Fundamental issues in modeling of mixed ionic-electronic conductors (MIECs)

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Abstract

The reaction at an MIEC/gas interface is electrochemical in nature when one of its charge-transfer steps influences the rate of the overall reaction. Changes in electrical states of the surfaces of an MIEC may not only enhance or hinder the rate of the reaction but also reverse the direction of the reaction (from anodic to cathodic or vice versa). Expressions similar to the Butler–Volmer equation are the most proper phenomenological description of the kinetics at an MIEC electrode, although the effect of the electrical state can be much smaller than that of the chemical state under certain conditions. Unless the kinetics are infinitely fast, the instantaneous relationship among concentrations of the species involved in a reaction is determined more by kinetics than thermodynamics. If an MIEC is assumed to be metallic in which bulk dielectric displacement cannot occur, both electric field and polarization in the bulk phase must vanish. If a huge capacitive response of an MIEC is indeed caused by space-dependent bulk polarization, displacement current density in the MIEC cannot be ignored in impedance analysis and the validity of local electroneutrality must be carefully evaluated. If local electroneutrality prevails, dielectric displacement vanishes, and the Fermi level is uniform in an MIEC, then the concentration of all defects must be uniform as must be the composition of the MIEC. It is important to adhere to these fundamental principles in order to obtain proper relations for the ionic, electronic, and oxygen fluxes and the correct influence of the interfaces on the charge-transfer and chemical reactions. © 1999 Published by Elsevier Science B.V. All rights reserved.

1. Introduction

Porous mixed ionic-electronic conductors (MIECs) have been widely used as electrodes [1–3] for various solid state ionic devices such as solid oxide fuel cells and gas sensors to extend the reaction sites beyond the triple-phase boundaries (TPBs). How-ever, many fundamental issues regarding electrode kinetics and transport of defects and gas through a porous MIEC electrode have not been totally resolved. Most misconceptions about MIECs have originated from misunderstanding of basic solid-state physics and solid-state electrochemistry [4]. These misconceptions hinder the modeling of MIECs and the performance prediction of solid-state systems involving MIECs. An equivalent circuit approximation [5] has been used to illustrate the reaction
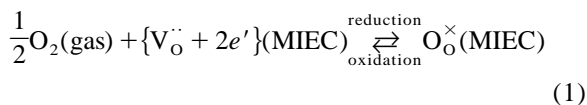
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paths in a solid-state cell with porous MIEC electrodes; it is clearly demonstrated that consideration of TPBs as parallel path to MIEC/gas interface is not a redundant, but a minimum requirement for any meaningful analysis of the system. Also, impedance spectroscopy [6] has been used to clarify some of the confusions on mechanism and electrode kinetics of porous MIEC electrodes; the reactions at a porous MIEC electrode are electrochemical in general and their impedance response is influenced not only by the properties of the MIEC but also by the interfaces between the MIEC and other cell components. While the distribution of immobile charges in an MIEC and the definition of thermodynamic factors have been discussed elsewhere [7], misconceptions on them will be elaborated in this paper. In particular, to be addressed in detail are the nature of the reactions at an MIEC/gas interface, the effect of thermodynamics and kinetics, the validity of electroneutrality and other assumptions, as well as the definition of dielectric displacement, polarization, and 'metallic' MIECs.
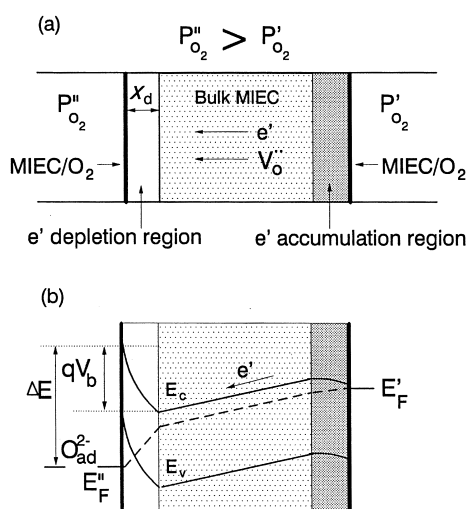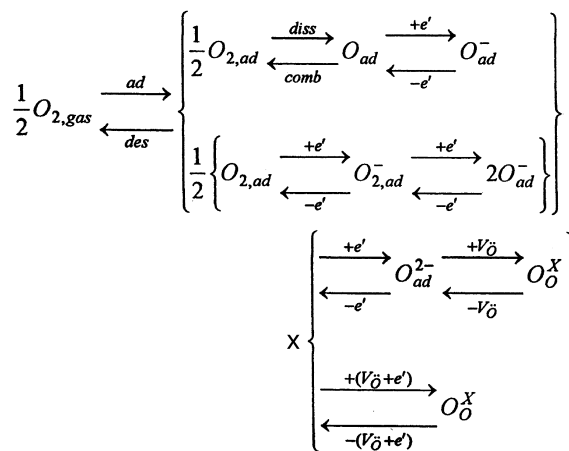

Fig. 1. (a) A schematic diagram showing that an electrically-isolated n-type MIEC membrane is subject to a chemical driving force – exposed to a gas having p'_{O_2} on one side (right) and to another gas having p''_{O_2} on the other side (left). (b) An energy band diagram for the n-type MIEC under the condition that $p''_{O_2} > p'_{O_2}$ i.e. oxygen permeating from left to right while electrons transporting from right to left.

