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Review Report for Ph.D. Thesis

Author: Emmanuel Pameté Yambou

Title of Dissertation "Design of ionic liquid based electrical double layer capacitors operating very effectively at low temperature"

Promoter: Professor François Béguin

Co-promoter: Dr. inż. Barbara Grórska

Prepared in Poznań University of Technology, Faculty of Chemical Technology, Institute of Chemistry and Technical Electrochemistry

Importance of the topic and objectives of the dissertation

As the main goal of his doctoral thesis, Mr. Emmanuel Pameté Yambou has chosen the design of ionic liquid-based electrical double-layer capacitors (EDLC) operating at low temperature. Achieving the assumed goal required the solution of specific issues, including (1) formulation of ionic liquid mixtures combining extended low-temperature liquidus range with relatively high conductivity and low viscosity, (2) design of hierarchical micro/meso-porous carbon electrodes with efficient performances for capacitors working at low temperature, (3) solving the leakage problem by confining the ionic liquid mixture in the solid polymer network.

The topic undertaken by the Author is important from the point of view of achieving the net-zero carbon dioxide emissions by 2050. Fossil-fuel-free economy requires the deployment of clean and efficient energy technologies, the integral components of which are energy storage systems. EDLCs based on ionic liquid electrolytes and porous carbon electrodes

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which perform from -40°C up to +70°C can be combined with high energy density components (batteries, fuel cells) to increase their lifespan. Thus, both the objective as the results obtained meet the demands of the transition to the Net Zero Emissions by 2050 Scenario (NZE) formulated by International Energy Agency.

Formal and content-related assessment

Doctoral dissertation is well structured and clearly presented. The main part of Mr. Pameté Yambou's dissertation is a collection of three scientific articles which were published in highly ranked journals (chapters II-IV) and one unpublished work (chapter V). The main part of the dissertation was preceded by a general introduction and a description of state of the art (chapter I). At the end of the dissertation, the Author included general conclusion, list of abbreviations and symbols, references, his scientific achievements, co-authorship statements and abstract (in English and Polish).

Chapter I is an exhaustive literature review containing an introduction to the working principles and properties of EDLCs, broad description of ionic liquids (IL) as electrolytes and carbon materials as electrodes for EDLCs. The author highlights the numerous advantages of ILs over conventional organic electrolytes: nonvolatility, non-flammability, a low vapor pressure, high thermal and high electrochemical stability. Combining specific cations and anions ILs can be implemented for EDLC applications. On the other hand, carbons are a good electrode material due to their availability, high electrical conductivity and moderate cost. From the point of view of applications in EDLC, the hierarchical structure of micro/mesopores is important. In the literature review, the issue of entrapping ILs in solid polymer network is discussed as well. Replacing ILs by ionogels allows to eliminate the risk of leakage. To summarize this chapter, it is evident that Mr. Emmanuel Pameté Yambou carefully selected the ILs, electrode carbon materials and ionogel formulation after in-depth literature studies in order to obtain the efficient IL-based EDLCs operating at low temperatures down to at least -40°C.

The first work (chapter II) in the collection entitled "**Binary mixtures of ionic liquids based on EMIm cation and fluorinated anions: physico-chemical characterization in view of their application as low-temperature electrolytes**" was published in 2020 in *Journal of Molecular Liquids* (IF: 5.065, MNiSW Points: 100). The PhD candidate is the first author of this publication. The main aim of the study was to evaluate the possibility of using ILs as an electrolyte in EDLC operating at low temperatures (at least down to -40 °C). The research was focused on ILs containing methylimidazolium $[EMIm]^+$ cations coupled with the fluorinated anions such as bis(fluorosulfonyl)imide $[FSI]^-$, bis(trifluoromethanesulfonyl)imide $[TFSI]^-$ or tetrafluoroborate $[BF_4]^-$ mixed with different molar ratios. Differential scanning calorimetry made it possible to trace the phase transitions (crystallization and melting) and determine the optimal molar ratios at which the mixtures remain liquid at low temperatures.

