The influence of surface inhomogeneity on the overcharge and lithium plating of graphite electrodes

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Abstract
We seek to clarify phenomena involved in the overcharge of a graphite electrode in a lithium ion battery, including lithium (Li) plating. In Baker and Verbrugge (2019 J. Electrochem. Soc.), we developed a set of equations that can be used to treat Li plating and subsequent electro-dissolution, and we analyzed how the equation system behaved for a particle of graphite, a fundamental unit of the negative (porous) electrode in lithium ion cells. In this work, we employ the same governing equations, but we render them in a two-dimensional setting to examine the graphite-electrolyte interface, allowing us to clarify phenomena involved in Li plating over graphitic electrode elements in the absence of complicating factors associated with the architecture of a porous electrode. For a variety of reasons described in the Introduction of this work, the surface of graphite is nonuniform in terms of reaction rates for Li insertion and plating, and we show that when the electrode is subjected to constant-current charging, as is commonly employed, such nonuniformities lead to early Li plating over the highly reactive surfaces. These observations underscore the importance of maintaining a uniform electrode surface, especially when the cell is to be subjected to high rates of charge.

Introduction
As lithium ion batteries become more prevalent, particularly in automotive electric-traction applications, clarification of phenomena that limit the charge rate of such batteries, including lithium (Li) plating over the graphite negative electrode [1–6], is becoming ever more important. The recent paper by researchers at Argonne National Laboratory (ANL) [7] provides a helpful summary of lithium-plating investigations. Of note, the ANL authors found that Li plating did not cause measurable discharge capacity loss for currents up to 6C for the conditions studied (see their discussion associated with figure 5 of [7]), despite the fact that their reference electrode measurement confirmed Li plating at the graphite electrode. Recent analyses [7–12] of lithium plating underscore its technological relevance. In [13], the authors developed a set of equations that can be used to treat Li plating and subsequent electro-dissolution in the context of a porous electrode, and simulations were provided for a single-particle model, which ignores all impedances associated with the electrolyte phase and considers each particle in the porous electrode to be identically spherical and isolated. In this work, we employ the same governing equations, but we render them in a two-dimensional (2D) setting to examine the graphite-electrolyte interface, allowing us to clarify phenomena involved in lithium plating over graphitic electrode element in the absence of complicating factors associated with a porous electrode architecture.

Schematics of the problem statement we pursue are shown in figure 1. As shown in figure 1(a), a solid strip of graphite of width \( a \) and thickness \( L_G \) contacts the electrolyte at \( z = 0 \) and the current collector is at \( z = -L_G \). Insulating boundary condition apply at \( y = 0 \) and \( a \). A Li counter and reference electrode is located at \( z = L \). All interfacial reactions take place at the interface between the solid-electrolyte interphase (SEI) and graphite, as indicated in figure 1(c). Impedance associated with the SEI is assumed negligible in this work.

If the interface at \( z = 0 \) is uniform in properties, then the problem is one-dimensional (1D), and there are no variations in \( y \). However, it is well known that the surface of graphitic materials used in the negative electrode of...
lithium ion batteries is nonuniform, with edge planes that are more reactive and basal planes that are far less reactive \([14–18]\). In addition, the use of ceramic materials over the graphite electrode, as employed in ceramic-enhanced separators \([19]\), leads to blockage of reactions over portions of the electrode. Insulating contaminants can also occlude portions of the graphite surface \([3, 5]\). It is thus important to understand how a nonuniform interface along the graphite surface, including substantially open as well as occluded regions, influences Li plating and overcharge of a graphite electrode. The system geometry associated with figure 1(a) may be viewed as a simple and reasonable model architecture to investigate salient features of the lithiation of graphite, including Li plating on overcharge.

What follows are sections entitled Model Formulation and Discussion of Results, after which is the Summary and Conclusions.

### Model formulation

We model the lithiation of graphite, corresponding to the charging of the graphite electrode in commonly employed lithium ion batteries in accordance with the schematic shown in figure 1(a).

### Thermodynamics and interfacial kinetics

For intercalation of graphite by lithium, the elementary insertion reactions at the particle surface for each gallery \(j\) are represented by

\[
\text{Li}^+_{\text{liquid}} + e_{\text{solid}}^- + H_{j,\text{solid}} \rightleftharpoons (\text{Li}_j - H_j)_{\text{solid}}. \tag{1}
\]

The thermodynamics of lithiated graphite are modeled using the multi-site, multi-reaction (MSMR) model as described in \([20–23]\). A practical aspect of the MSMR model is that, with few parameters that can be associated with the physical chemistry of the intercalation material, a quantitative fit of the open-circuit potential results, and this is key for the overall analysis. We refer the reader to \([21]\) for a complete discussion on the application of the MSMR model to graphite.
\[ U_1 = U_j^0 + \frac{1}{f} \ln \frac{a_{H,j}}{a_j} = U_j^0 + \frac{\omega_j}{f} \ln \frac{X_j - x_j}{x_j}, \quad f = \frac{F}{RT}, \]
\[ x_j = \frac{X_j}{1 + E_j}, \quad x(U_i) = \sum_j x_j, \quad \text{and} \]
\[ \frac{dx}{dU_i} = \sum_j \frac{dx_j}{dU_i} = \sum_j \frac{f}{\omega_j (1 + E_j)^2}, \quad \text{where} \quad E_j = e^{f(U_i-U_j^0)/\omega_j}, \quad (2) \]

where \( x \) is the total fraction of the filled sites in lithiated graphite and \( U_j \) refers to insertion-electrode equilibrium potential. The index \( j \) spans from 1 to \( J \), where \( f = 7 \) in this work for lithiated graphite (see table 2). From the first line of equation (2), we can represent the activities in the insertion electrode as
\[ a_j = x_j^{\omega_j} \quad \text{and} \quad a_{H,j} = (X_j - x_j)^{\omega_j}. \quad (3) \]

We found in computational simulations that there are times towards the end of lithiation of the graphite that \( x_j \rightarrow X_j \), \( X_j - x_j \) is small, and for some of the galleries, \( \omega_j \) is also small, giving rise to a small number being raised to a small power, leading to numerical problems; these problems can be removed by rearranging the expression for \( U_1 \) in equation (1) to yield:
\[ a_{H,j} = a_j e^{f(U_i-U_j^0)} = x_j^{\omega_j} e^{f(U_i-U_j^0)} \quad (4) \]
in place of the expression for \( a_{H,j} \) given in equation (3). While we did not have difficulties with \( a_j = x_j^{\omega_j} \) for small values of \( x_j \), one could employ a similar procedure to evaluate \( a_j \) when \( x_j \) is small.

