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Preparation and characterization of imidazolium-functionalized poly (ether sulfone) as anion exchange membrane and ionomer for fuel cell application

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ABSTRACT

Imidazolium-functionalized anion exchange membranes (AEMs) for anion exchange membrane fuel cells (AEMFCs) were synthesized by functionalization of chloromethylated poly (ether sulfone) (PES) with 1-alkylimidazole. The properties of AEMs can be controlled by the degree of chloromethylation of PES. Moreover, with the increment of the alkyl line length on the imidazolium group, the water uptake, swelling ratio and solubility of AEMs increased, whereas the hydroxide conductivity declined. By dissolving AEMs in the mixture of ethanol and water, IM-based anion exchange ionomers (AEIs) can be obtained. Electrochemical studies revealed that the catalytic activities of Pt/C towards oxygen reduction and hydrogen oxidation in the presence of imidazolium-functionalized AEIs were almost the same with that of commercial quaternary ammonium-based ionomers. The fabricated AEM and AEI were utilized to assemble H₂/O₂ AEMFC, yielding a peak power density of ~30 mW cm⁻² with open circuit potential larger than 1.0 V. The results obtained indicate that imidazolium-functionalized AEMs and AEIs may be candidates which are worth further investigation for the application in the AEMFCs.

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1. Introduction

In the near past decades, considerable attention has been paid to fuel cells because of high efficiency and low pollution levels. As especially developed for portable and electric vehicle applications, proton exchange membrane fuel cells (PEMFCs) received much attention and preferential development [1]. However, the utilization of Pt based cathode

electrocatalysts has become one of the obstacles that impede the large-scale commercialization of PEMFCs [2]. Compared with PEMFCs, numerous advantages, such as faster oxygen reduction reaction (ORR) kinetics, desirable applicability of non-precious metals as catalyst and milder corrosion environment [3,4], can be achieved under alkaline conditions. Therefore, increasing interests were attached to the exploitation of AEMFCs. Therein, AEM and AEI play inherently

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significant roles in improving fuel cell performance. The AEM transports hydroxide from the cathode to the anode and prevents the mix of reactants. The AEI was used to provide hydroxide conducting channels in the electrode to build three-phase boundaries where electrochemical reaction takes place [5].

Up to now, the quaternary ammonium (QA) has been the most extensively studied anion conductive head groups in AEMs [3,6]. However, the QA groups are usually suffered from poor solubility in low-boiling-point solvents [7,8] and degradation by Hofmann elimination and S_N2 displacement especially under high temperature and pH [4,9,10]. In the last few years, many efforts have been made to develop AEMs without QA groups [3]. Therein, imidazolium (IM)-based AEMs received much attention, due to their facile fabrication, high hydroxide conductivity, good chemical stability and desired selective solubility [7,11–16]. Nevertheless, the application of IM-based AEMs in H_2/O_2 fuel cell was very limited and the performances reported were far from satisfactory. Zhang et al. [16] used IM-functionalized polysulfone as the AEM and AEI spontaneously in H_2/O_2 fuel cells. The peak power density (P_{max}) of the fuel cell was 16 mW cm^{-2} but the cell performance could last only a few minutes and decayed gradually to zero. Furthermore, Deavin et al. [4] investigated the performances of QA and IM groups on non-aromatic polymer backbone. They found that IM-based and QA-based AEMs showed similar ion exchange capacity and anion conductivity, but the P_{max} of fuel cell utilizing IM-based polymer was only $\sim 1.1 \text{ mW cm}^{-2}$ which was far less than that of $\sim 150 \text{ mW cm}^{-2}$ for fuel cell having QA-based AEM and AEI. Although Ran et al. [14] reported a P_{max} of 30 mW cm^{-2} could be achieved by using IM-based poly (phenylene oxide) membrane, the ionomer applied in their work was still QA-based polymers. According to the results above, it appears that IM-based polymers are not suitable for the application in AEMFCs. But is it the truth?

