한국에너지공학회(2004년도)
추계 학술발표회 논문집 P133~138

Effects of surface modification of Nafion® Membrane on the Fuel Cell Performance

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Abstract

Proton exchange membrane fuel cell (PEMFC) is considered as a clean and efficient energy conversion device for mobile and stationary applications. Among all the components of the PEMFC, the interface between the electrolyte and electrode catalyst plays an important role in determining the cell performance since the electrochemical reactions take place at the interface in contact with the reactant gases. Therefore, to increase the interface area and obtain a high-performance PEMFC, surface of the electrolyte membrane was roughened by Ar^+ beam bombardment. The results imply that by modifying surface of the electrolyte membrane, platinum loading can be reduced significantly without performance loss. To optimize the surface treatment condition, effects of ion dose density on characteristics of the membrane/electrode interface were examined by measuring the cell performance, impedance spectroscopy, and cyclic voltammograms. Surface of the modified membranes were characterized using scanning electron microscopy and FT-IR.

1. Introduction

Surface morphology of an electrode or electrolyte is important for the electrochemical reaction which takes place at the 3-D zone of the reactant-electrode-electrolyte system. To enhance the electrochemical reaction, contact of the electrolyte (which includes membrane and electrolyte in the catalyst layer) with the catalyst particle should be improved. This can be done in two ways. One is by surface area enhancement of the membrane and other is by increasing the electrolyte content in the catalytic layer. Since the later is limited, due to surface coverage of Pt particle by ionomer, electrode resistance, and mass transport resistance caused by the ionomer in the catalytic layer surface enhancement of the membrane is an ideal way. Taking advantage of inherently limited penetration depth of ion beam irradiation, surface modification of the polymer can be done without altering the bulk properties of the membrane compared to other radiation treatments like electron, gamma, and X-rays. Commercialization of fuel cells requires high performance cost effective stack/kW, much importance is given to reduce the catalyst loading of the electrode since Pt is an expensive and limited resource. In our work we investigated the application of ion beam treatment in surface modification of Nafion® membrane and to know-how the surface morphology influences the cell performance.

2. Experimental

2.1. Preparation of ion beam treated samples

Precleaned and dried Nafion® 112 membrane (Du Pont, Inc.) was used for the surface modification. The Ar ion beam was generated by a cold hollow cathode-type ion source. Ion beam energy was controlled from 0.5 to 1.2 keV. Ion doses were changed from 10^{15} to 10^{17} ions/cm^2 by adjusting exposure time and ion beam current density. All the polymer specimens were cleaned by conventional method of ultrasonic cleaning. The working vacuum pressure was maintained at 0.133 ~5.3 $\times 10^{-5}$ kPa.

2.2. Preparation of membrane and electrode assemblies and single cell test

Catalyst ink was prepared by mixing 40 wt% Pt/C (Johnson Matthey, Inc.) with isopropyl alcohol (Baker Analyzed HPLC Reagent) and then, the mixture was ultrasonicated for 1 hr. 5 wt% Nafion® solution (Du Pont, Inc.) was added to the catalyst ink, which was sonicated again for 1 hr. MEA's was prepared by catalyst coated membrane (CCM) method, by spraying the prepared ink over the untreated and ion beam treated (IBT) membranes, then the prepared CCM was dried. Active electrode area was 25 cm^2 with the catalyst loading of 0.3 and 0.2 mg-Pt/cm^2 for anode and cathode, respectively. Single cells were assembled with the prepared CCMs, 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 at a cell temperature of 80 °C.

2.3. Electrochemical characterization

Performance of the single cell was evaluated by measuring the i-*V* characteristics using an electronic loader (Daegil Electronics Inc, EL 1000P). Polarization resistance (R_p) was investigated by measuring AC impedance of the single cells with the oxygen electrode as the working electrode and the hydrogen electrode as the reference and counter electrode. IM6 (ZAHNER) was used for the impedance measurement.

2.4. Characterization of membrane

Contact angle measurement of the membrane was performed by using contact angle micrometer (Cam Micro, Tantec) by sessile drop method at room temperature. Ion conductivity of the virgin and IBT samples was determined by a four probe method using IM6 (ZAHNER) at room temperature. FTIR (Nicolet Magna IR 560 model) was performed for the virgin and IBT samples in the ATR mode.

