Effects of platinum loading on performance of proton-exchange membrane fuel cells using surface-modified Nafion® membranes

M. Prasanna, E.A. Cho *, H.-J. Kim, T.-H. Lim,
I.-H. Oh, Sung-Ahn Hong

*Fuel cell Research Center, Korea Institute of Science and Technology, 39-1 Hawolgok-dong,
Sungbuk-gu, Seoul 136-791, South Korea*

Abstract

The interface between the electrolyte and electrode catalyst plays an important role in determining the performance of proton-exchange membrane fuel cells (PEMFCs) since the electrochemical reactions take place at the interface in contact with the reactant gases. To enhance catalyst activity by enlarging the interfacial area, the surface of a Nafion® membrane is roughened by Ar^+ ion beam bombardment that does not change the chemical structure of the membrane, as confirmed by FT-IR spectra. Among the membranes treated with ion dose densities of 0, 10^{15}, 10^{16}, 5×10^{16} and 10^{17} ions cm^{-2} at ion energy of 1 keV, the membrane treated at ion dose density of 5×10^{16} ions cm^{-2} exhibits the highest performance. Using the untreated and the treated membrane with 5×10^{16} ions cm^{-2}, the effects of platinum loading on cell performance are examined with Pt loadings of 01, 0.2, 0.3, 0.4 and 0.55 mg cm^{-2}. Except for a Pt loading of 0.55 mg cm^{-2} where mass transport limits the cell performance, the single cell using a treated membrane gives a higher performance than that using an untreated membrane. This implies that the cell performance can be improved and the Pt loading can be reduced by ion beam bombardment.
© 2006 Elsevier B.V. All rights reserved.

Keywords: Ion beam treatment; Surface morphology; Proton exchange membrane fuel cells; Platinum catalyst loading; Interface; Membrane characterization

1. Introduction

One of the technical challenges in developing proton-exchange membrane fuel cells (PEMFCs) is reduction of the stack fabrication cost possibly by lowering the platinum loadings for the electrodes. For this reason, control of the electrolyte|electrode interfacial structure is a key technique in fabricating PEMFC stacks since the electrochemical reactions producing electricity occur at the electrolyte|catalyst interfaces that are in contact with hydrogen or oxygen gas, the so-called three-phase boundaries (TPBs).

To improve Pt utilization by forming the electrolyte|catalyst interfaces into an effective structure, a proper amount of membrane ionomer has been added to the catalyst layer [1]. Alternatively, the surface of electrolyte membranes has been modified.

Sheppard et al. [2] showed that the Pt surface area could be increased by depositing Pt on a Nafion® membrane that was roughened by SiC paper. This was due to an increased number of nucleation sites on the membrane. Since it was difficult to control the surface roughness by using SiC paper [2] or plasma etching [3], membrane–electrode assemblies (MEAs) were fabricated by means of methods that did not consistently exhibit a performance improvement of PEMFCs.

Cho et al. [4] reported that by roughening the surface of a Nafion® membrane by ion beam bombardment, the maximum power density of a single cell operating on hydrogen and oxygen was almost doubled. This was attributed to the enlarged interfacial area between the electrolyte membrane and the electrode catalyst layer. Reduction of Pt loading is, however, more critical in PEMFCs operating on hydrogen and air due to the significant kinetic loss for the oxygen reduction reaction. In this work, to improve Pt utilization and hence to reduce Pt loading, effects of Pt loading and surface roughness of the Nafion® membrane on the electrochemical characteristics of a PEMFC

* Corresponding author. Tel.: +82 2 958 5279; fax: +82 2 958 5199.
E-mail address: eacho@kist.re.kr (E.A. Cho).

operating on hydrogen and air is examined by measuring cell performance, cyclic voltammograms (CVs), and impedance spectroscopy.

2. Experimental

2.1. Preparation of ion-beam-treated membranes

As an electrolyte, a Nafion® 112 (Du Pont, Inc) membrane was pretreated using H_2O_2, H_2SO_4 and de-ionized water before ion beam bombardment. 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, which was equal to the active area of the test fuel cells, and dried at 80 °C for 2 h.

The mounted membrane was put in a vacuum chamber that was equipped with a hollow cathode ion beam source as described in a previous study [4]. The ion dose was measured using a Faraday cup. The ion density bombarded on the membrane surface was 10^{15}, 10^{16}, 5×10^{16}, 10^{17} ions cm^{-2} at an ion energy of 1.0 keV. The vacuum level in the chamber was kept at 0.133–5.3×10^{-5} kPa during the bombardments.

2.2. Membrane characterization

To examine effects of ion beam treatment on the membrane characteristics, the surface morphology and the chemical structure of the membranes were analyzed by means of scanning electron microscopy (SEM, Hitachi S-4200) and FTIR spectoscopy (Nicolet Magna IR 560 model), respectively.

