Solvent Diffusion Model for Aging of Lithium-Ion Battery Cells

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This work presents a rigorous continuum mechanics model of solvent diffusion describing the growth of solid-electrolyte interfaces (SEIs) in Li-ion cells incorporating carbon anodes. The model assumes that a reactive solvent component diffuses through the SEI and undergoes electron reduction at the carbon-SEI interface. Solvent reduction produces an insoluble product, resulting in increased SEI thickness. The model predicts that the SEI thickness increases linearly with the square root of time. Experimental data from the literature for capacity loss in two types of prototype Li-ion cells validates the solvent diffusion model.

We use the model to estimate SEI thickness and extract solvent diffusivity values from the capacity loss data. Solvent diffusivity values have an Arrhenius temperature dependence consistent with solvent diffusion through a solid SEI. The magnitudes of the diffusivities and activation energies are comparable to literature values for hydrocarbon diffusion in carbon molecular sieves and zeolites. These findings, viewed in the context of recent SEI morphology studies, suggest that the SEI may be viewed as a single layer with both micro- and macroporosity that controls the ingress of electrolyte, anode passivation, and cell performance over the course of cycling as well as long-term operation.

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where \( k \) is a proportionality constant, \( \chi \) is the SEI specific conductivity (dependent only on temperature), \( A_{\text{anode}} \) is the anode surface area, and \( B = k\chi A_{\text{anode}} \) is constant. The SEI thickness, \( L(t) \), can be expressed as

\[
L = L_0 + AN_L
\]

where \( L_0 \) is the initial SEI thickness after the first few charge-discharge cycles, and \( A \) is another empirical parameter independent of both time and temperature. This expression assumes that lithium, electrons, and electrolyte react to produce an insoluble product \( P \) with constant composition and average molar volume.

Combining Eq. 1 and 2, integrating subject to the initial condition of \( N_L(0) = 0 \) at time \( t = 0 \), and rearrangement yield

\[
t = \frac{A}{2B} N_L^2 + \frac{L_0}{B} N_L
\]

Broussely et al.\(^{20}\) also assumed, implicitly, that the cell capacity is proportional to the available number of moles of lithium, \( N_0 - N_L \), with \( N_0 \) denoting the initial number of moles of lithium available for cycling. Then the fractional capacity loss can be expressed as \( x(t) = N_L(t)/N_0 \) and Eq. 3 becomes

\[
t = \frac{A'}{2B'} x^2 + \frac{L_0}{B'} x
\]

in accord with Eq. 5 of Ref. 20, except with \( A' = AN_0 \) and \( B' = B/N_0 \).

This quadratic relationship between time and SEI thickness (or its surrogate, fractional capacity loss) is by no means unique. In this work, we interpret the data of Broussely et al.\(^{20}\) in terms of a one-dimensional model of solvent diffusion through a porous SEI. Upon reaching the carbon/SEI interface, solvent (EC) undergoes two-electron reduction, thus growing the SEI at the internal interface. This scenario is consistent with the view that a robust SEI should be able to heal itself as damage occurs during charge-discharge cycling. As the SEI thickness increases, the solvent diffusion rate decreases, thus slowing the rate of SEI growth and fractional capacity loss. In fact, the solvent diffusion-limited model presented later leads to fractional capacity loss increasing with the square root of time, in accord with the data of Broussely et al.\(^{20}\).

**Model Development**

**Assumptions.—**Figure 1 presents a schematic diagram of the Li-ion half-cell illustrating the transport processes and reactions occurring near the surface of a carbon anode under float charge conditions. This diagram reflects several assumptions. First, we assume planar symmetry of the anode and consider only transport in one spatial Cartesian coordinate, valid away from the edges of the anode. Frame indifference\(^{22}\) enables us to work in reference frame in which the SEI-electrolyte interface is stationary, located for convenience at \( z = 0 \).

