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## Review of the PhD thesis

*Ionic liquid-based hybrid electrolyte membranes for proton conducting fuel cells*  
submitted by MSc Mohammad Ebrahimi

The review has been prepared at the request of the Discipline Council of Chemical Sciences of the Faculty of Chemistry of Nicolaus Copernicus University in Toruń. Prof. dr hab. Wojciech Kujawski (*Department of Chemistry UMK in Toruń*) and DSc Kateryna Fatyeyeva (*Université de Rouen Normandie*) are the supervisors of this dissertation.

### General characteristics of the dissertation

The doctoral dissertation submitted for review concerned the synthesis of the thermally stable and conductive ionic liquids (ILs) and the subsequent utilization of these ILs as an additive to prepare proton conductive membranes for polymer electrolyte membrane fuel cell (PEMFC) applied at elevated temperatures.

The main aim of this PhD thesis was the application of ILs containing different cations and anions as an additive to prepare proton conductive membranes. PhD student used three different polymers: cellulose acetate propionate, cellulose acetate butyrate, and polyamide-6 as the polymer matrix. Moreover, he investigated and

characterized the physical, chemical, electrochemical, transport, morphological, and thermal properties of fabricated membranes.

Energy generation is one of the most important challenges for people. Using non-renewable resources of energy causes environmental pollution (air contamination, water pollution, water scarcity, acid rains, and ozone depletion). Application of polymer electrolyte membrane fuel cell (PEMFC) is considered as a source of green energy because only water, heat, and electricity are the products of the reaction between hydrogen and oxygen used as the fuel and oxidizer, respectively. Therefore, the topic of the doctoral dissertation is current and very important.

The structure of the doctoral thesis is typical. The author presented the aim of the doctoral dissertation, the state of the art, materials and research methods, discussion of the results, conclusion and references.

The literature part includes sections related to the characterization of fuel cells, polymer electrolyte membranes, structure and properties of ionic liquids. The author listed types of fuel cells characterized by different electrolytes, operating conditions, design and technological parameters, namely molten carbonate fuel cells (MCFC), solid oxide fuel cells (SOFC), phosphoric acid fuel cells (PAFC), direct methanol (DMFC), alkaline fuel cell (AFC), and polymer electrolyte membrane fuel cell (PEMFC).

The analysis of this part of the thesis confirms my belief that the doctoral student has the ability to efficiently analyze various types of literature reports and is able to prepare a comprehensive study in the field of the subject covered by the doctoral dissertation, which is a necessary stage for the proper formulation of the research hypothesis and, consequently, the formulation of the aim of the research and the correct interpretation of obtained results and conclusions.

The research part of the work included a number of novelties such as: synthesis of new Pr-ILs showing excellent thermal stability and ionic conductivity; a deep discussion correlating the nature of IL with its thermochemical properties; a research work concerning the use of cellulose acetate butyrate (CAB) polymer in polymer electrolyte membrane fuel cell (PEMFC) for the application at elevated temperatures; and elaboration of new conductive polymer electrolyte membranes (PEM) based on a non-conductive polymer by utilization of only ionic liquids (ILs).



The research part of the work included the characteristics of the materials and research methods used, as well as a discussion of the research results, summary and conclusions. It is worth emphasizing that PhD student used modern research methods such as:

- Magnetic Resonance Spectroscopy (NMR),
- Fourier Transform Infrared Spectroscopy (FTIR),
- Atomic Force Microscopy (AFM),
- Thermogravimetric Analysis (TGA),
- Differential Scanning Calorimetry (DSC),
- Scanning Electron Microscopy (SEM)
- Coupled with Energy-Dispersive X-Ray (EDX) Spectroscopy.

Taking into account the scope of experimental work, it should be stated that the doctoral thesis contains a number of interesting and important results from both a cognitive and practical point of view. The research results were presented in an orderly, concise and communicative way, and their discussion was factual and exhaustive. The formal way of presenting the results in the form of tables and plots does not raise any major concerns, and the subchapters in which the discussion of the results are presented demonstrate the consistent implementation of the assumed research aims. The research material collected is extensive, which indicates that a lot of time and energy was devoted to it. Each issue was analyzed in detail, which also required a large amount of knowledge. In my opinion, the most important achievements of the PhD student are:

- It was found that the chemical nature of anion and cation influences the thermal stability of protic ionic liquids (Pr-ILs).
- The anion nature possessed dominant influence on the protic ionic liquids (Pr-IL) ionic conductivity measured in both dynamic and isothermal modes.
- Trifluoromethanesulfonate [TFS]-based Pr-ILs showed the highest values.

- The presence of long alkyl chains in the anion structure increased the viscosity for these Pr-ILs and, thus, reduced the ionic mobility.
- The change of the gelation time led to the change of the membrane morphology – higher gelation time provoked the formation of the porous membranes with smaller pores.

I positively evaluate the doctoral dissertation of Mohammad Ebrahimi, submitted for review. Nevertheless, I would like to address some comments and observations for the discussion.

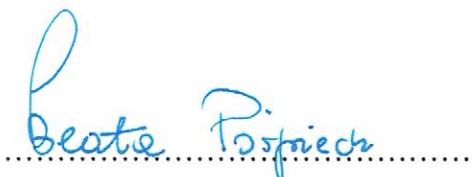
#### Detailed comments

- You wrote about a number of advantages of ionic liquids such as: good thermal and chemical stability, high proton conductivity, non-flammability, low vapor pressure, low toxicity, and great electrochemical stability. Can you precise which properties of ionic liquids are not favorable for ecological and practical reasons?
- As is widely known, life cycle assessment (LCA) is a systematic analysis of environmental impact over the course of the entire life cycle of a product, material, process. Do you have any information about the life cycle analysis for proton exchange membrane fuel cell (PEMFC)?
- In this work, you synthesized ionic liquids. You wrote that: “Several Pr-ILs containing different anions ([TFS]-, [TFA]-, [HS]-, [BUPH]-, and [EHPH]-based) and cations ([DETA]-, [DEPA]-, [MIM]-, and [BIM]-based) were prepared by acid-base neutralization reaction.” What criteria did you take into account when selecting cations and anions for the synthesis of these ionic liquids?
- You stated that *the obtained results showed that synthesized Pr-ILs have great potential to be used in PEMFC application. However, owing to the physical state of ILs, it is not possible to use them alone as the electrolyte in PEMFC. In order to have ion conductive PEM, composite membranes (polymer + IL) must be prepared.* My question is following: Why did you choose cellulose acetate propionate (CAP) and cellulose acetate butyrate (CAB) as the polymers for

obtaining composite membranes? Have you also investigated other polymers for the synthesis of composite membranes ?

The presented comments are of a debatable character and do not affect on the substantive assessment of the doctoral dissertation submitted by MSc Mohammad Ebrahimi

Taking into account the above and the fact that the doctoral dissertation submitted for review fully meets the 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), I apply for admission of MSc Mohammad Ebrahimi to the following stages of the PhD procedure and to publicly defend his doctoral dissertation.



Częstochowa, 15.04.2024

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