PROJECT ID # BAT458
U.S. DEPARTMENT OF ENERGY
VEHICLE TECHNOLOGIES OFFICE ANNUAL MERIT REVIEW
JUNE 1–4, 2020

XCEL
eXtreme Fast Charge Cell Evaluation of Lithium-ion Batteries

SPATIAL DESCRIPTION OF LITHIUM PLATING

DONAL FINEGAN
National Renewable Energy Laboratory (NREL)

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy
VEHICLE TECHNOLOGIES OFFICE
Argonne NATIONAL LABORATORY
SLAC NATIONAL ACCELERATOR LABORATORY
NREL NATIONAL RENEWABLE ENERGY LABORATORY
BERKELEY LAB Lawrence Berkeley National Laboratory
INL Idaho National Laboratory

OVERVIEW

Timeline

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

Barriers

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

Budget

- Funding for FY20 – $5.5M

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).

APPROACH

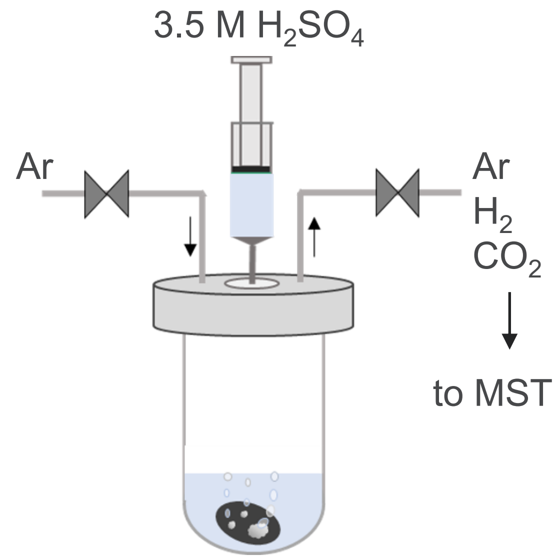
Creating a spatial description of Li plating

- 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

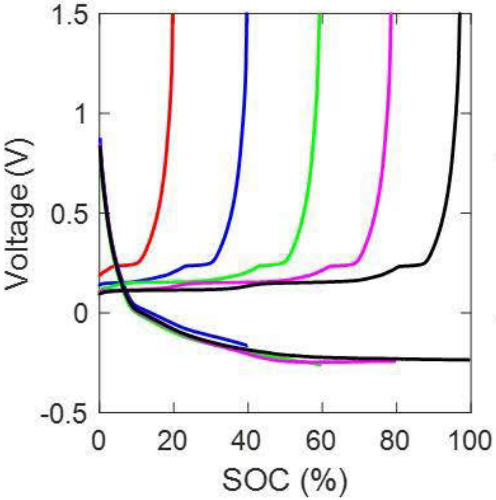
Mass Spectrometry titration (MST) Approach



$Li + H_2O \rightarrow LiOH + \frac{1}{2}H_2$

$Li_xC_6 + xH_2O \rightarrow xLiOH + C_6 + \frac{x}{2}H_2$

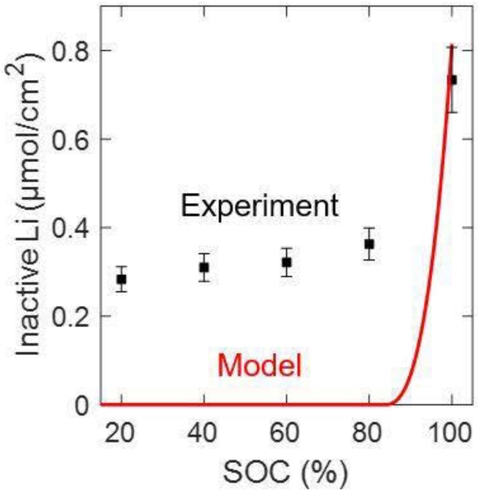
$ROCOOLi + H^+ \rightarrow ROH + Li^+ + CO_2$