For the MSMR approach, the electrochemical reactions for the lithiated-graphite can be expressed as was recently done for modeling the different reactions in spinel lithium manganese oxide \([23]\)

\[ \dot{i}_{ij} = i_{ij} \ell(y) [e^{f(U_i-U_j^0)} - e^{-f(U_i-U_j^0)}], \quad j = \sum_j i_{ij}, \]
\[ \eta_{i,j} = V - U_i - \Phi, \quad \text{and} \quad \dot{i}_{0,i} = \dot{i}_{0,i}^{\text{ref}} a_j^{-1/\beta} a_{H,j}^{-1/\beta} \left( \frac{c}{c_0} \right)^{1-\beta} \quad (5) \]
The function \( \ell(y) \) is used to examine the influence of resistance variations over the particle surface on the plating of lithium. For uniform resistance over the surface, \( \ell(y) = 1 \), the current distribution over the graphite surface is uniform, and the problem is 1D, with no variations in \( y \). The physical significance of the function \( \ell(y) \) is that it allows one to investigate surface inhomogeneities. When \( \ell(y) \) varies with \( y \), the problem is 2D. In this work, we examine the influence of a passivated surface adjacent to an active surface.

We now consider the lithium deposition reaction
\[ \text{Li}_i^{\text{solid}} + \frac{k_{e,\text{Li}}^{\text{solid}}}{k_{0,\text{Li}}} = \text{Li}_i^{\text{solid}} \quad (6) \]

As recently suggested in \([13]\), we express the open-circuit potential \( U_2 \) associated with deposited Li as
\[ U_2 = U_{Li}^0 - \frac{1}{f} \ln a_{Li} = -\frac{1}{f} \ln a_{Li}, \quad (7) \]

That is, we employ the convention that \( U_{Li}^0 = 0 \). For the activity of lithium \( a_{Li} \), we seek a function with the following attributes: (i) for \( \Gamma \ll 1, a_{Li} \rightarrow \Gamma \), where \( \Gamma \) is the surface concentration of lithium, (ii) for \( \Gamma \gg 1, a_{Li} \rightarrow 1 \), (iii) only one unknown parameter is needed that has physical significance \( (T)_{\text{ref}}, \) as will be described below, and (iv) the relation characterizing the \( a_{Li} \) versus \( \Gamma \) is monotonic and \( (v) \) continuously differentiable. A simple function with these attributes is
\[ a_{Li} = 1 - e^{-\Gamma/\Gamma_{\text{ref}}}, \quad (8) \]

where the lone parameter is \( \Gamma_{\text{ref}} \), a reference surface concentration (e.g. with units of mol cm\(^{-2}\)) that can be associated with the number of monolayers of Li needed to achieve bulk Li activity; i.e. after \( \Gamma \) exceeds \( \Gamma_{\text{ref}} \) the activity of the Li deposit asymptotes exponentially to that of bulk Li. More discussion and references underpinning the use of equation (8) can be found in \([13]\). Equation (8) is consistent with underpotential deposition of metals \([24-26]\), including Li on carbon \([15,27]\) and various other substrates \([28]\). Equations (7) and (8) allow us to write

\[ \text{See https://en.wikipedia.org/wiki/Zero_to_the_power_of_zero.} \]
At equilibrium, $U_1 = U_2$, and the total charge of Li $Q$ (e.g. with units of C cm$^{-1}$) is given by

$$Q(U) = Fc_T aL_G x(U) + Fa' (U)$$

or, in dimensionless form

$$\bar{Q} = \frac{Q}{Fc_T aL_G} = x + \frac{\Gamma}{c_T L_G} = \left(\sum_{j=1}^{N_j} \frac{X_j}{1 + E_j}\right) - \frac{\Gamma_{ref}}{c_T L_G} \ln (1 - e^{-\beta_j}),$$

where, as noted in equation (2), $E_j = e^{(U_j - U_{ref,j})/\omega}$. For differential voltage spectroscopy, the following relation is helpful:

$$d\bar{Q} \frac{dU}{dU} = \left(\sum_{j=1}^{N_j} \frac{X_j E_j}{(1 + E_j)^2}\right) - \frac{\Gamma_{ref}}{c_T L_G} \left(\frac{fe^{-\beta_j}}{1 - e^{-\beta_j}}\right).$$

The kinetics of equation (6) are modeled as an elementary charge-transfer reaction [29]

$$j_2 = i_{0, Li} \frac{e^{(U_j - U_{ref,j})/\omega}}{1 + e^{(U_j - U_{ref,j})/\omega}} - e^{-\beta_j, j} a_{Li, j}, \quad i_{0, Li} = i_{0, Li} a_{Li, j}, \text{ and } \eta_{h, j} = V - U_j - \Phi.$$  

The total current density normal to the electrode surface $j_T$ is given by

$$j_T = j_1 + j_2.$$  

At the interface between the lithiated graphite and the Li deposit, we postulate

$$k_j \text{Li}_{solid} + H_{j, solid} \rightarrow (\text{Li} - H_j)_{solid}$$

consistent with an elementary reaction when a Li deposit (Li$_{solid}$) is on top of the lithiated graphite (see figure 1(c)). The corresponding rate expression is taken to be

$$r_j = \frac{e^{(y_j)} (k_j a_{Li, j} - k_{h, j})}. $$

The exchange reaction cannot take place when the Li deposit is separated from the graphite by an insulating layer, corresponding to $e^{(y_j)} = 0$. At equilibrium, $r_j = 0$, $U_1 = U_2$, and

$$a_{Li} a_{Li, j} = k_{h, j} = e^{-\beta_j, e^{(y_j)}(U_j - U_{ref,j})} = e^{(U_j - U_{ref,j})} = e^{-\beta_j, j}$$

which, when combined with equation (16), yields

$$r_j = \frac{e^{(y_j)} (k_j a_{Li, j} - e^{-\beta_j, j} a_j)}{r_T} = \sum_j r_p$$

where $r_T$ is the total exchange rate between deposited Li and vacant sites in the graphite.

In this work, we examine currents below the 1C rate, and we ignore degradation of the plated Li, consistent with findings in [7], as noted in the Introduction.

**Transport phenomena and material balances**

We employ well-known equations to describe transport by diffusion and migration in the electrolyte phase based on irreversible thermodynamics (see [23] and references therein):

$$\nabla \cdot i = \nabla \cdot \left[-\kappa(c) \nabla \Phi + \vartheta(c) \nabla c\right] = 0, \text{ where } \vartheta(c) = \frac{2RT \kappa}{F} \left(1 + \frac{d \ln f_c}{d \ln c}\right) (1 - \epsilon^0),$$

$$\frac{\partial c}{\partial t} = \nabla \cdot \left[D \nabla c + (1 - \epsilon^0) \frac{1}{F}\right] = \nabla \cdot (D \nabla c).$$

The material balance on the salt concentration $c$ reflects our assumption of a constant transference number $\epsilon^0$.

