Equivalent Circuit Approximation to Porous Mixed-Conducting Oxygen Electrodes in Solid-State Cells

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ABSTRACT

While porous mixed ionic-electronic conductors (MIECs) have been widely used as electrodes for solid-state ionic devices, the electrochemical processes occurring in such an electrode are still not well understood. Equivalent circuit analyses indicate that there are three parallel paths for electrode reactions to occur in a cell with porous MIEC electrodes: (i) the triple-phase boundary (TPB) between the electrolyte, the MIEC, and O₂ gas, (ii) the TPB between the current collector, the MIEC, and O₂ gas, and (iii) the interface between the MIEC and O₂ gas. The relative significance of each path is determined not only by the transport and catalytic properties of the MIEC but also by the interfaces between the MIEC and other cell components. The effectiveness of the MIEC/gas interface is influenced by the rates of several sequential processes: transfer of ionic defects across the MIEC/electrolyte interface, transport of ionic and electronic defects in the MIEC, reaction at the MIEC/gas interface, and transport of O₂ in the pores of the MIEC. Accordingly, oxygen diffusion in the MIEC and reaction at the MIEC/gas interface are only part, not the entirety, of the electrode kinetics. In general, the TPBs cannot be ignored without careful analysis or adequate justification. Further, as a first-order approximation, it is demonstrated that the thickness of the electrochemically active layer of a porous MIEC electrode, δ, varies dramatically with the properties of the MIEC. Typically, δ decreases with increased rate of surface reaction and with decreased transport of ionic or electronic defects in the MIEC. In the absence of ionic or electronic transport in the MIEC, for instance, δ approaches zero, i.e., oxygen reduction or evolution can occur only at one of the TPBs.

Introduction

It is well recognized that, in contrast to an electrode of a pure electronic conductor (such as Pt), an electrode formed from a mixed ionic-electronic conductor (MIEC) has the potential to extend the reaction sites or zones beyond the triple-phase boundaries (TPBs) between the electrode, electrolyte, and O₂ gas. Accordingly, MIECs have been widely used as electrodes for solid-state ionic devices (e.g., solid oxide fuel cells, batteries, and gas sensors) and for electrochemical processes (e.g., gas separation or electrolysis). However, the detailed reaction paths and electrode kinetics in cells with porous MIEC electrodes are still not well understood. A recent model, for instance, predicts that the impedance of a cell with porous MIEC electrodes (of infinite thickness and uniform Fermi level) is determined merely by the properties of the MIEC, oxygen diffusivity in the MIEC and surface catalytic properties, and is independent of the properties of the interfaces between the MIEC and other cell components (electrolyte and current collector). This prediction, first of all, directly contradicts experimental observations; recent impedance spectroscopy studies demonstrate that the impedances of cells based on different electrolyte materials but with same MIEC electrodes are influenced dramatically by the interfaces between the MIEC and the electrolyte. Second, our analyses indicate that, in addition to the reactions at MIEC/gas interface, other reaction paths through the TPBs are an important part of the electrode kinetics and cannot be ignored without careful analysis and adequate justification.

In this paper, equivalent circuit analysis demonstrates conclusively that, in general, there are three parallel paths for electrode reactions to occur in a cell with porous MIEC electrodes: two types of triple-phase boundaries (TPBs) in parallel to the MIEC/gas interface. It is incorrect to assert that “consideration of a separate parallel triple-phase boundary (TPB) reaction would be redundant”; on the contrary, consideration of the TPBs as parallel paths to the MIEC/gas interface is a minimum requirement for any meaningful analysis of a solid-state system. TPBs are inherent to solid-state electrochemical systems and failing to address TPBs will lead to erroneous boundary conditions and ultimately to invalid conclusions. Further, it is demonstrated unequivocally that, for a cell based on MIECs of infinite thickness and uniform Fermi level, it is the TPB between the electrolyte, the MIEC, and O₂, rather than the bulk phase of the MIEC, that dominates the electrode kinetics and cell impedance, when the impedance of the TPB is smaller than the impedance of any of the following processes: ion transfer across the MIEC/electrolyte interface, oxygen transport in the MIEC, or the reaction at the MIEC/gas interface.

The observations that electrodes of MIECs with high rate of oxygen transport and surface reaction appear to show fast electrode kinetics do not necessarily mean that the oxygen transport in MIEC and surface reaction are the only processes dominating the electrode kinetics. The observed fast electrode kinetics may, for instance, result from enhanced catalytic activity of the TPBs. It should be recognized that the simultaneous transport of ionic and electronic defects in an MIEC electrode may not only extend the reaction sites from TPBs to the MIEC/gas interface, but also enhance the catalytic property of the TPBs. The latter advantages can not be well understood, particularly when the TPBs are ignored all together.

Clariﬁcation of reaction paths in a cell with porous MIEC electrodes is critical to gaining a profound understanding of the electrode kinetics (including the details of the reaction mechanisms) of such an electrode, to correct interpretation of impedance data of cells with such electrodes, and to meaningful modeling and effective design or improvement of porous MIEC electrodes for various applications.

Model Description

Schematically shown in Fig. 1 is a symmetrical cell consisting of a solid electrolyte of a pure ionic conductor (el, t, = 1), two porous electrodes of an MIEC (0 < t, < 1), and two current collectors (cc, t, = 1). Unless stated otherwise, it is further assumed that (i) the electrolyte is essentially homogeneous and there is no significant space charge polarization at grain boundaries, (ii) the MIEC electrode contains a continuous porous phase, through which O₂ gas may transport to or away from the TPBs and the MIEC/gas interface, (iii) the solid phase of the electrode is a single-phase, homogeneous MIEC (such as LaFeO₃- or LaCoO₃-based perovskite material) in which local charge neutrality is approximately observed and there is no significant bulk polarization, (iv) the electronic conductivity of the current collector is sufﬁciently greater than the conductivities of other cell components.

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components so that the variations in Fermi level in the current collector are negligible, (v) the properties of each cell component in a plane perpendicular to the direction \( x \) are the statistical average properties on the plane so that the system may be treated as a one-dimensional problem, and (vi) all current or mass fluxes are on a superficial area basis. The equations and conclusions derived under these assumptions, however, may be further extended to cells based on a mixed-conducting electrolyte (el, 0 < \( t \) < 1), as discussed in Appendix A, and to cells based on electrodes of composite MIECs consisting of two or more phases, as discussed in Appendix B.

**Electrochemical processes.**—The electrochemical processes which may occur in such a cell are schematically illustrated in Fig. 2 (only half of the cell is shown) and briefly described as follows.

In the electrolyte of uniform composition, the motion of the ionic defects is considered to be pure migration (driven by \( V_4 \)), i.e.

\[
J_i = -\sigma_{el} \nabla \phi, \quad \sigma_{el} = \sum_i z_i^2 F \mu_i c_i \tag{1a}
\]

At the MIEC/el interface (\( x = L \)), two types of processes can be differentiated: (i) the electrochemical reaction occurring at the triple-phase boundary (TPB1) between the el, the MIEC, and the O\(_2\) gas

\[
V^{\circ}(el) + 2e'(MIEC) + \frac{1}{2} O_2(gas) = O^{\circ}(el) \tag{1b}
\]

and (ii) the transfer of ionic defects (such as \( V^{\circ} \)) across the MIEC/el interface

\[
V^{\circ}(el) = V^{\circ}(MIEC) \tag{1c}
\]

In the region of the porous electrode (0 < \( x < L \)) with porosity \( p \), solid-phase tortuosity \( \tau_s \), and gas-phase tortuosity \( \tau_g \), three types of processes can be identified: (i) the transport of ionic and electronic defects in the solid phase MIEC through diffusion (driven by \( \nabla \mu_i \)) and migration (driven by \( \nabla \phi \))

\[
J_k = -z_k F \left( \frac{\mu_k}{\tau_s} \right) ([1 - p] c_k) \nabla \mu_k + z_k F \nabla \phi = J_{k,\text{diff}} + J_{k,\text{migr}} \tag{1d}
\]

\[
J_\tau = \sum_k J_k = J_{\text{ion}} + J_{\text{ele}}
\]

(ii) the transport of O\(_2\) gas in the pores of the MIEC through diffusion (driven by \( \nabla \mu_{O_2} \)) and convection (due to the motion of the gas in the pores with a bulk velocity \( v \))

\[
N_{O_2} = \left( \frac{\mu_{O_2}}{\tau_g} \right) \nabla \mu_{O_2} + u (p c_{O_2}) \tag{1e}
\]

and (iii) the interaction between the O\(_2\) gas and the MIEC at the MIEC/gas interface

\[
(V^{\circ} + 2e')(MIEC) + \frac{1}{2} O_2(gas) = O^{\circ}(MIEC) \tag{1f}
\]

At the cc/MIEC interface (\( x = 0 \)), three other types of processes can be identified: (i) the reaction occurring at the second triple-phase boundary (TPB2) between the cc, the MIEC, and O\(_2\) gas

\[
V^{\circ}(MIEC) + 2e'(cc) + \frac{1}{2} O_2(gas) = O^{\circ}(cc) \tag{1g}
\]

(ii) the transfer of electrons across the cc/MIEC interface

\[
e'(MIEC) = e'(cc) \tag{1h}
\]

and (iii) the reaction at the MIEC/gas interface at \( x = 0 \), which is the same reaction as described by Eq. 1f.