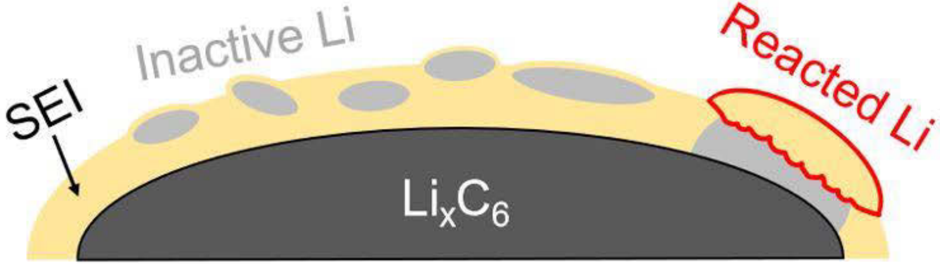
Fast charge (4C)

→

Acid titration quantifies:
-Inactive Li
-SEI ROCOOLi

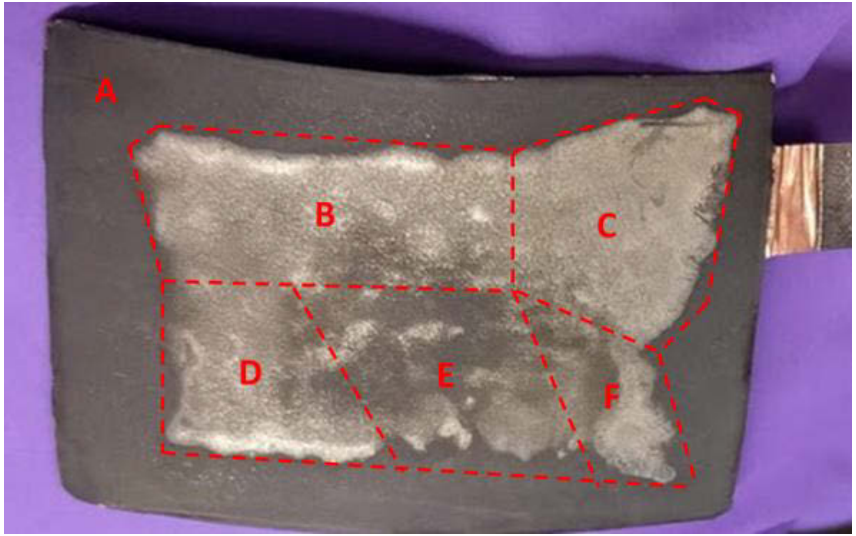


Plating onset at 85% SOC



TECHNICAL ACCOMPLISHMENTS

MST to quantify heterogeneity in Li plating



Capacity Fade: **22.4%**

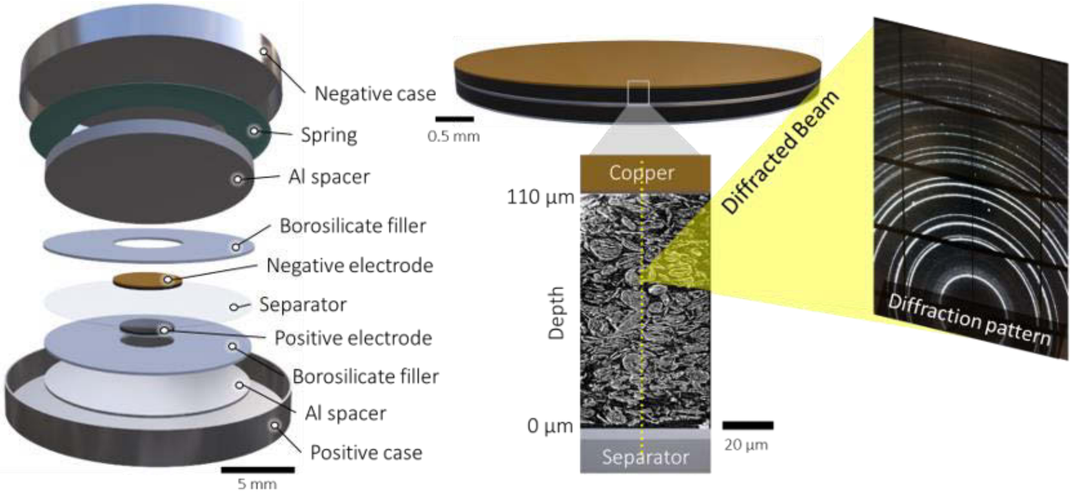
Region	Li + "dead" Li_xC_6 ($\mu mol/cm^2$)	Titration CO_2 ($\mu mol/cm^2$)
A	7.30	0.713
B	34.7	2.30
C	61.6	3.20
D	37.7	2.39
E	21.6	2.49
F	45.4	3.76

