

COMMENTS

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Comments should be sent to the Editor, Dr. Paul A. Kohl, The Electrochemical Society, Inc., 10 South Main St., Pennington, NJ 08534-2896.

Paul A. Kohl
Editor

Electrode Kinetics of Porous Mixed-Conducting Oxygen Electrodes

S. B. Adler, J. A. Lane, and B. C. H. Steele
(pp. 3554-3564, Vol. 143, No. 11, 1996)

M. Liu and J. Winnick: In this paper, Adler *et al.* attempt to model a solid-state device consisting of an ionically conducting electrolyte in contact with a mixed ionic-electronic conductor (MIEC) electrode, but do not correctly treat the MIEC electrode, as evidenced in several incorrect assumptions and boundary conditions in their analyses that invalidate their conclusions.

1. *Uniform Fermi level and charge neutrality.*—First, they assume that the Fermi level is locally uniform throughout the MIEC electrode. To illustrate the consequence of this assumption, consider an MIEC containing mobile defects of V_O^{**} , e' , and h^* . When $\nabla\tilde{\mu}_e = 0$, the electronic current density vanishes (*i.e.*, $J_e = J_h = 0$). Accordingly, any current passing through the MIEC electrode must be totally ionic. Evaluating the continuity equation for electrons or that for electron holes in a steady state, we find that $r = 0$, *i.e.*, the net rate of the reaction occurring at the MIEC/gas interface vanishes. Consequently, the electrochemical reaction may occur only at the triple-phase boundary (TPB) at $y = L$ (among the MIEC, the current collector, and the gas phase). In other words, the MIEC may act only as an extension of the electrolyte and is unable to function as an electrode and hence unable to extend the reaction zone beyond the TPB. However, the TPB was completely ignored in their analysis, as implied by Eq. 7d. Evaluating this equation, we find that $dc_v^*/dy|_{y=L} = 0$ since $r = 0$ and hence the ionic current passing through the MIEC must vanish as well (*i.e.*, $J_v = 0$). Thus, the total current passing through the cell or the MIEC vanishes (*i.e.*, $J_e = J_h = J_v = 0$) regardless of an applied cell voltage. As a result, the assumption of $\nabla\tilde{\mu}_e = 0$, together with ignoring the TPB, implies that the cell under consideration is not electrochemically functional.

Further, it is implicit, although not stated, that the electric field in the MIEC was assumed absent ($\nabla\phi = 0$) since the motion of V_O^{**} in the MIEC was characterized as "diffusion"² throughout their discussion. The assumption of $\nabla\phi = 0$ and $\nabla\tilde{\mu}_e = 0$, then, requires that the electrons distribute uniformly (*i.e.*, $\nabla c_e = 0$) while the thermal equilibrium between e' and h^* (which was also assumed to prevail in the MIEC) further requires that $\nabla c_h = 0$. Evaluating their charge neutrality equation (Eq. A-1c) under these conditions, we find that c_v must be constant throughout the MIEC, *i.e.*

$$c_v(y) = \frac{1}{2}(c_e - c_h - B) = \text{constant} \quad y \in [0, L] \quad [\text{C-1a}]$$

where B was defined as "uniform 'background' charge density of the solvent" in the solid MIEC. After some

mathematical manipulations, however, Adler *et al.* derived an expression for c_v , Eq. 9a, which indicates that c_v is not uniform, but a function of position y , as illustrated in Fig. 4. Clearly, Eq. 9a and Fig. 4 directly contradict the assumption of charge neutrality (Eq. C-1a or Eq. A-1c).

In order to avoid direct contradiction between Eq. 9a and Eq. A-1c, one must assume that c_e is nonuniform³ (so that c_v may vary with position without violating the assumption of charge neutrality). Any variation in c_e with position, however, requires that ϕ vary with position (*i.e.*, an electric field must be present) in order to maintain uniform Fermi level. This, unfortunately, directly contradicts their silent assumption of $\nabla\phi = 0$ in the MIEC. When $\nabla\phi \neq 0$ and $\nabla\tilde{\mu}_v \neq 0$, the current density due to the motion of V_O^{**} in the MIEC should be

$$J_v^* = -(4F^2 u_v c_v) \nabla\phi - (2F u_v c_v) \nabla\tilde{\mu}_v = J_{v,\text{migr}} + J_{v,\text{diff}} \quad [\text{C-1b}]$$

That is, the transport of V_O^{**} is no longer a pure "diffusion" process, as implied throughout their discussion; the "migration" of V_O^{**} under the influence of an electric field ($-\nabla\phi$) can no longer be ignored. In addition, the displacement current induced in a transient state must also be considered, as discussed later.

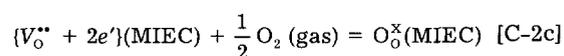
2. *The thermodynamic factor and the validity of the formalism.*—Even assuming that $\nabla\tilde{\mu}_e = 0$ does not contradict other assumptions, the governing equation (Eq. 1) and boundary conditions (Eq. 7a, c, and d) are still incorrect because the thermodynamic factor, A , was inadequately defined for these equations. The rigorous definition for A should be $A \equiv \partial \ln(a_v a_e^2) / \partial \ln c_v$. Thus, Adler's definition of

$$A = -\frac{1}{2} (\partial \ln p_{O_2} / \partial \ln c_v) \quad [\text{C-2a}]$$

requires that

$$a_v a_e^2 p_{O_2}^{\frac{1}{2}} = k_g \quad [\text{C-2b}]$$

which implies that the reaction at the MIEC/gas interface



is at equilibrium. Conceptually, this directly contradicts their fundamental assumption that the kinetics of this very reaction is finite, as formulated in Appendix A (Eq. A-15 to A-22); in fact, the central concern of their article is the kinetics of this reaction. Mathematically, Eq. C-2a or C-2b directly conflicts with their rate expression, Eq. A-17,⁴ unless $r = 0$ (which represents a trivial case of the problem). The surface reaction may approach equilibrium in the MIEC during cell operation only if the rate of the reaction is infinitely fast (*i.e.*, $r_o \rightarrow \infty$). Clearly, this cannot be assumed in their analysis. The use of Eq. A-

17 implies that the rate of the reaction is assumed to be finite. Thus, it is inconsistent, on one hand, to assume that r_o is finite in writing Eq. 1, 7a, 7c, and 7d, while on the other hand, assuming that $r_o \rightarrow \infty$ in defining A in the same equations. Even with their definition, A may vary in orders of magnitude or even approach ∞ and become ill behaved under certain conditions,⁵ although it may be treated as a constant within a narrow range of p_{O_2} . It is noted, however, that A was treated as a constant by Adler *et al.* without any explanation. At least, appropriate assumptions should be explicitly stated. Also, when A is not a constant, $\nabla A \neq 0$ and the term containing ∇A in Eq. A-3a cannot be ignored in obtaining the governing equation (Eq. 1). Thus, both the governing equations and the correct solutions to these equations should be quite different from those presented.

