A model for crack initiation in the Li-ion battery electrodes

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ABSTRACT
The development of high energy density Lithium-ion batteries is of intense interest due to their application in the electric car and consumer electronics industry. The primary limiter in using high energy density battery electrodes is the cracking of the electrode material due to the severe strain caused by the charging–discharging cycles. In this paper, a linear perturbation model is used to describe the evolution of the electrode surface under stress. The driving force for the surface undulation formation is the reduction in the electrode strain energy. The kinetics of mass transport is described by the surface and volume diffusion. The model predicts that the Si electrode will develop surface undulations of the order of sub-1 µm length scale on the electrode surface, showing a reasonable agreement with experimental results reported in literature. Such surface undulations roughen the anode surface and can form notches that can act as crack initiation sites. It is also shown that this model is applicable when the temperature of the system is not constant and the system is not isolated. The limitations of the model are also discussed.

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1. Introduction
The desire to achieve the highest possible time-between-charging for the electronic devices as well as the desire to reduce the fossil fuel usage is driving the development of high energy density Li-ion batteries [1]. A great deal of current research on the Li-ion batteries has concentrated on identifying novel electrode and electrolyte materials. Amongst the various material candidates for the Li-ion batteries, silicon (Si) is of particular interest as an anode due to its very high theoretical charge capacity (4200 mAh/g) [2] along with its abundance in earth’s crust. Although the capacity of Si electrode is about 10 times higher than the commercially used material graphite, Si undergoes large (~350 to 400%) volume expansion during charging cycle resulting in electrode pulverization and early capacity fade [3]. Several nano-geometries have been explored to overcome this problem in the form of nano-rod, core–shell nanostructures [6,7], nanotubes [8], Si nano films with [9] or without [10–15] soft substrates, hollow nanospheres [16], and coated nano-rods [17,18]. Although the nanostructured electrodes help accommodate the strain and prevent the build-up of stresses, the total electrode volume available in these cases, however, is limited primarily due to the low total volume of the nanostructures.

The major obstacle in using high energy density electrode materials (Si or otherwise) is the cracking and the resulting pulverization of the electrode due to high deformation during lithiation. This process involves crack initiation at the electrode surface or interior and its growth under the mechanical forces [3,19–21]. Several studies have been carried out to find a critical crack size and its growth in lithiated Si. Suo and co-workers [22–25] studied combined diffusion and the resulting stress accumulation at high and low charging rates. They also modeled the inelastic deformation in Si considering diffusion, elastic–plastic deformation, and fracture. Chiang and co-workers [26,27] have created an electrochemical shock map that shows the regime of failure depending upon the charging rate, particle size, and the inherent fracture toughness of the material. They also showed that minimizing the principal shear strain, rather than minimizing net volume change as previously suggested, is an important new design criterion for crystal chemical engineering of electrode materials for mechanical reliability. Medium range order in disordered Si is an important consideration for crack propagation in the electrodes [28–30]. Fluctuation electron microscopy experiments along with simulations have established a medium range orientational order in amorphous silicon [28,29]. This medium range order, as described by paracrystalline models, consists of topologically crystalline grains which are strongly strained and a disordered matrix between them [28]. Verbrugge and co-workers [31–33] have proposed a tensile stress-based criteria for the growth of cracks within a spherical insertion electrode. They considered both interfacial (electrochemical) kinetics and intercalate diffusion. Gao and co-workers [34,35] developed a cohesive model of crack nucleation in an initially crack-free strip electrode under galvanostatic intercalation and de-intercalation processes. They applied a cohesive zone model of crack nucleation in a cylindrical electrode under axisymmetric diffusion induced stresses. The cracks were assumed to exist at a certain
periodicity. The above models provide an excellent picture of the crack growth in a battery electrode under lithiation stresses. The exact mechanisms of how the surface cracks evolve from surface features, however, have not been fully investigated.

