Full length article

# Formulation of the coupled electrochemical–mechanical boundary-value problem, with applications to transport of multiple charged species

Giovanna Bucci[*], Yet-Ming Chiang, W. Craig Carter

Massachusetts Institute of Technology, Department of Materials Science and Engineering, 77 Massachusetts Avenue, Cambridge, MA 02139-4307, USA

A B S T R A C T

A framework is presented that treats the combined effects of nonlinear elastic deformation, lattice constraints, and electrochemical potentials. The electro-chemo-mechanical diffusion potential is derived, and the particular case where ionic species are subject to a crystal lattice constraint is also derived. By combining energy balance and local entropy production, the framework provides a consistent method to treat the evolution of charged species which also carry anelastic deformations in a crystal lattice. The framework is used to derive a finite element formulation that applies to general cases of interest for diffusion of active species in battery electrodes and in fuel cells. We demonstrate the application of the finite element formulation with two cases: ambipolar diffusion and kinetic demixing. The predicted system response demonstrates how mechanical effects cannot be disregarded, even in the presence of dominant electrostatic forces acting on ion transport. A cation rich surface layer is predicted when elastic forces, due to Vegard's stress, participate in the migration of defects in a multicomponent oxides. Simulations show how stress plays a central role in the cation segregation to interfaces, a phenomenon regarded as critical to power and durability of solid oxide fuel cells.

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## 1. Introduction

Materials for energy conversion and storage have complex microstructures and their physical behavior depends on coupling of multiple mechanisms and driving forces. Macroscopic models that account for such complex phenomena are a materials-modeling challenge. For instance, modeling of electrode and electrolyte materials for Li-ion batteries or solid oxide fuel cells (SOFCs) involves diffusion of multiple charged species in a solid medium in the presence of stress, electrostatic, and chemical potential gradients. Inclusion of these multiple fields and transport mechanisms into microstructural models can be performed by finite element methods. However, as a first step in the prediction of time-dependent species distribution, induced electric fields, deformation of the solid and the effect of stress on diffusion, it is necessary to construct a rigorous formulation of the coupled physics of mass transport, induced electric fields, and nonlinear continuum mechanics. The purpose is to predict the overall electrochemical performance–including limiting factors, failure mechanisms, sensitivity to external conditions and material properties–for electro-chemo-mechanical systems with complex microstructures.

The present article proposes a quantitative description of such multifunctional materials drawn from the study of a general non-homogeneous irreversible thermodynamic system under the action of multiple physical phenomena. From this analysis, we develop a finite-element formulation and present simulations that demonstrate its applicability to ambipolar diffusion and kinetic demixing. The predictive capability of the model depends on a consistent derivation and on the choice of appropriate numerical procedures to solve it. The formulation provides a foundation for subsequent models which treat the disparate length- and time-scales in complex battery and SOFC microstructures.

We present a derivation of the driving forces for the time-dependent evolution of the state variables. At each instant in time the system is considered to be in the state of local equilibrium. Mechanical equilibrium will be treated as instantaneous (i.e.,

* Corresponding author.
E-mail address: bucci@mit.edu (G. Bucci).

static), and the transport of species is transient. To that end, we follow Larché and Cahn (see §7 in Ref. [1]): the most common partial equilibrium occurs when all processes except diffusion have relaxed to equilibrium. The local equilibrium is still guaranteed and "The only suppressed condition is that [the diffusion potential][1] $M_{IK}$, need be constant, but $M_{IK}$, remains continuous across all interfaces that have reached equilibrium [1]".

Because the system under study is non-conservative, we use the entropy-production formulation stated in the form of the Clausius–Duhem [2] inequality. In particular we will consider natural isothermal processes, according to the definition proposed by Planck [3] and adopted by several authors, including Guggenheim [4]. For such cases the Clausius–Duhem inequality reduces to the Clausius–Planck inequality [2].

The dissipation-rate density is the difference between the external power expenditure and the rate of change of free energy of the system per unit volume. It includes contributions from the transport of chemical species and that of charges. It may incorporate mechanical dissipation typical of viscous and plastic materials, however, the treatment of such constitutive behaviors is not included in the finite formulation below.

