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Review of the of M.Sc. Emmanuel Pameté Yambou doctoral dissertation entitled „Design of ionic liquids based electrical double layer capacitors operating very effectively at low temperature".

Supervised by: Prof. François Béguin

Co-supervised by: Dr. inż. Barbara Górska

Mr Emmanuel Pamete Yambou doctoral dissertation was performer under supervision of Prof. François Béguin and co-supervised by dr. inż. Barbara Górska and focuses on improvement of the design of electrical double layer capacitors based on carbon electrodes and ionic liquids as electrolytes.

This PhD thesis was presented to me in mixed form, consisting of three scientific publications and one research chapter, prepared as ready manuscript, and is a single, coherent document. The work is thematically linked to the title of the dissertation. The work focuses on improvement of the performance of the electrical double layer capacitors at low temperatures, by designing new electrolytes in the form of ionic liquids mixtures and changing the active material for electrodes.

The dissertation is presented with distinctive sections and the document contains 183 pages, 35 figures, 16 equations, 3 tables and 1 scheme. Literature references contain 229 positions. The work consists of a table of contents (3 pages), an introduction with short description of the purpose of this work (6 pages), a literature review (37 pages), three chapters summarizing three scientific articles, presented as part of this work (6 pages), a chapter presented in a form of a manuscript (17 pages), general dissertation conclusions (3 pages), a list of abbreviations and symbols used (4 pages), references (18 pages), scientific achievements (4 pages), co-authorship statements (4 pages), summary in English (3 pages) and summary in Polish (3 pages).

The introduction to the dissertation concisely describes the aim of the doctoral dissertation and presents how increased demand for energy is forcing scientific research towards developing new technologies and new materials in electrochemical capacitors. In this section, before briefly describing each chapter, author presents main objectives of his studies, which include:

(i) Preparation and investigation of properties of ionic liquid mixtures with low-temperature liquidus range;

(ii) Selection and design of carbon electrodes enabling efficient performances at low temperatures in ionic liquid-based electrical double-layer capacitors (EDLCs);

(iii) Resolution of leakage problem associated with the usage of ionic liquids as electrolytes.

The literature review is divided into 6 main parts, directly linked to the topic of presented PhD thesis. First section begins with short introduction of the problem, which this work tries to overcome or at least improve existing solutions, and that is to enhance the performance of electrical double-layer capacitors. Next, author focuses on the EDLCs, presenting history of electrical double-layer capacitors models, mentioning Helmholtz, Gouy-Chapman-Stern or Bockris-Devanathan-Muller models. Following that, author presents operation principle of electrical double-layer capacitors and their properties. Rapid and reversible electrostatic accumulation of ions form an electrical double-layer at the interface of electrode and electrolyte is described. Author focuses a lot on practical and theoretical applicability of EDLC, highlighting the importance of the pore size control of the separator in order to increase the capacitance. Furthermore, the choice of electrolyte with high electrochemical stability window is also indicated, alongside other physicochemical properties such as low viscosity, low melting point or high dielectric constant. Subsequently, author presents up to date research on materials and chemical used for EDLCs.

In the next section, author focuses on ionic liquids as possibility to replace aqueous or organic electrolytes, currently dominating the market, due to their high operation potential window. As ionic liquids are know for their unique properties, especially large liquidous temperature range, author illustrates how the structure of ions influences melting points of ionic liquids, correctly stating that anion size has big effect on that property. Some ionic liquids however, have relatively high melting points, which excludes them form being used as electrolytes in EDLCs. In order to overcome this problem, binary mixtures have been presented as an solution to those problems, because proper selection of ionic liquids can result formation of binary mixtures without any phase transitions from -80 to 100°C, which in turn is beneficial for considering them as prospective electrolytes for EDLCs. The author states, that not only specific thermal properties are desirable but also high density and viscosity are important parameters. In this section, author proceeds with physical explanation of above-mentioned properties, with literature support of well-known ionic liquids experts, such as: D. R.

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McFarlane. It has been proven, that ionic liquids can be used as electrolytes for lithium batteries, and one of the best value to asses their potential is electrochemical window. In this section, Mr Yambou describes methods of measurements for electrochemical stability window, presenting, that the S-method, developed by Xu et al., as the most accurate one, for measurements on activated carbon electrodes. He follows up with couple of plots, displaying anodic and cathodic limits for ionic liquids, obtained using S-method. Last part of this section is devoted to the influence of ion sizes in ionic liquids on capacitance of EDLCs.

