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Referee Report on Doctoral Dissertation „Development of electrochemical capacitors based on protic ionic liquids" by Barbara Górska M. Sc supervised by Professor Francois Beguin

Problems related to proper conversion and storage of energy gained from removable energy sources are among the most important issues which are currently faced by humans. This is related to limited resources of fossil fuels combined with the growing input of energy get from sun, wind or water actions. 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. To this end batteries, fuel cells and super capacitors are considered each having different energy-power characteristic, sometimes contradictory, sometimes supplementary to each other. In view of this short introduction doctoral dissertation of Miss Barbara Górska meets expectation of today's society and is no doubt in the forefront of both basic and applied research in the field.

Recently growing interest in electrochemical capacitors (ECs) as high-power charge-storage devices that could possibly act as alternative or complementary energy storage systems to conventional secondary batteries has been observed. In comparison to batteries, ECs are typically characterized by lower specific energy but much higher specific power, in addition to longer cycle life.

Among important issues, there is a need to improve the EC's energy density, which is related to capacitance according to the Equation below,

$$E = {}^{1}/_{2}\, CV^2$$

Where C stands for capacitance (in F), $V$is the cell voltage (in V), and E refers to energy (in J). Details of capacitors characteristic and performance were carefully described by the Ph D candidate in section 2.1 of the dissertation. According to the description a reasonable strategy to improve the energy density is to develop and utilize highly capacitive materials. This strategy is well described and discussed in section 2.2. Among different electrode materials utilized in supercaps special emphasize was put on carbon based electrode materials of potential utility for Electrochemical Double Layer Capacitors (EDLCs), such as template carbons, carbon fabrics, fibers, nanotubes, onions, nanohorns, xerogels, carbon black and graphene. Additionally Miss Górska briefly describes other highly effective pseudo-capacitive materials, such as metal oxides (i.e. MnO_2 and RuO_2) or conducting polymers (i.e. polyaniline (PANI), polypyrrole (PPy)) that are characterized by fast electron transfers (between highly populated redox sites) responsible for their reversible charging/discharging processes .

Another option to increase the energy density is to enlarge the cell voltage that is often limited by the electrolyte decomposition at high potentials. This issue is a matter of section 2.3 of the dissertation. Application of aqueous electrolytes limits the voltage to 1.23 V range with the temperature stability from 0 to 100°C. Therefore, most of commercial super capacitors utilize non-aqueous organic electrolytes and, consequently, they can reach cell voltage as high as 3 V, and they can operate at temperatures ranging roughly from -30 °C to 60 °C. Little if not nothing is mentioned on application of solid, polymer or gel electrolytes in supercars which eventually can be comment by the candidate during the PhD defense. Generally these classes of electrolytes suffer from lower ionic conductivities compared to liquid ones but often their electrochemical or temperature stabilities are superior to liquid counter partners.

Based upon author's description as well as literature data there is a need to search for new electrolytes with extended electrochemical and temperature stability windows. These goals seem to be fulfilled by electrolytes based on ionic liquids. On top of former properties ionic liquids are also less flammable than conventional organic electrolytes which results in reduction of safety problems often related to conventional organic liquid based electrolytes. Ionic liquid based electrolytes and their application in super caps is well described and discussed by the authors in section 2.4. Most of the so far applied electrolytes are based on aprotic, often alkali metal, systems. In sections 2.4.5 and 2.4.6 Miss Górska draws our attention to possibility of use of new class of protic ionic liquids as electrolytes in super caps. This issue is the main line of her dissertation and is extensively explored and described in chapters from 2 to 4. I would like to emphasize that Miss Górska not only participates in the

synthesis of ionic liquids used but also characterizes them using wide variety of complementary physico-chemical techniques. On top of this candidate also shows some experience in the application of molecular modeling to study the structure of the synthesized systems. Details of the synthesis and methodology used are well described in appendices to the Thesis. In the body of the dissertation following problems are drawn and solved:

- Effect of type of binder on the performance of proton ionic liquid based electrochemical super caps
- Effect of traces of water on properties of ionic liquids and ions electro sorption in carbon porosity
- Development of novel family self prepared ionic liquids
- Application of protic ionic liquids with N-chloroalkyl functionalized cations as electrolytes for electrochemical super caps

The Dissertation is well written and I had difficulty even to find editorial mistakes. Not being a fun of raising detailed issues as a main content of the referee report I would like rather to concentrate on generalities. As not being an expert on super caps some of issues raised are rather view of battery guy but my point is that sometimes different perspective might be helpful for authors in their future work being an extension of current work.

First of all up to my best knowledge number of papers related to optimization of electrode materials in super caps greatly exceeds those related to electrolytes optimization. Further, even if number of combinations related to possible configuration of ionic liquids is practically unlimited they are rather rarely considered, so far, as candidates for electrolytes applied in electrochemical super capacitors. To continue, even if they are consider the system comprise aprotic ionic liquids rather than protic ones. All of these considerations clearly show that the approach taken in the refereed dissertation is unique one and deserves proper recognition. Clarity of the experiments, content of the Thesis, very good combination of the methodology applied is typical of all works performed in the group of Profs. Bequin and Frąckowiak of which I am aware and I am glad that Miss Górska took an advantage of possibility of co-operation with these work class experts in the field.

Just a few comments for future help of the author. Style of the description is a bit poetic especially in the literature section but it improves when it comes to description of own results. As I know from my own experience improvement in this matter usually comes with age. In the chapter 2 I found that from the described data the more hydrophobic is the binder the better is the electrochemical performance of capacitors. Is this something which misleads

me? Might be that my assumption is based on rather limited number of data. Nevertheless if this fact has something practical to do it might be a matter of future studies.

The effect of water is of particular interest for me. I do think that proton conduction mechanism especially in the presence of water requires further studies. In the view of NMR studies performed for other energy storage and conversion system I am not that certain that the H_3O^+ cation is the main carrier of proton for all water concentrations. Quite frequently NMR studies show that the main one is $H_5O_2^+$. Moreover recent results published for concentrated aqueous electrolytes in the battery field show quite new interested conceptual approach. Application of aqueous electrolytes solves very important troubles afflicting present technologies, like: danger of ignition, toxicity, environmental hazards and difficult recycling. A proof of concept has been tested and confirmed by K. Xu in US Army Laboratory using well-known commercially available lithium salt – lithium bis (trifluoromethylsulfo) imide LiTFSI. Maybe it will useful to explore this concept also in the field of super caps? Especially that the anion used e.g. TFSI is the one applied in the dissertation.

However I would personally consider changing TFSI anion to more electrochemically stable one in future studies.

At the end I would like to conclude 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 high quality and it deserves the highest ranking among PhD thesis. From the above considerations, it is my opinion that this work is perfectly appropriate to be defended to obtain a Ph.D. degree. Definitely this work is between 10% thesis that I have examined and therefore I suggest that to honour it with Summa Cum Laude recognition. To make my suggestion even stronger I would like to emphasized variety of scientific activities in which the candidate was involved. Miss Górska is a co- author of three scientific papers 11 patents, 10 patent applications. She also presented her data in 6 oral conference presentations and 11 posters. I particularly would like to highlight the fact that Miss Górska was involved in the scientific project and participated in two monthly short term scientific internships which is quite unusual for the Ph D candidate.