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Densely sulfonated block copolymer composite membranes containing phosphotungstic acid for fuel cell membranes

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ABSTRACT

The synthesis and properties of densely sulfonated poly(arylene biphenylsulfone ketone) block copolymer and its composite membranes including phosphotungstic acid (PWA) were investigated. The chemical structure of the block copolymers was characterized by FT-IR, ^{1}H-NMR, and GPC. The block copolymer composite membranes were prepared by mixing the block copolymer with a commercial PWA. The composite membranes have shown not only good thermal stability (decomposition temperature in nitrogen $>250\,^\circ$C), but also lower water uptake than the unfilled membranes. Their crystalline phases and morphologies have been confirmed by X-ray diffraction (XRD) and field-emission scanning electron microscopy (FSEM), respectively. The composite membranes displayed relevant ion exchange capacity (IEC), as well as good proton conductivity especially at elevated temperature. The proton conductivity of the Block-19/PWA-30 composite membrane (IEC 1.58 meq g^{-1}) reached the maximum of 97 mS cm^{-1} at 90 °C under 100% relative humidity (RH), which is comparable to Nafion-117. The fabricated composite membrane exhibited a maximum fuel cell power density of 150 mW cm^{-2}, which was much higher that of Block-19 membrane and can be considered as a candidate for potential application in fuel cells.

1. Introduction

Fuel cells have attracted considerable attention as energy-conversion systems for future applications in vehicles and for on-site power generation. The polymer electrolyte membrane (PEM) as a component of fuel cells is a very important material used to transfer protons from the anode to cathode. Commercialized Nafion has some advantages such as high ion conductivity, high efficiency, high energy density, and flexibility of the membrane. However, Nafion has still some limitations such as high cost, high methanol crossover, and limited operation temperature [1,2]. In order to overcome these drawbacks, many research groups have attempted to find alternative membranes superior to the Nafion. The hydrocarbon membrane is remarkable among alternative membranes, because it has advantages in low cost, thermal stability, elevated operation temperature, easy design structure, and simple synthesis. Aromatic hydrocarbon polymers such as poly (arylene ether sulfone)s (SPAES) [3–5], poly (ether ether ketone)s (SPEEK) [6,7], poly (sulfide sulfone)s (PSS) [8], and polyimides (SPI) [9] have been studied for fuel cells applications. Most of these polymeric membranes exhibited sufficient chemical and thermal stabilities, as well as low prices and a variety of applications. However, the performance of these membranes still did not satisfy the proton conductivity and mechanical strength requirements. Thus, their performance has been also investigated for blending membrane [10], organic–inorganic composite membrane [11,12], and cross-linking membrane applications [13]. Generally, a composite membrane has good thermal stability and high proton conductivity. For example, a heteropoly acid (HPA), such as PWA, is one of the most outstanding inorganic materials for proton exchange membranes, because in crystalline form they have demonstrated higher conductivity and thermal stability. Kreuer suggested that the HPA acts as a Bronsted acid toward water during hydration, which generally is loosely bound in the structure, resulting in high proton conductivity [14].

Recently, we have explored the synthesis and characterization of a range of tetrasulfonated copolymers originating from tetrasulfonated 4,4-bis[4-chloro-3-sulfonatophenylsulfonyl]biphenl-2,2-disulfonate (TsBCSBPD, 1) by direct condensation methods [15–17]. The major advantages of direct copolymerization

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includes well-defined location of sulfonic acid and ion conductor concentration, enhanced stability, the ability to generate much higher molecular weights than available commercial-based systems, precise control of sulfonation, and modestly higher acidity, which was due to the influence of the sulfonic acid group. Indeed, the acid form of these membranes showed good thermal stability by thermogravimetric analysis (TGA) (>250 °C in air) and a morphology evolution from phase-separated to co-continuous with increasing degree of sulfonation, which allows for controlled water sorption. The highly sulfonated acid form of the membrane had an ion conductivity of 75 mS cm^{-1} for the 30 mol% tetrasulfonated block copolymer at 90 °C and 100% RH [17]. These encouraging results lead us to suggest the utility of these materials not only as a proton exchange membrane (PEM), but also as an effective matrix for a composite membrane containing HPA for fuel cell applications at ambient or elevated temperatures.

