Electrochemical methods for determining ionic charge in solids

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Classical experiments from solid-state electrochemistry can be used to determine the charge of ions in solids. This comments also clarifies how the charge of point defects fits with the standard picture of ionic charge and highlights differences between these electrochemical experiments and methods that probe electrons directly.

The solid-state community evidently needs to be reminded every decade or so of the utility, but also of the limits, of the related, fundamental concepts of ionic charge, effective charge, formal charge and oxidation state. The latest instalment in this series is a timely perspective by Walsh et al.[1], in which the information and the understanding gained from electronic structure calculations are discussed. Some experimental techniques that are commonly used to determine the ionic charge are also mentioned, and this is where we would like to take up the baton from Walsh et al. In this comment, we discuss electrochemical experiments that can be used to determine the ionic charge. Our aims are to draw attention to experiments that, at least in this respect, have been widely ignored; and to provide some clarification on experiments that are plagued, to varying degrees, by misconceptions. We also briefly contrast these experiments with methods that probe electrons directly, taking as a representative method X-ray photoelectron spectroscopy (XPS).

According to Walsh et al.[1], each experimental technique will give a different answer to the question of how charge is apportioned between atoms in a solid. This is an eminently reasonable point of view: Each experiment will interrogate a solid in a different way, and hence different answers are to be expected from different experimental methods. In this regard, performing an experiment is analogous to taking a photograph with a specific objective lens and a specific filter. The image obtained will, of course, depend on the lens and on the filter.

It is surprising, therefore, to find three electrochemical experiments — the first that dates back to Faraday[2]; the second, to Nernst[3]; and the third, to the study of point defects[4-6] — that, despite being based on different physical observables, give the same answer to the question of an ion's charge. A further surprise is that the answer they give is the ion's formal charge. We describe these three experiments below, and we explain why, in the broadest sense, they all are concerned with a difference in charge or the movement of charge.

In concentrating on these experiments, we seemingly ignore an obvious choice: the calculation from electrical conductivity data. Since a measured ionic conductivity σ_{ion} can be expressed as the product of an ion's concentration c_{ion}, mobility u_{ion} and charge q_{ion} (*i.e.* $\sigma_{\text{ion}} = u_{\text{ion}}\, c_{\text{ion}}\, q_{\text{ion}}$), one can extract q_{ion} from σ_{ion}, if one knows c_{ion} and u_{ion}. The problem is the experimental determination of u_{ion}. Measurements utilising the Hall effect are challenging because the comparatively low ionic mobilities (relative to those of electronic charge carriers) translate into miniscule Hall voltages[7]. Indeed, the difficulties in determining u_{ion} directly mean that researchers often calculate it from σ_{ion} using the formal charge for q_{ion} (and knowing c_{ion}). An alternative route — using the Nernst−Einstein equation[8], which links an ion's mobility with its diffusivity: $u_{\text{ion}} = D_{\text{ion}}\, q_{\text{ion}} / (k_{\text{B}}\, T)$ — requires q_{ion} as input and can, therefore, be discounted. Hence, using the conductivity to determine the ionic charge is possible but seldom practicable.

Faraday's experiment

Most solids consist of one sublattice of (relatively) mobile ions and one or more sublattices of (relatively) immobile ions. This experiment relies on ions being mobile and thus yields the charge of the mobile ions. Let us consider, for simplicity and for illustration, a solid oxide in which only the oxygen ions are mobile (and with a suitably large bandgap so that electronic conductivity can be neglected). Yttria-stabilised zirconia (YSZ) is one such material, being an excellent oxygen-ion conducting electrolyte over a wide range of experimental conditions[9,10].

The experiment itself[2] is rather simple (Fig. 1a). We pass an electric current I for a time t through a YSZ sample that separates two compartments, A and B, and we determine the mass of oxygen, m_{O}, that disappears from A and appears in B. Faraday's law of electrolysis relates the amount of charge that has flowed through the external circuit to the mass of oxygen that has been pumped through the electrolyte (with F being Faraday's constant and M_{O}, the molar mass of oxygen):

$$I\, t = n\, F \frac{m_{\text{O}}}{M_{\text{O}}} \qquad (1)$$

The important quantity here is n, the number of electrons each ion carries with it as it moves through the electrolyte. Experiments[11,12] yield $n = 2$, indicating that the mobile ions are O^{2-}.

