

Distributions of Charged Defects in Mixed Ionic-Electronic Conductors

I. General Equations for Homogeneous Mixed Ionic-Electronic Conductors

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ABSTRACT

General analytical solutions to transport equations are presented for a mixed ionic-electronic conductor (MIEC) subject to various electrical and chemical conditions at the surfaces. The derived general expressions can be used to predict the steady-state distributions of defects and electrical potential within the MIEC as a function of an external stimulus for transport: an electric field, a gradient in chemical potential, or a combination of the two. Also, variations in conductivities, transference numbers, current carried by each type of defect, and chemical potential of oxygen within the MIEC can be readily calculated under different conditions. Analyses indicate that the distribution of mobile defects is approximately linear when the amount of uniformly distributed immobile charges is sufficiently small while the electrical potential distributes nearly linearly when the amount of uniformly distributed immobile charges is sufficiently large. In addition, the derived equations can be used to determine the transport properties of an MIEC from observed steady-state behavior of the MIEC under controlled conditions. The derived expressions are applicable to a variety of MIECs with vastly different transport properties, ranging from MIECs with predominant ionic disorders to the ones with overwhelming electronic disorders, from MIECs with intrinsic disorders to the ones with significant extrinsic disorders, and from the MIECs with uniform properties to the ones switching transport character through their thicknesses. Further, and in particular, the derived equations can provide valuable guidance in optimizing performances of devices or systems based on MIECs and in improving or redesigning MIECs for various applications.

Introduction

Mixed ionic-electronic conductors (MIECs) have been widely studied as dense membranes for electrosynthesis¹⁻⁴ (such as partial oxidation of methane and gas separation), as catalytic electrodes for solid-state ionic devices⁵ (such as solid oxide fuel cells,^{6,7} batteries,⁸⁻¹⁰ and chemical sensors¹¹), and as electrolytes^{12,13} or other components¹⁴ for various devices or systems. In all these applications, it is the ionic and electronic transport which dramatically influences the performance of the materials. Accordingly, fundamental understanding of mass and charge transport in MIECs is essential for accurately predicting the behavior of MIECs under various conditions, for optimizing the performance of devices or systems based on MIECs, and, of even greater significance, for rational designing of new MIECs and novel structures of devices based on MIECs.

Transport properties of mixed conductors have been formulated and investigated initially by Wagner¹⁵⁻¹⁹ and subsequently by many others.²⁰⁻²⁹ To date, a number of models³⁰⁻³⁴ have been developed to predict the transport behavior of MIECs under certain conditions. In all cases, however, some restrictive assumptions have been made on the properties of MIECs in order to obtain mathematically manageable solutions. While the existing models have provided important insight into the understanding of some MIECs, their applicability to others have suffered from the restrictive assumptions.

First, the ionic conductivities of MIECs are assumed to be relatively constant in some models under the conditions considered. This restrictive assumption limits the applicability of the developed models only to materials with predominant ionic disorder, which makes up only a very small portion of the family of MIECs. For instance, they may not even be applicable to transition metal oxide-doped CeO₂ and Bi₂O₃ under certain conditions, let alone perovskite-type MIECs such as La_{1-x}Sr_xMnO₃ (LSM), La_{1-x}Sr_xCoO₃ (LSC), and La_{1-x}Sr_xFeO₃ (LSF)-based materials, in which electronic disorders dominate and the ionic conductivities (or concentrations of ionic defects) can vary considerably with position in the direction in which a gradient in p_{O_2} exists.

Second, the electronic conductivities of MIECs are assumed to be a known function of p_{O_2} in order to take into account the effect of variation in electronic proper-

ties. The problem is, however, that the dependence of electronic conductivities on p_{O_2} may take very different forms under different conditions or even may not be available in some cases.

Third, most models developed consider only two types of mobile defects, oxygen vacancies and electrons (or electron holes), and the effect of other defects (particularly immobile ones) on charge and mass transport in MIECs is typically ignored. Accordingly, the models developed may not be applicable to materials in which intrinsic disorders prevail. For MIECs in which either ionic or electronic disorder is intrinsic in nature, more than two types of mobile defects must be considered. For an MIEC with intrinsic electronic disorder, for instance, both electrons and electron holes make significant contributions to the overall electronic behavior of the material and, hence, neither electrons nor electron holes can be neglected in the analysis.

Further, because of these restrictive assumptions, one of the most fascinating phenomena in MIECs has not been adequately addressed in the existing models: a transition in ionic or electronic character or a change in dominant defects from one type to another along the thickness of an MIEC when it is exposed to a large gradient in chemical potential. Frequently, an MIEC may exhibit n-type character on the side exposed to a reducing atmosphere and p-type character on the side exposed to an oxidizing atmosphere. Thus, the electronic character of the material must change continuously from n-type to p-type through the thickness of the MIEC. Accordingly, although the electronic behavior of the MIEC may be approximated by considering only the electrons in the n-type region and only the electron holes in the p-type region, in the transition region from the n-type to the p-type region, neither electrons nor electron holes can be neglected. Similarly, the ionic character of an MIEC may also change from oxygen vacancy predominant on one side to oxygen interstitial predominant on the other side. In this case, both oxygen vacancies and interstitials must be considered in formulating the ionic behavior of the MIEC. Another important point is that whenever there is a transition in character or a change in dominant defects, there must be a transformation of current carried by one type of defect to another, *i.e.*, from electrons to electron holes (or vice versa) for transition in electronic character and from positively charged ionic defects to negatively charged ionic defects (or vice versa) for transitions in ionic character.

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In this paper, analytical solutions to transport equations are first presented without restrictive assumptions on ionic or electronic conductivities, but with consideration of all significant defects (including both mobile and immobile ones). Thus, the obtained solutions are applicable to a variety of MIECs with vastly different transport properties, ranging from MIECs with predominant ionic transport (such as zirconia- and ceria-based electrolytes in which $\sigma_{ion} \gg \sigma_{ele}$) to the ones with overwhelming electronic transport (such as LSM, LSC, and LSF-based electrode materials in which $\sigma_{ele} \gg \sigma_{ion}$), from MIECs with intrinsic disorders (essentially pure or stoichiometric compounds in which three types of mobile defects make appreciable contributions to transport) to the ones with significant extrinsic disorders (doped or nonstoichiometric compounds in which there are only two types of significant mobile defects), and from the MIECs with uniform transport character through their thicknesses when exposed to a large gradient in chemical potential.

Variations in defect concentrations, conductivities, transference numbers, current carried by each type of defect, and chemical potential of oxygen along the thickness are expressed as a function of the two boundary conditions easiest to control and observe: oxygen partial pressures at the interfaces and the terminal voltage across MIECs.

With appropriate assumptions and approximations, the general expressions then reduce to some simple and familiar ones. The significance and utility of these expressions are illustrated with some examples. In particular, current-voltage- p_{O_2} relationships, distribution of defects and electrical potential, Hebb-Wagner experiment for characterization of MIECs, and the efficiencies of an SOFC based on MIECs are elucidated in light of the derived expressions. Applications of these equations to multilayered MIECs and the effect of interfacial polarization will be discussed in subsequent communications.³⁵

Model Description

Schematically shown in Fig. 1 is a homogeneous MIEC of thickness L , which is exposed to a gas having oxygen partial pressure of $p_{O_2}^I$ on one side at $x = 0$ and to another gas with $p_{O_2}^{II}$ on the other side at $x = L$. All properties of the MIEC are assumed to be uniform in a plane perpendicular to direction x so that the system under consideration reduces to a one-dimensional problem. Lattice defects present in the MIEC are described using Kroger-Vink notations³⁶ while the chemical and electrochemical potential of defect k inside the MIEC are defined, respectively, as³⁷

$$\mu_k = \mu_k^* + RT \ln \gamma_k c_k \quad [1.1a]$$

$$\tilde{\mu}_k = \mu_k + z_k F \phi \quad [1.1b]$$

where μ_k^* , γ_k , c_k , and z_k are the free energy at a reference state, activity coefficient, molar concentration, and the number of effective charge (with respect to a perfect crystal), respectively, of defect k and ϕ is the electrostatic potential inside the MIEC averaged over a volume element, which is sufficiently larger than atomic dimensions but much smaller than the dimensions of the MIEC.^{19,25} The properties of the MIEC at the surface exposed to $p_{O_2}^I$ (or $p_{O_2}^{II}$) are labeled with a superscript I (or II), such as c_k^I and μ_k^I (or c_k^{II} and μ_k^{II}), which correspond to the properties of the MIEC when it is immersed in and reaches equilibrium with a uniform atmosphere having oxygen partial pressure of $p_{O_2}^I$ (or $p_{O_2}^{II}$). Throughout this formulation, it is assumed that

1. Local equilibrium of reactions involving mobile defects (including the reactions occurring at the solid-gas interfaces) prevails in the MIEC so that partial thermodynamic properties of each defect have well-defined values;

2. Local charge neutrality is approximately, but not strictly, observed in the MIEC so that negligible deviations from electroneutrality may result in nonuniform electric field in the MIEC;

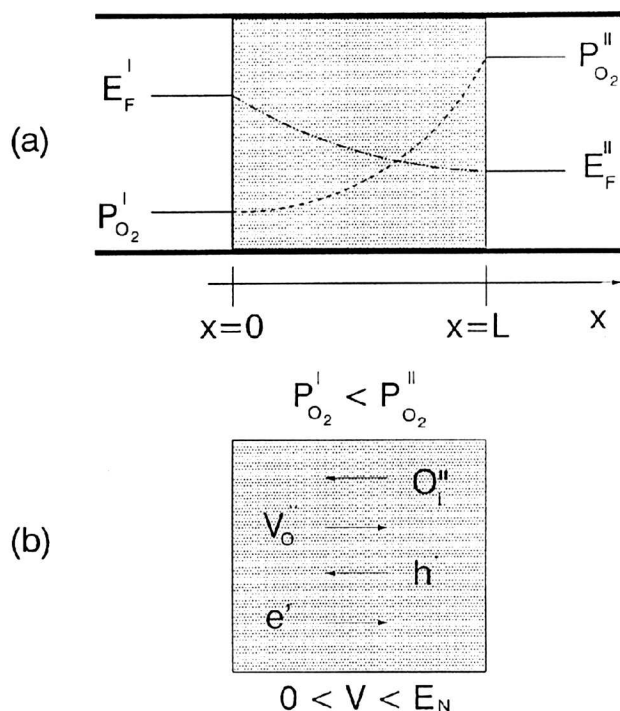


Fig. 1. Schematics showing (a) an MIEC exposed to a gas containing oxygen partial pressure $p_{O_2}^I$ at $x = 0$ and to another gas containing oxygen partial pressure $p_{O_2}^{II}$ at $x = L$ and (b) directions of fluxes due to the motion of defects in the MIEC.

3. The concentrations of defects in the MIEC are sufficiently small so that (i) the site fraction of each defect is much smaller than unity except the majority defects due to significant extrinsic disorders (resulting from doping or large departure from stoichiometry) and (ii) there are no significant interactions among defects;

4. Mobilities of all mobile defects are independent of position (x) and concentration (c_k) in the MIEC (a more rigorous formulation is possible if the dependence of mobilities on c_k is known); and

5. The gas phases in equilibrium with the MIEC are considered to be an ideal gas so that the activity of oxygen in each gas phase can be approximated by the partial pressure of oxygen.

When defect concentrations are sufficiently small (or more precisely, when the defects are distributed completely at random over the available sites in the MIEC), the activity coefficient approaches unity. For small deviations from ideal behavior in MIECs of ionic compounds, it is reasonable to approximate the activity coefficient by³⁸

$$\gamma_k = \gamma_k^o [k]^{g_k} = \gamma_k^* c_k^{g_k} \quad \text{with } g_k = \frac{\partial \ln \gamma_k}{\partial \ln c_k} \quad \text{and } \gamma_k^* = \gamma_k^o (M/d)^{g_k} \quad [1.1c]$$

where $[k]$ is the site fraction of defect k , g_k is a constant, d and M are the density and molecular weight of the lattice compound, and both γ_k^o and γ_k^* are proportionality constants [γ_k^o is dimensionless while γ_k^* has dimension of $(m^3/mol)^{g_k}$]. In this model, the activity coefficients are first considered constant ($g_k = 0$) for simplicity and then treated as a variable ($g_k \neq 0$) for extrinsic MIECs in Appendix A. This extends the validity of the model to the limit of defect concentration within which interactions among defects are insignificant while beyond which strong interactions among defects and site exclusion effect must be taken into consideration (this has been treated statistically for some special cases³⁹). Also, a thermodynamic factor may be introduced under certain conditions, which is also discussed in Appendix A.

Transport equations and boundary conditions.—According to the theory of irreversible thermodynamics,^{40,41} the transport of n types of mobile defects in a homogeneous MIEC, with respect to the immobile lattice elements as a reference frame under isothermal conditions, can be expressed as

$$N_k = - \sum_{i=1}^n L_{ki} \nabla \tilde{\mu}_i \quad k = 1, 2, \dots, n \quad [1.2]$$

where N_k is the molar flux of defect k and L_{ki} are the phenomenological coefficients. When the interactions among defects during transport are insignificant (assumption 3), *i.e.*, L_{ki} is small when $k \neq i$, the current density due to the motion of defect k can be adequately described by

$$J_k = z_k F N_k = -z_k F u_k c_k \nabla \tilde{\mu}_k = -z_k F R T u_k \left(1 + \frac{\partial \ln \gamma_k}{\partial \ln c_k} \right) \nabla c_k - z_k^2 F^2 u_k c_k \nabla \phi \quad [1.3a]$$

where u_k is the absolute mobility of defect k in the MIEC. The total or observable current density passing through the MIEC is then given by

$$J_T = \sum_{k=1}^n J_k \quad [1.3b]$$

At the interfaces between the MIEC and its surrounding atmosphere, oxygen atoms at regular or interstitial lattice sites may be extracted out of the crystal according to

$$O_O^x(\text{MIEC}) = \{V_O^{\bullet\bullet} + 2e'\}(\text{MIEC}) + \frac{1}{2} O_2(\text{gas}) \quad [V_O^{\bullet\bullet}] [e']^2 p_{O_2}^{\frac{1}{2}} = k'_g [O_O^x] \quad [1.4a]$$

$$\{O_i^{\bullet\bullet} + 2h^*\}(\text{MIEC}) = V_i^x(\text{MIEC}) + \frac{1}{2} O_2(\text{gas}) \quad [V_i^x] p_{O_2}^{\frac{1}{2}} = k_g [O_i^{\bullet\bullet}] [h^*]^2 \quad [1.4b]$$

when the partial pressure of oxygen in the atmosphere is less than the stoichiometric partial pressure of oxygen of the crystal. Conversely, oxygen molecules in the gas phases may incorporate into the crystal (*i.e.*, reactions 1.4a and 1.4b proceed from right to left) when the oxygen partial pressure in the atmosphere is greater than the stoichiometric oxygen partial pressure of the crystal. In general, the kinetics of these reactions may influence the transport of charged defects in MIECs; for simplicity, however, it is assumed that these reactions are sufficiently rapid so that the transport of defects within the MIEC is not altered by the kinetics of the surface reactions (assumption 1). Thus, the chemical condition imposed on the MIEC is determined by the partial pressures of oxygen at the two surfaces of the sample, $p_{O_2}^I$ and $p_{O_2}^{II}$, which is often expressed as a Nernst potential imposed across the MIEC

$$E_N = \frac{RT}{4F} \ln \left(\frac{p_{O_2}^{II}}{p_{O_2}^I} \right) \quad [1.5]$$

Further, the electrical state of the MIEC can be either observed or controlled through the surfaces of the MIEC. The voltage across the MIEC, V , determined by the difference in Fermi levels (or electrochemical potentials of electrons) of the two surfaces

$$V = \frac{-(E_F^{II} - E_F^I)}{F} = \frac{-(\tilde{\mu}_e^{II} - \tilde{\mu}_e^I)}{F} \quad [1.6]$$

which is further related to the electrostatic potential difference across the MIEC, $\phi^{II} - \phi^I$, and the ratio of electron concentrations at the two surfaces, c_e^{II}/c_e^I , as follows

$$\phi^{II} - \phi^I = \left(\frac{RT}{F} \right) \ln \left(\frac{c_e^{II}}{c_e^I} \right) + V \quad [1.7]$$

Defect equilibrium and electroneutrality.—For an MIEC of pure and stoichiometric ionic compound,^{36,38} intrinsic electronic disorder

$$nil = e' + h^*, \quad [e'] [h^*] = k_e \quad [1.8a]$$

may occur due to thermal excitation of electrons from the conduction band to the valence band. Similarly, thermal excitation of ions away from regular lattice sites may result in various intrinsic ionic disorders. To be specific, consider a metal oxide capable of being defective on either side of stoichiometry, $MO_{1\pm\delta}$, possible intrinsic ionic disorders include Frenkel disorder in the oxygen ion sublattice

$$O_O^x + V_i^x = O_i^{\bullet\bullet} + V_O^{\bullet\bullet}, \quad [O_i^{\bullet\bullet}] [V_O^{\bullet\bullet}] = k'_f [O_O^x] [V_i^x] \quad [1.8b]$$

Frenkel disorder in the metal ion sublattice

$$M_M^x + V_i^x = M_i^{\bullet\bullet} + V_M^{\bullet\bullet}, \quad [M_i^{\bullet\bullet}] [V_M^{\bullet\bullet}] = k_f [M_M^x] [V_i^x] \quad [1.8c]$$

Schottky disorder

$$nil = V_O^{\bullet\bullet} + V_M^{\bullet\bullet}, \quad [V_O^{\bullet\bullet}] [V_M^{\bullet\bullet}] = k_s \quad [1.8d]$$

interstitial disorder

$$MO = M_i^{\bullet\bullet} + O_i^{\bullet\bullet}, \quad [M_i^{\bullet\bullet}] [O_i^{\bullet\bullet}] = k_i \quad [1.8e]$$

and antistructure disorder

$$M_M^x + O_O^x = M_O^{\bullet\bullet\bullet\bullet} + O_M^{\bullet\bullet\bullet\bullet}, \quad [M_O^{\bullet\bullet\bullet\bullet}] [O_M^{\bullet\bullet\bullet\bullet}] = k_a [M_M^x] [O_O^x] \quad [1.8f]$$

where k_e , k'_f , k_f , k_s , k_i , and k_a are the equilibrium constant, respectively, for each defect reaction. The site fractions $[k]$ in the mass-action equations should be replaced with activities (*i.e.*, $\gamma_k [k]$) when the distributions of defects are not completely at random.

In addition, interactions between an MIEC and its surrounding atmosphere frequently cause additional departure from stoichiometry while the presence of impurities may further complicate the defect equilibrium. In theory, the list of possible extrinsic disorders can be quite long; in practice, however, often only one ionic disorder dominates the ionic defect equilibrium in a given MIEC. Accordingly, only one type of mobile ionic defect (or together with its thermal-equilibrium counterpart), in addition to electrons and electron holes, makes appreciable contributions to charge transport in a particular MIEC. To be specific, we take an MIEC with oxygen vacancies and interstitials being the predominant ionic defect as an example for derivation of equations. The equations derived for this case, however, can be readily applied to MIECs with any other types of ionic disorders (this is illustrated later).