2.3. Fuel cell tests

Catalyst ink was prepared by mixing 40 wt.% Pt/C (Johnson Matthey, Inc.) with isopropyl alcohol (Baker Analyzed HPLC Reagent) and then sonicated for 1 h. 5 wt.% Nafion® solution (Du Pont, Inc.) was added to the catalyst ink, which was sonicated again for 1 h. The MEA was prepared by spraying the prepared ink over the membranes. The active electrode area
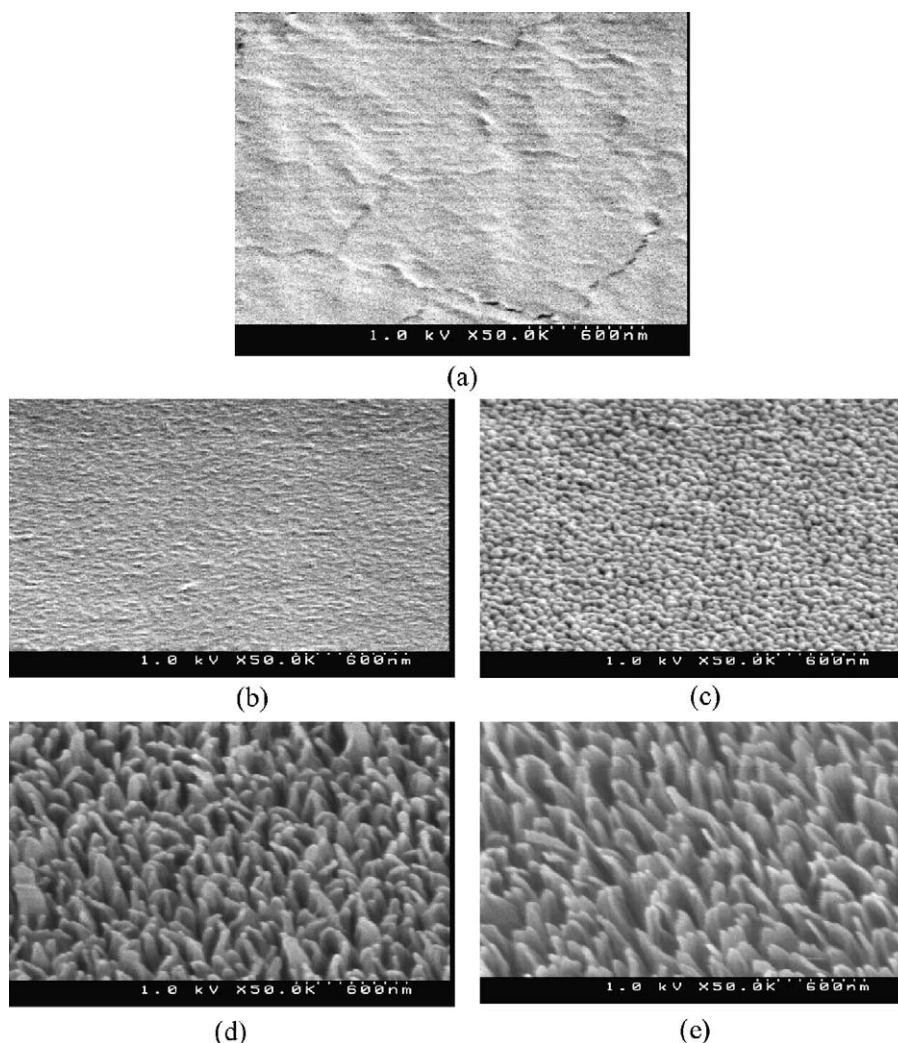

Fig. 1. Scanning electron micrographs of the surface of (a) untreated membranes, treated membrane with an ion beam dose of (b) 10^{15}; (c) 10^{16}; (d) 5×10^{16}; and (e) 10^{17} ions cm^{-2}. Ion beam energy = 1 keV.

was 25 cm^2 with a catalyst loading of 0.3 mg-Pt cm^{-2} for the anode. To examine the effects of Pt loading on the performance of single cells using an untreated or the treated membrane, the Pt loading for the cathode was in the range 0.1–0.55 mg-Pt cm^{-2} and was sprayed onto the treated side of the membranes.

Single cells were assembled with the prepared catalyst-coated membrane (CCM), a gas-diffusion layer (Sigracet®, SGL Carbon Inc.), gaskets, and graphite field-flow plates. Hydrogen and oxygen (or air) were fed to the anode and cathode, respectively, after passing through a bubble humidifier at a temperature of 80 °C (anode) and 65 °C (cathode). The cell temperature was 80 °C.

The performance of the single cells was evaluated by measuring the current–voltage (*i–V*) characteristics using an electronic load (Daegil Electronics Inc, EL 1000P). For *i–V* measurement, the open-circuit voltage (OCV) of the single cell was recorded after activation for 2 days at a constant current density of 800 mA cm^{-2}. The single cell was then subjected to a current density of 50 mA cm^{-2} and, when stabilized, the cell voltage was recorded. In the same way, *i–V* characteristics were measured at every 100 mA cm^{-2} in the current density range from 100 to 1100 mA cm^{-2}.

