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20th August 2026

REVIEW OF THE DOCTORAL THESIS SUBMITTED BY
AMELIA ALEKSANDRA KLIMEK

The doctoral dissertation entitled „*Sustainable electrochemical energy storage systems working in aqueous medium with high-voltage and long-term cyclability"* has been prepared by *mgr inż.* Amelia Aleksandra KLIMEK (M.Sc. Eng.) at *Institute of Chemistry and Technical Electrochemistry, Poznań University of Technology,* Poland as well as at *Institut de Science des Matériaux de Mulhouse, Université de Haute-Alsace*, France under supervision of *prof. dr hab. Elżbieta FRĄCKOWIAK* (Poznań University of Technology) and dr hab. (HDR) Camélia MATEI GHIMBEU (Université de Haute-Alsace) as a supervisor (thesis advisors).
The dissertation has been supported by French Government Scholarship *France Exellence* granted by the French Embassy in Poland, INPUTDoc Project "Toward Internationalization of Poznan University of Technology Doctoral School pursued within the STER Programme, co-financed by Polish National Agency for Academic Exchange (NAWA), as well as by National Science Centre, Poland through *Preludium 23* (granted to Amelia Klimek) and *Opus 16* (granted to Elżbieta Frąckowiak) projects.

The doctoral dissertation of Amelia Aleksandra Klimek is at the boundary of chemical sciences and materials engineering, and it refers to the concepts of preparation of advanced electrode materials and aqueous electrolytes toward substantial improvement of the performance of electrochemical capacitors, including such features as operating potential-output window, energy density and lifespan. Among important issues is advancement in safety through modification of neutral salt electrolytes and adjustment of the carbon electrodes' interfaces (texture/structure). In particular, the author concentrates on important challenges: (*i*) the development of neutral salt electrolytes with hydrogen bond donor additives with the ultimate goal of extending the capacitors' potential output and limiting corrosion; (*ii*) the considering the neutral aqueous electrolytes with redox-active additives toward boosting the potential output and energy density; (*iii*) the preparation of gel electrolyte using the waste-derived biopolymer (lignosulfonate), thus leading to safer and improved performance of electrochemical capacitors; (*iv*) the fabrication and characterization of soft-salt templated carbons through putting to use double alkali metal mixtures for the advancement of the electrode materials' textures/structures; and (*v*) the consideration of porous carbons functionalized by nitrogen-based carbon quantum dots toward the improvement of electrochemical properties of aqueous electrochemical capacitors.

On the whole, the dissertation significantly contributes to the development, preparation, characterization and performance of sustainable and high performance aqueous electrochemical capacitors. On fundamental grounds, the thesis addresses important strategies aiming at mitigation of existing constraints and enhancing the operation of electrochemical capacitors. Furthermore, particular emphasis has centered on ecological impact with respect to the designing of environmentally friendly electrolytes and carbon materials for cutting-edge electrochemical capacitors. The successful approaches have involved modification of neutral aqueous electrolytes, adjusting the interfacial properties and chemical identity of carbon electrode materials. Finally, the observations and conclusions are supported with results of measurements utilizing advanced analytical techniques and structure performance relationships.

The doctoral dissertation is organized in a way that it consists of distinct important parts: *Table of contents, Abstract, Abbreviations,* and *Introduction, as well as* description *of Electrochemical capacitors, Electrolytes and electrode materials used for electrochemical capacitors,* and *Characterization techniques,* together with five chapters referring to publications covering original research results, followed by *General conclusions, Doctoral thesis summary, Scientific achievement,* information about *Copyrights, Declaration of co-authors, and Acknowledgements.* The scientific part of *Introduction* refers to motivation, objective, research hypotheses and emphasizes the importance and novelty of the pursued research. Later, the author provides general literature review with crucial items of information concerning principles of operation of electrochemical capacitors including discussion of mechanisms of energy storage with respect to electrical double layer and pseudocapacitive pathways. When it comes to general overview of *Electrolytes used for electrochemical capacitors*, the author concentrates on their classification and description with special emphasis on aqueous, gel and redox active electrolytes. Having mind importance of *Electrode materials used for electrochemical capacitors*, special attention is paid to characterization of carbons, as well as to the influence of textural and structural effects on their practical performance. The *Characterization techniques* explored in the dissertation are numerous, and they have complimentary character, and they include X-ray diffraction, transmission electron microscopy, Raman spectroscopy, X-ray photoelectron spectroscopy, gas adsorption/desorption, thermal programmed desorption mass spectrometry to quantify active surface areas and to comment about nature of defects and active sites, as well as various electrochemical techniques, such as conventional voltammetric-type current potential responses, galvanostatic charging-discharging and electrochemical impedance spectroscopy. The broad scope of diagnostic experiments have permitted thorough characterization of the systems and correlation of interfacial features of utilized carbons with their performance in electrochemical capacitors.

