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A stable anion exchange membrane based on imidazolium salt for alkaline fuel cell

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ABSTRACT

A series of poly(arylene ether sulfone) containing bulky imidazole groups (PSf-Im-*x*) have been successfully synthesized based on a novel monomer 2,2′-bis-(2-ethyl-4-methyl-imidazole-1-ylmethyl)-biphenyl-4,4′-diol (EMIPO). After quaternized by n-bromobutane, these polymers are evaluated for alkaline anion exchange membranes (AEMs). The functional group, 2-ethyl-3-butyl-4-methyl-imidazolium, is employed in these new polymers for reason that attaching bulky groups around the imidazolium ring reduces the access of OH^- to imidazolium, which enhances the alkaline stability of the membranes. The membrane with an IEC value of 2.07 possesses ionic (OH^-) conductivity of 0.014 S cm^{-1} at 30 °C and 80% of the ionic conductivity is maintained after treatment in 1 M KOH at 60 °C for 144 h.

1. Introduction

Solid-state alkaline exchange membrane fuel cell (AEMFC) is considered to be a more promising energy conversion device for stationary and mobile applications compared with the acidic fuel cell because of the enhanced reaction kinetics for both oxygen reduction and fuel oxidation in the alkaline medium, which can lead to higher efficiencies and enable the use of non-precious metal catalysts, greatly reducing the cost of the device [1]. Anion exchange membrane (AEM), transporting hydroxide or other anions from the cathode to the anode, is one of the key components of AEMFC. An ideal AEM should exhibit high ionic conductivity, good mechanical integrity, and robust thermal and chemical stability. Up to date, quaternary ammonium (QA) containing AEM materials have been most extensively studied as the candidate electrolyte for AEMFC [1]. Various of polymer backbones containing QA groups have been investigated, such as radiation-grafted fluorinated polymers [2], poly(arylene ether sulfone) [3,4], poly (arylene ether ketone) [5–7], poly(2,6-dimethyl-1,4-phenylene oxide) [8,9], polyphenylene [10], as well as olefin-based cross-linked networks [11,12]. However, the main issue with QA-AEM is its low stability under the working condition of AEMFC (i.e. above 60 °C, and high pH) due to the degradation of QA groups via (i) Hoffmann elimination (E_2), (ii) nucleophilic substitution (S_N2) [13]. Although the E_2 reaction can be circumvented by avoiding a coplanar arrangement of β-hydrogen and nitrogen or by synthesizing β-hydrogen-absent quaternary ammoniums, most alkyl ammonium-functionalized polymers still have not realized sufficient stability because of the S_N2 reaction. In the S_N2 reaction, hydroxide ions attack the α-carbon of the ammonium cations. The extent of polymer degradation via the S_N2 reaction may be reduced by replacing alkyl ammonium with bulky cations such as guanidinium or phosphonium, which stabilize the α-carbon–nitrogen bond by charge delocalization of the cations [14].

More recently, interesting work has been carried out to explore the possibility of moving to non-QA AEMs, containing phosphonium [15–17], guanidinium [18,19] and imidazolium [20–22], for avoiding the drawbacks of QA membranes. Imidazolium-based AEMs are of interest due to the five-membered heterocyclic ring and π conjugated structure of the imidazolium cation, which is expected to have good stability in alkaline condition. However, a recent study which provides a thorough analysis of chemical stability for an imidazolium-based polymerized ionic liquid (PIL), showed that the imidazolium group was not stable as expected [7,23,24]. Benzylmethylimidazolium(BMI)-head-group is even less stable than the benzyltrimethylammonium(BTM)-head-group in alkaline conditions [24].

