Oxygen transport resistance in the cathode catalyst layer of polymer electrolyte fuel cells is discussed. The performance of the cell is first calculated using a 1-dimensional through-plane model in which the activation overpotential and the diffusion-limited current density are fitted to experimental results. Potential-dependent transport resistance is then introduced to bridge the gap between the model prediction and the experimental result in the intermediate potential region. The potential dependent resistance is discussed using an oxygen transport model near the ionomer-Pt interface, where the coverage of adsorbed species changes with the potential. The oxygen transport model predicts that the diffusion layer near the interface is thinner than the thickness of the ionomer that covers the Pt nanoparticles.

The cell performance was measured at 65°C. The cell was operated using a membrane-electrode assembly (MEA) with a active area of 1 cm². The MEA was composed of Nafion membrane (NR211, DuPont) sandwiched between in-house prepared catalyst layers on which gas diffusion layers (GDLs, FC Development Co., Ltd., Japan) were laminated. The catalyst layers were prepared from carbon-supported Pt catalyst (TEC10E50E, Toyota Central R&D Laboratories, Inc., Nagakute, Aichi 480-1192, Japan) which were first proposed.9,10 However, the large agglomerates that the model assumed were not observed in scanning electron micrographs of the catalyst layer cross sections.11 As a result, this model cannot give a clue to improve the structure of the catalyst layer; an obvious approach of agglomerate size reduction is irrelevant. Another diffusion resistance that depends on the coverage of Pt oxides was then proposed.2 However, the model was not able to account for the cell performance perfectly. The mass transport resistance was simulated using an agglomerate model in which the reaction zone is sporadic on the surface of the agglomerate.12 This result demonstrated that the lateral (along the agglomerate surface) transport in the ionomer film could behave as a mass transport resistance. The effective transport distance in the ionomer film was experimentally estimated and was longer than the actual film thickness.13,14 Another perspective of the transport path was proposed by Debe. He estimated the frequency of oxygen collision with the catalyst surface to compare the mass transport loss between the Pt/C catalyst layers and nanostructured thin-film electrodes.15

In this work, the cell performance is first predicted using a mathematical model. The prediction is then compared with experimental results to identify the discrepancy. Finally, an additional model is proposed for the oxygen transport resistance that bridges the gap.

**Experimental**

The cell performance was measured using a membrane-electrode assembly (MEA) with an active area of 1 cm². The MEA was composed of Nafion membrane (NR211, DuPont) sandwiched between in-house prepared catalyst layers on which gas diffusion layers (GDLs, FC Development Co., Ltd., Japan) were laminated. The catalyst layers were prepared from carbon-supported Pt catalyst (TEC10E50E, Toyota Central R&D Laboratories, Inc., Nagakute, Aichi 480-1192, Japan) were laminated. The catalyst layers were prepared from carbon-supported Pt catalyst (TEC10E50E, Toyota Central R&D Laboratories, Inc., Nagakute, Aichi 480-1192, Japan) were laminated. The catalyst layers were prepared from carbon-supported Pt catalyst (TEC10E50E, Toyota Central R&D Laboratories, Inc., Nagakute, Aichi 480-1192, Japan) were laminated. The catalyst layers were prepared from carbon-supported Pt catalyst (TEC10E50E, Toyota Central R&D Laboratories, Inc., Nagakute, Aichi 480-1192, Japan) were laminated.

In practice, fuel cells are typically operated at lower current densities than where the maximum power is achieved, which is around 0.5 V. A better understanding of the effect of the oxygen-transport resistance at the ionomer-Pt interface in the potential region of 0.5–0.7 V is crucial to increase the performance with decreased Pt loading. As a source of diffusion resistance in the catalyst layer in this potential range, agglomerates, which are composed of carbon-supported catalysts and an ionomer, were first proposed.9,10 However, the large agglomerates that the model assumed were not observed in scanning electron micrographs of the catalyst layer cross sections.11 As a result, this model cannot give a clue to improve the structure of the catalyst layer; an obvious approach of agglomerate size reduction is irrelevant. Another diffusion resistance that depends on the coverage of Pt oxides was then proposed.2 However, the model was not able to account for the cell performance perfectly. The mass transport resistance was simulated using an agglomerate model in which the reaction zone is sporadic on the surface of the agglomerate.12 This result demonstrated that the lateral (along the agglomerate surface) transport in the ionomer film could behave as a mass transport resistance. The effective transport distance in the ionomer film was experimentally estimated and was longer than the actual film thickness.13,14 Another perspective of the transport path was proposed by Debe. He estimated the frequency of oxygen collision with the catalyst surface to compare the mass transport loss between the Pt/C catalyst layers and nanostructured thin-film electrodes.15