For an MIEC containing mobile defects of oxygen vacancies ($V_O^{\bullet\bullet}$), oxygen interstitials ($O_i^{\bullet\bullet}$), quasi-free electrons (e'), and quasi-free electron holes (h^*), the directions of molar flux (N_k) for each type of defect in the MIEC are indicated in Fig. 1b for $p_{O_2}^I < p_{O_2}^{II}$ and $0 < V < E_N$. In terms of activities (or effective molar concentrations), the mass-action equations for reactions involving the mobile defects inside the MIEC (Eq. 1.8a and 1.8b) and at the surfaces (Eq. 1.4a or 1.4b) can be rewritten, respectively, in the form

$$(c_e \gamma_e) (c_h \gamma_h) = n_i^2 \quad n_i^2 = k_e \left(\frac{d}{M} \right)^2 \quad [1.9a]$$

$$(c_o \gamma_o) (c_v \gamma_v) = k_f^2 \left(1 - c_v \gamma_v \frac{M}{d} \right) \left(1 - c_o \gamma_o \frac{M}{d} \right) \quad k_f^2 = \kappa_f \left(\frac{d}{M} \right)^2 \quad [1.9b]$$

$$(c_v \gamma_v) (c_e \gamma_e)^2 p_{O_2}^{\frac{1}{2}} = k_g \left(1 - c_v \gamma_v \frac{M}{d}\right), \quad k_g = k'_g \left(\frac{d}{M}\right) \quad [1.9c]$$

where the subscripts v, o, e, and h represent the mobile charged defects, V_o^* , O_i' , e' , and h^* , respectively, in the mixed conductor, n_i represents the effective intrinsic concentration of electrons or electron holes while k_i corresponds to the effective intrinsic concentration of oxygen vacancies or interstitials (when $[V_o^*] \ll 1$ and $[O_i'] \ll 1$). The introduction of activity coefficients will be necessary for electrons and electron holes when their concentrations are beyond a certain value such as in MIECs with overwhelming electronic disorders (like degenerate semiconductors), where Boltzmann statistics is no longer applicable and the Fermi-Dirac distribution function must be used.^{37,38}

In addition to the mobile defects, the MIEC may also contain immobile or fixed defects, which can be divided into two categories: (i) randomly distributed defects such as ionized donors (D_M^*) and acceptors (A_M^*) and (ii) nonuniformly distributed defects such as partially reduced (M_M^*) or oxidized (M_M^x) lattice ions in the MIEC. The change in oxidation state of lattice ions (including dopant ions), and hence stoichiometry of the material, may occur (readily in MIECs containing transition metal ions) through capture or emission of quasi-free electrons and electron holes

$$M_M^x + e' = M_M^*, \quad [M_M^x] = k_R [M_M^*] [e']$$

$$\gamma_{ni} c_{ni} = k_R \gamma_e c_e \left(1 - \gamma_{ni} c_{ni} \frac{M}{d}\right) \quad [1.10a]$$

$$M_M^x + h^* = M_M^*, \quad [M_M^x] = k_O [M_M^*] [h^*]$$

$$\gamma_{pi} c_{pi} = k_O \gamma_h c_h \left(1 - \gamma_{pi} c_{pi} \frac{M}{d}\right) \quad [1.10b]$$

where c_{ni} and c_{pi} are the molar concentration of M_M^* and M_M^x , respectively, and k_R and k_O are the equilibrium constant for partial reduction and oxidation of lattice ions, respectively. Although the immobile defects do not contribute to charge transport, they do influence charge neutrality, the distribution of electrostatic potential, and hence the transport of mobile defects. For a homogeneous (without bulk polarization) MIEC containing n types of mobile and m types of immobile defects, approximation of local charge neutrality requires that

$$\sum_{k=1}^{n+m} z_k c_k \approx 0 \quad [1.11]$$

anywhere inside the MIEC. The summation must go over all types of charged defects, including both mobile and immobile defects in the MIEC (the effective charge of each defect is referred to the perfect crystal). The charge neutrality, however, is only an approximation, and it does not necessarily imply that

$$-\frac{d^2 \phi(x)}{dx^2} = \frac{F \sum_{k=1}^{n+m} z_k c_k(x)}{\epsilon} \quad [1.12]$$

vanishes inside the MIEC. In other words, the electric field may vary in a homogeneous MIEC in which charge neutrality is assumed (due to very small deviations from charge neutrality). In fact, Poisson's equation (Eq. 1.12) can be used to replace the charge neutrality equation (Eq. 1.11) for a more rigorous formulation.³⁰ In the presence of internal polarization, however, charge neutrality is no longer observed and Poisson's equation must be used to replace the charge neutrality equation.

Continuity equation and steady-state condition.—The population of defects in an infinitesimal volume inside the MIEC is influenced not only by transport (∇J_k) but also by various defect reactions and equilibrium among defects.

The basic continuity equation for each type of defect can be expressed as^{42,43}

$$\frac{\partial c_k}{\partial t} = -\frac{1}{z_k F} \nabla J_k + (G_k - R_k) \quad [1.13]$$

where $\partial c_k / \partial t$ is the rate of change in population of defect k in an infinitesimal volume inside the MIEC and G_k and R_k are the generation and recombination rates, respectively, in the volume for defect k . Combining the continuity equation for V_o^* and that for O_i' in a steady state ($\partial c_k / \partial t = 0$), we find

$$0 = \frac{1}{2F} \nabla (J_o + J_v) + (G_o - G_v) - (R_o - R_v) \quad [1.14a]$$

and, similarly, we have

$$0 = \frac{1}{F} \nabla (J_e + J_h) + (G_e - G_h) - (R_e - R_h) \quad [1.14b]$$

for electrons and electron holes in a steady state. At thermal equilibrium, the rate of capture of electrons by the localized states (e.g., Eq. 1.10a) must be equal to the rate of emission of electrons from the localized states (e.g., Eq. 1.10b). Further, because of the equilibrium between electrons and electron holes (Eq. 1.8a) and between oxygen vacancies and interstitials (Eq. 1.8b), the net generation or recombination rate of electronic or ionic defects within a dense MIEC vanishes. In other words, the only sink or source of any defects in a steady state must be located at the surfaces of the MIEC while the electron transfer processes which may convert ionic to electronic defects or vice versa within the MIEC, if there are any, must reach an equilibrium in a steady state. Accordingly, Eq. 1.14a and 1.14b reduce, respectively, to

$$\frac{d}{dx} (J_v + J_o) = \frac{d}{dx} J_{ion} = 0 \quad [1.15a]$$

$$\frac{d}{dx} (J_e + J_h) = \frac{d}{dx} J_{ele} = 0 \quad [1.15b]$$

for the MIEC shown in Fig. 1. It can be clearly seen from the last two equations that, in a steady state, the electronic current remains constant and so does the ionic current throughout the MIEC for a given E_N and V . In view of Eq. 1.3a, the ionic and electronic current density in a steady state can then be expressed, respectively, as

$$J_{ion} = 2FRT \left[u_o (1 + g_o) \frac{dc_o}{dx} - u_v (1 + g_v) \frac{dc_v}{dx} \right]$$

$$- 4F^2 (u_o c_o + u_v c_v) \frac{d\phi}{dx} \quad [1.16a]$$

$$J_{ele} = FRT \left[u_e (1 + g_e) \frac{dc_e}{dx} - u_h (1 + g_h) \frac{dc_h}{dx} \right]$$

$$- F^2 (u_e c_e + u_h c_h) \frac{d\phi}{dx} \quad [1.16b]$$

It must be noted, however, that the current carried by electrons may be transferred to electron holes (or vice versa) and, similarly, the current carried by oxygen vacancies may be transferred to oxygen interstitials (or vice versa) during transport within the MIEC. This occurs in MIECs that change character from one type of dominant defect on one side to another type of dominant defect on the other side when exposed to a large gradient in chemical potential.

Solutions for MIECs with Three Types of Significant Mobile Defects

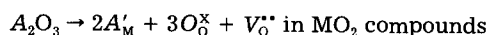
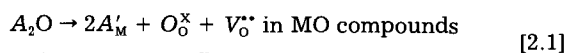
For MIECs containing significant amount of dopants, the presence of aliovalent impurities can shift the defect equilibrium into extrinsic regime where the concentration of one defect is much greater than the concentration of its thermal-equilibrium counterpart. Extrinsic disorders may also become significant when MIECs are exposed to an

extremely high or an extremely low p_{O_2} so that a considerable departure from the stoichiometric composition occurs. In either case, at least one type of mobile defect will be a minority defect throughout the MIEC and its contributions to transport may be ignored. For example, it is well known that a YSZ doped with transition metal oxides, $(Y_2O_3)_x(ZrO_2)_{92-x}(MO)_x$, exhibits extrinsic ionic disorder (i.e., $c_v \gg c_o$) over a wide range of p_{O_2} (from 1 to 10^{-20} atm). The electronic property of the material can, however, change from n-type to p-type (or vice versa) within the same p_{O_2} range. Accordingly, oxygen interstitials may be ignored in the analysis of the ionic behavior while both electrons and electron holes must be taken into consideration in the prediction of the electronic behavior of the material.

For simplicity, the activity coefficients for all defects are first considered constant (i.e., $g_k = 0$ and $\gamma_k = \gamma_k^*$), although the activity coefficients as defined by Eq. 1.1c can be incorporated into this model without too much difficulty. The effect of variable activity coefficients ($g_k \neq 0$) on the formulation of extrinsic MIECs is discussed in Appendix A.

MIECs with extrinsic ionic disorders.—The MIECs with extrinsic ionic disorders can be classified into two categories: the ones with the majority ionic defects being positively charged (such as V_O^{2+} and M_i^{2+}) and the ones with the majority ionic defects being negatively charged (such as O_i' and V_M''). In either case, however, both e' and h' make appreciable contributions to electronic transport and neither e' nor h' can be neglected in the analysis.

MIECs with V_O^{2+} as predominant ionic defect.—In MIECs based on metal oxides, V_O^{2+} may be created by doping of acceptors



or by departure from stoichiometry resulting from gas-solid interactions at the surface as described by Eq. 1.4a. This gas-solid interaction implies that, even for a metal oxide without dopants, extrinsic ionic disorder ($c_v \gg c_o$) may prevail if departure from stoichiometry can readily occur in the compound. Further, electrons or electron holes may be localized at lattice ions as implied by Eq. 1.10a and 1.10b. Thus, the population of quasi-free electrons and electron holes in the MIEC is generally influenced by the equilibrium of capture and emission of electrons or electron holes by lattice ions. Accordingly, the local charge neutrality approximation (Eq. 1.11) for an MIEC with $c_v \gg c_o$ can be rewritten as

$$c_{A_v} + c_{ni} + c_e \approx c_h + 2c_v + c_{pi} \quad [2.2a]$$

where c_{A_v} is the molar concentration of A'_M , which represents an ionized acceptor for creation of V_O^{2+} as implied by defect reaction Eq. 2.1, and the other terms as defined earlier. Doped electrolytes such as YSZ or doped perovskite compounds like LSM, LSC, and LSF are examples of these MIECs, in which V_O^{2+} is the majority ionic defect due to the presence of Y_{Zr} or Sr'_{La} and the effect of any minority ionic defects is negligible. If more than one type of ionized impurities (or any other types of immobile defects) are present in the MIEC, the compensation effect among l types of immobile defects can be taken into account by replacing c_{A_v} in Eq. 2.2a with a net concentration of ionized acceptors in the MIEC, c_A , defined as

$$c_A = -\sum_{j=1}^l z_j c_j \quad [2.2b]$$

where c_j represents the molar concentration of an ionized dopant (or any other immobile defect) j , while z_j corresponds to the number of effective charge (with respect to perfect crystal) carried by defect j (z_j is positive for donor-type defects and negative for acceptor-type defects).

All ionized dopants or any other types of defects are assumed to be immobile and distributed randomly in the

MIEC (and hence c_A is independent of x) whereas the concentrations of partially ionized lattice ions (such as M'_M and M''_M) may vary with position in the MIEC (i.e., c_{ni} and c_{pi} may be a function of x). This is because both c_{ni} and c_{pi} depend on c_e and c_h in the MIEC. Thus, the concentration of immobile charges may not be uniform in an MIEC in which partial oxidation ($k_o \neq 0$) or reduction ($k_r \neq 0$) of lattice ions occurs.

Among the unknown defect concentrations, only one of them is independent because of local charge neutrality (Eq. 2.2) and the equilibria among the defects as implied by Eq. 1.9a, 1.9b, 1.10a, and 1.10b. For instance, when c_e is chosen as an independent variable, the concentrations of other significant defects in the MIEC can be expressed in terms of c_e as follows

$$c_h(x) = \frac{n_i^2}{\gamma_e^* \gamma_h^* c_e(x)} \quad [2.3a]$$

$$c_{ni}(x) = \left(\frac{\gamma_e^* k_r}{\gamma_{ni}^*} \right) c_e(x) \quad [2.3b]$$

$$c_{pi}(x) = \left(\frac{k_o}{\gamma_{pi}^*} \right) \frac{n_i^2}{\gamma_e^* c_e(x)} \quad [2.3c]$$

$$c_v(x) = \frac{1}{2} \left[c_A + \left(1 + \frac{\gamma_e^* k_r}{\gamma_{ni}^*} \right) c_e(x) - \frac{n_i^2}{\gamma_e^* \gamma_h^* c_e(x)} \left(1 + \frac{\gamma_h^* k_o}{\gamma_{pi}^*} \right) \right] \quad [2.3d]$$

while the concentration of the minority ionic defect, O_i' , can be calculated as

$$c_o(x) = \frac{k_i^2 [1 - c_v(x)] \gamma_v^* M/d}{\gamma_o [\gamma_v^* c_v(x) + k_i^2 M/d]}$$

since $[V_O^{2+}][O_i'] \ll 1$. Alternatively, when c_h is chosen as an independent variable, the concentrations of other significant defects in the MIEC can be expressed in terms of c_h .

Since $c_v \gg c_o$ and $j_{ion} = J_v + J_o \approx J_v$, the terms containing c_o in Eq. 1.16a may be neglected. Eliminating $d\phi$ from Eq. 1.16a and 1.16b and substituting for c_v and c_h (using Eq. 2.3a to 2.3d) or for c_e and c_h (using similar expressions in terms of c_h), we find that the concentration of electrons ($k = e$) or electron holes ($k = h$) satisfies the following differential equation

$$\frac{dx}{B_1^k} = \left[\frac{Q_o^k + Q_1^k c_k + Q_2^k c_k^2 + Q_3^k/c_k + Q_4^k/c_k^2}{P_o^k + P_1^k c_k + P_2^k c_k^2} \right] dc_k \quad [2.4]$$

where the coefficients, B_1^k , P_n^k , and Q_n^k , depend on the electronic defect under consideration. When the distribution of electrons is considered, for instance, the coefficients are given by

$$B_1^e = -FRTu_v \quad [2.5]$$

$$P_o^e = \left[u_h J_{ion} + 2u_v J_{ele} \left(1 + \frac{\gamma_h^* k_o}{\gamma_{pi}^*} \right) \right] \left(\frac{n_i^2}{\gamma_e^* \gamma_h^*} \right)$$

$$P_1^e = -2u_v c_A J_{ele}$$

$$P_2^e = u_e J_{ion} - 2u_v \left(1 + \frac{\gamma_e^* k_r}{\gamma_{ni}^*} \right) J_{ele}$$

$$Q_o^e = \left[3u_h \left(1 + \frac{\gamma_e^* k_r}{\gamma_{ni}^*} \right) - u_e \left(1 + \frac{\gamma_h^* k_o}{\gamma_{pi}^*} \right) \right] \left(\frac{n_i^2}{\gamma_e^* \gamma_h^*} \right)$$

$$Q_1^e = 2u_e c_A$$

$$Q_2^e = 3u_e \left(1 + \frac{\gamma_e^* k_B}{\gamma_{ni}^*} \right)$$

$$Q_3^e = 2u_h c_A \left(\frac{n_i^2}{\gamma_e^* \gamma_h^*} \right)$$

$$Q_4^e = -u_h \left(1 + \frac{\gamma_h^* k_B}{\gamma_{pi}^*} \right) \left(\frac{n_i^2}{\gamma_e^* \gamma_h^*} \right)^2$$

Similarly, eliminating dx from Eq. 1.16a and 1.16b and in view of Eq. 2.3a to 2.3d (or similar expressions in terms of c_h), we find that the electrostatic potential satisfies the following differential equation

$$\frac{d\phi}{B_2^k} = \left[\frac{Q_5^k + Q_6^k c_k^2}{(P_o^k + P_1^k c_k + P_2^k c_k^2) c_k} \right] dc_k \quad [2.6]$$

Where $k = e$ for electrons or $k = h$ for electron holes and the coefficients, B_n^k , P_n^k , and Q_n^k , depend on which electronic defect is under consideration. For electrons, we have

$$B_2^e = RT/F \quad [2.7]$$

$$Q_5^e = (u_h J_{ion} + u_v J_{ele}) \left(\frac{n_i^2}{\gamma_e^* \gamma_h^*} \right)$$

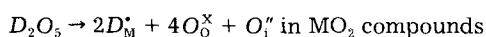
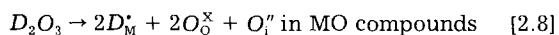
$$Q_6^e = u_e J_{ion} + u_v J_{ele} \left(1 + \frac{\gamma_e^* k_B}{\gamma_{ni}^*} \right)$$

and coefficients P_o^e , P_1^e , and P_2^e are the same as defined in Eq. 2.5.

Equations 2.4 and 2.6 can be solved analytically for a given V and E_N to determine the distributions of electronic defects and electrical potential. The analytical solutions to these equations under different conditions are summarized in Appendix B. With these analytical solutions (Eq. B-1 to B-6), the ionic and electronic current densities for a given V and E_N then can be determined from Eq. B-1 to B-6 evaluated for $k = e$ at $x = L$.

In addition, it is important to note that Eq. 2.2 to 2.7 remain the same for MIECs in which several ionic disorders may be significant but with V_o^{**} being the majority ionic defect. For instance, when both Frenkel disorder (Eq. 1.8b) and Schottky disorder (Eq. 1.8d) are significant, Eq. 2.2 to 2.7 are still valid as long as $[V_o^{**}] \gg [V_M^{**}]$ and $[V_o^{**}] \gg [O_i^{**}]$. Also, Eq. 2.2 to 2.7 are equally applicable to MIECs in which Frenkel disorder in the cation sublattice prevails (Eq. 1.8c) with $[M_i^{**}] \gg [V_M^{**}]$ and interstitial disorder prevails (Eq. 1.8e) with $[M_i^{**}] \gg [O_i^{**}]$, provided that the concentration of the majority ionic defect (M_i^{**}) is used in the place of c_v in the equations.

MIECs with O_i^{} as predominant ionic defect.**—Similarly, O_i^{**} may be created in MIECs of metal oxides by doping of donors



or by departure from stoichiometry due to solid-gas interaction such as Eq. 1.4b at the surface. Considering the effect of capture and emission of electrons or electron holes by lattice ions (Eq. 1.10a and 1.10b), we can approximate the local charge neutrality in an MIEC with $c_o \gg c_v$ by

$$c_{ni} + 2c_o + c_e \approx c_h + c_{pi} + c_{D,o} \quad [2.9a]$$

where $c_{D,o}$ represents the molar concentration of randomly distributed ionized impurities present in the MIEC to create O_i^{**} and the other terms are as defined earlier. If the MIEC contains l types of ionized impurities to create both ionic and electronic defects, the compensation effect

among different types of ionized impurities can be taken into account by replacing $c_{D,o}$ in Eq. 2.9a with a net concentration of ionized donors, c_D , defined as

$$c_D = \sum_{j=1}^l z_j c_j = -c_A \quad [2.9b]$$

where z_j and c_j are as defined earlier for Eq. 2.2b. It is important to note that all randomly distributed immobile defects are lumped to c_D or c_A so that either c_A or c_D is always uniform throughout the MIEC. The immobile charges due to emission or capture of electrons or electron holes by lattice ions (or other immobile ions) are represented by c_{ni} and c_{pi} , which may vary in general with c_e and c_h in an MIEC.

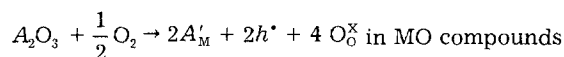
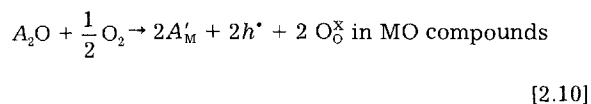
Analysis indicates that the forms of the equations describing the distribution of electrons or electron holes ($k = e$ or h) and electrical potential in an MIEC with $c_o \gg c_v$ are identical to the forms of the equations derived for an MIEC with $c_v \gg c_o$ (Eq. 2.4, 2.6, and B-1 to B-6) because of the inherent symmetry of the two cases. The only difference between the two sets of equations for the two types of materials is that the coefficients B_n^e , P_n^e , and Q_n^e defined in Eq. 2.5 and 2.7 will take different values for an MIEC with $c_o \gg c_v$. For instance, one modification needed is to replace subscript v by subscript o and c_A by c_D in Eq. 2.5 and 2.7 to get the coefficients for an MIEC with $c_o \gg c_v$.

