Chemical and mechanical degradation of component materials are major reasons for coulombic capacity fade in lithium ion batteries (LIBs). Chemical degradation occurs due to the instability of commonly used solvent electrolytes at the operating potentials, resulting in parasitic reactions. The parasitic electrochemical reactions that form the Solid Electrolyte Interphase (SEI) are generally solvent decomposition reactions that cause an irreversible capacity loss of LIBs. In spite of this, SEI formation is important for the durability of LIBs since a stable, coherent SEI passivates further decomposition of the electrolyte solvent and thus preserves battery life. Intense efforts to understand the composition, mechanical and transport properties as well as the formation mechanism of the SEI are underway in the research community. Electrolyte additives such as vinylene carbonate are being explored to improve the stability of the SEI. There are also attempts to make a more stable artificial SEI layer of polymeric material such as poly(ethylene-co-acrylic acid) and sodium carboxymethyl cellulose with methods such as electro-painting. Additionally, use of surface modifiers and surface coatings such as metals, metal oxides and conductive polymers on the electrode surface is demonstrated to improve battery durability.

During cycling of LIBs, the diffusion of lithium inside the lithium host active-material particles that comprise the electrodes result in mechanical stresses within these particles. This type of diffusion-induced stresses (DIS) can result in particle fracture, creating new electrode surface exposed to the solvent, and consequently, forming new SEI and concomitant loss of capacity. In order to understand this type of electrode mechanical degradation, we term Mode 1 fracture, several groups have attempted modeling these DISs in electrode particles. Most of the DIS models in the published literature concentrate on understanding the phenomenon of cracking of the lithium host material (i.e., Mode 1) as the major mechanism of cell capacity fade during cycling. For example, in an earlier publication, Deshpande et al. applied Paris’ Law from fatigue mechanics to model the electrode host particle cracking in LIBs, and an effect of particle cracking on battery capacity loss was developed.

Even though the cracking of the lithium host material may play a significant role in battery deterioration during high-rate cycling, its significance in capacity fade at low rates of charging/discharging may be questionable. Particularly, when operating temperatures are not very low, solid state diffusion is relatively fast and lithium concentration gradients inside the host particles are relatively small; hence, the electrode particle host material may not be stressed to the point of fracture. The internal stress may be well below the fatigue limit of the electrode material and thus may cause minimal damage to the particle. This reasoning is consistent with the observations made by Takahashi et al. in which they found that there was no significant damage to graphite host particles during room temperature cycling.

Previously several groups have proposed the SEI cracking, which we term Mode 2 fracture, as a reason for capacity fade during cycling of graphite-based LIBs, rather than cracking of the lithium host particle material (i.e. Mode 1). In this article we further explore the proposal of SEI cracking as a major mechanism of capacity loss during low-rate LIB operation. Intuitively, expansion and contraction of the host lithium material would invariably exert stress on the SEI layer that surrounds the particle, since the SEI does not act as a lithium host; that is, the SEI simply transports lithium ion and would not expand and contract during lithiation or delithiation the way host material does. Thus, even in the absence of concentration gradients inside the host particle material, the SEI would experience a tensile stress whenever the host material expands due to lithiation. It is possible that the SEI stress is larger than the lithium concentration gradient stress. In this case, the SEI fracture would dominate at lower rates. The phenomenon of SEI fracture in Mode 2 is considered analogous to multi-cracking of thermal coatings in which thermal expansion of the metal underneath fractures the thermal coating.

The work presented here is built upon earlier publications where a core-shell model was used to calculate stresses in the SEI layer. Here we develop an extension of these works that allows us to compare the development of mechanical stresses from the Mode 1 and Mode 2 mechanisms. We demonstrate that during low-rate charging of the battery (lithiation of the negative electrode), the stresses experienced by the SEI shell are actually much larger than the stresses experienced...
by the host core particle material. We focus on examining the stresses developed in the SEI layer that have the potential to promote SEI layer fracture. Using stress and strain energy calculations, we then develop a simple correlation between capacity loss and the state-of-lithiation (SOL) change (or ‘swing’) during a lithiation event while cycling, with the assumption that SEI cracking facilitates further solvent decomposition and that this “re-healing” of the SEI is the dominant mechanism of capacity loss.

Background

Under the operating conditions of the battery, all the freshly exposed surfaces of the graphite electrode give rise to new side reactions because of the electrochemical reduction of the electrolyte solvent. We assume that the newly exposed surface is covered by the products of the parasitic reactions.\(^2\),\(^10\),\(^28\),\(^29\) Thus, the host electrode particle and the parasitic reactions are represented by the host core particle material and the SEI is assumed to make a core-shell like structure. Figure 1 provides a schematic illustration of the Mode 2 SEI fracture associated with capacity loss.\(^3\) As a result of host material lithiation, the SEI may fracture instead of the active host material, exposing bare electrode surface to the solvent and resulting in new SEI formation. Cracking of the SEI causes the increased solvent reduction in Mode 2, whereas cracking of the host material causes the increased solvent reduction in Mode 1. In actuality both are modes would be possible as a “mixed mode” fracture mechanism.

Diffusion-induced Stresses in the Mode 1 and Mode 2 Mechanisms

We assume that the electrode consists of a large number of spherical graphite particles of uniform size. We further assume that every spherical electrode particle is encapsulated by an SEI layer formed uniformly around the particle (Fig. 1), and that the particle core and the SEI are homogeneous and isotropic in mechanical and transport properties.

Mechanics.—We begin with the equations describing DISs in the host particle material that would apply in both the Mode 1 and Mode 2 fracture mechanisms, as well as the SEI shell in the Mode 2 mechanism. These first three sets of equations have been developed previously\(^9\),\(^30\),\(^31\) and are reproduced here for clarity. We follow this development with a set of Equations 6 that are unique to this publication for the modeling of the Mode 2 mechanism. In this development the active host material is referred to as the \(\alpha\)-phase and the shell SEI layer as SEI. The radius of the active host material is \(R_\alpha\); hence, the interface between the \(\alpha\)-phase and the shell SEI layer is located at radial position of \(R = R_\alpha + w\). The thickness of SEI layer is shown with symbol \(w\). The radius of the entire particle \(R\) is the sum of the \(\alpha\)-phase radius and the SEI thickness, i.e., \(R = R_\alpha + w\). The first equation below is analogous to the constitutive law typically used for modeling thermal stress\(^31\),\(^32\) and has been used for modeling DISs\(^33\), including stresses in battery electrodes.\(^15\),\(^17\),\(^20\),\(^30\),\(^34\) The stress-strain relationships expressed in the spherical coordinate system for the radial and tangential components are:

\[
\varepsilon_r = \frac{1}{E_\alpha} (\sigma_r - 2\nu_\alpha \sigma_\theta) + \frac{1}{3} \Omega_\alpha (C(r,t) - C(0, t))
\]

\[
\varepsilon_\theta = \frac{1}{E_\alpha} ((1-\nu_\alpha) \sigma_\theta - \nu_\alpha \sigma_r) + \frac{1}{3} \Omega_\alpha (C(r,t) - C(0, t))
\]

where Young’s modulus is \(E_\alpha\), Poisson’s ratio is \(\nu_\alpha\), the partial molar volume of the solute is \(\Omega_\alpha\) for the respective \(\alpha\)-phase and SEI phase, molar concentration is \(C\), and the radial and tangential strains are represented by \(\varepsilon_r\) and \(\varepsilon_\theta\), and the radial and tangential stresses are represented by \(\sigma_r\) and \(\sigma_\theta\). We further assume that the elastic properties of any of the phases do not vary with the lithium composition variation in it.\(^4\)

Because of the spherical symmetry, the radial and tangential strains, in the infinitesimal formulation of deformation, can be expressed as functions of radial displacement, \(u\), as:

\[
e_r = \frac{du}{dr}, \quad \varepsilon_\theta = \frac{u}{r} \tag{2}
\]

Since atomic diffusion in solids is a much slower process than elastic deformation, mechanical equilibrium is established much faster than that of diffusion and can be treated as a static equilibrium problem. In the absence of a body-force such as gravity, the equation for static mechanical equilibrium for the radial component in spherical coordinates given by,\(^31\)

\[
\frac{d\sigma_r}{dr} + \frac{2(\sigma_r - \sigma_\theta)}{r} = 0 \tag{3}
\]

We first solve Equation 1 to get the radial and tangential stresses (\(\sigma_r\) and \(\sigma_\theta\)) in terms of the radial and tangential strains (\(\varepsilon_r\) and \(\varepsilon_\theta\)). Then, using Equation 2 we replace the \(\varepsilon_r\) and \(\varepsilon_\theta\) in terms of displacement \(u\) and thus, get the \(\sigma_r\) and \(\sigma_\theta\) in terms of \(u\). We replace the \(\sigma_r\) and \(\sigma_\theta\) in Equation 3 to get a second order ordinary differential equation in terms of \(u\). The solution of such differential equation gives the displacement \(u(r, t)\). For the case with constant \(E_\alpha\), \(\nu_\alpha\), and \(\Omega_\alpha\), it is given\(^9\),\(^30\),\(^31\)

\[
u(r, t) = \left(1 + \frac{\nu_\alpha}{1-\nu_\alpha}\right) \frac{\Omega_\alpha}{3r^2} \int C(r, t) - C(0, t) r^2 dr + r I_{1\alpha} + \frac{I_{2\alpha}}{r^3} \tag{4a}
\]

here, \(c\) is the lower integration boundary. For the host material \(\alpha\)-phase \(c = 0\), and for the SEI \(\varepsilon = R_\alpha\). The constants \(I_{1\alpha}\) and \(I_{2\alpha}\) can be obtained from the appropriate boundary conditions for both the \(\alpha\)-phase and the SEI layer.

