



Short communication

Modification of the pore structures of fuel cell electrodes using a dry etching technique

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H I G H L I G H T S

- ▶ An ion-beam treatment has been employed to modify pore structures of electrodes.
- ▶ The etching of surplus ionomer turns catalyst layers highly rough and porous.
- ▶ Modification results in a substantial improvement of mass-transport processes.
- ▶ The ion-beam-treated MEAs exhibit improved performance for the DMFC.

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The anodes of membrane-electrode assemblies (MEAs) have been treated with an argon ion-beam under vacuum to etch out a part of the ionomer present in the catalyst layers. The ion beam treatment alters the surface morphology of the catalyst layer by promoting the pore size and overall porosity, which reduces the mass transport resistance of the reactants and the products through the catalyst layers. As confirmed, the electrochemical surface areas of the electrodes are not affected by the treatment, and the ion-beam-treated MEAs exhibit improved performance toward direct methanol fuel cells (DMFCs). Physical and electrochemical analyses have been carried out to characterize the modified electrodes in greater detail.

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1. Introduction

The electrochemical reactions in fuel cells take place at the triple-phase boundary that consists of a catalyst particle, an ionomer and a reactant [1]. The triple-phase boundary and structure of the catalyst layer are strongly influenced by the electrode composition, which must be formulated precisely in terms of the choice of solvent, catalyst loading and ionomer content. Adequate morphology of the electrodes is critical to achieve a higher utilization of precious metal catalysts for better performance of the fuel

cells. An adequate morphology even assists to reduce the catalyst loading with no significant deterioration in performance. In order to facilitate the diffusion of reactants to active sites and the removal of the products from the electrodes, high electrode porosity is another crucial requirement for a membrane-electrode assembly (MEA).

Many reports have dealt with the optimization of electrode structures by modifying the porosity and catalyst aggregate size. Kim et al. and others [2,3] have controlled the pore size of fuel cell electrodes by taking advantage of the dielectric properties of the solvents that were used to make catalyst inks [4,5]. Another approach modified the electrode structure by using carbonaceous materials as additives in the catalyst layers [6]. Liu et al. manipulated the electrode fabrication process to modify the anode porosity of a direct methanol fuel cell (DMFC), which promoted the mass transport of reactants and products [7].

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One of the most frequently used methods has been the introduction of pore-forming agents in the catalyst inks to increase the electrode porosity [8,9]. These agents are then removed after MEA preparation using washing, heat treatment, or acid treatment processes. However, these additional steps are laborious, time consuming and can possibly increase the processing costs as well. Apart from that, the interfacial resistance between the electrodes and the membrane of the resultant MEAs can be increased during the processes that mostly include liquid phase extraction or evaporation under vacuum conditions. Also, there is a risk of electrode contamination if pore formers are not completely removed.

The methods mentioned above mostly include multiple steps that occur in the liquid phase. In the present study, we have adopted a different approach whereby a part of the ionomer is removed by a dry etching technique. The surfaces of polymeric materials can be modified by an ion-beam treatment technique under vacuum conditions [10,11]. Cho et al. [12] reported a method to modify the surface of a polymer electrolyte membrane (Nafion), which was then used to fabricate MEAs for polymer electrolyte fuel cells.

In this work, we used a novel and very effective technique, which proceeded under vacuum conditions to modify the pore structures of electrodes for fuel cells. The electrodes formed on the polymer electrolyte membrane were subjected to an ion-beam etching process in order to remove a part of the ionomer in the catalyst layer. The modified MEAs were characterized by using various physical and electrochemical techniques and their performance was tested for direct methanol fuel cells.

2. Experimental

Nafion® 115 (DuPont) was used as a polymer electrolyte membrane. PtRu/C (75 wt.%, HiSPEC 12100) and Pt/C (70 wt.%, HiSPEC 13100, Johnson Matthey Co.) were used as the anode and cathode catalysts, respectively. Catalyst inks were prepared by mixing respective catalyst powder, a 5 wt.% Nafion solution (DuPont) ionomer, de-ionized water and IPA in suitable proportions, and were then sonicated for 10 min to obtain well-dispersed catalyst inks.

The catalyst inks were directly sprayed onto the surface of the Nafion 115 membranes. The geometric area of the catalyst layer was 10.89 cm^2 with a loading of 2 mg cm^{-2} based on Pt metal weight for both anode and cathode. The ionomer content in each catalyst layer

was 30 wt.% of the catalyst used. Hot-pressing was carried out under a pressure of 8 MPa at $140 \text{ }^\circ\text{C}$ for 5 min.

