A Steady-State Impedance Model for a PEMFC Cathode

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Abstract

A model for the simulation of the steady-state impedance response of a polymer electrolyte membrane fuel cell (PEMFC) cathode is presented. The catalyst layer of the electrode is assumed to consist of many flooded spherical agglomerate particles surrounded by a small volume fraction of gas pores. Stefan-Maxwell equations are used to describe the multicomponent gas-phase transport occurring in both the gas diffusion layer and the catalyst layer of the electrode. Liquid-phase diffusion of O₂ is assumed to take place in the flooded agglomerate particles. Newman’s porous electrode theory is applied to determine over-potential distributions.

In a commercial polymer electrolyte membrane fuel cell (PEMFC), air is likely to be the ultimate candidate gas for the cathode due to its much lower cost compared to pure O₂. However, for an air cathode, the mass-transport limitation in its gas diffusion layer (GDL) becomes more and more significant with the increase of operating current density. Knowledge of the mass-transport limitations in an air electrode is important to us because this electrode is the most important source of loss in an air/H₂ PEMFC.¹

Two common models are available in the literature for the study of a PEMFC air cathode. They are the steady-state polarization model and the steady-state impedance model. Bernardi and Verbrugge² developed a steady-state polarization model for a PEMFC. In their model, multicomponent gas-phase transport was considered for both the GDL of an air cathode, and the O₂ diffusion as well as the liquid-phase diffusion of O₂ was considered for the catalyst layer (CAL). They found that the gas-phase transport limitation in the cathode GDL caused a limiting current in the cell. In their work, the cathode CAL was assumed to be completely flooded. This assumption was also adopted by a later work of Springer et al.,² who carried out an extensive study of the influence on cell performance of the multicomponent gas transport in the GDL and the ionic conduction as well as the liquid-phase diffusion of O₂ in a flooded CAL of an air cathode. Even if a model with the flooded CAL assumption was generally able to explain the experimental and the ionic conduction as well as the liquid-phase diffusion of O₂ in the cathode GDL, a better understanding of the transport limitations in the cathode is possible from a series of impedance experiments carried out at different steady-state operating current densities. Springer et al.³ developed a steady-state impedance model for an air cathode, where the multicomponent gas transport in the GDL and the liquid-phase diffusion of O₂ in a flooded CAL as well as the ionic conduction over there were taken into account. Due to the assumption of a flooded CAL in their work, the overestimation of the product of the diffusivity and the solubility of O₂ in the liquid phase was again not avoided.

The objective of this work is to extend Jaouen et al.’s work⁴ to the development of a steady-state impedance model for an air cathode. Gas-phase transport is assumed to occur in both the GDL and the CAL (see Fig. 1). The cathode CAL is assumed to have many flooded agglomerate particles, inside which the O₂ reduction reaction takes place. Outside the flooded agglomerate particles are gas pores. Similar to Springer et al.⁵ steady-state impedance model, liquid water transport is not considered in this work. Even if it is likely that with the increase of operating current density, the volume fraction of gas pores in either the GDL or the CAL decreases,⁶,⁷ we expect that a constant value of this parameter is maintained during each steady-state impedance measurement.

Mathematical Model

Multicomponent gas transport.—The multicomponent gas transport in a porous media such as the GDL and the CAL of a PEMFC cathode is described by the Stefan-Maxwell equation⁸

\[
\nabla x_i = - \sum_{j=1}^{n} \frac{1}{c_0 D_{ij}} (x_i N_j - x_j N_i)
\]

where \( x_i \) is the mole fraction of gas component i, \( \nabla x_i \) is the gradient vector of \( x_i \), \( n \) is the number of gas components, \( c_0 \) is the total gas concentration, \( N_j \) is the flux of gas component i, and \( D_{ij} \) is the effective binary diffusion coefficient related to a free stream binary diffusion coefficient \( D_{ij}^0 \) by

\[
D_{ij} = \varphi_i \varphi_j D_{ij}^0
\]

The cathode CAL was assumed to consist of many spherical agglomerate particles. The existence of a double Tafel slope on a steady-state polarization curve due to the transport limitation by either ionic conduction or liquid-phase diffusion of O₂ and the existence of a quadratic Tafel slope due to a combined limitation by both processes were extensively investigated by Jaouen et al.⁴

Compared to the steady-state polarization experiment, the steady-state impedance experiment is more useful for the study of mass-transport limitations in a PEMFC.⁵,⁷ After perturbing a cell from its steady-state operating condition by a small sinusoidal signal in the form of either cell potential or operating current over a wide range of frequency, all the processes occurring in the cell with different time constants are to be resolved on an impedance plot. Because the dominating process in a PEMFC often changes with the change of its steady-state operating condition, a better understanding of the transport limitations in the cell is possible from a series of impedance experiments carried out at different steady-state operating current densities. Springer et al.³ developed a steady-state impedance model for an air cathode, where the multicomponent gas transport in the GDL and the liquid-phase diffusion of O₂ in a flooded CAL as well as the ionic conduction over there were taken into account. Due to the assumption of a flooded CAL in their work, the overestimation of the product of the diffusivity and the solubility of O₂ in the liquid phase was again not avoided.

The objective of this work is to extend Jaouen et al.’s work⁴ to the development of a steady-state impedance model for an air cathode. Gas-phase transport is assumed to occur in both the GDL and the CAL (see Fig. 1). The cathode CAL is assumed to have many flooded agglomerate particles, inside which the O₂ reduction reaction takes place. Outside the flooded agglomerate particles are gas pores. Similar to Springer et al.⁵ steady-state impedance model, liquid water transport is not considered in this work. Even if it is likely that with the increase of operating current density, the volume fraction of gas pores in either the GDL or the CAL decreases,⁶,⁷ we expect that a constant value of this parameter is maintained during each steady-state impedance measurement.

Mathematical Model

Multicomponent gas transport.—The multicomponent gas transport in a porous media such as the GDL and the CAL of a PEMFC cathode is described by the Stefan-Maxwell equation⁸
where $w$ is the volume fraction of gas pores in the porous media, and $p$ is the Bruggeman coefficient, assumed to be 0.5 throughout this work, to account for tortuosity effect.\(^1\)

If a PEMFC and its two gas humidifiers are controlled at the same temperature, the isothermal and equilibrium water vapor saturation conditions are very likely to hold over the entire cell. If the gas pressures of a cell are well regulated, the isobaric condition is also valid in the gas pores of both the GDL and the CAL of the cathode. Unless it is mentioned otherwise, all the above conditions are assumed to be satisfied in this work, and the one-dimensional gas transport is considered to be valid (see Fig. 1).

For an O\(_2\) cathode, only two components, O\(_2\) and water vapor, exist in the gas phase of either the GDL or the CAL. Because a gas flow is always saturated by water vapor and the isobaric condition in the gas phase is maintained throughout, the partial pressure as well as the mole fraction of O\(_2\) does not vary with time and spatial coordinate. In this case, the flux of gaseous O\(_2\), $N_{O_2}$, is driven only by convection. The possible contribution to $N_{O_2}$ from the diffusion mechanism disappears due to the absence of a concentration gradient of O\(_2\). From Eq. 1, we find that there is a water vapor flux $N_W$ dragged along with an O\(_2\) flux

$$N_W = \frac{w}{1-w} N_{O_2}$$  \hspace{1cm} \text{[2]}$$

where $w$ is the mole fraction of water vapor. Equation 2 reveals that water vapor moves in the same direction as O\(_2\). As a result, we can conclude that water is removed out of a PEMFC in the liquid form rather than in the vapor form. Moreover, the total amount of water to be removed out of a cell includes not only the amount produced by the O\(_2\) reduction reaction assumed to follow a form

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O(l)$$  \hspace{1cm} \text{[3]}$$

but also the amount of water vapor dragged along with the O\(_2\) flux on the cathode side and the H\(_2\) flux on the anode side. (Similar to Eq. 2, one can derive a flux of water vapor on the anode side.) This conclusion is also valid for an air cathode, which can be seen from the water vapor flux $N_W$ given by Eq. 3 of Springer et al.’s work.\(^6\)

For an air cathode, the gas phase is usually treated as a ternary system, and O\(_2\), N\(_2\), and H\(_2\)O have to be considered simultaneously in Eq. 1. A differential material balance on O\(_2\) in the porous region $i$ of the air cathode gives

$$c_0 \phi_i \frac{dx}{dt} = - \frac{1}{l_i} \frac{\partial N_{O_2}}{\partial z} + j_O$$  \hspace{1cm} \text{[4]}$$

where $\phi_i$ is the volume fraction of gas pores in the porous region $i$, $x$ is the mole fraction of O\(_2\), $j_O$ is the accumulation rate of O\(_2\) in the gas pores and equal to the molar rate of O\(_2\) going to the gas pores from the flooded agglomerate particles per unit volume of the porous region $i$, and $z$ is the spatial coordinate normalized by the thickness $l_i$ of the porous region $i$.

