SPATIAL DESCRIPTION OF LITHIUM PLATING

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OVERVIEW

Timeline
- Start: October 1, 2017
- End: September 30, 2021
- Percent Complete: 75%

Budget
- Funding for FY20 – $5.5M

Barriers
- Cell degradation during fast charge
- Low energy density and high cost of fast charge cells

Partners
- Argonne National Laboratory
- Idaho National Laboratory
- Lawrence Berkeley National Lab
- National Renewable Energy Laboratory
- SLAC National Accelerator Lab
- Oak Ridge National Lab
RELEVANCE

Impact

• Avoid Li plating when fast charging Li-ion batteries
• Understand when and where Li plating occurs within cells
• Assist in identifying solutions to Li plating during fast charging.

Objective

• Build an understanding of how Li plates as a function of depth in graphite electrodes
• Map the distribution of Li plating within pouch cells
• Develop methods for operando, in situ, and ex situ detection and quantification of Li within cells.
MILESTONES

• MS 1: Identify and contrast strengths/weaknesses of nondestructive detection techniques to use on pouch cells.

• MS 2: Identify and contrast strengths/weaknesses of localized and/or destructive Li detection techniques. Identify where we can combine techniques to span length scales.

• MS 3: Combining at least 2 techniques to study when, where, and/or how Li plates on the same electrode. Combine to quantify techniques to discover detection limits.

• MS 4: Link detection of onset of Li with cell performance and other cell/cycling properties (aging).
A method to quantify the amount of plated Li, while also providing spatial and temporal insight into its presence, is sought to empower battery researchers with a means to quantitatively compare the efficacy of negative electrodes in handling fast-charge conditions while minimizing performance loss. Here, three approaches are taken to provide a quantitative spatial description of Li plating on graphite negative electrodes:

1. **Mass spectrometry titration (MST):** A post-test lab-based chemical method that quantifies inactive Li from off-gases.  
   - UC Berkeley

2. **Depth-profiling X-ray diffraction (XRD):** A synchrotron method for profiling along the depth of an electrode and measuring mass fractions of Li and graphite phases.  
   - NREL

3. **2D area profiling XRD:** A synchrotron method for mapping the quantity of Li plating and graphite phases present across the face of a pouch cell.  
   - SLAC
TECHNICAL ACCOMPLISHMENTS

Mass Spectrometry titration (MST) Approach

\[
\text{Li} + \text{H}_2\text{O} \rightarrow \text{LiOH} + ^1\text{H}_2
\]

\[
\text{Li}_x\text{C}_6 + x\text{H}_2\text{O} \rightarrow x\text{LiOH} + \text{C}_6 + \frac{x}{2}\text{H}_2
\]

\[
\text{ROCOO Li} + \text{H}^+ \rightarrow \text{ROH} + \text{Li}^+ + \text{CO}_2
\]

**Acid titration quantifies:**
- Inactive Li
- SEI ROCOOLi

**Fast charge (4C)**

**Plating onset at 85% SOC**
TECHNICAL ACCOMPLISHMENTS

MST to quantify heterogeneity in Li plating

<table>
<thead>
<tr>
<th>Region</th>
<th>Li + “dead” Li$_x$C$_6$ (μmol/cm$^2$)</th>
<th>Titration CO$_2$ (μmol/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>7.30</td>
<td>0.713</td>
</tr>
<tr>
<td>B</td>
<td>34.7</td>
<td>2.30</td>
</tr>
<tr>
<td>C</td>
<td>61.6</td>
<td>3.20</td>
</tr>
<tr>
<td>D</td>
<td>37.7</td>
<td>2.39</td>
</tr>
<tr>
<td>E</td>
<td>21.6</td>
<td>2.49</td>
</tr>
<tr>
<td>F</td>
<td>45.4</td>
<td>3.76</td>
</tr>
</tbody>
</table>

Capacity Fade: **22.4%**

Equivalent Li + Li$_x$C$_6$ Capacity Fade: **16.4%**

Capacity fade difference related to SEI formation

More carbonate species in high-Li regions
TECHNICAL ACCOMPLISHMENTS

High speed X-ray diffraction (XRD) depth profiling

- Modified 2032 coin cell with 4-mm diameter electrode
- 6C charge and discharge
- High-speed (100 Hz) and resolution (3 µm) at ESRF – The European Synchrotron
- 0.5 seconds for complete depth scan
- 13 seconds between scans

6C charge (red)
- 6C CC charge to 4.1 V, CV to C/5

2C charge (blue)
- 2C CC charge to 4.4 V, CV to C/5

Negative electrode:
- 91.83 wt%
- Superior graphite SLC1520P
- Thickness: 101 µm
- Porosity: 36.2%
- Loading: 13.97 mg/cm²
- Coating density: 1.38 g/cm³

