Surface modified Nafion® membrane by ion beam bombardment for fuel cell applications

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Abstract

The interfacial structure between an electrolyte membrane and an electrode catalyst layer plays an important role in determining performance of proton exchange membrane fuel cell (PEMFC) since the electrochemical reactions produce electricity occur on the interfaces that are in contact with hydrogen or oxygen gas, so-called three phase boundaries. To improve performance of the PEMFC by enlarging effective area of the interfaces, surface of Nafion® 115 membrane was roughened by Ar^+ ion beam bombardment before being coated with a catalyst ink to form the electrode layer. With increasing ion dose density from 0 to 1×10^{17} ions cm^{-2}, roughness and hydrophobicity of the membrane surface increased, which could be favored for a high-performance PEMFC. In fuel cell tests, the single cell using Nafion® membrane bombarded at an ion dose density of 10^{16} ions cm^{-2} exhibited maximum power density of 0.62 W cm^{-2}, which was two times higher than that of the single cell employing untreated Nafion® 115 membrane, i.e. 0.30 W cm^{-2}.
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Keywords: Nafion® membrane; Ion beam bombardment; Proton exchange membrane fuel cell (PEMFC); Surface roughness; Interfacial structure

1. Introduction

Polymer electrolyte membrane fuel cell (PEMFC) is considered as a promising power source for zero emission vehicles to replace the internal combustion engine with its favorable features such as high power density, low operating temperature, convenient fuel supply, etc. Although extensive R&D has been devoted to development of PEMFC for the last decades, high fabrication cost of PEMFC stacks still remains a barrier to commercialization. Cost reduction of PEMFC stacks could be achieved in two ways; development of new low-cost materials or improvement of fabrication methods with the currently used materials.

Among the structural factors of a PEMFC, the interfacial structure between an electrolyte membrane and an electrode catalyst layer plays an important role in determining the cell performance since the electrochemical reactions take place on the interfaces that are in contact with hydrogen or oxygen, so-called three phase boundaries. Thus, with enlarging effective area of the interfaces, cell performance would be improved and material usage would be reduced, leading to cost reduction of PEMFC stacks. For this purpose, surface of Nafion® membrane which is the most commonly used electrolyte for PEMFC was roughened by using SiC paper [1–2] or by plasma etching method [3]. However, the previous studies [1–3] did not consistently show that those surface modifications of Nafion® membrane improved performance of PEMFC.

In this work, to increase the effective area of the catalyst/electrolyte interface and hence to improve the fuel cell performance, surface of Nafion® membrane was roughened by ion beam bombardment that was reported to elaborately modify surface morphology of a polymer membrane without changing its bulk properties [4,5].

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2. Experimental

2.1. Membrane preparation

Nafion$^{®}$ 115 membrane (Du Pont, Inc.) was used as an electrolyte membrane for the fuel cells. Before ion beam bombardment onto the membrane surface, Nafion$^{®}$ 115 membrane as-received in Na^{+}-form was converted to H^{+}-form in H$_2$SO$_4$ solution and then rinsed with deionized water. The prepared membranes with a size of 8 cm × 8 cm were mounted on a bombardment frame with a window size of 5 cm × 5 cm, equal to the active area of the test fuel cells, and dried up at 80 °C for 2 h.

Then, the mounted membrane was brought in a vacuum chamber equipped with an ion beam source as depicted in Fig. 1. The ion beam was generated from a cold hollow cathode ion source with a diameter of 5 cm. Ion dose was measured using a Faraday cup. Ion density bombarded onto the surface of the membranes was 10^{15}, 10^{16}, and 10^{17} ions cm^{-2} at the ion energy of 1.2 keV. Vacuum level in the chamber was kept to be $(0.133–5.3) \times 10^{-5}$ kPa during the bombardments.

2.2. Characterization of the membranes

To investigate effects of the ion beam bombardment on the characteristics of Nafion$^{®}$ 115 membrane, morphology and roughness of the membrane surface, water contact angle, and proton conductivity were measured. Surface morphology was observed using scanning electron microscopy (SEM, Hitachi S-4200) and atomic force microscopy (AFM, Park Scientific Instrument) that provides data on surface roughness. To measure proton conductivity of the membranes, a test cell was assembled by placing the membrane between platinum electrodes [6] and then AC impedance of the test cell was measured with the frequency ranging from 10 Hz

to 10 kHz and an excitation voltage of 10 mV. As a measure of hydrophobicity of membrane surface, water contact angle was measured in sessile drop method using a contact angle micrometer (Cam Micro, Tantec).