Also, the derived equations are equally applicable to MIECs in which several ionic disorders prevail but with O_i^{**} being the predominant ionic defect. For instance, when both reactions described by Eq. 1.8b and 1.8e are important, the derived expressions will remain the same as long as $[O_i^{**}] \gg [V_o^{**}]$ and $[O_i^{**}] \gg [M_i^{**}]$. Further, for MIECs in which other negatively charged ionic defects (such as V_M^{**}) are the majority ionic defect, further modification needed is to replace c_o by the concentration of the majority ionic defect (V_M^{**}).

Extrinsic ionic disorders ($c_v \gg c_o$ or $c_o \gg c_v$) occur not only in MIECs with prevailing ionic disorders ($k_i \gg n_i$) such as YSZ or CSC but also in MIECs with overwhelming electronic disorders ($n_i \gg k_i$) such as LSM and LSC.

MIECs with extrinsic electronic disorders.—MIECs with extrinsic electronic disorder can also be classified into two categories: the ones with electrons as dominant electronic defects (n-type) and the ones with electron holes as the predominant electronic defects (p-type). In either case, however, both V_o^{**} and O_i^{**} make appreciable contributions to ionic transport and neither V_o^{**} nor O_i^{**} can be neglected in the analysis.

p-type MIECs ($c_h \gg c_n$).—In a p-type MIEC, quasi-free electron holes may be created by doping of acceptors



or by departure from stoichiometry resulting from solid-gas interactions at surfaces (Eq. 1.4a or 1.4b proceeding from right to left). The interaction between electron holes and lattice ions (Eq. 1.10b) is expected to be far more important than the interaction between electrons and lattice ions (Eq. 1.10a) because $c_h \gg c_e$. Under this condition, c_e and c_{ni} may be neglected and the local charge neutrality approximation in a p-type MIEC then takes the form

$$c_{A,h} + 2c_o \approx c_h + 2c_v + c_{pi} \quad [2.11]$$

where $c_{A,h}$ represents the molar concentration of ionized impurities present in the MIEC to create h^* . If the p-type MIEC contains l types of randomly distributed ionized

impurities, the compensation effect among different types of ionized impurities can be taken into account by replacing $c_{A,h}$ in Eq. 2.11 with a net concentration of ionized acceptors, c_A , as defined by Eq. 2.2b.

Again, among the unknown defect concentrations, only one of them is independent because of Eq. 1.9, 1.10, and 2.11. For example, when c_v is chosen as an independent variable, the concentrations of other significant defects in the MIEC can be expressed as

$$c_o(x) = \frac{k_t^2}{\gamma_o^* \gamma_v^* c_v(x)} \quad [2.12a]$$

$$c_h(x) = \frac{c_A + 2k_t^2 / [\gamma_o^* \gamma_v^* c_v(x)] - 2c_v(x)}{1 + \gamma_h^* k_o / \gamma_{pi}^*} \quad [2.12b]$$

$$c_{pi}(x) = \left(\frac{\gamma_h^* k_o}{\gamma_{pi}^*} \right) c_h(x) \quad [2.12c]$$

while the concentrations of the minority defects, c_e and c_{ni} , can be estimated, respectively, using Eq. 1.9a and 1.10a. In writing Eq. 2.12a, it is assumed that $[V_o^{\bullet}] \ll 1$ and $[O_i^{\bullet}] \ll 1$, which are usually true in MIECs in which both c_v and c_e are significant or intrinsic ionic disorders prevail. Alternatively, when c_o is chosen as an independent variable, the concentrations of other defects can be expressed in terms of c_o .

Under the assumption of $c_h \gg c_v$, $J_{ele} = J_e + J_h \approx J_h$ and the terms containing c_e in Eq. 1.16b may be neglected. Substituting for c_o and c_h (using Eq. 2.12a to 2.12c) or for c_v and c_h (using similar expressions in terms of c_o) in Eq. 1.16a and 1.16b and rearranging the equations, we find that the forms of the governing differential equations for distributions of ionic defects and electrical potential in p-type MIECs are identical to those of Eq. 2.4 and 2.6. In this case, however, the superscript or subscript k in the equations represents a mobile ionic defect, $k = v$ for oxygen vacancies and $k = o$ for oxygen interstitials. The coefficients B_n^k , P_n^k , and Q_n^k , of course, depend on the ionic species under consideration. When the distribution of V_o^{\bullet} is considered ($k = v$), the coefficients are defined as follows

$$B_1^v = 2FRTu_h \quad [2.13]$$

$$B_2^v = -2 \left(\frac{RT}{F} \right)$$

$$P_o^v = \left[4u_o J_{ele} \left(1 + \frac{\gamma_h^* k_o}{\gamma_{pi}^*} \right) - 2u_h J_{ion} \right] \left(\frac{k_t^2}{\gamma_v^* \gamma_o^*} \right)$$

$$P_1^v = -u_h c_A J_{ion}$$

$$P_2^v = 2u_h J_{ion} + 4u_v J_{ele} \left(1 + \frac{\gamma_h^* k_o}{\gamma_{pi}^*} \right)$$

$$Q_o^v = 2(3u_v + u_o) \left(\frac{k_t^2}{\gamma_v^* \gamma_o^*} \right)$$

$$Q_1^v = u_v c_A$$

$$Q_2^v = 2u_v$$

$$Q_3^v = u_o c_A \left(\frac{k_t^2}{\gamma_v^* \gamma_o^*} \right)$$

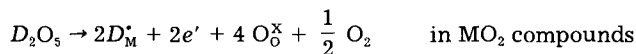
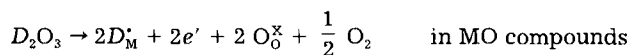
$$Q_4^v = 6u_o \left(\frac{k_t^2}{\gamma_v^* \gamma_o^*} \right)^2$$

$$Q_5^v = (u_h J_{ion} + u_o J_{ele}) \left(\frac{k_t^2}{\gamma_v^* \gamma_o^*} \right)$$

$$Q_6^v = u_h J_{ion} + u_v J_{ele} \left(1 + \frac{\gamma_h^* k_o}{\gamma_{pi}^*} \right)$$

Further, the forms of the analytical solutions to the differential equations for a p-type MIEC are identical to those of Eq. B-1 to B-6, in which $k = v$ or o . Accordingly, the ionic and electronic current densities for a given V and E_N can then be determined from Eq. B-1 to B-6 evaluated for $k = v$ at $x = L$.

n-type MIECs ($c_e \gg c_p$).—In an n-type MIEC, quasi-free electrons may be created by doping of donor impurities



[2.14]

or by solid-gas interactions (Eq. 1.4a or 1.4b proceeding from left to right). In this case, the interaction between electrons and lattice ions (Eq. 1.10a) is expected to be far more important than the interaction between electron holes and lattice ions (Eq. 1.10b) because $c_e \gg c_h$. Under this condition, c_h and c_{pi} may be neglected and the charge neutrality approximation in an n-type MIEC can be expressed as

$$c_{ni} + c_e + 2c_o \approx 2c_v + c_{D,e} \quad [2.15]$$

where $c_{D,e}$ is the molar concentration of ionized donor impurities present in the MIEC to create e' . If the n-type MIEC contains l types of randomly distributed ionized impurities, the compensation effect among different types of ionized impurities can be taken into account by replacing $c_{D,e}$ in Eq. 2.15 with a net concentration of ionized donors, c_D , as defined by Eq. 2.9b. Again, analysis indicates that the equations describing the distributions of the ionic defects and electrical potential in an n-type MIEC are similar to the equations for a p-type MIEC (Eq. 2.4, 2.6, and B-1 to B-6 with $k = v$ or o). One modification needed is to replace the subscript h by subscript e and c_A by c_D in Eq. 2.13 which defines coefficients B_n^v , P_n^v , and Q_n^v .

Extrinsic electronic disorders ($c_e \gg c_h$ or $c_h \gg c_p$) occur not only in MIECs with overwhelming electronic disorders ($n_i \gg k_t$) but also in MIECs with prevailing ionic disorders ($k_t \gg n_i$).

Variations in other properties.—Since conductivity and transference number are defined in the absence of chemical diffusion ($\nabla \mu_k = 0$ or $\nabla c_k = 0$), the variation in partial conductivity (due to the motion of each type of defect under the influence of electric field) can be calculated from

$$\sigma_k(x) \equiv \frac{J_{k,drift}(x)}{-d\phi/dx} = z_k^2 F^2 u_k c_k(x) \quad [2.16]$$

while variation in transference number for each type of defect can be determined as

$$t_k(x) \equiv \frac{J_{k,drift}(x)}{\sum_{k=1}^n J_{k,drift}(x)} = \frac{\sigma_k(x)}{\sum_{k=1}^n \sigma_k(x)} = \frac{z_k^2 u_k c_k(x)}{\sum_{k=1}^n z_k^2 u_k c_k(x)} \quad [2.17]$$

Clearly, the transport properties can vary considerably with position in MIECs in the direction in which there exists a gradient in p_{O_2} . Thus, the average conductivity over the thickness of a sample, $\langle \sigma_k \rangle$, can be determined as

$$\frac{1}{\langle \sigma_k \rangle} = \frac{1}{L} \int_{x=0}^{x=L} \frac{dx}{\sigma_k(x)} = \frac{1}{L} \left(\frac{1}{z_k^2 F^2 u_k} \right) \int_0^L \frac{dx}{c_k(x)} \quad [2.18]$$

whereas the average transference number over the thickness is given by

$$\langle t_k \rangle = \frac{\langle \sigma_k \rangle}{\sum_{k=1}^n \langle \sigma_k \rangle} \quad [2.19]$$

When the MIEC is in equilibrium with O₂ gas, Eq. 1.9c prevails and, hence, the variation in virtual partial pressure of oxygen within the MIEC can be determined from

$$\frac{p_{O_2}(x)}{p_{O_2}^I} = \left(\frac{1 - \gamma_v^* c_v(x) M/d}{1 - \gamma_v^* c_v^I M/d} \right)^2 \left(\frac{c_v^I}{c_v(x)} \right)^2 \left(\frac{c_e^I}{c_e(x)} \right)^4 \quad [2.20a]$$

which can be adequately approximated by

$$\frac{p_{O_2}(x)}{p_{O_2}^I} \approx \left(\frac{c_v^I}{c_v(x)} \right)^2 \left(\frac{c_e^I}{c_e(x)} \right)^4 = \left(\frac{\sigma_v^I}{\sigma_v(x)} \right)^2 \left(\frac{\sigma_e^I}{\sigma_e(x)} \right)^4 \quad [2.20b]$$

when $[V_O^{*}] \ll 1$ (this is true in MIECs in which intrinsic ionic disorders prevail or both c_v and c_o are significant).

Further, the variations in electrostatic potential, Fermi level, electrochemical potentials of ionic defects, and the current carried by each type of defect can also be calculated from the ionic and electronic current densities and the variations in concentrations and transport properties.

Solutions for MIECs with Two Types of Significant Mobile Defects

For MIECs in which both ionic and electronic disorders are extrinsic ($c_e \gg c_h$ or $c_h \gg c_e$ and $c_v \gg c_o$ or $c_o \gg c_v$), there are only two types of significant mobile defects, one ionic and one electronic. This is the simplest yet the most important class of MIECs. Under certain circumstances, in fact, many technologically important MIECs may be treated as an MIEC containing only two types of mobile defects, including materials based on doped zirconia, ceria, and bismuth oxides as well as perovskite-type compounds like LSM, LSC, and LSF.

For MIECs with two types of significant mobile defects, coefficients P_o^k , Q_o^k , Q_3^k , Q_4^k , and Q_5^k become negligible and, hence, Eq. 2.4 and 2.6 reduce, respectively, to

$$\frac{dx}{B_1^k} = \left[\frac{Q_1^k + Q_2^k c_k}{P_1^k + P_2^k c_k} \right] dc_k \quad [3.1a]$$

$$\frac{d\phi}{B_2^k} = \left[\frac{Q_6^k}{P_1^k + P_2^k c_k} \right] dc_k \quad [3.1b]$$

where the subscript or superscript k represents a mobile defect inside the MIEC ($k = e, h, v, \text{ or } o$). Equations 3.1a and 3.1b can also be obtained by eliminating $d\phi$ and dx , respectively, from Eq. 1.16a and 1.16b while noting that only two types of mobile defects are significant. For the general case, *i.e.*, $P_2^k \neq 0$ while P_1^k may take any value, integration of Eq. 3.1a and 3.1b over the thickness of the MIEC yields

$$\left(\frac{P_2^k}{B_1^k} \right) x = Q_2^k [c_k(x) - c_k^I] + \left(Q_1^k - \frac{P_1^k Q_2^k}{P_2^k} \right) \ln \left[\frac{P_2^k c_k(x) + P_1^k}{P_2^k c_k^I + P_1^k} \right] \quad [3.2a]$$

$$\frac{\phi(x) - \phi^I}{B_2^k} = \frac{Q_6^k}{P_2^k} \ln \left[\frac{P_2^k c_k(x) + P_1^k}{P_2^k c_k^I + P_1^k} \right] \quad [3.2b]$$

These two equations are the general expressions for distributions of defects and electrical potential in MIECs with

two types of significant mobile defects. They can also be obtained, respectively, by ignoring the terms containing coefficients P_o^k , Q_o^k , Q_3^k , Q_4^k , and Q_5^k in Eq. B-1 (or B-3) and B-2 (or B-4) in Appendix B.

Although P_2^k is apparently a function of J_{ele} and J_{ion} (as defined in Eq. 2.5), evaluating Eq. 3.2a and 3.2b at $x = L$, we find that P_2^k is, in fact, independent of J_{ele} and J_{ion} and is related to $(c_k^{II} - c_k^I)$ and $\phi^{II} - \phi^I$ as follows

$$P_2^k = \frac{B_1^k Q_2^k}{L} [(c_k^{II} - c_k^I) + \beta^k (\phi^{II} - \phi^I)] \quad [3.3]$$

where the coefficient β^k is given by

$$\beta^k = \frac{Q_1^k P_2^k - P_1^k Q_2^k}{B_2^k Q_2^k Q_6^k} \quad [3.3a]$$

which is independent of J_{ele} and J_{ion} and is determined primarily by c_A or c_D while $\phi^{II} - \phi^I$ is related to the electrical state of the MIEC as defined by Eq. 1.7. Thus, P_2^k is a known constant for a given electrical (V) and chemical (p_{O_2} and $p_{O_2}^I$) condition.

In order to gain some insight into the distributions of defects and electrical potential, let us examine the limits of the general equations (Eq. 3.2a and 3.2b) under some special conditions. In the absence of uniformly distributed immobile charges (*i.e.*, $c_A \rightarrow 0$ or $c_D \rightarrow 0$), coefficient P_1^k and Q_1^k vanish and, hence, Eq. 3.2a and 3.2b simplify, respectively, to

$$c_k(x) - c_k^I = (c_k^{II} - c_k^I) \frac{x}{L} \quad [3.4a]$$

$$\phi(x) - \phi^I = \left(\frac{B_2^k Q_6^k}{P_2^k} \right) \ln \left[1 + \left(\frac{c_k^{II}}{c_k^I} - 1 \right) \frac{x}{L} \right] \quad [3.4b]$$

indicating that the distribution of each mobile defect is linear while the distribution of the electrical potential is logarithmic along the thickness of the MIEC.

In the presence of uniformly distributed immobile charges (*i.e.*, $c_A \neq 0$ or $c_D \neq 0$ and, hence, $P_1^k \neq 0$ and $Q_1^k \neq 0$), however, Eq. 3.2a and 3.2b can be rewritten as

$$c_k(x) - c_k^I = (c_k^{II} - c_k^I) \frac{x}{L} + \beta^k \left[(\phi^{II} - \phi^I) \frac{x}{L} - [\phi(x) - \phi^I] \right] \quad [3.5a]$$

$$\phi(x) - \phi^I = (\phi^{II} - \phi^I) \frac{x}{L} + \frac{1}{\beta^k} \left[(c_k^{II} - c_k^I) \frac{x}{L} - [c_k(x) - c_k^I] \right] \quad [3.5b]$$

Evaluation of the last two equations indicates that, when $c_A \neq 0$ or $c_D \neq 0$, strictly speaking, the distribution of neither electrical potential nor each type of defect is linear since the last term in both equations is nonlinear. However, the distributions of mobile defects approach linear while the distribution of electrical potential approaches logarithmic as coefficient β^k (or c_A or c_D) becomes sufficiently small. In contrast, when β^k (or c_A or c_D) is sufficiently large, Eq. 3.2a and 3.5b reduce, respectively, to

$$c_k(x) + \frac{P_1^k}{P_2^k} \approx \left(c_k^I + \frac{P_1^k}{P_2^k} \right) \exp \left[\frac{P_2^k (\phi^{II} - \phi^I)}{B_2^k Q_2^k} \left(\frac{x}{L} \right) \right] \quad [3.6a]$$

$$\phi(x) - \phi^I \approx (\phi^{II} - \phi^I) \frac{x}{L} \quad [3.6b]$$

suggesting that the distribution of electrical potential approaches linear while the distributions of mobile defects approach exponential. Except these two limiting cases, however, the distributions of defects and electrical potential are nonlinear in general. The deviations from linear distribution depends on the value of β^k , which is deter-

mined primarily by c_A or c_D , the concentration of uniformly distributed immobile charges.

MIECs with two types of significant mobile defects can be divided into four groups and the coefficients for each type of MIEC depends on the defect equilibria prevailing in the MIEC. In this section, the equations for J_{ion} , J_{ele} , $c_k(x)$, and $\phi(x)$ are derived for each type of MIEC under the general conditions (i.e., $P_2^k \neq 0$). Similar equations for each type of MIEC under a special condition, $P_2^k = 0$, are summarized in Appendix C. Once $c_k(x)$ and $\phi(x)$ are determined, variations in other properties inside the MIEC, such as $\sigma_k(x)$, $t_k(x)$, $p_{O_2}(x)$, $\mu_{O_2}(x)$, and $\tilde{\mu}_k(x)$, can be readily obtained using Eq. 2.16 to 2.20 and Eq. 1.1.