2. The nature of the reactions at an MIEC/gas interface

Schematically shown in Fig. 1a is an MIEC membrane, with e' and $V_O^{\cdot\cdot}$ as the majority defects, exposed to a gas having p''_{O_2} on the left side and to another gas having p'_{O_2} on the right side. When $p''_{O_2} > p'_{O_2}$ oxygen will permeate through the MIEC from left to right. The overall reaction for oxygen reduction (on the left side) and evolution (on the right side) at the MIEC/O$_2$ interfaces can be expressed as

$$\frac{1}{2}O_2(gas) + \{V_O^{\cdot\cdot} + 2e'\}(MIEC) \underset{oxidation}{\overset{reduction}{\rightleftarrows}} O_O^{\times}(MIEC)$$

(1)

In order to determine the nature of this reaction, one must examine the nature of each elementary step, particularly the rate-limiting step, involved in the reaction [8]. Oxygen reduction or evolution may involve adsorption (ad) or desorption (des) of oxygen molecules on the surface of MIEC, dissociation (diss) of oxygen molecules to atoms or combination

(comb) of atoms to molecules, surface diffusion of adsorbed atoms from the adsorption sites to the active sites for electrochemical reactions or vice versa, charge transfer processes converting atomic or molecular species to ionic species or vice versa, and combination of oxygen ions with oxygen vacancies or removal of oxygen ions from regular lattice sites to form oxygen vacancies. Several reaction pathways are possible as follows,

$$\frac{1}{2}O_{2,gas} \underset{des}{\overset{ad}{\rightleftarrows}} \begin{cases} \frac{1}{2}O_{2,ad} \underset{comb}{\overset{diss}{\rightleftarrows}} O_{ad} \underset{-e'}{\overset{+e'}{\rightleftarrows}} O_{ad}^- \\ \frac{1}{2}\left\{O_{2,ad} \underset{-e'}{\overset{+e'}{\rightleftarrows}} O_{2,ad}^- \underset{-e'}{\overset{+e'}{\rightleftarrows}} 2O_{ad}^-\right\} \end{cases}$$

$$X \begin{cases} \overset{+e'}{\underset{-e'}{\rightleftarrows}} O_{ad}^{2-} \overset{+V_O^{\cdot\cdot}}{\underset{-V_O^{\cdot\cdot}}{\rightleftarrows}} O_O^X \\ \overset{+(V_O^{\cdot\cdot}+e')}{\underset{-(V_O^{\cdot\cdot}+e')}{\rightleftarrows}} O_O^X \end{cases}$$

If one of the charge transfer steps influences the rate of the overall reaction, the reaction should be considered electrochemical in nature. Consider one of the charge transfer steps,

$$O_{ad} + e' \rightarrow O_{ad}^{-} \tag{3a}$$

or

$$O_{ad}^{-} + e' \rightarrow O_{ad}^{2-} \tag{3b}$$

as an example to illustrate the electrochemical nature of this reaction. As electrons are brought to the MIEC surface (left) to form O_{ad}^{-} or O_{ad}^{2-}, an electron deficiency region is formed in the MIEC near the interface where net positive charges (ionized donor defects) are induced. The negative charges captured by the adsorbed oxygen on the surface are equal in number to the positive charges induced inside the MIEC. Schematically illustrated in Fig. 1b is an energy band diagram, in which V_b represents the potential barrier retarding the transfer of electrons from the interior of the MIEC to the MIEC/O_2 interface while ΔE corresponds to the energy barrier hindering the return of electrons back into the conduction band of the MIEC from the adsorbed oxygen ions due to thermal excitation of captured electrons. Even for degenerate semiconductors or metallic MIECs, when electrons are brought to surface to form O_{ad}^{-} or O_{ad}^{2-}, positive (image) charges are induced in the MIEC and a potential barrier exists at the interface. Thus, the essential features shown in Fig. 1b remain the same for all types of MIECs, although the thickness of the depletion layer (x_d) decreases with the density of charge carriers.

Clearly, the potential barrier at the interface can be raised or lowered by the external application of voltage across the interface, implying that the rate of the charge transfer step can be influenced by the electrical state of the MIEC.

2.1. Effect of electrical state on the rate of interfacial reactions

Schematically shown in Fig. 2a is a cell under the influence of a chemical and an electrical driving force. The chemical driving force is determined by p_{O_2}' and p_{O_2}'', which is also characterized by a Nernst potential,
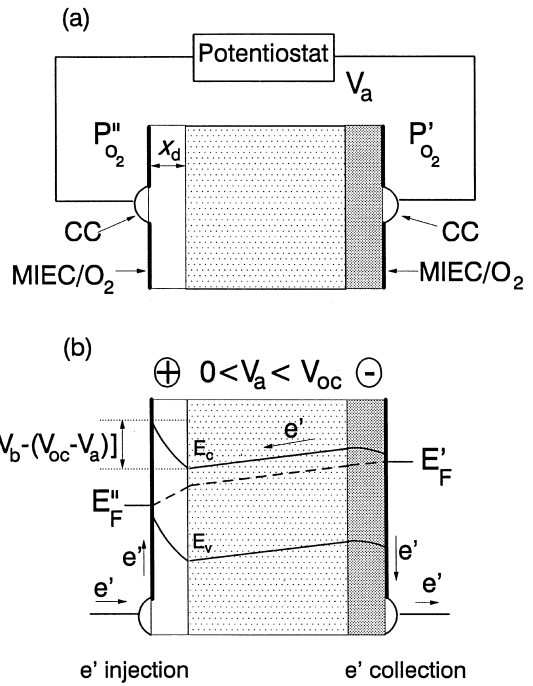

