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Referee Report on Doctoral Dissertation „Redox activity of pseudohalides in electrochemical capacitor application” by Paulina Bujewska supervised by Professor Krzysztof Fic

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. 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. 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. To extend this idea on one site fuel cells are characterized by high energy and low power densities whereas supercaps exhibit high power and relatively low energy densities. Despite considerable development of energy storage technology in the last 20-30 years still there is a need to search for new components (electrodes and electrolytes) assuring extended working temperature range, better safety, and wider electrochemical stability range together with extended lifetime of the device. With respect to supercapacitors there is a need to enhance the energy density of these devices keeping high power density. With consideration of all above aspects the choice of the topic of doctoral dissertation of Miss Paulina Bujewska seems to put the doctoral candidate in the fore front of currently ongoing research.

The main goal of the Thesis is to design and developed new generation of electrolytes based on systems utilizing pseudohalides as a redox shuttles extending energy density of supercapacitors. Electrolytes draw considerably less attention in the community working on novel energy storage and conversion devices compared to electrodes. Moreover there is a limited number of studies on role of electrolytes in enhancement of energy density of supercapacitors. Therefore the scope of the Thesis should be considered as a very important and novel compared to the available literature data.

As was already mentioned in comparison to batteries, supercapacitors are typically characterized by lower specific energy but much higher specific power, in addition to longer cycle life. The energy density of supercaps , 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 of the dissertation.

An option to increase the energy density is to enlarge the cell voltage that is often limited by the electrolyte decomposition at high potentials. 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. Therefore 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. However the temperature operating range of single ionic liquids is often limited by their tendency to crystallization or too high glass transition temperature which results in considerable increase of the solvent viscosity reflecting in the decrease in conductivity. It should also be emphasized that 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. The idea which is often used to enhance supercapacitors specific energy density is application of redox shuttles. The choice of the redox couple is related to the cell design mainly electrolyte pH, electrode material, current collector type and most important potential application of the system under study. The most often used ones are I^2/I^- couples.

In the present Thesis the last concept was widely explored with the application of pseudohalide redox couple based on thiocyanate and selenocyanate anions. Both systems are studied in aqueous electrolytes and in ionic liquid based electrolytes. The Thesis is based on 5 papers published in renowned international scientific journals such as Phys. Chem. Chem. Phys., Journal of Power Sources Advances, Synthetic Metals, Electrochimica Acta. On top of this the first section of the thesis comprises literature data describing electrochemical supercapacitors and specifically components used to their fabrication as electrodes and electrolyte materials. The part of this section is related to energy density enhancement procedures finishing with redox couple concept deeply explored by the author in the papers associated with the Thesis. It has to be emphasized that the role of each author of the paper contributing to the Thesis is well described. The input of Miss Paulina Bujewska ranges from 15 to 60 % highlighting her leading role at least in 3 out of 5 papers presented.

The Thesis is well organized and all experiments are properly designed. Most important it has been proved that pseudohalide anions can be successfully used to increase specific energy density in supercapacitors both when applied in aqueous solution or in ionic liquids. In particular it has been demonstrated that maximum voltage has been extended to 1.4 V in aqueous media and 1.6 V in ionic liquids with an enhancement in specific energy to values between 12 and 16 Wh/kg. The author used a concept of composite system adding gold nanoparticles which also result in considerable improvement in specific energy of supercaps studied. The system was capable to operate from 10000 to 100000 cycles depending on electrolyte composition with better cyclability achieved for thiocyanate systems compared to selenocyanate ones.

The Dissertation is well written and in the first section I hardly found any editorial mistakes. Below please find a few comments which might be helpful for the future works of the group of Professor Krzysztof Fic.

First of all up to my best knowledge number of papers related to optimization of electrode materials in supercaps greatly exceeds those related to electrolyte optimization. Therefore I consider a choice of the topic of this dissertation both highly challenging and novel. My first question to the author and supervisor is if they consider to try nonaqueous media as solvents in their electrolytes. If the answer is yes how the results obtained compare to the presented in the Thesis. The use of organic media should result in further extension of the voltage range therefore in further enhancement of energy density. The next step I would like to propose is to try to use gel type electrolyte comprising the system studied in the Thesis but

incorporated in polymeric matrix. The simplest system which should work for both aqueous, nonaqueous and ionic liquid systems should be poly (methyl methacrylate).

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 Miss Paulina Bujewska 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 14.03.2003 Dz. U. Nr 65 Poz. 595 z późniejszymi zmianami (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 hybrid supercapacitors under study hereby I strongly support the distinction of the reviewed Thesis.

