Introduction to the Materials Science of

Rechargeable Batteries

Week 4: Reversible and Irreversible Interfacial Reactions
Lecture 4.5: Week 4 Summary

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Elements of Reaction Theory

reacted charge:

\[ J_T = J_F - J_B \]

\[ J_T = z F c_s k_F - z F (c_T - c) k_B \]

backwards/forward reaction rates

\[ k_F = k_F^0 \exp \left( -\frac{\Delta G_f}{RT} \right) \]

\[ k_B = k_B^0 \exp \left( -\frac{\Delta G_b}{RT} \right) \]

The effective overpotential:

\[ \eta_T = \eta + \frac{RT}{zF} \ln \left( \frac{c_T - c}{c_s} \right) \]
Elements of Reaction Theory: Continued...

\[ Li \rightleftharpoons Li^+ + e^- \]

Detailing the rate at which Li intercalates

\[ LiM \rightleftharpoons e^- + Li^+ + M \]

The simplest interfacial kinetics

\[
\vec{J} \cdot \hat{n} = i_0 \left( \exp\left(\frac{\alpha_a F z \eta}{RT}\right) - \exp\left(-\frac{\alpha_c F z \eta}{RT}\right) \right)
\]

\[
i_0 = F k_r (c_T - c_s)^{\alpha_a} c_s^{\alpha_c}
\]
Irreversible Reactions

Butler-Volmer Kinetics:

\[
\vec{J} \cdot \hat{n} = i_0 \left( \exp\left(\frac{\alpha_a F z \eta}{RT}\right) - \exp\left(-\frac{\alpha_c F z \eta}{RT}\right) \right)
\]

\[+ \sum_{i=1}^{N} J_i\]

For a single side reaction:

\[
\frac{\partial \delta}{\partial t} = \frac{\Omega}{zF} j_{ir}
\]
Salt Precipitation Simulations

\[ R_c = \frac{Q_c}{Q_a - Q_{irr}} \]


Interface-Related Reactions

Negative Electrode
(Carbon or Graphite)

Electrolyte

Li$^+$

Li$_{\text{sol}}^+$ [desired reaction]

Ethers, Esters
(cyclic)

Polymerization

Solvent reduction

Soluble products

Insoluble products (Li$_2$CO$_3$)

Precipitation

LiF, LiCl

Salt reduction

Spatial Distribution of SEI Components

3 min of Cu-surface on EC:DEC (1:2)+1M of LiBF$_4$
Surface Morphology During Recharge

Surface Morphology During Discharge

## Summary of Anode Aging Mechanisms

### Table 1
Lithium-ion anode ageing—causes, effects, and influences

<table>
<thead>
<tr>
<th>Cause</th>
<th>Effect</th>
<th>Leads to</th>
<th>Reduced by</th>
<th>Enhanced by</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrolyte decomposition (→ SEI) (Continuous side reaction at low rate)</td>
<td>Loss of lithium</td>
<td>Capacity fade</td>
<td>Stable SEI (additives)</td>
<td>High temperatures</td>
</tr>
<tr>
<td></td>
<td>Impedance rise</td>
<td>Power fade</td>
<td>Rate decreases with time</td>
<td>High SOC (low potential)</td>
</tr>
<tr>
<td>Solvent co-intercalation, gas evolution and subsequent cracking formation in particles</td>
<td>Loss of active material (graphite exfoliation)</td>
<td>Capacity fade</td>
<td>Stable SEI (additives)</td>
<td>Overcharge</td>
</tr>
<tr>
<td></td>
<td>Loss of lithium</td>
<td></td>
<td>Carbon pre-treatment</td>
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<tr>
<td>Decrease of accessible surface area due to continuous SEI growth</td>
<td>Impedance rise</td>
<td>Power fade</td>
<td>Stable SEI (additives)</td>
<td>High temperatures</td>
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<td></td>
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<td>High SOC (low potential)</td>
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<tr>
<td>Changes in porosity due to volume changes, SEI formation and growth</td>
<td>Impedance rise</td>
<td>Power fade</td>
<td>External pressure</td>
<td>High cycling rate</td>
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<tr>
<td></td>
<td>Overpotentials</td>
<td></td>
<td>Stable SEI (additives)</td>
<td>High SOC (low potential)</td>
</tr>
<tr>
<td>Contact loss of active material particles due to volume changes during cycling</td>
<td>Loss of active material</td>
<td>Capacity fade</td>
<td>External pressure</td>
<td>High cycling rate</td>
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<td>High DOD</td>
</tr>
<tr>
<td>Decomposition of binder</td>
<td>Loss of lithium</td>
<td>Capacity fade</td>
<td>Proper binder choice</td>
<td>High SOC (low potential)</td>
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<tr>
<td></td>
<td>Loss of mechanical stability</td>
<td></td>
<td></td>
<td>High temperatures</td>
</tr>
<tr>
<td>Current collector corrosion</td>
<td>Overpotentials</td>
<td>Power fade</td>
<td>Current collector pre-treatment (?)</td>
<td>Overdischarge</td>
</tr>
<tr>
<td></td>
<td>Impedance rise</td>
<td></td>
<td></td>
<td>Low SOC (high potential)</td>
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<td></td>
<td>Inhomogeneous distribution of current and potential</td>
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</tr>
<tr>
<td>Metallic lithium plating and subsequent electrolyte decomposition by metallic Li</td>
<td>Loss of lithium (Loss of electrolyte)</td>
<td>Capacity fade</td>
<td>Narrow potential window</td>
<td>Low temperature</td>
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<td>High cycling rates</td>
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<td>Poor cell balance</td>
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<td>Geometric misfits</td>
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</tbody>
</table>