Fig. 2. (a) A schematic diagram showing that an n-type MIEC membrane is subject to both a chemical $p_{O_2}' < p_{O_2}''$ and an electrical ($V_\alpha \neq V_{oc}$) driving force. (b) An energy band diagram for the n-type MIEC under the condition that $0 < V_\alpha < V_{oc}$, i.e. electrons are injected by the cc into the left surface of the MIEC and collected by the cc from the right surface of the MIEC.

$$E_N = \left(\frac{RT}{4F}\right) \ln\left(\frac{p_{O_2}''}{p_{O_2}'}\right), \tag{4}$$

or an open circuit voltage across the MIEC [8],

$$V_{oc} = t_{V_O^{\cdot\cdot}}\{E_N - (\eta_a - \eta_c)\}. \tag{5}$$

The electrical driving force may be provided by a potentiostat, which sets the voltage across the MIEC (or the difference in Fermi levels of the two surfaces of the MIEC),

$$V_a = \frac{(E_F' - E_F'')}{F}. \tag{6}$$

Under the assumption of complete depletion of electrons in the electron deficiency region, the depletion region width can be estimated from [9]

$$x_d \approx \sqrt{\frac{2\epsilon_o \epsilon_r [V_b - (V_{oc} - V_a)]}{F \sum_i z_i c_i}} \qquad (7)$$

where ϵ_o is the permittivity of free space, ϵ_r is the relative permittivity (or dielectric constant) of the MIEC, F is Faraday's constant, z_i and c_i are charge and molar density of charge carriers in the depletion layer, and V_b is the potential barrier across the charge depletion layer when $V_{oc} = V_a$ (or in the absence of an applied electrical driving force). The effect of V_a on the rate and the direction of the reactions at the MIEC/gas interfaces depend on the relative amplitude of V_a, with respect to V_{oc} and E_N.

When $V_a = V_{oc}$, there is no external electrical driving force imposed on the MIEC; the reactions at MIEC/gas interface are driven merely by the chemical driving force. In this case, all electrons participating in the reduction of oxygen at the left surface,

$$\frac{1}{2} O_2(gas) + \{V_O^{\cdot\cdot} + 2e'\}(MIEC) \rightarrow O_O^{\times}(MIEC) \quad (1a)$$

must come from the right surface where electrons are generated by oxygen evolution (or oxidation),

$$O_O^{\times}(MIEC) \rightarrow \frac{1}{2} O_2(gas) + \{V_O^{\cdot\cdot} + 2e'\}(MIEC).$$
$$(1b)$$
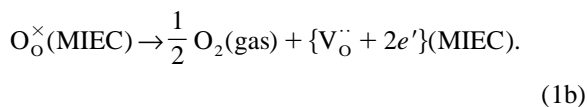
Thus, all electrons must transport through the interior of the MIEC and overcome the potential barrier, V_b, as schematically shown in Fig. 1b.

When $0 < V_a < V_{oc}$, the potential barrier near the left interface is reduced from V_b to $V_b - (V_{oc} - V_a)$ and x_d is reduced as well, as schematically shown in Fig. 2b. Accordingly, it is easier for electrons to transport to the left surface from the interior of the MIEC. Meanwhile, electrons are directly injected from the current collector (cc) into the left surface; these electrons may directly participate in oxygen reduction, Eq. (1a), without getting into the MIEC, further enhancing the kinetics of oxygen reduction. Similarly, electrons are directly collected by the cc away from the right surface, accelerating the rate of oxygen evolution, Eq. (1b). The smaller the voltage across the MIEC (V_a), the stronger the enhancement.

When $V_a = 0$, the Fermi level (or the driving force for electronic transport) is uniform throughout the MIEC and, thus, there is no net transport of electrons through the MIEC. All electrons participating in oxygen reduction at the left surface of the MIEC are injected from the cc while all electrons produced at the right surface of the MIEC by oxygen evolution are collected by the cc.

When $V_a < 0$, not only are the rates of the reactions at the MIEC/gas interfaces further enhanced but also the direction of electron transport within the MIEC is reversed, i.e. some of the electrons injected into the left surface are consumed by oxygen reduction at the surface and the rest transported from left to right.

When $V_{oc} < V_a < V_N$, however, not only the potential barrier but also the electron depletion layer thickness near the left interface increases with Va. Hence, the resistance to electron transport from the interior of MIEC to the left surface increases with V_a. At the same time, electrons are also taken away directly from the left surface and injected into the right surface, further hindering the rate of oxygen reduction and evolution. The larger the V_a, the stronger the retardation.

When $V_a = E_N$, the electrochemical potential of oxygen vacancies (or the driving force for ionic transport) is uniform throughout the MIEC, implying that there is no net transport of oxygen vacancies and hence the net rate of oxygen reduction and evolution vanishes.