A differential material balance on N\(_2\) in the porous region $i$ yields

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Illustration of the cathode for a polymer electrolyte membrane fuel cell.}
\end{figure}
Under a steady-state operating condition of a PEMFC, Eq. 5 yields a uniform \( N_N \) in the gas pores of the entire cathode. After applying an overall material balance on \( N_Z \) in the CAL, we find

\[
N_N = 0
\]

[13]

with which Eq. 10 is simplified to the first-order differential equation

\[
\frac{\beta_1 + \beta_2 \bar{x}}{(\beta_1 - \bar{x})(\beta_3 + \beta_2 \bar{x})} \frac{\partial \bar{x}}{\partial z} = \frac{I}{4F} \frac{\varphi^{c}}{\varphi^{b}D_{\text{cal-G}}^{0}/l_{c}}
\]

[14]

where an overbar is used for a variable to indicate a steady-state operating condition. Equation 14 can be used to find \( \bar{x} \), the steady-state mole fraction of \( O_2 \), in the GDL at the steady-state operating current density \( I \).

After applying Eq. 13 to Eq. 12 for the CAL, we can obtain a simplified second-order differential equation

\[
\frac{\beta_1 + \beta_2 \bar{x}}{(\beta_1 - \bar{x})(\beta_3 + \beta_2 \bar{x})} \frac{\partial \bar{x}}{\partial z} + \frac{\beta_4 + 2\beta_3 \beta_2 \bar{x} + \beta_2^2 \bar{x}^2 \partial^2 \bar{x}}{(\beta_1 - \bar{x})(\beta_3 + \beta_2 \bar{x})^2} = \frac{-\tilde{j}_{G,b}}{\varphi^{c}} \frac{D_{\text{cal-G}}^{0}}{l_{c}}
\]

[15]

where \( \beta_4 = \beta_1 \beta_2 - \beta_3 \beta_2 \beta_2^2 + \beta_1 \beta_2 \beta_3 \).

If the value of \( x \) at the GDL inlet is known, Eq. 14 can be integrated analytically to yield a solution of \( \bar{x} \) in the GDL (see Eq. 5 of Ref. 6). To find \( \bar{x} \) in the CAL from Eq. 15, we need two boundary conditions. One boundary condition can be specified by

\[
\bar{x}\big|_{z=0,c} = \bar{x}\big|_{z=-1,c} = 0
\]

[16]

to take advantage of the analytical solution of \( \bar{x} \) in the GDL (Eq. 5 of Ref. 6). Another boundary condition can be found by considering zero flux of \( O_2 \) going to the PEM.

After substituting Eq. 10 into Eq. 5 and applying \( \dot{\bar{x}}/\dot{t} = -\partial \bar{x}/\partial t \), we have a differential equation that can be used to find the dynamic response of \( x \) in the GDL. During an impedance experiment on a PEMFC, a small sinusoidal signal in the form of either operating current or cell potential is usually applied to the cell under a steady-state operating condition. Due to the slight perturbation to the operating condition of the cell, linear responses are obtained. If any state variable, i.e., \( x \), in a dynamic model equation is written to be the sum of a steady-state term, \( \bar{x} \), and a sinusoidal deviation term, \( R(\tilde{x}e^{i\omega t}) \), we can obtain a linear differential equation for the GDL in the frequency domain in terms of deviation variables such as \( \tilde{x} \)

\[
\frac{\beta_1 + \beta_2 \bar{x} \partial^2 \tilde{x}}{\beta_3 + \beta_2 \bar{x} \partial^2 \tilde{x}} + \left[ \frac{\beta_4 (\beta_1 - \beta_1) \partial \tilde{x}}{(\beta_3 + \beta_2 \bar{x})^2 \partial \tilde{x}} + \frac{\tilde{j}_{G,b}}{4F} \frac{\varphi^{c}}{\varphi^{b}D_{\text{cal-G}}^{0}/l_{c}} \right] \partial \tilde{x} = \frac{\beta_1 \beta_2 \partial \tilde{x}}{\varphi^{c}} \frac{D_{\text{cal-G}}^{0}}{l_{c}} \tilde{x} + \frac{1}{\varphi^{c}} \frac{D_{\text{cal-G}}^{0}}{l_{c}} \tilde{x}
\]

[18]

where a tilde is placed over a variable to indicate the deviation amplitude from a steady-state value of this variable. It is noted that all the deviation variables such as \( \tilde{x} \) and \( \tilde{j}_{G,b} \) are frequency-dependent complex variables.
After substituting Eq. 12 into Eq. 5, we have a differential equation that can be used to find the dynamic response of $x$ in the CAL.

Similar to the procedure to get Eq. 18, we can obtain a differential equation for the CAL in the frequency domain

$$\frac{\partial x}{\partial z} + \left[ \frac{l_j J_0}{\phi_c^{\text{GDL}}/c_{\text{GDL}}} + \frac{2}{3} \frac{B_2 (B_3 - B_1)}{(B_1 + B_3)^2} \frac{\partial \tilde{c}}{\partial z} \right] \left[ \frac{D_{\text{ON}}}{\phi_c^{\text{CAL}}/c_{\text{CAL}}} \right] = \frac{l_j J_0}{\phi_c^{\text{CAL}}/c_{\text{CAL}}},$$

where $H$ is Henry’s constant.

Once the concentration profile of the dissolved O$_2$ inside an agglomerate particle is found, we can calculate $4F_j$, the reaction current per unit volume of the CAL, by integrating $-4Fk c$ over all the agglomerate particles per unit volume of the CAL

$$4F_j = \frac{1 - \varphi_c}{4\pi R^3/3} \int_0^R 4Fk c r^2 dr = -12F(1 - \varphi_c) \int_0^R k c r^2 dr$$

where $j_i$ is the molar rate of O$_2$ reacted per unit volume of the CAL. We can also calculate $j_O$ by finding the flux of O$_2$ across all the surface of agglomerate particles per unit volume of the CAL

$$j_O = \left( \frac{1 - \varphi_c}{4\pi R^3/3} \right) \left( -\frac{e^{1+\phi_D} c \phi_r}{R_a^2} \right) \left( \frac{-1}{\partial \eta /\partial r}_{r=1} \right) = -3(1 - \varphi_c) e^{1+\phi_D} c$$

Under a steady-state operating condition, the time derivative term in Eq. 21 vanishes, and an analytical solution of $\tilde{c}$ is available (see Appendix A). After applying the solution of $\tilde{c}$ to Eq. 25 or 26, we can find

$$4F\tilde{J}_e = 4F\tilde{J}_O = -12F(1 - \varphi_c) e^{1+\phi_D}$$

subject to boundary conditions

$$\frac{\partial \tilde{c}}{\partial r}_{r=0} = 0$$

An analytical solution of $\tilde{c}$ is available (see Appendix A), and we can obtain the deviation of the CAL reaction current, $4F\tilde{J}_e$, in the frequency domain

$$\tilde{c}_{r=1} = c_G H\tilde{x}$$
We can also obtain the deviation of the accumulation rate of O$_2$ in the gas phase, $\bar{j}_O$, in the frequency domain

$$\bar{j}_O = -3(1 - \varphi_c) \frac{\epsilon^{1+\rho_D}}{R_a^2} c_G H \bar{x} \times \left\{ \frac{\sqrt{\frac{(k + j\omega)}{\epsilon^{1+\rho_D}}}}{R_a^2} \coth \left( \sqrt{\frac{(k + j\omega)}{\epsilon^{1+\rho_D}}} \right) - 1 }{1 + j \frac{e\omega}{k}} \right\}$$

