Electron-Ion Interference and Onsager Reciprocity in Mixed Ionic-Electronic Transport in TiO_2

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Onsager's reciprocity theorem has been extensively discussed for fluid systems and its validity generally accepted. The application of the theorem to solid state, however, is not always transparent due to additional complications that have no counterparts in fluids, and its validity has not been so exhaustively examined experimentally either. Here we show that in the phenomenon of mixed ionic-electronic conduction in TiO_2 (rutile), the theorem is verified experimentally, and the Onsager cross coefficient can be even larger than a direct one, contrary to the conventional belief.

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Mixed ionic-electronic conductor oxides have recently been attracting a wide attention for their electrochemical applications, e.g., permeation membranes for oxygen or hydrogen separation and electrodes for sensors and solid oxide fuel cells, to name but a few [1]. In principle [2–4], the flow of electrons in a mixed ionic-electronic conductor is induced not only directly by their own electrochemical potential gradient, but also indirectly by that of mobile ions, and vice versa for the flow of ions. However, the latter, indirect or electron-ion interference effect has been usually ignored or neglected in treatments of the mixed ionic-electronic transport. A recent report [5], that first dealt with this electron-ion interference effect in α-$Ag_{2+\delta}Se$ and β-$Cu_{2-\delta}S$ systems, concluded that the electron-ion interference effect was indeed negligible ($1 \sim 0.01\%$ of the direct effect at most). In contradistinction, for the $Co_{1-\delta}O$ and $Fe_{3-\delta}O_4$ systems, Yoo and coworkers [6,7] reported that the interference effect may not always be negligible depending on the nonstoichiometry δ.

Once the electron-ion interference effect is not negligible, then the validity of the Onsager reciprocity [8] of the effect is also of fundamental interest. The Onsager reciprocity theorem, a key hypothesis of irreversible thermodynamics, was originally derived for the causality between flows and forces that are scalar in character [2–4,8]. It was later theoretically proven to be also valid for those of vectorial character [2], and efforts have been exerted to experimentally verify the Onsager reciprocity relation (ORR) [4,9]. The overall conclusion is that "the experimental evidence is overwhelmingly in favor of the validity of the reciprocity" [9] and "it has not been disproved by experience" [10]. Concerning the mixed ionic-electronic transport phenomenon, in particular, there is one and only report [5] that is on the systems of α-$Ag_{2+\delta}Se$ and β-$Cu_{2-\delta}S$, that the ORR is satisfied within (not specified) experimental errors, but the electron-ion interference effect itself is negligible.

Recently, we succeeded in measuring, with sufficient precision, all the Onsager coefficients of the mixed ionic-electronic transport in $TiO_{2-\delta}$ (rutile) in the range of oxygen activity $-16 < \log_{10} a_{O_2} \leq -1$ at 800°, 900° and 1000 °C, respectively. We subsequently found that contrary to the conventional belief, the electron-ion interference effect was surprisingly large, and were able to demonstrate ORR with the highest ever precision. The purpose of this Letter is to report on these results.

It is common in mixed ionic-electronic conductors, e.g., $Co_{1-\delta}O$ that an ionic species, say, Co^{2+} is much more mobile than the other, O^{2-} so that the latter is normally regarded as fixed in space. The irreversible thermodynamic treatment of this common situation was first made by Wagner [11] and later by Yoo *et al.* [12] in more detail. For the present system $TiO_{2-\delta}$, however, both Ti^{4+} cations and O^{2-} anions may have comparable mobilities depending on the thermodynamic condition [13]. We will, thus, have to generalize the conventional transport equations first.

We choose the cations Ti^{4+}, anions O^{2-}, and electrons e^- as the mobile charged components [14]. Denoting these components by subscripts 1, 2, and 3, respectively, the energy dissipation, $T\sigma$, due to the flows of these components may be written in the isothermal and isobaric condition as [11,12]

$$T\sigma = j_1(-\nabla\eta_1) + j_2(-\nabla\eta_2) + j_3(-\nabla\eta_3), \tag{1}$$

where j_k and $\nabla\eta_k$ denote the flux and the force, the electrochemical potential gradient of the kth component ($k = 1, 2, 3$), respectively. Because of the local equilibrium postulate [11,12], one has $\nabla\eta_1 + 2\nabla\eta_2 = 0$ for $Ti^{4+} + 2O^{2-} = TiO_2$. Equation (1) may, thus, be rewritten in terms of the independent forces, say, $-\nabla\eta_1$ and $-\nabla\eta_3$, as

$$T\sigma = \left(j_1 - \frac{1}{2}j_2\right)(-\nabla\eta_1) + j_3(-\nabla\eta_3). \tag{2}$$

