The Ionomer Segregation in Composite Membrane Electrode Assemblies and the Effect on the Performance of Polymer Electrolyte Fuel Cells

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Introduction

The membrane electrode assembly (MEA) is formed by hot pressing the two thin catalyst layers on both sides of a membrane electrolyte [1]. The formed catalyst layer is a porous composite, consisting of the recast Nafion® ionomer, and the nano-particle precious metal catalyst supported on micro-particle carbon. As a gas electrode, the structure of catalyst layer needs to facilitate gas diffusion from outside to inside and water removal from the reverse direction. The surface features of the catalyst layer have an important impact on the performance of the MEA because both gas diffusion and water removal have to go through the surface. Here, we report our discovery that a perfluorosulfonated ionomer rich film, called the perfluorosulfonated ionomer skin hereafter, exists on the surface of the catalyst layer. We also present the study of the mechanism of this skin formation, and the effect of this skin on the performance of the catalyst layer. The effect of the decal surface and coating techniques on the skin and the improvement of performance of the catalyst layer has been investigated.

Experimental

The catalyst layer was prepared by the "decal process" [1,2]. Scanning electron microscopy (SEM) was used to examine both the cross-section and the surface of the catalyst layer. Atomic force microscopy (AFM) was used to study the membrane electrolyte, recast Nafion ionomer film, and the surface of the catalyst layer. The fuel cell test was carried out by measuring the polarization curve of each MEA. The active geometric area of the MEA is 5 cm².

Results and Discussions

The AFM examination of the Nafion® membrane electrolyte, recast Nafion® ionomer film and the catalyst layer reveals that the softness is a key character for identifying the existence of the Nafion®. AFM results also suggest the possible existence of a Nafion® skin on the surface of the catalyst layer as shown in Figure 1. The study of the cross-section of a catalyst layer using SEM and energy dispersive analysis x-ray (EDAX) concludes that a recast Nafion® ionomer skin exists on the surface of the catalyst layer as shown in Figure 2.

The mechanism for the formation of a recast Nafion® ionomer skin is proposed as follows: (1) the Nafion® ionomer aggregates in the catalyst ink are attracted onto the Teflon coated decal surface by the hydrophobic nature of the Teflon, and these aggregates accumulate on the surface of the decal; (2) the repeated cycle of deposition and dissolution of the catalyst layers during multi-layer painting provides both more ionomer aggregates by dissolving previous layers and more time for those aggregates to diffuse onto the Teflon decal surface. The proposed mechanism is supported by the SEM observations.

The formed Nafion® ionomer skin on the surface of the catalyst layer blocks gas access to the active catalytic sites and hinders water dissipation. The effective removal of the Nafion® ionomer skin greatly improves the performance of the catalyst layer. The effect of the Nafion® ionomer skin on the performance of the catalyst layer is found to be dependent on both coating techniques and the decals used to make the catalyst layer.

Conclusions

A Nafion® ionomer skin was found on the surface of a catalyst layer using AFM and SEM/EDAX. This skin blocks gas diffusion and water dissipation. Hence, it has a negative impact on the performance of the MEA. Removal of this skin can be done by using a less hydrophobic decal and the one-layer coating technique.

Acknowledgments

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References

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Figure 1. AFM "tapping height" image of carbon layer. This carbon layer was made by "decal process", multi-layer hand painting using the Teflon decal, and boiled with 0.5M H_2SO_4 and deionized water respectively. Scan box is 5×5 µm.



Figure 2. Scanning electron micrograph of the cross-section of the carbon layer made by multilayer hand painting using the Teflon decal with wt. 33% Nafion®. The thickness of the white skin is approximately $0.7 \mu m$.