



A path-independent integral for fracture of solids under combined electrochemical and mechanical loadings



Hamed Haftbaradaran^a, Jianmin Qu^{a,b,*}

^a Department of Civil and Environmental Engineering, Northwestern University, USA

^b Department of Mechanical Engineering, Northwestern University, USA

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ABSTRACT

In this study, we first demonstrate that the J -integral in classical linear elasticity becomes path-dependent when the solid is subjected to combined electrical, chemical and mechanical loadings. We then construct an electro-chemo-mechanical J -integral that is path-independent under such combined multiple driving forces. Further, we show that this electro-chemo-mechanical J -integral represents the rate at which the grand potential releases per unit crack growth. As an example, the path-independent nature of the electro-chemo-mechanical J -integral is demonstrated by solving the problem of a thin elastic film delaminated from a thick elastic substrate.

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1. Introduction

Solid state diffusion under both chemical and mechanical driving forces occurs in a number material systems used in energy conversion and storage devices such as fuel cells and batteries. Under such conditions, magnitude of the stress often exceeds that caused by the mechanical driving force alone. Therefore, to design reliable energy conversion and storage systems, the synergetic effects of mechanical and chemical (or electrochemical) driving force must be understood.

The earlier work on solid state diffusion in metallic system by Larche and Cahn (1973) established the general thermodynamic framework for metallic systems. Based on this framework, Larche and Cahn have studied a number of material science and engineering problems (Larche and Cahn, 1973, 1982, 1985, 1987, 1992). Following Larche and Cahn's approach, Swaminathan and Qu developed a stress-dependent electrochemical potential for ionic solids (Swaminathan et al., 2007a, 2007b), which enabled them to investigate the stresses developed in the electrolyte of planar (Swaminathan et al., 2007a, 2007b) and tubular (Swaminathan and Qu, 2007) solid oxide fuel cells under operation.

Recent interest in lithium ion batteries has attracted significant attention from the mechanics of materials community. In particular, silicon, when used as an anode material, experiences large volumetric expansion during charging. Such large deformation often causes high stress and material failure. To understand the lithiation process and the stresses induced by lithiation, a number of papers have been published recently, e.g., (Sethuraman et al., 2010; Liu et al., 2011; Ryu et al., 2011; Zhao et al., 2011; Cui et al., 2012a, 2012b; Haftbaradaran and Gao, 2012; Liu et al., 2012; Brassart et al., 2013; Cui et al., 2013).

Fracture is a major failure mode in electrodes, which involve cracking of the solid-electrolyte interphase (Wu et al., 2012), fracture within the electrodes (Liu et al., 2011; Ryu et al., 2011; Lee et al., 2012; Liu et al., 2012), delamination from the

* Corresponding author.

E-mail address: j-qu@northwestern.edu (J. Qu).

current collectors (Maranchi et al., 2006; Xiao et al., 2011; Haftbaradaran et al., 2012), and cyclic plasticity (Haftbaradaran and Gao, 2012; Brassart et al., 2013). Fracture within solid intercalation electrodes caused by diffusion-induced stresses has been investigated extensively in the literature, revealing particle size and cycling rate effects on the fracture behavior of the electrodes (Huggins and Nix, 2000; Bhandakkar and Gao, 2010; Woodford et al., 2010; Zhao et al., 2010; Bhandakkar and Gao, 2011; Grantab and Shenoy, 2011; Ryu et al., 2011). The interaction between the solute and stress field close to the crack tip has been widely studied in the context of hydrogen diffusion in metals, accounting for solute trapping at material defects, and plasticity ahead of the crack tip (Sofronis and Mcmeeking, 1989; Liang and Sofronis, 2003; Sobotka et al., 2009; Novak et al., 2010). It has been suggested that in Li-ion batteries, high Li mobility in the intercalation electrodes, particularly those with layered atomic structure (Van der Ven et al., 2008; Bhattacharya and Van der Ven, 2010; Persson et al., 2010), as well as in the electrolytes, can facilitate fast redistribution of Li around the crack tip, and thus might alter the fracture toughness and the energy available for the crack growth (Qi et al., 2012). In the limit of very high mobility, thermodynamics of crack growth should be studied in terms of a given Li chemical potential (Qi et al., 2012), which is related to the electric potential of the electrode (Sethuraman et al., 2010).

Among numerous existing studies on the fracture of solids under combined chemical and mechanical loadings, few have utilized the conventional J -integral of fracture mechanics to predict the onset of crack growth in electrodes (Ryu et al., 2011; Pupurs and Varna, 2014). This seems to be usual, because, ever since the seminal work of Cherepanov (1967), and Rice (1968), path-independent integrals have been widely developed and used to study fracture mechanics problem in a variety of materials and loadings, including finite deformations (Knowles and Sternberg, 1972), elastodynamics (Atkinson and Eshelby, 1968; Freund, 1972), elastoplastic materials (Hutchinson, 1968; Rice and Rosengren, 1968; Blackburn, 1972; Blackburn et al., 1977), thermal stresses (Wilson and Yu, 1979), viscoelastic materials (Schapery, 1984), bimaterial interfaces (Park and Earmme, 1986; Matos et al., 1989; Qu and Li, 1991; Qu and Bassani, 1993; Wei and Hutchinson, 1997), piezoelectric ceramics (Suo et al., 1992; Dascalu and Maugin, 1994; Gao and Barnett, 1996), nonhomogeneous materials (Honein and Herrmann, 1997), hygrothermal problems (Yang et al., 2006; Chen, 2007). For more references, see Chen and Lu (2003).

To take advantage of the path-independent integral, an electro-chemo-mechanical path-independent integral must be first identified. To this end, two questions naturally arise. Will the classical J -integral of Rice (1968) be path-independent under combined electrochemical and mechanical driving forces? If not, can a path-independent integral be developed?

The objective of the current study is to answer these two questions. The paper is organized as follows. For convenience and completeness, we present in Section 2 the pertinent governing equations for elastic solids under electro-chemo-mechanical equilibrium. In Section 3, we will first demonstrate that the classic J -integral of Rice becomes path-dependent when both electrochemical and mechanical driving forces are present at the same time. We then go on to derive a path-independent integral for an elastic solid under intercalation-induced stresses that is in electro-chemo-mechanical equilibrium with its surrounding. We will show that this electro-chemo-mechanical J -integral, once computed for a contour encircling a crack tip, renders the rate at which the grand potential of the system decreases. To illustrate the application of the developed path-independent integral, we investigate in Section 4 the problem of delamination of a thin elastic film from an infinitely thick substrate under chemo-mechanical driving forces. A solution is obtained for the chemo-mechanical field far away from the delamination front. This far-field solution is then used in Section 5 to calculate the chemo-mechanical J -integral. To verify that the chemo-mechanical J -integral so computed using the far-field solution is indeed path-independent, we obtain the full field solution in Section 6, from which the chemo-mechanical J -integral is computed again by using the near-tip fields. We show that the chemo-mechanical J -integrals computed from the far-field and the near-tip fields are indeed the same.

Finally, a summary and some concluding remarks are presented in Section 7.

2. Governing equations for solid state diffusion

Without loss of generality, we consider an elastic solid A_xB that consists of species A and species B. It is assumed that the concentration of A in A_xB may vary from $x=0$ to $x=x_{\max}$, where x_{\max} is the solvability of A in B. One may also view species A as the solute and species B as the solvent. Furthermore, we assume that the solid in consideration can be represented by the network model of Larche and Cahn (1973), namely, the lattice sites of species B form a network within which species A can move (diffuse). This allows the definition of a displacement and hence a strain of the solid. To simplify the mathematics, we will only consider small strain deformation in the rest of this paper.

In the following, it is convenient to define molar concentration per unit volume of the host matrix $c = x/V_m$, where V_m is the molar volume of species B in a stress-free state. We assume that the compositional change of the mixture of species A and species B causes a volumetric deformation according to

$$\varepsilon_{ij}^c = \eta x \delta_{ij} = \eta V_m c \delta_{ij}, \quad (1)$$

where δ_{ij} is the Kronecker delta, η is the coefficient of compositional expansion (CCE), which is a material property that characterizes the linear measure of the volumetric change due to unit change of the composition (Swaminathan et al., 2007a, 2007b). For a given material, the CCE can be obtained either experimentally, or by conducting molecular dynamic simulations (Swaminathan and Qu, 2009; Cui et al., 2012a, 2012b). The total strain caused by the compositional change and

applied load can be written as

$$\varepsilon_{ij} = \frac{1}{2}(u_{i,j} + u_{j,i}) = \varepsilon_{ij}^e + \varepsilon_{ij}^c, \quad (2)$$

where u_i is the displacement, and ε_{ij}^e is the elastic strain. We further assume that the solid is hyperelastic so that its elastic state is uniquely determined by the elastic strain energy function

$$w_e = \frac{E}{2(1+\nu)} \left(\varepsilon_{ij}^e \varepsilon_{ij}^e + \frac{\nu \varepsilon_{kk}^e \varepsilon_{mm}^e}{1-2\nu} \right), \quad (3)$$

and the stress tensor is given by

$$\sigma_{ij} = \frac{\partial w_e}{\partial \varepsilon_{ij}^e} = \frac{E}{(1+\nu)} \left(\varepsilon_{ij}^e + \frac{\nu \varepsilon_{kk}^e}{1-2\nu} \delta_{ij} \right), \quad (4)$$

where E and ν are Young's modulus and Poisson's ratio, respectively, of the solid. In the absence of body forces, the stress needs to satisfy the static equilibrium equations,

$$\frac{\partial \sigma_{ji}}{\partial x_j} = 0. \quad (5)$$

In this stressed-solid, the electrochemical potential of species A will depend on the stress (Larche and Cahn, 1973). By assuming small strain and composition-independent isotropic elasticity, the stress-dependent electrochemical potential (more precisely, the diffusion potential of species A in B) can be derived from the general expression (Swaminathan et al., 2007a, 2007b; Cui et al., 2012a, 2012b),

$$\mu = \mu_0 + R_g T \log \frac{c}{c_{\max} - c} - V_m \eta \sigma_{kk} + zF\phi, \quad (6)$$

where μ_0 is a constant representing the chemical potential at a standard state, R_g is the standard gas constant, T is the absolute temperature, $c_{\max} = x_{\max}/V_m$ is the solute concentration corresponding to the saturation state of the solution, z is the effective charge of species A, F is the Faraday constant, and ϕ is the electrostatic potential. The particular choice of the potential ensures that the stoichiometric state has the lowest energy (i.e., $\mu \rightarrow -\infty$ as $c \rightarrow 0$), and the state of saturation has the highest energy (i.e., $\mu \rightarrow \infty$ as $c \rightarrow c_{\max}$).