The electrolyte consists of one or more solvent components and a lithium salt. The reduction of various alkyl carbonates with lithium and lithiated carbon has been studied extensively. Experiments\(^{13,14,23,29}\) generally agree that among the various alkyl carbonates used in prototype Li-ion batteries, EC is the most reactive. Moreover, theory\(^{20}\) provides additional support for a reaction mechanism involving two-electron reduction of EC to produce either \( \text{Li}_2\text{CO}_3 \) or lithium alkyl carbonates at low or high EC concentrations, respectively. For our model, we assume that the reaction of one solvent component (S) dominates. This component undergoes two-electron reduction at the carbon-SEI interface via

\[
S + 2e^- + 2\text{Li}^+ \rightarrow P
\]

producing an insoluble product (P) with constant molar density \( c_P \). With respect to the experiments of Broussely et al.,\(^{20}\) we assume that S corresponds to EC, and P to \( \text{Li}_2\text{CO}_3 \). Within the SEI phase, component S is the only mobile component and has a constant effective diffusivity \( (D_S) \). Moreover, we shall assume that S is dilute within the SEI so that \( c_S \ll c_P \). Electrons and lithium cations are available in excess at the carbon-SEI interface.

**Transport equations.—**Under the assumptions described in the previous section, the SEI growth problem is very similar to that of the growth of silica layers on silicon surfaces limited by the diffusion of molecular oxygen through the growing silica layer.\(^{26}\) Assuming a constant \( c_P \) and a reference frame in which the SEI is stationary, the flux of P is zero and the differential mass balance for P is satisfied identically. The differential mass balance for the solvent in the SEI phase is

\[
\frac{\partial c_S}{\partial t} + \frac{\partial N_{LS}}{\partial z} = 0
\]

Assuming Fickian diffusion\(^{22}\) of the solvent with \( D_S \) as the effective binary diffusivity of S in P, we have

\[
N_{LS} = x_S \sum_{I} N_{L,I} - c_D I \frac{\partial x_S}{\partial z}
\]

where \( c \) denotes the total molar concentration and \( x_I \) the mole fraction of component I (S or P). Simplification of Eq. 7 is not trivial because \( c(z,t) \) is not constant. Recognizing that \( c = c_S + c_P \), \( x_S = c_S/c \), and that only the solvent has a nonzero flux, one may ultimately show that Eq. 7 reduces to

\[
N_{LS} = -D_S \frac{\partial c_S}{\partial z}
\]

Substitution of Eq. 8 into Eq. 6 yields

\[
\frac{\partial c_S}{\partial t} = D_S \frac{\partial^2 c_S}{\partial z^2}
\]

which governs solvent diffusion through the SEI.

Boundary conditions for this moving boundary problem are easily derived from jump mass balances\(^{22}\) for S and P at the carbon/SEI interface, yielding

\[
At \ z = L(t): \quad \frac{r_S}{M_S} = c_S \frac{dL}{dt}
\]

and

\[
At \ z = L(t): \quad 0 = \frac{r_P}{M_P} - c_P \frac{dL}{dt}
\]
respectively. Based on the stoichiometry of Eq. 5, the molar production rates \(r_i^a/M_P\) of the various species are related by
\[
\frac{r^a_p}{M_P} = -2 \frac{r^a_{\text{Li}^+}}{M_{\text{Li}^+}} = -2 \frac{r^a_{\text{S}}}{M_S} = \frac{r^a_s}{M_S} \tag{12}
\]
Adding Eq. 10 and 11 and eliminating the reaction rates using Eq. 12 gives
\[
\text{At } z = L(t): \quad \frac{dL}{dt} = \frac{N_{c,s}}{(c_p + C_S)} = \frac{N_{c,S}}{c_p} \tag{13}
\]
The second equality follows from the key assumption \(c_S \ll c_P\). Substituting this expression into Eq. 11 gives
\[
\text{At } z = L(t): \quad N_{c,s} = \frac{r^a_p}{M_P} = -\frac{r^a_s}{M_S} \tag{14}
\]
In turn, substituting this expression into Eq. 10 leads to the conclusion that
\[
\text{At } z = L(t): \quad c_S \approx 0 \tag{15}
\]
Thus all S that diffuses through the SEI is consumed at the carbon/SEI interface.

