}$ for TEDA-CQDs. Moreover, it was observed that the higher ionic conductivity of N-CQDs, the longest lifespan (floating time), emphasizing the beneficial effect of the N-CQDs incorporation. Ionic conductivity can increase when the solution concentration is higher,

however, bigger N-CQDs size, PDI and their aggregation results in lower conductivity. Even though, the highest concentration of oPDA-CQDs could lead to the highest ionic conductivity, but the highest PDI and relatively bigger particle size (unevenly distributed) caused the lowest ionic conductivity than other N-CQDs. On the other hand, well-dispersed TEDA-CQDs (the lowest particle size and PDI), with lower concentration than oPDA-CQDs showed the highest ionic conductivity. Abundant and diverse surface chemistry provides more interactions with water. The oPDA-CQDs present the lowest O-, N-functional groups, and the highest Csp², Csp³, thus, they are more hydrophobic and less dispersed than other materials, explaining the lower ionic conductivity as well. Moreover, the type of functional group is important, O-groups are more hydrophilic than N-groups. For example, TEDA-, HMTA-CQDs with the highest amount of O exhibit the highest ionic conductivity, while EDA- and oPDA-CQDs with the highest N-amount show much lower ionic conductivity.

Tab. 1 Summary of the physicochemical and electrochemical characteristics of N-CQDs (average size, PL emission $\lambda=360\text{nm}$) and Kynol (surface chemical composition). The gravimetric capacitance, capacitance retention and lifespan are shown for ECs based on Kynol and Kynol impregnated with N-CQDs.

Material	Average size	PL emission $\lambda=360\text{nm}$	Surface chemical composition			Gravimetric capacitance at 0.1 A g ⁻¹	Capacitance retention at 1 Hz	Lifespan; floating at 1.6V
			C	O	N			
	(nm)	(a.u.)	at. (%)	at. (%)	at. (%)	(F g ⁻¹)	(%)	(h)
EDA-CQDs	6.2±2.0	1.5·10 ⁹	61.95	18.00	20.05	134	40.3	148
HMTA-CQDs	5.7±1.3	4.3·10 ⁷	68.30	18.54	13.16	126	33.3	152
TEDA-CQDs	5.4±1.4	1.1·10 ⁶	66.30	23.02	10.68	146	33.9	200
oPDA-CQDs	5.6±2.8	1.7·10 ⁹	73.89	11.42	14.69	118	30.9	118
Kynol	-	-	96.52	3.48	0.00	116	34.0	74

A moderate correlation taking into account total amount of carbon obtained from XPS survey spectra and gravimetric capacitance ($R^2=0.47$), floating time ($R^2=0.25$) was noted (**Fig. S10 a**). The lower the carbon content, the higher gravimetric capacitance and floating time. On the other hand, a good correlation between total oxygen content and gravimetric capacitance

($R^2=0.85$), floating time ($R^2=0.92$) was observed (**Fig. 6 i**). On the contrary, a weak relationship of nitrogen content with gravimetric capacitance ($R^2=0.07$), and floating time ($R^2=0.28$) was observed (**Fig. S10 b**). All together, these correlations indicate that the oxygen functionalities play more important role in the EC gravimetric capacitance and lifespan than nitrogen functionalities. Indeed, the impact of the oxygen for the improvement of the EC gravimetric capacitance is well known, including improved wettability, and pseudocapacitance[13]. However, considering the lifespan, oxygen content could be not beneficial as demonstrated using classical porous carbons[61], but high R^2 (coefficient of determination) shows enhanced impact when using CQDs is used in combination with porous carbon. In fact, oxygen can be advantageous for the lifespan of the device through the redox pair quinone-hydroquinone, which can be formed during EC long-term testing[7]. These correlations were reported based on the overall N-CQDs composition (100%) derived from survey XPS spectra. However, there is just a portion of N-CQDs in the Kynol electrode (N-CQDs are adsorbed by the Kynol carbon cloth during impregnation process), which differ than the raw N-CQDs. Interestingly, good correlations of EC performance parameters and C_{sp}^2 , C_{sp}^3 (C=C; C-H), ($R^2=0.86$, 0.64) as well as O-, N-groups content ($R^2=0.96$, 0.76) from C 1s XPS spectra (**Fig. S10 c-d**) were reported. However, it is difficult to distinguish between the proportion of each type of oxygen and nitrogen groups from C 1s spectra, that is why the correlation of both O-, and N-functionalities are coupled. Though, if we consider the correlations using overall O-, N-amounts from survey XPS spectra, the R^2 was very high for O, contrary to N. Therefore, the O-based groups present more impact on performance, although a certain influence of N-groups cannot be neglected. Moreover, each surface functionality can act differently, some of them are beneficial for the capacitive/long-term performance and some of them act oppositely[48]. Overall, CQDs with high degree of disorder and high amount of O-groups contribute to enhanced performance.

Interestingly, these results led to the deeper questions: “Are the N-CQDs partially released from the N-CQDs impregnated Kynol electrodes to the electrolyte solution?” or “Is the electrochemical testing (EIS, CV, GCD) and/or applied current regimes forcing the N-CQDs to partially diffuse into the electrolyte solution?”. For that purpose, three specific samples of Kynol impregnated with EDA-CQDs were prepared in different conditions and the PL emission spectra were measured, as shown in **Fig. S11**. The first sample shown corresponds to the initial EDA-CQDs solution (dark blue line). Then, the solution left after the impregnation of Kynol in the EDA-CQDs (light blue line, denoted as solution after impregnation) is shown.

The third sample was prepared by directly putting Kynol-EDA-CQDs into the 1M Li_2SO_4 electrolyte solution (same quantity as used for the EC assembly) and then, the excess of the electrolyte solution, not adsorbed by the electrode was analyzed (red line, denoted as recovered electrolyte solution). As the fourth sample, Kynol-EDA-CQDs was used to assembly the EC, which was tested electrochemically using CV at 5 mV s^{-1} for 24 h. After electrochemical testing, the Kynol-EDA-CQDs electrodes were removed from the cell, put into the water, and further analyzed (violet line, denoted as solution after electrochemical testing). As observed, the RFU intensity and FWHM changes significantly. The RFU intensity of the initial EDA-CQDs (dark blue line), in the order of 10^9 was diminished significantly to $7.7 \cdot 10^8$ (solution after impregnation) confirming, that the EDA-CQDs were absorbed by the Kynol electrode successfully and some amount of N-CQDs was left. Then, the value of $1.3 \cdot 10^8$ was reported for

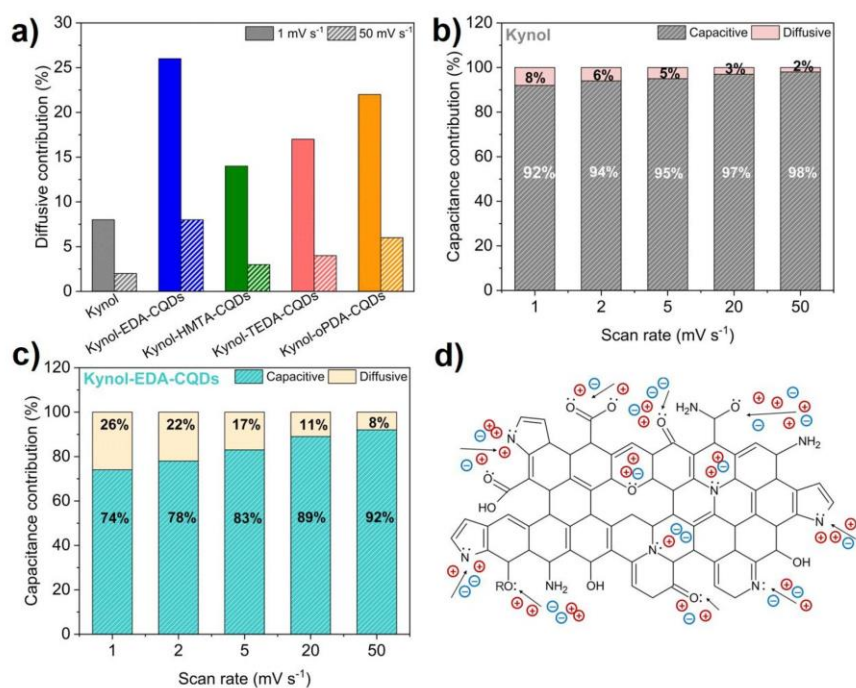


Fig. 7 a) Diffusive contribution to the total capacitance for Kynol and Kynol-N-CQDs based ECs operating in 1M Li_2SO_4 at 1 and 50 mV s^{-1} scan rates; diffusive and capacitive contributions to the total capacitance at 1, 2, 5, 20, 50 mV s^{-1} scan rates for: b) Kynol-based EC, c) Kynol-EDA-CQDs-based EC; d) scheme explaining the role of N-CQDs in the ECs (arrow shows charge attraction direction).

the recovered excess of electrolyte solution and $2.2 \cdot 10^6$ (solution after electrochemical testing). It revealed that some quantity of the EDA-CQDs is released to the electrolyte solution before and after electrochemical testing, which could enhance the ionic conductivity of the electrolyte, thus the lifespan.

In order to explain the mechanism of the N-CQDs impact, Dunn's method was used. It attains a more accurate comprehension of the diffusive and capacitive contributions at selected CV scan rates. As shown in **Fig. 7 a**), at 1 mV s^{-1} the diffusive contribution ranged from 26% (Kynol-EDA-CQDs) to 14% (Kynol-HMTA-CQDs), comparing with 8% for the Kynol. On the other hand, the diffusive contribution at 50 mV s^{-1} diminished significantly to 3-8% for N-CQDs and 2% for Kynol. Detailed diffusive and capacitive contributions to the total capacitance at 1-50 mV s^{-1} scan rates of Kynol and Kynol-EDA-CQDs are shown in **Fig. 7 b-e**). Typically, the diffusive contribution is decreasing with the increase of the scan rate. At small scan rates, the ions have sufficient time to diffuse into the electrode material[48]. This investigation proves that the mechanism for the charge accumulation is primarily influenced by the capacitive storage, however, the ion diffusion plays important role for the ECs containing N-CQDs. Moreover, the results of diffusive contribution provided by the presence of N-CQDs are in line with the TGA analysis, that gives the information about the quantity of the N-CQDs adsorbed by Kynol support material. The highest diffusive contribution for EDA- and oPDA-CQDs based ECs corresponds to the highest weight loss ($\sim 24 \text{ wt.}\%$) in the temperature range (200-540°C) associated with the decomposition of the O-, N- functional groups. In particular, it can be linked to the highest nitrogen content for EDA- and oPDA-CQDs evidenced by XPS. On the other hand, lower diffusive contribution for HMTA- and TEDA-CQDs based ECs matches the lower weight loss ($\sim 13 \text{ wt.}\%$).

The introduction of O-, N- functional groups by N-CQDs alter the charge distribution. Carbon atoms (accounting the carbon atoms from carbon skeleton) are predominantly located at the electron-rich zones including edge sites and defects. Furthermore, the charge properties of carbon atoms distant from the functional group (separated by several atoms) also have been altered. Consequently, functional groups and their surrounding areas can function as centers for ion attraction[30]. Hence, the extensive electron-rich areas of N-CQDs facilitate the transfer of the ions between the solution and the interface, enhancing the EC performance as illustrated in **Fig. 7 d**). Importantly, nitrogen and oxygen functional groups interact differently with the electrolyte. Nitrogen functionalities are typically associated with enhanced conductivity and redox activity, whereas oxygen groups mainly improve surface polarity[49]. Accordingly,

Kynol-EDA-CQDs (the highest N content) are expected to provide stronger conductivity and pseudocapacitive effects (the highest diffusive contribution), while Kynol-TEDA-CQDs (lower N content, relatively higher O content) may predominantly enhance wettability[64].

The features of CQDs – nanoscale size and high surface-to-volume ratio can increase external surface, thereby facilitating ion diffusion and adsorption[64,65]. Besides, CQDs offer unique effect called quantum capacitance. Due to the nanoscale size (< 10 nm) and low dimensionality (0 D), CQDs do not behave like bulk conductive carbons, instead, their ability to accept extra electrons is constrained by their electronic structure, making quantum capacitance an important factor that impacts the EC performance[64,66]. Moreover, the high O-, N-heteroatoms content in N-CQDs modifies electronic states, which cause the increase of quantum capacitance, impacting the overall capacitance[49].

3. Conclusions

The N-CQDs were synthesized using citric acid and various amines *via* hydrothermal carbonization process. Importantly, purification using centrifugation, dialysis and filtration was realized to remove unreacted products and larger particles. In-detailed physicochemical characterization revealed that N-CQDs possess uniformly spherical shape with size up to ~ 6 nm. The N-CQDs show a blue emission at $\lambda = 365$ nm attributed to the recombination of electron-hole pairs located within the Csp^2 . As-synthesized N-CQDs are rich in hydrophilic groups, emphasizing high content of O- (up to 23 at.%) and N- (up to 20 at.%) functionalities. It was found that EDA- and oPDA-CQDs are the most abundant in N-groups, C-N (for EDA-CQDs) and $-NH_2$ (for oPDA-CQDs) while TEDA and HMTA-CQDs contain predominant O-groups. The differences in the amount and type of the surface functionalities arise from the structural differences of selected amines.

A straightforward impregnation of Kynol carbon cloth by the N-CQDs was performed and the uniform distribution of the C, N, O elements in the Kynol electrode was confirmed by chemical mapping. Based on the XPS results, ~ 30 at.% of EDA-CQDs was present on the electrode surface after the impregnation, in line with TGA results.

The N-CQDs enhanced the gravimetric capacitance, achieving 146 F g^{-1} for Kynol-TEDA-CQDs compared to 116 F g^{-1} for pristine Kynol. This improvement is particularly notable in small current regimes, where the kinetics of redox reactions is not hindered.

Moreover, through the Dunn's method it was highlighted that charge storage in N-CQDs-based ECs is provided in majority by the capacitive phenomena associated with their S_{BET} and pore volume/size, but also pseudocapacitive contribution from the O- and N-functional groups. The addition of heteroatoms such as O- and N- from CQDs created higher electron density states on the electrode surface, which are ideal for the enhanced adsorption of ions coming from the electrolyte.

Notably, the N-CQDs improved the lifespan of ECs by extending the floating time up to 200 hours (Kynol-TEDA-CQDs, in contrast to the Kynol, which achieved only 74 hours). The long-term performance correlates well with a high amount of functional groups (especially O-groups) and low C_{sp^2} , C_{sp^3} content. The high O-content contributes to pseudocapacitive reactions, good wettability, but also to the better dispersion of N-CQDs. Moreover, due to their partial release in the electrolyte, the ionic conductivity is enhanced, therefore a synergetic enhancement of performance *via* electrode/electrolyte improvement is achieved.

In summary, this work provided insightful understanding to the current knowledge on as-synthesized N-CQDs effect on the EC performance. Particularly, the surface chemistry (O-, N-groups), quantum effects (nanoscale size/modification of electron density) and improved electrolyte conductivity promoted by partial release N-CQDs during electrochemical operation are at the origin of the improvement of capacitance and lifespan. This study offers a solid foundation for the further design of electrode/electrolyte interface using N-CQDs also for other energy storage devices.

Acknowledgements

This research was supported by a French Government Scholarship France Excellence, the Ministry of Higher Education of Poland (grant number 0911/SBAD/2601), Preludium 2024/53/N/ST5/02202 (partially) and ANR-10-LABX-76-01, STORE-EX (France). The authors acknowledge Loic Vidal (TEM), Cyril Vaultot (adsorption), Gautier Schrodj (TGA), Ludovic Josien (SEM/EDX) for their technical help within the IS2M platforms.

Conflict of interest

There are no conflicts of interest to declare.

Data availability statement

The data that support the finding of this study are available in the supplementary material (SI) of this article.

Author contributions

A.K. performed conceptualization, data curation, formal analysis, investigation, methodology, visualization, wrote the original manuscript, edited the final manuscript; E.S. performed investigation; S.H.G performed investigation; E.F. performed conceptualization, validation, funding acquisition, project administration, supervision, reviewed and edited the final manuscript; C.M.G. performed conceptualization, validation, funding acquisition, project administration, supervision, reviewed and edited the final manuscript.

References

- [1] R.A. Verzijlbergh, L.J. De Vries, G.P.J. Dijkema, P.M. Herder, Institutional challenges caused by the integration of renewable energy sources in the European electricity sector, *Renewable and Sustainable Energy Reviews* 75 (2017) 660–667. <https://doi.org/10.1016/j.rser.2016.11.039>.
- [2] J. Zhang, M. Gu, X. Chen, Supercapacitors for renewable energy applications: A review, *Micro and Nano Engineering* 21 (2023) 100229. <https://doi.org/10.1016/j.mne.2023.100229>.
- [3] M. Zhou, A. Gallegos, K. Liu, S. Dai, J. Wu, Insights from machine learning of carbon electrodes for electric double layer capacitors, *Carbon* 157 (2020) 147–152. <https://doi.org/10.1016/j.carbon.2019.08.090>.
- [4] P. Simon, Y. Gogotsi, Perspectives for electrochemical capacitors and related devices, *Nat. Mater.* 19 (2020) 1151–1163. <https://doi.org/10.1038/s41563-020-0747-z>.
- [5] S. Azmi, A. Klimek, E. Frackowiak, Why electrochemical capacitor electrolytes should not be ignored?, *Electrochimica Acta* 452 (2023) 142347. <https://doi.org/10.1016/j.electacta.2023.142347>.
- [6] A. Slesinski, S. Sroka, K. Fic, E. Frackowiak, J. Menzel, Operando Monitoring of Local pH Value Changes at the Carbon Electrode Surface in Neutral Sulfate-Based Aqueous Electrochemical Capacitors, *ACS Applied Materials & Interfaces* 14 (2022) 37782–37792. <https://doi.org/10.1021/acsami.2c09920>.
- [7] K. Fic, A. Platek, J. Piwek, J. Menzel, A. Ślesięński, P. Bujewska, P. Galek, E. Frackowiak, Revisited insights into charge storage mechanisms in electrochemical capacitors with Li₂SO₄-based electrolyte, *Energy Storage Materials* 22 (2019) 1–14. <https://doi.org/10.1016/j.ensm.2019.08.005>.
- [8] J.A.N. Friend, CCCIV.—The hydrates of lithium sulphate and their solubility in water between –16° and +103°, *J. Chem. Soc.* (1929) 2330–2333. <https://doi.org/10.1039/JR9290002330>.
- [9] S. Azmi, A. Klimek, E. Frackowiak, Electrochemical capacitor in aqueous electrolyte with long lifespan improved by hydrogen bond donor addition, *Materials Today* 68 (2023) 34–50. <https://doi.org/10.1016/j.mattod.2023.06.018>.
- [10] B.E. Conway, *Electrochemical Supercapacitors*, Springer US, Boston, MA, 1999. <https://doi.org/10.1007/978-1-4757-3058-6>.
- [11] E. Frackowiak, Carbon materials for supercapacitor application, *Phys. Chem. Chem. Phys.* 9 (2007) 1774–1785. <https://doi.org/10.1039/B618139M>.

- [12] T. Zhu, Z. Song, J. Lin, L. Fan, J.-Y. Lin, J. Wu, Ion-pore size match effects and high-performance cucurbit[8]uril-carbon-based supercapacitors, *Electrochimica Acta* 405 (2022) 139827. <https://doi.org/10.1016/j.electacta.2021.139827>.
- [13] A. Klimek, B. Réty, C. Matei Ghimbeu, E. Frackowiak, Impact of Disorder, Porosity, and Surface Chemistry of Salt Templated Carbons on Capacitance, *Advanced Science* 12 (2025) e05032. <https://doi.org/10.1002/advs.202505032>.
- [14] Q. Abbas, D. Pajak, E. Frackowiak, F. Béguin, Effect of binder on the performance of carbon/carbon symmetric capacitors in salt aqueous electrolyte, *Electrochimica Acta* 140 (2014) 132–138. <https://doi.org/10.1016/j.electacta.2014.04.096>.
- [15] E. Frackowiak, F. Béguin, Carbon materials for the electrochemical storage of energy in capacitors, *Carbon* 39 (2001) 937–950. [https://doi.org/10.1016/S0008-6223\(00\)00183-4](https://doi.org/10.1016/S0008-6223(00)00183-4).
- [16] J. Wang, T. Huo, Y. Zhao, R. Lu, X. Wu, Recent advances in heteroatoms-doped porous carbon electrode materials for supercapacitors: A review, *Journal of Energy Storage* 110 (2025) 115216. <https://doi.org/10.1016/j.est.2024.115216>.
- [17] J. Li, K. Han, D. Wang, Z. Teng, Y. Cao, J. Qi, M. Li, M. Wang, Fabrication of high performance structural N-doped hierarchical porous carbon for supercapacitors, *Carbon* 164 (2020) 42–50. <https://doi.org/10.1016/j.carbon.2020.03.044>.
- [18] A. Ilnicka, M. Skorupska, M. Szkoda, Z. Zarach, J.P. Lukaszewicz, N-doped carbon materials as electrodes for highly stable supercapacitors, *Materials Research Letters* 11 (2023) 213–221. <https://doi.org/10.1080/21663831.2022.2139163>.
- [19] G. Lota, B. Grzyb, H. Machnikowska, J. Machnikowski, E. Frackowiak, Effect of nitrogen in carbon electrode on the supercapacitor performance, *Chemical Physics Letters* 404 (2005) 53–58. <https://doi.org/10.1016/j.cplett.2005.01.074>.
- [20] N. Liu, J. Yu, Y. Li, Y. Liu, S. Jabeen, Y. Cheng, L. Zhou, D.L. Danilov, P.H.L. Notten, H. Li, Multifunctional Carbon Dots for Electrochemical Capacitors Reviewed: Their Opportunities and Challenges, *Advanced Science* 12 (2025) e08000. <https://doi.org/10.1002/advs.202508000>.
- [21] Z. Dong, J. Qi, L. Yue, H. Zhou, L. Chen, J. Gu, Y. He, H. Wu, Biomass-based carbon quantum dots and their agricultural applications, *Plant Stress* 11 (2024) 100411. <https://doi.org/10.1016/j.stress.2024.100411>.
- [22] T.H. Kim, F. Wang, P. McCormick, L. Wang, C. Brown, Q. Li, Salt-embedded carbon nanodots as a UV and thermal stable fluorophore for light-emitting diodes, *Journal of Luminescence* 154 (2014) 1–7. <https://doi.org/10.1016/j.jlumin.2014.04.002>.
- [23] S.K. Park, H. Lee, M.S. Choi, D.H. Suh, P. Nakhnivej, H.S. Park, Straightforward and controllable synthesis of heteroatom-doped carbon dots and nanoporous carbons for surface-confined energy and chemical storage, *Energy Storage Materials* 12 (2018) 331–340. <https://doi.org/10.1016/j.ensm.2017.10.008>.
- [24] J. Liu, R. Li, B. Yang, Carbon Dots: A New Type of Carbon-Based Nanomaterial with Wide Applications, *ACS Cent. Sci.* 6 (2020) 2179–2195. <https://doi.org/10.1021/acscentsci.0c01306>.
- [25] M.S. Alva, R.A. Nazareth, Y.N. Sudhakar, N. Desai, Carbon quantum Dot incorporated Xanthan gum based gel polymer electrolytes for high performance supercapacitors, *Sci Rep* 15 (2025) 18227. <https://doi.org/10.1038/s41598-025-02341-z>.
- [26] Y. Qing, Y. Jiang, H. Lin, L. Wang, A. Liu, Y. Cao, R. Sheng, Y. Guo, C. Fan, S. Zhang, D. Jia, Z. Fan, Boosting the supercapacitor performance of activated carbon by constructing overall conductive networks using graphene quantum dots, *J. Mater. Chem. A* 7 (2019) 6021–6027. <https://doi.org/10.1039/C8TA11620B>.
- [27] L. Wei, Z. Wu, J. Li, Y. Xiong, X. Wang, Inorganic salt-induced synthesis of lignin derived hierarchical porous carbon with self-embedded quantum dots and ultrahigh mesoporosity for supercapacitors, *New J. Chem.* 46 (2022) 13054–13064. <https://doi.org/10.1039/D2NJ01809H>.
- [28] L. Yu, C.-T. Hsieh, D.J. Keffer, H. Chen, G.A. Goenaga, S. Dai, T.A. Zawodzinski, D.P. Harper, Hierarchical Lignin-Based Carbon Matrix and Carbon Dot Composite Electrodes for High-Performance Supercapacitors, *ACS Omega* 6 (2021) 7851–7861. <https://doi.org/10.1021/acsomega.1c00448>.
- [29] Y. Xie, H. Du, Electrochemical capacitance of a carbon quantum dots–polypyrrole/titania nanotube hybrid, *RSC Adv.* 5 (2015) 89689–89697. <https://doi.org/10.1039/C5RA16538E>.