We note that the electrochemical potential (6) is a simplified version of the more general expression derived in (Swaminathan et al., 2007a, 2007b). This simplified version of the electrochemical potential is valid when the elastic constants are independent of the solute concentration and the deformation is small so that higher order stresses are negligible. For finite deformation, the full expression of electrochemical potential will need to be used.

The electrostatic potential needs to satisfy the Poisson's equation

$$-\kappa_\varepsilon \nabla^2 \phi = \frac{FzC}{\varepsilon_0}, \quad (7)$$

where $\varepsilon_0 = 8.854 \times 10^{-12}$ farad/m is the electric permittivity of free space, and κ_ε is the dielectric constant of the solid.

The system of Eqs. (1)–(7) describes the two-way coupling between the chemical and mechanical fields in that the solute concentration induces eigenstrain through (1), and the solute-induced eigenstrain (compositional strain) may cause mechanical stresses through (2)–(4). In return, the stresses so induced affect the solute diffusion through the stress-dependent electrochemical potential (6).

If the term $V_m \eta \sigma_{kk}$ is negligible in comparison with other terms on the right hand of (6), the solute diffusion will not be affected by the stress field. The diffusion will become purely entropy-driven, although the solute concentration will still induce the compositional strain, which may still cause stresses. Such coupling between the mechanical and chemical fields is only one way in that solute distribution generates stresses, but stresses do not affect solution diffusion.

Another case of one-way coupling is when the compositional strain ε_{ij}^c is negligible in comparison with the elastic strain in (2). In this case, the stress field is not affected by the solute distribution, but the solute diffusion is affected by the stresses through the stress-dependent electrochemical potential (6).

3. A path-independent contour integral under electro-chemo-mechanical equilibrium

The classical J -integral of Rice (1968) is defined over a closed contour $\partial\Omega$,

$$J_{\partial\Omega} = \oint_{\partial\Omega} \left(w_e n_1 - t_i \frac{\partial u_i}{\partial x_1} \right) d\Gamma, \quad (8)$$

where w_e is the elastic energy density, t_i is the traction vector on the contour $\partial\Omega$, n_i is the unit outward normal on $\partial\Omega$, u_i is the displacement vector, and $d\Gamma$ is the length element along the contour. In applying the J -integral to crack problems, the x_1 -direction is usually taken along the crack direction. Making use of the Cauchy equation $t_i = n_j \sigma_{ji}$ along the integration

path and the divergence theorem in (8), one obtains

$$J_{\partial\Omega} = \int_{\Omega} \left(\frac{\partial w_e}{\partial x_1} - \frac{\partial}{\partial x_j} \left(\sigma_{ji} \frac{\partial u_i}{\partial x_1} \right) \right) d\Omega. \quad (9)$$

By making use of (4), (5) and (2), the above integral reduces to

$$J_{\partial\Omega} = - \int_{\Omega} \sigma_{ij} \frac{\partial \varepsilon_{ij}^c}{\partial x_1} d\Omega. \quad (10)$$

Substitution of (1) into (10) leads to

$$J_{\partial\Omega} = -\eta V_m \int_{\Omega} \sigma_{kk} \frac{\partial c}{\partial x_1} d\Omega. \quad (11)$$

It follows from (11) that $J_{\partial\Omega}$ is zero for any arbitrary volume Ω if and only if $\sigma_{kk} = 0$ or $\partial c / \partial x_1 = 0$. If neither condition is satisfied, $J_{\partial\Omega}$ will not necessarily vanish for a closed contour. In other words, the conventional J -integral of Rice (1968) when calculated for a closed contour is no longer necessarily path-independent in general when solid state diffusion takes place. This is not a surprise in that the J -integral represents a balance between the total energy inside the closed contour and the energy passing through the contour line. In the presence of solid state diffusion, the total energy inside the closed contour is more than just the elastic strain energy. Energy associated with solute diffusion and distribution must also be considered. Thus, using the elastic energy w_e alone will no longer satisfy the balance between the total energy inside the closed contour and the energy passing through the contour line.

In what follows, we will construct an integral that is path-independent even when solid state diffusion takes place. We will limit our development to the case where the solute is in electrochemical equilibrium within the solid, preserving a uniform electrochemical potential throughout the volume Ω , i.e., $\mu = \mu_R$ is a given constant. Electrochemical equilibrium can be achieved if long enough time has elapsed, or if the rate of solute diffusion is much faster in comparison with other kinetic processes in the problem.

We will proceed by writing (11) into a contour integral in terms of the potentials. Solving the hydrostatic stress from (6) and substituting it into (11) lead to

$$J_{\partial\Omega} = - \int_{\Omega} \left(\mu_0 - \mu_R + R_g T \log \frac{c}{c_{\max} - c} + zF\phi \right) \frac{\partial c}{\partial x_1} d\Omega. \quad (12)$$

It follows from the entropy of mixing per volume of mixture (Hill, 1986)

$$s = -R_g c_{\max} \left(\frac{c}{c_{\max}} \log \frac{c}{c_{\max}} + \left(1 - \frac{c}{c_{\max}} \right) \log \left(1 - \frac{c}{c_{\max}} \right) \right), \quad (13)$$

that

$$\frac{\partial s}{\partial c} = -R_g c_{\max} \log \frac{c}{c_{\max} - c}. \quad (14)$$

Making use of the above in (12) with the divergence theorem yields

$$J_{\partial\Omega} = \oint_{\partial\Omega} [(\mu_R - \mu_0)c + Ts] n_1 d\Omega - zF \int_{\Omega} \phi \frac{\partial c}{\partial x_1} d\Omega, \quad (15)$$

where we have assumed T is uniform. The volume integral in the above can be further written as,

$$\int_{\Omega} \phi \frac{\partial c}{\partial x_1} d\Omega = \int_{\Omega} [(\phi c)_{,1} - c\phi_{,1}] d\Omega = \oint_{\partial\Omega} \phi c n_1 d\Gamma - \int_{\Omega} c\phi_{,1} d\Omega. \quad (16)$$

Writing the concentration c in the volume integral in terms of the electrostatic potential ϕ via the Poisson's Eq. (7) and making use of the divergence theorem, one has

$$\int_{\Omega} c\phi_{,1} d\Omega = -\frac{\kappa_e \varepsilon_0}{Fz} \int_{\Omega} \phi_{,kk} \phi_{,1} d\Omega = -\frac{\kappa_e \varepsilon_0}{Fz} \oint_{\partial\Omega} \left[\phi_{,k} \phi_{,1} n_k - \frac{1}{2} (\phi_{,k} \phi_{,k}) n_1 \right] d\Gamma. \quad (17)$$

Substituting (17) into (16), then into (15), we arrive at

$$J_{\partial\Omega} = \oint_{\partial\Omega} \left([(\mu_R - \mu_0)c + Ts + w_E - zF\phi c] n_1 - q_s \frac{\partial \phi}{\partial x_1} \right) d\Gamma, \quad (18)$$

where

$$w_E = \frac{\kappa_e \varepsilon_0}{2} \phi_{,k} \phi_{,k}, \quad q_s = \kappa_e \varepsilon_0 \phi_{,k} n_k \quad (19)$$

are, respectively, the electrical energy and surface charge carried by the solute per mole of the mixture.

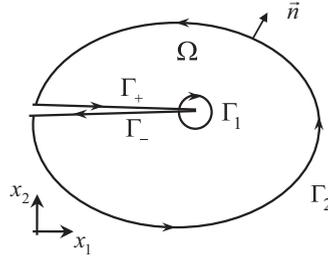


Fig. 1. A planar crack oriented along the x_1 direction. The figure shows a portion of the body Ω that is surrounded by the closed contour $\partial\Omega$ comprising Γ_+ , Γ_- , and Γ_2 . The unit outward normal \mathbf{n} points outward from Ω .

Making use of (18) and (8), one can now construct a contour integral that is identically zero along any closed contour $\partial\Omega$,

$$J_{\partial\Omega}^{ecm} = J_{\partial\Omega} - \oint_{\partial\Omega} \left([(\mu_R - \mu_0)c + Ts + w_E - zF\phi c] n_1 - q_s \frac{\partial\phi}{\partial x_1} \right) d\Gamma. \quad (20)$$

Substituting the original definition of $J_{\partial\Omega}$ given by (8) into the above, we arrive at

$$J_{\partial\Omega}^{ecm} = \oint_{\partial\Omega} \left(\psi n_1 - t_i \frac{\partial u_i}{\partial x_1} + q_s \frac{\partial\phi}{\partial x_1} \right) d\Gamma, \quad (21)$$

where

$$\psi = w_e - w_E - (\mu_R - \mu_0)c - Ts, \quad (22)$$

is identified as the grand potential of the system whose physical interpretation is as follows. The first and second terms in (22) correspond to the internal energy contributions from elastic and electrostatic fields, respectively. Whereas the third and fourth terms respectively account for the effect of mass and entropy exchange between the system and its surrounding. It is noteworthy to point out that the path-independent integral in (21) reduces to the one given by Suo et al. (1992) in the absence of piezoelectricity effects and the chemical fields ($c = s = 0$).

