

Proton Selectivity through Poly(vinyl alcohol) Based Polymer Electrolyte Membranes for Direct Methanol Fuel Cell

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Introduction

A direct methanol fuel cells (DMFCs) using polymer electrolyte membranes are one of the most attractive power sources due to the stable operation at a rarely low temperature, the high energy generation yield and energy density, the simplicity of system [1-2]. Most DMFC research has concentrated on polymer electrolyte membrane fuel cells (PEMFC) fed directly with methanol [3]. The proton diffusion across the membrane is associated with water transport in the membrane and methanol is also transported to the cathode by electro-osmotic drag. The methanol transport, that is called as methanol crossover, decrease in cell performance [4]. Considerable effort has been developed in order to reduce methanol crossover as well as to reach high proton conductivity. Poly(vinyl alcohol) (PVA) membrane has been used in ethanol dehydration to break the ethanol-water azeotrope because it selectively passes water molecule over ethanol or methanol [5]. The diffusion coefficient of water-soluble solutes and the ionic conductivity through charged PVA membranes depends on the water content and charge density [6]. Hence, it is important to examine the dependence of the water content and polyanion content of the membrane on the methanol permeability and proton conductivity.

In this study, we have prepared a polymer electrolyte membrane (PEM) by blending PVA and a polyanion changing polyanion content. The ionic conductivity, mechanical strength and methanol permeability of the PEMs has been measured as a function of the water content and polyanion content.

Experimental

PEM preparation. PEMs were prepared by casting mixed solution of poly(vinyl alcohol) and poly(vinyl alcohol-co-2-acrylamido-2-methylpropane sulfonic acid) (AP-2) on a glass plate and drying it at 50°C. The PEMs obtained were annealed at various temperatures for 20 min and then were cross-linked chemically by immersing them in a glutaraldehyde solution at 25°C for 24h to control their water content.

The water content. The water content was measured as follows: a PEM, weighted in the dry state, was immersed in an ion-exchanged water at 25°C for 3 days. The PEM was removed from the water, tapped with filter paper to remove excess water on the PEM surface, and was weighted in the wet state. The water content is given from the weights in the wet state, Ww , and in the dry state, Wd , as:

$$H \equiv \frac{(Ww - Wd)/1.0}{(Ww - Wd)/1.0 + Wd/1.3} \quad (1)$$

where 1.0 and 1.3 are the densities of water and PVA.

Proton conductivity. The ionic conductivity at 25°C was determined by impedance spectroscopy using a chemical impedance meter (HIOKI 3532-80) controlled by a personal computer.

Methanol permeability. Permeation experiments were performed by using an acrylic plastic cell of two parts separated by a PEM. One chamber of the cell was filled with 10M methanol solution and the other chamber an ion-exchanged water. The volumes of the chambers at the low- and the high-concentration sides were 120cm³ and 400 cm³, respectively. The effective membrane area of the cell was 7.07cm². The solution in the chamber at the low-concentration side was sampled to measure the concentration of methanol using an gas chromatograph.

Results and discussion

The water content of the PEMs increases with polyanion, AP-2 content because osmotic pressure in the PEMs increases with increasing the number of the charged groups. The water content decreases with increasing annealing temperature because the degree of crystallinity in the PVA matrix increases with increasing annealing temperature.

The proton conductivity (σ) and methanol permeability (P) of the PEMs increase with increasing AP-2 content because the water content

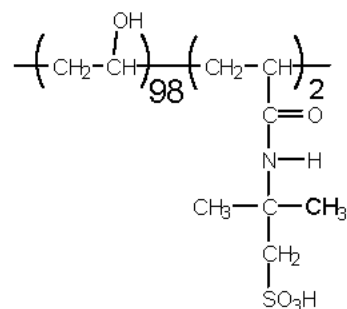


Figure 1. Chemical structure of AP-2.

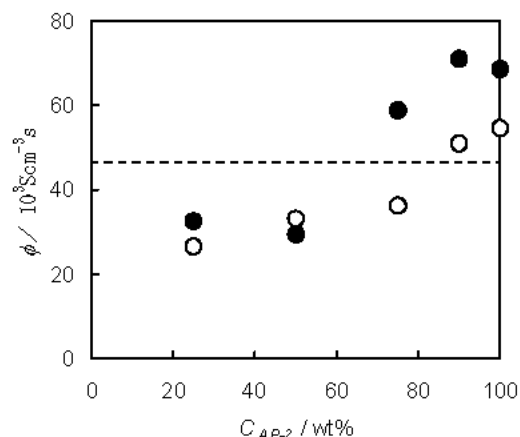


Figure 2. The proton permselectivity, ϕ , as a function of AP-2 content, C_{AP-2} . Measuring temperature: 25°C, MeOH concentration: 10M. Annealing temperature : ●, 170°C ; ○, 160°C. Dotted line: ϕ of Nafion@117 measured under the same conditions.

of the PEMs increases with increasing AP-2 content. Fig. 2 shows the proton permselectivity (ϕ) of the PEMs, which is defined as $\phi = \sigma/P$, as a function of AP-2 content. The proton permselectivity increases with increasing AP-2 content. The PEMs annealed at 170°C have higher proton permselectivity than Nafion@117.

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