In this work, the cell performance is first predicted using a mathematical model. The prediction is then compared with experimental results to identify the discrepancy. Finally, an additional model is proposed for the oxygen transport resistance that bridges the gap.
drying and flooding in the cathode. The cell potential was controlled with a potentiostat (PS-2100, Toho Technical Research Co., Ltd.). Triangular potential scans were applied between 0.04 and 0.86 V with a scan rate of 0.02 V · s⁻¹ until stable performance was obtained. The current density was then recorded during the anodic scan.

The electrochemical surface area (ECSA) of the cathode, oxide coverage of cathode Pt, and the membrane and catalyst layer resistances were measured using cyclic voltammetry under 10% H₂ balanced with N₂ in the anode (used as the counter and reference electrodes), and N₂ in the cathode (the working electrode). The ECSA was estimated from a cyclic voltamogram scanned between 0.08 and 0.9 V vs. RHE at a scan rate of 0.02 V · s⁻¹. The current density of double-layer charging was assumed to be the minimum current density observed at 0.43 V vs. RHE, denoted by $E_{DL}$, and was also assumed to be independent of the potential. The hydrogen desorption current observed at potentials less than $E_{DL}$, was integrated and converted to the ECSA by assuming a charge density of 210 μC · cm⁻². The double-layer current density was also measured at 0.005 and 0.05 V · s⁻¹ and extrapolated to 0 V · s⁻¹. The extrapolated value of the current density was assumed to be that from the oxidation of crossover hydrogen. The catalyst layer resistance was estimated from ac impedance spectra measured with a potentiostat/frequency response analyzer (1280Z, Solartron Analytical). The impedance was measured at 0.44 V vs. RHE with a voltage amplitude of 5 mV at frequencies from 1 to 20000 Hz. A transmission-line model was applied to obtain the resistances.

In a separate study on the effect of Pt loading, a PtCo alloy supported Pt catalyst. The catalyst layers were in-house-made. The model takes into consideration the loss of performance by Ohm’s loss in the membrane and cathode catalyst layer, the through-plane distribution of the oxygen reduction reaction (ORR) rate, which originates only from oxide formation. The values of $R_{DL}$ in Fig. 3a were obtained by subtracting the double-layer double-layer charging current from the oxidation current above this potential, as shown in Fig. 2b. The pressure dependence of $R_{DL}$ was well described by Eq. 2, as reported in the previous literature. The values of $R_{molc}$ and $R_{other}$ are listed in Table I.

Model

The cell performance was compared with the prediction from the model. The model takes into consideration the loss of performance by Ohm’s loss in the membrane and cathode catalyst layer, the through-plane distribution of the oxygen reduction reaction (ORR) rate, which originates only from oxide formation.

$\phi (0) = -R_{M} I,$

where $R_{M}$ is the area resistance of the membrane. The equations and boundary conditions, summarized in Fig. 1 with schematics of the MEA and catalyst layer, are implemented in gPROMS ModelBuilder version 4.1.0 (Process Systems Enterprise), an equation-based simulation program package.

Results and Discussion

Oxygen transport resistance.—Figure 2a shows performance curves with different total pressures of the cathode gas during the anodic sweep using 10% H₂-N₂ and 1% O₂-N₂ at the anode and cathode, respectively. The current density reached a local maximum and was independent of the potential between approximately 0.2 and 0.3 V under each condition. This value is considered to be the diffusion-limited current density. From this current density and oxygen partial pressure, the total oxygen transport resistance was calculated and plotted as a function of the total potential at the cathode, as shown in Fig. 2b. The pressure dependence of $R_{DL}$ is well described by Eq. 2, as reported in the previous literature. The values of $R_{molc}$ and $R_{other}$ are listed in Table I.

