



A facile approach toward preparing low methanol permeable sulfonated polyimide composites: The sulfonated polyimide blended with poly (vinyl alcohol-co-vinyl acetate)

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ABSTRACT

A series of sulfonated polyimide/poly (vinyl alcohol-co-vinyl acetate) (SPI/PVA-co-PVAc) composite membranes was facilely prepared from blending SPI salt with 80% hydrolyzed PVA-co-PVAc in *m*-cresol followed by casting. A miscible system of the prepared composite membranes was confirmed by scanning electron microscopy (SEM). Properties required for a proton exchange membrane, such as ion exchange capacity, water uptake, dimensional change, hydrolytic stability, proton conductivity, and methanol permeability, were measured and investigated in detail. The bound water distribution of the composite membranes was found to increase with PVA-co-PVAc contents due to the formation of the H-bonding between absorbed water and hydroxy groups of PVA-co-PVAc. In a direct methanol fuel cell (DMFC) test, an increase of PVA-co-PVAc in the composite membranes enhanced the cell performance of blend membranes. The composite membrane with 25 phr PVA-co-PVAc loading has shown high power output with 6 M methanol feed at a cell operating temperature of 80 °C.

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1. Introduction

Under increasing environmental concern, direct methanol fuel cells (DMFCs) have attracted considerable interest as a power source due to their high energy density and high energy conversion efficiency. These DMFCs have wide ranging potential uses, including stationary and portable power applications [1]. Notably, the proton exchange membrane (PEM) is the key component in DMFC systems and functions as a proton transmitter and fuel separator between anode and cathode. Perfluorosulfonate ionomers (PFSIs), such as DuPont's Nafion membranes, are commercially available and have the advantages of high proton conductivity, excellent chemical stability, and long-term stability. However, they have limited industrial applications due to their high cost, high methanol permeability, and the unfavorable environmental effects caused by their fluoride component [2,3]. Recent demand has increased markedly for non-fluorinated hydrocarbon membrane materials with low methanol permeability, enhanced environmental adaptability, and low production costs.

In the past decades, the use of various sulfonated polymers such as polyimide [4–9], poly (arylene ether sulfone) [10,11], poly (ether ether ketone) [12,13], polybenzimidazole [14,15] and polyvinyl alcohol [16–19] in DMFCs has been frequently investigated. Among these

sulfonated polymers, sulfonated polyimide (SPI) with a six-member imide ring are proved to be one of the promising materials for fuel cell applications due to their excellent properties of high thermal stability, excellent mechanical strength, superior chemical resistance, good film forming capability and very low methanol permeability [4–9]. However, the sulfonic group of SPI is a weaker acid than that of perfluorosulfonated polymers [8]. It results in the lower proton conductivity of SPI than that of perfluorosulfonated polymers; the SPI needs a high level of sulfonation to promote its proton conductivity. At high sulfonation levels, most SPI membranes encounter problems associated with swelling, poor hydrolytic stability and high methanol permeability. To solve these problems, SPI membranes modified by blending [20,21], crosslinking [22], and organic–inorganic hybrid [23,24] have demonstrated better performances and have attracted considerable attention.

Poly (vinyl alcohol-co-vinyl acetate) (PVA-co-PVAc) copolymers are obtained by partial hydrolysis of poly (vinyl acetate). The molar content of acetate groups in PVA-co-PVAc affects its physical–chemical properties, such as solubility, hydrophilic/hydrophobic interactions, crystallinity and melting point [25,26]. The good permselectivity of water over methanol in PVA is a matter of concern for DMFC applications [16–19,27]. Moreover, the hydrophilic nature of PVA results from the presence of abundant hydroxy groups that interact with sulfonic acid groups [17] or confer the potentiality for chemical crosslinking [18,19,27]. Yang [17], who examined sulfonated poly (ether ether

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ketone)/poly (vinyl alcohol) (SPEEK/PVA) blend membranes, showed that the hydroxy groups of PVA can interact with sulfonic acid groups of sulfonated poly (ether ether ketone).

In this study, an SPI membrane was modified by incorporating 80% hydrolyzed poly (vinyl alcohol-co-vinyl acetate) into the membrane. To obtain SPI/PVA-co-PVAc composite membranes, it addressed aspects associated with the choice of solvent, solvent evaporation temperature and speed, and the membrane post-treatment in the case of solution casting method. The SPI exhibits poor solubility in common organic solvents such as NMP, DMAc, DMSO, etc. due to their strong intermolecular interaction. Only SPI with TEA salt can dissolve in *m*-cresol well. On the other hand, the investigation has found that the 80% hydrolyzed poly (vinyl alcohol-co-vinyl acetate) exhibits excellent solubility in *m*-cresol due to the lower crystallinity and smaller crystalline domains. Therefore, *m*-cresol is the best choice for the co-solvent. Here we obtained the composite membranes with different parts of PVA-co-PVAc per hundred parts of SPI by weight, i.e., 0 phr, 5 phr, 10 phr, and 25 phr. The properties of PEM, such as ion exchange capacity, water uptake, dimensional variation, hydrolytic stability, proton conductivity, and methanol permeability, were investigated in detail. The DMFC performance of the SPI/PVA-co-PVAc composite membranes was tested with 2 M methanol and 6 M methanol as fuels and was compared to that of the performance of Nafion 117 membrane.

