Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he

Novel composite membranes based on dicationic ionic liquid and polybenzimidazole mixtures as strategy for enhancing thermal and electrochemical properties of proton exchange membrane fuel cells applications at high temperature

Khadijeh Hooshyari [a,b], *Mehran Javanbakht* [a,b,*], *Mina Adibi* [c]

[a] *Department of Chemistry, Amirkabir University of Technology, Tehran, Iran*

[b] *Solar Cell and Fuel Cell Lab, Renewable Energy Research Center, Amirkabir University of Technology, Tehran, Iran*

[c] *Gas Transportation and Processing Technology Development Division, Research Institute of Petroleum Industry (RIPI), P.O. Box 14665-137, Tehran, Iran*

ARTICLE INFO

Article history:
Received 8 January 2016
Received in revised form
17 April 2016
Accepted 28 April 2016
Available online 26 May 2016

Keywords:
Polybenzimidazole
Polymer electrolyte membranes
Composite membrane
Casting method
Dicationic ionic liquid

ABSTRACT

In this work, innovative proton exchange membranes containing dicationic ionic liquids are developed for elevated temperature fuel cells applications under anhydrous conditions. The composite membranes based on polybenzimidazole (PBI) and dicationic ionic liquid 1,6-di(3-methylimidazolium) hexane bis (hexafluorophosphate) (PDC_6) or monocationic ionic liquid 1-Butyl-3-methylimidazolium hexafluorophosphate (PMC_4) are prepared with solution casting method. The analyses of the results demonstrate promising characteristics such as high ionic conductivity and fuel cell performance of phosphoric acid (PA) doped PDC_6 composite membranes in comparison with PA doped PMC_4 and PA doped PBI membranes at high temperatures. Dicationic ionic liquid with high number of charge carriers provides suitable ionic channels for proton transfer in PA doped PDC_6 composite membranes. The ionic conductivity of 78 mS cm^{-1} and power density of 0.40 W cm^{-2} (at 0.5 V) are achieved for PA doped PDC_6 composite membranes with PBI/ionic liquid mole ratio: 4 at 180 °C under anhydrous condition.

Introduction

Nafion is the most common and commercially available proton exchange membrane (PEM) for PEM fuel cells [1,2]. However, it is limited for application at temperatures below 80 °C [3]. The improvement of membranes for use in high temperature PEM (HT-PEM) fuel cells under anhydrous conditions is rather ambitious [4]. HT-PEM fuel cells have attracted great interests in recent years due to their advantages

* *Corresponding author*. Department of Chemistry, Amirkabir University of Technology, Tehran, Iran.
E-mail address: mehranjavanbakht@gmail.com (M. Javanbakht).

http://dx.doi.org/10.1016/j.ijhydene.2016.04.245

compared with low temperature PEM fuel cells. Elevating the operating temperature provides improved carbon monoxide tolerance, faster electrode kinetics, simpler thermal and water management and more efficient recovery of waste heat as a practical energy source [5,6].

Polybenzimidazole (PBI) is an exceptional candidate for use in HT-PEM fuel cells [7]. PBI is commercially available at a relative low cost and shows outstanding stability in both reducing and oxidizing environments [8–10]. The intrinsic proton conductivity of PBI is low, about 10^{-9} mS cm^{-1}. Hence PBI needs to be doped with acid to achieve adequate proton conductivity for fuel cell operation [11]. Therefore conductors with less dependency on the hydration state are desired. Phosphoric acid (PA) is a good candidate which shows considerable proton conductivities in pure state that forms hydrogen bonding networks [12]. The PA doped PBI (PA-PBI) membranes at high acid-doping levels, in a range of 4–6 mol, exhibit high ionic conductivity (about 40–70 mS cm^{-1}) at high temperatures without humidifying [13,14]. Although the use of PA introduces high proton conductivity, the presence of PA has disadvantage regarding chemical stability at temperatures above 150 °C. PA was autodehydrated at temperatures above 150 °C to form lower conductivity oligomers like pyrophosphoric acid [15]. The deployment of ionic liquids (ILs) as proton transport carriers is clearly advantageous for operation above 150 °C when PA autodehydration becomes a serious limitation [16]. Pyrophosphoric acid obtained from PA autodehydration decreases ionic conductivity of PA-PBI membranes because of low ionic conductivity of pyrophosphoric acid compared PA.