Using the solution (4a), the equations for radial and tangential stresses are obtained:\(^9\),\(^30\),\(^32\)

\[
\sigma_r'(r, t) = -\frac{\Omega_\alpha E_\alpha}{3(1-\nu_\alpha)} \frac{2}{r^3} \int C(r, t) - C(0, t) r^2 dr + \left[\frac{E_\alpha I_{1\alpha}}{(1-\nu_\alpha)} - \frac{2E_\alpha I_{2\alpha}}{(1+\nu_\alpha)} \right] \tag{4b}
\]

\[
\sigma_\theta'(r, t) = \frac{\Omega_\alpha E_\alpha}{3(1-\nu_\alpha)} \frac{1}{r^3} \int C(r, t) - C(0, t) r^2 dr + \Omega_\alpha E_\alpha C(0, t) \frac{1}{3(1-\nu_\alpha)} + \left[\frac{E_\alpha I_{1\alpha}}{(1-\nu_\alpha)} + \frac{E_\alpha I_{2\alpha}}{(1+\nu_\alpha)} \right] \tag{4c}
\]

Note that Equation set 4 would apply in both the core and shell regions of the Mode 2 fracture mechanism, subject to the following boundary conditions. Without considering the effects of surface energy and surface stresses,\(^20\) the normal stress at the free surface of the spherical particle is \(\sigma_r(0) = 0\). Also the stress and the displacement are finite at \(r = 0\). Since the normal component of stresses and displacements are continuous at the interface between the \(\alpha\)-phase and the SEI layer, i.e., at \(r = R_\alpha\),

\[
\sigma_r(0) = \sigma_r(0) \varepsilon = \sigma_r^{SEI}(0) \varepsilon^{SEI} \tag{5}
\]

Here superscript “\(a\)” on radial location indicates points very close to the active material-SEI interface, on the active material side of the interface. Superscript “SEI” on radial location indicates points very close to the active material-SEI interface, on the SEI side of the
We note that, for the stresses $\sigma_r$ and $\sigma_\theta$ for the $\alpha$-phase within the core region $0 \leq r \leq R_0$ are

$$\sigma_r^{\alpha}(r, t) = \frac{2E_a}{3(1-v_\alpha)} \frac{\Omega_\alpha}{3} \left( C_{avg}(r, t) - C_{avg}(r, 0) \right) + \frac{E_a I_3\alpha}{1-2v_\alpha},$$  \[6a\]

$$\sigma_\theta^{\alpha}(r, t) = \frac{E_a}{3(1-v_\alpha)} \frac{\Omega_\alpha}{3} \left( C_{avg}(r, t) - C_{avg}(r, 0) \right) - \frac{E_a \omega_\alpha (C(r, t) - C(r, 0))}{3(1-v_\alpha)} + \frac{E_a I_3\alpha}{1-2v_\alpha},$$  \[6b\]

Here, $C_{avg}(r) = \int_0^r C(r) r^2 dr'$ is the average concentration in the $\alpha$-phase ($0 \leq r \leq R_\alpha$).

We note that, for the stresses $\sigma_r$ and $\sigma_\theta$ for the $\alpha$-phase within $0 \leq r \leq R_\alpha$, the stress and the displacement are finite at $r = 0$, the constant $I_3\alpha = 0$. To derive Equation 6c, we assume that $w \ll R$; therefore, the higher power terms of $(w/R)$ are neglected. Equation set 5 is reproduced from Deshpande et al.\textsuperscript{29} and applied in the Mode 2 mechanism in the present work. Note that radial and tangential stresses inside the particle would be zero at time $t = 0$, consistent with the assumption that the particle is in the relaxed state before any flux is applied to the surface of a particle. Moreover, if the SEI thickness is negligible ($w = 0$), Equations 6a, 6b, and 6c would reduce to the forms presented in an earlier publication\textsuperscript{15} on modeling the Mode 1 mechanism, in which the stresses in the electrode particle are modeled without consideration of the presence of the SEI. We reiterate that Appendix A shows the derivation of Equations 6a, 6b, and 6c in detail.

The results for the stresses $\sigma_r$ and $\sigma_\theta$ for the SEI shell region $R_\alpha \leq r \leq R$ are

$$\sigma_r^{SEI}(r, t) = 2 \left[ 1 - \frac{R^3}{r^3} \right] \left[ 1 - \frac{3w}{R} \right] \frac{\Omega_\alpha}{3(1-v_{SEI})} \left( C_{avg}(R_\alpha, t) - C_{avg}(R_\alpha, 0) \right)$$

$$E_{SEI} \frac{\Omega_\alpha}{3(1-v_{SEI})} \left( \frac{(1-2v_\alpha)E_{SEI}}{E_a} - (1 - 2v_{SEI}) \right) \frac{6w}{R}$$  \[6d\]

$$\sigma_\theta^{SEI}(r, t) = E_{SEI} \left[ \frac{2}{R^3} + \frac{1}{r^3} \right] \frac{\Omega_\alpha}{3(1-v_{SEI})} \left( \frac{(1-2v_\alpha)E_{SEI}}{E_a} - (1 - 2v_{SEI}) \right) \frac{6w}{R}$$  \[6e\]
Here in modeling the Mode 2 mechanism we assume that the SEI layer does not undergo lithiation or delithiation and only acts to transport lithium ions from the electrolyte to the active host material particle. For the SEI layer in the region of \( R_{SEI} \leq r \leq R \), we have \( \Omega_{SEI} = 0 \) (i.e., the SEI layer volume is not altered due to lithiation or de-lithiation of the particle). Equations 6c, 6d and 6e above are unique and are obtained using Equation sets 3, 4 and 5, the details of which are given in Appendix A.

At any radial position within the SEI location, \( r \leq R \), from Equation set 6, we may conclude
\[
\sigma_{r,SEI}(r, t), \sigma_{\theta,SEI}(r, t) \propto (C_{avg}(R_{SEI}, t) - C_{avg}(R_{SEI}, 0)) \quad [7]
\]
In the Equation 7, the term \((C_{avg}(R_{SEI}, t) - C_{avg}(R_{SEI}, 0))\) represents the change in average lithium concentration inside the host particle during the lithiation/delithiation operation.

We define the state-of-lithiation (SOL) of a particle as the ratio of average lithium concentration inside the host particle \((C_{avg})\) to the maximum theoretical lithium concentration the host material particle can store \((C_{max})\).

\[
\text{State of lithiation, SOL} = \frac{C_{avg}(R_{SEI})}{C_{max}}
\]

The state-of-lithiation swing \((\Delta \text{SOL})\) is defined as the ratio of change in lithium concentration in the host material particle during the lithiation/delithiation process to the maximum theoretical lithium concentration the host material particle can store.

\[
\Delta \text{SOL} = \frac{C_{avg}(R_{SEI}) - C_{avg}(R_{SEI}, 0)}{C_{max} - C_{avg}(R_{SEI}, 0)} \quad [8]
\]
Rewriting Equations 6c and 6d in terms of \( \Delta \text{SOL} \),
\[
\sigma_{r,SEI}(r, t) = \left\{ \frac{2}{R_{SEI}} \left[ 1 - \frac{R_{SEI}^2}{r^2} \right] \left( 1 - \frac{3w}{R_{SEI}} \right) \right\} \Delta \text{SOL} (t)
\]
\[
E_{SEI} = \left\{ \frac{3(1 - \nu_{SEI}) + \left( \frac{E_{SEI}(1 - 2\nu_{SEI})}{E_{SEI}} \right) \left( \nu_{SEI} \right)}{6 \nu_{SEI}} \right\} \Delta \text{SOL} (t)
\]
\[
\sigma_{\theta,SEI}(r, t) = \left\{ \frac{E_{SEI} \left[ 2 + \frac{1}{r} \right]}{3(1 - \nu_{SEI}) + \left( \frac{E_{SEI}(1 - 2\nu_{SEI})}{E_{SEI}} \right) \left( \nu_{SEI} \right)} \right\} \Delta \text{SOL} (t)
\] \quad [9a]

In Equations 9a and 9b, for a given location \( r \) inside the SEI, the terms in the curly brackets are constants for a given electrode particle. Hence we can conclude that the radial and tangential stresses at any given location inside the SEI are proportional to the state-of-lithiation swing \( \Delta \text{SOL} \). From Equation 9a and 9b, we can also observe that, for a given value of \( \Delta \text{SOL} \) for an electrode particle, the stresses in the SEI are actually independent of applied current.

\[
\sigma_{r,SEI}(r, t), \sigma_{\theta,SEI}(r, t) \propto \Delta \text{SOL} \quad [9c]
\]

The term ‘state-of-lithiation swing’ (i.e., \( \Delta \text{SOL} \)) can be used for each of the electrodes in a cell independently depending upon their respective storage capacities. In a full cell configuration, the ‘state-of-lithiation’ of the negative electrode may be calculated using the state-of-charge (SOC) of the cell, the cell capacity and the theoretical capacity of the negative electrode. It should be noted that a cell at the same SOC, but at different points during the life, will likely have differing states of lithiation of the negative electrode.

**Diffusion.**—For the case study analysis that we present in the next section, we make the assumption that the SEI layer acts only as a resistor for ions (or atoms, depending upon the location at which the charge transfer takes place) with no concentration gradient buildup inside SEI. To further simplify the analysis, we neglect diffusion that can result from mechanical stress; and hence, the Fickian diffusion equation is used. Fickian diffusion of a solute in the active \( \alpha \)-phase core for \( 0 \leq r < R_{SEI} \) is
\[
\frac{\partial C(r, t)}{\partial t} = \frac{D_a}{r^2} \left( \frac{\partial}{\partial r} \left( r^2 \frac{\partial C(r, t)}{\partial r} \right) \right) \quad [10a]
\]
where \( C(r, t) \) is the concentration of solute at a time \( t \) at a radial position \( r \).