2.3. Fuel cell tests

To evaluate performance of PEM fuel cells employing the surface treated membranes, single cells were prepared using the untreated and treated membranes. Catalyst ink for electrode was prepared by mixing 40 wt.% Pt/C (Johnson Matthey, Inc.) with isopropyl alcohol (Baker Analyzed HPLC Reagent) and 5 wt.% Nafion$^{®}$ solution (Du Pont, Inc.). For 1 g of the Pt/C catalyst powder, 330 mL of isopropyl alcohol and 6.6 g of the Nafion$^{®}$ solution was used. Then, the catalyst ink was sprayed on the prepared membrane with catalyst loading of 0.3 and 0.2 mg Pt cm^{-2} for anode and cathode, respectively. The ion beam bombarded surface was used for cathode side. Active electrode area was 25 cm^2.

Single cells were assembled with the prepared catalyst-coated membrane (CCM), gas diffusion media (Sigracet$^{®}$, SGL Carbon, Inc.), gaskets, and graphite blocks. Hydrogen and oxygen or air was fed to the anode and cathode, after passing through a bubble humidifier at a temperature of 80 and 65 °C, respectively. Operating temperature and pressure were 80 °C and 1 atm, respectively. Performance of the single cell was evaluated by measuring the i–V characteristics using an electronic loader (Daegil Electronics, EL 500P). For i–V measurement, open circuit voltage (OCV) of the single cell was recorded after supplying the humidified reactant gases for 2 h. Then, the cell voltage was lowered to 0.85 V and, after 1 h, current flowing through the electric load was recorded. In the same way, i–V characteristics were measured at every 50 mV in the voltage range from 0.8 to 0.3 V.

3. Results and discussions

3.1. Characteristics of the membranes

Fig. 2 presents scanning electron microscopy (SEM) images for surface of the untreated and the treated membranes, clearly showing that with increasing the bombarded ion density from 0 to 10^{17} ions cm^{-2}, surface of the membrane was roughened. Surface of the bombarded membranes seems to have nodules while the untreated membrane exhibits a flat surface. The higher the ion density was, the larger and the higher were the nodules on the membrane surface.

In addition to SEM images, surface morphology of the membranes was examined using atomic force microscopy (AFM). Fig. 3 shows AFM images for surface of the untreated and the treated membranes. With increasing the bombarded ion density from 0 to 10^{17} ions cm^{-2}, surface of the membranes was roughened, which was in good accordance with SEM analysis results in Fig. 2 (note that the scale of z-direction of the AFM images is different). From the AFM
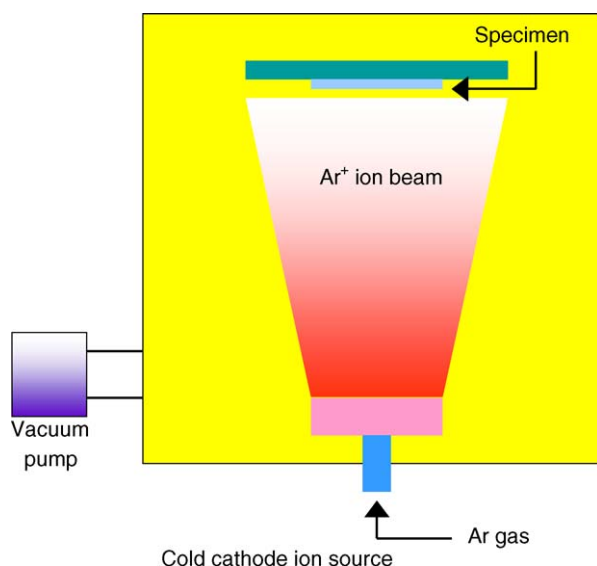

