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Cathode Polarizations of a Cathode-Supported Solid Oxide Fuel Cell

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cathode polarizations were theoretically and experimentally investigated. In the theoretical analysis, the exchange current density of the charge transfer was considered to be dependent on the $P_{O_2}$ determined by the preceding $O_2$ diffusion, resulting in an interrelationship between activation and concentration polarizations. The established nonlinear polarization equations were then applied to solve the key parameters with area specific resistances and overpotentials of the polarizations experimentally measured by electrochemical impedance spectroscopy on an operating cathode-supported SOFC. To ensure the consistency and meaningfulness of the solutions, the limiting current density in the concentration polarization equation was first solved, followed by the exchange current density of the activation polarization equation using the predetermined limiting current density. The model was finally verified by comparing the directly measured total overpotentials with the calculated ones using the obtained parameters. The agreement between the two favorably supported the proposed cathode polarization model.

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The performance of a cathode-supported solid oxide fuel cell (SOFC) is closely related to the manufacturing process, e.g., high processing temperature needed for achieving gastightness in layers of the electrolyte and the interconnect. The use of high temperature promotes chemical formations of insulating phases such as La$_2$Zr$_2$O$_7$ and SrZrO$_3$ at the interface of the cathode and the electrolyte. The rise of anode-supported SOFCs, however, does not implicate reduction of NiO to Ni and therefore independent of the electrolyte. The NiO–electrolyte composite anode is chemically more compatible with the electrolyte; co-sintering of the two at elevated temperatures produces no noticeable chemical reaction. The porosity in the anode is created in situ during operation by the reduction of NiO to Ni and therefore independent of the electrolyte sintering process. More importantly, these unique advantages have ensured to yield excellent performance for anode-supported SOFCs. It also becomes the reason why less and less research efforts have been spent on cathode-supported SOFC development in recent years.

The rise of anode-supported SOFCs, however, does not imply the end of cathode-supported SOFCs. The cathode-supported SOFCs have demonstrated the longest lifetime among all types of SOFCs (35,000 h at generator level and 50,000 h at single cell level). The merits of cathode-supported SOFCs are best manifested by the geometry of the cathode substrate and its role in the stack design. The tubular geometry of a cathode with one closed end, e.g., Siemens/Westinghouse’s, not only avoids the challenging gas seals requirement but also allows for the cell-to-cell connections in reducing atmospheres where inexpensive metals such as Ni can be readily used. The result is the excellent reliability of stack performance. Other types of geometry-substrate variations would have to deal with gas seals (planar anode and planar cathode), chemical reactions (planar cathode), and cell-to-cell connections (tubular anode). Today, high performance but with poor reliability planar anode-supported SOFCs with a metal interconnect stand out to compete with low performance but with good reliability tubular cathode-supported ones for commercialization.

Because the commercialization of the SOFC technology relies upon the coordination of two key elements, cost and reliability, the cathode-supported SOFC maintains its important and solid position in the course of SOFC development. In addition to years’ dedicated efforts by Westinghouse and Siemens to develop a product from the tubular cathode-supported SOFC technology, some fundamental research activities in this area can also be found in the literature among the systems of LaMnO$_3$-based/doped ZrO$_2$ and LaFeCoO$_3$-based/doped CeO$_2$. In most of these studies, the total cathode polarization was often considered as a sum of irrelevant concentration and activation contributions. A more comprehensive understanding and characterization on the cathode polarizations is still lacking but deemed critical in improving the overall performance of cathode-supported SOFCs.

In this paper, we present through a series of mathematical treatments more general polarization equations depicting coupled charge-transfer and gas-diffusion processes for the cathode of a cathode-supported SOFC. Experimental data such as current-dependent area specific resistances (ASRs) and overpotentials of concentration, activation, and total polarizations obtained from electrochemical impedance spectroscopy (EIS) are particularly utilized to verify the proposed model.

Cathode Polarization Model

Cathode polarizations of a cathode-supported SOFC, like other types of SOFCs, originate from two general sources: ordinary oxygen molecular diffusion through the porous substrate and subsequent charge transfer to reduce oxygen molecules into oxide ions at the interface of the cathode and the electrolyte.