Equivalent Li + Li_xC_6 Capacity Fade: **16.4%**
Capacity fade difference related to SEI formation
More carbonate species in high-Li regions

TECHNICAL ACCOMPLISHMENTS

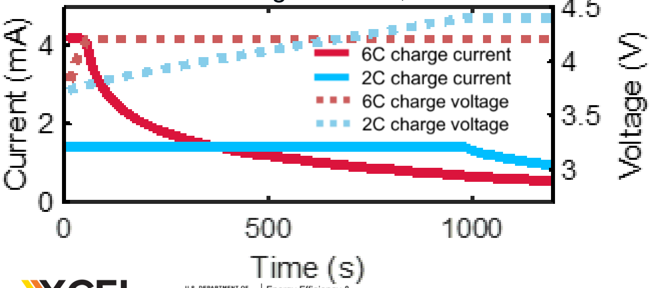
High speed X-ray diffraction (XRD) depth profiling

- 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



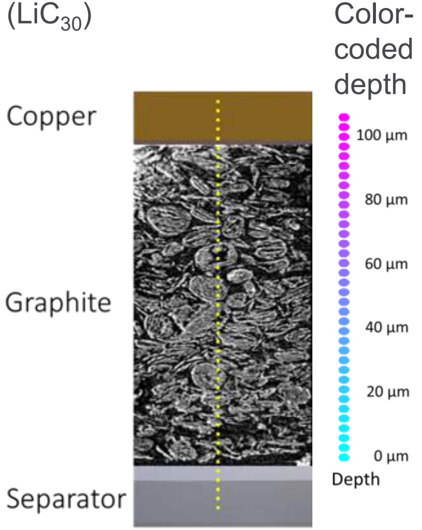
Negative electrode:
- 91.83 wt%
- Superior graphite SLC1520P
- Thickness: 101 μm
- Porosity: 36.2%
- Loading: 13.97 mg/cm^2
- Coating density: 1.38 g/cm^3

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

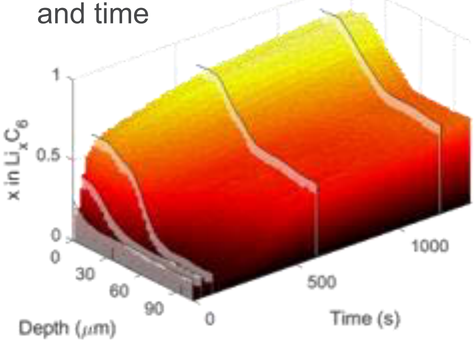
Quantifying lithiation gradients

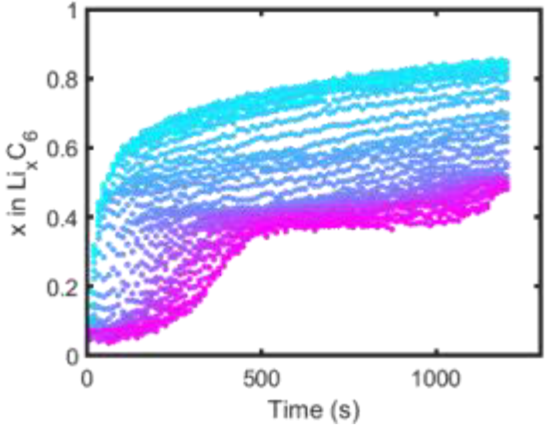
- Lithiation quantified for depth and time
- Contributions from distinct graphite phases quantified
  - Stage I (LiC_6)
  - Stage II (LiC_{12})
  - Stage III (LiC_{30})