We could consider, equally well, Li^+, Na^+, Cu^+, Ag^+ or F^- conducting solid electrolytes, but the higher charge of O^{2-} makes it a superior example. The benefit of considering, for example, a lithium-ion electrolyte sandwiched between two identical intercalation oxide electrodes is that the mobile ion (Li^+) does not undergo any redox reactions as it passes from one electrode through the electrolyte to the other electrode.

We emphasise two points. First, Faraday's experiment gives the charge carried by the ion as it moves, not the charge of the ion on its lattice site. In terms of our snapshots, the experiment gives us the difference between the ion sitting in one location and the ion sitting further along on the way from A to B. It does not give us the charge of an ion residing on its sublattice site (this information corresponding to a single snapshot), because this is not the observable. Second, when we talk of the charge that the ion carries with it, we do not mean the charge of the ion during the jump. As it executes a jump through the transition state, an oxygen ion may, for example, give up some charge to the environment during the jump, but it re-acquires this charge once it has completed the jump. Comparing before and after, we find that an oxygen atom and two electrons have moved. This is the charge that we refer to.

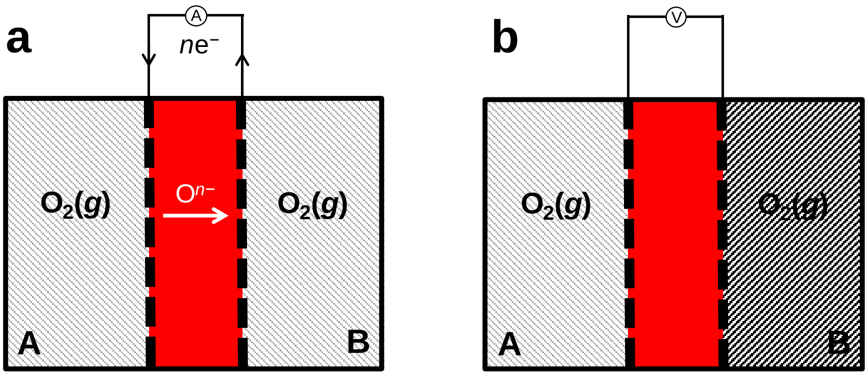


Fig. 1 | Two electrochemical experiments to determine the ionic charge. Both setups consist of an oxygen-ion conducting solid electrolyte YSZ sandwiched between porous Pt electrodes; they are run at elevated temperatures so that the electrochemical reactions at the electrodes proceed at a sufficient rate. **a**, Faraday's experiment, in which a current is passed for a time, and the amount of oxygen gas pumped from A to B is measured. **b**, Nernst's experiment, in which the partial pressures of oxygen in A and B are different, and the open-circuit voltage across the cell is measured.

The word “ion” was suggested to Michael Faraday by William Whewell (see Laidler’s book[13] for a more detailed description), after Faraday had asked Whewell’s help in coining terms to describe electrolysis. Whewell proposed “ion”, deriving it from a Greek word that means “to go”. In Laidler’s words: “An ion is therefore something that moves”. We propose that the term “ionic charge” is restricted in its use to the results of Faraday’s, Nernst’s and the defect-chemistry experiments.

The benefit of considering a pure ionically conducting material is that only one experiment needs to be performed; no other information is required. This is not the case if the material shows mixed ionic and electronic conductivity[8]. In such cases, some proportion of the current will be carried by electronic charge carriers and the remaining fraction by the ions. Further complications may arise from interactions between electronic and ionic charge carriers[14]. In other words, deviations from Eq. (1) do not necessarily indicate non-integral charges, but far more likely, the presence of significant electronic conductivity.

Nernst’s experiment

We keep the same set-up as previously, but we change the experiment and the physical observable. Instead of measuring a current and the mass of transported material, we expose the YSZ cell to different partial pressures of oxygen in the compartments A and B (Fig. 1b) and measure the electric potential difference E between the two Pt electrodes under open circuit conditions (no current flow). Nernst’s Law[3] for the concentration cell gives E in terms of the partial pressures of oxygen in the two compartments:

$$E = \frac{RT}{nF} \ln \left[\frac{p\mathrm{O}_2(\mathrm{A})}{p\mathrm{O}_2(\mathrm{B})} \right]^{½} \qquad (2)$$

n, here, refers to the number of electrons transferred from the Pt electrode to each atom of oxygen in the electrochemical reaction,

$$½\mathrm{O}_2(g) + ne^-(\mathrm{Pt}) \rightarrow \mathrm{O}^{n-}(\mathrm{YSZ}). \qquad (3)$$