The ohmic and charge-transfer resistances were estimated by measuring the a.c. impedance of the cathode of a single cell that was used as the working electrode. For impedance measurements, humidified air and hydrogen were supplied to the cathode and the anode, respectively. A IM6 (ZAHNER) instrument was used for the impedance measurements and the applied frequency was varied from 10 to 10 kHz with an excitation voltage of 5 mV (peak-to-peak). The Pt utilization or electrochemical active surface area (EASA) of the cathode was estimated from CVs that were recorded at a scan rate of 50 mV s^{-1} and a cell temperature of 80 °C. During measurement of the CVs, humidified nitrogen and hydrogen were fed to the working electrode and the counter electrode, respectively. For the measurements of a.c. impedance and CVs, the counter electrode also served as a reference electrode since the overpotential at the counter electrode

for the hydrogen oxidation or evolution reaction is negligible [5].

3. Results and discussions

3.1. Characterization of untreated and surface-treated membranes

Scanning electron micrographs of the surface of an untreated Nafion® 112 membrane and one treated with an ion dose density from 10^{15} to 10^{17} ions cm^{-2} at an ion beam energy of 1 keV are shown in Fig. 1. With increasing ion dose density, the surface of the membrane is clearly roughened. It has a nodule-like structure at ion dose densities of 10^{15} and 10^{16} ions cm^{-2} and a whisker-like structure at 5×10^{16} and 10^{17} ions cm^{-2}.
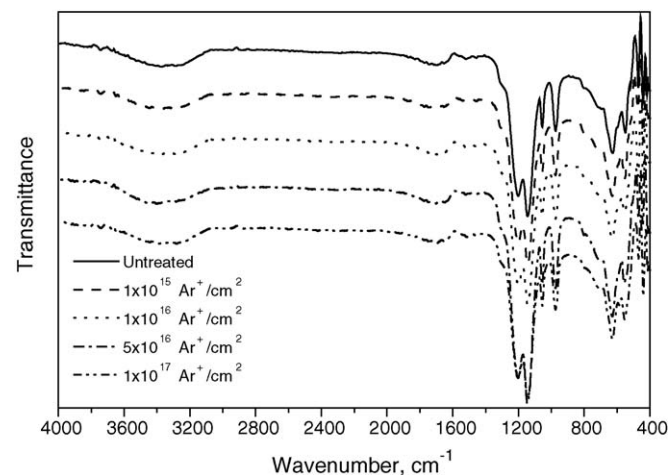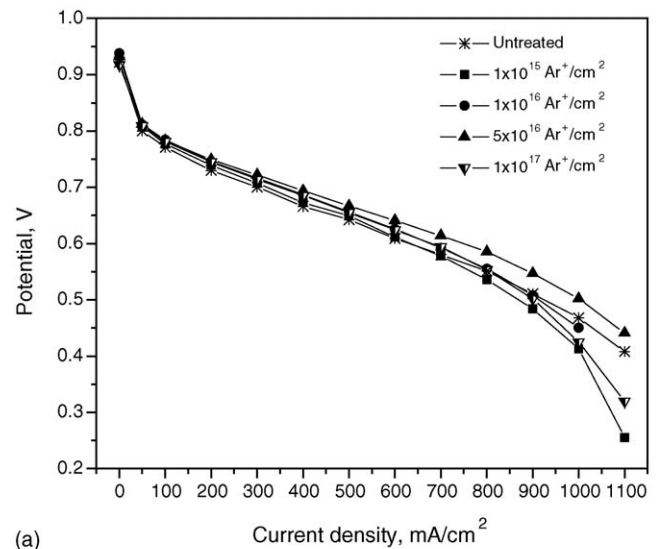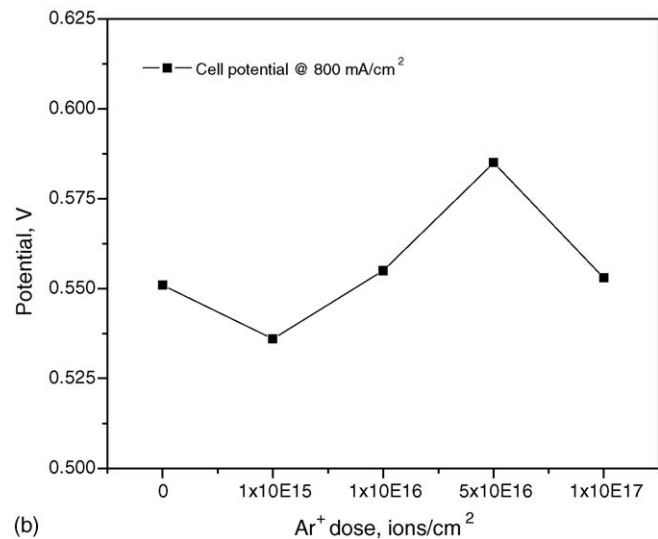

Fig. 3. Effects of ion dose density on (a) *i–V* curves and (b) cell potential at 800 mA cm^{-2} of single cells obtained from data in (a). Cathode catalyst loading = 0.2 mg-Pt cm^{-2}; H$_2$/air.

Fig. 2. FTIR-ATR spectra for untreated and the treated membranes.

