POLITECHNIKA GDAŃSKA
WYDZIAŁ CHEMICZNY

KATEDRA CHEMII I TECHNOLOGII MATERIAŁÓW FUNKCJONALNYCH

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Gdańsk, 12.12.2024

# Review

of the doctoral dissertation of Mr Andrés Camilo Parejo-Tovar titled "*Performance of symmetric and hybrid electrochemical capacitors*".

The review was prepared on the basis of a letter from the 29th of October 2024 of the Dean of the Faculty of Chemical Technology at the Poznan University of Technology, prof. Ewa Kaczorek based on the Resolution No. RD-15/1/2024 of the Council of the Chemistry Science Discipline of the Poznan University of Technology.

The mentioned above doctoral dissertation was conducted under the supervision of Prof. Françpoi Béguin and Dr. Paula Ratajczak at the Institute of Chemistry and Technical Electrochemistry, Faculty of Chemical Technology of Poznan University of Technology. The topic of the PhD thesis is focused on various aspects related to electrochemical capacitors i.e. the use of "water in salt" electrolytes and hybrid carbon-based lithium or sodium ion capacitors, including description and physicochemical and electrochemical characterization of synthesized materials as well as designing of the route in obtaining materials of desired properties.

Since Volta's discovery of electricity, electric energy has become one of the most critical aspects of modern life. Industry remains the primary beneficiary of this energy, driving a rapid increase in global energy demand. This surge has led to higher $CO_2$ emissions, contributing to climate change, pollution, and the intensification of global warming. It is predicted that till 2030 the temperature n Earth will increase of up to 6 °C due to greenhouse gases. Transitioning to a decarbonized energy sector is essential for reducing $CO_2$ emissions, and renewable energy sources offer a pathway to universal electricity access. However, despite significant advancements in renewable energy, it still falls short of meeting global electricity demands. Currently, more than 90% of the world's primary energy supply relies on fossil fuels, underscoring the urgent need to reduce their share in favour of low-emission alternatives. Even with a complete shift away from fossil fuels, the challenge of efficiently harvesting and utilizing

renewable energy remains. This highlights the critical need for advanced energy storage solutions.

Energy storage devices such as batteries, capacitors, and fuel cells play a vital role in this transition. Batteries provide high specific energy but suffer from low specific power. In contrast, capacitors offer high power density but low energy density. Electrochemical capacitors strike a balance by delivering relatively high energy and power densities, yet their performance still falls short compared to traditional batteries and capacitors. Therefore, the development of advanced materials with superior electrochemical properties is essential for enhancing the efficiency and capability of electrochemical capacitors, paving the way for more effective modern energy storage systems.

Many laboratories around the world are conducting research on the development of novel materials for electrochemical capacitors that exhibit high voltage originating from the battery, and high power capability coming from the capacitor. Among these laboratories, Prof. Béguin's team is one of the most recognizable groups in the scientific community in this field.

The doctoral dissertation of Mr Andrés Camilo Parejo-Tovar is in the form of the so-called thematically coherent set of articles published in scientific journals and has 255 pages. This set of articles is consisted of 4 published papers. These 4 articles are devoted to 3 main areas: 1) developing advanced water-in-salt (WIS) electrolytes for EDLCs to achieve high-voltage and stable operation, especially under low-temperature conditions to improve energy density and prolonging cycle life, 2) optimizing the pre-metalation process in MICs by utilizing the irreversible oxidation of a carefully selected cathodic sacrificial material to obtain stable SEI film and avoid by-products formation in the first cycle, 3) establishing an *operando* methodology to monitor ion population dynamics within the electric double layer (EDL) of the positive electrode in MICs during charge and discharge cycles, allowing optimization the electrode's performance and reliability.

The doctoral student's hirsch index is 1 (Scopus, December 12, 2024) and the total impact factor, IF, of 4 publications included in the doctoral dissertation, is 50.6 (December 12, 2024), which gives average value approx. 12.65. The average number of co-authors is 2.75, and suggests that Mr Andrés Camilo Parejo-Tovar was the main investigator, especially that he was the first author in all of the articles, however he was not a corresponding author in none of them. The total number of publications is 5 with IF=69.5. Mr. Parejo-Tovar is also co-author of 11 presentations (6 oral and 5 posters) presented at domestic and international conferences,

and was awarded the best poster presentation at ISEECap 2022 conference. He was participant in the scientific project POWROTY with Dr eng. Paula Ratajczak as the principal investigator, and beneficiary of the France Excellence scholarship called SSHN – research stay under the supervision of Dr Céline Merlet from CIRIMAT, Toulouse, France.

