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Referee Report on Doctoral Dissertation „Design of ionic liquid based electrical double layer capacitors operating very effectively at low temperature" by Emmanuel Pamete Yambou supervised by Professor Francois Beguin

Conversion of renewable energy and its storage is currently a vital issue for the society as a sustainable global world depends on renewable energy sources, instead of fossil fuels. 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. 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 development of energy storage technology 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. Assuming all above mentioned circumstances the doctoral dissertation of Mister Emmanuel Pamete Yambou is absolutely in line with the forefront research in the field of electrochemical energy conversion and storage.

The main goal of the Thesis is to design and developed new generation of Electrical Double Layer supercapacitors (EDLC) utilizing electrolytes based on binary or ternary mixtures of ionic liquids working efficiently at subambient temperatures down to -40°C. To reach this goals additionally self designed carbon based electrode materials are studied. In the

final chapter of the Thesis author presents preliminary results on application of gel type electrolytes in which liquid part consist of previously optimized ionic liquids.

Since the electrolyte part of energy storage devices draws considerably less attention in the community compared to electrodes studies the scope and scientific content of this Thesis should be beneficial for future development of subambient temperature EDLC.

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 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. This issue is a matter of section 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. 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. However the temperature operating range of single ionic liquids is often limited by their tendency to crystallization or two high glass transition temperature which results in considerable increase of the solvent viscosity reflecting in the decrease in conductivity. To extend operating temperature range Author proposed to use binary and ternary mixtures of ionic liquids which do not show any thermal transition down to about -90°C. 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. Although referee doubts about the green nature of ionic liquids due to use often harmful chemicals during their

synthesis. In the presented work ionic liquids base on immidazolium cations with variety of anions such as $TFSI^-$, FSI^-, $BF4^-$ have been investigated.

The experimental part of the dissertation composed of four chapters and is based on three scientific papers of which the candidate is co-author. The role of each co- author is carefully described in the supplementary part of the Thesis. In the last chapter preliminary results on the use of gel type electrolytes in subambient temperature supercaps are described. These gel electrolytes comprised commercially available PVdF matrix soaked with previously optimized ionic liquid which provides pathways for ionic transport.

The Thesis is well organized and all experiments are properly design and the results of former research are used as a background in forthcoming experiments. In the first experimental chapter the structure of binary ionic liquid mixture is optimized in the view of their performance in subambient temperature supercaps. The set of experiments starts from thermal investigation proving amorphous nature of electrolytes in the extended subambient temperature range, sometimes down to -90°C. This is followed by electrochemical characterization of the electrolyte itself ending with the presentation of characteristic of the EDLC performance. Conductivity and electrochemical stability window are properties of electrolytes to which the Candidate draws major attention. Similar experimental design is used in two other papers first of which compares properties of self developed carbon based electrode materials with commercially available ones when applied in supercaps utilizing previously optimized electrolyte. The results presented proves that when slef designed electrodes are used the EDLC performance is superior to that obtained when commercially available electrodes are used. In the third paper authors instead of binary ionic liquids decided to use the ternary mixture. This is a quite unique and novel approach which results in considerable improvement in the performance of electrolyte when used in supercapacitors. In the final chapter the Candidate decided to use gel type electrolytes with PVdF matrix and ionic liquid incorporated into it. Such procedure results in improvement of the electrolyte conductivity at the lowest temperature range which in the referee opinion is due to the fact that at these temperatures there is no considerable difference in ions mobility in gel and liquid electrolytes despite the quasi solid nature of the former ones. The use of gels should also be beneficial in the view of mechanical stability of the studied electrolytes.

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 the scientists involved in battery research 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 supercaps 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. The exception which is well known to the referee are former PhD Thesis of Barbara Górska also undertaken in Professors Bequin group dealing with application of protic ionic liquid as solvent for electrolytes used in supercapacitors. The reviewed Thesis seems to be a continuation of the former research and the referee acknowledge the fact that doctor Górska is co-supervisor of the Thesis. Also the experiments, content of the Thesis, very good combination of the methodology applied is typical of all works performed in the group of Prof. Bequin group of which I am aware and I am glad that Emmanuel Pamete Yambou took an advantage of possibility of co-operation with the internationally recognized experts in the field.

I would have two recommendations which in my opinion might be used by the Professor Bequin group in the future extension of the reviewed work. First is to use an immidazolium anion based ionic liquid being a part of binary or ternary mixture. For example BMImTDI 4,5-dicyjano-2-(trifluorometylo)imidazolan 1-butylo-3-metyloimidazolu ionic liquid is amorphous down to -70°C with a high fraction of empty space in the form of voids or even empty planes which should be beneficial for anion transport. Such ionic liquids are capable to easily incorporate even large glyme solvates without decrease in conductivity or an increase in the viscosity compared with the based ionic liquid. Therefore one can expect that they can act as a very effective part of binary or ternary mixtures of ionic liquids.

Secondly for the gelation of liquid electrolytes quite common procedure is to use nanosized fumed silica as the gelation agent (7nm provide by Degussa). Addition of even small amounts (few weight %) of the silica powder results in the creation of gel type structure without any loss in conductivity. This is an easy procedure commonly used in battery electrolytes and I presume it can be also tried in supercaps technology.

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 Mister Emmanuel Pamete Yambou to publically 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.