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Solute segregation and stress intensity factors at the edge of elastic thin-film electrodes under chemical equilibrium

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HIGHLIGHTS

- A fully coupled chemo-mechanical model is developed for a thin-film electrode.
- The model describes solute and stress distribution in the electrode.
- The stress intensity and solute segregation factors are derived at the film edge.
- Chemo-mechanical coupling significantly magnifies the stress intensity factor.
- A modified critical film thickness to avoid electrode delamination is proposed.

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ABSTRACT

High-capacity anodes hold great promise for the next-generation lithium-ion batteries. However, such electrodes are known to suffer from mechanical degradation during battery cycling. One important failure mode commonly observed in thin-film electrodes is film delamination from the underneath current collector. Here, by accounting for the nonlinear coupling between the chemical and mechanical fields, we derive the stress intensity and solute segregation factors close to the edge of a thin elastic film which is bonded to the surface of a thick elastic substrate. The film is considered in chemical equilibrium with an external mass reservoir. While in the limit of extremely weak coupling, our formulation reduces to the classical delamination theory, the results indicate that the chemo-mechanical coupling leads to magnification of the stress intensity factor and solute segregation near the film edge. The effect of coupling on the solute and stress distribution in the film is discussed. Further, an analytical expression is derived for the edge stress intensity factor in the limit of extremely strong chemo-mechanical coupling, based on which a modified critical film thickness to avoid edge delamination is proposed. Potential implication of the results for fatigue delamination growth is also discussed.

1. Introduction

Lithium-ion (Li-ion) batteries are gaining critical importance in a variety of technologies such as automobile, aerospace, and medical industries [1]. Increasing charge and energy capacity of Li-ion batteries have been the focus of many studies in the past. It has been shown that Li-alloy (Li_xM; M = Sn, Si, Ge, Al) anodes exhibit much higher charge capacity as compared to the conventional graphitic electrodes [2], and thus, hold great promise for application in the next-generation Li-ion batteries. For instance, the highest known theoretical charge capacity belongs to Si (4200 $mAhg^{-1}$ corresponding to the formation of $Li_{22}Si_5$) and is nearly ten times that of graphite [3]. However, most of the high-capacity anodes suffer from capacity fading after only a few cycles. Such capacity fading is often attributed to the mechanical disintegration of the host electrode which is caused by large mechanical stresses induced during solute insertion and extraction [1]. To alleviate the mechanical stresses and avoid the associated mechanical failure modes in electrodes, many recent studies have focused on various nano-scale electrodes, such as nano-films [4–7], nano-wires [3,8,9], and nano-particles [10].

Among various nano-structured materials, nano-scale thin-film electrodes deposited on thick substrates have been intensely studied in the recent years. Experimental studies have frequently reported mechanical degradation in such electrode systems. Significant effort has been devoted to improving mechanical stability of thin-film electrodes, for example via reducing the size of Si

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particles below a critical fracture-tolerant size [11] and enhancing adhesion at the film-substrate interface [12]. It has been shown that formation of a crystalline phase during lithium insertion/extraction which could lead to the emergence of large mechanical stresses and cause fracture in Si thin-film electrodes is suppressed when the film thickness decreases below about 2 μm [13]. In one study, it has been observed that 250 nm thick Si films on copper foils, due to fracture and delamination after only a limited number of cycles, lose a major fraction of their initial near theoretical charge capacity [5]. Theoretical studies which account for the plastic deformation of lithiated Si, estimate a critical film thickness between 50 nm and 200 nm to avoid fracture in Si thin films [14,15]. Through-the-thickness cracks have been observed in a more recent study on continuous Si films with thickness of 100 nm on thick copper foils [16]. The same study has investigated mechanical performance and delamination behavior of Si thin films by depositing patterns of Si square islands with different lateral sizes on copper substrates, concluding that the lateral size of the islands is a critical factor for their mechanical stability [16].