The primary objectives of this work were to prepare tetrasulfonated poly(arylene biphenylsulfone ether)/phosphotungstic acid (PWA) composite membranes with different PWA concentrations via solution blending methods to evaluate their performance at temperatures between 30 and 90 °C, and 100% RH. In addition, this study focuses on the structural analysis of the block copolymer, influence of the dispersed PWA on the membrane properties, oxidative and thermal stabilities, XRD and SEM spectra, water uptake, IEC, conductivity, and MEA (membrane electrode assembly) test.

2. Experimental

2.1. Materials

4,4′-Bis[(4-chlorophenyl)sulfonyl]-1,1′-biphenyl (BCPSBP), 4,4′-dichlorobenzophenone (DBP), 4,4′-(hexafluoroisopropylidene) diphenol (6F-BPA) and PWA were purchased from Sigma-Aldrich, and were dried at 50 °C in a oven for 15 h before use. Tetrasulfonated 4,4′-bis[(4-chlorophenyl) sulfonyl]-1,1′-biphenyl (TsBCPSBP, **1**) was prepared by sulfonating BCPSBP using fuming sulfuric acid at 110 °C for 12 h [15]. Fuming sulfuric acid (30%), N,N-dimethylacetamide (DMAc), anhydrous toluene, anhydrous potassium carbonate (K_2CO_3), and anhydrous DMSO were also purchased from Sigma-Aldrich, and used without further purification. Other reagents and solvents were used as received.

2.2. 2.2. Synthesis of hydrophilic and hydrophobic polymers

The polymerization for hydrophilic part was conducted in a 100 mL two-neck flask equipped with a mechanical stirrer and Dean-Stark trap under N_2 gas. TsBCPSBP (**1**; 7.50 g, 8.23 mmol), 6F-BPA (3.04 g, 9.05 mmol), and K_2CO_3 (2.28 g, 16.5 mmol) were added into the flask. Subsequently DMAc (25 mL) and toluene (25 mL) were added into the flask as solvents. The reaction mixture was heated under reflux at 135 °C for 6 h, and then most of the toluene was removed at 160 °C for 12 h. The temperature was raised slowly to 185 °C for 48 h until the solution was viscous. The viscous solution was slowly cooled to 60 °C and diluted with DMAc for easier filtering. The solution was poured into 800 mL of co-solvent (methanol/acetone/deionized water, 6:1:1, v/v/v). The precipitant was washed with methanol and deionized water several times and dried for 15 h at 100 °C in a vacuum oven. Hydrophilic polymer (**2**): FT-IR (KBr, cm^{-1}) 3459, 3076, 2939, 1631, 1597, 1512, 1466, 1428, 1399, 1318, 1248, 1206, 1171, 1152, 1135, 1107, 1066, 1027, 967, 929, 879, 850, 827, 746, 735, 704, 689, 619, 577, 547, 526, 503; ^{1}H-NMR (600 MHz, DMSO-d_6) δ 8.58 – 7.89 (4H), 7.79 – 7.7 (1H), 7.61 – 7.45 (3H), 7.45 – 7.38 (4H), 7.32 – 6.68 (8H).