Identifying the independent flows, J_i and J_e, and forces, $\nabla\eta_i$ and $\nabla\eta_e$, for ions and electrons, respectively, as $j_1 - j_2/2 \equiv J_i$; $j_3 \equiv J_e$; $\nabla\eta_1 \equiv \nabla\eta_i$; $\nabla\eta_3 \equiv \nabla\eta_e$, the generalized transport equations are written as [11,12]

$$J_i = -L_{ii}\nabla\eta_i - L_{ie}\nabla\eta_e \tag{3a}$$

$$J_e = -L_{ei}\nabla\eta_i - L_{ee}\nabla\eta_e \tag{3b}$$

Here, L_{mn} ($m, n = i, e$) are the Onsager coefficients. For the sake of simplicity, we define

$$\alpha_i^* \equiv L_{ie}/L_{ii}; \qquad \alpha_e^* \equiv L_{ei}/L_{ee} \tag{4}$$

which will henceforth be referred to as the "charge-of-transport" of ions and electrons, respectively [12]. If the Onsager reciprocity is valid, then the cross coefficients should be identical to each other or

$$L_{ie} = L_{ei}. \tag{5}$$

Again, by using the local equilibrium postulates [11,12], $\nabla\mu_{\mathrm{Ti}} = \nabla\eta_1 + 4\nabla\eta_3$ for $\mathrm{Ti} = \mathrm{Ti}^{4+} + 4e^-$ and $\nabla\mu_{\mathrm{Ti}} + \nabla\mu_{O_2} = 0$ for $\mathrm{Ti} + O_2 = \mathrm{TiO}_2$ (where μ_{Ti} and μ_{O_2} being the chemical potential of the neutral component Ti and O_2, respectively), Eq. (3) can be rewritten in terms of the ionic current density $i_i(= z_i F J_i)$ and electronic current density $i_e(= z_e F J_e)$ as

$$i_i/z_i F = L_{ii}\nabla\mu_{O_2} + L_{ii}(z_i - \alpha_i^*)\nabla\eta_e \tag{6a}$$

$$i_e/z_e F = L_{ee}\alpha_e^*\nabla\mu_{O_2} - L_{ee}(1 - z_i\alpha_e^*)\nabla\eta_e \tag{6b}$$

where $z_i(= +4)$ denotes the formal valence of Ti^{4+}, $z_e(= -1)$ that of e^-, and F the Faraday constant.

In Eq. (6), the partial current densities (i_i, i_e) and the gradients ($\nabla\mu_{O_2}$, $\nabla\eta_e$) are all experimentally measurable and controllable. Therefore, the four Onsager coefficients in Eq. (6) may be determined as follows: (i) By blocking the ionic flow ($i_i = 0$), one can determine from Eqs. (6a) and (6b), respectively

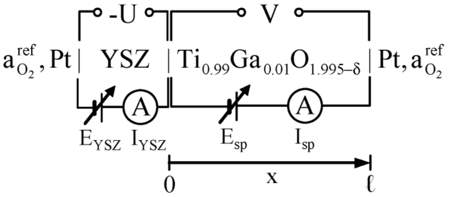
$$\begin{aligned} \left(\frac{\nabla\mu_{O_2}}{\nabla\eta_e}\right)_{i_i=0} &= -(z_i - \alpha_i^*); \\ \left(\frac{i_e}{F\nabla\eta_e}\right)_{i_i=0} &= L_{ee}(1 - \alpha_i^*\alpha_e^*). \end{aligned} \tag{7}$$

(ii) By blocking the electronic flow ($i_e = 0$), one can determine from Eqs. (6b) and (6a), respectively

$$\begin{aligned} \left(\frac{\nabla\mu_{O_2}}{\nabla\eta_e}\right)_{i_e=0} &= -(z_i - \alpha_e^{*-1}); \\ \left(\frac{i_i}{z_i F\nabla\mu_{O_2}}\right)_{i_e=0} &= L_{ii}\frac{1 - \alpha_i^*\alpha_e^*}{1 - z_i\alpha_e^*}. \end{aligned} \tag{8}$$