Summary of Cathode Interfacial Reactions

Base-Controlled Dendritic Growth


Fig. 9. Li plating on an MCMB electrode. The plating occurred while the voltage applied to the current collector was +2 mV, with (a) imaged about 8 h before (b). Videos showing the time dependence of the lithiation plating is available on the internet at www.lithiumontheweb.com [47].

Important Results of The Models

• Chazalviel’s Model
  - Critical Current Density: \( i^* \)
  - Dendrite Incubation Time: \( \tau_s \)
  - Deposition Rate: constant \( \nu \sim \mu_a E \)

• Monroe-Newman’s Model
  - Critical Current Density: \( 0.75i^* \)
  - Dendrite Incubation Time: \( \tau_s = 0 \)
  - Deposition Rate: accelerate
Thermodynamics of Lithium Nucleation

\[ \Delta G_T = \left( \Delta G_f + \frac{zF\eta}{\Omega} \right) S_V r^3 + S_A \gamma_{NE} r^2 + (\gamma_{SN} - \gamma_{SE}) \pi r^2 \sin^2 \theta \]

\[ S_V = \frac{\pi}{3}(2 + \cos \theta)(1 - \cos \theta)^2 \]

\[ S_A = 2\pi(1 - \cos \theta) \]

\[ \hat{\gamma} = (2 + \cos \theta) \sin^2(\theta/2) \]
Thermodynamics of Nucleation: Major Results

Nucleation is defined in terms of critical size and potential:

\[
\begin{align*}
    r_0 &= -\frac{2\gamma_{NE}\Omega}{\Omega\Delta G_f + zF\eta} \quad \text{(critical radius)} \\
    \eta_0 &= \frac{\Delta G_f\Omega}{zF} \quad \text{(critical potential)}
\end{align*}
\]

Barrier of nucleation depends on \( \eta \) and \( \theta \):

\[
\Delta \hat{G}_c = \frac{\Delta G_c}{\Delta G_0} = \frac{(2 + \cos \theta) \sin^4 \left( \frac{\theta}{2} \right)}{(1 + \hat{\eta})^2}
\]

\[
\begin{align*}
    S_V &= (\pi/3)(2 + \cos \theta)(1 - \cos \theta)^2 \\
    S_A &= 2\pi(1 - \cos \theta) \\
    \hat{\gamma} &= (2 + \cos \theta) \sin^2(\theta/2)
\end{align*}
\]
Kinetics Limited Critical Radius and Growth

\[ r(t) = -\frac{2\gamma_{NE}\Omega}{zF\eta} \left( 1 + W \left[ -\frac{zF\eta}{2\gamma_{NE}\Omega} \exp \left[ -1 - \frac{zF\eta}{2\gamma_{NE}\Omega} \left( r_0 + \frac{j_0 \Omega zF\eta t}{RT} \right) \right] \left( \frac{2\gamma_{NE}\Omega}{zF\eta} + r_0 \right) \right] \right) \]

Graph shows the relationship between \( r(t) \) and \( t \) with different initial conditions:

- \( r_0 > r_k^* \)
- \( r_0 = r_k^* \)
- \( r_0 < r_k^* \)

Other parameters include:

\[ j_0 \Delta G_f^2 \Omega^2 t \]

\[ -\frac{j_0 \Delta G_f^2 \Omega^2 t}{2\gamma_{NE} RT} \]
Summary of Growth Regimes

- Transient growth
- Steady state growth
- No growth (electrochemically isolated porosity)

\[ \frac{v}{\Delta G_f r / 2\gamma_{NE}} \geq 10^2 \tau_0 \]

\[ \frac{zF\eta}{\Delta G_f \Omega} \]

- Long incubation time (during storage)
- Short incubation time (surfaces facing the cathode)
Lithium Dendrite Inhibition

- Low Current Density Charging
- Intercalation Compound Anode
- Polymeric Solid Electrolyte
- Lithium Alloy Anode
- Additives in Electrolyte
- Pressure Application to the Cell
- Electrolyte Stirring