While formation of microcracks through the thickness of the films leads to partial capacity fading in thin-film electrodes, a far more critical issue for capacity fading of such electrodes is film delamination from the underneath current collector [5,16]. Recent theoretical studies have investigated this issue accounting for various effects including potential sliding at the film-substrate interface [17], plastic deformation in the film and/or substrate [18], and interface embrittlement [19]. Although film delamination due to thermal or lattice mismatch strain is a well-studied matter in the classical theory of thin films [20], not much attention has been directly focused on how interaction between mechanical stresses and solute distribution in the film could alter the classical theory of thin film delamination [21]. To investigate this, here we consider a semi-infinite elastic thin-film electrode which is bonded to the surface of a thick elastic substrate, and is in chemical equilibrium with an external mass reservoir. The goal of the current work is to investigate the effect of chemo-mechanical coupling on the stress and solute distribution in the film. Particular attention is directed to the effect of chemo-mechanical coupling on the stress intensity factor as well as on the solute segregation near the film edge. The paper is organized as the following. In Section 2, we first develop the equations which fully capture the nonlinear coupling between the stress and solute distribution in a nano-scale thin-film electrode under chemical equilibrium. A governing nonlinear singular integral equation for the shear stress at the film-substrate interface is derived. In Section 3, we focus our attention on two limiting cases. It is first demonstrated that in the limit of extremely weak coupling, the formulation presented here reduces to the classical thin film theory. Analytical expressions are then derived for the solute segregation and stress intensity factors near the edge of the film when the chemo-mechanical coupling is extremely strong. Results of the numerical analyses are presented in Section 4 along with in-depth discussions on the effect of chemo-mechanical coupling on the solute segregation and stress intensity factors. Potential implications of the results for prediction of a critical film thickness below which edge delamination is suppressed, and for prediction of fatigue life of thin-film electrodes, are also discussed in Section 4. In closure, a summary of the findings is presented in Section 5.

2. Formulation

Consider a semi-infinite thin elastic film of thickness h bonded to the surface of an infinitely-thick elastic substrate. A coordinate system (xyz) is introduced such that the film-substrate interface extends over the area $z = 0, x \geq 0$ with the edge of the film at $x = 0$ (Fig. 1). The film and substrate are both considered indefinitely extended in the y direction. The film, in contrast with the substrate, is assumed to be chemically active and over its entire surface exposed to an external mass reservoir such as a liquid electrolyte (Fig. 1). Suppose that at a given moment during battery cycling, solute concentration in the reservoir is altered via application of an external driving force. Solute therefore flows into the film, or out of it, until chemical equilibrium is established between the thin-film electrode and the reservoir. The goal of this Section is to derive the equations which fully capture the nonlinear coupling between stress and solute distribution in the film when chemical equilibrium is established.

2.1. Chemical equilibrium

Chemical potential of a solute in an ideal dilute solid solution is given by [22,23].

$$\mu = RT\log\frac{c}{c_0} - V_m\sigma_h, \tag{1}$$

where R is the gas constant, T is absolute temperature, c is the solute concentration, c_0 is a fixed reference 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 solution, and the second term is the elastic energy corresponding to insertion of volume V_m into the matrix under hydrostatic stress σ_h. In writing Eq. (1), we have assumed that solute carries no electrical charge in the electrode.

Since the film is considered sufficiently thin, its deformation can be approximated as that of a membrane with the only non-zero components of stress being the axial stresses σ_x and σ_y [24]. Following the classical analogy between the intercalation-induced stresses and thermal stresses [25], the corresponding normal components of strain are

$$\begin{aligned}\varepsilon_x &= \widehat{\sigma}_x - \nu\widehat{\sigma}_y + \varepsilon_c,\\ \varepsilon_y &= \widehat{\sigma}_y - \nu\widehat{\sigma}_x + \varepsilon_c,\end{aligned} \tag{2}$$

where

$$\varepsilon_c = \frac{1}{3}V_m c, \tag{3}$$

is the solute-induced strain, ν is Poisson's ratio of the film, and $\widehat{\sigma}_x = \sigma_x/E$, $\widehat{\sigma}_y = \sigma_y/E$ with E being the Young's modulus of the film. Under the assumptions stated above, deformation is essentially plane strain, i.e. $\varepsilon_y = 0$. Hence, from Eq. (2),

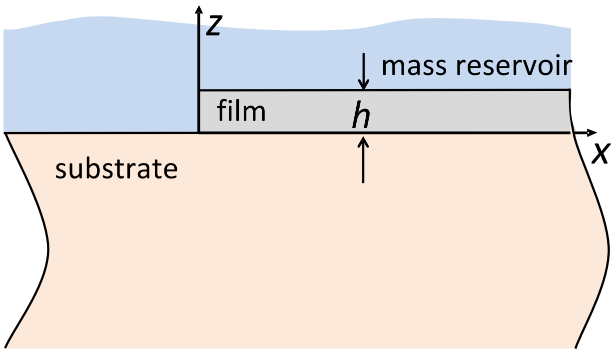

Fig. 1. A semi-infinite thin elastic film of thickness h, on a thick elastic substrate, in contact and in chemical equilibrium with a mass reservoir, such as a liquid electrolyte. The edge of the film is located at $x = 0$, and the film-substrate interface extends over the area $x \geq 0$, $z = 0$.