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SPAEEK-based binary blends and ternary composites as proton exchange membranes for DMFCs

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ABSTRACT

Naphthalene-containing blend membranes, comprising sulfonated polyaryletherketone (SPAEEK) as the primary matrix, and basic component polyazomethine (PAM), which has a chemical structure partially similar with SPAEEK, were investigated as proton exchange membranes (PEMs). Further, a ternary-composite membrane was successfully prepared by introducing acid-functionalized polysilsesquioxane (POSS-SO₃H) into SPAEEK/PAM composite using a sol-gel process. The relevant properties of the PEMs, such as proton conductivity, methanol permeability, water uptake, and morphology were determined, and it was shown that the ternary-composite membrane, SPAEEK/PAM/POSS-SO₃H, showed a superior combination of properties for proton conductivity and methanol resistance. Its selectivity was 7.5 times higher than Nafion.

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1. Introduction

In the 21st century, as easily recoverable fossil fuel resources diminish further, convenient alternative power sources are being urgently sought. Fuel cells, which transform chemical energy directly into electricity, have advantages such as environmental friendliness, high efficiency and quiet operation, and are widely regarded as promising clean energy sources [1]. Proton exchange membranes (PEMs) are the central components of membrane electrode assemblies (MEAs), the electrochemical heart of the fuel cell. Important properties such as high proton conductivity, limited fuel diffusion and dimensional stability, are required for use in these applications [2].

Nafion[®] membranes are commercial products manufactured by DuPont[™]. Although perfluorosulfonic acid structures in Nafion-type PEMs impart exceptional oxidative and chemical stability and high proton conductivity [3], these materials have some drawbacks such as high cost, low operating temperature, and high fuel permeability, which are limitations to widespread adoption. Alternative inexpensive proton-conducting materials with superior properties are required, such as sulfonated polyaryletherketones (SPAEEKs), which are being investigated due to

their higher temperature capability and overall thermooxidative and chemical stability performance [4].

It should be noted that most newly developed proton conducting materials have a typical profile of exhibiting unilateral improvements in properties, but fall short in integrated performance compared with Nafion [5,6]. Composite membranes (e. g., acid-base enhanced type PEMs), which have certain molecular interactions between different polymeric materials, can make multi-improvements for fuel cell applications. For example, most binary composite membranes have obvious improvements in dimensional stability and methanol resistance due to strong molecular interactions, such as hydrogen bonding between particular functional groups [7–11], but the proton conductivity is usually lower than that of the corresponding unitary membranes owing to decreased effective ion exchange capacity (IEC) values.

Sulfonated inorganic compounds introduced into PEMs to form organic-inorganic hybrid membranes have been shown to have some attractive membrane properties relevant to direct methanol fuel cells, since the sulfonic acid functionalization somewhat compensates for the lower IEC value of the added inorganic component (DMFCs) [12–17]. Recently, 3-trihydroxysilyl-1-propanesulfonic acid (THOPS) was used to form a multi-acid-functionalized polysilsesquioxane (POSS-SO₃H) via a sol-gel process, which was incorporated into polyarylether-type matrix. It was found that POSS-SO₃H containing hybrid membranes were highly proton conductive with enhanced water-holding capability [18,19]. In the present study, sulfonated poly(aryl ether ketone)

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(SPAEK) [11,15] was used as the primary PEM matrix, with 0–10% of a molecular-enhancing polyazomethine (PAM); each polymer contained naphthalene, ether and ketone structural units common to both [20]. A series of binary component composite SPAEK/PAM PEM films was prepared by solution casting and the properties were compared with a ternary-component composite (SPAEK/PAM/POSS-SO₃H) membrane.

2. Experimental

2.1. Materials

Sodium 6,7-dihydroxynaphthalene-2-sulfonate was purchased from Rintech Inc., and was recrystallized twice from a mixture (50:50 in volume) of water and ethanol. 1,4-Bis(4-fluorobenzoyl)benzene was obtained from Jilin University, China. Bisphenol AF was obtained from Sigma-Aldrich, and was recrystallized from toluene before use. 1,5-Bis[4-(4-aminophenoxy)]benzoyl-2,6-dimethoxynaphthalene, was synthesized via a Friedel–Crafts acylation reaction followed by an aromatic nucleophilic substitution reaction [20]. Terephthalaldehyde (Sinopharm Chemical Reagent Co., Ltd.) and anhydrous lithium chloride (Tianjin North Union Fine Chemicals Development Co., Ltd.) were used without purification. 3-Trihydroxysilyl-1-propanesulfonic acid (THOPS) was purchased from ABCR GmbH & Co KG. All other chemicals were reagent grade and obtained from commercial sources and used without further purification.