The former diffusion process is typically governed by Fick’s laws of diffusion and leads to a voltage loss known as the “concentration polarization.” The latter electrode process is generally described by the Butler–Volmer equation and results in the “activation polarization.” A simple model depicting the distributions of partial pressure of oxygen ($P_{O_2}$) across the cathode as well as other functional layers is schematically illustrated in Fig. 1. Two “virtual” layers representing gas diffusion and charge transfer for both the cathode and the anode are particularly shown. Under the open-circuit condition, the $P_{O_2}$ (in dotted lines) at the two electrode/electrolyte interfaces virtually remains the same as those in the corresponding bulk gas streams. No $P_{O_2}$ gradients are present across the cathode and anode layers. However, upon applying an electrical...
current, $P_{O_2}(c)$ and $P_{O_2}(d)$ at the cathode are lowered, whereas $P_{O_2}(k)$ and $P_{O_2}(m)$ at the anode are elevated, all as a result of the polarization losses. The higher the current applied, the smaller the $P_{O_2}$ gradient across the electrolyte. Because the main interest of this study is in the cathode polarizations, in what follows only cathode-related electrochemical properties are discussed. One of such properties is the partial pressure of oxygen [$P_{O_2}(c)$] between the two successive cathode polarization layers controlled by the leading $O_2$ diffusion process. Similarly, $P_{O_2}(d)$ at the electrolyte interface is influenced by the cumulative concentration and activation polarizations. If the activation polarization is described by the Butler-Volmer equation, where the exchange current density $i_0$ is $P_{O_2}$-dependent, the dependence of $i_0$ on $P_{O_2}(c)$ should be considered in the equation. Therefore, $P_{O_2}(c)$ can serve as a linking parameter to bridge the concentration and activation polarizations in the evaluation of the cathode performance.

Concentration polarization.—The $O_2$-diffusion induced concentration polarization of a cylindrical tubular porous cathode substrate has been previously studied. A geometry-independent, general form of $P_{O_2}(c)$ shown in Fig. 1 as a result of the concentration polarization is given by

$$P_{O_2}(c) = P_t - P_i(1 - x)^{i/x_i}$$

where $P_t$ is the total system pressure; $x = P_{O_2}(b)/P_t$ is the molar fraction of $O_2$ in air (0.209); $P_{O_2}(b)$ is the partial pressure of oxygen in bulk air, 0.209 atm at $P_t = 1$ atm; and $i$ and $i_0$ are the current density and limiting current density, respectively. The limiting current density ($i_0$), at which $P_{O_2}(c)$ becomes zero, is instead a geometry-dependent quantity. For a porous cylindrical tubular cathode, it has the form of

$$i_0 = \frac{\ln(1 - x)}{\ln(r_2/r_1)} \times \frac{4FD_{O_2}^{eff}(T)}{RT_2} \times P_t$$

where $r_2$ and $r_1$ are the outer and inner radii of the cathode tube, respectively, in centimeters; $R$ and $F$ have their usual meanings; $D_{O_2}^{eff}(T)$ is the temperature-dependent effective oxygen diffusivity in cm$^2$/s; $D_{O_2}(T)$ is the temperature-dependent ordinary $O_2$ molecular diffusivity in cm$^2$/s; and $e$ and $\tau$ are the porosity and tortuosity of the porous cathode substrate, respectively. Table I lists the $D_{O_2}(T)$ and $D_{O_2}^{eff}(T)$ values of some binary gas systems pertinent to SOFCs at representative temperatures, calculated by the dependence of $D_{O_2}(T)$ for $T > 1500^\circ C$. To be more accurate, the higher dependence closer to $T^{1.5}$ should also be considered to account for the collision integral. Equation 2 is used in this study to represent the effective oxygen diffusivity with the ratio of $e/\tau$ as a microstructural factor.

### Table I. Calculated $D_{O_2}$ and $D_{O_2}^{eff}$ values of some SOFC-related binary gas systems.

<table>
<thead>
<tr>
<th>$T$ (°C)</th>
<th>$D_{O_2}^{C2H}$ (cm$^2$/s)</th>
<th>$D_{O_2}^{H_2}$ (cm$^2$/s)</th>
<th>$D_{H_2}^{H_2}$ (cm$^2$/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0.204</td>
<td>0.743</td>
<td>0.924</td>
</tr>
<tr>
<td>800</td>
<td>1.799</td>
<td>6.183</td>
<td>8.294</td>
</tr>
<tr>
<td>850</td>
<td>1.947</td>
<td>6.679</td>
<td>8.930</td>
</tr>
<tr>
<td>900</td>
<td>2.056</td>
<td>7.162</td>
<td>9.579</td>
</tr>
<tr>
<td>950</td>
<td>2.237</td>
<td>7.693</td>
<td>10.248</td>
</tr>
<tr>
<td>1000</td>
<td>2.375</td>
<td>8.206</td>
<td>10.937</td>
</tr>
</tbody>
</table>

More comprehensive models with higher fidelity representations of porous-media transport can be found in Ref. 10-14 (just to name a few). In practice, Eq. 2 and 2’ are often applied to either estimate $i_0$ from known microstructural factors (e.g., $m = e/\tau$) or to estimate microstructural factors (e.g., $e$) from a measured $i_0$, often with an assumption of $\tau = 1/e$ or $\tau$ is unknown. In this study, we exercised using this assumption to estimate the porosity of the cathode from a measured $i_0$. The estimated porosity is listed in Table III.