**Current and mass fluxes.**—The ionic current flow pattern in the vicinity of the porous MIEC electrode is schematically sketched in Fig. 3a. Part of the ionic flux moving from the electrolyte toward the MIEC/el interface is directly converted to electronic flux by the reaction at the TPB1 (Eq. 1b). The remaining ionic flux, transferred into the MIEC through the MIEC/el interface, is then consumed either by the reaction at the MIEC/gas interface (Eq. 1f) or by the reaction at the TPB2 (Eq. 1g), depending primarily on the relative ionic and electronic transport properties of the MIEC, but also influenced by the nature.
Further, as the ionic current is converted to electronic current or vice versa by the electrode reactions (Eq. 1b, 1f, and 1g), O₂ gas is simultaneously consumed (or generated) at TPB₁, MIEC/gas interface, and TPB₂; this can be expressed, in a steady state, as
\[
J_{\text{e.o}}(x) = -4FN_{\text{O}_2}(x), \quad 0 \leq x \leq L
\]  
Continuous operation of such an electrode, then, requires that the O₂ gas transport to (or away from) these reaction sites through the pores of the MIEC. The rate of O₂ transport in the pores of MIEC may influence the partial pressure of O₂ near or at these reaction sites and hence may influence the rate of the interfacial processes and the impedance response of the interfaces.

Since the MIEC electrode must be porous to allow sufficient gas transport, the ionic current may heavily concentrate on the TPB₁ at \(x = L\); in fact, all current must pass through the TPB₁ when the mobility or concentration of the ionic defects in the electrode vanishes (e.g., when a Pt electrode is used). With the increase in transport of the ionic and electronic defects in the MIEC, the active sites or zones for reduction or evolution of oxygen (Eq. 1b and 1g) may be extended beyond the TPBs to the MIEC/gas interface (Eq. 1f). The degree of extension is primarily determined by the properties of the MIEC and the interfaces. In principle, when the rate of ionic and electronic transport in the MIEC is sufficiently fast in comparison to the rate of the surface reaction, the active reaction sites will be extended to the entire MIEC/gas interface.

The current or flux balances described by Eq. 2a to 2e are true in general for cells with MIEC electrodes; failing to consider TPBs will lead to erroneous boundary conditions, invalid conclusions, and incorrect interpretation of impedance data.

**Equivalent circuit.**—When the cell is exposed to a uniform atmosphere having oxygen partial pressure of \(P_{O_2}\) and under the influence of a small ac perturbation, such as in an impedance measurement, the electrochemical behavior of such a cell may be adequately approximated by the equivalent circuit shown in Fig. 4 (only half of the circuit is shown). The porous MIEC electrode is approximated by an electrical transmission line model, which has been widely used to model rough electrode surfaces, and porous electrodes of an electronic conductor involving liquid electrolytes. The transmission line model, however, is properly modified to reflect the fundamental differences between a porous MIEC electrode exposed to a gas and the systems exposed to a liquid handled previously. In the transmission line model shown in Fig. 4a, \(dR_e\), \(dR_i\), and \(dZ\) represent the impedance, respectively, to electronic transport, ionic transport, and to the reaction at the MIEC/gas interface of an MIEC layer with thickness of \(dx\) at a distance \(x\) away from the MIEC interface. Thus, integration along each path for electrochemical processes over the entire bulk phase of the porous MIEC results in three lumped circuit elements, \(R_{\text{MIEC}}, R_{\text{MIEC}}, \text{ and } Z_e\). The circuit shown in Fig. 4a is then transformed to the one shown in Fig. 4b. The impedance of each circuit element in Fig. 4 is normalized by the superficial area of the porous electrode (thus having dimension of \(\Omega \text{ cm}^2\)) and is defined as follows.

In the electrolyte, the resistance to the motion of the ionic defects, \(R_{\text{ electrolyte}}\), is defined as
\[
R_{\text{ electrolyte}} = L_e/\sigma_{\text{ electrolyte}}
\]

where \(\sigma_{\text{ electrolyte}}\) is the conductivity of the electrolyte at the MIEC/gas interface and \(J_f\) is the total current density as defined by Eq. 1d.

**Fig. 3.** A schematic diagram showing the flow patterns of (a) ionic and (b) electronic currents in the vicinity of a porous MIEC electrode. Note that the electron holes move in the direction opposite to the direction of the electronic current while the electrons move in the direction opposite to the direction of the electronic current.
where \( \sigma \) and \( L \) are the ionic conductivity and the thickness of the electrolyte, respectively. Since the polarization at grain boundaries of polycrystalline electrolyte is assumed to be negligible in order to focus on electrode processes, the impedance response of the electrolyte is approximated by a pure resistance, \( R_{\text{el}} \). The impedances to oxygen reduction or evolution at three different types of reaction sites, respectively.

Further, the kinetics of the interfacial reactions (Eq. 1b and 1c) are assumed to be finite in general. Accordingly, the defect concentrations at or near the MIEC/el or el/gas interface are influenced not only by thermodynamics but also by the kinetics of these reactions. Thus, significant interfacial polarizations due to charge and mass transfer are possible and the impedances to these processes, \( Z_{\text{TPB}} \) and \( Z_e \), are expected to be a complex quality (containing real and imaginary components) in general.

In the region of the porous electrode (0 < \( x < L \)), the properties of the MIEC may vary with position. If the local resistivity (\( \Omega \) cm), at a distance \( x \) away from the cc/MIEC interface, to transport of electrons and electron holes in the solid MIEC is \( p(x) \), the total resistance to the transport of electrons and electron holes through the entire MIEC of thickness, \( L \), can be expressed as

\[
R_{\text{MIEC}} = \int_0^L p(x) \, dx
\]

Similarly, if \( p(x) \) is the local resistivity to transport of ionic defects in the MIEC, the total resistance to the transport of ionic defects through the entire MIEC is given by

\[
R_{\text{MIEC}} = \int_0^L p(x) \, dx
\]

Because it is assumed that local charge neutrality is observed and bulk polarization is negligible in the bulk MIEC, the impedance of the bulk MIEC can be adequately approximated by resistance \( R_{\text{MIEC}} \) and \( R_{\text{MIEC}} \). When significant polarization occurs in the bulk phase of MIEC, \( p(x) \) and \( p(x) \) may no longer be pure resistive, as discussed in Appendix B.

The impedance of the MIEC/gas interface, however, should be a complex quality (frequency dependent) in general because the charge and mass transfer at or near the interface associated with the surface reaction may cause significant charge accumulation or depletion at the interface. If \( p(x) \) represents the local surface resistivity (\( \Omega \) cm) at an angular frequency \( \omega \) to the reaction at the MIEC/gas interface, the impedance to the reaction at the entire MIEC/gas interface (Eq. 1f) and to the transport of the species involved in the surface reaction, \( Z_e(L,\omega) \), can be expressed as

\[
\frac{1}{Z_e(L,\omega)} = \frac{1}{p(0,\omega)} + \left( 1 - \rho \right) \frac{1}{(1 - \theta_e)} + \int_0^L p(x) \, dx
\]

\[
+ \int_0^L \left[ \int_0^L \rho(x) \, dx \right] \rho(x) + \int_0^L \rho(x) \, dx + \int_0^L \rho(x) \, dx \left( \int_0^L \rho(x) \, dx \right) \rho(x)
\]
where $\theta_s$ is the fraction of the MIEC surface at $x = 0$ covered by the current collector and $a(x)$ is the local surface area of the porous MIEC per unit volume $(cm^2/cm^3)$, which characterizes the local microstructure of the MIEC electrode. The derivation of Eq. 3f is summarized in Appendix C. It is important to note that $\rho_i$ is influenced not only by the surface catalytic properties of the MIEC but also by the associated mass transfer in the vicinity of the MIEC/gas interface. For instance, concentration polarizations in the gas phase or in the MIEC adjacent to the MIEC/gas interface may result in larger $\rho_i$ at lower frequencies. In a steady state (i.e., $\omega \to 0$), however, $\rho_i$ becomes real and $Z_{re}$ reduces to a steady-state resistance, $R_e = \lim_{\omega \to 0} Z_{re}$.

