



Chemo-mechanical modeling of elastic thin-film electrodes on elastic substrates under chemical equilibrium



Hamed Haftbaradaran

Department of Civil Engineering, Faculty of Engineering, University of Isfahan, 81744-73441 Isfahan, Iran

ARTICLE INFO

Article history:

Received 30 April 2015

Revised 27 December 2015

Available online 24 February 2016

Keywords:

Thin-film electrodes

Delamination

Stress intensity factor

Chemical potential

Membrane approximation

ABSTRACT

High-capacity anodes hold great promise for the next-generation lithium-ion batteries. However, they are well known to suffer from mechanical failure during battery cycling. Among various nano-structured electrodes, nano-scale thin-film electrodes have been frequently observed to undergo fracture and delamination. In this work, we investigate the effect of nonlinear coupling between chemical and mechanical fields on the distribution of solute concentration and stress in a finite thin-film elastic electrode bonded to the surface of a thick chemically-inactive elastic substrate. The film is considered in chemical equilibrium with an external mass reservoir. It is demonstrated through numerical and analytical methods that chemo-mechanical coupling could lead to considerable solute segregation at the edges of the film. The coupling could also remarkably magnify the edge stress intensity factor beyond the classical predictions in the absence of coupling. Potential implications of the results in terms of prediction of a critical film thickness to avoid film delamination, and in terms of prediction of fatigue delamination growth are also discussed.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Rechargeable battery cells have recently attracted significant attention among researchers owing to their broad potential applications in a variety of technologies. Among various rechargeable cells, lithium-ion (Li-ion) batteries have gained critical importance due to their higher energy capacity, higher operating voltage, lower self-discharge and lower maintenance requirement (Tarascon and Armand, 2001). Therefore, increasing the charge and energy capacity of Li-ion batteries has been the centerpiece of many studies in the past. It has been shown that noticeable increase in the charge capacity is achievable through replacing the conventional carbonaceous anodes with high-capacity Li-alloy (Li_xM ; $\text{M} = \text{Sn}, \text{Si}, \text{Ge}, \text{Al}$) anodes (Kim et al., 2006). For instance, as compared to the conventional graphite providing a capacity of 372 mAhg^{-1} , Sn and Si respectively allow for capacities of 990 mAhg^{-1} and 4200 mAhg^{-1} corresponding to the formation of $\text{Li}_{4.4}\text{Si}$ and $\text{Li}_{4.4}\text{Sn}$ (Beaulieu et al., 2001). However, high-capacity anodes are well known to suffer from early capacity fading which is often attributed to the mechanical failure of the host material and loss of electronic contact with the current collector or other conductive phases (Beaulieu et al., 2001). To alleviate the mechanical stresses and avoid the associated mechanical failure modes, many recent studies have focused on nano-scale electrodes in the

form of particles (Liu et al., 2012), wires (Chan et al., 2008; Huang et al., 2010; Kushima et al., 2011; Liu et al., 2011) and films (Graetz et al., 2004; Li et al., 2011; Maranchi et al., 2006; Soni et al., 2011). Although nano-structured electrodes generally exhibit improved mechanical performance as compared to their bulk counterparts, recent theoretical as well as experimental studies reveal that mechanical failure can still take place in nano-electrodes (Liu et al., 2011; Liu et al., 2012; Wang et al., 2012; Xiao et al., 2011a).

Among various nano-structured electrodes, nano-scale thin films have been broadly investigated in the recent years. Cracks created through the film thickness and film delamination from the current collector have been frequently observed in thin-film electrodes. Many studies have therefore aimed to improve mechanical stability of thin-film electrodes during cycling, for example via reducing electrode particle size below a critical fracture-tolerant size (Graetz et al., 2003; Wang et al., 2012), enhancing adhesion at the film-substrate interface (Kim et al., 2008; Lee et al., 2004; Magagnin et al., 2001) and surface modification using atomic layer deposition (ALD) (He et al., 2011; Xiao et al., 2011b). It has been suggested that formation of a crystalline phase which leads to generation of large stresses in Si films can be suppressed by reducing the film thickness below a critical film thickness of about $2 \mu\text{m}$ (Hatchard and Dahn, 2004). Extensive plastic deformation, fracture and delamination induced by Li cycling have been observed in 250 nm Si thin films deposited on copper foils (Maranchi et al., 2006). More recent experiments indicate that fracture occurs in continuous 100 nm Si films deposited on copper substrates (Xiao

E-mail address: h.haftbaradaran@eng.ui.ac.ir

et al., 2011a). Mud-like crack patterns formed in thin films due to repeated cycling have been investigated both theoretically and experimentally (Li et al., 2011; Wang et al., 2012). Theoretical studies estimate a critical film thickness between 50 nm and 200 nm to avoid through-the-thickness fracture in Si thin films (Haftbaradaran et al., 2013; Zhao et al., 2011).

Although through-the-thickness cracks result in partial capacity loss due to the formation of solid-electrolyte interphase (SEI) at the crack faces, film delamination from the underneath current collector is a far more critical issue in terms of capacity fading in thin-film electrodes. Recent studies on patterned 100 nm-thick Si films have investigated effect of lateral size on the delamination behavior of Si islands (Haftbaradaran et al., 2012; Xiao et al., 2011a). The effect of diffusion-induced stresses on the onset of delamination in patterned thin films was considered by Lu et al. (2015). Effects of segregation-induced interface embrittlement (Pal et al., 2013) as well as plastic deformation both in the film (Liu, 2015) and substrate (Pal et al., 2014) have also been examined.