Li et al. [3] have observed that a flat bulk Si anode surface develops a characteristic surface roughness at a length scale of <1 μm upon lithiation. They observed that some surface cracks grow to form a fractal pattern at a higher length scale of tens of micrometers. Note that they observed that the Si surface roughness/undulations grow with time upon lithiation, although the amplitude and the dominant wavelength were not quantitatively characterized. Such sub-micron surface features can potentially act as crack initiation sites. Similar to the bulk silicon, the nanostructured Si anodes are also shown to form surface undulations upon lithiation. Direct TEM observations of Si nano-rod anodes undergoing lithiation [36] show clear Si surface undulations at a wavelength of about 100–200 nm and an amplitude of about tens of nm (Fig. 3d in Ref. [36]).

In this communication, we develop a linear perturbation model to describe the formation and evolution of surface undulations in Li-ion battery electrode films under stress caused by Li intercalation. The formulation takes into account the fact that the Li-ion battery electrode is not an isolated system and that the temperature can change during lithiation. Additionally, no assumptions are made regarding pre-existing flaws on the surface. It is shown that the formulation follows the description of the rumpling problem in metallic thin films previously addressed by the author [37]. A competition between surface energy and strain energy is shown to be the driver for the mass transport. The kinetics of mass transport is described by surface and volume diffusion. The model predicts that the surface undulations with 0.2 to 1 μm wavelength grow at the highest rate and dominate the surface in a reasonable agreement with experimental results from literature [3,36]. These undulations can give rise to notches that can act as crack initiation sites. Implications of the model in terms of the microstructural evolution at or near the surface of the battery electrode are discussed. Finally, the limitations of the model are discussed in detail.

2. Model

Consider a battery electrode film of Si as shown in Fig. 1. Consider for the time being that the Si is polycrystalline (i.e. diffusion is isotropic) and that the usual chemical potentials are driving the Li inside the electrode during charging cycle. As the charging goes on, the Si film will go under compressive stress during lithiation. The high diffusivity of the Li material inside and on the surface of Si, however, can give rise to some surface rearrangements driven by the desire to lower the free energy. To describe the roughness formation, the surface of the electrode can be decomposed into infinitely many sinusoidal undulations. The assumption is that we analyze each wave independently and the resultant surface is linear superposition of the waves. A single surface perturbation of wavelength is \( h(x, t) = a(t) \cos(\omega x) \), with \( \omega = 2/\lambda \) (Fig. 1b).

For a semi-infinite body of unit depth under a remote stress (Fig. 1b), the strain energy density in the body per unit volume is \( U(\varepsilon_{ij}) \). The internal energy of the system is comprised of the strain energy and surface energy, i.e.,

\[
\varepsilon = \int_V U(\varepsilon_{ij}) \, dV + \int_S \gamma \, dS. \tag{1}
\]

The system free energy is,

\[
F = \varepsilon - \int_V T_s(V) \, dV, \tag{2}
\]

where \( s(V) \) is the local entropy and \( T \) is the total absolute temperature of the solid. From Eqs. (1) and (2),

\[
F = \int_V U(\varepsilon_{ij}) \, dV + \int_S \gamma \, dS - \int_V T_s(V) \, dV. \tag{3}
\]

The time rate change of the free energy is,

\[
\frac{dF}{dt} = \int_V \frac{\partial U(\varepsilon_{ij})}{\partial t} \, dV + \int_V \frac{\partial V(V)}{\partial \varepsilon_{ij}} \frac{\partial V(V)}{\partial t} \, dV + \int_S \frac{\partial \gamma}{\partial t} \, dS + \int_V \frac{\partial T_s(V)}{\partial t} \, dV - \int_V T_s(V) \frac{\partial (dV)}{\partial t}. \tag{4}
\]

In writing Eq. (4), it is assumed that the spatial gradients of \( U \) and \( T \) are negligible compared with their time variations. The spatial gradient of \( U \) can be ignored if the surface stress is uniform, while for a thin layer such as a battery electrode, the spatial gradient of \( T \) can be ignored if the heat conduction is fast enough to make the gradients insignificant. A simple derivation [38,39] shows that,

\[
\int_S \gamma \frac{\partial (dS)}{\partial t} = -\int_S \kappa \gamma V_n \, dS. \tag{5}
\]