For equimolar counter diffusion of lithium in the host graphite, the total concentration of sites within the graphite $c_\gamma$ is constant, and the flux of lithium-filled sites is given by

$$N = c_\gamma f D_c x (1 - x) \frac{dU}{dx} \nabla x.$$

We shall assume the diffusion coefficient $D_c$ is a constant, reflecting the Li diffusion coefficient value at infinite dilution ($x \rightarrow 0$). A material balance yields

$$\nabla \cdot \left[\nabla \cdot \left(-\kappa(c) \nabla \Phi + \vartheta(c) \nabla c\right)\right] = 0.$$
\[
\begin{align*}
\frac{\partial c}{\partial t} &= -\nabla \cdot \mathbf{N} \quad \text{or} \quad \frac{\partial c}{\partial t} = -D \nabla \cdot \left[ x(1-x) \frac{dU_x}{dx} \nabla x \right].
\end{align*}
\]

A material balance on lithium at the interface \( z = 0 \) yields
\[
-c_T x(1-x) \frac{dU_x}{dx} \frac{\partial x}{\partial z} = -\frac{\dot{j}_x}{F} + r_T.
\]

For all times, the boundary condition for the potential over the graphite surface is given by
\[
-\kappa(c) \frac{\partial \Phi}{\partial z} + \vartheta(c) \frac{\partial c}{\partial z} = j_T.
\]

The average current density over the graphite surface is given by:
\[
i_{\text{avg}} = \frac{1}{a} \int_{y=0}^{y=a} j_T dy
\]
which constitutes a boundary condition for current-controlled operation, for which \( i_{\text{avg}} \) is specified and \( V \) must be chosen (calculated) so that the average current density matches the specified (input) value. For potential control, \( V(t) \) would need to be specified instead of equation (24), and equation (24) would be used to determine the average current density.

The net charge of Li in the graphite host per unit length in the dimension perpendicular to \( y \) and \( z \) (e.g. C cm\(^{-1}\)) can be obtained from
\[
Q_L(t) = Fc_T \alpha_L \left[ \frac{1}{L_G} \int_{z=-L_G}^{z=0} \left( \frac{1}{a} \int_{y=0}^{y=a} x(t, y, z) dy \right) dz \right]
= Fc_T \alpha_L \chi_{\text{avg}}(t),
\]
where \( \chi_{\text{avg}} \) is the average fraction of Li-filled sites in the host graphite. Similarly, the net charge of Li deposited corresponds to
\[
Q_L(t) = Fa \left[ \frac{1}{a} \int_{y=0}^{y=a} \Gamma(t, y) dy \right] = Fa \Gamma_{\text{avg}}(t),
\]
where \( \Gamma_{\text{avg}} \) is the average surface concentration of deposited Li. The total charge of Li is given by
\[
Q(t) = Q_L(t) + Q_z(t)
= Fa(c_T L_G \chi_0 + \Gamma_0) + \int_{t=0}^{t} \int_{y=0}^{y=a} (\dot{j}_x + j_z) dy dt.
\]

For the initial conditions in this work (equilibration of the system at 1 V versus a Li reference electrode), both the initial concentrations \( \chi_0 \) and \( \Gamma_0 \) are so small they can be ignored, but we retain the terms for completeness. A useful check on the efficacy of the numerical solution is to verify that the second line of equation (27) is satisfied.

### Remaining boundary conditions

We apply insulating boundaries at the left and right of the domain
\[
\begin{align*}
\frac{\partial \Phi}{\partial y} &= 0 \\
\frac{\partial c}{\partial y} &= 0 \\
\frac{\partial x}{\partial y} &= 0
\end{align*}
\quad y = 0 \text{ and } y = a
\]
and lithium cannot pass into the current collector for the graphite:
\[
\frac{\partial x}{\partial z} = 0 \quad \text{for } z = -L_G.
\]

At the Li counter electrode and at the graphite/current-collector interface, the salt flux is zero
\[
D \frac{\partial c}{\partial z} + \frac{(1 - \epsilon^f)}{F} \left[ -\kappa(c) \frac{\partial \Phi}{\partial z} + \vartheta(c) \frac{\partial c}{\partial z} \right] = 0 \quad \text{for } z = 0 \quad \text{for } z = L
\]
and the potential is grounded at the lithium counter electrode:
\[
\Phi = 0 \quad \text{for } z = L.
\]
Last, a material balance on deposited Li at the electrode surface is given by:

\[
\frac{\partial \Gamma}{\partial t} = -\frac{i}{F} - r_T.
\]  

(32)

**Dependent variable transformation for \(x(U_1)\)**

For numerical calculations, it is convenient to replace \(x\) with \(U_1\) as the dependent variable. Specifically, \(x\) and \(dx/dU_1\) in terms of \(U_1\) are provided in equation (2) above. The material balance on \(x\), equation (21), becomes

\[
\frac{dx}{dU_1} \frac{\partial U_1}{\partial t} = -fD_x \left[ x(1 - x) \nabla^2 U_1 + (1 - 2x) \frac{dx}{dU_1} \nabla U_1 : \nabla U_1 \right]
\]  

(33)

and equation (22) can be written as

\[
N_z = c_T fD_x(1 - x) \frac{\partial U_1}{\partial z} = \frac{i}{F} - r_T.
\]  

(34)

The initial conditions correspond to the initial value of \(U_1\). At the left and right of the volume element

\[
\frac{\partial x}{\partial y} = \frac{dx}{dU_1} \frac{\partial U_1}{\partial y} = 0 \text{ or } \frac{\partial U_1}{\partial y} = 0 \text{ for } y = 0 \text{ and } y = a
\]

and, because lithium cannot pass into the current collector for the graphite electrode,

\[
\frac{\partial U_1}{\partial z} = 0 \text{ for } z = -L_G.
\]

**Nondimensionalization and scaling**

We first introduce the following definitions:

\[
\gamma = \frac{y}{a}, \quad \zeta = \frac{z}{L}, \quad \zeta = -\frac{z}{L_G}, \quad \nabla = \left( \frac{L}{a} \right) \frac{\partial}{\partial \zeta} + \frac{\partial}{\partial \zeta}, \quad \tau = \frac{Dt}{L_G^2},
\]

\[
r_T = \frac{r_T}{k_i}, \quad \bar{Q} = \frac{Q}{F e_G a L_G}, \quad \bar{\Gamma} = \frac{\Gamma}{L_G \epsilon_T}, \quad \Gamma_{\text{ref}} = \frac{\Gamma_{\text{ref}}}{L_G \epsilon_T}, \quad \Theta = \Gamma_{\text{ref}},
\]

\[
\bar{\epsilon} = \frac{\epsilon}{\epsilon_0}, \quad \bar{\tau} = \frac{\tau}{L_G a}, \quad \bar{R}_e = \frac{R_e}{L_G \kappa}, \quad \bar{R}_{\text{diff}} = \frac{R_{\text{diff}}}{L_G \kappa}, \quad \bar{R}_d = \frac{R_d}{L_G \beta C_T}, \quad \bar{R}_k = \frac{1}{k_i},
\]

\[
\bar{R}_{1-2} = \frac{1}{\beta F_k}, \quad \bar{R}_e = \frac{R_{e,\text{ref}} L_G}{\kappa}, \quad \bar{R}_d = \frac{i_{e,\text{ref}} L_G}{\beta C_T}, \quad \bar{R}_{1-2} = \frac{k_i L_G}{\beta C_T - \epsilon_T}.
\]  

(35)

In addition, an overbar over a potential corresponds to \(f\) multiplied onto the potential, and an overbar over a current density corresponds to the current density divided by \(i_{e,\text{ref}}^{-1}\). Figure 1(b) shows the coordinates for the dimensionless formulation.