When $V_a > E_N$, the direction of oxygen vacancy transport is reversed and so is the direction of interfacial reaction. Oxygen reduction, Eq. (1a), now occurs at the right surface while oxygen evolution, Eq. (1b), occurs at the left surface; oxygen is pumped from right (low p_{O_2}) to left (high p_{O_2}) side of the MIEC.

Clearly, the rates of the reactions at the two MIEC/gas interfaces depend critically on the electrical states of the two surfaces of the MIEC; the reactions are, indeed, electrochemical reactions, in contrast to the conclusions found in recent treatments, e.g. [10,11]. This is also consistent with experimental observations; impedance spectra [6] and polarization behavior [12,13] of solid-state cells with porous MIEC electrodes depend strongly on the electrical states of the MIEC electrodes.

2.2. Phenomenological rate expression

When $c_V \gamma_V M / d \ll 1$ or the concentration of oxygen vacancies at the surface is sufficiently small [8], the kinetics of the reactions can be most generally described using a phenomenological expression similar to the Butler–Volmer equation,

$$J_V = 2Fr$$
$$= J_{V,o}\left[\left(\frac{c_V^*}{c_V}\right) \exp\left(\frac{\alpha_a}{RT} \Delta\tilde{\mu}_e\right) \right.$$
$$\left. -\left(\frac{p_{O_2}}{p_{O_2}^*}\right)^{1/2} \exp\left(\frac{-\alpha_c}{RT} \Delta\tilde{\mu}_e\right) \right] \qquad (8a)$$

where r is the rate at which oxygen vacancies are produced or consumed, $\Delta\tilde{\mu}_e$ is the difference in electrochemical potential of electrons,

$$\Delta\tilde{\mu}_e = RT\Delta\ln(\gamma_e c_e) - F\Delta\phi \qquad (8b)$$

and $J_{V,o}$ is the exchange current density,

$$J_{V,o} = 2Fr_o$$
$$= k^\circ\left(\frac{2F}{RT}\right)(p_{O_2}^*)^{(1/2)-(\alpha_c/4)}(c_V^*)^{-(\alpha_c/2)} \qquad (8c)$$

where r_o is the exchange rate and k° is the rate constant for the reaction.

In the limit of $\Delta\phi \to 0$ (or the effect of electrical conditions on kinetics is negligible), Eqs. (8a)–(8c) reduces to a rate expression for a pure chemical reaction (depending only on chemical conditions), which is therefore only a special case of a Butler–Volmer type expression (Eqs. (8a)–(8c)).

For porous MIEC electrodes in a solid-state cell, as schematically shown in Fig. 3, the application of a voltage across the cell may cause electron injection to the MIEC/gas interface of one electrode and electron collection from the MIEC/gas interface of another electrode, thus influencing the rates of the reactions at the MIEC/gas interfaces.

Under certain circumstances, the rate of the reaction at an MIEC/gas interface, just like any other electrochemical reactions, may be controlled primarily by chemical rather than electrical conditions. As a result, the effect of electrical conditions on the overall rate of the reaction may be negligible and the most general expression for electrode kinetics (such as Eqs. (8a)–(8c)) may reduce to an expression
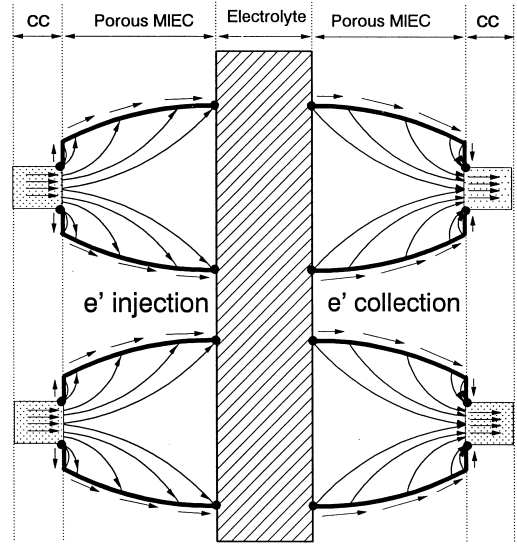

Fig. 3. A schematic diagram showing that, under the influence of an electrical driving force, electrons are injected by the cc into the porous MIEC electrode on the left side and collected by the cc from the porous MIEC electrode on the right side, thus influencing the rate of the reactions at the two porous MIEC electrodes.

depending primarily on chemical conditions. But, in general, both chemical and electrochemical reactions must be considered.

3. Effect of thermodynamics and kinetics

If the electrochemical potential of defect i in an MIEC is defined as

$$\tilde{\mu}_i = \mu_i^o + RT\ln c_i \gamma_i + z_i F\phi \qquad (9a)$$

elimination of ϕ from the expressions for $\tilde{\mu}_V$ and $\tilde{\mu}_e$ yields [7,14,15],

$$\nabla\tilde{\mu}_V = RT\xi_V\nabla\ln c_V - 2\nabla\tilde{\mu}_e \qquad (9b)$$

where ξ_V, known as the thermodynamic factor, is defined as

$$\xi_V \equiv \frac{\partial\ln[(c_V \gamma_V)(c_e \gamma_e)^2]}{\partial\ln c_V}. \qquad (10)$$

