**Special Feature: Popularizing Fuel Cell Vehicles: Designing and Controlling Electrochemical Reactions in the MEA**

**Research Report**

**Modeling of Oxygen Transport Resistance in Polymer Electrolyte Fuel Cells**

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**ABSTRACT** This contribution deals with the oxygen transport resistance in the vicinity of the cathode catalyst-ionomer interface in polymer electrolyte fuel cells (PEFCs). The transport resistance was measured using an ultramicroelectrode coated with a Nafion film less than 100 nm thick, and was resolved into inner (bulk) and interfacial resistances. The films were found to have almost the same inner transport resistivity as a 100 µm thick cast Nafion film. The interfacial resistance was equivalent to 30–70 nm of the Nafion film with only the inner resistance. The existence of a transport barrier at the Pt-Nafion interface was hypothesized. The interfacial transport resistance was included in a model that predicts the performance (current density vs. cell potential) of a membrane-electrode assembly as a pressure-independent transport resistance. The prediction is in agreement with the experimental curve in the intermediate potential region when the pressure-independent resistance is assumed to be potential dependent. The potential dependence suggests that the transport barrier is much thinner than the ionomer film.

**KEYWORDS** Polymer Electrolyte Fuel Cell, Oxygen Transport, Interfacial Transport Resistance, Thin Ionomer Film, Catalyst Layer

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1. Introduction

One of the biggest challenges to achieve the widespread use of polymer electrolyte fuel cell (PEFC) systems is to reduce the amount of electrode catalyst without sacrifice of the performance. This requirement is due to the cost of the catalyst, which is typically made of platinum group metals and accounts for a considerable portion of the cell cost. The voltage penalty in the reduction of catalyst loading often becomes a problem with respect to the oxygen reduction reaction (ORR) at the cathode rather than the hydrogen oxidation reaction (HOR) at the anode because the catalyst activity for the ORR is much lower than that for the HOR. Catalyst loading reduction generally leads to a reduction in the catalyst surface area and leads to an increase in the overall activation loss because the loss is characterized by the specific activity multiplied by the surface area of the catalyst. Reduction of the catalyst surface area is also regarded as a cause of the increase in mass-transport losses because the diffusional flux of reactants increases with a decrease in the catalyst surface area; therefore, the increase in diffusion flux leads to a decrease in the reactant concentration at the catalyst surface.

The origin of mass-transport losses has been separately investigated using a model system in which a planar Pt electrode was covered with a Nafion film facing O2-containing gas. The O2 transport resistance was larger than expected from the bulk diffusion coefficient of Nafion when a very thin film was applied. The O2 transport resistance could thus be another cause of the observed performance loss in addition to the local increase in the reactant flux with a reduction in catalyst loading. A diffusion barrier was then proposed to be located at the Pt-Nafion and/or Nafion-gas interfaces and the O2 transport resistance of the barrier was evaluated.

This article first examines the O2 transport resistance in a model system using a Nafion film with a thickness of 20 nm or less. The experiment reveals the difference between the inner (bulk) and interfacial transport resistance. The performance of a membrane-electrode assembly (MEA) is then predicted with a mathematical model that uses experimentally determined parameters. A potential dependence is introduced to the interfacial transport resistance by fitting the model prediction to the experimental result. The thickness of the diffusion...
barrier is then finally estimated using an O\textsubscript{2} transport model inside the barrier.

2. Interfacial Transport Resistance

2.1 Model

Figure 1 illustrates the steady-state concentration distribution of O\textsubscript{2} in an ionomer (e.g. Nafion) film of thickness \(x_0\) covering a planar Pt electrode at which the ORR occurs. When the diffusion-limited current density is observed, the O\textsubscript{2} concentration at the Pt-ionomer interface (\(x = 0\)) is regarded as zero. If there is some type of transport barrier at \(x = 0\), then the O\textsubscript{2} concentration just beyond the barrier is larger than zero (denoted \(c_p\)). At \(x = x_0\), there is a concentration jump again, assuming another transport barrier, so that the concentration (denoted \(c_{\text{ion}}\)) is lower than the equilibrium value (denoted \(c_{\text{eq}}\)). Inside the ionomer film (\(0 < x < x_0\)), the O\textsubscript{2} flux is assumed to obey Fick’s first law. The O\textsubscript{2} flux \(J_{\text{O2}}\) can be described as