The thermodynamic relations and reaction-rate expressions can now be stated as

\[
\mathcal{U}_1 = \mathcal{U}_1^0 + \omega_j \ln \left( \frac{x_j - x_j}{x_j} \right), \quad x_j = \frac{x_j}{1 + \exp \left( (\mathcal{U}_1 - \mathcal{U}_1^0) / \omega_j \right)},
\]

\[
x(\mathcal{U}_1) = \sum_j x_j, \quad \frac{dx}{d\mathcal{U}_1} = -\sum_j \frac{1}{\omega_j} \frac{x_j \exp \left( (\mathcal{U}_1 - \mathcal{U}_1^0) / \omega_j \right)}{1 + \exp \left( (\mathcal{U}_1 - \mathcal{U}_1^0) / \omega_j \right)},
\]

\[
\mathcal{U}_2 = -\ln (1 - e^{-\Theta}) \text{ or } \Theta = \frac{\Gamma}{\Gamma_{\text{ref}}} = -\ln (1 - e^{-\bar{\tau}}).
\]  

(36)

(37)

Note that as \(\mathcal{U}_2 \to 0, \quad \Theta = -\ln \mathcal{U}_2 \to +\infty\). The remaining thermodynamic and kinetic equations become

\[
\bar{Q} = x_{\text{avg}} + \Gamma_{\text{avg}} = \left\{ \begin{array}{ll}
\gamma_0 + \Gamma_0 + \frac{R_d}{R_k} \tau & \text{(general)} \\
\sum_j \frac{X_j}{1 + \exp(\mathcal{U}_1 - \mathcal{U}_1^0) / \omega_j} - \Gamma_{\text{ref}} \ln (1 - e^{-\bar{\tau}}) & \text{when } V = U = U_1 = U_2
\end{array} \right.
\]

(38)

\[
i_{\text{avg}} = i_{\text{avg}}(x_j(\mathcal{U}_1)) \epsilon(\gamma) [e^{1 - \beta} \bar{\eta}_{\text{ref}} - e^{-\beta} \bar{\eta}_{\text{ref}}], \quad \bar{y} = \sum_j \bar{y}_j, \quad \text{and } \bar{\eta}_{\text{ref}} = \nabla - \mathcal{U}_1 - \bar{\Phi}.
\]  

(39)
Table 1. Parameters and properties. For the simulations, \( k_1 = k_0 \) and \( k_2 \) is varied in the simulations (see \( R_d / R_{k2} \) in table 3).

| Quantity | Value | Comments |
|----------|-------|----------|
| \( a \) | 0.001 cm | Common graphite particle radius of 10 \( \mu \)m |
| \( c_0 \) | 0.001 mol cm\(^{-3}\) | Initial salt concentration |
| \( d \) | 0.0304 cm | Common separator thickness of 15 \( \mu \)m |
| \( D_{\text{eq}} \) | \( 2.58 \times 10^{-5} \text{ cm}^2 \text{s}^{-1} \) | [22, 23] |
| \( D_0 \) | \( 2 \times 10^{-10} \text{ cm}^2 \text{s}^{-1} \) | [30] |
| \( f = F/(RT) \) | 38.94 V\(^{-1}\) | \( T = 298 \text{ K} \) |
| \( F \) | 96 487 C mol\(^{-1}\) | |
| \( L \) | 0.0015 cm | Common graphite particle radius of 10 \( \mu \)m |
| \( L_G \) | 0.001 cm | Common graphite particle radius of 10 \( \mu \)m |
| \( i_{\text{seg}} \) | 0.816 \( \times 10^{-3} \text{ A cm}^{-2} \) | 1C current density |
| \( i_{\text{ref}, j} \) | 0.1 \( \times 10^{-3} \text{ A cm}^{-2} \) | for all \( j = 2-7 \) [29] |
| \( i_{\gamma, j} \) | 0.01 \( \times 10^{-3} \text{ A cm}^{-2} \) | [30] |
| \( U_{\text{b}0} \) | 1 V | Initial equilibrium potential, and \( U_1 = U_2 = U_{\text{b}0} \). See equations (2) and (9) to determine \( x_0 \) and \( \Gamma_{\text{b}} \), respectively. |
| \( \beta_j, \beta_{\gamma} \) | 0.5 | Assumes the same symmetry factor for all reactions [29, 30] |
| \( \Gamma_{\text{ref}} \) | \( 3.04 \times 10^{-8} \text{ mol/cm}^2 \) | 0.1% of the graphite capacity |
| \( \kappa \) | 0.01 S cm\(^{-1}\) | Representative value |

\[ \overline{j}_2 = \overline{i}_{0, \gamma} \epsilon(\gamma)[a^{1-\beta_2} e^{-\beta_2} f_{0, \gamma} - e^{-\beta_2} f_{0, \gamma}], \quad \overline{i}_{0, \gamma} = \overline{i}_{0, \gamma} a_{\gamma, i}, \quad \text{and} \quad \overline{f}_{0, \gamma} = \overline{U}_2 - \overline{\Phi}, \]  \( \overline{I}_2 = \overline{I}_2 \). \[ \overline{r}_T = \overline{\epsilon}(\gamma) \sum_j \frac{k_j}{k_i} (a_{\gamma, i} a_{\gamma, j} - e^{-\beta_j} a_j). \]  \( j_2 = \overline{j}_0, \gamma \epsilon(\gamma)[a^{1-\beta_2} e^{-\beta_2} f_{0, \gamma} - e^{-\beta_2} f_{0, \gamma}], \overline{j}_0, \gamma = \overline{j}_{0, \gamma} a_{\gamma, i}, \text{and} \overline{f}_{0, \gamma} = \overline{U}_2 - \overline{\Phi}, \]

The dimensionless fields equations for \( \overline{\Phi} \) and \( \overline{\tau} \) correspond to

\[ \overline{\nabla} \cdot [-\kappa \overline{\nabla} \overline{\Phi} + \overline{\nabla} \ln \overline{\tau}] = 0, \]

\[ \frac{\partial \overline{\tau}}{\partial \overline{\tau}} = \overline{\nabla} \cdot (\overline{D} \overline{\nabla} \overline{\tau}), \]  \( \xi = 0.015 \text{ cm}^{-1} \) (40)

For the values provided in table 1, \( \xi = 1.74 \times 10^{-5} \ll 1 \), as noted in table 3. This allows one to approximate equation (44) with \( \xi = 0 \), in which case, the equation represents a quasi-steady state condition. Since the salt flux vanishes on all boundaries of the electrolyte area, we can conclude that the salt flux is itself zero with this simplification. This, in turn, implies that \( \overline{\nabla} \overline{\tau} = 0 \) and \( \overline{\tau} = 1 \), a constant, and one can replace equation (43) with

\[ \left( \frac{L}{a} \right)^2 \frac{\partial \overline{\Phi}}{\partial \overline{\tau}^2} + \frac{\partial \overline{\Phi}}{\partial \overline{\tau}} = 0 \quad \text{for} \quad 0 < \overline{\tau} < 1. \]  \( \kappa = 0.015 \text{ cm}^{-1} \) (41)

