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A variational approach to surface cation segregation in mixed conducting perovskites

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ABSTRACT

A variational, phase-field methodology describing the segregation of dopant cations to the free surfaces of mixed conducting perovskite oxides is introduced. Based on the Cahn–Hilliard formalism for solute segregation in alloys and the Cahn theory of wetting of a solution at a solid surface, the model qualitatively predicts the experimentally observed behavior of solute segregation in oxides, which shows segregation layers on the order of tens of nanometers. Critical in this description are the interactions among defects and the gradient energy – two related concepts that can be expected to become influential at relatively high dopant concentrations. The analysis predicts that a first-order phase transition – a surface-mediated spinodal – may occur depending on the strength of dopant interactions and the affinity of dopant cations and oxygen vacancies for the free surface.

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1. Introduction

Mixed ionic–electronic conductors (MIECs) have found utility as electrode materials in solid oxide fuel cells, because they are capable of acting as both catalyst and transport medium for oxygen reduction and movement of oxygen ions towards the electrolyte. But the electrode behavior of these materials is complex, and they have proven to be fickle subjects for study: even chemically identical materials can exhibit vastly different electrochemical behaviors [1–4]. It is now widely accepted that dopant cation segregation at the gas-exposed surfaces of MIECs plays an important role in this phenomenon [5–12]. Due to the slow diffusion of cations even at elevated temperatures, different processing histories can lead to different electrochemical behaviors for the same bulk composition.

However, a holistic, quantitative thermodynamic framework for the segregation of cations at MIEC surfaces has not yet been established. Conventional space-charge calculations of the Gouy–Chapman or Mott–Schottky variety – that have been widely successful in relatively dilute systems [13–16] – cannot explain segregation layers on the order of 10 nm [10,11] in a highly-doped material where the Debye length is less than an angstrom. It is thus clear that the thermodynamics of dilute systems will not suffice and a framework pertaining to systems with high concentrations of solute must take its place.

Fortunately, such a theoretical framework is already available, in the family of variational phase-field methods: in particular the Cahn–Hilliard theory for the thermodynamics of solute segregation in alloys [17,18], supplemented for the scenario at a free surface by the Cahn theory of wetting at solid–liquid interfaces [19,20] and surface-mediated spinodal decomposition [21,22]. Variational methods have some history in the ionics field early theoretical work in the ionic solid-state demonstrated the utility of variational methods for interfaces [23,24]. In 2003, Bishop et al. [25] published a Cahn–Hilliard framework for spinodal decomposition in ionic solids. The following year, a number of studies treating electrochemical systems with a phase-field formalism appeared, including a general application of the Cahn–Hilliard framework in electrochemical systems by García et al. [26], a phase-field study of an electrode–electrolyte interface by Guyer et al. [27,28] and an application to the battery electrode LiFePO_4 by Han et al. [29]. Since then, others have adapted variational thermodynamic methods to electrochemical systems, often in the context of lithium-ion battery intercalation electrodes [30–33]. However, despite the importance of surface dopant segregation for the electrochemical behavior of mixed conductors, a general thermodynamic framework for this phenomenon which takes the defect chemistry of MIECs into account has not been reported.

Segregation is driven by short-range chemical (to include the short-range effects of cation size mismatch) as well as long-range electrostatic interactions, and as such any useful thermodynamic framework should incorporate both. A theoretical and experimental study of the segregation of dopants in lanthanum manganate

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perovskite MIECs was recently conducted by Lee et al. [34]. This study presented a hypothesis, supported by first principles calculations, that the principal driving forces for dopant segregation in these materials are the (positive) elastic energy created by the substitution of the larger strontium cation for lanthanum (other dopant and host cations were also considered), which is partially relieved at the surface, and an electrostatic interaction between the effectively negatively-charged dopant and positively-charged oxygen vacancies which also tend to aggregate at the surface. The modeling framework presented in this paper considers both types of driving forces, predicting dopant cation and oxygen vacancy concentrations as a function of temperature, the partial pressure of oxygen, material composition (bulk dopant concentration) and distance from the surface.

The concept of the gradient energy plays a critical role in the Cahn–Hilliard framework and related variational methods. Its phenomenological underpinning is that a gradient in concentration (or a gradient in the order parameter in the case of Allen–Cahn models treating two distinct phases) is associated with a strictly positive contribution to the free energy that will always be present in a concentrated system in which solute interactions (or defect interactions in an ionic context) can no longer be ignored. That the gradient energy is positive arises from the breaking of symmetry relative to the spatially homogeneous case: ordered configurations that extend infinitely in space (and represent major components of a free energy-minimizing distribution of such configurations) can no longer be realized when solute concentrations are not spatially uniform. Binder has shown that the gradient energy appearing in the Cahn–Hilliard formalism can be related to lattice models such as an Ising model [21]. In spinodal decomposition, the gradient energy coefficient determines the width of solute-rich and solute-poor regions in the spinodal. Analogously, in the segregation of charged cations to the surface, it is the gradient energy that controls the depth of cation enrichment.

