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Permeabilities of methanol, ethanol and dimethyl ether in new composite membranes: A comparison with Nafion membranes

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Abstract

New composite membranes were prepared by solution casting from sulfonated poly(ether ether ketone), poly(vinylidene fluoride) and phosphotungstic acid. Their structures were characterized using XRD, DSC and FT-IR. The permeability of methanol, ethanol and dimethyl ether in composite membranes ranged from 1.9 to 3.7×10^{-7}, 7.4 to 20×10^{-8} and 1.6 to 3.2×10^{-8} cm^2/s, respectively. These values were about or more than one order of magnitude lower than those of Nafion® 117 membrane measured under the same condition. The water uptake and the swelling ratio of composite membranes were also studied, and composite membranes showed good water stability within measurement range of temperature. Higher selectivity values were observed for composite membranes compared with Nafion® 117 membrane.

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1. Introduction

Fuel cells have attracted much attention because of their environmentally friendly nature and high efficiency [1,2]. The most frequently used solid electrolytes in fuel cells are Nafion® membranes (DuPont) due to their high conductivity, good chemical and mechanical stability [3]. One of the disadvantages of using Nafion® membranes in direct methanol fuel cells (DMFCs) is the high methanol permeability, which results in the reduction of cell performance [4]. In addition, the high cost of Nafion® membranes also blocks the commercialization of DMFCs. Therefore, new proton exchange membranes (PEMs) with low methanol permeability and low cost are given increasing attention. Sulfonated poly(aryl ether ketone) membranes are considered very promising as PEMs due to their high conductivity, high thermal stability and low cost [5–7]. It was also reported that sulfonated poly(ether ether ketone) (SPEEK) membranes have some advantages in microstructure over Nafion® membranes as PEMs for DMFCs [8]. The degree of sulfonation (DS) has significant impacts on the properties of SPEEK membranes. High proton conductivity can be obtained for membranes with high DS, but high methanol permeability, much water absorption and high swelling ratio, which lead to the reduction of water stability of membranes, are also accompanied. The water stability of membranes can be improved by reducing the DS, but the proton conductivity also decreases [5–7]. Therefore, SPEEK membranes with moderate DS may be a good choice to resolve the conflict.

In order to improve the performance of SPEEK membranes, some methods were used to modify SPEEK [9,10]. The aim of the modification is to reduce the methanol permeability and improve the water stability simultaneously without much loss of the proton conductivity. Phosphotungstic acid (PWA) is a kind of solid acid with high proton conductivity. It was demonstrated that the incorporation of PWA can facilitate the transport of protons in the membrane, but unfortunately the methanol permeability and the water uptake also increased [11,12], which are not desirable for DMFCs. Poly(vinylidene fluoride) (PVDF) is a kind of hydrophobic material, and can reduce the water absorption and methanol transport rate in PEMs. Though the proton conductivity of membranes modified with PVDF decreased, good cell performance was observed [13,14]. Therefore, materials mentioned above have their own advantages and disadvantages when applied in PEMs.

Besides methanol, some other fuels such as ethanol and dimethyl ether (DME) are also considered as promising fuels.

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Compared with methanol, benefits of using ethanol and DME in fuel cells include [15–18].

1. They are non-toxicity, and methanol is toxic for human beings and specially for optical nerve.
2. They have higher power density.
3. They have zero green-house contribution to the atmosphere.

In addition, ethanol can be readily and easily produced in great quantity by fermentation of sugar-containing raw materials, and DME can be stored as a high density liquid at a pressure of 0.6 MPa, which can be used to drive fuel flow for a pumpless portable DME system. The disadvantage of them is the lower activity in comparison with methanol. Therefore, many researchers have focused their attention on the development of new catalysts for such potential fuels [16,19–21]. The problem of fuel permeability in PEMs is as important as that of catalyst activity for a fuel cell system. The aim of developing new PEMs is to lower the cost as well as the fuel permeability simultaneously without much loss of the conductivity. But now the investigation of the fuel permeability in new PEMs is mainly limited to methanol, and there are few reports about the permeability of ethanol and DME, which are also attractive fuels.