For a one-dimensional planar geometry, $i_0$ can be further simplified into

$$i_0 = -\ln(1 - x) \times \frac{4FD_{O_2}^{eff}(T)}{RT} \times P_t$$

where $r$ is the wall thickness through which the $O_2$ diffusion takes place. The concentration polarization ($\eta_{con}$) of a solution-based electrochemical system is generally expressed by

$$\eta_{con} = i \int_0^\infty \left[ \frac{1}{\sigma_1} \frac{1}{\sigma_2} \right] dy + RT \sum_k \frac{c_{k0}}{c_{k0}} \ln \frac{c_{k0}}{c_k} + F \int_0^\infty \sum_j \frac{z_jD_j}{\sigma_2} \frac{\partial c_j}{\partial y}$$

where $\sigma_1$ and $\sigma_2$ are the electrical conductivities of active species in position $y$ to the surface of the electrode and in the electrolyte bulk, respectively; $c_{k0}$ is the stoichiometric coefficient of species $k$ in the electrode reaction; $c_{k0}$, and $c_{k0}$ are the concentrations of species $k$ at the electrode surface and the electrolyte bulk, respectively; and $z_j$ and $D_j$ are the charge number and diffusivity of species $j$, respectively. The first term relates to the ohmic loss due to the conductivity change by diffusion, and the last term refers to the “diffusion potential” caused by the concentration gradient. Applying Eq. 4 to the solid porous cathode through which molecular oxygen diffusion occurs, the first and last terms become zero. Therefore, substitutions of $n = 2, \alpha = -1/2, K = O_2$, $c \propto P_t$, and Eq. 1 into Eq. 4 yields the Nernst equation

$$\eta_{con} = \frac{RT}{4F} \ln \left[ \frac{P_{O_2}(b)}{P_{O_2}(c)} \right] = \frac{RT}{4F} \ln \left[ \frac{x}{1 - (1 - x)^{e/\tau}} \right]$$

where the electrode reaction is considered as: $1/2 O_2 + 2e^- = O_2$. This leads to the concentration polarization related ASR ($R_{con}$) by differentiating $\eta_{con}$ with regard to $i_0$ at a fixed temperature $T$

$$R_{con} = \frac{RT}{4F} \times \frac{\ln(1 - x)}{i_0} \times \frac{1}{1 - (1 - x)^{e/\tau}}$$

Clearly, both $\eta_{con}$ and $R_{con}$ follow an exponential dependence on $i_0$. The higher the $i_0$, the lower the polarization. A thinner wall and higher temperature help reduce $R_{con}$ and $\eta_{con}$ in the range of operating current densities. Both Eq. 4 and 5 can serve as the analytical models for solving $i_0$ from either a measured $\eta_{con}$ or $R_{con}$ data set. In this study, Eq. 5 is more preferable than Eq. 4 simply because $R_{con}$ is a directly measured quantity, whereas $\eta_{con}$ is a secondary computed value through integrating the $R_{con}$ data set.
Under one extreme condition, e.g., \( i = 0 \) (open circuit), the measured \( R_{\text{conc}} \) can lead to the knowledge of \( i_L \) directly from Eq. 5. In the following, \( i_L \) is primarily determined from the nonlinear least-square fitting of the \( R_{\text{conc}}-i \) data set with Eq. 5. The simpler open-circuit approach was not attempted in this study.