3. Triple-phase boundaries and steady-state boundary conditions.—In specifying boundary conditions, Adler *et al.* have neglected the most important portion of the electrode kinetics in a solid-state cell, the reactions occurring at the TPB among the electrolyte, the MIEC, and the gas at $y = 0$ and the TPB among the MIEC, the current collector, and the gas at $y = L$. As a result, Eq. 7a, 7b, and 7d are all incorrect. For a cell consisting of a pure ionic conductor (ic) of uniform composition and two porous electrodes of an MIEC, the ionic current heavily concentrates on the TPB at $y = 0$. This TPB cannot be ignored under any conditions unless the MIEC is not functioning as an electrode. The TPB at $y = L$ can be less important under certain conditions. In a steady state, the continuity of current density at $y = 0$ and $y = L$ should be expressed, respectively, as

$$[J_{v,migr}]_{ic,y=0} = [J_{TPB}]_{y=0} + [J_{v,migr} + J_{v,diff}]_{MIEC,y=0} \quad [C-3a]$$

$$[J_{v,migr} + J_{v,diff}]_{MIEC,y=L} = [J_{TPB}]_{y=L} + [J_r]_{y=L} \quad [C-3b]$$

where $[J_{v,migr}]_{ic}$ represents the current density due to the migration of V_o^* in the electrolyte, $[J_{TPB}]_{y=0}$ corresponds to the current density due to charge-transfer across the TPB at $y = 0$, $[J_{v,migr} + J_{v,diff}]_{MIEC}$ represent the current density due to migration and diffusion of V_o^* in the MIEC, $[J_{TPB}]_{y=L}$ corresponds to the current density due to charge-transfer across the TPB at $y = L$, while $[J_r]_{y=L}$ represents the current density due to the reaction occurring at the MIEC/gas interface at $y = L$. All current densities in the porous electrode are on a superficial area basis. Compared to Eq. 7a, it is clear that $[J_{TPB}]_{y=0}$ has been neglected. To illustrate that this is grossly wrong, imagine that the porous MIEC electrode is replaced with a porous Pt electrode, which has identical microstructure as the MIEC electrode (about 30% porosity). If Eq. 7a were correct, there would be no current passing through the cell simply because the term on the right side of Eq. 7 vanishes (note that $D_v \approx 0$ in Pt). In other words, the developed model predicts that Pt, or any other electrode material with little ionic transport, would not be functional at all as an electrode for solid-state cells such as SOFCs. The fact is just the contrary; many active metals (with proper microstructure) are far more active than most MIECs. In fact, porous Pt electrodes have been used for solid-state cells for many years and continue to be one of the best electrode materials for various solid-state cells based on ceramic electrolytes. Accordingly, any meaningful modeling of an MIEC electrode must include materials that have little or no ionic transport so that the effect of added ionic transport (or mixed transport) on the overall electrode kinetics can be meaningfully determined.

Similarly, Eq. 7d should be replaced with Eq. C-3b while Eq. 7b is invalid for the same reason. Any reduction or evolution of O_2 occurring at the TPB at $y = 0$ will create a gradient in p_{O_2} at $y = 0$, thus creating an O_2 flux at $y = 0$. Accordingly, an O_2 flux due to $[J_{TPB}]_{y=0}$ should be added to the right side of Eq. 7b.

4. Boundary conditions in a transient state.—In the MIEC electrode, as discussed earlier, $\nabla \phi \neq 0$ must be assumed in order to avoid conflicts among their assumptions. In the presence of a varying electric field, however, the displacement current in the MIEC can be quite significant because of the huge bulk capacitance reported by Adler *et al.* They claimed that the capacitance determined from their impedance data is associated with the bulk ("changes of oxygen stoichiometry in the mixed conductor"), not the MIEC/gas interface ("not confined to an interface-like double-layer polarization"), of the MIEC, implying that accumulation or depletion of charge occurred locally in the bulk of the MIEC. It was further estimated by Adler *et al.* using Eq. 19 that the capacitances associated with bulk reduction or oxidation of the MIEC are about three to five orders of magnitudes greater than the capacitances of electrochemical interfaces, suggesting that substantial bulk polarization has occurred locally in the bulk MIEC.⁶ Regardless of the detailed microscopic polarization mechanism, phenomenologically, the "effective" permittivity of the electrochemically active layer (with thickness δ) of the MIEC can be estimated from the apparent capacitance as $\epsilon_{MIEC} = \delta C_{chem}$. For the $La_{0.6}Ca_{0.4}Fe_{0.8}Co_{0.2}O_{3-\delta}$ electrode studied at 700°C, it was claimed that $C_{chem} \approx 0.81 \text{ F/cm}^2$ (from Fig. 6) and $\delta \approx 6 \mu\text{m}$ (from Table I) and, hence, $\epsilon_{MIEC} \approx 4.8 \times 10^{-2} \text{ F/m}$. Thus, the effective dielectric constant ($\epsilon_{MIEC}/\epsilon_o$) is in the order of 10^9 . With this extremely high effective dielectric constant, the displacement current density $[-\partial(\epsilon_{MIEC}\nabla\phi)/\partial t]$ in the MIEC cannot be ignored. The total current density must include both displacement current density and the current density due to migration and diffusion of mobile defects. It is this total current density which is space invariant at all times. Accordingly, the continuity of current density at $y = 0$ can be generally expressed as

$$\left[J_{v,migr} - \frac{\partial}{\partial t} \left(\epsilon \frac{d\phi}{dy} \right) \right]_{ic,y=0} = \left[J_{TPB} + C_{TPB} \frac{\partial \eta_{TPB}}{\partial t} \right]_{y=0} + \left[J_{v,migr} + J_{v,diff} - \frac{\partial}{\partial t} \left(\epsilon \frac{d\phi}{dy} \right) \right]_{MIEC,y=0} \quad [C-4]$$

where C_{TPB} and η_{TPB} are the capacitance of and overpotential across the TPB at $y = 0$, respectively. A similar equation may also be written for the interface at $y = L$. In general, the electric field ($-d\phi/dy$) in a two-layer system initially distributes according to the dielectric properties (ϵ_{ic} and ϵ_{MIEC}) of each layer while the steady-state distribution of electric field is determined by the transport properties (D_k^{ic} and D_k^{MIEC}) of each layer. The transition from an initial state to a final state (or a steady state) is characterized by accumulation or depletion of mobile charges at the interface due to unbalanced migration and diffusion currents at the interface. If there is polarization in either layer or at the interface, the migration or diffusion current density must vary with position.

It is noted that displacement current densities were not even mentioned in Adler's analyses. Any assumptions or approximations should be explicitly stated; otherwise, the boundary conditions specified by Eq. 7a, b, c, and d are all invalid in a transient state. For instance, Eq. 7a should be replaced by Eq. C-4. Even under the assumption that there were no electrochemical reaction occurring at the TPB at $y = 0$ (this is absolutely impossible in reality), the sum of the migration and diffusion current must be discontinuous at the interface ($y = 0$) in a transient state; it is the difference in this current at the interface that causes the interfacial polarization. Further, in a polycrystalline electrolyte such as doped CeO_2 , grain boundaries are the zones where mobile charges may accumulate, causing grain boundary polarization and displacement current. This effect is typically more pronounced at intermediate or lower temperatures. Grain boundary polarizations in ceramic electrolytes have been studied extensively using impedance spectroscopy and are well documented in the literature.⁷

In addition, the kinetics of other processes should also be considered. For instance, the condition stated by Eq. 7c is invalid in general; on the contrary, the total flux of oxygen in the electrode must be different from the total flux of oxygen in the boundary layer in a transient state. It is the difference in these fluxes which accounts for the polarization of the interface. For example, an adsorption or desorption of oxygen at the interface may create a flux of O₂ in the boundary layer, but not necessarily result in a current flux in the solid electrode at the same time since the induced current may lag behind to some degree. Equation 7b and d are invalid for the same reason as stated for Eq. 7a and c.

5. *Experimental verification.*—Because of the errors in Eq. 1 and 7 as well as the incorrect or inconsistent assumptions, the derived equations are invalid and so is the interpretation of the impedance data. For instance, Eq. 17 and Fig. 5 imply that in a cell with “a porous-electrode of infinite thickness,” the only contributions to the resistance of the cell are “diffusion of oxygen in the MIEC and exchange of O₂ at the mixed conductor/gas interface.” In fact, Z (defined by Eq. 17) is only part, not the entirety, of the total cell impedance, Z_{cell}; the contribution of Z to Z_{cell} decreases with the increase of Z, not increases with Z as predicted by Eq. 17. The incorrectness of Eq. 17 and 18 and Fig. 5 can be more clearly seen by evaluating Eq. 18, which predicts that the bulk resistance of the MIEC electrode, or the impedance of the cell, approaches infinity (R_{chem} → ∞) as r_o → 0 (or D_v → 0 or c_v → 0). In this limit, on the contrary, a correct model predicts that the impedance of the MIEC electrode must vanish since it is assumed that ∇μ_o = 0 (or equipotential) in the MIEC. The total impedance of a symmetric cell, cc/MIEC/electrolyte/MIEC/cc, in the limit of Z → ∞ can be expressed as

$$Z_{\text{cell}} = Z_{\text{el}} + 2(Z_{\text{TPB},y=0} + Z_2) \quad \text{[C-5]}$$

where Z_{el}, Z_{TPB,y=0}, and Z₂ are the impedance of the electrolyte, the TPB at y = 0, and the MIEC/cc interface, respectively. In fact, Eq. C-5 is true as long as r_o (or D_v or c_v) and ∇μ_o are sufficiently small (not necessarily vanishing). This equation implies that, when Z is sufficiently greater than the resistance to other processes occurring in the cell, neither oxygen transport in the MIEC nor the reaction at the MIEC/gas interface has much influence on the electrode kinetics and, hence, Z is not observable in an impedance measurement, rather than dominating the impedance response of the cell as predicted by Eq. 17 and Fig. 5.