Equation 3f implies that the actual rate of the reaction at MIEC/gas interface is determined not only by the local surface properties, $\rho_i$, but also by the local microstructure, $a(x)$, and the bulk transport properties of the MIEC, $\rho_b$ and $\rho_p$. In fact, the bulk ionic transport, local surface reaction, bulk electronic transport, and the transport of $O_2$ in the pores of the MIEC are several consecutive steps necessary in order for reduction or evolution of $O_2$ gas to occur at the MIEC/gas interface. Accordingly, when the rate of any one step is sufficiently slow, the MIEC/gas interface is ineffective for the electrode reaction. The effectiveness of the MIEC/gas interface is characterized by $1/Z_{re}$, which includes the impedance to surface reaction, to transport of $O_2$ in the boundary layer, and to the transport of $O_2$ gas in the pores of the MIEC (which is lumped in $\rho_i$).

At the cc/MIEC interface at $x = 0$, the impedance to the electrochemical reaction at the TPB2, $Z_{TPB2}$, can be expressed as

$$Z_{TPB2}(\omega) = \frac{\eta_{TPB2}(\omega)}{\partial J_{TPB2}(\omega)} = f(C_{cc}, J_{TPB2}, C_{TPB2})$$

where $\eta_{TPB2}, J_{TPB2}, C_{TPB2}$, and $C_{cc}$ are the overpotential across, the current density passing through, the exchange current density at, and the capacitance of the TPB2, respectively. The nature and the treatment of TPB2 are essentially the same as described for TPB1. The impedance to the electron transfer across the cc/MIEC interface (excluding the TPB2), $Z_{cc}$, is given by

$$Z_{cc}(\omega) = \frac{\eta_{cc}(\omega)}{\partial J_{cc}(\omega)} = f(C_{cc}, J_{cc}, C_{cc})$$

where $\eta_{cc}, J_{cc},$, and $C_{cc}$ are the overpotential across, the current density passing through, the exchange current density at, and the capacitance of the MIEC/el interface (excluding the TPB2), respectively. This interface can be considered as a typical metal/semiconductor interface and the $J_{cc} - \eta_{cc}$ relationship can be described using a diode equation. The contribution of the MIEC/gas interface at $x = 0$ to electrode kinetics has been included in Eq. 3f.

### Parallel Reaction Paths

The equivalent circuit shown in Fig. 4 clearly indicates that there are three parallel paths for oxygen reduction or evolution to occur in the cell:

1. The reaction at the TPB1 (Eq. 1b), which requires transport of electronic defects to or away from the TPB1 through the MIEC and transport of $O_2$ to or away from the TPB1 through the pores of the MIEC, but does not require any transport of ionic defects through the MIEC electrode.
2. The reaction at the MIEC/gas interface (Eq. 1h), which requires simultaneous transport of both ionic and electronic defects to or away from the MIEC/gas interface through the MIEC and transport of $O_2$ to or away from the MIEC/gas interface through the pores of the MIEC; and
3. The reaction at the TPB2 (Eq. 1g), which requires transport of ionic defects to or away from the TPB2 through the MIEC and transport of $O_2$ gas to or away from the TPB2, but does not require any transport of electronic defects through the MIEC electrode.

The relative significance of each path depends critically on the transport ($\rho_i, \rho_b, \text{and } \rho_p$) and the catalytic ($\rho_c$) properties of the MIEC electrode as well as the nature of the MIEC/el and cc/MIEC interfaces. The effect of $O_2$ transport in the pores of the MIEC is schematically included in the interfacial impedance $Z_{TPB1}, Z_{TPB2}, \text{and } \rho_i$. Clearly, oxygen transport in the MIEC and the reaction at the MIEC/gas interface are only part, not the entirety, of the electrode kinetics. Unlike liquid electrochemical systems (with porous electrodes involving liquid electrolytes), TPBs in a solid-state system (with porous MIEC electrodes exposed to a gas) are the most important sites for electrode reactions. In general, the reactions occurring at least at one of the TPBs are an important part of the electrode kinetics and cannot be ignored without careful analysis and adequate justification. Consideration of at least one of the TPBs is a minimum requirement for any meaningful modeling of a solid-state system and failing to recognize TPBs as parallel paths to the MIEC/gas interface may result in erroneous conclusions. For instance, in the absence of either ionic or electronic transport in the MIEC, electrode reaction may only occur at one of the TPBs.

### Effect of Transport and Catalytic Properties of the MIEC

**Limiting case I: zero ionic conductivity.**—In the limit of $\rho_i \to \infty$ (i.e., the electrode is, in fact, a pure electronic conductor such as Pt or Ag), $R_{MIEC} \to \infty$, and $Z_{cc} \to \infty$ and, hence, the reactions described by both Eq. 1f (the second path) and Eq. 1g (the third path) are unable to proceed. The only viable reaction path, then, is the first one, the reaction through the TPB1 described by Eq. 1b. Accordingly, the equivalent circuit shown in Fig. 4 reduces to the one shown in Fig. 5a. The total cell impedance, $Z_{cell}$, can then be expressed as

$$Z_{cell} - R_e = Z_{TPB1}$$

This equation is identical to Eq. C-5 in our earlier analysis, which may reduce to

$$Z_{cell} - R_e = Z_{TPB1}$$

since it is usually true that $Z_{cell} \ll Z_{TPB1}$ and $R_{MIEC} \ll R_e$ for cells with electrodes of good electronic conductors. This equation implies that the electrode kinetics and the cell impedance are dominated by the processes occurring at TPB1. In general, $Z_{TPB1}$ may include two contributions, the impedance to charge transfer across the TPB1 and the impedance to the associated mass transfer in the vicinity of the TPB. The impedance to mass transfer is frequency-dependent and can be approximated by the Warburg impedance.

$$Z_{M} = R_m \frac{\tanh(\sqrt{\omega}R_m/\sqrt{C_m})}{\sqrt{\omega}R_m}$$

where $R_m$ represents the steady-state mass-transfer resistance (since $Z_{M} \to R_m$ as $\omega \to 0$) and $\omega$ corresponds to the time constant of the mass transport in the boundary layer adjacent to the interface. Clearly, the mass-transfer impedance vanishes at sufficiently high frequencies ($Z_{M} \to 0 $ as $\omega \to \infty$) when the mass transport can no longer follow the changes in the applied perturbation.

Similarly, the impedance to charge transfer can be approximated by a resistance to charge transfer, $R_{ct}$, and an interfacial capacitance due to accumulation or depletion of charges at the TPB1, $C_{TPB1}$, as schematically shown in Fig. 5b. If the Butler-Volmer equation is used to approximate the charge-transfer process, the $R_{ct}$ can be defined as

$$R_{ct} = \lim_{\omega \to 0} \frac{\partial \eta_{TPB1}(\omega)}{\partial J_{TPB1}(\omega)} = \frac{RT}{F} \left( \frac{1}{\alpha_i + \alpha_e} \right) \frac{1}{J_{TPB1}}$$

where $\alpha_{anodic}$ and $\alpha_{cathodic}$ are the anodic and cathodic transfer coefficient, respectively, and $J_{TPB1}$ depends primarily on the...
intrinsic catalytic activity of the TPB1, which is critically influenced by the properties of the MIEC and the electrolyte, including oxygen transport in the MIEC and surface catalytic properties.