Again, we see that the charge probed in the experiment is a difference between two snapshots, being the charge transferred to the oxygen atom to make it into an oxygen ion. And again, we find that the charge obtained is not that of the oxygen ion on its lattice site in the solid; rather, it is the charge transferred to the oxygen moiety as it enters the solid. In experiment, the measured potential difference[9,11,15] is found to accord exactly with $n = 2$. (Again, deviations from the expected voltage do not indicate non-integral charges but electronic conductivity.) Indeed, the experiment is the basis of thermochemical analyses[9] and potentiometric oxygen sensors[15].

If we are willing to make an assumption, Nernst's experiment furnishes the charge of an oxygen ion on its lattice site, even though this quantity is not directly observed in the experiment (as indicated above, one should avoid calling this quantity the ionic charge). Specifically, if we assume that an O^{2-}, upon entering the oxide, does not lose (or acquire) any charge, Nernst's experiment implies that the charge of an oxygen ion on its lattice site is $-2e$. Taking this same assumption, one finds that the other two experiments also yield this conclusion. From a slightly different point of view, if one accepts that ionisation processes involve integer numbers of electrons and that they only occur at external interfaces, one has to accept that the incorporated ions carry integer charges.

The Brouwer approach

Point defects are defined as the zero-dimensional deviations from the ideal crystal that are present in real crystals: Point defects = real crystal – ideal crystal. Accordingly, the relative charge of a vacancy defect, say, is the charge present at the vacant lattice site in the real crystal minus the charge at that site in the ideal crystal. In the ionic limit, a vacant site has no charge (since we have removed an ion rather than an atom), and the charge of the ion is its formal charge. Thus, if an oxygen ion has a charge of $-2e$, the relative charge of an oxygen vacancy is $q_{\mathrm{real}} - q_{\mathrm{ideal}} = 0e - (-2e) = +2e$. The two snapshots in this case are the ideal crystal with no defects and the same crystal missing an oxygen ion. For oxides that are not fully ionic, the oxygen vacancy is still considered universally to possess a relative charge of $+2e$. Is this simply a standard approximation? Or worse, is it merely convention?

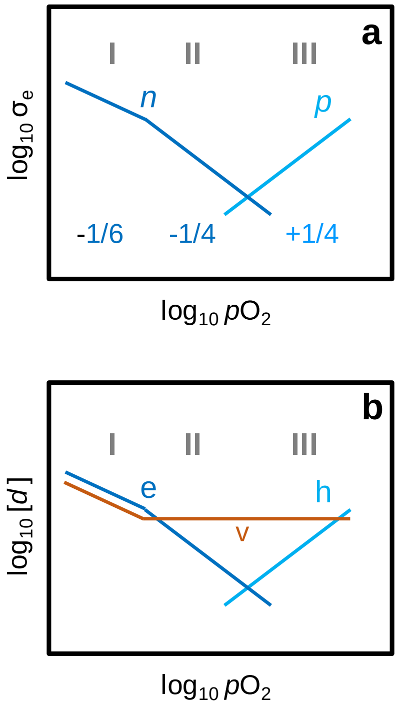
The Brouwer approach (Box 1) delivers the relative charge of an oxygen vacancy in an oxide; and we discuss literature data consistent with this relative charge being $+2e$ for oxides, such as YSZ, CeO_2, Ta_2O_5, $SrTiO_3$ and $(La,Sr)FeO_3$. These oxides certainly deviate from the fully ionic picture, and furthermore and more importantly, they deviate to varying degrees. It turns out that writing the relative charge of an oxygen vacancy as $+2e$ is not an approximation (and certainly not convention).

The key question, now, is what does the relative charge of an oxygen vacancy tell us about the charge of the missing oxygen ion? At first sight, nothing. If the absolute charge on an oxygen ion were, say,

−1.8*e* and the absolute charge at the vacancy (and its surroundings) were +0.2*e*, the vacancy's relative charge would be +2*e*. But what, then, is the physical mechanism that maintains the vacancy's relative charge of +2*e*, even if the oxygen ion's charge is less than –2*e*? Such a mechanism requires a crystal lattice, if its oxygen ions have a charge of –1.8*e* or –1.7*e* or –1.5*e*, to force –0.2*e* or –0.3*e* or –0.5*e* away from a vacancy's vicinity, in order to maintain a relative charge of +2*e*. This seems inconceivable. The simple alternative assumes the charge of the missing oxygen ion to be –2*e*.