The hydrophobic polymer (**3**) was synthesized as follows: 6F-BPA (5.00 g, 14.9 mmol), DBP (4.11 g, 16.4 mmol), K_2CO_3 (4.11 g, 29.7 mmol), DMAc (25 mL), and toluene (25 mL) were added to a 100 mL two-neck flask equipped with a mechanical stirrer and Dean-Stark trap. The reaction conditions and work-up procedures were carried out as described for the preparation of the hydrophilic polymer. Hydrophobic polymer (**3**): FT-IR (KBr, cm^{-1}) 3051, 1658, 1595, 1501, 1413, 1307, 1246, 1206, 1173, 1135, 1016, 968, 927, 872, 857, 833, 765, 738, 705, 686, 639, 610, 570, 559, 544, 522; ^{1}H-NMR (600 MHz, DMSO-d_6) δ 7.8 (4H), 7.65 (0.3H), 7.4 (4H), 7.2 (7.7H).

2.3. Synthesis of block copolymers-19 and control polymer

The block copolymer-19 (Block-19; **4**) was synthesized from hydrophilic and hydrophobic polymers via nucleophilic aromatic substitution polymerization. Hydrophilic polymer (**2**; 2.00 g, 0.59 mmol), hydrophobic polymer (**3**; 2.47, 0.59 mmol), K_2CO_3 (0.16 g, 1.2 mmol), DMAc (20 mL), and toluene (20 mL) were added to a 100 mL two-neck flask equipped with mechanical stirrer and Dean-Stark trap. The reaction conditions and work-up procedures were carried out as described for the preparation of the hydrophilic polymer. Block-19 (**4**): FT-IR (KBr, cm^{-1}) 3415, 3066, 2927, 2855, 1656, 1593, 1500, 1470, 1414, 1305, 1236, 1203, 1236, 1203, 1167, 1158, 1135, 1075, 1017, 967, 953, 927, 873, 853, 828, 765, 745, 735, 704, 683, 608, 558, 545, 522, 503; ^{1}H-NMR (600 MHz, DMSO-d_6) δ 8.58 (0.2H), 8.45-8.30 (1H), 8.11 (0.2H), 7.89 (0.2H), 7.79 (4H), 7.54 (0.4H), 7.41 (4H), 7.20 (8H).

Control polymer in Fig. 1 was synthesized from of the following polymer A and B (1:1 ratio) (The polymer A was prepared from BCPSBP and 6F-BPA in DMAc/toluene and the polymer B was prepared from DBP and 6F-BPA in the same co-solvent). The control polymer: FT-IR (KBr, cm^{-1}) 3065, 2933, 1656, 1593, 1508, 1491, 1412, 1324, 1247, 1207, 1175, 1154, 1106, 1076, 1016, 1004, 968, 953, 927, 872, 855, 832, 790, 766, 756, 726, 707, 682, 634, 609, 586, 569, 545, 523; ^{1}H-NMR (600 MHz, DMSO-d_6) δ 8.02 (8H), 7.92 (4H), 7.80 (4H), 7.40 (8H), 7.20 (16H).

2.4. Preparation of block-19/PWA composite membranes

The fabrication of composite membranes was carried out by the following solution casting method using PWA/acid form of Block-19. First, the PWA was dried at 100 °C in an air circulating oven for 12 h before use. The Block-19 and the PWA were added in DMSO (10% w/v) and stirred for 12 h at 80 °C; a transparent homogeneous solution was obtained. The weight ratio of PWA to the mixture of Block-19 and PWA was controlled from 0 to 30 wt%. The solutions were cast onto a glass plate, and then dried under heat oven at 80 °C for 24 h in sequence. Transparent composite membranes with a brown color were obtained with a thickness of about 60–80 μm.

2.5. Measurements

Solubility of the block copolymers were determined at room temperature at a concentration of 10% (w/v) in several solvents such as water, methanol, acetone, tetrahydrofuran (THF), chloroform, dimethylformamide (DMF), N-methyl-2-pyrrolidinone (NMP), DMAc, and DMSO.

Fourier transform infrared (FT-IR) spectroscopy was used to confirm the functional groups of the polymers. Measurements were recorded with a Nicolet Impact 400 FT-IR spectrometer in the range 400 – 4000 cm^{-1} using a KBr pellet. The ^{1}H-NMR (600 MHz) spectra were recorded using a JNM-ECA600 instrument