Figure 6 shows several predicted spectra of the interfacial impedance, $Z_{\text{TPB1}}$, using the equivalent circuit shown in Fig. 5b and Eq. 4b and c. In Fig. 6a, the resistance to charge transfer is assumed to be comparable to the resistance to mass transfer ($R_{\text{ct}} = R_{\text{mt}}$) and the relaxation time constant for mass transfer is varied in orders of magnitude (from 0.01 to 100 s). The shapes of the interfacial impedance, $Z_{\text{TPB1}}$, are greatly influenced by the ratio of the time constant for mass transfer to that for charge transfer. In Fig. 6b, $R_{\text{ct}}$ is assumed to dominate the interfacial impedance ($R_{\text{mt}} \gg R_{\text{ct}}$), and, again, the time constant for mass transfer has dramatic effect on the shapes of $Z_{\text{TPB1}}$. In Fig. 6c, $R_{\text{ct}}$ is assumed to dominate the interfacial impedance ($R_{\text{mt}} \gg R_{\text{ct}}$) and the shapes of $Z_{\text{TPB1}}$ are determined primarily by the charge-transfer process. The predicted spectra indicate that the equivalent circuits and derived equations can be used to interpret the impedance response of a cell with electrodes of a pure electronic conductor (such as Pt or Ag). Further, they can be used to approximate the impedance response of a cell with MIEC electrodes of infinite thickness and high electronic conductivity, when the rate of oxygen diffusion in the MIEC or the surface reaction rate is much slower than any other processes occurring in the cell, as described elsewhere.9

Limiting case II: zero electronic conduction.—In the limit of $\rho_e \to \infty$ (i.e., the electrode is, in fact, a pure ionic conductor), $R_{\text{MIEC}} \to \infty$ and $\eta_{\text{ed}} \to \infty$ and, hence, the reaction through either the first path (Eq. 1b) or the second path (Eq. 1f) is unable to proceed. The only possible reaction path, then, is the third one, the reaction through the TPB2 described by Eq. 1g. The total cell impedance can then be approximated by

$$Z_{\text{cell}} = R_{\text{ct}} + 2[Z_{\text{TPB1}} + Z_{\text{MIEC}}], \quad R_{\text{ct}} = R_{\text{ct}} + 2R_{\text{MIEC}} \tag{5}$$

Obviously, the porous electrode with $\rho_e \to \infty$ is unable to function as an electrode; it acts only as an extension of the electrolyte because of the lack of electronic transport. As a result, the electrode kinetics is dominated by the processes occurring at TPB2. Again, both charge and mass transfer at or near the TPB2 may significantly influence the electrode kinetics and hence cell impedance. The treatment of TPB2 is similar to that of TPB1 as discussed earlier.

Limiting case III: zero catalytic activity.—In the limit of $\rho_e \to \infty$, $\eta_{\text{ed}} \to \infty$, and, hence, the reaction described by Eq. 1f (the second path) is still unable to proceed, or the MIEC/gas interface is still inactive. The cell impedance can be expressed as

$$Z_{\text{cell}} = R_{\text{ct}} + 2\left[\frac{(Z_{\text{TPB1}} + R_{\text{MIEC}} + Z_{\text{ed}})(Z_{\text{ed}} + R_{\text{MIEC}} + Z_{\text{TPB2}})}{(Z_{\text{TPB1}} + R_{\text{MIEC}} + Z_{\text{ed}})(Z_{\text{ed}} + Z_{\text{TPB2}})}\right] \tag{6a}$$

which may be approximated by

$$Z_{\text{cell}} = R_{\text{ct}} + 2\left[\frac{(Z_{\text{TPB1}})(Z_{\text{TPB2}})}{Z_{\text{TPB1}} + Z_{\text{TPB2}}}\right] \tag{6b}$$

if the MIEC is sufficiently conductive both ionically and electronically so that $(R_{\text{MIEC}} + Z_{\text{ed}}) \ll Z_{\text{TPB1}}$ and $(R_{\text{MIEC}} + Z_{\text{ed}}) \ll Z_{\text{TPB2}}$. Under these conditions, the electrode kinetics and cell impedance are controlled by TPB1 and TPB2.

The representative case.—The most important class of MIECs for electrode applications are those which have overwhelming electronic conductivity, i.e., $\rho_e \ll \rho_p$, but with finite rate of ionic transport and finite rate of surface reaction ($\rho_p$ and $\rho_e$ are finite). Under this condition, $R_{\text{MIEC}}$ in the circuit may be neglected since $R_{\text{MIEC}} \ll Z_{\text{TPB1}}$. In order to simplify the circuit further, one may increase the thickness of the porous MIEC until $R_{\text{MIEC}} \gg Z_{\text{TPB1}}$ and $R_{\text{MIEC}} \gg Z_{\text{ed}}$, so that the reaction through the third path (Eq. 1g) may be neglected. Under these conditions, the equivalent circuit in Fig. 4 can be adequately approximated by the ones shown in Fig. 7. Thus, the impedance of the cell can be approximated by
1. The first path (TPB1) dominating.—When $Z_{TPB1} << (Z_n + Z_{el})$, e.g., when the interfacial impedance $Z_{TPB1}$ is sufficiently smaller than the impedance of the MIEC, $Z_n$, Eq. 7b reduces to Eq. 4b. In other words, Eq. 4b (or Eq. C-5 in Ref. 9) defines the impedance of a cell with porous MIEC electrodes of infinite thickness when $Z_{TPB1}$ is sufficiently smaller than the impedance of any one of the following processes occurring in the cell: the transfer of ionic defects across the MIEC/el interface, the transport of ionic defects in the MIEC, or the kinetics of the reaction at the MIEC/gas interface (including the associated mass transfer in both solid and gas phases). Accordingly, the impedance of the cell is primarily determined by the impedance to the reaction at TPB1 (including associated mass transfer processes) while neither $Z_n$ nor $Z_{el}$ is observable in an impedance measurement. The MIEC/gas interface is practically inactive. Any effect of the MIEC on electrode kinetics must be due to the influence of the MIEC on the catalytic property of the TPB1.

2. The second path dominating.—When the processes occurring at or near the TPB1 are completely ignored (i.e., assuming that $Z_{TPB1} \to \infty$), Eq. 7b reduces to

$$Z_{cell} - \frac{R_{el}}{2} = Z_n + Z_{el}$$  \[8a\]

Under these conditions, naturally, the impedance of the cell is determined only by $Z_n$ and $Z_{el}$ while $Z_{TPB1}$ is not observable in an impedance measurement. Further, when $Z_n$ is completely ignored (i.e., assuming that $Z_n \to 0$), Eq. 8a reduces to

$$Z_{cell} - \frac{R_{el}}{2} = Z_{el}$$  \[8b\]

This equation implies that the impedance of the cell is dominated by the reactions at the MIEC/gas interface and the transport of defects in the MIEC (if the transport of $O_2$ in the pores is sufficiently fast). However, this does not represent a general case or “a more complex version” as claimed by Adler et al.; it represents, at best, an unrealistic case where the electrolyte-electrode interface is completely ignored. In fact, it is a consequence of failing to recognize TPBs as parallel paths to the MIEC/gas interface and failing to appreciate the significance of TPBs in solid-state systems. In general, Eq. 7a should be used to describe the impedance of a cell with MIEC electrodes of infinite thickness ($L \to \infty$) and uniform Fermi level ($p_0 \to 0$).