For an air cathode, Eq. 32 and 33 are both required for the calculation of impedance responses, while only Eq. 32 is necessary for an O$_2$ cathode. For an O$_2$ cathode, $\bar{x}$ is equal to zero (x is uniform across the cathode). As a result, Eq. 32 can be further simplified to

$$4F\bar{j}_e = -12F(1 - \varphi_c) \frac{\epsilon^{1+\rho_D}}{R_a^2} c_G H \bar{x} \times \left\{ \frac{\sqrt{\frac{(k + j\omega)}{\epsilon^{1+\rho_D}}}}{R_a^2} \coth \left( \sqrt{\frac{(k + j\omega)}{\epsilon^{1+\rho_D}}} \right) - 1 }{1 + j \frac{e\omega}{k}} \right\}$$

In the above analysis, the liquid-phase diffusion of O$_2$ in a flooded agglomerate particle is modeled. The reaction currents, $4F\bar{j}_e$ and $4F\bar{j}_o$, as well as the accumulation rates of O$_2$ in the gas phase, $\bar{j}_o$ and $\bar{j}_O$, are solved analytically to be related to the local mole fractions of O$_2$, $\bar{x}$, and $\bar{x}$, and to the local overpotentials, $\bar{\eta}$ and $\bar{\eta}$, whose distributions are discussed as follows.

The modified Ohm’s law for the polymer electrolyte, which is assumed to be present only within the agglomerate particles (see Fig. 1), of the CAL of an air cathode gives$^{10}$

$$i_z = \frac{\kappa_{\text{eff}} R T}{4F \bar{j}_e} \frac{\partial \Phi_z}{\partial \bar{z}} + \frac{\kappa_{\text{eff}} R T}{4F \bar{j}_e} \frac{\partial \ln \chi}{\partial \bar{z}}$$
tial of a cathode measured with a reference $O_2$ electrode, to equal zero. The calculation of the cathode overpotential is then simplified to

$$\eta = \Phi_1 - \Phi_2 - U = \Phi_1 - \Phi_2$$  \[36\]

where $\Phi_1$ is the solid-phase potential assumed to be uniform in the CAL. The cathode potential in reference to a standard hydrogen electrode placed at the CAL/PEM interface can be calculated by

$$\Phi_1 = (E + \eta) \bigg|_{z=1,e}$$  \[37\]

where $E$ is the equilibrium potential of the $O_2$ reference electrode in reference to a standard hydrogen electrode and can be calculated by the Nernst equation

$$E = E^{\circ}_{O_2} + \frac{RT}{4F} \ln(Px)$$  \[38\]

where $E^{\circ}_{O_2}$ is the standard potential of the $O_2$ reference electrode in reference to a standard $H_2$ electrode and $P$ is the total cathode gas pressure.

Conservation of charge in the CAL is governed by

$$\frac{1}{I_c} \frac{\partial z}{\partial z} = 4FJ_e + (1 - \varphi_c)(1 - e)C_{d,e} \frac{\partial \eta}{\partial t}$$  \[39\]

where $C_{d,e}$ is the double-layer capacitance per unit volume of the Pt/carbon composite. Both the catalyst Pt and its carbon support are supposed to contribute to $C_{d,e}$.

A combination of Eq. 35, 36, and 39 yields

$$\frac{\partial^2 \eta}{\partial z^2} = \frac{1}{\kappa_{\text{eff}}} \left[ 4FJ_e + (1 - \varphi_c)(1 - e)C_{d,e} \frac{\partial \eta}{\partial t} \right] - \frac{RT}{4F} \frac{\partial \ln x}{\partial z}$$  \[40\]

subject to boundary conditions

$$\frac{\partial \eta}{\partial z} \bigg|_{z=0,c} = \frac{RT}{4F} \frac{\partial \ln x}{\partial z} \bigg|_{z=0,c}$$  \[41\]

and

$$\frac{\partial \eta}{\partial z} \bigg|_{z=1,e} = \frac{J_e}{\kappa_{\text{eff}}}$$  \[42\]

where zero $O_2$ gas flux going to the PEM is implicitly applied.

Equations 40-42 are valid for an air cathode at all times. Under a steady-state operating condition, no current goes to double-layer charging and Eq. 40 is simplified to

$$\frac{\partial^2 \eta}{\partial z^2} = \frac{1}{\kappa_{\text{eff}}} \left[ 4FJ_e \right] - \frac{RT}{4F} \frac{\partial^2 \ln x}{\partial z^2}$$  \[43\]

subject to the boundary conditions similar to Eq. 41 and 42 except that $\eta$ is replaced by $\bar{\eta}$, $x$ is replaced by $\bar{x}$ and $I$ is replaced by $\bar{I}$.

The substitution of $\eta = \bar{\eta} + \text{Re}(\varphi e^{i\omega t})$, $J_e = \bar{J}_e + \text{Re}(\varphi e^{i\omega t})$ and $x = \bar{x} + \text{Re}(\varphi e^{i\omega t})$ into Eq. 40 yields a differential equation in the frequency domain in terms of deviation variables

$$\frac{\partial^2 \bar{\eta}}{\partial z^2} = \frac{1}{\kappa_{\text{eff}}} \left[ 4F\bar{J}_e \right] + j\omega(1 - \varphi_c)(1 - e)C_{d,e} \bar{\eta}] - \frac{RT}{4F} \frac{\partial^2 \bar{x}}{\partial z^2}$$  \[44\]

subject to boundary conditions

For an $O_2$ cathode, neither $\bar{x}$ nor $\bar{\eta}$ is the variable to be solved for. Therefore, Eq. 43 to 45 can be simplified to

$$\frac{\partial^2 \bar{\eta}}{\partial z^2} = \frac{J_e}{\kappa_{\text{eff}}}$$  \[47\]

$$\frac{\partial^2 \bar{x}}{\partial z^2} = \frac{J_e}{\kappa_{\text{eff}}} [4F\bar{J}_e] + j\omega(1 - \varphi_c)(1 - e)C_{d,e} \bar{\eta}]$$  \[48\]

$$\frac{\partial \bar{\eta}}{\partial z} \bigg|_{z=1,e} = 0$$  \[49\]

The impedance response $Z$ of an air cathode under a steady-state operating condition can be calculated by finding the transfer function

$$Z = \bar{\Phi}_1 \bigg|_{z=1,e} = (\bar{E} + \bar{\eta}) \bigg|_{z=1,e} \frac{RT \bar{x}}{4F \bar{x}}$$  \[50\]

For convenience, we set $\bar{I}$ to be unity in our impedance calculation. Then, Eq. 50 is simplified to

$$Z = \bar{\Phi}_1 \bigg|_{z=1,e} = \frac{RT \bar{x}}{4F \bar{x}}$$  \[51\]

For an $O_2$ cathode, the impedance response at a steady-state operating condition can be calculated by

$$Z = \bar{\Phi}_1 \bigg|_{z=1,e} = \bar{\eta} \bigg|_{z=1,e}$$  \[52\]

Numerical solution.—The calculation of the impedance response of a PEMFC cathode under a steady-state operating condition requires the knowledge of steady-state profiles of the variables of interest. Therefore, these profiles are also part of our calculation in order to obtain the steady-state impedance response of a cathode.

