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Short communication

Modification of proton conducting membrane for reducing methanol crossover in a direct-methanol fuel cell

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Abstract

In order to reduce methanol cross-over to the positive electrode in a direct-methanol fuel cell (DMFC), the concept of modifying the morphology of the proton-conducting membrane is proposed. The method involves using plasma etching and palladium-sputtering on a NafionTM polymer membrane. Methanol permeability tests were conducted in a specially-designed cell. Plasma etching of NafionTM membrane increases the roughness of the membrane surface and decreases the methanol permeability. The sputtering of palladium on the plasma-etched NafionTM further decreases the methanol cross-over. Improved DMFC performance curves are obtained in a single cell which contains the modified NafionTM. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Direct-methanol fuel cell; Surface modification; Methanol cross-over; Methanol permeability

1. Introduction

The direct-methanol fuel cell (DMFC) is a promising power source for clean energy and is expected to be used as a portable power source. Methanol is in liquid form at room temperature, has high energy density, and is inexpensive [1]. One of the main impediments to practical realization of the DMFC as a portable power source is cross-over of methanol through the proton conducting polymer membrane. This results in poor cell performance [2,3]. Considerable research effort has recently been focused on DMFC proton conducting membranes, especially with respect to methanol cross-over [4–6]. Heinzel and Barragán [7] have reviewed the state-of-art.

It is accepted that NafionTM has a dual structure with a hydrophobic region interspersed with ion-rich hydrophilic domains [8]. The pore sizes of the latter domain are inaccessible by decane (and octane) molecules but accessible by water molecules [9]. It is known that methanol diffuses primarily through the water-rich domains. Thus, morphology of the pores in the water-rich domains must affect the rate of methanol cross-over.

We report here a new method for reducing methanol cross-over, namely, plasma-modification of the membrane

surface and palladium-sputtering. This results in a decrease in the pore diameter, an increase in the methanol permeation length, and a decrease in the hydrophilicity of membrane surface — all features which will decrease the extent of methanol cross-over.

2. Experimental

The following three proton-conducting membranes were prepared and compared: (i) plasma-etched membrane; (ii) palladium-sputtered membrane; (iii) plasma-etched and palladium-sputtered membrane.

2.1. Preparation of plasma-modified membranes

In order to fabricate a plasma-etched proton-conducting membrane, argon plasma etching was used. The reactor was a conventional parallel-plate diode type with the lower electrode coupled to a 13.56 MHz rf power supply through an impedance matching network. Typical plasma conditions were as follows: argon gas pressure = 5 mTorr; argon flow rate = 30 sccm; rf power = 100 W; bottom power = 100 W. For the preparation of a palladium-sputtered proton-conducting membrane, metallic palladium was deposited on the surface of a NafionTM 117 membrane under an argon pressure of 5×10^{-3} Torr at 30 W by sputtering from a

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palladium target (99.9% pure; Toshiba Co. Japan). Palladium was also deposited on Si(1 1 1) wafer under the same conditions and scanning electron microscopic analysis showed the thickness to be 20 nm. Palladium was deposited on the plasma-etched Nafion™ by means of the same sputtering method.

2.2. Methanol permeability measurement

Using the procedure reported elsewhere [10], the methanol permeability of the membranes was measured in a glass cell which contains the membrane clamped between two compartments. One compartment ($V_A = 18.03$ ml) was filled with a solution of methanol (8 vol.%) and 1-butanol (0.2 vol.%) in deionized water, and the other compartment ($V_B = 19.75$ ml) was filled with 1-butanol (0.2 vol.%) in deionized water. Both compartments were vigorously stirred during the permeation experiments. The concentrations of methanol in compartment (B) were analysed with a capillary (SUPELCO, Vocol™) gas chromatograph (HP5890) at various times. The methanol permeability was calculated from the slope of the straight-line plot of methanol concentration vs. permeation time.

2.3. Membrane/electrode assembly

Negative (anode) and positive (cathode) gas-diffusion electrodes were prepared from carbon paper (TORAY) which was coated on one side with a layer of an electrocatalyst (Electrochem) and a PTFE binder. The electrocatalysts were 20 wt.% Pt and 10 wt.% Ru/C for the anode and 20 wt.% Pt/C for the cathode. The average platinum loading of each electrode was 2 mg cm^{-2} . After activation, the electrodes were assembled with the modified membranes and hot pressed at 120°C and 100 cm^{-2} for 2 min.

2.4. Single-cell testing

A single cell was installed in a fuel-cell test station which was equipped with provisions for pressure control and flow-rate control of 2 M methanol and oxygen. Because the main aim of these experiments is to determine whether modification of the proton-conducting membrane reduces methanol cross-over, the single-cell testing was designed to feed gas-phase methanol solution and to maintain the pressure in the cathode compartment at 1 atm. A detailed explanation of single-cell testing is given elsewhere [11,12].

