



## Cohesive modeling of crack nucleation in a cylindrical electrode under axisymmetric diffusion induced stresses

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### ARTICLE INFO

#### Article history:

Received 2 June 2010

Received in revised form 18 March 2011

Available online 27 April 2011

#### Keywords:

Intercalation–deintercalation

Diffusion-induced stress

Lithium electrodes

Fracture

Flaw tolerance

Cohesive zone

Nanowire

### ABSTRACT

We have recently modeled crack nucleation in a 2D strip electrode as localization of a periodic array of cohesive zones subject to diffusion induced stresses in an initially crack-free thin strip under galvanostatic solute insertion and extraction. Here we generalize this model to crack nucleation in a cylindrical electrode under axisymmetric diffusion induced stresses, focusing on the effect of the cylindrical geometry on the crack nucleation condition. Similar to our previous findings for the 2D strip geometry, the present analysis identifies a critical electrode size, typically in the nanometer range, to avoid crack nucleation.

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### 1. Introduction

The technological needs to develop damage resistant lithium-ion battery electrodes with very large stresses and volume changes during Li intercalation–deintercalation cycles are calling for studies on crack nucleation under diffusion induced stresses. In the past, numerous models have been developed to describe the insertion/extraction of Li in an electrode as diffusion of interstitial atoms in a host material (García et al., 2005; Christensen and Newman, 2006a,b; Zhang et al., 2007, 2008; Cheng and Verbrugge, 2008, 2009; Deshpande et al., 2010a,b; Haftbaradaran et al., 2010, 2011; Yang, 2010), a subclass of problems more broadly referred to as the diffusion induced stresses (DIS) (Prussin, 1961; Li, 1978; Yang, 2005). In comparison, relatively few studies have explicitly considered crack nucleation under DIS. Huggins and Nix (2000) considered a bilayer plate with the top layer subjected to a swelling transformation strain and the bottom layer containing a crack. The Huggins–Nix model has been extended to the case of non-uniform distribution of DIS to predict relationships between charging rate, size and fracture toughness of an electrode particle for preventing growth of pre-existing cracks (Woodford et al., 2010; Zhao et al., 2010, 2011). In contrast, we have developed a cohesive model of crack nucleation in a strip electrode under galvanostatic

charge and discharge (Bhandakkar and Gao, 2010). Compared to the Huggins–Nix model and its extensions (Huggins and Nix, 2000; Woodford et al., 2010; Zhao et al., 2010, 2011) which used Griffith's criterion to predict a critical condition for crack growth, the Bhandakkar–Gao model considers spontaneous localization of a periodic array of cohesive zones during dynamic evolution of DIS in an initially crack-free electrode.

Recent years have seen the development of various forms of cylindrical electrodes such as nanorods, nanopillars and nanowires, with improved performance and cycle life compared to planar and spherical electrode geometries (Taberna et al., 2006; Chan et al., 2008). The exact mechanism behind the superior mechanical response of cylindrical electrodes is unresolved and is being actively pursued (e.g. Huang et al., 2010). In the present paper, we extend the 2D Bhandakkar–Gao model to localization of an array of cohesive zones in a cylindrical electrode under axisymmetric diffusion induced stress as the maximum DIS exceeds the cohesive strength of the material (Fig. 1). Such localized deformation is thought to be initially reversible, and crack nucleation is assumed to occur when the maximum surface separation within the cohesive zone reaches a critical value.

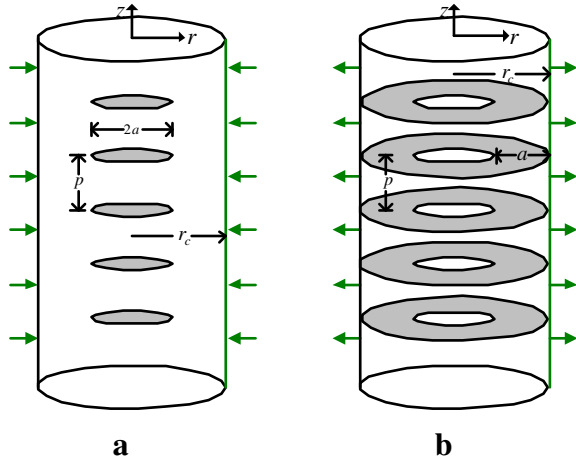
### 2. Diffusion induced stress in a cylindrical electrode

Fig. 1 shows a cylindrical electrode with diameter  $2r_c$  subject to insertion and extraction of an interstitial species such as Li. The electrode material is taken to be an isotropic linear elastic solid and the deformation is assumed quasi-static. Following an analogy

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**Fig. 1.** Schematic illustration of crack nucleation in a cylindrical electrode of diameter  $2r_c$  during galvanostatic (a) intercalation and (b) extraction, modeled as diffusion along the radial direction ( $r$ -axis). The axisymmetric crack nuclei are uniformly spaced with period  $p$  and modeled as localized cohesive zones obeying the triangular traction-separation law (Eq. (11)).

between DIS (Zhang et al., 2007, 2008; Cheng and Verbrugge, 2008, 2009; Deshpande et al., 2010a,b; Haftbaradaran et al., 2010, 2011; Yang, 2010) and thermal stresses, the transport of solute in the cylinder is modeled as a concentration driven diffusion process along the radial ( $r$ ) direction of the electrode (Crank, 1980),

$$\frac{\partial c}{\partial t} = D \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial c}{\partial r} \right), \quad (1)$$

where  $D$  is the diffusivity and  $c$  is the molar concentration of solute. The insertion of solute atoms into host causes a swelling transformation strain  $\Omega c/3$ ,  $\Omega$  being the partial molar volume of solute, which generates the following axial stress in the electrode (Timoshenko and Goodier, 1970),

$$\sigma_D(r, t) = \frac{E\Omega}{3(1-\nu)} \left[ \frac{2}{r_c^2} \int_0^{r_c} r' c(r', t) dr' - c(r, t) \right], \quad (2)$$

where  $E$  is the Young's modulus and  $\nu$  the Poisson ratio of the material.