\[
J_{\text{O2}} = -\frac{1}{R_{\text{pt}}}(x = 0),
\]

\[
J_{\text{O2}} = -D \frac{c_{\text{ion}} - c_p}{x_0} (0 < x < x_0),
\]

\[
J_{\text{O2}} = -\frac{1}{R_{\text{ion}}} (c_{\text{eq}} - c_{\text{ion}}) (x = x_0),
\]

\[
J_{\text{O2}} = -\frac{1}{R_{\text{ion}}} (c_{\text{eq}} - c_{\text{ion}})
\]

where \(R_{\text{pt}}\) and \(R_{\text{ion}}\) are the interfacial resistance at the Pt-ionomer and ionomer-gas interfaces, respectively, and \(D\) is the diffusion coefficient. The diffusion-limited current density \(I_d\) is expressed as

\[
I_d = -4FJ_{\text{O2}}(x = 0),
\]

where \(F\) is Faraday’s constant. When Henry’s law is assumed, \(c_{\text{eq}}\) is related to the partial pressure of O\textsubscript{2} gas \(p_{\text{O2}}\) as

\[
c_{\text{eq}} = Kp_{\text{O2}}^\text{ext},
\]

where \(K\) is Henry’s law constant. From Eqs. (1)–(5), the O\textsubscript{2} transport resistance for planar electrode \(R_{\text{O2}}\) is defined as

\[
R_{\text{O2}} = \frac{p_{\text{O2}}^\text{ext}/RT}{|I_d|/4F} = \frac{1}{RTK}x_0 + \frac{1}{RTK}(R_{\text{ion}} + R_{\text{pt}})
\]

\[
\equiv \rho_{\text{inner}}x_0 + R_{\text{interface}}.
\]

In Eq (6), \(\rho_{\text{inner}}\) corresponds to the diffusion coefficient inside the film (\(0 < x < x_0\)), which is called the inner transport resistivity, and \(R_{\text{interface}}\) corresponds to the barrier at the two interfaces, which is called the interfacial transport resistance.

2.2 Method

Figure 2 shows a schematic of the cell. The working electrode is a circular cross section of a 10 \(\mu\)m diameter Pt wire sealed in a glass tube. Nafion thin films with various thicknesses were prepared on the electrode from Nafion solution (DE2020, DuPont) diluted with 1-propanol by a solution casting technique. The counter electrode was comprised of a platinized Pt mesh coated with Nafion. The Nafion covering the mesh is in contact with the thin Nafion film coated on the working electrode. These electrodes were placed in a vessel into which humidified O\textsubscript{2}-N\textsubscript{2} mixture was flowed. The reference electrode was comprised of a platinized Pt mesh coated with Nafion and was placed in another vessel supplied with humidified 2\% H\textsubscript{2}-N\textsubscript{2} mixture. A Nafion membrane was used to bridge the Nafion films on the working and reference electrodes. The entire cell was placed in a temperature-controlled convection oven. Cyclic voltammetry was conducted between 0.1 and 1.1 V vs. RHE at a scan rate of
0.1 V·s⁻¹. Further experimental details can be found elsewhere.⁽¹⁰⁾

2.3 Mechanism

Representative cyclic voltammograms are shown in Fig. 3. The red and blue lines show that under N₂ and 1% O₂ atmospheres, respectively. The difference between these two voltammograms, shown in black, includes the ORR current. It does not show an apparent diffusion-limited current, which is often observed in experiments using liquid electrolytes.⁽¹¹⁾ This is because the diffusion resistance, indicated by the diffusion length divided by the diffusion coefficient, is much larger in liquid electrolytes than in thin Nafion films. In addition, the electrode area effective for the ORR is dependent on the potential because the species that covers the Pt surface, such as sulfonate anions of Nafion, (hydr)oxides, and H atoms, change their coverage depending on potential. The effects from such surface species are determined to be smallest around 0.25 V vs. RHE, and the current at this potential is regarded as the diffusion-limited current.