In the previous study [4], it was reported that with increasing ion dose density from 10^{15} to 10^{17} ions cm^{-2}, the RMS roughness of the ion-beam-bombarded membrane increased from 21 to 204 nm without changing the ionic conductivity of the membrane.

One of the advantages of ion beam bombardment for modifying a membrane is to roughen the surface structure without changing its bulk properties [6]. Thus, to examine the effects of ion beam bombardment on the chemical structure of the membrane, FTIR-ATR analysis was performed on untreated and the surface-treated membranes. The resulting spectra are shown in Fig. 2 and display the well-defined [7–10] peaks for Nafion®, namely: C–O–C symmetric stretching of the side chain at 975.81 cm^{-1}, SO$_3^-$ symmetric stretching at 1056.8 cm^{-1} and antisymmetric stretching masked by the strong CF$_2$ stretch-

ing at around 1300 cm^{-1}. The intense bands at 1145.51 and 1201.44 cm^{-1} correspond to CF$_2$ symmetric and antisymmetric stretching of the polymer. The peak positions were identical for all samples and this confirms that the chemical structure of the membrane is not affected by ion beam bombardment. These findings can be associated with the constant ionic conductivity of the untreated and the treated membranes [4].

3.2. Effects of ion dose density on cell performance

To investigate the effects of ion dose density on cell performance, single cells were prepared with either untreated or treated Nafion® 112 membranes. The i–V curves for the single cells measured at 80 °C are given in Fig. 3(a). The open-circuit voltages of the single cells are almost identical, viz., 0.94 V. At current densities from 50 to 1100 mA cm^{-2}, the
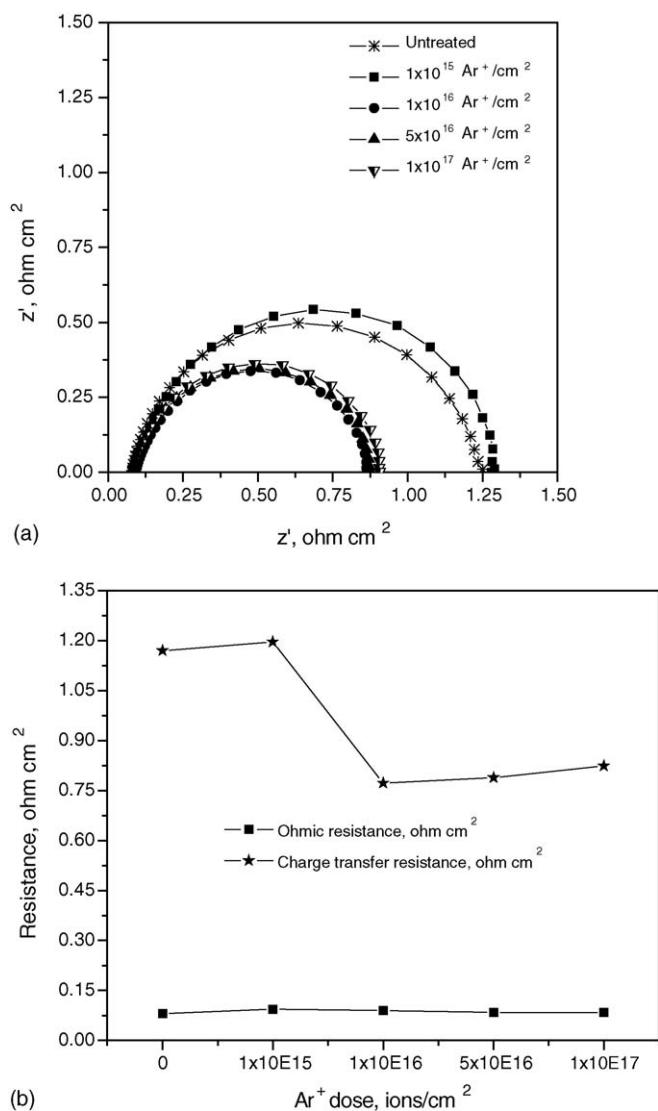