Furthermore, for small perturbations of the surface, the strain energy change in the bulk is negligible compared to that on the surface. Hence,

\[
\int_V U(\varepsilon_{ij}) \frac{\partial (dV)}{\partial t} = \int_S U(\varepsilon_{ij}) V_n \, dS. \tag{6}
\]
Similarly,\[
\int_0^1 T_s \frac{\partial (\Omega V)}{\partial t} = \int_0^1 T_s V_n dS. \tag{7}
\]

Note that the above system is not in thermodynamic equilibrium. From Eqs. (4), (5), (6), and (7), we obtain\[
0 = \int_0^1 \frac{\partial (U(e_{ij}))}{\partial t} dV + \int_0^1 \frac{\partial y}{\partial t} dS - \int_0^1 \frac{\partial T_s}{\partial T} dV - \int_0^1 T \frac{\partial (\nu (V))}{\partial t} dV. \tag{8}
\]

From Eqs. (4) and (8), we obtain,\[
\dot{\nu} = \int_0^1 (U(e_{ij}) - \kappa \gamma - T s) V_n dS. \tag{9}
\]

The factor \(V_n dS\) is equal to the atomic volume, \(\Omega\), times the atomic flux at \(dS\). The chemical potential, \(\chi\), along the surface of the solid can be obtained from Eq. (9) as,
\[
\chi = (U(e_{ij}) - \kappa \gamma - T s) \Omega, \tag{10}
\]

where \(U\) is the strain energy density along the film surface. Here \(\kappa\) is the curvature \((-\partial^2 h(x,t)/\partial x^2)\), \(\gamma\) is the surface energy and \(\Omega\) is the atomic volume. The value of \(\frac{\partial \chi}{\partial y}\) is of interest since it represents the gradient in the surface chemical potential. Although the system is not in thermodynamic equilibrium, the relation \(ds = dq/T\) is valid at every point along the solid surface (due to local thermodynamic equilibrium). The term \(dq\) represents the local change in the heat energy and is equal to \(C_p dT\), with \(C_p\) being the heat capacity of the solid. We can then write,
\[
Ts = \int_0^1 \frac{C_p dT}{T} = \frac{C_p}{T} \ln \left( \frac{T}{T_{ref}} \right). \tag{11}
\]

Eq. (11) is very important in determining the effect of entropy change on the system as the surface waviness is formed. From Eq. (11), if the temperature along the solid surface is constant at a given moment, we take \(\partial (Ts)/\partial x = 0\) (\(C_p\) is taken to be constant). Thus, the entropy term is shown not to contribute to the surface gradient of the chemical potential as given by Eq. (10). The problem formulation thus reverts back to that developed previously by the author and others [37–40] and is described below for clarity.

Note that the stress at the surface due to a ‘small’ perturbation of amplitude \(\nu\) and wavelength \(\lambda\) is: [41–43]
\[
\sigma_{xy}(x, y = 0) = \sigma_0 - 2\sigma_0 \nu \omega \cos(\omega x). \tag{12}
\]

Where \(\sigma_0\) is the remote stress caused by lithiation. Eq. (12) gives rise to strain energy density,
\[
U(x, t) = \frac{[1 - (1 - \nu)\alpha^2]}{4G} \left[ 1 - 4\nu \omega \cos(\omega x) \right]. \tag{13}
\]

The \(-\omega v\) sign indicates reduction in strain energy density due to undulation.

The flux of the atoms along the surface is proportional to the chemical potential gradient given by Eq. (10),
\[
J_s = \frac{-D_C}{kt} \frac{\partial (U(e_{ij})) - \kappa \gamma - T s}{\partial x} - \frac{\partial C_\nu}{\partial T} \sin(\omega x) \left[ \frac{1 - (1 - \nu)\alpha^2}{G} \alpha \omega^2 - \gamma \omega \right]. \tag{14}
\]

The normal velocity of the surface will then be \(-\Omega \frac{\partial y}{\partial t}\) (Fig. 1-c), giving,
\[
\frac{da(t)}{dt} = \frac{D_C \Omega^2 a(t)}{kt} \left[ \frac{(1 - \nu)\alpha^2}{G} \alpha \omega^2 - \gamma \omega \right]. \tag{15}
\]

From Eq. (15), the rate of growth of perturbation amplitude of the wave is dependent upon the amplitude itself. The first term in the bracket is the strain energy term that increases the wavelength while the second term is the surface energy term that will try to smoothen the surface. The dependence of the first term is \(1/\lambda^2\), while that for the second term is \(1/\lambda^4\).