Model prediction.—The charge for oxide formation on the Pt surface was determined to estimate the oxide-coverage dependent ORR kinetics. The solid line in Fig. 3a shows the voltammogram measured during the anodic sweep with 10% H₂-N₂ and N₂ at the anode and cathode, respectively. The current density increased just after it reached a local maximum at $E_{DL}$. The increase in current density with the potential may indicate the growth of surface oxides, sulfonate adsorption, and an increase in the double-layer capacitance. It was assumed that the double-layer capacitance is independent of the potential and that the current density observed at $E_{DL}$ is the double-layer current density, which is shown as $I_{DL}$ in Fig. 3a. It was also assumed that the current difference calculated by subtracting the double-layer current from the oxidation current above this potential originates only from oxide formation. With these assumptions, the charge for oxide formation is derived from Eq. 4, as shown by the circles in Fig. 3b. The charge-potential relationship was smoothed by a function, as shown by the solid line in Fig. 3b, within the accuracy of 2% above 0.7 V vs. RHE. The charge for oxide formation was used to determine the parameters of the ORR kinetics. Figure 4 (circles) shows the performance during the anodic sweep using 10% H₂-N₂ and 1% O₂-N₂ at the anode and cathode, respectively. The cell potential V is converted to the oxygen concentration in the pores of the catalyst layer $p_{O_2}^{CL}$.
The potential region was simultaneously determined by the maximum likelihood estimation, and was between 0.76 and 0.89 V vs. RHE. The fitting result was in reasonable agreement with the experimental result in the selected potential region, as shown by the solid line in Fig. 4. The parameter values are listed in Table I.

The cell performance was predicted using Eqs. 3–13 with the determined parameters and compared with the experimental results, as shown in Fig. 5a. The parameter values used in the model prediction are listed in Table I. The prediction (solid line) was fitted well to the experimental results (dotted line) above 0.76 and around 0.3 V vs. RHE. The performance below 0.3 V vs. RHE is not discussed here, because the effect of adsorbed hydrogen and the hydrogen evolution reaction is more significant than that of the ORR. It should be noted that the observed current density was significantly smaller than the model prediction between 0.45 and 0.7 V vs. RHE. The simple performance model described above, which includes reaction resistance (Eq. 3), ohmic resistance (Eq. 6), and mass transport resistance (Eqs. 8 and 10), requires an additional resistance model that accounts for the discrepancy in the intermediate potential region.

**Potential dependent mass-transport resistance.**—A potential-dependent oxygen-transport resistance caused by adsorbed species on the Pt surface was then introduced. The potential dependence should be implemented in $R_{\text{other}}$ because it includes the mass-transport resistance between the ionomer and Pt.

$R_{\text{other}}$ was modified at each potential, so that the current density predicted by the model agrees with the experimental result. Figure 5b shows the resulting potential-dependent $R_{\text{other}}$. As the potential increased, $R_{\text{other}}$ increased below 0.65 V vs. RHE but decreased above this potential. From 0.45 to 0.65 V vs. RHE, $R_{\text{other}}$ increased by a factor of 1.26. The oxygen flux decreased by a factor of 0.79 ($=1/1.26$) if the flux was inversely proportional to $R_{\text{other}}$.

**Effect of Pt loading.**—The results with the use of a PtCo catalyst are discussed in this subsection. Figure 6 shows $R_{\text{other}}$ determined from the diffusion-limited current density as a function of the inverse of the roughness factor. The expression

$$R_{\text{other}} = R_{\text{other}}^{f\rightarrow\infty} + \frac{R_{\text{Pt}}}{f}$$

was a good fit with the observed $R_{\text{other}}$, where $R_{\text{other}}^{f\rightarrow\infty}$ and $R_{\text{Pt}}$ are constants. The first term $R_{\text{other}}^{f\rightarrow\infty}$ may arise from Knudsen diffusion through the pores in the MPL and catalyst layer, and from diffusion through the ionomer in the catalyst layer. Equation 15 is transformed...
Figure 2. (a) Cell performance with different total pressures of 1% O₂-N₂ balanced gas. (b) Total oxygen transport resistance vs. total pressure of 1% O₂-N₂ balanced gas.

![Graph](image)

Figure 3. (a) Voltammogram measured during the anodic sweep using 10% H₂-N₂ and N₂ at the anode and cathode, respectively. (b) Cumulative charge for oxide formation during the anodic sweep.