6C charge

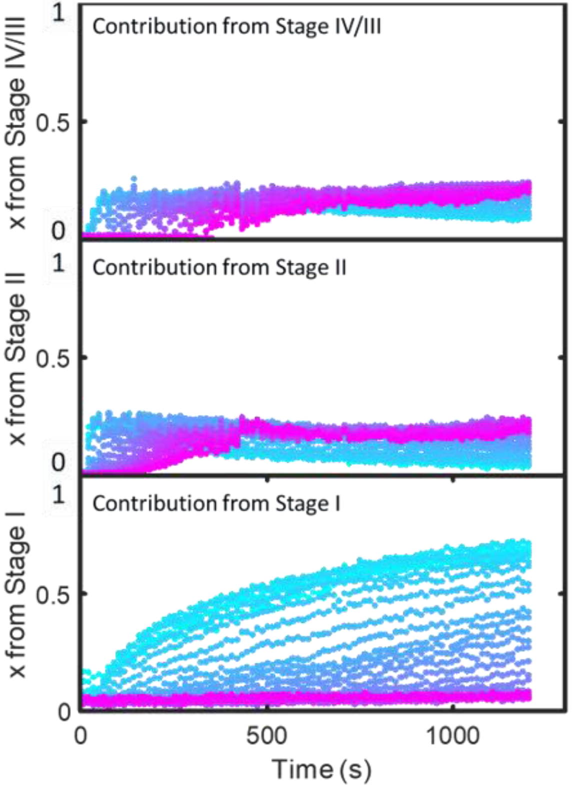
Lithiation state in depth and time





6C charge

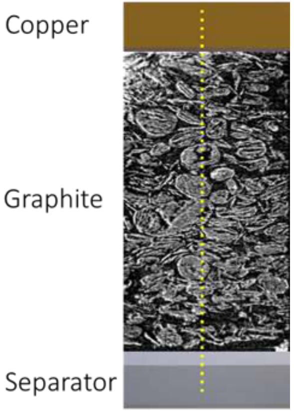
Contribution to x in Li_xC_6 from distinct phases

