

Irreversible Thermodynamic Analysis of the Cross Effect between Electron and Ion Currents in Ionic Compounds with Electronic Conduction Prevailing

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전자 전도체 이온결합 화합물에서 전자 흐름과 이온 흐름간 간섭 현상의 비가역 열역학적 분석

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요 약

전자 전도체 이온 결합 화합물, $A_{1-\delta}O$, 에서 전자의 흐름과 이온의 흐름 사이에서 일어나는 간섭 현상을 비가역 열역학적으로 분석하였다. 이 계를 가역 전극 사이에 두고 전기를 흘리던 주된 전하 나르제인 전자의 흐름에 의하여 잘 움직이는 양이온 빈자리들의 알짜 흐름이 유발되며, 이 빈자리의 흐름은 Fick 좌표계를 실험실 좌표계에 대하여 상대적으로 움직이게 한다는 것이 드러났다. 따라서 이 상대속도는 전자와 이온의 흐름간 간섭효과와 크기와 방향을 결정하는 양이온 유효전하의 척도가 되는 것이다. 이 상대속도를 측정하는 두가지의 실험을 고안 하였다.

ABSTRACT

The cross effect between an ion flux and an electronic current in a nonstoichiometric binary oxide, $A_{1-\delta}O$, has been analyzed in the light of irreversible thermodynamics. It has been shown that a net flux of the mobile cation vacancy is induced through the system in an electrical potential gradient applied across a pair of the reversible electrodes, which makes the Fick frame shift relative to the laboratory frame. As a consequence, the relative shift is a measure of the effective charge responsible for the cross effect. Two experiments are proposed to measure the shift.

INTRODUCTION

Transfer of matter in a condensed system is caused not only directly by a concentration

gradient (electrochemical potential gradient, more correctly) but also indirectly by an electronic current passed. The former direct effect is

usually called diffusion and the latter indirect phenomenon, for elemental metal systems in particular, electromigration or electrotransport.

This indirect phenomenon in a semiconducting compound is of practical and theoretical importance. It may cause a material component to fail in an extended period of service in an electrical field in a similar manner that an oxide material eventually fails in an oxygen potential gradient as extensively studied by Schmalzried and his coworkers[1-4, 11-13]. The extent of the interference between a material flux and an electronic electrical current is governed by a quantity called the effective charge of the various mobile components of the compound under consideration[5,6]. The effective charge of a component seems to carry the information on the innerworkings of the interaction between the electronic defect and the ionic defect that renders the component mobile, which is not yet fully understood.

Nevertheless, not many studies have been done on this cross effect in the ionic compounds. As far as we know, no experimental work has ever been made and only a few theoretical considerations in the light of linear irreversible thermodynamics[5-7] are available. In contrast, in the systems of elemental metals the cross effect electromigration has been studied experimentally and the effective charges are reported even if the systems studied are extremely limited in number [8-10].

In this paper we analyze the phenomenon in a binary oxide $A_{1-\delta}O_\nu$ as a model system in view of irreversible thermodynamics and subsequently a few experiments to measure the effective charge are designed. This result may apply to the other nonstoichiometric ionic compounds, e.g. sulfides with minor modifications.

PHENOMENOLOGICAL EQUATIONS

Consider a system of a nonstoichiometric

oxide $A_{1-\delta}O_\nu$ where δ denotes the metal deficit and $\nu \equiv z_1/|z_3|$, z_1 and z_3 being respectively the absolute valence of the cation and anion in the ideal lattice AO_ν at $T=OK$. As is the case for close-packed oxides[14], the mobility of the anion is so smaller compared with that of the cation that the anion sublattice may be considered essentially fixed to the laboratory frame of reference. Furthermore, we assume that the cation mobility is via a vacancy mechanism. We may then distinguish as the mobile components of our system the cation, A^{z_1} , and the electron (or hole), e' , relative to the anion sublattice-fixed frame of reference.