For a differential equation such as Eq. 18 involving some complex variables, even if its numerical solution can be handled in the complex domain by some numerical solvers, our available solver only allows its numerical solution in the real domain. Therefore, Eq. 18 has to be split into two equations

$$\beta_1 + \beta_3 \bar{x} \frac{\partial \bar{\eta}}{\partial z} + \beta_1 \beta_3 \bar{\eta} = \frac{2 \beta_3 (\beta_3 - \beta_1) \bar{x}}{(\beta_3 + \beta_2 \bar{x})^2} \frac{\partial \bar{x}}{\partial z} + \frac{I/4F}{\varphi_B^{1+PD_{ON}\sigma_c} \ell_B}$$

$$\frac{\partial \bar{\eta}}{\partial z} + \frac{\beta_3 (\beta_3 - \beta_1) \bar{x}}{(\beta_3 + \beta_2 \bar{x})^2} \frac{\partial \bar{x}}{\partial z} = \frac{2 \beta_3 (\beta_3 - \beta_1) \bar{x}}{(\beta_3 + \beta_2 \bar{x})^2} \frac{\partial \bar{x}}{\partial z}$$

$$\frac{\beta_1 \varphi_0}{\varphi_B^{1+PD_{ON}\sigma_c} \ell_B} \bar{x} = \frac{\partial \bar{\eta}}{\partial z} = \frac{1}{\kappa_{\text{eff}}} [4F\bar{J}_e] + j\omega(1 - \varphi_c)(1 - e)C_{d,e} \bar{\eta}]$$  \[53\]
Table I. Parameters used for the impedance simulation of a PEMFC cathode operated at 70°C.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{\text{GDL}}^0$</td>
<td>0.230 cm$^2$/s</td>
</tr>
<tr>
<td>$D_{\text{C}}^0$</td>
<td>0.282 cm$^2$/s</td>
</tr>
<tr>
<td>$D_{\text{G}}^0$</td>
<td>0.293 cm$^2$/s</td>
</tr>
<tr>
<td>$t_{\text{b}}$</td>
<td>0.04 cm</td>
</tr>
<tr>
<td>$\varphi_{\text{b}}$</td>
<td>0.36</td>
</tr>
<tr>
<td>$\varphi_{\text{c}}$</td>
<td>0.5</td>
</tr>
<tr>
<td>$l_{\text{c}}$</td>
<td>0.003 cm</td>
</tr>
<tr>
<td>$l_{\text{el}}/\gamma_{\text{el}}$</td>
<td>0.318 cm$^2$/s</td>
</tr>
<tr>
<td>$t_{\text{el}}/\gamma_{\text{el}}$</td>
<td>0.0015 s$^{-1}$</td>
</tr>
<tr>
<td>$C_{\text{d}}$</td>
<td>30 F/cm$^3$</td>
</tr>
<tr>
<td>$b$</td>
<td>0.0261 V</td>
</tr>
<tr>
<td>$D$</td>
<td>6.22 $\times$ 10$^{-5}$ cm$^2$/s</td>
</tr>
<tr>
<td>$H$</td>
<td>0.0277</td>
</tr>
<tr>
<td>$R_{\text{c}}$</td>
<td>1.0 $\times$ 10$^{-4}$ cm</td>
</tr>
<tr>
<td>$E_{\text{O}}$</td>
<td>1.20 V</td>
</tr>
</tbody>
</table>

where the subscripts Re and Im represent the real part and the imaginary part of a complex variable, respectively. A list of all the final equations such as Eq. 53 and 54 to be solved for the steady-state impedance response of a cathode are summarized in Appendix B, where the expressions for $\tilde{I}/(T_{\text{Re}}, I_{\text{Im}})$, $4 F_{\text{el}}$, and $4 F_{\text{el}}/\gamma_{\text{el}}$ in terms of other deviation variables such as $\tilde{X}_{\text{Re}}, \tilde{X}_{\text{Im}}, \tilde{V}_{\text{Re}},$ and $\tilde{V}_{\text{Im}}$ are available in Appendix C.

A three-point finite difference method is used to approximate the derivative of each variable in our model equations, a Trapezoidal’s rule is used to integrate a variable, and a general nonlinear equation solver in FORTRAN called GNES is used in our numerical calculation. It is noted that even if a banded Jacobian matrix is available for the calculation of the steady-state impedance response of a PEMFC cathode, both the steady-state polarization data and the steady-state impedance response can be predicted by the steady-state impedance model considered in this work. Figure 2a shows the simulated polarization curves of a PEMFC cathode operated under different gas pressures. One may observe that for an air cathode, each polarization curve displays a limiting current when the electrode potential goes below 0.4 V. The increase of the limiting current with the increase of gas pressure can be explained by an increase of the mole fraction of O$_2$ at the GDL inlet. One may also observe that the limiting currents predicted in this work are much higher than those reported in the literature. However, these values are observable in a laboratory on a PEMFC with up-to-date technologies. On the polarization curve of a cathode with an air pressure of 1.0 atm, four places are marked by the plus signs, where the steady-state impedance responses are to be calculated and compared later. For the air cathode, the mole fractions of gaseous O$_2$ at the CALPEM interface are also calculated with the change of the steady-state operating current density and these results are presented in Fig. 2b. A comparison between these two figures shows that a limiting current appears when the mole fraction of gaseous O$_2$ drops to a negligible value. Therefore, the mass-transport limitation in the gas pores of an air cathode is responsible for the appearance of a limiting current.

Throughout this work, each steady-state impedance plot is presented in a normalized form. Both the real part and the imaginary part of the impedance response are multiplied by the ratio of $-\tilde{I}$, the steady-state operating current density, to $b$, the normal Tafel slope, to yield a normalized impedance response. With this kind of representation, the width of an impedance plot (on the real axis) is directly related to the apparent Tafel slope observed on a steady-state polarization curve, $\tilde{V}_{\text{I}=1}=\ln(-\tilde{I})$, at the same steady-state operating current density. For example, if the width of a steady-state impedance plot reads 2, a double Tafel slope is shown on a polarization curve.

Under the ambient gas pressure, the impedance responses of a PEMFC air cathode are simulated for different steady-state operating current densities by this model (also called the full model below), and they are plotted in Fig. 3. In general, this model predicts an increase of the apparent Tafel slope with the increase of the steady-state operating current density. When a steady-state operating condition is close to open-circuit, only one impedance loop is observed and the apparent Tafel slope does not deviate much from the normal value, $b$. When a steady-state operating condition is away from open-circuit, two impedance loops are observed. In this case, the first one is due to the mass-transport limitation of O$_2$, and the second one is due to the mass-transport limitation of H$_2$.
from open-circuit, a second impedance loop appears and the apparent Tafel slope is larger than $b$. A limiting current is obtained when the second impedance loop becomes much bigger than the first one and when the apparent Tafel slope is infinitely large. Springer et al. attributed the first impedance loop to the effective charge-transfer resistance and double-layer charging and the second one to the mass-transport limitation in the gas phase. They explained that the effective charge-transfer resistance was influenced not only by the interfacial $O_2$ reduction reaction but also by ionic conduction and liquid-phase $O_2$ diffusion.

The steady-state impedance model developed in this work is largely motivated by a pioneering work of Springer et al. Unfortunately, there was an error associated with multicomponent gas transport in their work. This error was caused by their equating the uniform combined flux of $O_2$ and $N_2$ in the GDL to $I/(4F)$ instead of the $O_2$ flux at the GDLCAL interface, which indicated that the current for double-layer charging and liquid-phase $O_2$ storage was able to contribute to the combined flux of $O_2$ and $N_2$. Obviously, that is not true. To demonstrate the calculation accuracy of the impedance responses with such an error, a simplified model is developed from our full model by assuming and the calculated impedance responses are also presented in Fig. 3. If the simplified model can predict the steady-state impedance responses of an air cathode within an acceptable error, the integration terms in our full-model equations can be avoided (see Eq. 53 and 54) and a banded jacobian matrix can be used to allow much faster numerical calculations. It is seen from Fig. 3 that at high steady-state current densities, even if the impedance responses calculated by both models agree in the very high and very low frequency limits, the simplified model overestimated the impedance responses in most of the high frequency region (high frequency loops) and underestimated those in most of the low frequency region (low frequency loops). To understand this, we consider a simple air cathode with an ultrathin CAL. In this case, the CAL behaves like a thin-film
diffusion electrode, and the distributions of overpotentials and mole fractions of O\textsubscript{2} in the CAL can be neglected. The normalized impedance response of this air cathode can be calculated by

\[
\left( \frac{-\tilde{I}}{b} \right) Z = \left( \frac{-\tilde{I}}{b} \right) \hat{\eta} + \frac{\tilde{E}}{\tilde{I}} = \left( \frac{-\tilde{I}}{b} \right) \nabla \hat{\eta} + \frac{RT \tilde{\varepsilon}}{4F \tilde{x}I}
\]