Fig. 4. Effect of ion dose density on (a) Nyquist plot and (b) ohmic and charge-transfer resistance of single cells obtained from data in (a). Cathode catalyst loading = 0.2 mg-Pt cm^{-2}; H$_2$/air.
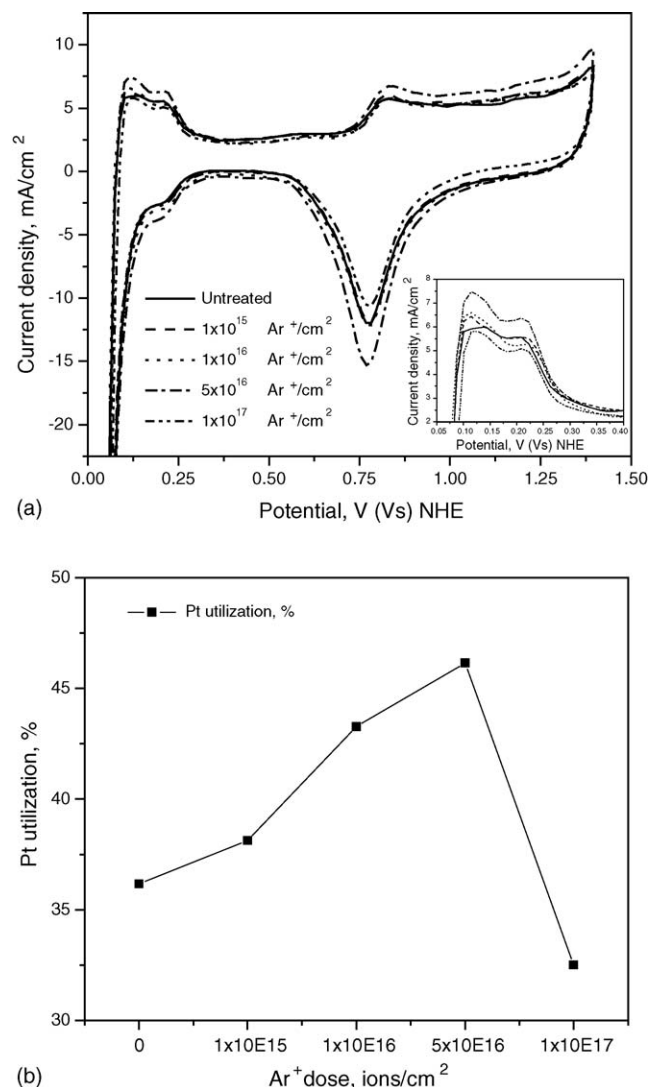

Fig. 5. Effect of ion dose density on (a) cyclic voltammogram and (b) Pt utilization of single cells obtained from data in (a). Scan rate = 50 mV s^{-1}.

single cell employing the membrane bombarded at an ion density of 5×10^{16} ions cm^{-2} exhibited the highest voltage; at a current density of 800 mA cm^{-2}, cell voltage was 0.55, 0.54, 0.56, 0.59 and 0.55 V at ion dose densities of 0, 10^{15}, 10^{16}, 5×10^{16} and 10^{17} ions cm^{-2}, respectively, as presented in Fig. 3(b). In the previous study [4], it was revealed that a single cell using a Nafion® 115 membrane bombarded at an ion density of 10^{16} exhibited the best performance among the single cells employing the membranes treated at ion dose densities of 0, 10^{15}, 10^{16} and 10^{17} ions cm^{-2}. It was reported that the enlarged interfacial area between the electrolyte membrane and the electrode catalyst layer by the ion beam bombardment could result in the enhanced cell performance and that at an ion dose density of 10^{17} ions cm^{-2}, the performance was lowered probably due to the loss of catalyst particles that became buried in the deep valleys formed by the bombardments.

To examine the ohmic and charge-transfer resistance of the single cells, electrochemical impedance spectroscopy was performed at 0.8 V after single-cell tests. The resulting Nyquist plots are shown in Fig. 4(a). The applied cell voltage was IR-corrected. The Nyquist plots are semi-circular; the left

point of intersection with the *x*-axis corresponds to the ohmic resistance and the diameter of the semi-circle to the charge-transfer resistance [11]. The ohmic resistance of the single cells is almost constant at 0.085 Ω cm^2, i.e., it is independent of surface roughness of the membranes, as illustrated in Fig. 4(b). This behaviour is in good agreement with previous results [4] that showed that ion beam bombardment does not affect the ionic conductivity of the membrane. By contrast, the charge-transfer resistance of the single cell is markedly reduced by ion beam bombardment at ion dose densities from 10^{16} to 10^{17} ions cm^{-2}. This can be associated with an enlarged interfacial area between the electrolyte membrane and the electrode catalyst layer.