**Activation polarization.**—In classical activation polarization models of the cathode in an SOFC, two elementary steps are generally considered: (i) \( O_2 \) surface adsorption/dissociation that converts \( O_2 \) into reactive oxygen species and (ii) charge transfer that converts the reactive oxygen species into oxide ions. In some cases, the surface diffusion of the adsorbed oxygen species should also be considered as one elementary step. Depending on the choice of cathode materials, either or both of them can be rate-limiting. It is generally accepted for LaMnO\(_3\)-based cathode materials (the same material used in this study), however, that the charge transfer is a slower process than the surface exchange, hence making it the rate-limiting step of the overall cathode kinetics. Furthermore, the rate-limiting charge-transfer step is often associated with single-electron electrode reactions such as \[ i_L = \frac{RT}{0.5F} \sinh^{-1} \left( \frac{i}{2i_L} \right) \] where \( i_L \) is the adsorbed reactive oxygen species; \( O_{\text{ad}}(s) \) and \( e^+ \) represent the negatively charged adsorbed oxygen species and free electrons, respectively; and \( k_L \) is the rate constant of the forward charge-transfer reaction (Eq. 6). To use the simplified two-term Butler–Volmer equation to describe the overpotential of the activation polarization, the charge-transfer coefficients of both the anodic and cathodic reactions are assumed to be equal, \[ \eta_{\text{act}} = \frac{RT}{0.5F} \sinh^{-1} \left( \frac{i}{2i_L} \right) \frac{1}{2} \sinh^{-1} \left( \frac{1 - (1 - x)^{1-\alpha/L}}{x} \right)^{0.25} + \frac{RT}{4F} \ln \left( \frac{x}{1 - (1 - x)^{1-\alpha/L}} \right) \] where \( x = P_{O_2}/P_C \), a form of molar fraction of oxygen related to \( P_{O_2} \). There are three independent constants \( i_L, \alpha, \) and \( x^* \) in the equation. One has to be cautious in attempting to solve the nonlinear equation (Eq. 9) because in many cases, the obtained values are just a set of numbers that meet the optimization criteria of computing algorithm but may not be physically meaningful. To minimize the number of unknown parameters in Eq. 9, the predetermined \( i_L \) by solving Eq. 5 with the \( R_{\text{conc}}-i \) data set is used as a fixed value throughout this study. Therefore, only two parameters \( i_L^* \) and \( x^* \) are left to be solved using the nonlinear equation (Eq. 9) with the \( \eta_{\text{act}}-i \) data sets.

**Combined cathode polarization.**—The sum of Eq. 4' and 9 gives the total cathode polarization

\[ \eta_{\text{tot}} = \frac{RT}{0.5F} \sinh^{-1} \left( \frac{i}{2i_L} \right) \frac{1}{2} \sinh^{-1} \left( \frac{1 - (1 - x)^{1-\alpha/L}}{x} \right)^{0.25} + \frac{RT}{4F} \ln \left( \frac{x}{1 - (1 - x)^{1-\alpha/L}} \right) \] for \( P_{O_2}\)-dependent \( i_L \) and the following for \( P_{O_2}\)-independent \( i_L \),

\[ \eta_{\text{tot}} = \frac{RT}{0.5F} \arcsin \left( \frac{i}{2i_L} \right) + \frac{RT}{4F} \ln \left( \frac{x}{1 - (1 - x)^{1-\alpha/L}} \right) \]  

In the discussions to follow, Eq. 10 and 10' are used as the model to independently verify the three parameters \( i_L, \alpha, \) and \( x^* \) obtained from Eq. 9 and 9 by directly comparing the measured and calculated \( \eta_{\text{tot}} \) values. The adequacy of the model can be judged by whether an agreement can be reached or not.

In a short summary, the attainment of the three critical electrochemical parameters involves three successive steps: (i) using Eq. 5 as the model to solve single constant \( i_L \) from the \( R_{\text{conc}}-i \) data set; (ii) using Eq. 9 as the model along with the predetermined \( i_L \) to solve the dual constants \( i_L^* \) and \( x^* \); and (iii) using Eq. 10 with all three constants to calculate \( \eta_{\text{tot}} \) and then compare with the measured values.

**Experimental**

**Preparation of testing cells.**—The cells used in this study were 11 mm long cutoff segments from a 1.5 m long cylindrical tubular SOFC. The effective surface area of each cell segment is \( \sim 5.0 \) cm\(^2\). Table II summarizes the attributes of each functional layer and their fabrication techniques.

### Table II. Attributes of each functional layer in the cathode-supported SOFC studied.

<table>
<thead>
<tr>
<th>Component</th>
<th>Material</th>
<th>Dimension</th>
<th>Fabrication technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cathode</td>
<td>LCM(^a)</td>
<td>i.d. 18 mm; o.d. 22 mm</td>
<td>Extrusion</td>
</tr>
<tr>
<td>Cathode interlayer</td>
<td>A mixture of LCM and ScSZ(^b)</td>
<td>20 ( \mu )m</td>
<td>Slurry dip coating</td>
</tr>
<tr>
<td>Electrolyte</td>
<td>ScSZ</td>
<td>60 ( \mu )m</td>
<td>Atmospheric plasma spray</td>
</tr>
<tr>
<td>Anode</td>
<td>A mixture of Ni and ScSZ</td>
<td>100 ( \mu )m</td>
<td>Atmospheric plasma spray</td>
</tr>
<tr>
<td>Interconnect</td>
<td>Ca- and Al-doped LaCo(_3)</td>
<td>100 ( \mu )m</td>
<td>Atmospheric plasma spray</td>
</tr>
<tr>
<td>Contact layer</td>
<td>Pure Ni</td>
<td>2 ( \mu )m</td>
<td>Electroplating</td>
</tr>
<tr>
<td>Current collector</td>
<td>Platinum mesh/leads</td>
<td>52 mesh/0.5 mm</td>
<td>Sintered on</td>
</tr>
</tbody>
</table>

