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How to interpret Onsager cross terms in mixed ionic electronic conductors

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Abstract

The interpretation of Onsager cross transport coefficients measured on mixed ionic electronic conductor (MIECs) oxides is examined. It is demonstrated that the cross terms are an artifact of the way the measurements are analyzed. When the proper, comprehensive defect model is considered for the MIEC, no cross terms are required.

Keywords: Onsager transport coefficients, cross terms, CeO_{2-x}, two ion valence states

Introduction.

In recent years cross terms of driving forces of currents were reported in a series of papers on mixed ionic electronic conductor (MIECs) oxides.[1] The measurements were done under constant and uniform temperature. These cross terms are also referred to as Onsager coefficients of transport. Cross terms appear if more than one kind of mobile particles exists in the sample and the driving force of one kind affects the flux of the other kind and vice versa. The materials investigated were MIECs oxides having mobile ions and electron or holes as electronic charge carriers. The cross terms L_{ie}, L_{ei} appear when one writes the flux equation for the two mobile species, ions (i) and electrons (e),

$$\begin{aligned} J_i &= -L_{ii}\nabla\tilde{\mu}_i - L_{ie}\nabla\tilde{\mu}_e \\ J_e &= -L_{ei}\nabla\tilde{\mu}_i - L_{ee}\nabla\tilde{\mu}_e \end{aligned} \tag{1.1}$$

where $\tilde{\mu}$ is the electrochemical potential of the charge carrier, L coefficients are the Onsager coefficients of transport and $L_{ei} = L_{ie}$. In most cases $L_{ie}=0$ and the ions are expected to be driven by the gradient $\nabla\tilde{\mu}_i$ only, while the electrons by the gradient $\nabla\tilde{\mu}_e$ only. When $L_{ie}\neq 0$, the ions are driven also by $\nabla\tilde{\mu}_e$ and the electrons also by $\nabla\tilde{\mu}_i$.

Similar cross terms appear in other electrochemical systems where solvating water is dragged together with the ions. An examples is Nafion®,[2-4] and related materials[5] where protons drag with them water molecules. Describing the transport in the material by the motion of protons and water molecules, two equations analogous to Eq. (1.1) appear with non-zero cross terms. (For the neutral water molecules the electrochemical potential is reduced to the chemical one).

For determining the Onsager coefficient in the MIEC oxides a sophisticated experimental system is used.[1] It allows for both electron blocking electrodes and material blocking electrodes. It uses two pairs of probes for measuring at two points along the sample, a difference $\Delta\tilde{\mu}_i$ and a difference $\Delta\tilde{\mu}_e$, simultaneously. For the measurement of $\Delta\tilde{\mu}_i$, it uses ionic probes made of yttria stabilized zirconia (YSZ) which are solid electrolytes and for measuring $\Delta\tilde{\mu}_e$ the probes used are Pt metal electrodes. Care is taken to seal all probe contacts on the oxide from the atmosphere while the other side of the ionic probes is exposed to a gas with well-defined oxygen partial pressure, $P(O_2)$. Under these conditions the voltage measured on the probes yields the above mentioned differences divided by the charge of the corresponding charge carrier.[6]

The existence of cross terms between electron and ion fluxes is known in the field of metals. They become significant under high current density.[7] There, due to the high current density the electrons are capable of pushing ions by momentum transfer regardless of the charge polarity of the ions. This phenomenon is known as electromigration and the electron current is sometimes referred to as electron wind. Extended collision of electrons and ions may result in significant failure of metal contacts due to motion of the ions.[8]

In the case of semiconductors which are MIECs there is no such electromigration effect as in metals. The authors[1] also state that they have no explanation for a mutual effect of a driving force of one species on the flux of the other species. Indeed there is non. We notice that an electrostatic force is taken into consideration by the Poisson equation and in some cases by forming new charge states for the mobile ions. In large samples the Poisson equation may be replaced by the local neutrality equation as most of the voltage drop takes place on the bulk and not on the space charge region near interfaces.

It turns out that the appearance of finite cross terms and the ability to measure them is due to an incomplete description of the system at hand. For the Nafion system mentioned before if the transport would be described not only by that of water and protons but also by complexes containing a proton and solvated water, $H^+\cdot(H_2O)_m$, the cross terms would not appear. Unfortunately, when the number of solvated water molecules in the complex may widely vary different flux equation need to be considered, one for each m value, and the use of effective cross terms is more convenient. Yet when there is a typical value for m three flux equations should be sufficient. The situation becomes even simpler when the flux of free proton and that of free water molecule are relative small. It was then shown that one can describe the transport within humid Nafion using a single flux equation with m~3 and no cross terms are required.[9]

In MIECs the situation is, usually, even simpler. The complexes formed between ions and electrons are ions in a different valence state. Wagner[10] and later Wiemhöfer and others[11] have shown that when there are two mobile ionic charge carries of the same chemical component, say singly and double charged oxygen vacancies, $V_O^{\bullet}$ and $V_O^{\bullet\bullet}$, in addition to electrons (or holes), the complete description of transport requires solving the flux density equations of all three mobile specie. If however, only two charge carriers are considered then the missing information manifest itself as cross terms in the theory and leads to misinterpretation of the measurements. An explanation is prenested below.

