XCEL
eXtreme Fast Charge Cell Evaluation of Lithium-ion Batteries

BAT339

IMPACT OF ANODE DESIGN ON FAST CHARGE PERFORMANCE

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June 12, 2019
Crystal City, VA

OVERVIEW

Timeline

- Start: October 1, 2017
- End: September 30, 2021
- Percent Complete: 37%

Barriers

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

Budget

- Funding for FY19 – 6390k
  - ANL – 2400k
  - NREL – 1600K
  - INL – 440K
  - SLAC – 1000K
  - LBNL – 950K

Partners

- Argonne National Laboratory
- Idaho National Laboratory
- Lawrence Berkeley National Lab
- National Renewable Energy Laboratory
- SLAC National Accelerator Lab

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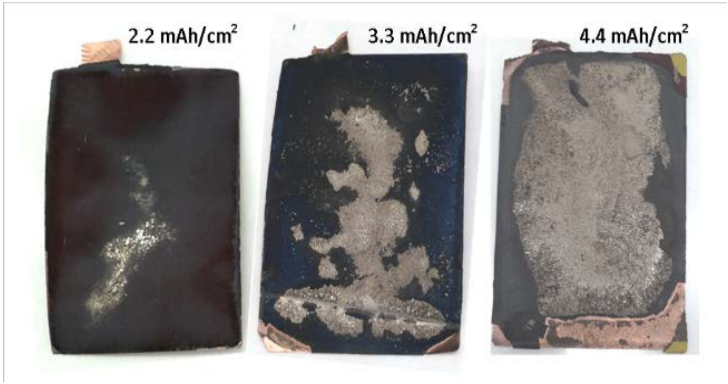
RELEVANCE

- Fast charging at rates over 2C can result in lithium plating on typical negative electrodes.
- Lithium plating is more likely with thicker electrodes and lower temperature.
- High tortuosity in the anode is also likely to favor lithium plating.
- Carefully selected design of experiments that include modeling, fabrication and testing of prototype cells, and post-test diagnostics are needed to develop a cell system that minimizes the possibility of lithium plating in EV batteries.



Gallagher, *et al., JES* 2016

OBJECTIVE

- The objective of this effort is to identify the causes of lithium plating on tailor-made graphitic anodes under fast charge conditions, and provide this information to XCEL teams to develop methods that enable fast charge.

APPROACH

- Argonne's CAMP Facility will develop advanced prototype electrodes and cells and provide them to the XCEL teams for their studies that include application of *operando* reference electrodes and XRD measurements during fast charge cycling
  - Baseline system is single-sided single-layer pouch cells with SLC1506T graphite vs. NMC532 at electrode loadings between 2 and 4 mAh/cm^2.
- Post-Test materials characterization to confirm and quantify the presence of lithium plating.
- These results are supplied to modeling teams for their feedback.

MILESTONES

Related milestones in XCEL

Milestone	End Date	Status
Fabricate pouch cells using baseline set of graphite and NMC electrodes with varying anode porosity for extended testing at INL/Argonne.	12/31/2018	Completed
Reference electrode cycling.	3/30/2019	Completed
Develop methods to modify the anode tortuosity/electrode structure to enable charge rates faster than FY18 baseline. Deliver pouch cells with these prototype electrodes to INL/Argonne for extended testing.	6/30/2019	On Track
Rationalize performance and degradation experimental findings from NREL, Argonne and Idaho National Labs using models to explain underlying mechanisms behind observed electrochemical performance and degradation.	6/30/2019	On Track

CAMP FACILITY ANODE DEVELOPMENT WORK

BASELINE ELECTRODES USED FOR FY18

19 mAh capacity in baseline xx3450 Single-Layer Pouch cells

Anode: A-A015

91.83 wt% Superior Graphite SLC1506T
2 wt% Timcal C45 carbon
6 wt% Kureha 9300 PVDF Binder
0.17 wt% Oxalic Acid

Lot#:1506-01 received 02/04/2015
Electrode ID: LN3107-110-5
"SS = single-side, DS = double-side"

Cu Foil Thickness: 10 µm
Total Electrode Thickness: 57 µm
Total Coating Thickness: 44 µm
Porosity: 37.4 %
Total SS Coating Loading: 6.38 mg/cm^2
Total SS Coating Density: 1.36 g/cm^3
Made by CAMP Facility

