Warszawa 2024.11.29

Prof. dr hab. inż. Władysław Wieczorek

Wydział Chemiczny

Politechniki Warszawskiej

Ul. Noakowskiego 3

00-664 Warszawa

Referee Report on Doctoral Dissertation „One -step assembly of metal-ion capacitors using redox-active electrolytes" by Adam Maćkowiak MSc supervised by Professor Krzysztof Fic

There is no doubt that the climate changes resulted from the use of fossil fuels are currently one of the vital issues faced by us. The urgent action leading to transformation of energy supplies and common use of renewable energy sources is needed and should be realized without further delay. In our climate zone sun, water and wind energy are under consideration as alternative sustainable energy resources which should substitute currently used coal, gas or oil supplies not only because of their predicted shortage but also due to negative environmental effect. However wind does not blow, sun does not shine on demand and therefore there is a need for highly efficient devices capable to both convert and stored produced energy in such way. One of obvious and efficient way to deal with these issues is the use of electrochemical energy conversion and storage systems. To this end batteries, fuel cells and super capacitors are considered each having different energy-power characteristic, sometimes contradictory, sometimes supplementary to each other. Fuel cells are characterized by high energy and low power densities whereas supercapacitors exhibit high power and relatively low energy densities with batteries power energy characteristic in between. Therefore hybrid systems comprising combination of two or even three systems is often considered as the most promising design. The next step is to combine power energy characteristic of two systems by putting them in one hybrid device. Such an idea is behind design and development of metal-ion capacitors which are combination of supercaps and

batteries in one system. This novel approach however still requires intensive studies to improve performance and assure long time stable cycling. Studies on metal-ion capacitors have been successfully undertaken in the lab headed by Profs. Frąckowiak, Bequin and Fic. One of the ideas is to use redox-active electrolytes as a component of the system under study. With consideration of all above aspects the choice of the topic of doctoral dissertation of Adam Maćkowiak seems to put the doctoral candidate in the fore front of currently ongoing research.

The main goal of the Thesis is to optimize the assembly of metal-ion capacitors using redox -active electrolytes as charge balancer which can facilitate the insertion of metal ions from the electrolyte into anode structure. The novelty of the approaches is based on the observation that until recently the design of new electrolytes for supercapacitors draw considerably less attention compared to design of novel electrode components. The group of Professor Fic is no doubt the leader in studies on role of electrolytes in enhancement of energy density of supercapacitors. The present Thesis can be considered as a very important step in these studies especially with respect to design of efficient metal-ion capacitors novel compared to the described in available literature.

The Thesis are based on 5 papers published or prepared for publication in renown international scientific journals such as Energy Storage Materials, Eleectrochimica Acta and Journal of Power Sources. The data not directly included in the Thesis were published in Frontiers in Energy Research, ChemElectrochem and Electrochemistry. The role of the candidate in writing all these works is well documented and described in the separate section of the Thesis.

In the section preceding presentation of the own results PhD candidate present literature review of energy storage and conversion systems. The short introduction to the area is followed by the chapters describing electrical double layer capacitors and lithium - ion batteries. These sections are followed by the separate subchapter devoted to the description of the metal-ion capacitors. The important part of this section is the discussion of the pres-insertion techniques used to enhance performance of metal-ion (particularly lithium-ion capacitors). Author present discussion on procedures used to this end including auxiliary metallic electrodes, use of composite cathode part of which is so called " sacrificial materials" and use of concentrated electrolytes. Author critically addressed positives and drawbacks of each methodology used concluding that still new approaches are needed to further improve performance of metal-ion (lithium-ion) capacitors. This section concludes with the presentation of the aim of doctoral project.

Finally author shortly presents all major experimental techniques used in his doctoral project. These methodology comprise variety of electrochemical techniques such as cyclic voltammetry (CV), galvanostatic cycling with potential limitation (GPLC), potentiostatic electrochemical impedance spectroscopy (PEIS), step-potential electrochemical spectroscopy (SPECS), galvanostatic internittent titration technique (GITT) coupled with spectroscopic techniques like Fourier Transformation Infra Red (FT-IR), Raman Microscopy, X-ray diffractometry, Gas Chromatography with Mass Spectroscopy (GC-MS) and transmition electron microscopy (TEM) used for surface characterization. Analyzing data included in publication I have got an impression that PhD candidate is capable of use of all these techniques with deep analysis of the complementary results.

The main body 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 includes studies on the use of redox electrolytes with addition of thiocyanate salts for one step pre-metalation procedure. The second introduce SPECS technique as a comprehensive tool for studying the intercalation process of the graphite anode. In the third chapter author introduce acetate salts as an alternatives to previously studied thiocyanates as redox active part of electrolytes.

I have no doubt that the approach presented is a novelty absolutely in the fore front of the current work on lithium-ion capacitors. Moreover it is worth to mention that the presented results are of significance not only for basic but also for industrial type research. In my opinion the lithium-ion capacitors design according to the presented approach can be used in variety of application including for instance hybrid train engines. The Dissertation is well written and I hardly found any editorial mistakes. Below I would like to draw the attention of the group of Professor Krzysztof Fic to the few ideas which might have been studied or can be used to foster the future experiments.

1. The idea of dual electrolytes containing two salts playing different roles in the system is not new and has been widely explored in the field of lithium-ion batteries. Usually the addition of the second salt changes the properties of the electrolyte (most frequently causing an increase in viscosity and decrease in conductivity) compared to the electrolyte containing only the main component. It is also seen in the Thesis (see Figure S19 at the page 97). Did the author study this problem more deeply in the case of $LiPF_6$ - LiSCN system? What about lithium co-ordination sphere? Is the concentration of LiSCN used optimized? For

some systems, previously studied in the case of lithium-ion batteries the conductivity decrease was lower and on top the lithium ion transference number increase which is beneficial for the long time cycling of the device. Authors please use FT-Ram and or FT-IR directly to study anion environment in your electrolytes in the future.

2. 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 "holy grail" is to obtain fully reduced conductive SEI. This can be achieved in various ways one of which is properly controlled decomposition of electrolyte components. The analysis of LISCN decomposition included in the Thesis (pages 118-121) does not suggest that the SEI formed has good properties. Decomposition of acetates can lead to carbonates which are also not the best SEI formers. What about the use of other salts combinations leading to better SEI? Do the authors consider to use any type of SEI forming additives? If yes which? What about the use of artificial SEI layers directly on anode not as " sacrificial materials"?

3. I strongly suggest to analyze the SEI formed for all studied electrolyte combinations? As a starting point to this I would like to draw attention to the review paper by Doron Aurbach and co-workers *Progress in Materials Science 147 (2025) 101349.*

At the end I would like to conclude that work performed within this Thesis shows high innovation potential and it will have high impact on the research society. Overall, the work presented is of good quality and I recommend allowing Mr Adam Maćkowiak 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 due to high quality of the Thesis and design and development of novel class of electrolytes capable to contribute to raise in the energy density of metal-ion capacitors I strongly support the distinction of the reviewed Thesis.