Numerical Simulation of the Reaction and Mass-Transfer Profiles in the Two-Layer Catalyst of a PEMFC

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A simple one-dimensional numerical simulation for cathode catalyst layers was conducted to elucidate the significance of a structure with a gradient in the ionomer content in the cross-plane direction. First, under an assumption of uniform (one-layer) catalysts, equivalent pairs of the effective ionic conductivity and effective gas diffusion coefficient were identified. Next, results with two-layer catalysts were calculated with two pairs of parameters among the equivalent pairs obtained earlier. Comparison of the performance of the two-layer catalysts revealed that ionic conductivity is more important near the PEM, and gas diffusivity is more important near the GDL.

Key Words: PEMFC, Simulation, Catalyst Layer, Mass Transfer

1 Introduction

Even if a catalyst layer of a proton exchange membrane fuel cell (PEMFC) is assumed to be uniform without any consideration of its microstructure, a distribution in the reaction develops in the cross-plane direction according to the combination of two kinds of mass transfer, i.e., proton conductivity and oxygen diffusivity. These two phenomena oppose each other, since they are positively and negatively correlated with the ionomer content, respectively. Therefore, optimization of the ionomer content in a catalyst layer requires a balance of these two phenomena. 1,2 It is reasonable to ask, if a gradient in the ionomer content can be made in a catalyst layer, what is the preferred direction of the gradient? One might expect that a higher ionomer content near the gas diffusion layer (GDL) (and therefore a lower ionomer content near the proton exchange membrane (PEM)) would lead to better performance, since the limitation of the reaction near the gas diffusion layer is due to a lack of ionic access (and that near the PEM is due to lack of gas access), and such an electrode might mitigate these limitations. On the other hand, one might also expect that an electrode with an opposite gradient (rich in ionomer near the PEM and poor in ionomer near the GDL) would be better, since ionic flux is greater near the PEM (the flux of gas is greater near the GDL), and an improvement in ionic conductivity seems to be more effective near the PEM (and an improvement in gas diffusivity seems to be more effective near the GDL). Although a multi-layer catalysts 14 tend to show that rich in ionomer near the PEM is preferable, some studies show different results. 1 This is probably due to change of the platinum utilization, since a catalyst layer with a catalyst gradient is also fairly effective. 15 In this study, we examined the performance of two-layer catalysts with different values of ionic conductivity and gas diffusivity by numerical simulations. This simple model were used to elucidate the effects of graded catalysts, and the effects of the direction of differences in conductivity and diffusivity on performance.

2 Mathematical Model

The model used for the numerical simulation is one-dimensional and isothermal, and gives steady-state conditions based on quite simplified assumptions. The catalyst layer is assumed to be uniform without a microstructure. The oxygen concentration profile is assumed to be determined only by Fick’s first law with uniform diffusion coefficient throughout the material, without considering the influence of liquid water. The local electrolyte potential profile in the ionomer phase is determined by Ohm’s law with a given ionic conductivity. The electronic resistance is ignored. Electrochemical reaction (faradaic current, which is equal to the divergence of the ionic current passing through the ionomer phase) is determined by the Tafel equation with a constant Tafel slope. The parameters used in the model are summarized in Table 1. Calculations were performed by obtaining a self-consistent faradaic current distribution by fitting using Microsoft Excel Solver 9.

Although such a primitive model may not give quanti-
tatively exact results, qualitative findings suitable for the scope of this paper should be expected. Indeed, if some realistic factors, such as the effects of liquid water flux, 3D effect, etc. are introduced, the results may become more accurate. However, the effects of such factors should depend on the characteristics of the material used. The purpose of this study was to obtain basic and general findings regarding the significance of a catalyst layer with a gradient in the ionomer content under simple assumptions.

3 Results and Discussion

First, a simulation was conducted for uniform (one-layer) catalyst to obtain proper parameters. The effective ionic conductivity was varied within the range of 2 to 10 mS cm$^{-1}$, and the effective diffusion coefficient of oxygen was adjusted so that the electrode would exhibit a target performance point (0.6 V at 0.8 A cm$^{-2}$). Figure 1 (a) shows the obtained pairs of conductivity and diffusivity, which result in $I-E$ curves that share a common target performance point as shown in Fig. 1 (b). For the lowest conductivity, the local reaction (faradaic current) is localized near the electrolyte membrane, as shown in Fig. 1 (c). This is a typical behavior when ionic access is hindered.