In my opinion, the part of the literature review devoted to ionic liquids and its characterization, should include information about synthesis and more importantly purification of ionic liquids, since the application of mentioned substances is electrochemistry, where even smallest impurities can cause faulty results. Moreover, it would also be beneficial to include some examples of application of ionic liquids, not only in the presented research as electrolytes, but also other fields, such as extraction processes, reaction solvents, catalysis, photonics, etc. Nonetheless, the absence of those sections does not diminish the importance of the issue presented by the author, as he mainly focuses on binary mixtures of ionic liquids as potential electrolytes for EDLCs.

In the next section of literature review, author presents different types of active materials for ionic liquid based electrical double-layer capacitors, giving extensive research background on different forms of carbon, that can be used, such as graphene, activated carbon, carbon nanotubes or templated carbon. Last section is devoted to EDLCs based on ionogels, as alternative to simple IL electrolytes. Entrapment of ionic liquid in a host network, such as silica, produces solid-state electrolytes, which ensures no leakage that continues to be a problem for using ionic liquids as electrolytes. Author proceeds to present advantages of ionogels over liquids electrolytes, with improved safety, limiting packaging constraints and good interfacial stability to name a few.

At the end of this chapter, Mr Yambou provides brief conclusions regarding literature review, highlighting the steps that must be addressed while designing ionic liquids based electrical double-layer capacitors.

The literature section has been prepared thoroughly and meritoricaly correct by the author. The knowledge presented in the abovementioned sections is necessary to describe the results and conduct a discussion in the following chapters of the dissertation, therefore it constitutes an integral part of the dissertation.

The next chapter summarizes the results obtained in the first publication that is part of this PhD thesis, with the application of binary mixtures of ionic liquids based od 1-ethyl-3-methylimidazolium cation, as low-temperature electrolytes. The first objective of presented doctoral dissertation was to prepare binary mixtures of ionic liquids in order to surpass the problem of standalone ionic liquids which is high melting

temperature. It is well known in the literature, that ionic liquids with fluorinate based anions, have great electrochemical properties, thus it is not surprising that Mr Yambou chose ionic liquids with different fluorinated anions, such as tetrafluoroborate or bis(trifluoromethanesulfonyl)imide. All ionic liquids researched in this publication, are based on 1-ethyl-3-methylimidazolium [EMIM] cation. The author prepared multiple binary mixtures, with different molar ratios of individual ionic liquids, ranging from 0.1 to 0.9. After conducting differential scanning calorimetry analysis for all obtained mixtures, Mr Yambou concluded that mixtures of EMIM bis(trifluorosulfonyl)imide and EMIM tetrafluoroborate, with molar ratios from 0.2 to 0.8, can be used as electrolytes for ionic liquid based electrical double-layer capacitors. Even though, several other mixtures did not present any phase transitions, after studies of their densities and viscosities it was determined, that only binary mixtures mentioned above, have sufficient properties for being considered as electrolytes. To confirm the hypothesis, author conducted electrochemical studies, in order to determine the electrochemical stability window, which for the best mixture is 3.1 V. Furthermore, at the end of this chapter, author concludes that ionic liquid mixtures can be an effective alternative to commercially used electrolytes for electrical double-layer capacitors.

Third chapter summarizes the research done in the second publication that is part of presented doctoral dissertation and is focused on fitting the porous texture of carbon electrodes. After completing the first objective of his work, Mr Yambou had to continue his work and select the best electrode material for previously obtained binary mixtures of EMIM FSI and EMIM BF_4, which had the pest properties of all tested mixtures. Consequently, addressing the issues present in the literature, author decided to select carbon black and hierarchical carbon, which both can be characterized as mesoporous materials with different textures. instead of carbon nanotubes. After proceeding with cyclic voltammetry measurements, author concluded that the EDLC with electrodes made form the hierarchical carbon exhibited good specific outputs, higher than those obtained with EDLC with electrodes made form carbon black, which in turn had superior volumetric parameters. Thus, author decided to prepare electrodes with mixed carbons. Electrical double-layer capacitors with such electrodes retained the best qualities of each individual carbon.