3. Results and discussions

3.1 Effects of ion dose density on cell performacne

Surface morphology of the membrane was modified with Ar ion fluence in the range of 10^{15} to 10^{17} ions/cm^2 with constant beam energy of 1keV and the cell performance of these IBT membrane results were compared with the untreated membrane. Polarization curve (Fig.1a) reveals that the cells with modified membrane shows higher performance in the activation and ohmic controlled region compared to untreated. IBT membrane with low doses shows mass transport limitation. Fig. 1b shows impedance spectra of cell at various treatment conditions. Membranes with low doses of 10^{15} ions/cm^2 show higher R_p as that of untreated membrane. This shows that at low ion fluence, the surface morphology change is subtle or the attributed surface roughness is low. Whereas membranes treated with high fluence $>10^{15}$ Ar ions/cm^2 exhibits low R_p. This ensures that the surface morphology of membrane greatly affects the structure of the coated catalytic layer.

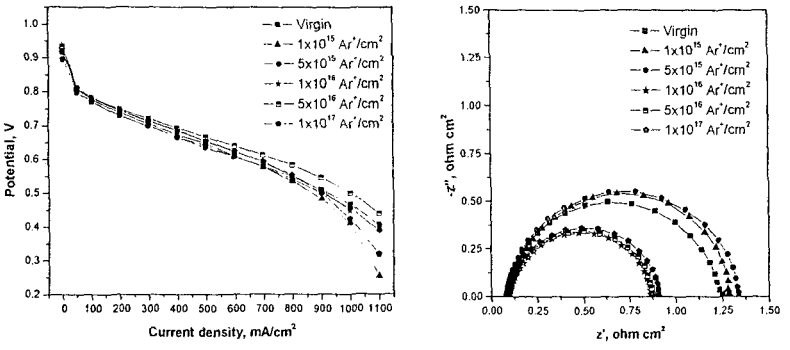


Fig. 1 Effects of ion dose density on (a) cell performance (b) Nyquist plot of the membrane. Cathode catalyst loading = 0.2 mg-Pt/cm^2, H_2/air.

Scanning electron micrograph (Fig. 2) shows the surface morphology of the virgin membrane is smooth with some little cracks. In case of IBT membrane, as the ion fluence increases from 10^{15} to $1x10^{16}$ (not shown), nodule like structure appears and intensifies on the surface. At fluence of $5x10^{16}$, the surface of Nafion® disintegrates to form whisker like appearance, and this

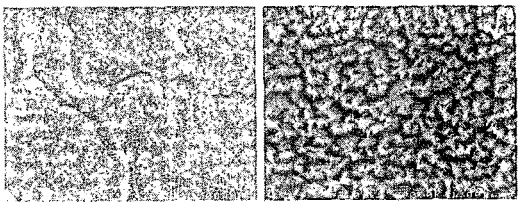


Fig.2 Scanning electron micrograph of (a) Untreated, (b) IBT membranes at $5x10^{16}$ ions/cm^2.

Table. 1 Properties of membrane at various ion fluences.

Ion fluence ions/cm^2	Pt Utilization %	Ionic conductivity S/cm	Water contact angle, θ
Virgin	36	0.119	108
$1x10^{15}$	38	0.113	111
$5x10^{15}$	29	0.125	117
$1x10^{16}$	43	0.111	121
$5x10^{16}$	46	0.119	111
$1x10^{17}$	32	0.127	123

whisker length increases with decrease in diameter and found more in numbers per unit area at higher fluences of 10^{17}.

From CV (Table. 1), the calculated Pt utilization for virgin is 36 % whereas a maximum of 46% is obtained for the IBT membrane ($5x10^{16}$ ions/cm^2). Except for IBT membranes at $5x10^{15}$ and 10^{17} ions/cm^2, other membranes shows higher Pt utilization compared to virgin. This increase in Pt utilization is mainly due to the interfacial contact of the catalyst with the surface modified membrane. As the membrane surface is roughened, the valleys and peaks appeared on the surface gives an irregular structure. This provides higher surface for the contact of the catalyst with the polymer electrolyte.