![Graph](image)

Local diffusion model.—The increase in \( R_{\text{other}} \) and \( R_{\text{Pt}} \) can be ascribed to the decrease in the diffusion coefficient of O₂ through the ionomer that covers the Pt particles, and/or the decrease in the Pt area effective for the ORR, which increases the local diffusive flux. The following analysis focuses on the decrease in the Pt area because the amount of adsorbed species, specifically sulfonates in the ionomer\(^2\) and Pt oxides,\(^1\) are likely to be dependent on potential; the intrinsic diffusivity can be affected by the mass density, for example, but the density is less likely to be affected by a change in the electrode potential.

If the ionomer covering the Pt particles had been infinitely thin, \( R_{\text{Pt}} \) 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 O₂ diffuses from the ionomer-Pt interface that faces the adsorbed species as well as from that facing the unpoisoned Pt. If the ionomer is sufficiently thick, then the oxygen flux from the interface that faces the adsorbed species may exceed that from the interface that faces the unpoisoned Pt.

Thus, the oxygen transport through the ionomer was modeled as follows. The Pt surface was modeled as a straight line of width \( 2w \).

The diffusion layer, of which the thickness is not necessarily the same as the ionomer thickness, was modeled as a rectangular domain of thickness \( t \) above the line, as shown in Fig. 8 with coordinate axes.

The ionomer-Pt interface is at \( y = 0 \) and the interface is effective for the ORR only at \(-(1 - \theta)w \leq x \leq (1 - \theta)w\), where \( 0 \leq \theta \leq 1 \). This effective region represents the unpoisoned Pt. The parameter \( \theta \) is regarded as the coverage of adsorbed species that prohibits the ORR, and \( 2w \) can be regarded as a yardstick of the distance between

### Table I. Parameters used in the model prediction shown in Fig. 5a.

| Symbol | Parameter | Value       |
|--------|-----------|-------------|
| \( b \) | Tafel slope | 125 mV · decade\(^{-1} \) |
| \( f \) | Roughness factor | 74 cm\(^2\)Pt · cm\(^{-2} \) |
| \( i_0 \) | Reference current density | 3.07 A · m\(^{-2} \) |
| \( L \) | Thickness of the cathode catalyst layer | 5 \( \mu \)m |
| \( P_0 \) | Reference pressure | 101325 Pa |
| \( Q_0 \) | Reference charge density | 20.1 mC · cm\(^{-2} \) |
| \( R_{\text{molec}} \) | Molecular diffusion resistance at \( P_0 \) | 53 s · m\(^{-1} \) |
| \( R_{\text{other}} \) | Oxygen transport resistance in Eq. 2 | 28 s · m\(^{-1} \) |
| \( r_M \) | Membrane resistance | 53 mΩ · cm\(^{2} \) |
| \( k \) | Ionic conductivity of the cathode catalyst layer | 5.6 mS · cm\(^{-1} \) |
Figure 4. Cell performance during the anodic sweep using 10% H₂-N₂ and 1% O₂-N₂ at the anode and cathode, respectively; circles: experimental results, line: best-fit result.

The active sites on the Pt surface. The oxygen concentration $c$ (in an arbitrary unit) and the $x$ and $y$ components of the oxygen flux, $J_x$ and $J_y$, were modeled as:

$$c = 0 \text{ for } -(1 - \theta)w \leq x \leq (1 - \theta)w \text{ and } y = 0,$$

$$c = 1 \text{ for } y = t,$$

The oxygen flux was assumed to obey Fick’s law:

$$J_x = -D \frac{\partial c}{\partial x},$$

$$J_y = -D \frac{\partial c}{\partial y},$$

The oxygen flux was assumed to obey Fick’s law:

$$J_x = 0 \text{ at } x = \pm w,$$

$$J_y = 0 \text{ for } |x| > (1 - \theta)w \text{ and } y = 0.$$

Figure 5. (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.

Figure 6. $R_{\text{other}}$ determined using $I_d$ as a function of the inverse of the roughness factor, $f$.

Figure 7. Potential-dependent $R_{\text{Pt}}$ with different Pt loadings.

Figure 8. Model geometry near the ionomer-Pt interface.
Equations 23 has to be solved only at \( x \geq 0 \) by imposing
\[ J_x = 0 \quad \text{at} \quad x = 0 \] from the symmetry. The overall flow rate \( q \) was calculated by integrating \( J_y \) as
\[ q = \frac{1}{2} \left( \int_0^w J_y \bigg|_{y=0} dx + \int_0^w J_y \bigg|_{y=t} dx \right). \] The first and second terms in the parenthesis should be exactly the same. These terms were averaged because they are different within the tolerance used in the numerical calculation.

