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**Review of the PhD Thesis entitled**
**"Ionic liquid-based hybrid electrolyte membranes**
**for proton conducting fuel cells"**
**submitted by MSc Mohammad Ebrahimi**

The dissertation under review has been prepared under the joint supervision of prof. dr. hab. Wojciech Kujawski (Department of Chemistry UMK in Torun) and DSc Kateryna Fatyeyeva. (Université de Rouen Normandie). This PhD Thesis is a joint project between Nicolaus Copernicus University in Toruń (NCU) (Poland) and University of Rouen Normandie (URN) (France) supported by NCU, Normandy region (HERMES project, 2020–2023) and the Graduate School of research XL-Chem (ANR-18-EURE-0020 XL-Chem).
This dissertation is related to the very modern topics, importnat both from the scientific point of view and practical application in modern technique and simple life. Proton conducting fuel cells are one of possible „green" energy solutions and Ionic Liquids offer new possibilities for their development and improvements.

This dissertation is written in the traditional way: it comprises five chapters on 207 pages with 172 references, 23 pages of abbreviations and list of figures. The first chapter "State of the Art" is presenting the energy generation, fuel cell, and the use of IL-based composite membranes for PEMFC application. The second chapter "Materials and Characterization Methods" describes used chemical materials (e.g. polymers, solvents, ILs, and other chemical reagents) and the techniques used for the membrane preparation, IL synthesis, there are also briefly described

characterization methods. The third chapter "Ionic Liquids: Synthesis and Characterization" describes synthesis of novel protic ionic liquids by acid-base neutralization reaction. Several new imidazolium- and hydroxylammonium-based ionic liquids were synthesized and the influence of anion and cation nature on their thermal stability and ionic conductivity was investigated and what is especially interesting – these physical properties were correlated with the IL structure. Data presented in Figures 3.1 – 3.12 and in Tables 3.1 – 3.3 are very impressive and show complete characterization of the new synthesized IL. These data and discussion (Chapter 3.6) is very well prepared and described, especially in Figure 3.10 (page 86) analysis of Einstein and Grotthuss mechanism of proton conduction (vehicle mechanism or proton hopping – page 86) and therefore is worth to be published as a separate paper. Also the final conclusion (page 93) … *The obtained results prove that the [TFS]-based Pr-ILs are the ideal choice for high temperature industrial applications and long-term processes (e.g. HT-PEMFC) owing to their excellent thermal stability and ionic conductivity* in nice way summarizes made hard and vast research and I hope this direction of experiments will be continued both at the UMK and the Université de Rouen Normandie. The fourth chapter "Polyamide 6-based Membrane" focuses on the preparation according to the original method developed at the UMK [Ref. 122] porous polyamide-6 membrane by nonsolvent-induced phase separation technique. In this chapter, the physical, morphological, and transport properties of polyamide-6 membranes with different gelation time are evaluated. The Author in discussion is showing postive properties of PA-6 membrane but also is showing its weaker points, like poor water flux (page 111) and states, that this kind of membrane is still good for SILM applications in the PEMFC applications.The fifth chapter is crucial to all this PhD Thesis, forms kind of summary and conclusions of the all done research. Chapter V entitled "Ionic Liquid-based Membranes" is dedicated to fabrication of IL-based membranes by a phase inversion method. Chemical, physical, thermal, and mechanical properties of fabricated composite membrane are presented and discussed. The main problem with currently used Nafion membranes is related with loss of ionic conductivity at elevated temperatures, so the ionic conductivity of IL-based membranes at elevated temperature and under anhydrous conditions is analyzed. Discussion on page 166 comparing Nafion ionic conductivity and CAB/[DETA][TFS]-[DEPA][BUPH] conductivity at RT (~ 0.1 $Scm^{-1}$ vs $10^{-5}$ $Scm^{-1}$) but at temperatures exceeding $80^0C$ this phenomena is reversed ($10^{-8}$ $Scm^{-1}$ vs $10^{-4}$ – $10^{-3}$ $Scm^{-1}$at $120^0C$ in anhydrous conditions leads to very crucial statement: *The obtained results confirm that the prepared CAB/[DETA][TFS]- [DEPA][BUPH] composite membranes are promising candidates for using in electrochemical applications, namely, electrodialysis and fuel cell.* The subchapter 5.4 „Conclusions" and the next part "General Conclusion and Prospects" section is devoted to the summary of the obtained results and provides some suggestions for the future study. Finally in the Annex part there are collected 1H NMR and 19F NMR spectra of new synthesized 16 ILs, abstracts in English, Polish and French and the last

but not the leasts scientific achievements of MSc M. Ebrahimi – four articles already published in good journals, with high IFs:

M. Ebrahimi W. Kujawski, K. Fatyeyeva, "Different Approaches for the Preparation of Composite Ionic Liquid-Based Membranes for Proton Exchange Membrane Fuel Cell Applications—Recent Advancements", Membranes, 2023, 13, 593 (IF: 4.562). DOI: https://doi.org/10.3390/membranes13060593;

M. Ebrahimi, W. Kujawski, K. Fatyeyeva, "Fabrication of Polyamide-6 Membranes—The Effect of Gelation Time towards Their Morphological, Physical, and Transport Properties", Membranes, 2022, 12, 315 (IF: 4.565). DOI: https://doi.org/10.3390/membranes12030315;