Consider a planar crack parallel to the x_1 direction, and let $\partial\Omega$ be constructed of four parts: Γ_1 , Γ_2 around the crack tip starting on one face of the crack and ending on the opposite face; and Γ_+ , Γ_- parts of the crack face (see Fig. 1.). Assuming that the mechanical traction and the surface charge (i.e., normal component of the electric field, $-\phi_{,2}$) identically vanish on the crack faces, and noting that $n_1 = 0$ on the crack faces, it can readily be verified that the integrals along Γ_+ , Γ_- vanish, and hence the integrals along Γ_1 and Γ_2 must cancel each other. Thus, by reversing the direction of normal along Γ_1 to point away from the crack tip, one can write

$$J_{\Gamma}^{ecm} = \int_{\Gamma_2} \left(\psi n_1 - t_i \frac{\partial u_i}{\partial x_1} + q_s \frac{\partial\phi}{\partial x_1} \right) d\Gamma = \int_{\Gamma_1} \left(\psi n_1 - t_i \frac{\partial u_i}{\partial x_1} + q_s \frac{\partial\phi}{\partial x_1} \right) d\Gamma. \quad (23)$$

This means J_{Γ}^{ecm} is path-independent along any contour enclosing the crack tip, as long as the mechanical tractions t_i and the normal component of the electric field $-\phi_{,2}$ identically vanish on the crack faces.

It is worthwhile to mention that while electrochemical equilibrium is assumed in the above derivations, no use has been made of electrochemical equilibrium in the direction normal to the crack faces. In fact, the derivation remains valid even when μ_R varies with x_2 .

For future reference, the J_{Γ}^{ecm} defined by (23) will be called the electro-chemo-mechanical J -integral. When the electrical field is not present, i.e., when $\phi \equiv 0$, the integral reduces to the chemo-mechanical J -integral,

$$J_{\Gamma}^{cm} = \int_{\Gamma} \left(\psi n_1 - t_i \frac{\partial u_i}{\partial x_1} \right) d\Gamma, \quad (24)$$

where

$$\psi = w_e - (\mu_R - \mu_0)c - Ts. \quad (25)$$

In this case, it can be easily shown from (6) that, under chemical equilibrium $\mu = \mu_R$, the concentration is bounded, $0 \leq c \leq c_{\max}$, regardless whether the stress field is bounded. Further, for $0 \leq c \leq c_{\max}$, the entropy s is also bounded. It thus follows that near the crack tip, the field quantities c and s are negligible in comparison with the stresses and strains. Consequently, very close to the crack tip, the generalized grand potential is approximately equal to the strain energy, i.e., $\psi \approx w_e$. Thus, for a sufficiently small contour enclosing the crack tip, one must have

$$\lim_{\Gamma \rightarrow 0} \oint_{\Gamma} \left(\psi n_1 - t_i \frac{\partial u_i}{\partial x_1} \right) = \lim_{\Gamma \rightarrow 0} \oint_{\Gamma} \left(w n_1 - t_i \frac{\partial u_i}{\partial x_1} \right) d\Gamma, \quad (26)$$

which means that, when evaluated along an infinitesimal contour enclosing the crack tip, the classical J -integral yields the same value as the chemo-mechanical J -integral. In other words, to calculate J_{Γ}^{cm} , one only needs to evaluate the classical J -integral (8) along an infinitesimal contour enclosing the crack tip. In doing so, one must keep in mind that (1) the stresses

and strains used in evaluating the classic J -integral must be the solution to the chemo-mechanical fields, and (2) that the equality between the chemo-mechanical J -integral and the classical J -integral holds only for infinitesimal contours enclosing the crack tip, because the classical J -integral is path-dependent so its value will differ when evaluated along any other contours away from the crack tip, while the chemo-mechanical J -integral remains the same regardless the contour used.

In the following, we will return to the electro-chemo-mechanical J_{Γ}^{ecm} in (23). We will show that J_{Γ}^{ecm} represents the rate at which the grand potential ψ flows into the crack tip. To this end, we assume that the planar crack showing in Fig. 1 extends its length at the speed of v in the x_1 direction under certain loading conditions. We further assume that the mechanical traction and the surface charge identically vanish on the crack faces. Now, consider a small contour Γ_0 encircling the crack tip that moves with the crack tip without changing its size, shape and orientation. Therefore, by using the Cauchy equation $t_i = n_j \sigma_{ji}$ and the second of (19) at any instantaneous time, Eq. (23) can be recast into

$$J_{\Gamma_0}^{ecm} = \frac{1}{v} \int_{\Gamma_0} (\psi v n_1 + \varphi_j n_j) d\Gamma \quad (27)$$

where

$$\varphi_j = v \left(-\sigma_{ij} \frac{\partial u_i}{\partial x_1} + \kappa_\epsilon \epsilon_0 \frac{\partial \phi}{\partial x_1} \frac{\partial \phi}{\partial x_j} \right). \quad (28)$$

It can be verified, see Appendix A, that the φ_j defined above satisfies the conservation law,

$$\dot{\psi} = \frac{\partial \varphi_j}{\partial x_j}. \quad (29)$$

It has been shown by Moran and Shih (1987) that the right hand side of (27) is the instantaneous rate at which the grand potential ψ flows through Γ_0 . Since J_{Γ}^{ecm} is path-independent, the rate at which the grand potential ψ is being lost to the crack tip, or the energy release rate, can then be obtained by shrinking Γ_0 to the crack tip,

$$G = \lim_{\Gamma_0 \rightarrow 0} J_{\Gamma_0}^{ecm} = \lim_{\Gamma_0 \rightarrow 0} \frac{1}{v} \int_{\Gamma_0} (\psi v n_1 + \varphi_j n_j) d\Gamma. \quad (30)$$

Again, in view of the path-independency of J_{Γ}^{ecm} , one can calculate the energy release rate via the following line integral along any contour Γ that encircles the crack tip,

$$G = J_{\Gamma}^{ecm} = \int_{\Gamma} \left(\psi n_1 - t_i \frac{\partial u_i}{\partial x_1} + q_s \frac{\partial \phi}{\partial x_1} \right) d\Gamma. \quad (31)$$

It is noteworthy to point out that the J -integral derived here consists of a single line integral. This is different from those obtained by Yang et al. (2006) and Gao and Zhou (2013), where an area integral appears. However, in the absence of the electrical field and under chemical equilibrium, the area integral in Gao and Zhou (2013) can be converted into a line integral (Zhou, 2014). Therefore, under these conditions, one can show that the J -integral of Gao and Zhou (2013) can be reduced to (21).

To close this section, we note that, by taking Eq. (6) to be the universal condition for electrochemical potential, we have not differentiated the electrochemical equilibrium in the bulk from that on the crack faces. Furthermore, we have not accounted for the variations in the elastic properties caused by solute concentration.

4. Delamination of a thin film from a thick substrate

To illustrate the application of the path-independent integral derived above, we consider an elastic film of thickness h attached onto an infinitely thick (half space) elastic substrate. We adopt a Cartesian coordinate system (xyz) such that the film-substrate interface lies within the plane $z = 0$. The film is considered delaminated from the substrate over the area $(-\infty < x \leq 0, -\infty < y < \infty)$ as depicted in Fig. 2. Since the film is very thin, one may use the membrane assumption so that $\tau_{zx} = \tau_{zy} = \sigma_z = 0$ (Erdogan and Joseph 1990). Further, the film is assumed chemically active, but the substrate is not. To simplify the algebra, we further assume that neither the film, nor the substrate carries any electrical charges. Thus, the electrical potential is identically zero, i.e., $\phi = 0$. Finally, we assume that the rate of diffusion is extremely fast so that chemical equilibrium is achieved instantaneously.

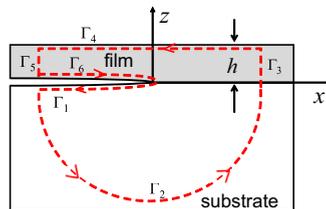


Fig. 2. Delamination of a thin film from an infinitely thick substrate.

For the applied mechanical load, we prescribe a uniform eigenstrain in the film to represent the (thermal or lattice) mismatch between the film and the substrate. In addition, a uniform chemical potential $\mu = \mu_R$ is prescribed in the film, which provides the chemical loading. Under such combined mechanical and chemical loadings, we are interested in obtaining the stress and solute concentration distribution in the film and along the film/substrate interface, particularly, the singular fields near the crack tip.

Under the above assumptions, the deformation is essentially plane strain, and the stress, strain and solute concentration in the film become functions of x only. Thus, the only non-zero stress components in the film are the normal stresses in the x and y directions, respectively denoted by σ_x , and σ_y , with corresponding normal strain components ε_x and ε_y . It follows from the Hooke's law that the plane strain deformation requires

$$\varepsilon_y = \hat{\sigma}_y - \nu \hat{\sigma}_x + \varepsilon_c + \varepsilon_m = 0, \quad (32)$$

where $\hat{\sigma}_x = \sigma_x/E$, $\hat{\sigma}_y = \sigma_y/E$, $\varepsilon_c = \eta V_m c$ is the compositional strain, ε_m is the prescribed eigenstrain in the film, and E and ν are, respectively, the Young's modulus and Poisson ratio of the film. From the above, one can obtain $\hat{\sigma}_y$, in terms of $\hat{\sigma}_x$ and c as

$$\hat{\sigma}_y = \nu \hat{\sigma}_x - (\varepsilon_c + \varepsilon_m), \quad (33)$$

and hence,

$$\hat{\sigma}_{kk} = \hat{\sigma}_x + \hat{\sigma}_y = (1 + \nu) \hat{\sigma}_x - (\varepsilon_c + \varepsilon_m). \quad (34)$$

Moreover, chemical equilibrium implies that

$$R_g T \log \frac{c}{c_{\max} - c} - \eta V_m \sigma_{kk} = \mu_R - \mu_0 \equiv R_g T \log \frac{c^{eq}}{c_{\max} - c^{eq}}, \quad (35)$$

where c^{eq} is introduced as the solute concentration in a stress-free solid which is in chemical equilibrium with the mass reservoir, and therefore with the thin film electrode. In this sense, the quantity c^{eq} can be considered as an applied chemical load.