- [30] J.S. Wei, C. Ding, P. Zhang, H. Ding, X.Q. Niu, Y.Y. Ma, C. Li, Y.G. Wang, H.M. Xiong, Robust Negative Electrode Materials Derived from Carbon Dots and Porous Hydrogels for High-Performance Hybrid Supercapacitors, *Advanced Materials* 31 (2019) 1806197. <https://doi.org/10.1002/adma.201806197>.
- [31] Y. Hiejima, M. Kanakubo, Hydrothermal Synthesis of Photoluminescent Nanocarbon from Hydroxylic Acids and Amines, *J Solution Chem* 45 (2016) 1560–1570. <https://doi.org/10.1007/s10953-016-0531-5>.
- [32] Y. Song, S. Zhu, S. Zhang, Y. Fu, L. Wang, X. Zhao, B. Yang, Investigation from chemical structure to photoluminescent mechanism: a type of carbon dots from the pyrolysis of citric acid and an amine, *J. Mater. Chem. C* 3 (2015) 5976–5984. <https://doi.org/10.1039/C5TC00813A>.
- [33] S. Zhu, Q. Meng, L. Wang, J. Zhang, Y. Song, H. Jin, K. Zhang, H. Sun, H. Wang, B. Yang, Highly Photoluminescent Carbon Dots for Multicolor Patterning, Sensors, and Bioimaging, *Angewandte Chemie International Edition* 52 (2013) 3953–3957. <https://doi.org/10.1002/anie.201300519>.
- [34] S. Elkun, M. Ghali, T. Sharshar, M.M. Mosaad, Green synthesis of fluorescent N-doped carbon quantum dots from castor seeds and their applications in cell imaging and pH sensing, *Sci Rep* 14 (2024) 27927. <https://doi.org/10.1038/s41598-024-78745-0>.
- [35] P. Yang, Z. Zhu, M. Chen, W. Chen, X. Zhou, Microwave-assisted synthesis of xylan-derived carbon quantum dots for tetracycline sensing, *Optical Materials* 85 (2018) 329–336. <https://doi.org/10.1016/j.optmat.2018.06.034>.
- [36] K.G. Nguyen, I.-A. Baragau, R. Gromicova, A. Nicolaev, S.A.J. Thomson, A. Rennie, N.P. Power, M.T. Sajjad, S. Kellici, Investigating the effect of N-doping on carbon quantum dots structure, optical properties and metal ion screening, *Sci Rep* 12 (2022) 13806. <https://doi.org/10.1038/s41598-022-16893-x>.
- [37] C.M. Carbonaro, D. Chiriu, L. Stagi, M.F. Casula, S.V. Thakkar, L. Malfatti, K. Suzuki, P.C. Ricci, R. Corpino, Carbon Dots in Water and Mesoporous Matrix: Chasing the Origin of their Photoluminescence, *J. Phys. Chem. C* 122 (2018) 25638–25650. <https://doi.org/10.1021/acs.jpcc.8b08012>.
- [38] C.M. Carbonaro, R. Corpino, M. Salis, F. Mocci, S.V. Thakkar, C. Olla, P.C. Ricci, On the Emission Properties of Carbon Dots: Reviewing Data and Discussing Models, *C* 5 (2019) 60. <https://doi.org/10.3390/c5040060>.
- [39] S.E. Elugoke, G.E. Uwaya, T.W. Quadri, E.E. Ebenso, Carbon Quantum Dots: Basics, Properties, and Fundamentals, *ACS Symposium Series* 1 (2024) 3–42. <https://doi.org/10.1021/bk-2024-1465.ch001>.
- [40] K.G. Nguyen, M. Huš, I.-A. Baragau, J. Bowen, T. Heil, A. Nicolaev, L.E. Abramiuc, A. Sapelkin, M.T. Sajjad, S. Kellici, Engineering Nitrogen-Doped Carbon Quantum Dots: Tailoring Optical and Chemical Properties through Selection of Nitrogen Precursors, *Small* 20 (2024) 2310587. <https://doi.org/10.1002/smll.202310587>.
- [41] Y. Zheng, G. Xie, X. Zhang, Z. Chen, Y. Cai, W. Yu, H. Liu, J. Shan, R. Li, Y. Liu, B. Lei, Bioimaging Application and Growth-Promoting Behavior of Carbon Dots from Pollen on Hydroponically Cultivated Rome Lettuce, *ACS Omega* 2 (2017) 3958–3965. <https://doi.org/10.1021/acsomega.7b00657>.
- [42] P. He, Y. Shi, T. Meng, T. Yuan, Y. Li, X. Li, Y. Zhang, L. Fan, S. Yang, Recent advances in white light-emitting diodes of carbon quantum dots, *Nanoscale* 12 (2020) 4826–4832. <https://doi.org/10.1039/C9NR10958G>.
- [43] Z. Gan, H. Xu, Y. Hao, Mechanism for excitation-dependent photoluminescence from graphene quantum dots and other graphene oxide derivatives: consensus, debates and challenges, *Nanoscale* 8 (2016) 7794–7807. <https://doi.org/10.1039/C6NR00605A>.
- [44] H. Ding, X.X. Zhou, Z.H. Zhang, Y.P. Zhao, J.S. Wei, H.M. Xiong, Large scale synthesis of full-color emissive carbon dots from a single carbon source by a solvent-free method, *Nano Research* 15 (2021) 3548–3555. <https://doi.org/10.1007/s12274-021-3891-0>.
- [45] J. Manioudakis, F. Victoria, C.A. Thompson, L. Brown, M. Movsum, R. Lucifero, R. Naccache, Effects of nitrogen-doping on the photophysical properties of carbon dots, *J. Mater. Chem. C* 7 (2019) 853–862. <https://doi.org/10.1039/C8TC04821E>.

- [46] H. Tao, K. Yang, Z. Ma, J. Wan, Y. Zhang, Z. Kang, Z. Liu, In Vivo NIR Fluorescence Imaging, Biodistribution, and Toxicology of Photoluminescent Carbon Dots Produced from Carbon Nanotubes and Graphite, *Small* 8 (2012) 281–290. <https://doi.org/10.1002/smll.201101706>.
- [47] L. Zhang, R. Sun, Y. Liang, X. Wang, J. Liu, Q. Ning, Q. Yuan, H. He, S. Qiu, Y. Ren, J. Xu, X. Yin, Carbon quantum dot dual-regulation for constructing high-performance NFPP cathode: Synergistic breakthrough in electron conductivity and ion transport, *Energy Storage Materials* 81 (2025) 104548. <https://doi.org/10.1016/j.ensm.2025.104548>.
- [48] B. Réty, H.-Y. Yiin, C. Matei Ghimbeu, Quantification of activated carbon functional groups and active surface area by TPD-MS and their impact on supercapacitor performance, *Energy Storage Materials* 74 (2025) 103963. <https://doi.org/10.1016/j.ensm.2024.103963>.
- [49] A. Adeniji, A. Beda, P. Fioux, C. Matei Ghimbeu, Engineering nitrogen-doped porous carbon positive electrodes for high-performance sodium-ion capacitors: the critical role of porosity, structure and surface functionalities, *J. Mater. Chem. A* 13 (2025) 14896–14914. <https://doi.org/10.1039/D5TA01075F>.
- [50] M. Thommes, K. Kaneko, A.V. Neimark, J.P. Olivier, F. Rodriguez-Reinoso, J. Rouquerol, K.S.W. Sing, Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report), *Pure and Applied Chemistry* 87 (2015) 1051–1069. <https://doi.org/10.1515/pac-2014-1117>.
- [51] M. He, K. Fic, E. Frackowiak, P. Novak, E.J. Berg, Ageing phenomena in high-voltage aqueous supercapacitors investigated by in situ gas analysis, *Energy & Environmental Science* 9 (2016) 623–633. <https://doi.org/10.1039/C5EE02875B>.
- [52] O. Gharbi, M.T.T. Tran, B. Tribollet, M. Turmine, V. Vivier, Revisiting cyclic voltammetry and electrochemical impedance spectroscopy analysis for capacitance measurements, *Electrochimica Acta* 343 (2020) 136109. <https://doi.org/10.1016/j.electacta.2020.136109>.
- [53] A. Platek, J. Piwek, K. Fic, E. Frackowiak, Ageing mechanisms in electrochemical capacitors with aqueous redox-active electrolytes, *Electrochimica Acta* 311 (2019) 211–220. <https://doi.org/10.1016/j.electacta.2019.04.117>.
- [54] H. Wu, S. Lu, B. Yang, Carbon-Dot-Enhanced Electrocatalytic Hydrogen Evolution, *Acc. Mater. Res.* 3 (2022) 319–330. <https://doi.org/10.1021/accountsmr.1c00194>.
- [55] Z. Liu, B. Li, Y. Feng, D. Jia, C. Li, Y. Zhou, N-Doped sp²/sp³ Carbon Derived from Carbon Dots to Boost the Performance of Ruthenium for Efficient Hydrogen Evolution Reaction, *Small Methods* 6 (2022) 2200637. <https://doi.org/10.1002/smt.202200637>.
- [56] N. Jackel, P. Simon, Y. Gogotsi, V. Presser, Increase in Capacitance by Subnanometer Pores in Carbon, *ACS Energy Letters* 1 (2016) 1262–1265. <https://doi.org/10.1021/acsenenergylett.6b00516>.
- [57] A. Parejo-Tovar, F. Béguin, The NaClO₄-water eutectic electrolyte for environmentally friendly electrical double-layer capacitors operating at low temperature, *Energy Storage Materials* 69 (2024) 103387. <https://doi.org/10.1016/j.ensm.2024.103387>.
- [58] B.A. Mei, O. Munteshari, J. Lau, B. Dunn, L. Pilon, Physical Interpretations of Nyquist Plots for EDLC Electrodes and Devices, *J. Phys. Chem. C* 122 (2018) 194–206. <https://doi.org/10.1021/acs.jpcc.7b10582>.
- [59] K.B. Li, D.W. Shi, Z.Y. Cai, G.L. Zhang, Q.A. Huang, D. Liu, C.P. Yang, Studies on the equivalent serial resistance of carbon supercapacitor, *Electrochimica Acta*, 174, 2015, 596–600. <https://doi.org/10.1016/j.electacta.2015.06.008>.
- [60] L. Wang, T. Wei, L. Sheng, L. Jiang, X. Wu, Q. Zhou, B. Yuan, J. Yue, Z. Liu, Z. Fan, “Brick-and-mortar” sandwiched porous carbon building constructed by metal-organic framework and graphene: Ultrafast charge/discharge rate up to 2 V s^{−1} for supercapacitors, *Nano Energy* 30 (2016) 84–92. <https://doi.org/10.1016/j.nanoen.2016.09.042>.
- [61] E. Pamete, L. Kops, F.A. Kreth, S. Pohlmann, A. Varzi, T. Brousse, A. Balducci, V. Presser, The Many Deaths of Supercapacitors: Degradation, Aging, and Performance Fading, *Advanced Energy Materials* 13 (2023) 2301008. <https://doi.org/10.1002/aenm.202301008>.
- [62] P. Ratajczak, K. Jurewicz, P. Skowron, Q. Abbas, F. Béguin, Effect of accelerated ageing on the performance of high voltage carbon/carbon electrochemical capacitors in salt aqueous electrolyte, *Electrochimica Acta* 130 (2014) 344–350. <https://doi.org/10.1016/j.electacta.2014.02.140>.

- [63] D. Salinas-Torres, S. Shiraishi, E. Morallón, D. Cazorla-Amorós, Improvement of carbon materials performance by nitrogen functional groups in electrochemical capacitors in organic electrolyte at severe conditions, *Carbon* 82 (2015) 205–213.
<https://doi.org/10.1016/j.carbon.2014.10.064>.
- [64] F.A. Permatasari, M.A. Irham, S.Z. Bisri, F. Iskandar, Carbon-Based Quantum Dots for Supercapacitors: Recent Advances and Future Challenges, *Nanomaterials* 11 (2021).
<https://doi.org/10.3390/nano11010091>.
- [65] Enriched carbon dots/graphene microfibers towards high-performance micro-supercapacitors - *Journal of Materials Chemistry A* (RSC Publishing) DOI:10.1039/C8TA02124D, (n.d.).
<https://pubs.rsc.org/en/content/articlehtml/2018/ta/c8ta02124d> (accessed March 3, 2026).
- [66] S. Ilani, L.K. Donev, M. Kindermann, P.L. McEuen, Measurement of the quantum capacitance of interacting electrons in carbon nanotubes, *Nature Phys* 2 (2006) 687–691.
<https://doi.org/10.1038/nphys412>.

Supplementary information

Insights of N-Carbon Quantum Dots Effect on Charge Storage in Supercapacitors

Amelia Klimek^{1,2,3}, Emmanuel Salomon⁴, Samar Hajjar-Garreau^{2,3},
Elzbieta Frackowiak^{*1}, Camélia Matei Ghimbeu^{*2,3,5}

¹Institute of Chemistry and Technical Electrochemistry, Poznan University of Technology, Berdychowo 4,
61-131, Poznan, Poland

²Institut de Science des Matériaux de Mulhouse (IS2M), Université de Haute-Alsace, F-68100 Mulhouse,
France

³Université de Strasbourg, F-67081 Strasbourg, France

⁴Laboratoire d'Innovation Moléculaire et Applications (LIMA), Université de Haute-Alsace, Université de
Strasbourg, CNRS, LIMA UMR 7042, F-68100 Mulhouse, France

⁵Réseau sur le Stockage Electrochimique de l'Energie (RS2E), 80039 Amiens Cedex, France

*Corresponding authors

elzbieta.frackowiak@put.poznan.pl, camelia.ghimbeu@uha.fr

Materials and methods

Materials

Citric acid ($\geq 99.5\%$), ethylenediamine (EDA) ($\geq 99\%$), hexamethylenetetramine (HMTA) ($\geq 99\%$), o-phenylenediamine (oPDA) (99.5%), lithium sulphate monohydrate (Li_2SO_4) ($\geq 99\%$) were purchased from Sigma Aldrich. 1,4-diazabicyclo[2.2.2]-octane (TEDA) (98%) was acquired from Alda Aesar. A carbon cloth Kynol 5092-20 was provided from Kynol Europa GmbH. GF-A glass microfiber discs, which served as separators were given by Whatman. Dialysis membrane (Spectra/Por Dialysis Membrane) MWCO: 100-500 D was purchased by Biotech CE Tubing. Cell culture Bottle Top Filtration unit, 0.22 μm (polyethersulfonate) was purchased from the Starlab.

N-CQDs preparation

N-CQDs were synthesized from citric acid and amine (EDA, HMTA, TEDA, oPDA, respectively, through a hydrothermal carbonization treatment (HTC), by modifying the existing protocol[1] as illustrated in **Fig. 1**. Firstly, citric acid and selected amine (1:2 molar ratio) were mixed in distilled water at RT until being dissolved. The solution (30 mL) was transferred to a Teflon-lined stainless-steel autoclave. The reactor was placed in the oven and heated at 200°C for 4 hours. After the reaction, the autoclave was taken out of the oven and cooled down at RT. The recovered solution was initially centrifugated (20,000 rpm, 10 min) to eliminate the residual reactants with larger sizes. Then, the solution was subsequently subjected to dialysis using a membrane (100-500 Da) for 24 hours and filtered with 0.22 μm membrane to further remove reaction residues and by-products. The resultant solution containing dispersed N-CQDs was stored at the temperature $\sim 4^\circ\text{C}$. The purified liquid solutions of N-CQDs, without any further modifications were used for the physicochemical and electrochemical testing. Additionally, to estimate the concentration, N-CQDs solutions were freeze dried to obtain the solid powder products and its weight. The resulting average yield was: 6 mg mL^{-1} (EDA-, HMTA-CQDs), 8 mg mL^{-1} (TEDA-CQDs), 16 mg mL^{-1} (oPDA-CQDs).

Kynol-N-CQDs preparation

Self-standing electrodes were cut out of the Kynol carbon cloth sheet into the 10 mm of diameter (thickness: 460 μm , mass: ~ 11 mg). A single Kynol electrode was impregnated with a 1 mL of the selected N-CQDs solution over 24 h and dried at 80°C for 10 min. The change

of the color of EDA-CQDs solution after immersing Kynol electrodes was tracked in time as shown in **Fig. S4**. The Kynol-EDA-CQDs solution changed color, from yellowish to no-color after 24 hours.

Physicochemical characterization of the materials

Transmission electron microscopy (TEM) was employed to investigate the morphology and microstructural properties of the N-CQDs on a JEOL ARM-200F with acceleration voltage of 200 kV. The N-CQDs (2 drops of the solution) were applied onto a carbon holey mesh grid (Agar) and allowed to air dry. The particle size distribution was determined using the ImageJ program and the ~1000 of particles were counted for EDA-CQDs, ~900 for HMTA-, TEDA-CQDs and ~300 for oPDA-CQDs. Additionally, polydispersity index (PDI) was calculated, considering the mean particle diameter and standard deviation of the size distribution. The Philips Scanning Electron Microscope XL30 served for SEM micrographic images and energy dispersive X-ray (EDX) mapping of the Kynol and Kynol-N-CQDs. X-ray photoelectron spectroscopy (XPS) was used to analyze the surface chemical composition and functional groups of N-CQDs, Kynol and Kynol-N-CQDs within the energy range of 300-1500 eV. The analysis was done using a VG SCIENTA SES-2002 spectrometer equipped with a monochromatic X-ray source (Al K α = 1486.6 eV). Before the XPS analysis, the N-CQDs were freeze dried. A conductivity meter and pH meter (both purchased from Mettler Toledo®, Switzerland) were utilized to measure the ionic conductivity and pH of the N-CQDs at ambient temperature. Fourier transform infrared spectroscopy (FTIR) spectrometer, Thermo fisher Scientific iS50, with the ATR (attenuated total reflectance) mode was performed on the N-CQDs solutions. A SpectraMax iD3 multimode microplate reader (absorbance, fluorescence, luminescence) was used to measure absorbance (λ = 230 nm to 1000 nm) and fluorescence emission (λ_{exc} = 40 nm to 850 nm) of N-CQDs. The-EDA-CQDs, HMTA-CQDs, and oPDA-CQDs solutions were diluted by 100, and TEDA-CQDs solution was diluted by 50. The thermal stability and oxidation behavior of the Kynol and Kynol-N-CQDs were investigated using Mettler Toledo TGA/DSC 3+. The analyses were performed under oxygen (Air) and an inert atmosphere (N₂) with heating rate of 5°C min⁻¹ up to 900°C. The texture of the Kynol and Kynol-N-CQDs was investigated using ASAP 2420 Micromeritics, by nitrogen sorption at 77K. The samples were degassed before the analysis at 80°C for 24 hours. The specific surface area (SSA) was calculated by the Brunauer-Emmett-Teller (BET) equation from the linear dependence at relative pressures ranging from 0.01 to 0.05. The micropore volume (V_{micro}) was

determined using Dubinin-Radushkevich model. The mesopore volume (V_{meso}) was determined by subtracting V_{micro} from the total pore volume of nitrogen adsorbed at relative pressure (p/p_0) of 0.99. The average micropore ($L_0 \text{ micro}$) and mesopore ($L_0 \text{ meso}$) size was calculated according to the formula reported in[2]. The pore size distribution (PSD) was determined using two-dimensional nonlocal density functional theory (2D-NLDFT) from SAIEUS software[3], where the slit pores and adsorption branch are considered. The model for heterogenous surface pores for carbon materials was applied.

Electrochemical characterization of the materials

Two electrodes made of Kynol or Kynol-N-CQDs, separated by GF-A separator were soaked with 150 μL of 1 mol L^{-1} Li_2SO_4 electrolyte (pH ~ 8 , ionic conductivity $\sim 65 \text{ mS cm}^{-1}$) and placed in 2-electrode Swagelok® system with stainless steel 316L current collectors. A VMP3 multi-channel potentiostat/galvanostat (BioLogic, France) was utilized for the electrochemical capacitor testing at RT. Cyclic voltammetry (CV) at scanning rates 1 – 100 mV s^{-1} , galvanostatic charge-discharge (GCD) at current densities 0.1 – 5 A g^{-1} , electrochemical impedance spectroscopy (EIS) at frequency range 100 kHz – 1 mHz (0 V) were used. Gravimetric capacitance values calculated after 2-electrode cell measurement are expressed per one electrode. The formulas (I,II) used for the calculation of the gravimetric capacitance (extracted from[2,4]) are presented below:

$$I \quad C_{CV} = \frac{2I}{v m_a} \quad [F g^{-1}]$$

where: I – current, v – scan rate, m_a – active mass of the electrode.

$$II \quad C_{GCD} = \frac{4 A_{int} t}{U^2 m_a} \quad [F g^{-1}]$$

where: A_{int} – integration of constant current discharge curve, t – time of discharge, m_a – active mass of the electrode, U – applied voltage.

Additionally, a reference electrode $\text{Hg}|\text{Hg}_2\text{SO}_4$ was used for three electrode measurements. A Dunn's method served for the calculation of capacitive and diffusive contributions according to[5,6]. Capacitance normalized by the specific surface area (S_{BET}) was calculated by dividing the capacitance from CV by the S_{BET} . The floating procedure was employed to assess the lifespan of the ECs[7]. Three GCD cycles (1 A g^{-1}) at the U_{max} (1.6 V) were followed by a 2-

hour voltage hold at $U_{\max}$. The floating procedure was reiterated until one of end-of-life requirements was reached, a 20% decrease in initial gravimetric capacitance (C/C_0) and/or a 100% increase of initial resistance (R_e/R_{e0}) according to [8,9].

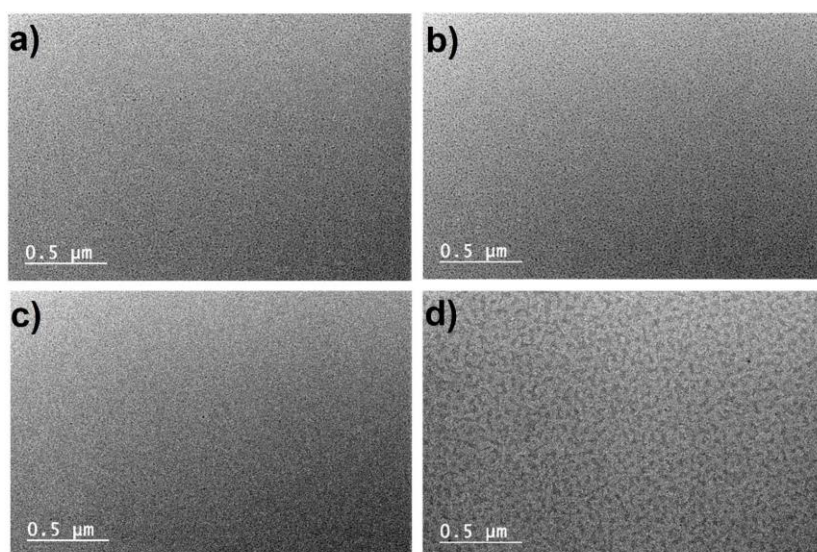


Fig. S1 TEM images of N-CQDs: **a)** EDA-CQDs, **b)** HMTA-CQDs, **c)** TEDA-CQDs, **d)** oPDA-CQDs.

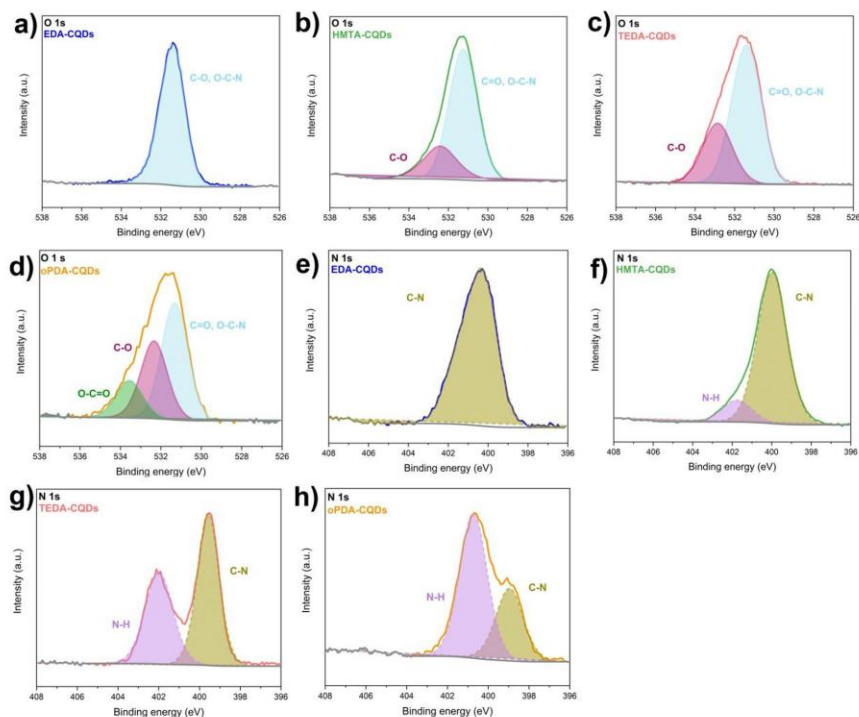


Fig. S2 Deconvolution of O 1s XPS spectra: **a)** EDA-CQDs, **b)** HMTA-CQDs, **c)** TEDA-CQDs, **d)** oPDA-CQDs. Deconvolution of N 1s XPS spectra: **e)** EDA-CQDs, **f)** HMTA-CQDs, **g)** TEDA-CQDs, **h)** oPDA-CQDs.

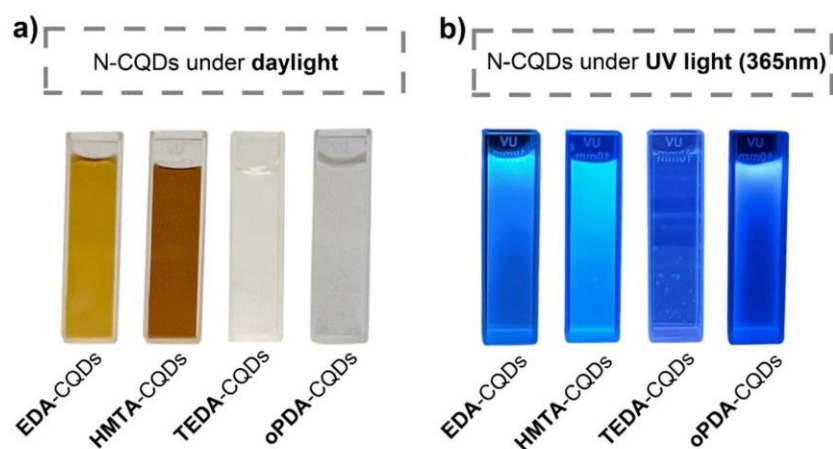


Fig. S3 Optical photographs of N-CQDs solutions under **a)** daylight, **b)** UV light (365 nm).

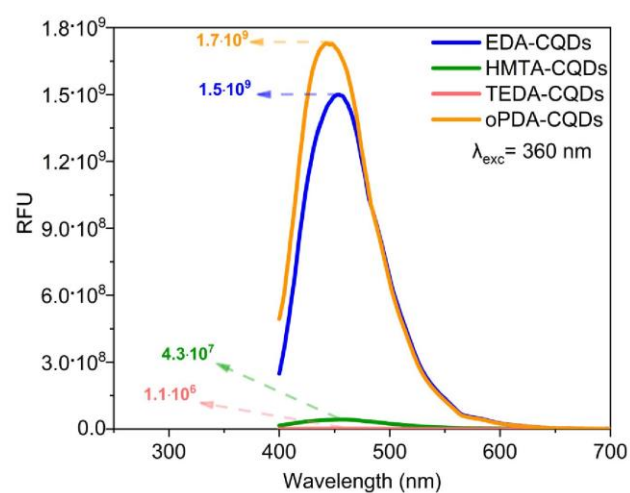


Fig. S4 The PL emission spectra at $\lambda_{\text{exc}} = 360 \text{ nm}$ of CQDs.

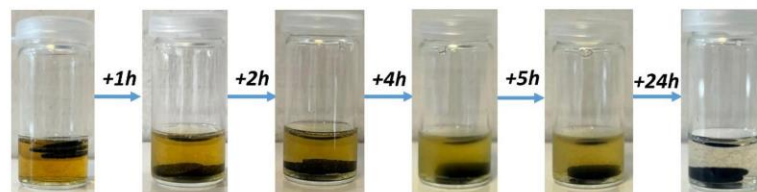


Fig. S5 The change of the color of EDA-CQDs solution as a function of the time of impregnation with Kynol electrodes.