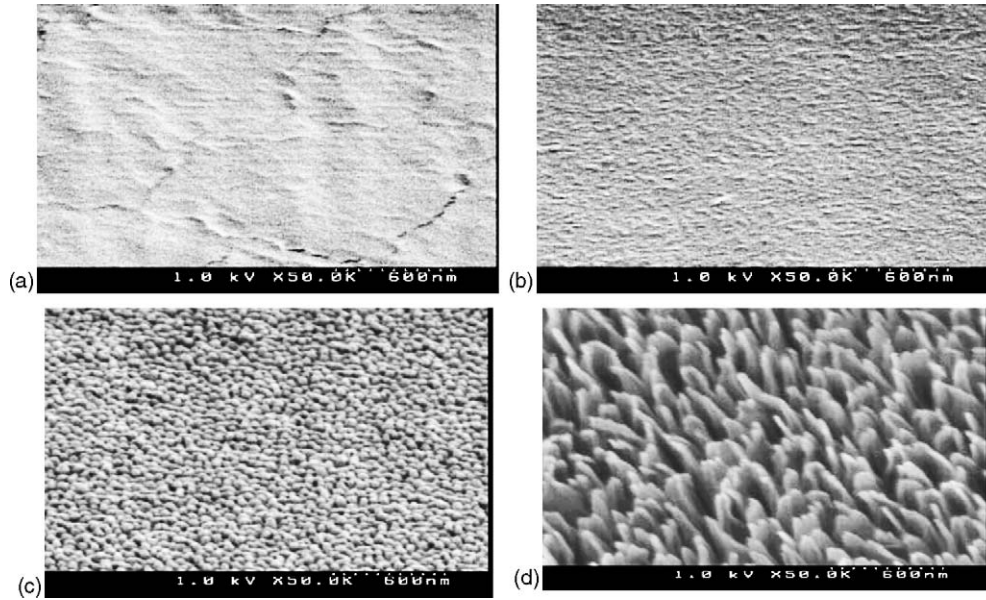Fig. 1. A schematic diagram of the apparatus for ion beam bombardment.

Fig. 2. SEM surface images of (a) the untreated and the surface treated membranes at (b) 10^{15}, (c) 10^{16}, and (d) 10^{17} ions cm^{-2} at an ion energy of 1 keV.

Table 1
Geometrical properties of the untreated and the surface-treated Nafion® 115 membranes analyzed by AFM

Parameter	Untreated	Ion dose density (ions cm^{-2}) at 1 keV		
		1×10^{15}	1×10^{16}	1×10^{17}
Peak to valley (nm)	247	410	836	1790
Mean height (nm)	75	146	473	1130
RMS roughness (nm)	21	32	87	204

analysis, RMS roughness, peak to valley, and mean height were obtained and summarized in Table 1. As ion density increased from 0 to 10^{17} ions cm^{-2}, RMS roughness drastically increased from 21 to 204 nm. Peak to valley and mean

height also increased from 247 to 1790 nm and from 75 to 1130 nm, respectively. Based on the results, it was expected that by the ion beam bombardment resulting in a roughened membrane surface, effective area of the interface between the membrane and electrode catalyst layer could be increased for fuel cell applications.

For PEM fuel cells, proton conductivity of the membrane is one of the most important parameters. Fig. 4 shows effects of ion density on proton conductivity of Nafion® 115 membrane. Without the ion beam bombardment, proton conductivity of the membrane was measured to be 0.119 S cm^{-1}. At ion densities of 10^{15}, 10^{16}, and 10^{17} ions cm^{-2}, proton conductivity was 0.113, 0.111, and 0.127 S cm^{-1}. Those results
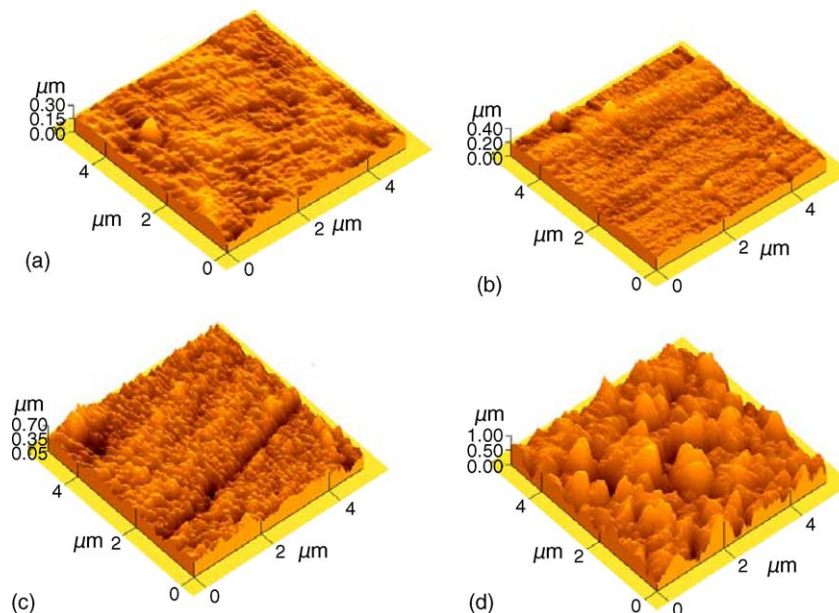