Box 1| Relative charge of oxygen vacancies

Many defect-dependent properties of oxides vary as a function of oxygen partial pressure, pO_2. This experiment is based on determining the exponent m in the power-law description, property $\propto (pO_2)^m$. Brouwer's approximation in defect chemistry[6] yields values of m that are often either reciprocal integers ($\pm{}^1/_2$, $\pm{}^1/_4$, $\pm{}^1/_6$, *etc.*) or zero. Here, on account of the wealth of available experimental data, we consider, as the defect-dependent property, the electronic conductivity (σ_e), and as oxide systems, wide-bandgap oxides.



Three Brouwer regimes (denoted I, II, III, see text) for a wide-bandgap oxide as a function oxygen partial pressure: **a**, electronic conductivity; **b**, point-defect concentrations.

In Kröger−Vink notation[5], the reduction of an oxide can be written as

$$\mathrm{O}_\mathrm{O}^{\times} \rightleftharpoons \mathrm{v}_\mathrm{O}^{r\bullet} + r\mathrm{e}^{/} + \tfrac{1}{2}\mathrm{O}_2(g) \tag{4}$$

That is, removing an oxygen ion (of unspecified charge) sitting on its regular lattice site (it is, therefore, relatively neutral) yields a vacant site with relative positive charge $r\bullet$, the equivalent number of electrons (each having a single negative relative charge) and half an oxygen molecule. Applying the law of mass action, we obtain the equilibrium constant

$$K_{\mathrm{red}} = \frac{[\mathrm{v}_\mathrm{O}^{r\bullet}][\mathrm{e}^{/}]^{r}(p\mathrm{O}_2)^{1/2}}{[\mathrm{O}_\mathrm{O}^{\times}]} \tag{5}$$

(with $[d]$ denoting the concentration of the defect d). We now consider three Brouwer[6] approximations. Regime I: Under highly reducing conditions, vacancies are compensated by electrons: $r[\mathrm{v}_\mathrm{O}^{r\bullet}] = [\mathrm{e}^{/}]$. Substituting this condition into eq. (5) yields $\sigma_\mathrm{e} \propto [\mathrm{e}^{/}] \propto p\mathrm{O}_2^{-1/(2+2r)}$. Regime II: At more moderately reducing conditions, the vacancy concentration is fixed either by an acceptor dopant or by an intrinsic disorder reaction. Consequently, with $[\mathrm{v}_\mathrm{O}^{r\bullet}]$ being constant in eq. (5) one finds $\sigma_\mathrm{e} \propto [\mathrm{e}^{/}] \propto p\mathrm{O}_2^{-1/2r}$. Regime III: Under oxidising conditions, the electron concentration is so low that through the electron–hole equilibrium the concentration of electron holes becomes more important. Consequently, $\sigma_\mathrm{e} \propto [\mathrm{h}^{\bullet}] \propto p\mathrm{O}_2^{+1/2r}$.

Taking $\mathrm{SrTiO_3}$ (Ref. 16) as our example, we find experimentally that, with increasing oxygen partial pressure, $\sigma_\mathrm{e} \propto p\mathrm{O}_2^{-1/6}$ (consistent with $r = 2$), changes to $\sigma_\mathrm{e} \propto p\mathrm{O}_2^{-1/4}$ (also consistent with $r = 2$), which then changes to $\sigma_\mathrm{e} \propto p\mathrm{O}_2^{+1/4}$ (yet again consistent with $r = 2$). For $\mathrm{(La,Sr)FeO_3}$ (Ref. 17), $\mathrm{CeO_2}$ (Ref. 18) and YSZ (Ref. 10), the experimental data accord with $m = -^1/_4$ and $+^1/_4$ (and thus $r = 2$) for regions II and III. For $\mathrm{Ta_2O_5}$ (Ref. 19), regions I and II (with $m = -^1/_6$ and $-^1/_4$, and thus $r = 2$) are seen. Such results indicate unambiguously that the oxygen vacancies possess a relative charge of $+2e$.