The thermodynamic framework is constructed along the lines of theories formulated by Larché and Cahn [1], Truesdell [5], and Ortiz [6]. It also borrows from more recent application to the analysis of electrochemical systems, in particular Li-ion batteries, proposed by Bower [7] [8], Anand [9], Suo [10], Wu [11]. As observed by Larché and Cahn [1], in many cases the mutual interaction between stress and diffusion cannot be ignored, therefore it will solve the equations of mechanical equilibrium and diffusion simultaneously. Furthermore, our model extends previous work by accounting for electrostatic forces and multiple charged mobile-species. This includes the internal electric field induced by the transport and distribution of ions and vacancies in order for the system to maintain local electroneutrality. The nonlinear theory of electro-elasticity cast into the Coleman-Noll formalism was originally proposed by Toupin [12], followed by several other contributions, including papers by Ogden and coauthors (see Ref. [13] for a literature review). We demonstrate the electro-chemo-mechanical applications of our model by presenting simulations of ambipolar diffusion and kinetic demixing (as defined in Ref. [14])–both being relevant phenomena in SOFCs.

Kinetic demixing (i.e., the production of non-homogeneous compositions and defect populations due to mobility differences between species) can lead to interfacial segregation. For example, some chemistries and extreme operating conditions will be shown to produce demixing at the surfaces of SOFCs' cathodes. Under operation, SOFC electrodes experience electrical biases that can redistribute their charged defects (e.g. oxygen and cation vacancies [15]). While the oxygen vacancy rapidly moves in response to this bias, cation defects, due in large part to their much lower mobility in these systems, migrate very slowly to establish a new equilibrium. Over time, a cation rich surface layer is often observed to develop in many of the advanced cathodes, blocking the critical oxygen reduction reaction and thus reducing SOFC power [16–19]. With changes in the oxidation state of the electrode (i.e., vacancy content), the relative amount of cation segregation has been shown to be modified [15]. In extreme conditions, this may even result in decomposition of the electrode material [20]. In another recent example, the oxidation state of the electrode has been controlled to intentionally segregate catalytically active cations from the bulk

oxide to the surface, with corresponding improvements in SOFC power [21].

Elastic and electrostatic interactions of dopants with the surrounding lattice have been described as the driving forces for segregation on perovskite compounds of the type $Ln_{1-x}D_xMnO_3$ (host cation Ln = La, Sm, dopant D = Sr, Ca, Ba) [15] which are among the most commonly used SOFC cathode-materials. Elastic energy differences are created by differences in the atomic volume of dopants compared to the host cations (La, Sm). Gradients in elastic energy density can affect the stability of cathode surfaces.

Atomistic studies also provide insight for some experimentally observed demixing phenomena [15,22]. Kinetic demixing has also been investigated at the continuum level for oxide solid solutions in which oxygen ions can be regarded as an immobile species [23,24]. However, these continuum approaches do not account for stress effects on diffusion and segregation of species. Stress driven kinetic demixing and decomposition has been treated by Dimos and coauthors [25].

However, a combined electro-chemo-mechanics is necessary to model complex dynamics of these multifunctional materials under a variety of external conditions and microstructures. The rigorous continuum-model proposed herein is amenable for numerical treatment and for the investigation of a wide range of technologically relevant systems in a rigorous quantitative manner. Central to the formulation is the derivation of a diffusion potential for each independent species–the gradients of which drive mass transport. Below, we simplify the formulation by assuming that the diffusion potential can be written as a sum of the chemical, electrostatic, and stress potentials and adopt a mixed finite-element method [26].

Three example applications have been selected for demonstration of the formulation's capability:

- In Section 4.2, simulations of kinetic demixing, in the presence of Vegard's stresses and in the absence of stress are presented. The simulation shows that stress plays a central role in the segregation to interfaces: the time-dependent evolution of stress should not be ignored in the formulation, even when there are large electric fields. The results have direct applicability to electrode surface properties in SOFCs.
- Simulations that illustrate stress-effect ambipolar diffusion are presented in Section 4.1. These simulations show the predominance of electrostatic compared to chemical and mechanical driving forces: stresses on the order of 1 GPa are insufficient to decouple the transport of charges of opposite sign.
- The example of mechanically driven diffusion in Section 4.3 illustrates the role of stress as a driving force in cases where intercalation is coupled with anelastic deformation of the host lattice. Furthermore, it treats a highly non-homogeneous stress field in addition to the Vegard's stresses.[2]

The range of applications that can be approached goes well beyond the one proposed here and can be further extended in a straightforward manner. The development of this model has been motivated by the need for a rigorous and robust tool

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[1] In this paper, we use $\varpi_i$ as notation instead of the Larché-Cahn notation $M_{iK}$. The second dependent species $K$ is treated explicitly.

[2] Larché and Cahn's work mostly focused on the effect of self-stress, i.e., stress induced by non-homogeneous concentration. In [27] Larché and Cahn took into account problems, which require "the simultaneous solution of the equations of elasticity and those of chemical equilibrium". However, they were able to decouple the chemo-mechanical problem under the assumption of constant diffusion potential. The use of numerical methods permits solutions to a fully coupled electrochemical-mechanical problem with external applied loads.