**Effect of Electrode Thickness ($L$)**

The effectiveness of the MIEC/gas interface of a porous MIEC electrode, characterized by $Z_n$, is determined not only by the transport and catalytic properties of the MIEC but also by the thickness of the MIEC, as implied by Eq. 3f. In order to estimate the effect of $L$ on $Z_n$, it is assumed in the following discussion that $p_0, p, \rho, \rho_0$ are relatively uniform throughout the thickness of the MIEC (or consider them to be the average values over the thickness of the MIEC electrode). Under this assumption, Eq. 3f reduces to

$$\frac{1}{Z_n(L)} = G_1(L) + G_2(L)$$  \[9a\]

where

$$G_1(L) = \frac{1}{(1 - \rho)(1 - \rho_0)} + \frac{\rho L}{(1 - \rho_0)}$$  \[9b\]

$$G_2(L) = \int_0^L \left( -\rho x^2 + \rho_0 a + \rho_0 (L - x)^2 \right) dx$$  \[9c\]

Clearly, the $G_1$ represents the contribution from the surface (or MIEC/gas interface) at $x = 0$ of the MIEC electrode. While the effect of $L$ on $G_1$ is apparent as implied by

---

**Fig. 7.** (a) An equivalent circuit for a cell with electrodes of a porous MIEC of infinite thickness and (b) an approximation to the circuit shown in (a) when $Z_{TPB1}$, $R_{el}$, and $Z_{el}$ are negligible. Further, similar to the approximation made to $Z_{TPB1}$ in Fig. 5, the $Z_n$ is approximated by a capacitor, $C_n$, in parallel to a charge-transfer resistance, $R_{CT, MIEC}$, and a Warburg impedance, $Z_{W, MIEC}$, where $R_{CT, MIEC} = R_{n, MIEC} + \lim_{L \to \infty} Z_{W, MIEC}$.

$$Z_{cell} = R_{el} + 2 \left[ Z_n + \frac{Z_{TPB1}(Z_n + Z_{el})}{Z_{TPB1} + (Z_n + Z_{el})} \right]$$  \[7a\]

This is the expression for the impedance of a cell with two identical MIEC electrodes of infinite thickness and sufficiently high electronic conductivity. Since the interfacial impedance, $Z_{cell}$, is typically small under the assumptions (particularly when the contact between the MIEC and the current collector is made ohmic, which can be accomplished by tailoring the Fermi levels of the two materials), Eq. 7a simplifies to

$$\frac{Z_{cell} - R_{el}}{2} = \frac{Z_{TPB1}}{Z_n + Z_{el}} = \frac{Z_{el}}{Z_n + Z_{el}}$$  \[7b\]

Equations 7a and 7b as well as the equivalent circuit shown in Fig. 7 imply that the oxygen reduction or evolution has two parallel paths. One path is the direct electrochemical reaction at the TPB1 at $x = L$ while the other path is the MIEC/gas interface. The second path involves several sequential steps: transfer of ionic defects across the MIEC/el interface ($Z_n$), transport of ionic defects to or away from the MIEC/el interface through the MIEC ($\rho_0$), and the kinetics of the reaction at MIEC/gas interface ($\rho$), which may also be influenced by the $O_2$ transport in the pores. Similar to the approximation made to $Z_{TPB1}$ shown in Fig. 5b, the circuit element characterizing the effectiveness of the MIEC/gas interface, $Z_n$, may also be approximated by a proper combination of a charge-transfer resistance ($R_{CT, MIEC}$), a capacitance ($C_n$), and a Warburg impedance to mass transfer ($Z_{W, MIEC}$), as shown in Fig. 7b.

When the impedance of one path is much greater than that of the other path, Eq. 7b can be simplified further.
Eq. 9b, the dependence of $G_\alpha$ on $L$ is complex and further analysis is necessary in order to gain some insight. In particular, $G_\alpha$ diminishes as $a_\alpha \rightarrow 1$ and as $p_\alpha$ or $L$ increases. When $p_\alpha \gg p_\alpha$ or $L$ is sufficiently large, in fact, $G_\alpha$ is negligible and $1/\Sigma_a = G_\alpha$. Thus, in the following discussions, we focus only on the effect of $L$ on $G_\alpha$.

Depending on the relative values of $p_\alpha$ and $p_\alpha$, integration of Eq. 9c may result in different expressions for $G_\alpha$ ($L$).

Since the most representative MIECs for electrode applications are those with overwhelming electronic conductivity, the case with $p_\alpha > p_\alpha$ is discussed here in detail while the other two cases, $p_\alpha > p_\alpha$ and $p_\alpha = p_\alpha$, are briefly summarized in Appendix D.

Integrating Eq. 9c under the condition of $p_\alpha > p_\alpha$, we find that $G_\alpha (L)$ is given by

$$G_\alpha (L) = \frac{1}{f(L)} \arctan \left[ \frac{L \sqrt{f(L)}}{p_\alpha / a} \right], \quad 0 < L < \frac{p_\alpha - p_\alpha}{a \rho_\alpha \rho_\alpha}$$

or

$$G_\alpha (L) = \frac{1}{2 \sqrt{f(L)}} \ln \left[ \frac{p_\alpha / a + L \sqrt{f(L)}}{p_\alpha / a - L \sqrt{f(L)}} \right], \quad \frac{p_\alpha - p_\alpha}{a \rho_\alpha \rho_\alpha} < L < \frac{p_\alpha - p_\alpha}{2 \rho_\alpha \rho_\alpha}$$

or

$$\left[ \frac{p_\alpha - p_\alpha}{a \rho_\alpha \rho_\alpha} \right]^{1/2} < L < \left[ \frac{p_\alpha - p_\alpha}{a \rho_\alpha \rho_\alpha} \right]^{1/2}$$

Differentiating Eq. 10a and b with respect to $L$, we find that the variation in $G_\alpha (L)$ with $L$ in each range of $L$ can be expressed, respectively, as

$$\frac{\partial}{\partial L} \left[ G_\alpha (L) \right] = \frac{p_\alpha L}{f(L)^{1/2}} \arctan \left[ \frac{L \sqrt{f(L)}}{p_\alpha / a} \right]$$

or

$$\frac{\partial}{\partial L} \left[ G_\alpha (L) \right] = \frac{1}{2 \sqrt{f(L)}} \ln \left[ \frac{p_\alpha / a + L \sqrt{f(L)}}{p_\alpha / a - L \sqrt{f(L)}} \right]$$

or

$$\frac{\partial}{\partial L} \left[ G_\alpha (L) \right] = \frac{1}{p_\alpha / a + p_\alpha L^2}$$

From a practical point of view, however, most MIECs for electrode applications satisfy the condition of $L < (p_\alpha / a)(p_\alpha / a)(p_\alpha / a)$. Accordingly, Eq. 10a and 12a may be adequate for most MIECs with $p_\alpha > p_\alpha$. In the limit of $p_\alpha \rightarrow 0$ (or $p_\alpha < p_\alpha$ and $p_\alpha L^2 << p_\alpha / a$), Eq. 10 and 12 reduce, respectively, to

$$G_\alpha (L) = \frac{1}{p_\alpha / a} \left[ L \sqrt{f(L)} \right]$$

or

$$\frac{\partial}{\partial L} \left[ G_\alpha (L) \right] = \frac{1}{p_\alpha / a + p_\alpha L^2}$$

Evaluation of Eq. 13 indicates that $G_\alpha (L)$, the effectiveness of the MIEC/gas interface for the electrode reaction, increases monotonically with thickness, $L$, and approaches a maximum as $L \rightarrow \infty$ (note that $G_\alpha (L)$ is an arctan functio
Ionic transport is sufficiently fast or the surface reaction is sufficiently slow [i.e., the ratio \( \rho/\rho_s \) is sufficiently large], \( G_{\text{el}}(L) \) increases linearly with the thickness of the MIEC, indicating that increase in thickness improves the effectiveness of the MIEC/gas interface. In the limit of \( \rho \to 0 \) and \( \rho_s \to 0 \), i.e., the transport of both ionic and electronic defects in the MIEC is much faster than the rate of surface reaction, the thicker the MIEC, the greater the \( G_{\text{el}}(L) \) for a given \( \rho/\rho_s \), simply because a thicker MIEC has more MIEC/gas interface area available for the reaction to take place. Under this condition, the entire MIEC/gas interface is electrochemically active for the electrode reactions.

Finally, it is important to recognize that the effect of electrode thickness on electrode kinetics is important only when the reaction passing through the MIEC/gas interface is significant. The relative significance of each path is influenced by the properties of the MIEC as well as the MIEC/el and cc/MIEC interface (including the TPBs). When \( Z_{\text{TPB}} \ll Z_s \) or \( Z_{\text{TPB}} \ll Z_{\text{el}} \), for instance, the reaction passing through the MIEC/gas interface is insignificant; the electrode kinetics are dominated by the TPBs and largely independent of electrode thickness. Under this condition, \( L_s \) or \( \delta \) has no practical significance.