We assume local equilibrium at the SEI/electrolyte interface implies a relationship between the concentrations of S in the SEI and the electrolyte
\[
\text{At } z = 0: \quad c_S = c_{eq} \tag{16}
\]
Lacking detailed thermodynamic information about partitioning at this interface, we assume that \(c_{eq}\) equals the concentration of the reactive solvent component S in the electrolyte solution.

**Analytical solution.**—Equations 9, 15, and 16 are the final set of equations to be solved. The same set of equations has been solved previously\(^{22,26}\) in the context of silicon oxidation. Dimensional analysis shows that these equations can be solved through the similarity transformation of the form
\[
u = \frac{z}{\sqrt{4D_S t}} \tag{17}
\]
without the need for an initial condition. Employing this change of variable, Eq. 9 becomes
\[
\frac{d^2c_S}{du^2} + 2u \frac{dc_S}{du} = 0 \tag{18}
\]
with the boundary conditions
\[
\text{At } u = \lambda: \quad c_S \approx 0 \tag{19}
\]
and
\[
\text{At } u = 0: \quad c_S = c_{eq} \tag{20}
\]
In Eq. 19, we have
\[
\lambda = \frac{L(t)}{\sqrt{4D_S t}} \tag{21}
\]
Since \(c_S(\lambda) = 0\) from Eq. 19, \(\lambda\) must be a constant.

The solution of Eq. 18 consistent with Eq. 19 and 20 is\(^{22,26}\)
\[
c_S(u, t) = c_{eq} \left( 1 - \frac{\text{erf}(u)}{\text{erf}(\lambda)} \right) \tag{22}
\]
where \(\lambda\) may be found from the solution of
\[
\lambda = \frac{c_{eq}}{\sqrt{\pi c_p}} \text{exp}(-\lambda^2) \tag{23}
\]
Equation 21 gives
\[
L(t) = 2\sqrt{D_S t} \tag{24}
\]
As one might expect for diffusion-limited film growth, the SEI thickness increases with the square root of time.

In order to compare the predicted trend, Eq. 24, with experimental data for capacity loss, we must invoke some additional assumptions. First, cell capacity is proportional to the moles of Li available for cycling, and all capacity loss must be due to Li consumption associated with electrolyte reduction. This produces an insoluble product, \(P\), having constant composition and molar volume. Under these conditions, a lithium mass balance gives
\[
x(t) = \frac{N_z(t)}{N_0} = \frac{Z_p c_{eq} A_{\text{anode}}}{N_0} = \frac{2Z_p c_{eq} A_{\text{anode}} \lambda}{N_0} \sqrt{D_S t} \tag{25}
\]
for the fractional capacity loss \(x(t)\), where \(Z_p\) is the stoichiometric coefficient of Li in \(P\). If we know (or assume) the electrolyte composition and the molar volume of \(P\) in the SEI, the values of \(c_{eq}\), \(c_P\), \(\lambda\) (from Eq. 23), and \(Z_p\) are all determined. The anode area \(A_{\text{anode}}\) is a cell design parameter, and the initial capacity \(N_0\) is a measured value. If experimental data for \(x(t)\) is linear when plotted vs. \(\sqrt{t}\), then we may extract \(D_S\) from the slope of this plot.