The dissertation, besides 5 chapters consisted of literature review (Chapter I) and summary of the attached publications (Chapters II-V), contains General introduction, General conclusion, References, Scientific achievements, Abstract, Streszczenie and Co-authorship statements.

The motivation of the research is placed in General introduction, but in my opinion it should be stated as a separate chapter because placing it in the General introduction diminished its importance. This is crucial information as to why the Author decided to start PhD studies in the Doctoral School at Poznan University of Technology. I have one comment to General introduction chapter:

1. The abbreviation of solid electrolyte interphase is SEI not S.E.I.

Chapter I is a very detailed introduction including theory of the electrical double-layer capacitors (EDLC), materials use as electrode in EDLC, types of EDLC, electrolytes used in EDLC. This is well written chapter.

2. The symbol * is not a multiplication symbol.
3. In the negative electrode in a lithium-ion battery energy is stored by the intercalation process. Same for lithium-ion capacitors. Thus, what is the difference between them?

Chapter II is a summary of the article *The $NaClO_4$-water eutectic electrolyte for environmentally friendly electrical double-layer capacitors operating at low temperature*. This article deals with the use of eutectic electrolyte at low temperature. It was evidenced that such eutectic electrolyte can be successfully use down to -35 °C. Additionally, the comparison of computational analysis with experimental results showed that the presence of hydrogen-bonded water channels enhance ionic conductivity.

4. It is known that ionic conductivity of salt of strong acid and strong base increases with the increase of the concentration of the salt soluble in water. Did you expect a decrease in the ionic conductivity of the $NaClO_4$ solution with the increase of the $NaClO_4$ before its saturation? Otherwise the word “interestingly” seems to be not

the best choice in the statement *Interestingly, the eutectic electrolyte demonstrated a high ionic conductivity of 180 mS cm$^{-1}$*.

5. Could you comment the reason of decrease of the ionic conductivity for $NaClO_4$ mass fraction above 45% (Fig S1, page 90)?
6. Could you comment why the pH of eutectic electrolyte was 6.1?
7. Could you compare the determination coefficient for Arrhenius-type dependence and VTF approach for conductivity measurements?
8. How many charge/discharge cycles were performed at different temperatures?
9. What cycle number does coulombic efficiency refer to?

Chapter III is about using sodium azide ($NaN_3$) as a sacrificial cathodic material to improve electrochemical performance of AC//$Na_x$HCM sodium-ion capacitor. The idea of the use of a sacrificial material is to enhance the electrochemical performance of the energy storage system due to the addition of ions that will be consumed during the formation of a protective SEI layer, but which will not originate from electrolyte. The use of $NaN_3$ is reasonable because any by-products are generated during $NaN_3$ oxidation.

10. The cycle life of the sodium-ion capacitor is impressing reaching capacity retention over 95% in 15000 cycles. The discharge capacity was 40 F/g. Do you think that this value is interesting from practical point of view?
11. The typical current density used for battery cycling, in C-rate unit, is from 0.5C to 2C, for ECDL it is much higher, even up to 100C. Thus, for hybrid ion capacitors this value should be in the range from 1C to 20C. Could you comment why the chosen current density was only 200 mA/g, that is approximately equal to 0.5C?

Chapter IV, *Comprehensive potentiodynamic analysis of electrode performance in hybrid capacitors*, presents a methodology for precisely evaluating the properties of individual electrodes in hybrid capacitors. This an important issue due to fact that in any energy storage system there are 2 electrodes, while in electrochemical measurements usually only one is set as so called working electrode, and investigated. The article demonstrates how optimizing electrode composition and mass ratios can balance energy density and power output, leading to enhanced performance in hybrid capacitors.

12. During a typical charging/discharging process, constant current followed by constant voltage is applied. Do you have any idea how such procedure affects electrode performance in hybrid capacitors?

