Influence of Catalyst Layer Structure on the Current Distribution of PEMFCs

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A modified subcell approach was adopted to evaluate the current density distributions of proton exchange membrane fuel cells (PEMFCs) with different electrodes. Conventional hydrophobic electrodes showed better performance under flooding conditions compared to hydrophilic electrodes. The thin-film hydrophilic electrode performed better in the absence of liquid water, but it was more readily flooded. A composite catalyst layer was designed with 2/3 of the area from the inlet prepared hydrophilic and the remaining 1/3 area hydrophobic. The composite catalyst layer with commercial scale dimension showed notable enhanced performance in the concentration polarization region.

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Proton exchange membrane fuel cells (PEMFCs) are promising for both stationary and mobile applications due to their significant advantages such as high efficiency and the absence of noxious emissions. But the commercial success of PEMFCs depends on their cost competitiveness with other energy conversion and power generation devices. Enhancing performance and lowering material and fabrication costs can achieve cost reduction of PEMFCs.

The performance of a PEMFC is affected by many internal and external factors, such as catalyst type and loading, Nafion content, polytetrafluoroethylene (PTFE) content, cell temperature, humidity level, channels configuration of the bipolar plate, and so on.

Until now, with or without PTFE, two main types of the catalyst layer preparation methods were developed to lower the catalyst loading on the electrodes and improve the cell performance at the same time. With regard to the hydrophobic catalyst layer, the electrocatalyst slurry mixed with carbon-supported Pt (Pt/C) as catalyst agent and PTFE as binder was applied to a wetproofed carbon support. After that, solubilized Nafion was impregnated into a catalyst layer by spraying or dipping the electrode upon/within a Nafion solution. Another method, referred to as thin-film hydrophilic catalyst layer, was developed by Wilson et al. to mix carbon-supported catalysts with a Nafion solution in the presence of adding additional organic solvents or not. Then, the resulting mixture was brushed or sprayed directly on the carbon paper surface, or the membrane surface.

To achieve maximum performance from commercial scale fuel cells, distribution of reactant and performance over the electrode surface should be primarily optimized. The problem raises the issue of methods to determine high spatial and time resolution of an operating fuel cell, which can give additional information to that obtained by standard electrochemical methods, e.g., current-voltage curves. To this end, several techniques were developed in a few papers to measure the current density distribution and the species distribution in an operating cell. These measured results provided direct information about what was really taking place in the cell at various operating conditions.

In this paper, two different electrodes, i.e., a conventional hydrophobic electrode and a thin-film hydrophilic electrode, were evaluated with the instrumented cell described previously. The current density distribution of each electrode was demonstrated and discussed. From viewpoints of designing a suitable catalyst layer for commercial scale PEMFC, a composite catalyst layer was designed, and its performance was compared with other conventional electrodes.

Experimental

Preparation of electrodes.—All electrodes used here were prepared with the same anode, cathode backing layer but different cathode catalyst layer. The cathode backing layer was made of carbon paper (SGL TECHNIK, PE704) wetproofed with PTFE emulsion. Then, a diffusion layer consisting of about 1 mg/cm² of carbon black (Vulcan XC72) and 0.43 mg/cm² of PTFE was applied on the backing layer by brushing technique. After that, the substrate was subjected to sintering at 330°C for 40 min to give a homogeneous dispersion of PTFE.

The hydrophobic catalyst layer was prepared over the diffusion layer by brushing a slurry of Pt/C and PTFE. After sintering, the cathode electrode thus prepared was impregnated with 5 wt % solubilized Nafion (DuPont Company). Regarding the thin-film hydrophilic catalyst layer preparation, the procedure proposed by Tang was used. The slurry mixed with Pt/C, alcohol, and Nafion solution was stirred thoroughly in an ultrasonic bath before being brushed on the diffusion layer. Then, the electrode was dried at room temperature for 30 min and subsequently at 70°C for another 60 min. In Table I, the characteristics and fabrication conditions of electrodes are summarized in detail. The cathode catalyst layers of E1 and E2 are hydrophobic and hydrophilic, respectively.

