Novel alkaline anion exchange membranes containing pendant benzimidazolium groups for alkaline fuel cells

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ABSTRACT

Novel benzimidazolium (BIm) functionalized anion exchange membranes (AEMs) are synthesized and characterized for alkaline fuel cells (AFCs). Poly(phenylene oxide) (PPO) is firstly brominated followed by nucleophilic substitution reaction with methylbenzimidazole to obtain the objective BIm-PPO AEMs. Such solution-casting AEMs show good mechanical and thermal stabilities as well as the favorable fuel cell-related indicators, including high ion exchange capacity, proper water uptake and high ionic conductivity. In addition, a single H_2/O_2 fuel cell test by employing the optimal BIm-PPO-0.54 AEM yields a peak power density of 13 mW cm^{-2} at 35 °C, indicating the potential application of BIm-PPO AEMs in AFCs. Compared with the analogous AEMs based on PPO containing the classical pendant quaternary ammonium and imidazolium cations, BIm-PPO AEMs show the advantages in dimensional, mechanical and thermal stabilities, while simultaneously exhibiting the higher ionic conductivity. Compared with polybenzimidazolium based AEMs, where BIm cations distribute within the polymer backbone, AEMs herein present the higher ionic conductivity and power density (produced from a single cell test) due to the better mobility and aggregation abilities of pendant BIm cations attached to the backbone *via* a side chain relative to those distribute within the polymer backbone.

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1. Introduction

In recent years, alkaline anion exchange membrane fuel cells (AAEMFCs) have deserved the increasing attention primarily because of the low over potential derived from the fast electrochemical reaction at high pH [1–3], and therefore, the use of non-precious-metal-based electro-catalysts such as silver [4], cobalt [5] or nickel [6] to replace expensive platinum-based ones is allowed. Moreover, AAEMFCs also offer enhanced cell efficiency, depressed fuel crossover and facile fuel oxidation [3].

As the core component of AAEMFCs, anion exchange membranes (AEMs) with favorable properties are desired. To data, the quaternary ammonium (QA) functionalized AEMs are the most intensively researched ones for AAEMFCs application. They are typically synthesized by immersing the pre-formed existing polymers with halomethyl [7–9] in aqueous trimethylamine (TMA) solution to introduce quaternary ammonium (QA) groups into the membrane matrix. However, such post-amination method proceeds heterogeneously and is adverse to the formation of the

micro-phase-segregated structure in the membrane matrix, affording the resultant QA-AEMs with insufficient ionic conductivity. Moreover, QA-AEMs always suffer from the poor alkaline stability due to the degradation of QA groups by the direct nucleophilic substitution at α-carbon position [10–13].

More recently, the soluble imidazolium (Im) functionalized AEMs become a hot spot [14–19]. Although the alkaline stability (especially in the harsh conditions) is disputed [15,19], the superiority in the ion conduction yet endows the Im-type AEMs with highly scientific value [16,17]. Benzimidazolium (BIm), with the similar structure to Im, could act as another kind of alkaline functionalized agents for AEM preparation. Theoretically, for the BIm-AEMs, the originally favorable properties of Im-AEMs are expected to be preserved and the further improved performance can be expected because of the presence of the additional benzene ring. Until now, the research on BIm functionalized AEMs are insufficient and all of them are based on polybenzimidazolium, where BIm cations distribute within (and become a part of) the polymer backbone [20–23]. However, it is usually considered that the pendant ion exchange groups should possess the better mobility and aggregation abilities than those of the corresponding ones distributing within the polymer backbone. Hence, the higher ionic conductivity of the membranes containing pendant ion

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exchange groups is expected [24]. To the best of our knowledge, the research on AEMs containing pendant BIm cations has not been reported so far. As a consequence, the aim of this study is to synthesize and characterize such BIm-AEMs by grafting the charged BIm cations to poly (phenylene oxide) (PPO), which was chosen due to the excellent mechanical and thermal stabilities [25]. Specifically, AEMs in this study were prepared from PPO via benzyl bromination followed by nucleophilic substitution reaction of the generated –CH₂Br with 1-methylbenzimidazole (MBIm). The preparation process will be investigated in detail and optimized to produce AEMs with elegant fuel-cell properties. Moreover, the general properties of the target BIm-PPO AEMs such as ion exchange capacity (IEC), water uptake (WU) and ionic conductivity (σ) will be evalutated for their appliaciton in AAEMFCs as the polymer electrolyte materials. In addition, the QA and Im functionalized AEMs [26] based on PPO were also summarized for the purpose of the comparison in this paper.

2. Experimental

2.1. Materials

Poly(phenylene oxide) (PPO) of intrinsic viscosity equal to 0.57 dl g⁻¹ in chloroform at 25 °C was kindly provided by Tianwei Membrane Company of Shandong. 1-methylbenzimidazole (MBIm) was purchased from Aladdin Scientific Co., Ltd. Shanghai. All reagents were of analytical grade and used as received. Deionized water was used throughout.