In the limiting case of very large solubility c_{\max} (or equivalently for a dilute solute), one can write a simplified version of the equation of chemical equilibrium by letting $c_{\max} \rightarrow +\infty$, as

$$R_g T \log c - \eta V_m \sigma_{kk} = R_g T \log c^{eq}, \quad (36)$$

which can be cast into the following dimensionless form

$$\varepsilon_c \exp(-\hat{\eta} \hat{\sigma}_{kk}) = \varepsilon_c^{eq}, \quad (37)$$

where $\hat{\eta} = \eta V_m E / RT$, $\varepsilon_c = \eta V_m c$, and $\varepsilon_c^{eq} = \eta V_m c^{eq}$. It can be easily shown that if $\hat{\eta} = 0$, then $\varepsilon_c = \varepsilon_c^{eq}$, or $c = c^{eq}$, throughout the film. This corresponds to the one-way coupling case where the solute distribution generates compositional strain $\varepsilon_c^{eq} = \eta V_m c^{eq}$, but the solute diffusion is unaffected by the stress. In this case, the process is purely entropy-driven.

Let us now consider the field quantities at $x = \pm\infty$. It is obvious that the solute concentration is uniform at $x = -\infty$, and the corresponding stress field is $\hat{\sigma}_x = 0$. At $x = +\infty$, the stress in the film should be equi-biaxial, i.e., $\hat{\sigma}_x^{+\infty} = \hat{\sigma}_y^{+\infty}$. Thus, it follows from (33) that

$$\hat{\sigma}_y^{-\infty} = -(\varepsilon_c^{-\infty} + \varepsilon_m), \quad \hat{\sigma}_x^{+\infty} = \hat{\sigma}_y^{+\infty} = -\frac{1}{1-\nu}(\varepsilon_c^{+\infty} + \varepsilon_m), \quad (38)$$

where $\varepsilon_c^{\pm\infty} = \eta V_m c^{\pm\infty}$. Consequently,

$$\hat{\sigma}_{kk}^{-\infty} = -(\varepsilon_c^{-\infty} + \varepsilon_m), \quad \hat{\sigma}_{kk}^{+\infty} = -\frac{2}{1-\nu}(\varepsilon_c^{+\infty} + \varepsilon_m), \quad (39)$$

In the above and the rest of the paper, the superscript $\pm\infty$ indicates the values at $x = \pm\infty$ of the field quantity represented by the base letter. Chemical equilibrium (37) with the aid of (39) implies that

$$\varepsilon_c^{-\infty} \exp(\hat{\eta}(\varepsilon_c^{-\infty} + \varepsilon_m)) = \varepsilon_c^{+\infty} \exp\left(\frac{2\hat{\eta}}{1-\nu}(\varepsilon_c^{+\infty} + \varepsilon_m)\right) = \varepsilon_c^{eq} \equiv \eta V_m c^{eq}. \quad (40)$$

These equations suggest that once the applied mechanical load ε_m and the chemical load c^{eq} are prescribed, the quantities $\varepsilon_c^{\pm\infty} = \eta V_m c^{\pm\infty}$ can be uniquely determined from (40). For example, the second of (40) can be solved for $\varepsilon_c^{+\infty}$,

$$\varepsilon_c^{+\infty} = \frac{(1-\nu)}{2\hat{\eta}} W\left(\frac{2\hat{\eta}\varepsilon_c^{-\infty}}{1-\nu} e^{-\frac{2\hat{\eta}\varepsilon_m}{1-\nu}}\right), \quad (41)$$

where $W(z)$ is the Lambert W -function, whose real branch has an asymptotic expression near $z = 0$, and increases monotonically with increasing $z > 0$ (Abramowitz and Stegun, 1964),

$$W(z) = \sum_{n=1}^{\infty} \frac{(-n)^{n-1}}{n!} z^n. \quad (42)$$

Thus, $\varepsilon_c^{+\infty}$ increases monotonically with increasing $\varepsilon_c^{-\infty}$, and $\varepsilon_c^{+\infty} \rightarrow 0$ in the limit of $\varepsilon_c^{-\infty} \rightarrow 0$. In this sense, one can view $\varepsilon_c^{+\infty}$ as a proxy of the chemical load. Thus, in the remainder of this paper, we will use ε_m and $\varepsilon_c^{+\infty}$ as the two independent variables to represent the applied mechanical load and the applied chemical load, respectively.

The first of (40) can be solved for $\varepsilon_c^{-\infty}$,

$$\varepsilon_c^{-\infty} = \frac{1}{\hat{\eta}} W(z), \quad (43)$$

where

$$z = \hat{\eta} \varepsilon_c^{+\infty} \exp \left[\frac{2\hat{\eta}}{1-\nu} (\varepsilon_c^{+\infty} + \varepsilon_m) - \hat{\eta} \varepsilon_m \right]. \quad (44)$$

Thus, by substituting (44) into (42), and expanding the result for small $\hat{\eta}$ one may write (43) asymptotically to the order of $\hat{\eta}^2$ as

$$\varepsilon_c^{-\infty} = \varepsilon_c^{+\infty} (1 + a_1 \hat{\eta} + a_2 \hat{\eta}^2), \quad (45)$$

where

$$a_1 = \frac{1+\nu}{1-\nu} (\varepsilon_c^{+\infty} + \varepsilon_m), \quad a_2 = \frac{1}{2} \left(\frac{1+\nu}{1-\nu} \right)^2 (\varepsilon_c^{+\infty} + \varepsilon_m) \left(\varepsilon_m - \frac{1-3\nu}{1+\nu} \varepsilon_c^{+\infty} \right). \quad (46)$$

In the sections to follow, this asymptotic solution will be invoked to calculate some of the quantities of interest to the problem of film delamination from the substrate including the chemo-mechanical J integral.

As discussed earlier, $\hat{\eta} = 0$ corresponds to the one-way coupling case where the solute distribution generates compositional strain $\varepsilon_c^{eq} = \eta V_m c^{eq}$, but the solute diffusion is unaffected by the stress. In this case, it follows from (45) and (37) that $\varepsilon_c^{-\infty} = \varepsilon_c^{+\infty} = \varepsilon_c^{eq}$.

5. The chemo-mechanical J -integral

In this section, we will make use of the chemo-mechanical J -integral to obtain the energy release rate at the crack tip in the film/substrate problem stated in the previous section. To calculate the chemo-mechanical J integral, the contour Γ is taken as shown in Fig. 2, going through both the film and substrate at points infinitely far from the crack tip. It is straightforward to see that $n_x = 0$, and $t_x = t_z = 0$ on Γ_1 , Γ_4 and Γ_6 , and $\psi = 0$, $t_x = t_z = 0$ on Γ_2 as it is located infinitely far from the delamination front. Furthermore, $t_x = t_z = 0$ on Γ_5 , and $\partial u_x / \partial x = \partial u_z / \partial x = 0$ on Γ_3 . Therefore, in the absence of the electrical field, the chemo-mechanical J -integral of (23) is reduced to

$$J_{\Gamma}^{cm} = \int_{\Gamma} \left(\psi n_x - t_x \frac{\partial u_x}{\partial x} - t_z \frac{\partial u_z}{\partial x} \right) d\Gamma = h(\psi^{+\infty} - \psi^{-\infty}), \quad (47)$$

where the grand potential in the film as defined in (22) is simplified to

$$\psi = w_e - (\mu_R - \mu_0)c - Ts. \quad (48)$$

For convenience, we rewrite (47) in the following form

$$J_{\Gamma}^{cm} = h(\Delta w_e - \Delta w_{ch}), \quad (49)$$

where $\Delta w_e = w_e^{+\infty} - w_e^{-\infty}$, and $\Delta w_{ch} = (\mu_R - \mu_0)(c^{+\infty} - c^{-\infty}) + T(s^{+\infty} - s^{-\infty})$ are the elastic and chemical energy contributions. In the following, we proceed to calculate Δw_e and Δw_{ch} based on the asymptotic solution obtained in the preceding section.

The problem is considered plane strain in the xz plane. The film-substrate interface is located at $z = 0$, with delamination front at $x = 0$. The closed contour $\Gamma = \sum_{n=1}^6 \Gamma_n$ going around the crack tip is shown.

First, for the case considered here, it can be easily shown by using (3) that the strain energy density in the film is given by

$$w_e = \frac{1}{2} (\sigma_x (\varepsilon_x - \varepsilon_m - \varepsilon_c) + \sigma_y (\varepsilon_y - \varepsilon_m - \varepsilon_c)) = \frac{E}{2} \left((\varepsilon_c + \varepsilon_m)^2 + \frac{(1-\nu^2)\sigma_x^2}{E^2} \right). \quad (50)$$

Thus,

$$w_e^{-\infty} = \frac{E}{2} (\varepsilon_m + \varepsilon_c^{-\infty})^2, \quad w_e^{+\infty} = \frac{E}{2} (\varepsilon_m + \varepsilon_c^{+\infty})^2, \quad (51)$$

where, in deriving the second of (51), we have used the second of (38). Consequently,

$$\Delta w_e = w_e^{+\infty} - w_e^{-\infty} = \frac{E}{2} \left(\frac{2}{1-\nu} (\varepsilon_m + \varepsilon_c^{+\infty})^2 - (\varepsilon_m + \varepsilon_c^{-\infty})^2 \right) \quad (52)$$

gives the difference between elastic energy density far behind and far ahead of the delamination front. Note that $\varepsilon_c^{-\infty}$ in the above is given as a function of ε_m and $\varepsilon_c^{+\infty}$ through (43), so that Δw_e is a function of the applied loads, ε_m and $\varepsilon_c^{+\infty}$.

