



Theoretical analysis of space charge layer formation at metal/ionic conductor interfaces

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ABSTRACT

We examine the space charge layer formation at metal/ionic conductor interfaces by solving Poisson's equation using defect energetics calculated from first principles. The scheme is applied to zirconia, and we find that oxidizing atmosphere and high valence band offset result in negative space charge accumulation at the interface, while reducing atmosphere and low valence band offset result in positive charge accumulation. This is explained in terms of the alignment of the Fermi levels in the metal and the ionic conductor.

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1. Introduction

In recent years, an ever increasing number of works on ionic transport in solids have demonstrated that the conductivity can sometimes be modified drastically through the introduction of interfaces (see, e.g., Refs. [1–3] and references therein). This has opened up whole new possibilities for materials and device design, with applications in electrochemical devices such as batteries and fuel cells. In many cases, these phenomena have been explained in terms of the space charge model [1], where space charge layers are formed adjacent to charged interface “cores”. The concept has been applied widely to ionic conductor/ionic conductor and ionic conductor/insulator interfaces, as well as grain boundaries. However, despite the ubiquitousness of the metal/ionic conductor interfaces in electrochemical devices, relatively few works have dealt with the space charge layer formation in such systems [4–6]. The few available works have reported decreases in conductivity adjacent to the interface due to carrier depletion [5,6]. The present issue is to circumvent this negative effect on conduction and to see if it is possible to enhance the conductivity at metal/ionic conductor interfaces.

In this work, we take a theoretical approach to this problem, and attempt to clarify when, why and to what extent space charge layers are formed at the metal/ionic conductor interface. The defect energetics calculated from first principles are coupled with a self-consistent solution of Poisson's equation to calculate space charge profiles. We examine how the polarity and extent of space charge

layers depend on the atmosphere (temperature and partial pressures), as well as the valence band offset (VBO) at the interface. We will consider yttria stabilized zirconia (YSZ) as a concrete example, but it should be noted that this scheme and the general understanding obtained from it are applicable to any metal/ionic conductor interface. Furthermore, the present work is also relevant in the context of semiconductor devices, as ionic solids such as zirconia and hafnia (the so-called high-k oxides) have come to be used as the oxide layer in metal-oxide-semiconductor field effect transistors (MOSFETs).

2. Computational methodology

Ion conduction in YSZ occurs through oxygen vacancies, which are generated by doping with yttria (Kröger–Vink notation is used to represent point defects hereafter):



Trivalent Y ions replace tetravalent Zr ions in the lattice, and oxygen vacancies are generated to satisfy charge neutrality. However, this is not the case at interfaces, where in general, local charge neutrality is violated in order to keep the electrochemical potential constant. We will show how to handle this situation below.

We consider doubly positive and neutral oxygen vacancies ($V_{O}^{\bullet\bullet}$ and V_{O}^{\times}), doubly negative and neutral oxygen interstitials (O_i^{\bullet} and O_i^{\times}), yttrium dopants (Y'_{Zr}), conduction band electrons (e'), and valence band holes (h^*). We do not consider singly charged defects because of their theoretically predicted negative-U behavior [7–10] (i.e., singly charged defects are unstable with respect to disproportionation into

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doubly charged and neutral defects, and would therefore exist in negligible amounts).

The concentration of a point defect D with charge q is written as

$$[D^q] = \frac{n_D}{V_{f.u.}} \times \frac{\exp(-\Delta G_f\{D^q\}/\theta)}{1 + \sum_{q'} \exp(-\Delta G_f\{D^{q'}\}/\theta)}, \quad (2)$$

where $\Delta G_f\{D^q\}$ is the formation energy of the defect D with charge q , n_D is the number of possible defect sites in the lattice per formula unit of ZrO_2 , $V_{f.u.}$ is the volume per formula unit, q' denotes possible charge states of the defect, and $\theta = k_B T$ where k_B is the Boltzmann constant and T is the absolute temperature (see Appendix A for derivation). We use this equation for oxygen vacancies and interstitials. On the other hand, we consider Y_{Zr}^{3+} immobile and that its concentration is determined by the initial dopant distribution. The assumption that cations are immobile is reasonable in the temperature range considered in this work [11].

We employ VASP code [12,13] based on density functional theory (DFT) for calculation of defect formation energies. The projector augmented wave method is used to describe the ion–electron interactions. A plane wave energy cutoff of 500 eV is chosen for the wavefunction expansion. The exchange–correlation functional based on the generalized gradient approximation by Perdew et al. [14] is employed. A supercell consisting of 32 cubic ZrO_2 units is used for the calculations. The Gaussian smearing method is employed with a $2 \times 2 \times 2$ Monkhorst–Pack mesh for k-point sampling. We apply Makov–Payne correction for the calculation of the system with a charged vacancy [15].

We note here that this work suffers somewhat from the well known shortcoming of present-day DFT methods in reproducing the band gap [16]. In fact, the calculated band gap of cubic zirconia is 3 eV, while experiments report values in the range of about 5–7 eV [17,18]. To correct for this discrepancy, we simply shift up the conduction band minimum (CBM) until the gap reaches 5 eV while keeping the valence band maximum (VBM) and defect levels fixed to the calculated values. This is obviously an approximation that we are forced to make, and thus we limit ourselves to semi-quantitative analysis of the results. More sophisticated methods are being explored to overcome this problem (see, e.g., Ref. [16] and references therein), but those methods are much more computationally demanding and their reliability has not been tested as rigorously as conventional DFT methods.

