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Referee Report on Doctoral Dissertation
"Performance of symmetric and hybrid electrochemical capacitors"
"Działanie symetrycznych i hybrydowych kondensatorów elektrochemicznych"

by **Andrés Camilo Parejo-Tovar**
supervised by Prof. Francois Beguin and co-supervised by Paula Ratajczak Ph. D

Transformation of energy supplies from fossil fuels to renewable sources such as wind, sun or water is currently emerging issue both in terms of the shortage of fossil fuels as well as need for environmental protection. The renewable energy is often considered as a dissipative energy and therefore requires to be efficiently store and use when needed. To achieve these goals novel sustainable and efficient energy storage and conversion devices need to be designed. To this end batteries, fuel cells and super capacitors are considered each having different energy-power characteristic, sometimes contradictory, sometimes supplementary to each other. Practically none of these devices satisfies both high energy and high power densities and therefore hybrid systems comprising combination of two or even three systems is often considered as the most promising design. Currently the idea of use hybrid devices comprising supercapacitors characterized by high power density and batteries with high energy densities is widely explored. The technologically advancing approach is the construction of device baring supercaps and battery functionalities. This idea has been extensively studied in the electrochemical team from the Poznań University of Technology headed by Profs. Frąckowiak, Beguin and Fic which is no doubt among world leading groups on supercaps technology and currently extended studies on new generation of devices called metal-ion capacitors.

These relatively new systems still requires novel design to improve their long time performance and sustainability. One of the vital issues is the use of the pres-insertion techniques to metalate negative electrode. To this end various procedures including auxiliary metallic electrodes, use of composite cathode part of which is so called " sacrificial materials", use of concentrated electrolytes or electrolytes with redox type additives have been previously studied.

The main goal of the Thesis was to addressed vital challenges in advancing the performance of symmetric and hybrid electrochemical capacitors which should create a new insight in designing novel energy storage systems. The Thesis is based on four papers published in renowned scientific journals such *as Energy Storage Materials, Journal of Power Sources* and *Electrochemistry Letters* in which problems related to use highly concentrated Water-in-Salt (WIS) electrolytes for Electrical Double Layer Capacitors (EDLCs), the innovative use of sacrificial materials for pre-metalation in Sodium-Ion Capacitors (SICs), and extensive studies on understanding of ion dynamics within electrodes during operation have been discussed. Through these studies, the research highlights the role of electrolyte composition, electrode textural and structural properties as well as ion population behavior in determining the overall performance and lifespan of electrochemical capacitors (ECs). The role of the candidate in writing all these works is well documented and described in the separate section of the Thesis.

The Thesis start with the literature review addressing issues related to various energy storage and conversion devices. In the first subchapter electrical double layer capacitors EDLC are described with the special emphasize on discussion on type of electrode materials used. To this end carbon based electrodes are widely presented. This is followed by the presentation on various type of electrolytes with more deeper presentation of concentrated water in salt system (WISE) . Finally carbon based metal-ion capacitors are discussed. These section ends with the discussion of pre-metalation techniques used to enhance performance of metal-ion capacitors in which doctorate candidate defines the scope of his own works comprising PhD dissertation.

There is no separate section describing experimental techniques used in the Thesis. I presume that author assumes that the referee can find the information in the following papers constituting the body of the research and discussion part of the Thesis. This is essentially true but for the reader not being a specialist in the field separate experimental section will be helpful and made it easier to follow. In the PhD Thesis variety of electrochemical techniques like galvanostatic cycling with potential limitation (GPLC), potentiostatic

electrochemical impedance spectroscopy (PEIS), operando electrochemical dillatometry are used. These studies are coupled with thermo gravimetric techniques such as differential scanning calorimetry (DSC) or thermal gravimetry TG and also density and viscosity measurements to characterize electrolytes.

The main part of the Thesis is the presentation of own results in three separate chapters ending with the conclusions and future plans in the very last chapter of the Thesis. Each chapter starts with the short summary of papers comprising this part of the Thesis followed by copies of papers and manuscript to be sent for publication. The first chapter describes properties on EDLC in which concentrated $NaClO_4$-water eutectic electrolyte is used. This is followed the studies on sodium-ion capacitors in which pre-metalation is realized by the used of sacrificial Na_3N layer which after electrochemical decomposition (oxidation) generates artificial sodium layer on the negative electrode. In the referee opinion this is the crucial part of the Thesis and novel approach considering the fact that so far mostly lithium-ion capacitors were studied. Since the abundance of sodium in the Earth crust is much higher than lithium the designing of novel sodium based metal-ion capacitors and its good long life cycling abilities can have considerable effect not only on basic research but also for industrial application. Following two chapter deals with the characterization of electrode performance in hybrid supercapacitors.

I consider the Thesis under review as a very important research on novel type of hybrid energy conversion and storage devices. Below I would like to address few points as a possible tasks for future studies in the group of Prof. Beguin being the extension of the presented results.

For the long time performance of the battery one of the crucial issue is to get a stable solid electrolyte interface SEI at the negative electrode. The focus is to obtain fully reduced conductive SEI. This can be achieved in various ways one of which is properly controlled decomposition of electrolyte components. Do the authors analyze the SEI composition in the studied hybrid supercaps? Electrochemical impedance spectroscopy EIS will be no doubt useful to analyze how the properties of SEI change during long time cycling? Why not to use the simple approach of designing artificial SEI layer directly on negative electrode using Na_3N? The reference 165 is very old original study of SEI by Prof. Emmanuel Peled back in 1979. Many strategies of SEI design change since this publication and to learn about them I would like to draw authors attention to the review paper by Doron Aurbach and co-workers *Progress in Materials Science 147 (2025) 101349*.

When applying WISE type electrolytes what is the water and anion coordination around sodium cations? Do authors analyze whether free water molecules still exists in the system and if so what will be their effect on long time stability of the studied system including safety aspects?

Generally I strongly recommend to use spectroscopic techniques FT-IR, FT-Raman to study structure and ion-ion ion solvents interactions in the electrolytes.

Despite the above comments or rather suggestions for future studies I am of the opinion that the Thesis under review is of good quality and I recommend allowing Mr Parejo - Tovar to publicly defend it. It should also be mentioned that the Thesis presented satisfies all requirements mentioned in Ustawa o Stopniach i Tytule Naukowym oraz o Stopniach i Tytule w Zakresie Sztuki z dnia 20 lipca 2018 r. Prawo o szkolnictwie wyższym i nauce (Dz.U. z 2021 r. poz. 478) (tekst ujednolicony) related to procedure leading to award of the PhD degree. Moreover considering overall high quality of papers comprising the Thesis and their publication in well respected scientific journals I strongly support the distinction of the reviewed Thesis. Particularly design and studies of novel sodium-ion supercapacitors in my opinion can be considered as the very important step forward both for basic and technological aspects.