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Alkaline stable C2-substituted imidazolium-based cross-linked anion exchange membranes for alkaline fuel cell applications

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HIGHLIGHTS

- C2-substituted imidazolium salt was synthesized and used both as crosslinker and hydrophilic phase.
- The imidazolium-based AEMs show the conductivity up to 2.0×10^{-2} S cm^{-1} at 90 °C.
- The imidazolium-based AEMs show good chemical stability in 1 M KOH solution.

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ABSTRACT

Novel C2-substituted imidazolium-based cross-linked anion exchange membranes (AEMs) are prepared via irradiation with ultraviolet light cross-linking of styrene, acrylonitrile and 1,3-diallyl-2-methyl imidazolium bromine ([DAMIm][Br]), and followed by anion exchange with hydroxide ions. [DAMIm][Br] is synthesized and used both as crosslinker and hydrophilic phase. The ionic conductivity of the AEMs increases with increasing [DAMIm][Br] content due to the hydrophilic regions and the continuous hydrophilic polymeric networks formed in the membranes. The imidazolium-based cross-linked AEMs show excellent thermal stabilities, and the membrane which containing 30% mass fraction of [DAMIm][Br] shows ionic conductivity up to 2.0×10^{-2} S cm^{-1} and good long-term chemical stability in 1 M KOH solution. The results of this study suggest that the C2-substituted imidazolium-based cross-linked AEMs have good perspectives for alkaline fuel cell applications.

1. Introduction

Fuel cells have been recognized as one of the most promising power generation technologies that could provide clean and efficient energy for stationary, transportation, and portable electronics [1–3]. Among all kinds of fuel cells, proton exchange membrane fuel cells (PEMFCs) attracted much attentions due to their high power density, high energy-conversion efficiencies, low starting temperature, and ease of handling [4,5]. Nafion® perfluorosulfonic acid membranes, the most established and state-of-the-art proton exchange membranes (PEMs) used in PEMFCs, have high proton conductivities, good mechanical properties and excellent chemical stability [6,7]. However, the application of Nafion in PEMFCs is limited by their high production cost, environmental incompatibility of the perfluorinated materials, high gas permeability and insufficient thermomechanical properties above 80 °C [8,9]. In addition, the dependence of platinum catalysts of PEMFCs is an important consideration because of the high cost and the limited platinum resource in nature [10–12].

To solve these problems mentioned above, recently, great interests have been evoked on alkaline anion exchange membrane fuel cells (AEMFCs) which are a type of fuel cells using anion exchange membrane (AEM) instead of PEM as electrolyte. Compared with PEMFCs, the high pH operation of AEMFCs could both enhance the electrokinetics and reduce CO poisoning. In addition, the basic conditions of AEMFCs enable the use of non-precious metal catalysts (such as nickel and silver) instead of platinum catalysts [10,11],

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which dramatically lowers the cost of fuel cells. The advantages mentioned above make the AEMFC technology financially and technically doable.

As the core component of AEMFCs, AEMs have attracted much attentions. An excellent AEM for an AEMFC must have good chemical and thermal stability, sufficient mechanical strength, and high ionic conductivity. In the past several years, the AEMs containing quaternary ammonium cationic groups have been extensively studied [13–16]. They are commonly prepared by attachment of chloromethyl groups to polymer backbones and followed by quaternization to form ammonium salts. However, it has been demonstrated that quaternary ammonium-based AEMs are unstable in alkaline medium, especially at elevated temperatures [17,18]. Since the chemical stability of an AEM is strongly dependent on the nature of the cations, cations such as guanidinium cations [19–21], quaternary phosphonium cations [22–25], imidazolium cations [26–36] and benzimidazolium cations [37–40] other than quaternary ammonium cation groups based polymers have been recently extensively studied. Among the different kinds of AEMs, imidazolium-based AEMs have attracted much attention. Fang et al. [29] reported an imidazolium-based AEMs which prepared via free radical copolymerization and solution-casting method. After treatment with 10 M NaOH solution at 60 °C for 120 h, the conductivity of the membranes showed no significant change, which indicated the good chemical stability of the imidazolium-based AEMs. Yan et al. [33] reported a cross-linked imidazolium-based AEM which displays an excellent chemical stability up to 400 h in high pH solution without obvious loss of ion conductivity and mechanical properties. Though imidazolium cations show relatively higher chemical stability than ammonium cations in a wide range of alkaline condition, degradation was observed for imidazolium-based AEMs under vigorous conditions (such as dry conditions, higher temperature and alkaline concentrations) in our previous work [41]. These results suggest that imidazolium cations have considerable chemical stability in alkaline condition, but it still needs to be improved. The protection of cationic groups by steric hindrance and/or mesomeric stabilization might be a prospect way to enhance the chemical stability of cations. In our previous work, we found that C2-substituted imidazolium salts showed much more chemical stability than C2-unsubstituted imidazolium salt under alkaline condition at elevated temperature, and the compound with methyl at C2 position of imidazole ring (3-ethyl-1,2-dimethyl imidazolium bromine) showed the best alkaline stability in the four kinds of imidazolium salts [41].

