Mechanistic Details of the spontaneous Intercalation of Li metal into Graphite Electrodes

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- Supporting Information -

S1 Details of the electrochemical model

The graphite electrode is modelled as porous, homogeneous medium, similar to porous electrode theory. The transport of Li ions in the electrolyte within the electrode is described by

\[
\frac{\partial (\varepsilon c_{El})}{\partial t} = -\nabla \cdot N_{El}^{eff} \tag{1}
\]

\[
0 = -\nabla \cdot j_{El}^{eff} \tag{2}
\]

With the effective particle flux density N and effective charge flux density J given by

\[
N_{El}^{eff} = -D_{El}^{eff} \nabla c_{El} + \frac{t_{\pm}}{F} j_{El}^{eff} \tag{3}
\]

\[
j_{El}^{eff} = -\kappa_{El}^{eff} \nabla \phi_{El} + \kappa_{El}^{eff} \frac{1 - t_{\pm}}{F} \left( \frac{\partial \mu_{El}}{\partial c_{El}} \right) \nabla c_{El} \tag{4}
\]
Due to the size of the Li disk, the limiting step in the lithiation process is the transfer of Li ions through the electrolyte towards the active material. Therefore, the diffusion of Li inside the graphite particles which happens on much smaller timescales (4 orders of magnitude) is neglected. Still, we keep track of the Li concentration within the Graphite phase according to

$$\frac{\partial c_{So}}{\partial t} = -\nabla \vec{N}_{So}$$  \hspace{1cm} (5)

Where the transport of Li within the Graphite domain is given by the effective diffusion in the phase

$$\vec{N}_{So} = -D_{So}^{eff} \nabla c_{So}$$  \hspace{1cm} (6)

The electronic connection between the Li disk and the graphite electrode is critical for the lithiation process. Without electrical contact, charge transfer between Li and graphite is impossible which will stop the dissolution process. In order to keep track of local electrical currents we solve the charge conservation equation inside the solid regions of the model cell:

$$0 = -\nabla j_{So}^{eff}$$  \hspace{1cm} (7)

With the electronic current density given by

$$j_{So}^{eff} = \sigma_{So} \nabla \Phi_{So}$$  \hspace{1cm} (8)

At the interface between the electrolyte and the graphite, the Li de-/intercalation is described by a classical Butler-Volmer expression

$$i_{BV} = i_{00} c_{el}^{1-\alpha} (c_{So}^{max} - c_{So})^{1-\alpha} \times \left[ \exp\left(\frac{\alpha F}{RT} \eta\right) - \exp\left(-\frac{(1-\alpha) F}{RT} \eta\right) \right]$$  \hspace{1cm} (9)

with the exchange current density $i_{00}$, the maximum Li concentration in graphite $c_{So}^{max}$, the symmetry factor $\alpha$, and the overpotential $\eta$ driving the reaction. The overpotential is given by

$$\eta = \Phi_{So} - \varphi_{el} - U_0(c_{So})$$  \hspace{1cm} (10)

The experiments on model electrodes without conductive salt demonstrate that direct intercalation of Li from the disk into graphite is minor. Therefore, we only include de-/intercalation from the electrolyte.

A challenge of simulating the chemical lithiation using a metallic Li disk is the complete dissolution of the metallic Li phase. This kind of extensive volume change is expected to introduce convection into the electrolyte. On the other hand, the chemical lithiation takes place in a long period of time, therefore, it can be expected, that the convection
is negligibly small. In this work, we use a simplified description of the Li disk, where we do not take into account changes of our computational domain during dissolution. Still, we keep track of the amount of Li within the disk by solving the conservation equation for the Li phase:

$$\frac{\partial c_{Li}^{disk}}{\partial t} = -\nabla N_{Li}^{disk}$$

(11)

In this lumped model dissolved Li is immediately replaced by electrolyte. The transport of Li within the domain is then given by effective transport in the electrolyte

$$N_{Li}^{disk} = -D_{Li}^{disk} \nabla c_{Li}^{disk}$$

(12)

Therefore, the effective transport parameter within the Li disk $D_{Li}^{disk}$ is chosen to represent transport inside the electrolyte.

Since we do not change the computational domain, the geometry of the Li disk affects transport in the electrolyte even after the complete dissolution. A similar effect is expected due to the remains of the Li disk observed in the experiments. However, this thinner layer is probably more permeable for Li ions. Therefore, our model assumption probably overestimates this blocking effect where Li ions in electrode pores underneath the disk can only diffuse through the electrode pore space and not towards the counter electrode. The distribution of Li in this region is therefore probably slightly overestimated.