When the reaction at an MIEC/gas interface (Eq. (1)) is infinitely fast, the relationship among equilib-

rium concentrations of species involved in the reaction can be expressed as [7],

$$(c_V \gamma_V)(c_e \gamma_e)^2 p_{O_2}^{1/2} = k_g \left(1 - c_V \gamma_V \frac{M}{d} \right)$$

$$\approx k_g \quad \text{when } c_V \gamma_V \frac{M}{d} \ll 1 \qquad (11)$$

In view of Eq. (11), Eq. (10) can be rewritten as,

$$\xi_V = \frac{\partial \ln(1 - c_V \gamma_V M/d)}{\partial \ln c_V} - \frac{1}{2} \left(\frac{\partial \ln p_{O_2}}{\partial \ln c_V} \right) \qquad (12a)$$

which can be approximated, when $c_V \gamma_V / d \ll 1$, by

$$\xi_V \approx -\frac{1}{2} \left(\frac{\partial \ln p_{O_2}}{\partial \ln c_V} \right). \qquad (12b)$$

Accordingly, the relationship between p_{O_2} and c_V as defined by Eqs. (12a) and (12b) requires that the MIEC be at equilibrium with oxygen in the gas phase (or the surface reaction, Eq. (1), be infinitely fast). The use of Eqs. (12a) and (12b) in transport equations, then, implies that the concentration of oxygen vacancies at the surface of the MIEC changes instantaneously with the p_{O_2} in the gas. This is the assumption often made in order to restrict a model just to transport of defects in an MIEC without the influence of the kinetics of surface reaction [7,16].

When the rate of the surface reaction is assumed finite, however, the instantaneous vacancy concentration at the surface of the MIEC is no longer dictated merely by thermodynamics (Eq. (11) or Eqs. (12a) and (12b)), but increasingly by the kinetics of the reaction (Eqs. (8a)–(8c)). In general, when p_{O_2} is changed, the vacancy concentration at the surface of the MIEC will change gradually toward the new equilibrium value. The slower the kinetics of the surface reaction, the longer it will take for the vacancy concentration to reach the equilibrium value. In other words, a change in p_{O_2} in the pores of the MIEC may not induce an instant change in c_V at the same time; the induced change in c_V may lag behind. Likewise, a change in c_V due to transport in the MIEC may not induce an instant change in p_{O_2} in the gas phase at the same time. For many MIECs, in fact, it takes time (typically from minutes to hours) for c_V to reach an equilibrium value when p_{O_2} in the gas phase is changed in order to determine the

equilibrium relationship between c_V and p_{O_2}, from which a thermodynamic factor may be estimated [17,18].

During the operation of an MIEC electrode (e.g. in an impedance measurement), the instantaneous relationship among the concentrations of defects at the surface of the MIEC and p_{O_2} in the pores of the MIEC can only be adequately described using a kinetic or rate expression such as the Butler–Volmer equation (Eqs. (8a)–(8c)) [8]. Combination of this kinetic expression with appropriate transport equations allows investigation into the effect of the kinetics of surface reaction on defect transport in MIEC, or conversely, the effect of defect transport on the rate of surface reaction. A correctly-formulated kinetic equation (such as Eqs. (8a)–(8c)), however, should reduce to the corresponding thermodynamic expression (Eq. (11)) in the limit of infinitely-fast kinetics ($J_{V,o} \to \infty$ or $r_o \to \infty$).

Conceptually, it is inconsistent to use Eqs. (12a) and (12b), which specifies the equilibrium relationship, to describe the instantaneous relationship between c_V and p_{O_2} for an MIEC electrode under active operation. The time required for c_V or p_{O_2} to reach the equilibrium value depends on the rate of the reaction.

The misuse of Eq. (12b) can be seen by examining the limiting case of $r_o \to 0$, i.e. the rate of the reaction at the MIEC/gas interface is infinitely slow. In this limit [5], the entire MIEC/gas interface is inactive (so that Eq. (1) cannot proceed) and the only active sites are the TPBs for oxygen reduction or evolution. Accordingly, c_V must remain constant throughout the MIEC while p_{O_2} may vary with position within the porous MIEC electrode due to production or consumption of O_2 gas at the TPB at the MIEC–electrolyte interface. However, Eq. (12b) would erroneously predict that any variation in p_{O_2} must produce an instant variation in c_V. Thus, Eq. (12b) is incorrect when the rate of the reaction at MIEC/gas interface is not infinitely fast.

While thermodynamic factors have been properly defined and used in other cases [7,16], the use of Eq. (12b) as the definition for thermodynamic factor in a recent treatment [10,11] is inconsistent with their formulation of the electrode kinetics. This conceptual inconsistency results in a mathematical contradiction: the definition of thermodynamic factor, Eq. (12b),

directly contradicts their rate expression unless $r_o = \infty$ (i.e. the kinetics are infinitely fast) [4].