More recently, Hickner's study showed that the main chain backbone structure of the polymers significantly influenced on the alkaline stability of the quaternary ammonium cations [42]. Their results indicated that the quaternary ammonium cations on vinyl polymer (QA-PS) have much more alkaline stability than that on main chain type aromatic polymers. However, vinyl polymer-based membranes generally have poor mechanical properties, especially when hydrated [42]. Thus, strategies to reinforce the mechanical properties of functionalized vinyl polymer-based AEMs are required. Chemical cross-linking is a feasible and effective method for improving the mechanical properties of membranes. Yan et al. synthesized an imidazolium-based cross-linked AEMs, and divinylbenzene (DVB) used as the crosslinker [33]. The mechanical properties of membranes increased with the increment of DVB content. However, the conductivity of the membranes decreased with increasing of DVB content because of DVB shows no ionic conductivity.

In the present work, a cross-linked vinyl polymer-based AEMs were synthesized and characterized. 1,3-Diallyl-2-methyl imidazolium bromine ([DAMIm][Br]) was synthesized and used both as crosslinker and hydrophilic phase. The properties of the membranes, such as water uptake, swelling degree, thermal stability, mechanical properties, ion exchange capacity (IEC), hydroxide ion conductivity and chemical stability were investigated.

2. Experimental

2.1. Materials

Styrene, acrylonitrile, ethyl ether, ethyl acetate, acetonitrile, chloroform, potassium hydroxide, anhydrous $MgSO_4$, sodium hydroxide and hydrochloric acid were purchased from Aladdin (Shanghai). 2-Methylimidazole, 3-bromo-1-propene and benzoin ethyl ether were purchased from Alfa Aesar. All of the vinyl monomers were made inhibitor-free by passing the liquid through a column filled with base Al_2O_3. Distilled deionized water was used for all experiments.

2.2. Synthesis of 1-allyl-2-methylimidazole

1-Allyl-2-methylimidazole was synthesized as follows: a mixture containing 2-methylimidazole 4.10 g (0.05 mol), 3-bromo-1-propene 6.05 g (0.05 mol), and 5.61 g (0.10 mol) KOH in acetonitrile (40 mL) was stirred at room temperature for 4 h under an argon atmosphere. The solvent was removed under dynamic vacuum, and the crude product was extracted with $CHCl_3$ three times. The combined organic phase was washed with distilled water and dried over anhydrous $MgSO_4$, and the solvent was removed under vacuum. The resultant yellow oil was dried in dynamic vacuum at room temperature. ^1H NMR (400 MHz, $CDCl_3$): δ: 6.87–6.89 (d, 1H), 6.76–6.78 (d, 1H), 5.82–5.90 (m, 1H), 5.16–5.19 (d, 2H), 4.92–4.96 (d, 1H), 4.39–4.41 (m, 2H), 2.30 (s, 3H).

2.3. Synthesis of 1,3-diallyl-2-methyl imidazolium bromine ([DAMIm][Br])

[DAMIm][Br] was synthesized by stirring the mixture of 1-allyl-2-methylimidazole with an equivalent molar amount of 3-bromo-1-propene at room temperature under nitrogen atmosphere. The resultant viscous oil was washed with ethyl ether three times and then dried in dynamic vacuum at room temperature for 24 h. ^1H NMR (400 MHz, D_2O): 7.35 (s, 2H), 5.90–6.00 (m, 2H), 5.32–5.34 (d, 2H), 5.09–5.14 (d, 2H), 4.71–4.73 (d, 4H), 2.52 (s, 3H).

2.4. Preparation of cross-linked composite membranes

A mixture of styrene/acrylonitrile (1:3 weight ratio, 90–70 wt%), [DAMIm][Br] (10–30 wt%), and benzoin ethyl ether (photo-initiator 1 wt% to the formulation based on the weight of monomer) was stirred and ultrasonicated to obtain a homogeneous solution, which was then cast into a glass mold and photo-cross-linked by irradiation with UV light of 250 nm wavelength in a glass mold for 30 min at room temperature. The resultant composite membranes were immersed in a N_2 saturated 1 M KOH solution at 60 °C for 24 h to convert the membrane from Br^- to OH^- form [43]. Then the converted membranes were immersed in a N_2 saturated deionized water and washed with N_2 saturated deionized water until the pH of residual water was neutral.

2.5. Characterization

^1H NMR spectra were recorded on a Varian 400 MHz spectrometer. Fourier transform infrared (FT-IR) spectra of the membranes were recorded on a Varian CP-3800 spectrometer in the range of 4000–400 cm^{-1}. Thermal analysis was carried out by Universal Analysis 2000 thermogravimetric analyzer (TGA). Samples were heated from 30 to 600 °C at a heating rate of 10 °C min^{-1}