Pretreated Nafion 1035 membrane, hydrophobic anode (Pt/C from Johnson-Mathey, Pt loading: 0.3 mg/cm²) and cathode are hot pressed at 10 MPa, 140°C for 1 min to obtain membrane electrode assembly (MEA). The active areas of the MEAs used here were all 130 cm².

Instrumented cell design.—The MEA was incorporated in the single-cell test fixture. Special details and geometry of the instrumented fuel cell with 15 subcells were given previously. Figure 1 shows the structure of the cathode side testing plate with parallel channels flow field. The matrix of the cathode plate was made of polymethyl methacrylate and the current collectors of the subcells were made from carbon rods. As a result, parallel channels flow field contained 15 conductive segments with diameter of 8.0 mm acting as electrically isolated current collectors. Thus, each carbon rod could be seen as a probe to monitor local MEA activity and local membrane conductivity. The flow field channels were 0.8 mm wide, 0.6 mm deep, and the shoulders were 1.0 mm wide. On both sides of the anode and cathode, distributing channels 2.0 mm in width and 0.4 mm in depth were positioned at the top and bottom of the flow field plate, respectively.

The anode plate consisted of flow field plate, current collector plate, and end plate. The flow field plate was made from a piece of porous graphite sheet, which was hot pressed to shape the parallel channels pattern. The current collector plate and the end plate were made of stainless steel. The lead welded to each carbon rod was connected to a load unit through a 0.05 Ω high-resolution resistor. The voltage drop over each resistor was monitored with a data col-
lector and a computer, by which the performance of each subcell was recorded.

In PEMFC performance test, the cell temperature was kept at 40°C with both hydrogen and oxygen humidified at 40°C. The operating partial pressures $p_{O_2}$ and $p_{H_2}$ were controlled at 0.13 and 0.12 MPa, respectively. The stoichiometric coefficients for hydrogen and oxygen were 1.25 and 2.38, respectively.

**Results and Discussion**

*Effect of different catalyst layers on current distribution.*—Figure 2 shows the overall performance of all subcells with two different electrodes E1 and E2. In the whole current density range, it is obvious that E2 demonstrates better performance compared to E1. It can be explained that, in the low current density region (activation polarization), the absence of PTFE increases the contact area between Nafion and catalyst, and at the same time, increases the electrochemically active surface area. Integrity of the membrane-electrode interface of E2 is greatly improved in the sense that the electrolyte is continuous across the interface. In E1, it is difficult to make Nafion distribution homogeneous, and the excess addition of Nafion leads to reduction of cell performance due to the lower diffusion rate of reactant gases in Nafion film covering Pt catalyst.

![Figure 1](image1.png)

Figure 1. Schematic of the testing cathode structure with parallel channels flow field.

![Figure 2](image2.png)

Figure 2. Cell performance of different electrodes, $p_{O_2} = 0.13$ MPa, $p_{H_2} = 0.12$ MPa, $T_{cell} = 40°C$, $T_{H} = 40°C$.

![Figure 3](image3.png)

Figure 3. Scanning electron micrographs of cross sections of (a) E1 and (b) E2.

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**Table I. Characteristics and fabrication conditions of electrodes.**

<table>
<thead>
<tr>
<th>Cathode</th>
<th>45.6 wt % Pt loading (mg/cm²)</th>
<th>Ionomer loading (mg/cm²)</th>
<th>PTFE loading (mg/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E1</td>
<td>0.4</td>
<td>0.6</td>
<td>0.37</td>
</tr>
<tr>
<td>E2</td>
<td>0.4</td>
<td>0.29</td>
<td>0</td>
</tr>
<tr>
<td>E3</td>
<td>0.4 (2/3 area from the inlet) + 0.4 (the rest)</td>
<td>0.29 (2/3 area from the inlet) + 0.6 (the rest)</td>
<td>0 (2/3 area from the inlet) + 0.37 (the rest)</td>
</tr>
</tbody>
</table>

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*Electrochemical and Solid-State Letters, 7 (6) 1-0 (2004)*
Figure 4. Contours of current density distribution of E1 (V = 0.35 V), $p_{O_2} = 0.13$ MPa, $p_{H_2} = 0.12$ MPa, $T_{cell} = 40^\circ$C, $T_{Hi} = 40^\circ$C.