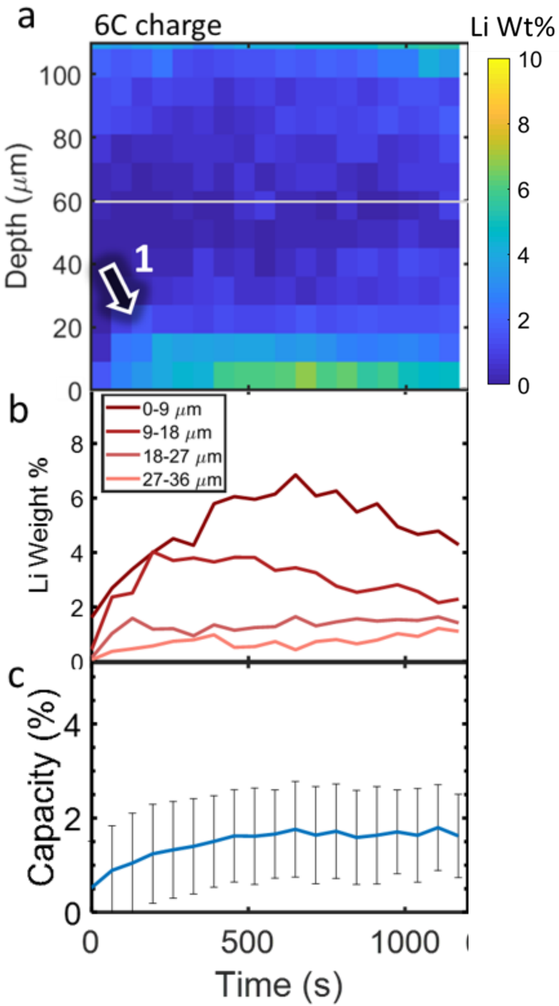


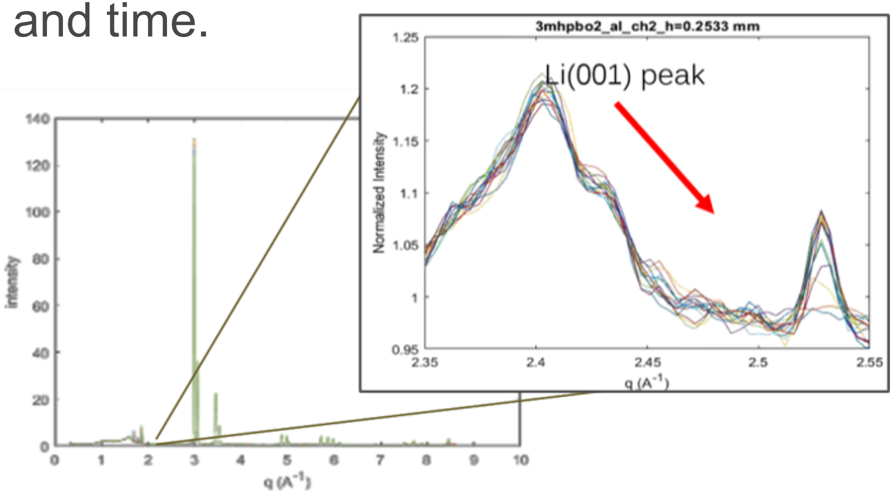
TECHNICAL ACCOMPLISHMENTS

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.

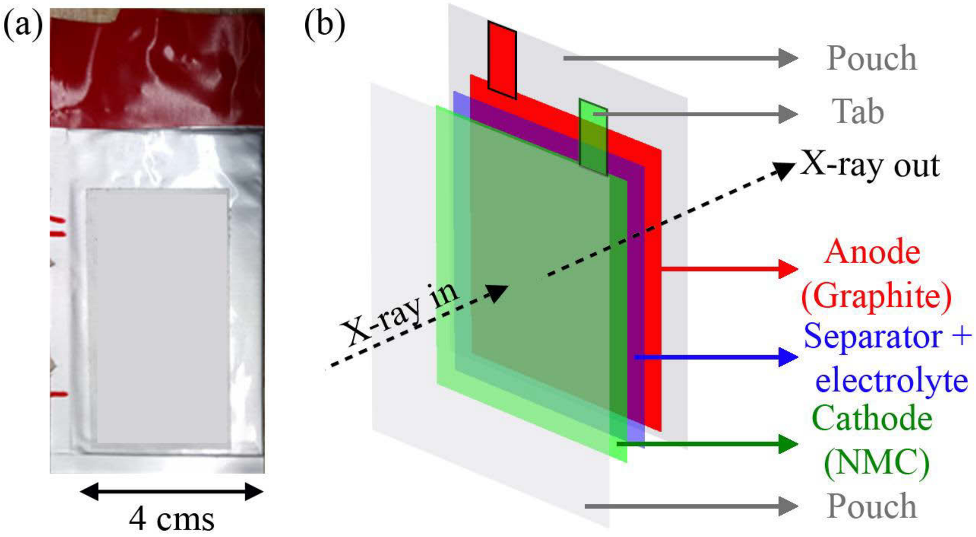


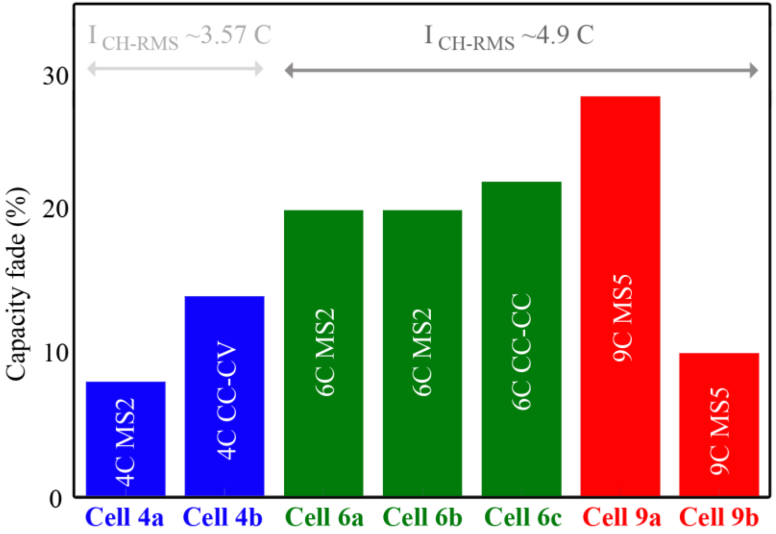




TECHNICAL ACCOMPLISHMENTS

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





- Round II cells
- Transmission mode scans → no teardown of cell; all components of cell studied simultaneously