MIECs with V_O^{*} and e' .—When $c_v \gg c_o$ and $c_e \gg c_h$, the electroneutrality equation, Eq. 2.2 or 2.15, reduces to

$$c_A + c_{ni} + c_e \approx 2c_v \quad [3.7]$$

The distribution of V_O^{*} or e' is determined by Eq. 3.2a with $k = v$ or e while the electrical potential distributes according to Eq. 3.2b with $k = v$ or e . When the electrons are under consideration (i.e., $k = e$), the coefficients B_n^k , P_n^k , and Q_n^k in Eq. 3.1 and 3.2 are the same as defined in Eq. 2.5 and 2.7 whereas Eq. 3.3 takes the specific form of

$$P_2^e = \frac{-FRTu_e u_v}{L} \left\{ 3 \left(1 + \frac{\gamma_e^* k_R}{\gamma_{ni}} \right) (c_e^{II} - c_e^I) + 2c_A \left[\ln \left(\frac{c_e^{II}}{c_e^I} \right) + \frac{VF}{RT} \right] \right\} \neq 0 \quad [3.8]$$

where

$$1 + \frac{\gamma_e^* k_R}{\gamma_{ni}} = \frac{2c_v^I - c_A}{c_e^I} \quad [3.8a]$$

Thus, P_2^e is indeed independent of J_k and is a known constant for a given V and E_N (or $P_{O_2}^I$ and $P_{O_2}^{II}$). Evaluating Eq. 3.2a at $x = L$, we find that, in terms of P_2^e and other known constants, the electronic current density can be determined from the following implicit expression

$$J_{ele} = \frac{P_2^e}{3u_v \left(1 + \frac{\gamma_e^* k_R}{\gamma_{ni}} \right)} \left\{ \frac{\frac{RT}{F} \ln \left(\frac{c_e^{II}}{c_e^I} \right) + V}{\frac{RT}{F} \ln \left(\frac{P_2^e c_e^{II} - 2u_v c_A J_{ele}}{P_2^e c_e^I - 2u_v c_A J_{ele}} \right)} - 1 \right\} \quad [3.9a]$$

while the corresponding ionic current density can be determined from

$$J_{ion} = \frac{1}{u_e} \left[P_2^e + 2u_v \left(1 + \frac{\gamma_e^* k_R}{\gamma_{ni}} \right) J_{ele} \right] \quad [3.9b]$$

The distribution of electrons in the MIEC is then given implicitly by

$$\frac{-P_2^e x}{FRTu_v u_e} = 3 \left(\frac{2c_v^I - c_A}{c_e^I} \right) [c_e(x) - c_e^I] + \left[2c_A - \frac{3P_2^e}{P_2^e} \left(\frac{2c_v^I - c_A}{c_e^I} \right) \right] \ln \left[\frac{P_2^e c_e(x) + P_1^e}{P_2^e c_e^I + P_1^e} \right] \quad [3.10a]$$

whereas the distribution of electrical potential is given explicitly by

$$\phi(x) - \phi^I = \frac{RT}{F} \left[1 + \frac{3u_v J_{ele}}{P_2^e} \left(\frac{2c_v^I - c_A}{c_e^I} \right) \right] \ln \left[\frac{P_2^e c_e(x) + P_1^e}{P_2^e c_e^I + P_1^e} \right] \quad [3.10b]$$

In the absence of impurities (i.e., $c_A = 0$), the extrinsic disorders in the MIEC may arise merely from considerable departure from stoichiometry due to reactions at the surface (Eq. 1.4). Accordingly the general expressions Eq. 3.9 and 3.10 then simplify, respectively, to

$$J_{ele} = \frac{\sigma_e^I}{L} \left[\frac{-V}{\ln \left(\frac{c_e^{II}}{c_e^I} \right)} \right] \left(\frac{c_e^{II}}{c_e^I} - 1 \right) \quad [3.11a]$$

$$J_{ion} = \frac{\sigma_v^I}{L} \left[\frac{-V}{\ln \left(\frac{c_e^{II}}{c_e^I} \right)} - \frac{3RT}{2F} \right] \left(\frac{c_e^{II}}{c_e^I} - 1 \right) \quad [3.11b]$$

$$\frac{c_e(x)}{c_e^I} = 1 + \left(\frac{c_e^{II}}{c_e^I} - 1 \right) \frac{x}{L} \quad [3.12a]$$

$$\phi(x) - \phi^I = \left[\frac{V}{\ln \left(\frac{c_e^{II}}{c_e^I} \right)} + \frac{RT}{F} \right] \ln \left[1 + \left(\frac{c_e^{II}}{c_e^I} - 1 \right) \frac{x}{L} \right] \quad [3.12b]$$

where

$$\frac{c_e^{II}}{c_e^I} = \frac{c_v^{II}}{c_v^I} = \frac{\sigma_e^{II}}{\sigma_e^I} = \frac{\sigma_v^{II}}{\sigma_v^I} = \left(\frac{P_{O_2}^I}{P_{O_2}^{II}} \right)^{1/6} \left[\frac{1 - c_v^{II} \gamma_v^* M/d}{1 - c_v^I \gamma_v^* M/d} \right]^{1/3} \approx \left(\frac{P_{O_2}^I}{P_{O_2}^{II}} \right)^{1/6} \quad [3.12c]$$

The last approximation is under the assumption of $[V_O^{*}] \ll 1$. Thus, the ratio of c_e^{II}/c_e^I in Eq. 3.11 and 3.12 can be replaced by σ_e^{II}/σ_e^I or σ_v^{II}/σ_v^I or approximated by $(P_{O_2}^I/P_{O_2}^{II})^{1/6}$. Once $c_e(x)$ is determined, the concentrations of other significant defects can be calculated as

$$c_v(x) = \frac{1}{2} \left[\left(\frac{2c_v^I - c_A}{c_e^I} \right) c_e(x) + c_A \right] \quad [3.13a]$$

$$c_{ni}(x) = \left(\frac{2c_v^I - c_A}{c_e^I} - 1 \right) c_e(x) \quad [3.13b]$$

while the concentrations of the minority defects, c_o and c_h , can be determined from Eq. 1.9a and 1.9b. When the uniformly distributed charges arise merely from ionized acceptors for creation of V_O^{*} and donors for creation of e' , we can define $c_A = c_{A,v} - c_{D,e}$ to take account of the effect of both donor and acceptor defects.

MIECs with V_O^{*} and h' .—When $c_v \gg c_o$ and $c_h \gg c_e$, Eq. 2.2 or 2.11 reduces to

$$c_A \approx c_h + 2c_v + c_{pi} \quad [3.14]$$

The distribution of V_O^{*} or h' is determined by Eq. 3.2a with $k = v$ or h while the electrical potential distributes according to Eq. 3.2b with $k = v$ or h . When oxygen vacancies are under consideration (i.e., $k = v$), the coefficients B_n^k , P_n^k , and Q_n^k in Eq. 3.1 and 3.2 are the same as defined in Eq. 2.13 while Eq. 3.3 can be rewritten as

$$P_2^v = \frac{4FRTu_v u_h}{L} \left\{ (c_v^{II} - c_v^I) + c_A \left[\ln \left(\frac{c_e^{II}}{c_e^I} \right) + \frac{VF}{RT} \right] \right\} \neq 0 \quad [3.15]$$

which is independent of J_k and is a known constant for a given V and E_N . Evaluating Eq. 3.2a at $x = L$, we find that, in terms of P_2^v and other known constants, the ionic current density can be determined from the following implicit expression

$$J_{ion} = \frac{-P_2^v}{u_h} \left\{ \frac{\frac{RT}{F} \ln \left(\frac{c_e^{II}}{c_e^I} \right) + V}{\frac{RT}{F} \ln \left(\frac{P_2^v c_v^{II} - u_h c_A J_{ion}}{P_2^v c_v^I - u_h c_A J_{ion}} \right)} + \frac{1}{2} \right\} \quad [3.16a]$$

the corresponding electronic current density can be determined from

$$J_{ele} = \frac{P_2^v - 2u_h J_{ion}}{4u_v \left(1 + \frac{\gamma_h^* k_o}{\gamma_{pi}^*} \right)} \quad [3.16b]$$

while the distributions of V_o^{**} and electrical potential can be expressed, respectively, as

$$\frac{-P_2^v x}{2FRTu_v u_h} = 2[c_v(x) - c_v^I] + \left(c_A - \frac{2P_1^v}{P_2^v} \right) \ln \left[\frac{P_2^v c_v(x) + P_1^v}{P_2^v c_v^I + P_1^v} \right] \quad [3.17a]$$

$$\phi(x) - \phi^I = \frac{RT}{F} \left[\frac{2u_v J_{ele}}{P_2^v} \left(1 + \frac{\gamma_h^* k_o}{\gamma_{pi}^*} \right) - 1 \right] \ln \left[\frac{P_2^v c_v(x) + P_1^v}{P_2^v c_v^I + P_1^v} \right] \quad [3.17b]$$

where

$$1 + \frac{\gamma_h^* k_o}{\gamma_{pi}^*} = \frac{c_A - 2c_v^I}{c_h^I} \quad [3.17c]$$

The concentrations of other significant or minority defects as well as variations in properties of the MIEC can be further calculated as discussed earlier. When the uniformly distributed charges arise merely from ionized acceptors for creation of both V_o^{**} and h^* , we can define $c_A = c_{A,v} + c_{A,h}$ to take into account of the effect of all acceptor defects.

MIECs with O_i'' and h^* .—When $c_o \gg c_v$ and $c_h \gg c_e$, Eq. 2.9 or 2.11 reduces to

$$c_A + 2c_o \approx c_h + c_{pi} \quad [3.18]$$

The distribution of O_i'' or h^* is determined by Eq. 3.2a ($k = o$ or h) while the electrical potential distributes according to Eq. 3.2b ($k = o$ or h). When electron holes are under consideration (*i.e.*, $k = h$), the coefficients in Eq. 3.1 and 3.2 are given by

$$B_1^h = FRTu_o \quad [3.19]$$

$$B_2^h = \left(\frac{RT}{F} \right)$$

$$P_1^h = -2u_o c_A J_{ele}$$

$$P_2^h = 2u_o \left(1 + \frac{\gamma_h^* k_o}{\gamma_{pi}^*} \right) J_{ele} - u_h J_{ion}$$

$$Q_1^h = 2u_h c_A$$

$$Q_2^h = -3u_h \left(1 + \frac{\gamma_h^* k_o}{\gamma_{pi}^*} \right)$$

$$Q_6^h = u_o \left(1 + \frac{\gamma_h^* k_o}{\gamma_{pi}^*} \right) J_{ele} + u_h J_{ion}$$

and in view of Eq. 3.3, P_2^e can also be expressed as

$$P_2^h = \frac{-FRTu_h u_o}{L} \left\{ 3 \left(1 + \frac{\gamma_h^* k_o}{\gamma_{pi}^*} \right) (c_h^{II} - c_h^I) - 2c_A \left[\ln \left(\frac{c_e^{II}}{c_e^I} \right) + \frac{VF}{RT} \right] \right\} \neq 0 \quad [3.20]$$

where

$$1 + \frac{\gamma_h^* k_o}{\gamma_{pi}^*} = \frac{2c_o^I + c_A}{c_h^I} \quad [3.20a]$$

Thus, the electronic and ionic current density can be expressed, respectively, as

$$J_{ele} = \frac{P_2^h}{3u_o \left(\frac{2c_o^I + c_A}{c_h^I} \right)} \left\{ \frac{\frac{RT}{F} \ln \left(\frac{c_e^{II}}{c_e^I} \right) + V}{\frac{RT}{F} \ln \left(\frac{P_2^h c_h^{II} - 2u_o c_A J_{ele}}{P_2^h c_h^I - 2u_o c_A J_{ele}} \right)} + 1 \right\} \quad [3.21a]$$

$$J_{ion} = \frac{1}{u_h} \left[2u_o \left(\frac{2c_o^I + c_A}{c_h^I} \right) J_{ele} - P_2^h \right] \quad [3.21b]$$

while the distributions of h^* and electrical potential can be expressed, respectively, as

$$\frac{P_2^h x}{FRTu_h u_o} = -3 \left(1 + \frac{\gamma_h^* k_o}{\gamma_{pi}^*} \right) [c_h(x) - c_h^I] + \left[2c_A + \frac{3P_1^h}{P_2^h} \left(1 + \frac{\gamma_h^* k_o}{\gamma_{pi}^*} \right) \right] \ln \left[\frac{P_2^h c_h(x) + P_1^h}{P_2^h c_h^I + P_1^h} \right] \quad [3.22a]$$

$$\phi(x) - \phi^I = \frac{RT}{F} \left[\frac{3u_o J_{ele}}{P_2^h} \left(1 + \frac{\gamma_h^* k_o}{\gamma_{pi}^*} \right) - 1 \right] \ln \left[\frac{P_2^h c_h(x) + P_1^h}{P_2^h c_h^I + P_1^h} \right] \quad [3.22b]$$

When the uniformly distributed charges are due merely to impurities for creation of h^* and O_i'' , define $c_A = c_{A,h} - c_{D,o}$ to take into account of any compensation effect of donor and acceptor defects. For MIECS with V_m'' and h^* being the majority defects, Eq. 3.18 to 3.22 remain the same provided that the c_o in the equations is replaced with the concentration of V_m'' .

MIECs with O_i'' and e' .—When $c_o \gg c_v$ and $c_e \gg c_h$, Eq. 2.9 or 2.15 reduces to

$$c_{ni} + 2c_o + c_e \approx c_D \quad [3.23]$$

The distribution of O_i'' or e' is determined by Eq. 3.2a ($k = o$ or e). While the electrical potential distributes according to Eq. 3.2b ($k = o$ or e). When oxygen interstitials are considered (*i.e.*, $k = o$), the coefficients in Eq. 3.1 and 3.2 can be defined as follows

$$B_1^o = -2FRTu_e \quad [3.24]$$

$$B_2^o = 2 \left(\frac{RT}{F} \right)$$

$$P_1^o = -u_e c_D J_{ion}$$

$$P_2^o = 2u_e J_{ion} + 4u_o \left(1 + \frac{\gamma_e^* k_R}{\gamma_{ni}^*} \right) J_{ele}$$

$$Q_1^o = u_o c_D$$

$$Q_2^o = 2u_o$$

$$Q_6^o = u_e J_{ion} + u_o \left(1 + \frac{\gamma_e^* k_R}{\gamma_{ni}^*} \right) J_{ele}$$

while P_2^o can also be expressed as

$$P_2^o = \frac{-4FRTu_o u_e}{L} \left\{ (c_o^{II} - c_o^I) + c_D \left[\ln \left(\frac{c_e^{II}}{c_e^I} \right) + \frac{VF}{RT} \right] \right\} \neq 0 \quad [3.25]$$

Thus, the ionic and electronic current density can be expressed, respectively, as

$$J_{ion} = \frac{P_2^o}{u_e} \left\{ -\frac{1}{2} + \frac{\frac{RT}{F} \ln \left(\frac{c_e^{II}}{c_e^I} \right) + V}{\frac{RT}{F} \ln \left(\frac{P_2^o c_o^{II} - u_e c_D J_{ion}}{P_2^o c_o^I - u_e c_D J_{ion}} \right)} \right\} \quad [3.26a]$$

$$J_{ele} = \frac{P_2^o - 2u_e J_{ion}}{4u_o \left(1 + \frac{\gamma_e^* k_R}{\gamma_{ni}^*} \right)} \quad [3.26b]$$

while the distributions of O_2^o and electrical potential can be expressed, respectively, as

$$\frac{-P_2^o x}{2FRTu_o u_e} = 2[c_o(x) - c_o^I] + \left[c_D + \frac{2P_1^o}{P_2^o} \right] \ln \left[\frac{P_2^o c_o(x) + P_1^o}{P_2^o c_o^I + P_1^o} \right] \quad [3.27a]$$

$$\phi(x) - \phi^I = \frac{RT}{F} \left[1 - \frac{2u_o J_{ele}}{P_2^o} \left(1 + \frac{\gamma_e^* k_R}{\gamma_{ni}^*} \right) \right] \ln \left[\frac{P_2^o c_o(x) + P_1^o}{P_2^o c_o^I + P_1^o} \right] \quad [3.27b]$$

where

$$1 + \frac{\gamma_e^* k_R}{\gamma_{ni}^*} = \frac{c_D - 2c_o^I}{c_e^I} \quad [3.27c]$$

When the uniformly distributed charges are due only to donor impurities for creation of both e' and O_2^o , define $c_D = c_{D,e} + c_{D,o}$ to take account of the effect of all donor impurities.

Discussion of Solutions

Integration of transport equations for a given set of boundary conditions (V and E_N) yields analytical expressions for (i) steady-state distributions of defects, $c_k(x)$, and electrical potential, $\phi(x)$, in the MIEC; (ii) variation in transport properties such as partial conductivity, $\sigma_k(x)$, and transference numbers, $t_k(x)$, in the MIEC; and (iii) current carried by each defect, $J_k(x)$, chemical potential of oxygen, $\mu_{O_2}(x)$, and the electrochemical potential of each defect, $\tilde{\mu}_k(x)$, in the MIEC.

Equations B-1 to B-6 are the general expressions for distributions of defects and electrical potential in MIECs containing three types of significant mobile defects whereas Eq. 3.2, C-1, and C-2 are expressions for distribution of defects and electrical potential in MIECs with two types of significant mobile defects. These expressions can be used not only to predict the steady-state behavior of an MIEC under the influence of various chemical and electrical stimuli applied to the MIEC, but also to predict the terminal voltage across the MIEC (the electrical state) for a given J_T and E_N , or to determine the expected oxygen partial pressures at the interfaces (the chemical state) for a given J_T and V . These expressions are applicable to a variety of MIECs with very different characteristics.

The model, however, requires prior knowledge of the following properties of the MIEC as input parameters

1. Mobility (u_k) and equilibrium concentrations (c_k^I and c_k^{II}) of each defect (or alternatively, the partial conductivity due to the motion of each defect, σ_k^I and σ_k^{II}) in the MIEC when immersed in a uniform atmosphere having oxygen partial pressure of $p_{O_2}^I$ and $p_{O_2}^{II}$ at a given temperature.

2. Activity coefficient of each defect (γ_k) if it is deviated from unity.

3. Equilibrium constants for defect reactions which appreciably influence the defect equilibrium in the MIEC. For MIECs in which both ionic and electronic disorders are extrinsic, however, n_i and k_i are not needed to determine the distribution of significant defects and electrical potential; they would be needed to calculate the concentrations of the minority defects.

These properties primarily determine the coefficients (Q^k and P^k) in the general Eq. 2.4, 2.6, 3.1, and 3.2 and the coefficients, in turn, determine the behavior of a particular MIEC. Accordingly, modeling the behavior of an MIEC starts with identifying these coefficients for the MIEC under consideration.

In this section, we take an MIEC with V_o^{**} and e' being the predominant defects as an example to illustrate how to use Eq. 3.9 and 3.10 for predicting the steady-state behavior of an MIEC under the influence of various electrical (V) and chemical ($p_{O_2}^I$ and $p_{O_2}^{II}$) conditions. Also, for some conditions discussed below, the derived general expressions are further simplified by letting $c_A \rightarrow 0$ in order to gain an easy insight into the derived equations. For an MIEC containing negligible amount of uniformly distributed immobile defects (i.e., $c_A \rightarrow 0$), only two independent transport properties of the MIEC are required as input data: σ_v^I and σ_v^I as measured in a uniform atmosphere with $p_{O_2}^I$.

Current-voltage- p_{O_2} relationship.—Combination of Eq. 3.9a and 3.9b yields the total current density passing through the MIEC

$$J_T = \frac{P_2^o}{3u_e u_v (2c_v^I - c_A)} \left\{ u_v (2c_v^I - c_A) - u_e c_e^I + \frac{[2u_v (2c_v^I - c_A) + u_e c_e^I] \left[\frac{RT}{F} \ln \left(\frac{c_e^{II}}{c_e^I} \right) + V \right]}{\frac{RT}{F} \ln \left(\frac{P_2^o c_e^{II} - 2u_v c_A J_{ele}}{P_2^o c_e^I - 2u_v c_A J_{ele}} \right)} \right\} \quad [4.1a]$$

When $c_A \rightarrow 0$ and in view of Eq. 3.12c, Eq. 4.1a simplifies to

$$J_T = \left[\left(\frac{\sigma_v^I + \sigma_e^I}{L} \right) \frac{6V}{\ln \left(\frac{p_{O_2}^{II}}{p_{O_2}^I} \right)} - \frac{3RT}{2F} \frac{\sigma_v^I}{L} \right] \left[\left(\frac{p_{O_2}^I}{p_{O_2}^{II}} \right)^{\frac{1}{6}} - 1 \right] \quad [4.1b]$$

Equations 4.1a and 4.1b are the general relationship among the observable current density (J_T), voltage across the MIEC (V), and the partial pressures of oxygen to which the MIEC is exposed (or E_N). Shown in Fig. 2 are some typical current-voltage characteristics for MIECs with different properties under a specified chemical condition ($P_{O_2}^I/P_{O_2}^{II} = 10^{20}$ or $E_N = 1.07$ V at 800°C). The current densities were calculated using Eq. 3.9a, 3.9b, and 4.1. Three interesting cases need special attention.

