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"Reply to the 'Comment on "How to interpret Onsager cross terms in mixed ionic electronic conductors" ' by H.-I. Yoo, M. Martin, and J. Janek, Phys. Chem. Chem. Phys., 2015, 7, DOI: 10.1039/C4CP05737F".

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Abstract

The origin of the Onsager cross terms in mixed-ionic-electronic-conductor (MIEC) oxides is re-examined. Experiments are suggested to determine which of the two suggested explanations is applicable.

Ref. 9 in the Comment[1] discusses a sufficient condition for obtaining cross terms, L_{ie}. It shows that in a MIEC that has mobile ionic defects with two charge states; if only the current of one is considered (plus the electronic one) cross terms appear. As the concentration and mobility of ionic defects in ionic solids is usually low in comparison to liquid electrolytes, Coulomb interactions were neglected. In Ag_2Se (Ref. 8 in the Comment[2]) with a high defect concentration, high ionic conductivity, σ_i~3 S/cm at T=162°C, and even higher electronic conductivity, the cross terms are small, $L_{ie}/L_{ii}<10^{-2}$. Is this small cross term due to the Coulomb interaction? If so, this interaction is weak even in a favorable MIEC.

The authors ignore the specific examples discussed in Ref. 9 in the Comment[1] that demonstrate how two ionic currents and an electron current are generated in an MIEC, of the kind mentioned above, under dc conditions though the electrodes may block material transfer or block electron transfer. The authors suggest an interaction mechanism between ions and electrons that lead to cross terms, L_{ie}, in MIECs. It is based on short and long range Coulomb interaction. While this is the case in high concentration and high mobility systems such as in liquid electrolytes (Refs. 22, 23 in the Comment[3,4]), it is questionable if it prevails in systems such as CeO_{2-x}. The experimental evidence (in Ref. 10-18, 24, 25 in the Comment[5-15],) refer mainly to oxides which either conduct cation defects having two charge states or oxygen vacancies where the existence of both $V_O^{\bullet\bullet}$, $V_O^{\bullet}$ cannot be excluded. In particular in CeO_{2-x} there are indications that two mobile ionic defects, $V_O^{\bullet\bullet}$ and $V_O^{\bullet}$ are present. In this case a finite, artificial L_{ie}, should appear if the system is analyzed in terms of only one of these ionic defects. For CeO_{2-x} we have observed rapid oxidation, in the 40-200°C temperature range, indicating fast bipolar oxygen diffusion. At this low temperature $V_O^{\bullet}$ is expected to be the dominant charged vacancy not $V_O^{\bullet\bullet}$. One has then to conclude that $V_O^{\bullet}$ is mobile and that at more elevated temperatures both $V_O^{\bullet}$ and $V_O^{\bullet\bullet}$ may contribute to the ionic current. Some oxides referred to by the authors have a more complicated composition and the variations and uncertainty are even bigger. We recommend that at this stage of knowledge experiment will be conducted on binary solids.

A definite answer which of the two mechanisms is the one prevailing has to be provided experimentally. The experiments mentioned by the authors (e.g. Ref. 7 and 8 in the Comment[16,2]) cannot tell apart which of the two mechanisms is definitely the relevant one. There are, however, two methods that can provide an answer.

Method A: Looking for the Coulomb interaction, the type of measurements used to determine the cross terms (Ref. 7 and 8 in the Comment[16,2]) should be applied to a MIEC where it can be clearly anticipated that there are no mobile ionic defects with two valence states. In particular let the MIEC contain mobile ionic defects (ions or vacancies) that have unit charge, e.g. F^- (ignoring positive F ions) and Li^+ ions. In particular, the system Li-Si may be of interest as both Li and Si exhibit a single, stable charge, the concentration of Li ions and conduction electrons can be largely varied and their conductivities are significant. It would be interesting to look for cross terms vs. the concentration of Li. If in this system large cross terms appear it will support the Coulomb interaction mechanism as the alternative solution of the omission of a current equation (Ref. 9 in the Comment[1]) is not applicable in this case.