\(^a\)Ca-doped LaMn\(_3\).  
\(^b\)Sc-doped ZrO\(_2\).
The constructed test-cell assembly is first heated up in a furnace to a dependent electrode resistance studies. Both air and fuel flows are set to 500 mL/min. After initial stabilization at the measuring temperature, a desirable current is then gradually applied to the cell. The current convention mimics the current flow in a practical SOFC. To assist in separating concentration and activation polarizations, a method known as “He–O₂ shift” is also employed. The basic principle of the method is described in the next section. With the known \( R_{\text{conc}} \) and the total cathode ASR \( (R_{\text{act}}) \) being readily obtained from the spectrum, the activation polarization ASR \( (R_{\text{act}}) \) can then be taken as \( R_{\text{act}} = R_{\text{conc}} \). After the completion of these characterizations, the cell temperature was then changed and the same measurements were repeated. The maximum ranges of temperature and current density varied from 850 to 1000°C and 0 to 0.6 A/cm², respectively. Obviously, the instrumentation was more capable of providing a higher current density at higher temperatures due to a lowered overall cell resistance. For repeatability check, each run was conducted on two identical cells in one furnace. The final ASRs were the average values produced from the two cells in each run.

The polarization overpotentials \( \eta \) were obtained from numerically integrating the measured ASRs with respect to \( i \) because the exact analytical expressions between them were unknown and usually complex. Specifically, the “trapezoid rule” was applied to perform the numerical integrations.

**Helium–oxygen shift.**—The method of helium–oxygen (He–O₂) shift is aimed at determining the concentration polarization resistance of a cathode. The principle of this method is based on the fact that the O₂ diffusivity in the He–O₂ mixture is roughly 4 times higher than that in the N₂–O₂ (air) mixture. Therefore, switching air to a mixture of He–O₂ gas at the cathode should reduce the concentration polarization resistance markedly as a result of an enhanced O₂ diffusivity. The selection of 20% O₂ for the He–O₂ mixture was to minimize the effect of \( P_{\text{O}_2} \) on activation polarization. Furthermore, the \( P_{\text{O}_2} \) effect on the electrical conductivity of the cathode and ceramic interconnect, both of which are p-type conductors and contribute to the ohmic resistance, could also be avoided. Therefore, the change induced by switching from air to He–20% O₂ reflected largely the change in the concentration polarization of the cathode. Applying Eq. 5 to air, a mixture of roughly 20% O₂ and 80% N₂, the concentration ASR \( [R_{\text{conc}}] \) can be written as

\[
R_{\text{conc}}(\text{air}) = A \times \frac{1}{I_{\text{lim}}(\text{air})} \times \frac{1}{[1 - (1 - x)^{\frac{m}{iL,O_2He}}]} \tag{11}
\]

where \( I_{\text{lim}}(\text{air}) \) is the limiting current density of cathode in air. A similar equation can also be written for the He–20% O₂ mixture

\[
R_{\text{conc}}(\text{O}_2\text{He}) = A \times \frac{1}{I_{\text{lim}}(\text{O}_2\text{He})} \times \frac{1}{[1 - (1 - x)^{\frac{m}{iL,O_2He}}]} \tag{13}
\]

where \( I_{\text{lim}}(\text{He}) \) is the limiting current density of the cathode in He–20% O₂. The difference \( \Delta R_{\text{conc}} \) between \( R_{\text{conc}}(\text{air}) \) and \( R_{\text{conc}}(\text{O}_2\text{He}) \), which is experimentally measurable, is obviously given by

\[
\Delta R_{\text{conc}} = A \times \left[ \frac{1}{I_{\text{lim}}(\text{air})} \times \frac{1}{[1 - (1 - x)^{\frac{m}{iL,O_2He}}]} \times \frac{1}{[1 - (1 - x)^{\frac{m}{iL,O_2He}}]} \right] \tag{14}
\]

The significance of Eq. 14 is that the microstructural factor \( m = e/\gamma \) can be first determined by the measurable \( \Delta R_{\text{conc}} \) at a given \( i \) with known theoretical oxygen diffusivities for air and He–20% O₂ (see Table I). The attainment of \( m \) can then be utilized to calculate the absolute \( R_{\text{conc}}(\text{air}) \) using Eq. 11 with assumed constant \( m \). For convenience, Ref. 21 lists a number of tables in Appendix 3 and plots several graphs under a few representative conditions to facili-
tate the simultaneous attainments of \( m \) and \( R_{\text{conc}}(\text{air}) \) from a measured \( \Delta R_{\text{conc}} \). In this study, all \( R_{\text{conc}} \) values were obtained by the above-described He–O\(_2\) shift method.