1. When $V = 0$ and $E_N \neq 0$, Eq. 4.1a and 4.1b reduce, respectively, to

$$J_T = \frac{-RT}{2F} \left(\frac{\sigma_v^I}{L} \right) \left[3 \left(\frac{c_e^{II}}{c_e^I} - 1 \right) + \left(\frac{c_A}{c_v^I} \right) \ln \left(\frac{2c_v^{II} - c_A}{2c_v^I - c_A} \right) \right] = J_{ion} \quad [4.2a]$$

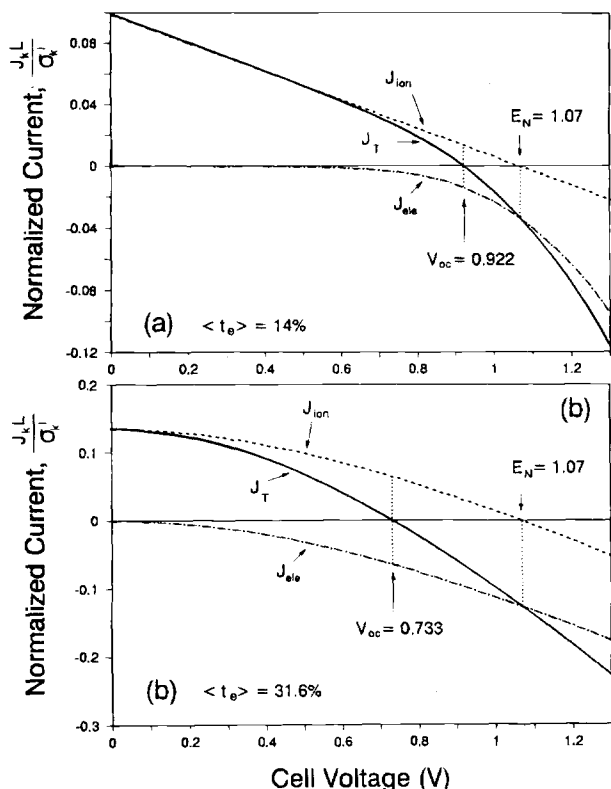


Fig. 2. Current-voltage characteristics of MIECs with different properties: (a) $\langle t_e \rangle \approx 14\%$ ($c_A = 5 \times 10^{-4}$, $c_e^I = 2.52 \times 10^{-4}$, $c_e^II = 2.5 \times 10^{-4}$, and $c_A^I = 4.0 \times 10^{-6}$ mol/cm³) and (b) $\langle t_e \rangle \approx 31.6\%$ ($c_A = 5 \times 10^{-3}$, $c_e^I = 2.5 \times 10^{-3}$, $c_e^II = 2.5 \times 10^{-3}$, and $c_A^I = 1.0 \times 10^{-9}$ mol/cm³). It is assumed that $p_{O_2}^II/p_{O_2}^I = 10^{20}$, $u_e = 1.0 \times 10^{-6}$, $u_v = 1.0 \times 10^{-9}$ mol cm² J⁻¹ s⁻¹, $T = 800^\circ\text{C}$ and $L = 0.1$ cm.

$$J_T = -\frac{\sigma_v^I}{L} \left(\frac{3RT}{2F} \right) \left[\left(\frac{p_{O_2}^I}{p_{O_2}^II} \right)^{\frac{1}{6}} - 1 \right]$$

$$= -3 \left[2FD_v \left(\frac{c_v^{II} - c_v^I}{L} \right) \right] = +3J_{diff,v} \quad [4.2b]$$

implying that the electronic current vanishes (i.e., $J_{ele} = 0$) and the observable current is due merely to the motion of ionic defects (i.e., $J_T = J_{ion}$). This can be readily interpreted by noting that, when $V = 0$, Eq. 1.7 can be rewritten as

$$RT \ln \left(\frac{c_e^{II}}{c_e^I} \right) - F(\phi^{II} - \phi^I) = \tilde{\mu}_e^{II} - \tilde{\mu}_e^I = 0$$

Thus, $V = 0$ implies that $\nabla \tilde{\mu}_e = \nabla \tilde{\mu}_h = 0$ (i.e., there is no driving force for transport of electronic defects) and hence $J_{ele} = 0$.

2. When $V = E_N$ and $E_N \neq 0$, on the other hand, Eq. 4.1a and 4.1b reduce, respectively, to

$$J_T = \frac{RT}{2F} \left(\frac{\sigma_e^I}{L} \right) \left[3 \left(\frac{c_e^{II}}{c_e^I} - 1 \right) - \left(\frac{c_A}{c_e^I} \right) \ln \left(\frac{c_v^{II}}{c_v^I} \right) \right] = J_{ele} \quad [4.3a]$$

$$J_T = \frac{\sigma_e^I}{L} \left(\frac{3RT}{2F} \right) \left[\left(\frac{p_{O_2}^I}{p_{O_2}^II} \right)^{\frac{1}{6}} - 1 \right] = \frac{3}{2} \left[FD_e \left(\frac{c_e^{II} - c_e^I}{L} \right) \right] = \frac{3}{2} J_{diff,e} \quad [4.3b]$$

suggesting that the ionic current vanishes (i.e., $J_{ion} = 0$) so that the observable current is due merely to the motion of the electronic defects (i.e., $J_T = J_{ele}$). This is because, when $V = E_N$, Eq. 1.7 can be rewritten as

$$\phi^{II} - \phi^I = \frac{RT}{2F} \ln \left[\left(\frac{c_e^{II}}{c_e^I} \right)^2 \left(\frac{p_{O_2}^II}{p_{O_2}^I} \right)^{\frac{1}{2}} \right]$$

which is identical to

$$RT \ln \left(\frac{c_v^{II}}{c_v^I} \right) + 2F(\phi^{II} - \phi^I) = \tilde{\mu}_v^{II} - \tilde{\mu}_v^I = 0$$

Thus, $V = E_N$ implies that $\nabla \tilde{\mu}_v = \nabla \tilde{\mu}_o = 0$ (i.e., the driving force for ionic transport vanishes) and hence $J_{ion} = 0$.

3. When $J_T = 0$ and $E_N \neq 0$, to an outside observer, the transport of defects within the MIEC is apparently driven merely by the chemical potential gradient of oxygen, although it is an electrochemical process in nature. The observed voltage across an MIEC is the open-circuit voltage (OCV), which can be either readily determined experimentally or calculated as follows

$$V_{oc} = V(J_T = 0)$$

$$= \frac{RT}{F} \left\{ \frac{u_e c_e^I - u_v (2c_v^I - c_A)}{u_e c_e^I + 2u_v (2c_v^I - c_A)} \ln \left(\frac{\sigma_v^{II} + \sigma_e^{II}}{\sigma_v^I + \sigma_e^I} \right) - \ln \left(\frac{c_e^{II}}{c_e^I} \right) \right\} \quad [4.4a]$$

When $c_A \rightarrow 0$ and in view of Eq. 3.12c, Eq. 4.4a reduces to

$$V_{oc} = \left(\frac{\sigma_v^I}{\sigma_v^I + \sigma_e^I} \right) \left(\frac{RT}{4F} \right) \ln \left(\frac{p_{O_2}^II}{p_{O_2}^I} \right) = t_v^I E_N \quad [4.4b]$$

Equation 4.4b agrees with the expression for OCV derived initially by Wagner under the assumption that the interfacial reactions are sufficiently fast. Thus, the effective or average ionic transference number of an MIEC under the conditions can be expressed as

$$\langle t_v \rangle = \frac{4}{\ln \left(\frac{p_{O_2}^II}{p_{O_2}^I} \right)} \left\{ \frac{u_e c_e^I - u_v (2c_v^I - c_A)}{u_e c_e^I + 2u_v (2c_v^I - c_A)} \ln \left(\frac{\sigma_v^{II} + \sigma_e^{II}}{\sigma_v^I + \sigma_e^I} \right) - \ln \left(\frac{c_e^{II}}{c_e^I} \right) \right\} \quad [4.5a]$$

which reduces, when $c_A \rightarrow 0$, to

$$\langle t_v \rangle = \frac{\sigma_v^I}{\sigma_v^I + \sigma_e^I} = t_v^I = \frac{\sigma_v^{II}}{\sigma_v^{II} + \sigma_e^{II}} = t_v^{II} \quad [4.5b]$$

That is, the transference numbers are independent of position in an MIEC with $c_A \rightarrow 0$.

Clearly, any deviation in voltage across the MIEC away from OCV, $V - V_{oc}$, represents an alteration of the electrical state of the MIEC through an external circuit. When $V = V_{oc}$ or when the MIEC is not connected to a circuit, however, there still exists a built-in electric field within the MIEC induced by an applied $E_N \neq 0$. Under an open-circuit condition, the total or observable current vanishes so that the ionic current is exactly balanced by the electronic current

$$J_{ion} = -J_{ele} = \frac{-RTFu_e u_v c_e^I}{[u_e c_e^I + 2u_v (2c_v^I - c_A)]L} \left\{ 3(2c_v^I - c_A) \left(\frac{c_e^{II}}{c_e^I} - 1 \right) + 2c_A \left[\frac{u_e c_e^I - u_v (2c_v^I - c_A)}{u_e c_e^I + 2u_v (2c_v^I - c_A)} \right] \ln \left(\frac{\sigma_v^{II}}{\sigma_v^I} \right) \right\} \quad [4.6a]$$

When $c_A \rightarrow 0$ and in view of Eq. 3.12c, Eq. 4.6a reduces to

$$J_{\text{ion}} = \frac{\sigma_v^i (t_v^i - 1)}{L} \left(\frac{3RT}{2F} \right) \left[\left(\frac{p_{\text{O}_2}^i}{p_{\text{O}_2}^{\text{II}}} \right)^{\frac{1}{6}} - 1 \right]$$

$$= -3 \left[2F(D_v t_e) \left(\frac{c_v^{\text{II}} - c_v^i}{L} \right) \right]$$

$$-J_{\text{ele}} = \frac{-\sigma_v^i t_v^i}{L} \left(\frac{3RT}{2F} \right) \left[\left(\frac{p_{\text{O}_2}^i}{p_{\text{O}_2}^{\text{II}}} \right)^{\frac{1}{6}} - 1 \right]$$

$$= -\frac{3}{2} \left[F(D_e t_e) \left(\frac{c_e^{\text{II}} - c_e^i}{L} \right) \right] \quad [4.6b]$$

where

$$\sigma_v^i t_v^i = \sigma_v^i (1 - t_v^i) = \sigma_v^i t_e^i = \frac{\sigma_v^i \sigma_e^i}{\sigma_v^i + \sigma_e^i} \quad [4.7a]$$

and

$$D_v t_e^i = D_e t_e^i \quad [4.7b]$$

are the ambipolar conductivity and diffusivity of the MIEC, respectively. These two parameters characterize the ability of an MIEC to transport both ionic and electronic species simultaneously. Equation 4.7a and 4.7b are identical to those derived previously to describe ambipolar transport properties of MIECs.²⁴ The current density given by Eq. 4.6 is also called permeation current density since the transport of charged defect results in "oxygen permeation" through the MIEC.

Thus, the examination of the current-voltage- p_{O_2} relationship indicates that the derived general equations (Eq. 3.9a and 3.9b) reduce to some simple and familiar ones (Eq. 4.4b, 4.7a, and 4.7b) in the limit of $c_A \rightarrow 0$ (i.e., for an essentially pure MIEC).

Efficiencies of SOFCs based on mixed-conducting electrolytes.—Mixed-conducting electrolytes, such as CeO_2 - and BaCeO_3 -based electrolytes,²³ have been proposed as electrolytes for SOFCs because of their high ionic conductivities. However, the transport of electronic defects through the electrolyte for an SOFC represents an energy loss process. This is because the chemical energy is consumed at a rate corresponding to the ionic current whereas the current delivered to the external circuit is the observable or the total current. In view of Eq. 3.9a, 3.9b, and 4.1, the current efficiency for an SOFC based on a mixed-conducting electrolyte can be expressed as

$$\eta_i \equiv \frac{J_T}{J_{\text{ion}}} = 1 + \frac{J_{\text{ele}}}{J_{\text{ion}}} = 1 + \left[\frac{u_e c_e^i}{u_v (2c_v^i - c_A)} \right]$$

$$V + \frac{RT}{F} \left\{ \ln \left(\frac{c_e^{\text{II}}}{c_e^i} \right) - \ln \left(\frac{P_2^e c_e^{\text{II}} - 2u_v c_A J_{\text{ele}}}{P_2^e c_e^i - 2u_v c_A J_{\text{ele}}} \right) \right\}$$

$$2V + \frac{RT}{F} \left\{ 2 \ln \left(\frac{c_e^{\text{II}}}{c_e^i} \right) + \ln \left(\frac{P_2^e c_e^{\text{II}} - 2u_v c_A J_{\text{ele}}}{P_2^e c_e^i - 2u_v c_A J_{\text{ele}}} \right) \right\} \quad [4.8a]$$

where V is the voltage of the cell ($0 \leq V \leq V_{\text{oc}} \leq E_N$) when an observable current density of J_T is drawn through the cell. The overall energy efficiency of the cell is given by

$$\eta_E = \frac{V}{E_N} \left(\frac{J_T}{J_{\text{ion}}} \right) \quad [4.9a]$$

where V/E_N is the voltage efficiency of the cell. As $c_A \rightarrow 0$, Eq. 4.8a and 4.9a reduce, respectively, to

$$\eta_i = \frac{J_T}{J_{\text{ion}}} = 1 - \frac{\sigma_e^i}{\sigma_v^i} \left(\frac{V}{E_N - V} \right) \quad [4.8b]$$

$$\eta_E = \frac{V}{E_N} \left[1 - \frac{\sigma_e^i}{\sigma_v^i} \left(\frac{V}{E_N - V} \right) \right] \quad [4.9b]$$

The use of a mixed-conducting electrolyte in an SOFC may also reduce interfacial polarization because of perceived high catalytic activity of MIECs. However, the OCV of the cell is reduced due to the electronic transport in the electrolyte, as implied by Eq. 4.4. Thus, the viability of using a mixed-conducting electrolyte for SOFCs depends on the overall energy efficiency expressed by Eq. 4.9.

Figure 3 shows the effect of cell voltage on the efficiencies of a SOFC based on mixed-conducting electrolytes with different transport properties. Clearly, the electronic transport is suppressed rapidly as the cell voltage is reduced. Accordingly, there is an optimal operating cell voltage at which the energy efficiency reaches a maximum, depending on the transport properties of the electrolyte. In particular, it is noted that, for MIECs with $\langle t_e \rangle$ smaller than 10%, the energy loss due to electronic transport through the MIECs is reasonably small when the cell is operated at voltages lower than 0.7 V.

Distributions of defects, electrical potential, and other properties.—Shown in Fig. 4, 5, and 6 are the distributions of defects, virtual partial pressure of oxygen, electrical potential, and the electrochemical potentials of mobile defects in an MIEC for a given chemical condition ($P_{\text{O}_2}^i$ and $p_{\text{O}_2}^{\text{II}}$) under the influence of the electrical states (V) of the surfaces.

In Fig. 4, it is assumed that the MIEC has predominant ionic disorder. The corresponding current-voltage characteristics of the MIEC are shown in Fig. 2a. With dopant concentration of 5×10^{-4} mol/cm³ and $P_{\text{O}_2}^{\text{II}}/p_{\text{O}_2}^i = 10^{20}$, the concentration of V_o^{**} is relatively constant (varied less than 1 m/o) throughout the MIEC while the concentration of

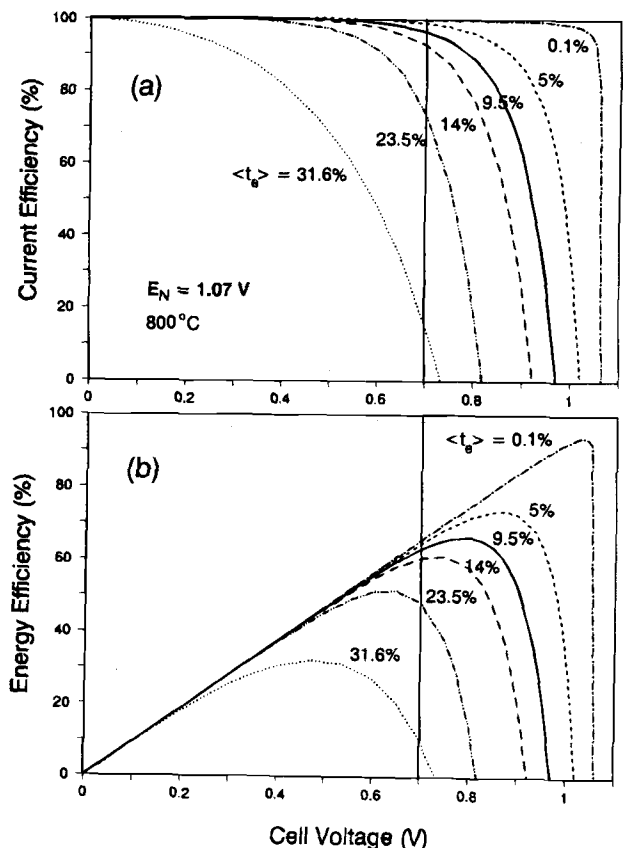


Fig. 3. Calculated (a) current and (b) energy efficiency of an SOFC based on an electrolyte of MIEC with different properties: $\langle t_e \rangle = 0.1, 5, 9.5, 14, 23.5,$ and 31.6% (it is assumed that $p_{\text{O}_2}^{\text{II}}/p_{\text{O}_2}^i = 10^{20}$, $u_o = 1.0 \times 10^{-6}$, $u_v = 1.0 \times 10^{-9}$ mol cm² J⁻¹ s⁻¹, and $L = 0.1$ cm).

electrons varied about five orders of magnitude. Accordingly, the ionic transference number varied from $t_v^I \approx 0.99996$ to $t_v^I = 0.2$. The effective or average ionic transference number of the MIEC under the conditions is calculated to be 0.86 using Eq. 4.5 and the OCV is 0.922 V calculated using Eq. 4.4. As shown in Fig. 4a and b, the distributions of defects, and hence conductivities and

transference numbers, are strongly influenced by the electrical states of the MIEC (*i.e.*, the voltage across the MIEC). The variation in p_{O_2} , calculated using Eq. 2.20, is shown in Fig. 4c whereas the distribution of electrical potential, calculated using Eq. 3.10b, is shown in Fig. 4d, which is approximately linear. Clearly, the variations in both $p_{O_2}(x)$ and $\phi(x)$ are also strongly influenced by the

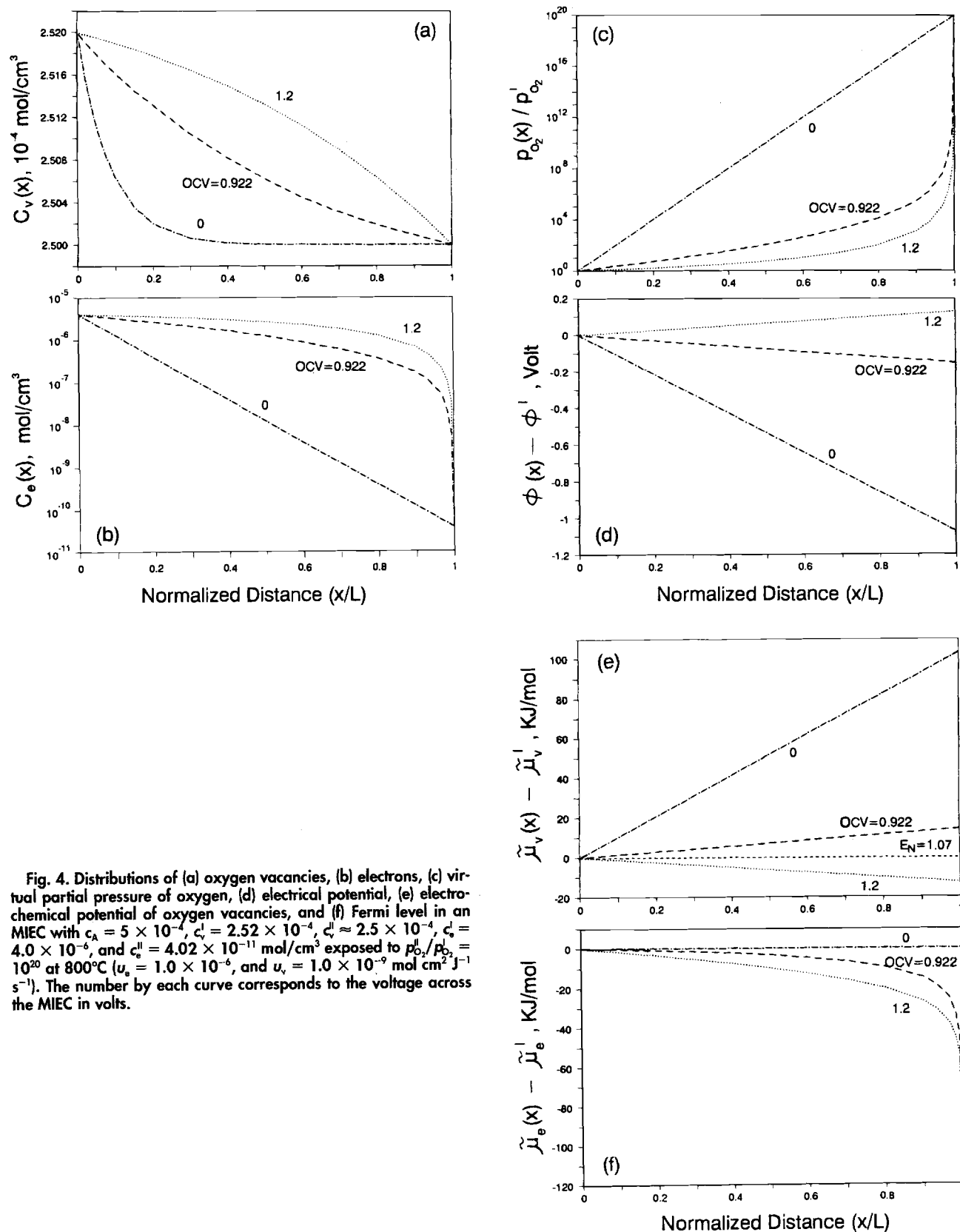


Fig. 4. Distributions of (a) oxygen vacancies, (b) electrons, (c) virtual partial pressure of oxygen, (d) electrical potential, (e) electrochemical potential of oxygen vacancies, and (f) Fermi level in an MIEC with $c_a = 5 \times 10^{-4}$, $c_v^I = 2.52 \times 10^{-4}$, $c_e^I \approx 2.5 \times 10^{-4}$, $c_e^I = 4.0 \times 10^{-6}$, and $c_e^{II} = 4.02 \times 10^{-11} \text{ mol/cm}^3$ exposed to $p_{O_2}^I / p_{O_2}^I = 10^{20}$ at 800°C ($u_a = 1.0 \times 10^{-6}$, and $u_v = 1.0 \times 10^{-9} \text{ mol cm}^{-2} \text{ s}^{-1}$). The number by each curve corresponds to the voltage across the MIEC in volts.

voltage across the MIEC. Further, shown in Fig. 4e and f are the variations in electrochemical potentials of oxygen vacancies and electrons using Eq. 1.1. The slopes of these curves are the overall driving forces for transport of defects in the MIEC. It can be clearly seen from the plots that $\nabla \mu_e = 0$ for $V = 0$ and $\nabla \mu_v = 0$ for $V = E_N$ as discussed earlier.