CVs were measured for the single cells to evaluate Pt utilization, see Fig. 5. On increasing the ion dose density from 0 to 5×10^{16} ions cm^{-2}, the Pt utilization increased from 36 to 46% due to the enlarged interfacial area between the electrolyte membrane and the electrode catalyst layer. At 10^{17} ions cm^{-2}, however, the utilization decreases to 33%, which is probably due to loss of catalyst particles that are buried in the deep valleys formed by the bombardments. All these obser-
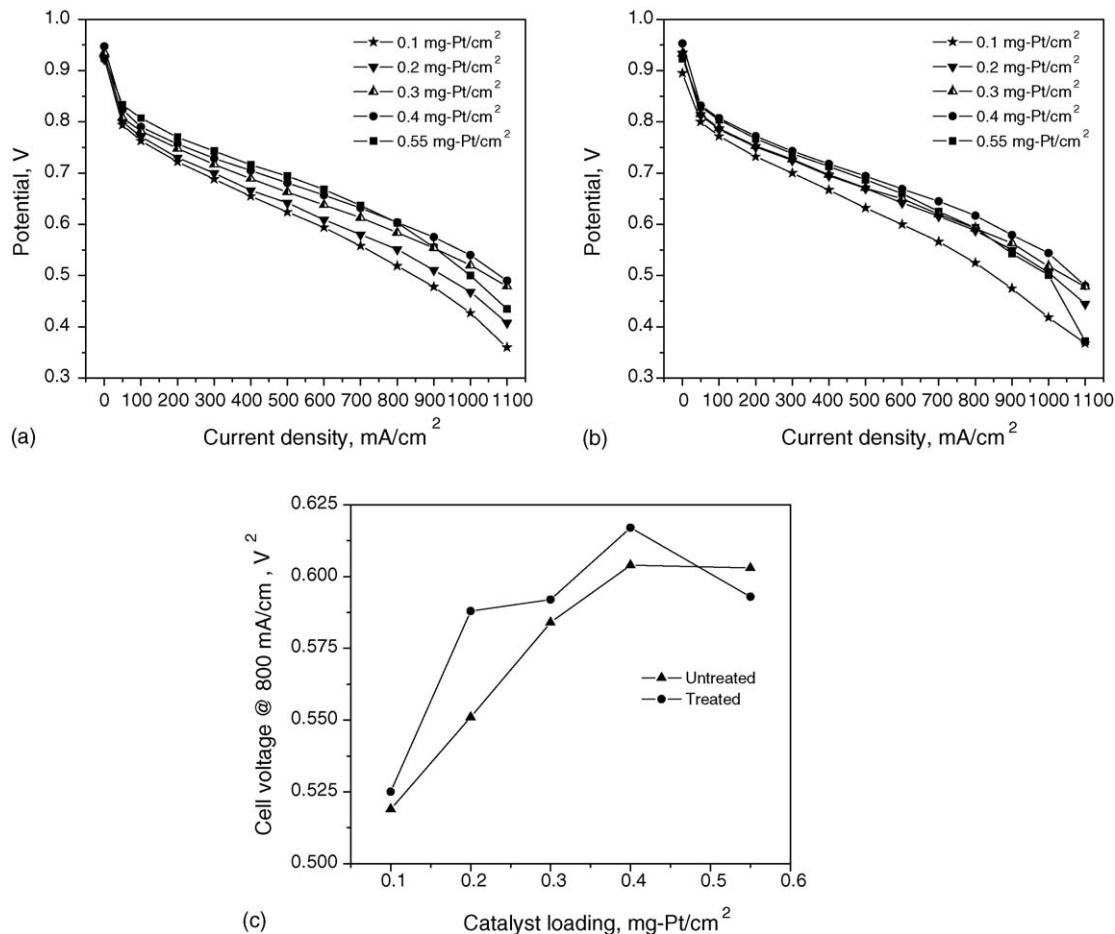

Fig. 6. Effect of catalyst loading on *i–V* curves of single cells using (a) untreated and (b) treated membrane (5×10^{16} ions cm^{-2} and 1 keV) and on (c) cell voltage at 800 mA cm^{-2} obtained from data in (a) and (b).
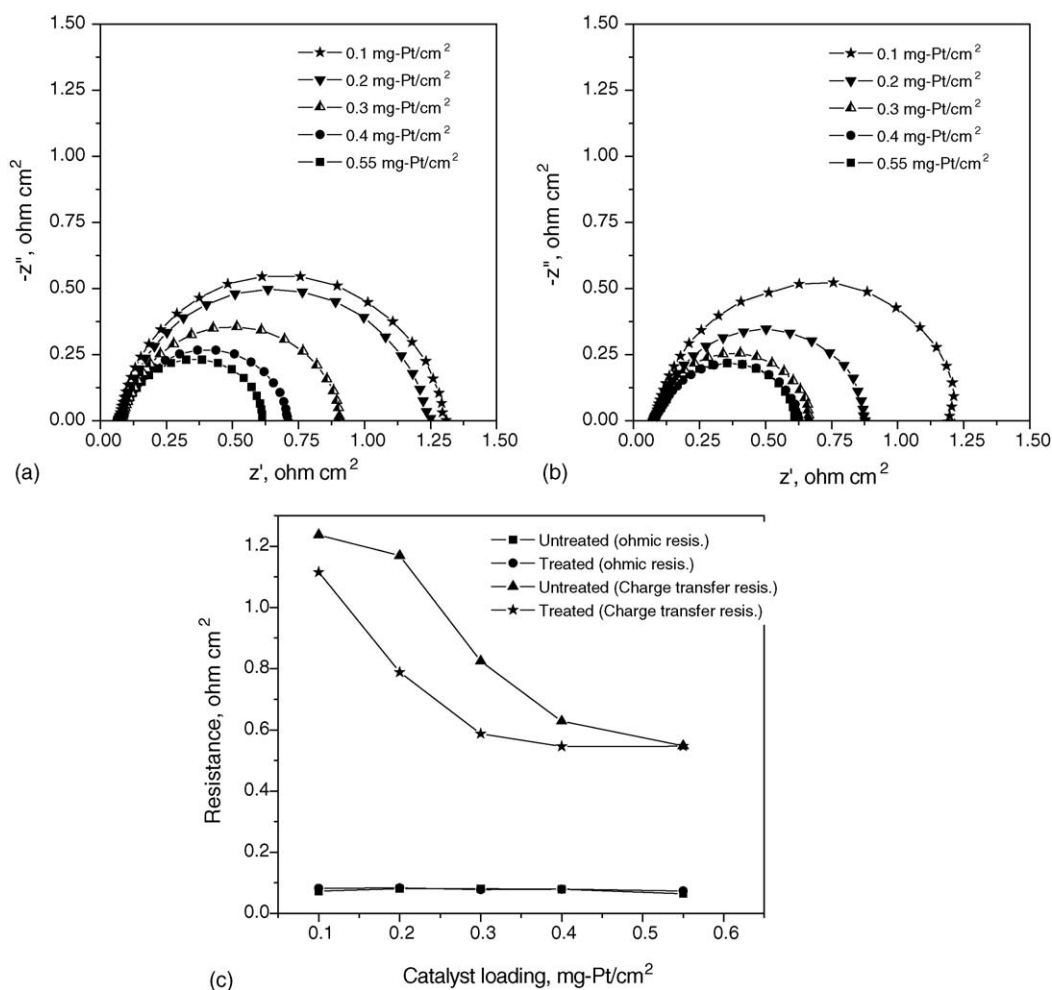
Fig. 7. Effect of catalyst loading on Nyquist plots of single cells using (a) untreated and (b) treated membrane (5×10^{16} ions cm^{-2} and 1 keV) and on (c) ohmic and charge-transfer resistances obtained from data in (a) and (b).