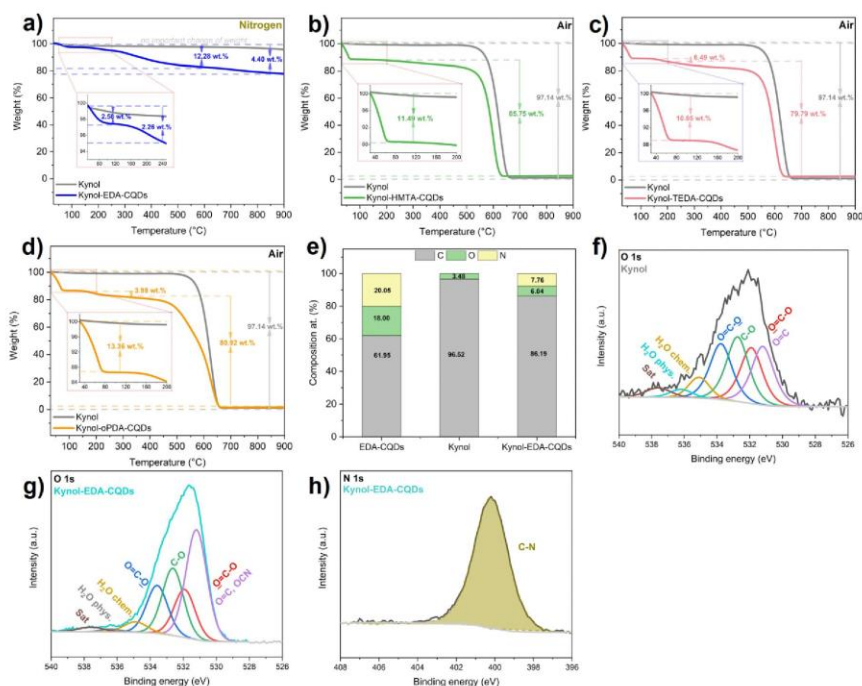


Fig. S6 a) TGA curves (Nitrogen) of Kynol and Kynol-EDA-CQDs. TGA curves (Air) of Kynol and: b) Kynol-HMTA-CQDs, c) Kynol-TEDA-CQDs, d) oPDA-CQDs; e) surface chemical composition from XPS analysis of EDA-CQDs, Kynol and Kynol-EDA-CQDs; O-functional groups derived from the deconvoluted O 1s XPS spectra: f) Kynol g) Kynol-EDA-CQDs; N-functional groups derived from the deconvoluted N 1s XPS spectra: h) Kynol-EDA-CQDs.

Tab. S1 Textural properties of Kynol carbon cloth and Kynol impregnated with EDA-CQDs determined by N₂ sorption at 77K: S_{BET} , V_{micro} , V_{meso} , $L_0 \text{ micro}$, and $L_0 \text{ meso}$.

Material	S_{BET} ($\text{m}^2 \text{ g}^{-1}$)	V_{micro} ($\text{cm}^3 \text{ g}^{-1}$)	V_{meso} ($\text{cm}^3 \text{ g}^{-1}$)	$L_0 \text{ micro}$ (nm)	$L_0 \text{ meso}$ (nm)
Kynol	1955	0.72	0.12	0.84	2.01
Kynol-EDA-CQDs	1060	0.38	0.08	0.87	2.05

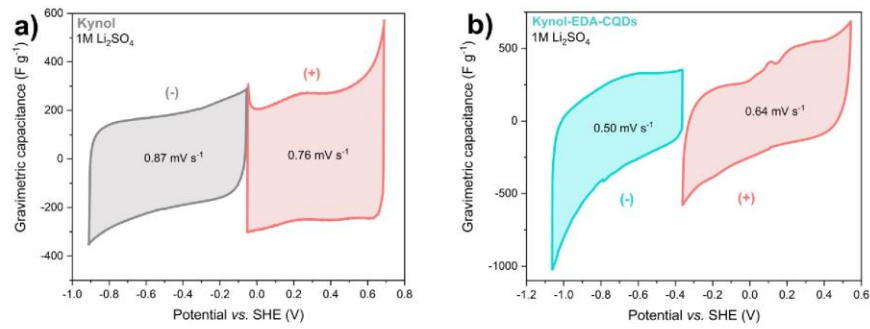


Fig. S7 Cyclic voltammetry profiles of negative and positive electrodes of **a)** Kynol and **b)** Kynol-EDA-CQDs based ECs.

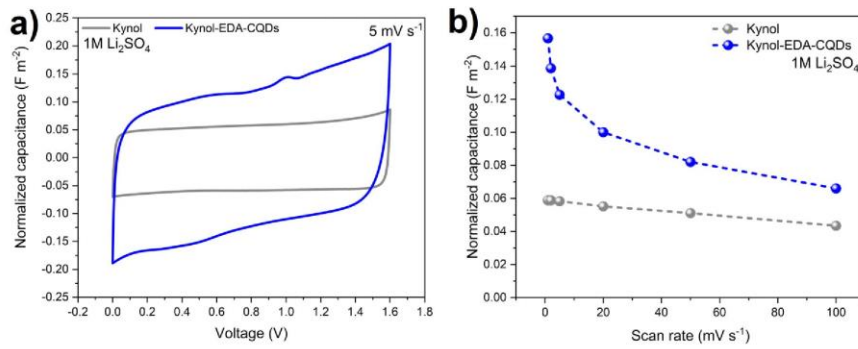


Fig. S8 Capacitance normalized by S_{BET} value for Kynol and Kynol-EDA-CQDs-based ECs: **a)** cyclic voltammetry at 5 mV s^{-1} , **b)** scan rate at $1 - 100 \text{ mV s}^{-1}$.

Tab. S2 Parameters of the equivalent circuit for Kynol and Kynol-N-CQDs.

Material	R_e^a (Ω)	R_i^b (Ω)	R_{ct}^c (Ω)	R_{diff}^d (Ω)	f_0^e (Hz)	τ_0^f (s)
Kynol	0.68	0.94	0.26	2.63	0.50	2.0
Kynol-EDA-CQDs	0.53	0.87	0.34	2.13	0.65	1.5
Kynol-HMTA-CQDs	0.76	0.99	0.23	2.59	0.48	2.1
Kynol-TEDA-CQDs	0.62	0.84	0.22	2.10	0.49	2.0
Kynol-oPDA-CQDs	0.78	1.93	0.85	4.21	0.45	2.2

^a R_e – electrode resistance

^b R_i – internal resistance

^c R_{ct} – charge transfer resistance

^d R_{diff} – diffuse layer resistance

^e f_0 – operating frequency at which capacitance is 50% of the maximum

^f τ_0 – characteristic relaxation time constant

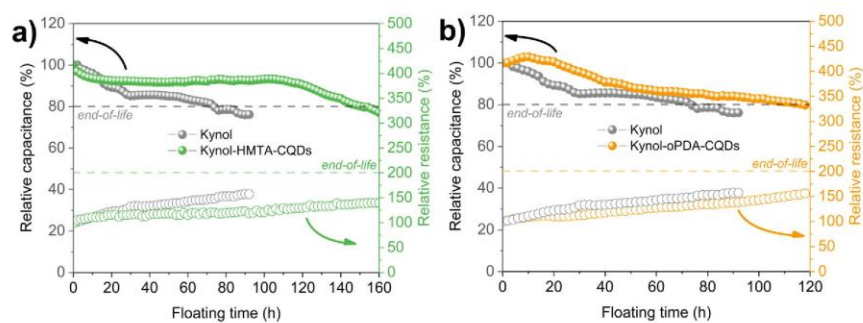


Fig. S9 Relative capacitance and resistance vs. floating time of Kynol and **a)** Kynol-HMTA-CQDs, **b)** Kynol-oPDA-CQDs.

Tab. S3 Summary of the ionic conductivity and pH values of the initial N-CQDs aqueous solutions.

Material	Ionic conductivity ($\mu\text{S cm}^{-1}$)	pH
EDA-CQDs	73.7 ± 1.42	7.3 ± 0.06
HMTA-CQDs	129.4 ± 2.03	7.1 ± 0.04
TEDA-CQDs	317.4 ± 8.29	7.0 ± 0.01
oPDA-CQDs	52.3 ± 0.84	7.0 ± 0.01

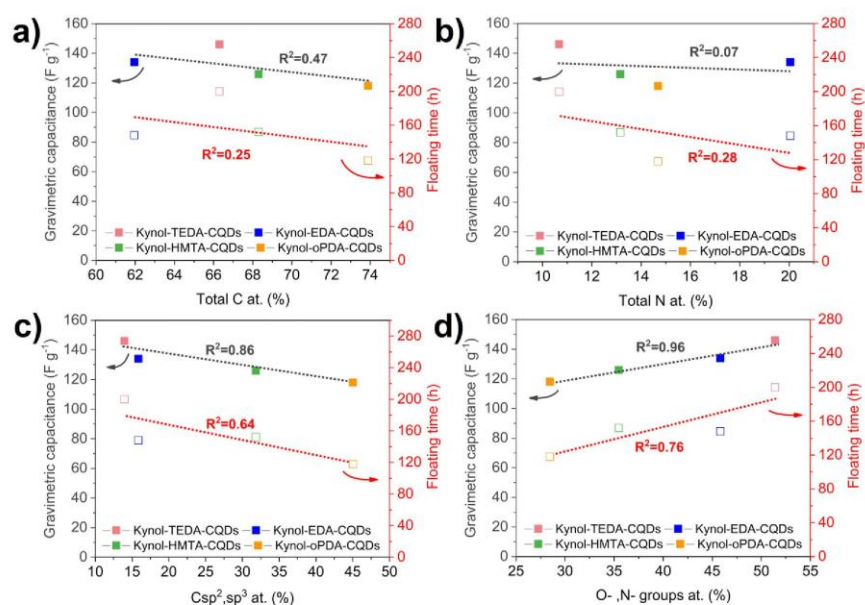


Fig. S10 Gravimetric capacitance and floating time presented as a function of: **a)** total carbon content derived from XPS survey spectra **b)** total nitrogen content derived from XPS survey spectra, **c)** Csp^2 , sp^3 content derived from C 1s XPS spectra, **d)** O-, N-groups content derived from C 1s XPS spectra.

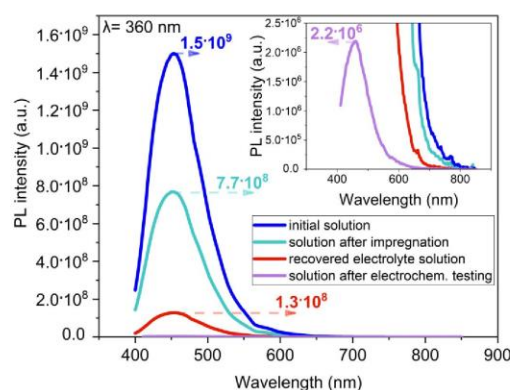


Fig. S11 PL emission spectra at $\lambda=360$ nm of: initial EDA-CQDs solution (blue line), solution of EDA-CQDs after Kynol electrodes impregnation (light blue), recovered electrolyte solution before the electrochemical testing (red line), solution after electrochemical testing (violet line).

References

- [1] Y. Hiejima, M. Kanakubo, Hydrothermal Synthesis of Photoluminescent Nanocarbon from Hydroxylic Acids and Amines, *J Solution Chem* 45 (2016) 1560–1570. <https://doi.org/10.1007/s10953-016-0531-5>.
- [2] A. Platek-Mielczarek, C. Nita, C. Matei Ghimbeu, E. Frackowiak, K. Fic, Link between Alkali Metals in Salt Templates and in Electrolytes for Improved Carbon-Based Electrochemical Capacitors, *ACS Appl. Mater. Interfaces* 13 (2021) 2584–2599. <https://doi.org/10.1021/acsami.0c18627>.
- [3] J. Jagiello, J.P. Olivier, 2D-NLDFT adsorption models for carbon slit-shaped pores with surface energetical heterogeneity and geometrical corrugation, *Carbon* 55 (2013) 70–80. <https://doi.org/10.1016/j.carbon.2012.12.011>.
- [4] S. Azmi, M.F. Koudahi, E. Frackowiak, Reline deep eutectic solvent as a green electrolyte for electrochemical energy storage applications, *Energy Environ. Sci.* 15 (2022) 1156–1171. <https://doi.org/10.1039/D1EE02920G>.
- [5] J. Wang, J. Polleux, J. Lim, B. Dunn, Pseudocapacitive Contributions to Electrochemical Energy Storage in TiO₂ (Anatase) Nanoparticles, *J. Phys. Chem. C* 111 (2007) 14925–14931. <https://doi.org/10.1021/jp074464w>.
- [6] A. Adeniji, A. Beda, P. Fioux, C. Matei Ghimbeu, Engineering nitrogen-doped porous carbon positive electrodes for high-performance sodium-ion capacitors: the critical role of porosity, structure and surface functionalities, *J. Mater. Chem. A* 13 (2025) 14896–14914. <https://doi.org/10.1039/D5TA01075F>.
- [7] E. Pamete, L. Kops, F.A. Kreth, S. Pohlmann, A. Varzi, T. Brousse, A. Balducci, V. Presser, The Many Deaths of Supercapacitors: Degradation, Aging, and Performance Fading, *Adv. Energy Mater.* 13 (2023) 2301008. <https://doi.org/10.1002/aenm.202301008>.
- [8] A. Klimek, B. Réty, C. Matei Ghimbeu, E. Frackowiak, Impact of Disorder, Porosity, and Surface Chemistry of Salt Templated Carbons on Capacitance, *Adv. Sci.* 12 (2025) e05032. <https://doi.org/10.1002/advs.202505032>.
- [9] A. Parejo-Tovar, F. Béguin, The NaClO₄-water eutectic electrolyte for environmentally friendly electrical double-layer capacitors operating at low temperature, *Energy Storage Materials* 69 (2024) 103387. <https://doi.org/10.1016/j.ensm.2024.103387>.

General conclusions

This PhD thesis introduces several strategies for the development of electrochemical capacitors (ECs), ensuring their high capacitive performance and long-term lifespan. The EC performance relies on both the electrolyte and the electrode, facing persistent limitations. Important contributions presented in this thesis consist of the modification of neutral salt aqueous electrolytes and tailoring of the texture/structure of carbon electrode materials, considering sustainability.

EC electrolyte challenges, including low voltage, corrosive characteristics, short lifespan, and safety concerns are critical, prompting deeper investigation of these limitations. For the first time, the study on urea as a hydrogen bond donor (HBD) additive to a 1M Li_2SO_4 aqueous electrolyte was reported. This achievement is already published (*Azmi et al., Mat. Tod. 2023, 68, 34-50*) and patented (*Patent no. 246396, 6.11.2024, approved by the Polish Patent Office*). EC with urea additive showed an excellent lifespan - over 60 000 cycles and 350 floating hours at 1.6 V. The molecular dynamics modeling proved that the formation of the hydrogen bond network (strong urea-water- Li_2SO_4 hydrogen bonding) is at the origin of such improved EC performance. For elucidation of the HBD effect, *operando* Raman spectroscopy and gas chromatography coupled with mass spectrometry were used. It was confirmed that urea suppresses CO_2 evolution and electrode degradation by reducing free-water activity. Moreover, the additive of urea to 1M Li_2SO_4 reduced corrosion current ten-fold and shifted the corrosion potential to more negative values, showing a strong protective effect toward stainless-steel current collectors. Such an EC electrolyte offers an advantageous and cost-effective solution having, in addition to its anticorrosive character, a stable electrochemical window. The additive of HBD provides new insights into the development of reliable, environmentally friendly electrolytes to produce highly durable ECs.

Interestingly, the capacitance of EC operating in a neutral aqueous electrolyte could be subsequently improved through the additive of redox active pair providing a beneficial pseudocapacitive effect. In the publication *Klimek et al. Green Chem. 2024, 26, 6684-6695*, a new aqueous electrolyte combining buffer solutions (acetate, citrate, phosphate) and a redox additive ($I_2/2I^-$) was investigated. The buffer solution maintained a stable pH, hindering the evolution of oxygen and hydrogen, which led to the increase of the operating voltage (1.5 V). On the other hand, the iodide/iodine redox pair provided enhancement of capacitance (e.g., from 91 F g⁻¹ acetate buffer to 149 F g⁻¹ for acetate buffer/Nal based-EC). During the ageing test, such EC exhibited a prolonged lifespan (100 floating hours without additive vs. 310 floating hours with additive of $I_2/2I^-$). The stabilization of the pH at the electrode/electrolyte interface prevented the formation of insoluble products (e.g., IO_3^-) during accelerated ageing. The buffer/iodide electrolyte-based EC is a cheap, green, and reliable system with significant promise for future widespread application.

To further enhance the safety of aqueous EC, the use of gel electrolytes is considered as a promising approach, ensuring its favorable characteristics (high solution uptake, mechanical stability). A novel and environmentally benign strategy for effective utilization of lignosulfonate (LS), a waste-derived technical lignin from wood, as a renewable precursor for EC components (electrolyte, separator, electrodes) was proposed and published *Klimek et al. Green Chem. 2026, 28, 4225-4242*. Importantly, LS gel electrolyte composed of 72% of LS was further tailored with 5m KOAc and achieved high solution uptake, stability, as well as ionic conductivity. Acetates, working as structural templates and self-activating agents resulted in the tailored texture/structure of LS-carbons. The ECs assembled with LS-components operated at 1.6 V, showed reduced self-discharge, and achieved a lifespan of 170 floating hours, while also benefiting from improved safety due to suppressed electrolyte leakage. Notably, this strategy facilitated a reduction in CO₂ emissions of 32-49%, illustrating its significant potential for advancing more sustainable, safe and high-performance ECs.

The research on EC electrolytes provided great insights, nevertheless the carbon electrode aspect is also important. The current literature lacks the study where the all possible structural/textural/surface chemistry characteristics are related to the capacitance, but also to other parameters of importance such as lifespan, and retention. Further research revealed that salt templated carbons with increased disorder, characterized by a greater I_{D1}/I_G Raman ratio display enhanced capacitance throughout a broad spectrum of current densities, confirmed as well by the active surface area (ASA) approach. The results are published in the article *Klimek et al. Adv. Sci. 2025, 12, e05032*.

Importantly, the degree of disorder is not the only factor that impacts the capacitance. The specific surface area, pore size distribution, and surface functionalities cannot be neglected. The novelty, and impact of this work encompass three principal aspects:

i) The soft-salt templating route modified by the use of mixtures of alkali metal chloride salts in their eutectic ratio, led to the preparation of a series of porous carbons. The differences in cations' binding energy to the carbon core and cations' size resulted in the modifications in the structure/texture of carbons.

ii) Two complementary techniques: Raman spectroscopy and temperature programmed desorption coupled with mass spectrometry (TPD-MS) combined with oxygen chemisorption and further TPD-MS quantification (ASA estimation) served for the investigation of the defects of the synthesized carbons. Both techniques gave different information about the defects, i.e., defects in the graphene basal planes and the carbon edges (Raman), the exact area occupied by the basal and edge carbon defects (ASA). A universal Raman spectra deconvolution procedure with special attention to the use of the integrated areas of D_1 and G bands was performed for the proper degree of disorder value (I_{D1}/I_G).

iii) The determined physicochemical parameters (I_{D1}/I_G , ASA, amount of oxygen functional groups, specific surface area and volume/size of micro- and mesopores) were correlated with capacitance, retention, and lifespan of 1M Li_2SO_4 -based EC. The more disordered carbon, with accessible microporosity matching the solvated ions of the electrolyte, but also with the presence of some mesoporosity (fast kinetics) and balanced surface functionalities content led to boosted capacitance but shorter lifespan. Even if highly disordered carbon supplied enhanced capacitance, defects were responsible for lifespan shortage. On the contrary, the carbons abundant in graphitic domains (e.g., LiCl-templated) enhanced the EC lifespan significantly. Similar property-performance relationships were observed for LS-based salt templated carbons. Overall, these studies provide a universal insight into the design of EC electrode material.

Another strategy to improve the performance of carbon electrodes is linked with the use of the materials that provide pseudocapacitance. Carbon quantum dots (CQDs) are recently proposed for that purpose, nevertheless their real effect on capacitance, retention, and EC lifespan is not well elucidated. Therefore, a straightforward approach to enhance the performance of porous carbon electrodes for ECs through N-doped CQDs is reported. N-CQDs synthesized *via* hydrothermal carbonization using different amines, exhibited particle size of ~6 nm, blue fluorescence under UV light and significant N, O functional groups. The N-CQDs integrated to porous carbon cloth demonstrated

improved capacitance (116 F g⁻¹ without N-CQDs vs. 146 F g⁻¹ with N-CQDs) and markedly enhanced stability during prolonged lifespan (74 floating hours without N-CQDs vs. 200 floating hours with N-CQDs), compared to the pristine carbon electrodes. Through linear correlations, it was identified that N-CQDs possessing high amount of surface groups and low content of Csp²/Csp³ core, are at the origin of better EC performance. These functional groups improved the wettability of the carbon surface, provided additional redox-active sites and electron rich zones, that facilitated pseudo-capacitance, charge transfer within the porous network and protective barrier against degradation. The enhanced electrolyte ionic conductivity, promoted by partial release N-CQDs during EC electrochemical testing, contributed to the performance improvement as well. This work provides insightful understanding of the N-CQDs effect on the EC performance. Particularly, the surface chemistry (O-, N-groups), quantum effects (nanoscale size/modification of electron density), and electrolyte conductivity are at the origin of the improvement of capacitance and lifespan.

Consequently, the outcomes of this thesis show new light on the design of neutral salt aqueous electrolytes and the carbon electrodes for the desired electrochemical performance of ECs, but also other energy storage/conversion systems.

For the perspectives, the electrode materials, abundant and low-cost biomass precursors rich in carbon such as coconut shells, coffee grounds, olive pits, or lignin should be considered, depending on their geographical availability. Ideally, precursors originally containing heteroatoms (O, N, S) or activating functionalities are particularly attractive for simplifying synthesis and improving the electrochemical performance (e.g., chitosan, lignin, sodium alginate). Salt templating approach could be further advanced by use of the components that act simultaneously as structural/textural agent and self-activating source, while being easily removable through the water washing (e.g., acetates, oxalates, carbonates, urea). Further advances also require deeper understanding of the structure–property relationships governing charge storage mechanisms. Advanced characterization techniques (also in *operando* and/or *in-situ* mode), e.g., electron paramagnetic resonance could provide deeper insights into the relationship between paramagnetic sites and capacitance. The role of machine learning and computational chemistry is inevitable for accelerating the design of materials.

Regarding electrolytes, the development of multifunctional systems presents a promising direction, simultaneously ensuring ionic transport, improving safety, and enhancing lifespan. While iodide-based redox couples have demonstrated remarkable efficiency for enhancing the capacitance of positive electrode, identifying bi-redox species capable of

improving the performance of both electrodes would present a major breakthrough. In parallel, combining redox-active species with anti-corrosive additives (hydrogen bond donors) could offer an effective strategy to increase energy density and improve lifespan. Also, the electrolyte could provide additional functionalities into the device (e.g., leakage protection, flammability suppression, elimination of shuttle effects).

The targeted application should guide the design of electrodes and electrolytes, since achieving high energy and high power at the same time in electrochemical capacitors remains challenging. Energy storage coupled with renewable sources harvesting prioritizes high energy density over ultra-fast charge/discharge, especially for stationary applications, e.g., grid stabilization, UPS.

In contrast, automotive applications require high power devices capable of rapid energy delivery (e.g., start/stop systems, regenerative braking). Flexible electrochemical capacitors are promising for wearable electronics, while military and aerospace applications demand devices combining high power, wide operating temperature range, and enhanced safety. Overall, the key challenge is to establish the right balance between performance, sustainability, safety, and application requirements in order to develop the next generation of electrochemical capacitors.

Wnioski końcowe

W niniejszej pracy doktorskiej przedstawiono kilka strategii rozwoju kondensatorów elektrochemicznych (*ang. electrochemical capacitors - ECs*), zapewniających ich wysoką wydajność pojemnościową i długą żywotność. Działanie ECs zależy zarówno od elektrolitu, jak i od elektrody, przy czym w obu przypadkach istnieją pewne ograniczenia. Istotnym osiągnięciem pracy doktorskiej jest modyfikacja elektrolitów wodnych na bazie neutralnych soli oraz dostosowanie tekstury/struktury węglowych materiałów elektrodowych do rozmiaru jonów z uwzględnieniem zasad zrównoważonego rozwoju.

Wyzwania związane z wodnymi elektrolitami, w tym niskie napięcie, właściwości korozyjne, krótka żywotność oraz kwestie bezpieczeństwa, mają kluczowe znaczenie i skłaniają do wnikliwej analizy tych ograniczeń. Nowatorskie wyniki badań dotyczących stosowania mocznika jako dodatku pełniącego rolę donora wiązania wodorowego (*ang. hydrogen bond donor - HBD*) w 1M wodnym elektrolicie Li_2SO_4 zostały opublikowane (*Azmi et al., Mat. Tod. 2023, 68, 34-50*) oraz opatentowane (*nr patentu 246396, 6.11.2024, zatwierdzony przez Urząd Patentowy RP*). EC z dodatkiem mocznika wykazał doskonałą żywotność – ponad 60 000 cykli i 350 godzin stałonapięciowej polaryzacji (1.6 V). Modelowanie z wykorzystaniem dynamiki molekularnej wykazało, że u podstaw tak poprawionej żywotności EC leży tworzenie się sieci wiązań wodorowych (silne wiązania wodorowe pomiędzy mocznikiem, wodą i Li_2SO_4). Aby dodatkowo potwierdzić teoretyczne badania dotyczące efektu HBD, spektroskopia Ramana oraz chromatografia gazowa sprzężona ze spektrometrią mas w trybie *operando* wykazały, że mocznik hamuje wydzielanie CO_2 oraz degradację elektrody poprzez zmniejszenie aktywności niezwiązanej wody. Ponadto dodatek mocznika do 1M Li_2SO_4 dziesięciokrotnie zmniejszył prąd korozyjny i przesunął potencjał korozyjny w kierunku bardziej ujemnych wartości, powodując silne działanie ochronne w stosunku do kolektorów prądowych ze

stali nierdzewnej. Taki elektrolit jest korzystnym i ekonomicznym rozwiązaniem, zapewnia doskonale właściwości antykorozyjne oraz stabilne napięcie EC. Dodatek HBD pokazuje nowe podejście dotyczące opracowywania niezawodnych, przyjaznych dla środowiska elektrolitów do produkcji ECs o wydłużonej żywotności.