After fabricating the MEA, the anode catalyst layer was treated by an Ar^+ ion-beam under vacuum conditions of $8 \times 10^{-5} \text{ kPa}$. The plasma was generated with argon gas while hydrogen gas was introduced to the vacuum chamber to make a hydrogen atmosphere at a flow rate low enough to maintain a predetermined vacuum level. Three different ion doses were used with an ion energy of 1.5 keV: 5×10^{16} , 1×10^{17} , and $5 \times 10^{17} \text{ ions cm}^{-2}$.

The performance of the MEAs for DMFC was measured with a cell fixture having a serpentine flow field by using a commercial test station (Won-A tech, Korea). The DMFC tests were carried out at $60 \text{ }^\circ\text{C}$ and 1 atm, while supplying a 1.0 M methanol solution to the anode and air to the cathode. After single-cell testing, electrochemical analyses were conducted using a potentiostat (AutoLab, EcoChemie). Electrochemical impedance (EIS) of anode was measured at 0.4 V using a potentiostatic mode. Methanol solution with a concentration of 1.0 M was fed to the anode at 1 ml min^{-1} and humidified hydrogen was supplied to the cathode at 100 sccm, which functioned as a counter and reference dynamic hydrogen electrode (DHE) [13]. The frequency range was varied from 1 kHz to 0.1 Hz, and the amplitude of the applied AC voltage was 5 mV. Linear sweep voltammetry (LSV) was conducted to measure the anode overpotential for a methanol oxidation reaction (MOR) in a potential range of 0–0.8 V at a scan rate of 1 mV s^{-1} . Methanol stripping voltammetry (MSV) was carried out to analyze the electrochemical active surface area (ECSA) of the anode. For MSV measurement, methanol solution was fed to the anode for 20 min by holding anode potential at 0.1 V so that methanol can be adsorbed on the catalyst layer and then de-ionized water supplied to anode to remove the un-adsorbed methanol at the same holding potential. Afterward, adsorbed methanol was oxidized by cycling the anode potential between 0.1 and 0.7 V and MSV curve was recorded [14]. Morphological and structural characteristics of the anode catalyst layers were investigated using a scanning electron microscope (XL-30 FEG-ESEM, FEI Inc.). A mercury porosimeter (AutoPore IV, Micromeritics) was used to analyze pore structure of the pristine and ion beam treated anodes.

3. Results and discussion

Fig. 1 shows a schematic diagram of the change in the electrode morphology caused by an ion-beam irradiation that has the ability

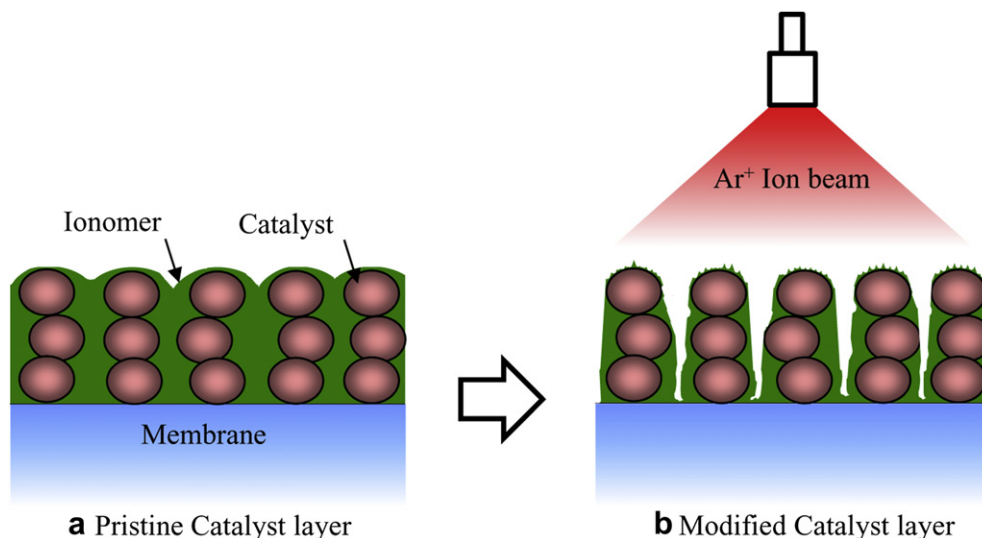


Fig. 1. A schematic diagram showing the change in the electrode structure by ion beam irradiation.

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