Next, to calculate the chemical energy difference, we first notice that according to (13),

$$w_{ch} = \left[(\mu_R - \mu_0) - R_g T \log \frac{c}{c_{\max} - c} \right] c - R_g T c_{\max} \log \left(1 - \frac{c}{c_{\max}} \right). \quad (53)$$

With the aid of the equation of chemical equilibrium (35), the expression inside the square bracket is recognized as $-\eta V_m \sigma_{kk}$. Furthermore, letting $c_{\max} \rightarrow +\infty$, we can reduce $R_g T c_{\max} \log(1 - c/c_{\max})$ to $-R_g T c$. Thus, in terms of the dimensionless parameters $\hat{\sigma}_{kk}$, $\hat{\eta}$ and ε_c , Eq. (53) can be rewritten as

$$w_{ch} = -E \left(\hat{\sigma}_{kk} - \frac{1}{\hat{\eta}} \right) \varepsilon_c. \quad (54)$$

Making use of (39) in (54) leads to

$$\Delta w_{ch} = w_{ch}^{+\infty} - w_{ch}^{-\infty} = \frac{2E}{1-\nu} \varepsilon_c^{+\infty} (\varepsilon_m + \varepsilon_c^{+\infty}) - E \varepsilon_c^{-\infty} (\varepsilon_m + \varepsilon_c^{-\infty}) + \frac{E}{\hat{\eta}} (\varepsilon_c^{+\infty} - \varepsilon_c^{-\infty}). \quad (55)$$

We are now ready to compute the chemo-mechanical J -integral. Making use of (52) and (55) in (49) yields

$$J_I^{cm} = \frac{(1+\nu)}{2(1-\nu)} Eh (\varepsilon_m)^2 + Eh \left[\frac{(\varepsilon_c^{-\infty})^2}{2} - \frac{(\varepsilon_c^{+\infty})^2}{(1-\nu)} - \frac{1}{\hat{\eta}} (\varepsilon_c^{+\infty} - \varepsilon_c^{-\infty}) \right]. \quad (56)$$

Once again, the quantity $\varepsilon_c^{-\infty}$ in the above is related to the applied loads through (43). Eq. (56) gives the exact solution to the chemo-mechanical J -integral for the thin films problem stated in the previous section.

When the applied chemical load is zero, i.e., $\varepsilon_c^{+\infty} = 0$, it follows from (43) that $\varepsilon_c^{-\infty} = 0$. Thus, the chemo-mechanical J -integral given by (56) reduces to $J_I^{cm} = ((1+\nu)/2(1-\nu)) Eh (\varepsilon_m)^2$. This is the classical J -integral for the thin-film problem in the absence of any solute.

In the one-way coupling case where the solute distribution induces compositional strain $\varepsilon_c^{eq} = \eta V_m c^{eq}$, but the solute diffusion is unaffected by the stress, one has $\varepsilon_c^{-\infty} = \varepsilon_c^{+\infty} = \varepsilon_c^{eq}$. Thus, it follows from (56) that

$$J_I^{cm} = \frac{Eh(1+\nu)}{2(1-\nu)} (\varepsilon_m + \varepsilon_c^{eq})^2, \quad (57)$$

where in deriving (57), we have used the following limit

$$\lim_{\hat{\eta} \rightarrow 0} \frac{1}{\hat{\eta}} (\varepsilon_c^{+\infty} - \varepsilon_c^{-\infty}) = -\frac{1+\nu}{1-\nu} (\varepsilon_c^{eq} + \varepsilon_m) \varepsilon_c^{eq}, \quad (58)$$

which can be easily proven by using (45). It is seen from (57) that the chemical and mechanical loads are additive in this case. In other words, the solute distribution induced compositional strain acts like a thermal or lattice mismatch induced eigenstrain.

In the case of weakly two-way coupling, i.e., $\hat{\eta} \ll 1$, the chemo-mechanical J -integral of (56) may be simplified by keeping only the leading order $\hat{\eta} \ll 1$ in (45),

$$J_I^{cm} = \frac{(1+\nu)Eh}{2(1-\nu)} (\varepsilon_m + \varepsilon_c^{+\infty})^2 \left[1 + \frac{1+\nu}{1-\nu} \hat{\eta} \varepsilon_c^{+\infty} \right]. \quad (59)$$

This result suggests that the total free energy available for crack growth increases with increasing $\hat{\eta}$, namely, the higher the coupling between the chemistry and mechanics, the higher the driving force for crack growth.

6. Full field solution

The chemo-mechanical J -integral gives the energy release rate. It does not provide the stress and concentration distributions near the crack tip. In this section, we will derive and solve an integral equation to obtain the full field solution. In addition to the distributions of stress and solute concentration, our numerical solutions also allow the computation of energy release rate directly. Therefore, the numerically calculated energy release rate can be compared to the analytical results derived in the previous section.

6.1. Singular integral equations

To begin, let $q(x)$ denote the shear stress induced at the interface between the film and substrate. Its sign is defined positive when it generates tension in the film. A simple equilibrium argument relates the normal stress σ_x in the film to the interfacial shear stress $q(x)$ through

$$\hat{\sigma}_x(x) = \frac{1}{Eh} \int_0^x q(\xi) d\xi. \quad (60)$$

The interfacial shear stresses $q(x)$ induces a normal strain $\varepsilon_x^s(x)$ on the substrate side of the film/substrate interface (Johnson, 1985),

$$\varepsilon_x^s(x) = \frac{2(1-\nu_s^2)}{\pi E_s} \int_0^\infty \frac{q(\xi)}{\xi-x} d\xi, \quad (61)$$

where E_s and ν_s stand for Young's modulus and Poisson ratio, respectively, of the substrate. Compatibility condition at the interface requires $\varepsilon_x = \varepsilon_x^s$ for all $x \geq 0$. Thus, making use of (61) in conjunction with (60) leads to the following singular

integral equation for $q(x)$,

$$\frac{2(1-\nu_s^2)}{\pi E_s} \int_0^\infty \frac{q(\xi)}{\xi-x} d\xi - \frac{(1-\nu^2)}{Eh} \int_0^x q(\xi) d\xi = (1+\nu)(\varepsilon_c + \varepsilon_m), \quad \text{for } x > 0. \quad (62)$$

By introducing the dimensionless variable, $\alpha = E_s(1-\nu^2)/E(1-\nu_s^2)$, $\chi = \alpha\xi/h$, and $s = \alpha x/h$, Eqs. (60) and (62) can be cast in the following dimensionless form

$$\frac{1}{\pi} \int_0^\infty \frac{\hat{q}(\chi)}{\chi-s} d\chi - \frac{1}{2} \int_0^s \hat{q}(\chi) d\chi = \frac{1}{2} \frac{\alpha}{1-\nu} [\varepsilon_c(s) + \varepsilon_m], \quad \text{for } s > 0, \quad (63)$$

$$\hat{\sigma}_x(s) = \frac{1}{\alpha} \int_0^s \hat{q}(\chi) d\chi, \quad (64)$$

where $\hat{q}(\chi) = (1/E)q(h\chi/\alpha)$. In addition, chemical equilibrium (37) in conjunction with (34) and the second of (39) requires that

$$\varepsilon_c(s) \exp[-\hat{\eta}((1+\nu)\hat{\sigma}_x(s) - \varepsilon_c(s) - \varepsilon_m)] = \varepsilon_c^{+\infty} \exp\left[\frac{2\hat{\eta}}{1-\nu}(\varepsilon_m + \varepsilon_c^{+\infty})\right]. \quad (65)$$

Eqs. (63)–(65) provide a set of coupled nonlinear equations for $\varepsilon_c(s)$, $\hat{\sigma}_x(s)$, and $q(s)$. To proceed, we will use an asymptotic approach whereby the aforementioned unknown field quantities are expanded in terms of $\hat{\eta}$ which is assumed to be small compared to unity,

$$\hat{q}(\chi) = \hat{q}_0(\chi) + \hat{q}_1(\chi)\hat{\eta}, \quad \varepsilon_c(s) = \varepsilon_c^{+\infty}[1 + b(s)\hat{\eta}], \quad (66)$$

where $\hat{q}_0(\chi)$, $\hat{q}_1(\chi)$ and $b(s)$ are unknown functions to be determined by solving (63)–(65). In the expansion of $\varepsilon_c(s)$, we have used the fact that $\varepsilon_c = \varepsilon_c^{+\infty}$ when $\hat{\eta} = 0$, see (65).