If the dissolved O\textsubscript{2} storage in the flooded agglomerate particles is neglected, either Eq. 32 or Eq. 33 yields

\[
4F\tilde{J}_{d} = 4F\tilde{J}_{cd} = \hat{\eta} \left( \frac{-\tilde{I}}{b} \right) \left( \frac{1}{k_1} - \frac{\hat{\eta}(\tilde{I}b)}{\hat{\eta}(\tilde{I}b)} \right)
\]

where

\[
k_1 = \frac{2[\sqrt{k'} \coth(\sqrt{k'}) - 1]}{\sqrt{k'} \coth(\sqrt{k'}) + k' - k' \coth(\sqrt{k'})^2},
\]

\[
k' = k\ell \left( \frac{e^{1+\eta D}}{\ell R_a} \right), \text{ and } \tilde{I} = 4F\tilde{J}_{d}
\]

where \(k_1\) ranges from 1 to 2 and reflects the change of the apparent Tafel slope with the change of the steady-state operating condition for a single agglomerate particle cathode. Equations 56 and 57 can be combined to yield

\[
\left( \frac{-\tilde{I}}{b} \right) Z = \left( \frac{1}{k_1} - \frac{\hat{\eta}(\tilde{I}b)}{\hat{\eta}(\tilde{I}b)} \right) + \frac{RT \tilde{\varepsilon}}{4F \tilde{x}I}
\]

In the high-frequency region, we expect that the majority of the perturbation current goes to double-layer charging and \(\tilde{x}\), the deviation of mole fraction of O\textsubscript{2}, has a much smaller amplitude at the same frequency than that predicted from the simplified model, where all the perturbation current is assumed to influence \(\tilde{x}\). It is not difficult for one to conclude from Eq. 59 that the overestimation of \(\tilde{x}\) in the high-frequency region by the simplified model leads to a high estimation of \(Z\). An explanation for the underestimation of \(Z\) in the low-frequency region by the simplified model is offered later.

The failure of the simplified model to predict accurately the impedance responses of a cathode motivates our interest in finding out how the total accumulation current of O\textsubscript{2} in the gas-phase changes, subject to the current perturbation, with frequency. Figure 4 shows the plots of \(4F\tilde{J}_{d} \frac{\partial \tilde{J}_d}{\partial \tilde{z}}\tilde{I}\), the transfer function for the deviation of the total accumulation current of O\textsubscript{2} in the gas phase. Interestingly, this figure displays a transfer function profile similar to an impedance plot in Fig. 3. When the steady-state operating current density is small, \(\tilde{I} = 0.05 \text{ A/cm}^2\), the transfer function profile has an almost exact semicircular shape. When the steady-state current density becomes high, two loops are displayed. These transfer function profiles can be understood by considering a similar air cathode with an ultrathin CAL (the dissolved O\textsubscript{2} storage in the flooded agglomerate particles is again neglected).

\[
\frac{4F\tilde{J}_{d} \frac{\partial \tilde{J}_d}{\partial \tilde{z}}}{\tilde{I}} = 1 - \frac{\bar{I} - j\omega(1 - \varphi_e)(1 - e)\Gamma_{d}c}{\bar{I}} \left( \frac{1}{k_1} - \frac{\hat{\eta}(\tilde{I}b)}{\hat{\eta}(\tilde{I}b)} \right) + j\omega(1 - \varphi_e)(1 - e)\Gamma_{d}c
\]

which predicts an exact semicircular profile whose width equals unity. At a high steady-state operating current density, \(\tilde{x}(\tilde{I})\) becomes comparable to \(\hat{\eta}(\tilde{I}b)\) in the low frequency region due to a reduced value of \(\tilde{x}\) (\(\tilde{x}\) does not change much with the change of the steady-state operating current density, as is justified later) and a reduced value of \(\hat{\eta}(\tilde{I}b)\), and consequently Eq. 60 is simplified to

\[
\frac{4F\tilde{J}_{d} \frac{\partial \tilde{J}_d}{\partial \tilde{z}}}{\tilde{I}} = 1 - \frac{\bar{I} - j\omega(1 - \varphi_e)(1 - e)\Gamma_{d}c}{\bar{I}} \left( \frac{1}{k_1} - \frac{\hat{\eta}(\tilde{I}b)}{\hat{\eta}(\tilde{I}b)} \right) + j\omega(1 - \varphi_e)(1 - e)\Gamma_{d}c
\]
The normalized impedance response of a PEMFC air cathode includes two contributions. One is from \(E / I\), the impedance of gas-phase transport, and another is from \(h / I\), an interfacial impedance. The computer simulation of the impedance response of a PEMFC cathode allows the separation of the total cathode impedance into the contributions from different sources, which is helpful for us in evaluating the relative importance of each impedance contribution. A comparison of the normalized impedance response of a full PEMFC air cathode operated under the ambient gas pressure with contributions from different sources is shown. Even if the steady-state mole fraction of O\(_2\) adjacent to the PEM drops significantly with the increase of the steady-state operating current density (Fig. 5a), the transfer function \(x / (x / I)\) profile does not change much (Fig. 5b). As a result, the size of \(x / (x / I)\) profile grows with the increase of the steady-state operating current density. This explains that for an air cathode, the low-frequency impedance loop increases its size with the increase of the steady-state operating current density (see Eq. 59).

We recall from Eq. 50 that the total impedance response of a PEMFC air cathode includes two contributions. One is from \(E / I\), the impedance of gas-phase transport, and another is from \(h / I\), an interfacial impedance. The computer simulation of the impedance response of a PEMFC cathode allows the separation of the total cathode impedance into the contributions from different sources, which is helpful for us in evaluating the relative importance of each impedance contribution. A comparison of the normalized impedance response of a full PEMFC air cathode operated under the ambient gas pressure with contributions from different sources is shown.
for the low-frequency impedance loops generated by the simplified model in Fig. 3.

To understand the difference between an air cathode and an O₂ cathode, it is helpful to look at Fig. 7, where the normalized impedance responses of a high pressure air cathode are compared with those of a low pressure O₂ cathode for different steady-state operating current densities. It is seen that at a very small operating current density, i.e., \( \bar{I} = 0.05 \, \text{A/cm}^2 \), both the air cathode and the O₂ cathode exhibit almost the same impedance profile and a normal Tafel slope. This indicates the absence of gas-phase transport limitation. With the increase of the steady-state operating current density, the O₂ cathode begins to display an increasingly apparent Tafel slope. When the steady-state operating current is equal to 3.0 A/cm², an almost quadric Tafel slope is obtained on the O₂ cathode, which is caused by a combined limitation from slow ionic conduction and double-layer charging. 4 For an air cathode, besides the increasing Tafel slope observed from the high-frequency impedance loop with the increase of the steady-state current density, a second impedance loop begins to grow and adds an extra Tafel slope. As explained above, this extra Tafel slope is the combined effect of the gas-phase transport limitation and the effective charge-transfer resistance.

In Fig. 7, the peak frequency for the high-frequency impedance loop increases with the increase of the steady-state operating current density. An explanation is that the charge-transfer resistance decreases with the increase of the steady-state operating current density and consequently leads to the increase of the time constant for the charge-transfer reaction and double-layer charging.

One might suspect that, in addition to the high-frequency impedance loop associated with the effective charge-transfer resistance and double-layer charging, the liquid-phase diffusion of O₂ inside an agglomerate particle is able to yield a low-frequency semicircle-like loop on the impedance plot of an O₂ cathode. To evaluate this possibility, let us consider a simple O₂ cathode with an ultrathin CAL. After neglecting double-layer charging, Eq. 34 is normalized to yield the cathode performance over a wide range of operating current

\[
\frac{(-\bar{I})}{b} = \frac{\sqrt{k} \coth(\sqrt{k}) - 1}{k' + j\omega' \coth(\sqrt{k'} + j\omega') - 1} \frac{\omega'}{1 + j\frac{\omega'}{k'}} \left[ \sqrt{k'} \coth(\sqrt{k'}) - 1 \right] \frac{j\omega'}{k'} \tag{62}
\]

where

\[
\omega' = e \omega \left( \frac{e^{1+\frac{1}{pD}}}{R_s} \right) \tag{63}
\]

The impedance responses of the O₂ cathode under different steady-state operating conditions are compared in Fig. 8. One may notice that a semicircle-like impedance loop is indeed predicted even if double-layer charging is not considered. With the increase of \( k' \), the impedance loop grows to a semicircle with its diameter up to 2. However, if we look at the dimensionless peak frequency \( \omega' / \bar{I} \) for the impedance loop, we can find that \( \omega' \) increases with the increase of \( k' \) (the steady-state operating current density). This behavior indicates that it is very unlikely that the diffusion process inside an agglomerate particle yields a low-frequency impedance loop since its peak frequency has never been observed experimentally to become bigger and bigger with the increase of the steady-state operating current density.

