PERFORMANCE IMPROVEMENT OF THE PEMFC BY USING PORE FORMING ADDITIVES IN THE ACTIVE LAYER OF THE OXYGEN (AIR) DIFFUSION ELECTRODE

Sergei Gamburzev, Christopher Boyer, and A. John Appleby

Center for Electrochemical Systems and Hydrogen Research, Texas Engineering Experiment Station, Texas A&M University, College Station, TX 77843 - 3402

The influence of pore forming additives introduced into the active layer of oxygen (air) gas diffusion electrodes for PEMFCs was studied. Two types of electrodes, with low (LL) and high (HL) platinum loading respectively, were investigated. In both cases, optimal amounts of pore-forming additives were used after experimentation on the increase in the volume porosity of the active layer. The increased volume porosity resulted in a significant reduction in the mass transport resistance in the active layer of the oxygen (air) cathode and therefore in a substantial improvement in electrode performance. Possible positive and negative aspects of changing the volume porosity of the active layer by means of additional pore formation are discussed.

INTRODUCTION

During the past few years, research on proton exchange membrane fuel cells (PEMFCs) has often appeared to have reached a saturation point in regard to performance improvement. Data and scientific efforts and achievements in the performance area were recently summarized by the Ballard team (1). It was concluded that further improvement in PEMFC performance might be achieved by systematic research in: (i) new oxygen reduction electrocatalysts; (ii) new types of polymer electrolyte; and (iii) profound changes in oxygen (air) diffusion electrode structure to minimize all transport limitations. The first direction needs systematic profound research and experimental work in the area of catalyst "construction," while the second mainly involves polymer chemistry. The most promising direction for improvement of PEMFC performance is based on minimization of all transport resistances occurring in the electrochemical reaction by making appropriate changes in the overall electrode structure. One way to minimize the transport resistances in gas diffusion electrodes is to increase their pore volume by using different pore-forming additives (2). It was shown that the pore volume of gas diffusion electrodes could be increased in both the gas distribution layer and the active layer. This paper gives performance results for a hydrogen-oxygen (air) PEMFC which incorporates pore-forming additives during the fabrication of the active layer of the oxygen electrode.
EXPERIMENTAL

Two types of PEMFC with *in-house* fabricated gas diffusion electrodes (3) were studied, namely high platinum loading (HL) with a total of 1.25 mg platinum per cm$^2$ of membrane-electrode assembly (MEA) and low platinum loading (LL) with 0.25 mg platinum cm$^2$. Every set of cathodes used proprietary pore-forming (PF) additives in the active layer in amounts varying from 20 to 60 wt %. The pore former was added to the catalyst-Nafion mixture (ink), followed by ultrasonic agitation. After painting the active layers onto the substrate, the electrodes were treated to extract the pore-former. MEAs were fabricated by hot pressing of the cathodes thus prepared and low-platinum-loading (0.05 mg/cm$^2$) anodes on to Nafion 112 membranes as the polymer electrolyte. The working area of the MEAs was 50 cm$^2$. The performance of the MEAs was evaluated at 50°C with humidified hydrogen, oxygen and air at atmospheric pressure.

RESULTS AND DISCUSSION

Figure 1 shows the hydrogen-air cell potential versus current density for the set of MEAs with LL-oxygen electrodes as a function of different amounts of the pore-forming additive (PF). The results show that the performance improves when the amount of PF is increased up to a level of 33 wt %. Further increase in the quantity of PF results in a reduction in performance. Figure 2 shows the hydrogen-oxygen cell performance for the above set of MEAs. The influence of amount of pore forming additive on mass transport processes in the active layer of oxygen electrode may be evaluated from both sets of data.

