



Synthesis and characterization of novel anion exchange membranes based on imidazolium-type ionic liquid for alkaline fuel cells

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ABSTRACT

Novel anion exchange membranes based on the copolymers of 1-allyl-3-methylimidazolium chloride (AmimCl) ionic liquid either with methyl methacrylate (MMA) or butyl methacrylate (BMA) have been prepared via free radical polymerization. The structures and characteristic properties of the membranes are studied. It is found that the hydroxyl ionic conductivity of the synthesized membrane can reach $3.33 \times 10^{-2} \text{ S cm}^{-1}$ in deionized water at 30 °C. The methanol permeability is less than $10^{-9} \text{ mol cm}^2 \text{ s}^{-1}$ even at 60 °C. These membranes with imidazolium salt functional groups exhibit superior stability both chemically and thermally as well compared to the alkyl quaternary ammonium functionalized polymers. Therefore, the membranes have good perspectives and great potential for alkaline fuel cell applications.

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1. Introduction

The direct methanol fuel cell (DMFC) is regarded as a promising green energy conversion solution for electric vehicles and portable power applications due to the high fuel energy density, readily stored and available liquid fuel [1]. The polymer electrolyte membrane, which separates methanol and oxygen and transfers ions between the anode and cathode, is the core component of the DMFC. Nafion® membrane (produced by DuPont), a proton exchange membrane, is widely used as the polymer electrolyte membrane in DMFC due to its high ionic conductivity, excellent thermal and chemical stability. However, this membrane suffers from high methanol crossover and high cost [2,3].

Alkaline direct methanol fuel cell (ADMFC) is receiving more and more attentions recently [4]. It uses the anion exchange membrane (AEM) as polymer electrolyte membrane instead of proton exchange membrane and has several merits, such as: (a) both methanol oxidation and electrode-kinetic of oxygen reduction are enhanced [1,5]; (b) methanol crossover can be reduced by electro-osmotic, because the pathway of OH⁻ anion movement is opposite to the direction of the methanol flux through the membrane [1,6,7]; (c) in alkaline medium, platinum-based catalysts are not necessary, non-precious metal catalysts can be used [8,9]; (d) since the water

is produced at the anode and consumed at the cathode, the water management can be simplified [7,10].

Up to date, most of the research works on the development of AEMs for application in fuel cells were focused on the quaternized polymers [7,10]. Some AEMs were prepared via quaternization following chloromethylation of the commercial available polymers containing aromatic rings, such as, poly(phthalazinone ether sulfone ketone) (PPESK) [6], polyepichlorohydrin homopolymer [11], polysulfone [12], polyetherketone cardo (PEK-C) [13], and polyethersulfone cardo [14]. And the others were synthesized via quaternization of the polymers containing vinylbenzyl chloride (VBC) units, which could be produced by radio grafting method [15] or free radical polymerization route [10]. However, the materials using alkyl quaternary ammonium groups as anion exchange groups are verified to be unstable in alkaline medium, especially at elevated temperatures [16]. Low ionic conductivity, poor thermal and chemical stabilities are serious obstacles on the way towards commercially applying AEMs to alkaline fuel cells.

Ionic liquids, a new class of organic molten electrolytes at or near ambient temperature, are novel environmentally benign solvents and have remarkable physicochemical properties, such as ideal conductivity, wide electrochemical window, and excellent thermal and chemical stability. They are also considered to be designer solvents, since their properties can be appropriately tuned and developed for different applications [17–20]. Aiming to explore novel anion exchange membranes which are high conductive, stable at elevated temperatures and soluble in certain solvents, imidazolium-type ionic liquids have been using as monomers for

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polymerization in our works. In this study, we originally report the preparation and characterization of anion exchange membranes based on the copolymers of 1-allyl-3-methylimidazolium chloride (AmimCl) ionic liquid and methyl methacrylate (MMA)/butyl methacrylate (BMA). These membranes using imidazolium salt as functional groups are stable up to 80 °C in a concentrated sodium hydroxide aqueous solution (6 mol L⁻¹). The hydroxyl ionic conductivity of the membrane can reach 3.33 × 10⁻² S cm⁻¹ in deionized water at 30 °C. These results suggest that the membranes could provide an attractive alternative for alkaline anion exchange membrane fuel cell applications.

2. Experimental section

2.1. Materials

AmimCl (98%) was purchased from Alfa Aesar Company and used as received. The other reagents used in this study were analytical grade and purchased from China National Medicines Corporation Ltd. Methyl methacrylate (MMA) and butyl methacrylate (BMA) were distilled before use. Azobisisobutyronitrile (AIBN) was recrystallized before used as an initiator for radical polymerization.

2.2. Preparation of alkaline anion exchange membrane

The preparation of alkaline anion exchange membrane was carried out in three steps: copolymerization, membrane preparation and alkalization.