Figure 5. Contours of current density distribution of E2 (V = 0.35 V), $p_{O_2} = 0.13$ MPa, $p_{H_2} = 0.12$ MPa, $T_{cell} = 40^\circ$C, $T_{Hi} = 40^\circ$C.

Figure 6. Contours of current density distribution of E3 (V = 0.35 V), $p_{O_2} = 0.13$ MPa, $p_{H_2} = 0.12$ MPa, $T_{cell} = 40^\circ$C, $T_{Hi} = 40^\circ$C.

particles. The proton penetration and gas accessibility together defines the active reaction region in the catalyst layer. As the current density increases (ohmic polarization), the active reaction region narrows and closes to the interface of membrane and electrode. Figure 3a and b show the scanning electron micrographs of the cross sections of E1 and E2, respectively. The measured thickness of the catalyst layer of E1 is about 40 $\mu$m while E2 shows an evident thinner catalyst layer (about 30 $\mu$m). The thickness of the catalyst layer depends on three factors: PTFE content, Nafion content, and the catalyst type and loading. Compared to E2, the presence of PTFE and the higher ionomer loading result in a thicker catalyst layer than that of E1. E2 provides better performance because of its thinner catalyst layer and higher active density compared to the thicker catalyst layer E1. E2 provides better performance because of its thinner catalyst layer and higher active density compared to the PTME and the higher ionomer loading result in a thicker catalyst layer than that of E1. E2 provides better performance because of its thinner catalyst layer and higher active density compared to the microporous structure of E1. But, as illustrated in Fig. 2, it is obvious to note that the difference between the performances of two electrodes decreases in the high current density region.

An explanation of this behavior can be derived from the current density distribution of the electrodes. When the fuel cell was operated at different voltage, the performances of the subcells were recorded. Then, the contour of current density distribution over the whole electrode was obtained by calculating with cubic interpolation. Figure 4 and 5 illustrate the contours of E1 and E2 operated at 0.35 V. It is demonstrated that the current density decreases steeply at the outlet region of the cell. It is mainly attributed to that as the electrochemical reaction occurs, water gradually accumulates and condenses along the gas flow channel as a by-product, a condition known as “flooding.” This is consistent with the results of Mench12 and Geiger,13 according to whom the liquid water was observed mainly at the outlet region of the flow field and consequently resulted in flooding at this region. Comparing the results shown in Fig. 4 and 5, the flooding of E2 is more marked. Liquid water reduces the pore spaces for oxygen transport to the reaction surface and results in gas permeability limitation as well as renders part of the electrode electrochemically inactive. For E2, Nafion is used instead of PTFE to bind the structure together, which makes it more prone to be flooded. As for E1, PTFE is effective as a binder and imparts hydrophobicity to the electrode, the gas conduit in the catalyst layer lined with a thin coating of PTFE allows passageway for the gas, even in the presence of liquid water.

Composite catalyst layer study.—Based on the above discussions, a composite catalyst structure, which is defined as E3, was prepared. The 2/3 area from the inlet of the electrode was prepared according to E2 and the rest was prepared as E1. The carbon black loading at the different regions of the cathode diffusion layer was adjusted to obtain a homogeneous thickness. In Fig. 2, it can be seen that the cell voltage for E2 is slightly higher than that of E3 at low current density. But, it drops rapidly with the increase of the current density due to the presence of liquid water at the outlet region of electrode until E3 yields a notably better performance. The performance of the outlet region of E3 has a marked increase compared to E2, as illustrated in Fig. 6. This is due to the composite catalyst layer, which ensures both high activity of the hydrophilic electrode and excellent waterproofness of the hydrophobic electrode.

Conclusions

The current density distribution and the performance of the hydrophilic electrode and hydrophobic electrode were evaluated and discussed. The hydrophilic electrode showed better performance in the activation polarization region and the ohmic polarization region. However, under flooding conditions, the hydrophobic electrode demonstrated better performance. A composite catalyst layer, which included both the advantages of hydrophilic and hydrophobic electrodes was designed based on those results, and an improved performance was obtained in the concentration polarization region.
The Chinese Academy of Sciences assisted in meeting the publication costs of this article.

References