If \( I \) is the current density over the electrode particle, at the interface \( r = R_{SEI} \) between the shell and the core, the flux is constant
\[
D_a \frac{\partial C}{\partial r} \bigg|_{r=R_{SEI}} = \frac{I}{F} \quad [10b]
\]
We may assume, initially, \( t = 0 \), and both phases are equilibrated.
\[
C(r, 0) = C_{ini} \quad [10c]
\]
We also assume that the solution is well behaved at the center of the particle \( r = 0 \)
\[
\frac{\partial C(0, t)}{\partial r} = 0 \quad [10d]
\]
Such an equation system is solved on numerous occasions earlier and an analytical solution is well reported in the literature\(^5\) and reproduced here
\[
C(r, t) = C_{ini} + \frac{IR_{SEI}}{FD_a} \left\{ 3x - \frac{1}{2} x^2 - \frac{3}{10} - 2 \sum_{n=1}^{\infty} \frac{\sin(\lambda_n x)}{\lambda_n^2 \sin(\lambda_n)} e^{-\lambda_n^2 \tau} \right\} \quad [10e]
\]
where \( \tau = \frac{D_a}{R_{SEI}^2} \), \( x = \frac{r}{R_{SEI}} \), and \( \lambda_n = (1, 2, 3, \ldots) \) are the solutions of \( \tan(\lambda_n) = \lambda_n \). Here this equation serves to give the concentration of lithium atoms inside the spherical host particle at different radial locations as a function of time during lithiation/delithiation process.

The state-of-lithiation of a particle at any point in time is obtained by normalizing the average lithium concentration over the entire particle with the theoretical capacity of the host material.
\[
SOL(t) = \frac{1}{c_{max}} \left( \frac{3}{x^3} \int_{0}^{1} C^\alpha(x, \tau) x^2 dx \right) \quad [11a]
\]
By putting Equation 10e into Equation 11a, we obtain
\[
SOL(t) = \frac{1}{c_{max}} \left( \frac{3}{x^3} \int_{0}^{1} C_{ini} + \frac{IR_{SEI}}{FD_a} \left\{ 3x - \frac{1}{2} x^2 - \frac{3}{10} \right. \right. \]
\[
- \left. \left. 2 \sum_{n=1}^{\infty} \frac{\sin(\lambda_n x)}{\lambda_n^2 \sin(\lambda_n)} e^{-\lambda_n^2 \tau} \right\} x^2 dx \right) \quad [11b]
\]
Upon integration, Equation 11b becomes
\[
SOL(t) = \frac{1}{c_{max}} \left[ C_{ini} + 3 \frac{IR_{SEI}}{FD_a} \left\{ \tau - \frac{1}{10} (x^2 - 1) - \frac{2}{x^3} \sum_{n=1}^{\infty} \frac{\sin(\lambda_n x)}{\lambda_n^2 \sin(\lambda_n)} e^{-\lambda_n^2 \tau} \right\} \right]_{0}^{1} \quad [11c]
\]
On applying the integration limits on Equation 11c, we get
\[
SOL(t) = \frac{1}{c_{max}} \left[ C_{ini} + 3 \frac{IR_{SEI}}{FD_a} \tau \right] \quad [11d]
\]
Table I. List of parameters.

| Symbol | Description | Unit |
|--------|-------------|------|
| C      | Charge/discharge rate | \( \text{hour}^{-1} \) |
| \( C_{\text{max}} \) | Saturation lithium concentration in graphite phase | \( \text{mol m}^{-3} \) |
| \( D_a \) | Lithium diffusion coefficient in graphite phase | \( \text{m}^{2} \text{sec}^{-1} \) |
| \( E_a \) | Young’s modulus of the unlithiated graphite material | \( \text{Nm}^{-2} \) |
| \( E_{\text{SEI}} \) | Young’s modulus of the lithium carbonate SEI | \( \text{Nm}^{-2} \) |
| \( F \) | Faraday’s constant (C) | 96500 C mol\(^{-1} \) |
| \( R \) | Radius of the spherical electrode particle including the SEI | \( \text{m} \) |
| \( w \) | SEI thickness | \( \text{nm} \) |
| \( v_\alpha, v_{\text{SEI}} \) | Poisson’s ratio of the ‘\( \alpha \)’ phase and the SEI layer | |
| \( \rho_{\text{graphite}} \) | Density of unlithiated graphite | \( \text{g m}^{-3} \) |
| \( \Omega_a \) | Partial molar volume of the lithium in host material | \( \text{m}^{3} \text{mol}^{-1} \) |
| - | Specific capacity of graphite | \( \text{mAh g}^{-1} \) |

Since, \( \tau = \frac{t R_a^2}{E_a} \), the Equation 11d can be re-written as,

\[
SOL(t) = SOL(0) + \frac{1}{C_{\text{max}}} \left( \frac{3 I}{FR_a} \right) t \quad [11e]
\]

If the initial state-of-lithiation \( SOL(0) = C_{\text{ini}}/C_{\text{max}} \) and the theoretical capacity of an electrode are known, the final state-of-lithiation can also be calculated based on integration of the applied current over the duration of charging/discharging operation.

Analysis of Stresses: Case Study

Using the Equation set 10 lithium concentration profiles inside the spherical host particle can be obtained as a function of time during lithiation/delithiation process. Combining the solution of Equation set 10 with Equation set 6, the radial and tangential stresses in the core-shell configuration can be calculated. As an example, we present the analysis of stresses inside a graphite electrode particle covered with SEI layer during constant current lithiation and delithiation process. For these calculations here, we assume that there is no mass transfer limitation in the electrolyte at low rates of operation; therefore, the current distribution over the entire composite electrode would be uniform. This allows us to represent the composite electrode with a single electrode particle. The material and chemical properties of the graphite electrode and the SEI layer used for these calculations are listed in Table I. We use 0.5 C as the rate of lithiation/delithiation. We note that the C rate is calculated based on the assumption that graphite has 1.2 times the initial cell capacity. The theoretical capacity of anode is assumed to be 330 mAh g\(^{-1} \).\(^{36} \)

Additionally, we assume that the electrode particle is a 10 micron diameter spherical graphite particle with a non-porous, 50 nm thick SEI layer surrounding it. The density of unlithiated graphite is assumed to be \( 2.11 \times 10^6 \text{g m}^{-3} \).\(^{36} \) Here, for simplification, we neglect the variation of graphite density as a function of state-of-lithiation. The SEI thickness reported in the literature varies from few angstroms to several hundred angstroms.\(^{37} \) Although the SEI is postulated to have inorganic and organic components that may undergo dissolution during battery operation,\(^{28,36} \) we simplify the problem with the assumption that the SEI is a non-dissolvable inorganic layer consisting of materials such as lithium carbonate (\( Li_2 CO_3 \)), lithium oxide (\( Li_2 O \)) etc. This is consistent with the assumptions previously used in the battery life modeling literature.\(^{1,2} \) The stress calculations are also based on the assumption that the SEI does not crack during the lithiation process, since any fracture in the SEI would alter the stress level.

We begin by transforming the stresses into dimensionless form follows

\[
\xi_i = \frac{\sigma_i}{\frac{2}{3} \frac{E_a}{1 - \nu_\alpha} \frac{C_{\text{max}}}{\rho_{\text{graphite}}} \Omega_a} \quad [12]
\]

where ‘\( i \)’ represents the radial (\( r \)), azimuthal (\( \theta \)), or polar (\( \phi \)) direction.

For the above mentioned conditions of lithiation, we calculate the radial stresses using Equations 6a, 6d and 10e. Figure 2 shows the radial stress distribution in the active material core-SEI shell system

\[ 0.5 \text{ (hour)}^{-1} \]
\[ 25 \times 10^3 \text{ (mol m}^{-3} \)\]
\[ 10^{-14} \text{ (m}^{2} \text{sec}^{-1}) \]
\[ 3.3 \times 10^{10} \text{ (Nm}^{-2} \]}
\[ 6.6 \times 10^{10} \text{ (Nm}^{-2} \]}
\[ 96500 \text{ Cmol}^{-1} \]
\[ 5 \times 10^{-6} \text{ (m} \]
\[ 50 \times 10^{-9} \text{ m} \]
\[ 0.3^{47,48} \]
\[ 2.11 \times 10^{10} \text{ (gm}^{-3} \]
\[ 8.9 \times 10^{-6} \text{ (m}^{2} \text{mol}^{-1} \]
\[ 330 \text{ (mAh g}^{-1} \]}

\[ ^{36} \]

\[ ^{37} \]

\[ ^{1,2} \]

\[ ^{10} \]

\[ ^{1,29,38} \]

\[ ^{1} \]

\[ ^{1} \]
Figure 2. Normalized radial stress in the electrode particle at different radial locations as a function of dimensionless time $\tau$ in the particle core as well as the SEI shell during lithiation at the 0.5 C rate, with a zoomed-in view of the stresses near the host material core-SEI shell interface.

maximum at the shell/core interface, and decreases slightly throughout the layer as the electrolyte interface is reached. We note that, the radial and tangential stresses presented above are qualitatively similar to the stress distributions of previously published two-phase core-shell models.\textsuperscript{27,38–40}

The dashed blue curve in Figure 4 presents the relationship of this maximum tangential in the SEI during lithiation as a function of $\Delta \zeta_1$. As expected from Equation 9, the maximum tensile stress in the SEI is proportional to the $\Delta \zeta_1$. We should note that the stress in the SEI is independent of the rate of lithiation. In other words, even at vanishing lithiation rates, the stresses in SEI would be finite and the dashed blue curved would be valid. This is in contrast to previous analyses of DISs\textsuperscript{17,19} without consideration of the SEI where stresses vanish as the rates of lithiation/delithiation vanish.