The specimens of $\mathrm{Ti}_{0.99}\mathrm{Ga}_{0.01}\mathrm{O}_{1.995-\delta}$ were prepared by thoroughly mixing the starting powders of TiO_2 and $\mathrm{Ga}_2\mathrm{O}_3$ (both 99.99% purity from Aldrich) into an appropriate proportion, followed by sintering at 1450 °C in air for 6 hours. Doping of the aliovalent impurity Ga^{3+} is to extrinsically fix the defect structure in the near stoichiometric regime ($\delta \approx 0$) of $\mathrm{TiO}_{2-\delta}$ as $[\mathrm{Ga}'_{\mathrm{Ti}}] \approx 2[V_O^{\bullet\bullet}] + 4[\mathrm{Ti}_i^{\bullet\bullet\bullet\bullet}]$ in terms of Kröger-Vink notation [15]. The sintered specimens were found, via both x-ray diffractometry and scanning electron-microscopy, to be of single phase with an average grain size of 33 ± 4 μm and an apparent density of 99% of the theoretical value.

The Onsager coefficients L_{mn} were measured on the basis of Eqs. (7) and (8) from an electrochemical cell with the configuration of Cell (I),



, (I)

where the specimen, with a cross-section A, extends from $x = 0$ to ℓ. The role of the yttria-stabilized zirconia (YSZ) is to block electron flow as well as to measure the oxygen activity ($a_{O_2} \equiv P_{O_2}/\mathrm{atm}$) at the YSZ/specimen interface relative to a reference electrode with an oxygen activity of $a_{O_2}^{\mathrm{ref}}$. E_{sp} and I_{sp} stand for the terminal voltage applied and the current passed across the specimen, respectively, and similarly E_{YSZ} and I_{YSZ} for the YSZ.

We operated the cell galvanostatically under the ion-blocking condition and under the electron-blocking condition, respectively, in identical $a_{O_2}^{\mathrm{ref}}$-atmospheres. In the former, a constant current (in the range of 3 μA to 20 mA) was passed through the specimen only, while monitoring open-circuit voltage U across the YSZ and V across the specimen (corrected against the lead wire voltage drop at measurement temperature). In the latter, U and V were monitored while passing a constant current (in the range of 0.5 μA to 0.1 mA) through the specimen and YSZ. In either mode of operation, the extent of chemical polarization across the specimen was kept as small as possible (normally $|U| \leq 51$ mV and $|V| \leq 63$ mV) so that one might approximate as

$$\nabla\eta_e = -FV/\ell; \qquad \nabla\mu_{O_2} = 4FU/\ell, \tag{9}$$

and assign the results unambiguously to the reference oxygen activity ($a_{O_2}^{\mathrm{ref}}$) imposed. Details of the experimental setup, including the construction, design, and performance of this apparently simple cell, which in reality is extremely delicate, will be reported elsewhere.

From the steady state values for U, V, and the value of I applied in the ion-blocking mode (denoted as U^I, V^I, and I^I, respectively), we obtain due to Eqs. (7) and (9)

$$4 - \alpha_i^* = \frac{4U^I}{V^I}; \qquad -\frac{\ell}{A}\cdot\frac{I^I}{F^2 V^I} = L_{ee}(1 - \alpha_i^*\alpha_e^*). \tag{10}$$

Similarly from the steady state values for U, V, and the constant current (denoted as U^E, V^E, and I^E, respectively) in the electron-blocking mode, we obtain due to Eqs. (8) and (9)

$$4 - \frac{1}{\alpha_e^*} = \frac{4U^E}{V^E}; \qquad \frac{\ell}{A}\cdot\frac{I^E}{16F^2U^E} = L_{ii}\frac{1 - \alpha_i^*\alpha_e^*}{1 - 4\alpha_e^*}. \tag{11}$$

From Eqs. (10) and (11) have been evaluated α_i^*, α_e^*, L_{ee}, and L_{ii} and subsequently all the Onsager coefficients L_{mn} due to Eq. (4), for the identical thermodynamic conditions. In Fig. 1, we plot $L_{ie}(= L_{ii}\alpha_i^*)$ vs $L_{ei}(= L_{ee}\alpha_e^*)$ and in Figs. 2(a) and 2(b), α_i^* and α_e^* vs $\log_{10}a_{O_2}$, respec-