**Conclusions**

Equivalent circuit analyses indicate that, in general, there are three parallel paths for reduction or evolution of oxygen in a cell with porous MIEC electrodes: (i) the reaction at the TPB between the electrolyte, the MIEC, and the gas phase, (ii) the reaction at the MIEC/gas interface, and (iii) the reaction at the TPB between the MIEC, the current collector, and the gas. The relative significance of each path is determined not only by the transport and catalytic properties of the MIEC electrode but also by the nature of the interfaces between the MIEC and other cell components (such as electrolyte and current collector). In general, the interfacial processes cannot be ignored without careful analysis and adequate justification and it is improper to state that oxygen diffusion in the MIEC electrode and the reaction at the MIEC/gas interface are the only processes that dominate the electrode kinetics of a cell with a porous MIEC electrode. In the absence of electronic transport in the MIEC, for instance, only the reaction at TPB1 may occur while in the absence of electronic transport in the MIEC, only the reaction at TPB2 may occur. Accordingly, failing to recognize TPBs as parallel paths to the MIEC/gas interface may result in erroneous conclusions.

The effectiveness of the MIEC/gas interface of a porous MIEC electrode is characterized by \( Z_{\text{el}} \), which is determined by the rates of several sequential processes necessary for the surface reaction to occur, including simultaneous transport of ionic and electronic defects in the MIEC, reaction at the MIEC/gas interface, and the transport of \( O_2 \) in the pores of the MIEC.

Further, as a first-order approximation, it is demonstrated that the thickness of the electrochemically active layer of the porous MIEC electrode, \( \delta \), varies dramatically with the properties of the MIEC and the nature of the interfaces. In general, \( \delta \) decreases with the increased rate of surface reaction and with decreased transport of ionic or electronic defects in the MIEC. In the absence of ionic or electronic transport, for instance, the \( \delta \) approaches zero, implying that oxygen reduction or evolution can occur only at TPB1 or TPB2. When the rate of ionic and electronic transport is much faster than the rate of the surface reaction, on the other hand, the thicker the electrode, the smaller the \( Z_{\text{el}} \) because more surface area becomes available for the reaction at the MIEC/gas interface to occur. Under this condition, the entire MIEC/gas interface is active for electrode reaction.
and the porous MIEC electrodes, the cell impedance can be approximated by

$$Z_{\text{cell}} - R_b = Z_{\text{el}}$$  \[A-2\]

where $R_b$ represents the "bulk resistance" of the cell and can be expressed as

$$R_b = R_{\text{el}} + 2R_{\text{MIEC}}$$  \[A-3\]

Further, when the dense electrolyte and porous electrodes are made of the same MIEC, impedance $Z_{\text{el}}$ at the MIEC/el interface may be neglected. Thus, $Z_{\text{el}}$ and $R_{\text{MIEC}}$ may be determined from impedance measurements of a cell with a configuration of $\text{Po}_{t_1}\text{cc}/\text{porous MIEC}/\text{dense MIEC}/\text{porous MIEC}/\text{cc}, t_2$. This cell can be used to determine the contact resistance between the cc and MIEC electrode, $R_{\text{MIEC}}$, and the electronic resistance of the MIEC electrode, $R_{\text{MIEC}}$.

**APPENDIX B**

**Composite MIEC Electrodes and Bulk Polarization**

When the porous MIEC electrode in the cell shown in Fig. 1 is a composite MIEC consisting of two or more phases, the equivalent circuit (Fig. 4) for approximation of the electrochemical behavior of such a cell will remain the same as long as the space-charge polarization within the solid phase of the MIEC is assumed to be insignificant. However, the electrochemical processes occurring in the porous electrode are different. For instance, the reaction at the MIEC/gas interface can no longer be described using Eq. 1f; the proper reaction should be written as

$$\text{V}^{\text{ic}}(\text{ic}) + 2e^{\text{ec}}(\text{ec}) + \frac{1}{2} \text{O}_2(\text{gas}) = \text{O}_2^+(\text{ic})$$  \[B-1\]

where ic and ec represent, respectively, the ionically conductive and electronically conductive phase of the composite MIEC electrode. Accordingly, the active sites for electrode reactions at the MIEC/gas interface are, in fact, the TPB between the ic, the ec, and O$_2$ gas. The nature and the treatment of the TPB at the MIEC/gas interface should be similar to those of the TPBs at the MIEC/el and cc/MIEC interfaces discussed earlier.

If the polarization processes are extended to the bulk of the MIEC, not confined to the MIEC/gas interface, the assumption of local charge neutrality in the MIEC may no longer be valid; the displacement current induced in the bulk phase of the MIEC, when a time-dependent electric field is applied, may become significant. Under these conditions, the impedance to the motion of electronic and ionic defects in the MIEC can no longer be adequately approximated by a pure resistance; the $R_{\text{MIEC}}$ and $R_{\text{MIEC}}$ as defined by Eq. 3d and 3e should be a complex quality because $R_b$ and $R_b$ are no longer pure resistive. In this case, the electrochemical behavior of an arbitrary element $m(1 \leq m \leq n)$ of the MIEC electrode can be approximated by the equivalent circuit shown in Fig. 1B-1. Compared to the circuit shown in Fig. 1a, two capacitances, $C_{\text{el}}$, and $C_{\text{el}}$, are added to element $m$ in order to take into consideration the polarization of, respectively, electronic and ionic defects in the bulk of the MIEC.

In general, the local specific impedance ($\Omega$ cm$^{-1}$) at an angular frequency $\omega$ to the motion of defect $k$ in an MIEC can be expressed as

$$p_k(x,\omega) = \frac{1}{x F} \left[ \frac{\partial N_p(x,\omega)}{\partial x} \right]$$  \[B-2\]

Thus, the specific impedance to the motion of electronic and ionic defects can then be expressed, respectively, as

$$\frac{1}{p_e(x,\omega)} = \sum_k \left( \frac{1}{p_k(x,\omega)} \right)$$  \[B-3a\]  $k = \text{electronic defects}$

$$\frac{1}{p_i(x,\omega)} = \sum_k \left( \frac{1}{p_k(x,\omega)} \right)$$  \[B-3b\]  $k = \text{ionic defects}$

In a steady state ($\omega \to 0$) or in the absence of significant bulk polarization (i.e., $V_{\text{c}} = 0$), Eq. B-3a and B-3b reduce, respectively, to

$$p_e(x) = \frac{1}{F^2[u_e(x) + u_c(x)]}$$  \[B-4a\]

$$p_i(x) = \sum_k \frac{1}{x_k^2 F^2 u_i(x)}$$  \[B-4b\]  $k = \text{ionic defects}$
APPENDIX C

Transmission Line Model and Derivation of Eq. 3f

Imagine that the MIEC electrode of thickness \( L \) is sliced into \( n \) layers, each with thickness of \( L/n \). If \( Z_{rm,m} \) and \( Z_{rm} \) represent the impedance to electronic transport, ionic transport, and the impedance to the reaction at the MIEC/gas interface of a single layer \( m \) (where \( 1 \leq m \leq n \)), the electrochemical behavior of the cell can be approximated by a discretized form of a transmission line model as schematically shown in Fig. 4a. In the absence of bulk polarization, \( R_{in} \) and \( R_{om} \) may be considered to be real while \( Z_{in} \) should be treated as a complex quantity in general due to interfacial polarization.

Consider an arbitrary element \( m \) (\( 1 \leq m \leq n \)) of the MIEC electrode. The reaction at the MIEC/gas interface (described by Eq. 1f) of element \( m \) requires that \( \nu_e \) ions transport from the electrolyte to the element, electrons \( (e') \) move from the cc to the element, and \( O_2 \) gas move to the element \( m \) through the pores of the MIEC. The impedance to the motion of electronic defects through the MIEC from the \( cc \) to the element \( m \) (or from the element \( m \) to the \( cc \)) can be expressed as

\[
\sum_{i=1}^{\infty} R_i = \sum_{i=1}^{\infty} \rho_i \left( \frac{L}{n} \right) \tag{C-1a}
\]

Similarly, the impedance to the motion of ionic defects through the MIEC to the element \( m \) (or from the element \( m \) to the electrolyte) is given by

\[
\sum_{j=1}^{\infty} R_{j} = \sum_{j=1}^{\infty} \rho_{j} \left( \frac{L}{n} \right) \tag{C-1b}
\]

While the impedance at an angular frequency \( \omega \) to the reaction at the MIEC/gas interface of element \( m \) can be expressed as

\[
Z_{rm}^{(m)}(\omega) = \frac{\rho_{m}^{(m)}(\omega)}{a_{m} \left( \frac{L}{n} \right)} \tag{C-1c}
\]

where the frequency-dependent \( \rho_{m} \) includes the impedance to the charge-transfer at the interface and the impedance to the associated mass-transfer near the interface of element \( m \). The \( a_m \) represents the specific area of the element, i.e., the ratio of the MIEC/gas interface area to the volume of element \( m \). Further, if the surface of the porous MIEC at \( x = 0 \) is not completely covered by the current collector \( (cc) \), the impedance to the reaction at this surface (or MIEC/gas interface at \( x = 0 \)) can be expressed as

\[
Z_{rm}^{(m)}(\omega) = \frac{\rho_{m}^{(m)}(\omega)}{(1-p)(1-\theta_{in})} \tag{C-1d}
\]

where \( p \) is the porosity of the MIEC and \( \theta_{in} \) is the fraction of the MIEC surface at \( x = 0 \) covered by the current collector.