An optimization of a PEMFC cathode is usually associated with overcoming one or more transport limitations, such as the mass-transport limitations in both the gas and liquid phase. In this work, the influences of the change of some important parameters, such as \( \ell / \kappa_{st}, i_{\text{act}}/(4F \varepsilon_{\text{act}}), I_g \), and \( R_g \), on the electrode performance are briefly studied for an air cathode operated under the ambient gas pressure, and these results are presented in Fig. 9a-d. The polarization curves in Fig. 9a show that the decreases of \( \ell / \kappa_{st}, I_g \), and \( R_g \) as well as the increase of \( i_{\text{act}}/(4F \varepsilon_{\text{act}}) \) lead to the improvements of the cathode performance over a wide range of operating current
densities. Moreover, the decrease of $l_B$ yields a much larger limiting current, which is expected to be caused by the decrease of the gas-phase transport path. The impedance responses calculated at the steady-state operating current densities equal to 0.05, 1.0, and 2.0 A/cm$^2$ are plotted in Fig. 9b-d. One may notice that the increase of $\frac{i_{ref}}{4Fc_{ref}}$ does not cause any change of the steady-state impedance response. However, one should not simply conclude that $\frac{i_{ref}}{4Fc_{ref}}$ has no influence on the cathode performance. The polarization curves in Fig. 9a demonstrate clearly the improvement of the cathode performance due to an increase of $i_{ref}/(4Fc_{ref})$. An explanation for the insensitivity of the steady-state impedance response to the change of $i_{ref}/(4Fc_{ref})$ is available in Appendix D. In Fig. 9b-d, we also observe that the decrease of any of the other parameters, $l_c/\kappa_{att}$, $R_f/B$, causes the decrease of the apparent Tafel slope, an indication of the improvement of existing mass-transport limitations.

Discussion.—The peak frequency for the second impedance loop

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**Figure 9.** (a) Comparison of the polarization curves of a PEMFC air cathode operated under the ambient gas pressure. Only one parameter value is changed at one time. (b) Comparison of the normalized impedance responses of a PEMFC air cathode operated under the ambient gas pressure and at the steady-state operating current density $\bar{I} = 0.05$ A/cm$^2$. Only one parameter value is changed at one time. (c) Comparison of the normalized impedance responses of a PEMFC air cathode operated under the ambient gas pressure and at the steady-state operating current density $\bar{I} = 1.0$ A/cm$^2$. Only one parameter value is changed at one time. (d) Comparison of the normalized impedance responses of a PEMFC air cathode operated under the ambient gas pressure and at the steady state operating current density $\bar{I} = 2.0$ A/cm$^2$. Only one parameter value is changed at one time.
(low-frequency region) is an important characteristic quantity, from which the length of the mass-transport path in the gas pores can be possibly determined. If the mass-transport path in the gas phase were fixed, one would expect to observe an almost constant peak frequency, which can be verified by evaluating Eq. 11 of Ref. 6. However, special care must be taken before too much credit is given to this characteristic frequency. Figure 3 shows that this quantity decreases slightly with the increase of the steady-state operating current density. One explanation is the increase of the gas-phase transport path, and another explanation is the increase of the gas-phase diffusion resistance. If the mass-transport path in the gas phase is attributed to the effective gas-phase diffusion resistance, Springer et al.’s impedance solution for a planar liquid film diffusion model is useful \[ Z = b \left( \frac{1 + i \exp \left( \frac{-\eta}{B} \right)}{1 + i \exp \left( -\frac{-\eta}{B} \right)} \right) \]

\[ + \frac{1}{I_F} \left( \frac{1 + i \exp \left( -\frac{-\eta}{B} \right)}{I_F} \right) \tan \left( \frac{j \omega L^2}{D} \right) \]

where \( i^* \) is the effective exchange current density for the \( O_2 \) reduction reaction, \( l \) is the thickness of the liquid film, and \( I_F \) is a characteristic current density. After evaluating Eq. 64, we can find the impedance peak frequency \( f_p \) from

\[ \frac{2 \pi f p l^2}{D} = 2.5406 \]

By using a value of 20.0 Hz for the experimentally observed impedance peak frequency and a value of 6.22 \( \times 10^{-6} \) cm/s for \( D \), we can find from Eq. 65 that \( l = 3.55 \mu m \). To have such a thick liquid film outside each agglomerate particle, an average pore size of no less than 7.1 \( \mu m \) in the CAL is required. This is unlikely to be true. Therefore, we conclude that the attribution of a low-frequency impedance loop observed on an \( O_2 /H_2 \) PEMFC to the \( O_2 \) cathode is not justified by the thin liquid film diffusion. The poor water management in the PEM may be useful for explaining this low-frequency impedance loop. Unfortunately, the study of the water management in the PEM is not covered in the present work.

**Conclusions**

A steady-state impedance model for a PEMFC cathode is presented in this work to include the feature of multicomponent gas transport in the CAL. Two impedance loops are predicted for an air cathode at high steady-state operating current densities. The high-frequency impedance loop is attributed to the effective charge-transfer resistance and double-layer charging, and the low-frequency loop is attributed to a combined effect of the gas-phase transport limitation and the effective charge-transfer resistance.

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**Appendix A**

Under a steady-state operating condition, Eq. 21 is simplified to

\[ \frac{e^{1+\gamma D}}{R_i^2} \left[ \frac{\partial e}{\partial \gamma} \right] - \bar{e} = 0 \]

subject to boundary conditions

\[ \frac{\partial \bar{e}}{\partial \gamma} \bigg|_{\gamma=0} = 0 \]

\[ \bar{e} \bigg|_{\gamma=1} = c_\gamma H \]

After substituting \( \bar{e} = \bar{C} \gamma \) into Eq. A-1, we have

\[ \frac{\partial \bar{C}}{\partial \gamma} \left( \frac{e^{1+\gamma D}}{R_i^2} \bar{C} \right) = 0 \]

from which we can write the solution of \( \bar{C} \) as

\[ \bar{C} = c_1 \sinh \left( \frac{\tilde{k}}{e^{1+\gamma D} R_i^2} \right) + c_2 \cosh \left( \frac{\tilde{k}}{e^{1+\gamma D} R_i^2} \right) \]

where \( c_1 \) and \( c_2 \) are constants.