On the basis of the literature, the hydroxide conductivity of IM-based membranes can reach as high as that of QA-based membranes, at least 10 mS cm^{-1} at room temperature [4,13,16]. That is, the IM-based membranes meet the conductivity requirement for the fuel cell application [17]. As a result, the poor performance of AEMFCs adopting IM-based AEM and AEI may be resulted from the poor performance of ionomer or the poison effect on the catalyst applied by ionomer. In the electrode, the ionomer directly contacts the catalysts, and whether the groups on the ionomer will deteriorate the activity of catalysts should be well understood. Recently, our group found that imidazole-based ionic liquids were not suitable for the application of PEMFCs, because imidazole-based ionic liquids strongly poisoned the Pt/C catalyst in acidic medium [18]. To date, in the development of AEI, studies of the interaction between AEI and catalysts, and the effect of AEI towards the activity of catalysts has not been reported.

Based on the existing literature, the IM groups of reported AEMs were mainly methyl substituted [4,7,11,13–15]; the effect of the aliphatic substituent group length of IM on the properties of IM-functionalized polymer was, to the best of our knowledge, seldom reported. In addition, as the backbone matrix of the AEM, good chemical stability and mechanical

strength are required [7,14]. PES is a well-known engineering polymer with good solubility, thermal stability, chemical resistance and mechanical properties, thus PES is suitable to serve as the backup matrix of AEMs.

Herein, we made use of PES as the polymer backbone to prepare IM-functionalized polymers. The properties of IM-based AEMs can be controlled by the degree of chloromethylation (DCM) of PES. The effect of the alkyl line length of the IM group on the properties of IM-based PES was studied. Furthermore, the influence of IM-based and commercial QA-based AEI on the catalytic activity of Pt/C catalysts towards hydrogen oxidation reaction (HOR) and ORR were evaluated in 0.1 M KOH aqueous solutions. On the basis of the fabricated AEM and AEI, H_2/O_2 AEMFCs with varied ionomer contents in the electrode were assembled, and a P_{max} of $\sim 30 \text{ mW cm}^{-2}$ could be yielded at $45 \text{ }^\circ\text{C}$, which is as high as that of fuel cell with QA-based ionomer reported by Ran et al. [14], indicating the feasibility of IM-based ionomer in fuel cells.

2. Experimental

2.1. Chloromethylation of PES

Typically, 2 g PES (reduced viscosity = 0.36 dl g^{-1} in N,N-Dimethylformamide (DMF) at $25 \text{ }^\circ\text{C}$, produced by Changchun Jilin University Special Plastic Engineering Research) was dissolved into 30 mL ice-cold 98% concentrated H_2SO_4 followed by addition of 5 mL of 1, 4-bis (chloromethoxy) butane (BCMB) ($\geq 95\%$, Xi'an Langene Bioscience Co. Ltd). Subsequently, the reaction was kept in the ice-water bath for some time and the product was separated by precipitation the mixture in ice water, followed by thorough washing with de-ionized water, and then drying at $50 \text{ }^\circ\text{C}$ in air. Then the chloromethylated PES (CMPES) was obtained.

2.2. IM-functionalized PES fabrication

For the fabrication of 1-methylimidazole functionalized PES (PES-MeIm), CMPES was dissolved in 1-methylimidazole ($>99\%$, Aladdin) to give a polymer concentration of $5 \text{ wt. } \%$, and this polymer solution was stirred at room temperature for 24 h . Then the solution was poured onto a glass plate to cast the membrane and dried in oven at $80 \text{ }^\circ\text{C}$ for 24 h . The membrane obtained was denoted as PES-MeIm/Cl. The average thickness of PES-MeIm/Cl membrane with different DCM was close (Table S1). Subsequently, the PES-MeIm/Cl membranes were immersed in a 1 M KOH solution for 24 h , converting the membranes from the Cl^- form into the OH^- form (PES-MeIm/OH), followed by washing with de-ionized water several times and storing in de-ionized water for another 48 h to completely remove the residual KOH prior to further experiments.

The procedures for the fabrication of 1-ethylimidazole functionalized PES (PES-EtIm) were the same as that of PES-MeIm, except that 1-methylimidazole was replaced by 1-ethylimidazole ($>99\%$, TCI). For the fabrication 1-butylimidazole functionalized PES (PES-BuIm), 0.4 g CMPES was dissolved in 1-methyl-2-pyrrolidone (NMP) followed by

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