The problems associated with the use of imidazolium-based ionic liquids under strongly basic conditions may arise from the hydrolysis of the imidazolium cations as shown in Scheme 1 [25]. In the first step, the OH^- was added to the C2, yielding a non-aromatic 2,3-dihydro-1,3-dimethylimidazole-2-ol with a saturated carbon atom. This intermediate is quite polarized, and is therefore destabilized and undergoes ring open to an aminoketal. On the basis of above hydroxide decomposition mechanisms of small-molecule

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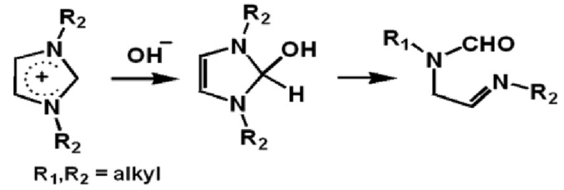
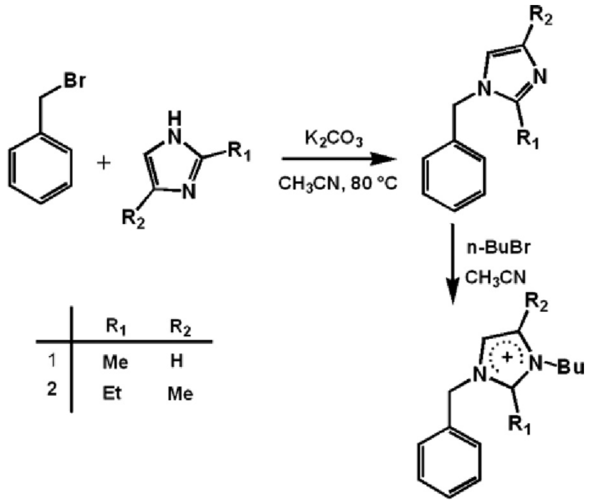


Scheme 1. Decomposition of imidazolium cation.



Scheme 2. Synthesis of the model compounds.

imidazolium salts, installation of bulky groups around the reactive C2 position may hinder nucleophilic attack by OH^-, thus improving the stability of the hydroxide form [26–29]. Recently, Varcoe and coworkers reported the enhanced stability of imidazolium salts with shielding of C2 position through comparing the C2-unsubstituted imidazolium salts with the C2-substituted imidazolium salts [26]. Yan and coworkers demonstrated that installation of bulky groups around in C2-position could improve the stability of the imidazolium salts due to the steric hindrance effect and the σ–π hyperconjugative effect of the C2-substituted groups [27a]. To examine this, we prepared and compared the imidazolium salts 1 and 2 (Scheme 2) with a bulky group and a less-bulky group, respectively, attached at the C2 position in this paper.

Our group has previously reported polymer networks bearing pendant imidazole groups [30]. Using a similar strategy, we synthesized a biphenol monomer containing sterically crowded imidazole groups, of which the hydrogen at the C-2, 4 position has been replaced by bulky group. Use the novel monomer, we prepared a series of poly(arylene ether sulfone) polymers containing imidazolium groups. Membranes based on the polymers were characterized by water uptake, conductivity, and stability under strong alkaline condition.

2. Experimental

2.1. Materials

4, 4′-Biphenol (BP), 4, 4′-bifluorodiphenylsulfone, 2-methylimidazole and 2-ethyl-4-methylimidazole were purchased from Aldrich. Formaldehyde solution (37%), dimethylamine solution (33%), potassium carbonate (K_2CO_3), n-bromobutane, N,N-dimethylacetamide (DMAc) and dimethylbenzene were purchased from Sinopharm Group Chemical Reagent Co., Ltd. All other reagents were obtained from commercial sources and used as received. 2, 2′-Bimethylaminemethylene-4, 4′-biphenol was synthesized as reported in our previous paper [31].