The diffusivity of Li on Si surfaces as well as surface Li concentration has not been measured. The only measurement of \(D_C\) for Li was at room temperature in ultra-high vacuum on graphite [44]. The diffusivity, \(D_0\), at 300 K was \(5 \times 10^{-6} cm^2/s\), the activation energy was 0.16 to 0.02 eV, and \(C_s\) was \(8 \times 10^{14} atoms/cm^2\). This is very low activation energy and at room temperature, a very high \(D_0\) value. For comparison, the activation energy for surface self-diffusion of Ni is 1.5–1.8 eV, while \(D_0\) is 3 \(\times 10^{-6} cm^2/s\). The \(D_C\) in Ref. [44] was calculated in ultra-high vacuum, while in the actual battery electrodes this value is expected to be lower by a few orders of magnitude due to surface contaminants.

The volume diffusion of Li in Si can also give rise to Si surface roughening. The expression for surface evolution due to vacancy diffusion was derived by the author previously as [37],
\[
\frac{da(t)}{dt} = \frac{D_1 \Omega a(t)}{kt} \left[ \frac{2(1 + \nu)\alpha^2}{3} \alpha \omega^2 - \gamma \omega \right]. \tag{16}
\]

Where \(D_1\) is the volume self-diffusivity of the solid. The first term has \(1/\lambda^2\) dependence on \(da/dt\), similar to \(1/(\text{grain size})\) [2] dependence in creep. The diffusivity of Li in Si has been calculated by several recent studies at room temperature to be about \(10^{-12} \text{ to } 10^{-13} cm^2/s\) (Ref. [45]). We approximate \(D_1\) to be this value and evaluate between the measured range of values. A combination of surface and volume diffusion is combined to get the final expression for rate of amplitude growth for a given surface undulation:
\[
\frac{da(t)}{dt} = \frac{D_C \Omega^2 a(t)}{kt} \left[ \frac{(1 - \nu)\alpha^2}{G} \alpha \omega^2 - \gamma \omega \right] + \frac{D_1 \Omega a(t)}{kt} \left[ \frac{2(1 + \nu)\alpha^2}{3} \alpha \omega^2 - \gamma \omega \right]. \tag{17}
\]

We integrate Eq. (17), to get the following time dependent evolution equation.
\[
\ln \left( \frac{a(t)}{a(0)} \right) = \frac{8\nu^2 D_C \sigma_0^2 t}{kT G} \left( \frac{\omega G}{2\pi \sigma_0^2} \right)^3 \left[ \frac{[1 - (1 - \nu)\alpha^2]}{G} \alpha \omega^2 - \gamma \omega \right] + \frac{D_1 \sigma_0^2}{3 \Omega} \left( \frac{2(1 + \nu)\alpha^2}{3} \alpha \omega^2 - \gamma \omega \right) \left[ \frac{\omega G}{2\pi \sigma_0^2} \right]^3. \tag{18}
\]

Here, \(2m \Omega^2 \omega G\), represents dimensionless wavelength. The terms in the curly bracket will be taken on the LHS since we are interested in determining the relative rate of each perturbation and plotted as normalized growth rate (see next section).

3. Discussion

Figs. 2(a) and (b) show the growth of the amplitude of perturbations for different perturbation wavelengths for parameters noted in Table 1 and a compressive stress of 2 GPa and 1 GPa, respectively. Note that in the case of a battery electrode (Table-1), the contribution from all the four smoothing and roughening mechanisms given by Eq. (18) is
significant, unlike the case for thick films at low stresses observed in thermal barrier systems [37]. For 2 GPa stress in the film, we see that the surface perturbations with waviness less than 0.18 μm decay in amplitude with time, while perturbations with waviness close to about 0.2–0.4 μm grow at a very fast rate. For longer wavelengths, the amplitude grows very slowly at λ > 0.6 μm. For a stress of 1 GPa (Fig. 2b), the eventual dominant wavelength over the surface is predicted to be about 1 μm. The sub-μm dominant surface features observed in experiments [3,36] are very close to that predicted by the current formulation.

