Continuum and atomistic models of strongly coupled diffusion, stress, and solute concentration

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ABSTRACT

Poor cyclic performance of electrodes in lithium-ion rechargeable cell batteries is calling for efforts to develop continuum models of diffusion under very large stresses and high solute concentrations. The present work is aimed to develop such a model based on input from atomistic simulations. We consider four fundamental features of highly nonlinear behavior associated with diffusion at high solute concentrations. First, the effect of solute-induced stresses on the activation energy of solute diffusion could be important. Second, the solute concentration may be subject to an upper limit if there exists a stoichiometric maximum concentration. Third, the strong influence of the change in local chemical environment on the interaction energy between solute and host atoms could play a significant role. Fourth, we include the effect of the solute concentration on the Young's modulus of the host material. A continuum model is developed and validated based on atomistic simulations of hydrogen diffusion in nickel. The influences of each feature above are clearly discussed through parametric studies.

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1. Introduction

Rechargeable battery cells have recently received much attention due to their broad potential applications in a variety of technologies including military, automobile, aerospace and medical industries [1,2]. Among various types of rechargeable batteries, lithium-ion (Li-ion) cells featuring higher energy capacity, higher operating voltage, lower self-discharge and lower maintenance requirement have become the most widely used secondary battery systems [3]. In the past, significant research has been directed toward increasing the charge and energy capacity of Li-ion batteries [1]. It has been shown that a noticeable increase in the charge capacity of batteries is achievable using Li-alloy (Li_xM; M = Sn, Si, Ge, Al) anodes [4]. Silicon (Si) possesses the highest known theoretical charge capacity (4200 mAh g^{-1}) corresponding to the formation of $Li_{22}Si_5$ but this capacity is accompanied by a 400% volume expansion [5]. Very large mechanical stresses associated with such a huge volume change during Li intercalation/deintercalation are responsible for poor cyclic behaviors of the Si anodes by inducing pulverization, fracture, loss of integrity and loss of electric contact with current collector. This major liability is obstructing the way toward widespread application of the Si anodes [2,6–11].

Much theoretical work has been devoted to continuum modeling of diffusion in battery electrodes. A number of continuum thermodynamics and kinetics models have been proposed in the literature such as the theory of porous electrodes [12,13] and the Dualfoil cell-sandwich model [14,15]. In addition, a large volume of publications has been devoted to the study of stress generation, deformation and fracture during diffusion. Study of diffusion-induced stresses based on an analogy with thermal stresses can be traced back to the work of Prussin [16]. The study was broadened to include the development of stresses during mass transfer in thin plates, solid cylinders and spheres, where the stress-diffusion coupling was considered by including the elastic inclusion energy of solute in the chemical potential [17–19]. During the past decade, an increasing number of continuum models of diffusion-induced stresses during charging/discharging of electrodes have been developed [20–26], some even accounting for the effects of surface tension and surface modulus [27–29]. Criteria for fracture in electrodes have also been discussed based on the maximum tensile stress criterion [22,23,25] and cohesive crack nucleation model [30].

Despite these developments, continuum models of diffusion under very large stresses and high solute concentrations usually face the challenge of strongly nonlinear system behavior. Validation of such models is often subject to limitations in experimental techniques. For instance, Christensen and Newman [22] presented an integrative model accounting for a number of different physical effects whose experimental validations are still lacking. Moreover, most of the existing models are either strictly applicable only in the limit of dilute concentrations [20,21,24,25] or do not account for non-conventional stress-diffusivity couplings

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that could be of importance for concentrated solutions and large stresses [22,23,26].

The aim of the present paper is to explore a simulation-based approach to developing continuum models of strongly nonlinear and coupled diffusion under very large stresses and high solute concentrations. Our model includes the effects of solute-induced stresses on the activation energy of solute diffusion, an upper limit for solute concentration, the interaction energy between solute and host atoms, as well as the effect of the solute concentration on the Young's modulus of the host material. On the other hand, we neglect the effects of surface tension and surface modulus [27–29] so that our model is really trying to capture the "bulk" behavior starting just inside the surface (associated with the flow of the material into the "bulk" due to an imposed flux at the "real" interface). In this way, our model is not a nanoscale model and has no special kinetics or energetics at the continuum surface. Although our atomistic simulations will be at nanoscale, the simulations are specially designed to avoid complications at a real electrolyte/material interface by artificially imposing an input flux inside the material just away from the outermost surface atomic layer, where bulk thermodynamics and kinetics applies (see more discussions later).

The paper is organized as follows. In Section 2, we introduce a continuum analytical model taking into account the four nonlinear features mentioned above. In Section 3, we discuss hydrogen in nickel as a test system to provide data against which the analytical model can be compared. The underlying material parameters needed in the continuum model are computed and the methods to accomplish direct molecular dynamics (MD) modeling of the charging of Ni by H at various rates are discussed. Section 4 contains our comparison of the analytical model against the MD, and demonstrates the role of the factors noted above in achieving quantitative predictions in the continuum model. We then investigate the influence of each individual physical effect on the overall charging process. A comparative study between the MD results and two versions of the classical models is also presented in Section 4. We conclude this section with a discussion on the applicability of the present model to the case of Li-ion batteries with Si anodes. A summary of our results is given in Section 5.