vations consistently show that the most effective ion dose for ion beam bombardment is 5×10^{16} ions cm^{-2} at an ion energy of 1 keV.

3.3. Effects of catalyst loading on cell performance

The effect of cathode catalyst loading on cell performance was investigated for both untreated and treated membranes at 5×10^{16} ions cm^{-2} with increasing Pt loading of the cathode from 0.1 to 0.55 mg-Pt cm^{-2}. Fig. 6(a) and (b) show i–V curves for a single cell using either an untreated or a treated membrane, respectively, at various Pt loadings. On increasing the Pt loading from 0.1 to 0.4 mg-Pt cm^{-2}, the cell voltage at a given current density increases gradually. For a Pt loading of 0.55 mg-Pt cm^{-2}, however, the cell voltage is drastically lowered at high current densities due to mass transport limitations caused by the thick catalytic layer. The cell voltage measured at 800 mA cm^{-2} is plotted as a function of cathode catalyst loading in Fig. 6(c). Below 0.4 mg-Pt cm^{-2}, the single cell using the treated membrane exhibited a higher cell voltage of 10–40 mV. This suggests that by using a treated membrane, the cell per-

formance can be improved and hence the Pt loading can be reduced. The lower performance of the single cell using the treated membrane compared with that using the untreated membrane at 0.55 mg-Pt cm^{-2} can be attributed to higher mass transport resistance from the gas channel to the catalyst particles in the deep valleys formed on the membrane surface by the bombardments.

Nyquist plots for the single cells measured at 0.8 V are shown in Fig. 7. With increasing Pt loading, the charge-transfer resistance of the single cells is reduced, while the ohmic resistance remains almost constant. As revealed in Fig. 7(c), single cell using the treated membrane exhibited lower charge-transfer resistance than that using the untreated membrane. The latter is due to the enlarged interfacial area between the electrolyte and the catalyst layer.