When our system is isothermal and subject to no other external forces than an external electrical field, the phenomenological equations for the two mobile components are given, according to linear irreversible thermodynamics[5-7, 15], as:

$$j_1 = L_{11} \nabla \eta_1 + L_{12} \nabla \eta_2 \quad (1)$$

$$j_2 = L_{21} \nabla \eta_1 + L_{22} \nabla \eta_2 \quad (2)$$

where the subscripts 1 and 2 denote A^{z_1} , and e' , respectively. The thermodynamic forces, the electrochemical potential gradients of A^{z_1} and e' are denoted by $\nabla \eta_1$ and $\nabla \eta_2$, and their fluxes in moles/cm²-sec by j_1 and j_2 , respectively. The phenomenological coefficients are represented by L_{ij} , which are symmetric due to the Onsager reciprocity theorem[15]:

$$L_{21} = L_{12} \quad (3)$$

From the analysis of self-diffusion[5, 16], it has been well established that

$$L_{11} = -D_A C_A / RT \quad (4)$$

where D_A and C_A are the self-diffusion coefficient and the molar concentration of the cation, respectively, and R and T have the usual meaning. Equation 4 will be invoked later when necessary.

According to Eq. 1, a flux of the cation is driven not only by its direct cause $\nabla \eta_1$ but indirectly by $\nabla \eta_2$ also. The latter indirect phenomenon is used to be called electromigration or electrotransport in the systems of elemental metals. We may, thus, have a cation flux even when $\nabla \eta_1=0$ or vice versa an electron flux when $\nabla \eta_2=0$ due to Onsager[15]. Combining Eq's 1 and 2 with $\nabla \eta_2=0$, we have

$$j_2 = (L_{12}/L_{11}) j_1 \quad (5)$$

In words, a flux of the electron is brought about even by an ion flux alone, the direction and magnitude of which is determined by the ratio L_{12}/L_{11} . This ratio is defined as the "effective charge" of the cation[5, 6], α_1^* :

$$\alpha_1^* \equiv L_{12}/L_{11} \quad (6)$$

Instead of the effective charge of the mobile ionic component, we may define the effective charge of the ionic defect which is responsible for the mobility of the cation in question. Due to the constraint of the local lattice conservation in our system where the cation vacancy is the major defect type,

$$j_1 = -j_v \quad (7)$$

where j_v denotes a flux of the vacancy with reference to the anion sublattice-fixed frame. Combining Eq's 5, 6 and 7, we obtain

$$j_2 = -\alpha_v^* j_v \quad (8)$$

The opposite of the ionic effective charge, $-\alpha_1^*$, may be identified with the effective charge of the vacancy, α_v^* :

$$\alpha_v^* \equiv -\alpha_1^* \quad (9)$$

As a matter of fact, if we started, instead of the cation, with the vacancy as a mobile component, we would then end up with the definition of α_v^* : $j_2 = \alpha_v^* j_v$.

In the literature[7, 11, 13], one may oftentimes encounter the term, the average effective

charge, \bar{n} , of e.g. the cation vacancy, which has been estimated from the vacancy diffusion coefficient, D_v , and the chemical diffusion coefficient, \tilde{D}_v , with the help of the relationship[11]:

$$\tilde{D}_v = (1 + \bar{n}) D_v \quad (10)$$

But it is yet to be confirmed experimentally if the so-called average effective charge is the very quantity that is identical to the effective charge defined above in Eq. 6. The average effective charge is understood literally as:

$$\bar{n} = \frac{\sum_n [V_{Me}^{n'}] n}{\sum_n [V_{Me}^{n'}]} \quad (11)$$

where $[V_{Me}^{n'}]$ denotes the concentration of the (cation) vacancy of the effective negative charge of n .

Due to the thermodynamic equilibrium, $A \rightleftharpoons A^{z_1} + z_1 e'$,

$$\nabla \mu_A = \nabla \eta_1 + z_1 \nabla \eta_2 \quad (12)$$

where μ_A is the chemical potential of the neutral metal component A. Substituting for $\nabla \eta_1$ in Eq's 1 and 2 from Eq 12, we have

$$j_1 = L_{11} \nabla \mu_A - z_1 L_{11} (1 - \alpha_1^*/z_1) \nabla \eta_2 \quad (13)$$

$$j_2 = L_{21} \nabla \mu_A + L_{22} (1 - z_1 \alpha_1^* L_{11}/L_{22}) \nabla \eta_2 \quad (14)$$

