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Analytical solutions for composition and stress in spherical elastic–plastic lithium-ion electrode particles containing a propagating phase boundary

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ABSTRACT

Analytical solutions are derived for the distribution of Li concentration, chemical potential, and stress in a spherical particle of an active Li insertion material containing a propagating phase boundary. Results are presented both for elastic and inelastic host materials. We focus in particular on understanding the coupling between the solution thermodynamics, transport, and mechanical forces in the particle. It is shown that solution chemistry can have a strong influence on the stress state; and conversely, the stress state may significantly alter the equilibrium conditions at the phase boundary and the driving forces for phase boundary migration.

1. Introduction

Nearly all Li ion insertion electrode materials phase separate when lithium is removed from or inserted into the host material. Cathode materials Li_xCoO_2, $Li_xMn_2O_4$ form as many as seven different Li compounds (Mukhopadhyay and Sheldon, 2014) while cathodes of lithiated $LiFePO_4$ experience a first order phase transformation to $FePO_4$ when delithiated (Tang et al., 2010). Similarly, the widely used LiC_x anodes exhibit staging, which is attributed to phase separation; crystalline Si anodes undergo a crystalline–amorphous phase transformation; and lithiated Sn anodes form five compounds with progressively increasing stoichiometric lithium concentrations (Mukhopadhyay and Sheldon, 2014). Recent experiments have reported a sharp interface that appears to resemble a phase boundary even in amorphous Si thin-film electrodes, although little is known at present about the structure or origin of this interface.

The interfaces that form between phases play a critical role controlling both the rates at which the material can be charged and discharged, as well as the stress induced in the particle during lithiation. For example, the superior charge–discharge response of nanoscale doped $LiFePO_4$ has been attributed to a lower mismatch strain between its phases, as well as a higher mobility of the phase boundary (Meethong et al., 2007). Hysteresis losses in cathodes have been attributed to the collective dynamics of phase separating particles (Dreyer et al., 2010, 2011; Delmas et al., 2008). The degradation of candidate high-capacity anode materials, including Sn (Li et al., 2014) and crystalline Si (Limthongkul et al., 2003) is associated with the low mobility of phase boundaries in these materials (McDowell et al., 2012).

This has motivated numerous studies that aimed to predict and characterize the behavior of an electrode particle containing one or more propagating phase boundaries. These can be divided into two broad groups: in one approach, the particle geometry is approximated as a sphere, with a core consisting of one phase encapsulated within a shell of the second phase (Subramanian and White, 2001; Subramanian et al., 2000; Zhang and White, 2007; Srinivasan and Newman, 2004; Park et al., 2011; Deshpande et al., 2011; Renganathan et al., 2010). In this case, analytical expressions can often be obtained for stresses and Li concentration distributions within the particle. If the solution thermodynamics or kinetic relations are too complicated to permit an analytical solution, the governing equations reduce to a simple ordinary differential equation that can be solved numerically. These simple models are insightful but are restricted to simple geometries and isotropic material behavior. The effects of material anisotropy or complex particle geometries can only be predicted with the aid of numerical simulations. The phase field method is widely used for this purpose. In this approach, the free energy of the host is represented as a non-convex function of the concentration, but the formation of sharp discontinuities in concentration is prevented by including a term in the free energy that is proportional to the concentration gradient. By selecting appropriate forms for the free energy and

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mobility, a wide range of phenomena can be included in phase field simulations (Cogswell and Bazant, 2012; Dargaville and Farrell, 2013; Di Leo et al., 2014; Anand, 2012; Han et al., 2004; Huttin and Kamlah, 2012; Singh et al., 2008; Tang et al., 2009).

These prior studies have used a wide range of different descriptions of the thermodynamics and kinetics associated with the phase transformation. In some cases, a concentration distribution that resembles phase separation is produced by introducing a concentration dependent diffusion coefficient (Liu et al., 2011; Drozdov, 2014) or by adopting a chemical potential for Li that has near flat regions (Baker and Verbrugge, 2012). The latter approach can be interpreted as modeling a two-phase mixture, without explicitly considering the motion of the phase boundaries or the evolution of the underlying microstructure (Bohn et al., 2013). Under non-equilibrium conditions, these materials will develop regions with approximately uniform Li concentration, which are separated by narrow regions with large concentration gradient. If the materials are allowed to equilibrate, however, they will always return to a uniform concentration: the possibility of a stable microstructure consisting of two coexisting phases in which the Li concentration differs is precluded. In another approach, a sharp phase boundary is introduced, which separates solids with different equilibrium Li concentrations. Equilibrium conditions in sharp-interface models can be calculated by straightforward energy minimization: for example, Meethong et al. (2007) use energy arguments to determine the influence of elasticity on phase equilibria and nucleation of a second phase in Olivine based cathode particles. Modeling the transient conditions that develop during Li insertion is more challenging, but has been treated in several studies (Subramanian and White, 2001; Subramanian et al., 2000; Zhang and White, 2007; Srinivasan and Newman, 2004; Park et al., 2011; Deshpande et al., 2011; Renganathan et al., 2010). These have focused primarily on understanding the influence of the moving phase boundary on the transient evolution of concentration in the particle, and in some cases also consider the resulting effects on the behavior of a full cell. In these models, the phase boundary is assumed to be highly mobile in comparison to the rate of Li transport through the bulk, and the influence of stresses on Li transport and phase boundary motion is neglected. Most studies also assume ideal solution thermodynamics in the bulk phases.