For the system geometry (see figure 1(b)), we can express equation (33) as

\[ \frac{dx}{dU_k} \frac{\partial U_k}{\partial \overline{\tau}} = -x(1 - x) \left[ \left( \frac{L_k}{a} \right)^2 \frac{\partial^2 U_k}{\partial \overline{\tau}^2} + \frac{\partial U_k}{\partial \overline{\tau}} \right] - (1 - 2x) \frac{dx}{dU_1} \left[ \left( \frac{L_k}{a} \right)^2 \left( \frac{\partial U_k}{\partial \overline{\tau}} \right)^2 + \left( \frac{\partial U_k}{\partial \overline{\tau}} \right)^2 \right] \quad \text{for} \quad 0 < \overline{\tau} < 1 \]  \( \kappa = 0.015 \text{ cm}^{-1} \) (42)

and at \( \overline{\tau} = 0 \),

\[ U_1(0, \overline{\tau}, \overline{\tau}) = U_2(0, \overline{\tau}) = U_{b0} |_{\overline{\tau}=0}. \]  \( \kappa = 0.015 \text{ cm}^{-1} \) (43)

At the electrode–electrolyte interface, \( \overline{\tau} = \overline{\tau} = 0 \), and we have three equations for the three dependent variables \( \overline{\Phi}, U_1, \) and \( U_2 \):

\[ -\frac{\partial \overline{\Phi}}{\partial \overline{\tau}} = \frac{R_d}{R_k} j_2 \quad \text{for} \quad \overline{\tau} = 0, \]  \( \kappa = 0.015 \text{ cm}^{-1} \) (44)

\[ x(1 - x) \frac{\partial U_1}{\partial \overline{\tau}} = -\frac{R_d}{R_k} j_2 + \frac{R_d}{R_{k2}} \overline{r}_T \quad \text{for} \quad \overline{\tau} = 0, \]  \( \kappa = 0.015 \text{ cm}^{-1} \) (45)
and
\[ \Gamma_{rf} \frac{d\Theta}{dU_2} \frac{\partial U_2}{\partial \tau} = -\frac{R_d \tau}{R_k} - \frac{R_d}{R_{k-2}} \tau_T \quad \text{where} \quad \frac{d\Theta}{dU_{\text{Li}}} = - \frac{e^{-\Theta}}{1 - e^{-\Theta}}, \] (50)

Equation (50) is similar to the treatment of the graphite host, equation (49), as the dependent variable \( \Theta \) has been replaced with \( U_2 \), which exhibits less variation. For small \( U_2 \), \( d\Theta / dU_2 \approx -1 / U_2 \). Hence, for very small \( U_2 \), we can replace equation (50) with \( U_2 = 0 \). Upon solution for \( U_1 \) and \( U_0 \), one can integrate the following equation to determine \( \Theta \):

\[ \Theta(\tau, \varphi) = -\frac{1}{\Gamma_{rf}} \int_{0}^{\tau} \left( \frac{R_d \tau}{R_k} (\tau, \varphi) + \frac{R_d}{R_{k-2}} \tau_T (\tau, \varphi) \right) d\varphi. \] (51)

Problems can arise in the use of equation (50) to calculate \( U_2 \) and equation (51) to calculate \( \Theta \) when \( U_2 \) is so small that equation (50) is replaced with \( U_2 = 0 \). Upon current reversal, leading to dissolution of deposited Li, one needs to evaluate equation (51) after each time step to determine when \( U_2 = 0 \) again. Then use equation (50) to solve for \( U_2 \) instead of employing \( U_2 = 0 \). This problem motivates a dependent variable transformation as first proposed in [13]:

\[ s = -\ln(e^{U_2} - 1), \quad \bar{U}_2 = \ln(1 + e^{-s}), \quad \text{and} \quad \Theta = -\ln(1 - e^{-\bar{U}_2}) = \ln(1 + e^s). \] (52)

This allows us to write

\[ \frac{d\Theta}{ds} = \frac{e^s}{1 + e^s} = \frac{1}{1 + e^{-s}}, \quad \text{and} \quad \frac{\partial \Theta}{\partial \tau} = \frac{1}{1 + e^{-s}} \frac{\partial s}{\partial \tau}. \] (53)

Equation (50) becomes

\[ \Gamma_{rf} \frac{d\Theta}{ds} \frac{\partial s}{\partial \tau} = -\frac{R_d \tau}{R_k} - \frac{R_d}{R_{k-2}} \tau_T \quad \text{or} \quad \Gamma_{rf} \frac{\partial s}{\partial \tau} = -\frac{R_d \tau}{R_k} - \frac{R_d}{R_{k-2}} \tau_T. \] (54)

Equations (52) and (54) replace equation (50).

Last, we note that in the limit of large \( k_j \) (see equation (17)), reaction (15) becomes facile. To avoid the evaluation of \( \tau_T \) in the limit of large \( k_j \), we sum equations (49) and (54) to obtain a total Li material balance along the electrode surface:

\[ \frac{\Gamma_{rf} \frac{\partial s}{\partial \tau}}{1 + e^{-s}} + x(1 - x) \frac{\partial U}{\partial \tau} = -\frac{R_d \tau}{R_k} - \frac{R_d}{R_{k-2}} \] (55)

and equation (49) can be replaced by

\[ \bar{U}_1 = \bar{U}_2(s) \text{ at } \bar{s} = 0 \text{ for } k_j \to \infty \] (56)

consistent with equilibrium prevailing between the deposited Li and Li within the graphite host.

The remaining boundary conditions can be written as

\[ \begin{align*}
\frac{\partial \bar{x}}{\partial \bar{s}} &= 0, \\
\frac{\partial \bar{U}}{\partial \bar{s}} &= 0, \\
\bar{x} &= 0 \text{ and } \bar{y} = 1, \\
\bar{\Theta} &= 0 \text{ for } \bar{s} = 1, \\
\frac{\partial x}{\partial \bar{s}} &= 0 \text{ for } \bar{s} = 1.
\end{align*} \] (57)

The dimensionless average current density is given by

\[ i_{\text{avg}} = \int_{\bar{s}=0}^{\bar{s}=1} \bar{i} \, d\bar{s}. \] (60)

For numerical calculations, it is convenient to replace the integral equation (60) with a differential equation (and a boundary condition):

\[ \frac{\partial i_{\text{avg}, \bar{\varphi}}}{\partial \bar{\varphi}} = \bar{i}_{\bar{\varphi}} \quad \text{and} \quad i_{\text{avg}, \bar{\varphi}} = 0 \text{ at } \bar{\varphi} = 0, \] (61)

where \( i_{\text{avg}, \bar{\varphi}} \) is the average current over the range 0 to \( \bar{\varphi} \). To determine potential \( \bar{\varphi} \), we first note that the potential is taken to be uniform in the current collector,
\[
\frac{\partial \mathcal{V}}{\partial \mathcal{V}} = 0
\]

and the lone boundary condition for the potential corresponds to

\[
i_{\text{avg}, \mathcal{V}} = i_{\text{avg}} \text{ for } \mathcal{V} = 1,
\]

where \(i_{\text{avg}}\) is the specified (dimensionless) average current density over the entire electrode surface, \(0 \leq \mathcal{V} \leq 1\).