Substituting (66) into (65) in conjunction with (64), and expanding the exponentials in terms of $\hat{\eta}$, one can show that

$$b(s) = \frac{1+\nu}{1-\nu}(\varepsilon_c^{+\infty} + \varepsilon_m) + \frac{1+\nu}{\alpha} \int_0^s \hat{q}_0(\chi) d\chi. \quad (67)$$

Making use of (66) in (63) and collecting terms with similar order of $\hat{\eta}$ yields

$$\frac{1}{\pi} \int_0^\infty \frac{\hat{q}_0(\chi)}{\chi-s} d\chi - \frac{1}{2} \int_0^s \hat{q}_0(\chi) d\chi = \frac{1}{2} \frac{\alpha}{1-\nu} (\varepsilon_c^{+\infty} + \varepsilon_m), \quad \text{for } s > 0, \quad (68)$$

$$\frac{1}{\pi} \int_0^\infty \frac{\hat{q}_1(\chi)}{\chi-s} d\chi - \frac{1}{2} \int_0^s \hat{q}_1(\chi) d\chi = \frac{1}{2} \frac{1+\nu}{1-\nu} \varepsilon_c^{+\infty} \left(\frac{\alpha}{1-\nu} (\varepsilon_c^{+\infty} + \varepsilon_m) + \int_0^s \hat{q}_0(\chi) d\chi \right), \quad \text{for } s > 0. \quad (69)$$

Note that (68) and (69) are singular integral equations for $\hat{q}_0(\chi)$ and $\hat{q}_1(\chi)$. Clearly, once (68) is solved for $\hat{q}_0(\chi)$, the right hand side of (69) is known, thus can be solved as well. Analytical solutions to these singular integral equations do not seem to be feasible. In this work, they are solved numerically, see Appendix B.

6.2. Crack-tip stress intensity factor

Once the interfacial shear stress $q(x)$ is obtained, the mode II stress intensity factor can be written as (Erdogan and Joseph, 1990),

$$K_{II} = \lim_{x \rightarrow 0} \sqrt{2\pi x} q(x) = -\frac{\sqrt{hE}}{1-\nu} \sqrt{\alpha} \left(1 + \frac{1+\nu}{2} \frac{\hat{\eta}}{1-\nu} \varepsilon_c^{+\infty} \right) (\varepsilon_m + \varepsilon_c^{+\infty}). \quad (70)$$

In deriving the last equality, we have used (B11) and (B12).

6.3. Calculating the chemo-mechanical J -integral using the near-tip solution

Knowing the shear stress distribution at the film-substrate interface, one can calculate the chemo-mechanical J integral for a vanishingly small contour encircling the crack tip, $\Gamma_\varepsilon = \sum_{n=1}^6 \Gamma_n$,

$$J_{\Gamma_\varepsilon}^{cm} = \int_{\Gamma_\varepsilon} \left(\psi n_x - t_x \frac{\partial u_x}{\partial X} - t_z \frac{\partial u_z}{\partial X} \right) d\Gamma. \quad (71)$$

To this end, consider a small piecewise smooth closed contour, see Fig. 3, comprising (i) Γ_3 and Γ_5 : straight lines normal to the interface at $x = +r_\varepsilon$, $x = -r_\varepsilon$ within the film, (ii) Γ_6 : a straight line from $x = r_\varepsilon$ to $x = -r_\varepsilon$ in the film surface, (iii) Γ_2 : a semicircle centered at the crack tip of radius r_ε within the substrate, and (iv) Γ_1 and Γ_4 : straight lines on the lower and upper crack surfaces. As usual, the unit normal vector is considered pointing away from the crack tip. Contribution from (ii) vanishes because $t_x = t_z = 0$ and $n_x = 0$ on (ii) under the membrane assumption. For the same reason, shear stress vanishes in the film. Hence $t_z = 0$ on the parts of the contour in (i). Again, under the membrane assumption, the stresses and strains in the film are continuous at $x = 0$, so is the elastic energy density. Therefore, under chemical equilibrium, the solute

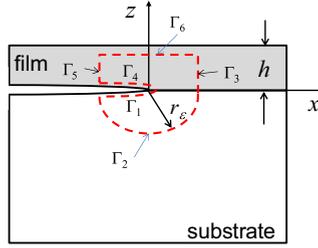


Fig. 3. A vanishingly small contour encircling the crack tip, $\Gamma_\epsilon = \sum_{n=1}^6 \Gamma_n$.

concentration field is also continuous at $x = 0$. As $r_\epsilon \rightarrow 0$, both Γ_3 and Γ_5 approach to $x = 0$. Since the integrand is continuous, the integrals along Γ_3 and Γ_5 cancel out. Thus the contribution from (i) vanishes. Finally, contributions from (iv) also vanish because $t_x = t_z = 0$ and $n_x = 0$ on the crack surfaces. Consequently, the only non-trivial contribution is from (iii), which lies entirely within the substrate. Since the substrate is inactive chemically, i.e. $c = s = 0$, we have $\psi = w_e$, i.e.,

$$J_{\Gamma_\epsilon}^{cm} = \int_{\Gamma_2} \left(w_e n_x - t_x \frac{\partial u_x}{\partial x} - t_z \frac{\partial u_z}{\partial x} \right) d\Gamma, \tag{72}$$

where Γ_2 is the semicircle of radius r_ϵ centered at the crack tip in the substrate. One can readily show that the above integral can be written in terms of the stress intensity K_{II} as (Erdogan and Joseph, 1990),

$$J_{\Gamma_\epsilon}^{cm} = \frac{1 - \nu_s^2}{2E_s} K_{II}^2. \tag{73}$$

Making use of (70) in (73) and neglecting higher terms in $\hat{\eta}$ yield

$$J_{\Gamma_\epsilon}^{cm} = \frac{hE(1+\nu)}{2(1-\nu)} (\epsilon_m + \epsilon_c^{+\infty})^2 \left(1 + \frac{1+\nu}{1-\nu} \hat{\eta} \epsilon_c^{+\infty} \right). \tag{74}$$

This chemo-mechanical J -integral computed along a vanishingly small contour encircling the crack tip is identical to (59), which was computed along a contour far away from the crack tip. This verifies path-independency property of J^{cm} .

Further, we note that (72) is actually the classical J -integral given by (8). Thus, the fact that (74) is identical to (59) also confirms (26) in that the chemo-mechanical J -integral $J_{\Gamma_\epsilon}^{cm}$ is equal to the classical J -integral when computed along a vanishingly small contour encircling the crack tip.

7. Summary and concluding remarks

We showed in this study that the classical J -integral is no longer path-independent under electro-chemo-mechanical equilibrium. We further derived an electro-chemo-mechanical path-independent J -integral. The integral is formulated in terms of the grand potential energy of the system that governs the thermodynamics of a grand canonical ensemble. It was shown that this integral, once computed for a contour encircling a crack tip, yields the rate at which the grand potential energy of the system decreases with crack growth. To illustrate the applicability of this integral, we considered the delamination of an elastic thin film from an elastic thick substrate under combined chemical and mechanical loadings. The chemo-mechanical fields were obtained by solving a singular integral equation. The corresponding chemo-mechanical J -integral was then calculated using a contour far away from the delamination front, and a contour near the delamination front, respectively. We demonstrated that both ways of calculating the chemo-mechanical J -integral yield identical results, indicating the path-independent nature of the chemo-mechanical J -integral.

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Appendix A

Consider the material derivative of the grand potential ψ ,

$$\dot{\psi} \equiv \frac{\partial \psi}{\partial t} - v \frac{\partial \psi}{\partial x_1}. \tag{A1}$$

Under electro-chemo-mechanical equilibrium, the local rate of change of the grand potential vanishes, i.e., $\partial\psi/\partial t = 0$. It thus follows from (22) that

$$-\frac{1}{\nu}\dot{\psi} = \sigma_{ij} \frac{\partial \varepsilon_{ij}^e}{\partial x_1} - \frac{\partial u}{\partial x_1} + zFc \frac{\partial \phi}{\partial x_1} - (\mu_R - \mu_0 - zF\phi) \frac{\partial c}{\partial x_1} - T \frac{\partial s}{\partial x_1}, \quad (\text{A2})$$

where we have used the fact that μ_R , μ_0 and T are independent of x_1 . Eq. (A2) can be simplified with the aid of (5), and (7), to obtain

$$-\frac{1}{\nu}\dot{\psi} = \frac{\partial}{\partial x_j} \left(\sigma_{ij} \frac{\partial u_i}{\partial x_1} - \kappa_\varepsilon \varepsilon_0 \frac{\partial \phi}{\partial x_1} \frac{\partial \phi}{\partial x_j} \right) - \left(\eta V_m \sigma_{kk} + (\mu_R - \mu_0) + T \frac{\partial s}{\partial c} - zF\phi \right) \frac{\partial c}{\partial x_1}. \quad (\text{A3})$$

Furthermore, electrochemical equilibrium $\mu = \mu_R$, with μ given in (6), suggests that the second term in (A3) identically vanishes. Hence,

$$\dot{\psi} = \frac{\partial \varphi_j}{\partial x_j}. \quad (\text{A4})$$

Appendix B

We begin by considering,

$$\frac{1}{\pi} \int_0^\infty \frac{f^{(0)}(\chi)}{\chi-s} d\chi - \frac{1}{2} \int_0^s f^{(0)}(\chi) d\chi = 1, \quad (\text{B1})$$

$$\frac{1}{\pi} \int_0^\infty \frac{f^{(1)}(\chi)}{\chi-s} d\chi - \frac{1}{2} \int_0^s f^{(1)}(\chi) d\chi = \int_0^s f^{(0)}(\chi) d\chi. \quad (\text{B2})$$

Once the above are solved for $f^{(0)}$ and $f^{(1)}$, it is straightforward to show that the solutions to (68) and (69) can be written as,

$$\hat{q}_0 = \frac{1}{2} \frac{\alpha}{1-\nu} (\varepsilon_c^{+\infty} + \varepsilon_m) f^{(0)}, \quad (\text{B3})$$

$$\hat{q}_1 = \frac{1}{2} \frac{\alpha(1+\nu)}{(1-\nu)^2} (\varepsilon_c^{+\infty} + \varepsilon_m) \varepsilon_c^{+\infty} \left(f^{(0)} + \frac{1}{2} f^{(1)} \right). \quad (\text{B4})$$