In addition, it is not clear how the thickness (L) of the porous electrode could have as dramatic effect on cell impedance, as implied by simplification of Eq. 12 to Eq. 17 in the limit of L → ∞. According to their analysis, oxygen diffusion in the MIEC and the reaction at the MIEC/gas interface occur significantly only within a layer adjacent to the electrolyte with thickness of δ, which is on the order of microns. Thus, the impedance of the cell should be independent of L as long as L > δ and ∇μ_o = 0 (or equipotential).

While the predicted impedance spectrum shown in Fig. 5 is incorrect, the data shown in Fig. 6 represent the typical impedance response of such a cell. In Fig. 5, the two intercepts of the impedance spectrum with the real-axis are Re(Z)/R_{chem} = 0 and 1, implying that Z constitutes the entirety of the total cell impedance. In Fig. 6, on the other hand, the two intercepts are Re(Z)/R_{chem} ≈ 9.4 and 10.4, suggesting that Z represents only a small part (about 10%), not the entirety, of the total cell impedance. Clearly, the two spectra are fundamentally different; the spectrum shown in Fig. 6 cannot be explained using Eq. 17 which requires Z_{cell} = Z. Yet, Adler *et al.* claim that “The plot (Fig. 6) shows that the measured response of the cell agrees well with the Gerischer behavior (Eq. 17) predicted in Fig. 5. This agreement suggests strongly that the electrode kinetics is dominated by surface exchange and solid-state diffusion.” Further, as an experimental verification of

their model, they claim that the “chemical” resistance (R_{chem} = 0.63 Ω cm²) and capacitance (C_{chem} = 0.81 F/cm²), as determined from the data shown in Fig. 6, are due merely to the diffusion of oxygen in the MIEC and to exchange of O₂ at the MIEC/gas interface. Still further, they asserted that “homogeneous electrochemical reactions in aqueous electrolytes” are mathematically isomorphic to “heterogeneous chemical reactions” in the solid MIEC electrode.

In fact, if the impedance to oxygen diffusion in the MIEC or to the reaction at the MIEC/gas interface is indeed significantly greater than the impedance to any other processes occurring in the cell, the impedance data shown in Fig. 6 should be interpreted using Eq. C-5, not Eq. 17. That is, the determined resistance (0.63 Ω cm²) and capacitance (0.81 F/cm²) should be due to just what was ignored, the interface impedance (Z_{TPB} and Z₂), and have nothing to do with the impedance to oxygen diffusion and surface reaction (Z). In general, the contributions of the interfaces to cell impedance cannot be ignored without careful analysis and adequate justification. In conclusion, the impedance data presented cannot verify the validity of their model; on the contrary, they demonstrate that the developed model is invalid.

LIST OF SYMBOLS

a _k	activity of defect k (k = e, h, v)
A	thermodynamic factor
c _k	molar concentration of defect k, mol m ⁻³
C _{TPB}	capacitance of triple-phase boundary (TPB), Fm ⁻²
D _k	diffusivity of defect k (D _k = RTu _k), m ² s ⁻¹
e [•] , h [•]	an electron and electron hole, respectively
E _F	Fermi energy of electrons (E _F = μ _e), J
F	Faraday's constant, 96,487 C · eq ⁻¹
J _k	current density due to the motion of defect k, J _k = J _{k,migr} + J _{k,diff} , A m ⁻²
J _{k,diff}	current density due to diffusion of defect k under the influence of ∇μ _k , A m ⁻²
J _{k,migr}	current density due to migration of defect k under the influence ∇φ, A m ⁻²
J _{TPB}	current density passing through triple-phase boundary (TPB), A m ⁻²
k _g	equilibrium constant for the reaction at MIEC/gas interface
L	thickness of the MIEC, m
p _{O₂}	partial pressure of oxygen, atm
r	net rate of the reaction at MIEC/gas interface
r _o	exchange rate of the reaction at MIEC/gas interface
u _k	absolute mobility of defect k, mol m ² J ⁻¹ s ⁻¹
V _O ^{••}	an oxygen vacancy
y	distance away from MIEC/electrolyte interface, m
Z	impedance to oxygen diffusion in MIEC and the reaction at MIEC/gas interface, Ω
Z ₁	impedance of the MIEC/electrolyte interface (excluding the TPB), Ω
Z ₂	impedance of the MIEC/current collector interface (excluding the TPB), Ω
Z _{el}	impedance of the electrolyte, Ω
Z _{cell}	impedance of a symmetrical cell, cc/MIEC/electrolyte (ic)/MIEC/cc, Ω
δ	thickness of electrochemically active layer of an MIEC electrode, m
γ _k	activity coefficient of defect k
η _{TPB}	overpotential across the TPB, V
ε _o	permittivity of vacuum, 8.854 × 10 ⁻¹² F m ⁻¹
ε _{ic} , ε _{MIEC}	effective permittivity of electrolyte (ic) and MIEC, respectively, F m ⁻¹
μ _k	chemical potential of defect k (μ _k = μ _k [*] + RT ln γ _k c _k), J mol ⁻¹
μ̃ _k	electrochemical potential of defect k (μ̃ _k = μ _k [*] + RT ln γ _k c _k + z _k Fφ), J mol ⁻¹
φ	electrostatic potential in a plane at distance y, V
Abbreviations	
cc	current collector
ic	ionic conductor
MIEC	mixed ionic-electronic conductor
TPB	triple-phase boundary

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2. "Diffusion" refers only to a transport process driven merely by a gradient in chemical potential, $\nabla\mu_c$.

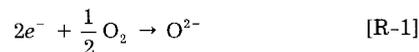
3. The validity of $\nabla c_c \neq 0$ (or $\nabla\phi \neq 0$) in an MIEC with uniform Fermi level depends on the transport properties of the MIEC. For instance, when u_c is finite, it may be possible to sustain an electron concentration gradient and an electric field while maintaining uniform Fermi level. When $u_c \rightarrow \infty$ (e.g., in a superconductor), however, it becomes questionable to sustain $\nabla c_c \neq 0$ (or $\nabla\phi \neq 0$).

4. Even assuming that their formulation of the kinetics of the reaction is correct, c_v and c_i in Eq. A-16 and A-17 should be replaced, respectively, with the corresponding activities a_v and a_i to be consistent with their formulation. For instance, they have used activity ($a_k = \gamma_k c_k$) for each defect in writing transport equations. Also, Eq. A-17 should reduce to Eq. C-2b when $r = 0$, i.e., when the reaction at the MIEC/gas interface (Eq. C-2c) is at equilibrium.

5. T. M. Gur and R. A. Huggins, "Oxygen Transport Measurements in Mixed-Conducting A-Site and B-Site Doped Perovskites", GRI Report, 1992; M. Liu, *This Journal*, **144**, 1813 (1997).

6. If the observed capacitances in their impedance spectra are indeed associated with the bulk phase of the MIEC, the assumption of local charge neutrality is incorrect. The charge neutrality equation (Eq. A-1c) should be replaced with Poisson's equation. Charge neutrality is an approximation, not a fundamental law. In the absence of bulk polarization in a homogeneous phase, it may be adequate to assume that local charge neutrality is approximately observed. In the presence of significant bulk polarization, however, the validity of the local charge neutrality approximation must be carefully evaluated.