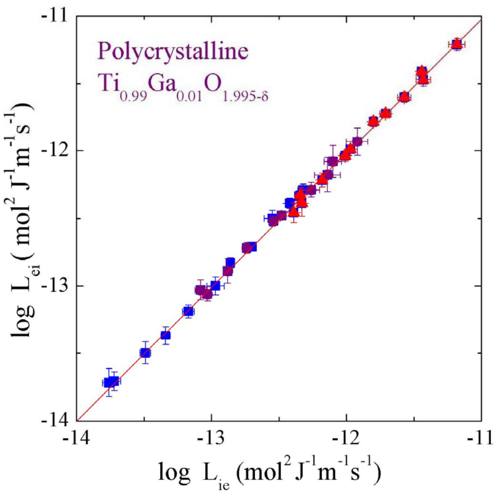


FIG. 1 (color online). Cross coefficient L_{ei} vs L_{ie} of the system 1 mol% Ga-doped TiO_2 at 1073 K (■), 1173 K (●), and 1273 K (▲). Note that $L_{ei}/L_{ie} = 0.993 \pm 0.013$ as depicted by the solid line, precisely demonstrating the validity of the ORR in the phenomenon of mixed ionic-electronic transport.

tively. It is important to emphasize here that while the accuracy of each Onsager coefficient L_{mn} is affected by the systematic error associated with the geometric factor ℓ/A of the specimen via Eqs. (10) and (11), the ratios of transport coefficients, say, L_{ie}/L_{ei}, α_i^* and α_e^*, are absolutely free from this effect and even free from any other systematic error (because of being a ratio).

As depicted by the solid straight line in Fig. 1, it is found that the cross coefficient ratio is

$$L_{ei}/L_{ie} = 0.993 \pm 0.013. \tag{12}$$

Hereby, the ORR, Eq. (5) is experimentally verified, within a relative error of 1.3%, in the mixed ionic-electronic transport.

To the best of the authors' knowledge, the most precise and extensive experimental demonstration of the ORR in vectorial phenomena is with the thermoelectric phenomenon in metals: The cross coefficients ratio between the heat (q) and charge (e) flow, say, L_{qe}/L_{eq}, is in the range of 0.77 to 1.08, depending on the types of thermocouples [4,9]. Upon averaging all the data available in the literature [4,9], one may have $L_{qe}/L_{eq} = 0.978 \pm 0.096$. The ORR in the other vectorial phenomena, particularly matter transfer, however, is subject to much larger uncertainty. In the recent studies on isothermal diffusion in CaO-Al_2O_3-SiO_2 liquid solutions at 1550°–1450 °C [16] and Cu-Zn-Sn solid solutions at 800 °C [17], for example, the cross coefficient ratio between the two independent fluxes (of, say, component 1 and 2) was reported to be $L_{12}/L_{21} = 1.29 \sim 1.46$ and $= 0.85 \sim 1.55$, respectively. It is reminded that there is a single report [5] for the mixed ionic-electronic conduction in solids that $L_{ie} = L_{ei}$ within the experimental error that, however, was not specified, but $\alpha_i^* (= L_{ie}/L_{ii}) \ll 1$.

Attention is now drawn to the magnitude of α_i^* and α_e^* in Figs. 2(a) and 2(b): As the electronic conductivity is predominant for the present system [13] and hence, $L_{ee} \gg L_{ii}$, L_{ei}, L_{ie}, it is easy to guess that $\alpha_e^* < 1$, but it is surprising that $\alpha_i^* > 1$: it takes a value in the range of 1.5 to 3.7 depending on the oxygen activity. This fact clearly indicates that the cross coefficient L_{ie} is not only not negligible, but can be even larger than the direct coefficient L_{ii} also. It is noted that the only constraint on the cross coefficients is $\alpha_i^* \alpha_e^* < 1$ due to the positive-definiteness of the energy dissipation, $T\sigma$, in Eq. (2) [2–4].