As mentioned earlier, the SEI is assumed to be a dense inorganic layer. Because we could not obtain the actual tensile strength of the SEI from the published literature, we proceed with the following analysis by comparing our calculated stress values to the tensile strength of similar materials. In other words, the inorganic SEI layer would perhaps be a brittle layer with tensile strength similar to those of ceramic materials such as flat soda lime glass (a mixture of oxides), which has a reported value of 0.045 GPa.\textsuperscript{41} According to Hasselman’s criteria, crack initiates when the material is subjected to a stress level ($\sigma$) that exceeds the fracture strength ($\sigma_f$) of the material, i.e., $\sigma > \sigma_f$.\textsuperscript{34}

Figure 3. Normalized tangential stress as a function of dimensionless time $\tau$ during lithiation of the particle at the 0.5 C rate at different radial locations in the active material core as well as the SEI shell, with a zoomed-in view of the stresses near the host material core-SEI shell interface.
From Figure 4, the tensile stresses in the SEI during lithiation clearly exceed this value, even for small $\Delta$SOL. Hence, once the $\Delta$SOL exceeds a certain threshold value (i.e., a $\Delta$SOL value at which the stress in SEI equals the strength of SEI layer ($\sigma_{SEI}^f = \sigma_{SEI}^{SOL}$)), the fracture tendency (i.e., ratio of maximum stress to the tensile strength of the material) of the SEI shell becomes high. We therefore propose that, during lithiation, once $\Delta$SOL is above the threshold $\Delta$SOL, the SEI cracks exposing a new electrode surface to the solvent, facilitating irreversible side reactions and eventually, the cell capacity decay. The calculations shown in Figure 4 indicate that $\Delta$SOL as low as 1% could result in SEI fracture.

For the stress calculations presented above, the SEI layer is assumed to be a non-porous layer. It should be noted that the porosity of the SEI will affect both the modulus of elasticity and the fracture strength of the SEI in the same direction and hence we expect the results presented here to remain qualitatively the same.

It has been established previously that, for constant current lithiation/delithiation processes, the maximum tensile stress that a particle experiences in the tangential direction at the surface of the particle during delithiation. Cheng et al. also establishes that the maximum stress experienced by the particle is proportional to the current density at the surface of the particle. Thus, lower the current of operation, lower is the stress on the electrode particle. Here, we compare this maximum tensile stress experienced by the host material core at the surface of the core $r = R$ during delithiation to the maximum stress experienced by the SEI shell during lithiation for different $\Delta$SOLs at different rates of operation. The solid curves in Figure 4 gives the maximum tangential tensile stress experienced by the core active material particle as a function of the $\Delta$SOL when an electrode particle is delithiated at different rates. To reiterate, we chose the delithiation condition for plotting stresses in the host particle, because a particle experiences maximum tensile stress at the surface during delithiation.

From the zoomed-in view of Figure 4 we observe that as the rate of delithiation decreases from 2 C to 0.1 C, the maximum tensile stress experienced by the host material core decreases significantly (moving from green curve to sky blue curve). This implies that at vanishing lithiation rates the stresses at the host material core surface would be infinitesimally small, yet the SEI would fracture when the threshold $\Delta$SOL is exceeded. Upon comparison of the dashed blue curve with the solid curves we observe that, at low rates of operation, the stress experienced by the host material core is much smaller than that experienced by the SEI shell. In effect, the fracture tendency of the graphite core would be presumably low at low-rate cycling conditions. Previously, Takahashi et al. came to the similar conclusion that at low rate, the stresses in graphite electrode are very small as compared to the fracture strength of the particles.

Therefore, we may conclude that during low rate cycling, the SEI layer fracture rather than the host material core fracture would be dominant mode of degradation.

**Strain Energy Calculations for SEI Cracking**

From the stress analysis in the previous section, it is clear that the SEI has higher fracture tendency than the core active material during low rate operation. The cracked SEI exposes new electrode particle surface to the solvent electrolyte and new SEI is formed in the exposed area (see in Figure 1). To correlate the capacity loss to SEI cracking, it is important to quantify the number of cracks on the SEI layer. The crack density will then be related to strain energy released during SEI cracking.

Following Cheng and Verbrugge, we calculate the bulk strain energy per unit volume (i.e., the bulk strain energy density) $e(r)$ accumulated as a result of the elastic deformation for the isotropically deformed sphere as

$$e(r) = \frac{1}{2E} (\sigma_r^2 + 2\sigma_\theta^2) - \frac{\nu}{E} (2\sigma_r\sigma_\theta + \sigma_\theta^2).$$

Because the total strain energy can be obtained by integrating the strain energy density over the entire volume, in the core-shell model, the total energy is the sum of the strain energies in both the phases. The total strain energy therefore in dimensionless form is

$$\Pi_{\text{total}} = \frac{4\pi}{2\pi R^3 E_a \xi \xi \frac{E_{\text{SOL}}}{(1-\nu)} \left[ (\xi_1^2 + 2\xi_2^2) - 2\nu \xi_3 (2\xi_4 + \xi_5) \right] x^2 dx$$

$$+ \int_0^1 \frac{E_a}{E_{\text{SEI}} \xi} \left[ (\xi_1^2 + 2\xi_2^2) - 2\nu \xi_3 (2\xi_4 + \xi_5) \right] x^2 dx [14a]$$
where $\xi_i$ is the normalized stress (Equation 12) in the direction $r$, $\theta$, or $\varphi$ and $x = r/R$ is the dimensionless radial position of a point from the center.  

If the SEI cracks, only a part of this total strain energy will be released, because the SEI fracture process would result in only a partial relaxation of the stresses in the core region. When the SEI cracks, the part of the stresses developed in the core as an effect of SEI confinement will be released along with the stresses developed in the SEI region. At the same time, the active particle core may still have finite stresses due to presence of the lithium concentration gradients are present inside the active material particle. In a simplified formulation, we assume that, the residual stresses in the electrode particle just after SEI fracture would be same as those in an electrode particle with no SEI but with a similar lithium concentration profile inside it. The strain energy of the particle with a cracked SEI ($\Pi_{\text{cracked,SEI}}$)  can be calculated with the assumption of no SEI constraints on the active material core, i.e., by setting $w = 0$ in Equation set 6.

$$\Pi_{\text{cracked,SEI}} = \frac{4\pi \int_0^R \frac{e(r)r^2 dr}{2\pi R^3 E_a \left(\frac{\nu_a C_a}{\Omega_a (1-\nu_a)}\right)^2}}{\int_0^R \left[\left(\xi_r^2 + 2\xi_\theta^2\right) - 2\nu_a \xi_r^2 \left(2\xi_r + \xi_\theta\right)\right] x^2 dx}$$

where $\xi_j^\prime$ represents normalized stress in a particle if there are no SEI constraints to the particle expansion and $j\prime$ represents direction $r$, $\theta$, or $\varphi$.  

The energy to be released during the SEI cracking would be the difference between the total strain energy of the particle before and after the SEI cracking takes place. We define this excess strain energy ($\Pi_{\text{excess}}$) as the difference between the total strain energy ($\Pi_{\text{total}}$) and the strain energy in the particle after the SEI fractures ($\Pi_{\text{cracked,SEI}}$).

$$\Pi_{\text{excess}} = \Pi_{\text{total}} - \Pi_{\text{cracked,SEI}}$$  \hspace{1cm} [15]$$

Once the SEI fractures, the stresses in the SEI layer are relieved. Since, the stresses in the host material core may not be completely relieved even after the SEI fracture, there might be a finite strain energy ($\Pi_{\text{cracked,SEI}}$) stored in the particle after the SEI fracture event. We assume that once the SEI fracture stops, the residual stresses in SEI layer are small and thus are insufficient to continue further cracking of SEI at that point of time. For above mentioned example of graphite electrode particle with 10 micron diameter and 50 nm SEI layer, we calculate the excess strain energy based on Equations 14a, 14b and 15. In Figure 5 we plot the excess strain energy $\Pi_{\text{excess}}$ as a function of %\Delta SOL for 0.5 C rate of lithiation, and we find that the excess strain energy has a quadratic relation with the state-of-lithiation swing $\Delta SOL$ and has a very weak linear dependency on $\Delta SOL$.  