Excluding the parameters in the thermodynamic models (equations (36) and (37)), the dimensionless groups impacting the problem are: \(\varepsilon, \frac{i_{\text{avg}, x}}{i_{\text{avg}, y}}, \frac{i_{\text{avg}, y}}{i_{\text{avg}, x}}, \frac{k_i}{k_{\ell}}, (j = 2-7), (\frac{L}{a})^2, (\frac{R_1}{a}) \text{ and } (\frac{R_2}{a}) \text{ for } \mathcal{V} \text{ and } \mathcal{U} \text{ at } \tau = 0\). Values used in this work can be found in table 3.

**Numerical analysis**

We employed the finite difference method to solve the equation system with a Fortran program. For all calculations presented in the work, 161 mesh points were used for the \(\mathcal{V}\) and \(\mathcal{X}\) coordinates, and 160 mesh points for the \(\mathcal{Y}\) coordinate. The mesh spacing will be discussed in the context of figures 7 and 8. A variable time-stepping routine was used for short times, involving very small time steps, which were increased with time to (and subsequently held at) \(\Delta \tau = 0.0005\), where \(\Delta \tau\) refers to the dimensionless time step. We found that smaller time steps and finer meshes did not affect the results as plotted in this work. In addition, the equations were solved using COMSOL Multiphysics (finite element software)\(^3\), specifically, the mathematics module. The COMSOL routine also used variable time stepping and variable element sizes. We found that we obtained identical results upon comparing calculations from the two routines.

**Discussion of results**

The parameters and properties for the base case are provided in table 1, and table 3 provides the relevant dimensionless groups that govern the problem for the base case. The thermodynamic parameters for the MSMR model of lithiated graphite are identical to those of [21] with the exception of the LiC\(_{12}\) to LiC\(_6\) phase transition \((j = 1)\); for this gallery, two percent of the capacity is split off to yield ideal, Nernstian behavior as the graphite completes lithiation (see \(j = 7\)), consistent with the formation of an ideal solution as \(x \rightarrow 1\) and \(x_{Li} \rightarrow 0\). The base case involves the charging of a large graphite particle at the 1 h rate (the 1C rate), which is known to be a challenge for lithium ion traction batteries today if a full charge is desired (i.e. charge to full lithiation of the graphite). Prior models [1–6] have assumed \(R_d/R_{k-2} = 0\), even though the plated Li is immediately adjacent to the graphite surface (and is covered by the SEI, as shown in figure 1(\(c\))). Hence, we chose \(R_d/R_{k-2} = 0\) for the base case, but we also examine large values of \(R_d/R_{k-2}\).

The relevant thermodynamics for the problem formulation are depicted in figure 2 (see equation (38)). The primary conclusion one can draw from this figure is that for \(\Pi_{\partial U, x, y}\) below 0.001, which corresponds to the reference surface coverage of Li being 0.1% of the area-specific graphite capacity for lithium, further reductions in \(\Pi_{\partial U, x, y}\) do not influence the results as plotted. The lower plot in figure 2 portrays the highly nonlinear behavior in \(d\mathcal{U}/d\mathcal{Q}\) and the effective diffusion coefficient \(\frac{d\mathcal{Q}}{d\mathcal{X}}\) (see equation (20)). In addition, we see that differentiation of the ocv curve \(\partial \mathcal{U}/\partial \mathcal{Q}\) versus \(\mathcal{Q}\) yields a sharp valley (a pronounced minimum) as \(i\) the graphite fills with Li and \(x \rightarrow 1\), leading to a sharp decline in the potential and \(\partial \mathcal{U}/\partial \mathcal{Q}\), followed by (ii) Li plating, causing \(U \rightarrow 0\) \(V\), a constant, and causing \(\partial \mathcal{U}/\partial \mathcal{Q}\) to transition from a large, negative value to nearly zero. These observations underscore the relevance of evaluating \(\partial \mathcal{U}/\partial \mathcal{Q}\) to approximate the onset of Li plating.

**1D results**

\(\varepsilon(\mathcal{V}) = 1\) for all \(\mathcal{V}\)

The problem is 1D when \(\varepsilon(\mathcal{V}) = 1\), and only variations in \(\mathcal{V}\) and \(\mathcal{X}\) result (see equations (39) and (40)). Results for the base case with \(\varepsilon(\mathcal{V}) = 1\) and \(R_d/R_{k-2} = 0\) are shown in figure 3. The results for \(R_d/R_{k-2} \rightarrow \infty\) look similar to those of figure 3, with the exception that the curve for \(U_1\) plots over that of \(U_2\) shown in figure 3 before plating, and, after plating, \(U_1 = U_2 = 0\) (see equation (56)). The current employed is the 1C rate, 0.816 mA cm\(^{-2}\). Charging a present-day electric vehicle in 1 h is aggressive with current graphite-electrode technology. The potentials \(U_1, U_2, V\), including \(d\mathcal{V}/d\mathcal{X}\), are associated with the left ordinate, and the concentrations \(\Gamma, \Theta, \text{ and } x\) are associated with the right ordinate. The cell potential is initially at 1 V versus Li, and declines immediately as charging (lithiation of graphite) begins. Because \(R_d/R_{k-2} = 0\), \(r_j\) and \(r_{ij} = \sum_{i} r_i\) are zero, and Li transfers between the graphite galleries and deposited Li by electrochemical reactions only (see equations (1), (5), (6), and (13)). In addition, because \(R_d/R_{k-2} = 0\), the potential associated with plated Li, \(U_2\), remains near the cell.

\(^3\) https://en.wikipedia.org/wiki/COMSOL_Multiphysics.
potential \( V \), as the current density \( j_2 \) is nearly zero (see equation (13)), as is the overpotential \( \eta_b \), leading to \( U_2 \approx V - \Phi \approx V \), as \( \Phi \) is small (due to the small value of \( R_c / R_k = 5.84 \times 10^{-4} \)).

