METHODS FOR THE DETECTION AND QUANTIFICATION OF LITHIUM PLATING

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OVERVIEW

Timeline
- Start: October 1, 2017
- End: September 30, 2021
- Percent Complete: 94%

Budget
- Funding for FY20 – $5.6M

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
- Decrease charging time without sacrificing lifetime
- Connect Li plating to cell degradation mechanisms
- Identify and mitigate unfavorable Li plating to reduce capacity fade from extreme fast charging (XFC)

Objectives
- Develop approaches to accurately detect and quantify Li deposition during extreme fast charge conditions
- Link detection of onset of Li with cell performance, age, and local heterogeneity
# MILESTONES

## High level Li detection related milestones in XCEL

<table>
<thead>
<tr>
<th>Milestone</th>
<th>End Date</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Determine where the lost Li inventory is trapped using a combination of at least two Li detection techniques.</td>
<td>12/31/2020</td>
<td>Completed</td>
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<tr>
<td>2. Submit review paper on Li detection techniques which will outline where each technique is in terms of detection accuracy and correlations between multiple techniques.</td>
<td>12/31/2020</td>
<td>Completed</td>
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<tr>
<td>3. Connect “dead Li” to cycling age and determine if dead Li accelerates additional Li plating. Understand how intentional Li plating in the first few cycles affects future capacity fade during standard CCCV cycling.</td>
<td>6/30/2021</td>
<td>On Track</td>
</tr>
<tr>
<td>4. Identify if and what are the early warning signs of Li plating for different Li detection techniques. Identify which detection techniques that could be incorporated on a vehicle.</td>
<td>6/30/2021</td>
<td>On Track</td>
</tr>
<tr>
<td>5. Determine if the hero cell-1 plates less Li or later in life or SOC compared to R-II cells?</td>
<td>9/30/2021</td>
<td>On Track</td>
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Any proposed future work is subject to change based on funding levels.
Leveraging different Li detection techniques to answer:

- Where is the lost Li inventory trapped?
  - Combine multiple detection techniques to gain holistic understanding of degradation processes during fast charge
- What *operando*, readily accessible techniques could be used for early detection?
  - Explore inexpensive, non-invasive detection & connect to modeling
- Will a small amount of Li plating result in irreversible damage contributing to cell failure?
XRD quantification of dead Li

- Depth-averaged XRD gives ‘quantitative’ spatial maps of crystalline Li-containing species
- When summed up over the cell, we can get the total amount of such species over the cell

Dead (plated) Li

Dead LiC$_6$

NMC532/Graphite Round 2 pouch cell after 450 XFC
Mass Spectrometry Titration (MST)

Graphite anodes from NMC532/Gr Round 2 pouch cell after 450 XFC

After 450 XFC cycles (6C charge, C/2 discharge)

- Plated Li
- $\text{Li}_x\text{C}_6$
- Solid Carbonates
- $\text{Li}_2\text{C}_2$
- Other (LiF, Li$_2$O, soluble species, etc.)
Other Li species – XPS depth profiling

Atomic concentration from surface to bulk

Detailed peak fitting of Li1s region

- Cannot compare same electrode as MST and XPS depth profiling are destructive
- But estimate of undetectable species (LiF, Li₂O, etc.) reasonable

Graphite anodes after 50 XFC (NMC532/Gr Round 2 coin cell)
dQ/dV and dOCV sensitive to cycling conditions

**dQ/dV:**
- reliable at low C-rates
- disappears at moderate/high rates

**dOCV/dt:**
- reliable at low & moderate C-rates
- signal highly variable at high C-rates and disappears after a few cycles

For confident detection, need multi-modal EC approach that includes modeling
Galvanostatic impedance

Measure impedance during fast charging

- Fast impedance scans (~6 s/scan) at up to 6C
- Increase in graphite solid electrolyte interphase resistance ($R_{\text{SEI}}$) indicates plating
- Cross-validation with MST suggests detection sensitivity: <0.5% of graphite
- Ongoing work:
  - Implement in 2 electrode full cells
  - Detection of plating in aged cells
  - Detection during CCCV (currently only CC)
SOC sweep protocol to detect onset with CE’s
Graphite/Li coin cell to determine Li plating onset during CC charging

Protocol overview
Three C/10 formation
Fast charge cycling at 5-10% increments
All C/5 deintercalation, OCV between steps

Convert CE% to normalized irreversible Li plating
Li plating onset with CE experiments & modeling

Estimate irreversible Li plating from coulombic inefficiencies

Define 0.1 mol% as the onset charge capacity, state-of-charge (SOC)