**Equivalent circuit.**—The collected impedance spectra were analyzed with ZView [version 2.8, Scribner Associates] with its built-in equivalent circuits. Figure 3 shows the equivalent electrical circuit used in this study. The element \( DX2 \) (DXII-Bisquert #2) was selected from the library of ZView equivalent circuits to simulate the cathode polarization process because the two-phase composite network present in the cathode can be better represented by a chain-conductor model. For the anode polarization, only one charge-transfer process, namely activation polarization, was represented by one R-CPE parallel circuit because the concentration polarization of the anode is negligible for the cathode-supported SOFC. CPE (constant phase element) is a general form of impedance that covers from pure resistors to pure capacitors. All ohmic contributions from the different functional layers were lumped into \( R_{\text{act}} \). To account for the inductance effect caused by the measuring wires, an inductor was also included in the circuit model.

**Results and Discussion**

**Identification of cathode polarization process.**—The first step to determine the cathode ASRs from an impedance spectrum measured from an SOFC is to identify which semicircle (or arc) corresponds to the cathode kinetics. A representative impedance spectrum of an operating cathode-supported SOFC is shown in Fig. 4. It features two distinct semicircles (or arcs) spreading across the frequency domain on a complex plane with the smaller one at higher frequency and the large one at lower frequency. To determine which one is cathode-related, the aforementioned He–O\(_2\) shift method was employed. It is evident from Fig. 4 that a marked reduction in ASR only occurs at the low frequency semicircle after the oxidant is switched from air to the He–20% \( \text{O}_2 \) mixture while the fuel composition is kept the same. The implications of such an ASR reduction are threefold. First, it identifies that the low frequency semicircle is indeed associated with the cathode kinetics. The high frequency semicircle has been previously identified to be related to the anode kinetics in a Siemens’ internal study,\(^5\) in which the only semicircle that responded to the anode gas change was the first high frequency one. Second, the degree to which the ASR is shrunk by switching oxidants with the same concentration of \( \text{O}_2 \) mainly reflects the change in \( R_{\text{conc}} \) with a marginal influence on \( R_{\text{act}} \). Third, it allows for a quantitative determination of \( R_{\text{conc}} \) from Eq. 14, and \( R_{\text{act}} \) can be further determined as \( R_{\text{act}} = R_{\text{conc}} \). The rationality of the above identification is also understandable in that the insignificant anode polarization of a cathode-supported SOFC signals a higher exchange current density and a negligible \( \text{H}_2 \) diffusion-related concentration polarization (very thin anode layer and higher \( \text{H}_2 \) diffusivity) for the fuel oxidation and therefore should appear at a high frequency range. In contrast, the slower cathode kinetics with smaller exchange current density and larger \( \text{O}_2 \) diffusion related concentration polarization (very thick cathode layer and relatively lower \( \text{O}_2 \) diffusivity) should mainly occupy the low frequency domain of the spectrum. It is further estimated from the peak frequencies shown in Fig. 4 that the time constant for the anode kinetics is \( \sim 19 \) \( \mu \)s, whereas the time constants for the cathode kinetics are 155 ms with air and 40 ms with He–20% \( \text{O}_2 \), respectively. The magnitudes of the time constants for the anode and cathode semicircles place the anode and cathode kinetics in the charge-transfer and gas-diffusion regimes, respectively. The following results evidently support this assertion.

**Cathode ASRs vs current density.**—With the separation of the cathode-related ASRs, Fig. 5 plots the individual ASR of (a) total, (b) concentration, and (c) activation polarizations as a function of current density at four temperatures. At first glance, one can easily capture the similarity in the \( R_{\text{act}}^{-1} \) and \( R_{\text{conc}}^{-1} \) curves, e.g., a slow increase at low current density followed by a pronounced increase at high current density (lack of high current density data points for 900 and 850°C prevents showing the sharp increase). Different from the \( R_{\text{act}}^{-1} \) and \( R_{\text{conc}}^{-1} \) curves, the \( R_{\text{act}} \) in Fig. 5c displays its own dependence on \( i \) at different temperatures, e.g., flat at 1000°C, slight increase at 950 and 900°C, and slight decrease at 850°C. The opposite trend between \( R_{\text{act}}^{-1} \) and \( R_{\text{conc}}^{-1} \) at 850°C seems to cancel out to yield a flat \( R_{\text{act}}^{-1} \) curve in the current density range plotted.