2.2. Synthesis of benzyl brominated poly (phenylene oxide) (BPPO)

PPO was benzyl brominated using bromine according to our previous work (see Scheme 1) [27]: Chlorobenzene-diluted bromine (33% (V/V)) was added slowly into a chlorobenzene solution of PPO (8% (m/v)) under stirring at 130 °C. The molar ratio of bromine to PPO was varied to obtain a series of BPPO with different extent of benzyl bromination. The solution was precipitated with methanol, washed and dried. The resultant brominated polymers were denoted as BPPO-X, where X is the extent of benzyl bromination and measured by nuclear magnet resonance (NMR) analysis (X=0.09, 0.20, 0.30, 0.43, 0.54 [28]).

2.3. Synthesis of benzimidazolium functionalized poly (phenylene oxide) (BIm-PPO)

BIm-PPO was obtained via the nucleophilic substitution reaction of BPPO-X with MBIm and the resultant polymer was denoted

Scheme 1. Synthetic route of BIm-PPO AEMs.

as BIm-PPO-X (see Scheme 1). A typical example is as follows: 1 g BPPO-0.43 (–CH₂Br: 2.7 mmol) was dissolved in 20 ml NMP in a 50 ml round bottom flack, upon complete dissolution, 1.1 g (8.1 mmol) MBIm was added slowly. The mixture was kept stirring at 50 °C for 24 h, and then the resultant solution was cast onto a pre-cleaned glass substrate for solvent volatilization. After washing thoroughly with water, the final BIm-PPO-0.43 AEM was obtained (92% yield).

2.4. Synthesis of the benchmark quaternized poly (phenylene oxide) (QPPO)

The QPPO AEM was prepared from BPPO-0.30 by its reaction with trimethylamine (TMA). Specifically, BPPO-0.30 was immersed in an aqueous TMA solution (33% (m/v)) for 5 days at room temperature to ensure the complete conversion of –CH₂Br to quaternary ammonium (QA) groups and then washed thoroughly with water to get the target QPPO AEM.

2.5. Membrane characterizations

2.5.1. NMR and FTIR
¹H nuclear magnet resonance (NMR) spectra were recorded on an AVIII 400 NMR spectrometer (Bruker) operating at 400 MHz.
Infrared spectroscopy (FTIR) spectra were measured using a Vector 22 Fourier transform infrared spectrometer (Bruker).

2.5.2. SEM
The morphology of the membrane was investigated using scanning electron microscopy (XT30 ESEM-TMP PHILIP). The membrane was dried and then coated with gold before observation.

2.5.3. IEC
Ion exchange capacity was measured as previously reported [27]. The sample was dried to a constant weight and then converted to its Cl⁻ form by immersing in an aqueous NaCl solution (1 mol cm⁻³). The sample was thoroughly washed with water to remove the excess NaCl and then immersed in an aqueous Na₂SO₄ solution (0.5 mol cm⁻³) for 2 days. The amount of Cl⁻ released from the polymer sample was then determined by titration with an aqueous AgNO₃ aqueous solution (1 mol cm⁻³) using K₂Cr₂O₇ as an indicator. The IEC value was calculated as amount of Cl⁻ (in mmol) per g of dry membrane (assuming a 1:1 reaction ratio between the Cl⁻ anions and Ag⁺).

2.5.4. Water uptake and swelling ratio
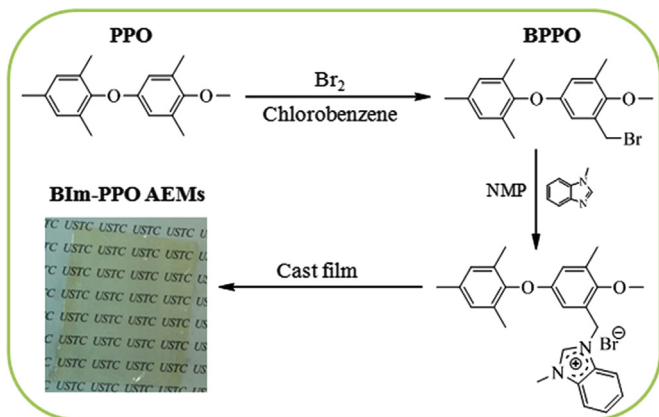Water uptake and swelling ratio were measured according to our previous work [27,28].
Water uptake (WU) was tested as follows: the sample was dried at 50 °C until a constant weight (m_{dry}) was attained, and then the sample was immersed in water at a given temperature for 2 days, afterwards, the weight of wet sample was attained and WU of membrane was calculated according to the following equation:

$$WU = \frac{m_{wet} - m_{dry}}{m_{dry}} \times 100\% \quad (1)$$

The swelling ratio was characterized by linear expansion ratio (LER), which was determined by the difference between wet and dry dimensions of a membrane sample (4 cm in length and 1 cm in width). The calculation was based on the equation as follow:

$$LER = \frac{L_{wet} - L_{dry}}{L_{dry}} \times 100\% \quad (2)$$

where L_{wet} and L_{dry} are the lengths of wet and dry membranes, respectively.