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Review on the PhD thesis report of Mr. Mohammad EBRAHIMI
Entitled " Ionic liquid-based hybrid electrolyte membranes for proton conducting fuel cells"

The PhD thesis was prepared in the frame of a collaborative work supervised by Prof. Wojciech KUJAWSKI, Department of Physical Chemistry and Physical Chemistry of Polymers, Faculty of Chemistry, Nicolaus Copernicus University in Toruń, Poland and Dr hab Kateryna FATYEYEVA, laboratoire Polymères, Biopolymères et Surfaces, UMR CNRS 6270, Université de Rouen Normandie, France.

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The long-term objective of this thesis is to contribute to energy production in a different way than the one using fossil fuels, in order to have stable and sustainable energy resource, but also less environmental and human health impacts. This is in good agreement with policy of many states and countries. Among the possibilities is the use of fuel cells, in the core of this study.

A fuel cell is an electro-chemical device able to produce energy from a chemical reaction. The most popular is the one called polymer electrolyte membrane fuel cell (PEMFC) in which hydrogen and oxygen are consumed as the fuel and oxidizer, respectively, and water, heat, and electricity are the products of the reaction. Thus, it is a green way to produce energy without carbon production.

Beside the catalyst, the most vital part of PEMFC is the polymer electrolyte membrane that must ensure the transport of the protons from the anode to the cathode with a high desired proton conductivity.

The reference membrane is made of Nafion ® but this perfluorated and sulfonated polymer suffers from some disadvantages among which are degraded performances when temperature is greater than 80°C. A second drawback is the mandatory use of pure hydrogen to avoid the Pt catalyst poisoning by CO.

A PEMFC that can be used at temperature higher than 80°C (HT-PEMFC) is thus desirable as well as the possibility to use less pure hydrogen and oxidizer. Aiming at this, a non-conductive polymer membrane can be impregnated with a protic ionic liquid to ensure the conductivity. However, even if it is a promising material, the IL leaching has still to be better controlled to optimise the IL(s)-HT-PEMFC performances.

The first aim of this study was the synthesis of thermally stable and conductive ILs in order to use them as an additive to prepare proton conductive membranes for PEMFC application at high temperature.

Accordingly, several ILs were synthesized and used to prepare composite membranes that have been obtained from 3 non-conductive polymers known for their film formation ability: cellulose acetate propionate (CAP), cellulose acetate butyrate (CAB), and polyamide-6 (PA6). The physical, chemical, electrochemical, transport, morphological, and thermal properties of prototype membranes were in-depth investigated.

Report structure

Besides the general introduction and general conclusion & perspectives, the thesis report (207pages) is classically divided in 5 chapters.

Chapter 1 is a bibliographic review, presenting the state of the art on fuel cells and the use of IL-based composite membrane for PEMFC application.

Chapter 2 is devoted to the experimental part, presenting either the chemical reactions or the membrane fabrication and all the characterisation tools that have been used and appeared relevant.

Chapter 3 describes the Ionic Liquid synthesis and their characterizations. Several new ILs were prepared. Besides NMR and FTIR characterisations, the thermal stability (TGA, DSC) and ionic conductivity (EIS, isothermal and dynamic modes) were studied aiming at the selection of the most promising one(s) for the further membrane fabrication. The discussion provides correlation between the ILs structure and the performances.

The obtained results proved that the Trifluoromethansulfonate ([TFS]) based protic ILs were very promising candidates for high temperature industrial applications and long-term processes.

According to the Table evidencing all prepared ILs, the cations and anions, nomemclature was the following one (only giving the ones that will be discussed in the following):
2-hydroxy-N,N-dimethylethanaminium ([DETA]
3-hydroxy-N,N-dimethylpropan-1-aminium ([DEPA]
Trifluoromethanesulfonic acid ([TFS])
di-n-butyl phosphate ([BUPH])
and
[DEPA][BUPH] is liquid at room temperature
[DETA][TFS] is liquid at room temperature

So I do not understand why, it was written that the most promising ILs were solid, leading to the conclusion that it was not possible to use them directly as electrolyte in the PEMFC. I feel, that this point must be clarified in the last version of the PhD report.

Chapter 4 focuses on the preparation of a Polyamide 6-based Membrane by the non-solvent-induced phase separation technique (NIPS), that is well-known technique able to provide more or less porous membranes.

These membranes were self supported ones (PA6: 13.5 wt%; 200 µm thickness (knife); 10 mm.s^{-1}). It is not clear for me what is the hydrophobic glass used (mistake with hydrophilic or special composition? Page 50, chapter 2).

Among the parameters inducing the membrane morphology and porosity, was the gelation time before the immersion in the non-solvent. The impact of this time (0-10 min) has been carefully studied: pore size by porometer 3G (here from 0.2 to 0.7 µm), swelling ability, roughness (AFM), water contact angle with limitations due to water penetration inside the membranes with the sessile drop technique and change for captive bubble, tensile strength, membrane water flux, etc..