In order to solve (B1) and (B2), we will reduce them to a system of linear algebraic equations following the numerical procedure outlined in Erdogan et al. (1973). By introducing the change of variables $\hat{\chi} = \chi - 1/\chi + 1$, $\hat{s} = s - 1/s + 1$, and $f^{(m)}(\chi) = f^{(m)}(1 + \hat{\chi}/1 - \hat{\chi}) = \hat{f}^{(m)}(\hat{\chi})$ for $m = 0, 1$, Eqs. (B1) and (B2) can be transformed to the standard form of Cauchy singular integral equation of the second kind,

$$\frac{1}{\pi} \int_{-1}^1 \frac{\hat{f}^{(m)}(\hat{\chi})}{\hat{\chi} - \hat{s}} d\hat{\chi} + \int_{-1}^1 K(\hat{s}, \hat{\chi}) \hat{f}^{(m)}(\hat{\chi}) d\hat{\chi} = b^{(m)}(\hat{s}), \quad m = 0, 1, \quad (\text{B5})$$

where $K(\hat{s}, \hat{\chi}) = 1/\pi(1 - \hat{\chi}) - \text{H}(\hat{s} - \hat{\chi})/(1 - \hat{\chi})^2$, $b^{(0)}(\hat{s}) = 1$, and $b^{(1)}(\hat{s}) = \int_{-1}^{\hat{s}} 2\hat{f}^{(0)}(\hat{\chi})/(1 - \hat{\chi})^2 d\hat{\chi}$. Here $\text{H}(z)$ is the Heaviside unit step function. Using the Jacobi polynomials $P_{j-1}^{(1/2, -1/2)}$ (Abramowitz and Stegun, 1964), the solutions to (B5) can be written in the form of

$$\hat{f}^{(m)}(\hat{\chi}) = \sqrt{\frac{1-\hat{\chi}}{1+\hat{\chi}}} \sum_{j=1}^n c_j^{(m)} P_{j-1}^{(1/2, -1/2)}(\hat{\chi}), \quad m = 0, 1, \quad (\text{B6})$$

where $c_j^{(i)}$ is obtained by solving the following systems of linear algebraic equations,

$$\varphi^{*(m)}(\hat{\chi}_i) = \sum_{j=1}^n c_j^{(m)} P_{j-1}^{(1/2, -1/2)}(\hat{\chi}_i), \quad m = 0, 1, \quad (\text{B7})$$

$$\sum_{k=1}^n A_{ki} \varphi^{*(m)}(\hat{\chi}_i) = b^{(m)}(\hat{s}_k), \quad i = 1, \dots, n, \quad m = 0, 1, \quad (\text{B8})$$

In the above, $\hat{\chi}_i = \cos(2i\pi/(2n+1))$, $\hat{s}_k = \cos((2k-1)\pi/(2n+1))$, $A_{ki} = 2(1 - \hat{\chi}_i)/(2n+1)[1/(\hat{\chi}_i - \hat{s}_k) + \pi K(\hat{s}_k, \hat{\chi}_i)]$ for $i, k = 1, \dots, n$ (Erdogan et al., 1973). Strength of the singularity of $f^{(m)}$ at $s = 0$ can be obtained as

$$\lim_{s \rightarrow 0} \sqrt{2s} f^{(m)}(s) = \lim_{\hat{s} \rightarrow -1} \sqrt{2} \sqrt{\frac{1+\hat{s}}{1-\hat{s}}} \hat{f}^{(m)}(\hat{s}) = \sqrt{2} \sum_{j=1}^n c_j^{(m)} P_{j-1}^{(1/2, -1/2)}(-1). \quad (\text{B9})$$

Our numerical solutions indicate that one can write, with errors less than a few percent,

$$\lim_{s \rightarrow 0} \sqrt{2s} f^{(0)}(s) = -\lim_{s \rightarrow 0} \sqrt{2s} f^{(1)}(s) = -\frac{2}{\sqrt{\pi}}. \quad (\text{B10})$$

Thus, combining (B3) and (B4) with (B10) leads to

$$\lim_{x \rightarrow 0} \sqrt{2\pi x} q_0(x) = \frac{\sqrt{hE}}{\sqrt{\alpha}} \lim_{s \rightarrow 0} \sqrt{2\pi s} \hat{q}_0(s) = -\sqrt{hE} \frac{\sqrt{\alpha}}{1-\nu} (\epsilon_c^{+\infty} + \epsilon_m), \quad (\text{B11})$$

$$\lim_{x \rightarrow 0} \sqrt{2\pi x} q_1(x) = \frac{\sqrt{hE}}{\sqrt{\alpha}} \lim_{s \rightarrow 0} \sqrt{2\pi s} \hat{q}_1(s) = -\frac{1}{2} \sqrt{hE} \sqrt{\alpha} \frac{1+\nu}{(1-\nu)^2} \epsilon_c^{+\infty} (\epsilon_c^{+\infty} + \epsilon_m). \quad (\text{B12})$$

References

- Abramowitz, M., Stegun, I.A., 1964. Handbook of Mathematical Functions with Formulas, Graphs, and Mathematical Tables. U.S. Govt. Print. Off. Washington.
- Atkinson, C., Eshelby, J.D., 1968. Flow of energy into tip of a moving crack. *Int. J. Fract. Mech.* 4 (1), 3–8.
- Bhandakkar, T.K., Gao, H.J., 2010. Cohesive modeling of crack nucleation under diffusion induced stresses in a thin strip: implications on the critical size for flaw tolerant battery electrodes. *Int. J. Solids Struct.* 47 (10), 1424–1434.
- Bhandakkar, T.K., Gao, H.J., 2011. Cohesive modeling of crack nucleation in a cylindrical electrode under axisymmetric diffusion induced stresses. *Int. J. Solids Struct.* 48 (16–17), 2304–2309.
- Bhattacharya, J., Van der Ven, A., 2010. Phase stability and nondilute Li diffusion in spinel $\text{Li}_1+x\text{Ti}_2\text{O}_4$. *Phys. Rev. B* 81, 10.
- Blackburn, W.S., 1972. Path Independent integrals to predict onset of crack instability in an elastic plastic material. *Int. J. Fract. Mech.* 8 (3), 343–346.
- Blackburn, W.S., Jackson, A.D., Hellen, T.K., 1977. Integral associated with state of a crack tip in a non-elastic material. *Int. J. Fract.* 13 (2), 183–200.
- Brassart, L., Zhao, K.J., Suo, Z.G., 2013. Cyclic plasticity and shakedown in high-capacity electrodes of lithium-ion batteries. *Int. J. Solids Struct.* 50 (7–8), 1120–1129.
- Chen, X.H., 2007. Coupled hydro-thermo-viscoelastic fracture theory. *Int. J. Fract.* 148 (1), 47–55.
- Chen, Y.-H., Lu, T.J., 2003. Recent developments and applications of invariant integrals. *Appl. Mech. Rev.* 56 (5), 515–552.
- Cherepanov, G.P., 1967. Crack propagation in continuous media. *J. Appl. Math. Mech.-Ussr* 31 (3), 503–8.
- Cui, Z., Gao, F., Qu, J., 2013. Interface-reaction controlled diffusion in binary solids with applications to lithiation of silicon in lithium-ion batteries. *J. Mech. Phys. Solids* 61, 293–310.
- Cui, Z.W., Gao, F., Cui, Z.H., Qu, J.M., 2012a. A second nearest-neighbor embedded atom method interatomic potential for Li-Si alloys. *J. Power Sources* 207, 150–159.
- Cui, Z.W., Gao, F., Qu, J.M., 2012b. A finite deformation stress-dependent chemical potential and its applications to lithium ion batteries. *J. Mech. Phys. Solids* 60 (7), 1280–1295.
- Dascalu, C., Maugin, G.A., 1994. Energy-release rates and path-independent integrals in electroelastic crack-propagation. *Int. J. Eng. Sci.* 32 (5), 755–765.
- Erdogan, F., Gupta, G.D., Cook, T.S., 1973. Numerical Solution of Singular Integral Equations. Noordhoff International Pub, Leyden.
- Erdogan, F., Joseph, P.F., 1990. Mechanical modeling of multilayered films on an elastic substrate—Part i: analysis. *J. Electron. Packag.* 112 (4), 309–316.
- Freund, L.B., 1972. Energy flux into the tip of an extending crack in an elastic solid. *J. Elast.* 2 (4), 341–349.
- Gao, H.J., Barnett, D.M., 1996. An invariance property of local energy release rate in a strip saturation model of piezoelectric fracture. *Int. J. Fract.* 79 (2), R25–R29.
- Gao, Y.F., Zhou, M., 2013. Coupled mechano-diffusional driving forces for fracture in electrode materials. *J. Power Sources* 230, 176–193.
- Grantab, R., Shenoy, V.B., 2011. Location- and orientation-dependent progressive crack propagation in cylindrical graphite electrode particles. *J. Electrochem. Soc.* 158 (8), A948–A954.
- Haftbaradaran, H., Gao, H.J., 2012. Ratcheting of silicon island electrodes on substrate due to cyclic intercalation. *Appl. Phys. Lett.* 100 (12).
- Haftbaradaran, H., Xiao, X.C., Verbrugge, M.W., Gao, H.J., 2012. Method to deduce the critical size for interfacial delamination of patterned electrode structures and application to lithiation of thin-film silicon islands. *J. Power Sources* 206, 357–366.
- Hill, T.L., 1986. An Introduction to Statistical Thermodynamics. Dover Publications, New York.
- Honein, T., Herrmann, G., 1997. Conservation laws in nonhomogeneous plane elastostatics. *J. Mech. Phys. Solids* 45 (5), 789–805.
- Huggins, R.A., Nix, W.D., 2000. Decrepitation model for capacity loss during cycling of alloys in rechargeable electrochemical systems. *Ionics* 6 (1–2), 57–63.
- Hutchinson, J.W., 1968. Singular behaviour at end of a tensile crack in a hardening material. *J. Mech. Phys. Solids* 16 (1), 13–31.
- Johnson, K.L., 1985. Contact Mechanics. Cambridge University Press, Cambridge Cambridgeshire; New York.
- Knowles, J.K., Sternberg, E., 1972. Class of conservation laws in linearized and finite elastostatics. *Arch. Rational Mech. Anal.* 44 (3), 187–211.
- Larche, F., Cahn, J.W., 1973. Linear theory of thermochemical equilibrium of solids under stress. *Acta Metall.* 21 (8), 1051–1063.
- Larche, F.C., Cahn, J.W., 1982. The Effect of Self-Stress on Diffusion in Solids. *Acta Metall.* 30 (10), 1835–1845.
- Larche, F.C., Cahn, J.W., 1985. The interactions of composition and stress in crystalline solids. *Acta Metall.* 33 (3), 331–357.
- Larche, F.C., Cahn, J.W., 1987. Stress effects on III–V solid–liquid equilibria. *J. Appl. Phys.* 62 (4), 1232–1239.
- Larche, F.C., Cahn, J.W., 1992. Phase-changes in a thin plate with nonlocal self-stress effects. *Acta Metall. Mater.* 40 (5), 947–955.
- Lee, S.W., McDowell, M.T., Berla, L.A., Nix, W.D., Cui, Y., 2012. Fracture of crystalline silicon nanopillars during electrochemical lithium insertion. *Proceedings of the National Academy of Sciences of the United States of America* 109 (11), 4080–4085.
- Liang, Y., Sofronis, P., 2003. Micromechanics and numerical modelling of the hydrogen-particle-matrix interactions in nickel-base alloys. *Model. Simul. Mater. Sci. Eng.* 11 (4), 523–551.
- Liu, X.H., Zheng, H., Zhong, L., Huan, S., Karki, K., Zhang, L.Q., Liu, Y., Kushima, A., Liang, W.T., Wang, J.W., Cho, J.H., Epstein, E., Dayeh, S.A., Picraux, S.T., Zhu, T., Li, J., Sullivan, J.P., Cummings, J., Wang, C.S., Mao, S.X., Ye, Z.Z., Zhang, S.L., Huang, J.Y., 2011. Anisotropic swelling and fracture of silicon nanowires during lithiation. *Nano Lett.* 11 (8), 3312–3318.
- Liu, X.H., Zhong, L., Huang, S., Mao, S.X., Zhu, T., Huang, J.Y., 2012. Size-dependent fracture of silicon nanoparticles during lithiation. *Acs Nano* 6 (2), 1522–1531.
- Maranchi, J.P., Hepp, A.F., Evans, A.G., Nuhfer, N.T., Kumta, P.N., 2006. Interfacial properties of the a-Si/Cu: active-inactive thin-film anode system for lithium-ion batteries. *J. Electrochem. Soc.* 153 (6), A1246–A1253.
- Matos, P.P.L., Mcmeeking, R.M., Charalambides, P.G., Drory, M.D., 1989. A method for calculating stress intensities in bimaterial fracture. *Int. J. Fract.* 40 (4), 235–254.
- Moran, B., Shih, C.F., 1987. A general treatment of crack tip contour integrals. *Int. J. Fract.* 35 (4), 295–310.
- Novak, P., Yuan, R., Somersday, B.P., Sofronis, P., Ritchie, R.O., 2010. A statistical, physical-based, micro-mechanical model of hydrogen-induced intergranular fracture in steel. *J. Mech. Phys. Solids* 58 (2), 206–226.