We now focus on the corresponding concentrations \( x, \Gamma, \) and \( \Theta \). In figure 3, \( x(0) \) is the fraction of filled sites at the graphite surface \( \mathcal{F} = 0 \), which can be contrasted with \( x(1) \), the fraction of filled sites at the current collector \( \mathcal{F} = 1 \). When the graphite is nearly filled with Li at the surface, near \( \tau = 0.3 \), only about 25% of the sites are filled with Li near the current collector. To examine the behavior of the equation system over a wide range of conditions, the simulations are carried out until \( \tau = 1 \), at which time only about 60% of the sites are filled with Li near the current collector, and the average state of lithiation \( x_{\text{avg}} \) (see equation (25)) is just over 75%. At \( \tau = 1 \), \( \Gamma \) is about 0.6, which means that the amount of Li plated corresponds to 60% of the Li capacity of the graphite. To an observer, the total dimensionless charge passed would be \( Q = x_{\text{avg}} + \Gamma_{\text{avg}} \approx 0.75 + 0.6 = 1.35 \) (see equation (38)), which, if the observer were to assume that first all of the graphite fills with Li and then Li plating begins, might be interpretable as 35% overcharge, but the ratio of plated Li to intercalated Li is about 0.6/ (0.6 + 0.75), or 44% overcharge. It is clearly important to be able to determine the individual currents \( j_1 \) and \( j_2 \) to avoid overcharge, and modeling of the electrochemical system can assist in the endeavor.
The dependent variable for the field equation (46) is $U_1$, which is plotted versus $z$ for various times in the upper plot of figure 4 for the conditions of figure 3 and $R_d/R_{1-2} = 0$. The curves for times $t > 0.5$ are shifted to lower potentials but are otherwise like those for $t = 0.5$. The corresponding traces in $x$ are shown in the lower plot. There is more variation in $x$ with $z$ than there is in $U_1$ with $z$; the plateau-like patterns in figure 4 are due to the influence of the different galleries (phases) in graphite, as described in the context of figure 2.

Sensitivity to the geometric parameters $a$ and $L_G$ is shown in figure 5. Other than changes to $a$ and $L_G$, the parameters are identical to those employed for the plot of figure 3. The values for $a$ and $L_G$ were chosen by first reducing $L_G$ from 10 $\mu$m (figures 3) to 5 $\mu$m (figure 5) and then increasing $a$ so as to keep the graphite capacity the same; by equation (10), we see that the graphite capacity at equilibrium is given by $F_G a L_G x U$. Because the C-rate for the current density is inversely proportional to $a$, the 1C rate is halved to 0.408 mA cm$^{-2}$. The resistance $R_d$ is halved, and the results look like those of figure 3, but with reduced impedance. As seen previously, the minimum in $dV/d\tau$ near $\tau = 2$ corresponds to the time when $U_2$ approaches 0 V. The graphite is substantially filled throughout with Li by the time $t = 4$, i.e. $x_{avg} \approx 1$, but $\Gamma$ is about 0.4, implying an overcharge of $0.4/(1 + 0.4)$ or about 30%.

2D results. $\ell (\Psi)$ varies with $\Psi$

The problem becomes 2D when $\ell (\Psi)$ varies with $\Psi$ (see equations (39), (40), and (42)). As noted in table 3, for the 2D investigations in this work $\ell (\Psi)$ is 0.9 for $0 \leq \Psi < 0.5$, the more reactive surface, and 0.1 for $0.5 \leq \Psi < 1$, indicative of a kinetically-hindered surface. Plots analogous to those in figure 3 for the 1D case are provided in figure 6 for the 2D case. Other than introducing variations in $\ell (\Psi)$, all parameters are the same for the 1D and 2D cases, including the 1C charge rate, and the potentials $U_1$, $U_2$, and $V$ (as well as $dV/d\tau$) are associated with the left ordinate, while the concentrations $\Gamma$, $\Theta$, and $x$ are associated with the right ordinate. The ordinate axes are the same for the figures, but the abscissa ranges from $0 \leq \tau \leq 1$ in figure 3 and $0 \leq \tau \leq 0.5$ in figure 6. For the 2D
plots, the two arguments associated with $x$ and $U_1$ correspond to $y$ and $z$, and the lone argument to $Q$ and $U_2$ refers to $y$, as they are evaluated along the electrode surface only. The vertical dashed lines indicate when $\text{ref } G = G$ and $\text{ref } 1Q = 1$ at $y_0 = (0.6 + 0.1)$ or about 15%. For $0 \leq \tau \leq 0.5$, the average values for $x$ and $\Gamma$ are similar for all results presented in figures 3 and 6, because the average current density is the same for all plots, corresponding to 1C. In a similar vein, the derivatives $dV/d\tau$ shown in figures 3 and 6 exhibit a minimum near $\tau = 0.3$, close to the time when $U_1$ at $\varphi = 0$ falls below 0 V versus a Li reference. The increased impedance associated with the results of figure 6, relative to those of figure 3, yields smaller magnitudes in the valleys associated with $dV/d\tau$, but the resolution is still sufficient to identify when substantial Li plating takes place.

For the 2D results of figure 6, relative to their 1D counterparts in figure 3, the cell voltages $V$ and the ocv’s at $\varphi = 0$, $U_1(0, 0)$ and $U_2(0)$, are shifted to lower values due to the increased impedance. Similarly, the concentrations at $\varphi = 0$, $x(0, 0)$ and $\Gamma(0)$, are shifted to higher values, associated with more Li intercalation and plating, and, at $\varphi = 1$, $x(1, 0)$ and $\Gamma(1)$ are shifted to lower values due to the impeding surface for...
0.5 < \varphi < 1, which substantially blocks current flow and leads to less Li intercalation and subsequent plating of Li. The Li fractions in the graphite at the far end of current collector below the impeding surface, x(1, 1) at \varphi = 1, is much less than x(1) of the 1D cases.

Profiles in the potential \( U_0(\tau, 0, \varphi) \) and the fraction of filled sites in the graphite \( x(\tau, \varphi, \varphi, 0) \), \( \varphi = 0 \) (solid lines) and 1 (dashed lines), are provided in figure 7. The conditions are identical to those associated with figure 6. Very similar profiles \( U_1(\tau, 0, \varphi) \) and \( x(\tau, \varphi, \varphi, \varphi) \) result for \( R_{1-2} = 10000 \). The mesh used in the \( \varphi \) and \( \varphi \) directions for calculations is shown by the symbols of the \( \tau = 0.5 \) trace (81 mesh points for \( 0 \leq \varphi \leq 0.15 \) and

\[ \begin{array}{lcccc}
 j & U_0^j, V & X_0^j & \omega_0^j \\
 1 & 0.08843 & 0.41336 & 0.08611 \\
 2 & 0.12799 & 0.23963 & 0.08009 \\
 3 & 0.14331 & 0.15018 & 0.72469 \\
 4 & 0.16984 & 0.05462 & 2.53277 \\
 5 & 0.21446 & 0.00644 & 0.09470 \\
 6 & 0.36325 & 0.05476 & 5.97354 \\
 7 & 0.08843 & 0.02000 & 1.00000 \\
\end{array} \]
81 mesh points for $0 < z < 1.15$. As $x$ nears 1, a boundary forms near $z = 0$, which motivates the depicted mesh allocation. For all the plots presented in this work, further refinement in the mesh (in time and in the two spatial coordinates) did not alter the results as plotted. The plot in figure 7 is analogous to the 1D results depicted in the upper plot of figure 3, as all parameters are the same except for $y$. Consistent with the comparison of the plots of figure 3 with those in figure 6, $x(\tau, 0, \bar{z})$ (respectively, $x(\tau, 1, \bar{z})$) values are larger (respectively, smaller) at a selected time in the 2D case of figure 7 as compared to those of the upper plot of figure 3. The practical ramification associated with the analysis of figure 7, as compared to that of the upper plot of figure 3, is that insulating layers or contaminants can induce Li plating in the surrounding areas [3, 5].