3. Results and discussion

The concentration of methanol which has permeated through the clamped membrane is reported in Fig. 1 as a function of time. The permeability values at room temperature are listed in Table 1. Clearly, the surface-modified Nafion™ membranes reduced markedly the degree of methanol permeability. The permeability of the Pd-sputtered membrane is lower than that of the plasma-etched membrane, and membrane modified by both plasma etching and palladium-sputtering shows the lowest permeability. Atomic force microscopy (AFM) was used to provide surface images of both the plasma-etched Nafion™ membrane and the unmodified membrane, see Fig. 2. The etching process increases the surface roughness and hence increases the specific surface area. The rate of methanol permeation is proportional to the permeability and surface area, and is inversely proportional to the permeation length. Thus, decrease in the permeability may be due to a decrease in the pore size after plasma etching and to an increase in the hydrophobicity arising from the preferential etching of $-\text{SO}_3\text{H}$ groups.

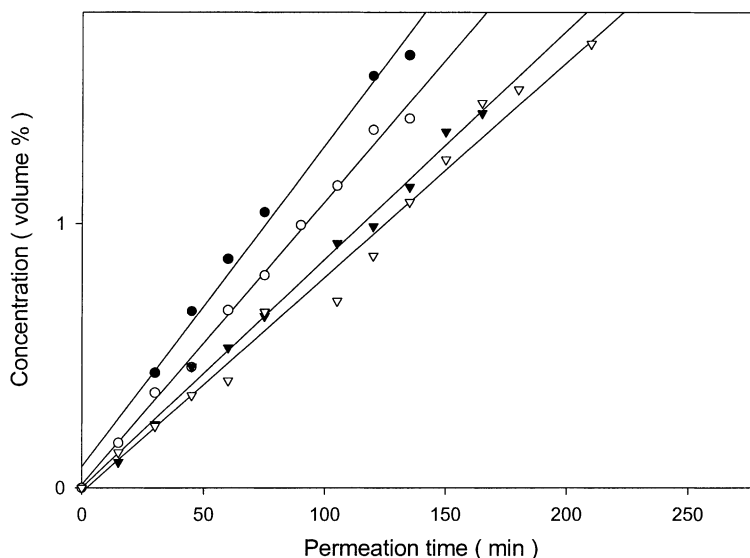


Fig. 1. Concentration of methanol in compartment B permeated through a clamped membrane as a function of time: unmodified membrane (●); plasma-etched membrane (○); Pd-sputtered membrane (▼); plasma-etched and Pd-sputtered membrane (▽).

Table 1
Methanol permeabilities at room temperature of membranes

	Type of membrane			
	Unmodified membrane	Plasma-etched membrane	Pd-sputtered membrane	Plasma-etched and Pd-sputtered membrane
Permeability ($\text{cm}^2 \text{s}^{-1}$)	2.392×10^{-6}	2.106×10^{-6}	1.700×10^{-6}	1.598×10^{-6}