The EASA was evaluated from CVs since the Pt loading was not constant (Fig. 8). A higher EASA value is observed for the single cell using the treated membrane than for the untreated membrane. These results show that by ion beam bombardment of the membrane surface, catalyst activity can be improved, and hence enhance cell performance.
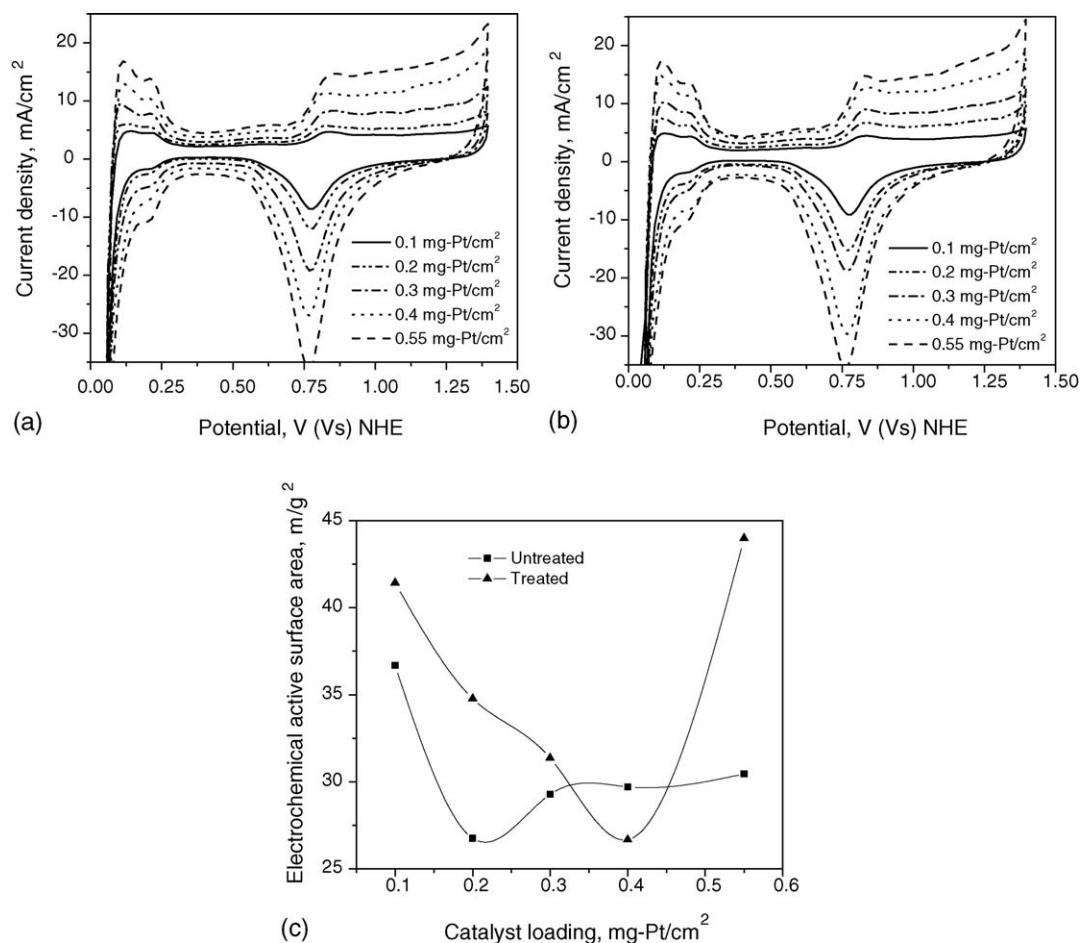
Fig. 8. Effects of catalyst loading on cyclic voltammograms of single cells using (a) untreated and (b) treated membrane (5×10^{16} ions cm^{-2} and 1 keV) and on (c) electrochemical active surface area obtained from data in (a) and (b). Scan rate = 50 mV s^{-1}.

4. Conclusions

Ion beam bombardment of a Nafion® 112 membrane using Ar ions with ion dose densities from 10^{15} to 10^{17} ions cm^{-2} at an ion energy of 1 keV, roughens the surface of the membrane without changing its chemical structure. On increasing the ion dose density up to 5×10^{16} ions cm^{-2}, the cell performance and the Pt utilization increase while the charge-transfer resistance decreases, which indicates that the interfacial area between the electrolyte membrane and the electrode catalyst increases with the surface roughness. With an ion dose density of 10^{17} ions cm^{-2}, however, a portion of catalyst probably could fall into the deep valleys of the roughened membrane and hence be isolated from the electrode, which results in decreases of cell performance and Pt utilization and an increase in the charge-transfer resistance.

With increasing the catalyst loading from 0.1 to 0.55 Pt-mg cm^{-2}, the performance of single cells using untreated or treated (5×10^{16} ions cm^{-2}, 1 keV) membranes is improved up to a Pt loading of 0.4 Pt-mg cm^{-2} and then lowered at 0.55 Pt-mg cm^{-2} due to mass-transport limitations. Compared with the single cell using the untreated membrane, the single cell using the treated membrane exhibits higher performance, higher

EASA and lower charge-transfer resistance. This implies that by the ion beam bombardment of the membrane surface, cell performance can be improved and hence catalyst loading can be reduced.

References

[1] G. Sasikumar, J.W. Ihm, H. Ryu, J. Power Sources 132 (2004) 11–17.
[2] S.-A. Sheppard, S.A. Campbell, J.R. Smith, G.W. Lloyd, T.R. Ralph, F.C. Walsh, Analyst 123 (1998) 1923–1929.
[3] P. Millet, T. Alleau, R. Durand, J. Appl. Electrochem. 23 (1993) 322.
[4] S.A. Cho, E.A. Cho, I.-H. Oh, H.-J. Kim, H.Y. Ha, S.-A. Hong, J.B. Ju, J. Power Sources 155 (2006) 286–290.
[5] T.E. Springer, T.A. Zawodzinski, M.S. Wilson, S. Gottesfeld, J. Electrochem. Soc. 143 (1996) 587–599.
[6] R.L. Clough, Nucl. Instrum. Methods Phys. Res. Sect. B-Beam Interact. Mater. Atoms 185 (2001) 8–33.
[7] M. Ludvigsson, J. Lindgren, J. Tegenfeldt, Electrochim. Acta 45 (2000) 2267–2271.
[8] Z. Liang, W. Chen, J. Liu, S. Wang, Z. Zhou, W. Li, G. Sun, Q. Xin, J. Membr. Sci. 233 (2004) 39–44.
[9] S.R. Lowry, K.A. Mauritz, J. Am. Chem. Soc. 102 (1980) 4665–4667.
[10] W. Kujawski, Q.T. Nguyen, J. Neel, J. Appl. Polym. Sci. 44 (1992) 951–958.
[11] A.J. Bard, Electrochemical Methods, John Wiley & Sons, 1980, p. 351.