We shall demonstrate our claims by considering ceria (CeO_2) for which cross terms were measured under steady state conditions.[12] We shall then refer to the oxide $Ce_{0.8}Pr_{0.2}O_{2-x}$ [1] and to the fact that in this case the measurements were not done under steady state conditions. The discussion holds for systems under uniform and fixed temperature.

2. Two valence state of mobile ions and electrons, the ceria example.

2a. The charge carries in CeO_{2-x}

Tuller and Nowick [13] have shown that CeO_2, at elevated temperatures, contains both singly and doubly charged oxygen vacancies. The more the oxide is reduced the higher is the concentration of $V_O^{\bullet}$ due to a recombination reaction between $V_O^{\bullet\bullet}$ and the conducting electrons $e^{\backslash}$. As the stoichiometry of the oxide could readily be changed both under high $P(O_2)$, where $V_O^{\bullet\bullet}$ is dominant, and under low $P(O_2)$, where $V_O^{\bullet}$ is dominant, we conclude that not only $V_O^{\bullet\bullet}$ but also $V_O^{\bullet}$ defects are mobile at elevated temperatures, $T \geq 800^oC$. Hence, there are three mobile charge carriers, $e^{\backslash}$, $V_O^{\bullet\bullet}$ and $V_O^{\bullet}$, to be considered.

2b. The use of electrodes that block material exchange.

Let us first discuss the measurement done using platinum as electrodes that block material exchange. One possible flux partition is presented schematically in Fig. 1. This flux partition is the only one possible if local equilibrium prevails. We consider this case.

As shown in Fig. 1 the two ion fluxes (and currents) need **not** be blocked by the electrodes. The metal electrode blocks material exchange not necessarily ion currents within the neighboring MIEC. The electrodes block the net ion flux. The blocking leads to a link between the two ion fluxes which, under steady state, have to be equal in magnitude and opposite in direction,

$$J_{i,1} + J_{i,2} = 0 \qquad (1.2)$$

where J denotes flux and 1 and 2 refer to the charge state of the vacancy. Under the applied voltage with the polarity as indicated in Fig. 1 the charged oxygen vacancies are attracted towards the cathode. The oxide is polarized and the chemical potential of neutral vacancies, V_O^x, near the cathode increases while near the anode it decreases until a steady state value, $\Delta\mu_x > 0$, is reached. This difference can be expressed as a Nernst voltage. However, one has first to specify a Nernst voltage for which charge carrier. The Nernst voltage $V_{th,2}$ for $V_O^{\bullet\bullet}$ is,

$$V_{th,2} = -\frac{\Delta\mu_x}{2q} \tag{1.3}$$

where q is the elementary charge. However, the Nernst voltage for $V_O^{\bullet}$ is twice as large,

$$V_{th,1} = -\frac{\Delta\mu_x}{q} = 2V_{th,2} \tag{1.4}$$

One can show,[14] based on Eq. (1.2) and Eq. (1.5), that in the steady state $|V_{th,2}|<|V|$ (V is the applied voltage) while $|V_{th,1}|>|V|$. In the present example V, $V_{th,1}$, $V_{th,2}$ are negative.

For the case of local equilibrium the ion currents are uniform and given by,[15]

$$\begin{aligned} I_1 &= qJ_{i,1} = \frac{V_{th,1} - V}{R_{i,1}} \\ I_2 &= 2qJ_{i,2} = \frac{V_{th,2} - V}{R_{i,2}} \end{aligned} \tag{1.5}$$

where R is the resistance of the MIEC for the corresponding ionic charge carrier. Hence, $J_{i,1}<0$ and $J_{i,2}>0$ as indicated in Fig. 1 (the current is positive when flowing to the right). At the MIEC/electrode interface an electrochemical reaction takes place. At the anode it is,

$$V_O^{\bullet} \rightarrow V_O^{\bullet\bullet} + e' \tag{1.6}$$

while at the cathode it is the inverse one,

$$V_O^{\bullet\bullet} + e' \rightarrow V_O^{\bullet} \tag{1.7}$$

The net result is that electrons are transferred by $V_O^{\bullet}$ from the cathode to the anode. In addition there is an electron current that flows through the oxide, as it is a MIEC.