Chapter V titled *Operando tracking of ion population changes in the EDL electrode of a lithium-ion capacitor during its charge/discharge* investigates charge transport and charge transfer phenomena in activated carbon electrode materials in metal-ion capacitor. The article shows the importance of the porosity of electrode material on its electrochemical performance. The results obtained from the experimental data were in agreement with the results obtained by computational analysis.

13. Could you clarify why you used different equations for calculating coulombic efficiency?
14. How did you distinguish interactions e.g. $Li^+ - O_{EC}$ from $Li^+ - O_{DMC}$ or $PF_6^- - C_{EC}$ from $PF_6^- - C_{EC}$?
15. Could you comment why the value of the point of zero charge (PZC) differs from the open circuit potential (OCP) value?
16. What is the difference between PZC and OCP?
17. Could you clarify the meaning of $G_1$, $G_2$, $D_1$ and $D_2$?
18. Deconvolution of the Raman spectra is confusing for D2 band. This band is too broad. Why did you deconvolute the spectra only with 4 peaks? According to Sadezky et. al. (https://doi.org/10.1016/j.carbon.2005.02.018) carbonaceous material may be with 3, 4 or 5 bands. From my experience, I noticed that Origin is not the best software for deconvolution of any spectra. I would recommend Fityk software (https://doi.org/10.1107/S0021889810030499).

In general, the doctoral dissertation is of a very high standard, both substantively and editorially. It addresses issues related to the broad range of energy storage systems including choosing the right electrolyte, optimization of the negative electrode in a hybrid metal-ion capacitor, and investigation of the ion population in the electrode material. All these aspects were undertaken to improve the electrochemical performance and lifespan of electrochemical capacitors. Publication of all articles in very prestige journals confirms that the quality of the results is very high, and from the reviewer's point of view it was really very difficult to revise the already published articles. According to co-authorship statements Mr. Andrés Camilo Parejo-Tovar demonstrated his ability to plan and conduct experimental work, to select appropriate research techniques, to discuss the results, and to conclude.

In summary, although mentioned above comments, the doctoral dissertation submitted by Mr Andrés Camilo Parejo-Tovar represents very high scientific work. The literature review

conducted by the PhD student and the publication of the previously mentioned articles, which constitute a critical study of the research on individual components of hybrid ionic capacitors, taking into account various measurement methods and techniques together with the analysis and interpretation of the obtained results, meets all requirements set up in Article 187 of the Act dated July 20, 2018. Law on higher education and science (Journal of Laws of 2023, item 742, as amended. d.), and I recommend to the Council of the Faculty of Chemical Technology, Poznan University of Technology for the admission of Mr Andrés Camilo Parejo-Tovar to the next stages of the doctoral dissertation.

Sincerely,

ık, Profesor PG

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## Application for awarding of doctoral dissertation

The doctoral dissertation of Mr Andrés Camilo Parejo-Tovar is an example of very well planned and performed investigation of symmetric and hybrid metal-ion capacitors. It is addressed not only to one component of electrochemical capacitor but rather to overall electrochemical performance of complete energy storage system. The investigations are focused on eutectic electrolyte, pre-sodiation or pre-lithiation process of negative electrode, and charge/discharge mechanism depending on electrode including charge transport, ion adsorption/desorption, ion trapping in the host material. It evidences that Mr Andrés Camilo Parejo-Tovar is focused on broad aspects of electrochemical phenomena occurring in the studied systems. The obtained results have very high cognitive value in terms of both scientific and application approach. The most crucial achievement is to prove that negative and positive electrode material in hybrid metal-ion capacitor shall not be charge/discharge with the same potential sweep rate. In other words, the process controlled by diffusion taking place at negative electrode is much more complex and current dependent in comparison with the charge storage at positive electrode. It is a challenge for the industry to propose a charger that allows the charge/discharge rate adjustment individually for each electrode. Mr Andrés Camilo Parejo-Tovar is co-author of 5 articles of the total impact factor equal to 69.5 and 840 points, in the rank given by Polish Ministry of Science and Higher Education. In all 4 out of 4 articles PhD student is the first author showing his main role in articles' formation. It proves his scientific maturity and is an exception at this stage of his scientific career.

Thus, I **strongly recommend awarding the doctoral dissertation of Mr Andrés Camilo Parejo-Tovar by the Council of the Chemistry Science Discipline of the Poznan University of Technology**.