Equations 17–24 were solved by a finite-difference method. The concentration profiles for different aspect ratios of the diffusion layers with the same coverage of \( \theta = 0.9 \) are compared in Fig. 9. Figure 9a shows a contour plot of the oxygen concentration for \( w = 5 \) and \( t = 1 \). The oxygen flux is large where the contour interval is small. The interval between the contour lines is large above the adsorbed species, which indicates that the oxygen flux is small compared with the region above the unpoisoned Pt. Figure 9b shows a contour plot of the oxygen concentration for \( w = 0.5 \) and \( t = 1 \). The contour interval above the adsorbed species is smaller in Fig. 9b than in Figs. 9a.

The effectiveness factor \( H \) is defined as the flow rate \( q \) divided by the flow rate when the coverage is zero:
\[ H = \frac{q}{wD_T}. \]
With the limit of small $r$, $H$ becomes $1 - 0$. The values of $H$ for the cases of Figs. 9a and 9b are 0.14 and 0.45, respectively. Thus, the flux is dependent on the distance between the active sites and the thickness of the diffusion layer, as well as the coverage of the adsorbed species.

**The thickness of the diffusion layer.**—The dimensionless solutions of Eq. 23 are identical for dynamically similar systems. Therefore, the effectiveness factor $H$ is a function of $w/t$ and $\theta$, as shown in Fig. 10a. Given the coverage was $\theta_0$ at $E_{DL}$, the coverage $\theta_H$ at a higher potential can be calculated from the decrease in $H$ or the increase in $R_{other}$ from $R_i$ to $R_H$. The prerequisites are as follows:

(a) The distance between the active sites should be larger than the interatomic distance (ca. 0.3 nm) and smaller than the size of the Pt nanoparticles (ca. 2–3 nm).
(b) The thickness of the diffusion layer should be smaller than the thickness of the ionomer that covers Pt (ca. 10 nm).
(c) The oxide coverage at 0.45 and 0.65 V vs. RHE was zero and 0.075, respectively, as shown in Fig. 3.

Although a distinct peak in the voltammogram that shows an increase in the sulfonate coverage with the potential was not observed for an MEA with Pt nanoparticles, it is likely that the coverage increases at a constant rate and is therefore difficult to distinguish from other reactions. The initial coverage was assumed to be 0.1 in the following discussion because the sulfonate coverage was approximately 0.1 for 30% Pt/high-surface area carbon at 0.45 V vs. RHE. Given the value of $R_{other}$ increased by 1.26 from 0.45 to 0.65 V vs. RHE, the ranges of $w$ and $t$ were inferred from this relationship. Figure 10b shows $\theta_H$ as a function of $w/t$ with different values of $R_H/R_i$. If $2w = 3$ nm and $t = 10$ nm ($w/t = 0.15$) are assumed, then the increase in $R_{other}$ by 1.26 ($R_H/R_i = 1.26$) can be achieved only when $\theta_H$ is larger than 0.9. Such a large coverage should result in a significant decrease in the ORR activity, and therefore a diffusion layer as thick as the ionomer thickness may not be reasonable. The final coverage $\theta_H$ decreases with decreasing $w/t$, and reaches $\theta_H = 0.46$ for $w/t = 1.5$. If $t = 1$ nm, the value that was predicted by the molecular dynamics simulation, is selected, then the value of $2w$ becomes 3 nm, which is the same order of magnitude of the Pt particle size.

**Conclusions**

A model for the potential-dependent oxygen-transport resistance in the cathode catalyst layer of a PEFC is proposed by comparison of the predictions from a model including constant transport resistances with experimental results. The transport resistance increases and then decreases with an increase in the potential. The origin of the increase in resistance with the potential is discussed using a local diffusion model near the ionomer-Pt interface partially blocked with adsorbed species. The local diffusion model predicts that the thickness of the diffusion layer near the interface should be thinner than that of the ionomer that covers the Pt particles. This conceptual model requires further enhancement by incorporation into the performance model, so that the activation loss and diffusion loss can be discussed simultaneously. In addition, data for sulfonate coverage at potentials higher than $E_{DL}$, which may be obtained by spectroscopic methods and electrochemical methods, are required.