2. Experimental

2.1. Materials

The 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTDA, 95% pure; Aldrich) was dried under vacuum before use. The 2,2'-benzidinedisulfonic acid (BDSA, 70% pure; Tokyo Chemical Industry Co.) was dissolved in ethanol and was neutralized with triethylamine (TEA, 99.9% pure; Sigma-Aldrich) at 60 °C. The BDSA-TEA was purified by recrystallization from the ethanol solution and was dried under vacuum for 3 days. The 4,4'-oxydianiline (ODA, 98% pure; Aldrich) and benzoic acid (BA, 99.5% pure; Sigma-Aldrich) were used without further purification. Poly (vinyl alcohol-co-vinyl acetate) (PVA-co-PVAc) (80% hydrolyzed, degree of polymerization of 2000; Tokyo Chemical Industry Co.), *m*-Cresol (99% pure; Sigma-Aldrich) and Nafion-containing solution (Nafion® PFSA polymer dispersions, 5 wt.%; DuPont Fuel Cells) were also used without further purification.

2.2. Synthesis of sulfonated polyimide

Sulfonated polyimide (SPI) was prepared from NTDA, BDSA-TEA and ODA according to a method that has been described elsewhere [28], with an NTDA:BDSA-TEA:ODA molar ratio of 0.93:0.64:0.29. The BDSA-TEA and ODA were dissolved in 30 mL *m*-cresol and poured into a 100 mL three-necked flask, and then stirred with a magnetic stirrer under nitrogen atmosphere. Finally, NTDA and benzoic acid were added. The mixture was stirred under ambient temperature for 30 min and then heated to 80 °C for 4 h and 180 °C for 24 h. After cooling back to room temperature, 10 mL *m*-cresol was added to dilute the highly viscous solution and then the products were precipitated into the acetone pool. The fiber-like precipitate was collected by filtration, and then dried under vacuum at 80 °C for 24 h.

2.3. Preparation of SPI/PVA-co-PVAc composite membranes

The SPI (with TEA salt form) and PVA-co-PVAc were dissolved in *m*-cresol, respectively. The composite membranes obtained with different parts of PVA-co-PVAc per hundred parts of SPI by weight, i.e., 5 phr, 10 phr, and 25 phr, are named M-5, M-10, and M-25, respectively. The blended solutions were stirred at room temperature for 24 h, and then cast onto a glass plate and dried at 80 °C for 12 h.

The prepared membranes were soaked in 1 M H₂SO₄ at room temperature for 24 h to convert TEA salt into protonic acid form. These membranes were then thoroughly washed with de-ionized water.

2.4. Characterization of SPI/PVA-co-PVAc composite membranes

2.4.1. Fourier transform infrared spectroscopy and ion exchange capacity

The prepared membranes were examined by Fourier transform infrared (FT-IR) spectroscopy with attenuated total reflection (ATR) (Spectrum One, Perkin Elmer). A minimum of 8 scans was used and signal was averaged with a resolution of 2 cm⁻¹ in the 4000–650 cm⁻¹ range. Ion exchange capacity was measured using the titration method. Dried membranes were crushed using a cryogenic crusher followed by soaking in 1 M NaCl solution for 48 h to release the protons. Released protons were titrated with 0.01 M NaOH solution, using phenolphthalein as the indicator. The IEC value was recorded at an average value of each sample in milliequivalent NaOH per gram polymer (meq g⁻¹).

2.4.2. Morphological analysis

The cross-section morphology of the composite membranes was examined by Field Emission Scanning Electron Microscopy (FE-SEM) (JSM-7401F; JEOL). Membrane samples were fractured after immersing in liquid nitrogen for about 60 s and then were examined by the FE-SEM.

2.4.3. Water uptake and dimensional change

Water absorption of the SPI/PVA-co-PVAc composite membranes was determined at 30 °C. These membranes were dried in a vacuum at 100 °C for 24 h, weighed, and then immersed in de-ionized water at 30 °C for 24 h. Wet membranes were dried by wiping and weighed immediately. Water uptake (WU) of membranes was based on the calculation of the weight percentage, using the following equation:

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

Dimensional changes were calculated using the following equation:

$$\Delta l_c = \frac{l_w - l_d}{l_d} \times 100\%$$

$$\Delta t_c = \frac{t_w - t_d}{t_d} \times 100\%$$

where t_d and l_d are the thickness and length of a membrane dried in a vacuum at 100 °C for 24 h, respectively; and t_w and l_w are the thickness and length of a membrane immersed in de-ionized water at 30 °C for 24 h, respectively.

2.4.4. Thermal analysis

Thermogravimetric analysis (TGA) (Q500, TA Instruments) was performed to characterize the thermal stability of membranes and water weight loss of the hydrated membranes. Temperature was increased to 900 °C at 10 °C min⁻¹ under a nitrogen atmosphere. Sample weight was about 7 ± 2 mg.

2.4.5. Water states

Freezing and nonfreezing water in the hydrated membranes were determined by the melting transition obtained from the Differential Scanning Calorimeters (DSC) (Q100, TA Instruments) [19,29]. Hydrated membranes were first cooled to -40 °C (cooling rate: 5 °C min⁻¹) and then heated up to 40 °C (heating rate: 5 °C min⁻¹).

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