The gradient of μ_A may be replaced by the oxygen potential gradient $\nabla \mu_0 (\equiv \nabla \mu_{O_2}/2)$ via the Gibbs-Duhem equation for $A_{1-\delta} O_\nu$ with $\delta \ll 1$ $\nabla \mu_A + \nu \nabla \mu_0 = \nabla \mu_{A_{0\nu}} \approx 0$ or

$$\nabla \mu_A = -\frac{\nu}{2} \nabla \mu_{O_2} \quad (15)$$

Equations 13 and 14 are, thus, rewritten:

$$j_1 = -(\nu/2) L_{11} \nabla \mu_{O_2} - z_1 L_{11} (1 - \alpha_1^*/z_1) \nabla \eta_2 \quad (16)$$

$$j_2 = -(\nu/2) L_{21} \nabla \mu_{O_2} + L_{22} (1 - z_1 \alpha_1^* L_{11}/L_{22}) \nabla \eta_2 \quad (17)$$

MEASUREMENT OF THE EFFECTIVE CHARGE

Suppose now that we put our system between the reversible electrodes as illustrated in Fig. 1.

Pt 1, $P_{O_2(1)} | A_{1-\delta}O_x | P_{O_2(2)}$, Pt (2)

Fig. 1. Configuration of the cell to measure the effective charge, α_1^* .

By keeping the ambient oxygen potential constant, say $P_{O_2(1)} = P_{O_2(2)}$, and applying an external electrical potential gradient $\nabla\phi$ across the system, we may realize an experimental condition:

$$\nabla\mu_{O_2} = 0 ; \nabla\eta_z = -F\nabla\phi \quad (18)$$

where F is the Faraday constant (96,500 coul). Under this experimental condition, the transport equations, Eq's 16 and 17 become:

$$j_1 = z_1 F L_{11} (1 - \alpha_1^*/z_1) \nabla\phi \quad (19)$$

$$j_2 = -F L_{22} (1 - z_1 \alpha_1^* L_{11}/L_{22}) \nabla\phi \quad (20)$$

The ratios $-z_1 F j_1 / \nabla\phi$ and $F j_2 / \nabla\phi$ in Eq's 19 and 20 can be identified with the partial ionic conductivity, σ_1 , and the partial electronic conductivity, σ_2 , respectively.

It is noted in Eq. 19 that, being placed between the reversible electrodes as shown in Fig. 1, a net flux of the cation j_1 arises through our oxide only due to a gradient of electrical potential applied externally at constant T and P_{O_2} . It consists of two contributions; one driven directly by the external electrical field (the 1st term in the parentheses) and the other due to the coupling with the electronic current (the 2nd term in the parentheses). The extent and direction of the latter coupling effect is entirely dependent on the magnitude and sign of the effective charge.

This net flux of the ion, Eq. 19, is counterbalanced by a net flux of the vacancy, j_v , due to Eq. 7. Inserting Eq. 4 into Eq. 19,

$${}_L j_v = -{}_L j_1 = (F D_A / V_m^0 RT) (z_1 - \alpha_1^*) \nabla\phi \quad (21)$$

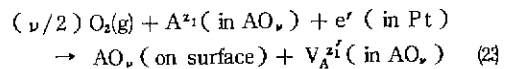
where we employed the relation, $C_i = 1/V_m^0$, V_m^0 being the molar volume of AO_x , on the assumption

of $\delta \ll 1$ and the subscript L of ${}_L j_v$ is to emphasize that the flux is relative to the anion sublattice-fixed frame of reference which is congruent with the laboratory frame in the present example. The self-diffusion coefficient, D_A , in the present case where $\nabla\delta = 0$ (this is ensured by the reversible electrode condition in Fig. 1), is related to the tracer diffusion coefficient, D_A^* , or the vacancy diffusion coefficient, D_v :

$$D_A = D_A^* / f = N_v^0 D_v \quad (22)$$

where f is the geometric correlation factor and N_v^0 the equilibrium vacancy fraction at the uniform temperature, T , and the uniform oxygen potential, P_{O_2} .