In Fig. 5, it is assumed that the dopant concentration is 5×10^{-5} mol/cm³, i.e., one order of magnitude smaller than the value assumed for c_A in Fig. 4. The corresponding current-voltage characteristics of the MIEC are shown in Fig. 2b. The concentration of V_o^{**} varied about two orders of magnitude while the concentration of electrons varied about four orders of magnitude for $P_{O_2}^II/P_{O_2}^I = 10^{20}$. Accordingly, the ionic transference number varied from $t_v^II = 0.99$ to $t_v^I = 0.5$, with an effective or average ionic transference number of 0.684 and an OCV of 0.733 V. In comparison to the case shown in Fig. 4, it is noted in Fig. 5 that (i) the voltage across the MIEC has much less effect on variations in $c_v(x)$ and p_{O_2} , and (ii) the distribution of electrical potential is clearly nonlinear.

In Fig. 6, it is assumed that the MIEC contains negligible amount of uniformly distributed charges (i.e., $c_A \rightarrow 0$). Accordingly, Eq. 3.11 and 3.12 (instead of Eq. 3.9 and 3.10) were used in predicting the behavior of the MIEC. In this case, $c_e(x)/c_e^I = c_v(x)/c_v^I$ throughout the MIEC and, hence, the ionic transference number is independent of position in the MIEC. Further, unlike the cases shown in Fig. 4 and 5, the distributions of defects and p_{O_2} are completely independent of the voltage across the MIEC. However, the electrostatic potential distribution is still influenced by the voltage across the MIEC.

Now, let us examine the effect of uniformly distributed charges (c_A) on the distributions of mobile defects and electrical potential. For MIECs with V_o^{**} and e^- being the majority defects, Eq. 3.5a and 3.5b take, respectively, the form of

$$c_e(x) - c_e^I = (c_e^{II} - c_e^I) \frac{x}{L} + \frac{2c_A}{3 \left(\frac{2c_v^I - c_A}{c_e^I} \right) \frac{RT}{F}} \left[(\phi^{II} - \phi^I) \frac{x}{L} - (\phi(x) - \phi^I) \right] \quad [4.10a]$$

$$\phi(x) - \phi^I = (\phi^{II} - \phi^I) \frac{x}{L} + \frac{3}{2} \left(\frac{2c_v^I - c_A}{c_e^I} \right) \frac{RT}{F} \left[\left(\frac{c_e^{II} - c_e^I}{c_A} \right) \frac{x}{L} - \left(\frac{c_e(x) - c_e^I}{c_A} \right) \right] \quad [4.10b]$$

Thus, strictly speaking, the distribution of neither electrical potential nor electrons is linear when $c_A \neq 0$. In practice, however, when c_A is sufficiently large so that

$$\left| \frac{c_e^{II} - c_e^I}{c_A} \right| \ll \left| \frac{\phi^{II} - \phi^I}{\frac{3RT}{2F} \left(\frac{2c_v^I - c_A}{c_e^I} \right)} \right| = \left| \frac{\ln \left(\frac{c_e^{II}}{c_e^I} \right) + \frac{FV}{RT}}{\frac{3}{2} \left(\frac{2c_v^I - c_A}{c_e^I} \right)} \right| \quad [4.11]$$

for the range of E_N and V of interest, the nonlinear term (or the last term) in Eq. 4.10b becomes negligible and, hence, the distributions can be adequately approximated by

$$\frac{\phi(x)}{\phi^I} \approx 1 + \left(\frac{\phi^{II}}{\phi^I} - 1 \right) \frac{x}{L} \quad [4.12a]$$

$$c_e(x) + \frac{P_1^e}{P_2^e} \approx \left(c_e^I + \frac{P_1^e}{P_2^e} \right) \exp \left[\frac{P_2^e (\phi^{II} - \phi^I)}{3u_e \left(\frac{2c_v^I - c_A}{c_e^I} \right) \frac{RT}{F}} \left(\frac{x}{L} \right) \right] \quad [4.12b]$$

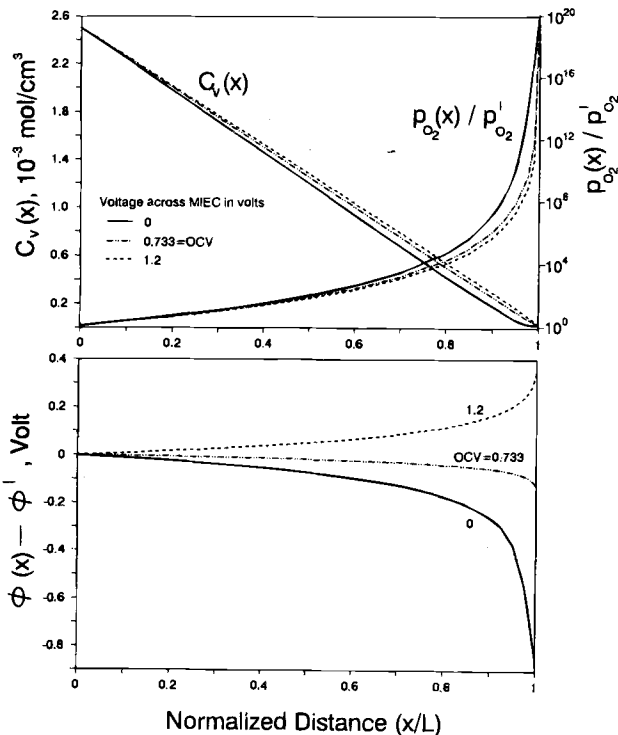


Fig. 5. Distributions of (a, top) oxygen vacancies and virtual partial pressure of oxygen and (b, bottom) electrical potential in an MIEC with $c_A = 5 \times 10^{-5}$, $c_v^I = 2.5 \times 10^{-3}$, $c_e^I = 2.5 \times 10^{-5}$, and $c_e^II = 1.0 \times 10^{-5}$, and $c_e^{II} = 1.0 \times 10^{-9}$ mol/cm³ exposed to $p_{O_2}^II/p_{O_2}^I = 10^{20}$ at 800°C ($u_v = 1.0 \times 10^{-6}$ and $u_e = 1.0 \times 10^{-9}$ mol cm² J⁻¹ s⁻¹).

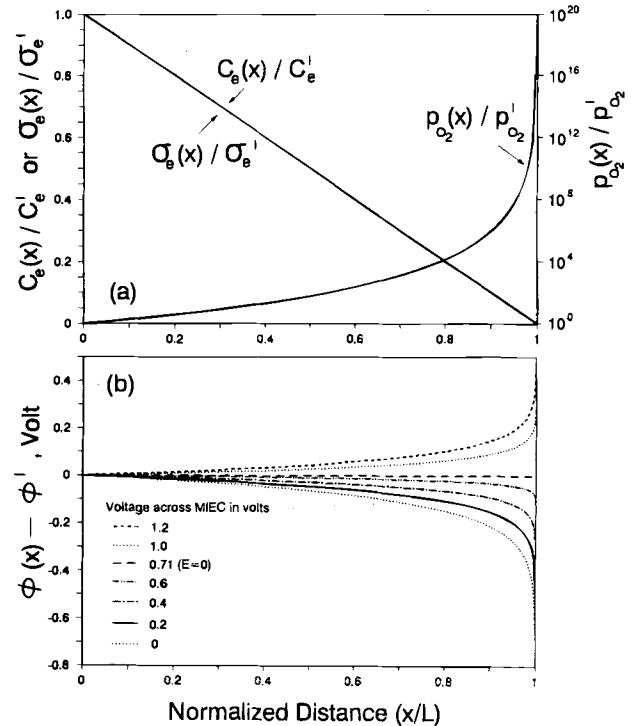


Fig. 6. Distributions of (a) electrons and virtual partial pressure of oxygen and (b) electrical potential in an MIEC with $c_A^I/c_e^I = 4.64 \times 10^{-4}$ exposed to $p_{O_2}^II/p_{O_2}^I = 10^{20}$ at 800°C. The electric field in the MIEC vanishes when the applied voltage is 0.71 V while the distributions of defects and p_{O_2} are independent of the voltage across the MIEC.

That is, the distribution of electrical potential is approximately linear while the distribution of electrons is approximately exponential. It is noted, of course, that both the chemical and electrical conditions imposed on the MIEC will also influence the distributions of mobile defects and electrical potential. An example of MIECs satisfying inequality 4.11 is illustrated in Fig. 4, where $|(c_e^{\text{II}} - c_e^{\text{I}})/c_A| \approx 0.008$, $\ln(c_e^{\text{II}}/c_e^{\text{I}}) \approx -11.5$, and $(2c_v^{\text{I}} - c_A)/c_e^{\text{I}} \approx 1$. Accordingly, inequality 4.11 reduces to

$$4.96 \times 10^{-4} \ll |-1.07 + V| \quad [4.11a]$$

which is true except when the voltage across the MIEC is approaching the Nernst potential (*i.e.*, $V \rightarrow E_N = 1.07$ V). For most applications, the electrical state of an MIEC varies from a short-circuit ($V = 0$) to an open-circuit ($V = V_{oc}$) condition. In particular, for $0 \leq V \leq V_{oc} = 0.922$ V, the electric field in this MIEC can be adequately approximated by a constant, implying that the charge neutrality is nearly strictly observed from a practical point of view and the Poisson's equation (Eq. 1.12) may be adequately approximated by Laplace's equation ($\nabla^2\phi = 0$). The physical implication of this mathematical consequence is that the larger the concentration of uniformly distributed immobile charges (c_A) in comparison to the changes in concentration of mobile defects ($c_e^{\text{II}} - c_e^{\text{I}}$), the better the charge neutrality is observed in the MIEC. If the electric field can be adequately approximated by a constant, mathematical formulation of the MIEC can be greatly simplified. For instance, the implicit equations for $j_k(x)$ and $c_k(x)$, such as Eq. 3.9a and 3.10a, become explicit.

Similarly, when c_A is sufficiently small so that

$$\left| \frac{c_e^{\text{II}} - c_e^{\text{I}}}{c_A} \right| \gg \left| \frac{\ln\left(\frac{c_e^{\text{II}}}{c_e^{\text{I}}}\right) + \frac{FV}{RT}}{\frac{3}{2}\left(\frac{2c_v^{\text{I}} - c_A}{c_e^{\text{I}}}\right)} \right| \quad [4.13]$$

for the range of E_N and V of interest, the nonlinear term (or the last term) in Eq. 4.10a becomes negligible and the distributions can be approximated by Eq. 3.12a and 3.12b, *i.e.*, the distributions of electrons is nearly linear while the distribution of electrical potential is close to logarithmic. An example of MIECs satisfying inequality 4.13 is illustrated in Fig. 5, where $|(c_e^{\text{II}} - c_e^{\text{I}})/c_A| \approx 0.2$, $\ln(c_e^{\text{II}}/c_e^{\text{I}}) \approx -9.21$, and $(2c_v^{\text{I}} - c_A)/c_e^{\text{I}} \approx 495$. Accordingly, inequality 4.13 reduces to

$$6.145 \gg |-0.857 + V| \quad [4.13a]$$

which is approximately true for $0 \leq V \leq E_N = 1.07$ V and, as expected, the distributions of mobile defects are approximately linear as shown in Fig. 5. Further, as $c_A \rightarrow 0$, $|(c_e^{\text{II}} - c_e^{\text{I}})/c_A| \rightarrow \infty$, Eq. 3.12a and 3.12b become exact and, hence, the distribution of electrons is completely linear while the distribution of electrical potential is perfectly logarithmic as shown in Fig. 6.

When neither inequality 4.11 nor 4.13 is satisfied, neither electrical potential nor each type of mobile defect distributes linearly and, thus, the distributions can only be adequately described using Eq. 3.10a and 3.10b.

Figures 5b and 6b clearly indicate that the electric field ($-\nabla\phi$) is not necessarily constant in an MIEC in which local charge neutrality is assumed. Analyses suggest that the smaller the concentration of uniformly distributed immobile charges (c_A) in comparison to the variations in concentrations of mobile charges ($c_e^{\text{II}} - c_e^{\text{I}}$), the larger the deviations from strict charge neutrality and, hence, the greater the deviation in electrostatic potential from linear distribution. Charge neutrality is almost strictly observed only when c_A is sufficiently large in comparison to $c_e^{\text{II}} - c_e^{\text{I}}$.

The Hebb-Wagner experiment.—Now, let us examine the classical Hebb⁴⁴-Wagner¹⁹ experiment using Eq. 3.10a and 3.10b, which determine the distributions of defects and electrical potential in an MIEC and, thus, allow us to estimate the effect of these distributions on the observed con-

ductivities of an MIEC in Hebb-Wagner experiments. The electronically blocked conditions are examined in detail while the ionically blocked conditions are discussed further because of the similarities of the two cases.

When the electronic current is completely blocked (*i.e.*, $J_{ele} = 0$), the observable current is due merely to the motion of ionic defects, as implied by Eq. 4.2. Evaluating Eq. 3.10a under this condition, we find that the e' distributes according to

$$c_e(x) = c_e^{\text{I}} - \frac{J_{ion}x}{3RTFu_v\left(\frac{2c_v^{\text{I}} - c_A}{c_e^{\text{I}}}\right)} = c_e^{\text{II}} + \frac{J_{ion}(L-x)}{3RTFu_v\left(\frac{2c_v^{\text{I}} - c_A}{c_e^{\text{I}}}\right)} \quad [4.14a]$$

Inserting Eq. 4.14a into Eq. 3.13a, we find that the distribution of the V_o^{**} is given by

$$c_v(x) = c_v^{\text{I}} - \frac{J_{ion}x}{6RTFu_v} = c_v^{\text{II}} + \frac{J_{ion}(L-x)}{6RTFu_v} \quad [4.14b]$$

Since both electrons and oxygen vacancies distribute linearly when $J_{ele} = 0$, the average concentrations of e' and V_o^{**} in the MIEC are related to their surface concentrations as

$$\langle c_e \rangle = \frac{c_e^{\text{I}} + c_e^{\text{II}}}{2} = \hat{c}_e \quad [4.15a]$$

$$\langle c_v \rangle = \frac{c_v^{\text{I}} + c_v^{\text{II}}}{2} = \hat{c}_v \quad [4.15b]$$

which are also identical to the uniform concentrations of e' and V_o^{**} as $J_{ion} \rightarrow 0$. If we define the conductivities of the MIEC with uniform composition (*i.e.*, $\nabla c_k = 0$ or without polarization) as

$$\hat{\alpha}_e = F^2 u_e \hat{c}_e \quad [4.16a]$$

$$\hat{\alpha}_v = 4F^2 u_v \hat{c}_v \quad [4.16b]$$

Equations 4.14a and 4.14b can be rewritten, in terms of the properties of an MIEC with uniform composition, as

$$\frac{c_e(x)}{\hat{c}_e} = 1 + \lambda_e \left(1 - \frac{2x}{L}\right) \quad \lambda_e = \frac{FLu_e J_{ion}}{6RTu_v \hat{\sigma}_e \left(\frac{2\hat{c}_v - c_A}{\hat{c}_e}\right)} \quad [4.17a]$$

$$\frac{c_v(x)}{\hat{c}_v} = 1 + \lambda_v \left(1 - \frac{2x}{L}\right) \quad \lambda_v = \frac{FLJ_{ion}}{3RT\hat{\sigma}_v} \quad [4.17b]$$

On the other hand, evaluating Eq. 3.10b at $J_{ele} \rightarrow 0$ and in view of Eq. 4.17, we find that the electrical potential distributes according to

$$\begin{aligned} \phi(x) - \phi^{\text{I}} &= \frac{RT}{F} \ln \left[\frac{1 + \lambda_e \left(1 - \frac{2x}{L}\right)}{1 + \lambda_e} \right] \\ &= \frac{RT}{F} \ln \left[\frac{2c_v(x) - c_A}{2c_v^{\text{I}} - c_A} \right] \quad [4.18] \end{aligned}$$

As expected, the distribution of electrical potential under these conditions is logarithmic since the distributions of mobile defects are linear. Shown in Fig. 7 are some typical profiles of oxygen vacancies and electrical potential inside an MIEC at different ratios of $J_{ion}/\hat{\alpha}_v$. It can be seen that the slopes of these plots depend critically on the ratio $J_{ion}/\hat{\alpha}_v$ for a given sample at a given temperature. The conductivity of the MIEC due to the motion of V_o^{**} , when the transport of e' is completely suppressed, can then be estimated as¹⁹

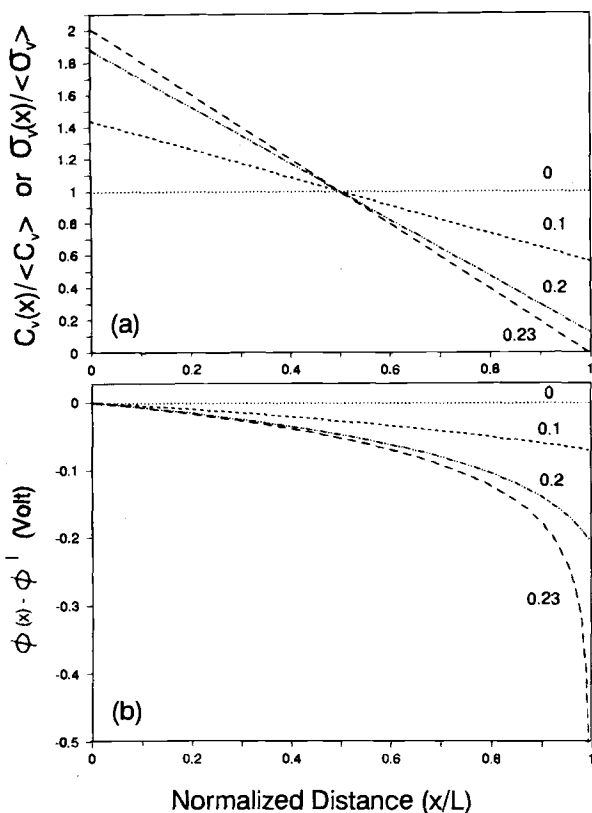


Fig. 7. Distributions of (a) oxygen vacancies and (b) electrical potential in an MIEC under electronically blocked conditions ($J_{ele} = 0$) in a Hebb-Wagner experiment ($L = 1$ cm and $J_{ion}/\alpha_x = 0.1, 0.2, 0.23$ V cm $^{-1}$ at 600°C). The numbers by the curves correspond to the ratio of J_{ion}/α_x , in V cm $^{-1}$.

$$\sigma_v = \frac{J_{ion}}{-d\phi/dx} \approx \frac{J_{ion}}{(\phi^I - \phi^{II})/L} \quad [4.19]$$

Clearly, the conductivity calculated using this equation may depend on the distribution of electrical potential inside the MIEC. The distribution should be sufficiently linear so that $d\phi/dx$ can be adequately approximated by $(\phi^I - \phi^{II})/L$ since it is the potential difference, $\phi^I - \phi^{II}$, not the potential gradient, $d\phi/dx$, that can be readily measured experimentally. As seen from Fig. 7, the logarithmic distribution of electrical potential will be close to linear only when the applied J_{ion} is sufficiently small (or the ratio of J_{ion}/α_x is sufficiently small).