2.2.1. Copolymerization and membrane preparation

According to the designed synthetic protocol, AmimCl ionic liquid and MMA/BMA were selected as monomers for copolymerization using AIBN as an initiator.

The schematic diagram for copolymerization of AmimCl with MMA is shown in Fig. 1. The copolymerization of AmimCl with BMA using the same synthetic route and the structure of the resultant copolymer is shown in Fig. 2. The *x* and *y* in Figs. 1 and 2 can be calculated by measuring N content by elemental analysis.

The copolymerization was performed at 65 °C for 12 h in dry DMF under a nitrogen atmosphere. The resultant copolymers, either poly(AmimCl–MMA) or poly(AmimCl–BMA) were precipitated by cooled methanol three times and dried at 60 °C overnight. A gram of the copolymer was dissolved in 20.12 mL DMF to make a 5 wt% solution. The solution was filtered and poured onto a glass dish and dried at 70 °C for 10 h. The Cl⁻ form membranes were made and removed from the glass dishes [21].

2.2.2. Alkalization

The Cl⁻ form membranes were immersed in 1 mol L⁻¹ NaOH solution at room temperature for 24 h to convert the membrane from Cl⁻ form to OH⁻ form. After that, the membranes were washed with distilled-deionized water until neutral and stored in deionized water for further use. The thickness of the anion exchange membranes were controlled between 30 and 60 μm.

2.3. Morphological and structure characterization

The chemical structure of the anion exchange membranes were confirmed with a FT-IR 740SX spectrophotometer (Thermo Electron Corporation, USA). The morphologies of the membranes were with a HITACHI S-4800 (field emission scanning electron microscope, Japan). The thermal analysis of the membrane samples were performed by using a TG209F1 (NETZSCH, Germany) with the controlled heating rate of 10 °C min⁻¹ in the temperature from 30 to 600 °C under a nitrogen atmosphere.

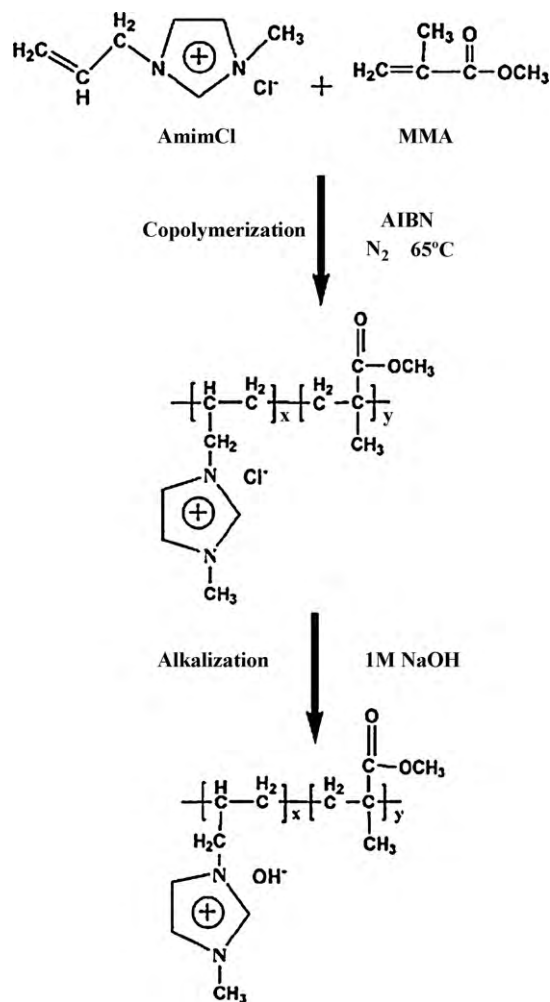


Fig. 1. Synthesis of poly(AmimCl–MMA) membrane in OH⁻ form: copolymerization and alkalization.

The viscosities of the copolymers were determined by Ubbelohde viscometer at room temperature (298.15 K). The N contents of the membranes were measured by Elementar Vario EL III (Elementar Analysen System GmbH, Germany).

2.4. Liquid uptake

Liquid uptake of the membranes were determined by the method reported by Kolhe and Kumar [22], which was carried out

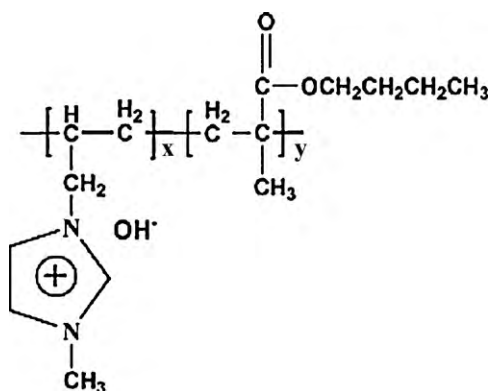


Fig. 2. Structure of poly(AmimCl–BMA) anion exchange membrane in OH⁻ form.

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