ILs are purely ionic materials with a melting temperature often around room temperature. They typically consist of a large organic cation and an anion that possesses a highly delocalized charge. The advantage of ILs over PA is their excellent thermal stability at higher temperatures (>150 °C) and their more environmentally friendly character [14]. ILs have very interesting properties as high temperature electrolytes due to their negligible volatility, chemical and thermal stability, non-flammability and high ionic conductivity [17,18]. Thus, they could be good candidates for HT-PEM fuel cells. The ionic conductivity values for monocationic ILs were obtained in the range 0.1–10 mS cm^{-1}, depending on the cation used [19]. One of the most widely used and studied IL families is based on imidazolium cations, in particular 1-Butyl-3-methylimidazolium hexafluorophosphate [20,21]. The reason is that these ILs are very versatile and easy to prepare. Hexafluorophosphate (PF_6) anion is a typical anion in ILs that, because of its relatively large size. Therefore the resulting salt has a melting point around or below room temperature in monocationic ILs.

Several composite membranes based on PBI and imidazolium based ILs have been prepared and analyzed for application in HT-PEM fuel cells [22–26]. ILs are able to transport protons due to their acid-base character and their capability for hydrogen bonding. Greenbaum et al. used the 1-propyl-3-methylimidazolium dihydrogen phosphate to increase the proton conductive character of PBI membrane for operation in high temperatures [24]. These developed composite membranes were flexible and freestanding with good thermal stability. The ionic interaction between PBI and ILs resulted in the formation of homogeneous membranes. Jacob et al. prepared PBI/1-hexyl-3-methylimidazolium trifluoromethanesulfonate composite membranes which demonstrated high thermal stability and achieved high ionic conductivity at 250 °C under anhydrous conditions [25].

So far, most studies have primarily involved the monocationic type ILs but less attention has been paid to dicationic ILs with respect to electrochemical applications [27–29]. Dicationic ILs are new family of ILs and consist of a doubly charged cation that are composed of two singly charged cations linked by an alkyl chain spacer and paired with two singly charged anions [30,31]. The greater number of possible combinations of cation and anion in dicationic ILs allows a broader variability of the properties for dicationic ILs compared with monocationic ILs would be possible [31]. The results obtained from dicationic ILs have shown that these ILs have high density, glass transition temperature (T_g), and melting point. Also, the surface tension was large, and the viscosity was high in comparison with the reference monocationic ILs [32,33].

The main advantage of dicationic ILs is that they have a higher thermal stability compared to traditional monocationic ILs [28]. The ionic conductivity values of dicationic ILs still have not been studied in detail, and few studies have been devoted to conductivity mechanism in dicationic ILs. However, some recent studies have shown that the ionic conductivity of dicationic ILs, depending on used cations and anions, was obtained in conductivity range of the monocationic ILs [27]. In these studies, a series of imidazolium-based geminal dicationic ILs with cations consisting of two identical imidazolium rings linked together by alkyl chains of different lengths were studied [34]. Several researchers have reported that dicationic ILs, similar to monocationic ILs, can be used equally well as electrolytes in secondary batteries [35,36], supercapacitors [37,38], solar cells [39] and catalysts [40,41] particularly at high temperatures due to their high stability. In this work for the first time we prepared composite membranes based on dicationic ILs and PBI to improve thermal properties of those conventional based on monocationic ILs and PBI. We improved novel composite membranes based on PBI and dicationic IL 1,6-di(3-methylimidazolium) hexane bis (hexafluorophosphate). For comparison purpose, PBI membranes containing monocationic IL 1-Butyl-3-methylimidazolium hexafluorophosphate were also prepared. We found that the composite membranes based on PBI and dicationic IL demonstrated high ionic conductivity, mechanical stability and thermal stability. PA uptake values of the prepared composite membranes have been systematically analyzed and the results displayed that the dicationic IL has best interaction with PA in PBI matrix. The performance of PBI membranes containing dicationic IL in HT-PEM fuel cells applications is evaluated in terms of ionic conductivity and fuel cell power output under anhydrous conditions compared to that of PBI membranes containing monocationic IL.

Experimental

Materials

PBI was obtained from Fuma tech. PA and N,N-dimethylacetamide (DMAc) were purchased from Merck. LiCl was purchased from Aldrich. The highly pure monocationic IL