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Polybenzimidazoles with pendant quaternary ammonium groups as potential anion exchange membranes for fuel cells

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ABSTRACT

A series of novel polybenzimidazoles with pendant quaternary ammonium groups (QPBIs) have been synthesized by grafting 4-methyl-4-glycidylmorpholin-4-ium chloride (MGMC) onto the polybenzimidazole with pendant amino groups (H_2N-PBI) at 80 °C for 10 h. The grafting yields are estimated to be 104, 84 and 50% by elemental analysis, respectively at the feed ratio of MGMC/H_2N-PBI = 2:1, 3:2 and 1:1. The remaining unreacted pendant amino hydrogen atoms of the H_2N-PBI were further used to react with the epoxy groups of bisphenol A diglycidyl ether (BADGE) for cross-linking. The hydroxide conductivity of the cross-linked QPBI membranes increases with an increase in ion exchange capacity (IEC) and temperature. The highest hydroxide conductivity of 0.056 S cm^{-1} has been achieved with the QPBI-2/1 (here, the '2/1' refers to the molar ratio of MGMC to H_2N-PBI in feed) membrane at 80 °C under fully hydrated state. All the QPBI main chains show extremely good chemical stability in strong alkaline solution (6.0 M NaOH) at 60 °C. However, the quaternary ammonium groups of the QPBI membranes except the QPBI-1/1 are unstable (degradable) in 6.0 M NaOH at 60 °C leading to large reduction in hydroxide conductivity.

1. Introduction

Recently alkaline anion exchange membrane fuel cells (AAEMFCs) have attracted increasing attention because they have many advantages over proton exchange membrane fuel cells (PEMFCs) such as possible utility of non-precious metal electro-catalysts (nickel, silver, etc.), facile oxidation kinetics of fuels (e.g. methanol), faster reduction kinetics of oxygen, reduced fuel (e.g. methanol) crossover, enhanced carbon monoxide tolerance of catalyst and relatively simple water management [1–6]. An anion exchange membrane (AEM) is one of the key components of an AAEMFC system. From viewpoint of practical applications, an ideal AEM should meet the following requirements: (1) low cost, (2) high anion (hydroxide) conductivity under fuel cell operating conditions, (3) good mechanical properties preferably with resistance to swelling, (4) long term chemical and mechanical stability at elevated temperatures in oxidizing and reducing environment, (5) interfacial compatibility with catalyst layer. Quaternary ammonium hydroxide is a typical organic base and is relatively easy to synthesize, and therefore almost all the anion exchange polymer resins developed so far are quaternized polymers. The commercially available anion exchange polymers are mainly based on the quaternized polystyrene. However, it seems that they are not ideal AEMs because of their poor stability at elevated temperatures (>60 °C) as well as their poor mechanical properties [7]. To improve the stability and other properties, a large number of AEMs have been developed in recent years such as quaternized polystyrene with long spacers [7], quaternized poly(ether sulfone)s [8–14], quaternized polyphenylene [15], quaternized poly(phenylene oxide) [16,17], quaternized poly(vinyl alcohol) [18–22], imidazolium-based copolymers [23], quaternary-guanidinium-functionalized poly(arylene ether sulfone) [9], and phosphonium hydroxide ionomer [24]. It is well known that quaternary ammonium groups are generally unstable at elevated temperatures (e.g. >80 °C) due to Hofmann degradation. Recently Pivovar et al. [25,26] have reported that the hydroxide-attack-induced degradation could be elucidated by three mechanisms: (1) an S_N2 pathway leading to alcohol formation, (2) an ylide pathway that gives rise to unstable intermediates, and (3) Hofmann elimination. To avoid Hofmann degradation, in principle the quaternary ammonium groups must contain no β hydrogen. However, the relationship between the structure and stability of quaternary ammonium groups still needs to be clarified. For example, Tomoi et al. reported that the quaternized polystyrene with β-hydrogen-containing long spacers showed much higher stability than the one with a β-hydrogen-free short spacer ($-CH_2$) [7]. Imidazolium-based copolymers have also been reported to

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have excellent stability despite the presence of β hydrogen in the polymer structure. On the other hand, the elimination reaction is another important degradation mechanism but the effects of quaternary ammonium structure on the elimination reaction rate have far less been studied yet.

Since quaternary ammonium hydroxides are strong bases comparable to potassium hydroxide, the stability of polymer backbone in such a strong alkaline environment should be also an important issue which is expected to have large effects on the lifetime of AAEMFCs. Hibbs et al. reported that the poly(phenylene)-based AEMs could maintain mechanical strength after being soaked in 4 M sodium hydroxide solution at 60 °C for four weeks, whereas the poly(ether sulfone)-based AEMs became extremely brittle after only a few days under the same conditions [15]. Polybenzimidazole (PBI) is well known for its excellent stability under basic and oxidative environments. PBIs can be doped with strong alkaline such as potassium hydroxide and the alkaline-doped PBI membranes have been reported to have good fuel cell performance [27,28]. In this study, the polybenzimidazole with pendant amino groups (H_2N-PBI) was synthesized and subsequently reacted with 4-methyl-4-glycidylmorpholin-4-ium chloride (MGMC) to yield the quaternized polybenzimidazoles. The thermal stability, mechanical properties, hydroxide conductivity and membrane stability were also investigated.