The impedance to the reaction at the MIEC/gas interface of the element \( m \) and to the transport of the species involved in the reaction, \( Z_{m}^{(m)}(\omega) \), can be expressed as

\[
Z_{m}^{(m)}(\omega) = \sum_{i=1}^{\infty} R_{i} + Z_{rm}^{(m)}(\omega) + \sum_{j=1}^{\infty} R_{j} \tag{C-2a}
\]

Similarly, the impedance to the reaction at the MIEC/gas interface at \( x = 0 \) and to the transport of the species involved in the reaction, \( Z_{m}(\omega) \), can be expressed as

\[
Z_{m}(\omega) = \frac{\rho_{m}(\omega)}{(1-p)(1-\theta_{in})} + \sum_{j=1}^{\infty} R_{j} \tag{C-2b}
\]

Accordingly, summation of \( Z_{m}^{(m)}(\omega) \) over all elements (from \( m = 1 \) to \( m = n \)), together with \( Z_{m}(\omega) \), results in \( Z_{in}(L, \omega) \), the total impedance to the reaction at the entire MIEC/gas interface (of a porous MIEC electrode of thickness \( L \)) and to the transport of the species involved in the surface reaction

\[
\frac{1}{Z_{in}(L, \omega)} = \frac{1}{Z_{rm}(L, \omega)} + \sum_{m=1}^{n} \left[ \frac{1}{Z_{m}^{(m)}(\omega)} \right]
\]

\[
= \frac{1}{\rho_{m}^{(m)}(\omega)} \left( 1-p \right) \left( 1-\theta_{in} \right) + \sum_{m=1}^{n} \rho_{m} \left( \frac{L}{n} \right)
\]

\[
+ \sum_{m=1}^{n} \left[ \sum_{i=1}^{\infty} \rho_{i} \left( \frac{L}{n} \right) + \rho_{m}^{(m)}(\omega) \left[ a_{m} \left( \frac{L}{n} \right) + \sum_{j=1}^{\infty} \rho_{j} \left( \frac{L}{n} \right) \right] \right] \tag{C-3}
\]

The first term represents the contribution from the MIEC/gas interface at \( x = 0 \) while the second term corresponds to the contribution from the rest of the MIEC (\( 0 < x < L \)).

As the number of layers, \( n \), approaches infinity (or the thickness of each layer, \( L/n \), approaches infinitesimal), the discretized form of the transmission line model is transformed to a continuous form of the model. In this limit, \( R_{in}, R_{om}, R_{pm}, R_{om}, \rho_{m}, \rho_{pm}, \rho_{om}, \) and \( L/n \) of an arbitrary element in the discretized model should be replaced, respectively, with \( dR_{in}, dR_{om}, dZ_{in}, dZ_{om}, \rho_{in}, \rho_{om}, \) and \( dx \) for a differential element at a distance \( x \) away from the cc/MIEC interface in the continuous model. The differential circuit elements \( (dR_{in}, dR_{om}, \) and \( dZ_{in} \) to \( dZ_{om} \)) are related to the local properties of the MIEC, \( \rho_{in}, \rho_{om}, \) and \( \alpha(x) \), as follows

\[
dR_{in} = \rho_{in}(x) \frac{dx}{z}\]

\[
dR_{om} = \rho_{om}(x) \frac{dx}{z}\]

\[
dZ_{in}(\omega) = \frac{\rho_{in}(x, \omega)}{\alpha(x) \frac{dx}{z}} \tag{C-4}
\]

Accordingly, the summations in Eq. C-1 to C-3 should be replaced with integrals and Eq. C-3 is then transformed to Eq. 3f.

APPENDIX D

Effect of \( L \) on \( G_{fr} \), for \( \rho_{fr} > \rho_{in} \) and \( \rho_{in} > \rho_{fr} \)

MIECs with predominating ionic conduction (\( \rho_{fr} > \rho_{in} \)). Integrating Eq. 9e under the condition that \( \rho_{fr} > \rho_{in} \) (i.e., the rate of ionic transport is faster than that of electronic transport), we arrive at equations similar to Eq. 10 and 12 because of the symmetrical contribution of ionic and electronic transport in the MIEC to \( G_{fr} \). The only modifications needed are to redefine \( x = 0 \) at the MIEC/cc interface and to exchange the position of \( \rho_{fr} \) and \( \rho_{in} \) in the Eq. 9e, 10 to 12, and 17. For instance, the \( f(L) \) defined by Eq. 11 should be redefined as

\[
f(L) = \frac{\rho_{fr}(\rho_{fr} - \rho_{in})}{a_{fr} L_{fr}^{2}} \tag{D-1}
\]

These changes, however, have no effect on the description of the MIEC electrode or the cell, since \( Z_{in} \) is defined as the total impedance of an MIEC electrode with thickness \( L \). Accordingly, all discussions and conclusions described earlier for the case \( \rho_{fr} < \rho_{in} \) also applicable to the case \( \rho_{fr} > \rho_{in} \) provided that the position of ionic transport is exchanged with that of electronic transport.

For instance, in the limit of \( \rho_{fr} \to 0 \) or \( \rho_{fr} \gg \rho_{fr} \), the characteristic thickness \( L_{fr} \) is then determined primarily by the rate of electronic transport and surface reaction. The mathematical description is identical to Eq. 13 to 16, provided that the \( \rho_{fr} \) is in the equations are replaced with \( \rho_{fr} \).

The only difference between the case of \( \rho_{fr} > \rho_{fr} \) and that of \( \rho_{fr} < \rho_{fr} \) is the distribution of the reaction at the MIEC/gas interface along the thickness of the electrode. For the case \( \rho_{fr} > \rho_{fr} \), the rate of the reaction at MIEC/gas interface (Eq. 1f) increases toward the MIEC/cc interface. In contrast, for the case \( \rho_{fr} > \rho_{fr} \), the rate of the same reaction increases toward the cc/MIEC interface.
MIECs with equal ionic and electronic conduction ($\rho_i = \rho_e$).—When the rate of ionic transport is identical to the rate of electronic transport, integration of Eq. 9c yields

$$\frac{1}{Z_n(L)} = \left(\frac{1}{2L_p}\right) \ln \left(\frac{\rho_i/a + L_p}{\rho_i/a - L_p}\right), \quad \rho_i = \rho_e \quad \text{[D-2]}$$

Differentiating this equation with respect to $L$, we find that the variation in $G_n(L)$ with $L$ is given by

$$\frac{\partial}{\partial L} G_n(L) = \frac{1}{2L_p} \ln \left(\frac{\rho_i/a + L_p}{\rho_i/a - L_p}\right) + \frac{2\rho_i/a}{(\rho_i/a)^2 - (L_p)^2} \quad \text{[D-3]}$$

Thus, Eq. D-2 and D-3 can be used to determine how the transport ($\rho_i$ or $\rho_e$) and catalytic ($\rho_i/a$) properties and the thickness ($L$) of an MIEC electrode influence the effectiveness of the MIEC/gas interface, $G_n(L)$.