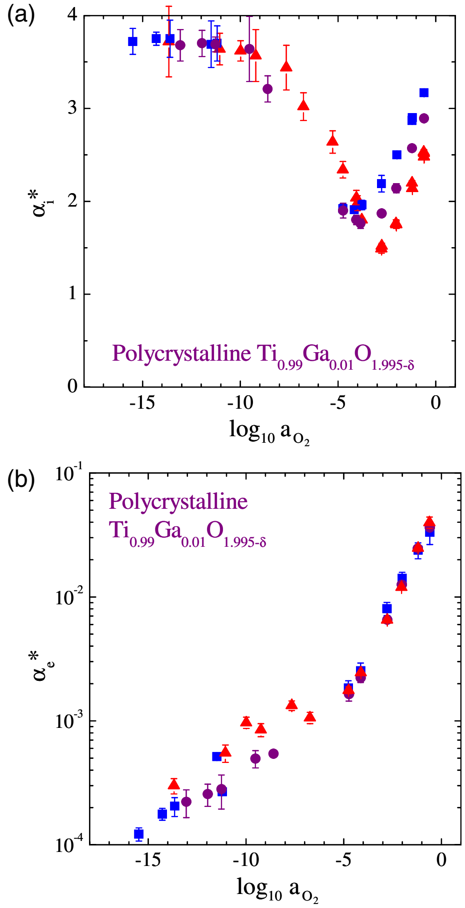


FIG. 2 (color online). Ionic charge-of-transport α_i^* (a), and electronic charge-of-transport α_e^* (b) of Ga-doped TiO_2 vs oxygen activity a_{O_2} at different temperatures: ■, 1073 K ; ●, 1173 K; ▲, 1273 K.

Now that the ORR is verified, the charges-of-transport defined in Eq. (4) may be expressed by using Eq. (3), as

$$\alpha_i^* = \frac{L_{ei}}{L_{ii}} = \left(\frac{J_e}{J_i}\right)_{\nabla\eta_e=0}; \qquad \alpha_e^* = \frac{L_{ie}}{L_{ee}} = \left(\frac{J_i}{J_e}\right)_{\nabla\eta_i=0}. \tag{13}$$

It follows that phenomenologically α_i^* corresponds to the number of electrons dragged by a mobile ion (Ti^{4+} in the present context) upon its transfer in the absence of the direct cause for electron transfer ($\nabla\eta_e = 0$). Similarly, α_e^* is the number of ions dragged by an electron in the absence of a direct driving force for the mobile ions ($\nabla\eta_i = 0$). According to the data in Fig. 2(a), a Ti^{4+} ion drags 1.5 to 3.7 electrons depending on the thermodynamic conditions.

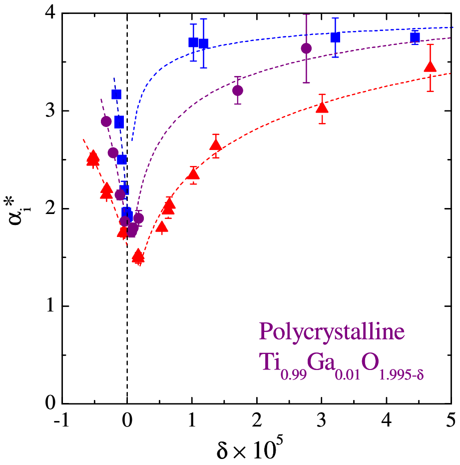


FIG. 3 (color online). The ionic charge-of-transport α_i^* vs nonstoichiometry δ. Note that the minimum falls at the stoichiometric composition, $\delta = 0$. Dotted lines are for visual guidance only.

In other words, only $(0.3 \sim 2.5)F$ charge is transported by a mole of Ti^{4+} transferred, or the effective charge unit of Ti^{4+} ions is not the formal valence $+4(= z_i)$, but only $0.3 \sim 2.5(= z_i - \alpha_i^*)$. On the other hand, Fig. 2(b) indicates that approximately up to one ion is dragged by ten electrons even in the absence of the ionic driving force, as a_{O_2} increases up to 1.

At this point, one may suspect that the validity of the ORR, Eq. (12), may possibly be impaired by the choice of the formal charge z_1. It is emphasized that the ORR remains unimpaired by arbitrary choice of z_1, see Ref. [18].