In present study low cost new composite membranes including SPEEK with a moderate DS, PVDF and PWA were successfully prepared. The permeability of methanol, ethanol and DME in composite membranes were investigated and compared with those of Nafion® 117 membrane. The proton conductivity, water uptake and swelling ratio were also studied to evaluate the possibility of using such composite membranes in fuel cells for portable applications such as mobile phones and laptops operating at low temperature.

2. Experimental

2.1. Materials and membrane preparation

SPEEK polymer was obtained by sulfonation of Victrex® PEEK using concentrated sulfuric acid (95–98 wt.%) under argon atmosphere. Detailed procedures for the sulfonation reaction can be found elsewhere [6]. The PWA and PVDF were commercially obtained from Tianjin China and ATO Chemical Co., respectively. Other reagents were obtained commercially and used as received.

Dried SPEEK polymer was dissolved in DMAc (10–15 wt.%), then PVDF powder and PWA were added into the SPEEK polymer solution, which was stirred for several hours. After all the components were fully dissolved, the solution was cast onto a glass plate, then dried at ambient condition for several days, and kept under vacuum at 100 °C for 24 h.

2.2. Instruments

The ^{1}H NMR spectra, which can be used to determine the DS of SPEEK, was recorded on a 600 MHz Bruker Avance spectrometer at room temperature. For analysis, ~4 wt.% polymer solution was prepared in DMSO-d_6. The chemical shift of tetramethylsilane (TMS) was used as internal standard reference. XRD analysis was carried out for PVDF powder and composite membranes with a D/max-rB (Japan) diffractometer using a Cu Kα X-ray source. The XRD patterns were obtained at a scanning rate of $5^\circ\,\mathrm{min}^{-1}$ with an angular resolution of 0.05° of the 2θ scan. The DSC measurements were carried out at a scanning rate of 10 °C/min using a Setaram DSC 141 calorimeter. FT-IR spectra were measured with a Perkin-Elmer spectrum one FT-IR spectrometer.

2.3. Measurements of water uptake and swelling ratio

The membrane was vacuum dried at 100 °C for 24 h and weighed. Then the membrane was immersed into water at room temperature. The wet membrane was quickly wiped to remove surface water and weighed again. Water uptake of the membrane was calculated by:

$$\text{water uptake} = \frac{W_\mathrm{w} - w_\mathrm{d}}{W_\mathrm{d}} \times 100\% \tag{1}$$

where W_w and W_d are the weights of wet and dry membranes, respectively.

swelling ratio of the membrane was calculated by:

$$\text{swelling ratio} = \frac{l_\mathrm{w} - l_\mathrm{d}}{l_\mathrm{d}} \times 100\% \tag{2}$$

where l_w and l_d are the lengths of wet and dry membranes, respectively.

2.4. Measurements of conductivity and permeability

Transverse proton conductivity of the membrane was measured by AC impedance spectroscopy using an EG&G PARC Potentiostat/Galvanostat Model 273. Before measurement, the membrane was immersed in deionized water for more than 24 h, and then the fully hydrated membrane was clamped between two stainless steel electrodes (two-probe method), which was put into a teflon cell. A spring, which was inserted between the bottom of the teflon cell and one stainless steel electrode, was used to keep constant pressure between the two stainless steel electrodes. The membrane dehydration from its edge was also reduced by sandwiching edges of the membrane between two teflon rings. The teflon cell was placed in a temperature-controlled set-up. The measurement temperature ranged from 22 to 60 °C. The conductivity was calculated from:

$$\sigma = \frac{L}{(RA)} \tag{3}$$

where σ is the proton conductivity, L the thickness of the membrane, A the face area of the membrane, and R the bulk resistance value measured.

The permeability of methanol, ethanol and DME were measured using a diffusion cell, which consists of two compartments. For measurements of methanol and ethanol, 10 vol% alcohol solution was put into the feed compartment, for DME, saturated

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