Beam conditions:
- 60 keV beam
- 0.6 µm × 0.3 µm beam
- 3 µm step sizes
- 148 XRD points at 100 Hz
- 1.5 s per line scan
- 13 s between line scans
TECHNICAL ACCOMPLISHMENTS

Quantifying lithiation gradients

- Lithiation quantified for depth and time
- Contributions from distinct graphite phases quantified
  - Stage I (LiC₆)
  - Stage II (LiC₁₂)
  - Stage III (LiC₃₀)

6C charge
Lithiation state in depth and time

6C charge
Contribution to x in LiₓC₆ from distinct phases

Copper
Graphite
Separator

Color-coded depth

Contribution from Stage I
Contribution from Stage II
Contribution from Stage IV/III
TECHNICAL ACCOMPLISHMENTS

Quantifying Li plating gradients

- Li plating was detected but the signal was faint
- Data were summed across 3 depths and 5 times (15 point measurements) to improve signal-to-noise ratio
- Weight fractions of Li were quantified for depth and time.
• Round II cells
• Transmission mode scans → no teardown of cell; all components of cell studied simultaneously

TECHNICAL ACCOMPLISHMENTS

Quantifying spatial heterogeneities in Li plating using X-ray diffraction (XRD)

- 4C, 6C, and 9C charging rates
- 450 extreme fast charge (XFC) cycles
- All scans done at 0% SOC (3.0 V)
Loss mechanisms:

- Dead (irreversibly plated) Li
- Prevents deintercalation of Li (trapped Li as C₆Li) → loss of Li inventory
- Dead anode regions → loss of active surface area
- SEI-related reactions are not accounted for (nanocrystalline/amorphous)

Charging time: 10 min, 28% capacity fade

**TECHNICAL ACCOMPLISHMENTS**

Spatial correlations between species
• Independence of intensity and location of regions of plated Li with angle of incidence (between X-ray beam and pouch cell)

• Plated Li is polycrystalline, without any preferred crystallographic orientation.
Correlating Li plating to global cell performance

Irreversible Li plating $\alpha$ XFC capacity fade

- 4C charged cells show lower plating in general, irrespective of capacity fade
- For 6C and 9C cells, the capacity fade during XFC $\alpha$ amount of irreversible Li plating
- Large heterogeneity in Li plating (and performance) of 9C cells.
RESPONSES TO PREVIOUS YEAR REVIEWERS’ COMMENTS

• This topic was not reviewed last year
COLLABORATION AND COORDINATION WITH OTHER INSTITUTIONS

• Mass Spectroscopy Titration experiments were led by Bryan McCloskey at University of California Berkeley.

• Depth profiling X-ray diffraction experiments were led by Donal Finegan at the National Renewable Energy Laboratory (NREL).

• X-ray diffraction of pouch cells was led by Partha Paul at Stanford Linear Accelerator (SLAC).
REMAINING CHALLENGES AND BARRIERS

- Understand why Li plates unevenly throughout pouch cells.
- Gain insight into how Li nucleates on graphite.
- Understand how Li plating changes over many cycles.
- Construct modelling methods that can predict experimental observations of Li plating.
PROPOSED FUTURE RESEARCH

MST FUTURE WORK
• Quantify inactive Li and SEI species spatially as a function of cycles
  o Post-formation, 75, 225 cycle pouch cells from Idaho National Laboratory
• Correlate spatial degradation on anode and cathode
  o Cut anode and cathode symmetrically, quantify carbonate species on cathode surface with similar titration
  o Correlate high-carbonate areas on cathode to inactive Li and SEI on corresponding region of anode.

XRD FUTURE WORK
• Use retrieved data to guide and validate models to more accurately predict Li plating
• Integration of cathode analysis along with anode analysis → role of cathode in degradation in Round II cells
• XRD in pristine condition and after XFC cycling → role of initial cell state (as measurable by XRD) in plating heterogeneity across the electrode
• Evolution of degradation mechanisms (dead and trapped Li) with increasing cycles → XRD on same cell after 10 s of cycles
• Mechanism for cell capacity (reversible plating/stripping vs. intercalation/deintercalation into graphite) → XRD on same cycle at different SOCs
• Probe heterogeneity of plating along depth of the electrode → X-ray and neutron imaging on selected portions of the anode.

Any proposed future work is subject to change based on funding levels.
SUMMARY

- Lab-based and synchrotron techniques can effectively map the quantity and location of Li plating.
- Li plating occurs mostly near the separator interface of the graphite electrode, reaching about 20 µm deep.
- In pouch cells, Li plating occurs unevenly with higher quantities observed near the center of the electrode sheets.
- Some regions in the graphite anode become less active after cycling at high rates.
- Plated Li is polycrystalline without any preferred orientations.
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