In Fig. 3, we plot α_i^* against, instead of a_{O_2}, the nonstoichiometry δ by using the nonstoichiometry data (as a function of T and a_{O_2}) of the system [13]. It is seen that α_i^* becomes minimum $(\alpha_i^* = 1.5)$ apparently at the stoichiometric composition $(\delta = 0)$ and tends to saturate to a value of 3.7 as $|\delta|$ increases. The knee of α_e^* vs $\log_{10} a_{O_2}$ in Fig. 2(b) also corresponds approximately to the stoichiometric composition. Considering that the electron-ion cross effect is a consequence of the short- and/or long-range interaction between the oppositely charged carriers [11,12] and δ is a measure of the overall concentration of the defects, the variation of α_i^* vs δ is very much suggestive, but its quantitative understanding is yet to be sought for.

Nevertheless, the fact that the electron-ion cross effect is non-negligible and even larger than the direct effect $(\alpha_i^* > 1)$ will have far-reaching consequences. All the theories or relationships dealing with mass and charge transport phenomena in mixed conductor compounds have, so far, been developed on the ground that the carrier ions and electrons migrate independently or $L_{ie} = L_{ei} = 0$. Now that the electron-ion cross effect is by no means negligible, all those should be corrected against the cross effect.

In conclusion, the Onsager reciprocity relation is firmly confirmed in the phenomenon of mixed ionic-electronic conduction in the system of Ga-doped $TiO_{2-\delta}$ with a unprecedented precision or $L_{ei}/L_{ie} = 0.993 \pm 0.013$. The charge-of-transport of Ti^{4+} ions $\alpha_i^*(\equiv L_{ei}/L_{ii})$, a measure of the ion-electron cross effect that corresponds phenomenologically to the number of electrons dragged by the ion upon its transfer, takes a value of 1.5 to 3.7 depending on the extent of nonstoichiometry (δ), with its minimum value $(\alpha_i^* = 1.5)$ falling at the stoichiometric composition $(\delta = 0)$. All the mass and charge transport theories and relationships in mixed ionic-electronic conductor compounds that have so far been based upon the assumption of independent migration of ions and electrons should thus be corrected against the electron-ion cross effect.

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[1] H. J. M. Bouwmeester and S. McIntosh, *Proc. 26th Riso International Symposium on Materials Science*, edited by S. Linderoth *et al.* (Riso National Lab., Roskilde, Denmark, 2005), pp. 1–14.
[2] S. R. de Groot and P. Mazur, *Non-Equilibrium Thermodynamics* (North-Holland, Amsterdam, 1962), Chap. 6.
[3] A. R. Allnatt and A. B. Lidiard, *Atomic Transport in Solids* (Cambridge University Press, Cambridge, England, 1993), Chaps. 4 and 5.
[4] D. Kondepudi and I. Prigogine, *Modern Thermodynamics: From Heat Engines to Dissipative Structures* (Wiley, West Sussex, England, 1998), Chap. 16.
[5] S. Miyatani, Solid State Commun. **38**, 257 (1981).
[6] J.-H. Lee and H.-I. Yoo, J. Electrochem. Soc. **141**, 2789 (1994).
[7] J.-O. Hong and H.-I. Yoo, J. Mater. Res. **17**, 1213 (2002).
[8] L. Onsager, Phys. Rev. **37**, 405 (1931).
[9] D. G. Miller, Chem. Rev. **60**, 15 (1960).
[10] J. O'M Bockris and A. K. N. Reddy, *Modern Electrochemistry* (Plenum, New York, 1970), Vol. 1, p. 413.
[11] C. Wagner, Prog. Solid State Chem. **10**, 3 (1975).
[12] H.-I. Yoo, H. Schmalzried, M. Martin, and J. Janek, Z. Phys. Chem. Neue Folge **168**, 129 (1990).
[13] D.-K. Lee, Ph.D thesis, Seoul National University, 2005.
[14] In the present system of $Ti_{0.99}Ga_{0.01}O_{1.995-\delta}$, Ga^{3+} is considered to be immobile because Ga substitutes Ti and cation disorder in the majority is Ti-interstitials.
[15] F. A. Kröger and H. J. Vink, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1956), Vol. 3, pp. 307–435.
[16] F. J. Spera and A. F. Trial, Science **259**, 204 (1993).
[17] T. Takahashi *et al.*, J. Mater. Sci. **22**, 3194 (1987).
[18] H.-I. Yoo, J.-H. Lee, M. Martin, J. Janek, and H. Schmalzried, Solid State Ionics **67**, 317 (1994).