From Table. 1 it is evident that membrane treated at different ion fluence, the ionic conductivity does not vary much whereas the water contact angle shows difference in value. This shows that the treated membrane is not different from the untreated membrane in terms of chemical nature of the polymer.

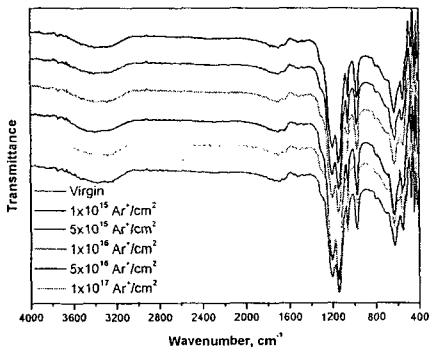


Fig.3 Infrared spectra of untreated and ion beam treated membrane at different ion fluence.

To further confirm the hydrophilic-hydrophobic nature of the membrane which causes little difference in the water contact angle, FTIR-ATR of the virgin and IBT membrane was investigated. The spectra (Fig. 3) shows clearly well defined peaks, C-O-C symmetric stretching of the side chain at 975.81 cm^{-1}, SO_3^- symmetric stretching at 1056.8 cm^{-1} and anitsymmetric stretching masked by the strong CF_2 stretching around 1300 cm^{-1}. Moreover strong intense band in the region at 1145.51 cm^{-1} and 1201.44 cm^{-1} corresponds to CF_2 symmetric and antisymmetric stretching of the polymer. Additionally the OH bending and stretching band in the region of 1600-2000 cm^{-1} and 3000-3700 cm^{-1} corresponds to water present in the membrane. The peak positions for these strong intense bands for the virgin and IBT membrane was found to be identical. This implies that chemical environment of the polymers was not changed during or/after Ar^+ bombardment. Since the treatment conditions set for the Ar^+ bombardment was under vacuum, the possibilities for the formations of surface polar groups after the treatment conditions, where the membrane was kept in air environment was undetectable. Since the aim of this work is to know-how the surface roughness of the membrane influences the electrode-electrolyte contact and its affect on electrochemical active area, the designed Ar^+ treatment conditions achieved its objective.

3.2 Effects of catalyst loading on cell performance

Effects of the cathode catalyst loading on the cell performance was investigated for both untreated and IBT membrane ($5x10^{16}$ Ar^+/cm^2, 1keV) by varying the Pt loading from 0.1 to 0.55 mg-Pt/cm^2. Fig. 4a shows that for the

untreated membrane as the Pt loading increases from 0.1 to 0.3 mg-Pt/cm^2, current density improves gradually which becomes less significant as the loading increased to 0.4 mg Pt/cm^2. As the Pt content increased further to 0.55 mg-Pt/cm^2 obvious difference in mass transport was found at high current density regime. This ensures that the cathode is mass transport limited due to diffusion hindrance of oxidant in the water bound thick catalytic layer at higher loading of Pt/C. Comparing the performance of untreated with the IBT membrane (Fig. 4b), the improvement is larger from 0.1 to 0.2 mg-Pt/cm^2 where as it increases slightly from 0.2 to 0.4 mg-Pt/cm^2. At higher loading of 0.55 mg-Pt/cm^2, mass transport arises earlier compared with cell fabricated with the untreated membrane at the same loading. This shows clearly that for cells with IBT membrane the performance is better than untreated at all catalyst loading except at very high catalyst loading. Fig. 5 shows in situ impedance analysis of the cell at 0.8V, it was found that charge transfer resistance (Fig.