Fig. 3. AFM surface images of (a) the untreated and the surface treated membranes at (b) 10^{15}, (c) 10^{16}, and (d) 10^{17} ions cm^{-2} at an ion energy of 1 keV.
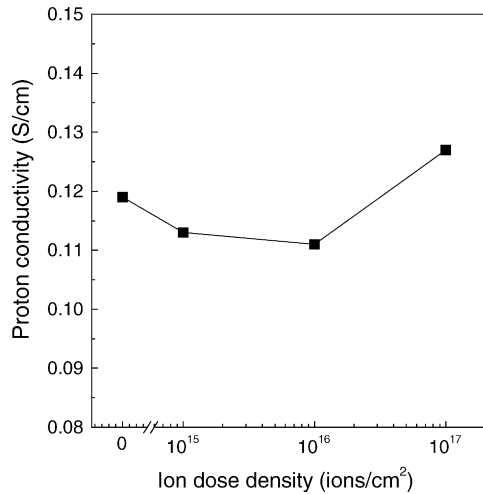
Fig. 4. Effects of ion dose density on proton conductivity of the membrane.

demonstrate that the ion beam bombardment had little effect on proton conductivity of the membrane.

As a measure of hydrophobicity of membrane surface, water contact angle was measured for the untreated and the treated membranes and presented in Fig. 5. With increasing ion density, water contact angle increased from 80° to 140°, the membrane surface became more hydrophobic. Since proton conductivity of all the membrane was almost constant, hydrophobic surface could be favored for fuel cell applications especially at high current densities where water should be properly removed from the electrode catalyst layer.

3.2. Fuel cell performance

Before fuel cell testing, interfacial structure of the catalyst coated membrane were observed. Fig. 6 shows cross-sectional SEM images of the catalyst-coated membranes prepared using the untreated and the treated membrane at ion density of 10^{16} ions cm^{-2}. The interface between the treated
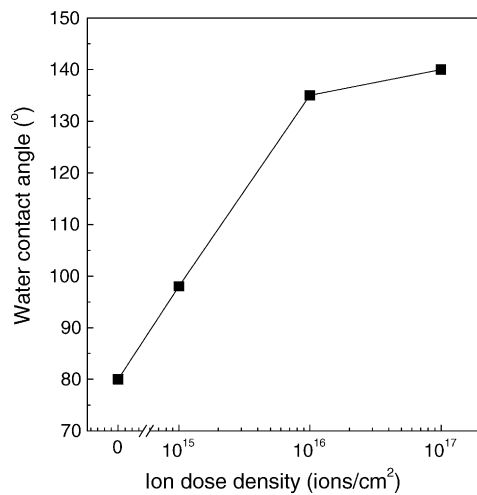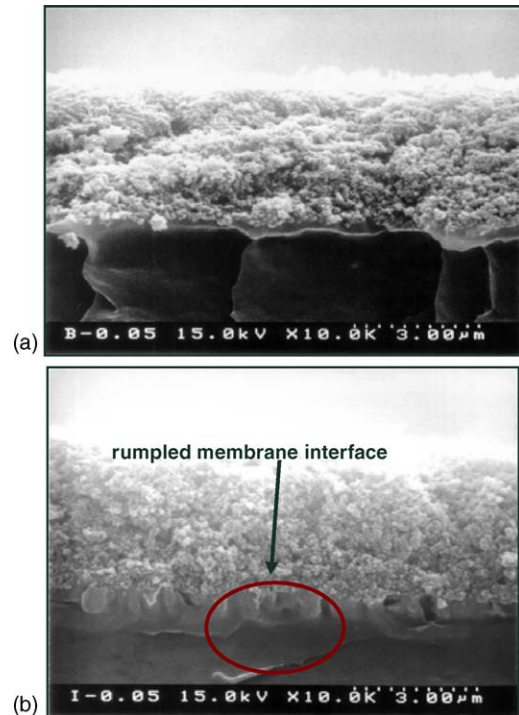

Fig. 6. Cross-sectional SEM images of the MEA fabricated using (a) the untreated and (b) the treated membrane at an ion dose density of 10^{16} ions cm^{-2}.

membrane and electrode catalyst layer seemed to be rumpled while the interface between the untreated membrane and electrode catalyst layer seemed to be flat, implying that effective area of the electrochemical active site could be increased by the ion beam bombardment.