Table 3. Relevant dimensionless groups arising from the values provided in table 1. Other relevant values that can be deduced for those of tables 1 and 3 are $L_{D1}/D = 5000$ s $= 1$ h, $R_d = 43.7$ Ohm cm$^2$, $R_e = 0.15$ Ohm cm$^2$, $R_0 = 257$ Ohm cm$^2$, and $R_{d-1}$ (Ohm cm$^2$) is infinite (and is varied in the simulations). For calculations, $\varepsilon$ was set to zero per the discussion immediately below equation (44).

| Quantity | Value |
|----------|-------|
| $\varepsilon$ | $1.74 \times 10^{-3}$ |
| $i_{avg}/i_{ref,1}$ | 8.16 (for the 1C rate) |
| $i_{ref,j}/i_{ref,3}$ | 1 for all $j$ |
| $i_{ref,Li}/i_{ref,3}$ | 0.1 |
| $(L/a)^2$ | 2.25 |
| $(L_{Li}/a)^2$ | 1 |
| $R_d/R_{d-2}$ | 0 (varied in simulations) |
| $R_d/R_k$ | 0.17 |
| $R_0/R_k$ | $5.84 \times 10^{-4}$ |
| $U$ at $\tau = 0$ | $(1 V)' (fV^{-1}) = 38.94$ |
| $\Gamma_{ref}$ | 0.001 corresponding to 0.1% of the graphite capacity |
| $\ell'(\bar{z})$ | 1 for the one-dimensional case |
| | $0.9$ for $0 < \bar{z} < 0.5$ |
| | $0.1$ for $0.5 < \bar{z} < 1$ |

Figure 8. Fraction of Li-filled sites along the graphite surface, $x(\tau, \bar{z}, 0)$ versus $\bar{z}$ for various times $\tau$. The conditions are the same as those of figure 6. The vertical arrow to the right of the plot reflects increasing times for the curves.
Profiles in the fraction of filled sites in the graphite $x(\tau, \gamma, 0)$ along the graphite surface for various times $\tau$ are displayed in figure 8 for $R_{\text{Li}^{-2}} = 0$. Very similar profiles result for $R_{\text{Li}^{-2}} = 10000$. For the 1D analysis shown in the upper plot of figure 3, $\ell(\gamma) = 1$, $x$ is independent of $\gamma$, and $x$ along the surface corresponds to $x(0)$ in that figure; the only difference between the simulations for the upper plot of figures 3 and 8 is the influence of the variable $\ell(\gamma)$ (see table 3). Under the impeding surface along $0.5 < \gamma < 1$, the intercalation reaction is hindered (see equation (39)), and $x(\tau, \gamma, 0)$ grows with time at a slower rate. The mesh used in the $\gamma$ direction for calculations is shown by the symbols for the $\tau = 0.2$ trace (54 mesh points for each of the three regions $0 \leq \gamma \leq 0.4$, $0.4 \leq \gamma \leq 0.55$, and $0.55 \leq \gamma \leq 1$).

Profiles in the relative surface concentration of lithium $\Theta = \Gamma / \Gamma_\text{ref}$ along the graphite surface for various times $\tau$ are displayed in figure 9 for $R_{\text{Li}^{-2}} = 0$ (upper plot) and $R_{\text{Li}^{-2}} = 10000$ (lower plot). Both ordinates have logarithmic scaling, and they differ in range. When $R_{\text{Li}^{-2}} = 0$, the deposited Li is largely independent of the intercalated Li, as the two can only communicate with one another by electrochemical reactions (39) and (40). In contrast, when $R_{\text{Li}^{-2}} = 10000$, the two are nearly equilibrated (see the discussion associated with equation (55)), and the curvature in $\Theta$ near $\gamma = 0.5$ reflects the curvature in $x$ near $\gamma = 0.5$ (see figure 8).

**Summary and conclusions**

We show how the model equations developed in [13], can be applied to examine a graphitic electrode element and overcharge that leads to lithium plating. Two new features of this work and [13] involve the development of an expression for the activity of Li on graphite, equation (8), and the exchange of Li between plated and inserted Li.
reaction (15) and equation (16). The equation system involves multiple electrochemical and nonelectrochemical reactions, and significant diffusion resistance within the graphite when high charge rates are employed, as investigated in this work. Dependent variable transformations are described (equations (33), (50), and (54)) that simplify the numerical analysis. Results obtained from two different software routines were compared (and found to agree), as described in the brief ‘Numerical analysis’ subsection.

We find that if the amount of deposited Li needed to obtain the activity of bulk Li is significantly less than the capacity of the graphitic host, i.e. if $\Gamma_{\text{ref}} \ll L_{\text{G},C_7}$, where the reference surface concentration of plated lithium $\Gamma_{\text{ref}}$ (mol cm$^{-2}$) reflects the surface concentration above which the activity of deposited Li rises quickly to that of bulk Li, and $L_{\text{G},C_7}$ is the total amount of Li that can be stored in the graphitic host per unit geometric area, then the calculated results of the model equations, as plotted in this work, are close to those of $\Gamma_{\text{ref}} = 0$. To be specific, equation (8) provides the activity of plated Li, which tends to that of bulk Li for $\Gamma \gg \Gamma_{\text{ref}}$. A precise value for $\Gamma_{\text{ref}}$ is not known, but it should be on the order of a monolayer to several monolayers of Li. When $\Gamma_{\text{ref}}$ is on the order of 0.1% of the specific capacity of the graphite, the model results plotted, for example, in figure 5 are indistinguishable from those in which deposited Li immediately acquires the activity of bulk Li (i.e. $\Gamma_{\text{ref}} = 0$). Care must be exercised in supporting this observation with calculations, for the equations as presented in the work become singular when $\Gamma_{\text{ref}} = 0$.

Past modeling studies of Li plating on graphite, e.g. [1–6], have assumed that the plated Li does not react directly with graphite vacancies at the interface (see reaction (15)), even though the plated Li resides directly on the graphitic surface (figure 1(c)), i.e. atoms of deposited Li are within angstroms of vacant sites within the graphite. For this reason, we compare the conventional approach of no Li exchange ($k_j = 0$ for all $j$ in equation (17)) to that of nearly facile exchange of Li ($k_j \to \infty$ for all $j$ in equation (17)). We find that during constant current charging the time traces of the calculated electrode potential, as well as those for the open-circuit potentials for the Li insertion and plating reactions, are very sensitive to the ratio of the resistance to Li diffusion in graphite to that of the Li exchange reaction, $R_d / R_{\text{T_Li}}$.

For a variety of reasons, the surface of graphite is nonuniform in terms of reaction rates for Li insertion and plating, as overviewed in the Introduction, and we show that when the electrode is subjected to constant-current charging, as is commonly employed, such nonuniformities lead to early Li plating over the highly reactive surfaces (see figures 6 through 9). These results underscore the importance of maintaining a uniform electrode surface, especially when the cell is to be subjected to high rates of charge.

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