LIST OF SYMBOLS

- **a** surface area of a porous MIEC electrode per unit volume, $\text{cm}^2$
- **$C_{\text{MIEC}}$, $C_{\text{CMIEC}}$** capacitance due to polarization of electronic and ionic defects, respectively, in bulk phase of element $m$ ($1 \leq m \leq n$) in Fig. B-1, $F/\text{cm}^2$
- **$C_{\text{C}}$** capacitance of the MIEC/gas interface per superficial area of electrode, $F/\text{cm}^2$
- **$C_{\text{TPB}}$, $C_{\text{TPB2}}$** capacitance of TPB1 per superficial area of electrode, $F/\text{cm}^2$
- **$f(L)$** Faraday's constant, 96,487 C equiv$^{-1}$
- **$G_n$** as defined by Eq. 9c, $\Omega^{-1}$ cm$^{-2}$
- **$G_{\alpha}$** as defined by Eq. 9b, $\Omega^{-1}$ cm$^{-2}$
- **$j_e$, $j_m$** electronic and ionic current density, respectively, $A/\text{cm}^2$
- **$J_{\text{TPB1}}, J_{\text{TPB2}}$** current density passing through TPB1 and TPB2, respectively, $A/\text{cm}^2$
- **$L$** thickness of a porous MIEC electrode, $\text{cm}$
- **$L_i$** characteristic thickness of a porous MIEC electrode, $\text{cm}$
- **$L_{el}$** thickness of electrolyte, $\text{cm}$
- **$N_k$** molar flux of species $k$, mol cm$^{-2}$ s$^{-1}$
- **$P$** porosity of the MIEC electrode, dimensionless
- **$P_{0}$** partial pressure of oxygen, atm
- **$r$** net consumption rate of $V^+_0$ at the MIEC/gas interface, mol cm$^{-2}$ s$^{-1}$
- **$R$** universal gas constant, 8.314 J mol$^{-1}$ K$^{-1}$
- **$R_{\text{ct}}$, $R_{\text{rel}}$** bulk resistance of a cell ($R_{\alpha} = \lim Z_{\alpha}(s)$), $\Omega$ cm$^2$
- **$R_{\alpha}$**, $R_{\alpha MIEC}$, $R_{\alpha,\text{cc/MIEC}}$, $R_{\alpha MIEC, MIEC}$ resistance to the motion of electronic and ionic defects, respectively, in the entire MIEC as defined by Eq. 3d and 3e, $\Omega$ cm$^2$
- **$R_{\alpha,\text{MIEC}}$, $R_{\alpha,\text{MIEC}}$** resistance to the motion of electronic and ionic defects, respectively, through the entire MIEC as defined by Eq. 3d and 3e, $\Omega$ cm$^2$
- **$t_e$, $t_i$** electronic and ionic transference number, dimensionless
- **$t_{\text{rel}}$** relaxation time constant for mass-transfer, s
- **$T$** absolute temperature, K
- **$u_k$** absolute mobility of species $k$, mol cm$^{-2}$ s$^{-1}$ K$^{-1}$
- **$v$** bulk velocity of gas in the pores of MIEC, $\text{cm}$ s$^{-1}$
- **$x$** distance away from the cc/MIEC interface, $\text{cm}$
- **$x_k$** number of effective charge carried by defect $k$, dimensionless
- **$Z_{\alpha}$** impedance to the reaction at the entire MIEC/gas interface and to the transport of the species involved in the surface reaction (as defined by Eq. 3f), $\Omega$ cm$^2$
- **$Z_{\alpha,\text{cc}}$, $Z_{\alpha,\text{MIEC}}$, $Z_{\alpha,\text{el}}$** impedance to electron transfer across cc/MIEC and MIEC/el interface, respectively, $\Omega$ cm$^2$
- **$Z_{\text{cm}}$** impedance to ion transfer across MIEC/el interface, $\Omega$ cm$^2$
- **$Z_{\text{cm}}$** impedance to reaction at MIEC/gas interface of element $m$ in Fig. 4a, $\Omega$ cm$^2$
- **$Z_{\alpha,\text{TPB1}}, Z_{\alpha,\text{TPB2}}$** impedance to the reaction at TPB1 and TPB2 (including the impedance to the mass transfer associated with the reaction), respectively, $\Omega$ cm$^2$
- **$Z_w$** Warburg impedance as defined by Eq. 4c, $\Omega$ cm$^2$

Greek

- **$\alpha$, $\omega$** anodic and cathodic transfer coefficient, dimensionless
- **$\delta$** thickness of the electrochemically active layer of a porous MIEC electrode, cm
- **$\phi$** electrostatic potential, V
- **$\theta_{\text{er}}$** fraction of MIEC surface at $z = 0$ covered by current collector, dimensionless
- **$\eta$** overpotential across an interface due to charge and mass transfer [$\eta_l = \Delta V[5 + RT \ln (\gamma_c x_c) / F ]$, $J$ mol$^{-1}$]
- **$\mu_k$** electrochemical potential of defect $k$ ($\mu_k = \mu_{0,k} + RT \ln (\gamma_k x_k)$, $J$ mol$^{-1}$)
- **$\rho_e$** resistivity to motion of electronic and ionic defects in MIEC, respectively, $\Omega$ cm$^2$
- **$\rho_i$** resistivity to the reaction at the MIEC/gas interface (including the resistance to the mass transfer associated with the reaction), $\Omega$ cm$^2$
- **$\sigma_k$** partial conductivity ($\sigma_k = g_k F \mu_k c_k$) due to the motion of defect $k$, $\Omega$ cm$^{-2}$

Solid-phase and gas-phase tortuosity of the porous MIEC, respectively.

Subscripts

- **e** electronic
- **i** ionic
- **ct** charge transfer
- **mt** mass transfer

Abbreviations

- **el** electrolyte
- **MIEC** mixed ionic-electronic conductor
- **cc** current collector
- **TPB** triple-phase boundary
- **TPB1** TPB between the el, the MIEC, and $O_2$
- **TPB2** TPB between the cc, the MIEC, and $O_2$

REFERENCES

Characterizations of Iron-Containing Clay Modified Electrodes and Their Applications for Glucose Sensing

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ABSTRACT

An amperometric biosensor was constructed on the basis of ruthenium purple-containing clay and glucose oxidase for the direct assay of glucose. These clay-modified electrodes were characterized by cyclic voltammetry and flow injection techniques. The electrodes were very sensitive to the presence of glucose. Linear calibration curves between 10 μM and 15 mM with an electrode sensitivity of 3.88 μA/M and a detection limit of 10 μM were registered in aerated solutions (pH 5.1). Uric acid, ascorbic acid, and oxygen interfere very little with the detection of glucose. Long-term tests showed these clay electrodes were quite durable, e.g., the electrode sensitivity only decreases by ca. 25% over a period of six weeks.

Introduction

Metal ions are essential to living cells. For example, Na⁺, K⁺, and Ca²⁺ are important where transport of metabolites and energetic processes are occurring, and transition metals are active catalysts involved in many electron-transport systems. Among the transition metals, iron is the principal electron carrier in biological oxidation-reduction reactions. Haem groups (Fe²⁺) and hematin (Fe³⁺), often associated with protoporphyrin IX, are the coenzymes for a number of redox enzymes. These include catalase, which catalyzes the dismutation of hydrogen peroxide, and peroxidases, which catalyze the reduction of alkyl hydroperoxides. However, the role of iron-containing complexes in the catalysis of biochemical or chemical reactions still needs to be explored.

Recently amperometry-based glucose biosensors have received increased attention due to a clinical demand. Research activity has focused on accelerating the slow electron transfer between the reduced glucose oxidase (GOXred) and the probe material and enhancing the sensitivity of the probe to hydrogen peroxide, which is generated by the enzyme-catalyzed reactions. To date, excellent results in terms of sensitivity and reproducibility in the detection of glucose have been reported and a substantial number of papers have been published. The results indicate that the amperometric biosensor is easy to fabricate and has a low detection limit.

Electrode preparations.—Clay-modified electrodes were fabricated on conductive SnO₂ glass (indium-doped 0.7 mm thick, 20 Ω/cm², Delta Technologies). Typically, 20 μl/cm² of a clay slurry (1 g/liter water, denoted solution A) was first cast on the glass squares and dried at an ambient temperature (ca. 25°C). After this, 20 μl/cm² of a GOX solution (denoted solution B) was cast onto the resulting glass squares (denoted sandwich-type clay electrodes). Solution B contained 5 ml GOX (25 g/liter water), 3 ml of the aqueous glutaraldehyde (GA, 4%), and 5 ml BSA (20 g/liter water). Poly(methyl methacrylate (PMMA) or poly(o-phenylenediamine) (PPD) were also used instead of the glutaraldehyde described elsewhere. The clay/RP particles were prepared by reacting 9 mg of ruthenium hexamine with 100 mg of the clay in 20 ml sulfuric acid (0.2 M) with constant stirring for 4 h.

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