At the interface between the electrolyte and the Li disk the kinetic expression is given by

$$i_{BV} = i_{00} c_{El}^{n} \left[ \exp \left( \frac{\alpha F}{RT} \eta \right) - \exp \left( -\frac{(1 - \alpha)F}{RT} \eta \right) \right]$$

(13)

During the experiment the Li disk is able to completely dissolve. This effect is taken into account through a variation of the activity of the Li metal for vanishing Li content.

$$\eta_{Li-Disk} = \Phi_{Li} - \varphi_{El} + \frac{RT}{F} \ln(a_{Li}(c_{Li}))$$

(14)

As long as the Li concentration is sufficiently large, the activity of bulk Li metal $a_{Li}$ is one by definition. In our model the activity and, thus the corresponding Faradaic current, will approach zero for vanishing amounts of Li.
The Li metal counter electrode serves as a reference in the electrochemical measurements. In the simulations, the counter electrode is modeled as infinite reservoir for Li ions following the kinetic description given in Eq. 9. The electrochemical parameters for the electrolyte and the graphite are taken from Hein et al.\textsuperscript{25} and are listed in Table S1-1. The transport inside the electrolyte phase of the electrode (index \textit{El}) and the long range diffusion within Graphite (index \textit{So}) are reduced according to $e^\beta$ with the corresponding volume fraction of the respective phase and a classical Bruggeman factor $\beta_{\textit{So}} = \beta_{\textit{El}} = 1.5$. The volume fraction of the pore space is 30% and the solid fraction of the electrode is 70%. This Bruggeman expression is related to a tortuosity expression according to $\epsilon_i^\beta = \frac{\epsilon_i}{\tau_i}$. The reaction rate of the Li dissolution reaction at the Li disk together with the diffusion of Li inside the disk describe the Li dissolution process. The value of the diffusion was set to $D_{Li} = 3.8279 \times 10^{-4} \text{ cm}^2/\text{s}$ and the rate constant was chosen to $i_{00}^{Li\text{Disk}} = 0.002511886 \frac{A}{\sqrt{\text{cm mol}}}$ in order to qualitatively reproduce the dissolution process.

The open circuit voltage of Graphite is given by the following equation:

$$U_0(x) = 0.6379 + 0.5416 \cdot \exp(-305.5309 \cdot x) + 0.44 \cdot \tanh\left(-\frac{x - 0.1958}{0.1088}\right) - 0.1978 \cdot \tanh_{\text{mod}}\left(\frac{x - 0.99}{0.05}\right) - 0.6875 \cdot \tanh\left(\frac{x + 0.0117}{0.0529}\right) - 0.0175 \cdot \tanh\left(\frac{x - 0.5692}{0.0875}\right)$$

where $\tanh_{\text{mod}}(x) = \frac{\exp(20 \cdot x) - \exp(-x)}{2 \cdot \cosh(x)}$

The expression is based on the work of Safari et al. [SI-2].

Table S1: List of the electrochemical parameters used for the simulations.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c_{\textit{So}}^0$ / mol/cm$^3$</td>
<td>3.137e-6</td>
<td>Initial Li concentration</td>
</tr>
<tr>
<td>$c_{\textit{So}}^{\text{max}}$ / mol/cm$^3$</td>
<td>31370e-6</td>
<td>Maximum Li concentration [SI-2]</td>
</tr>
<tr>
<td>$D_{\textit{So}}$ / cm$^2$/s</td>
<td>3e-10</td>
<td>Li ion diffusion coefficient [SI-2]</td>
</tr>
<tr>
<td>$\kappa_{\textit{So}}$ / S/cm</td>
<td>10</td>
<td>Electronic conductivity of Graphite (estimated)</td>
</tr>
<tr>
<td>Symbol</td>
<td>Value</td>
<td>Description</td>
</tr>
<tr>
<td>-------</td>
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</tr>
<tr>
<td>$U_0 / V$</td>
<td>See Ref. 13</td>
<td>Open circuit potential of Graphite</td>
</tr>
<tr>
<td>$c_{El}^0 / \text{mol/l}$</td>
<td>1</td>
<td>Concentration of Li salt</td>
</tr>
<tr>
<td>$\kappa_{El} / \text{S/cm}$</td>
<td>Eqn (4) in [SI-1] based on [SI-3]</td>
<td>Conductivity</td>
</tr>
<tr>
<td>$D_{El} / \text{cm}^2/\text{s}$</td>
<td>Eqn (3) in [SI-1] based on [SI-3]</td>
<td>Li ion diffusion coefficient</td>
</tr>
<tr>
<td>$f_{El}^{\text{Li}} / -$</td>
<td>Eqn (3) in [SI-1] based on [SI-3]</td>
<td>Activity factor</td>
</tr>
<tr>
<td>$t_\pm / -$</td>
<td>Eqn (2) in [SI-1] based on [SI-3]</td>
<td>Transference number</td>
</tr>
</tbody>
</table>