Assuming that there is no sink (or source) inside the crystal, a net vacancy flux, Eq. 21, makes the crystal shift as a whole in its opposite direction via the reaction at the surface where the vacancy flux initiates:



and the reverse reaction where the vacancy flux terminates as illustrated in Fig. 2. The reference frame attached to the crystal that is moving relative to the laboratory frame may be taken as the Fick' frame as the molar volume of our crystal has been assumed constant V_m^0 . The shift velocity of the crystal or the moving velocity of the Fick's frame relative to the laboratory frame, $u_F - u_L$, is then related to the net vacancy flux as:

$$u_F - u_L = -V_m^0 j_v \quad (24a)$$

or, due to Eq. 21,

$$u_F - u_L = -(z_1 F D_A / RT) (1 - \alpha_1^* / z_1) \nabla\phi \quad (24b)$$

If $0 < \alpha_1^* < z_1$ as would be expected, the crystal or the Fick's frame shifts down the gradient as shown in Fig. 2. The shift distance of the crystal, $\Delta x_0 (= x_F^{(1)} - x_L^{(1)} = x_F^{(2)} - x_L^{(2)})$, may be given for the 1-

dimensional transport by the equation:

$$\Delta x_0 = (u_F - u_L) t = - (FD_A/RT)(z_1 - \alpha_1^*) (\Delta\phi / L_0) t \quad (25)$$

on the assumption that the stationary state with respect to the vacancy transfer is readily achieved as is the case[1] since $D_V \gg D_1$ (see Eq. 22). Here we replaced $\nabla\phi$ with $\Delta\phi/L_0$, $\Delta\phi$ being the electrical potential difference applied across the electrodes Pt(1) and Pt(2) in Fig. 1 and L_0 the interelectrode distance or the thickness of the crystal, $x_F^{(2)} - x_F^{(1)} (= x_L^{(2)} - x_L^{(1)})$ in Fig. 2. As a consequence, the effective charge can be determined from the relative shift, Δx_0 , in the configuration of Fig. 1.

At this point, it may be helpful to make an

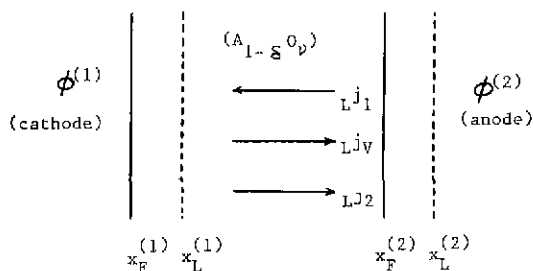


Fig. 2. Position of the crystal (Fick's frame, delineated by the solid lines) relative to the original position (delineated by the dotted lines) after an elapse of time t . Each frame is distinguished by the subscript, F and L, respectively. The planar boundaries of the crystal are denoted by $x^{(1)}$ and $x^{(2)}$. It is envisaged that a net vacancy flux, L_j^V , dragged by an electron current, L_j^2 , causes the crystal to shift as a whole.

order to magnitude calculation of the duration of annealing, t , to yield a shift which is large enough to be measured with the precision of the experiment available. For Co_{1-s}O , for example, $D_V = 2.2 \times 10^{-6} \text{ cm}^2/\text{sec}$ at $T=1483 \text{ K}$ [13]. As the standard Gibbs free energy of CoO at

about 1500 K is ca. -50 kcal/mole [18], the maximum potential difference, $\Delta\phi$, allowable across the crystal is approximately 2 V . If we take $L_0 \sim 0.1 \text{ cm}$ and $N_V^0 \sim 10^{-3}$ as the typical values, the shift velocity will be ca. $12 \mu\text{m/hr}$, taking the order of magnitude of the term $(z_1 - \alpha_1^*)$ as unity [13]. For about $100 \mu\text{m}$ shift at this temperature, it will take around 8 hours, a time scale that is more than viable.

The accurate measurement of the shift of the crystal as a whole, Δx_0 , may not be a trivial task presumably because of the possible disturbances by the presence of the Pt particles which are to be applied onto the surfaces $x_L^{(1)}$ and $x_L^{(2)}$ of the crystal in order to ensure the reversibility of the oxygen exchange across the electrodes. It is expected that the presence of the Pt particles causes morphological changes of both the crystal surfaces which are to be well-finished previously; at the anode may form microvoids and at the cathode microhumps. This sort of surface morphology has also been observed on the surface of the lower oxygen potential side of a crystal subject to an oxygen potential gradient [19, 20].