7. D. Y. Wang and A. S. Nowick, in *Grain Boundary Phenomena in Electronic Ceramics*, L. M. Levinson, Editor, publisher, p. 130 (1981).



On the contrary, the purpose of our model is to investigate one mechanism by which this three-phase boundary reaction may occur. Consideration of a separate parallel three-phase boundary (TPB) reaction would be redundant.

Perhaps at issue is not whether we address the three phase-boundary reaction, but what conclusions we draw from our analysis. Indeed, Liu and Winnick appear to reject our conclusion that electrode polarization in a mixed-conducting electrode involves bulk reduction/oxidation of the mixed conductor. Their criticism invokes a more phenomenological paradigm in which polarization must occur locally at the one-dimensional interface between catalyst, electrolyte, and gas.^{11,12}

Yet it is well established that this paradigm fails to explain several key features of mixed conducting electrodes: (i) large faradaic capacitances (up to 1 farad/cm²),^{13,14} (ii) semi-infinite diffusion behavior at intermediate frequencies,¹⁵ (iii) nearly linear i - V characteristics at moderate overpotential,¹⁶ and (iv) strong correlation between electrode kinetics and bulk diffusion and surface-exchange properties.^{17,18} In contrast, our model is able to explain these features of the data, in some cases quantitatively.

The counter example of platinum on yttria-stabilized zirconia does not seem pertinent, since our model is only valid for materials with high rates of internal mass transfer and surface exchange. We show specifically that our model breaks down for poor mixed-conductors such as LSM, in which other, more localized mechanisms must dominate.

With any material, however, the paradigm of a one-dimensional interface is an oversimplification. Poorly understood faradaic processes such as those treated in our paper appear to play a role in all three-phase boundary reactions, even in Liu's and Winnick's own example of platinum.¹⁹⁻²¹ Indeed, despite being a poor mixed conductor, LSM exhibits large electrode capacitances that cannot be explained solely in terms of interfacial polarization.²² At low p_{O_2} , the reaction zone appears to extend over much of the mixed-conductor surface.²³ It is likely mixed-conduction on some level is important in all metal-oxide electrode reactions.

Thus we disagree philosophically with Liu's and Winnick's limited view of modeling in terms of fitting specific sets of data. The methods presented here serve a much broader purpose of allowing us to pose scientific questions about solid-state electrochemical systems in a rigorous manner, so that we can address them thoroughly. A model does not have to treat all general cases to be useful and enlightening. It is often differences between observation and model that are the most educational.

Electrical state and charge-density issues.—(Response to comment 1).—*Proper treatment of disparate mobilities.*—In our model, we assume that electronic transport in the mixed conductor is facile, and thus the Fermi level will be approximately uniform throughout the material. Liu and Winnick argue that finite electronic current (as predicted by our model) is inconsistent with this assumption since a uniform Fermi level implies zero electronic current.

This argument is based on a misunderstanding of our assumptions. In reality, we do not assume that the gradient of the Fermi level is identically zero; we assume only that electronic transport is facile. The consequence of this assumption can be seen by examining Eq. A-1a. As the product $c_i D_i$ for the electronic species (electrons or holes) approaches infinity, then for any finite (nonzero) value of the electronic flux, the gradient of the Fermi level must go to zero. This statement is not an assumption entering Eq. A-1a, it is an approximate solution which we use in place of Eq. A-1a in order to simplify the system of equations.²⁴ Thus our approach here implies only that oxygen

Fundamental Issues in Modeling of Mixed-Conductors

(A rebuttal to comments on "Electrode Kinetics of Porous Mixed-Conducting Oxygen Electrodes")

S. B. Adler,⁸ J. A. Lane,⁹ and B. C. H. Steele⁶: The following is a discussion of some fundamental issues of modeling mixed-conductors.

Introduction.—It has long been theorized that oxygen reduction at a porous mixed-conducting electrode may involve O₂ reduction at the mixed conductor surface followed by solid-state transport of oxygen through the mixed-conductor to the electrolyte. In our paper, we establish theoretical justification for this view by modeling this mechanism and comparing our predictions to electrode kinetic data.¹⁰

In their criticisms, Liu and Winnick disagree with two aspects of our work: (i) the conclusion that the kinetics of a mixed conducting electrode may be dominated by solid-state diffusion and surface exchange, and (ii) the method that we use to model these phenomena. In this rebuttal, we provide additional support for our method and conclusions, and show that these criticisms either lack factual support or contain theoretical misconceptions.

Some of these misconceptions raise issues that are worth discussing in detail, as they touch upon the theoretical underpinnings of solid-state electrochemistry. In developing our model, it was necessary for us to address these issues in depth, some of which are not obvious nor fully understood. Since these issues are likely to arise repeatedly in modeling of similar systems, we hope to highlight them for the reader, show what choices we made and why, and illustrate their importance in constructing useful, self-consistent continuum-mechanical descriptions of solid-state electrochemical systems.

Each of the following sections respond to one of Liu's and Winnick's numbered comments.

Role of modeling in solid-state electrochemical systems.—(Response to comment 3).—Liu and Winnick comment that our model ignores the electrochemical reaction occurring at the three-phase boundary

transport in the mixed-conductor will be limited by ion transport, not that electronic transport is zero.

This assumption is analogous (in a one-dimensional, single-phase system) to approximating the electronic transference number in Wagner's equation as unity prior to integration.¹⁶ Setting $t_e = 1$ does not mean the transference number of ions (and thus the integrand) is zero, only that it is very small and thus $t_e = 1$ is a reasonable approximation.

Returning to the model, we find that the current in the mixed conductor is defined to be 100% electronic at the current-collector/mixed-conductor interface, while being 100% ionic at the electrolyte/mixed-conductor interface. As illustrated in our Fig. 2,¹⁰ this change from electronic to ionic current over the thickness of the electrode is accommodated by the incorporation of neutral oxygen from the gas into the mixed conductor, and corresponds to the overall electrode reaction: $2e^- + 1/2 O_2 \rightarrow O^{2-}$.

Choice of electrical state variable.—In the text, we often refer to vacancy transport in the mixed conductor as “diffusion.” Liu and Winnick express concern that we are ignoring “migration” by assuming that gradient of the electric potential is zero.

This concern appears to be semantic. In reality, we do not assume $\nabla\Phi = 0$. Indeed, we expect the driving force for vacancy transport to involve gradients in electric potential as well as concentration. However, the mathematical definitions of “diffusion” and “migration” are not universal, they depend on our choice of electrical state variable, as do the definitions of activity coefficients and the thermodynamic factor.^{26–28} Although strictly arbitrary, this choice strongly influences the difficulty of the mathematics, as well as the semantics.

For example, let us consider a reformulation of the model in which we choose the quasi-electrostatic potential, Φ , to be the electrical state variable in the mixed conductor. The quasi-electrostatic potential (based on electrons) is defined as²⁹

$$\mu_e = RT \ln(c_e) - F\Phi \quad [\text{R-2}]$$

Substitution of this definition into the flux equation for vacancies yields

$$\mathbf{N}_v = - \left(-\frac{1}{2} \frac{\partial \ln(p_{O_2})}{\partial \ln c_v} - \frac{\partial \ln(c_e^2)}{\partial \ln c_v} \right)_{\text{eqb.}} D_v \nabla c_v - \frac{2Fc_v D_v}{RT} \nabla \Phi \quad [\text{R-3}]$$

This shows that the vacancy flux is composed of a “diffusion” and a “migration” term. Since in our problem we anticipate large gradients in vacancy concentration and potential, we expect both these terms to be important. Thus the choice to apportion transport in this manner is inconvenient since now the driving force for transport involves gradients of two separate state variables (c_v and Φ). Reformulation of the conservation Eq. A-3 using these definitions results in a complex problem involving coupled partial differential equations.