**Results and Discussion**

**Capacity loss.**—Broussely et al.\(^{20}\) measured the capacity loss of various prototype Li-ion cells as functions of time, storage temperature, and float potential. Table I summarizes the design details of these cells, including the measured values of initial capacity \(N_0\). Figure 2 shows data (symbols from Ref. 20, Fig. 5, cell 2) for capacity loss vs. \(\sqrt{t}\) for HE prototype cells stored at 30 and 60°C and at a float potential of 3.8 V. The solid curves are one parameter linear fits of the data. Likewise, Fig. 3 shows data (symbols from Ref. 20, Fig. 1) for capacity loss vs. \(\sqrt{t}\) for MP prototype cells stored at various temperatures and at a float potential of 3.9 V. Despite the scatter in the data, one-parameter linear regression again provides a satisfactory fit. Table II shows linear correlation coefficients \(R^2\) for the two-parameter linear regressions reported by Broussely et al.\(^{20}\) (on data in their Fig. 6 and 7) as well as our corresponding one-parameter regressions (our Figures 2 and 3). The overall quality of the linear regressions of the capacity loss data in Fig. 2 and 3 demonstrates that the solvent diffusion model provides a satisfactory description of capacity loss in these Li-ion cells. Considering that the solvent diffusion model has only one adjustable parameter, the fidelity of this model is perhaps better than that of the two-parameter electronic conductivity model (Eq. 4) employed by Broussely et al.\(^{20}\)

**SEI thickness.**—The solvent diffusion model can be used to estimate the SEI thickness and extract the solvent diffusivity from capacity loss data via Eq. 25. First, we assume that in the HE and MP prototype cells studied by Broussely et al.\(^{20}\) EC reduction produces Li2CO3 as the predominant product, so we use \(Z_p = 2\) and \(c_P = 2.11 \text{ g/cm}^3\) in Eq. 25. Although Broussely et al.\(^{20}\) identified the solvents used in the cells, they did not specify the mixing ratios, so we assumed the volume ratios shown in the lower part of Table I. The solvent compositions are used to calculate \(c_{eq}\) for EC in the mixture and thus \(\lambda\) from Eq. 23 (values given in Table I).

The final parameter required to estimate SEI thickness is the anode area, \(A_{\text{anode}}\), representing the actual carbon surface area that is both electrochemically active and accessible to electrolyte. For composite carbon anodes typically based on graphite powders, values of \(A_{\text{anode}}\) are generally unknown. The area of the underlying...
current collector provides a lower bound on $A_{\text{anode}}$ and would be appropriate if the carbon anode were a perfect sheet of highly ordered pyrolytic graphite (HOPG). At the other extreme, the carbon surface area obtained through gas absorption measurements, e.g., Brunauer-Emmett-Teller (BET), might serve as the upper bound on $A_{\text{anode}}$. However, it has been noted that “the surface of a composite graphite electrode, which is accessible to the electrolyte, can be expected to differ considerably from the surface of a graphite powder... accessible to $N_2$ at 77 K.” Here we use an order-of-magnitude estimate of $A_{\text{anode}}$ to show that the resulting predictions of SEI thickness are in reasonable accord with other experimental observations.

First, we note that Broussely et al.20 did not report, for any of their cells, the actual anode current collector areas, the two types of synthetic graphites they used, the loading of the active material, or any details about how the anodes were fabricated. Our previous studies28,29 of commercial Li-ion cells indicate that anode area is, on average, directly proportional to rated capacity. From the rated capacities given in Table I, we used the same proportionality constant to estimate the values of the current collector areas given in the lower part of Table I. To estimate $A_{\text{anode}}$ from the current collector areas, we need values of the carbon loading in the composite anode and the specific surface area of the active carbon. Lacking this information for the SAFT cells,20 we instead used information from the work of Winter et al.27,30 for estimation purposes. Based on carbon loadings30 of 0.00923 g/cm$^2$ (i.e., 1.2 mg/1.3 cm$^2$) and a specific surface area27 of 1.41 m$^2$/g for the prismatic surface area of TIMREX KS75 graphite, we can easily convert the current collector areas into the estimates for $A_{\text{anode}}$ given in the lower part of Table I.