Co istotne, pojemność EC działającego w neutralnym elektrolicie wodnym można było następnie zwiększyć poprzez dodanie pary aktywnej redoks, co zapewniło dodatkową pseudopojemność. W publikacji *Klimek et al., Green Chem. 2024, 26, 6684-6695* zaproponowano nowy elektrolit wodny łączący roztwory buforowe (octanowy, cytrynianowy, fosforanowy) oraz dodatek pary redoks ($I_2/2I^-$). Roztwór buforowy utrzymywał stabilne pH, hamując wydzielanie tlenu i wodoru, co doprowadziło do wzrostu stabilnego napięcia EC (1.5 V). Z drugiej strony para redoks jodek/jod zapewniła zwiększenie pojemności (np. z 91 F g⁻¹ dla EC z buforem octanowym do 149 F g⁻¹ dla EC z buforem octanowym/Nal). Podczas testu starzenia taki EC wykazał wydłużoną żywotność (100 godzin stałonapięciowej polaryzacji bez dodatku $I_2/2I^-$ w porównaniu z 310 godzinami stałonapięciowej polaryzacji z dodatkiem $I_2/2I^-$). Stabilizacja pH na granicy faz elektroda/elektrolit zapobiegała tworzeniu się nierozpuszczalnych produktów (np. IO_3^-) podczas testu żywotności. EC wykorzystujący jako elektrolit bufor/jodek stanowi tanią, ekologiczną i niezawodną opcję, która ma duże szanse na szerokie zastosowanie w przyszłości.

W celu zwiększenia bezpieczeństwa elektrolitów wodnych, za obiecujące rozwiązanie uznaje się stosowanie elektrolitów żelowych, które dodatkowo zapewniają wysoką zdolność wchłaniania roztworu elektrolitu oraz stabilność mechaniczną. Nowatorska oraz przyjazna dla środowiska strategia skutecznego wykorzystania lignosulfonianu (LS) - ligniny technicznej pochodzącej z odpadów drzewnych - jako odnawialnego prekursora do produkcji komponentów EC (elektrolitu, separatora, elektrod) została przedstawiona w publikacji *Klimek et al., Green Chem. 2026, 28, 4225-4242*. Co ważne, zaproponowany elektrolit żelowy, składający się w 72% z LS, został dodatkowo zmodyfikowany i osiągnął wysoką zdolność wchłaniania roztworu 5m KOAc, stabilność, a także przewodnictwo jonowe. Octany, działające jako matryce strukturalne i samoczynne aktywatory, doprowadziły do uzyskania zróżnicowanej tekstury/struktury węgla na bazie LS. ECs złożone z lignosulfonianowych komponentów działały stabilnie przy napięciu 1.6 V, wykazywały zmniejszone samowyladowanie i osiągnęły żywotność 170 godzin stałonapięciowej polaryzacji, a jednocześnie zyskały na bezpieczeństwie dzięki zapobieganiu wycieku elektrolitu. Poza tym, strategia ta umożliwiła zmniejszenie emisji CO₂ o 32-49%, co ilustruje jej znaczny potencjał w zakresie rozwoju bardziej zrównoważonych, bezpiecznych i wydajnych ECs.

Badania nad elektrolitami dostarczyły wielu cennych spostrzeżeń, aczkolwiek elektrody węglowe również mają duże znaczenie. W obecnej literaturze brakuje prac, w których wszystkie możliwe cechy strukturalno-teksturalne oraz powierzchniowe grupy funkcyjne węgla zostałyby powiązane nie tylko z pojemnością, ale także z innymi istotnymi parametrami EC, takimi jak żywotność i retencja. Dalsze badania wykazały, że węgle o zwiększonym nieuporządkowaniu struktury, wytworzone przy użyciu matrycy solnej i charakteryzujące się wyższym stosunkiem Ramana I_{D1}/I_G , wykazują zwiększoną pojemność w szerokim zakresie gęstości prądu, co potwierdza również analiza aktywnej powierzchni (*ang. active surface area - ASA*). Wyniki zostały opublikowane w artykule Klimek et al., *Adv. Sci.* 2025, 12, e05032. Aczkolwiek, stopień nieuporządkowania nie jest jedynym czynnikiem wpływającym na pojemność. Nie można pominąć powierzchni właściwej, rozkładu wielkości porów i powierzchniowych grup funkcyjnych. Nowatorski charakter i znaczenie tej pracy obejmują trzy główne aspekty:

i) Metoda matrycy solnej, zmodyfikowana poprzez zastosowanie mieszanin soli chlorków metali alkalicznych w ich stosunku eutektycznym, pozwoliła na przygotowanie serii porowatych węgli. Energia wiązania kationów soli z rdzeniem węglowym oraz ich rozmiar spowodowały różnice w strukturze/teksturze węgli.

ii) Do badania defektów w syntetyzowanych węglach wykorzystano dwie uzupełniające się techniki: spektroskopię Ramana oraz desorpcję programowaną temperaturowo sprzężoną ze spektrometrią mas (*ang. temperature programmed desorption coupled with mass spectrometry - TPD-MS*) w połączeniu z chemisorpcją tlenu i dalszą kwantyfikacją TPD-MS w celu określenia ASA. Obie techniki dostarczyły różnych informacji na temat defektów, tj. defektów w płaszczyznach bazowych grafenu i krawędziach węglowych (Raman) oraz powierzchni zajmowanej przez te defekty (ASA). W celu uzyskania właściwej wartości stopnia nieuporządkowania (I_{D1}/I_G) przeprowadzono uniwersalną procedurę dekonwolucji widm Ramana, ze szczególnym uwzględnieniem zintegrowanych powierzchni pasm D_1 i G .

iii) Określone parametry fizykochemiczne (m.in., I_{D1}/I_G , ASA, zawartość tlenowych grup funkcyjnych, powierzchnia właściwa oraz objętość/wielkość mikro- i mezoporów) skorelowano z pojemnością, retencją i żywotnością ECs z 1M Li_2SO_4 jako elektrolitem. Węgiel o większym stopniu nieuporządkowania, z dostępnymi mikroporami dopasowanymi do solwatowanych jonów elektrolitu, ale również z obecnością mezoporów (szybka kinetyka) i umiarkowaną zawartością powierzchniowych grup funkcyjnych, wpłynął na zwiększoną pojemność, ale krótszą żywotność ECs. Nawet jeśli węgiel o wysokim stopniu nieuporządkowania zapewniał polepszoną pojemność EC,

defekty były odpowiedzialne za skrócenie żywotności EC. Podobne zależności między właściwościami fizykochemicznymi a wydajnością ECs zaobserwowano w przypadku węgla otrzymanych z LS metodą szablونowania z wykorzystaniem soli. Niniejsze badania dostarczają uniwersalne korelacje, które są istotne dla projektowania przyszłych materiałów elektrodowych dla urządzeń do magazynowania energii.

Kolejna strategia mająca na celu poprawę wydajności elektrod węglowych wiąże się z wykorzystaniem materiałów elektrodowych, które dostarczają pseudopojemność. W tym celu zaproponowano ostatnio użycie węglowych kropek kwantowych (*ang. carbon quantum dots - CQDs*), jednak ich rzeczywisty wpływ na pojemność, retencję i trwałość elektrod węglowych nie jest jeszcze dobrze znany. W związku z tym, w prezentowanym manuskrypcie opisano badania nad prostym sposobem poprawy wydajności elektrod z porowatego węgla poprzez zastosowanie CQDs domieszkowanych azotem. N-CQDs, zsyntetyzowane w procesie karbonizacji hydrotermalnej z wykorzystaniem różnych amin, charakteryzowały się wielkością cząstek wynoszącą około 6 nm, niebieską fluorescencją w zakresie światła UV oraz znaczną zawartością azotowych i tlenowych grup funkcyjnych. N-CQDs zintegrowane z porowatą tkaniną węglową wykazały zwiększoną pojemność (116 F g⁻¹ bez N-CQDs vs. 146 F g⁻¹ z N-CQDs) oraz znacznie poprawioną żywotność EC (74 godzin stałonapięciowej polaryzacji bez N-CQDs vs. 200 godzin stałonapięciowej polaryzacji z N-CQDs) w porównaniu z elektrodami węglowymi. Dzięki korelacom liniowym ustalono, że ulepszona pojemność/żywotność EC wynika z faktu, iż N-CQDs posiadają dużą ilość powierzchniowych grup funkcyjnych oraz niską zawartość Csp²/Csp³ w rdzeniu. Grupy te poprawiły zwilżalność powierzchni węgla, zapewniając dodatkowe miejsca aktywne o większej gęstości elektronowej, co sprzyjało pseudopojemności, transferowi ładunku w porowatej sieci oraz tworzeniu bariery ochronnej przed degradacją. Zwiększone przewodnictwo jonowe elektrolitu, poprzez częściowe uwalnianie N-CQDs podczas badań elektrochemicznych, również przyczyniło się do poprawy charakterystyki EC. Niniejsza praca zapewnia wnikliwe zrozumienie wpływu N-CQDs na działanie ECs. W szczególności grupy funkcyjne (grupy O-, N-), efekty kwantowe (rozmiar w nanoskali/modyfikacja gęstości elektronowej) oraz przewodnictwo jonowe elektrolitu są przyczyną poprawy pojemności/żywotności EC.

Podsumowując, niniejsza praca wnosi istotny wkład w rozwój wodnych elektrolitów na bazie neutralnych soli oraz elektrod węglowych pod kątem uzyskania pożądanej charakterystyki kondensatorów elektrochemicznych, a także innych systemów magazynowania i przetwarzania energii.

W kontekście dalszego rozwoju materiałów elektrodowych należy rozważyć wykorzystanie bogatych w węgiel, łatwo dostępnych i niedrogich prekursorów pochodzących z biomasy, takich jak łupiny orzechów kokosowych, fusy z kawy, pestki oliwek czy ligninę, w zależności od ich dostępności w danym regionie. W idealnym przypadku szczególnie interesujące są prekursory zawierające heteroatomy (O, N, S) lub aktywujące grupy funkcyjne, co pozwoli uprościć syntezę i poprawić właściwości elektrochemiczne (np. chitozan, lignina, alginian sodu). Metodę opartą na zastosowaniu matryc solnych można udoskonalić poprzez użycie odczynników, które działają strukturalno/teksturalnie oraz są źródłem samoczynnej aktywacji, a jednocześnie są łatwe do usunięcia poprzez płukanie wodą (np. octany, szczawiany, węglany, mocznik). Dalszy postęp wymaga również głębszego zrozumienia mechanizmu magazynowania ładunku oraz zależności między strukturą materiału a właściwościami pojemnościowymi oraz żywotnością EC. Zaawansowane techniki charakteryzacji (również w trybie *operando* oraz/lub *in situ*), np. elektronowy rezonans paramagnetyczny, mogłyby zapewnić głębsze wyjaśnienie związku między miejscami paramagnetycznymi a pojemnością. Rola uczenia maszynowego i chemii obliczeniowej jest nieunikniona dla przyspieszenia projektowania materiałów.

W przypadku elektrolitów, obiecującym kierunkiem rozwoju jest tworzenie systemów wielofunkcyjnych, które jednocześnie zapewniają transport jonów, zwiększają bezpieczeństwo i wydłużają żywotność. Chociaż pary redoks oparte na jodkach wykazały niezwykłą skuteczność w zwiększaniu pojemności elektrody dodatniej, to zidentyfikowanie związków o dwufunkcyjnej aktywności redoks, zdolnych do poprawy działania obu elektrod, stanowiłoby znaczący przełom. Równoległe połączenie aktywnych związków redoks z dodatkami antykorozyjnymi (donorami wiązań wodorowych) mogłoby stanowić skuteczną strategię zwiększenia gęstości energii i wydłużenia cykliczności. Dodatkowo, elektrolit mógłby zapewnić urządzeniu dodatkowe funkcje (np. ochronę przed wyciekiem, ograniczenie palności, eliminację efektów związanych z samowyladowaniem).

Docelowe zastosowanie urządzenia powinno determinować konstrukcję elektrod i elektrolitów, ponieważ jednoczesne osiągnięcie wysokiej pojemności energetycznej oraz dużej mocy w kondensatorach elektrochemicznych nadal stanowi wyzwanie. Magazynowanie energii zintegrowane z odnawialnymi źródłami energii nadaje priorytet wysokiej gęstości energetycznej, zamiast ultraszybkiemu ładowaniu/wyładowaniu, zwłaszcza w zastosowaniach stacjonarnych, np. w stabilizacji sieci energetycznej czy zasilaczach awaryjnych (UPS).

Natomiast zastosowania motoryzacyjne wymagają urządzeń o dużej mocy, zdolnych do szybkiego dostarczania energii (np. systemy start/stop, hamowanie regeneracyjne). Elastyczne kondensatory elektrochemiczne są obiecujące w przypadku elektroniki nadającej się do noszenia, podczas gdy zastosowania wojskowe i lotnicze wymagają urządzeń łączących dużą moc, szeroki zakres temperatur roboczych i zwiększone bezpieczeństwo. Kluczowym wyzwaniem jest ustalenie balansu między wydajnością, zrównoważonym rozwojem, bezpieczeństwem i planowanym zastosowaniem w celu opracowania kondensatorów elektrochemicznych nowej generacji.

Conclusion générale

Cette thèse de doctorat introduit plusieurs stratégies de développement de condensateurs électrochimiques (EC) présentant des performances capacitives élevées et une longue durée de vie. Les performances des EC sont liées simultanément à la nature de l'électrolyte et des électrodes, et font face à des limitations persistantes. Les contributions importantes présentées dans cette thèse consistent en la modification d'électrolytes aqueux à base de sels neutres et l'adaptation de la texture/structure des matériaux d'électrode en carbone, dans une optique de durabilité.

Les défis posés par les électrolytes des CE, notamment la faible tension, les caractéristiques corrosives, la courte durée de vie et les problèmes de sécurité sont critiques, et incitent à approfondir l'étude de ces limitations. Pour la première fois, une étude sur l'introduction de l'urée comme additif donneur de liaisons hydrogène (DLH) à un électrolyte aqueux 1 M de Li_2SO_4 est rapportée. Cette réalisation a déjà fait l'objet d'une publication (*Azmi et al., Mat. Tod. 2023, 68, 34-50*) et d'un dépôt de brevet (*brevet n° 246396, 6.11.2024, délivré par l'Office polonais des brevets*). Le CE contenant l'électrolyte avec l'urée comme additif démontre une excellente durée de vie, supérieure à 60 000 cycles et 350 heures de fonctionnement à tension de 1,6 V. La modélisation par dynamique moléculaire a prouvé que la formation d'un réseau de liaisons hydrogène (liaisons hydrogène fortes urée-eau- Li_2SO_4) est à l'origine de ces performances améliorées du CE. La spectroscopie Raman *operando* et la chromatographie en phase gazeuse couplée à la spectrométrie de masse ont été utilisées pour élucider l'effet donneur de liaisons hydrogène (DLH). Cela a permis de confirmer que l'urée supprime le dégagement de CO_2 et la dégradation de l'électrode en réduisant l'activité de l'eau libre. De plus, l'ajout d'urée à une solution 1 M de Li_2SO_4 permet de réduire le courant de corrosion d'un ordre de grandeur et de déplacer le potentiel de corrosion vers des valeurs plus négatives, démontrant ainsi un fort effet protecteur sur les collecteurs de

courant en acier inoxydable. Outre son caractère anticorrosif, cet électrolyte pour CE offre une solution avantageuse et économique permettant d'obtenir une fenêtre électrochimique stable. L'ajout d'un DLH ouvre de nouvelles perspectives pour le développement d'électrolytes fiables et respectueux de l'environnement, permettant ainsi la production de CE de haute durabilité.

Il est intéressant de noter que la capacité d'un CE fonctionnant dans un électrolyte aqueux neutre peut être améliorée par l'ajout d'un couple redox actif, induisant un effet pseudocapacitif bénéfique. Dans la publication de *Klimek et al., Green Chem. 2024, 26, 6684-6695*, un nouvel électrolyte aqueux combinant des solutions tampon (acétate, citrate, phosphate) et un additif redox ($I_2/2I^-$) a été utilisé. La solution tampon maintient un pH stable, tout en limitant le dégagement d'oxygène et d'hydrogène, ce qui permet d'augmenter la tension de fonctionnement (1,5 V). Par ailleurs, le couple redox iodure/iode permet d'améliorer la capacité (par exemple, de 91 à 149 F g⁻¹ pour un CE à base de tampon acétate/Nal). Lors d'un test de vieillissement, ce CE a présenté une durée de vie prolongée (310 heures avec l'additif $I_2/2I^-$, au lieu de 100 heures seulement en présence de la solution tampon seule). La stabilisation du pH à l'interface électrode/électrolyte empêche la formation de produits insolubles lors du vieillissement accéléré. Le CE à base d'électrolyte tampon/iodure est un système économique, écologique et fiable, présentant un fort potentiel pour de futures applications à grande échelle.

Afin d'améliorer encore plus la sécurité des CE en milieu aqueux, l'utilisation d'électrolytes gélifiés a été considérée comme une approche prometteuse, grâce à leurs caractéristiques avantageuses (forte absorption de solution, stabilité mécanique). Une stratégie novatrice et respectueuse de l'environnement pour une utilisation efficace du lignosulfonate (LS, une lignine technique de bois issue de déchets) comme précurseur renouvelable des composants d'un CE (électrolyte, séparateur, électrodes), a été proposée et publiée par *Klimek et al., Green Chem. 2026, 28, 4225-4242*. Un électrolyte gélifié composé de 72 % de LS a été optimisé avec 5 m KOAc, permettant d'atteindre une forte absorption de solution, une grande stabilité et une conductivité ionique élevée. Les acétates, utilisés comme matrices structurales et agents d'auto-activation, ont permis d'obtenir des carbones LS de texture/structure contrôlée. Les CE assemblés avec ces composants LS fonctionnent à 1,6 V, et présentent une autodécharge réduite et une durée de vie de 170 heures à 1,6 V, tout en bénéficiant d'une sécurité accrue grâce à la suppression des fuites d'électrolyte. Cette stratégie a notamment permis de réduire les émissions de CO₂ de 32-49 %, démontrant ainsi son potentiel important pour le développement de CE plus durables, plus sûrs et plus performants.

Même si les recherches sur les électrolytes pour CE ont apporté des éclairages précieux, la contribution des électrodes de carbone demeure importante. La littérature actuelle ne présente pas d'étude reliant l'ensemble des caractéristiques structurales et texturales à la capacité, ni à d'autres paramètres importants tels que la durée de vie et la rétention. Des recherches complémentaires ont révélé que les carbones à matrice saline présentant un désordre accru, caractérisé par un rapport Raman I_{D1}/I_G plus élevé, confirmé également par l'approche de la surface active (ASA), affichent une capacité améliorée sur une large gamme de densités de courant. Ces résultats sont publiés dans l'article de *Klimek et al.*, *Adv. Sci.* 2025, 12, e05032. Il est important de noter que le degré de désordre n'est pas le seul facteur influençant la capacité. La surface spécifique, la distribution de la taille des pores et les fonctionnalités de surface sont également des facteurs déterminants. L'originalité et l'impact de ce travail reposent sur trois aspects principaux :

i) La méthode de synthèse par matrice saline, modifiée par l'utilisation de mélanges de chlorures de métaux alcalins dans leur rapport eutectique, a permis la préparation d'une série de carbones poreux. Les différences d'énergie de liaison des cations au cœur carboné et leur taille ont entraîné des modifications de la structure/texture des carbones.

ii) Deux techniques complémentaires, la spectroscopie Raman et la désorption programmée en température couplée à la spectrométrie de masse (TPD-MS), combinées à la chimisorption d'oxygène accompagnée d'une quantification TPD-MS (estimation de l'ASA), ont permis d'étudier les défauts des carbones synthétisés. Ces deux techniques ont fourni des informations différentes sur les défauts, à savoir les défauts dans les plans basaux de graphène et sur les bords du carbone (Raman), et surface exacte occupée par ces défauts (ASA). Une procédure universelle de déconvolution des spectres Raman, avec une attention particulière portée à l'utilisation des aires intégrées des bandes D_1 et G, a été appliquée pour obtenir la valeur appropriée du degré de désordre (I_{D1}/I_G).

iii) Les paramètres physico-chimiques déterminés (I_{D1}/I_G , ASA, quantité de groupements fonctionnels oxygénés, surface spécifique et volume/taille des micro- et mésopores) ont été corrélés à la capacité, à la rétention et à la durée de vie d'un CE à base de 1M Li_2SO_4 . Le carbone le plus désordonné, présentant une microporosité accessible adaptée aux ions solvatés de l'électrolyte, mais également une certaine mésoporosité (cinétique rapide) et une teneur équilibrée en groupements fonctionnels de surface, a permis d'accroître la capacité, mais de réduire la durée de vie. Même si ce carbone très désordonné offrait une capacité accrue, les défauts étaient responsables de la réduction

de la durée de vie. À l'inverse, les carbones riches en domaines graphitiques (par exemple, synthétisés par matrice LiCl) permettent d'améliorer considérablement la durée de vie des CE. Des relations propriétés-performances similaires ont été observées pour les carbones synthétisés par matrice LS. Globalement, ces études offrent une vision universelle sur la conception des matériaux d'électrode pour CE.

Une autre stratégie pour améliorer les performances des électrodes de carbone repose sur l'utilisation de matériaux conférant une pseudocapacité. Les points quantiques de carbone (PQC) ont récemment été proposés à cette fin ; toutefois, leur effet réel sur la capacité, la rétention et la durée de vie des CE reste mal compris. C'est pourquoi une approche simple visant à améliorer les performances des électrodes de carbone poreuses pour CE grâce à des PQC dopés à l'azote (PQC-N) est présentée. Les PQC-N synthétisés par carbonisation hydrothermale à l'aide de différentes amines, présentent une taille de particules d'environ 6 nm, une fluorescence bleue et une quantité importante de groupements fonctionnels azotés et oxygénés. Les PQC-N intégrés à un tissu de carbone poreux permettent d'obtenir une capacité améliorée (146 F g^{-1} contre 116 F g^{-1}) et une durée de vie prolongée (200 heures contre 74 heures à tension maximale), comparativement aux électrodes de carbone non dopées. Des corrélations linéaires ont permis d'identifier que les PQC possédant une quantité élevée de groupements de surface sont à l'origine des meilleures performances des CE. Ces groupes fonctionnels améliorent la mouillabilité de la surface du carbone, fournissent des sites redox actifs supplémentaires et des zones riches en électrons, ce qui stimule la pseudocapacité, le transfert de charge au sein du réseau poreux et la formation d'une barrière protectrice contre la dégradation. L'amélioration de la conductivité ionique de l'électrolyte, induite par la libération partielle de PQC-N lors des tests électrochimiques des CE, contribuent également à l'amélioration des performances. Ce travail apporte un éclairage nouveau sur l'effet des PQC-N sur les performances des CE. Plus précisément, la chimie de surface (groupes O- et N-), les effets quantiques (taille nanométrique/modification de la densité électronique) et la conductivité de l'électrolyte sont à l'origine de l'amélioration de la capacité et de la durée de vie.

Par conséquent, les résultats de cette thèse offrent de nouvelles perspectives pour la conception d'électrodes de carbone et d'électrolytes aqueux à base de sels neutres, en vue d'obtenir les performances électrochimiques souhaitées pour les condensateurs électrochimiques, mais aussi pour d'autres systèmes de stockage et de conversion d'énergie.

Concernant les matériaux d'électrode, il conviendrait d'envisager des précurseurs issus de la biomasse riches en carbone, abondants et peu coûteux, tels que les coques de noix de coco, le marc de café, les noyaux d'olive ou la lignine, en fonction de leur disponibilité géographique. Idéalement, les précurseurs contenant initialement des hétéroatomes (par exemple, O, N, S) ou des groupements fonctionnels activants sont particulièrement intéressants pour simplifier la synthèse et améliorer les performances électrochimiques (par exemple, le chitosane, la lignine, l'alginate de sodium). L'approche par templating salin pourrait être perfectionnée en utilisant des composants agissant simultanément comme agent structural/textural et source d'auto-activation, tout en étant facilement éliminables par lavage à l'eau (par exemple, des acétates, oxalates, carbonates, l'urée). Pour réaliser de nouvelles avancées, il est également nécessaire de mieux comprendre les relations structure-propriétés régissant les mécanismes de stockage de charge. Des techniques de caractérisation avancées (y compris en mode *operando* ou *in situ*), telles que la résonance paramagnétique électronique, pourraient fournir des informations plus précises sur la relation entre les sites paramagnétiques et la capacité. Le rôle de l'apprentissage automatique et de la chimie computationnelle est incontournable pour accélérer la conception des matériaux.

Concernant les électrolytes, le développement de systèmes multifonctionnels représente une voie prometteuse, assurant simultanément le transport ionique, améliorant la sécurité et prolongeant la durée de vie. Si les couples redox à base d'iodure ont démontré une efficacité remarquable pour améliorer la capacité de l'électrode positive, l'identification d'espèces bi-redox capables d'améliorer les performances des deux électrodes constituerait une avancée majeure. Parallèlement, la combinaison d'espèces redox actives avec des additifs anti-corrosifs (par exemple, des donneurs de liaisons hydrogène) pourrait offrir une stratégie efficace pour augmenter la densité énergétique et prolonger la durée de vie. L'électrolyte pourrait conférer des fonctionnalités supplémentaires au dispositif (par exemple, la protection contre les fuites, la réduction de l'inflammabilité, l'élimination des effets navette).

L'application visée devrait orienter la conception des électrodes et des électrolytes, car l'obtention de condensateurs électrochimiques délivrant simultanément une énergie et une puissance élevées reste un défi. Le stockage d'énergie associé à l'exploitation des énergies renouvelables privilégie une densité énergétique élevée à une charge/décharge ultrarapide, notamment pour les applications stationnaires telles que la stabilisation du réseau et les systèmes d'alimentation sans coupures (UPS).

À l'inverse, les applications automobiles exigent des dispositifs de forte puissance capables de fournir rapidement de l'énergie (par exemple, les systèmes start/stop et le freinage régénératif). Les condensateurs électrochimiques flexibles sont prometteurs pour l'électronique portable, tandis que les applications militaires et aérospatiales requièrent des dispositifs alliant puissance élevée, large plage de températures de fonctionnement et sécurité renforcée. En définitive, le principal défi consiste à trouver le juste équilibre entre performance, durabilité, sécurité et exigences de chaque application afin de développer la prochaine génération de condensateurs électrochimiques.