On the other hand, let us now examine the same flux equation with the Fermi level as the electrical state variable (as we use in our model)³⁰

$$\mathbf{N}_v = - \left(-\frac{1}{2} \frac{\partial \ln(p_{O_2})}{\partial \ln c_v} \right)_{\text{eqb.}} D_v \nabla c_v + \frac{2c_v D_v}{RT} \nabla \mu_e \quad [\text{R-4}]$$

Again, we have a “diffusion” term and a “migration” term. However, if we substitute the approximate solution $\nabla \mu_e = 0$ into this expression, we eliminate “migration” and are left only with “diffusion,” with the driving force being the gradient of a single-state variable (c_v). This allows us to simplify the equations and to solve the problem analytically. In addition, this definition of the thermodynamic factor is more accessible experimentally.

As with the choice of speciation, our choice of electrical state variable is dictated by convenience. Since we know that the material is a good electronic conductor, it is natural to choose the Fermi level as the electrical state variable in order to simplify the mathematical description. Contrary to the concern expressed in the comments, this choice does not imply that Φ or c_e is uniform. We specify that c_e and c_h are tied to c_v through electron-hole equilibrium and electroneutrality.

Electroneutrality.—In our model, we specify that electroneutrality is obeyed in the bulk of the mixed-conductor. Liu and Winnick state that this specification is inconsistent with our results, since bulk oxidation and reduction predicted by our model implies significant deviation from electroneutrality. This concern is reiterated in comment 4. (See above, Winnick and Liu's footnote 6).

On the contrary, electrochemical oxidation or reduction of the mixed conductor does not violate electroneutrality, since these processes involve loss or gain of neutral combinations of ionic and electronic species, without storage of charge. Electrochemical oxidation or reduction is equivalent thermodynamically to chemical oxidation or reduction, as occurs by absorption or desorption of oxygen gas.

Although electroneutrality is “not a fundamental law,” it is a valid approximation to Poisson's equation in the bulk of a material. As discussed by Newman,³¹ its validity only breaks down at extremely low concentrations ($\sim 10^{-8}$ eq/cm³), well below those encountered in most electrochemical systems, even lightly doped semiconductors.

The relevant issue is not whether electroneutrality is obeyed in the bulk of the mixed conductor; the issue is how far from a polarized interface do regions of charge separation extend into the bulk. This distance is characterized by the Debye length, λ , which is related to the bulk concentration of mobile charges

$$\lambda = \sqrt{\frac{\epsilon RT}{F^2 \sum_i z_i^2 c_i}} \quad [\text{R-5}]$$

where ϵ is the dielectric permittivity of the solvent (in the absence of any mobile charges). For a 0.1 M aqueous solution of a univalent salt,³² the Debye length is less than 10 Å. For a highly defective perovskite we expect this distance to be much smaller (less than a unit cell) since concentrations of charges are much higher.³³ Thus all but the first monolayer of the material is “bulk,” and obeys electroneutrality. Any deviations from electroneutrality are confined to the interfaces, as treated by Eq. A-11 and A-13.

Distribution and effect of immobile, unreactive charges.—In our model, we define the “background charge,” B , as the uniform charge density of all immobile and unreactive ions or localized charges in the mixed conductor, which we lump together as part of the lattice “solvent.” Liu has asserted that this definition of B as uniform is invalid since oxidation or reduction causes compositional gradients of immobile charges.³⁴

The misconception in this argument can be seen by examining the electroneutrality Eq. A-1c. Under conditions of thermodynamic equilibrium, the charge density of the explicitly defined species must be uniform. Thus for electroneutrality to be obeyed, B must also be uniform at equilibrium. Since all charges contributing to B are by definition immobile and unreactive, they cannot move or transfer their charge during nonequilibrium conditions. Thus B is by definition uniform under all conditions. Oxidation or reduction can only cause compositional gradients of explicit species (in our case vacancies, electrons, and holes).

The conceptual difficulty with this definition of B appears to be a concern that we are not properly accounting for the reduction or oxidation of reducible transition-metal cations (e.g., Co or Fe). However, with the speciation used in the model, a separate consideration of cation con-

centrations would be redundant. For example, in $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$, the hole concentration c_h (in our notation) is equal to $[\text{Co}'_{\text{Co}}]$ (in Kröger-Vink notation). Likewise, c_e is equal to $[\text{Co}'_{\text{Co}}]$. The vacancy concentration c_v is equal to $[\text{V}^{\bullet\bullet}_{\text{O}}]$. We account for neutral oxygen, $\text{O}^{\times}_{\text{O}}$, cobalt, $\text{Co}^{\times}_{\text{Co}}$, lanthanum, $\text{La}^{\times}_{\text{La}}$, and charged strontium, Sr'_{La} , as part of the solvent, having a background charge $B/F = [\text{Sr}'_{\text{La}}]$.³⁵

One could define each defect as an explicit species, with the neutral lattice as the solvent. Species such as Sr'_{La} would then appear explicitly in the charge neutrality sum. However, these species are thermodynamically and kinetically indistinguishable from the solvent, as is their contribution to electroneutrality. We therefore gain nothing useful by defining them explicitly, and instead prefer to lump them together for convenience.³⁶ This approach is useful when many such species are present.

Thermodynamic and transport issues.—(Response to comment 2).—*Definition of thermodynamic properties and state variables.*—In our model, we define the thermodynamic factor as

$$A = -\frac{1}{2} \left(\frac{\partial \ln(p_{\text{O}_2})}{\partial \ln c_v} \right)_{\text{eqb}} \quad [\text{R-6}]$$

Liu and Winnick assert that this definition is incorrect, since the mixed-conducting electrode will not be at equilibrium and thus A will depend on rate properties of the mixed conductor.

This criticism confuses the definition of A as a thermodynamic property with the actual value of A in the electrode under operation. Certainly since A depends on composition, its value in the electrode will depend on kinetic properties influencing local composition, such as the surface exchange rate, τ , as well as other properties of the system. Indeed, our model predicts the composition profile in the electrode, and how this profile is manifest in the electrode kinetics.

However, the definition of A as a thermodynamic property cannot involve any kinetic or transport properties of the material. Although there are various definitions in the literature for the thermodynamic factor (or “thermodynamic enhancement factor” as it is often called), all self-consistent definitions known to the authors share a common feature: A is defined as a thermodynamic property of the material describing the equilibrium relationship between activity and composition in the solid.

Expression A-5, to which Liu and Winnick do not object, is equivalent to definition R-6. This can be seen by examining the equilibrium expression for the oxygen-exchange reaction

$$-\frac{1}{2} \mu_{\text{O}_2} = \mu_v + 2\mu_e \quad [\text{R-7}]$$

Substituting A-2b, assuming O_2 is ideal, and differentiating with respect to $\ln c_v$ we obtain

$$-\frac{1}{2} \frac{\partial \ln(p_{\text{O}_2})}{\partial \ln c_v} = 1 + \frac{\partial \ln(f_{v,e})}{\partial \ln c_v} + \frac{\partial \ln(c_e^2)}{\partial \ln c_v} \quad [\text{R-8}]$$

This expression shows that A-5 is a restatement of R-6 in terms of composition variables in the mixed-conductor.

Part of the confusion may arise from the practice of calculating “thermodynamic factors” based on transport properties (e.g., ionic conductivity and diffusion³⁷) rather than measuring them independently. Although the various transport models used to make this calculation incorporate a thermodynamic factor, the thermodynamic factor itself is not a transport property, nor do these models form the basis for its definition. The thermodynamic factor is defined independently as an equilibrium property, and can only be measured independently using an equilibrium experiment (e.g., material weight as a function of p_{O_2} and T ^{38,39}).

The fundamental premise required by any continuum transport theory is that a phase in a nonequilibrium sys-

tem can be described locally by thermodynamic state variables defined under conditions of equilibrium, such as temperature, pressure, and composition.⁴⁰ In this case, due to electroneutrality and electron-hole equilibrium, we have one independent composition variable, which we choose out of convenience to be c_v . We then express all other composition-dependent variables (c_e , c_h , $f_{v,e}$, κ , A) in terms of that one variable. This approach guarantees the proper number of independent macroscopic state variables and transport properties.⁴¹

Importance of proper speciation.—Liu and Winnick also state that we implicitly assume constant A in the mixed conductor, and that this assumption is invalid since the thermodynamic factor can vary by orders of magnitude.