Cathode: A-C013B

90 wt% Toda NMC 532
5 wt% Timcal C45
5 wt% Solvay 5130 PVDF

Matched for 4.2V full cell cycling
Prod:NCM-04ST, Lot#:7720301, Elect:LN3107-141-3

Al Foil Thickness: 20 µm
Al Foil Loading: 5.36 mg/cm^2
Total Electrode Thickness: 62 µm
Coating Thickness: 42 µm
Porosity: 33.1 %
Total Coating Loading: 11.40 mg/cm^2
Total Coating Density: 2.71 g/cm^3
Made by CAMP Facility

Referred to as "Round 1" (2 mAh/cm^2 anode loading)

BASELINE ELECTRODES USED FOR FY19

32 mAh capacity in baseline xx3450 Single-Layer Pouch cells

Anode: LN3107-190-4A

91.83 wt% Superior Graphite SLC1506T
2 wt% Timcal C45 carbon
6 wt% Kureha 9300 PVDF Binder
0.17 wt% Oxalic Acid

Lot#: 573-824, received 03/11/2016
Single-sided coating, CFF-B36 anode

Cu Foil Thickness: 10 µm
Total Electrode Thickness: 80 µm
Total Coating Thickness: 70 µm
Porosity: 34.5 %
Total SS Coating Loading: 9.94 mg/cm^2
Total SS Coating Density: 1.42 g/cm^3

Made by CAMP Facility

Cathode: LN3107-189-3

90 wt% Toda NMC532
5 wt% Timcal C45
5 wt% Solvay 5130 PVDF

Matched for 4.1V full cell cycling
Prod:NCM-04ST, Lot#:7720301
Single-sided coating, CFF-B36 cathode

Al Foil Thickness: 20 µm
Al Foil Loading: 5.39 mg/cm^2
Total Electrode Thickness: 91 µm
Coating Thickness: 71 µm
Porosity: 35.4 %
Total Coating Loading: 18.63 mg/cm^2
Total Coating Density: 2.62 g/cm^3

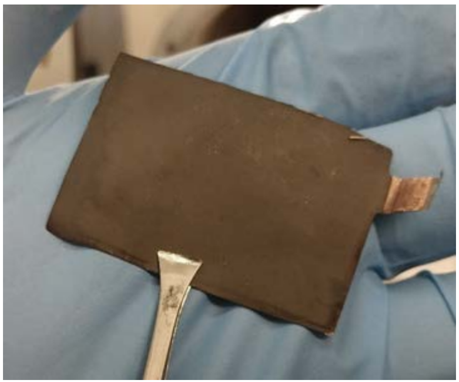
Made by CAMP Facility

Referred to as “Round 2” (3 mAh/cm^2 anode loading)

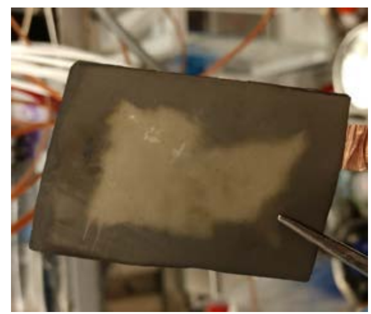
INCREASING CAPACITY LOADING LEADS TO MORE LITHIUM PLATING

Need to develop anodes with electrode structures that minimize lithium plating at higher loadings