Doctoral thesis summary

1) Introduction

The widespread use of fossil fuels contributes significantly to greenhouse gas emissions, environmental degradation, and climate change¹. Renewable energy sources provide a sustainable alternative; however, their intermittent nature requires efficient energy storage technologies^{1,2}. Among currently available systems, electrochemical capacitors (ECs), are particularly attractive due to their high power density, rapid charge/discharge capability, and excellent cycling stability, hence enable the storage of renewable energy^{3,4}. Nevertheless, ECs still face limitations related to energy density, electrolyte safety, narrow operating voltage, corrosion processes, limited lifespan, and sustainability of electrode materials^{5,6}.

The main objective of the thesis is to enhance the capacitance, functioning voltage, and sustainability of ECs. This thesis focuses on the development of sustainable aqueous electrochemical capacitors through two complementary approaches: (i) modification of neutral aqueous electrolytes to enhance voltage stability, corrosion resistance, and lifespan; (ii) tailoring the texture, disorder, and surface chemistry of carbon electrode materials to optimize capacitance and lifespan. Particular emphasis is placed on environmentally friendly materials, advanced characterization techniques, and structure–performance relationships.

2) Results and discussion

Electrochemical capacitor in aqueous electrolyte with long lifespan improved by hydrogen bond addition; <https://doi.org/10.1016/j.mattod.2023.06.018>

A major limitation of aqueous ECs based on neutral electrolytes is the corrosion of stainless-steel current collectors, which shortens device lifespan and decreases electrochemical stability. To address this issue, the effect of urea as a hydrogen bond

donor (HBD) additive to 1 M Li_2SO_4 electrolyte was investigated employing, e.g., electrochemistry tests, computational modelling, *operando* Raman spectroscopy and gas chromatography coupled with mass spectrometry (GC-MS) (**Figure 1**).

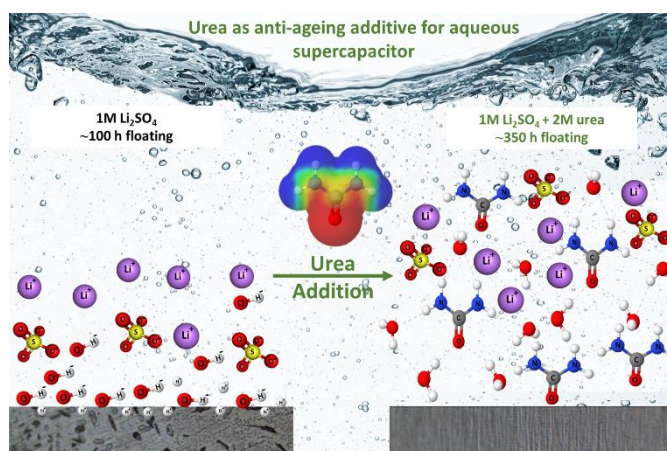


Figure 1 Anti-corrosive and anti-ageing effect on EC due to the formation of hydrogen bond donor network after urea additive to 1M Li_2SO_4 .

The addition of urea only slightly decreased ionic conductivity while maintaining favorable pH values and electrochemical stability. Corrosion testing revealed a substantial reduction of corrosion current from $6.60\ \mu\text{A}$ to $0.55\ \mu\text{A}$ with increasing urea concentration, demonstrating the strong anticorrosive effect of urea. Raman analysis confirmed suppression of Fe_2O_3 formation

and stabilization of protective FeOOH surface layers. Symmetric ECs operating with urea-containing electrolytes-maintained capacitance values of approximately $100\ \text{F g}^{-1}$ at 1.6 V, indicating that the additive did not negatively affect capacitive performance. Importantly, a significant improvement in lifespan was achieved. The EC containing 2 M urea exhibited over 60 000 cycles and approximately 350 floating hours, compared with 47 000 cycles and 96 floating hours for pure 1 M Li_2SO_4 . *Operando* Raman spectroscopy and GC-MS demonstrated that urea reduces free-water activity through formation of an extensive hydrogen bond network, thereby limiting electrode degradation and CO_2 evolution. Density functional theory calculations further confirmed strong interactions between urea, water, and Li_2SO_4 species, leading to modified solvation structures and suppressed water reactivity. Overall, the incorporation of urea enabled the development of a low-cost, eco-friendly electrolyte combining high ionic conductivity, reduced corrosion, and enhanced EC lifespan.

Effect of buffer/iodide electrolyte on the performance of electrochemical capacitors;
<https://doi.org/10.1039/D4GC01748J>

To improve the relatively low capacitance of aqueous ECs, buffer solutions combined with iodide/iodine redox chemistry were investigated. Acetate, citrate, and phosphate buffers containing NaI were studied as multifunctional electrolytes capable of stabilizing pH and introducing pseudocapacitive charge storage (**Figure 2**).

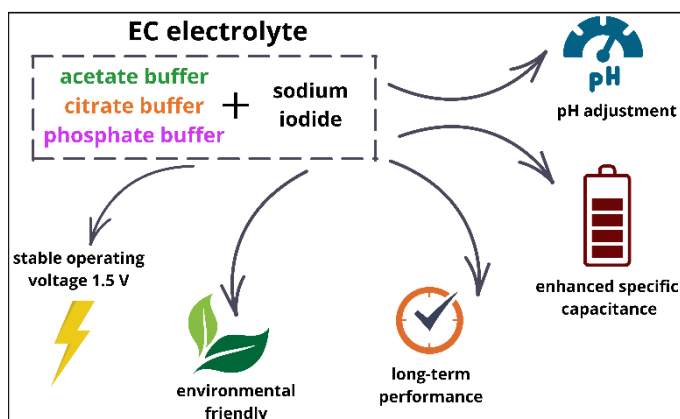


Figure 2 Graphical presentation of the novel buffer-iodide/iodine EC electrolyte with its advantages.

The addition of NaI significantly increased electrolyte conductivity while preserving stable pH conditions. Electrochemical testing demonstrated that iodide-containing electrolytes enabled stable EC operation up to 1.5 V. Three-electrode measurements confirmed that the positive electrode exhibited reversible faradaic reactions

associated with the I^-/I_2 redox couple. The incorporation of 0.2 M NaI markedly enhanced capacitance. For example, capacitance increased from 91 to 149 F g⁻¹ in acetate buffer systems. Simultaneously, the lifespan improved substantially during floating tests. The citrate buffer containing 0.2M NaI achieved more than 1000 floating hours, whereas the corresponding buffer without iodide reached only 30 floating hours. The electrolyte performance strongly depended on pH and iodide concentration. Slightly acidic conditions favored reversible redox activity and minimized formation of undesirable polyiodides and iodates. Excessive iodide concentrations promoted pore blocking and accelerated degradation processes. *Post-mortem* analyses using XPS and XRD showed limited electrode oxidation and lack of insoluble deposits on the carbon surface. The results demonstrated that the synergistic combination of buffering action and iodide redox chemistry simultaneously enhanced capacitance, operating voltage, and stability.

Lignin as a precursor of a gel electrolyte and salt templated carbon for sustainable electrochemical capacitors; <https://doi.org/10.1039/D5GC05533D>

This work further explored the use of liginosulfonate (LS), a waste-derived technical lignin, as a multifunctional precursor for sustainable EC components, including gel electrolytes (GEs), separators, and porous carbons (**Figure 3**). GEs were composed of LS, poly(ethylene glycol) diglycidyl ether (PEGDGE) and acetate salt solutions. Among investigated systems, LS–5 m KOAc gel exhibited the best balance between ionic conductivity, mechanical stability, and reduced water content. In parallel, salt-templated LS-derived carbons were prepared using acetate salts as both structural templates and self-activating agents. The resulting carbons displayed tunable microporosity, structural disorder, and graphitic character depending on the salt composition. Specific surface areas ranged from 881 to 1754 m² g⁻¹. Electrochemical testing demonstrated nearly ideal

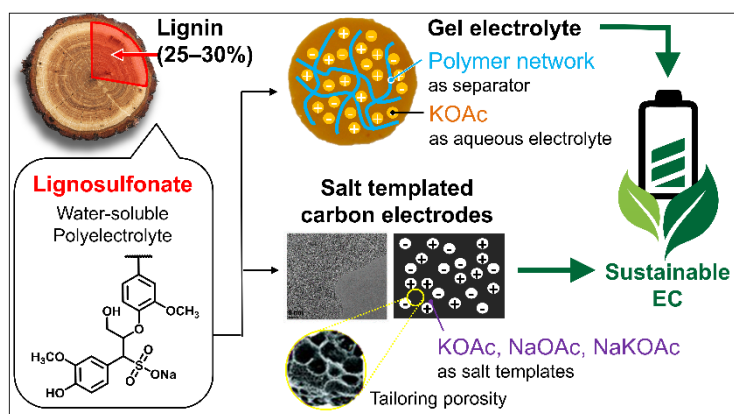


Figure 3 Novel and environmentally friendly strategy for effective utilization of a waste-derived technical lignin from wood, as a renewable precursor of EC electrolyte, electrodes, and separator.

electrical double-layer behavior up to 1.6 V. Capacitance values between 46 and 82 F g⁻¹ were obtained, with higher capacitance observed for highly disordered and microporous carbons. Importantly, the gel electrolyte significantly reduced self-discharge and electrolyte leakage, while

improving device safety. ECs assembled entirely from LS-derived components achieved up to 170 floating hours and reduced voltage loss compared with glass-fiber separators. Life-cycle considerations indicated a reduction in CO₂ emissions of 32–49% compared with conventional EC fabrication methods. The study demonstrated that LS can serve as a renewable and efficient precursor for sustainable ECs.

Impact of disorder, porosity, and surface chemistry of salt templated carbons on capacitance; <https://doi.org/10.1002/adv.202505032>

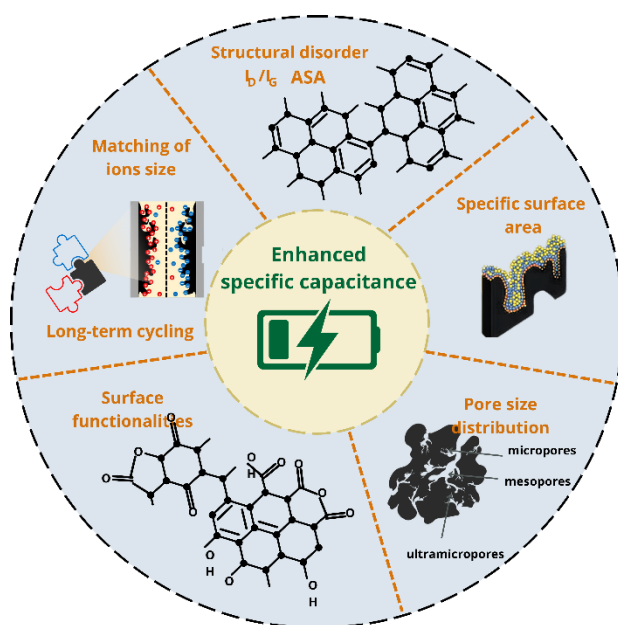


Figure 4 The parameters of importance considered for the enhanced EC performance.

The relationships between carbon texture/structure and electrochemical performance (**Figure 4**) were investigated using porous carbons synthesized by a soft-salt templating approach employing eutectic alkali metal chlorides. Comprehensive characterization using Raman spectroscopy, XRD, TEM, gas sorption, and temperature-programmed desorption coupled with mass spectrometry revealed significant variations in disorder degree, accessible surface area, microporosity, and oxygen functional groups. Highly

disordered CsCl-templated carbons exhibited increased defect density and microporosity, whereas LiCl-based templates promoted graphitic ordering and mesopore formation.

Electrochemical testing in 1 M Li₂SO₄ showed capacitance values up to 244 F g⁻¹ with stable operation at 1.6 V. Strong linear correlations were established between capacitance and several physicochemical parameters. The capacitance increased with: higher disorder degree (I_D/I_G ratio), greater active surface area, larger micropore volume, and appropriate oxygen functional groups. Micropores were identified as dominant charge storage sites, while mesopores mainly facilitated ion transport. Although highly disordered carbons exhibited superior capacitance, they also demonstrated shorter lifespan due to increased structural instability. In contrast, more graphitic carbons provided enhanced durability but lower capacitance. These findings provide a general framework for optimizing carbon electrodes by balancing disorder, porosity, conductivity, and surface chemistry.

Insights of N-carbon quantum dots effect on charge storage in supercapacitors

The final part of the thesis concerned the effect of nitrogen-doped carbon quantum dots (N-CQDs) on EC performance (**Figure 5**). N-CQDs were synthesized by hydrothermal carbonization using citric acid and different amines. The obtained N-CQDs exhibited particle sizes of approximately 6 nm, blue fluorescence under UV light, and high concentrations of oxygen- and nitrogen-containing surface groups.

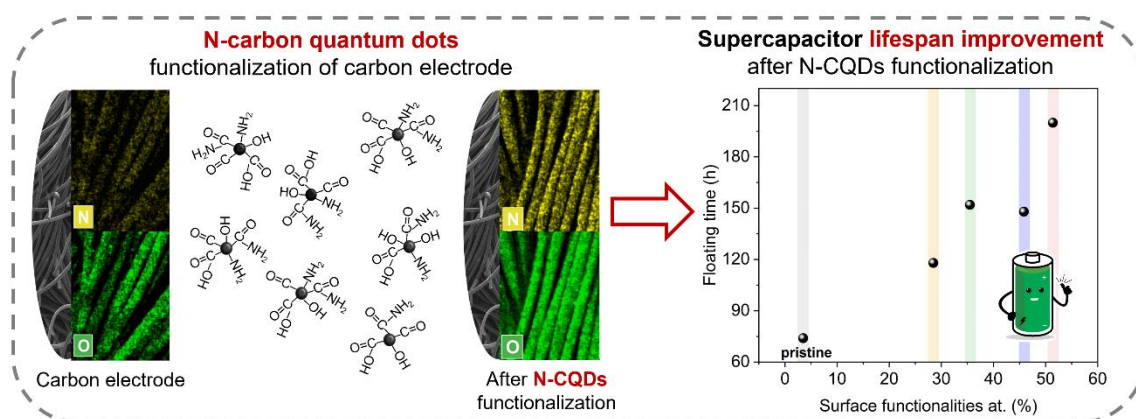


Figure 5 The beneficial effect of the electrode functionalization by carbon quantum dots abundant in oxygen and nitrogen functional groups on the EC lifespan.

Porous carbon cloth electrodes impregnated with N-CQDs were subsequently evaluated in aqueous ECs. The incorporation of N-CQDs improved capacitance from 116 to 146 F g⁻¹ and substantially enhanced lifespan from 74 to 200 floating hours. Dunn analysis revealed increased diffusive contribution associated with pseudocapacitive processes. The improvement originated mainly from the abundant surface functionalities, which enhanced electrode wettability, introduced additional redox-active sites, and facilitated charge transfer. Partial release of N-CQDs into the electrolyte additionally increased ionic conductivity. Correlations between N-CQD properties and EC performance

demonstrated that highly functionalized CQDs with lower graphitic core content provided the best electrochemical behavior.

3) General conclusions

This thesis presents several complementary strategies for the development of sustainable and high-performance aqueous electrochemical capacitors. The incorporation of HBD additives into neutral aqueous electrolytes effectively suppressed corrosion, reduced water activity, and significantly improved EC lifespan without sacrificing electrochemical performance. Buffer/iodide electrolytes introduced reversible pseudocapacitance and enabled simultaneous enhancement of capacitance, voltage window, and stability.

The use of lignosulfonate as a renewable precursor demonstrated the possibility of producing sustainable gel electrolytes and porous carbons considering environmental impact. Furthermore, systematic investigations of salt-templated carbons established clear structure–performance relationships linking disorder, porosity, and surface chemistry to capacitance and lifespan.

Finally, N-CQDs were identified as promising functional additives capable of enhancing both capacitance and long-term stability through surface-functional-derived pseudocapacitance and improved charge transport.

The results provide important insights into the design of environmentally friendly electrolytes and carbon materials for next-generation electrochemical capacitors. The presented strategies contribute to the advancement of safe, durable, and environmentally friendly energy storage technologies.

In perspectives, ECs will likely rely on combining sustainable heteroatom-rich biomass-derived carbon electrodes with multifunctional electrolytes that simultaneously enhance energy density, safety, and lifespan. Supported by advanced characterization techniques (also in *operando* mode), computational chemistry, and machine learning, this integrated approach could accelerate the further development of high-performance devices tailored for applications ranging from renewable energy integration, automotive systems, and wearable electronics.

4) References

- 1 Wolf, S.; Bullard, R.; Buonocore, J. J.; Donley, N.; Farrelly, T.; Fleming, J.; González, D. J. X.; Oreskes, N.; Ripple, W.; Saha, R.; Willis, M. D. Scientists' Warning on Fossil Fuels. *Oxford Open Climate Change* **2025**, 5 (1) kgaf011. <https://doi.org/10.1093/oxfclm/kgaf011>
- 2 Ripple, W.J., Wolf, C., Gregg, J.W., Rockstorm, J., Mann, M.E., Oreskes, N., Lenton, T.M., Rahmstorf, S., Newsome, T.M., Xu, C., Svenning, J.C., Pereira, C.C., Law, B.E., Crowther, T.W., The 2024 state of the climate report: Perilous times on planet Earth. *BioScience* **2024**, 74 (12), 812-824. <https://doi.org/10.1093/biosci/biae087>
- 3 Conway, B. E. *Electrochemical Supercapacitors*; Springer US: Boston, MA, **1999**. <https://doi.org/10.1007/978-1-4757-3058-6>
- 4 Miller, J. R.; Simon, P. Electrochemical Capacitors for Energy Management. *Science* **2008**, 321 (5889), 651–652. <https://doi.org/10.1126/science.1158736>
- 5 Burke, A. F.; Zhao, J. Past, Present and Future of Electrochemical Capacitors: Technologies, Performance and Applications. *Journal of Energy Storage* **2021**, 35, 102310. <https://doi.org/10.1016/j.est.2021.102310>
- 6 Béguin, F.; Presser, V.; Balducci, A.; Frackowiak, E. Carbons and Electrolytes for Advanced Supercapacitors. *Advanced Materials* **2014**, 26 (14), 2219–2251. <https://doi.org/10.1002/adma.201304137>

Podsumowanie pracy doktorskiej

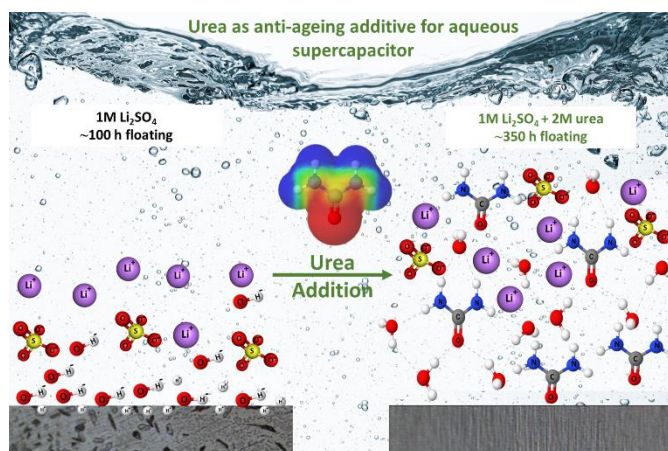
1) Wprowadzenie

Powszechne stosowanie paliw kopalnych w znacznym stopniu przyczynia się do emisji gazów cieplarnianych, degradacji środowiska i zmian klimatu¹. Odnawialne źródła energii stanowią przyjazną środowisku alternatywę; jednak ich okresowość wymaga zastosowania wydajnych technologii magazynowania energii^{1,2}. Spośród obecnie dostępnych technologii, kondensatory elektrochemiczne (*ang. electrochemical capacitors – ECs*), są szczególnie interesujące ze względu na wysoką gęstość mocy, możliwość szybkiego ładowania/wyładowania oraz doskonałą stabilność cykliczną, co pozwala na efektywne magazynowanie energii odnawialnej^{3,4}. Niemniej jednak ECs charakteryzują się ograniczeniami związanymi z gęstością energii, bezpieczeństwem elektrolitu, wąskim zakresem napięcia roboczego, procesami korozji, ograniczoną żywotnością oraz wyborem ekologicznych materiałów elektrodowych^{5,6}.

Głównym celem pracy doktorskiej jest zwiększenie pojemności, napięcia oraz żywotności ECs. Niniejsza praca dotyczy opracowania zrównoważonych kondensatorów elektrochemicznych na bazie roztworów wodnych poprzez zastosowanie dwóch uzupełniających się strategii: (i) modyfikację neutralnych elektrolitów wodnych w celu poprawy pojemności i stabilności napięcia, odporności na korozję oraz żywotności; (ii) dostosowanie tekstury, nieuporządkowania strukturalnego i właściwości powierzchniowych węglowych materiałów elektrodowych w celu uzyskania wysokiej pojemności i długotrwałej żywotności. Szczególny nacisk położono na materiały przyjazne dla środowiska, zaawansowane techniki charakteryzacji oraz zależności między strukturą/teksturą a właściwościami elektrochemicznymi.

2) Wyniki i dyskusja

Electrochemical capacitor in aqueous electrolyte with long lifespan improved by hydrogen bond addition; <https://doi.org/10.1016/j.mattod.2023.06.018>



Rysunek 1 Działanie antykorozyjne i przeciwdziałające starzeniu ECs spowodowane tworzeniem się sieci donorów wiązań wodorowych po dodaniu mocznika do 1M Li_2SO_4 .

Głównym ograniczeniem wodnych ECs wykorzystujących elektrolity na bazie neutralnych soli, jest korozja kolektorów prądowych ze stali nierdzewnej, która skraca żywotność urządzenia i obniża stabilność elektrochemiczną. Aby rozwiązać ten problem, zbadano wpływ mocznika jako dodatku donora wiązania wodorowego (*ang. hydrogen bond donor – HBD*) do 1M Li_2SO_4 , wykorzystując m.in. testy elektrochemiczne, modelo-

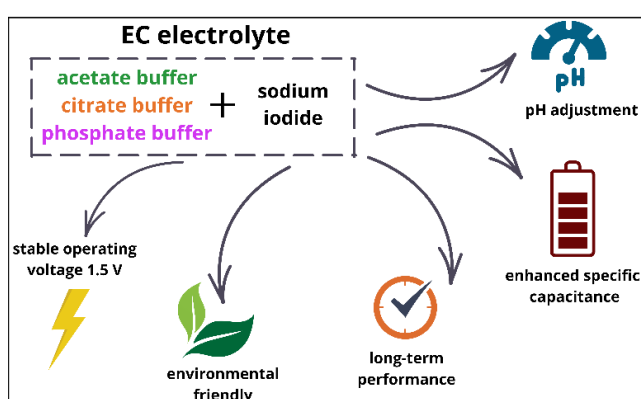
wanie, spektroskopię Ramana oraz chromatografię gazową sprzężoną ze spektrometrią mas (*ang. gas chromatography coupled with mass spectrometry – GC-MS*) w trybie *operando* (**Rysunek 1**).

Dodanie mocznika spowodowało jedynie nieznaczny spadek przewodnictwa jonowego, przy jednoczesnym utrzymaniu korzystnych wartości pH i stabilności elektrochemicznej. Badania korozyjne wykazały znaczne zmniejszenie prądu korozyjnego z $6.60 \mu\text{A}$ do $0.55 \mu\text{A}$ wraz ze wzrostem stężenia mocznika, co wskazuje na silne działanie antykorozyjne. Analiza widm Ramana potwierdziła zahamowanie tworzenia się Fe_2O_3 oraz utworzenie powłoki pasywacyjnej (FeOOH). Symetryczne ECs na bazie elektrolitu zawierającego mocznik utrzymywały wartości pojemności około 100 F g^{-1} przy 1.6 V , co wskazuje, że dodatek ten nie wpłynął negatywnie na pojemność. EC zawierający dodatek 2M mocznika osiągnął ponad 60 000 cykli i około 350 godzin stałonapięciowej polaryzacji w porównaniu z 47 000 cyklami i 96 godzinami stałonapięciowej polaryzacji dla 1M Li_2SO_4 bez dodatku mocznika. Wykorzystując *operando* spektroskopię Ramana oraz GC-MS udowodniono, że mocznik zmniejsza aktywność niezwiązanej wody poprzez tworzenie rozległej sieci wiązań wodorowych, ograniczając w ten sposób degradację elektrody i wydzielanie CO_2 . Modelowanie dodatkowo potwierdziło silne oddziaływania między cząsteczkami mocznika, wody i Li_2SO_4 , prowadzące do zmodyfikowania solwatacji oraz zmniejszonej aktywności wody. Podsumowując, dodatek mocznika umożliwił

opracowanie niedrogiego, ekologicznego elektrolitu łączącego wysokie przewodnictwo jonowe, zmniejszoną korozyjność i wydłużoną żywotność EC.

Effect of buffer/iodide electrolyte on the performance of electrochemical capacitors;
<https://doi.org/10.1039/D4GC01748J>

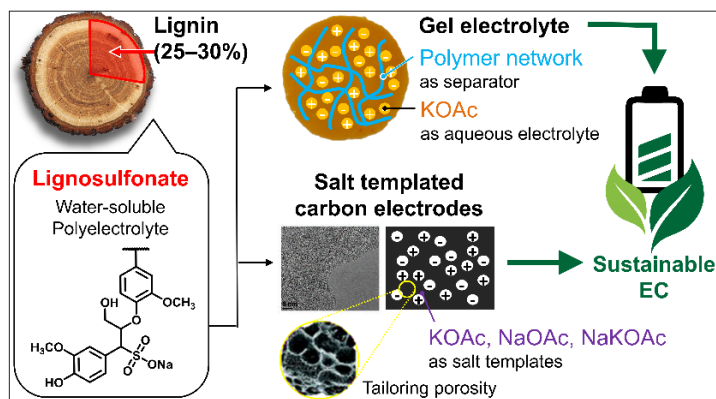
W celu poprawy stosunkowo niskiej pojemności wodnych elektrolitów wykorzystano roztwory buforowe w połączeniu z reakcjami redoks jodek/jod. Bufory octanowe, cytrynianowe i fosforanowe zawierające NaI jako wielofunkcyjne elektrolity zapewniły stabilizację pH oraz dodatkowe pseudopojemnościowe magazynowanie ładunku (**Rysunek 2**).



Rysunek 2 Graficzna prezentacja nowego elektrolitu dla EC na bazie buforu oraz pary redoks jod/jodek wraz z korzyściami wynikającymi z jego zastosowania.