- Park, J.H., Earmme, Y.Y., 1986. Application of conservation integrals to interfacial crack problems. *Mech. Mater.* 5 (3), 261–276.
- Persson, K., Sethuraman, V.A., Hardwick, L.J., Hinuma, Y., Meng, Y.S., van der Ven, A., Srinivasan, V., Kostecki, R., Ceder, G., 2010. Lithium diffusion in graphitic carbon. *J. Phys. Chem. Lett.* 1 (8), 1176–1180.
- Pupurs, A., Varna, J., 2014. Modeling mechanical stress and exfoliation damage in carbon fiber electrodes subjected to cyclic intercalation/deintercalation of lithium ions. *Compos. Part B: Eng.* <http://dx.doi.org/10.1016/j.compositesb.2013.11.007>, in press.
- Qi, Y., Xu, Q.C., Van Der Ven, A., 2012. Chemically induced crack instability when electrodes fracture. *J. Electrochem. Soc.* 159 (11), A1838–A1843.
- Qu, J., Bassani, J.L., 1993. Interfacial fracture-mechanics for anisotropic bimetals. *J. Appl. Mech.-Trans. ASME* 60 (2), 422–431.
- Qu, J.M., Li, Q.Q., 1991. Interfacial dislocation and its applications to interface cracks in anisotropic bimetals. *J. Elast.* 26 (2), 169–195.
- Rice, J.R., 1968. A path independent integral and approximate analysis of strain concentration by notches and cracks. *J. Appl. Mech.* 35 (2), 379–386.
- Rice, J.R., Rosengren, G.F., 1968. Plane strain deformation near a crack tip in a power-law hardening material. *J. Mech. Phys. Solids* 16 (1), 1–12.
- Ryu, I., Choi, J.W., Cui, Y., Nix, W.D., 2011. Size-dependent fracture of Si nanowire battery anodes. *J. Mech. Phys. Solids* 59 (9), 1717–1730.
- Schaperly, R.A., 1984. Correspondence principles and a generalized J integral for large deformation and fracture-analysis of viscoelastic media. *Int. J. Fract.* 25 (3), 195–223.
- Sethuraman, V.A., Chon, M.J., Shimshak, M., Srinivasan, V., Guduru, P.R., 2010. In situ measurements of stress evolution in silicon thin films during electrochemical lithiation and delithiation. *J. Power Sources* 195 (15), 5062–5066.
- Sethuraman, V.A., Srinivasan, V., Bower, A.F., Guduru, P.R., 2010. In situ measurements of stress-potential coupling in lithiated silicon. *J. Electrochem. Soc.* 157 (11), A1253–A1261.
- Sobotka, J.C., Dodds, R.H., Sofronis, P., 2009. Effects of hydrogen on steady, ductile crack growth: computational studies. *Int. J. Solids Struct.* 46 (22–23), 4095–4106.
- Sofronis, P., McMeeking, R.M., 1989. Numerical-analysis of hydrogen transport near a blunting crack tip. *J. Mech. Phys. Solids* 37 (3), 317–350.
- Suo, Z., Kuo, C.M., Barnett, D.M., Willis, J.R., 1992. Fracture-mechanics for piezoelectric ceramics. *J. Mech. Phys. Solids* 40 (4), 739–765.
- Swaminathan, N., Qu, J., 2007. Interactions between non-stoichiometric stresses and defect transport in a tubular electrolyte. *Fuel Cells* 7 (6), 453–462.
- Swaminathan, N., Qu, J., 2009. Evaluation of thermomechanical properties of non-stoichiometric gadolinium doped ceria using atomistic simulations. *Model. Simul. Mater. Sci. Eng.* 17 (4), 045006.
- Swaminathan, N., Qu, J., Sun, Y., 2007a. An electrochemomechanical theory of defects in ionic solids. I. Theory. *Philos. Mag.* 87 (11), 1705–1721.
- Swaminathan, N., Qu, J., Sun, Y., 2007b. An electrochemomechanical theory of defects in ionic solids. Part II. Examples. *Philos. Mag.* 87 (11), 1723–1742.
- Van der Ven, A., Thomas, J.C., Xu, Q.C., Swoboda, B., Morgan, D., 2008. Nondilute diffusion from first principles: Li diffusion in $\text{Li}(x)\text{TiS}_2$. *Phys. Rev. B* 78, 10.
- Wei, Y.G., Hutchinson, J.W., 1997. Nonlinear delamination mechanics for thin films. *J. Mech. Phys. Solids* 45 (7), 1137–1159.
- Wilson, W.K., Yu, I.W., 1979. Use of the J -integral in thermal-stress crack problems. *Int. J. Fract.* 15 (4), 377–387.
- Woodford, W.H., Chiang, Y.M., Carter, W.C., 2010. “Electrochemical Shock” of intercalation electrodes: a fracture mechanics analysis. *J. Electrochem. Soc.* 157 (10), A1052–A1059.
- Wu, H., Chan, G., Choi, J.W., Ryu, I., Yao, Y., McDowell, M.T., Lee, S.W., Jackson, A., Yang, Y., Hu, L.B., Cui, Y., 2012. Stable cycling of double-walled silicon nanotube battery anodes through solid-electrolyte interphase control. *Nat. Nanotechnol.* 7 (5), 309–314.
- Xiao, X., Liu, P., Verbrugge, M.W., Haftbaradaran, H., Gao, H., 2011. Improved cycling stability of silicon thin film electrodes through patterning for high energy density lithium batteries. *J. Power Sources* 196 (3), 1409–1416.
- Yang, F., Wang, J., Chen, D.P., 2006. The energy release rate for hygrothermal coupling elastic materials. *Acta Mech. Sin.* 22 (1), 28–33.
- Zhao, K.J., Pharr, M., Vlassak, J.J., Suo, Z.G., 2010. Fracture of electrodes in lithium-ion batteries caused by fast charging. *J. Appl. Phys.* 108, 7.
- Zhao, K.J., Wang, W.L., Gregoire, J., Pharr, M., Suo, Z.G., Vlassak, J.J., Kaxiras, E., 2011. Lithium-assisted plastic deformation of silicon electrodes in lithium-ion batteries: a first-principles theoretical study. *Nano Lett.* 11 (7), 2962–2967.
- Zhou, M. 2014. Private Communication.