2. Theory and implementation

The notation used in the following derivation will conform to the conventions of defect thermodynamics.

Consider a perovskite oxide (ABO_3) with an aliovalently doped cation (D) at the A-site, compensated by oxygen vacancies and a bound hole state at the B-site (i.e., $[D'] = [B'] + 2[V_O^\bullet]$, where the brackets indicate concentrations and the Kröger–Vink notation has been used to indicate dopants, B-site cations and oxygen vacancies). The dopant cation is assumed to be larger than the host, and as such there is a negative energy associated with a dopant cation located at the surface relative to the bulk; similarly, oxygen vacancies are energetically favored at the surface relative to the bulk. Oxygen adsorbs dissociatively at the gas-exposed surface, and is incorporated into the bulk by combining with a vacancy according to the reactions



where s is a site on the surface of the material, O' is a negatively-charged adsorbed oxygen, B' is a positively-charged B-site cation, V_O^\bullet is an effectively +2 charged oxygen vacancy, and O_O^x is a lattice oxygen ion. The domain of the problem is semi-infinite (see Fig. 1), which means either a bulk material or a film thick enough that segregation and charge separation at the free surface is not affected by segregation and charge separation at the substrate.¹

Following the development found in Refs. [19,26,20], the semi-grand potential per unit surface area is

$$\begin{aligned} \Omega[y, h, v, \phi, \theta; T, \mu_{O_2}] = & \Phi(y(0), v(0), \theta, T) - Fn_\theta \phi(0) - \frac{1}{2} \mu_{O_2} n_\theta \theta \\ & + \int_0^\infty \left[W(y, v, h, T) + \frac{1}{2} c \left(\frac{dy}{dx} \right)^2 \right. \\ & + \frac{1}{2} c_v \left(\frac{dv}{dx} \right)^2 - \frac{1}{2} \epsilon_r \epsilon_0 \left(\frac{d\phi}{dx} \right)^2 \\ & \left. + F\phi(nh + 2n_v v - ny) + \frac{1}{2} \mu_{O_2} n_v v \right] dx \quad (2) \end{aligned}$$

where $y(x)$ is the dopant site fraction, $h(x)$ the site fraction of B', $v(x)$ is the site fraction of vacancies, $\phi(x)$ is the electrostatic potential, μ_{O_2} the chemical potential of oxygen in the gas, n , n_v and n_θ are the molar densities of A or B cation sites in the bulk, oxygen sites in the bulk and adsorption sites at the surface, respectively, ϵ_r the relative permittivity, ϵ_0 the permittivity of free space and c and c_v are gradient energy coefficients. The free energy densities W and Φ pertain to the bulk and the surface, respectively. Here the gradient energy for holes along with the cross-term gradient energies are ignored.

In equilibrium, this functional is minimized with respect to the functions y , h , v and ϕ , as well as the scalar θ . The minimization is subject to two constraints related to the conservation of mass in the system:

$$\int_0^\infty (y - \bar{y}) dx = 0 \quad (3a)$$

$$\int_0^\infty (nh + 2n_v v - n\bar{y}) dx = n_\theta \theta \quad (3b)$$

where \bar{y} is the average dopant site fraction in the material. These constraints are added to the functional using Lagrange multipliers.

Obtaining the Euler–Lagrange equations involves conventional differentiation with respect to θ , and variational differentiation with respect to v , h , ϕ and y . Differentiating with respect to θ and setting the result equal to zero, it becomes clear that

$$\lambda_\theta = \frac{1}{n_\theta} \frac{\partial \Phi}{\partial \theta} \quad (4)$$

where λ_θ is the Lagrange multiplier corresponding to the constraint (3b). λ_θ can thus be eliminated from the Euler–Lagrange equations. Aside from the potential at infinity, which is fixed to zero as reference, all boundary terms are natural. However, the condition of a zero derivative at infinity for y and v , when combined with the mass conservation constraints, yields a Dirichlet condition for y , and an electroneutrality condition, which reflects the absence of charge separation in the bulk of the material. The Euler–Lagrange equations arising from the minimization of the free energy functional are thus

¹ For the purposes of this demonstrative study, the Schottky equilibrium (i.e., the influence of cation vacancies) has been expressly ignored, since this would add at least two additional field variables to the simulation. The same formalism could, however, be used to model Schottky disorder as well.

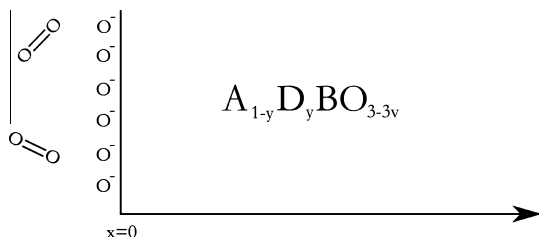


Fig. 1. The semi-infinite computational domain: the surface is in equilibrium with the bulk and the gas.

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