The relation between excess strain energy $\Pi_{\text{excess}}$ and the state-of-lithiation swing can be derived analytically as below. If we assume that the SEI thickness is extremely small compared to the particle radius, (i.e., $w \to 0$) then within the active material (i.e., $r \leq R_a$) the stresses $\xi_j \approx \xi_j^\prime$. In other words, if the SEI is extremely thin, the stresses in the active material would be mostly unaffected by the presence of the SEI. In that case, the excess strain energy would be the strain energy stored in the SEI portion before the SEI fractures. The Equation 15 for excess strain energy $\Pi_{\text{excess}}$ would become

$$\lim_{w \to 0} \Pi_{\text{excess}} = \int_{\Delta_0}^1 \frac{E_a}{E_{\text{SEI}}} \left[\left(k_r^2 + 2k_\theta^2\right) - 2\nu_{\text{SEI}} k_r (2k_1 + k_2)\right] (\Delta SOL)^2 x^2 dx$$  \hspace{1cm} [16a]$$

From Equation 7, the stresses in the SEI are proportional to $\Delta SOL$. Hence, we rewrite Equation 16a as

$$\lim_{w \to 0} \Pi_{\text{excess}} = \int_{\Delta_0}^1 \frac{E_a}{E_{\text{SEI}}} \left[\left(k_r^2 + 2k_\theta^2\right) - 2\nu_{\text{SEI}} k_r (2k_1 + k_2)\right] (\Delta SOL)^2 x^2 dx$$  \hspace{1cm} [16b]$$

where $k_r = k_1 \Delta SOL$ and $k_\theta = k_2 \Delta SOL$. Equations for $k_1$ and $k_2$ can be obtained using Equations 9a and 9b.

$$k_1 = \left\{\begin{array}{l}2 \left[1 - \frac{R^2}{r^2}\right] \left[1 - \frac{3w}{R}\right] \\ \frac{\Omega_a C_a}{\Omega_a (1-\nu_a)} \left(3 (1-\nu_{\text{SEI}}) + \left(\frac{E_{\text{SEI}}(1-2\nu_{\text{SEI}})}{E_a} - (1 - 2\nu_{\text{SEI}})\right) \frac{\Omega_a C_a}{\Omega_a (1-\nu_a)} \right) \end{array}\right\}$$

$$k_2 = \left\{\begin{array}{l}E_{\text{SEI}} \left[\frac{2}{r^2} + \frac{1}{R^2}\right] \\ \frac{\Omega_a C_a}{\Omega_a (1-\nu_a)} \left(1 - 2\nu_{\text{SEI}}\right) \left(\frac{E_{\text{SEI}}(1-2\nu_{\text{SEI}})}{E_a} - (1 - 2\nu_{\text{SEI}})\right) \end{array}\right\}$$

Since, the state-of-lithiation swing $\Delta SOL$ is independent of the position vector $x$, we can take it out of the integration sign

$$\lim_{w \to 0} \Pi_{\text{excess}} = (\Delta SOL)^2 \int_{\Delta_0}^1 \frac{E_a}{E_{\text{SEI}}} \left[\left(k_r^2 + 2k_\theta^2\right) - 2\nu_{\text{SEI}} k_r (2k_1 + k_2)\right] x^2 dx$$  \hspace{1cm} [16c]$$

For a given electrode particle, the term in the square bracket is a constant and is independent of state-of-lithiation swing.

$$\lim_{w \to 0} \Pi_{\text{excess}} = \text{const} \ast (\Delta SOL)^2$$  \hspace{1cm} [16d]$$

Here, $\text{const} = \int_{\Delta_0}^1 \frac{E_a}{E_{\text{SEI}}} \left[\left(k_r^2 + 2k_\theta^2\right) - 2\nu_{\text{SEI}} k_r (2k_1 + k_2)\right] x^2 dx$ is a constant.

Hence we may write

$$\lim_{w \to 0} \Pi_{\text{excess}} \propto (\Delta SOL)^2$$  \hspace{1cm} [16e]$$

From Equation 16e, we show that the excess strain energy is proportional to the 'square of the state-of-lithiation swing' (i.e., $(\Delta SOL)^2$) of the electrode particle. This is consistent with the earlier observation from Figure 5. The excess strain energy stored is transferred to surface energy during fracture by creating new surfaces. Note that, here the term 'new surface' refers to the two surfaces of the SEI layer created when the SEI layer cracks. With the stress analysis presented in Analysis of stresses:
case study section, we could prove that at lower rates of operation, the fracture tendency of the SEI layer is higher than the fracture tendency of the graphite material core. Unlike the assumption of crack propagation in the electrode particle core presented in Deshpande et al., we assume that the SEI thickness does not change significantly once initial SEI is formed; hence, from Equation 16 and 17, \( l_{crack} \) would be proportional to the energy released and in turn to \((\Delta SOL)\)^2.

\[
l_{crack} \propto \Pi_{excess}, \text{ i.e., } l_{crack} \propto (\Delta SOL)^2.
\]

We assume that, upon fracture, the two newly formed surfaces of SEI are left a distance ‘d’ apart from each-other (Figure 1b). The crack between two SEI surfaces allows the electrolyte transport to the electrode surface, and thus facilitates more side reactions causing a crack between two SEI surfaces allows the electrolyte transport to the electrode surface, and thus facilitates more side reactions causing a crack between two SEI surfaces allows the electrolyte transport to the electrode surface, and thus facilitates more side reactions causing a crack between two SEI surfaces allows the electrolyte transport to the electrode surface, and thus facilitates more side reactions causing.

\[
A_{new, electrode} \propto l_{crack}
\]

Hence, the new surface of the electrode particle exposed to the electrolyte is proportional to the length of crack.

\[
\frac{A_{new, electrode}}{\Delta SOL} \propto (\Delta SOL)^2.
\]

**SEI Cracking and Cell Capacity Loss**

To correlate the capacity loss with SEI cracking we detail our assumptions:

a. At low rate operation SEI cracking and re-healing is the main mechanism of capacity loss and the host material particle itself would not undergo cracking and pulverization.

b. There is no loss of host material in either electrode during low rate cycling. It’s been shown previously that at low rates of operation for well-made cells the loss of host material is minimal. In this article, Figure 6 (discussed later) supports this conclusion for the graphite electrode in NMC/graphite cells.

c. Parasitic electrochemical reactions resulting in the capacity loss occur only at the graphite electrode in the cell.

d. Coulombic loss of cell capacity is equal to the cumulative coulombic throughput of the parasitic reactions.

e. During cycling, the rate of SEI re-healing reactions is only a function of the exposed graphite area \( A_{new, electrode} \) and the composition and potential dependencies of the reaction rates are negligible.

With the assumptions mentioned above, the capacity loss \( Q_{loss} \) of a cell during electrochemical cycling would be proportional to the surface area of the host material core newly exposed to the electrolyte,

\[
Q_{loss} \propto A_{new, electrode}
\]

\[
\frac{Q_{loss}}{\Delta SOL} = 2\gamma (Area \ of \ cracked \ SEI \ surface) = 2\gamma \times w \times l_{crack}
\]

where \( \gamma \) is the surface energy of the newly created SEI surfaces, \( w \) is the thickness of the SEI, and \( l_{crack} \) is the sum of lengths of all the cracks present on the SEI surface.

\[
l_{crack} = \sum_{i=1}^{N} l_i
\]

\[
N: \text{Number of cracks}
\]

\[
l_i: \text{Length of a crack}
\]

We assume that the SEI thickness \( w \) does not change significantly once initial SEI is formed; hence, from Equation set [16] and [17], \( l_{crack} \) would be proportional to the energy released and in turn to \((\Delta SOL)\)^2.

\[
l_{crack} \propto \Pi_{excess}, \text{ i.e., } l_{crack} \propto (\Delta SOL)^2.
\]

Combining Equation 22 with Equation 21,

\[
Q_{loss} \propto (\Delta SOL)^2
\]

here \( a > 0 \) is a constant and is a function of various parameters such as the rate of reaction (thus temperature), the number of lithium atoms involved in the reaction, the mechanical properties of SEI material as well as the electrode material, radius of particles, and diffusion properties of lithium in the electrode material etc.

Equation 23 shows that the cell capacity loss during a cycle would be proportional to the square of state-of-lithiation swing of the negative electrode. In other words, larger is the state-of-lithiation swing larger is the capacity loss during cycling. Although it’s widely recognized in the literature that SOC swing is one of the major factors affecting the battery cycle life, the exact relation between the capacity loss and the SOC is mostly empirically calculated. The quadratic relation presented with the Equation 24, to our knowledge, is the first physics based derivation relating the capacity loss to the state-of-lithiation swing.

**Battery Cycle Life**

Using above mentioned relation (Equation 24) between the cell capacity loss and \( \Delta SOL \), we develop a model for estimating capacity loss for a case in which a cell is continuously cycled. The SEI facture and re-healing on the negative electrode is assumed as the major mechanism of capacity fade during low rate cycling and we neglect the calendar aging during the cycling period while deriving the equations below. We also assume that, the constant \( a \) does not change significantly during cycling.

For the discussion below we define the cell capacity \( Q_i \) after \( i \) cycles as the low rate discharge capacity from 100% state-of-charge to 0% state-of-charge on \( i^{th} \) cycle. The cycle capacity after \( (n+1) \) cycles \( (Q_{n+1}) \), can be obtained by subtracting the capacity lost during the \( (n+1)^{th} \) cycle \( (Q_{loss,Jn+1}) \) from the cell capacity at the end of previous cycle \( (Q_n) \).

\[
Q_{n+1} = Q_n - Q_{loss,Jn+1}
\]

As we have shown with Equation 24, the capacity loss during any cycle \( (Q_{loss,Jn}) \) is proportional to the square of state-of-lithiation swing during that cycle \( (\Delta SOL)^2 \). Here \( \Delta SOL \) represents the final state-of-lithiation swing that the negative electrode undergoes during the \( i^{th} \) cycle when lithiation is complete. Note that, with this definition,
\[ \Delta SOL_i \] is a function the cycle number and is independent of the time during cycling.