In addition, the actual ionic conductivity (as defined by Eq. 2.16) is a function of position since c_v is nonuniform when $J_{ele} = 0$. Thus, the conductivity determined using Eq. 4.19 is, in fact, a conductivity averaged over the thickness of the sample. In order to estimate the effect of defect distribution on the observed conductivity, inserting Eq. 4.17b into Eq. 2.18 and integrating the equation, we find that the average ionic conductivity of the MIEC over its thickness is given by

$$\langle \sigma_v \rangle = \hat{\sigma}_v \left[\frac{2\lambda_v}{\ln \left(\frac{1 + \lambda_v}{1 - \lambda_v} \right)} \right] \rightarrow \hat{\sigma}_v \text{ as } \lambda_v \rightarrow 0 \text{ or } \frac{J_{ion}}{\hat{\sigma}_v} \rightarrow 0 \quad [4.20]$$

Thus, the average ionic conductivity determined under an electronically blocked condition, $\langle \sigma_v \rangle$, is a function of J_{ion} . Strictly speaking, $\langle \sigma_v \rangle$ approaches the true conductivity α_x , only when $J_{ion} \rightarrow 0$. Shown in Fig. 8 are the calculated ionic

conductivity as a function of the applied current density under electronically blocked conditions. The errors introduced in the measurements increase with the applied current density and approach infinity as the applied J_{ion} approaches the diffusion-limited current density of the MIEC. The diffusion-limited current densities can be quite small for MIECs. For instance, for an MIEC with $\alpha_x = 0.02$ Ω^{-1} cm $^{-1}$, the diffusion-limited current density is about 4.5 mA/cm 2 , as can be seen from Fig. 8.

Distributions of defects and variations in properties of multiple layers of MIECs can also be predicted and, hence, the performance of devices or systems based on MIECs with layered structures can be analyzed using these equations.

Conclusion

General expressions for distributions of defects, electrical potential, and other properties in an MIEC have been derived from integration of transport equations with specified electrical (V) and chemical ($p_{O_2}^I$ and $p_{O_2}^{II}$) conditions. Equations 2.4 and 2.6 are the governing differential equations while Eq. B-1 to B-6 are the analytical solutions for MIECs with three types of significant mobile defects. For MIECs with two types of significant mobile defects, Eq. 3.1a and 3.1b are the governing differential equations whereas Eq. 3.2a, 3.2b, C-1, and C-2 are the analytical solutions under various conditions. These expressions are very general and are applicable to a variety of MIECs with vastly different properties. Once the properties of an MIEC in a uniform atmosphere are known, the derived expressions can be used to predict the steady-state behavior of the MIEC under the influence of various chemical and electrical stimuli applied to the MIEC, including steady-state distributions of defects, conductivities, transference numbers, chemical potential of oxygen, and current car-

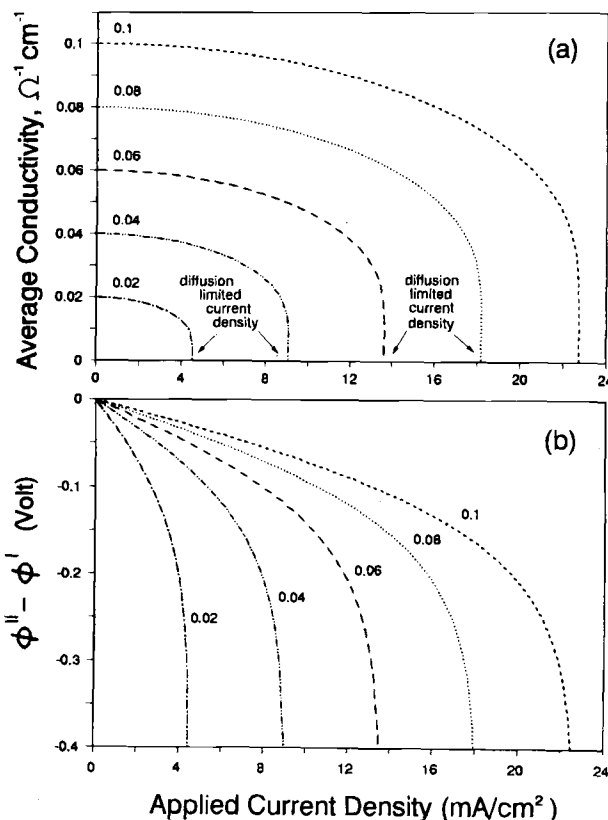


Fig. 8. Effect of the applied J_{ion} on (a) the observed average conductivity, $\langle \sigma_v \rangle$, of and (b) the electrical potential drop across an MIEC under electronically blocked conditions ($J_{ele} = 0$) in a Hebb-Wagner experiment at 600°C ($L = 1$ cm and $\alpha_x = 0.02, 0.04, 0.06, 0.08, \text{ and } 0.1$ Ω^{-1} cm $^{-1}$). The numbers by the curves correspond to the conductivity α_x in Ω^{-1} cm $^{-1}$.

ried by each type of defect inside the MIEC. Further, the expressions can also be used to predict the terminal voltage across an MIEC for a given J_T and E_N or to determine the expected oxygen partial pressures at the interfaces for a given J_T and V .

Large variations in electric field may occur in a homogeneous MIEC in which charge neutrality is assumed. The smaller the concentration of uniformly distributed immobile charges (c_A or c_D) in comparison to the variations in concentrations of mobile defects ($c_k^{\text{II}} - c_k^{\text{I}}$), the larger the deviations from electroneutrality and the greater the deviation in electrical potential from linear distribution. When c_A (or c_D) is sufficiently large in comparison to $c_k^{\text{II}} - c_k^{\text{I}}$ however, the electroneutrality can be strictly observed and the electric field in the MIEC can be adequately approximated by a constant.

Conversely, the derived equations can be used to determine the transport properties of an MIEC from the observed steady-state behavior of the MIEC under controlled electrical and chemical conditions. Since conductivities and transference numbers of an MIEC can vary considerably along the direction in which an electrochemical potential gradient exists, however, the properties determined from an experiment under the influence of an electrochemical driving force are, in general, the average properties over the thickness under the testing conditions. Further, partial conductivity measurements under ionically or electronically blocked conditions may introduce significant error when the distribution of electrical potential is no longer linear due to severe concentration polarizations.

The derived equations are applicable to a variety of MIECs with very different characteristics. Applications of these equations to characterization of MIECs and to prediction of performance of devices or systems based on homogeneous and multilayered MIECs will be discussed in subsequent communications.

Acknowledgment

The author would like to acknowledge Dr. Benjamin Abeles and Professor Jack Winnick for their careful review of this manuscript and for their valuable suggestions. This work was supported by NSF (Award No. DMR-9357520) and EPRI (Contract No. RP 1676-19) and their financial support of this research is gratefully acknowledged.

Manuscript submitted July 29, 1996; revised manuscript received Feb. 7, 1997.

Georgia Institute of Technology assisted in meeting the publication costs of this article.

APPENDIX A

Effect of Activity Coefficient on Formulation

Variable activity coefficient ($g_k \neq 0$).—Although the assumption of constant activity coefficient (*i.e.*, $\gamma_k = \gamma_k^*$ and $g_k = 0$) may be adequate for many MIECs, variable activity coefficient as defined by Eq. 1.1c can be incorporated in the model for generality. For MIECs with significant extrinsic disorders, in particular, the concentrations of the majority defects can be sufficiently large that their activity coefficients may have to be treated as a variable. To be specific, consider an extrinsic MIEC in which $c_v \gg c_o$ and $c_e \gg c_h$. When $g_k \neq 0$, Eq. 3.1 to 3.6 and coefficients B_1^e , B_2^e , and P_1^e defined by Eq. 2.5 and 2.7 remain the same while coefficients P_2^e and Q_n^e may take different values. In the presence of emission or capture of electrons by lattice ions (*i.e.*, $k_R \neq 0$ and $c_{ni} \neq 0$), c_{ni} is related to c_e as

$$c_{ni} \approx \left(\frac{k_R \gamma_e^*}{\gamma_{ni}^*} \right)^{\left(\frac{1}{g_{ni}+1} \right)} c_e^{\left(\frac{g_e+1}{g_{ni}+1} \right)} \quad \text{if } \gamma_{ni} c_{ni} \ll \frac{d}{M} \quad [\text{A-1}]$$

When $g_e \approx g_{ni}$ or $g_e \ll 1$ and $g_{ni} \ll 1$, coefficients, P_2^e , Q_1^e , Q_2^e , and Q_6^e defined in Eq. 2.5 and 2.7 should be replaced, respectively, by

$$P_2^e = u_e J_{\text{ion}} - 2u_v J_{\text{ele}} \left[1 + \left(\frac{k_R \gamma_e^*}{\gamma_{ni}^*} \right)^{\left(\frac{1}{g_{ni}+1} \right)} \right] \quad [\text{A-2}]$$

$$Q_1^e = 2u_e (1 + g_e) c_A$$

$$Q_2^e = u_e (1 + g_v) + 2u_e (1 + g_e) \left[1 + \left(\frac{k_R \gamma_e^*}{\gamma_{ni}^*} \right)^{\left(\frac{1}{g_{ni}+1} \right)} \right]$$

$$Q_6^e = u_e (1 + g_e) J_{\text{ion}} + u_v (1 + g_v) J_{\text{ele}} \left[1 + \left(\frac{k_R \gamma_e^*}{\gamma_{ni}^*} \right)^{\left(\frac{1}{g_{ni}+1} \right)} \right]$$

When the conditions of $g_e \approx g_{ni}$ or $g_e \ll 1$ and $g_{ni} \ll 1$ are not satisfied, however, the solution to the problem depends on the specific values of g_e and g_{ni} . For other types of MIECs, expressions similar to Eq. A-2 can be readily derived.

The use of a thermodynamic factor.—Another approach is to use the thermodynamic data determined from the dependence of c_k on p_{O_2} . Eliminating ϕ from the expressions for $\tilde{\mu}_v$ and $\tilde{\mu}_e$ (Eq. 1), we have

$$\nabla \tilde{\mu}_e = \frac{1}{2} (RT \xi_e \nabla \ln c_e - \nabla \tilde{\mu}_v) = -\nabla \tilde{\mu}_h \quad [\text{A-3a}]$$

$$\nabla \tilde{\mu}_v = RT \xi_v \nabla \ln c_v - 2 \nabla \tilde{\mu}_e \quad [\text{A-3b}]$$

where ξ_e and ξ_v are thermodynamic factors defined, respectively, as

$$\xi_e = \frac{\partial [\gamma_v c_v (\gamma_e c_e)^2]}{\partial \ln c_e} = 2(1 + g_e) + (1 + g_v) \left(\frac{\partial \ln c_v}{\partial \ln c_e} \right) \quad [\text{A-4a}]$$

$$\xi_v = \frac{\partial [\gamma_v c_v (\gamma_e c_e)^2]}{\partial \ln c_v} = (1 + g_v) + 2(1 + g_e) \left(\frac{\partial \ln c_e}{\partial \ln c_v} \right) \quad [\text{A-4b}]$$

When the MIEC is in equilibrium with O_2 gas, *i.e.*, Eq. 1.4a or 1.9c prevails, the thermodynamic factors can be expressed as

$$\xi_k = \frac{\partial \ln \left(1 - \gamma_v c_v \frac{M}{d} \right)}{\partial \ln c_k} - \frac{1}{2} \left(\frac{\partial \ln p_{O_2}}{\partial \ln c_k} \right), \quad k = v, e \quad [\text{A-5a}]$$

which can be approximated by

$$\xi_k \approx - \frac{1}{2} \left(\frac{\partial \ln p_{O_2}}{\partial \ln c_k} \right), \quad k = v, e \quad [\text{A-5b}]$$

when $[V_0^{**}] \ll 1$. Thus, ξ_v can be estimated from the dependence of c_v on p_{O_2} determined using thermogravimetric analysis (TGA)⁴⁵ while ξ_e may be determined from the dependence of σ_e on p_{O_2} . For MIECs containing aliovalent dopants ($c_A \neq 0$ or $c_D \neq 0$), the slope, $\partial \ln c_k / \partial \ln p_{O_2}$, in each p_{O_2} region in a Brouwer diagram is relatively constant and is bounded as follows

$$0 \leq \frac{-\partial \ln c_v}{\partial \ln p_{O_2}} = \frac{\partial \ln c_o}{\partial \ln p_{O_2}} \leq \frac{1}{4} \quad [\text{A-6a}]$$

$$0 \leq \frac{-\partial \ln c_e}{\partial \ln p_{O_2}} = \frac{\partial \ln c_h}{\partial \ln p_{O_2}} \leq \frac{1}{4} \quad [\text{A-6b}]$$

For an essentially pure MIEC ($c_A \approx 0$ and $c_D \approx 0$), the slope is bounded as

$$0 \leq \frac{-\partial \ln c_v}{\partial \ln p_{O_2}} = \frac{\partial \ln c_o}{\partial \ln p_{O_2}} \leq \frac{1}{6} \leq \frac{-\partial \ln c_e}{\partial \ln p_{O_2}} = \frac{\partial \ln c_h}{\partial \ln p_{O_2}} \leq \frac{1}{4}, \quad \text{for } k_i > n_i \quad [\text{A-6c}]$$

$$0 \leq \frac{-\partial \ln c_e}{\partial \ln p_{O_2}} = \frac{\partial \ln c_h}{\partial \ln p_{O_2}} \leq \frac{1}{6} \leq \frac{-\partial \ln c_v}{\partial \ln p_{O_2}} = \frac{\partial \ln c_o}{\partial \ln p_{O_2}} \leq \frac{1}{4} \quad \text{for } n_i > k_i \quad \text{[A-6d]}$$

It is important to note, however, that the thermodynamic factors as defined in Eq. A-4a and A-4b may be treated as a constant only under certain conditions. In fact, ξ_k may vary dramatically with p_{O_2} near the boundaries between two adjacent p_{O_2} regions in which the slope $\partial \ln c_k / \partial \ln p_{O_2}$ is constant; further, in a p_{O_2} region where $\partial \ln c_k / \partial \ln p_{O_2} \rightarrow 0$, ξ_k may approach infinity and become ill behaved. This can be clearly seen in a Brouwer diagram, $|\xi_v| \rightarrow \infty$ in the p_{O_2} region where $c_v = c_o$ while $|\xi_v| \rightarrow \infty$ in the p_{O_2} region where $c_e = c_h$. This is true even for MIECs with constant activity coefficients. Thus, either when c_v is independent of p_{O_2} or when the p_{O_2} of interest is not entirely within one of the p_{O_2} regions with constant $\partial \ln c_v / \partial \ln p_{O_2}$, ξ_v cannot be treated as a constant.

The thermodynamic factor, ξ_v , may be treated as a well-defined constant only when p_{O_2} of interest is within a p_{O_2} region in which $\partial \ln c_v / \partial \ln p_{O_2}$ is a nonzero constant. Under this condition, Eq. 1.16a and 1.16b can be written as

$$J_{ele} = F(u_e c_e + u_h c_h) \nabla \tilde{\mu}_e \quad \text{[A-7a]}$$

$$J_{ion} = -2F(u_v c_v + u_o c_o) [RT \xi_v \nabla \ln c_v - 2 \nabla \tilde{\mu}_e] \quad \text{[A-7b]}$$

In writing Eq. A-7b, it is assumed that $[V_o^{**}] \ll 1$ and $[O_i^*] \ll 1$ so that $\nabla \tilde{\mu}_v \approx -\nabla \tilde{\mu}_o$. Eliminating $\nabla \tilde{\mu}_e$ from Eq. A-7a and A-7b and noting that $u_e c_v \gg u_o c_o$, we arrive at Eq. 2.4 with $k = e$, in which the coefficients B_n^e and P_n^e remain the same (as defined in Eq. 2.5) while the coefficients Q_n^e must be redefined as follows

$$Q_o^e = \left[u_e \left(1 + \frac{\gamma_h k_o}{\gamma_{pi}} \right) + u_h \left(1 + \frac{\gamma_e k_R}{\gamma_{ni}} \right) \right] \left(\frac{n_i^2}{\gamma_h \gamma_e} \right) \xi_v \quad \text{[A-8]}$$

$$Q_1^e = Q_3^e = 0$$

$$Q_2^e = u_e \left(1 + \frac{\gamma_e k_R}{\gamma_{ni}} \right) \xi_v$$

$$Q_4^e = u_h \left(1 + \frac{\gamma_h k_o}{\gamma_{pi}} \right) \left(\frac{n_i^2}{\gamma_e \gamma_h} \right)^2 \xi_v$$

The solutions to Eq. 2.4 and Eq. B-1, B-3, and B-5, remain the same provided that the coefficients Q_n^k are as defined by Eq. A-8. For MIECs with two types of significant mobile defects, the distribution of defects as described by Eq. 3.1a, 3.2a, and C-1 also remain the same if Q_1^k and Q_2^k are properly defined.

APPENDIX B

Solutions to Eq. 2.4 and 2.6

The analytical solutions to Eq. 2.4 and 2.6 depend on the values of the coefficients P_o^k and P_2^k , which are determined by the ionic and electronic current densities passing through the MIEC or by the electrical (V) and chemical ($p_{O_2}^I$ and $p_{O_2}^{II}$) conditions imposed on the MIEC. Clearly, $P_2^k = 0$ or $P_o^k = 0$ corresponds to a special case where the ratio of J_{ele} / J_{ion} must be constant while $p_o^k \neq 0$ and $p_2^k \neq 0$ represents the general case where either J_{ele} or J_{ion} may take any value except for $P_2^k = 0$ or $P_o^k = 0$.