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For particular mixtures, the glass transition temperature around -90°C occured. Binary mixtures offered improved transport properties (low viscosity, high electrical conductivity) with a slight decrease of electrochemical stability window. Among the series of binary ILs, the $[EMIm][FSI]_{0.5}[BF_4]_{0.5}$ and $[EMIm][FSI]_{0.6}[BF_4]_{0.4}$ showed the highest electrical conductivity and low viscosity. Their properties are superior to the other mixtures under investigation as well as electrolytes reported in literature.

The second article (chapter III) from the series entitled "**Fitting the porous texture of carbon electrodes to a binary ionic liquid electrolyte for the realization of low temperature EDLCs**" appeared in *Electrochimica Acta* in 2020 (IF:6.215, MNiSW Points: 100). Mr. Pameté Yambou is listed as the first author of the publication. The main research topic was related to determine the effect of carbon electrode texture on the performance of low temperature EDLC. As an electrolyte was used the binary ILs $[EMIm][FSI]_{0.5}[BF_4]_{0.5}$ with a superior transport properties to other IL mixtures tested (chapter II). The electrode materials chosen for this study were commercial carbon black (SCA2, Cabot) and home-made hierarchical MgO-templated carbon. The choice of carbon materials was well thought out and not accidental. Both carbon materials exhibit similar values of specific surface area of about 1500 m^2/g but represent different kind of porosity. As revealed by the gas adsorption isotherms, carbon black is characterized by external porosity resulting from the existence of voids between carbon aggregates. Similar texture have electrodes made of carbon nanotubes. On the other hand, templated carbon offers uniform mesopores (~3.5 nm) that play a role of ion reservoirs and the transportation channels to the micropores. Carbon black with agglomerated dense microporous spherical particles displays high volumetric capacitance and volumetric energy. However, an apparent performance deterioration was detected at low temperatures. On the other hand, templated carbon has low density but exhibits better charge propagation and greater specific capacitance. The pure box-like shape of cyclic voltammograms was retained down to -40°C. To combine the advantage of the two materials, the mixture of carbon black and templated carbon was studied as well. The mixed electrode combined the advantages of both types of electrodes. Namely, the specific outputs of the EDLC were similar to the EDLC with templated carbon electrodes, whereas its volumetric energy was alike in the carbon black electrode.

The third article (chapter IV) included in the doctoral dissertation entitled "**Electrical double-layer capacitors based on a ternary ionic liquid electrolyte operating at low temperature with realistic gravimetric and volumetric energy outputs**" was published in 2021 in *ChemSusChem* (IF: 7.962, MNiSW Points: 140). Also in this work the PhD candidate appears as the first author. Here, the results of research on low temperature EDLC obtained in the two first publications was extended by ternary mixture $[EMIm][FSI]_{0.6}[BF_4]_{0.1}[TCB]_{0.3}$, in which the tetracyanoborate admixture was intended to lower the viscosity of the electrolyte. Indeed, this ternary mixture was superior to binary ones owing to its lower viscosity and higher conductivity. For further enhancement of EDLC efficiency, a hierarchical

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carbon with better-adjusted mesopore-size and greater density was used as electrode. Texture and density of the hierarchical carbon was successfully adjusted by chose of proper size of silica and carbon-to-template ratio, respectively. The EDLC thus obtained was able to operate down to -50°C. The EDLCs demonstrated high and almost stable specific and volumetric energy outputs down to -20°C, and as high as 43% retention down to -40°C.