Combining Equations 24 and 25, we obtain

\[ Q_{n+1} = Q_n - a(\Delta SOL_{n+1})^2 \]  

[26]

For example, the discharge capacity after the 1st cycle is

\[ Q_1 = Q_0 - a(\Delta SOL_1)^2 \]  

[27]

here \( \Delta SOL_1 \) is the state-of-lithiation swing of the negative electrode during the first cycle. Similarly, the capacity after second and third cycle would be

\[ Q_2 = Q_1 - a(\Delta SOL_2)^2 \]

\[ Q_3 = Q_0 - a(\Delta SOL_1)^2 - a(\Delta SOL_2)^2 \]  

[28]

And the capacity after n cycles would be

\[ Q_n = Q_0 - a(\Delta SOL_1)^2 - a(\Delta SOL_2)^2 - \cdots - a(\Delta SOL_n)^2 \]  

[29]

Equation 29 is a significant result of this work. It is generally applicable and represents the cell capacity after n cycles as a function of state-of-lithiation swing during those cycles. Since, the final state-of-lithiation during a lithiation event in a cycle is independent of the magnitude of current applied during that cycle, Equation 29 would also apply to non-constant current cycling and voltage-limited cycling. Since, the current during electric vehicle drive profiles is generally non-constant, the result above would still apply and thus is significant from the automotive application point of view. We note that only integration of current over time during a lithiation event can be used to calculate \( \Delta SOL_n \), not during delithiation events. In Experimental procedure and model validation section we compare predictions of capacity loss using this equation to actual experimental data.

If capacity fade due to calendar aging is significant during cycling, an additional expression for calendar capacity fade can be incorporated in Equation 29, as is often done.\(^{10,42}\) In that scenario, total capacity loss can be calculated as the total of the loss due to calendar aging and the loss due to cycle aging.\(^{10}\)

\[ Q_n = Q_0 - a \left[ \sum_{i=1}^{n} (\Delta SOL_i)^2 \right] - Q_{lost,cal} \]  

[30]

In the above equation \( Q_{lost,cal} \) Represents the capacity loss due to calendar aging.

As in Deshpande et al.,\(^ {10} \) we may assume that the capacity loss due to calendar aging \( (Q_{lost,cal}) \) is proportional to the square root of duration of aging.

\[ Q_{lost,cal} = K (\text{aging time})^{0.5} \]  

[31]

here K is the proportionality constant for calendar aging. The cell capacity at any cycle would be a resultant of capacity lost due to cycle aging and capacity lost due to calendar aging

\[ Q_n = Q_0 - a \left[ \sum_{i=1}^{n} (\Delta SOL_i)^2 \right] - K (\text{aging time})^{0.5} \]  

[32]

**Simplifications to Equation 29** - Here we derive an expression for capacity loss when a cell is cycled between \( V_{max} \) and \( V_{min} \) at a low rate with constant current operation. Consistent with the observation reported in Deshpande et al.,\(^ {36} \) we assume that there is a negligible resistance rise in the cell due to cycle aging.

When a cell is cycled between two voltage limits \( V_{max} \) and \( V_{min} \), the state-of-lithiation swing of the negative electrode during a cycle would be:

\[ \Delta SOL = \frac{Q'}{Q_{gr}^{theor}} \]  

[33]

Here \( Q' \) is the cell charge capacity in a cycle when the cell is charged from \( V_{min} \) to \( V_{max} \). The quantity \( Q' \) can be obtained by integrating current over time during the charging event, i.e., \( Q' = \int i dt \). Note that for full cell configuration, when the cell is charging, the graphite electrode is lithiated. The term \( Q_{gr}^{theor} \) represents theoretical capacity of the graphite electrode.

We also assume that, on any \( n^{th} \) cycle we first lithiate the negative electrode based on the previous cycle’s capacity (i.e., \( Q_{n-1} \)) and then side reactions take place to decrease the cell capacity to \( Q_n \), therefore the state-of-lithiation swing of \( n^{th} \) cycle is related to the capacity available after \((n-1)\) cycles. If we assume that the state-of-charge (SOC) vs. Open circuit voltage (OCV) relationship of a cell does not significantly change over cycling, then the cell capacity between \( V_{max} \) and \( V_{min} \) would decrease proportionally to the overall cell capacity fade of the cell during cycling. Hence

\[ Q_n \propto Q_{n-1} \]  

[34]

\[ Q_n' = p Q_{n-1} \]  

[35]

\( Q_n' \) represents the cell charge capacity when the cell is charged from \( V_{min} \) to \( V_{max} \) during the \( n^{th} \) cycle and \( Q_{n-1} \) is the cell maximum capacity available for lithiation on the \( n^{th} \) cycle, which is normally measured by a low-rate discharge test. With an invariant SOC-OCV, \( p \) is positive constant.

Since there is no loss of graphite material during slow cycling,\(^ {10,28,36} \) (verified with Figure 6, explained in Experimental procedure and model validation section), the theoretical capacity of the graphite electrode \( Q_{gr}^{theor} \) remains constant. Hence, combining Equation 33 and 35

\[ \Rightarrow \Delta SOL_n = \frac{p Q_{n-1}}{Q_{gr}^{theor}} \]  

[36]

\[ \Delta SOL_n = k Q_{n-1} \]  

[37]

here \( k = \frac{p}{Q_{gr}^{theor}} \).

Equation 37 implies that the state-of-lithiation swing when the cell is charged from \( V_{min} \) to \( V_{max} \) during any cycle \( n \) is proportional cell capacity available at the end of previous cycle \((n-1)\). We note that as we cycle the cell, the capacity of the \( Q_{n-1} \) decreases. From Equation 37, the state-of-lithiation swing during the next cycle \( \Delta SOL_{n+1} \) decreases proportionally. As the capacity loss is proportional to state-of-lithiation swing during that cycle (Equation 24), we proceed in cycling the rate of capacity loss due to SEI cracking-reformation decreases.

Combining Equation 29 and Equation 37, we obtain the cell capacity \( Q_n \)

\[ Q_n = Q_0 - a \left[ \sum_{i=1}^{n} (k Q_{i-1})^2 \right] \]  

[38]

When the Equation 38 is applied to 1st cycle, the cell capacity after 1st cycle of cycling is

\[ Q_1 = Q_0 - a(k Q_0)^2 \]  

[39]

Similarly, the cell capacity after 2nd cycle

\[ Q_2 = Q_0 - a(k Q_0)^2 - a(k Q_1)^2 \]  

[40]

\[ \Rightarrow Q_2 = Q_0 - 2a(k Q_0)^2 - 2a(k Q_0)^2 - a(k Q_1)^2 \]  

[41]

In Appendix B, we show that \( k Q_0 \) is a very small number. Here, \((k' = k^2)\) Hence, as an approximation we may neglect higher power \((> 4)\) terms \( k' Q_0 \) and the equation for the capacity on after n cycles
would be:

\[
Q_n = Q_0 - (n) ak^2(Q_0)^2 + 2(n)(n - 1) (ak)^2(Q_0)^3
- \sum_{i=2}^{n} (i - 1)(3i - 5) (ak)^3(Q_0)^4 \tag{42}
\]

Equation 44 represents the cell capacity at any cycle \(n\) when the cell is cycled continuously between \(V_{\text{max}}\) and \(V_{\text{min}}\) at low rates of charge and discharge. The capacity retention during slow cycling between \(V_{\text{max}}\) and \(V_{\text{min}}\) normalized to initial cell capacity \(Q_0\). Interestingly, with the SEI cracking as a major mechanism of capacity loss during cycling, the battery capacity retention after \(n\) cycles can be described with only one variable parameter \(k\), initial capacity of the cell \(Q_0\) is known.

It should be noted that since value of \(k Q_0\) is small (see Appendix B), the terms with higher powers of \(k Q_0\) have comparatively smaller effect during initial cycling (i.e., small value of \(n\)). As the value of \(n\) grown, the effect of these terms increases.

Equation 44 can be written in terms of initial state-of-lithiation swing by replacing \(k Q_0\) with \(\Delta SOL\) (Equation 37) in Equation 44

\[
\bar{Q}_n = \frac{Q_0}{Q_0} = 1 - (n) k (\Delta SOL_1) + (n)(n - 1) 2(ak)^2(\Delta SOL_1)^2
- \sum_{i=2}^{n} (i - 1)(3i - 5) (ak)^3(\Delta SOL_1)^3 \tag{45}
\]

For the same initial cell capacity \(Q_0\) and similar cycling voltage limits, a cell with larger graphite electrode capacity would have smaller value of \(k\) (for the same chemistry). Hence, from Equation 38, for a given cell capacity, larger the graphite electrode smaller would be the initial state-of-lithiation swing (\(\Delta SOL_1\)) if the cells are cycled between same voltage limits. From Equation 45, a cell with smaller (\(\Delta SOL_1\)) would have smaller initial capacity fade rate. In an interesting set of experiments, Xu et al.\(^\text{28}\) cycled two cells with similar initial capacity but different graphite anode loading between similar voltage window. It was observed that the cell with higher graphite anode loading has lower initial capacity fade rate as compared to the cell with lower anode loading (please refer to Figure 2b in Xu et al.\(^\text{28}\)).

The presented theory provides a theoretical backing to the experimental observations in Xu et al.\(^\text{28}\).

This equation will be valid only when there is no loss of electrode particles through cracking or isolation. At high charge discharge rates or at low operating temperatures other mechanisms such as host electrode material cracking (i.e., Mode 1), binder degradation, lithium plating, SEI growth etc. might affect the described mechanism of degradation. We note that, any isolation of graphite material from the composite matrix during cycling would increase the \(\Delta SOL\) of the remaining graphite electrode in the subsequent cycles, and thus may increase the rate of capacity fade further.