It is worth noting, first, that the total electrical conductivity of an oxide may also contains contributions from mobile ions. Second, that point defects can alter their charge state if they trap electrons or holes, so that the defect’s relative charge does not necessarily give the ion’s charge. An oxygen vacancy ($\mathrm{v}_\mathrm{O}^{\bullet\bullet}$), for example, can trap one electron to form $\mathrm{v}_\mathrm{O}^{\bullet}$ and then a second to form $\mathrm{v}_\mathrm{O}^{\times}$; such reactions in general modify how defect-dependent properties vary with $p\mathrm{O}_2$ (see, e.g., Ref. 20). Third, that for oxides in which cation vacancies dominate the defect chemistry information on the vacancies' charge state can also be obtained by varying pO_2 (see, e.g., Refs. 21,22).

Probing electrons directly to obtain the ionic charge

Though used to determine the ionic charge, methods that are based on probing the electrons directly do not (indeed, cannot) provide the ionic charge because they do not utilise charge (or some property connected to charge) as an observable. Such methods, to return to our camera analogy, constitute a single snapshot rather than a difference between two snapshots. X-ray photoelectron spectroscopy (XPS) is one such method. As discussed by Walsh et al.[1], it is a widely applied technique. It serves here as the most direct representative of those methods that are based on probing the electrons or electronic states themselves.

XPS probes the energy and the symmetry of the state that the electron occupies in the solid. These quantities are governed not only by the parent atom but also by the atomic arrangement in the compound. Consequently, the appearance or the disappearance or the shift in energy of features in X-ray photoelectron spectra upon compositional variation may arise from changes in the parent atom's electronic energy levels and their occupation, but also and more importantly, from changes in the inter-atomic arrangement. In particular, the often-used shift in binding energy can have multiple origins, with changes in formal oxidation state being only one of them[23]. Furthermore, changes in formal oxidation state do not necessarily lead to changes in spectral features.

We stress that standard XPS cannot give the charge of the ion. On its own it is unable to deliver an unambiguous assignment of spectral changes. The assignment is made by the researcher on the basis of chemical intuition or electronic structure calculations. Generally, the best that can be achieved is the establishment of a link *from* oxidation states *to* spectroscopic signatures (but not vice versa).

Hence, there are cases for which XPS works well in confirming changes in oxidation state, one example being the change of Ti oxidation state from +4 to +3 in the isostructural $Ca_{1-x}Y_xTiO_3$ series[24], evident in Ti 2*p* core level and valence-band spectra. But there are also cases where there are no links. $YTiO_3$ and Ti_2O_3, for example, exhibit qualitatively different Ti 2*p* core level spectra, even though the formal oxidation state of Ti is the same in both compounds; this is due to the different crystal structures of the two compounds[25]. And in the case of $La_xSr_{1-x}FeO_3$, unambiguous spectroscopic evidence of *changes* in the oxidation state of Fe upon variation of the Sr/La ratio are absent from the Fe 2*p* spectra[26]. Such behaviour arises because the $La_xSr_{1-x}FeO_3$ perovskites are negative charge-transfer materials, in which holes are predominantly located on the ligand[27]. From a (defect-)chemical point of view, one cannot differentiate between a hole on the ligand and a hole on the transition metal cation. But from the point of view of chemical reactions, there is a difference, and for the $La_xSr_{1-x}FeO_3$ compounds, x-ray spectroscopic studies indicate that the ligand holes are the active species in redox reactions[28].

With this in mind, we maintain that the electrochemical concept of ionic charge does not have any correspondence in the physics of XPS (or X-ray spectroscopy in general). Consequently, results obtained by XPS or any other direct technique (for example, that oxygen is *not* O^{2-} in a solid) can contradict those obtained from the electrochemical experiments. The bottom line is that such techniques *may* yield valuable information that can be translated into a formal oxidation state, but this is not guaranteed a priori.

Concluding remarks

Arguably, the question of charge (ionic, effective, formal) comes down to the issue of observables and to distinguishing between different concepts[29]. If one is observing charge, either being transported (Faraday), being transferred (Nernst) or being additionally present or absent (Brouwer), one can determine the ionic charge. And one gets the same value, the formal charge of the ion, from all three experiments. If, however, one is probing the electrons' distribution or their energy or their symmetry, one is not observing charge. From this point of view, it is hardly surprising that such methods provide no unique answer to the question of charge.

Finally, this comment should serve as a call to arms. These three electrochemical experiments should be applied to determine the ionic charge in solids. They are used widely by researchers, who assume the formal ionic charge, but the experiments can be reversed so that they deliver (from easily measurable quantities) the ionic charge in solids.

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