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

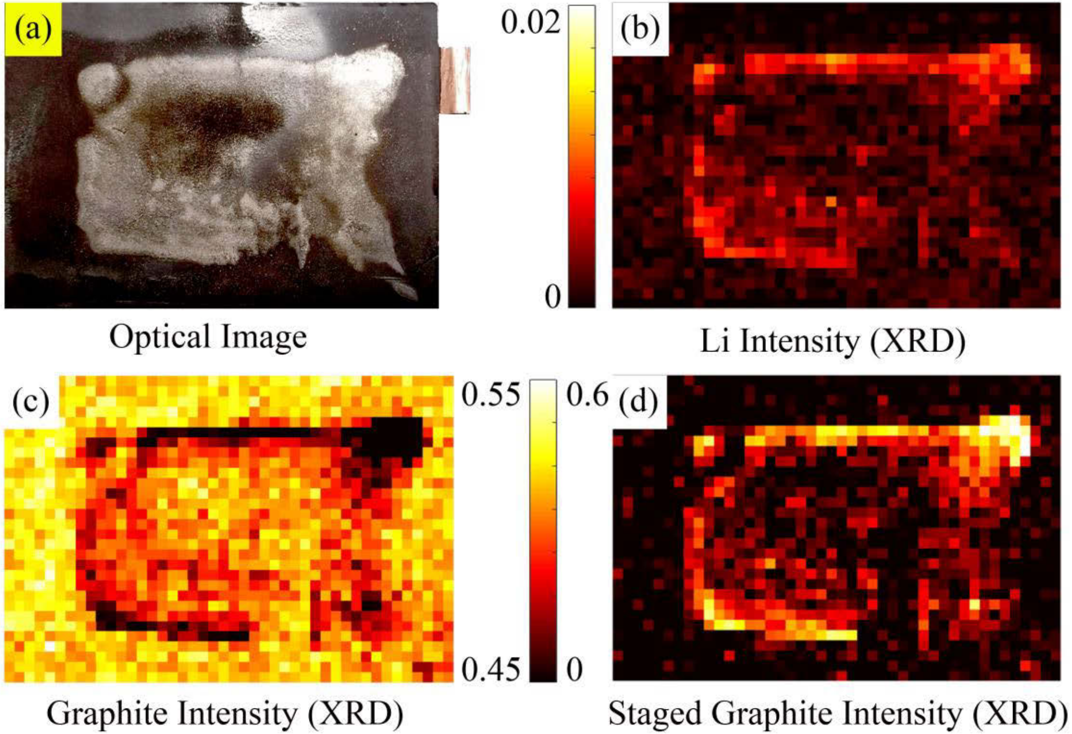
TECHNICAL ACCOMPLISHMENTS

Spatial correlations between species

Loss mechanisms:

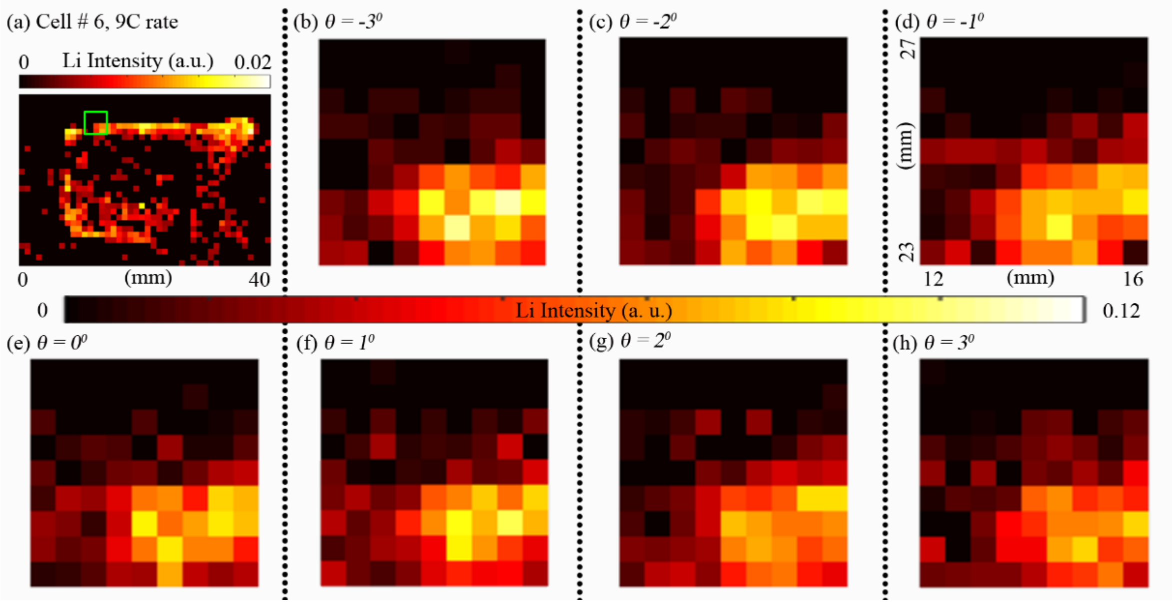
- Dead (irreversibly plated) Li
- Prevents deintercalation of Li (trapped Li as C_6Li) → loss of Li inventory
- Dead anode regions → loss of active surface area
- SEI-related reactions are not accounted for (nanocrystalline/amorphous)

Charging time: **10 min, 28%** capacity fade



TECHNICAL ACCOMPLISHMENTS

Crystallographic orientations of plated Li on graphite



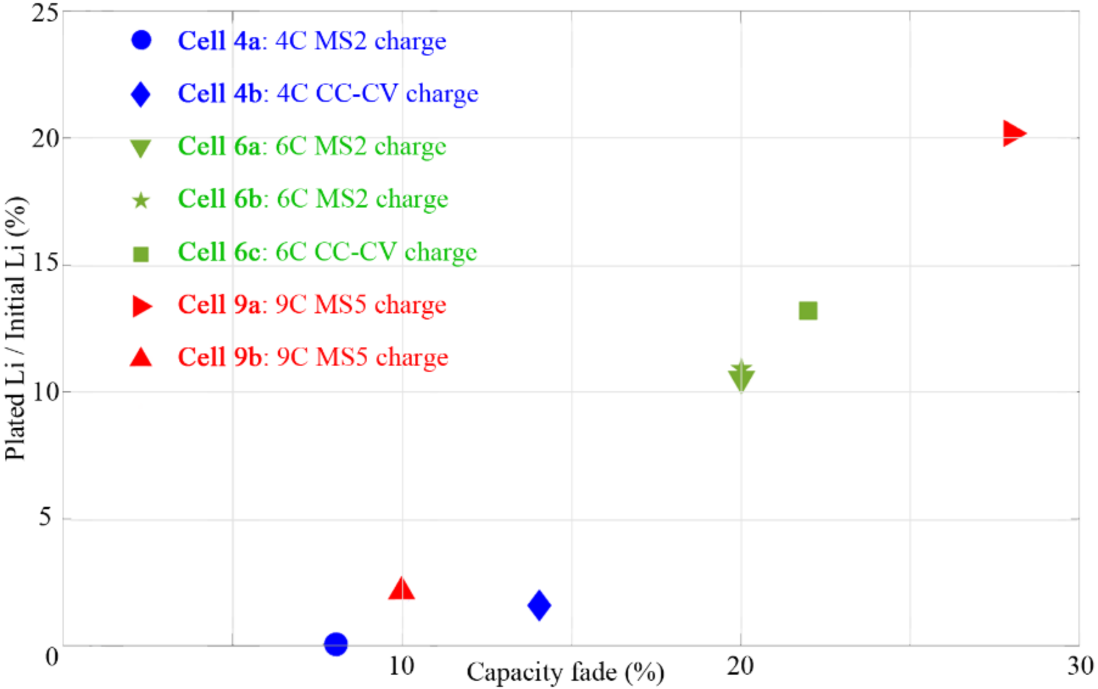
- Independence of intensity and location of regions of plated Li with angle of incidence (between X-ray beam and pouch cell)
- Plated Li is polycrystalline, without any preferred crystallographic orientation.