Method B: The second method is aimed to test the consistency of the mechanism suggested in Ref 9 in the Comment[1] under local equilibrium conditions as discussed there. Let us consider an oxide such as CeO_{2-x} which is supposed to have mobile ionic defects with two valence states, $V_O^{\bullet}$ and $V_O^{\bullet\bullet}$.

Case I, current carrying electrodes that block material transfer: Using the analysis in Ref. 9 in the Comment[1] the ratio between $R_{i,1}$, the resistance to the current of $V_O^{\bullet}$, and $R_{i,2}$, the resistance to the current of $V_O^{\bullet\bullet}$, is,

$$\frac{R_{i,1}}{R_{i,2}} = 2\left(\frac{V_{e,I}}{V_{i,I}} - 2\right) \equiv f_{12} \qquad (1.1)$$

where $V_{e,I}$ and $V_{i,I}$ are, respectively, in case I, the voltage measured on the inert metallic probes (e.g. Pt) and between the ionic conducting probes based on YSZ, in an arrangement as shown in Ref 7 in the Comment[16], Fig. 1. When the resistance $R_{i,1}$ is high, $R_{i,1} >> R_{i,2}$, then $V_{i,I} << V_{e,I}$ and the cross term determined experimentally, $L_{ie}/L_{ii} = 2V_{i,I}/V_{e,I} << 1$, is small.

Case II, current carrying electrodes are based on ionic conductors (YSZ) and the electron current is blocked: The ratio between $R_{i,1}$ and R_e, the resistance to electron current, is,

$$\frac{R_{i,1}}{R_e} = 2\frac{V_{i.II}}{V_{e,II}} - 1 \equiv f_{1e} \qquad (1.2)$$

For a small driving force the composition is quite uniform and one can refer to the average oxygen chemical potential and oxygen partial pressure as the typical ones. Repeating the experiment under different oxygen partial pressures, $P(O_2)$, $R_{i,1}$, $R_{i,2}$ and R_e change in a known manner since the concentration of the corresponding charge carrier changes with $P(O_2)$. This is controlled by the mass action law,

$$P(O_2)^{1/2}[V_O^{\bullet\bullet}]n^2 = K_2 \qquad (1.3)$$

$$P(O_2)^{1/2}[V_O^{\bullet}]n = K_1 \qquad (1.4)$$

Taking the mobility, ν, of those defects to be independent of $P(O_2)$ and combining Eqs.(1.1)-(1.4), leads to,

$$f_{12}(P)^{-1} = \frac{\nu_{i,1}}{2\nu_{i,2}}\frac{[V_O^{\bullet}]}{[V_O^{\bullet\bullet}]} = \frac{\nu_{i,1}K_1}{2\nu_{i,2}K_2}n \ , \quad P \equiv P(O_2) \qquad (1.5)$$

and

$$f_{1e}(P)^{-1} = \frac{\nu_{i,1}}{\nu_e}\frac{[V_O^{\bullet}]}{n} \qquad (1.6)$$

Eq. (1.5) yields an experimental expression for the n-P relation. Using then Eq. (1.6), the $[V_O^{\bullet}]$-P relation can be determined from which, with the help of Eq.(1.5), the $[V_O^{\bullet\bullet}]$-P relation can be determined. The consistency test requires that the three concentrations fulfil the neutrality equation for all P values, $n=[V_O^{\bullet}]+2[V_O^{\bullet\bullet}]$, which yields,

$$\left(1+\frac{\nu_{i,1}}{\nu_{i,2}}f_{12}(P)\right)f_{1e}(P)^{-1}=\frac{\nu_{i,1}}{\nu_{e}} \tag{1.7}$$

The experimental expression in Eq. (1.7) should be a constant under $P(O_2)$ variations with the mobility ratios as fitting parameters being independent of $P(O_2)$.

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