Dodanie NaI znacznie zwiększyło przewodnictwo jonowe, zachowując jednocześnie stabilne pH. Badania elektrochemiczne wykazały, że elektrolity zawierające jodki umożliwiły stabilną pracę EC przy napięciu 1.5 V. Pomiar trójelektrodowy potwierdził, że elektroda (+) charakteryzowała się odwracalnymi reakcjami redoks I^-/I_2 . Dodatek 0.2M NaI znacznie zwiększył pojemność EC, np.

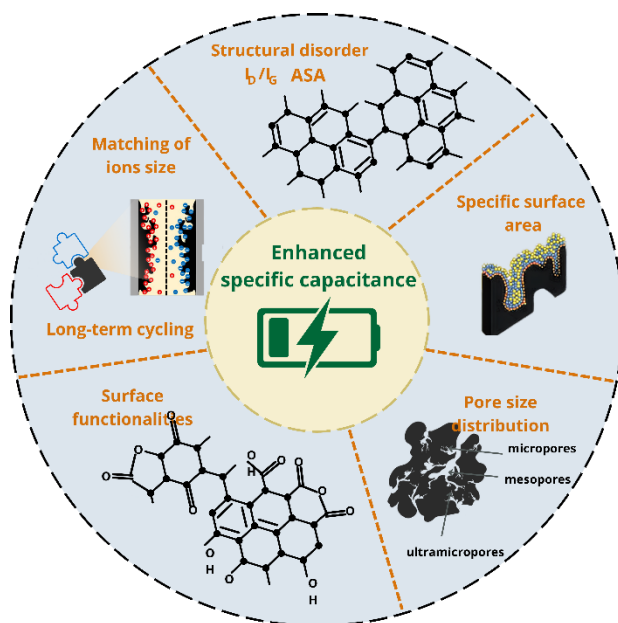
pojemność wzrosła z 91 F g^{-1} (bufor octanowy) do 149 F g^{-1} (bufor octanowy z jodkiem). Jednocześnie żywotność EC została znacznie wydłużona podczas stałonapięciowej polaryzacji. Bufor cytrynianowy zawierający 0.2M NaI osiągnął ponad 1000 godzin, podczas gdy bufor cytrynianowy bez dodatku jodku uzyskał jedynie 30 godzin stałonapięciowej polaryzacji. Działanie elektrolitu silnie zależało od pH i stężenia jodku. Lekko kwaśne warunki sprzyjały odwracalnej aktywności pary redoks i minimalizowały tworzenie się niepożądanych polijodków i jodanów. Nadmierne stężenia jodku sprzyjały blokowaniu porów i przyspieszały proces degradacji. Analizy po zakończeniu eksperymentu z wykorzystaniem spektroskopii fotoelektronów w zakresie promieniowania rentgenowskiego (*ang. X-ray photoelectron spectroscopy – XPS*) i dyfrakcja rentgenowska (*ang. X-ray diffraction – XRD*) udowodniły zredukowane utlenianie elektrody oraz brak obecności nierozpuszczalnych osadów na powierzchni węgla. Wyniki wskazują, że synergiczne połączenie działania buforu, stabilizującego pH roztworu i pary redoks jod/jodek zwiększyło pojemność, napięcie oraz żywotność ECs.



Rysunek 3 Innowacyjna i przyjazna dla środowiska strategia skutecznego wykorzystania ligniny technicznej pozyskanej z odpadów drzewnych jako odnawialnego prekursora elektrolitu, elektrod i separatora EC.

W niniejszej pracy przeprowadzono badania dotyczące wykorzystania lignosulfonianu (*ang. lignosulfonate – LS*) jako wielofunkcyjnego prekursora do produkcji ekologicznych komponentów ECs, w tym elektrolitów żelowych (*ang. gel electrolytes – GEs*), separatorów i porowatych węgla (**Rysunek 3**).

Elektrolity żelowe składały się z LS, eteru diglicydylowego glikolu polietylenowego (*ang. poly(ethylene glycol) diglycidyl ether – PEGDGE*) oraz roztworów soli octanowych. Spośród badanych układów, GE LS-5m KOAc osiągnął najbardziej korzystny balans pomiędzy przewodnictwem jonowym, stabilnością mechaniczną i ograniczoną zawartością wody. Jednocześnie przygotowano LS-węgle z wykorzystaniem soli octanowych jako zarówno matryc strukturalnych, jak i środków samoczynnie aktywujących. Otrzymane węgle charakteryzowały się optymalną mikroporowatością, nieuporządkowaniem strukturalnym i zwiększoną obecnością domen grafitowych w zależności od składu soli. Powierzchnie właściwe LS-węgla mieściły się w przedziale od 881 do 1754 m² g⁻¹. Badania elektrochemiczne wykazały niemal idealne zachowanie pojemnościowe w zakresie napięcia do 1.6 V. Uzyskano wartości pojemności od 46 do 82 F g⁻¹, przy czym wyższą pojemność zaobserwowano w przypadku węgla o wysokim stopniu nieuporządkowania i bardziej mikroporowatych. Co ważne, elektrolit żelowy znacznie ograniczył samowyladowanie i wyciek elektrolitu, poprawiając jednocześnie bezpieczeństwo urządzenia. ECs złożone w całości z LS komponentów osiągnęły do 170 godzin stałonapięciowej polaryzacji i spowolniły samowyladowanie w porównaniu z separatorami z włókna szklanego. Analiza aspektów cyklu życia wykazała zmniejszenie emisji CO₂ o 32-49%, w porównaniu z konwencjonalnymi metodami produkcji materiałów węglowych. Podsumowując, udowodniono, że LS może służyć jako odnawialny i wydajny prekursor dla zrównoważonych ECs.



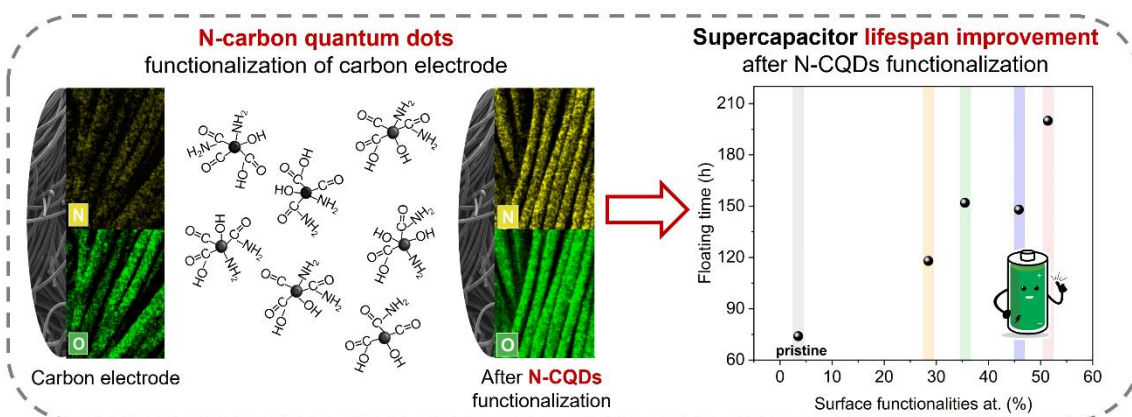
Rysunek 4 Istotne parametry brane pod uwagę w celu poprawy działania EC.

Zbadano zależności między teksturą/strukturą węgla a właściwościami elektrochemicznymi EC (**Rysunek 4**) przy użyciu węgla porowatych zsyntezowanych metodą matrycy solnej, wykorzystując chlorki metali alkalicznych w stosunku eutektycznym. Kompleksowa charakteryzacja przeprowadzona przy użyciu spektroskopii Ramana, XRD, transmisyjnej mikroskopii elektronowej (ang. *transmission electron microscopy* – TEM), sorpcji gazów oraz desorpcji programowanej temperaturowo w połączeniu ze

spektrometrią mas wykazała znaczne różnice w stopniu nieuporządkowania, dostępnej powierzchni, mikroporowatości oraz tlenowych grup funkcyjnych. Węgłe o wysokim stopniu nieuporządkowania, zsyntezowane wykorzystując matrycę CsCl, charakteryzowały się zwiększoną gęstością defektów i mikroporowatością, podczas gdy matryce na bazie LiCl sprzyjały większemu uporządkowaniu, natomiast tworzeniu mezoporów. Testy elektrochemiczne w 1M Li₂SO₄ wykazały wartości pojemności do 244 F g⁻¹ przy stabilnym napięciu 1.6 V. Zaobserwowano silne korelacje liniowe między pojemnością a kilkoma parametrami fizykochemicznymi. Pojemność wzrastała wraz z: wyższym stopniem nieuporządkowania (stosunek I_D/I_G), większą powierzchnią aktywną, większą objętością mikroporów oraz odpowiednimi grupami funkcyjnymi tlenu. Mikroporowatość została zidentyfikowana jako dominujące miejsce magazynowania ładunku, podczas gdy mezopory ułatwiały głównie transport jonów. Chociaż węgle o wysokim stopniu nieuporządkowania wykazywały lepszą pojemność, charakteryzowały się jednak krótszą żywotnością ze względu na zwiększoną niestabilność strukturalną. Natomiast węgle o bardziej uporządkowanej strukturze zapewniały większą żywotność, ale niższą pojemność. Wyniki te stanowią ogólne ramy dla modyfikacji elektrod węglowych poprzez dostosowanie nieuporządkowania, porowatości, przewodnictwa i powierzchniowych grup funkcyjnych materiału.

Insights of N-carbon quantum dots effect on charge storage in supercapacitors

Ostatnia część pracy doktorskiej dotyczyła określenia wpływu węglowych kropek kwantowych domieszkowanych azotem (*ang. nitrogen doped carbon quantum dots – N-CQDs*) na właściwości kondensatorów elektrochemicznych (**Rysunek 5**). N-CQDs zsyntezowano metodą karbonizacji hydrotermalnej z wykorzystaniem kwasu cytrynowego i różnych amin. Otrzymane N-CQDs charakteryzowały się wielkością



Rysunek 5 Korzystny wpływ funkcjonalizacji elektrod węglowymi kropkami kwantowymi, zawierającymi liczne grupy funkcyjne tlenu i azotu, na żywotność ECs.

cząstek wynoszącą około 6 nm, niebieską fluorescencją w zakresie światła UV oraz wysokim stężeniem tlenowych i azotowych powierzchniowych grup funkcyjnych. Elektrody węglowe z porowatej tkaniny, impregnowane N-CQDs zostały następnie przetestowane w ECs z 1M Li₂SO₄ jako elektrolitem. Obecność N-CQDs poprawiła pojemność z 116 F g⁻¹ (bez N-CQDs) do 146 F g⁻¹ (z N-CQDs) i znacznie ulepszyła żywotność EC z 74 godzin (bez N-CQDs) do 200 godzin stałonapięciowej polaryzacji (z N-CQDs). Analiza Dunna wykazała zwiększony udział dyfuzji związany z procesami pseudopojemnościowymi. Poprawa pojemności i żywotności ECs wynikała głównie z obecności licznych grup funkcyjnych, które zwiększyły zwilżalność elektrody, wprowadziły dodatkowe centra aktywne redoks i ułatwiły transfer ładunku. Częściowe uwolnienie N-CQDs do elektrolitu dodatkowo zwiększyło przewodnictwo jonowe. Korelacje między właściwościami N-CQDs a wydajnością ECs wykazały, że wysoce sfunkcjonalizowane N-CQDs o niższej zawartości sp² w rdzeniu zapewniły ulepszenie właściwości elektrochemicznych.

3) Wnioski

Niniejsza praca doktorska przedstawia kilka komplementarnych strategii rozwoju zrównoważonych i wysokowydajnych wodnych ECs. Wprowadzenie dodatku HBD do elektrolitu na bazie soli neutralnej skutecznie ograniczyło korozję, zmniejszyło

aktywność niezwiązanej wody oraz znacząco poprawiło trwałość ECs bez pogorszenia ich właściwości elektrochemicznych. Elektrolity buforowo-jodkowe umożliwiły odwracalne reakcje pseudopojemnościowe, umożliwiając jednocześnie zwiększenie pojemności, rozszerzenie napięcia oraz wzrost cykliczności ECs.

Wykorzystanie lignosulfonianu jako odnawialnego prekursora pozwoliło na otrzymanie zrównoważonych elektrolitów żelowych oraz porowatych materiałów węglowych z uwzględnieniem aspektów środowiskowych. Ponadto badania materiałów węglowych otrzymywanych metodą matrycy solnej pozwoliły określić zależności struktura-właściwości, łączące stopień nieuporządkowania, porowatość oraz powierzchniowe grupy funkcyjne z pojemnością i żywotnością ECs.

Węglowe kropki kwantowe domieszkowane azotem zidentyfikowano jako obiecujące dodatki funkcjonalne, zdolne do zwiększania zarówno pojemności, jak i długoterminowej stabilności dzięki pseudopojemności wynikającej z obecności grup funkcyjnych na powierzchni oraz poprawie transportu ładunku.

Uzyskane wyniki dostarczają istotnych informacji dotyczących projektowania przyjaznych środowisku elektrolitów i materiałów węglowych do kondensatorów elektrochemicznych nowej generacji. Przedstawione strategie przyczyniają się do rozwoju bezpiecznych, trwałych i zrównoważonych technologii magazynowania energii.

W przyszłości rozwój kondensatorów elektrochemicznych będzie prawdopodobnie związany z łączeniem przyjaznych środowisku elektrod węglowych otrzymywanych z biomasy bogatej w heteroatomy z wielofunkcyjnymi elektrolitami, które jednocześnie zwiększają gęstość energii, bezpieczeństwo, oraz żywotność ECs. Wspierane przez zaawansowane techniki charakteryzacji (również w trybie *operando*), chemię obliczeniową oraz uczenie maszynowe, takie zintegrowane podejście może przyspieszyć dalszy rozwój wysokowydajnych urządzeń dostosowanych do zastosowań związanych z integracją odnawialnych źródeł energii, elektroniką stosowaną w odzieży noszonej oraz systemami motoryzacyjnymi.

4) Referencje

- 1 Wolf, S.; Bullard, R.; Buonocore, J. J.; Donley, N.; Farrelly, T.; Fleming, J.; González, D. J. X.; Oreskes, N.; Ripple, W.; Saha, R.; Willis, M. D. Scientists' Warning on Fossil Fuels. *Oxford Open Climate Change* **2025**, 5 (1) kgaf011. <https://doi.org/10.1093/oxfclm/kgaf011>
- 2 Ripple, W.J., Wolf, C., Gregg, J.W., Rockstorm, J., Mann, M.E., Oreskes, N., Lenton, T.M., Rahmstorf, S., Newsome, T.M., Xu, C., Svenning, J.C., Pereira, C.C., Law,

- B.E., Crowther, T.W., The 2024 state of the climate report: Perilous times on planet Earth. *BioScience* **2024**, 74 (12), 812-824. <https://doi.org/10.1093/biosci/biae087>
- 3 Conway, B. E. *Electrochemical Supercapacitors*; Springer US: Boston, MA, **1999**. <https://doi.org/10.1007/978-1-4757-3058-6>
- 4 Miller, J. R.; Simon, P. Electrochemical Capacitors for Energy Management. *Science* **2008**, 321 (5889), 651–652. <https://doi.org/10.1126/science.1158736>
- 5 Burke, A. F.; Zhao, J. Past, Present and Future of Electrochemical Capacitors: Technologies, Performance and Applications. *Journal of Energy Storage* **2021**, 35, 102310. <https://doi.org/10.1016/j.est.2021.102310>
- 6 Béguin, F.; Presser, V.; Balducci, A.; Frackowiak, E. Carbons and Electrolytes for Advanced Supercapacitors. *Advanced Materials* **2014**, 26 (14), 2219–2251. <https://doi.org/10.1002/adma.201304137>

Ecole Doctorale résumé

1) Introduction

L'utilisation généralisée des combustibles fossiles contribue de manière significative aux émissions de gaz à effet de serre, à la dégradation de l'environnement et au changement climatique¹. Les sources d'énergie renouvelables offrent une alternative durable; cependant, leur caractère intermittent impose des technologies de stockage d'énergie efficaces^{1,2}. Parmi les systèmes actuellement disponibles, les condensateurs électrochimiques (ECs) sont particulièrement intéressants en raison de leur forte densité de puissance, de leur capacité de charge/décharge rapide et de leur excellente stabilité cyclique, ce qui leur permet de stocker l'énergie renouvelable^{3,4}. Néanmoins, les ECs conventionnels se heurtent encore à des limites liées à leur densité d'énergie, à la sécurité de l'électrolyte, à la plage de tension de fonctionnement étroite, aux processus de corrosion, à la durée de vie limitée et à la durabilité des matériaux d'électrodes^{5,6}.

L'objectif principal de cette thèse est d'améliorer la capacité, la tension de fonctionnement et la durabilité des ECs. Ainsi, la dissertation se concentre sur le développement de condensateurs électrochimiques aqueux durables en suivant deux approches complémentaires: (i) la modification d'électrolytes aqueux neutres pour améliorer la stabilité de tension, la résistance à la corrosion et la durée de vie ; (ii) l'adaptation de la texture, du désordre et de la chimie de surface des matériaux d'électrodes en carbone afin d'optimiser la capacité et la durée de vie. Un accent particulier est mis sur les matériaux respectueux de l'environnement, les techniques de caractérisation avancées et les relations structure-performance.

2) Résultats et discussions

Electrochemical capacitor in aqueous electrolyte with long lifespan improved by hydrogen bond addition; <https://doi.org/10.1016/j.mattod.2023.06.018>

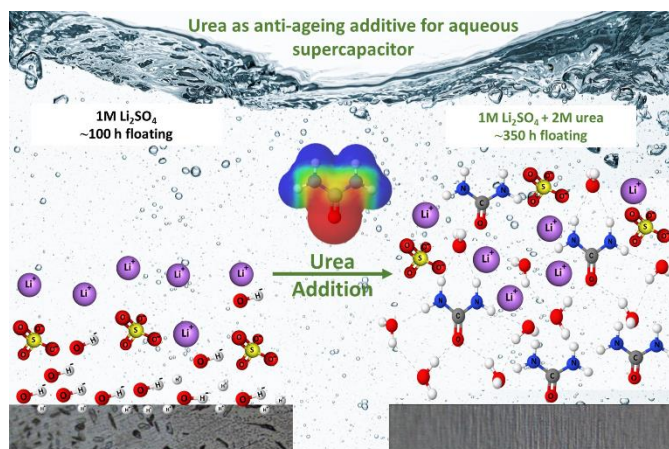


Figure 1 Effet anticorrosion et anti-vieillessement sur l'EC dû à la formation d'un réseau de donneurs de liaisons hydrogène après ajout d'urée à une solution de Li_2SO_4 à 1 M.

L'une des principales limites des ECs à base d'électrolytes neutres aqueux réside dans la corrosion des collecteurs de courant en acier inoxydable, qui réduit la durée de vie des dispositifs et diminue leur stabilité électrochimique. Pour remédier à ce problème, l'effet de l'urée en tant qu'additif donneur de liaisons hydrogène (HBD) dans un électrolyte à base de Li_2SO_4 1 M a été étudié à l'aide, par exemple,

de tests électrochimiques, de modélisation numérique, de spectroscopie Raman *operando* et de chromatographie en phase gazeuse couplée à la spectrométrie de masse (GC-MS) (**Figure 1**). L'ajout d'urée ne réduit que légèrement la conductivité ionique tout en maintenant des valeurs de pH favorables et une bonne stabilité électrochimique. Avec l'accroissement de la concentration en urée, les tests de corrosion révèlent une réduction substantielle du courant de corrosion, passant de 6,60 μA à 0,55 μA , démontrant ainsi le fort effet anticorrosif de l'urée. L'analyse Raman confirme que la formation de Fe_2O_3 est supprimée et que les couches de surface protectrices de FeOOH sont stabilisées. Les ECs symétriques fonctionnant avec des électrolytes contenant de l'urée conservent des valeurs de capacité d'environ 100 F g^{-1} à 1,6 V, indiquant que l'additif n'a pas d'effet négatif sur les performances capacitives. Il est important de noter que la durée de vie est améliorée significativement. Le condensateur électrochimique contenant de l'urée à 2 M présente plus de 60 000 cycles et environ 350 heures à tension nominale, contre 47 000 cycles et 96 heures à tension nominale lorsque l'électrolyte est seulement Li_2SO_4 pur à 1 M. La spectroscopie Raman *operando* et la GC-MS démontrent que l'urée réduit l'activité de l'eau libre par la formation d'un vaste réseau de liaisons hydrogène, limitant ainsi la dégradation des électrodes et l'évolution de CO_2 . Des calculs de théorie de la fonctionnelle de la densité confirment en outre de fortes interactions entre l'urée, l'eau et les espèces de Li_2SO_4 , conduisant à des structures de solvation modifiées et à une réactivité de l'eau réduite. Dans l'ensemble, l'incorporation

d'urée permet de développer un électrolyte peu coûteux et respectueux de l'environnement, combinant une conductivité ionique élevée, une corrosion réduite et une durée de vie prolongée des condensateurs électrochimiques.

Effect of buffer/iodide electrolyte on the performance of electrochemical capacitors;
<https://doi.org/10.1039/D4GC01748J>

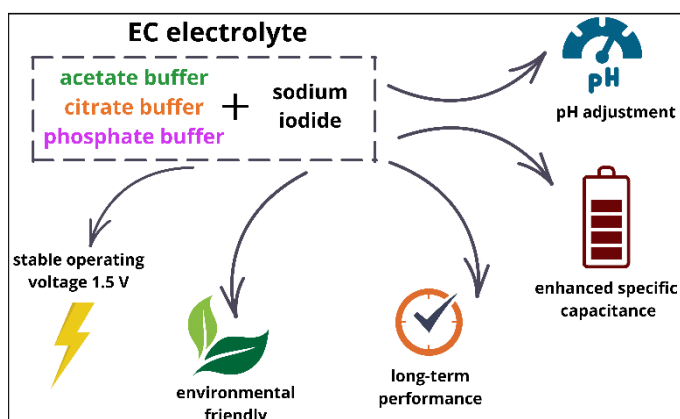


Figure 2 Représentation graphique du nouvel électrolyte EC à base de tampon iodure/iode et de ses avantages.

Afin d'améliorer la capacité relativement faible des condensateurs électrochimiques en milieu aqueux, des solutions tampons associées à une chimie redox iodure/iode sont étudiées. Des tampons acétate, citrate et phosphate contenant du NaI sont utilisés en tant qu'électrolytes multifonctionnels capables de stabiliser le pH et

d'introduire un stockage de charge pseudocapacitif (**Figure 2**). L'ajout de NaI accroît considérablement la conductivité de l'électrolyte tout en préservant des conditions de pH stables. Les essais électrochimiques démontrent que les électrolytes contenant un iodure permettent un fonctionnement stable des ECs jusqu'à 1,5 V. Des mesures en cellules à trois électrodes confirment que l'électrode positive présente des réactions faradaïques réversibles associées au couple redox I^-/I_2 . L'incorporation de NaI 0.2 M améliore considérablement la capacité. Par exemple, la capacité passe de 91 à 149 F g⁻¹ dans les systèmes à tampon acétate. Parallèlement, la durée de vie est considérablement améliorée lors des essais à tension nominale. Le condensateur électrochimique à base de tampon citrate contenant NaI à 0,2 M atteint plus de 1 000 heures à tension nominale, contre seulement 30 heures avec le tampon correspondant sans iodure. Les performances de l'électrolyte dépendent fortement du pH et de la concentration en iodure. Des conditions légèrement acides favorisent une activité redox réversible et minimisent la formation de polyiodures et d'iodates indésirables. Des concentrations excessives d'iodure favorisent l'obstruction des pores et accélèrent les processus de dégradation. Les analyses *post-mortem* par XPS et XRD montrent une oxydation limitée de l'électrode et l'absence de dépôts insolubles dans la porosité du carbone. Les résultats démontrent que la combinaison synergique de l'action tampon et de la chimie redox de l'iodure améliore simultanément la capacité, la tension de fonctionnement et la stabilité.

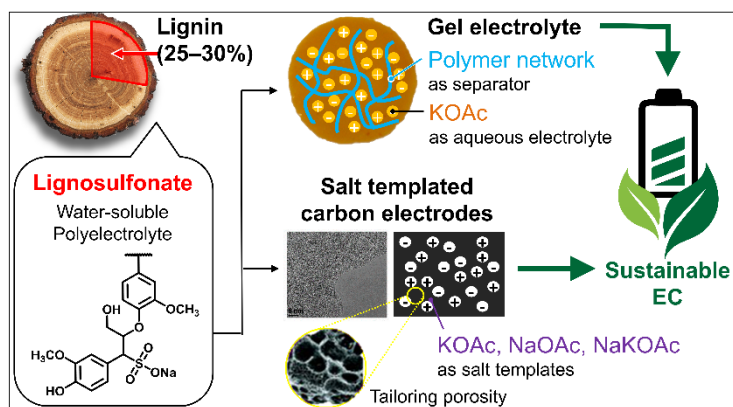


Figure 3 Une stratégie novatrice et respectueuse de l'environnement pour l'utilisation efficace d'une lignine technique issue de déchets de bois, en tant que précurseur renouvelable d'électrolytes, d'électrodes et de séparateurs pour batteries rechargeables.

Ces travaux explorent l'utilisation du lignosulfonate (LS), une lignine technique issue de déchets, en tant que précurseur multifonctionnel de composants durables pour ECs, notamment des électrolytes gélifiés (GE), des séparateurs et des carbones poreux (**Figure 3**). Les GE sont composés de LS, de poly(éthylène glycol) diglycidyl éther (PEGDGE) et

de solutions de sels d'acétate. Parmi les systèmes étudiés, le gel LS–5 m KOAc présente le meilleur équilibre entre conductivité ionique, stabilité mécanique et teneur en eau réduite. Parallèlement, des carbones dérivés du LS par salt templating sont préparés en utilisant des sels d'acétate à la fois comme template structuraux et comme agents d'auto-activation. Les carbones obtenus présentent une microporosité, un désordre structural et un caractère graphitique ajustables en fonction de la composition du sel. Les surfaces spécifiques varient de 881 à 1754 m² g⁻¹. Les essais électrochimiques mettent en évidence un comportement de double couche électrique quasi idéal jusqu'à 1,6 V. Des valeurs de capacité comprises entre 46 et 82 F g⁻¹ sont obtenues, les carbones hautement désordonnés et microporeux présentant une capacité plus élevée. Il est important de noter que l'électrolyte sous forme de gel réduit considérablement l'autodécharge et les fuites d'électrolyte, tout en améliorant la sécurité des dispositifs. Les EC entièrement assemblés à partir de composants dérivés de LS atteignent jusqu'à 170 heures à tension nominale et sont moins affectés par une perte de tension que les ECs contenant des séparateurs en fibre de verre. Les analyses de cycle de vie indiquent une réduction des émissions de CO₂ de 32 à 49 % par rapport aux méthodes de fabrication conventionnelles des EC. L'étude démontre que le lignosulfonate peut servir de précurseur renouvelable et efficace pour des EC durables.