The first part of this statement is a misunderstanding of our assumptions. As defined by R-6, A depends explicitly on the composition of the mixed conductor. The apparent constancy of A in our analysis arises because in the specific system of equations that we solve, only the zeroth-order (constant) term in the expression for A as a function of c_v is important when the equations are linearized. This assumption of linearity is made implicitly by anyone (including Liu) measuring ac impedance.⁴² For solving nonlinear problems, such as estimating i - V characteristics at modest potential, one would account for the composition dependence of A as shown in Eq. A-23a.

However, since nonlinear problems may be of interest, it is worth addressing the secondary question of how strongly $A(c_v)$ depends on c_v . In order to estimate this dependency, let us consider a typical nonstoichiometric perovskite of the type studied in this paper. These materials are often described over wide ranges of p_{O_2} with a power law

$$c_v = c_v^0 p_{\text{O}_2}^\beta \quad [\text{R-9}]$$

where the constant β has a value between $-1/2$ and $-1/16$.^{43,44} Applying our definition of the thermodynamic factor (Eq. R-6), we find that A is given by

$$A = \frac{-1}{2\beta} \quad [\text{R-10}]$$

which predicts A will be composition-independent. Although the true dependence of the stoichiometry may deviate from a power law over the full range of composition, Eq. R-9 is usually valid over the p_{O_2} range relevant to an electrode, and thus serves as an excellent approximation.

While Liu and Winnick reference a counter example in which the thermodynamic factor varies by orders of magnitude,⁴⁵ they fail to appreciate that the definition of the thermodynamic factor (and thus its composition dependence) is determined by the choice of speciation in the mixed conductor. Depending on which independent species are chosen to write conservation equations for, the thermodynamic factor can be a constant, or a highly composition-dependent function.⁴⁶

In order to illustrate this principle, let us consider an alternative speciation of the mixed conductor in which oxygen ions rather than oxygen-ion vacancies are defined as the mobile oxygen species. In this case we would replace c_v with $c_{\text{O}} = c_{\text{mc}} - c_v$ as the independent composition variable, where c_{O} is the oxygen ion concentration and c_{mc} is the concentration of lattice sites. The linearized porous electrode equation describing the mixed conductor (Eq. 1) then becomes

$$(1 - \epsilon) \frac{\partial c_{\text{O}}^*}{\partial t} = \frac{(1 - \epsilon)}{\tau} A' D_{\text{O}} \frac{\partial^2 c_{\text{O}}^*}{\partial y^2} + ar \quad [\text{R-11}]$$

where $c_{\text{O}}^*(y, t) = c_{\text{O}}(y, t) - c_{\text{O}}(i = 0)$, and A' is defined as

$$A' = \frac{1}{2} \frac{\partial \ln(p_{\text{O}_2})}{\partial \ln c_{\text{O}}} = 1 + \frac{\partial \ln(f_{\text{O},e})}{\partial \ln c_{\text{O}}} - \frac{\partial \ln(c_e^2)}{\partial \ln c_{\text{O}}} \quad [\text{R-12}]$$

Although Eq. R-11 is an equivalent expression of the problem in terms of a different set of composition variables, the parameters entering this equation are more likely to be

composition dependent than the ones used in our model. This can be understood by examining the relationship between the thermodynamic factor A' as defined in R-12 and our definition of A as defined in R-6

$$A' = \frac{-1}{2\beta} \frac{c_{mc} - c_v}{c_v} \quad [\text{R-13}]$$

Assuming β is constant, A' becomes inversely proportional to c_v at moderate vacancy concentrations, and diverges to infinity as c_v approaches zero. Likewise (for consistency between Eq. 1 and R-11) D_o must be related to D_v by

$$D_o = D_v \frac{c_v}{c_{mc} - c_v} \quad [\text{R-14}]$$

indicating that if D_v is roughly constant,⁴⁷ D_o becomes proportional to c_v at moderate vacancy concentrations, and vanishes to zero as c_v approaches zero.

Although these strong compositional dependencies are "valid," they are inconvenient since we must now account for them throughout the analysis. For example, if we choose to solve the full nonlinearized problem using numerical methods, we cannot assume that the diffusion coefficient, D_o , is a constant (as we do for D_v in A-3a and A-3b). Likewise we cannot assume $\nabla A' = 0$ (as we would for A when β is constant). The extra terms required to handle these composition dependencies may create numerical difficulties such as rounding errors or stiffness near geometric features. Indeed, the mathematics become more difficult as the defect chemistry becomes more "ideal" (i.e., as D_v and β approach constant values).

Since various choices of speciation are equivalent, the choice is strictly arbitrary. However, as illustrated above, proper speciation is not a matter of "correctness;" it is a matter of convenience.⁴⁸ In our model, we use knowledge of the material properties to choose a composition variable, c_v , and electrical state variable, μ_e , that naturally minimize compositional and spatial dependencies. This approach allows us to more easily make valid *a priori* physical assumptions that simplify the analysis, while providing a useful framework for evaluating the origin and validity of those assumptions.⁴⁹

Interfacial polarization and kinetic issues.—(Response to comment 4).—*Bulk polarization.*—Liu and Winnick assert that any capacitances associated with the bulk of the mixed conductor must be caused by bulk dielectric displacement, which they claim our boundary conditions improperly ignore.

This criticism misunderstands the origins of bulk polarization. Since the mixed conductor is metallic, bulk dielectric displacement cannot occur.^{50,53} Rather, the large capacitance predicted by the model is caused by electrochemical oxidation and reduction. By definition, these processes should appear in the conservation equations describing the bulk, not in the boundary conditions describing the interfaces. Indeed, continuum Eq. 1 through 4 are associated with changes in composition of the mixed conductor and gas. As discussed above, electrochemical oxidation or reduction is consistent with electroneutrality because it involves gain or loss of neutral combinations of ionic and electronic species.

Interfacial polarization.—In our model, we employ boundary conditions that are statements of current continuity across the electrolyte/mixed-conductor interface and the mixed-conductor/current-collector interface. Liu and Winnick claim that these boundary conditions ignore interfacial polarization since it is the difference in current from one side of the interface to the other that results in storage of charge.

Although capacitors are often said to "store charge," this is a semantic description. In fact, capacitors do not store charge, they store energy in the form of charge polarization. A capacitor as a whole remains electrically neutral, with the charge " q " on one side of the capacitor being

equal and opposite to the charge " $-q$ " on the other side.^{51,52} Thus the current across a capacitor is continuous. Indeed, the governing equation for a capacitor is defined in terms of a single current

$$i = C \frac{dV}{dt} \quad [\text{R-15}]$$

where V is the potential difference across the capacitor, and C is the capacitance.⁵³

At an electrochemical interface, where a charge-transfer reaction occurs in parallel with interfacial polarization, the total current will be the sum of the faradaic current and the polarization current (or the "drift" and "displacement" currents, respectively)

$$i = f(\eta) + C \frac{d\eta}{dt} \quad [\text{R-16}]$$

where η is an interfacial overpotential (analogous to V on a capacitor), and $f(\eta)$ is the faradaic current driven by non-zero η .⁵⁴ This equation shows that during the transient state, part of the current will be faradaic and part will be involved in polarizing the interface. However, as implied by R-16, the current is at all times continuous across the interface.

Returning to the model, we find that the faradaic and polarization processes at the electrolyte/mixed-conductor interface and the mixed-conductor/current-collector interface are handled by equations analogous to R-16 (A-11 and A-13). Thus our model properly takes into account both "drift" and "displacement" current. Charge continuity across these interfaces is provided by Eq. 7a and the implied equivalency of the current in Eq. 5 and 6.

It is correctly noted that we ignore polarization effects in the grain boundaries of the electrolyte. Indeed, we chose to restrict our model to electrode processes.

Surface adsorption.—Liu and Winnick correctly note that we ignore any capacitive effects of surface adsorption at the gas/mixed-conductor interface (Eq. 7c and 7d). We believe this assumption is justified for the following reasons

1. The concentration of oxygen species in the bulk is high, while the surface area of the electrode is low. Thus at low frequency, we expect capacitive effects caused by changes in bulk stoichiometry to overwhelm those caused by changes in surface composition. This expectation is supported by our impedance data that shows semi-infinite diffusion behavior above ~ 1 Hz (Fig. 6 and 7¹⁰), suggesting that the large, low-frequency, capacitances have bulk rather than interfacial origins.