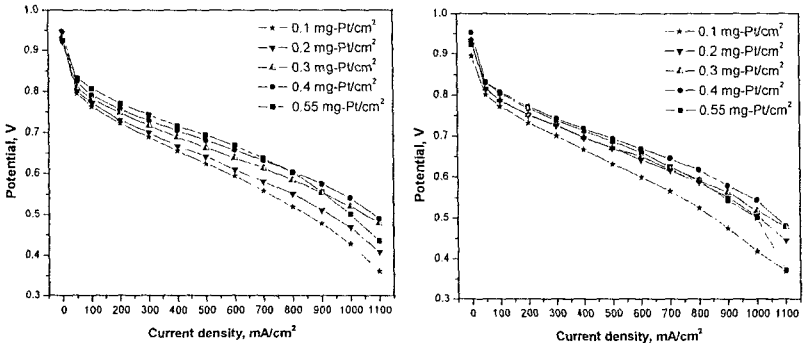
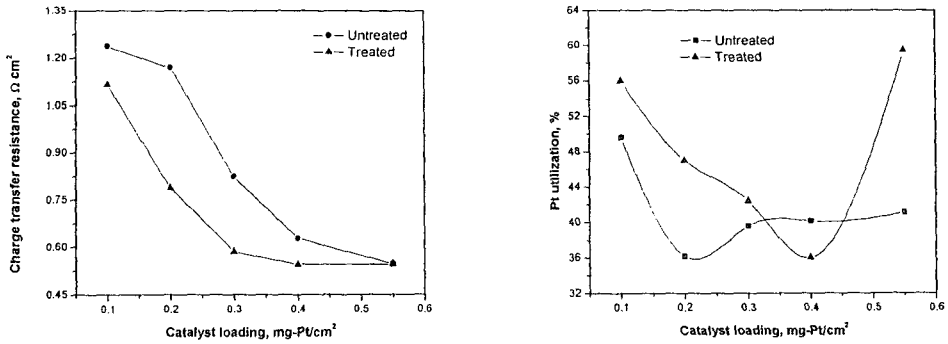


Fig.4 Effects of catalyst loading on performance of the single cells using the (a) untreated and (b) the surface treated membrane at 5 x 10^{16} ions/cm^2 and 1 keV. Anode catalyst loading = 0.3 mg-Pt/cm^2, H_2/air.



5a) is low for the cells with IBT membrane compared to untreated. This shows that at very low catalyst loading, cells with IBT membrane exhibits lower resistance for oxygen reduction reaction and thus higher catalytic activity.

Fig. 5 Effects of catalyst loading on (a) charge transfer resistance and (b) Pt utilization of the single cells using untreated and surface treated membrane at 5 x 10^{16} ions/cm^2 and 1 keV. Anode catalyst loading = 0.3 mg-Pt/cm^2, H_2/air.

Fig. 5b shows Pt utilization reaches a maximum of 50% for 0.1 mg-Pt/cm^2 where as it maintains around 40% for lower loading for the cells with untreated membrane. In case of cells using IBT membrane, 60% utilization was observed for 0.55 mg-Pt/cm^2 whereas it decreases and then increased for catalyst loading from 0.55 to 0.1 mg-Pt/cm^2. This difference in trend is attributed to the change in structure of the catalytic layer coated on IBT membrane with catalyst loading. This shows that how the surface morphology of the membrane changes the interface between the electrode and electrolyte, and the electrochemical active surface area. IBT membrane shows excellent performance at very low catalyst loading compared to untreated Nafion membrane.

4. Conclusions

By bombarding Ar ions on the surface of Nafion 112 membrane to ion dose of 1 x 10^{17} ions/cm^2 at 1 keV, roughness of the membrane surface increased from without changes in ionic conductivity, hydrophobicity, and chemical structure of the membrane.

With increasing the ion dose density, Pt utilization and the cell performance increased, exhibited the maximum at 5 x 10^{16} ions/cm^2, and then decreased, reflecting that interfacial area between the electrolyte membrane and the electrode catalyst increased with the surface roughness to a certain level. However, if the surface roughness is higher than that level, a portion of catalyst probably could fall into the deep valleys of the roughened membrane and hence be isolated from the electrode, resulting in the reduction of Pt utilization and the cell performance.

Performance of the single cells using untreated and ion beam bombarded (5 x 10^{16} ions/cm^2) Nafion 112 membranes was evaluated at various catalyst loadings from 0.1 to 0.55 mg/cm^2. Except 0.55 mg/cm^2, the ion beam treated membrane exhibited the higher cell performance, implying that by the ion beam bombardment on the membrane surface, catalyst loading could be reduced.