After applying boundary conditions A-2 and A-3 to Eq. A-5, we can find

\[ c_1 = \frac{c_{\gamma} H}{\sinh \left( \frac{\tilde{k}}{e^{1+\gamma D} R_i^2} \right)}, \quad c_2 = 0 \]

Equation A-5 is updated with Eq. A-6 to yield

\[ \bar{e} = \frac{c_{\gamma} H}{r \sinh \left( \frac{\tilde{k}}{e^{1+\gamma D} R_i^2} \right)} \]

The steady-state reaction current per unit volume of the CAL, \( 4F \bar{J}_e \), can be calculated by either
from which we can write the solution of $C_{\text{as}}$

$$C \approx \rho C_{\text{as}} = c_3 \sinh \left( \sqrt{ \frac{\tilde{E} + j \omega}{e^{1/2} R_s^2} } \right)$$

$$+ c_4 \cosh \left( \sqrt{ \frac{\tilde{E} + j \omega}{e^{1/2} R_s^2} } \right)$$

$$\times \left[ \sqrt{\frac{k}{e^{1/2} R_s^2}} \cosh \left( \sqrt{ \frac{\tilde{E} + j \omega}{e^{1/2} R_s^2} } \right) - 1 \right]$$

Equation A-11 is updated with Eq. A-12 to yield

$$\tilde{E} = c_3 H\tilde{x}$$

$$- \frac{\tilde{x}}{\tilde{x} + \rho C_{\text{as}}} \frac{\sinh \left( \sqrt{ \frac{\tilde{E} + j \omega}{e^{1/2} R_s^2} } \right)}{\text{sinh} \left( \sqrt{ \frac{\tilde{E} + j \omega}{e^{1/2} R_s^2} } \right) - \frac{\tilde{q}}{\tilde{x} b} \frac{\sqrt{k}}{j \omega}}$$

The deviation of the accumulation rate of $O_2$, $\tilde{J}_O$, in the gas phase per unit volume of the CAL can be calculated by substituting Eq. A-13 into Eq. 26

$$\tilde{J}_O = -3(1 - \rho) \frac{e^{1/2} R_s^2}{\tilde{q} H\tilde{x}} c_3 H\tilde{x} \times$$

$$\left[ \sqrt{\frac{(\tilde{E} + j \omega)}{e^{1/2} R_s^2}} \cosh \left( \sqrt{ \frac{(\tilde{E} + j \omega)}{e^{1/2} R_s^2} } \right) - 1 \right] \frac{\tilde{x}}{\tilde{x} + \rho C_{\text{as}}} \frac{\sinh \left( \sqrt{ \frac{(\tilde{E} + j \omega)}{e^{1/2} R_s^2} } \right)}{\text{sinh} \left( \sqrt{ \frac{(\tilde{E} + j \omega)}{e^{1/2} R_s^2} } \right) - \frac{\tilde{q}}{\tilde{x} b} \frac{\sqrt{k}}{j \omega}}$$

The deviation of the $O_2$ reduction current per unit volume of the CAL can be calculated by substituting Eq. A-13 into Eq. 25
For an O₂ cathode, the steady-state overpotential profile in the CAL is found by solving

\[
\frac{\partial \eta}{\partial z} = \frac{l_i}{k_{\text{eff}}} \frac{4Fj_{i}}{j_{i}}
\]
subject to boundary conditions

\[
\left. \frac{\partial \eta}{\partial z} \right|_{z=0} = 0
\]
and

\[
\left. \frac{\partial \eta}{\partial z} \right|_{z=l} = \frac{l_j}{k_{\text{eff}}}
\]

The deviation profiles of \( \eta_{R_a} \) and \( \eta_{I_m} \) are found by solving

\[
\frac{\partial^2 \eta_{R_a}}{\partial z^2} = \frac{l_j}{k_{\text{eff}}} \left( 4Fj_{i} \right)_L - \omega (1 - \varphi_c) (1 - \varepsilon) C_d j_{i} \eta_{I_m}
\]
subject to boundary conditions

\[
\left. \frac{\partial \eta_{R_a}}{\partial z} \right|_{z=0} = 0, \left. \frac{\partial \eta_{I_m}}{\partial z} \right|_{z=l} = 0
\]
and

\[
\left. \frac{\partial \eta_{R_a}}{\partial z} \right|_{z=l} = \frac{l_j}{k_{\text{eff}}}
\]

The steady-state overpotential profile in the CAL is found by solving

\[
\frac{\partial \eta}{\partial z} = \frac{l_i}{k_{\text{eff}}} \frac{4Fj_{i}}{j_{i}} - \frac{RT \left. \frac{\partial \ln \chi_j}{\partial z} \right|_{z=0}}{4F \frac{\partial \chi_j}{\partial z}}
\]
subject to boundary conditions

\[
\left. \frac{\partial \eta}{\partial z} \right|_{z=0} = 0
\]
and

\[
\left. \frac{\partial \eta}{\partial z} \right|_{z=l} = \frac{l_j}{k_{\text{eff}}}
\]

The deviation profiles of \( \eta_{R_a} \), \( x_{c_1} \), \( \eta_{I_m} \), and \( \eta_{I_m} \) are found by solving

\[
\frac{\partial^2 \eta_{R_a}}{\partial z^2} = \frac{l_j}{k_{\text{eff}}} \left( 4Fj_{i} \right)_L + \omega (1 - \varphi_c) (1 - \varepsilon) C_d j_{i} \eta_{I_m}
\]
subject to boundary conditions

\[
\left. \frac{\partial \eta_{R_a}}{\partial z} \right|_{z=0} = 0, \left. \frac{\partial \eta_{I_m}}{\partial z} \right|_{z=0} = 0
\]
and

\[
\left. \frac{\partial \eta_{R_a}}{\partial z} \right|_{z=l} = \frac{l_j}{k_{\text{eff}}}
\]

The steady-state impedance responses, \( Z_{R_a} \) and \( Z_{I_m} \), of an O₂ cathode can be calculated by

\[
Z_{R_a} = \eta_{R_a}|_{z=0} \quad \text{and} \quad Z_{I_m} = \eta_{I_m}|_{z=0}
\]

For an air cathode, the steady-state mole fraction of O₂ profile in the GDL is found by solving

\[
\frac{\partial x_2}{\partial z} = \frac{1}{(\beta_1 - \varphi_c \beta_3 + \beta_2) \frac{\partial z}{\partial z}} = \frac{7}{4F \varphi_{\text{eff}} j_{i} \left( 4Fj_{i} \right)_L}
\]
subject to boundary condition

\[
\left. x_2 \right|_{z=0} = x_0
\]
where \( x_0 \) is the mole fraction of O₂ at the inlet of the GDL.

The steady-state mole fraction of O₂ profile in the CAL is found by solving

\[
\left( \frac{\hat{E} + j\omega}{\varepsilon^1 + j\omega D} \right) \coth \left( \frac{\hat{E} + j\omega}{j\omega D} \right) - 1 + \frac{j\omega}{k} \leq \frac{\hat{E} + j\omega}{\varepsilon^1 + j\omega D} \coth \left( \frac{\hat{E} + j\omega}{j\omega D} \right) - 1
\]

subject to boundary conditions

\[
\left. \frac{\partial \eta}{\partial z} \right|_{z=0} = x_0
\]

for the GDL and by solving

\[
\frac{\partial \eta}{\partial z} = \frac{l_i}{k_{\text{eff}}} \frac{4Fj_{i}}{j_{i}} - \frac{RT \left. \frac{\partial \ln \chi_j}{\partial z} \right|_{z=0}}{4F \frac{\partial \chi_j}{\partial z}}
\]
subject to boundary conditions

\[
\left. \frac{\partial \eta}{\partial z} \right|_{z=0} = 0
\]
and

\[
\left. \frac{\partial \eta}{\partial z} \right|_{z=l} = \frac{l_j}{k_{\text{eff}}}
\]
The steady-state impedance responses, \( j \tilde{\eta}_{\text{obs}} \), and \( \tilde{\eta}_{\text{obs}} \), of an air cathode can be calculated by

\[
Z_a = \frac{RT \tilde{\eta}_a}{4F} + \eta_a \quad \text{at} \quad t \to \infty
\]

and

\[
\eta_{\text{obs}} = \frac{RT \tilde{\eta}_{\text{obs}}}{4F} + \eta_{\text{obs}} \quad \text{at} \quad t \to \infty
\]

The steady-state impedance responses, \( \tilde{z}_{O,1n} \), and an imaginary part, \( j \tilde{\eta}_{O,1n} \), Eq. A-14 is expressed as

\[
\tilde{z}_{O,1n} = -3(1 - \phi) \frac{e^{i+4D}}{R_e} c_DHS_{32}
\]

where

\[
S_{11} = (S_{21} - 1) \frac{\eta_e}{\phi} - S_{21} \frac{\eta_a}{\phi} - \left[ \left( S_{21} - \sqrt{\kappa} \coth (\sqrt{\kappa}) \right) \frac{\eta_e}{\phi} + S_{21} \frac{\eta_a}{\phi} \right]
\]

\[
S_{22} = (S_{21} - 1) \frac{\eta_e}{\phi} + S_{21} \frac{\eta_a}{\phi} + \left[ \left( S_{21} - \sqrt{\kappa} \coth (\sqrt{\kappa}) \right) \frac{\eta_e}{\phi} - S_{21} \frac{\eta_a}{\phi} \right]
\]

and where

\[
k' = \frac{\phi}{e^{i+4D} / R_e}, \quad w' = \frac{\phi}{e^{i+4D} / R_e}
\]