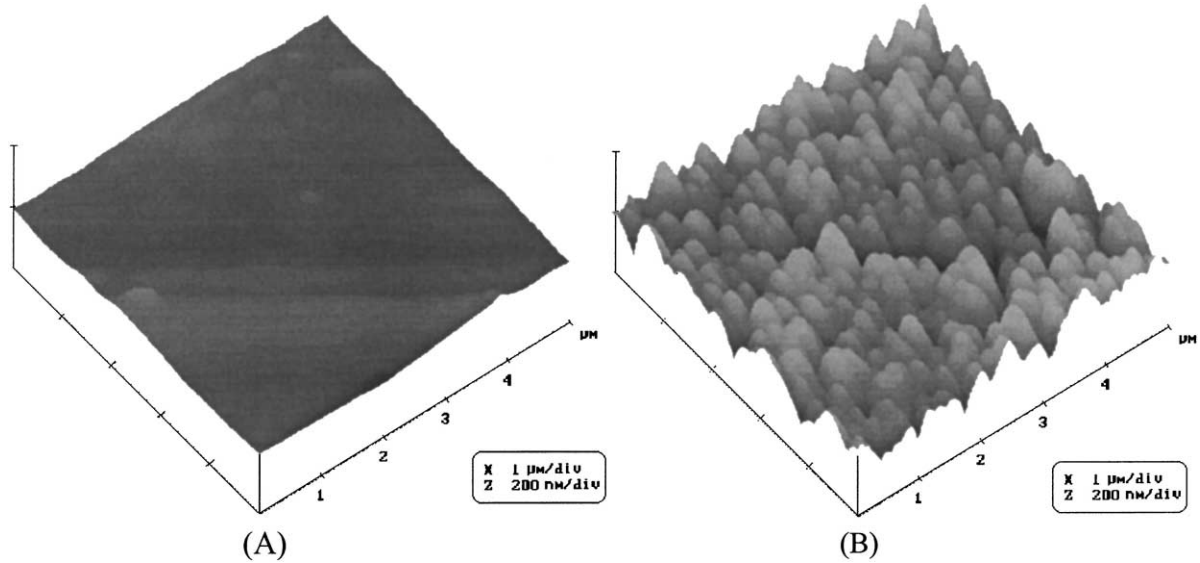


Fig. 2. AFM surface images of (A) unmodified Nafion™ membrane and (B) plasma-etched Nafion™ membrane.

Palladium was chosen to plug the pores of membrane; the metal is known to be an effective storage medium for hydrogen and can easily form palladium hydride. As expected, the methanol cross-over rate decreases without

decreasing the proton transfer rate. This results in better current–voltage characteristics, as shown in Fig. 3.

Current–voltage (I – V) curves for a single cell fabricated with modified membranes, as well as the open-circuit

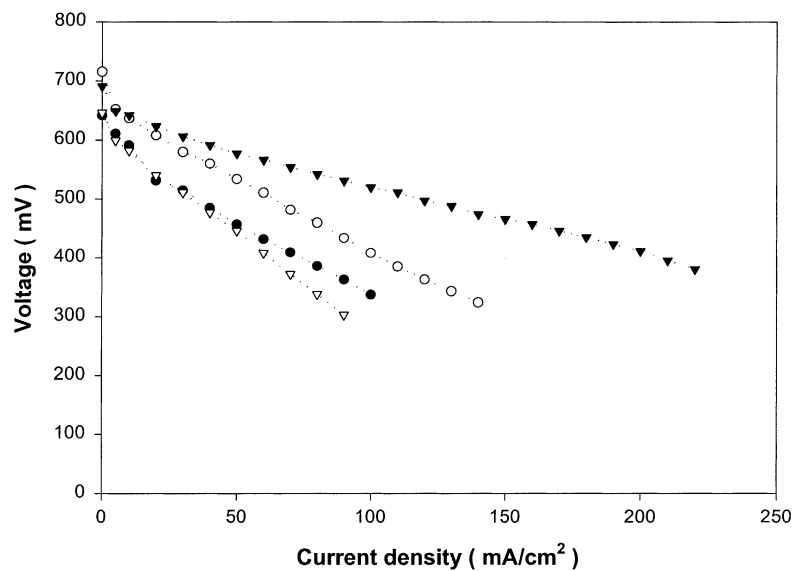


Fig. 3. Current–voltage (I – V) curves of DMFC single cell with: unmodified membrane (●); plasma-etched membrane (○); Pd-sputtered membrane; (▼) plasma-etched and Pd-sputtered membrane (▽). All experiments conducted at $95 \pm 2^\circ\text{C}$.

voltage (OCV), are given in Fig. 3. Methanol diffuses from the anode to the cathode through the proton-conducting membrane with a change in the OCV. Methanol cross-over makes the potential of the cathode shift from an oxygen reduction potential, to a mixed potential with electrooxidation of methanol. The OCV and the I - V performance of a fuel cell fabricated with a modified membrane are higher than those of a fuel cell with an unmodified membrane. The fuel cell with the palladium-sputtered NafionTM membrane exhibits the best performance. It should be noted that etching could have a deleterious effect in that $-\text{SO}_3\text{H}$ functional groups of the NafionTM membrane can be affected by this treatment and result in a decrease in the ion conductivity of the membrane. The fuel cell fabricated with the palladium-sputtered membrane shows the best I - V performance, because during the deposition of palladium, the $-\text{SO}_3\text{H}$ group was not affected and methanol cross-over was reduced. Despite the large reduction in methanol cross-over, the OCVs of both the palladium-sputtered and the plasma-etched membranes are lower than that of the Pd-sputtered membrane. An exact explanation for this behaviour has yet to be found. It can be speculated, however, that uneven palladium-deposition on the very rough plasma-etched membrane might increase the contact resistance between the electrocatalyst layer and the membrane.

4. Conclusion

The surface modification of NafionTM membrane by plasma etching, palladium-sputtering and a combination of plasma etching and palladium-sputtering decreases methanol cross-over significantly. The OCVs and current-voltage

performance of fuel cells fabricated with membranes which have undergone plasma etching and Pd-sputtering are improved significantly, compared with those of a fuel cell fabricated with an unmodified membrane. It is necessary to optimize the balance between the methanol cross-over rate and the ion conductivity of surface-modified membranes.

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