2. At higher frequencies, where we might expect to see surface-capacitive effects, our model predicts that bulk composition fluctuations will not reach much of the mixed-conductor surface. Thus we expect interfacial polarization as expressed in Eq. 5 and 6 to dominate over any adsorptive effects. Indeed, experiments below $\sim 600^\circ\text{C}$ only show evidence for charge-transfer resistance at the electrolyte/mixed-conductor interface.⁵⁵ At higher temperatures we observe no high-frequency polarization of any type.

Part of the concern regarding "polarization" at the gas/mixed-conductor interface may arise from a misunderstanding of the driving force for the oxygen exchange reaction. As explained below, oxygen exchange does not involve a net flow of charge across the interface, and thus there can be no "polarization" due to net changes in charge separation, as considered in Eq. A-11 and A-13. Prediction of adsorptive capacitance would require direct consideration of transients in the elementary reaction steps (A-15).⁵⁶

Kinetics of oxygen exchange at the gas/mixed-conductor interface.—In our model, we treat the driving force for the oxygen exchange reaction at the gas/mixed-conductor interface as independent of the electrical state in the mixed conductor. Liu⁵⁷ and others have commented that

this is inconsistent, since the driving force for the electrode reaction as a whole is electrical in nature. Indeed, Liu employs a rate expression that invokes an electrical state-dependent driving force.⁵⁸

However, the oxygen exchange reaction is a net chemical reaction involving molecules and neutral combinations of charged species, whose thermodynamic states are by definition independent of electrical state. Thus the driving force for the reaction cannot depend on electrical state,⁵⁹ and a rate expression such as R-16 (or Liu's similar rate expression) would be incorrect.

It may help to illustrate this concept with the following paradox. Imagine two macroscopic pieces of a mixed conductor that have been allowed to come to chemical equilibrium with the ambient p_{O_2} , but are subsequently polarized 100 mV relative to each other through a dc power supply. According to Liu's rate expression, the electrical state difference would cause one of the pieces to reduce (evolving O_2), while the other oxidizes (absorbing O_2). Yet we know logically that without an electrolyte connecting them, both pieces must remain in equilibrium with the ambient p_{O_2} .

The resolution is that although the thermodynamic state of any specific charged species differs by 100 mV between the two pieces, the thermodynamic state of O_2 (or its manifestation as neutral combinations in the solid) is equivalent everywhere. Electrochemical oxidation and reduction of the solid relative to the gas can only occur by selective ion transport through an electrolyte. This change in composition ultimately provides the driving force for O_2 exchange, but only when it reaches the gas-exposed surface. Parts of the electrode whose composition is unaffected by current remain equilibrated with the gas, despite being polarized 100 mV relative to each other electrostatically.

A consequence of this principle is that the current through the cell and the rate of O_2 reduction/oxidation at the surface are not correlated directly. They are coupled indirectly via solid-state and gas-phase diffusion (see our paper Fig. 2¹⁰). As discussed in the paper, this indirect coupling between electrochemical and chemical reduction/oxidation is relatively slow, and thus large capacitances are observed.

Comparison to experiment.—(Response to comment 5).—“Chemical” vs. charge-transfer contributions to the electrode impedance.—Based on Eq. C-5, Liu and Winnick assert that if the electrical resistance of the electrode material and the impedances of the interfaces are small, the impedance of the electrode must also be small. Hence, the impedance observed in our measurements must have interfacial origins.

To illustrate the fallacy of this conclusion, consider the example of a highly conductive Pt electrode on zirconia that has been encased in a thick coating of a microporous material. In this example, we specify that without the coating the measured interfacial impedance is small, but with the coating the current becomes limited by oxygen diffusion through the pores of the microporous material. Thus we observe experimentally that the kinetics of the coated electrode are poor, even though the electrical conductivity of Pt is high and the interfacial kinetics are fast.

Equation C-5 cannot explain this observation because it assumes implicitly all contributions to impedance are charge-transfer related. In this example, however, the current is limited by a noncharge-transfer process: the supply of molecular oxygen. The mixed conducting electrode treated in our model is a more complex version of the same principle, in which the supply of oxygen is additionally limited by solid-state oxygen transport and surface exchange. Unlike Eq. C-5, our model (Eq. 12) includes these processes, and is supported by our data and the measurements of other workers.

Electrode thickness effects and electrolyte contributions.—Liu and Winnick correctly observe that if the electrode reaction does not extend more than a distance δ from the electrolyte, the electrode impedance should become

independent of electrode thickness for $L \gg \delta$. Indeed, Eq. 14-19 predict this independence, as illustrated in Fig. 4.¹⁰

We hope it is clear, however, that Eq. 17 is an asymptotic limit of the model. As the electrode becomes thick, or as the p_{O_2} becomes small, O_2 -diffusion in the pores becomes rate limiting. The full solution (Eq. 12) includes these gas-phase effects.

Liu and Winnick also correctly note that the data in Fig. 6¹⁰ include electrolyte resistance, whereas Eq. 17 does not. Indeed, the figure caption is in error. We actually fit the data below 1000 Hz to the sum of Eq. 17 and a positive real constant in order to separate the electrode and electrolyte contributions.

Parallel electrode processes.—Finally, Liu and Winnick correctly observe that if a second, more localized reaction mechanism is active in parallel with our chemical mechanism, then as R_{chem} goes to infinity, the electrode resistance will be dominated by the more local process. We fully agree, as illustrated in Fig. 9.¹⁰ However, as R_{chem} becomes small, as is the case with a good mixed conductor, we expect our mechanism to dominate.

Others have commented that during bonding, constituents of the electrode material may dope the electrolyte surface such that it becomes mixed-conducting, while also modifying the properties of the mixed-conductor locally. We believe this is likely and may result in a dependence of the electrode performance on the electrolyte material and the bonding conditions. We expect this dependence to be most pronounced when the active region (δ) is small. When δ is large, the electrode is less likely to be interface dependent, since the electrode contributes most of the active area ($\sim 95\%$ with $\delta = 2.5 \mu\text{m}$, $\epsilon = 0.3$, and $a = 20,000 \text{ cm}^2/\text{cm}^3$). Little is known experimentally that addresses this issue.⁶⁰

This issue raises an interesting possibility for the more “localized” mechanism for poor mixed-conductors such as LSM. Perhaps local changes in electrolyte and electrode composition during bonding cause significant local mixed conduction, creating a much larger reaction zone than predicted by the model. Indeed, local reactions are known to effect charge-transfer resistance, why not mixed conduction? An approach similar to ours might be used to investigate this possibility theoretically, in conjunction with a careful analysis of the true materials at the interface.

