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Referee Report on Doctoral Dissertation „Research on the electrode charging and carbon degradation in electrochemical capacitors" written by Sylwia Ślesińska, supervised by Professor Krzysztof Fic and co-supervised by Dr. Jakub Menzel

Conversion of renewable energy and its storage is currently a vital issue for society as a sustainable global world depends on renewable energy sources, instead of fossil fuels. Despite development of novel technologies such as lithium-ion batteries, fuel cells and supercapacitors, there is still a need to search for new components (electrodes and electrolytes) assuring higher capacities, longer and more efficient cyclability, better safety and wider electrochemical stability range together with extended lifetime of the device. In view of shortages of raw materials vital for construction of new generations of energy storage and conversion devices the urgent matter is the design of new electrodes and electrolytes based on easily accessible materials of low cost and ease manufacturing procedures.

Another approach is to better understand phenomena occurring in up-to-date technologies which helps us to optimize their performance and benefit when designing novel systems.

Among the currently explored devices, supercapacitors are characterized by the highest power density and extending cycling stability compared to batteries or fuel cells. However, low energy density is no doubt the drawback of these systems. To solve it hybrid systems comprising a combination of supercapacitors and batteries has been developed and is considered as the most promising design. The next step is to combine supercapacitors 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. To benefit from these new arrangement extensive studies of ageing mechanisms in existing electrodes used in supercapacitors is a need. Coupling these observations with fundamental studies on the effect of cycling conditions, electrolyte type and electrode electrolyte characteristics should be of great importance for the future development of supercapacitors as well as dual systems mentioned above.

The referee has no doubts that the reviewed Thesis combines all the aspects already pointed out in this report. The Thesis comprise of three chapters first of which is the introduction to the field and second as well as the third is the presentation of own studied mainly based on three papers published in *ACS Applied Materials and Interfaces*, *Advanced Science* and *ACS Applied Energy Materials*. Additionally, in chapter 3 unpublished paper is also included.

The main goal of the Thesis is to optimize various aspects of the long-term performance of supercapacitors neglected or not deeply studies so far (Papers 1-2) in the chapter 2 together with the studies of ageing phenomena (paper 3 and article 1) in chapter 3. The Thesis were supervised by Prof. Krzysztof Fic and co-supervised by Dr. Jakub Menzel.

In the first chapter, candidate presents 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 capacitors. These sections are followed by the separate subchapter devoted to ageing studies of supercapacitors. Authors deeply discussed the state of art in ageing studies of lithium-ion batteries, supercapacitors and metal-ion supercapacitors. The importance of use of *in-situ* and *operando* techniques for the extensive characterization of ageing phenomena is highlighted.

Finally author shortly presents all major experimental techniques used in his doctoral project. The methodology comprises variety of electrochemical techniques such as cyclic voltammetry (CV), galvanostatic charge- discharge, current interrupt technique, step-potential electrochemical spectroscopy (SPECS), staircase potentio electrochemical impedance spectroscopy (SPEIS), electrochemical quartz microbalance (EQCM) coupled with *operando* and *in-situ* studies using Raman Spectroscopy, and Gas Chromatography with Mass Spectroscopy (GC-MS). Data analysis is included in publication I have got an impression that PhD candidate is capable of use of all these techniques with deep examination 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. In the second chapter paper 1 deals with the studies of local pH changes at carbon electrode surface for supercapacitors in which electrolyte is based on neutral sulfate aqueous solutions. The author identifies that pH changes at electrode surface are dynamic, strongly dependent on the working potential and differ at each electrode. The changes start at relatively low potential and are coupled with electrolyte decomposition and formation of side products. These changes affect the overall performance of supercapacitors and should be monitored in order to enhance the cyclability of supercapacitors. The second paper which deals with point of zero charge determination using EQCM technique is in my opinion the most important discovery of the Theis. The author highlights the fact that point zero charge should not be treated at the single value but rather as the potential range thus introducing new description zero charge range RZC. The use of EQCM has been proved to be a very efficient way of RZC determination.

Chapter 3 starts with the description of ageing phenomena occurring on porous electrode surface in contact with organic electrolyte. The observed trends are generally the same as described for lithium-ion batteries and depends on the voltage used. The higher the voltage applied the faster the degradation of the electrolyte. This presentation is lacking from the studies in which SEI forming agents are added to the electrolyte or artificially SEI layers are formed on the electrode surface. It will be interesting to study the effect of both above approaches on the kinetics of degradation phenomena. In the second part of the chapter the effect of oxygen surface functionalities on ageing of electrodes are described. The studies in the function of intentional formation or (and) removal of oxygen containing groups on behavior of electrodes are studied. It has been found that removal of oxygen functionalities does not promote long time operation of carbon - based electrodes. In contrast to this incorporation of surface acidic functionalities promote the formation of surface polymer protective layers thus resulting in extension of lifetime of the studied systems.

The presented Thesis deals with important issues for the future development of supercapacitors as well as hybrid systems. The papers included in the Thesis have been published in renown international scientific journals and the PhD candidate is the first author of in the two of them. Overall, the Dissertation is well written, and I hardly found any editorial mistakes. There is one major remark which sort of bothers me and I feel a need to share it with the candidate and the doctoral committee. The presented Thesis more resembles self-review for habilitation than PhD dissertation. This is because it consists of four papers each dealing with the different issues to be solved. Although the scope of the Thesis is defined but it is rather broad. There is no clear identification which is the major problem author wishes to solve in the

frame of the Theis. It will be helpful if the body text of the Thesis PhD candidate would include a chapter with the clear view of the problem and way of its solution. Since it is not as straightforward, I strongly encourage the candidate to include one-two slides which can be presented during the defense and bring up front the main issue of the Thesis and way of its solution.

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 Mrs Sylwia Ślesińska to publicly defend it. It should also be mentioned that the Thesis presented satisfies all requirements included in Ustawy z dnia 20 lipca 2018 r. Prawo o szkolnictwie wyższym i nauce ((Dz.U.2024 r., poz. 1571)). related to procedure leading to award of the PhD degree in the field of natural sciences, discipline chemical sciences.

Moreover, due to high quality of the Thesis, publication of three papers in the renown international scientific journal of high impact factor, which give a new insight on both processes occurring at electrodes as well as ageing of electrode materials I strongly support the distinction of the reviewed Thesis. Particularly the paper describing investigation on proper assignment of point of zero charge is of great importance and interest of the scientific community working in the field of energy storage and conversion devices.