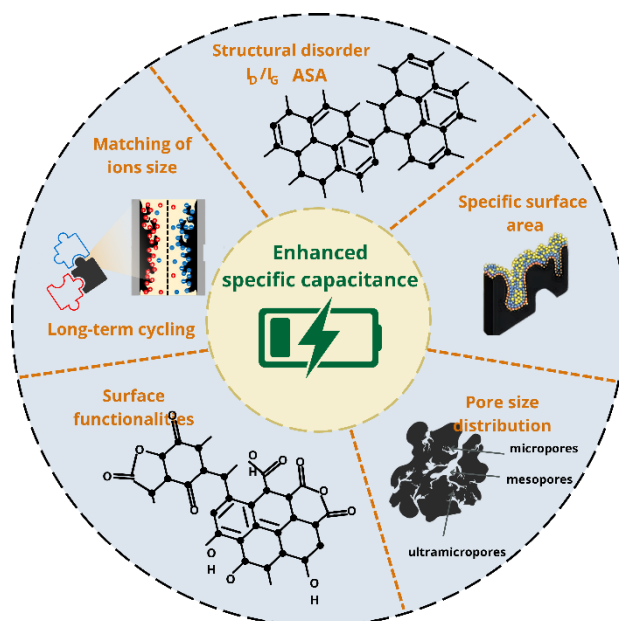


Figure 4 Les paramètres jugés importants pour améliorer les performances de l'EC.

Les relations entre la texture/structure du carbone et les performances électrochimiques (**Figure 4**) sont étudiées à l'aide de carbones poreux synthétisés par *soft-salt templating* utilisant des eutectiques de chlorures de métaux alcalins. Une caractérisation complète par spectroscopie Raman, diffraction des rayons X, microscopie électronique à transmission (MET), sorption de gaz et désorption programmée en température couplée à la spectrométrie de masse révèle des variations significatives du degré de

désordre, de la surface spécifique accessible, de la microporosité et des groupes fonctionnels oxygénés. Les carbones hautement désordonnés obtenus à partir de CsCl templating présentent une densité de défauts et une microporosité accrues, tandis que les templates à base de LiCl favorisent un ordonnancement graphitique et la formation de mésopores. Les essais électrochimiques réalisés dans une solution de Li_2SO_4 à 1 M révèlent des valeurs de capacité pouvant atteindre 244 F g^{-1} avec un fonctionnement stable à 1,6 V. Des corrélations linéaires marquées sont établies entre la capacité et plusieurs paramètres physico-chimiques. La capacité augmente avec : un degré de désordre plus élevé (rapport I_{D1}/I_G), une surface active plus importante, un volume de micropores plus grand et la présence de groupes fonctionnels oxygénés appropriés. Les micropores sont identifiés comme les principaux sites de stockage de charge, tandis que les mésopores facilitent essentiellement le transport ionique. Bien que les carbones hautement désordonnés conduisent à une capacité supérieure, ils sont également responsables d'une durée de vie plus courte en raison d'une instabilité structurale accrue. En revanche, les carbones plus graphitiques offrent une durabilité améliorée mais une capacité plus faible. Ces résultats fournissent un cadre général pour optimiser des électrodes de carbone en équilibrant le désordre, la porosité, la conductivité et la chimie de surface.

Insights of N-carbon quantum dots effect on charge storage in supercapacitors

La dernière partie de la dissertation porte sur l'effet des points quantiques de carbone dopés à l'azote (N-CQDs) sur les performances des condensateurs électrochimiques (**Figure 5**). Les N-CQDs ont été synthétisés par carbonisation hydrothermale à l'aide d'acide citrique et de différentes amines. Les N-CQDs obtenus présentent une taille de

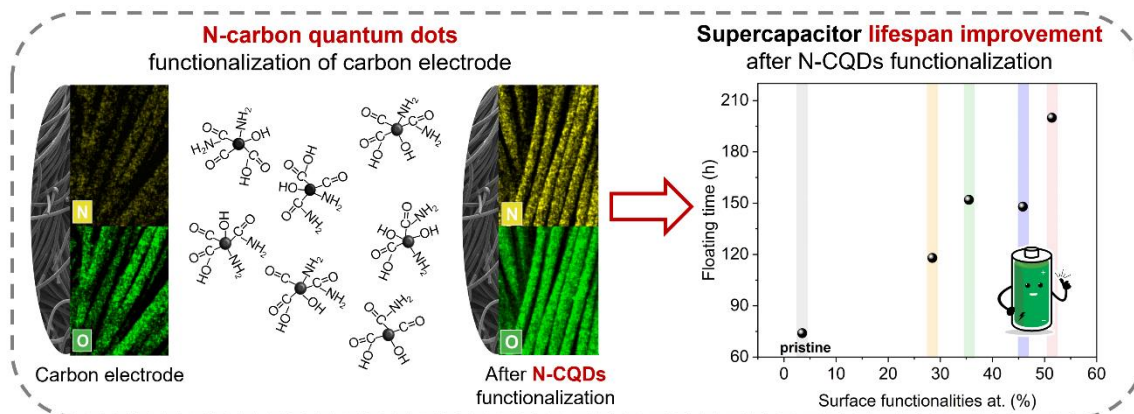


Figure 5 L'effet bénéfique de la fonctionnalisation des électrodes à l'aide de points quantiques de carbone riches en groupes fonctionnels oxygénés et azotés sur la durée de vie des cellules électrochimiques.

particules d'environ 6 nm, une fluorescence bleue et des concentrations élevées de groupes de surface contenant de l'oxygène et de l'azote. Des électrodes en tissu de carbone poreux imprégnées de N-CQDs sont ensuite évaluées dans des électrolytes aqueux. L'incorporation de N-CQDs permet de porter la capacité de 116 F g^{-1} (sans N-CQDs) à 146 F g^{-1} (avec N-CQDs) et d'augmenter considérablement la durée de vie de 74 heures à tension nominale (sans N-CQDs) à 200 heures (avec N-CQDs). L'analyse de Dunn met en évidence une contribution diffusive accrue liée à des processus pseudo-capacitifs. Cette amélioration provient principalement de l'abondance des fonctionnalités de surface, qui améliorent la mouillabilité des électrodes, introduisent des sites redox actifs supplémentaires et facilitent le transfert de charge. La libération partielle de N-CQDs dans l'électrolyte accroît en outre la conductivité ionique. Les corrélations entre les propriétés des N-CQDs et les performances des condensateurs électrochimiques démontrent que les N-CQDs fortement fonctionnalisés, et avec une teneur réduite en noyaux graphitiques, offrent le meilleur comportement électrochimique.

3) Conclusion générale

Cette thèse présente plusieurs stratégies complémentaires permettant de développer des condensateurs électrochimiques aqueux durables et hautement performants.

L'incorporation d'additifs HBD dans des électrolytes aqueux neutres permet de supprimer efficacement la corrosion, de réduire l'activité de l'eau et d'améliorer significativement la durée de vie des ECs sans compromettre leurs performances électrochimiques. Les électrolytes tampons/iodures introduisent une pseudocapacité réversible et permettent simultanément d'améliorer la capacité, la fenêtre de tension et la stabilité.

L'utilisation du lignosulfonate comme précurseur renouvelable démontre la possibilité de produire des électrolytes gélifiés et des carbones poreux durables, tout en tenant compte de l'impact environnemental. De plus, les études systématiques conduites sur les carbones formés par salt templating permettent d'établir des corrélations claires entre la structure et les performances, reliant le désordre, la porosité et la chimie de surface à la capacité et à la durée de vie.

Enfin, les N-CQDs ont été identifiés comme des additifs fonctionnels prometteurs, capables d'améliorer à la fois la capacité et la stabilité à long terme grâce à une pseudocapacité dérivée de la fonctionnalisation de surface et à un transport de charge optimisé.

Ces résultats apportent des informations importantes pour la conception d'électrolytes et de matériaux carbonés respectueux de l'environnement destinés aux condensateurs électrochimiques de nouvelle génération. Les stratégies présentées contribuent à l'avancement de technologies de stockage d'énergie sûres, durables et respectueuses de l'environnement.

À l'avenir, les condensateurs électrochimiques s'appuieront probablement sur la combinaison d'électrodes en carbone durables issues de la biomasse et riches en hétéroatomes, avec des électrolytes multifonctionnels qui améliorent simultanément la densité énergétique, la sécurité et la durée de vie. S'appuyant sur des techniques de caractérisation avancées (également en mode *operando*), la chimie computationnelle et l'apprentissage automatique, cette approche intégrée pourrait accélérer le développement de dispositifs de haute performance adaptés à des applications allant de l'intégration des énergies renouvelables aux systèmes automobiles, en passant par l'électronique portable.

4) Références

- 1 Wolf, S.; Bullard, R.; Buonocore, J. J.; Donley, N.; Farrelly, T.; Fleming, J.; González, D. J. X.; Oreskes, N.; Ripple, W.; Saha, R.; Willis, M. D. Scientists' Warning on Fossil Fuels. *Oxford Open Climate Change* **2025**, 5 (1) kgaf011. <https://doi.org/10.1093/oxfclm/kgaf011>
- 2 Ripple, W.J., Wolf, C., Gregg, J.W., Rockstorm, J., Mann, M.E., Oreskes, N., Lenton, T.M., Rahmstorf, S., Newsome, T.M., Xu, C., Svenning, J.C., Pereira, C.C., Law, B.E., Crowther, T.W., The 2024 state of the climate report: Perilous times on planet Earth. *BioScience* **2024**, 74 (12), 812-824. <https://doi.org/10.1093/biosci/biae087>
- 3 Conway, B. E. *Electrochemical Supercapacitors*; Springer US: Boston, MA, **1999**. <https://doi.org/10.1007/978-1-4757-3058-6>
- 4 Miller, J. R.; Simon, P. Electrochemical Capacitors for Energy Management. *Science* **2008**, 321 (5889), 651–652. <https://doi.org/10.1126/science.1158736>
- 5 Burke, A. F.; Zhao, J. Past, Present and Future of Electrochemical Capacitors: Technologies, Performance and Applications. *Journal of Energy Storage* **2021**, 35, 102310. <https://doi.org/10.1016/j.est.2021.102310>
- 6 Béguin, F.; Presser, V.; Balducci, A.; Frackowiak, E. Carbons and Electrolytes for Advanced Supercapacitors. *Advanced Materials* **2014**, 26 (14), 2219–2251. <https://doi.org/10.1002/adma.201304137>

Scientific achievements

Publications

1. **A. Klimek**, E. Salomon, S. Hajjar-Garreau, E. Frackowiak*, C. Matei Ghimbeu*
 “Insights of N-carbon quantum dots effect on charge storage in supercapacitors”
 (2026) under revision
2. **A. Klimek**, L. Amro, N. Pakkang, C. Matei Ghimbeu, E. Frackowiak*, S. Suzuki*
 “Lignin as precursor of gel electrolyte and salt templated carbon for sustainable
 electrochemical capacitor” *Green Chemistry* 28 (2026) 4225-4242
<https://doi.org/10.1039/D5GC05533D> **IF: 9.2, MNiSW: 200**
3. **A. Klimek**, B. Réty, C. Matei Ghimbeu*, E. Frackowiak*
 “Impact of disorder, porosity and surface chemistry of salt templated carbons on
 capacitance” *Advanced Science* 12 (2025) e05032
<https://doi.org/10.1002/advs.202505032> **IF: 14.3, MNiSW: 200**
4. **A. Klimek**, M. Tobis, E. Frackowiak*
 “Effect of a buffer/iodide electrolyte on the performance of electrochemical capacitors”,
Green Chemistry 26 (2024) 6684-6695
<https://doi.org/10.1039/D4GC01748J> **IF: 9.2, MNiSW: 200**
5. S. Azmi, **A. Klimek**, E. Frackowiak*
 “Electrochemical capacitor in aqueous electrolyte with long lifespan improved by
 hydrogen bond donor addition”, *Materials Today* 68 (2023) 34-50
<https://doi.org/10.1016/j.mattod.2023.06.018> **IF: 21.1, MNiSW: 200**
6. S. Azmi, **A. Klimek**, E. Frackowiak*
 “Why electrochemical capacitor electrolytes should not be ignored?”, *Electrochimica
 Acta* 452 (2023) 142347
<https://doi.org/10.1016/j.electacta.2023.142347> **IF: 5.5, MNiSW: 100**
7. S. Azmi, **A. Klimek**, E. Frackowiak*
 “Anticorrosive performance of green deep eutectic solvent for electrochemical
 capacitor”, *Chemical Engineering Journal* 444 (2022) 136594
<https://doi.org/10.1016/j.cej.2022.136594> **IF: 13.3, MNiSW: 200**

Total Impact Factor (IF) of published papers: 72.6, Total MNiSW points of published papers: 1100; *denotes corresponding author

Granted patent

1. E. Frackowiak, S. Azmi, **A. Klimek**
“Kondensator elektrochemiczny o wysokiej trwałości cyklicznej”
Pat. 246396
06.11.2024

Oral presentations at conferences

1. E. Frackowiak*, **A. Klimek**, B. Rety, C. Matei Ghimbeu
“How disorder, porosity and surface chemistry of salt templated carbons interplay with capacitance”
The World Conference on Carbon (Carbon 2025)
29.06-04.07.2025, Saint-Malo, France
2. **A. Klimek***
“How to improve the performance of energy storage systems?”
The Perspektywy Women in Tech Summit 2025
04.06-05.06.2025, Warsaw, Poland
3. **A. Klimek***
“Świat potrzebuje naszej ciekawości: kobiety w nauce inspirują – kropki kwantowe”
Poznaj Kobiące Perspektywy w czasie Drzwi Otwartych Politechniki Poznańskiej
15.04.2025, Poznan, Poland
4. **A. Klimek***, H. Negi, N. Pakkang, Y. Uraki, S. Suzuki, E. Frackowiak
“Development of lignin-based gel electrolytes for energy storage system”
66. Zjazd Naukowy Polskiego Towarzystwa Chemicznego (PTChem 2024)
15-20.09.2024, Poznan, Poland
5. E. Frackowiak*, **A. Klimek**, C. Matei Ghimbeu
“Tailoring the properties of salt-templated carbons for energy storage systems”
The 11th Torunian Carbon Symposium – Copernican Revolution in Carbon Science (TCS 2024)
15-18.09.2024, Torun, Poland
6. E. Frackowiak*, **A. Klimek**
“Electrode/Electrolyte interplay in electrochemical capacitors”
The International Symposium on Enhanced Electrochemical Capacitors (ISEECap 2024)
08-12.07.2024, Vitoria-Gasteiz, Spain

7. E. Frackowiak*, **A. Klimek**,
 "Protic vs aprotic supercapacitor electrolyte"
International Conference on Advanced Capacitors (ICAC)
 26-29.09.2023, Kamakura, Japan
 8. **A. Klimek***, S. Azmi, E. Frackowiak
 "Intriguing role of hydrogen bond addition into neutral electrolyte for carbon-based supercapacitor"
IV Polish Carbon Society Workshop
 24.06.2023, Tokai Cobex Poland, Nowy Sacz, Poland
 9. E. Frackowiak*, **A. Klimek**
 "Green and cheap supercapacitor based on reline DES electrolyte"
The International Society of Electrochemistry Regional Meeting
 15-19.08.2022, Kamakura, Japan
 10. **A. Klimek***, S. Azmi, E. Frackowiak
 "Long-term performance of carbon-based electrochemical capacitor operating in reline deep eutectic solvent"
III Polish Carbon Society Workshop
 24.06.2022, Academy of Mining and Metallurgy, Cracow, Poland
- *denotes presenting author

Poster presentations at conferences

1. A.C. Parejo-Tovar*, N. Pakkang, **A. Klimek**, J. Nishiyama, H. Negi, S. Suzuki
 "Development of lignin-derived gel electrolytes and carbon materials for energy storage devices"
Co-Creation Symposium of Hokudai Soft Materials 2025
 01.10.2025, Sapporo, Japan
2. **A. Klimek***, L. Vidal, E. Salomon, E. Frackowiak, C. Matei Ghimbeu
 "Unraveling the impact of physicochemical properties of carbon quantum dots for energy storage"
The World Conference on Carbon (Carbon 2025)
 29.06-04.07.2025, Saint-Malo, France
3. **A. Klimek***, H. Negi, N. Pakkang, Y. Uraki, S. Suzuki, E. Frackowiak
 "Mechanism of aqueous electrolyte uptake by the hydrophilic lignin gel and its application as electrolyte for supercapacitor"
2nd Workshop on Multi-Functional Materials and Sustainability
 03-05.07.2024, Catania, Italy
4. **A. Klimek***, S. Azmi, E. Frackowiak
 "Carbon-based electrochemical capacitor in aqueous electrolyte with hydrogen bond donor"
9th International Conference on Carbon for Energy Storage and Environmental Protection (CESEP'23)
 24-28.09.2023, Budapest, Hungary

5. **A. Klimek***, S. Azmi, E. Frackowiak
 "Electrochemical capacitor in aqueous electrolyte improved by hydrogen bond donor addition"
74th Annual Meeting of the International Society of Electrochemistry
 03-08.09.2023, Lyon, France
6. **A. Klimek***, E. Frackowiak
 "Iodides additive as the capacitance booster for aqueous electrochemical capacitors"
64. Zjazd Naukowy Polskiego Towarzystwa Chemicznego
 11-16.09.2022, Lublin, Poland
7. **A. Klimek***, J. Piwek, E. Frackowiak
 "Iodides additive as the capacitance booster for aqueous electrochemical capacitors"
The International Symposium on Enhanced Electrochemical Capacitors
 11-15.07.2022, Bologna, Italy
8. **A. Klimek**, M. Tobis*, J. Piwek*, E. Frackowiak
 "CoAl-LDH/activated carbon composite for electrochemical capacitor"
XIII Scientific and Technical Conference, Carbon Materials and Polymer Composites: Science – Industry 2021
 25-28 November 2021, Ustron-Jaszowiec, Poland
III Prize of the Best Poster Competition

*denotes presenting author

Participation in scientific projects

1. **OPUS 29** (2025/57/B/ST4/01691) National Science Centre
Project title: Effect of the structural disorder in carbon material on capacitive and faradaic charge storage
Place of stay: Poznan University of Technology, Faculty of Chemical Technology, ICTE
Role: **PhD student researcher**
Principal investigator: prof. dr hab. Elzbieta Frackowiak
Period of realization: 01.2026 – 01.2028 (24 months)
Project budget: 1 613 450 PLN
2. **Preludium 23** (2024/53/N/ST5/02202) National Science Centre
Project title: Carbon materials decorated by quantum dots – synthesis, characterization
Place of stay: Poznan University of Technology, Faculty of Chemical Technology, ICTE,
Role: **Principal investigator**
Scientific advisor: prof. dr hab. Elzbieta Frackowiak
Period of realization: 01.2025 – 01.2027 (24 months)
Project budget: 140 000 PLN
3. **OPUS 16** (2018/31/B/ST4/01852) National Science Centre
Project title: Study of electrode/electrolyte interface of high stability and quick charge

response

Place of stay: Poznan University of Technology, Faculty of Chemical Technology, ICTE

Role: **Student researcher**

Principal investigator: prof. dr hab. Elzbieta Frackowiak

Period of realization: 06.2019 – 04.2023

Project budget: 1 663 000 PLN

Participation in summer schools and trainings

1. **REUNICE Summer School “Multifunctional Materials and Sustainability”**

01-05.07.2024, University of Catania, Italy

2. Course on the **safe use of compressed gases**

10.2023, Proactive Gas Safety, Ltd, Poznan, Poland

3. **REUNICE 1st Doctoral Summer School on Sustainable Science**

10-14.07.2023, University of Catania, Italy

4. **International Summer School (ISS) on Energy Storage Systems – New Developments and Directions**

18-20.07.2022, University of Zaragoza, Spain

5. Micromeritics ASAP2020 (**N₂/CO₂ sorption**)

03.2022, SYL&ANT Instruments, Poznan, Poland

Scientific internships, research stays

1. **Research stay** for the inductance and permittivity measurements of electrode materials and electrolytes

Project title: Inductance and permittivity of electrodes, electrolytes and their electrochemical cells

Place of stay: **University at Buffalo**, The State University of New York, Department of Mechanical and Aerospace Engineering, School of Engineering and Applied Sciences, Buffalo, USA

Scientific advisors: prof. Deborah Chung, prof. dr hab. Elzbieta Frackowiak

Period of stay: 09.02.2025 – 17.02.2025 (1 week)

2. **Research stay** under the **STER Mobility program (co-financed by NAWA)**

Project title: Investigation of the mechanism of aqueous electrolyte uptake by hydrophilic lignin gels and its application to gel electrolytes for energy storage systems

Place of stay: **Hokkaido University**, Research Faculty of Agriculture, Division of Fundamental Agriscience Research, Research Group of Forest Science, Laboratory of Wood Chemistry, Sapporo, Japan

Scientific advisors: Prof. Yasumitsu Uraki, Associate prof. Shiori Suzuki

Period of stay: 01.02.2024 – 30.04.2024 (3 months)

3. **Co-tutelle research stays** within the framework 2023 – 2025 **French Government Scholarship France Excellence**, granted by the **French Embassy in Poland**

Project title: Sustainable electrochemical energy storage systems working in aqueous medium with high-voltage and long-term cyclability

Place of stay: **University of Haute-Alsace**, Institute of Materials Science of Mulhouse, Mulhouse, France

Scientific advisor: Dr hab. Camelia Matei Ghimbeu

Period of stay: 01.10.2023 – 31.01.2024 (4 months), 01.10.2024 – 31.01.2025 (4 months), 01.09.2025 – 31.12.2025 (4 months)

Awards, scholarships

1. **Honorary Mention** in the **TOP 10 Women in Engineering** in Poland (Category: Rising Stars in Engineering) by Perspektywy Educational Foundation (05.06.2025)
2. **Nomination** by Perspektywy Educational Foundation to the **TOP 100 Women in Engineering** in Poland list (28.04.2025)
3. **Themed collection** “Celebrating International Women’s Day 2025: **Women in Green chemistry**” by the Royal Society of Chemistry, of the article *Klimek et al.* Green chem. 26 (2024) 6684-6695 (03.2025)
4. **Scholarship** for a 3-month research stay awarded to the top PhD students of Doctoral School of Poznan University of Technology in the framework of INPUTDoc **STER “Mobility”** competition co-financed by **Polish National Agency for Academic Exchange** NAWA (02.2024)
5. **French Government Scholarship** Excellence granted by the French Embassy in Poland (02.2023)
6. **Research Scholarship** for Doctoral Students of Poznan University of Technology in the academic year 2023/2024, 2024/2025, 2025/2026
7. **Increase in the Doctoral Scholarship** for the best PhD students of Poznan University of Technology in the academic year 2022/2023, 2023/2024, 2024/2025, 2025/2026

Memberships, responsibilities

1. Member of the **French Chemical Society** (SCF)
01.2024 – 11.2024
2. Ambassador of program “**Girls to Science**” (Dziewczyny do Nauki)
08.2023 – now

3. Member of the **International Society of Electrochemistry** (ISE)
05.2023 – now
4. **Coordinator** of the Department of Applied Electrochemistry for the **eLearning platform** at Poznan University of Technology
06.2023 – now
5. Member of the **Polish Carbon Society** (PTW)
06.2023 – now
6. Member of Science Club **PUT Chemistry** at Poznan University of Technology
12.2021 – 06.2023
7. Member of the **Independent Student's Association** (NZS)
07.2019 – 06.2023

Copyrights

Figure 3 Schematic presentation of electrical double layer models on the surface of positively charged electrode in electrolytic solution: **a)** Helmholtz model, **b)** Gouy-Chapman model, **c)** Stern model. The electrical potential φ diminishes as it moves from the electrode (φ_e) to the bulk electrolyte (φ_s). Adapted from reference: F. Beguin, V. Presser, A. Balducci, E. Frackowiak "Carbons and Electrolytes for Advanced Supercapacitors" *Advanced Materials*, 26 (2014) 2219-2251 with permission from John Wiley and Sons [license no. 6262391509922; 5 May 2026].

Figure 4 Scheme presenting three different types of pseudocapacitance: **a)** adsorption pseudocapacitance, **b)** redox pseudocapacitance, **c)** intercalation pseudocapacitance. Adapted from reference: S. Fleischmann, J.B. Mitchell, R. Wang, C. Zhan, D. Jiang, V. Presser, V. Augustyn "Pseudocapacitance: From Fundamental Understanding to High Power Energy Storage Materials" *Chemical Reviews*, 120 (2020) 6738-6782 with permission from American Chemical Society [license no. 6262400473394; 5 May 2026].

Publication P1 "Electrochemical capacitor in aqueous electrolyte with long lifespan improved by hydrogen bond donor addition"

Authors: Sara Azmi*, Amelia Klimek, Elżbieta Frackowiak*

Journal metrics: *Materials Today*, 68 (2023) 34-50

Publisher, DOI: Elsevier, <https://doi.org/10.1016/j.mattod.2023.06.018>

As an Elsevier journal author, you retain the right to Include the article in a thesis or dissertation (provided that this is not to be published commercially) whether in full or in part, subject to proper acknowledgment; see <https://www.elsevier.com/about/policies/copyright> for more information. As this is a retained right, no written permission from Elsevier is necessary.

As outlined in our permissions licenses, this extends to the posting to your university's digital repository of the thesis provided that if you include the published journal article (PJA) version, it is embedded in your thesis only and not separately downloadable.

Thank you.

Kind regards,

Thomas Rexson Yesudoss
Copyrights Specialist
ELSEVIER | HCM - Health Content Management

Publication P2 “Effect of a buffer/iodide electrolyte on the performance of electrochemical capacitors”

Authors: Amelia Klimek, Maciej Tobis, Elżbieta Frąckowiak*
Journal metrics: Green Chemistry 26 (2024) 6684-6695
Publisher, DOI: Royal Society of Chemistry, <https://doi.org/10.1039/D4GC01748J>

Effect of a buffer/iodide electrolyte on the performance of electrochemical capacitors

A. Klimek, M. Tobis and E. Frackowiak, *Green Chem.*, 2024, **26**, 6684 DOI: 10.1039/D4GC01748J

To request permission to reproduce material from this article, please go to the [Copyright Clearance Center request page](#).

If you are **an author contributing to an RSC publication**, **you do not need to request permission** provided correct acknowledgement is given.