In the next chapter, author summarizes the work presented in the publication titled "Electrical double-layer capacitors based on ternary ionic liquid electrolyte operating at low temperature with realistic gravimetric and volumetric energy outputs". Based on the results obtained in the first two publications, author decided to further the research and implemented ternary mixtures of ionic liquids, introducing new anion, namely tetracyanoborate. Introduction of such ionic liquid allowed for lower viscosity and higher conductivity of ternary mixture of EMIM FSI, EMIM BF_4 and EMIM TCB in comparison to the binary mixture presented in the first paper (EMIM FSI and EMIM BF_4). Author in a convincing manner addressed the viscosity and conductivity

issues stemming from binary mixture. In order to find the best formulation of three ionic liquids, several different ternary mixtures were prepared with varying molar ratios of ILs, from which the mixture comprised of 0.6 mol of EMIM FSI, 0.1 mol of EMIM BF_4 and 0.3 EMIM TCB was the best, with low viscosity and high conductivity. In addition, in this paper author adjusted the mesopore size to the hierarchical carbon as electrode material. Both of those adjustments enabled significant increase in the performance of EDLCs.

Second to last chapter is presented as a ready to publish manuscript and introduces ionogels as an electrolyte to the electrical double-layer capacitors. This section begins with thorough introduction, presenting latest research on the employment of ionic liquids and their mixtures as electrolytes, furthermore highlighting downside of their application as well as their limitations. Having in mind all previous presented research, Mr Yambou proposed utilization of ionogels as a response to the problems arising from using ionic liquids, mainly leakage problems. Poly(vinylidene fluoride) and poly(vinylidene fluoride-co-hexafluoropropylene) have been characterized as polymers with high thermal stability and relatively high ionic conductivity, thus author decided to implement the latter polymer as a solid carrier for binary mixture of EMIM FSI and EMIM BF_4. In the experimental section of this chapter, the author presents preparation and characterization techniques of ionogels, and films based on PVdF-HFP, which include SEM and energy dispersive X-Ray analysis. For electrode material, hierarchical micro/mesoporous MgO-templated carbon was used, and cell manufacturing is presented in the last part of the experimental section. In the section devoted to the results, author concludes that ionogels of binary mixture can be adapted as solid-state electrolyte, because of its thermal properties and lack of phase transitions changes on thermogram, with only glass transition being present at -101°C. Next, the conductivity measurements confirmed the increased value for ionogels-binary mixture at temperature lower than -30°C. Scanning electron microscopy allowed for investigation of the morphology and microstructure of PVdF-HFP and ionogels-binary films, proving that the ionic liquid occupies the pores of the polymer. Finally, the electrochemical properties of prepared cells with hierarchical micro/mesoporous MgO-templated carbon, have been studied, from which Mr Yambou concludes, that the EDLc with 100 µm ionogels-binary film could outperform the capacitors made with liquid electrolytes in terms of energy, capacitance and cycle life.

The last chapter of presented doctoral dissertation is devoted to general conclusions and coherently informs the reader about the achievements made during this work, highlighting that all the objectives of this PhD thesis have been fulfilled. The hypothesis assumed, that ionic liquids can be an effective electrolytes for electrical double layer capacitors, operating at low temperatures. Work plan for verification of this hypothesis was well thought of and executed with each subsequent study (publication) resulted form the results obtained previously (or from the literature). Therefore, the author demonstrated that adjusting

physicochemical properties of electrolyte and the texture of the electrode material, EDLCs performance can exhibit better and promising performance while operating at low temperatures.

To sum up, the presented doctoral dissertation was written correctly, with minor editorial errors, however they do not affect the significance of this work and my positive opinion about presented PhD thesis. M.Sc. Emmanuel Pameté Yambou presented himself as an experienced experimenter who knows how to design an experiment, select appropriate research method and draw correct conclusions. The innovative aspect of his work is further highlighted by the fact, that the results obtained in the course of this work were published as three individual articles in very good scientific journals (Electrochim. Acta, ChemSusChem, J. Mol. Liq.). The results were also presented at several international conferences, including 10 oral presentations. Mr Yambou also received three awards, including one for best creative work in 2020 by the Polish Academy of Sciences branch in Poznań.

I declare that the doctoral dissertation of Mr Emmanuel Pameté Yambou meets the conditions and requirements specified in Art. 13. 1. act on academic degrees and academic title. I apply to the Council of the Faculty of Chemical Technology of the Poznan University of Technology for the admission of a PhD degree and allow Mr Yambou to proceed to the next stages of doctoral procedure.