2.2. Synthesis of monomers and polymers

2.2.1. Synthesis of model compound

2-Ethyl-4-methylimidazole (2.18 g, 19.8 mmol) or 2-methylimidazole (1.62 g, 19.8 mmol), K_2CO_3 (2.76 g, 20 mmol) were added to a solution of benzyl bromide (2.26 g, 13.2 mmol) in acetonitrile (50 mL). The reaction mixture was kept at reflux under stirring for 3 h and then filtered to eliminate K_2CO_3 and then acetonitrile was evaporated under reduced pressure. Water (50 mL) and dichloromethane (50 mL) were added to the residue. The organic phase was separated, and the solvent was evaporated under reduced pressure to give a pale yellow liquid (1.52 g, 8.30 mmol; 72% yield) [32]. Then 10 ml acetonitrile, n-bromobutane (3 mmol) was added to the pale yellow liquid, the reaction was stirred for 24 h at 80 °C. The reaction mixture was dried under reduced pressure to provide the model compound [33]. ^1H NMR of model compound 1 (DMSO-d_6, ppm): δ 7.20–7.24 (2H, dd), 7.05–7.06 (2H, d), 6.89 (2H, s), 6.86 (2H, s), 6.74–6.75 (2H, d), 5.05 (4H, s) and 3.42 (6H, s). ^1H NMR of model compound 2 (DMSO-d_6, ppm): δ 7.20–7.24 (2H, dd), 7.05–7.06 (2H, d), 6.89 (2H, s), 6.86 (2H, s), 6.74–6.75 (2H, d), 5.05 (4H, s) and 3.42 (6H, s).

2.2.2. Synthesis of monomer 2,2′-bi(2-ethyl-4-methylimidazole methylene)-4,4′-biphenol (EMIBP)

To a 250 mL round-bottomed flask, 2,2′-bimethylaminemethylene-4,4′-biphenol (30.0 g, 0.10 mol) was dissolved in dimethylbenzene, and 2-ethyl-4-methylimidazole (24.0 g, 0.30 mol) were added. The solution was stirred at 140 °C with a nitrogen inlet for 12 h. The precipitated solid was collected by filtration, washed with ethanol several times and was dried under vacuum at 80 °C for 24 h to produce the final product (80% yield). ^1H NMR (DMSO-d_6, ppm): δ 7.20–7.24 (2H, dd), 7.05–7.06 (2H, d), 6.89 (2H, s), 6.76 (2H, s), 5.05 (4H, s), 2.47–2.55 (4H, q), 2.03 (6H, s), 1.06–1.18 (6H, td).

2.2.3. Synthesis of poly(arylene ether sulfone) containing pendent imidazole groups (PSf-Im-x)

The DF values of the copolymers, where DF represented the degree of functionalization (the number of imidazole groups/repeat unit), were controlled by adjusting the molar ratio of EMIBP to BP (4, 4′-biphenol monomer). A typical synthesis procedure of PSf-Im-60, where 60 refers to the feed percent of EMIBP, was as follows. A flame-dried 100 mL three-necked flask equipped with a nitrogen inlet and overhead stirrer was charged with EMIBP (2.9914 g, 6 mmol), BP (0.7448 g, 4 mmol), 4,4′-bifluorodiphenylsulfone (2.5425 g, 10 mmol), K_2CO_3 (2.90 g, 21 mmol), and dry DMAc (50 mL; 10% solids). The mixture was kept at room temperature for a few minutes and then slowly heated at 120 °C for 12 h. After cooling to room temperature, an additional 30 mL of DMAc was added so as to dilute the highly viscous solution, after which the solution was filtered and dropped into stirred deionized water. The fiber like precipitate was filtered off and washed with hot water three times prior to being dried under vacuum to produce the final product.

2.2.4. Synthesis of poly(arylene ether sulfone) containing pendent imidazolium groups (PSf-Imm-x)

A typical synthesis procedure of PSf-ImmBr-60 was as follows. PSf-Im-60 (1.0 g, 2.4 mmol) was dissolved in 20 mL of dimethylacetamide (DMAc), and then n-bromobutane (0.7 g, 4.8 mmol) was added. The reaction mixture was stirred at 80 °C for 24 h and then