We can now show why ionic probes applied onto that MIEC oxide measure a difference $\Delta\tilde{\mu}_i \neq 0$ (on top of $\Delta\tilde{\mu}_e \neq 0$) despite the fact that the total ion flux (though not ion current) vanishes. For that, one has to examine the ionic probes used in the measurement. They are YSZ which can be considered as only $V_O^{\bullet\bullet}$ conductors. Thus the voltage measured by those probes yields the difference, $\Delta\tilde{\mu}_{i,2}/2q$, of the electrochemical potential (divided by 2q) of the $V_O^{\bullet\bullet}$ defects but not of the $V_O^{\bullet}$ ones. Since there is a current of $V_O^{\bullet\bullet}$ defects, (see Fig. 1) it is not surprising that a finite driving force $\Delta\tilde{\mu}_{i,2} \neq 0$ is being measured. This, however, has nothing to do with cross terms $L_{ie} \neq 0$. There are two ion currents each being driven by the corresponding driving force $\nabla\tilde{\mu}_{i,1}$, $\nabla\tilde{\mu}_{i,2}$ and no cross terms L_{ie} need be called upon. The sign of the voltage measured on the ionic probes is negative.

We summarize this section by reiterating that in the present case the net ionic current within the MIEC does **not** vanish. It is only the net ion flux which vanishes by the use of the Pt blocking electrodes. The electrochemical reactions at the MIEC/electrodes interfaces transfer the net ionic current within the MIEC into an electron current within the metal electrodes.

2c. The use of electrodes that block the electron current.

A rather similar explanation applies when the electrodes are solid electrolytes which block the electron current through them. We shall show that voltage probes made of Pt, applied to the MIEC should measure a finite voltage, though the electrodes block the electron current. We claim that an electron current is induced within the MIEC CeO_{2-x} despite the blocking nature of the nearby electrodes.

The possible currents, assuming local equilibrium, are shown in Fig 2. The oxygen chemical potential in the surrounding is assumed uniform, i.e. $P(O_2)$ is uniform. Under this condition the applied voltage drives oxygen vacancies from the anode towards the cathode. While in the electrodes only $V_O^{\bullet\bullet}$ defects are mobile, in the MIEC both $V_O^{\bullet}$ and $V_O^{\bullet\bullet}$ are mobile and driven through it (as well as electrons). At the anode/MIEC interface an electrochemical reaction takes place whereby some of the $V_O^{\bullet\bullet}$ defects are reduced to $V_O^{\bullet}$ (Eq. (1.7)). At the cathode the inverse reaction (Eq. (1.6) occurs. The electrons required for the reduction process at the anode are generated at the cathode and flow through the MIEC from the cathode to the anode.

The electron current is related to a voltage, V_0 that must be generated on the MIEC,[15]

$$I_e = -\frac{V_0}{R_e} \tag{1.8}$$

Since $V_0 \neq 0$ the voltage probes applied to the MIEC at x_1 ad x_2 (Fig. 2) will measure a finite voltage despite the fact that the electrodes block the electron current. I_e is driven only by $\nabla\tilde{\mu}_e$ and no cross terms need be called upon, i.e. $L_{ie}=0$.

3. The $Ce_{0.8}Pr_{0.2}O_{2-x}$ system

The discussion of the $Ce_{0.8}Pr_{0.2}O_{2-x}$ oxide is based on the same experimental system used to the measurements on CeO_{2-x} [12] (with a slight improvement) while the theory has been extended to adapt to the defect model and to the measuring procedure.[1] The conclusion that the electron driving force acts also on the oxygen vacancies and vice versa, i.e. $L_{ie} \neq 0$, is questionable for the same reason as for CeO_{2-x} as the same mobile ionic defects, $V_O^{\bullet}$ and $V_O^{\bullet\bullet}$ (and electrons, $e^{\backslash}$) are in both oxides.

4. Question concerning the approximation used for determining the diffusion coefficient

In the case of $Ce_{0.8}Pr_{0.2}O_{2-x}$ [1] the theory was modified to derive the diffusion coefficient form non steady state experiments. The fact the procedure is not a steady state one and therefore may be far from local equilibrium raises a question concerning the approximation done in the derivation. In the continuity equations used in the analysis no generation terms appear. This may hold exactly only in the steady state and under local equilibrium.[16] The error introduced by that approximation is still an open question.