Again, if the calendar aging is significant during the cycling period, form similar to Equation 32, we can write

\[
Q_n = Q_0 - \sum_{i=2}^{n} (i - 1)(3i - 5) (ak)^3(Q_0)^3
\]

Experimental Procedure and Model Validation

Graphite and NMC333 electrode laminates were prepared, calendared and punched and used in Graphite/NMC333 coin cells. The electrode preparation and cell fabrication procedure is described in earlier publications.\(^\text{28,36}\) A charge-discharge rate of \(C/10\) with a 15 min rest after every charge and discharge and the voltage limits of 4.4 V to 2.0 V were used for formation cycles. After the formation cycles, the cells were cycled at the \(C/2\) charge discharge rate with voltage limits of 4.2 V to 2.0 V. The theoretical specific capacity of graphite is taken to be 330 mAh g\(^{-1}\) and that for NMC333 is be 165 mAh g\(^{-1}\) in the given voltage range.\(^\text{36}\) A low cycling rate of \(C/2\) was chosen to minimize Mode 1 host material cracking. Though, the threshold value of ‘low rate’ (i.e., maximum rate above which particle cracking becomes significant) would depend on parameters such as the diffusion coefficient of lithium in the electrode particle material, the temperature of operation and the mechanical properties of electrode material as well as SEI layer etc.; for the graphite electrode, the stresses in the particle during \(C/2\) charge/discharge at 25 °C are shown to be much lower than its tensile strength.\(^\text{22}\) After every 40 cycles at C/2 rate, a couple of C/10 cycles with the same voltage limits are used to measure the cell capacity, which serves to avoid the effects of impedance rise during cycling. In Figure 6, we plot the voltage profile of the cell at different stages during cycling (i.e., at cycle 1, 212, and 379). At cycle 379 the cell has much lower discharge capacity (green voltage curve) than at the beginning of life (red voltage curve) within the given voltage limits. To confirm that there is no graphite material degradation we also plot differential voltage against the cell capacity (dV/dQ vs Q) for different cycle numbers in Figure 6. The distance between the peaks of a differential voltage curve in graphite/NMC cell chemistry indicates the amount of negative electrode material available for lithium storage.\(^\text{28,36}\) The distance between the peaks of a differential voltage curve in graphite/NMC cell chemistry indicates the amount of negative electrode material available for lithium storage.\(^\text{28,36}\) In this figure, if we compare the differential voltage curves for the cell at the beginning of life (red curve) to that after 379 cycles (green curve), we find that the distance between peaks remain unchanged over cycling, i.e., \(\Delta V_1 \approx \Delta V_2\). We therefore conclude that there is no major loss of graphite electrode material from the composite electrode matrix.

In Figure 7, we plot the normalized capacity of the cell against the cycle number (black circles). In this figure the circles showing higher capacity represent the capacity of the cells at C/10 rate that were performed to measure the capacity of the cell independent of the impedance rise. We also compare the experimental results with the model (Equation 29) fitting (represented by purple line) and see that the model results match very closely to the experimental results with parameter constant of \(a = 0.0011\). While fitting Equation 46, we
assume that the calendar life degradation in 3 months of cycling test is negligible. The good agreement between model and the experimental data suggests that, the model fairly accurately captures the capacity retention of a cell over cycling.

**Conclusions**

Even though the Mode 2 SEI cracking mechanism of capacity loss during cycling of lithium ion batteries has been discussed previously in various articles, the relationship between SEI cracking and capacity loss presented in these articles has been mostly qualitative. To our knowledge, we present the first mathematical formulation relating SEI cracking to fade during cycle aging. We show that the SEI layer experiences a large tensile stress when a graphite electrode particle is lithiated.

We perform an analysis that allows us to compare the development of mechanical stresses from the Mode 1 and Mode 2 particle fracture mechanisms. The analysis leads us to the conclusion that during relatively low-rate operation, Mode 2 dominates with the SEI layer experiencing relatively larger stresses than the graphite host material and at the same time, the SEI layer having much lower fracture strength than the host graphite material; that is, the SEI layer has a much larger fracture tendency than the particle host material itself. In the context of electric vehicle (EV) applications, we surmise that the Mode 1 mechanism would be more prominently presented in standard hybrid-electric vehicles (HEVs) and the Mode 2 mechanism would be more prominently presented in EVs because HEV charging events are exclusively due to regenerative braking and typically at relatively high currents. Another way of looking at this hypothetical comparison is to consider two identical plug-in HEVs (PHEVs) that are designed to have the option of operating exclusively as an EV or exclusively as a standard HEV. After operation under the same vehicle drive duty, we suggest that the battery capacity loss of the vehicle operated as an HEV will be dominated by Mode 1 and that as an EV will be dominated by Mode 2.

For low-rate lithiation, unlike Mode 1 particle cracking, which is predicted to happen mostly during delithiation,10,20 the Mode 2 SEI cracking may happen during lithiation of the electrode. Since, the negative electrode is lithiated during cell charging, the cell charging conditions may have a significant effect on the cell capacity fade rate. The tensile stress in the SEI layer is shown to be proportional to the state-of-lithiation swing of the negative electrode. Thus, the larger the state-of-lithiation window of operation (ΔSOL), the larger the tensile stress on the SEI layer, resulting in larger SEI fracture tendency. Additionally, we demonstrate that the strain energy released during SEI cracking is proportional to the square of the SOL swing and in turn, the cell capacity loss during a lithiation event is proportional to the square of the event’s SOL swing. We developed a model based on this SEI fracture theory to predict capacity loss of cells cycled continuously between two voltage limits, and we find good agreement between the modeling results and experimental observations.

Although the model predicts that the SEI has a high fracture tendency, the SEI cracking phenomenon is very difficult to observe experimentally. To improve the model, a better understanding of SEI properties as well as the parasitic reactions is needed. Certainly many questions remain unanswered by the presented theory. For example, how much of the total SEI reformation products actually deposit on the electrode? How do the properties of SEI-reformation products affect the SEI fracture in subsequent cycles? There is the possibility that the SEI reformation products deposited on the exposed electrode experience a compressive force during subsequent delithiation. Factors such as the porosity of the SEI, the organic/inorganic structure of SEI, the chemical/mechanical properties of SEI-reformation products etc. may have significant effects that warrant further investigations in subsequent analyses.

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**Appendix A: Derivation of Equation set 6**

Rewriting the Equation 4a for the displacement $u_x(t)$:

$$u_x(t) = \left(1 + \frac{\nu}{1 - \nu}\right) \frac{\Omega_i}{\Omega} \int_0^{r_i} (C(r, t) - C(0, t)) r^2 dr + \frac{\Omega_i}{\nu R}$$  \[4a\]

Rewriting the Equations 4b and 4c for the radial and tangential stresses:

$$\sigma_r(r, t) = -\frac{\Omega_i}{3(1 - \nu)} \int_0^{r_i} (C(r, t) - C(0, t)) r^2 dr$$

$$\sigma_r(r, t) = -\frac{\Omega_i}{3(1 - \nu)} \int_0^{r_i} (C(r, t) - C(0, t)) r^2 dr$$

$$\sigma_\theta(r, t) = \frac{E_i}{(1 + \nu)} \frac{\Omega_i}{\Omega} \int_0^{r_i} (C(r, t) - C(0, t)) r^2 dr$$  \[4b\]

$$\sigma_\phi(r, t) = \frac{E_i}{(1 + \nu)} \frac{\Omega_i}{\Omega} \int_0^{r_i} (C(r, t) - C(0, t)) r^2 dr$$  \[4c\]

For the $x$-phase in the region of $0 \leq r < R_s$, since the stress and the displacement are finite at $r = 0$, the term $I_{SEI}$ has to be zero for the $x$-phase. Hence the radial stress and the tangential stress in the host material $x$-phase core would take forms as below:

$$\sigma_r^x(r, t) = -\frac{2E_i}{3(1 - \nu)} \int_0^{R_s} (C_{SEI}(r, t) - C_{SEI}(0, t)) \frac{E_i I_{SEI}}{(1 - 2\nu)}$$  \[6a\]

$$\sigma_\theta^x(r, t) = \frac{E_i}{(1 + \nu)} \frac{\Omega_i}{\Omega} \int_0^{R_s} (C_{SEI}(r, t) - C_{SEI}(0, t)) \frac{E_i I_{SEI}}{(1 - 2\nu)}$$  \[6b\]

For the SEI layer phase in the region of $R_s \leq r \leq R$, we have $\Omega_{SEI} = 0$, i.e., there is no expansion in the SEI layer, since SEI acts only as an ionic conductor. Hence the radial stress and tangential stresses (Equation 4a and 4b) for the SEI shell $(R_s \leq r \leq R)$ would take forms as below:

$$\sigma_r^{SEI}(r, t) = \frac{E_{SEI} I_{SEI}}{(1 - 2\nu_{SEI})} \frac{E_{SEI} I_{SEI}}{(1 + \nu_{SEI})} \frac{E_{SEI} I_{SEI}}{R^2}$$  \[A1\]

$$\sigma_\theta^{SEI}(r, t) = \frac{E_{SEI} I_{SEI}}{(1 - 2\nu_{SEI})} \frac{E_{SEI} I_{SEI}}{(1 + \nu_{SEI})} \frac{E_{SEI} I_{SEI}}{R^2}$$  \[A2\]

Since the normal stress at the free surface of the spherical particle is $\sigma_r(R) = 0$; putting $r = R$ in Equation A1, we get

$$I_{SEI} = \frac{E_{SEI} I_{SEI}}{(1 - 2\nu_{SEI})} \frac{E_{SEI} I_{SEI}}{(1 + \nu_{SEI})} \frac{E_{SEI} I_{SEI}}{R^2}$$  \[A3\]

Combining Equation A3 with Equation A1,

$$\sigma_r^{SEI}(r, t) = \frac{2E_{SEI} I_{SEI}}{(1 - 2\nu_{SEI})} \frac{E_{SEI} I_{SEI}}{(1 + \nu_{SEI})} \frac{E_{SEI} I_{SEI}}{R^2}$$  \[A4\]