Figure 3 shows the current density generated by hydrogen-air cells at two different cell potentials with LL-oxygen electrodes as a function of amount of PF. It appears that the optimal amount of PF is 33 wt % at 0.6 V, and 25 wt % at 0.3 V. This difference may be attributed to the specific distribution of hydrophilic/hydrophobic properties of the pore volume formed in the active layer after extraction of the PF. At high cathode polarization (e.g., at 0.3 V cell voltage) the rate of water production in the electrochemical reaction is probably higher that its rate of evaporation. This results in an accumulation of liquid water in part of the hydrophilic pores in the electrode active layer. Thus, this part becomes inaccessible for fast gas-phase diffusion of oxygen from air, which leads to increase in gas diffusion resistance and loss of performance.

Figure 4 shows the influence of the amount of PF on ohmic resistance in the MEAs studied. The ohmic resistance of the MEAs was calculated from the slopes of the linear part of the potential vs. current density plots of PEMFCs operating on hydrogen and oxygen. Because the same membrane (Nafion 112) and MEA structure was used in each case, the only variable parameter was the amount of PF used in the preparation of the
active layer of the cathodes, which would be the main influence on the ohmic resistance. The results show the same optimal value (33 wt %) of PF at 0.6 V as in Figure 3.

The set of MEAs with HL oxygen cathodes showed similar behavior to that of the LL electrodes (Figures 5-8). The optimal amounts of PF appeared to be 40 wt %. The higher value for HL compared with LL cathodes results from the different characteristics of the carbon-supported platinum catalysts used in each case. The 30 wt % Pt/C catalyst used to fabricate LL oxygen cathodes gave a higher initial active layer porosity because of its smaller particle size compared with the larger particles of 60 wt % Pt/C catalyst used in HL oxygen oxygen cathodes. If we accept that the optimal porosity (from point of view of transport resistance) of the active layer is practically constant, then more pore forming additive (40 wt. %) is required compared with LL electrodes (33 wt %).

CONCLUSIONS

1. Introduction of PF into the fabrication procedure for the active layer of LL and HL oxygen gas diffusion cathodes, followed by extraction of the additive, results in an increase in the volume porosity of the active layers and in a consequent significant decrease in mass transport resistance.

2. It was found that volume porosity had an optimal value which was different for both types of electrodes investigated. The electrode performance improvement of the optimal porosity value is correlated in a simple manner with the improved mass transport properties of the electrode active layer.

3. A further increase of porosity beyond the optimal value negatively influences electrode performance because of the appearance of discontinuity of the solid phase in the active layer, and an increase in the active layer thickness. These respectively result in increased ohmic resistance and unfavorable gas diffusion. An unfavorable change in the hydrophobic/hydrophilic pore volume ratio also occurs.

4. At optimal PF loadings, the current density at 0.7 V increased from 200 mA/cm² to 320 mA/cm² on hydrogen-air with LL cathode and from 370 mA/cm² to 480 mA/cm² with HL cathodes.

REFERENCES

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Figure 1. Cell potential vs. current density plots of H₂-air PEMFCs with LL cathodes as a function of amount of pore forming additive in the active layer of air electrode. T = 50°C, P = 1 atma.

Figure 2. Cell potential vs. current density plots of H₂-O₂ PEMFCs with LL cathodes as a function of amount of pore forming additive in the active layer of air electrode.
Figure 3. Current density (at $E_{cell} =$ constant) of H$_2$-air PEMFCs with LL cathodes as a function of amount of pore forming additive in the active layer.

Figure 4. Linear IR resistance of H$_2$-O$_2$ PEMFCs with LL cathodes as a function of amount of pore forming additive in the active layer.
Figure 5. Cell potential vs. current density plots of H₂-air PEMFCs with HL cathodes as a function of amount of pore forming additive in the active layer.

Figure 6. Cell potential vs. current density plots of H₂-O₂ PEMFCs with HL cathodes as a function of amount of pore forming additive in the active layer.
Figure 7. Current density (at $E_{\text{cell}} =$ constant) of H$_2$-air PEMFCs with HL cathodes as a function of amount of pore forming additive in the active layer.

Figure 8. Resistance of H$_2$-O$_2$ PEMFCs with HL cathodes as a function of amount of pore forming additive in the active layer.