<table>
<thead>
<tr>
<th>Table I. Published and assumed characteristics of the HE and MP prototype Li-ion cells studied by Broussely et al.20</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Published characteristics</strong>20</td>
</tr>
<tr>
<td>Cell design</td>
</tr>
<tr>
<td>Positive electrode</td>
</tr>
<tr>
<td>Negative electrode</td>
</tr>
<tr>
<td>Electrolyte salt</td>
</tr>
<tr>
<td>Electrolyte solvents</td>
</tr>
<tr>
<td>Rated capacity (Ah)</td>
</tr>
<tr>
<td>Storage temperatures</td>
</tr>
<tr>
<td>Float potentials</td>
</tr>
<tr>
<td>Capacity measurement</td>
</tr>
<tr>
<td>Initial capacity$^a$ (Ah)</td>
</tr>
<tr>
<td></td>
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<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Assumed characteristics</td>
</tr>
<tr>
<td>Solvent volume ratio</td>
</tr>
<tr>
<td>$c_{\text{eq}}$ (mol/cm$^3$)</td>
</tr>
<tr>
<td>$\lambda$</td>
</tr>
<tr>
<td>Anode current collector area$^b$ (m$^2$)</td>
</tr>
<tr>
<td>Carbon surface area,$^b$ $A_{\text{anode}}$ (m$^2$)</td>
</tr>
</tbody>
</table>

$^a$ Initial capacity values from Ref. 20, Fig. 5 (HE prototypes) and Fig. 1 (MP prototypes).

$^b$ Estimated; see text.
Recent AFM measurements of SEI films formed on HOPG after one or two charge-discharge cycles provide at least a qualitative basis for comparison. Hirasawa et al. 31 used AFM to estimate a minimum film thickness of 50-70 nm for the SEI formed on HOPG in 1.0 M Li$_2$ClO$_4$ + 1:1 EC-EMC solution during one charge-discharge cycle. Thicker particulate films, on the order of hundreds of nanometers, were implied by the measurements of Chu et al. 32 for HOPG in similar electrolytes. Interpretation of these early AFM measurements may be problematic because the SEI films may have been damaged due to excessive contact force. More recent, lower force AFM measurements by Alliata et al. 19 indicated film thicknesses in excess of 25 nm for SEIs formed over two charge-discharge cycles on HOPG in 1.0 M Li$_2$ClO$_4$ + 1:1 EC-DMC. These studies all suggest that relatively thick SEI layers form after just a few charge-discharge cycles.

The additional growth in thickness expected over months or years of self-discharge under float potential conditions has not been measured. However, if the initial formation of a 10-100 nm thick SEI is accompanied by a 10-20% initial capacity loss, then a subsequent 10% capacity loss during long-term self-discharge ought to produce SEI thickness growth of the same order of magnitude. Thus the SEI thicknesses predicted by the solvent diffusion model are reasonable, notwithstanding all of the assumptions required to generate the estimates. For a given value of capacity loss, the predicted SEI thickness would be smaller if some of the reduction products were soluble in the electrolyte. The predicted SEI thickness could be greater if the reduction product has a lower average molar density or significant porosity. The thickness varies most significantly with the true active carbon area, which depends on a host of material properties and the details of how the anode is fabricated.

**Solvent diffusivity.**—We may extract values of solvent diffusivity in the SEI from the slopes of the lines in Fig. 2 and 3 and the values of λ in Table I. The diffusivity values are given in Table III and depicted in an Arrhenius plot in Fig. 4. The diffusivity values in Table III, on the order of $10^{-13}$ m$^2$/s, are about a factor of ten lower than the smallest experimental values for hydrocarbon diffusion in zeolites (e.g., $50 \times 10^{-21}$ m$^2$/s for n-hexane in 4A zeolite at 50°C, Table 12.2 in Ref. 33). Ordinary diffusion in microporous carbons, zeolites, and solids in general 33 should have a temperature dependence obeying the Eyring expression

$$D_S = D_0^S \exp \left( - \frac{E_a}{RT} \right)$$

where $E_a$ is the apparent activation energy for the diffusion process. The linearity of the corresponding Arrhenius plot (Fig. 4) for solvent diffusivities in MP cells is therefore consistent with solvent diffusion through a solid SEI. For the MP prototype cells, we find $E_a = 9.5$ kcal/mol, which compares well with values for interstitial diffusion in crystalline solids 30 as well as hydrocarbon diffusion in zeolites (e.g., 8.5-9.5 kcal/mol for n-butane in 4A zeolite at 50°C, Table 12.2 in Ref. 19; 8-10 kcal/mol for aromatic hydrocarbons in silicalite, Fig. 14.16 in Ref. 33). The magnitudes of the diffusivity values, their conformance to the Eyring expression, and the activa-