While film delamination induced by thermal or lattice mismatch strain is a classical problem in the theory of thin films (Freund and Suresh, 2003), not much attention has been directly focused on how coupling between mechanical stresses and solute distribution in a thin-film electrode could alter results of the classical theory of thin film delamination (Haftbaradaran, 2015; Haftbaradaran and Qu, 2014). Here, we consider a finite thin-film elastic electrode bonded to the surface of a thick chemically-inactive elastic substrate. The goal of the present study is to investigate the effect of chemo-mechanical coupling on the distribution of solute concentration and axial stress in the film as well as on the distribution of shear stress along the film-substrate interface when solute particles in the film are in chemical equilibrium with an external mass reservoir. The paper is organized as the following. In Section 2, the fundamental equations capturing the nonlinear coupling between chemical and mechanical fields are first outlined. The governing equation is then derived in the form of a nonlinear singular integral equation in terms of the interface shear stress. Special cases of the governing equation where the chemo-mechanical coupling is either extremely weak or extremely strong are examined in Section 3. It is shown that in the presence of sufficiently strong chemo-mechanical coupling, there exists a strong tendency for solute to segregate at the edges of the film and the stress intensity factor could considerably exceed beyond the classical predictions where such coupling is not present. In Section 4, we present results obtained via numerical solution of the governing equations for a broad range of chemo-mechanical coupling. The effects of chemo-mechanical coupling on the solute distribution and segregation behavior, axial stress distribution and maximum stress in the film are scrutinized in detail. Numerical values of the stress intensity factors are also given for various film aspect ratios at any level of coupling. In closure, a summary of the results is presented in Section 5.

2. Formulation

Consider a thin-film elastic island of width $2b$, and thickness h on a thick elastic substrate as shown in Fig. 1. The coordinate system (xyz) is introduced such that the center of island is located at $x = 0$, and the film-substrate interface extends over $z = 0$, $+b \geq x \geq -b$. Both the island and substrate are considered indefinitely extended in the y direction. The thin-film island, as opposed to the underneath substrate, is considered chemically active. The surface of the island is considered in contact with an infinitely large mass reservoir such as a liquid electrolyte (see Fig. 1). In this work, we consider a quasi-static intercalation process during which chemical equilibrium between the film and reservoir is achieved instantaneously. In other words, it is assumed that the charging rate is

sufficiently small so that solute particles in the film can be considered in instantaneous equilibrium with those in the reservoir. Further, since this work is focused on the effect of chemo-mechanical coupling on solute and stress distribution in the film, for the sake of simplicity, the surface effects which could arise at the free surfaces of the film are not taken into consideration.

2.1. Chemical equilibrium

Chemical potential of a solute in an ideal dilute solid solution and in the presence of internal stresses is given by Larché and Cahn (1973),

$$\mu = RT \log(c/c_0) - V_m \sigma_h, \quad (1)$$

where R is the gas constant, T is the absolute temperature, c is the solute concentration, c_0 is a fixed concentration, V_m is the partial molar volume of the solute, and σ_h is the hydrostatic stress in the host solid. The first term on the right hand side of Eq. (1) is due to the entropy of the solution, and the second term is the elastic energy associated with insertion of volume V_m into the host solid under the hydrostatic stress σ_h .

Here, the thin-film island is assumed sufficiently thin so that its deformation can be approximated as that of a membrane (Erdogan and Joseph, 1990). Therefore, the only non-zero stress components in the film are σ_x , σ_y . Invoking the analogy between the intercalation-induced stresses and thermal stresses (Prussin, 1961), the normal components of strain in the film can be written as

$$\varepsilon_x = \hat{\sigma}_x - \nu \hat{\sigma}_y + \varepsilon_c, \quad (2)$$

$$\varepsilon_y = \hat{\sigma}_y - \nu \hat{\sigma}_x + \varepsilon_c, \quad (3)$$

where

$$\varepsilon_c = \frac{1}{3} V_m c, \quad (4)$$

is the solute-induced strain in the island, ν is Poisson's ratio of the film, $\hat{\sigma}_x = \sigma_x/E$, $\hat{\sigma}_y = \sigma_y/E$ are dimensionless stresses, and E is the Young's modulus of the film. Under the assumptions stated above, deformation of the film is essentially plane strain, with $\varepsilon_y = 0$. Thus, using Eq. (3), one may write

$$\hat{\sigma}_y = \nu \hat{\sigma}_x - \varepsilon_c, \quad (5)$$

and therefore, the hydrostatic stress in the film can be written as

$$\sigma_h = \frac{1}{3}(\sigma_x + \sigma_y) = \frac{1}{3}[(1 + \nu)\sigma_x - E\varepsilon_c]. \quad (6)$$

Here, we assume that solute particles in the film are in chemical equilibrium with an infinitely large mass reservoir which maintains a uniform chemical potential everywhere in the film,

$$\mu = \mu_R, \quad (7)$$

where μ_R represents the chemical potential of solute in the reservoir. Eqs. (1), (6) and (7) together can be cast into the following dimensionless form

$$\varepsilon_c \exp[\eta \varepsilon_c] \exp[-\eta(1 + \nu)\hat{\sigma}_x] = \frac{1}{3} V_m c_0 \exp\left[\frac{\mu_R}{RT}\right], \quad (8)$$

where $\eta = \frac{V_m E}{3RT}$ is a dimensionless constant representing the strength of interaction between chemical and mechanical fields. One should note that the coupling parameter η as defined above, at a given temperature, depends only on the properties of the solute and matrix, and is independent of the actual stress which arises in the film due to solute insertion. Room-temperature values of the chemo-mechanical coupling parameter η are given in Table 1 for the materials involved in several energy-storage systems. This table indicates that η varies about two orders of magnitude in typical materials systems.

Download English Version:

<https://daneshyari.com/en/article/277102>

Download Persian Version:

<https://daneshyari.com/article/277102>

[Daneshyari.com](https://daneshyari.com)