2.2. Polymer synthesis

2.2.1. Synthesis of the naphthylated sulfonated paek

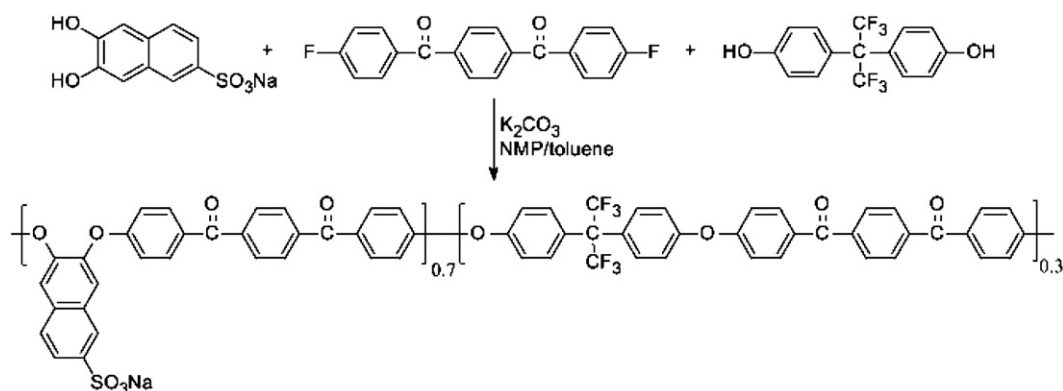
Naphthalene-containing sulfonated poly(aryl ether ketone) (SPAEK) was synthesized from sodium 6,7-dihydroxynaphthalene-2-sulfonate, 1,4-bis(4-fluorobenzoyl)benzene, and bisphenol AF, following a previously reported procedure [11,15]. The SPAEK (IEC ~ 1.30 meq/g) structure is shown in Scheme 1. The inherent viscosity measured at 25.0 °C using a Ubbelohde viscometer and a polymer concentration of 0.5 g/dL in DMAc was 1.08 dL/g.

FTIR (KBr, cm⁻¹): 1032, 1103 (–SO₃); 1660 (C=O).

¹H NMR (DMSO-d₆, ppm): 8.21 (s, 0.7H); 8.01–7.73 (m, 10.6H); 7.45–7.07 (m, 6.6H).

2.2.2. Synthesis of the naphthylated PAM containing ether and ketone linkages

Naphthalene-containing polyazomethine (PAM) was synthesized according to a previously reported procedure [20]. The PAM structure is shown in Scheme 2. The inherent viscosity in DMAc at 25.0 °C was 0.13 dL/g.



Scheme 1. Synthesis of a naphthylated SPAEK as a matrix.

FTIR (KBr, cm⁻¹): 1610 (C=N); 1670 (C=O).

¹H NMR (DMSO-d₆, ppm): 8.74 (s, 1H); 8.06 (s, 2H); 7.78–7.05 (m, 10H); 3.70 (s, 3H).

2.3. Membrane preparation

Powdered SPAEK in sodium form (5 g) was stirred overnight in 500 mL of 2 M H₂SO₄, then washed with water until it was neutral. The resulting SPAEK was dried at 120 °C in vacuum for 4 h before use. Different samples of SPAEK/PAM in the relative weight proportions of 1/0, 0.98/0.02, 0.95/0.05, 0.92/0.08 and 0.9/0.1 (0.5 g in total weight) were separately dissolved in 5 mL of *N,N*-dimethylacetamide (DMAc). After 6 h of stirring, the solutions were filtered and cast onto 10 cm × 10 cm glass plates and then dried at 60 °C for 24 h and at 100 °C, 120 °C for 12 h separately. The resulting films were immersed in deionized water and separated from the glass.

The ternary-composite membrane, SPAEK/PAM/POSS-SO₃H, was cast from SPAEK/PAM/THOPS (0.75/0.1/0.15 in weight). Two drops of concentrated hydrochloric acid were added before stirring. It was fabricated in the same way mentioned above. All the samples could be cast into transparent membranes. The thickness of the PEM samples was in range of 30–60 μm.

3. Measurements

3.1. Characterization

The ¹H NMR spectra were obtained on a Bruker 510 spectrometer operating at a proton frequency of 500 MHz. DMSO-d₆ was selected as solvent. FT-IR spectra were measured on a Nicolet Impact 410 Fourier-transform infrared spectrometer.

3.2. Water uptake and swelling ratio measurements

Membrane samples were vacuum dried at 120 °C until constant weight and measured as *W*_{dry}. Then the membranes were soaked in deionized water at different temperatures of 20 °C, 50 °C, 80 °C and 100 °C for 2.5 h separately. After each procedure, the wet membranes were quickly weighed with surface water removed by filter paper and noted as *W*_{wet}. Water uptake was calculated by:

$$\text{water uptake (\%)} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100$$

where *W*_{wet} and *W*_{dry} are the weights of wet and dry membrane samples, respectively.

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