Sharp interface models have also shown that the presence of a phase boundary has a significant influence on the stress state in electrode particles. The stresses in turn influence Li transport through the particle. The fully coupled problem has been solved with the aid of numerical simulations (Park et al., 2011; Renganathan et al., 2010). Deshpande et al. (2011), were also able to find analytical expressions for the stresses by neglecting the influence of stress in driving diffusion. The phase boundaries were treated approximately in these studies, by assuming that the Li concentrations remain at their stress-free stoichiometric equilibrium values, and assuming that the phase boundary is perfectly mobile. In addition, they assumed that the particle remains elastic, which is a good approximation for most cathode materials and for graphitic anodes.

High capacity materials such as Sn and crystalline Si are known to deform plastically during phase changes that accompany Li insertion and removal (Sethuraman et al., 2010). Recent experiments and calculations suggest that plastic flow significantly alters the stress state in a particle containing a propagating phase boundary. For example, experiments have revealed fracture initiation at the surface of crystalline Si particles during the first lithiation cycle (Liu et al., 2012). Elastic solutions predict that Li insertion generates compressive stress at the particle surface (Deshpande et al., 2011), and consequently cannot account for this failure mechanism. In addition, the kinetics of the crystalline/amorphous phase boundary is believed to be the rate limiting process during lithium insertion into these materials (McDowell et al., 2012; Zhao et al., 2012). Experiments show that the mobility of the interface is strongly anisotropic (Yang et al., 2012), and the deformation associated with the transformation from a crystalline to amorphous state also appears to depend on the orientation of the interface with respect to the crystalline phase (Liu et al., 2012; Lee et al., 2011). A number of recent studies have helped to explain and quantify these observations. Models have shown, for example, that plastic flow occurs concurrently with the phase transformation just behind the crystalline–amorphous phase boundary, and that one consequence of this plasticity is that the stresses at the surface of a particle are tensile (Liu et al., 2012; Zhao et al., 2012; Huang et al., 2013). Models have also confirmed the important role of the kinetics of the crystalline/amorphous phase boundary in controlling both the Li insertion rate at constant chemical potential (McDowell et al., 2012), as well as the stress state in the particle (Zhao et al., 2012; Yang et al., 2012). Despite these advances, however, these have treated the phase boundary approximately, either by introducing a concentration dependent diffusion coefficient (Yang et al., 2012), or by estimating the driving force for a sharp interface based on the volume expansion across the phase boundary (Zhao et al., 2012).

Numerical phase-field simulations are capable of providing a more detailed picture of phase separation in electrode materials. Early models adapted the Cahn–Hilliard equations to model phase separation in isotropic, stress free particles (Han et al., 2004), and have since been extended to account for elasticity (Cogswell and Bazant, 2012), finite strain plasticity (Anand, 2012), non-ideal solution thermodynamics, (Bazant et al., 2009) and to model explicitly the charge-transfer reactions at the particle surface (Singh et al., 2008). They have also been incorporated into homogenized porous electrode models (Ferguson and Bazant, 2012). Phase-field simulations can treat complex microstructural evolution in phase-separating particles, and give predictions that are in good agreement with experiment. Their disadvantage is that their governing equations can only be solved numerically. In particular, in these models the kinetics of the phase boundary are determined by the details such as the gradient terms in the free energy and the variation of diffusivity with concentration, and it is consequently difficult to isolate their effects.

In this paper, our intent is to clarify the roles of solution thermodynamics, mechanical stress, and kinetics, on the behavior of electrode particles containing propagating phase boundaries. For simplicity, we restrict attention to a material that forms only two phases; and furthermore, approximate an electrode particle as a perfect sphere, in which the core and a surrounding shell contain the two phases. This has the advantage that (with a few simplifying approximations) exact solutions can be found for concentrations, stress, and chemical potential for both elastic and elastic–plastic materials, and also that key material parameters that control material behavior can easily be identified. Our analysis aims to answer the following questions: (1) How do solution thermodynamics (quantified by the variation of free energy of a stress free material as a function of its composition) influence stresses in a particle? (2) How does stress influence deviations from the stoichiometric composition in the particle; (3) how do the kinetics of phase boundary migration influence stresses and composition; and (4) how does plasticity influence the stress and composition in a phase separating particle?

We begin by reviewing briefly the standard thermodynamic treatment of phase separation in a stress-free particle. In particular, equilibrium conditions that determine the stoichiometric Li concentrations in the two phases are reviewed, and the influences of the kinetics of Li transport through the bulk phases, as well as the kinetics of phase boundary migration on concentration distributions in the particle are calculated. Conditions where phase