2. Continuum modeling of diffusion

For simplicity, consider one-dimensional diffusion in a plate under large stresses and high solute concentrations. We start by introducing a chemo-mechanical potential including the effect of high solute concentrations on the entropy of the system, the work required to insert an inclusion into an elastic matrix, and the concentration-dependent heat of solution. The diffusion-induced stresses are then presented for an infinitely extended free-standing plate using small-deformation theory, considering that the Young's modulus of the plate may vary with the solute concentration. We then introduce the stress-diffusivity coupling through the effect of internal stress field on the activation energy of diffusion. Finally, the generalized governing 1D diffusion equation is derived and the solution methodology is discussed.

2.1. Chemo-mechanical potential

To demonstrate the basic approach of simulation-based continuum modeling, we consider interstitial diffusion of solute atoms in a host solid. The interstitial sites of the host solid form a sublattice. With respect to this sublattice, the diffusion of the solute atoms can be viewed as a substitutional mechanism. The total number of interstitial sites in the original host lattice is assumed to be preserved.

In the continuum modeling of diffusion in solids, the drift velocity v and hence the flux of the diffusing species in the host material

is given by [20,31,32]

$$J = cv = -Mc\nabla\mu^*, \tag{1}$$

where M is the mobility of the diffusing component, c is the solute concentration and μ^* is the chemo-mechanical potential incorporating the chemical and mechanical energies of the system. In the presence of internal stresses, the chemo-mechanical potential is expressed in terms of the chemical potential of the solute atoms μ_s and vacancies μ_v, partial molar volume of the solute Ω and the hydrostatic stress in the host solid σ_h as [32,33]

$$\mu^* = \mu_s - \mu_v - \Omega\sigma_h, \tag{2}$$

where

$$\mu_i = \mu_i^0 + RT \log a_i. \tag{3}$$

Here, $i \equiv s, v$ corresponds to the solute and vacancy components, respectively, μ_v^0 is the free energy of the host solid accommodating 1 mol of the vacant interstitial sites, μ_s^0 is the free energy of the same system when the interstitial sites are occupied by the solute atoms, R is the gas constant and T is the absolute temperature. The activity a_s accounts for the interaction energy between the host and solute atoms. A similar treatment of vacancies can be found in the thermodynamic description of adsorption equilibrium via vacancy solution theory [34,35], where activity of the vacancies is interpreted as the interaction between the adsorbate molecules and the host solid [36–38].

Recognizing the existence of a stoichiometric maximum concentration c_{max}, activities of the components are related to their site fractions through $a_s = \gamma_s\tilde{c}$ and $a_v = \gamma_v(1 - \tilde{c})$, where $\tilde{c} = c/c_{max}$ and, γ_v and γ_s are the activity coefficients of the vacancies and solute atoms, respectively.

Therefore, the chemo-mechanical potential takes the following form:

$$\mu^* = \mu_0^{sv} + RT\log\frac{\tilde{c}}{1-\tilde{c}} - \Omega\sigma_h + RT\log\frac{\gamma_s}{\gamma_v}, \tag{4}$$

where $\mu_0^{sv} = \mu_0^s - \mu_0^v$ is a constant. Eq. (4) accommodates three important physical effects associated with high solute concentrations and large stresses as follows.

The second term on the right hand side of Eq. (4) is due to the entropy of a simple solution where the solutes occupy a fixed set of sites, such as interstitial or substitutional sites in the host material. For dilute solutions, where $\tilde{c} \ll 1$, this term reduces to the usual form $RT \log \tilde{c}$. However, the entropy of the system should reduce to zero as all the available sites in the host are filled with the solutes and so it is not possible to reach the saturation point. Introduction of this effect enables the present model to recognize a saturation limit for the host solid. Throughout this paper, this effect is referred to as the saturation effect.

The third term on the right hand side of Eq. (4) is the elastic energy associated with insertion of an inclusion of volume Ω into the matrix under the hydrostatic stress σ_h. This term was considered by Li [17], and is well-established in other contexts including diffusion around dislocations [39,40]. This effect is interchangeably referred to as the effect of hydrostatic stress or inclusion energy in the rest of this paper.

The last term on the right hand side of Eq. (4) represents the deviation of the solution behavior from an ideal solution which is ideal over the entire range of its composition [41]. This term reduces to a constant for dilute solutions and vanishes for an ideal solution. However, at high solute concentrations, the change in the chemical environment of the solution influences the interaction energy of the solute and host atoms. Since the activity coefficients γ_v and γ_s are related through the Gibbs–Duhem equation, they are determined based on the excess molar Gibbs free energy of the solution $G_{Ex}(\tilde{c})$ via $(\tilde{c}(1 - \tilde{c})/RT)(d^2G_{Ex}/d\tilde{c}^2) = (\partial\log\gamma_s/\partial\log\tilde{c}) = (\partial\log\gamma_v/\partial\log$