The similarity between \( R_{\text{act}}^{-1} \) and \( R_{\text{conc}}^{-1} \) curves at 950 and 1000°C is an indication of the domination of cathode polarization by \( R_{\text{conc}} \). This is also supported by the fact that the magnitude of \( R_{\text{conc}} \) is markedly greater than \( R_{\text{act}} \) and the degree to which \( R_{\text{conc}} \) varies with \( i \) is appreciably larger at these two higher temperatures. The \( R_{\text{conc}} \) dominance with temperature is primarily ascribed to the difference in the activation energies of the charge-transfer and gas-diffusion processes, i.e., the charge-transfer process is more temperature-sensitive (or higher activation energy) than the gas-diffusion (projected \( i_L \propto T^{0.5} \)). At the lower temperature (850°C), the overall cathode polarization is dominated by \( R_{\text{act}} \) as is evidenced not only by the high \( R_{\text{act}} \) values shown in Fig. 5c but also by the decrease in \( R_{\text{act}} \) with \( i \). The latter is a characteristic of the Butler–Volmer equation (Eq. 7) as the slope of \( (\partial \eta_{\text{act}}/\partial i) \) decreases with increasing \( i \).

The importance of Fig. 5b is that it provides a theoretical foundation for using experimental data to solve \( i_L \). The lines shown in the figure represent the nonlinear least-square fittings of the measured values using DataFit software (version 9.0, Oakdale Engineering). The fittings are generally good, except for one data point at \( i = 0.50 \) A/cm\(^2\) and 950°C. The obtained \( i_L \) at different temperatures are listed in the second column of Table III; it is used as the fixed value for subsequent simulations. Along with \( i_L \) values, the corresponding effective oxygen diffusivities and substrate porosity calculated by assuming \( \tau = 1/e \) are also listed in Table III. The
porosity remains reasonably constant with temperature as it should be. To further support the obtained porosity values, Fig. 6 shows the microstructure of a Siemens/Westinghouse cathode substrate before electrolyte densification. The average porosity is estimated to be \( \approx 33\% \). A following densification of the electrolyte at 1345°C further reduces the porosity to below 30%, which agrees well with the values in Table III. To verify the dependence of \( \bar{\rho} \) on temperature as suggested by Eq. 2, the obtained \( \bar{\rho} \) is plotted against \( T^{0.5} \) and shown in Fig. 7. A stronger dependence than that predicted as \( \bar{\rho} \propto T^{0.5} \) in Eq. 2 is probably an indication of the effect of He–20% \( \text{O}_2 \) on \( R_{\text{act}} \) as well as a coupled relationship between \( R_{\text{act}} \) and \( R_{\text{conc}} \).

**Activation polarization vs current density.**—The overpotentials of activation polarization \( (\eta_{\text{act}}) \), numerically integrated from \( R_{\text{act}} \) are plotted in Fig. 8 as a function of \( i \) for four temperatures. Along with the data points are solid lines representing nonlinear least-square fitting using Eq. 9 as the model and the predetermined \( \bar{i}_L \) as a fixed value. The model appears to predict an upward bending at \( i > 0.50 \text{ A/cm}^2 \) for 950 and 1000°C where \( i > 0.50 \text{ A/cm}^2 \) data points are available. Also plotted in dotted lines are the simulations using Eq. 7 as the model, in which \( \bar{i}_L \) is considered to be independent of \( P_{\text{O}_2} \). The difference begins to be noticeable at higher \( i \), e.g., \( >0.50 \text{ A/cm}^2 \). This trend appears to suggest a more pronounced \( P_{\text{O}_2} \) dependence of \( \bar{i}_L \) at higher current densities. The outcomes of solving nonlinear Eq. 9 are the two best fit parameters \( \bar{i}_L^* \) and \( x^* \). They are listed in the fifth and sixth columns of Table III, respectively. There is no apparent trending among \( x^* \) values with temperature, particularly the value at 900°C, which could be caused by insufficient data points. In all cases, the obtained \( x^* \) values are small, implying a large but temperature-insensitive equilibrium constant for the adsorption/desorption reaction \( (\text{P}_{\text{O}_2}^* = 1 \text{K}, \text{see Ref. 20}) \). The concentration of the surface adsorbed oxygen species is high and well-equilibrated. They are also quite different from those reported by Matsuzaki and Yasuda\(^{23} \) on a Pt/8YSZ (where YSZ is yttria-stabilized zirconia) system. The different cathode materials could account for the disagreement. For comparison, the last column also lists the \( \bar{i}_L \) values obtained from solving Eq. 7. These values are comparable to those reported in Ref. 24 (e.g., 0.450 A/cm\(^2\) at 900°C) where the La\(_{0.6}\)Sr\(_{0.4}\)MnO\(_3\)/YSZ cathode was investigated by the ac impedance technique. An Arrhenius plot of \( \bar{i}_L^* \) and \( x^* \) given in Fig. 9 reveals an almost identical activation energy of \( E_a = 1.197 \text{ eV} \) between the two, suggesting that \( P_{\text{O}_2}(c)/P_{\text{O}_2}^* \) is rela-

![Figure 5](image-url)  
**Figure 5.** Cathode-related ASRs of polarization as a function of current density at four different temperatures: (a) Total, (b) concentration [lines representing fittings with Eq. 5], and (c) activation.