The inner transport resistivity  \( \rho_{\text{inner}} \) and interfacial transport resistance  \( R_{\text{interface}} \) were determined by fitting the  \( \rho_{\text{planar}} \) vs.  \( x_0 \) data to Eq. (6), as shown by the dotted lines in Fig. 4. Figure 5 shows the temperature and relative humidity (RH) dependence of  \( \rho_{\text{inner}} \) and  \( R_{\text{interface}} \). The data for a 100 µm thick Nafion film are also plotted in Fig. 5(a). Both thin (from 20 to 100 nm) and thick (100 µm) films have almost the same inner resistivity, which indicates that the structure that determines the O₂ transport inside Nafion (0 <  \( x < x_0 \)) is not affected by the structure of the interfaces ( \( x = 0, x_0 \)). The interfacial resistance has different temperature and RH dependence from the inner resistivity, as observed by comparison of Figs. 5(a) and (b). The equivalent film thicknesses of the interfacial resistance, given by  \( R_{\text{interface}}/\rho_{\text{inner}} \), were between 30 and 70 nm in the studied temperature and RH ranges. The O₂ flux is predominantly controlled by the interfacial transport resistance when the film is much thinner than the value of  \( R_{\text{interface}}/\rho_{\text{inner}} \).

3. Transport Resistance in Catalyst Layers

3.1 Model

The O₂ transport resistance in an MEA  \( R_{\text{O₂}}^{\text{MEA}} \), is formally defined as

\[
R_{\text{O₂}}^{\text{MEA}} \equiv \frac{P_{\text{O₂}}^{\text{MEA}}/RT}{I_{\text{d}}/4F}.
\] (7)

Fig. 2 Geometry of the electrodes.
This includes the diffusion resistance originated from the molecular diffusion through the pores in the gas diffusion layer (GDL) and catalyst layer, as well as the transport resistance from the ionomer surface to the Pt surface. The molecular diffusion coefficient is inversely proportional to the total pressure $P$; therefore, $R_{O_2}^{MEA}$ can be separated into pressure dependent and independent terms, as

$$R_{O_2}^{MEA} = R_{molec}(P) + R_{\text{other}}^{0} = R_{molec}^{0} \times \frac{P}{P_0} + R_{\text{other}}, \quad (8)$$

where $R_{molec}(P)$ is the molecular diffusion resistance as a function of $P$, $R_{\text{other}}$ is the pressure independent term, $P_0$ is the reference pressure, and $R_{molec}^{0}$ is the molecular diffusion resistance at $P_0$. $R_{\text{other}}$ includes the interfacial transport resistance discussed in Sec. 2, and is expressed as

$$R_{\text{other}} = \left( \frac{p_{O_2}^{CL} - p_{O_2}(z)}{P_0} \right) \frac{RT}{4F}, \quad (9)$$

where $p_{O_2}^{CL}$ (assumed constant) is the $O_2$ partial pressure in the pores of the catalyst layer, $p_{O_2}(z)$ (assumed as a function of the distance from the membrane, $z$) is the equivalent $O_2$ partial pressure at the Pt-ionomer interface. $i_{\text{local}}(z)$ is the local current density described by

$$i_{\text{local}}(z) = -i_0 (1 - \theta_{\text{ox}}) f \left( \frac{p_{O_2}(z)}{P_0} \right)^{10^{-\eta(z)/b}}, \quad (10)$$

where $i_0$ is the reference current density, $\theta_{\text{ox}}$ is the oxide coverage on the Pt surface, $f$ is the roughness

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**Fig. 3** Cyclic voltammograms of the Pt electrode with 39 nm-thick Nafion film under $N_2$ (red) and 1% $O_2$ (blue) atmosphere at 313 K and 60% RH. The black curve is the difference in current between the two conditions.

**Fig. 4** Oxygen transport resistance for planar electrode $R_{O_2}^{\text{planar}}$ planar as a function of Nafion film thickness $x_0$ at 313 K.