2. Experimental

2.1. Materials

3,3′-Diaminobenzidine (DAB) and 5-aminoisophthalic acid (APTA) were purchased from Acros and used without further purification. Polyphosphoric acid (PPA), epichlorohydrin, 4-methylmorpholine, bisphenol A diglycidyl ether (BADGE), acetonitrile and dimethylsulfoxide (DMSO) were purchased from Sinopharm Chemical Reagent Co., Ltd. (SCRC). APTA was dried at 80 °C in vacuo for 10 h. Other materials were used as received.

2.2. Synthesis of polybenzimidazole with pendant amino groups (H_2N-PBI) [29]

To a 100 mL dry three-neck flask were added 55 g of PPA containing 85 wt% P_2O_5, 2.172 g (12.0 mmol) of APTA and 2.568 g (12.0 mmol) of DAB. The reaction mixture was mechanically stirred under nitrogen flow at 140 °C for 2 h and 190 °C for 20 h. After cooling to room temperature, the extremely viscous solution mixture was precipitated from ice-water. The resulting precipitate was filtered and subsequently boiled with excess 10% ammonium hydroxide over night under nitrogen flow to remove the residual phosphoric acid. After cooling to room temperature, the mixture was filtered and the solid was thoroughly washed with deionized water, and finally dried in vacuo at 80 °C for 20 h.

2.3. Synthesis of 4-methyl-4-glycidylmorpholin-4-ium chloride (MGMC)

To a 100 mL dry three-neck flask were added 18.21 g (~20 mL, 180 mmol) of 4-methylmorpholine, 16.65 g (~14.1 mL, 180 mmol) of epichlorohydrin and 5 mL of acetonitrile. The mixture was magnetically stirred at room temperature for 0.5 h and then heated at 40 °C for 48 h. After cooling to room temperature, ~50 mL of diethyl ether was added and stirred, and then the reaction mixture was filtered. The solid was thoroughly washed with diethyl ether and acetone successively, and finally dried at 50 °C in vacuum. Yield: 70%.

2.4. Synthesis of quaternized polybenzimidazole (QPBIs)

The QPBIs were synthesized by grafting the MGMC to the H_2N-PBI at the feed ratio by mole of MGMC/H_2N-PBI = 2:1, 3:2 and 1:1, respectively, and the resulting polymers are accordingly denoted as QPBI-2/1, QPBI-1.5/1 and QPBI-1/1. A typical procedure is described as follows using the QPBI-1/1 as an example.

To a 100 mL dry three-neck flask were added 0.646 g (2.0 mmol) of the above synthesized H_2N-PBI and 10 mL of DMSO. The mixture was magnetically stirred under nitrogen flow. After H_2N-PBI was completely dissolved, 0.387 g (2.0 mmol) MGMC was added to the flask. The mixture was stirred and heated at 85 °C for 10 h. After cooling to room temperature, the reaction mixture was poured into acetone. The precipitate was collected by filtration, thoroughly washed with acetone and hot deionized water and dried at 60 °C for 10 h in vacuum.

2.5. Membrane formation and hydroxide exchange

For the preparation of cross-linked membranes, the synthesized QPBIs (QPBI-1/1, QPBI-3/2 or QPBI-2/1) and the cross-linker BADGE were dissolved in DMSO to form ~8 w/v% solutions. The weight ratio of QPBI to BADGE was controlled at 100:6 to give a certain cross-linking density. The solutions were cast on glass plates and dried in an air oven at 80 °C for 10 h. The resulting membranes were peeled off from glass plates, soaked in methanol at 50 °C for 24 h and dried in vacuum at 60 °C for 10 h. For the preparation of non-cross-linked membranes, the same experimental procedures were followed except that the QPBI solutions without BADGE were used. The dry membrane thickness was controlled at ~50 μm.

Hydroxide anion exchange was performed by immersing the membranes in 2.0 M KOH solution at room temperature for 48 h. The membranes were taken out, rinsed with deionized water till it became neutral and finally dried at 60 °C for 24 h.

2.6. Measurements

FT-IR spectra were recorded on a Perkin-Elmer Paragon 1000PC Spectrometer. ^1H NMR spectra were recorded on a Varian Mercury Plus 400 MHz instrument. Reduced viscosity (η) was measured in DMSO at a polymer concentration of 0.5 g dL^{-1} with an Ubbelohde viscometer at 30 °C. Thermogravimetric analysis (TGA) was performed in nitrogen with a TGA2050 instrument at a heating rate of 20 °C min^{-1}. Tensile measurements were carried out with an Instron 4456 instrument under ambient atmosphere (room temperature, ~50% relative humidity) at a crosshead speed of 1 mm min^{-1}. For each kind of membrane, three sheets of samples were used for the measurements and the tensile stress (TS) and the elongation at break (EB) was estimated by the averaged values of the three samples.

Elemental analysis was performed on a Perkin Elmer PHI 5000 ESCT System X-ray photoelectron spectroscopy (XPS) instrument with an aluminum K-alpha X-ray source. The chemical formulae of the polymer backbone and the pendant MGMC unit are $(C_{20}H_{13}N_5)_n$ and $C_8H_{16}NClO_2$, respectively. Thus the grafting degree (y) can be calculated from the following equation:

$$y = \frac{20n_{\mathrm{Cl}}/n_{\mathrm{C}}}{1 - 8n_{\mathrm{Cl}}/n_{\mathrm{C}}} \times 100\% \quad (1)$$

where n_{Cl} and n_{C} refer to the molar contents of chlorine and carbon, respectively, determined by the elemental analysis.