The permeate flux to water was found low, that seems me logical with respect to the membrane thickness; this could be overcome by decreasing the thickness, but I feel that no acceptable limit were given in the report and just the conclusion was, in brief, the prototype membranes did not evidence sufficient transport properties for filtration process.

PEG (20 000 g.mol^{-1}) was the solute used for the retention measurements in dead-end filtration at 1000 rpm and 2 bar (page 60, chapter2 + page 110). I was surprise that the PEG concentration was measured by UV-Vis (page 60, Chapter 2) as I feel that PEG do not absorb in UV. Was it a modified PEG or a mistake in the redaction? Except membrane characterisation is there any interest in the determination of the rejection of such macromolecule by the microfiltration membranes with respect to the PEMFC ?

Finally, such membranes could act as "the support" of the ILs when these last ones are liquid (SILM) allowing the proton conduction (not tested); but the ILs leaching remains unsolved.

Chapter 5 is dedicated to the ILs-PEM membrane fabrication by the phase inversion induced by solvent evaporation method. The selected polymers were cellulose acetate propionate (CAP) and cellulose acetate butyrate (CAB).

With respect to the different number of carbon, CAB is less hydrophobic than CAP; consequently CAB can have more electrostatic interactions with ILs than CAP.

Multiples tests, well explained, have been made in order to found the best preparation of a flexible and sufficiently stable membrane (summary Table 5.7, page 142).

These membranes were self supported ones (CAP or CAB: 10 wt%; hydrophobized Petri dish, thickness of the fluid before evaporation was not given neither an estimation of the evaporation time nor the temperature, I guess it was at room temperature, page 51, chapter 2). The mixing between the polymer and the added ILs was achieved at the stage of the dope solution preparation. The CAP-based membrane had 110-140 µm thickness (page 118), while the CAB-based ones were close to 50-100 µm thickness (page 145)

The chemical, physical, thermal, and mechanical properties as well as the ionic conductivity of the prototype membranes are presented and discussed.

Pictures of CAP- based membranes given page 115 are not clear (see contrast for better quality) idem for CAB- based membranes given page 133 and all related pictures.

More promising results were obtained with the CAB-based composite membranes than with the CAP ones. This was partly attributed to the higher concentration of IL load in the CAB matrix, from 23 to 41 wt.%, while it ranged from 9 to 23wt% with the CAP-matrix.

Finally, the composite membranes based on CAB as polymer and [DETA][TFS]-[DEPA][BUPH] as mixed ILs, in which the last one was the dominant whatever the tested mixture (see Table 5.8 page 143), appeared as the most promising for further fuel cell applications. The thermal degradation occurred at high temperature Tdeg ~ 256–265 °C.

The ionic conductivity of Nafion® membrane at 25 °C (~ 0.1 S·cm^{-1}) is much higher than the prepared "best" CAB/[DETA][TFS]-[DEPA][BUPH] composite membrane (M3, 41% ILs, CAB/[DETA][TFS](18wt%)-[DEPA][BUPH] (23%); ~ 10^{-5} S·cm^{-1}).
However, conductivity of Nafion® membrane significantly drops above 80 °C (~ 10^{-8} S·cm^{-1}) because of the dehydration phenomenon and the conductivity of the "best" membrane (M3) remained high (~ 10^{-4}–10^{-3} S·cm^{-1} at 120 °C under anhydrous condition.

The general conclusion/perspectives part gives a nice overview of results and a list of perspectives.

I have a question dealing with middle or long-term use of the CAB/[DETA][TFS]-[DEPA][BUPH] composite membrane. As the most perfoming membrane (M3) is also the one that can leach the more ILs amount, do you have an estimation of the life-time of the composite membrane, or at least what is the maximum acceptable ILs leaching to keep acceptable performances? On this particular point, the perspectives delt with polymerized ILs. Is there any anticipated drawback associated with their polymerisation (membrane fabrication difficulties, conductivity change?, …) ?

As a general impression the thesis is well written and presented, however I feel that some minor corrections are needed (see above) and that there is too much abbreviations in the conclusion for an easy read and I recommend to perhaps develop more the sigles in the final version of the PhD report.

Valorization: The study has been valorized by the mean of 3 papers in peer reviewed international journals plus one submitted and several oral communications.

In conclusion, this thesis shows an important experimental work and relevant analyses at different scales for an interesting topic related to green energy production. It also delves into more fundamental aspects, discussing interactions between ILs and polymers, for instance.

I am therefore very much in favour of the oral defence of the doctoral thesis of Mr. **Mohammad EBRAHIMI** in order to get the doctoral diploma of the Uniwersytet Mikołaja Kopernika W Toruniu.

Rennes, April 17, 2024

Prof. Dr. Ing. Murielle Rabiller-Baudry