2 mAh/cm²



3 mAh/cm²



CHANGE ANODE POROSITY - XX3450 SLP CELLS

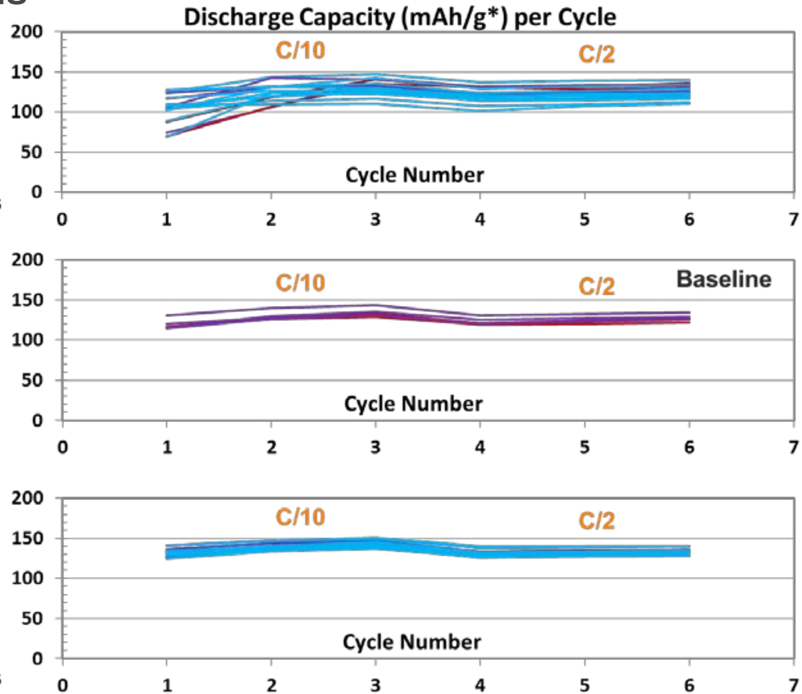
Test effect of porosity (thickness) by altering calendering of Round 2 anodes to 26%, 36% (baseline), and 47% porosities

Cells provided to teams

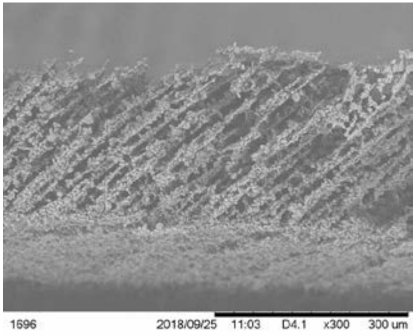
CFF-B36-LOW
26.1% Porosity
555 µL of Gen2
(4.13 PVF)
18 S.L. Pouch Cells

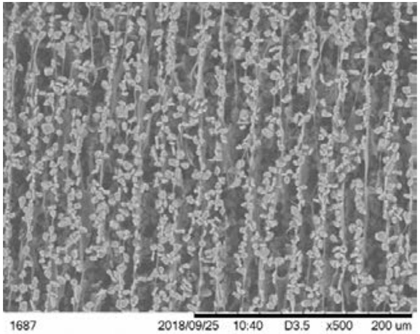
CFF-B36A
36.4% Porosity
615 µL of Gen2
(4.12 PVF)
6 S.L. Pouch Cells

CFF-B36-HIGH
47.3% Porosity
710 µL of Gen2
(4.14 PVF)
18 S.L. Pouch Cells

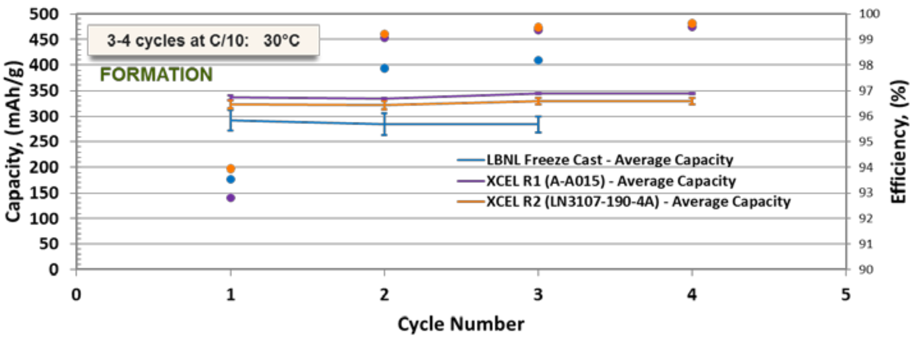


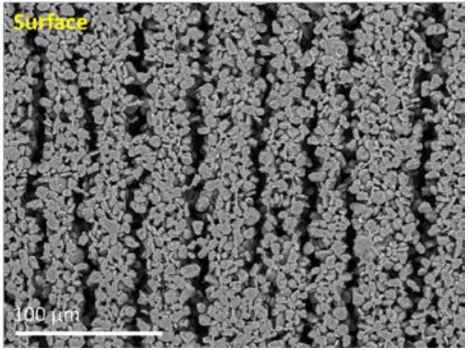
WORK WITH LBNL FREEZE-CAST ELECTRODES MADE WITH SLC1506T GRAPHITE





- Electrodes have nearly ideal low tortuosity structure
  - LBNL is developing methods for lowering porosity





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CAMP FACILITY FY19 SUPPORT OF XCEL TEAMS