The last, **fourth work** (chapter V) in the collection entitled "**An all-solid-state electrical double-layer capacitor operating at low temperature with the help of an ionogel electrolyte and a hierarchical micro-mesoporous carbon**" has not published yet. Mr Pameté Yambou is the first author of this work as well. The research was closely related to the results presented in previous published articles and focused on the design of efficient low temperature EDLC in which solid-state electrolyte was used. Replacement of ILs with ionogels, i. e. liquid electrolytes confined in solid matrix, allows to solve the leakage problem which affects the interfacial stability and life time of capacitor. As a polymer network, poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP) was chosen. Based on previous results, the equimolar binary mixture of [EMIm][FSI] and [EMIm][BF_4] as a liquid electrolyte and a hierarchical micro/mesoporous MgO-templated carbon as electrodes were selected. As revealed by DSC, low-temperature thermal properties of the ionogel based on the binary ILs were comparable with the liquid state binary IL electrolyte. Below -30°C, electrical conductivity of the binary IL confined in polymer matrix is higher than for liquid electrolyte. Down to -30°C, capacitive properties of the EDLC with the 100 µm thick ionogel-binary were comparable with the device made with liquid IL mixture. At -40°C and a power density of 1000 W kg^{-1}, the device based on the ionogel exhibits a specific energy output which is more than twice higher than the value obtained for EDLC with liquid electrolyte. Viability of the EDLC cells were assessed as well. At -30°C, capacitance retention was evaluated 89% and 82% for the cell-based on ionogel and liquid IL electrolyte, respectively.

In 'General conclusion', Author summarized all research works constituting the content of chapters II-V. The conclusions are fully justified by the results presented in chapters II-V and prove the great knowledge as well as the great criticism of the Author. The most important conclusion is that matching the electrode porous texture and IL electrolyte transport properties is an effective design strategy for alternative cost effective, high conductivity, and eco-friendly low temperature EDLCs. Finally, the Author concludes that further optimization of EDLC performance requires refinement of the templating methods of carbon electrodes, improving the properties of IL mixtures, enhancing the ionogel conductivity and adjusting the ionogel thickness in the EDLC cells.

Specific comments

The role of the reviewer is facilitated in the case of a dissertation constituting a collection of published articles, as they have already undergone the review process.

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Nevertheless, there are two remarks which occurred to me and need to be explained in details.

- ✓ In chapters III-V, the EIS data in the form of Nyquist plots are presented. On the basis of these plots, parameters of EDLC such as equivalent series resistance (ESR), ionic resistance (R_{ionic}) and equivalent distributed resistance (EDR) were determined. However, physical interpretation of these parameters is missing. There is also a question whether the obtained data can be modeled with the use of the equivalent circuit shown in Figure 4 (chapter I)?
- ✓ One of the key conclusions from the research conducted as part of the doctoral dissertation is that the performance of low-temperature EDLCs requires matching the texture of carbon electrodes to electrolytes. The most prospective strategy in the light of presented results is the use of templated carbons as the electrode material which are superior to carbon materials with external porosity (carbon blacks, carbon onions, carbon nanotubes). A comment regarding the overall assessment of the scalability of the use of templated carbon compared with other carbon materials is expected.

Final conclusions

The doctoral dissertation shows the generally high substantive level of the candidate for the doctoral degree in the discipline of chemical science and proves the ability to independently conduct scientific work. Mr. Emmanuel Pameté Yambou presented a series of four thematically related works. In each of the works, the candidate is the first author. According to the statements of the co-authors, his contribution to these works was in the range 40-50%. Results presented in that works constitute an original solution to the scientific problem of design of ionic liquid based electrical double layer capacitors operating effectively at low temperature.

Apart from the series of articles included in the dissertation, candidate is a co-author (the first author) in another two publications in journals indexed in JCR. The total IF of the published works is 36.758 and total number of MNiSW Points is 580.

Mr. E. Pameté Yambou gave 10 oral and 9 poster presentations at international conferences. One oral presentation given at the the 8th International Conference on Carbon for Energy Storage and Environmental Protection (CESEP'19) was awarded as the best oral presentation. The poster presented at 71st Annual Meeting of the International Society of Electrochemistry (ISE) received a similar distinction in 2020. He was awarded by the Polish Academy of Sciences, Branch in Poznań, with the Award for the best creative work in 2020.

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In view of the above, I conclude that the assessed dissertation of Mr. Emmanuel Pameté Yambou, entitled "Design of ionic liquid based electrical double layer capacitors operating very effectively at low temperature" **fulfills all requirements posed on theses aimed for obtaining PhD degree set out in the Act of 20 July 2018 – Law on Higher Education and Science (Dz. U. 2018, item. 1668) – and is ready to be defended orally in front of respective committee.**

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