Fig. 7 demonstrates fuel cell performance using the untreated and the treated membranes as an electrolyte. Open circuit voltage of the single cells was almost constant to be 0.95 V. With increasing ion density to 10^{16} ions cm^{-2}, the cell performance was significantly improved and then, low-

Fig. 5. Effects of ion dose density on water contact angle of the membrane.

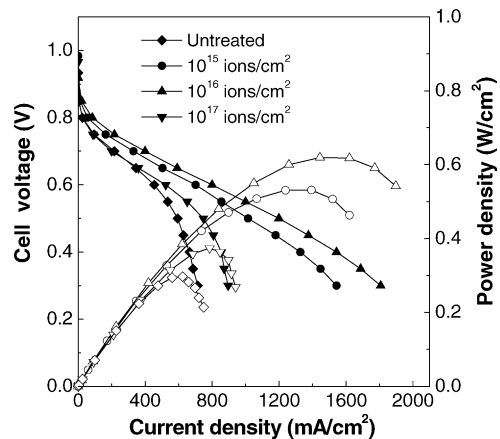Fig. 7. Effects of ion dose density on performance of the fuel cells using the untreated and the treated membrane at an ion dose density of 10^{15}, 10^{16}, and 10^{17} ions cm^{-2} at 1 keV. $T_{cell} = 80\,°C$, $U_{H_2} = 0.25$, $U_{O_2} = 0.5$, and $P = 1$ atm.

ered at ion density of 10^{17} ions cm^{-2}; at a cell voltage of 0.6 V, current density was 454, 702, 800, and 523 mA cm^{-2}. Maximum power density was also increased by the ion beam bombardment from 0.3 to 0.53, 0.62, and 0.37 W cm^{-2} at ion densities of 10^{15}, 10^{16}, and 10^{17} ions cm^{-2}. The cell performance evaluated as current density at a cell voltage of 0.6 V and maximum power density increased with ion beam bombardment up to 10^{16} ions cm^{-2} with the enlarged interfacial area between the electrolyte and the catalyst layer, and then decreased at 10^{17} ions cm^{-2} probably due to utilization loss of catalyst particles buried in the deep valleys. Compared with the single cell using untreated membrane, the single cells employing treated membrane at 10^{15} and 10^{16} ions cm^{-2} showed markedly higher performance at high current density region, i.e. higher than 1000 mA cm^{-2}; single cell using untreated membrane exhibited abrupt voltage drop with flooding at current densities higher than 400 mA cm^{-2}. Those results could be associated with the more hydrophobic surface of the surface-treated membranes as revealed in Fig. 5.

4. Conclusions

By bombarding Ar ions onto the surface of Nafion® 115 membrane at ion dose of 10^{15}, 10^{16}, and 10^{17} ions cm^{-2} at 1 keV, proton conductivity of the membrane was not affected while hydrophobicity and roughness of the membrane surface was significantly increased. As a result, the single cells using the treated membranes exhibited significantly improved performance in terms of current density at a cell voltage of 0.6 V and maximum power density, up to ion dose density of 10^{16} ions cm^{-2}; the single cell using the membrane bombarded at an ion dose density of 10^{16} ions cm^{-2} exhibited maximum power density of 0.62 W cm^{-2}, which was two times higher than that of the single cell employing untreated membrane, i.e. 0.30 W cm^{-2}. Those results could be attributed to the enlarged interfacial area between the electrolyte membrane and the electrode catalyst layer and more hydrophobic membrane surface to prevent flooding at high current density region, resulting from roughened membrane surface by the ion beam bombardment. However, at ion dose density of 10^{17} ions cm^{-2}, the performance was lowered probably due to the loss of catalyst powders buried in the deep valleys formed by the bombardments.

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