4. Bulk polarization and electroneutrality

As shown in Fig. 1 and Fig. 2, polarization occurs primarily within an interfacial region with thickness x_d. For a metallic MIEC with high charge density, polarization is restricted only to a layer near the surface. For MIECs with low charge density, on the other hand, x_d can be significant relative to the thickness of the MIEC, leading to 'bulk' polarization. The smaller the charge density and the larger the dielectric constant, the wider the polarization layer (x_d) or the further the polarization extends into the bulk. Examining Poisson's equation,

$$\sum_i z_i c_i = \frac{-\epsilon_o}{F}(\epsilon_r \nabla \phi) \tag{13}$$

we find that electroneutrality is no longer valid in an MIEC with effective dielectric constant on the order of $\epsilon_r \approx 10^9$. For an MIEC with reported capacitance of 0.81 F/cm^2 over a layer of about 6 μm thick [10], a rough estimate indicates that the term on the right side of Eq. (13) is, at least, about the same order of magnitude as the average concentration of oxygen vacancies in the MIEC, 10^{-3} eq/cm^3; it is not near zero, nor much smaller than the concentrations of the majority defects in the MIEC, as required by electroneutrality.

While electroneutrality may break down in a liquid electrochemical system ($\epsilon_r < 10^2$) only at extremely low concentrations ($\sim 10^{-8}$ eq/cm^3) [19], it can break down in a solid-state system at concentrations much higher than $\sim 10^{-8}$ eq/cm^3, depending on the dielectric constant of the material or the state of polarization. The dielectric constant and electric field can significantly influence the validity of electroneutrality. For instance, if electroneutrality breaks down in a liquid electrochemical system with $\epsilon_r < 10^2$ at concentrations of $\sim 10^{-8}$ eq/cm^3, it may break down in a solid system in which $\epsilon_r \approx 10^9$ at concentrations as high as $\sim 10^{-1}$ eq/cm^3, much greater than the concentrations expected in any MIECs. Electroneutrality is not a fundamental law, but an approximation to Poisson's equation in a homogeneous material without bulk polarization. In the presence of significant bulk polarization, the validity of electroneutrality must be carefully evaluated. It is inconceivable that local electroneutrality prevails in a material with phenomenal bulk polarization ($\epsilon_r \approx 10^9$).

Although the reactions at an MIEC/gas interface involve 'loss or gain of neutral combinations of ionic and electronic species' [11], they may invalidate local electroneutrality in the MIEC. It is the distribution of charge, not the total amount of charge, that determines local electroneutrality. 'Loss or gain of neutral combinations of ionic and electronic species' may imply that the total amount of charge in the MIEC is conserved; it does not imply that electroneutrality would be preserved locally at every point (averaged over a small area) within the MIEC. When the same amount of charge in a material is distributed in such a way that positive charges accumulate in one area and negative charges accumulate in another, local electroneutrality in the material is violated. For example, electroneutrality is violated in the polarized surface layer (with thickness x_d) of the MIEC shown in Fig. 1; however, the MIEC as a whole is electrically isolated, without loss or gain of any charge.

Further, the reactions at an MIEC/gas interface may cause polarization at or near the interface, although they 'do not involve a net flow of charge' to or away from the MIEC [11]. Electrical polarization is a process of acquiring electric dipoles or aligning existing dipoles in a particular direction; it is a consequence of non-uniform distribution of charge, not necessarily a change in total amount of charge. Thus, electrical polarization can occur in an electrically-isolated material without a net flow of charge to or away from it. As shown in Fig. 1b, the surface layer (with thickness x_d) of the MIEC is polarized; but there is no net flow of charge to or away from the MIEC because it is electrically isolated. As another example, an electrically-isolated ferroelectric material (such as BaTiO$_3$), without a net flow of charge to or away from it, can polarize spontaneously when its temperature falls below the Curie (or critical) temperature, even in the absence of an external electric field. In this case, the electrical polarization is caused by rearrangement (or redistribution) of ions in the crystal so that the center of positive charges and the center of negative charges in

each unit cell no longer coincide; it has nothing to do with a net flow of charge to or away from the material.

5. Validity and consistency of assumptions

While it is necessary to make assumptions in order to simplify a physical model, any assumptions made for a given model must be consistent and meaningful. Contradictory or inconsistent assumptions may lead to erroneous conclusions [4,11].

5.1. $\vec{D}=0$ requires $\nabla\phi=0$ and $\vec{P}=0$

If an MIEC is assumed to be 'metallic' in which bulk dielectric displacement cannot occur ($\vec{D}=0$), both the electric field and polarization in the bulk phase must vanish ($\nabla\phi=0$ and $\vec{P}=0$). This is apparent by examining $\vec{D}=-\epsilon_o\epsilon_r\nabla\phi$ and $\vec{P}=-\chi_e\epsilon_o\nabla\phi$. Clearly, $\vec{D}=0$ requires that $\nabla\phi=0$ since $\epsilon_r\geq1$ and ϵ_o is a constant (8.854×10^{-12} F/m) whereas $\nabla\phi=0$ directly leads to $\vec{P}=0$.

It is inconceivable therefore that, in a material of any kind, bulk dielectric displacement cannot occur yet electric field does not vanish and bulk polarization is enormous. Under any conditions, if an MIEC is indeed 'metallic' in which $\vec{D}=0$ and the Fermi level is uniform, any observable capacitive response of the porous MIEC electrode must be caused by interfacial polarizations (at the MIEC/gas interface, electrolyte–electrode interface, or TPBs), not by polarizations in the bulk phase of the MIEC [4]. While chemical polarization due to changes in stoichiometry may occur in the bulk phase of an MIEC, they cannot be detected from impedance measurements if the Fermi level is indeed uniform throughout the MIEC [20].