<table>
<thead>
<tr>
<th>( T ) (°C)</th>
<th>( \bar{i}_L ) (A/cm(^2))</th>
<th>( D_{\text{O}_2} ) (cm/s)</th>
<th>( \varepsilon )</th>
<th>( \bar{i}_L^* ) (A/cm(^2))</th>
<th>( x^* )</th>
<th>( \bar{i}_L ) (A/cm(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>0.629 ± 0.001</td>
<td>0.160</td>
<td>0.26</td>
<td>2.301 ± 0.025</td>
<td>0.056 ± 0.010</td>
<td>1.120 ± 0.010</td>
</tr>
<tr>
<td>950</td>
<td>0.621 ± 0.001</td>
<td>0.152</td>
<td>0.26</td>
<td>1.611 ± 0.044</td>
<td>0.089 ± 0.027</td>
<td>0.752 ± 0.023</td>
</tr>
<tr>
<td>900</td>
<td>0.560 ± 0.017</td>
<td>0.131</td>
<td>0.25</td>
<td>1.130 ± 0.040</td>
<td>0.608 ± 0.236</td>
<td>0.526 ± 0.004</td>
</tr>
<tr>
<td>850</td>
<td>0.499 ± 0.010</td>
<td>0.112</td>
<td>0.24</td>
<td>0.509 ± 0.001</td>
<td>0.068 ± 0.006</td>
<td>0.253 ± 0.001</td>
</tr>
</tbody>
</table>
Figure 7. (Color online) A representative microstructure of the cathode substrate before the electrolyte densification.

Figure 8. (Color online) Activation polarization of cathode as a function of current density at four different temperatures along with nonlinear least-square fitting with Eq. 9 and 7 as the models.

Figure 9. (Color online) Arrhenius plots of effective and intrinsic exchange current densities of the cathode.

Figure 10. (Color online) Total polarization of cathode as a function of current density at four different temperatures along with nonlinear least-square fittings using Eq. 10 (solid lines) and Eq. 10’ (dotted lines) as the models.

Total polarization vs current density.—To verify the model, the numerically integrated total polarizations $\eta_{\text{tot}}$ as a function of $i$ at four temperatures are shown in Fig. 10. $R_{\text{net}}$, from which $\eta_{\text{tot}}$ is derived, is determined with the highest accuracy as a result of direct reading from the spectrum. The solid and dotted lines represent the simulations using Eq. 10 and 10’ as the models, respectively, and the corresponding parameters listed in Table III. It is evident that the use of Eq. 10 produces the best fit to the measured data points, whereas the use of simplified Eq. 10’ yields deviations at higher current densities. Therefore, it is reasonable to conclude that the proposed coupled polarization model is a more general representation over a broader range of current density. It also becomes much clearer in Fig. 10 than in Fig. 8 that the effect of $P_{\text{O}_2}$ on $i_o$ begins to play a significant role at higher current densities.

Conclusions

The total cathode polarization of a cathode-supported SOFC has been considered in this study as a result of two interrelated contributions: concentration polarization of $\text{O}_2$ diffusion and activation polarization of charge transfer. The leading $\text{O}_2$ diffusion is shown to determine the $P_{\text{O}_2}$ that would affect the subsequent charge transfer. With this $P_{\text{O}_2}$ as the linking parameter, polarizations of concentration and activation are coupled. The conventional EIS technique in conjunction with the He–O$_2$ shift method is employed to experimentally separate $R_{\text{conc}}$ from $R_{\text{act}}$. This allows for the attainment of $i_o$, which is used as a fixed value for subsequent simulations and verification of the model by fitting $R_{\text{conc}}$–$i$ data. The obtained $i_o$ and $i'_o$ share an almost identical activation energy at a higher level, indicating a strong temperature-dependent charge-transfer process. The $i'_o$ and $x^*$ obtained by solving the nonlinear equation (Eq. 9) with the $\eta_{\text{act}}$–$i$ data set and the predetermined $i_o$ are also applied to calculate $\eta_{\text{tot}}$ using Eq. 10. The excellent agreement between the measured and calculated values favorably confirms the proposed polarization model. The model is more suitable for a broader range of current density. Overall, the cathode performance of the Siemens/Westinghouse cathode-supported SOFCs is mainly dominated by oxygen diffusion, especially at higher current density for temperatures greater than 900°C, below which it is largely limited by the charge-transfer polarization.

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