The actual results are presented in a form of publications preceded by short but precise introductory remarks. Here the author addresses new approaches based on own concepts of the application of aqueous electrolytes improved by hydrogen-bond-donor addition, buffer ($pH < 7$) electrolytes to stabilize operation of the iodide/iodine redox couple, or lignosulfonate (a waste-derived technical lignin) as precursor of gel electrolyte and salt templated carbon, as well as describes the importance of degree of disorder, specific surface area, pore size distribution, and correlates the physicochemical identity of ions with surface functional groups, the feasibility of enhancing the electrochemical capacitors' performance through integrating N-doped carbon dots with porous carbon cloth electrodes. For example, incorporation of urea as the hydrogen-bond-donor additive to lithium sulphate electrolyte has significantly reduced corrosion of stainless-steel current collectors and limited aging processes. The buffer environment with stable pH has facilitated broadening of the operating potential out-put of aqueous iodine-based electrochemical capacitors up to 1.5 V and improved the capacitor's cycle life. The electrochemical capacitor utilizing lignosulfonate-based gel-electrolyte and precursor for carbon electrodes via salt-templating approach with use of acetate salts has yielded a stale operating potential out-put (on the level of 1.6 V), significant lowering of the self-discharge effect, and considerable life-span (170 h of floating). On fundamental grounds, such issues as accessible microporosity (in more disordered carbons) capable of matching the electrolyte solvated ions, in addition to some mesoporosity (favoring fast kinetics) and the presence of certain functional groups has been emphasized and demonstrated to improve the systems' capacitance. On the other hand, highly ordered carbons with high population of graphitic domains have exhibited an extended life span. All these features has to be taken into account when it comes to optimization of the design of novel materials. The originality and importance of the new concept based on impregnation of porous carbon cloth N-carbon quantum dots, and the successful application (improvement of capacity and possibly of lifespan) in the aqueous (lithium sulfate electrolyte) electrochemical capacitors should be emphasized.

The research results described in the Amelia Klimek's dissertation seem to significantly contribute to the state of the art of the science and technology of electrochemical capacitors. On the whole, Amelia Klimek appears as coauthor of seven publications. These works have been published in very good journals of international circulation (e.g., *Advanced Science, Green Chemistry, Materials Today, Electrochimica Acta, Chemical Engineering Journal*). Going to the substantive evaluation of the dissertation, I would like to mention the importance of observations and achievements described therein. The main accomplishments concern development of strategies, synthesis, characterization and possible applications of sustainable and high-performance aqueous electrochemical capacitors. Among other important issues is detailed characterization of developed systems using various analytical techniques. Furthermore, the results presented in the dissertation should contribute to the progress of safe, durable, and eco-friendly sustainable energy-storage technologies.

Upon reading the doctoral dissertation, my general impression is that the work is very well-written: electrochemical capacitors, electrolytes and electrode carbon materials and their properties are broadly addressed, as well as the results obtained are carefully described and interpreted. Both the results and conclusions are convincing.

I have got a few questions or comments that could be easily answered or explained during the doctoral defense.

(1) While discussing pseudocapacitance in Chapter 2.2.2 and presenting schemes of three different types of pseudocapacitane, it should be mentioned that not all faradaic reactions lead to capacitive behavior. It would be valuable to mention the need of examination of charging/discharging curves. Certainly, not in all cases mentioned in Figure 4, electrochemical characteristics (e.g., cyclic voltammograms) would have rectangular shapes typical of capacitive systems. In such case, instead of the capacitance (in F/g), capacity (in C/g) should be considered. True pseudocapacitive electrode materials display electrochemical behavior typical of that observed for a capacitive carbon electrode (i.e. rectangular CVs and linear charge/discharge characteristics). The difference between these two classes of materials has been explained in the following articles: P. Simon et al., Perspective: Where do batteries end and supercapacitors begin? Science, 343, 1210-1211, 2014 and T. Brousse et al., To Be or Not To Be Pseudocapacitive? Journal of The Electrochemical Society, 162 (5) A5185-A5189, 2015.

(2) The statement about the “low hydration degree of Li^+ cations” (in the context of sorption of water on the positive carbon electrode on page 46, second paragraph) requires clarification. If we refer to the basic inorganic chemistry of alkali metal cations, the hydration sphere of lithium is relatively the largest.

(3) The choice of urea as the hydrogen bond donor additive, and its ability to inhibit the corrosion of stainless steel and to enhance the lifespan of electrochemical capacitor seems to be of primary practical importance. But urea is also known as a potential fuel that undergoes readily oxidation (in low-temperature fuel cells) at fairly low potentials. Is there any danger of instability of urea when it comes to application in electrochemical capacitors?

In conclusion, I would like to express my high appreciation to the efforts of the author, emphasize high scientific value of the obtained results and evaluate very positively the doctoral dissertation. Furthermore, I would like to state that the dissertation meets the formal and customary criteria and expectations for doctoral works in the area of exact and natural sciences and chemistry discipline. I am in favor of the Ph.D. defense of Ms. Amelia Klimek in the view of obtaining the Ph.D. degree from the Poznań University of Technology, Poland and University of Haute-Alsace, Mulhouse, France. I am convinced that Amelia Klimek should be readily admitted to the public doctoral defense that will be held at Poznan University of Technology.

Having in mind the importance of pursued research, the quality, the high scientific value and the application potential of results obtained (presented in six valuable publications onto which the dissertation is based), I would like to recommend awarding the dissertation and conferring the Ph.D. degree to Amelia Klimek with distinction (honors).

Signed by / Podpisano przez:

Paweł Józef Kulesza
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Date / Data: 2026-08-21 11:49

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