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Fabrication of sulfonated poly(aryl ether ketone sulfone) membranes blended with phosphotungstic acid and microporous poly(vinylidene fluoride) as a depository for direct-methanol fuel cells

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ABSTRACT

A series of sulfonated poly(aryl ether ketone sulfone)/poly(vinylidene fluoride) phosphotungstic acid (SPAEEKS/PVDF-HPW) composite membranes were prepared and characterized by Fourier transform infrared spectroscopy. No phase separation was observed by scanning electron microscopy. The HPW particles are evenly dispersed in the membranes, probably because the microporous structure of PVDF stabilized the dispersion of HPW particles in the membranes. Thermogravimetric analysis showed that the thermal stability of the membranes increased with increase in HPW content. Moreover, the composite membranes exhibited outstanding oxidative stability. The methanol permeability coefficient of the SPAEEKS/PVDF-HPW10% membrane at 20 °C was $1.68 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, and the highest proton conductivity of the membrane at 80 °C was 0.098 S cm^{-1} , slightly lower than that of Nafion[®] 117. However, the relative selectivity of the membrane was higher than that of Nafion[®] 117. The swelling ratio of the membrane at 80 °C was 16%, and the methanol uptake of the membrane at room temperature was only 10.2%, much lower than those of Nafion[®] 117. The results indicate that the SPAEEKS/PVDF-HPW membranes can be used as an alternative proton exchange membrane for direct-methanol fuel cells.

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Introduction

Direct-methanol fuel cells (DMFCs) are eco-friendly, safe and energy efficient device [1–6]. As a key component of DMFCs, a proton exchange membrane (PEM) should have a high proton conductivity and low methanol permeability coefficient at a high temperature and low relative humidity (RH). Nafion[®], a commercially available PEM, not only has a high proton conductivity, but also has excellent chemical stability at a moderate temperature (≤ 80 °C) [7,8]. However, Nafion[®] has a disadvantage: severe loss of fuel, common problem in PEMs [9]. Therefore, studies have been conducted to overcome this disadvantage of Nafion[®] membrane in the recent decades, for example, by blending Nafion[®] with other components [10–12] and by modifying the Nafion[®] surface [13]. The development of a new PEM material for application in DMFCs may be more efficient.

In the past few years, the studies on PEMs focused on sulfonated aromatic polymers because of their high proton conductivity, excellent mechanical and chemical properties, and outstanding thermal stability [14–18]. The hydrophilic $-\text{SO}_3\text{H}$ groups in these aromatic copolymers are responsible for transporting protons in the membranes. Therefore, a certain degree of sulfonation (DS) is necessary for sufficient proton conductivity. However, a high DS causes a poor dimensional stability and high methanol permeability coefficient simultaneously [19]. Therefore, a simple and effective method is needed to reduce the fuel crossover by incorporating hydrophobic materials into sulfonated aromatic polymers. Therefore, hydrophobic polymers such as poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-co-HFP), poly(vinylidene fluoride) (PVDF), and poly(ether sulfone) (PES) have been utilized because of their extremely hydrophobic nature and good chemical stability. The addition of these hydrophobic polymers decreased the methanol permeability coefficient and significantly increased the dimensional stability of the membranes [20–23]. However, the water uptake (WU) and proton conductivity decreased [21], hindering further development of these membranes.

Phosphotungstic acid (HPW), a solid heteropoly acid, is a proton conductor because of its unique structure and strong acidity. The primary structure of HPW is represented by Keggin units, where 12 edge-sharing metal–oxygen octahedral WO_6 units surround the P atom in the center of a tetrahedron. The acidic protons exist in the form of isolated protons or formed protonated water molecules such as H_3O^+ and H_5O_2^+ by water solvation [24]. As the origin of the strong acidity in the pseudoliquid phase, the isolated protons migrate rapidly between the adjacent polyanions, resulting in a high inherent proton conductivity of $0.02\text{--}0.1\text{ S cm}^{-1}$ at room temperature [25–27]. Although the proton conductivity of the HPW-containing PEMs increased, the HPW particles easily leached away in water with time. It was a challenge to retain HPW in the membranes to maintain a high proton conductivity.

In this study, PVDF and HPW were added to sulfonated poly(aryl ether ketone sulfone) (SPAEEKS) membranes to fabricate a new composite PEM. The introduction of hydrophobic PVDF was expected to reduce the swelling rate (SR), particularly the methanol permeability coefficient of the

membranes. The microporous PVDF accommodated HPW particles in its micropores and thus prevented them from leaching away in water. Furthermore, the HPW particles helped to transfer protons among the $-\text{SO}_3\text{H}$ groups and maintained a high level of proton conductivity. The thermal stability, chemical capacity and methanol permeability coefficient of the composite membranes were investigated in detail, and the results were compared to those of Nafion[®] 117 and SPAEKS-100 (100% DS) membranes.

Experimental

Material

Disodium-3,3'-disulfonate-4,4'-dichlorodiphenylsulfone (SDCDPS) was prepared in laboratory. Nafion[®] 117 membrane was purchased from commercial sources. Tetramethylene-sulfone (TMS), 2,2-bis(4-hydroxyphenyl) propane (bisphenol A), and potassium carbonate (K_2CO_3) (AR grade) were purchased from Tianjin XingFu Fine Chemical Industry Research Institute, China. Toluene and HCl were obtained from Beijing Chemical plant, and *N*-methyl-2-pyrrolidinone (NMP) was purchased from Tianjin FuChen Chemical Reagent Factory, China. HPW and PVDF (99% purity) were provided by Aladdin Industrial Co. 4,4'-Difluorobenzophenone (DFB) was obtained from YanBian Long Jing Chemical Company, China, and the solid reagents were used after drying for 12 h at 60 °C under vacuum.

Synthesis of SPAEKS-100

SPAEEKS-100 was obtained by adjusting the molar ratio of DFB, bisphenol A and SDCDPS as shown in Scheme 1. The detailed procedure is as follows: DFB (7.5 mmol), bisphenol A (15 mmol), SDCDPS (7.5 mmol), K_2CO_3 (15 mmol), TMS (18 mL) and toluene (13 mL) were added into a 100 mL three-neck round-bottom flask equipped with a heating jacket and reflux condenser under nitrogen atmosphere. The mixture was refluxed at 130 °C for 4 h under stirring to remove the water produced in reaction by azeotropic distillation. After 4 h, toluene was evaporated, and the temperature of the reaction mixture was raised to 190 °C and maintained at 190 °C for several hours. During this period, the color of the reaction mixture changed from white to brown. When the system viscosity was sufficiently high, the solution was cooled to 160 °C and poured into deionized water in a beaker. The obtained strip copolymer was cut into pieces, washed with boiling water, and dried in a vacuum oven at 60 °C for 24 h affording the final product (in the sodium form).

Preparation of composite membranes

The dried copolymer (in the salt form) was immersed in 2 M HCl for 24 h to transform into the acid form of the copolymer, washed with distilled water to remove excess HCl, and dried at 80 °C for 24 h. Then, the acid copolymer was dissolved in NMP forming a 10wt% solution. PVDF and HPW were also dissolved in NMP and added to the 10wt% solution of acid copolymer, stirred, and stand for several minutes to remove

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