M. Ebrahimi, W. Kujawski, K. Fatyeyeva and J. Kujawa, "A Review on Ionic Liquids-Based Membranes for Middle and High Temperature Polymer Electrolyte Membrane Fuel Cells (PEM FCs)", Int. J. Mol. Sci., 2021, 22, 5430 (IF: 5.923). DOI: https://doi.org/10.3390/ijms22115430;

M. Ebrahimi, Y. Kobzar, W. Kujawski, K. Fatyeyeva, "New hydroxylammonium-based protic ionic liquids: Influence of cation and anion structure on thermal, viscosity and conductive properties" Journal of Molecular Liquids 401 (2024) 124574 (IF: 6.6)
https://doi.org/10.1016/j.molliq.2024.124574
and 4 oral presentations (one awarded) and one poster, all presented in the international conferences.

It must be stated here in this part, that this PhD Thesis has been prepared with great care and is excellent by means of clarity of presentation and language. This is not easy task to present so numerous experimental results, starting from the synthesis and characterization of new ILs, preparing three kinds of porous membrane supports PA-6; CAP; CAB; impregnation with ILs and finally measuring their physicochemical properties with advanced analytical methods (NMR; FTIR; ATR; TGA; DSC; CA; SEM; EDX; AFM; mechanical testing, ionic conductivity swelling degree; water uptake; contact angle; porosity; filtration and leaching tests; – pages 52 - 62). Presented discussion of membranes structure and properties (Chapter V) is even in my opinion more interesting, elaborated and advanced than also good discussion describing IL properties (Chapter III). Especially way of obtained results presentation (data scattering, averages, standard deviations, 3D plots) is very convincing and shows, that MSc M. Ebrahimi is now a well educated, mature scientist satisfactory prepared to run his own research work and present results in advanced way. Both scientific advisers, DSc Kateryna Fatyeyeva and prof. dr hab. Wojciech Kujawski and two participating scientific institutions (Université de Rouen Normandie and Department of

Chemistry UMK in Torun) have done a good educational and scientific job and the way how they have spent support from the European Funds can be shown as an example how to positively complete educational program in Europe.

BTW, in this moment, I feel pressure to add, that currently I am writing an opinion about PhD Thesis written in cooperation between German company and the University of Luxembourg. Results presented in this one work are so intermixed and there is hard to follow the research idea, that I will suggest in my opinion to send the Author to the UMK for predoc stay to learn how to write the PhD Thesis in so well organized and clear way.

But writing the opinion about this PhD Thesis I have an obligation to be also critical and find some drawbacks or missing elements. For me there is one important topic unanswered. How this work is located in the whole project of fuel cells ? Is this work located between the top several solutions or this is just medium, standard position or may be the results are meaningless and without any practical, real value ? What is the current situation of the fuel cells in the world market and how this work located within this field ? Partly these questions are answered in this PhD Thesis in very fundamental and well prepared Table 1.1; Table 1.2 and Table 1.3 and in Ref. [7] coauthored by MSc M. Ebrahimi. But there are presented data from the literature analysis and situation in the commercial market is only briefly mentioned. I am sure that the Author knows the answer to these questions and during the public presentation will give the answer to the mentioned topics. Another topic in my opinion not sufficiently explained in this PhD Thesis is the selection of polymeric membranes for the FC. Why MSc M. Ebrahimi has selected porous PA-6 membrane, cellulose acetate propionate CAP and cellulose acetate butyrate CAB ? Of course these materials have some advantages being for example „green" materials, PA-6 membrane has a long and interesting history of research done at the UMK. But the procedure for their preparation, phase inversion methods, application of solvents like chloroform, formic acid, dimethylformamide, 1,4-dioxane, large ammounts of water causes, that this is an interesting method for their preparation but only on laboratory scale (page 51, page ). These methods will be never applied on big commecial scale. Why MSc M. Ebrahimi did not even discussed possibilities of application of another kind of porous membranes like for example track Nuclepore membranes, Celgard membranes, interesting polypropylene membranes developed at the Polymem Ltd with foaming PP with gaseous water vapors or membranes made from PVC or PSAn materials ? There is also another editorial mistake, simple to correct but repeated several times (pages 3; 4; 9; 12; 14; 15; 16; 21; 26 and so on) – there should be no space between digits and $^0$C units. Note, that Flash Point FP is correctly presented (without space, page 45). Page 22 in Figure 1.5 second time is unnecessary repeated „Phosphonium", page 29 should be …poly(vinyl chloride)...

In summary all this PhD Thesis shows, that the Author is mature, well educated and correctly prepared to run independently responsible scientific research.

Therefore, in my opinion the PhD thesis prepared by MSc Mohammad Ebrahimi fulfils all formal and customary requirements for the doctoral degree in chemical sciences in accordance with the statutes in the Journal of Laws of the Republic of Poland (Dziennik Ustaw 2023 poz. 742, the law of 20th July 2018), and I am applying for admission of MSc Mohammad Ebrahimi to the following stages of the PhD procedure.

Wojciech Fabianowski, PhD, DSc