**Fig. 5** Inner transport resistivity $\rho_{\text{inner}}$ and interfacial transport resistance $R_{\text{interface}}$ as a function of relative humidity at different temperatures.
factor of the electrode, $\eta$ is the overpotential, and $b$ is the Tafel slope.

The MEA performance model deals with the ORR rate distribution in the through-plane direction of the cathode catalyst layer, the ohmic loss in the membrane, and the O$_2$ concentration decrease in the GDL. The details are available elsewhere.$^{(12)}$ The model is applicable to operating conditions in which moderately and equally humidified gases are supplied at high stoichiometry and the O$_2$ concentration is sufficiently low. This condition ensures the in-plane homogeneity of the reaction rate, through-plane homogeneity of the water content of the ionomer, and a negligibly small temperature distribution. The value of $i_0$ was fitted to the experimental data in the high-potential region, and the values of $R_{\text{molec}}$ and $R_{\text{other}}$ were fitted to the data where $I_d$ was observed (between ca. 0.2 and 0.3 V). Even after fitting the parameters in the model, a significant discrepancy still remained between the model and experimental results$^{(12)}$ in the intermediate potential region, as shown in Fig. 6(a). The discrepancy was assumed to be caused by the potential dependence of $R_{\text{other}}$, which includes the interfacial transport resistance. The value of $R_{\text{other}}$ was adjusted at each potential so that the model prediction agreed with the experimental result. As the cathode potential increased, the potential dependent $R_{\text{other}}$ increased between 0.45 and 0.65 V vs. RHE, and decreased above 0.65 V vs. RHE, as shown in Fig. 6(b).

### 3.2 Mechanism

The potential dependence of $R_{\text{other}}$ is more likely to be ascribed to the change in the Pt-ionomer interface than that in the ionomer-gas interface because the coverage of the Pt surface species is dependent on the potential. The influence of the decrease in the Pt area with an increase in the potential is considered in the following discussion. If the ionomer covering the Pt is infinitely thin, then $R_{\text{interface}}$ discussed in Sec. 2 and the interfacial resistance component in $R_{\text{other}}$ would have been inversely proportional to the fraction of the unpoisoned Pt area in the total Pt area. In reality, the ionomer has a finite thickness and hence O$_2$ diffuses from the ionomer-gas interface that faces the adsorbed species, as well as from that facing the unpoisoned Pt. The situation is shown by a simple 2D model in Fig. 7, where the Pt surface is repeatedly covered with adsorbed species at a coverage of $\theta$.

The O$_2$ concentration profile in the diffusion barrier, which exists in the ionomer, is shown in Fig. 8 for different aspect ratios of the distance between the unpoisoned Pt sites ($2w$) to diffusion layer thicknesses ($t$) with the same $\theta$ of 0.9. Figure 8(a) shows a contour plot for $w = 5$ and $t = 1$. The O$_2$ concentration is almost uniform above the adsorbed species at the cathode electrode potential.

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**Fig. 6** (a) Comparison of performance curves; dash: experimental, solid: model prediction. (b) Potential-dependent $R_{\text{other}}$ determined so that the model prediction fits the experimental results. $E$ is the cathode electrode potential.

**Fig. 7** Ionomer-Pt interface model with equations and boundary conditions that determine the concentration (denoted $c$) distribution. $J_x$ and $J_y$ are the flux in $x$ and $y$ directions, respectively, and $D$ is the diffusion coefficient.
4. Conclusion

The existence of an interfacial transport barrier at a Pt-ionomer interface with a different feature from the bulk ionomer was clarified using a model system of a planar Pt electrode coated with thin Nafion films. The equivalent thickness of the interfacial resistance against the inner resistivity was ca. 30–70 nm. A model for the potential dependent interfacial resistance was proposed by comparing the model prediction for the performance of an MEA with the experimental result. The interfacial resistance increases and then decreases with an increase in the potential. The origin of the increase in the interfacial resistance was discussed using a local diffusion model near the Pt-ionomer interface partially blocked by adsorbed species. The model predicts that the interfacial transport barrier should be thinner than the ionomer that covers the Pt particles in the catalyst layer.

References

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Fig. 1

Figs. 2 and 3

Figs. 6-8