Influence of Cathode Ionomer Content on PEFC MEA Structure and Performance

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Introduction

For MEAs made by the thin-film decal method [1,2], the recast ionomer plays two key roles in determining performance of the catalyst layer. It serves as a binder by holding the catalyst and carbon aggregates together to form a porous layer with structural integrity and robustness. Also, it acts as a proton conductor by allowing proton migration to and from the membrane. Early studies on the optimization of Nafion® content in MEAs made by different techniques yielded different results, suggesting that optimized Nafion® content is dependent on the materials and technique used in MEA preparation. However, the effects of ionomer content on catalyst-layer performance and structure of MEAs made by the decal method have not yet been reported, which was the goal of this work. Preliminary results from our study focusing on the cathode are presented here.

Experimental

Scanning electron microscopy (SEM) was used to examine both the cross-section and surface of the catalyst layer. Atomic force microscopy (AFM) was used to study the membrane, recast ionomer film, and surface of the catalyst layer. Polarization curves for each MEA were measured (geometric active area was 5 cm^2), and the electrochemically-active surface area of the cathode catalyst layer was measured by *in-situ* hydrogen adsorption-desorption cyclic voltammetry (CV).

Results and Discussions

The effect of cathode catalyst-layer ionomer (Nafion®) content on MEA performance is shown in Figure 1, where a significant impact over the entire polarization range (*i.e.*, kinetic, Ohmic and mass-transport regions) is seen. Kinetic performance (0.9 V and 0.8 V curves in Fig. 2) increases slightly with ionomer content up to 28 wt%, followed by a gradual decline at higher loadings, suggesting that ionomer content indeed has an effect on oxygen reduction reaction (ORR) kinetics. Ohmic region analysis (0.7 V and 0.6 V curves in Fig. 2) also shows a slight increase in performance up to 28 wt% ionomer, followed by a sharp decrease beyond 33 wt%. In the mass-transport region (0.4 V and 0.3 V curves in Fig. 2), a performance decrease at low ionomer content is seen, with a slight increase at 25 wt% and reaching a maximum at 28 wt%, again followed by a sharp decrease similar to that of the Ohmic performance.

The microstructure of the MEA is shown in Figure 2, where an inhomogeneous distribution of Pt_3Cr catalyst clusters on the carbon support surfaces can be seen, with some areas having densely agglomerated clusters (arrow D of Fig. 2). Carbon-support aggregates are seen that penetrate deeply into the Nafion® membrane (*i.e.* >150 nm), effectively increasing the volume of the interfacial zone between the catalyst layer and membrane. This overlapping facilitates proton transport through the membrane. Inside the catalyst layer, Figure 2 shows ample recast ionomer distributed among the carbon aggregates, indicating good aggregate dispersion. Both secondary (large) pores and primary (small) pores can easily be seen as regions of light gray with a white perimeter (arrows denoted as "E" in Fig. 2) and scattered white spots (arrows denoted as "F" in Fig. 2), respectively.

Conclusions

It was found that Nafion® content affects both the PEFC performance over the entire range of polarization curves, as well as the structure of the catalyst layer. Changes in size and distribution of catalyst and carbon aggregates, pore size and pore size distribution, and ionomer coverage on the surface of metal catalyst particles were collectively observed with AFM, SEM, TEM and Hg porosimetry.

Acknowledgments

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References

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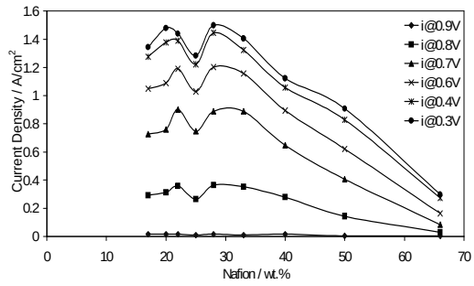

Figure 1. Current density as a function of cathode ionomer content plotted at different voltages.

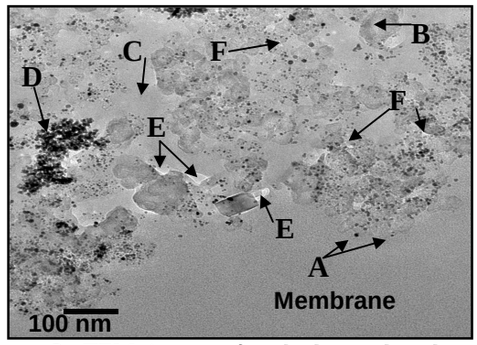

Figure 2. TEM image of cathode catalyst layer with arrow demarcation: (A) Pt_3Cr catalyst particles, d=4-12 nm; (B) carbon aggregates, $d\approx$340 nm; (C) recast Nafion® ionomer; (D) coalesced Pt_3Cr particles; (E) secondary pores, d=40-80 nm; (F) primary pores, $d\leq$17 nm.