After splitting \( 4F \tilde{J}_a \) into a real part, \( 4F \tilde{J}_{R_a} \), and an imaginary part, \( j(4F \tilde{J}_{I_a}) \), Eq. A-15 is expressed as

\[
4F \tilde{J}_a = 4F \tilde{J}_{R_a} + j(4F \tilde{J}_{I_a})
\]

where

\[
4F \tilde{J}_{R_a} = -12F(1 - \phi) \frac{e^{i+4D}}{R_e} c_DHS_{43}
\]

\[
4F \tilde{J}_{I,a} = -12F(1 - \phi) \frac{e^{i+4D}}{R_e} c_DHS_{43}
\]

and where

\[
S_{41} = k'(S_{21} - 1) + w'S_{22} \frac{\eta_e}{\phi} - k'(S_{21} - 1) \frac{\eta_a}{\phi}
\]

\[
k' = 1 + \frac{w'^2}{k''}
\]

\[
k'(S_{21} - 1) + w'S_{22} = k'(S_{21} - 1) + w'(\sqrt{\kappa} \coth (\sqrt{\kappa}) - 1) + \frac{1}{1 + \frac{w'^2}{k''}} \frac{\eta_e}{\phi}
\]

\[
- \frac{1}{1 + \frac{w'^2}{k''}} \frac{\eta_a}{\phi}
\]

\[
k'(S_{21} - 1) + w'S_{22} = k'(S_{21} - 1) + w'(\sqrt{\kappa} \coth (\sqrt{\kappa}) - 1)
\]

\[
- \frac{1}{1 + \frac{w'^2}{k''}} \frac{\eta_e}{\phi}
\]

\[
k'(S_{21} - 1) + w'S_{22} = k'(S_{21} - 1) + w'(\sqrt{\kappa} \coth (\sqrt{\kappa}) - 1) + \frac{1}{1 + \frac{w'^2}{k''}} \frac{\eta_a}{\phi}
\]

where the expressions for \( S_{11}, S_{12}, S_{21}, S_{22}, k' \), and \( w' \) are the same as those used in Eq. C-1.
Appendix D

Equation 28 can be rewritten as

$$\eta = -b \ln F + b \ln \left( \frac{i_{\text{cal}}}{4Fj c} (1 - e) \right)$$  \hfill [D-1]

Substitution of Eq. D-1 into Eq. B-14, B-15, and B-16 yields

$$\frac{a}{\sigma_{e}} \ln \left( \frac{U_{c}}{\sigma_{e}} \right) = \frac{i_{l}}{w_{\text{eff}}} = \frac{RT \ln \left( \frac{U_{c}}{\sigma_{e}} \right)}{4F}$$  \hfill [D-2]

$$b \frac{a}{\sigma_{e}} \ln \left( \frac{U_{s}}{\sigma_{e}} \right) = \frac{i_{l}}{w_{\text{eff}}}$$  \hfill [D-3]

$$b \frac{a}{\sigma_{e}} \ln \left( \frac{U_{c}}{\sigma_{e}} \right) = \frac{i_{l}}{w_{\text{eff}}}$$  \hfill [D-4]

After combining Eq. 27 and Eq. B-9 to B-13 with Eq. D-1 to D-4, we can find that the \( F \) profile as well as the \( r \) profile is uniquely determined for the same steady-state operating current density, regardless of the change of \( i_{\text{cal}}(4Fj c) \). To calculate the impedance response of an air cathode, we need to solve Eq. B-17 to B-28 and C-1 to C-2, which are directly related to the \( F \) profile instead of the value of \( i_{\text{cal}}(4Fj c) \). With an unique \( F \) distribution in the cathode CAL for the same steady-state operating current density, we find that the impedance responses, \( Z_{\text{ref}} \) and \( Z_{\text{cal}} \), of an air cathode are independent of the change of \( i_{\text{cal}}(4Fj c) \). This conclusion is also valid for an O₂ cathode.

Further inspection of Fig. 9a reveals that the change of \( i_{\text{cal}}(4Fj c) \) causes a translational movement of a polarization curve in the \( \Phi_{1} \) direction. The translational distance can be estimated by Eq. D-1.

List of Symbols

- \( b \) Tafel slope, \( b = 0.0261 \) V
- \( c_{o} \) concentration of the dissolved O₂ in the liquid phase, mol/cm³
- \( c_{d} \) a reference concentration of the dissolved O₂ in the liquid phase, mol/cm³
- \( c \) steady-state concentration of the dissolved O₂ in the liquid phase, mol/cm³
- \( D \) diffusion coefficient of the dissolved O₂ in a free liquid stream, cm²/s
- \( D_{\text{dl}} \) binary diffusion coefficient of O₂-N₂ in the gas pores of a porous media, cm²/s
- \( D_{\text{row}} \) binary diffusion coefficient of O₂-water vapor in the gas pores of a porous media, cm²/s
- \( E \) equilibrium potential of a cathode, V
- \( E_{0} \) standard equilibrium potential of an O₂ electrode in reference to a standard H₂ electrode (at the temperature of T and the O₂ partial pressure of 1.0 atm), V
- \( f_{0} \) impedance peak height, Hz
- \( F \) Faraday constant, 96,487 C/equiv.
- \( H \) Henry's constant, mol/cm³/(mol/cm³¹)
- \( I_{l} \) operating current density of the cathode, A/cm²
- \( I_{c} \) characteristic current density, A/cm²
- \( T \) steady-state operating current density of the cathode, A/cm²
- \( a_{\text{eff}} \) exchange current density of the O₂ reduction reaction per unit volume of the Pt/carbon composite evaluated at \( c_{o} \), A/cm²
- \( j_{0} \) electrolyte current, A/cm²
- \( j_{0} \) reaction current per unit volume of the CAL, A/cm³
- \( j_{0} \) steady-state reaction current per unit volume of the CAL, A/cm³
- \( j_{0} \) deviation amplitude of reaction current per unit volume of the CAL, A/cm³
- \( J_{0} \) steady-state accumulation rate of O₂ in the gas pores of the CAL, mol/cm³/s
- \( J_{0} \) deviation amplitude of the accumulation rate of O₂ in the gas pores of the CAL, mol/cm³/s
- \( i_{l} \) thickness of the CAL, cm
- \( i_{l} \) thickness of the GDL, cm
- \( N_{w} \) O₂ flux, cm²/s
- \( N_{w} \) water vapor flux, cm²/s
- \( P \) total gas pressure, atm
- \( p \) Bruggeman coefficient, 0.5
- \( R \) universal gas constant, 8.3143 J/mol/K
- \( R_{s} \) radius of a spherical agglomerate particle, cm
- \( r \) normalized spherical coordinate
- \( T \) absolute cell temperature, K
- \( U \) equilibrium potential of an O₂ electrode, V
- \( x \) mole fraction of O₂ in the gas pores
- \( z \) steady-state mole fraction of O₂ in the gas pores
- \( \delta \) deviation amplitude of the mole fraction of O₂ in the gas pores
- \( \zeta \) mole fraction of N₂
- \( \zeta_{n} \) normalized spatial coordinate in either the GDL or CAL, \( 0 \leq \zeta \leq 1 \)

Greek

- \( \epsilon \) volume fraction of the liquid phase in an agglomerate particle
- \( \eta \) overpotential, V
- \( \eta_{s} \) steady state overpotential, V
- \( \delta \) deviation amplitude of the overpotential, V
- \( \phi_{B} \) volume fraction of gas pores in the GDL
- \( \psi \) volume fraction of gas pores in the CAL
- \( \kappa_{\text{eff}} \) effective ionic conductivity of the electrolyte, S cm⁻¹
- \( \Phi_{1} \) solid-phase potential, V
- \( \Phi_{2} \) electrolyte potential, V

Subscripts

- \( C \) CAL
- \( B \) GDL
- \( \text{Re} \) real part
- \( \text{Im} \) imaginary part

References