5. Conclusion:

Cross Onsager coefficient of transport, L_{ie}, when measured on a MIEC which conducts ionic defects in two oxidation states, such as $V_O^{\bullet}$ and $V_O^{\bullet\bullet}$, will “appear” if the experimental results are analyzed in terms of only one valence state of the mobile ionic defects and electrons (or holes). In the case of ceria two oxidation states of mobile ionic defects, $V_O^{\bullet}$ and $V_O^{\bullet\bullet}$, exist at elevated temperatures, their concentration varying with $P(O_2)$. No mechanism for a real link between the driving force for ions and the electron flux and the driving force for electron and the ion flux is known in those oxides. The only one known is electromigration in metals and it requires high current density that may appear in metals but are not in semiconductor oxides, in particular those with the rather low electron mobility of small polarons, as is the case in many oxides. In the example discussed we have assumed local equilibrium which allowed making the drawings in Figs. 1 and 2. If local equilibrium does not prevail the currents need be calculated in detail. The same conclusions hold in the steady state also when local equilibrium does not prevail.

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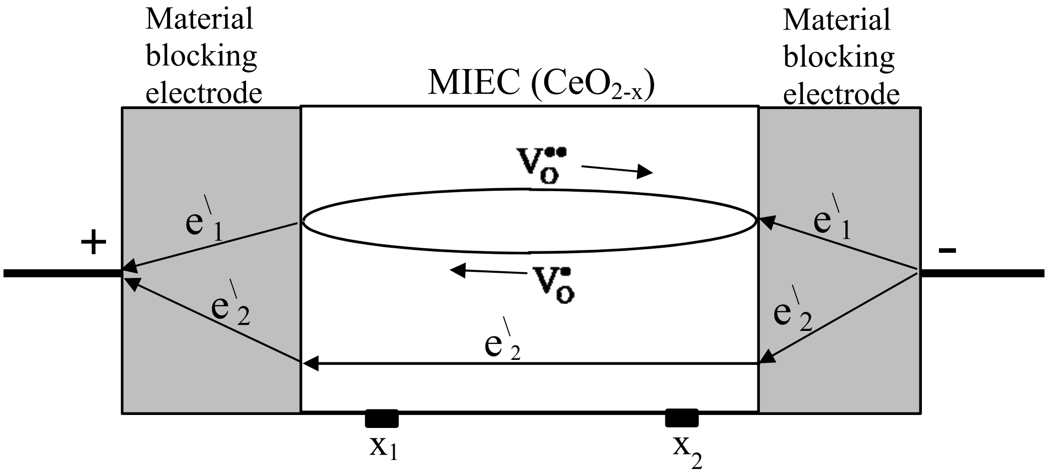

Fig. 1: The fluxes in a MIEC which conducts $e^{\backslash}$, $V_O^{\bullet}$, $V_O^{\bullet\bullet}$ when the electrodes conduct electrons and block material transfer through them, under steady state and local equilibrium. The polarity of the applied voltage is indicated by + and -. x_1 and x_2 are the locations where the probes are supposed to be attached to the MIEC.

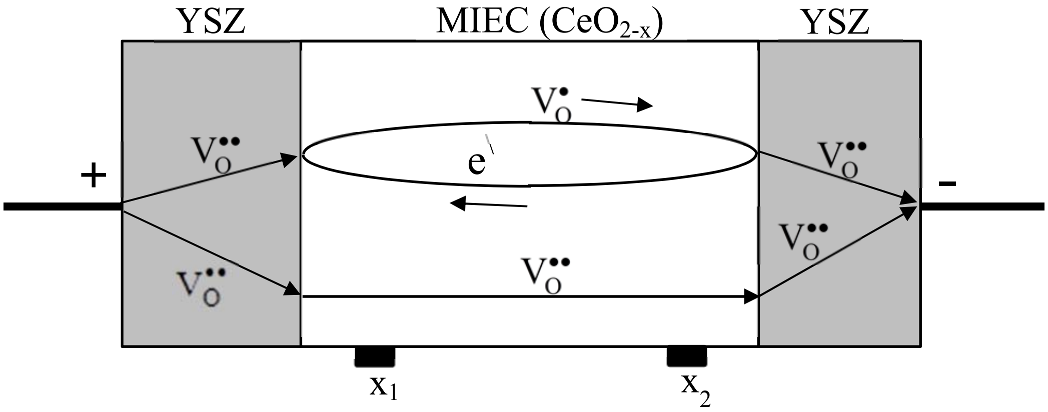

Fig. 2: The fluxes in a MIEC which conducts $e^{\backslash}$, $V_O^{\bullet}, V_O^{\bullet\bullet}$ when the electrodes conduct $V_O^{\bullet\bullet}$ and block electron transfer through them, under steady state and local equilibrium. The polarity of the applied voltage is indicated by + and -. x_1 and x_2 are the locations where the probes are supposed to be attached to the MIEC.