If you are **the author of this article**, **you do not need to request permission to reproduce figures and diagrams** provided correct acknowledgement is given. If you want to reproduce the whole article in a third-party publication (excluding your thesis/dissertation for which permission is not required) please go to the [Copyright Clearance Center request page](#).

Publication P3 “Lignin as precursor of gel electrolyte and salt templated carbon for sustainable electrochemical capacitor”

Authors: Amelia Klimek, Lina Amro, Nutthira Pakkang, Camélia Matei Ghimbeu, Elżbieta Frąckowiak*, Shiori Suzuki*
Journal metrics: Green Chemistry 28 (2026) 4225-4242
Publisher, DOI: Royal Society of Chemistry, <https://doi.org/10.1039/D5GC05533D>

Lignin as a precursor of a gel electrolyte and salt templated carbon for sustainable electrochemical capacitors

A. Klimek, L. Amro, N. Pakkang, C. Matei Ghimbeu, E. Frackowiak and S. Suzuki, *Green Chem.*, 2026, **28**, 4225 DOI: 10.1039/D5GC05533D

This article is licensed under a [Creative Commons Attribution 3.0 Unported Licence](#). You can use material from this article in other publications without requesting further permissions from the RSC, provided that the correct acknowledgement is given.

Publication P4 “Impact of disorder, porosity and surface chemistry of salt templated carbons on capacitance”

Authors: Amelia Klimek, Bénédicte Réty, Camélia Matei Ghimbeu*,
Elżbieta Frąckowiak*

Journal metrics: Advanced Science 12 (2025) e05032

Publisher, DOI: Wiley, <https://doi.org/10.1002/adv.202505032>

Details

© 2025 The Author(s). Advanced Science
published by Wiley-VCH GmbH

This is an open access article under the terms of
the [Creative Commons Attribution](#) License,
which permits use, distribution and reproduction
in any medium, provided the original work is
properly cited.

Declaration of co-authors

The contributions of all authors of the peer-reviewed articles (P1-P4) within this PhD thesis are provided in the Table below. The specific contributions of the all authors to the peer-reviewed articles (P1-P4) are encompassed in this PhD thesis.

Author	P1	P2	P3	P4
Amelia Klimek	•	•	•	•
Sara Azmi	•			
Elzbieta Frackowiak	•	•	•	•
Maciej Tobis		•		
Camélia Matei Ghimbeu			•	•
Benedicte Réty				•
Lina Amro			•	
Nutthira Pakkang			•	
Shiori Suzuki			•	



POZNAN UNIVERSITY OF TECHNOLOGY

Sara Azmi
FACULTY OF CHEMICAL TECHNOLOGY
Institute of Chemistry and Technical Electrochemistry
Berdychowo 4, 60-965 Poznan, Poland
e-mail: sara.azmi@put.poznan.pl



Poznan, August 18th, 2023

Statement of individual contribution in publication

As the co-author of the following article:

“Electrochemical capacitor in aqueous electrolyte with long lifespan improved by hydrogen bond donor addition”

Authors: **Sara Azmi**, Amelia Klimek, Elzbieta Frackowiak

Journal metrics: Materials Today, 68 (2023) 34-50

Publisher: Elsevier

DOI: <https://doi.org/10.1016/j.mattod.2023.06.018>

I hereby declare that my contribution to this work included:

Conceptualization, methodology, validation, formal analysis, investigation (SEM images, TEM images, testing of anticorrosive properties of the electrolytes towards stainless steel, Raman investigation of stainless steel disc electrodes, electrochemical capacitors testing in two and three electrode cells), data curation, writing – original draft, writing – review & editing, visualization.

.....*S.Azmi*.....
signature



POZNAN UNIVERSITY OF TECHNOLOGY

Amelia Klimek

FACULTY OF CHEMICAL TECHNOLOGY
Institute of Chemistry and Technical Electrochemistry
Berdychowo 4, 60-965 Poznan, Poland
e-mail: amelia.klimek@doctorate.put.poznan.pl



Poznan, March 6th, 2026

Statement of individual contribution in publication

As the co-author of the following article:

“Electrochemical capacitor in aqueous electrolyte with long lifespan improved by hydrogen bond donor addition”

Authors: Sara Azmi, **Amelia Klimek**, Elzbieta Frackowiak

Journal metrics: Materials Today, 68 (2023) 34-50

Publisher: Elsevier

DOI: <https://doi.org/10.1016/j.mattod.2023.06.018>

I hereby declare that my contribution to this work included:

Conceptualization, methodology, validation, formal analysis, investigation (ionic conductivity and pH measurements of electrolytes, realization of sorption of nitrogen at 77K of electrode materials, testing of anticorrosive properties of the electrolytes towards stainless steel, Raman investigation of stainless steel disc electrodes, electrochemical capacitors testing in two and three electrode cells, electrochemical impedance spectra fitting, pouch cells investigation, Raman investigation in operando mode, operando gas chromatography-mass spectrometry experiments), data curation, writing – original draft, writing – review & editing, visualization.

Amelia Klimek

signature



POZNAN UNIVERSITY OF TECHNOLOGY

Elżbieta Frackowiak
FACULTY OF CHEMICAL TECHNOLOGY
Institute of Chemistry and Technical Electrochemistry
Berdychowo 4, 60-965 Poznań, Poland
phone.: +48 (61) 665 36 32
e-mail: elzbieta.frackowiak@put.poznan.pl



Poznań, March 6th, 2026

Statement of individual contribution in publication

As the co-author of the following article:

“Electrochemical capacitor in aqueous electrolyte with long lifespan improved by hydrogen bond donor addition”

Authors: Sara Azmi, Amelia Klimek, **Elżbieta Frackowiak**

Journal metrics: Materials Today, 68 (2023) 34-50

Publisher: Elsevier

DOI: <https://doi.org/10.1016/j.mattod.2023.06.018>

I hereby declare that my contribution to this work included:

Conceptualization, supervision, methodology, funding acquisition, writing – review & editing.

signature



POZNAN UNIVERSITY OF TECHNOLOGY

Amelia Klimek

FACULTY OF CHEMICAL TECHNOLOGY
Institute of Chemistry and Technical Electrochemistry
Berdychowo 4, 60-965 Poznan, Poland
e-mail: amelia.klimek@doctorate.put.poznan.pl



Poznan, March 6th, 2026

Statement of individual contribution in publication

As the co-author of the following article:

“Effect of a buffer/iodide electrolyte on the performance of electrochemical capacitors”

Authors: **Amelia Klimek**, Maciej Tobis, Elzbieta Frackowiak

Journal metrics: Green Chemistry, 26 (2024) 6684-6695

Publisher: Royal Society of Chemistry

DOI: <https://doi.org/10.1039/D4GC01748J>

I hereby declare that my contribution to this work included:

Conceptualization, methodology, validation, formal analysis, investigation (preparation of electrodes and electrolytes for physicochemical and electrochemical testing, realization of sorption of nitrogen at 77K of electrode materials, ionic conductivity and pH measurements of electrolytes, FTIR investigation of electrolytes, SEM images, electrochemical capacitors testing in two-electrode cells using cyclic voltammetry, galvanostatic charge/discharge, electrochemical impedance spectroscopy), data curation, writing-original draft, writing-review & editing, visualization.

Amelia Klimek

signature



POZNAN UNIVERSITY OF TECHNOLOGY

Maciej Tobis

FACULTY OF CHEMICAL TECHNOLOGY
Institute of Chemistry and Technical Electrochemistry
Berdychowo 4, 60-965 Poznań, Poland
e-mail: maciej.p.tobis@doctorate.put.poznan.pl



Poznań, April 22nd, 2024

Statement of individual contribution in publication

As the co-author of the following article:

"Effect of a buffer/iodide electrolyte on the performance of electrochemical capacitors"

Authors: Amelia Klimek, Maciej Tobis, Elzbieta Frackowiak

Journal metrics: Green Chemistry, 26 (2024) 6684-6695

Publisher: Royal Society of Chemistry

DOI: <https://doi.org/10.1039/D4GC01748J>

I hereby declare that my contribution to this work included:

Investigation (electrochemical capacitor testing in three-electrode cells, preparation of electrode material/electrolytes for physicochemical investigation), data curation (X-ray diffraction, X-ray photoelectron spectroscopy), writing - review & editing, visualization.

signature



POZNAN UNIVERSITY OF TECHNOLOGY

Elżbieta Frackowiak
FACULTY OF CHEMICAL TECHNOLOGY
Institute of Chemistry and Technical Electrochemistry
Berdychowo 4, 60-965 Poznan, Poland
phone.: +48 (61) 665 36 32
e-mail: elzbieta.frackowiak@put.poznan.pl



Poznan, March 6th, 2026

Statement of individual contribution in publication

As the co-author of the following article:

“Effect of a buffer/iodide electrolyte on the performance of electrochemical capacitors”

Authors: Amelia Klimek, Maciej Tobis, **Elżbieta Frackowiak**

Journal metrics: Green Chemistry, 26 (2024) 6684-6695

Publisher: Royal Society of Chemistry

DOI: <https://doi.org/10.1039/D4GC01748J>

I hereby declare that my contribution to this work included:

Conceptualization, resources, writing – review & editing, supervision, project administration, funding acquisition.

signature



POZNAN UNIVERSITY OF TECHNOLOGY

Amelia Klimek
FACULTY OF CHEMICAL TECHNOLOGY
Institute of Chemistry and Technical Electrochemistry
Berdychowo 4, 60-965 Poznan, Poland
e-mail: amelia.klimek@doctorate.put.poznan.pl



Poznan, March 6th, 2026

Statement of individual contribution in publication

As the co-author of the following article:

“Impact of disorder, porosity and surface chemistry of salt templated carbons on capacitance”

Authors: **Amelia Klimek**, Bénédicte Rety, Camélia Matei Ghimbeu, Elzbieta Frackowiak

Journal metrics: Advanced Science, 12 (2025) e05032

Publisher: Wiley

DOI: <https://doi.org/10.1002/advs.202505032>

I hereby declare that my contribution to this work included:

Conceptualization, methodology software, validation, formal analysis, investigation (Raman spectroscopy of carbons, preparation of carbons for TEM and XRD analyses, realization of nitrogen sorption at 77K and carbon dioxide sorption at 273K of carbons, realization of temperature programmed desorption coupled with mass spectrometry and active surface area, electrochemical capacitor investigation in two and three electrode cells using cyclic voltammetry, galvanostatic charge/discharge, electrochemical impedance spectroscopy, contact angle measurement), data curation, writing – original draft, writing – review & editing, visualization.

Amelia Klimek

signature

Mulhouse, February 19th, 2026

Statement of individual contribution in publication

As the co-author of the following article:

“Impact of disorder, porosity and surface chemistry of salt templated carbons on capacitance”

Authors: Amelia Klimek, Bénédictte Réty, Camélia Matei Ghimbeu, Elzbieta Frackowiak

Journal metrics: Advanced Science, 12 (2025) e05032

Publisher: Wiley

DOI: <https://doi.org/10.1002/advs.202505032>

I hereby declare that my contribution to this work included:

Investigation and data curation (temperature programmed desorption coupled with mass spectrometry of salt templated carbons), writing – review & editing, visualization.



.....
signature



Dr Camelia Matei Ghimbeu, HDR
Mulhouse Materials Science Institute
Carbon and Hybrid Materials Team
15 rue Jean Starcky, 68057 Mulhouse, FRANCE
phone: +33 389 508 743
e-mail: camelia.ghimbeu@uha.fr



Mulhouse, March 6th, 2026

Statement of individual contribution in publication

As the co-author of the following article:

“Impact of disorder, porosity and surface chemistry of salt templated carbons on capacitance”

Authors: Amelia Klimek, Bénédicte Rety, Camélia Matei Ghimbeu, Elzbieta Frackowiak

Journal metrics: Advanced Science, 12 (2025) e05032

Publisher: Wiley

DOI: <https://doi.org/10.1002/advs.202505032>

I hereby declare that my contribution to this work included:

Conceptualization, funding acquisition, project administration, supervision, validation, writing – review & editing.

.....
signature



POZNAN UNIVERSITY OF TECHNOLOGY

Elżbieta Frackowiak
FACULTY OF CHEMICAL TECHNOLOGY
Institute of Chemistry and Technical Electrochemistry
Berdychowo 4, 60-965 Poznań, Poland
phone.: +48 (61) 665 36 32
e-mail: elzbieta.frackowiak@put.poznan.pl



Poznań, February 18th, 2026

Statement of individual contribution in publication

As the co-author of the following article:

“Impact of disorder, porosity and surface chemistry of salt templated carbons on capacitance”

Authors: Amelia Klimek, Bénédicte Rety, Camélia Matei Ghimbeu,
Elzbieta Frackowiak

Journal metrics: Advanced Science, 12 (2025) e05032

Publisher: Wiley

DOI: <https://doi.org/10.1002/advs.202505032>

I hereby declare that my contribution to this work included:

Conceptualization, funding acquisition, project administration, supervision, validation,
writing – review & editing.

signature



POZNAN UNIVERSITY OF TECHNOLOGY

Amelia Klimek
FACULTY OF CHEMICAL TECHNOLOGY
Institute of Chemistry and Technical Electrochemistry
Berdychowo 4, 60-965 Poznań, Poland
e-mail: amelia.klimek@doctorate.put.poznan.pl



Poznań, March 6th, 2026

Statement of individual contribution in publication

As the co-author of the following article:

“Lignin as a precursor of a gel electrolyte and salt templated carbon for sustainable electrochemical capacitors”

Authors: **Amelia Klimek**, Lina Amro, Nutthira Pakkang, Camélia Matei Ghimbeu, Elzbieta Frackowiak, Shiori Suzuki

Journal metrics: Green Chemistry, 28 (2026) 4225-4242

Publisher: Royal Society of Chemistry

DOI: <https://doi.org/10.1039/D5GC05533D>

I hereby declare that my contribution to this work included:

Conceptualization, methodology, validation, formal analysis, investigation (preparation of gel electrolyte, water-in-salt electrolytes and salt templated carbons, solution uptake and swelling degree measurements, FTIR analysis, Cryo SEM analysis, ionic conductivity, pH and viscosity measurements, TEM analysis, Raman spectroscopy, nitrogen sorption at 77K, elemental analysis, electrochemical capacitor investigation in two and three electrode cells using cyclic voltammetry, galvanostatic charge/discharge, electrochemical impedance spectroscopy), data curation, writing – original draft, writing – review & editing, visualization.

Amelia Klimek

signature



POZNAN UNIVERSITY OF TECHNOLOGY

Lina Amro

FACULTY OF CHEMICAL TECHNOLOGY
Institute of Chemistry and Technical Electrochemistry
Berdychowo 4, 60-965 Poznan, Poland
e-mail: lina.amro@student.put.poznan.pl



Poznan, March 3rd, 2026

Statement of individual contribution in publication

As the co-author of the following article:

“Lignin as a precursor of a gel electrolyte and salt templated carbon for sustainable electrochemical capacitors”

Authors: Amelia Klimek, **Lina Amro**, Nutthira Pakkang, Camélia Matei
Ghimbeu, Elzbieta Frackowiak, Shiori Suzuki

Journal metrics: Green Chemistry, 28 (2026) 4225-4242

Publisher: Royal Society of Chemistry

DOI: <https://doi.org/10.1039/D5GC05533D>

I hereby declare that my contribution to this work included:

Investigation (preparation of gel electrolyte, water-in-salt electrolytes and salt templated carbons, solution uptake and swelling degree measurements, FTIR analysis, Raman spectroscopy, electrochemical investigation in two and three electrode cells using cyclic voltammetry, galvanostatic charge/discharge, electrochemical impedance spectroscopy), writing – review & editing.



FACULTY OF ENGINEERING
Department of International Collaborative Program in
Sustainable Materials and Technology for Industries
Nagoya University and Chulalongkorn University
Furo-cho, Chikusa-ku, Nagoya, Aichi, 4648601 Japan
phone.: +81 (52) 789 3260
e-mail: pakkang.nutthira.r7@f.mail.nagoya-u.ac.jp

Nagoya, March 3rd, 2026

Statement of individual contribution in publication

As the co-author of the following article:

“Lignin as a precursor of a gel electrolyte and salt templated carbon for sustainable electrochemical capacitors”

Authors: Amelia Klimek, Lina Amro, **Nutthira Pakkang**, Camélia Matei
Ghimbeu, Elzbieta Frackowiak, Shiori Suzuki

Journal metrics: Green Chemistry, 28 (2026) 4225-4242

Publisher: Royal Society of Chemistry

DOI: <https://doi.org/10.1039/D5GC05533D>

I hereby declare that my contribution to this work included:

Investigation (preparation of steam activated carbon).

.....
signature



Dr Camelia Matei Ghimbeu, HDR

Mulhouse Materials Science Institute
Carbon and Hybrid Materials Team
15 rue Jean Starcky, 68057 Mulhouse, FRANCE
phone: +33 389 508 743
e-mail: camelia.ghimbeu@uha.fr



Mulhouse, March 6th, 2026

Statement of individual contribution in publication

As the co-author of the following article:

“Lignin as a precursor of a gel electrolyte and salt templated carbon for sustainable electrochemical capacitors”

Authors: Amelia Klimek, Lina Amro, Nutthira Pakkang, **Camélia Matei Ghimbeu**, Elzbieta Frackowiak, Shiori Suzuki

Journal metrics: Green Chemistry, 28 (2026) 4225-4242

Publisher: Royal Society of Chemistry

DOI: <https://doi.org/10.1039/D5GC05533D>

I hereby declare that my contribution to this work included:

Conceptualization, funding acquisition, project administration, supervision, validation, writing – review & editing.

.....
signature



POZNAN UNIVERSITY OF TECHNOLOGY

Elżbieta Frackowiak
FACULTY OF CHEMICAL TECHNOLOGY
Institute of Chemistry and Technical Electrochemistry
Berdychowo 4, 60-965 Poznań, Poland
phone.: +48 (61) 665 36 32
e-mail: elzbieta.frackowiak@put.poznan.pl



Poznań, March 6th, 2026

Statement of individual contribution in publication

As the co-author of the following article:

“Lignin as a precursor of a gel electrolyte and salt templated carbon for sustainable electrochemical capacitors”

Authors: Amelia Klimek, Lina Amro, Nutthira Pakkang, Camélia Matei Ghimbeu, **Elżbieta Frackowiak**, Shiori Suzuki

Journal metrics: Green Chemistry, 28 (2026) 4225-4242

Publisher: Royal Society of Chemistry

DOI: <https://doi.org/10.1039/D5GC05533D>

I hereby declare that my contribution to this work included:

Conceptualization, funding acquisition, project administration, supervision, validation, writing – review & editing.

signature

Dr Shiori Suzuki
Research Faculty of Agriculture
Division of Fundamental Agriscience Research
Research Group of Forest Science
Laboratory of Wood Chemistry
Kita 9, Nishi 9, Kita-ku, Sapporo, Japan
phone.: +81-11-706-2512
e-mail: suzuki-s@agr.hokudai.ac.jp



HOKKAIDO
UNIVERSITY

Sapporo, March 3rd, 2026

Statement of individual contribution in publication

As the co-author of the following article:

“Lignin as a precursor of a gel electrolyte and salt templated carbon for sustainable electrochemical capacitors”

Authors: Amelia Klimek, Lina Amro, Nutthira Pakkang, Camélia Matei Ghimbeu, Elzbieta Frackowiak, **Shiori Suzuki**

Journal metrics: Green Chemistry, 28 (2026) 4225-4242

Publisher: Royal Society of Chemistry

DOI: <https://doi.org/10.1039/D5GC05533D>

I hereby declare that my contribution to this work included:

Conceptualization, investigation (preparation of gel electrolytes, Cryo SEM analysis), funding acquisition, project administration, supervision, validation, writing – review & editing.

Shiori Suzuki
.....
signature

Acknowledgements

I would like to sincerely thank my supervisor – **Prof. Elżbieta Frąckowiak** for the countless valuable comments, suggestions, and for being the best example of a scientist. You were the first person to notice my hidden ambitions, abilities and offered me the opportunity to work in your research group during my engineering studies. I knew nothing about the electrochemistry and materials science. Even worst, my English language skills were not existing... and you still invested your time, and your energy in my development. Your encouraging and inspiring mentorship gave me the confidence to spread my wings and aim even higher – to do co-tutelle PhD. You will always have a special place in my heart. *“Jeśli zabałaganione biurko jest oznaką zabałaganionego umysłu, oznaką czego jest puste biurko” ~ Albert Einstein*

I am also profoundly grateful to my supervisor, **Dr HDR Camèlia Matei Ghimbeu**. You broadened my understanding of the textural and structural properties of carbon materials and guided me through the fascinating field of carbon quantum dots - a material particularly challenging in terms of synthesis, characterization, and applications. Your creativity, extensive knowledge, dedication to research, and inspiring leadership have been truly remarkable. I deeply admire the way you manage your team and support your students while maintaining balance beyond academic life. You are an exceptional role model, and, in my eyes, the definition of excellence in research.

I would like to thank present and past members of **Power Sources Group** in Poznan. Together, we contributed to the strong international visibility of the group, and our research still continues to attract the interest of scientific community. **Maciej**, thank you for being my first lab mate. I really enjoyed working with you on LDH and buffers. Special thanks to my office mates – **Sara** and **Andrii**. You accepted me even though I was still unexperienced student, while you were decent postdoctoral researchers. **Sara**, you believed in me and inspired me to do a PhD. *“There is no force more powerful than a woman determined to rise”*. **Andres**, thanks for your support, scientific discussions and non-scientific life lessons. *“You are owner of your silence and slave of your words”*. **Adam, Sylwia** you were here to help everybody no matter what – thank you for that. I would like to express my gratitude to **Prof. François Béguin** for his help, advices and

excellent French language skills, improving the quality of this thesis. **Paula**, you were the first one who introduced me the mystery behind TPD-MS – thank you. Additionally, sincere thanks to **Prof. Krzysztof Fic** for the help and support of every member of the group.

I am deeply grateful to the members of **Carbon and Hybrid Material Group** at IS2M, Mulhouse. Just like the carbon materials we study, we are highly diverse, yet united by shared values – much like carbon materials composed of carbon atoms with different hybridizations. **Adrian**, thank you for your daily dose of humor, excellent taste in music as well as dealing with the equipment that suddenly decided to not cooperate. **Benedicte**, there is no better specialist on TPD-MS than you, I am honored that I could learn from you. **Ademola**, I think our scientific discussions on texture/structure/surface chemistry - performance relationships should be available online. Please, remember what you promised to me and Fatima, we keep our fingers crossed for you! **Fatima**, thank you for always finding a time to talk and help me, even though you were busy. **Khoi**, you were the best neighbor office mate I had! **Colleen**, since the first time we met, I knew we share the same life attitude. Thank you for always making the workday brighter. **Peet**, thanks for continuously making me laugh, but also academic/life advices. **Hugo**, thanks for your expertise in the French language/culture, I also really enjoyed our 7 am scientific and non-scientific discussions. **Loic**, I cannot promise you that I will not provide you more carbon quantum dots for TEM analysis. **Jean-Marc**, thank you for being always so supportive regarding XRD analysis. **Cyril**, there is no better specialist on gas sorption than you – thank you for your help and all advices.

Special thanks are owed to the members of the **Wood Chemistry Group** in Sapporo for their kindness, openness, and warm welcome despite our cultural and scientific differences. **Sensei Shiori Suzuki**, thank you for introducing me to the field of biopolymers and for your invaluable guidance, both in and outside the laboratory. I greatly admire your ability to balance so many responsibilities while always finding time to help and support me - even beyond office hours. It is truly an honor to continue collaborating with you after my internship. To my brilliant colleagues, **Nutthira** and **Himani** - it is finally my turn to complete this thesis and join you as a doctor. **Nutthira**, your enthusiasm and dedication to science made my time in Sapporo especially enjoyable. **Himani**, I will always remember our discussions on issues related with lignin-based gels, your kindness, sense of humour and hospitality. I would also like to sincerely thank **Sensei Yasumitsu Uraki** for his advice on gel electrolyte formulations and for his willingness to help me during laboratory experiments despite his many responsibilities.

Ogromne podziękowania należą się mojemu **tacie Zbigniewowi**, który najbardziej motywował mnie podczas pisania niniejszej pracy. W tym samym czasie konsekwentnie pracował nad budową altanki w ogrodzie. Za każdym razem, gdy brakowało mi siły do pisania spoglądałam przez balkon i widziałam jak ciężko pracuje, nie ważne czy padał deszcz, wiał wiatr czy było zimno. W takich momentach wracałam do pisania bez narzekania. Kto pierwszy skończy swoją pracę, ten pomaga przegranemu...

Nie ukończyłabym doktoratu bez wsparcia mojej **mamy Beaty**. Dziękuję za Twoją obecność, cierpliwość, nieustającą troskę oraz wiarę we mnie – zarówno w chwilach wzlotów, jak i upadków. Dziękuję również mojemu **bratu Adamowi** za to, że był obok na każdym etapie tej drogi, za wsparcie i przypominanie mi, do podążania drogą zgodną z własnymi pasjami i wartościami.

Chciałabym serdecznie podziękować moim wspianiałym **babciom Jadwidze i Ewie** oraz **dziadkom Henrykowi i Józefowi**. Jestem wdzięczna za Waszą miłość, nieustanne wsparcie i dumę, którą od Was czuję. Jesteście najlepszymi kibicami na świecie, na dobre i na złe! Dziękuję **cioci Iwonie, cioci Marii, cioci Beacie i cioci Zofii** za ich życzliwość, troskę oraz wsparcie. Dziękuję, że inspirujecie mnie do nieustannego rozwoju i sięgania po więcej.

Ponadto nie mogę przejść obojętnie, nie wspominając o mojej przyjaciółce **Marcie**. Przez te wszystkie lata wspieramy się nawzajem i motywujemy do działania. *„Czasem poświęcamy zbyt dużo uwagi złym rzeczom i zajęci narzekaniem, często zapominamy o przyszłości, której naprawdę chcemy, albo o tym, co chcielibyśmy osiągnąć.”* Nawet po całym dniu spędzonym razem zawsze znajduje się jeszcze coś do dodania podczas wieczornej rozmowy telefonicznej.

Dziękuję również **Patrycji, Karolinie, Asi, Kasi G., Nataszce, Kasi M., Włodkowi, Robertowi, Elham, Matthiasowi, Batoul, Linie, Ewie** za obecność, rozmowy, śmiech, wsparcie i ogromne pokłady cierpliwości, szczególnie podczas doktoratu. *„W życiu nie chodzi o to, co posiadamy, lecz o ludzi, których mamy obok siebie”.*