Mapping Li plating onset

Onset as a function of: C-rate, temperature, loading

Model development will be invaluable for full-cell plating predictions
Map Li Concentration Gradient in Anode

Stronger gradient precursor to Li plating

thermal wave sensor:

Typically
0.01 Hz – 100 Hz

cross section view

Points = sensor measurements
Shading = agnostic predictions from
electrochemical simulations

\[ \text{In-Phase Data} \]
\[ \text{Out-of-Phase Data} \]

Voltage, \( V_{\text{th}} \) [mV]

Heating Frequency, \( f \) [Hz]

Local relative Li concentration

1C charging

\[ \text{Very bad} \]
\[ \text{Less good} \]
\[ \text{Ok} \]

66% SOC
47% SOC
28% SOC

thermal wave sensor:
Pressure evolution with cycling

Pressure changes at discharged state correlate with dead Li

30 psi  3rd cycle  6th cycle  8th cycle  10th cycle  10th cycle

Average pressure vs. time

0 psi

Graphite

Voltage vs. time
Does Li plating create irreversible damage?

Preliminary electrochemical results for two cases studied

- **Case 1**: plate small amount of Li then cycle cell under “safe” (no plating) conditions
  - No additional Li is plated while cycling
  - No effect on long term capacity

- **Case 2**: repeatedly expose cell to plating conditions
  - Each cycle results in more irreversible plating per exposure

➢ **Preliminary conclusion**: small amounts of Li plating may not necessarily trigger cell failure

**System**: Coin-cells (no spring) LFP vs. Round 1 graphite (N/P <<1)
Responses to previous year reviewers’ comments

Not reviewed last year
COLLABORATION ACROSS LABS AND UNIVERSITIES

Argonne National Laboratory

Cell and electrode design and building, performance characterization, post-test, cell and atomistic modeling, cost modeling

Performance characterization, failure analysis, electrolyte modeling and characterization, Li detection, charging protocols

Li detection, electrode architecture, diagnostics

Idaho National Laboratory

Thermal characterization, life modeling, micro and macro scale modeling, electrolyte modeling and characterization

Detailed Li plating kinetic models, SEI modeling

Berkeley Lab

Li detection, novel separators, diagnostics

National Renewable Energy Laboratory

Oak Ridge National Laboratory

SLAC National Accelerator Laboratory

XCEL Energy

BYU

ESRF

UCL

VEHICLE TECHNOLOGIES OFFICE
Remaining Challenges and Barriers

- Does the nature of lost Li inventory (metal, SEI, etc.) correlate to capacity fade or cycling conditions?
- How can we use models in combination with electrochemistry techniques as a reliable, readily-accessible, multimodal Li detection technique?
  - Should work with both new and aged cells
  - Should work under realistic charging conditions
- Can we find a reliable predictor of Li plating?
- How does Li plating (and stripping efficiency) evolve with battery age

Any proposed future work is subject to change based on funding levels
Next steps

- Connect differences in SEI components and Li plating to capacity fade and cycle rate (XRD/MST analyses)
- Compare relative differences in SEI components with cycling temperature (30°C vs. 45°C) with XPS depth profiling
- Study reversibility of Li plating and Li_xC with XPS depth profiling and in situ XRD mapping
- Leverage models to extend the limitations of echem detection methods
- Quantify how much Li plating is acceptable before irreversible damage
- Compare Li plating conditions of “hero” cell compared to round 2 cells

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

- Identify and contrast approaches to accurately detect and quantify Li plating during extreme fast charge conditions resulting in a review paper
- Holistic approach to determine where the lost Li inventory is trapped
- Shown standard electrochemical techniques don’t work in all cycling conditions
  - Need to combine techniques and support with robust modeling
- Small amounts of reversible Li plating does not contribute to long term capacity fade
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TECHNICAL BACKUP SLIDES
Ongoing work: Perform similar analyses on 3 additional electrodes with varying amounts of plating
• Li plating detection with dQ/dV technique sensitive to cycling conditions
• Reliable at low C-rate conditions but disappears at moderate and high C-rate conditions even with Li plating
LITHIUM PLATING DETECTION

- Li plating detection with dOCV/dt technique sensitive to cycling conditions
- Reliable at low and moderate C-rate conditions
- High C-rate conditions makes signal highly variable and vanishes after few cycles
- Multi-modal EC techniques helps to improve Li plating identification and improves confidence in EC detection sensitivity and reliability
Galvanostatic impedance

- Current work is in 3-electrodes cells
- We have also demonstrated that technique works, in principle, for 2-electrode full cells
- Implementing with CCCV cycling in future
Thermal Wave Sensors

Thermal wave frequency controls measurement

Cross Section View

Typically 0.01 Hz – 100 Hz