The general case (i.e., $P_2^k \neq 0$ and $P_o^k \neq 0$).—Integrating Eq. 2.4 over the thickness of the MIEC under these conditions, we find that the distributions of electronic defects inside the MIEC are determined by the following implicit expression

$$\frac{x}{B_1^k} = S_o^k \ln \left(\frac{c_k(x)}{c_k^I} \right) + S_1^k [c_k(x) - c_k^I] + S_2^k \ln \left[\frac{y_k^2(x) - f_1^k}{(y_k^I)^2 - f_1^k} \right] + S_3^k \left[\frac{1}{c_k(x)} - \frac{1}{c_k^I} \right] + S_4^k \ln \left[\frac{u_k^2(x) - f_2^k}{(u_k^I)^2 - f_2^k} \right] + \Psi_1^k(x) \quad \text{[B-1]}$$

where

$$\begin{aligned} \Psi_1^k(x) &= \frac{S_5^k}{2\sqrt{f_1^k}} \ln \left[\frac{(y_k(x) - \sqrt{f_1^k})(y_k^I + \sqrt{f_1^k})}{(y_k(x) + \sqrt{f_1^k})(y_k^I - \sqrt{f_1^k})} \right] \\ &\quad + \frac{S_6^k}{2\sqrt{f_2^k}} \ln \left[\frac{(u_k(x) - \sqrt{f_2^k})(u_k^I + \sqrt{f_2^k})}{(u_k(x) + \sqrt{f_2^k})(u_k^I - \sqrt{f_2^k})} \right], \quad f_1^k > 0 \\ &= -S_5^k \left[\frac{1}{y_k(x)} - \frac{1}{y_k^I} \right] - S_6^k \left[\frac{1}{u_k(x)} - \frac{1}{u_k^I} \right], \quad f_1^k = 0 \\ &= \frac{S_5^k}{\sqrt{-f_1^k}} \left[\arctan \frac{[y_k(x) - y_k^I] \sqrt{-f_1^k}}{-f_1^k + y_k^I y_k(x)} \right] \\ &\quad + \frac{S_6^k}{\sqrt{-f_2^k}} \left[\arctan \frac{[u_k(x) - u_k^I] \sqrt{-f_2^k}}{-f_2^k + u_k^I u_k(x)} \right], \quad f_1^k < 0 \end{aligned}$$

$$y_k(x) = c_k(x) + \frac{P_1^k}{\pm 2P_2^k}, \quad y_k^I = y_k(0), \quad y_k^{II} = y_k(L)$$

$$f_1^k = \frac{(P_1^k)^2 - (\pm)4P_o^k P_2^k}{4(P_2^k)^2}, \quad \text{"+" for } P_2^k > 0, \quad \text{"-" for } P_2^k < 0$$

$$S_o^k = Q_3^k / P_o^k$$

$$S_1^k = Q_2^k / (\pm P_2^k)$$

$$S_2^k = (Q_1^k - P_2^k S_o^k - P_1^k S_1^k) / (\pm 2P_2^k)$$

$$S_5^k = \frac{Q_o^k - P_1^k S_o^k - P_1^k (Q_1^k - P_2^k S_o^k)}{\pm P_2^k} - \frac{P_1^k (Q_1^k - P_2^k S_o^k)}{2(P_2^k)^2} + S_1^k \left(f_1^k + \frac{(P_1^k)^2}{4(P_2^k)^2} \right)$$

$$u_k(x) = \frac{1}{c_k(x)} + \frac{P_1^k}{\pm 2P_o^k}, \quad u_k^I = u_k(0), \quad u_k^{II} = u_k(L)$$

$$f_2^k = \frac{(P_1^k)^2 - (\pm)4P_o^k P_2^k}{4(P_o^k)^2}, \quad \text{"+" for } P_o^k > 0, \quad \text{"-" for } P_o^k < 0$$

$$S_3^k = -Q_4^k / (\pm P_o^k)$$

$$S_4^k = -P_1^k S_3^k / (\pm 2P_o^k)$$

$$S_6^k = S_3^k \left(f_2^k + \frac{(P_1^k)^2}{4(P_o^k)^2} \right)$$

Similarly, integrating Eq. 2.6 under the same conditions, we find that the electrical potential distributes inside the MIEC according to

$$\frac{\phi(x) - \phi^I}{B_2^k} = S_7^k \ln \left[\frac{c_k(x)}{c_k^I} \right] + S_8^k \ln \left[\frac{y_k^2(x) - f_1^k}{(y_k^I)^2 - f_1^k} \right] + \Psi_2^k(x) \quad \text{[B-2]}$$

where

$$\begin{aligned} \Psi_2^k(x) &= \frac{S_9^k}{2\sqrt{f_1^k}} \ln \left[\frac{(y_k(x) - \sqrt{f_1^k})(y_k^I + \sqrt{f_1^k})}{(y_k(x) + \sqrt{f_1^k})(y_k^I - \sqrt{f_1^k})} \right], \quad f_1^k > 0 \\ &= -S_9^k \left[\frac{1}{y_k(x)} - \frac{1}{y_k^I} \right], \quad f_1^k = 0 \\ &= \frac{S_9^k}{\sqrt{-f_1^k}} \left[\arctan \frac{[y_k(x) - y_k^I] \sqrt{-f_1^k}}{-f_1^k + y_k^I y_k(x)} \right], \quad f_1^k < 0 \end{aligned}$$

$$\begin{aligned} S_7^k &= Q_5^k/P_0^k \\ S_8^k &= (Q_6^k - P_2^k S_7^k)/(\pm 2P_2^k) \\ S_9^k &= -P_1^k(S_7^k + S_8^k)/(\pm P_2^k) \end{aligned}$$

Further, Eq. B-1 and B-2 reduce, respectively, to Eq. 3.2a and 3.2b for MIECs with two types of significant mobile defects.

The special case I, $P_0^k = 0$.—When $P_1^k \neq 0$ and $P_2^k \neq 0$ (otherwise $J_{\text{ele}} = J_{\text{ion}} = 0$ and the case is trivial), $P_0^k = 0$ implies that the ratio of $J_{\text{ele}}/J_{\text{ion}}$ must be a constant while J_{ele} and J_{ion} may flow in the same or opposite direction, depending on the nature of the majority defects. Under this condition, integration of Eq. 2.4 results in

$$\begin{aligned} \frac{x}{B_1^k} &= S_{10}^k \ln \left[\frac{P_1^k + P_2^k c_k(x)}{P_1^k + P_2^k c_k^I} \right] + \frac{Q_2^k}{P_2^k} [c_k(x) - c_k^I] \\ &+ S_{11}^k \ln \left[\frac{c_k(x)}{c_k^I} \right] + S_{12}^k \left[\frac{1}{c_k(x)} - \frac{1}{c_k^I} \right] - \frac{Q_4^k}{2P_1^k} \left[\frac{1}{c_k^2(x)} - \frac{1}{(c_k^I)^2} \right] \end{aligned} \quad [\text{B-3}]$$

where

$$S_{10}^k = -Q_2^k P_1^k / (P_2^k)^2 + Q_1^k / P_2^k - Q_0^k / P_1^k + Q_3^k P_2^k / (P_1^k)^2 - Q_4^k (P_2^k)^2 / (P_1^k)^3$$

$$S_{11}^k = Q_0^k / P_1^k - Q_3^k P_2^k / (P_1^k)^2 + Q_4^k (P_2^k)^2 / (P_1^k)^3$$

$$S_{12}^k = -Q_3^k / P_1^k + Q_4^k P_2^k / (P_1^k)^2$$

whereas integration of Eq. 2.6 yields

$$\begin{aligned} \frac{\phi(x) - \phi^I}{B_2^k} &= \left[\frac{Q_5^k}{P_2^k} + \frac{Q_5^k P_2^k}{(P_1^k)^2} \right] \ln \left[\frac{P_1^k + P_2^k c_k(x)}{P_1^k + P_2^k c_k^I} \right] \\ &- \frac{Q_5^k}{P_1^k} \left[\frac{1}{c_k(x)} - \frac{1}{c_k^I} \right] - \frac{Q_5^k P_2^k}{(P_1^k)^2} \ln \left[\frac{c_k(x)}{c_k^I} \right] \end{aligned} \quad [\text{B-4}]$$

Equations B-3 and B-4 also reduce, respectively, to Eq. 3.2a and 3.2b for MIECs with two types of significant mobile defects.

The special case II, $P_0^k = 0$.—When $P_1^k \neq 0$ and $P_2^k \neq 0$ (otherwise $J_{\text{ele}} = J_{\text{ion}} = 0$), $P_0^k = 0$ implies that the ratio of $J_{\text{ele}}/J_{\text{ion}}$ must be a constant while J_{ele} or J_{ion} reverses the direction in comparison to the case where $P_0^k = 0$, depending on the nature of the majority defects. Under this condition, integration of Eq. 2.4 gives

$$\begin{aligned} \frac{x}{B_1^k} &= S_{13}^k \ln \left[\frac{P_0^k + P_1^k c_k(x)}{P_0^k + P_1^k c_k^I} \right] + S_{14}^k [c_k(x) - c_k^I] \\ &+ S_{15}^k \ln \left[\frac{c_k(x)}{c_k^I} \right] + \frac{Q_2^k}{2P_1^k} [c_k^2(x) - (c_k^I)^2] - \frac{Q_4^k}{P_0^k} \left[\frac{1}{c_k(x)} - \frac{1}{c_k^I} \right] \end{aligned} \quad [\text{B-5}]$$

where

$$S_{13}^k = Q_0^k / P_1^k + Q_1^k P_0^k / (P_1^k)^2 + Q_2^k (P_0^k)^2 / (P_1^k)^3 - Q_3^k / P_0^k + Q_4^k P_1^k / (P_0^k)^2$$

$$S_{14}^k = Q_1^k / P_1^k - 2P_0^k Q_2^k / (P_1^k)^2 + 2P_0^k P_1^k$$

$$S_{15}^k = Q_3^k / P_0^k - Q_4^k P_1^k / (P_0^k)^2$$

while integration of Eq. 2.6 yields

$$\begin{aligned} \frac{\phi(x) - \phi^I}{B_2^k} &= \left[\frac{-Q_5^k}{P_0^k} - \frac{P_0^k Q_5^k}{(P_1^k)^2} \right] \ln \left[\frac{P_0^k + P_1^k c_k(x)}{P_0^k + P_1^k c_k^I} \right] \\ &+ \frac{Q_5^k}{P_1^k} [c_k(x) - c_k^I] + \frac{Q_5^k}{P_0^k} \ln \left[\frac{c_k(x)}{c_k^I} \right] \end{aligned} \quad [\text{B-6}]$$

Further, Eq. B-5 and B-6 reduce, respectively, to Eq. C-1 and C-2 for MIECs with two types of significant mobile defects.

APPENDIX C

Solutions to Eq. 3.1a and 3.1b when $P_2^k = 0$

When $P_1^k \neq 0$ and $c_A \neq 0$ (otherwise $J_{\text{ele}} = J_{\text{ion}} = 0$), $P_2^k = 0$ implies that the ratio of $J_{\text{ele}}/J_{\text{ion}}$ must be a constant while J_{ele} and J_{ion} may flow in the same or opposite direction, depending on the nature of the majority defects. Under this condition, integration of Eq. 3.1a and 3.1b over the thickness of the MIEC yields

$$Q_1^k [c_k(x) - c_k^I] + \frac{Q_2^k}{2} [c_k^2(x) - (c_k^I)^2] = \left(\frac{P_1^k}{B_1^k} \right) x \quad [\text{C-1}]$$

$$\phi(x) - \phi^I = \left(\frac{B_2^k Q_5^k}{P_1^k} \right) [c_k(x) - c_k^I] \quad [\text{C-2}]$$

It is noted that Eq. C-1 and C-2 can also be obtained by ignoring the terms containing coefficients P_0^k , Q_0^k , Q_3^k , Q_4^k , and Q_5^k in Eq. B-5 and B-6. This is because these coefficients become negligible in MIECs with two types of significant mobile defects. Summarized below are the expressions for ionic and electronic current densities and for distribution of defects and electrical potential in each class of MIECs with two types of significant defects under the condition of $P_2^k = 0$.

*MIECs with V_0^{**} and e' .*—Charge neutrality in these MIECs is described by Eq. 3.7 and the coefficient B_1^k , P_1^k , and Q_n^k are defined by Eq. 2.5 and 2.7. In this case, $P_2^k = 0$ implies that

$$J_v = \frac{2u_v}{u_e} \left(\frac{2c_v^I - c_A}{c_e^I} \right) J_e \quad [\text{C-3}]$$

where J_e , as determined from evaluating Eq. C-1 for $k = e$ at $x = L$, is given by

$$J_e = \frac{FRTu_e}{L} \left\{ (c_e^{II} - c_e^I) + \frac{3}{4c_A} \left(\frac{2c_v^I - c_A}{c_e^I} \right) [(c_e^{II})^2 - (c_e^I)^2] \right\} \quad [\text{C-4}]$$

The distributions of electrons and electrical potential are given, respectively, by

$$[c_e(x) - c_e^I] + \frac{3}{4} \left(\frac{2c_v^I - c_A}{c_e^I} \right) \left[\frac{c_e^2(x) - (c_e^I)^2}{c_A} \right] = \left(\frac{J_e}{FRTu_e} \right) x \quad [\text{C-5}]$$

$$\phi(x) - \phi^I = -3 \left(\frac{RT}{F} \right) \left[\frac{c_v(x) - c_v^I}{c_A} \right] \quad [\text{C-6}]$$

*MIECs with V_0^{**} and h^* .*—

$$J_h = \frac{-u_h}{2u_v} \left(\frac{c_h^I}{c_A - 2c_v^I} \right) J_v \quad [\text{C-7}]$$

$$J_v = \frac{-2FRTu_v}{L} \left\{ (c_v^{II} - c_v^I) + \frac{1}{c_A} [(c_v^{II})^2 - (c_v^I)^2] \right\} \quad [\text{C-8}]$$

$$[c_v(x) - c_v^I] + \left[\frac{c_v^2(x) - (c_v^I)^2}{c_A} \right] = \left(\frac{-J_v}{2FRTu_v} \right) x \quad [\text{C-9}]$$

$$\phi(x) - \phi^I = \left(\frac{RT}{F} \right) \left[\frac{c_v(x) - c_v^I}{c_A} \right] \quad [\text{C-10}]$$

MIECs with O_i'' and h^* .—

$$J_o = \frac{2u_o}{u_h} \left(\frac{2c_o^I + c_A}{c_h^I} \right) J_h \quad [C-11]$$

$$J_h = \frac{FRTu_h}{L} \left\{ -(c_h^{II} - c_h^I) + \frac{3}{4c_A} \left(\frac{2c_o^I + c_A}{c_h^I} \right) [(c_h^{II})^2 - (c_h^I)^2] \right\} \quad [C-12]$$

$$[c_h(x) - c_h^I] + \frac{-3}{4} \left(\frac{2c_o^I + c_A}{c_h^I} \right) \left[\frac{c_h^2(x) - (c_h^I)^2}{c_A} \right] = \left(\frac{J_h}{FRTu_h} \right) x \quad [C-13]$$

$$\phi(x) - \phi^I = -3 \left(\frac{RT}{F} \right) \left[\frac{c_o(x) - c_o^I}{c_A} \right] \quad [C-14]$$

MIECs with O_i'' and e' .—

$$J_e = \frac{-u_e}{2u_o} \left(\frac{c_e^I}{c_D - 2c_o^I} \right) J_o \quad [C-15]$$

$$J_o = \frac{-2FRTu_o}{L} \left\{ (c_o^{II} - c_o^I) + \frac{1}{c_D} [(c_o^{II})^2 - (c_o^I)^2] \right\} \quad [C-16]$$

$$[c_o(x) - c_o^I] + \left[\frac{c_o^2(x) - (c_o^I)^2}{c_D} \right] = \left(\frac{J_o}{FRTu_o} \right) x \quad [C-17]$$

$$\phi(x) - \phi^I = - \left(\frac{RT}{F} \right) \left[\frac{c_o(x) - c_o^I}{c_D} \right] \quad [C-18]$$

LIST OF SYMBOLS

- B_n^k coefficients ($k = e, h, v, o; n = 1, 2$) defined by Eq. 2.5, 2.7, 2.13, 3.19, and 3.24
- c_A net molar concentration of ionized acceptors as defined by Eq. 2.2b, mol cm⁻³
- c_D net molar concentration of ionized donors as defined by Eq. 2.9b, mol cm⁻³
- c_k molar concentration of defect k ($c_k = [k]d/M$), mol cm⁻³
- $\langle c_k \rangle$ average concentration of defect k over the thickness, mol · cm⁻³
- \hat{c}_k uniform concentration of defect k when $\nabla c_k = 0$, mol cm⁻³
- d density of lattice compound, g cm⁻³
- D_k diffusivity of defect k ($D_k = RTu_k$), cm² s⁻¹
- E_F Fermi energy of electrons ($E_F = \tilde{\mu}_e$), J
- E_N Nernst potential across an MIEC as defined by Eq. 1.5, V
- F Faraday's constant, 96,487 C eq⁻¹
- g_k exponent as defined by Eq. 1.1c, $g_k = \partial \ln \gamma_k / \partial \ln c_k$
- G_k generation rate of defect k inside an MIEC, mol cm⁻³ s⁻¹
- k_R, k_o equilibrium constant for partial reduction and oxidation of lattice ions
- k_f intrinsic concentration of ionic defects for Frenkel disorder, mol cm⁻³
- $[k]$ site fraction of defect k , dimensionless
- J_k current density carried by defect k , A cm⁻²
- J_T total (or observable) current density, A cm⁻²
- J_{ele} electronic current density, A cm⁻²
- J_{ion} ionic current density, A cm⁻²
- L_{kl} general transport coefficients, mol² cm⁻¹ J⁻¹ s⁻¹
- M molecular weight of lattice compound, g mol⁻¹
- n_i intrinsic concentration of electrons or holes at a given temperature, mol cm⁻³
- N_k molar flux of defect k , mol cm⁻² s⁻¹
- p_{O_2} partial pressure of oxygen, atm
- P_n^k, Q_n^k coefficients ($k = e, h, v, o; n = 0, 1, \dots$) defined by Eq. 2.5, 2.7, 2.13, 3.19, and 3.24
- R universal gas constant, 8.314 J mol⁻¹ K⁻¹
- t_k transference number of defect k , dimensionless
- $\langle t_k \rangle$ average transference number of defect k over thickness, dimensionless

- t_{ele} electronic transference number, dimensionless
- t_{ion} ionic transference number, dimensionless
- T absolute temperature, K
- u_k absolute mobility of defect k , mol cm² J⁻¹ s⁻¹
- V voltage across an MIEC as defined by Eq. 1.6 and 1.7, V
- V_{oc} open-cell voltage as defined by Eq. 4.4, V
- x distance from the surface of the MIEC exposed to a gas containing p_{O_2} , cm
- z_k number of effective charge (with respect to perfect crystals) of defect k , dimensionless

Greek

- β^k coefficient defined by Eq. 3.3a
- γ_k activity coefficient of defect k , dimensionless
- ϵ permittivity of an MIEC, F cm⁻¹
- η_i, η_E current and energy efficiency, dimensionless
- μ_k chemical potential of defect k ($\mu_k = \mu_k^* + RT \ln \gamma_k c_k$), J mol⁻¹
- $\tilde{\mu}_k$ electrochemical potential of defect k ($\tilde{\mu}_k = \mu_k^* + RT \ln \gamma_k c_k + z_k F \phi$), J mol⁻¹
- σ_k partial conductivity ($\sigma_k = z_k^2 F^2 u_k c_k$) due to the motion of defect k , Ω^{-1} cm⁻¹
- $\langle \sigma_k \rangle$ average conductivity over thickness due to the motion of defect k , Ω^{-1} cm⁻¹
- $\hat{\sigma}_k$ conductivity of MIEC with uniform composition (*i.e.*, when $\nabla c_k = 0$), Ω^{-1} cm⁻¹
- ϕ average electrical potential in a plane at distance x , V
- λ_e, λ_v coefficient defined, respectively, by Eq. 4.17a and Eq. 4.17b
- ξ_k thermodynamic factor defined by Eq. A-4

Subscripts or superscripts

- A an acceptor impurity (immobile but distributed uniformly)
- A,h an acceptor impurity to create an electron hole
- A,v an acceptor impurity to create an oxygen vacancy
- D a donor impurity (immobile but distributed uniformly)
- D,e a donor impurity to create an electron
- D,o a donor impurity to create an oxygen interstitial
- k a defect in an MIEC
- j an ionized dopant which is immobile and distributed uniformly
- e an electron, e'
- h an electron hole, h^*
- o an oxygen interstitial, O_i''
- v an oxygen vacancy, $V_o^{..}$
- pi an immobile ion with an effective positive charge (such as M_M^+ and D_M^+)
- ni an immobile ion with an effective negative charge (such as M_M^- and D_M^-)
- ele electronic
- ion ionic
- I properties of MIEC when exposed to an atmosphere containing $p_{O_2}^I$ at $x = 0$
- II properties of MIEC when exposed to an atmosphere containing $p_{O_2}^{II}$ at $x = L$

Acronyms

- BCG gadolinia-doped barium cerate (BaCe_{1-x}Gd_xO₃)
- CSC calcia-stabilized ceria (Ce_{1-x}Ca_xO₂)
- LSC strontium-doped lanthanum cobaltite (La_{1-x}Sr_xCoO₃)
- LSF strontium-doped lanthanum ferrite (La_{1-x}Sr_xFeO₃)
- LSM strontium-doped lanthanum manganide (La_{1-x}Sr_xMnO₃)
- MIEC mixed ionic-electronic conductor
- SOFC solid oxide fuel cell
- YSZ yttria-stabilized zirconia (Zr_{1-x}Y_xO₂)

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