LIST OF SYMBOLS

A	the thermodynamic factor relating oxygen fugacity to solid composition
B	uniform background charge of all immobile and unreactive species
$f_{i,e}$	activity coefficient for a neutral combination of (species $i + z_i$ electrons)
r	reaction rate of the O_2 -reduction reaction at the mixed-conductor surface (area specific)
r_0	rate constant for the oxygen reduction reaction (area specific)
z_i, D_i	charge, single-component diffusion coefficient for species i
β	power law constant for oxygen nonstoichiometry in a mixed conducting perovskite
δ	thickness of the active region in a mixed-conducting electrode
ϵ, τ, a	porosity, solid tortuosity, internal surface area of the mixed-conducting electrode
μ_i, c_i	electrochemical potential, concentration of species i
μ_e	electrochemical potential of electrons (the Fermi level)
Φ	quasi-electrostatic potential based on electrons

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31. J. S. Newman, *Electrochemical Systems*, 2nd ed., p. 258, Prentice Hall, Englewood Cliffs, NJ.
32. J. S. Newman, *ibid.*, p. 88.
33. In semiconductors or dilute electrolytes, the dielectric solvent can be defined as the upped insulator, e.g., S. B. Adler and J. W. Smith, *J. Chem. Soc., Faraday Trans.*, **89**, 3123 (1993). However, this approach loses meaning when a material becomes metallic: S. B. Adler and J. A. Reimer, *Solid State Ionics*, **91**, 175 (1996). Strictly speaking, the Debye length of the mixed-conductor should be taken as zero by definition, since it is metallic, not dielectric.
34. M. Liu, Private communication, 1996.
35. More complex speciation may be necessary if other defects or defect-interactions are considered, but this changes the number of explicitly defined species, not the uniformity of the solvent charge. In $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$, for example, one would add $(V_{\text{La}}^{\bullet})$ and $(\text{Mn}_{\text{Mn}}^{\bullet} - V_{\text{O}}^{\bullet} - \text{Mn}_{\text{Mn}})$ in order to treat oxygen excess and nonideality. See B. A. van Hassel, T. Kawada, N. Sakai, H. Yokokawa, and M. Dokiya, *Solid State Ionics*, **66**, 295 (1993).
36. This approach is commonly taken in ion-exchange resins. See G. Klein, in *Ionic Exchange: Science and Technology*, NATO ASI Series, Vol. 107, A. E. Rodrigues, Editor, p. 206, (1986).
37. W. Weppner and R. A. Huggins, *Ann. Rev. Mater. Sci.*, **8**, 269, 274 (1978).
38. T. Ishigaki, S. Yamauchi, K. Kishio, J. Mizusaki, and K. Fueki, *J. Solid State Chem.*, **73**, 179 (1988).
39. In Ref. 28, p. 204, M. Liu defines a "thermodynamic factor" that cannot be measured independently because it is based on activity coefficients that are defined ambiguously (see Ref. 27).
40. S. R. DeGroot, *Thermodynamics of Irreversible Processes*, North Holland Pub. Co., Amsterdam (1951).
41. The independent macroscopic state variables and transport properties defining a system are determined by speciation of the solution, choice of electrical state variable, homogeneous reactions, and electroneutrality. Discussions on these subjects can be found in J. S. Newman, *Electrochemical Systems*, 2nd ed., Chap. 2, 3, and 11, Prentice Hall, Englewood Cliffs, NJ (1991).
42. J. R. MacDonald, *Impedance Spectroscopy*, John Wiley & Sons, Inc., New York (1987).
43. J. Mizusaki, M. Yoshihiro, S. Yamauchi, and K. Fueki, *J. Solid State Chem.*, **58**, 259 (1985).
44. J. Mizusaki, Y. Mima, S. Yamauchi, and K. Fueki, *ibid.*, **80**, 102 (1989).
45. T. M. Gur and R. A. Huggins, "Oxygen Transport Measurements in Mixed-Conducting A-Site and B-Site Doped Perovskites," GRI Report (1992).
46. J. Maier addresses how the composition-dependence of the thermodynamic factor depends on the choice of oxygen speciation in *J. Am. Ceram. Soc.*, **76**, 1212 (1993).
47. D_v depends weakly on composition, as well as material. See J. Mizusaki, *Solid State Ionics*, **52**, 79 (1992).
48. J. S. Newman compares the virtue of different speciation choices for dilute H_2SO_4 in *Electrochemical Systems*, 2nd ed., p. 107, Prentice Hall, Englewood Cliff, NJ (1991).
49. In Ref. 28, p. 207, Liu rederives and integrates Wagner's equation for mixed conductors. When integrating, he specifies all transport properties as composition independent, rather than accounting for composition dependencies prior to integration. The resulting flux equation is therefore not generally valid. A more useful approach is taken by Bouwmeester *et al.* in Ref. 25.
50. The dielectric constant is a parameter describing charge polarization in a dielectric medium. See R. P. Feynman, *Lectures on Physics*, Vol. 2, Chap. 10, Addison Wesley Pub. Co., Reading, MA (1964).
51. D. Halliday and R. Resnick, *Fundamentals of Physics*, 2nd ed., p. 484, John Wiley & Sons, Inc., New York (1981).
52. Current continuity breaks down at radio frequencies, but is valid at the frequencies discussed here. See R. P. Feynman, *Lectures on Physics*, Vol. 2, p. 23-2, Addison Wesley Pub. Co., Reading, MA (1964).
53. R. J. Smith, *Circuits, Devices, and Systems*, 4th ed., p. 12, John Wiley & Sons, Inc., New York (1984).
54. J. S. Newman, *Electrochemical Systems*, 2nd ed. p. 198, Prentice Hall, Englewood, NJ (1991).
55. J. A. Lane, S. Adler, P. H. Middleton, and B. C. H. Steele, in *Solid Oxide Fuel Cells IV*, M. Dokiya, O. Yamamoto, H. Tagawa, and S. C. Singhal, Editors, PV 95-1, p. 584, The Electrochemical Society Proceedings Series, Pennington, NJ (1995).
56. This consideration would be outside the realm of continuum mechanics, as would the direct use of rate expression A-18. Indeed, Liu's suggestion (in his Comment Ref. 4) to replace concentrations with activities in A-17(18) confuses the distinction between a continuum rate expression such as A-21 (which does include activities), with a microscopic reaction model such as A-18 (which is used only to rationalize the form of r_0). See J. S. Newman, *Electrochemical Systems*, 2nd ed., pp. 197-198, Englewood Cliffs, NJ (1991).

57. M. Liu, Private communication, 1966.

58. In Ref. 23, p. 207, M. Liu derives rate expressions for the oxygen exchange reaction that depend explicitly on the potential. This is incorrect for reasons stated in the text.

59. For example, the corrosion of iron in H_2SO_4 is a balanced superposition of cathodic dissolution of Fe and anodic H_2 formation. Although the individual currents, i_c

and i_a , depend on electrical state, the corrosion rate at zero current, $r = |i_a/2F| = |i_c/2F| = i_0/2F$, is only a function of composition. See C. Wagner and W. Traud, *Z. Elektrochem.*, **44**, 396 (1938) and S. Barnartt, in *Electrochemical Techniques for Corrosion*, R. Baboian, Editor, NACE Symposium (1976).

60. M. Levy, J. Fouletier, and M. Kleitz, *J. Phys.*, **41**, 335 (1980).

ERRATA

In the article "Vibrational Spectroscopic Investigation of Polyacrylonitrile-Based Electrolytes with a Dimethylformamide Plasticizer" [*This Journal*, Vol. 144, No. 1, pp. 44-48, 1997] the authors should be Zhaoxiang Wang, Biying Huang, Sumin Wang, Xuejie Huang, Rongjian Xue, and Liqun Chen.

In the article "Quantitative Study of Charge-to-Breakdown of Thin Gate Oxide for a p^+ -Poly-Si Metal Oxide Semiconductor Capacitor," [*This Journal*, Vol. 144, No. 2, pp. 698-704, 1997] the authors should be Li-shuenn Wang, Fongshan Huang, and Mou-shiung Lin.

In the article "Deformation of Porous Silicon Lattice Caused by Absorption/Desorption Processes" by Aleksei R. Chelyadinsky, Alexander M. Dorofeev, Nikolai M. Kazuchits, Sandro La Monica, Serguei K. Lazarouk, Gabriella Maiello, Gianlorenzo Masini, Nataly M. Penina, Vechteslav F. Stelmakh, Vitaly P. Bondarenko, and Aldo Ferrari, [*This Journal*, Vol. 144, No. 4, pp. 1463-1467, 1997] S. K. Lazarouk's name should be spelled as herein. On p. 1464, right column, seventh line from the bottom, the sentence should read, "We can conclude that this disordered film probably consists of amorphous silicon and products of chemical processes taking place during anodization of silicon in HF solution and storage of PS samples in air ambient before the TEM study." On page 1467, left column, the sentence beginning on the 20th line down should read, "Both our PS samples and a-Si targets of Ref. 17 show similar behavior at temperatures higher than 500°C. Paduschek *et al.*¹⁷ explained the observed behavior as due to the outgassing of hydrogen from the samples, being supported in this by the measured decrease of the infrared absorption peaks related to silicon hydrogen bonds."