TECHNICAL ACCOMPLISHMENTS

Correlating Li plating to global cell performance

Irreversible Li plating *α* 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 *α* 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
    - Post-formation, 75, 225 cycle pouch cells from Idaho National Laboratory
- Correlate spatial degradation on anode and cathode
    - Cut anode and cathode symmetrically, quantify carbonate species on cathode surface with similar titration
    - 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.

CONTRIBUTORS AND ACKNOWLEDGEMENTS

Abhi Raj
Alison Dunlop
Alex Quinn
Andy Jansen
Andrew Colclasure
Antony Vamvakeros
Anudeep Mallarapu
Aron Saxon
Bryan McCloskey
Bryant Polzin
Chuntian Cao
Charles Dickerson
Daniel Abraham
Daniel Steingart
Dave Kim
David Brown
David Robertson
David Wragg
Dean Wheeler
Dennis Dees
Donal Finegan
Eongyu Yi
Eric Dufek
Eric McShane
Eva Allen
Francois Usseglio-Viretta
Guoying Chen
Hakim Iddir
Hans-Georg Steinrück
Hansen Wang
Harry Charalambous
Ilya Shkrob
Ira Bloom
James W. Morrissette
Jiayu Wan
Jeffery Allen
Johanna Nelson Weker
Josh Major
John Okasinski
Juan Garcia
Kae Fink
Kandler Smith
Kamila Wiaderek
Kevin Gering
Maha Yusuf
Marca Doeff
Marco DiMichiel
Marco Rodrigues
Matt Keyser
Michael Evans
Michael Toney
Nancy Dietz Rago
Ning Gao
Nitash Balsara
Orkun Fura
Partha Mukherjee
Partha Paul
Parameswara Chinnam
Paul Shearing
Pierre Yao
Quinton Meisner
Ravi Prasher
Robert Kostecki
Ryan Brow
Sang Cheol Kim
Sangwook Kim
Sean Wood
Seoung-Bum Son
Shabbir Ahmed
Sean Lubner
Shriram Santhanagopalan
Srikanth Allu
Steve Trask
Susan Lopykinski
Tanvir Tanim
Uta Ruett
Venkat Srinivasan
Victor Maroni
Vince Battaglia
Vivek Bharadwaj
Vivek Thampy
Volker Schmidt
Wei Tong
Weijie Mai
Wenxiao Huang
William Chueh
William Huang
Xin He
Yang Ren
Yanying Zhu
Yi Cui
Yifen Tsai
Zachary Konz
Zhenzhen Yang

Support for this work from the Vehicle Technologies Office, DOE-EERE – Samuel Gillard, Steven Boyd, David Howell

This work was authored in part by the National Renewable Energy Laboratory, operated by Alliance for Sustainable Energy, LLC, for the U.S. Department of Energy (DOE) under Contract No. DE-AC36- 08GO28308. Funding provided by the DOE Office of Energy Efficiency and Renewable Energy, Vehicle Technologies Office (VTO). The views expressed in the article do not necessarily represent the views of the DOE or the U.S. Government. The U.S. Government retains and the publisher, by accepting the article for publication, acknowledges that the U.S. Government retains a nonexclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this work, or allow others to do so, for U.S. Government purposes.

NREL/PR-5400-76737

XCEL

eXtreme Fast Charge Cell Evaluation of Lithium-ion Batteries

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

VEHICLE TECHNOLOGIES OFFICE

Argonne NATIONAL LABORATORY

SLAC NATIONAL ACCELERATOR LABORATORY

NREL NATIONAL RENEWABLE ENERGY LABORATORY

BERKELEY LAB Lawrence Berkeley National Laboratory

INL Idaho National Laboratory