### Electrolyte

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Value</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\kappa_{CC} / \text{S/cm}$</td>
<td>10</td>
<td>Electronic conductivity of Current collector (estimated)</td>
</tr>
<tr>
<td>$D_{Li} / \text{cm}^2/\text{s}$</td>
<td>3.8279e-4</td>
<td>Li “diffusion coefficient” inside Li disk (model parameter)</td>
</tr>
</tbody>
</table>

### Kinetic parameter

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Value</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$i_{CE}^{00} / \text{A/cm}^2$</td>
<td>0.0364</td>
<td>Exchange current density factor at counter electrode [SI-1]</td>
</tr>
<tr>
<td>$i_{Li}^{00} / \text{Acm}^{1.5}/\text{mol}^{0.5}$</td>
<td>0.002511886</td>
<td>Exchange current density factor at Li disk (model parameter)</td>
</tr>
<tr>
<td>$i_{So}^{00} / \text{Acm}^{2.5}/\text{mol}^{1.5}$</td>
<td>0.0657</td>
<td>Exchange current density factor for intercalation[SI-2]</td>
</tr>
</tbody>
</table>

### Geometrical parameter

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Value</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A / \text{cm}^2/\text{cm}^3$</td>
<td>1.125e3</td>
<td>Specific surface area of Graphite electrode (calculated)</td>
</tr>
</tbody>
</table>

S2 Simulations with reduced counter electrode

In the experiments, we observe a complete dissolution of the Li metal disk in a setup with counter electrode, which was introduced for OCP measurements. This is not seen in experiments without the additional counter-electrode. The influence of the geometry of the counter electrode is also investigated by one additional simulation. The simulation domain with a reduced counter electrode can be seen on the left side of Figure S1. The counter electrode is reduced to a fraction of the size and is located at the bottom of the pouch cell. This setup is similar to the experiments without counter-electrode. Still, we are able to additionally simulate the corresponding OCP which is not tracked in the experiments. The electrochemical simulations reveal, that the cell potential decreases slower compared to the large counter electrode. This is the result of the reduced dissolution of the Li disk. This supports our claim, that the extended counter electrode enhances the Li dissolution. In Figure S2, the Li ion concentration in the electrolyte right next to the counter electrode in both cases are shown. The location of the Graphite electrode and its current collector, roughly 290 µm and 350 µm below the shown slice, are schematically shown in the first image on the left. When Li is dissolving, it is reflected by the increased Li concentration in the electrolyte. Without the metallic Li counter facing the surface, only at the position close to the Li metal disk, an increase of Li ion concentration can be observed. Remarkably, this concentration can reach up to 3 mol/l and consequently we also observe concentrations lower than the initial salt concentration away from the Li disk. In the lower panel, with the additional diffusion/reaction path given by the large counter electrode, the increase in Li ion concentration can not only be seen at the Li metal disk but also at the edges of the electrode. Therefore, the counter-electrode accelerates redistribution of the Li ions in the electrolyte. The asymmetric concentration profile is caused by the asymmetry in cell setup due to the current collectors. The current collector is blocking the electrolyte transport on the top right which causes an inhomogeneous transport and Li concentration distribution. This can be seen in the first image of the lower row in Figure S2 and the shape and position of the electrode and current collector is indicated by the black mesh. Since, high concentrations also reduce dissolution kinetics this
phenomenon is responsible for the residual Li disk in the experiments without counter electrode. Due to this additional diffusion path, equilibration of Li ions in the electrolyte can be achieved within 700 h, whereas no equilibrium is reached when the Li metal counter electrode is not facing the graphite electrode.

Figure S1: (left) Geometry of the pouch cell with a reduced counter electrode, which is located on the bottom. (right top) The cell potential of the small counter electrode exhibits exponential behavior. (right bottom) The remaining amount of Li in the Li disk. The small CE leads to a slower dissolution of the Li disk.
Figure S2: Li ion distribution in the electrolyte right next to the counter electrode during the dissolution and re-intercalation (upper panel) with no metallic Li counter electrode facing the graphite electrode surface (lower panel) with a metallic Li counter electrode facing the graphite electrode surface. The black mesh indicates the shape and position of the electrode and current collector.