5.2. $\epsilon_r\approx10^9$ and $\nabla\phi\neq0$ implies $\partial\vec{D}/\partial t\neq0$

The definition of displacement current density,

$$\frac{\partial\vec{D}}{\partial t}=-\epsilon_o\frac{\partial}{\partial t}(\epsilon_r\nabla\phi)$$
$$=-\epsilon_o\left[\nabla\phi\frac{\partial\epsilon_r}{\partial t}+\epsilon_r\frac{\partial}{\partial t}\nabla\phi\right] \qquad (14)$$

is applicable to an MIEC of any kind. It implies that whenever there is a time-varying polarization ($\partial\epsilon_r/\partial t\neq0$) or a time-varying electric field ($\partial(\nabla\phi)/\partial t\neq0$), there must be a displacement current. This is true in a medium of any kind (including vacuum); it is not just defined for dielectrics. A dielectric constant, $\epsilon_r=\epsilon/\epsilon_o$, may be defined for an MIEC of any kind, naturally including the 'metallic' MIEC in which bulk polarization is enormous [4]. It is implicit that, under the influence of an AC stimulus (such as the condition for an impedance measurement), both bulk polarization and electric field vary with time and position in an MIEC in which $\epsilon_r\approx10^9$ and $\nabla\phi\neq0$, implying that displacement current is significant no matter whether the MIEC is labeled 'metallic' or not. Accordingly, displacement current density cannot be ignored in writing boundary conditions nor in impedance analysis of the MIEC electrode. Misunderstanding of this principle may lead to erroneous conclusions [4]. For instance, it is an illogical conclusion that the impedance of a cell with porous MIEC electrodes (of uniform Fermi level) depends only on the properties of the MIEC and is independent of the interfaces between the MIEC and other cell components, since it directly contradicts experimental observations [6].

5.3. $\vec{D}=0$, $\nabla\tilde{\mu}_e=0$, and $\sum_i z_ic_i=0$ require $\nabla c_i=0$

For an MIEC containing electrons, electron holes, and oxygen vacancies as majority mobile defects, the assumption of $\vec{D}=0$ leads to $\nabla\phi=0$, which implies $\nabla c_e=0$ when the Fermi level is assumed uniform,

$$\nabla\tilde{\mu}_e=RT\frac{\nabla c_e}{c_e}-F\nabla\phi=0 \qquad (15)$$

Further, $\nabla c_e=0$ requires that $\nabla c_h=0$ when electrons and electron holes are assumed at thermal equilibrium, i.e.
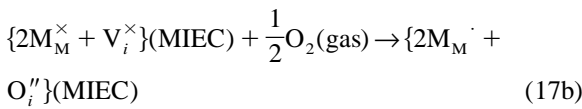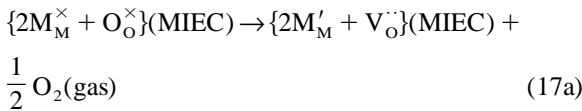
$$c_hc_e=n_i^2 \qquad (16)$$

where n_i is the intrinsic electron density in the MIEC, a constant at a given temperature. The uniform distribution of electrons and electron holes then requires that the concentration of oxygen vacancies be uniform throughout the MIEC when the local electroneutrality is assumed to prevail and the

immobile charges are assumed to distribute uniformly. As a result, these assumptions require that the composition or stoichiometry of the MIEC be space-invariant and the concentration of all defects be uniform ($\nabla c_i = 0$) throughout the MIEC under any conditions. Clearly, this represents a trivial case, implying that the assumptions are meaningless. Incidently, chemical polarization due to changes in stoichiometry cannot occur in the bulk phase of the MIEC under these assumptions.

5.4. Distribution of immobile charges may not be uniform

In general, the distribution of the so-called 'background' charges, or immobile charges, may not be uniform throughout an MIEC [7]. Reduction or oxidation of lattice ions (including dopant ions) may occur readily in MIECs containing transition metal ions by departure from stoichiometry resulting from MIEC–O_2 gas interactions at surfaces,

$$\{2M_M^\times + O_O^\times\}(MIEC) \rightarrow \{2M_M' + V_O^{\cdot\cdot}\}(MIEC) +$$
$$\frac{1}{2} O_2(gas) \tag{17a}$$

$$\{2M_M^\times + V_i^\times\}(MIEC) + \frac{1}{2}O_2(gas) \rightarrow \{2M_M^\cdot +$$
$$O_i''\}(MIEC) \tag{17b}$$

or through capture or emission of quasi-free electrons or electron holes within the MIEC,

$$M_M^\times + e' = M_M', \quad c_{ni} = \frac{k_R c_e}{1 + k_R \gamma_e c_e M/d} \left(\frac{\gamma_e}{\gamma_{ni}} \right) \tag{18a}$$

$$M_M^\times + h^\cdot = M_M^\cdot,$$
$$c_{pi} = \frac{k_O c_h}{1 + k_O \gamma_h c_h M/d} \left(\frac{\gamma_h}{\gamma_{pi}} \right) \tag{18b}$$

where c_{ni}, and c_{pi} represent the molar concentration of immobile charges M_M' and $M_M^\cdot$, respectively, and k_R and k_O correspond to the equilibrium constant of reduction and oxidation of lattice ions, respectively. For an MIEC containing electrons, electron holes, and oxygen vacancies as majority mobile defects, as discussed elsewhere [7], local electroneutrality can be expressed as,