Consider the variations of solute concentration and the corresponding DIS during charging and discharging. The initial solute concentration in the electrode is assumed to be zero. Under galvanostatic boundary conditions as shown in Fig. 1,

$$-D \frac{\partial c}{\partial r} \Big|_{r_c} = -\frac{I}{F}; \quad -D \frac{\partial c}{\partial r} \Big|_0 = 0, \quad (3)$$

where  $I$  is the surface current density and  $F = 96486.7$  C/mol is Faraday's constant, the solute concentration during insertion can be found as (Crank, 1980)

$$\frac{c(r, t)}{I r_c / FD} = \frac{2Dt}{r_c^2} + \frac{r^2}{2r_c^2} - \frac{1}{4} - 2 \sum_{n=1}^{\infty} \frac{J_0(\alpha_n r / r_c)}{\alpha_n^2 J_0(\alpha_n)} \exp \left\{ -\frac{Dt \alpha_n^2}{r_c^2} \right\}, \quad (4)$$

and the associated DIS is

$$\sigma_D(r, t) = \frac{E\Omega}{3(1-\nu)} \frac{I r_c}{FD} \left[ \frac{1}{4} - \frac{r^2}{2r_c^2} + 2 \sum_{n=1}^{\infty} \frac{J_0(\alpha_n r / r_c)}{\alpha_n^2 J_0(\alpha_n)} \exp \left\{ -\frac{Dt \alpha_n^2}{r_c^2} \right\} \right], \quad (5)$$

where  $J_0(r)$  is the Bessel function of the first kind and  $\alpha_n$  are the roots of  $J_1(\alpha)$ . At the end of charging, the stress approaches a steady state while the solute concentration rises steadily with time. This situation persists until the saturation limit of material is reached.

The steady state solution then acts as the initial condition for the extraction process,

$$c(r, 0) = c_1 + \frac{I r_c}{FD} \left[ \frac{r^2}{2r_c^2} - \frac{1}{4} \right], \quad (6)$$

where

$$c_1 = \frac{2I t_c}{F r_c}, \quad (7)$$

$t_c$  denoting the charging time. During extraction, the solute concentration evolves as

$$\frac{c(r, t) - c_1}{I r_c / FD} = -\frac{2Dt}{r_c^2} - \frac{r^2}{2r_c^2} + \frac{1}{4} + 4 \sum_{n=1}^{\infty} \frac{J_0(\alpha_n r / r_c)}{\alpha_n^2 J_0(\alpha_n)} \exp \left\{ -\frac{Dt \alpha_n^2}{r_c^2} \right\}, \quad (8)$$

with the associated DIS

$$\sigma_D(r, t) = \frac{E\Omega}{3(1-\nu)} \frac{I r_c}{FD} \left[ \frac{r^2}{2r_c^2} - \frac{1}{4} - 4 \sum_{n=1}^{\infty} \frac{J_0(\alpha_n r / r_c)}{\alpha_n^2 J_0(\alpha_n)} \exp \left\{ -\frac{Dt \alpha_n^2}{r_c^2} \right\} \right]. \quad (9)$$

Fig. 2 plots the variations of solute concentration and the associated DIS during the first charging and discharging cycle. During insertion, the solute concentration continuously rises with time (Fig. 2a) while the stress approaches a steady state with tension near the center and compression near the free surface of the electrode (Fig. 2b). The peak tensile stress occurs at the centre when reaching the steady state, with magnitude equal to (Fig. 2b)

$$\sigma_{peak} = E\Omega I r_c / 12(1-\nu) FD. \quad (10)$$

During extraction, the surface current is reversed, and the solute concentration continuously decreases with time (Fig. 2c) while the stress approaches a steady state with compression near the center and tension at the surface of the electrode. The peak tensile stress occurs at the surface with the same magnitude as Eq. (10) when reaching the steady state (Fig. 2d).

Note that the above solutions to DIS neglect a number of nonlinear coupling effects and may be oversimplified in a number of ways. The reader is referred to Christensen and Newman (2006) for some detailed discussions. The current density  $I$  in the surface flux boundary condition of Eq. (3) couples the diffusion induced stress problem with electrochemical kinetics described by the Butler-Volmer reaction (Newman and Thomas, 2004; Zhang et al., 2008; Golmon et al., 2010). Heat generation in the electrode during charge and discharge also affects DIS. A fully coupled electrochemical-mechanical model with heat generation identified resistive heating as the most important heat source for electrode particles (Zhang et al., 2008). By introducing a coupling between internal stresses and activation energy for diffusion, Haftbaradaran et al. (2010) discovered a class of nonconventional solutions to DIS with a surface choking instability once the product between electrode dimension and charging rate exceeds a critical value. The nonlinear coupling between DIS and solute concentration in high capacity electrodes was also demonstrated through validation of continuum modeling with atomistic simulations of hydrogen diffusion in nickel, taking into account the coupling between DIS and the activation energy for diffusion, an upper bound to solute concentration based on stoichiometric limit and a concentration-dependent binding energy between the host and solute (Haftbaradaran et al., 2011). The effect of concentration-dependent binding energy between the host and solute on DIS was also analyzed by Yang (2010) for the thin plate geometry. First principle calculations have shown

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