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Proton-conducting membranes with high selectivity from phosphotungstic acid-doped poly(vinyl alcohol) for DMFC applications

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Abstract

Proton-conducting hybrid membranes composed of poly(vinyl alcohol) (PVA) and phosphotungstic acid (PWA) were prepared by solution-blending. The effect of PWA doping on the membrane properties such as water uptake, ion-exchange capacity (IEC), proton conductivity and methanol permeability was investigated. Up to 20 wt.% PWA content, both water uptake and methanol permeability slightly increased then decreased continuously until 90 wt.%. Fourier transform infrared spectra indicate that significant amount of PWA was maintained in the polymer matrix even after several hours of immersion in water. Combining FTIR results and the similarity in water uptake and methanol permeability of PVA/PWA hybrid membranes suggests that the variations in associated properties are ascribed to intermolecular hydrogen bonding interaction between hydroxyl groups of PVA and PWA. Methanol permeabilities of hybrid membranes were significantly lower than that of Nafion115. The proton conductivity of hybrid membranes was in the order of 10^{-4} S cm^{-1} and generally increases with PWA content. Finally, the possibility of PVA/PWA hybrid membranes for use in PEMFC was explored. In H_2/O_2 mode, the performance increases with PWA content and a maximum current density of 46 mA cm^{-2} was obtained with PVA 20 wt.% and PWA 80 wt.% (PVA20PWA80) sample. Performance of DMFC with PVA20PWA80 increases with temperature and reached to 80 mA cm^{-2} at 80 °C.

Keywords: Solution-blending; Proton-conducting PVA/PWA hybrid membranes; Methanol permeability; Selectivity; DMFC

1. Introduction

The proton exchange membrane fuel cells (PEMFC) technology is receiving a great deal of attention for the last several years because of its specific advantages over other type of fuel cells [1–3]. One of the important areas of research interest in PEMFC is the development of a low cost membrane for high temperature operation (>100 °C) with little or no dependence on humidity for hydrogen-based fuel cells (H_2/O_2FC) and with low methanol permeability for direct methanol fuel cells (DMFC). The main reason for this intense interest is high cost, limit of low operating cell temperature and methanol cross-over problems associated with presently used plain perflurosulfonic acid membranes [4–6]. High temperature operation has several advantages including improvement of electrode kinetics, enhancement of CO tolerance of electrocatalysts and reduction in catalyst loading. Cross-over of methanol from anode to cathode will strongly affect the DMFC performance since the presence of methanol at the cathode side not only lowers the fuel efficiency but also further polarizes the cathode, and may adversely affect the cathode performance through wetting the hydrophobilized electrode structure and poisoning the catalyst sites for oxygen reduction [7].

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The developments of alternative membrane materials to commercially available Nafion include various new modified per-fluorinated, partially per-fluorinated and non-per-fluorinated membranes [4,5]. A common problem of fluorine-free membranes such as sulfonated phenol formaldehyde [8], vinyl polymers [9], phosphazine-based cation-exchange membranes [10,11] and homogeneous partially sulfonated arylene main chain-polymers [12,13] is that they are too swelling in water and lose their mechanical property. Although some improvements have been achieved with hydrocarbon ionomer membranes at low temperatures, the proton conductivity of these materials at elevated temperature is still unsatisfactory because of the lack of water retention at temperature above 100 °C. Recently, Kim et al. [14] showed that incorporation of heteropolyacid (HPA) into sulfonated poly(arylene ether sulfone) copolymer significantly reduced the water swelling behavior of resulting composite membrane and the conductivity increased up to 0.15 S cm^{-1} in the temperature range from 100 to 130 °C. The heteropolyacids (HPAs) are one of the most attractive inorganic fillers because these materials in crystalline form have been demonstrated to be highly conductive and thermally stable [15]. Taking the advantages of HPAs, several research groups have explored to prepare proton-conducting membranes doped with HPA for PEMFC [14–26].

Due to its high selectivity of water to alcohols, poly(vinyl alcohol) (PVA) membranes have been used in alcohol dehydration to break the alcohol–water azeotrope [17–20]. Taking advantage of this high selectivity, Pivovar et al. [21] explored the potentiality of PVA as proton exchange membrane in DMFC from proton conductivity and methanol permeability experiments. The authors reported that the PVA membranes employed in pervaporation process were much better methanol barriers than Nafion. Later, Li and Wang [22,23] have prepared proton-conducting membranes based on PVA with embedded phosphotungstic acid (PWA) and found that water uptake, proton conductivity and methanol permeability were increased with PWA content. In order to improve the reagent endurance and thermal stability of PVA/PWA membrane, SiO_2 was added [24]. Recently, Rhim and coworkers [25,26] have prepared and characterized cross-linked PVA membranes containing sulfonic acid group for DMFC applications. Most of the previous studies on PVA/PWA composites membranes have mainly devoted to the aspects related to preparation and transport properties but none of them focused on fabrication of membrane electrode assemblies (MEA) and fuel cell tests.

This paper describes the preparation of PWA/PVA hybrid membranes via slightly modified solution-blending method. The influence of the dispersed PWA on the membrane properties such as water uptake, ion-exchange capacity (IEC), proton conductivity and methanol permeability was studied. In addition, fuel cell tests were carried out in both hydrogen/oxygen and methanol/oxygen mode. To the best of our knowledge, there is no report presently available on applications of PVA/PWA hybrid membrane in either H_2/O_2FC or DMFC.

2. Experimental

2.1. Chemicals

The following chemicals were used: poly(vinyl alcohol) (Aldrich, molecular weight: 89,000–98,000 average; degree of alcoholysis: 99%), phosphotungstic acid (Sigma, 99%). All the reagents were ACS grade and used as received without further purification.

2.2. Preparation of PWA-doped PVA proton-conducting hybrid membranes

To prepare 10 wt.% (mass) solution, PVA was dissolved in water at 60 °C with continuous stirring. Similarly, PWA was dissolved in water at room temperature (RT). To 5 g of 10 wt.% PVA solution, PWA solution of desired concentration was added and the resulting mixture was stirred at 60 °C until homogeneous solution was obtained (∼for about 3 h). The amount of PWA in the membrane was changed from 0 to 90 wt.% with respect to PVA. Higher amount of PWA was limited due to too brittle nature of membrane in practical use. After that, the homogeneous hot solution was poured into Petri disc and allowed at 60 °C for 6 h to remove the solvents. Membrane was peeled off from the disc and annealed at 120 °C for 1 h. After cooled down to room temperature suddenly, the resultant membrane was stored in deionized water. The thickness of these composite membranes in the dry state is about 60 to 100 μm.

2.3. Water uptake

The water uptake of the hybrid membrane was determined by measuring the change in the weight before and after the hydration. The membrane was immersed in deionized water for 24 h, and then surface-attached water onto the membrane was removed with filter paper. After that, the wetted membrane weight (W_{wet}) was determined as quickly as possible. Weight of dry membrane (W_{dry}) was determined after completely drying in vacuum at 100 °C for 24 h. The water uptake was calculated by using the following equation:

$$\frac{W_{wet} - W_{dry}}{W_{dry}} \qquad (1)$$

2.4. Ion-exchange capacity

Titration method was used to determine the ion-exchange capacity. Each hybrid membrane was soaked in 1 M sodium chloride aqueous solution for 24 h to exchange protons with sodium ions. The ion-exchanged solution was titrated with 0.01 M sodium hydroxide solution. The ion-exchange