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DOCTORAL DISSERTATION ABSTRACT

Scientific discipline: Chemistry

Title of the doctoral dissertation: **Ionic liquid-based hybrid electrolyte membranes for proton conducting fuel cells**

Doctoral dissertation abstract:

Proton exchange membrane fuel cell (PEMC) has attracted a lot of attention in the both, laboratories and industries because PEMFC is considered as the green source of energy. Polymer electrolyte membrane (PEM) is the most important part in PEMFC owing to the fact that it is responsible for carrying protons between electrodes. Nafion® is the most commonly used polymer for PEM preparation because of its good thermal, mechanical, and chemical stability as well as high ionic conductivity. This polymer has excellent performance at low up to moderate temperatures under humidified condition. However, working at elevated temperature (higher than 80 °C) is more desirable and under these conditions the ionic conductivity of Nafion® membrane drops down significantly owing to the water evaporation. To obtain PEMs which can be applied at higher temperatures under anhydrous conditions, ionic liquids (ILs) are used as the proton carrier. The aim of this PhD thesis was to synthesis thermally stable and conductive ILs and use them as the additive to prepare proton conductive membranes for PEMFC application at elevated temperature.

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. The chemical structure of synthesized Pr-ILs was evaluated by NMR (^{1}H and ^{19}F) and FTIR analysis. It was found that the IL nature has a strong influence on the thermal and electrochemical properties of obtained ILs. In addition, the influence of anion nature on the thermal stability and ionic conductivity of synthesized Pr-ILs is much more pronounced than cation nature. The dynamic TGA results showed that there is a direct link between the acidity of acid and thermal stability of IL and [TFS]-based ILs demonstrated the highest thermal stability (T_{deg} ~ 415–435 °C) owing to the high acidity of trifluoromethanesulfonic acid (pK_a ~ -14). The following thermal stability order was proposed: [TFS] > [HS] > [EHPH] > [BUPH] > [TFA]. The ionic conductivity measurements were carried out in two heating/cooling cycles and no hysteresis was observed. Such results confirm the ionic conductivity of ILs. Furthermore, it was observed that the anion nature has the dominant influence on the ionic conductivity of synthesized Pr-ILs. [TFS]-based ILs showed the highest ionic conductivity values (~ 34.5–63.7 mS·cm^{-1} at 150 °C) because trifluoromethanesulfonic acid is a stronger acid as compared to the other used acids for IL synthesis. According to the results, the following ionic conductivity order of

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studied anions can be proposed: [TFS] > [HS] > [TFA] > [BUPH] > [EHPH]. 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.

CAB/[DETA][TFS]-[DEPA][BUPH] composite membranes were prepared by a phase inversion technique. Composite membranes containing 0, 23, 33, and 41 wt.% of ILs were prepared (M_0, M_1, M_2, and M_3, respectively) by the phase inversion method. The presence of ILs in the membrane was confirmed by FTIR and EDX analysis. SEM analysis showed a homogenous and dense structure of M_0 and M_1 membranes. However, in case of M_2 and M_3 membranes (containing 33 and 41 wt.% of Pr-ILs), some aps and cavities were observed. AFM analysis revealed that the surface roughness of pure CAB membrane increased by rising the concentration of ILs because of incompatibility between [DETA][TFS] and CAB polymer. Thermal analysis revealed the lower thermal stability of composite membranes (T_{deg} ~ 256–265 °C) in comparison with pure CAB membrane (T_{deg} ~ 360 °C). Composite membrane also showed lower T_g values as compared with the pure CAB membrane, confirming the plasticizing behavior of ILs. The addition of ILs led to reduction of the mechanical stability of composite membrane in comparison with pure CAB membrane, while the membrane flexibility increased. Composite membranes showed good ionic conductivity (0.1–1 mS·cm^{-1} at 120 °C) and it was found that an increase of ILs concentration from 23 to 41 wt.% resulted in rising the membrane ionic conductivity owing to the increase of conductive regions. Furthermore, membrane ionic conductivity increased by rising the operating temperature from 25 to 120 °C owing to the ionic mobility enhancement. M_3 membrane showed the highest ionic conductivity of 0.443 mS·cm^{-1} at 120 °C under anhydrous condition. The stable ionic conductivity of composite membranes (M_1, M_2, and M_3) at 100 °C during 24 h reveals the excellent potential of CAB/[DETA][TFS]-[DEPA][BUPH] composite membranes for HT-PEMFC application for long-term utilization. It was confirmed the proton conduction takes place by Grotthuss mechanism since the calculated E_a > 14 kJ·mol^{-1}. The results prove that the fabricated CAB/[DETA][TFS]-[DEPA][BUPH] composite membranes are promising candidates for using in electrochemical applications, namely fuel cell.

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