Next, two-layer catalysts were simulated. As parameters for each layer (PEM side and GDL side) in the calculation, two of the pairs shown in Fig. 1 (a) were used. Figure 2 (a) shows the electrode activities of two-layer catalyst represented by potentials at 0.8 A cm$^{-2}$. As shown, higher conductivity is preferred on the PEM side, albeit lower diffusivity, and higher diffusivity is preferred on the GDL side, but with lower conductivity. Comparisons of $I-E$ curves under a fixed conductivity in the GDL side are shown in Fig. 2 (b). Although performance was improved by an increase in ionic conductivity on the PEM side, the relatively large change in the shapes of the $I-E$ curves at high-current regions suggests that this improvement is due to an improvement in gas diffusivity. This discordance can be understood by considering the reaction profiles in detail, as follows: Fig. 2 (c) shows calculated profiles of the electrode potential (local potential difference between the carbon and ionomer), oxygen concentration, and faradaic current (electrochemical reaction) when the conductivity on the PEM side is high. Based on a comparison with the uniform case shown in Fig. 1 (c), it is apparent that the reaction has a more relaxed localization and is distributed more homogeneously. This shortens the average diffusion distance required for the reaction, which results in the apparent improvement in gas diffusivity observed in the $I-E$ curve.

The calculations in this paper are for equivalent pairs of ionic conductivity and gas diffusivity. However, changes in the ionomer content in an actual catalyst layer generally do not guarantee such equivalence. The significance of the obtained findings is as follows: Both an excess and a deficiency of the ionomer in an actual catalyst layer could lead to inferior performance. Furthermore, the behavior of such performance should change depending on the materials used and the fabrication method. Therefore, we can not provide a quantitative explanation of the change in performance without obtaining the ionic conductivity and gas diffusivity as functions of the ionomer content. Thus, there apparently is no general method for optimizing a two-layer catalyst. However, despite this limitation, an analytical consideration

\begin{figure}[h]
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\includegraphics[width=\textwidth]{fig1.png}
\caption{(a) Pairs of ionic conductivity and gas diffusivity for which the calculation shows a target performance (0.6 V at 0.8 A cm$^{-2}$). (b) Three examples of the calculated $I-E$ performance among the combinations shown in (a). (c) Calculated profiles of the local electrode potential, $E$, normalized oxygen concentration, $c$, and normalized faradaic current, $i$, under operation at 0.8 A cm$^{-2}$ when the conductivity and diffusivity are set at 2 mS cm$^{-1}$ and 2.9 $\times$ 10$^{-3}$ cm$^{2}$ s$^{-1}$, respectively. The PEM is on the left (x < 0 $\mu$m) and the GDL is on the right (x > 30 $\mu$m).}
\end{figure}
independent of the material used or fabrication method can be made if the discussion is limited to the situation at and near the optimum amount of ionomer used. As shown schematically in Fig. 3, we can imagine a performance curve as a function of the ionomer content. The differential coefficient is zero at the maximum point.

This means that a small change in the ionomer content at and near the maximum point approximately satisfies the condition of “equivalent pairs”, as represented in Fig. 1. Therefore, the results shown in Fig. 2 (a) may answer the question regarding which direction is desirable when a small gradient is formed into an optimized uniform catalyst layer.

4 Conclusion
Several pairs of ionic conductivity and gas diffusivity were obtained by a numerical simulation as equivalent pairs from the viewpoint of the compatibility of mass transfer. Various combinations of these pairs were used to compose two-layer catalysts for simulation. Based on the potential of the electrode at a target current density as an index of the activity, the results indicate that a higher conductivity is preferred on the PEM side and a higher diffusivity is preferred on the GDL side. This tendency can be explained by relaxation of the localized reaction observed with a homogeneous (one-layer) catalyst. While this finding does not depend on the characteristics of the catalyst layer, it is theoretically valid only when the ionomer content is already optimized and the degree of gradient is not large.

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References