Since the radial stress is continuous at the $x$-phase core-SEI shell interface (Equation 5), equating Equations A3 and (6a) at $r = R_s$:

$$\sigma_r^{x}(r_{SEI}) = \sigma_r^{SEI}(r_{SEI})$$  \[5\]

If the thickness of SEI shell is $w$, then

$$R_s = R - w$$  \[A6\]

Putting Equation A6 in Equation A5:

$$2E_{SEI} I_{SEI} \frac{2E_{SEI} I_{SEI}}{(1 + \nu_{SEI})} \frac{E_{SEI} I_{SEI}}{R^2} = \frac{E_s}{3(1 - \nu)} \frac{\Omega_i}{\Omega} \int_0^{r_i} (C_{SEI}(r, t) - C_{SEI}(0, t))$$  \[A7\]
Rearranging some of the terms of the equation above,
\[
\frac{2E_{SEI} I_{SEI}}{(1 + \nu_{SEI})} \left( \frac{R - w}{R} \right)^2 \left( R - \frac{R^2}{w} \right)^2 \left[ \frac{R}{R - w} \right] = \frac{-2E_a}{3(1 - \nu_a) \frac{Q}{Q_n}} \left( \frac{C_{avg}(R_a, t) - C_{avg}(R_e, 0)}{R} \right) \\
+ \frac{E_a I_{se}}{(1 - \nu_a)} \left[ A7 \right]
\]

Since, the SEI is very thin we neglect higher powers of \( w \).
\[
\frac{2E_{SEI} I_{SEI}}{(1 + \nu_{SEI})} \left( \frac{R - w}{R} \right)^2 \left( R - \frac{R^2}{w} \right)^2 \left[ \frac{R}{R - w} \right] = \frac{-2E_a}{3(1 - \nu_a) \frac{Q}{Q_n}} \left( \frac{C_{avg}(R_a, t) - C_{avg}(R_e, 0)}{R} \right) \\
+ \frac{E_a I_{se}}{(1 - \nu_a)} \left[ A8 \right]
\]

\( I_{se} = -2 \frac{E_{SEI} (1 - \nu_a)}{E_a (1 + \nu_{SEI})} \frac{3w}{R} \left( R - \frac{R^2}{w} \right) \left( \frac{C_{avg}(R_a, t) - C_{avg}(R_e, 0)}{R} \right) \)

\( I_{se} = -2 \frac{E_{SEI} (1 - \nu_a)}{E_a (1 + \nu_{SEI})} \frac{3w}{R} \left( R - \frac{R^2}{w} \right) \left( \frac{C_{avg}(R_a, t) - C_{avg}(R_e, 0)}{R} \right) \left[ A9 \right]

Similarly, the radial displacement is continuous at the \( \alpha \)-phase core-SEI shell interface (Equation 5), equating equations for radial displacement \( (4a) \) for the active core and shell at the interface \( r = R_e \),
\[
u_r \mid_{r = R_e} = \nu_r \mid_{r = 0} \tag{5}
\]

\[
\left( \frac{1 + \nu_a}{1 - \nu_a} \right) \frac{Q}{Q_n} \left( \frac{R_e}{3R_e^2} \right) \int_0^{R_e} \left( C(r, t) - C(0, 0) \right) r^2 dr + R_a I_{se} = R_e I_{SEI} + \frac{I_{SEI}}{R_e} \left[ A10 \right]
\]

Putting Equation A3 in A10
\[
\left( \frac{1 + \nu_a}{1 - \nu_a} \right) \frac{Q}{Q_n} \left( \frac{R_e}{3R_e^2} \right) \int_0^{R_e} \left( C(r, t) - C(0, 0) \right) r^2 dr + R_a I_{se} = R_e \left( \frac{2(1 - 2\nu_{SEI)} I_{SEI}}{(1 + \nu_{SEI}) \frac{R}{R^2}} \right) \left[ A11 \right]
\]

Dividing both sides of Equation A11 by \( R_e \)
\[
\left( \frac{1 + \nu_a}{1 - \nu_a} \right) \frac{Q}{Q_n} \left( \frac{R_e}{3R_e^2} \right) \int_0^{R_e} \left( C(r, t) - C(0, 0) \right) r^2 dr + \frac{I_{SEI}}{R_e} \left[ A12 \right]
\]

Rearranging (A12) to obtain \( I_{se} \) in terms of \( I_{SEI} \)
\[
I_{se} = -\left( \frac{1 + \nu_a}{1 - \nu_a} \right) \frac{Q}{Q_n} \left( \frac{C_{avg}(R_e, t) - C_{avg}(R_e, 0)}{R_e} \right) \\
+ 2(1 - 2\nu_{SEI}) I_{SEI} \left( \frac{R_e}{R^2} \right) \left[ A13 \right]
\]

Combining (A9) and (A13), we obtain an expression for \( I_{SEI} \)
\[
-2 \frac{E_{SEI} (1 - \nu_a)}{E_a (1 + \nu_{SEI})} \frac{3w}{R} \left( R - \frac{R^2}{w} \right) \\
\frac{2\Omega_a}{9(1 - \nu_a)} \left( C_{avg}(R_e, t) - C_{avg}(R_e, 0) \right) \\
= -\left( \frac{1 + \nu_a}{1 - \nu_a} \right) \frac{Q}{Q_n} \left( \frac{C_{avg}(R_e, t) - C_{avg}(R_e, 0)}{R_e} \right) + \left( \frac{2(1 - 2\nu_{SEI}) I_{SEI}}{(1 + \nu_{SEI}) \frac{R}{R^2}} \right) \left[ A14 \right]
\]

Rearranging terms from Equation A14,
\[
I_{SEI} = R_e \left( \frac{2\Omega_a}{9(1 - \nu_a)} \left( C_{avg}(R_e, t) - C_{avg}(R_e, 0) \right) \right. \\
\left( \frac{1 + \nu_a}{1 - \nu_a} \right) \frac{Q}{Q_n} \left( \frac{C_{avg}(R_e, t) - C_{avg}(R_e, 0)}{R_e} \right) \left[ A15 \right]
\]

Combining Equation A15 with A3, we get an expression for \( I_{SEI} \)
\[
I_{SEI} = \frac{2(1 - 2\nu_{SEI}) I_{SEI}}{(1 + \nu_{SEI}) \frac{R}{R^2}} \\
I_{SEI} = \frac{2(1 - 2\nu_{SEI}) I_{SEI}}{(1 + \nu_{SEI}) \frac{R}{R^2}} \left( \frac{2\Omega_a}{9(1 - \nu_a)} \left( C_{avg}(R_e, t) - C_{avg}(R_e, 0) \right) \right. \\
\left( \frac{1 + \nu_a}{1 - \nu_a} \right) \frac{Q}{Q_n} \left( \frac{C_{avg}(R_e, t) - C_{avg}(R_e, 0)}{R_e} \right) \left[ A16 \right]
\]

Combining Equation A16 with A9 and rearranging, we get an expression for \( I_{se} \)
\[
I_{se} = \frac{2E_{SEI} (1 - \nu_a)}{E_a (1 + \nu_{SEI})} \frac{3w}{R} \left( \frac{2\Omega_a}{9(1 - \nu_a)} \left( C_{avg}(R_e, t) - C_{avg}(R_e, 0) \right) \right. \\
\left( \frac{1 + \nu_a}{1 - \nu_a} \right) \frac{Q}{Q_n} \left( \frac{C_{avg}(R_e, t) - C_{avg}(R_e, 0)}{R_e} \right) \left[ A17 \right]
\]
diffusion coefficient of the solute in a phase (m^2 sec^{-1})

\( d \) distance between the cracked SEI surfaces (m)

\( E_i \) Young’s modulus of phase ‘i’ (Nm^{-2})

\( e(r) \) local strain energy density (Jm^{-3})

\( F \) Faraday constant C mol^{-1}

\( I \) current density on the electrode particle (Am^{-2})

\( L_{crack} \) length of crack on SEI (m)

\( p \) proportionality constant

\( Q_n \) cell capacity retained after n cycles (Ah)

\( Q_{0} \) initial cell capacity (Ah)

\( Q_{loss} \) cell capacity loss (Ah)

\( Q_{loss_n} \) cell capacity lost during n\(^{th}\) cycle (Ah)

\( Q_{total} \) theoretical capacity of the graphite electrode in the cell (Ah)

\( V_{max} \) discharge voltage limit used during cycling (V)

\( V_{min} \) charge voltage limit used during cycling (V)

\( w \) thickness of SEI (m)

\( x \) dimensionless radius

\( x_a \) dimensionless radial location of interface

\( \gamma \) surface energy of SEI material (Jm^{-2})

\( \gamma_s \) radial strain

\( \eta \) cell cyclic efficiency

\( \eta_i \) Poisson’s ratio of phase ‘i’

\( \xi_i \) dimensionless stress in i direction for a particle with SEI

\( \xi_{i'} \) dimensionless stresses in i direction for a particle with no SEI constraint

\( \Pi_{total} \) normalized total strain energy for a particle with SEI layer

\( \Pi_{cracked,SEI} \) normalized strain energy of the electrode particle after SEI fracture

\( \Pi_{excess} \) normalized strain energy released after SEI fracture

\( \sigma_{0s} \) radial stress (Nm^{-2})

\( \sigma_{0s'} \) tangential stress in the i phase (Nm^{-2})

\( \sigma_{t} \) fracture strength of a material (Nm^{-2})

\( \tau \) dimensionless time

\( \Omega_d \) partial molar volume of the solute in the α phase (m^3mol^{-1})

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