The defect formation energies are obtained according to, e.g., Refs. [19–21] as

$$\Delta G_f\{V_O^x\} = 5.56 \text{ eV} + \mu_O, \quad (3)$$

$$\Delta G_f\{V_O^{x*}\} = -0.70 \text{ eV} + \mu_O + 2\Delta E_F, \quad (4)$$

$$\Delta G_f\{O_i^x\} = 4.10 \text{ eV} + \mu_O, \quad (5)$$

$$\Delta G_f\{O_i^{x*}\} = 4.65 \text{ eV} - \mu_O - 2\Delta E_F, \quad (6)$$

where μ_O is the oxygen chemical potential with respect to half that of an isolated oxygen molecule at 0 K and $\Delta E_F (= E_F - E_V)$ is the position of the Fermi level E_F with respect to the VBM E_V . Volume change and vibrational entropy due to defect formation are not considered here (this is a good approximation in most cases [20]). Note that these equations do not assume any type of “mechanism” such as cation doping for the generation of defects. Such effects are taken into account as changes in the value of E_F and μ_O . When considering a system in equilibrium with the gas phase, μ_O is related to the temperature T and partial pressure p_{O_2} of oxygen gas as

$$\mu_O(T, p_{O_2}) = \mu_O(T, p^\circ) + \frac{1}{2} k_B T \ln \left(\frac{p_{O_2}}{p^\circ} \right), \quad (7)$$

where p° is an arbitrary reference pressure. $\mu_O(T, p^\circ)$ can be obtained from thermochemical tables [22]. We do not consider defect–defect and defect–dopant interactions in this work, and use the formation energy of an isolated vacancy and interstitial in all concentration calculations. However, it should be noted that electrostatic interactions between charged defects are taken into account in a mean-field way through the value of ΔE_F (ΔE_F corresponds to the electrostatic potential, which we determine from the charge density; the explicit relation will be given later).

In addition, the concentration of electrons and holes are written as

$$\begin{aligned} [e'] &= N_C \exp[-(E_C - E_F)/\theta] \\ &= N_C \exp\left[-(\Delta E_{\text{gap}} - \Delta E_F)/\theta\right], \end{aligned} \quad (8)$$

$$\begin{aligned} [h^*] &= N_V \exp[-(E_F - E_V)/\theta] \\ &= N_V \exp[-\Delta E_F/\theta], \end{aligned} \quad (9)$$

where N_C and N_V are the effective density of states of the conduction and valence bands, E_C is the position of the CBM, E_V is that of the VBM, E_F is the Fermi level, $\Delta E_{\text{gap}} (= E_C - E_V)$ is the band gap, and ΔE_F is the Fermi level measured from the VBM. N_C and N_V are related to electron and hole effective masses in the band edges as

$$N_{C(V)} = 2 \left(\frac{2\pi m_{e(h)} \theta}{h^2} \right)^{\frac{3}{2}}, \quad (10)$$

where m_e and m_h are electron and hole effective masses and h is the Planck constant. Here, we simply approximate electron and hole masses with the free electron mass. In this work, these values have very little impact on the results, because hole and electron concentrations turn out to be negligibly small compared to the dominant charged defects in each case. Using the above equations, we can now calculate the total charge density

$$\rho = \sum_{D,q} q [D^q] + [h^*] - [e'] \quad (11)$$

as a function of p_{O_2} , T , and ΔE_F .

In bulk, ΔE_F is determined so as to satisfy charge neutrality ($\rho = 0$) under given p_{O_2} and T [20]. Fig. 1 shows the variation of ΔE_F with respect to the oxygen partial pressure calculated for 10 mol% YSZ (20% of Zr^{4+} sites are substituted by Y^{3+}) at 300 K and 1000 K. Low oxygen partial pressure and high temperature (reducing atmosphere) result in higher ΔE_F . Fig. 2 shows the Brouwer diagrams (oxygen partial pressure vs. defect concentration relationship) calculated using these ΔE_F values. The major defect is the oxygen vacancy introduced through the defect reaction of Eq. (1).

In situations where the bulk periodicity is broken, such as at an interface, we must consider spatial variations in the electrostatic potential. In this work, we consider a simple parallel capacitor structure

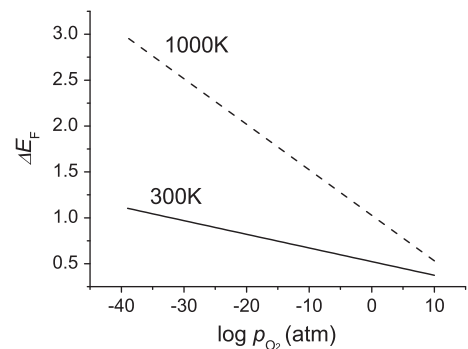


Fig. 1. Fermi level position in bulk YSZ with respect to the oxygen partial pressure at 300 K and 1000 K.

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