$$\sum_i z_i c_i = c_h - c_e + 2c_V + (c_D + c_{pi} - c_{ni}) = 0 \tag{19}$$

where c_D represents the net concentration of uniformly-distributed, ionized donors [7] while c_{ni}, and c_{pi}, correspond to the concentrations of immobile lattice ions with an effective negative and positive charge, respectively. Clearly, c_{pi}, and c_{ni}, depend on c_e, c_h, and p_{O_2} unless there is no oxidation ($k_O = 0$) or reduction ($k_R = 0$) of lattice ions. Thus, the concentration of the immobile charges in the MIEC,

$$B = c_D + c_{pi} - c_{ni} \tag{20}$$

cannot be constant throughout an MIEC in which space-dependent reduction or oxidation of lattice ions occurs [4].

6. Conclusions

Oxygen reduction and evolution at MIEC/gas interfaces are electrochemical in nature when one of its charge-transfer steps influences the rate of the overall reaction. Expressions similar to the Butler–Volmer equation are the most proper phenomenological description of the kinetics at an MIEC electrode. Unless the kinetics are infinitely fast, the instantaneous relationship among concentrations of the species involved in an electrode reaction is determined more by kinetics than by thermodynamics; the use of an inadequately-defined thermodynamic factor is improper in formulation of electrode kinetics.

It is the distribution of charge, not the total amount of charge, that determines local electroneutrality; 'loss or gain of neutral combinations' does not imply that electroneutrality would be preserved locally at every point (averaged over a small area) within the material. Electrical polarization is a process of acquiring electric dipoles or aligning dipoles in a particular direction; it is a consequence of non-uniform distribution of charge, not necessarily a change in total amount of charge. While chemical polarization due to changes in stoichiometry may occur in the bulk phase of an MIEC, they cannot be detected from impedance measurements if the Fermi level is uniform throughout the MIEC.

If an MIEC is indeed metallic in which dielectric

displacement cannot occur, the electric field and polarization in the bulk phase must vanish whereas the observed huge capacitive response of the MIEC electrode must be caused by interfacial polarizations, not bulk polarization. Conversely, if an MIEC does display enormous bulk polarization in which the electric field does not vanish, bulk dielectric displacement cannot vanish, local electroneutrality may not prevail, and displacement current densities cannot be ignored in specifying boundary conditions nor in impedance analysis.

The distribution of immobile charges cannot be uniform in an MIEC in which there exists significant, space-dependent reduction or oxidation of lattice ions. Electroneutrality is not a fundamental law, but an approximation to Poisson's equation in a homogeneous material without bulk polarization. In the presence of enormous bulk polarization, the validity of electroneutrality must be carefully evaluated.

7. List of symbols

c_D net molar concentration of ionized donors, mol cm^{-3}

c_i molar concentration of species i, mol cm^{-3}

c_i^* molar concentration of species i at a reference state (e.g. in the bulk), mol cm^{-3}

c_{pi} molar concentration of immobile ion with an effective positive charge, mol cm^{-3}

c_{ni} molar concentration of immobile ion with an effective negative charge, mol cm^{-3}

d density of lattice compound, g cm^{-3}

$\vec{D}$ dielectric displacement or electric induction, C cm^{-2}

E_F Fermi energy of electrons ($E_F = \tilde{\mu}_e$), J or eV

E_N Nernst potential across an MIEC as defined by Eq. (4), V

ΔE energy barrier hindering electron transfer from an absorbed oxygen to the conduction band of an MIEC, J or eV

F Faraday's constant, 96 487 C equiv^{-1}

k_R, k_O equilibrium constant for partial reduction and oxidation of lattice ions

k_g equilibrium constant for oxygen–MIEC interaction

M   molecular weight of lattice compound, g mol^{-1}

n_i intrinsic concentration of electrons or holes at a given temperature, mol cm^{-3}

p_{O_2} partial pressure of oxygen, atm

P electric polarization or dipole moment density, C cm^{-2}

r consumption or production rate of $V_O^{\cdot\cdot}$ at an MIEC/gas interface, mol cm^{-2} s^{-1}

R universal gas constant, 8.314 J mol^{-1} K^{-1}

T absolute temperature, K

V_a voltage across an MIEC as defined by Eq. (6), V

V_b potential barrier retarding electron transfer from the interior to surface, V

V_{oc} open cell voltage across an MIEC, V

x_d thickness of charge depletion layer as defined by Eq. (7), cm

z_i number of effective charge of species i (with respect to perfect crystal)

α_a, α_c anodic and cathodic transfer coefficient, dimensionless

η_a, η_c anodic and cathodic overpotential, V

γ_i activity coefficient of species i

ϵ permittivity of a material, F cm^{-1}

ϵ_o permittivity of vacuum, 8.854×10^{-14} F/cm

ϵ_r relative permittivity or dielectric constant, dimensionless

χ_e electric susceptibility of a material, dimensionless

$\tilde{\mu}_i$ electrochemical potential of defect i as defined by Eq. (9a), J mol^{-1}

ϕ electrical potential, V

ξ_V thermodynamic factor as defined by Eqs. (12a) and (12b)

cc   current collector

MIEC   mixed ionic-electronic conductor

TPB   triple-phase boundary

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