An alternative experiment to measure the relative shift velocity, $u_F - u_L$, is based on the tracer diffusion experiment in the electrical potential gradient. An instantaneous planar source of the radioactive tracer A^* , e.g. Co^* , and the Darken's chips, e.g. thin Pt wire chips, are inserted simultaneously at $x_L = x_L^{(0)}$ ($=0$) within our crystal as illustrated in Fig. 3. The experimental condition with the cell configuration of Fig. 1 is still the same as before, Eq. 18. The flux of tracer j_{A^*} with respect to the laboratory (or Hittorf) frame of reference is then given by the sum of the two contributions, one due to random walks under its own concentration gradient, ∇C_{A^*} , and the other due to the directional walks against the net vacancy flux, Eq. 21:

$$L j_{A^*} = -D_{A^*} \nabla C_{A^*} - N_{A^*} j_v \quad (26)$$

or, due to Eq. 24a,

$$L j_{A^*} = -D_{A^*} \nabla C_{A^*} + C_{A^*} (u_F - u_L) \quad (27)$$

where $N_{A^*} (= C_{A^*}/V_m^0)$ is the mole fraction of the tracer.

The distribution profile of the tracer $C_{A^*}(x_L, t)$ with respect to the laboratory frame fixed to the Darken's chips, i.e. the inert marker is obtained by solving the continuity equation, $\partial C_{A^*}/\partial t = -\nabla_L j_{A^*}$. Assuming a stationary state as before where $u_F - u_L$ is constant, the solution for the instantaneous planar source is given[21]:

$$C_{A^*} = \frac{M}{2\sqrt{\pi D_{A^*} t}} \exp \left\{ -\frac{[x_L - (u_F - u_L)t]^2}{4D_{A^*} t} \right\} \quad (28)$$

where M is the total amount of the tracer per unit area and t the duration of diffusion anneal.

The profile expected, Eq. 28, is as illustrated in Fig. 3. One may notice that the centroid of the profile shifts from the Darken's chip which remain at $x_L = x_L^0 = 0$. The displacement of the centroid, Δx_0 , from $x_L = 0$ is again given by Eq. 25. Thus, by measuring the displacement of the centroid, we can determine the effective charge as:

$$\alpha_i^* = z_1 + \frac{RT}{FD_{A^*}} \frac{1}{(\Delta\phi/L_0)} \frac{\Delta x_0}{t} \quad (29)$$

In the system of CoO, for example, the period of diffusion anneal at 1500 K is again about 8 hours for a shift of as much as 100 μm for $\Delta\phi \sim 2\text{V}$ and $L_0 \sim 0.1\text{ cm}$.

This sort of experiment is highly viable on the basis of experience in the self-diffusion studies[22]. Furthermore, measurement of the shifts of the centroid of the tracer profile and the crystal as a whole can be made simultaneously on the same piece of crystal.

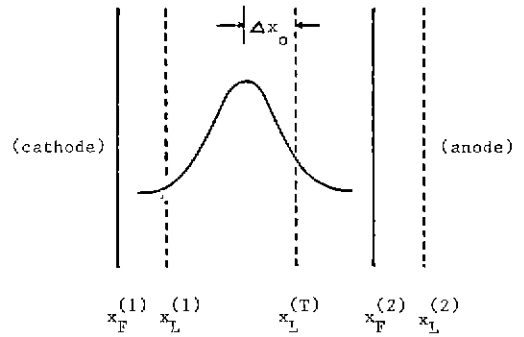


Fig. 3. Tracer diffusion profile expected from the instantaneous planar source placed originally at the origin of the laboratory reference frame, $x_L = 0$. It is noted that the Darken's chip, denoted by the dotted lines, has been fixed at the laboratory frame while the centroid of profile has been fixed at the Fick's frame denoted by the solid lines.

SUMMARY AND CONCLUSION

It has been shown that, when a semiconducting crystal is placed between the reversible electrodes with an electrical potential gradient applied, a net vacancy flux is induced relative to the laboratory frame fixed to the anion sublattice due to the coupling with the electronic current in addition to the partial ionic conduction or

$$j_v = (FD_A/V_m^0 RT) (z_1 - \alpha_1^*) \nabla\phi \quad (21)$$

$$u_F - u_L = -V_m^0 j_v \quad (24 a)$$

This net vacancy flux makes the Fick frame of reference fixed to the crystal move relative to the laboratory frame in the opposite direction of the vacancy flux at a relative velocity,

Thus by measuring the relative velocity, one can determine the effective charge of the cation. For the experimental determination of the effective charge, two steady state experiments are proposed; measurement, in an electrical potential gradient, of the shift relative to the laboratory frame of the crystal as a whole or the centroid of

the tracer profile developed from an instantaneous planar source. An order of magnitude calculation has shown that these experiments are highly reliable.

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