Fig. 3 shows the maximum wavelength as a function of \( D_i/D_sC_i \) for different stress levels. The max wavelength increases with decreasing stress, indicating that the dominant wavelength moves to larger values with lower stresses, but the rate of growth drops down. All the direct observations of the lithiation point to a stress of the level of 1–2 GPa in bulk materials [19,20]. Even for nanostructured Si anodes over a soft substrates, the anode stress have been calculated to be of the order of 1 GPa [9]. Note that although we have taken the stress to be compressive in the current formulation, the max wavelength is not affected significantly by the sign of the stress. Note also that in the absence of stress (or even for low stress), the surface roughening cannot happen since the surface energy increase will dominate over the strain energy decrease during roughening. Only surface smoothing can happen in such cases. The results also point to the fact that already undulating surfaces of a battery electrode can help in stress relaxation and avoid crack initiation at the surfaces.

From Fig. 2, it is clear that the perturbations with wavelengths in a small range of values will dominate the surface once enough time is given for the surface to evolve. For the perturbations smaller than the critical wavelength, the surface energy dominates and the amplitude dies down. For large wavelength perturbations, the time scale is too large before any meaningful amplitude increase can happen. It is noted that once the amplitude is large compared to the wavelength, the small scale assumption is no longer valid and the present formulation is not applicable. In addition, if the thermal conductivity of the electrode material is poor, the assumption of the surface gradient of \( T_s \) being small is not valid either. Although the current formulation assumes that the Li atoms move through Si bulk and help create the waviness, we note that the breakdown of Si structure during intercalation may result in Si atoms contributing to the roughening process as well. The medium range order in amorphous Si can also affect crack propagation [30] and not considered in the current formulation. Clearly, critical experiments are needed to observe the diffusive processes at or near the electrode surface in order to gain a full understanding of this phenomenon in the Li-ion batteries. Lastly, we note that if Li is not cleaned properly from the electrode surface in the dry box after battery disassembly, several electrochemical features associated with the SEI layer are formed over the electrode surface that can prevent clean experiments to observe the surface roughening. In spite of the several limitations discussed above, the present formulation provides a highly useful insight into a possible crack initiation mechanism during the electrochemical fatigue in battery electrode films.

### 4. Conclusion

In this paper, a linear perturbation model is applied to the crack initiation problem in Li-ion battery electrodes undergoing lithiation–delithiation cycles. The driving force for the surface undulation formation is the reduction in the electrode strain energy. The kinetics of mass transport is described by the surface and volume diffusion. The model allows the temperature of the battery to change and does not require the system to be isolated. The Si electrode is predicted to develop surface undulations of the order of sub-1 μm length scale on the electrode surface in a reasonable agreement with experimental results.
reported in literature. Such surface undulations roughen the electrode surface and can form notches that can act as crack initiation sites. It is also shown that this model is applicable when the temperature of the system is not constant and the system is not isolated. The limitations of the model are also discussed.

5. List of symbols

- $h(t, \tau)$: height of perturbation
- $a(t)$: amplitude of perturbation
- $\omega$: perturbation frequency associated with wavelength $\lambda$
- $U(\varepsilon_l)$: electrode strain energy density
- $\gamma$: electrode surface energy
- $s(V)$: local entropy
- $T$: electrode temperature
- $V_a$: normal velocity of the electrode surface
- $\Omega$: atomic volume for the diffusing species
- $C$: electrode surface energy
- $a$: atomic volume of the diffusing species
- $G$: electrode strain energy density
- $t$, $i$, $j$: volume diffusivity of diffusing species
- $D$: surface diffusivity of diffusing species
- $C_s$: surface concentration of diffusing species
- $D_i$: volume diffusivity of diffusing species

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