**Table III. Estimated values of $D_s$ at various temperatures for HE and MP prototype cells, and corresponding infinite temperature diffusivities and activation energies from the Arrhenius plot in Fig. 4.**

<table>
<thead>
<tr>
<th>Cell prototype</th>
<th>Storage temp. (°C)</th>
<th>$D_s/10^{-21}$ (m$^2$/s)</th>
<th>$D_0^S$ (m$^2$/s)</th>
<th>$E_a$ (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HE</td>
<td>30</td>
<td>3.07</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>15.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$1.50 \times 10^{-15}$</td>
<td></td>
<td>10.7</td>
</tr>
<tr>
<td>MP</td>
<td>15</td>
<td>0.722</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>1.35</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>1.93</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>6.94</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$1.03 \times 10^{-16}$</td>
<td></td>
<td>9.50</td>
</tr>
</tbody>
</table>
The capacity loss of Li-ion cells during storage under float conditions is the prediction that capacity loss increases with the square root of time. An Arrhenius plot of diffusivities extracted from experimental data is linear, consistent with the behavior expected for temperature-dependent diffusivity of solvent through a solid, perhaps microporous SEI. The solvent diffusivities for two different cell prototypes differ by a constant factor that may be explained by uncertainties in details of cell design.

Although the model invokes many simplifying assumptions, it points toward the possibility of a new, realistic, tractable picture of the SEI on carbon anodes in Li-ion cells. The current “working model” is Peled’s bilayer SEI,13 consisting of an ultrathin, nonporous passivation barrier with non-negligible electronic conductivity, covered by a thick, macroporous, permeable layer with little relevance for passivation. Instead, we envision a single SEI layer with continuously varying properties including composition and porosity, much like the picture resulting from the simulations of Nainville et al.34-37 A more sophisticated solvent diffusion model should be able to predict initial passivation characteristics as well as long-term capacity loss and SEI growth, all governed by the ability of reactive solvents to diffuse to within electron tunneling distance of the anode surface. One should be able to use this model to design “good” electrolytes by including reactive components that readily undergo reduction to form dense, low-porosity, insoluble products with low permeability to other electrolyte components.

Electrolyte composition.—It is well known in practice that the solvent composition in the electrolyte plays a critical role in controlling SEI formation, anode passivation, and long-term capacity fade. The solvent diffusion model provides a starting point for understanding and predicting the effect of solvent composition on SEI growth and capacity fade. For example, we may use the model to explore the effect of varying EC concentration on long-term capacity loss and SEI layer growth for cells under float potential conditions. Predictions for HE and MP prototype cells are given in Fig. 5 and 6. The symbols are the capacity loss data of Broussely et al., measured for different ratios of EC:DEC:DMC in the electrolyte mixture for MP prototype cells. Symbols are measured capacity loss data20 for an MP cell stored at 30°C with the SEI thickness estimate based on 1:1:1 EC:DEC:DMC.

Conclusions

We have presented a one-dimensional solvent diffusion model to explain the capacity loss of Li-ion cells during storage under float potentials at various temperatures. The primary result of the model is the prediction that capacity loss increases with the square root of time, in accord with experimental data.20 Additional reasonable assumptions about the composition of the SEI lead to plausible estimates of SEI thickness, which also grows in proportion to the square root of time. The solvent diffusivity may be obtained from linear regression of capacity loss plotted vs. square root of time. An Arrhenius plot of diffusivities extracted from experimental data is linear, consistent with the behavior expected for temperature-dependent diffusivity of solvent through a solid, perhaps microporous SEI. The solvent diffusivities for two different cell prototypes differ by a constant factor that may be explained by uncertainties in details of cell design.
References