Organization	Electrodes	Purpose/Comments	No. Pouch Cells
INL	Round 2	Charge protocol, electrolyte, porosity	24+11+12
Argonne	Round 2 R2 pos/R1 neg	Temperature effect, porosity XRD beamline	16+24 1
NREL	Round 2 R2 pos/Li R2 neg/Li	Micro-calorimetry, XRD	4+4+6 4 4
SLAC/Stanford	Round 2	XRD beamlines metallized separator (3-tabs)	4+6 6
Princeton	Round 2	XRD beamlines	9
UC-Berkeley	R2-pos/R1 neg	XRD	5
Does not include numerous coin cells, electrode sheets, or powders			

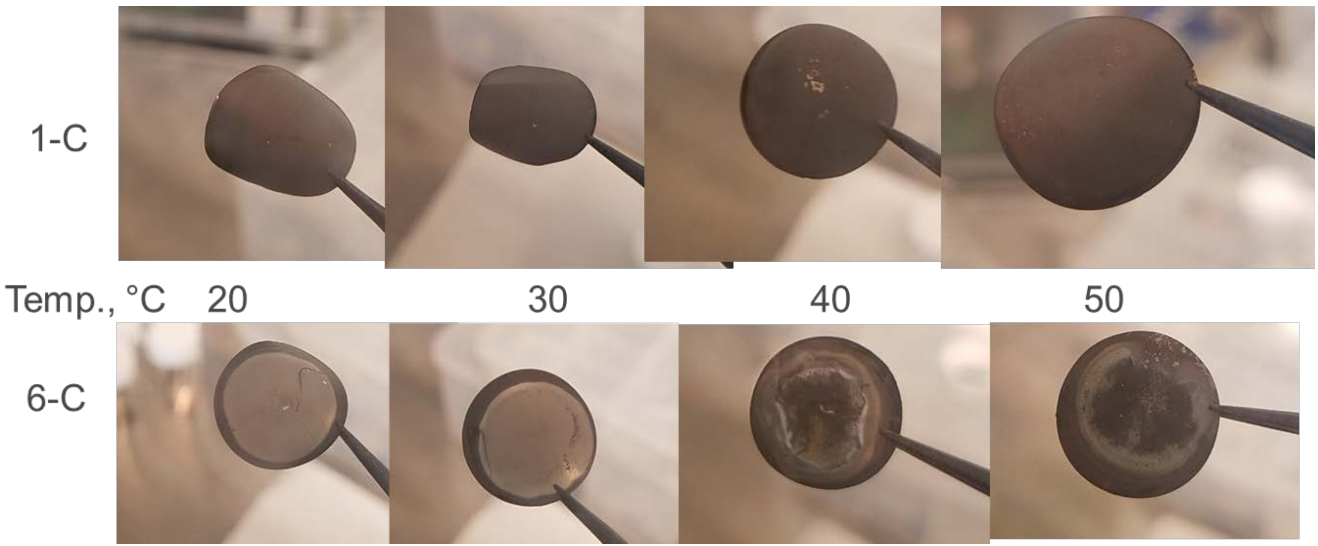
Total over 140 pouch cells

POST-TEST QUANTIFICATION OF LITHIUM CONTENT

QUANTIFY LITHIUM PLATING IN CYCLED CELLS

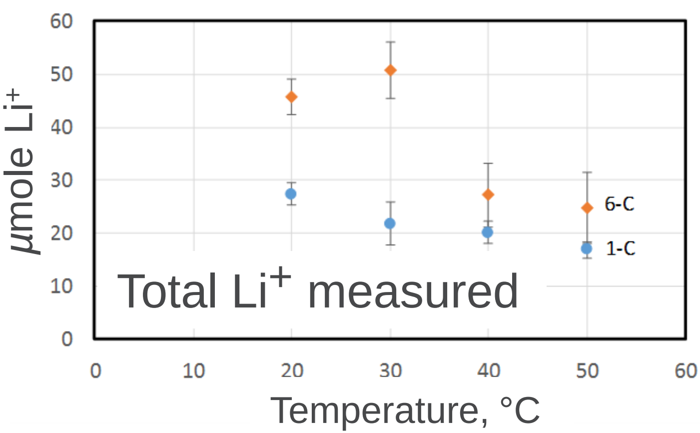
Developed new analytical technique to measure plated Li post-test

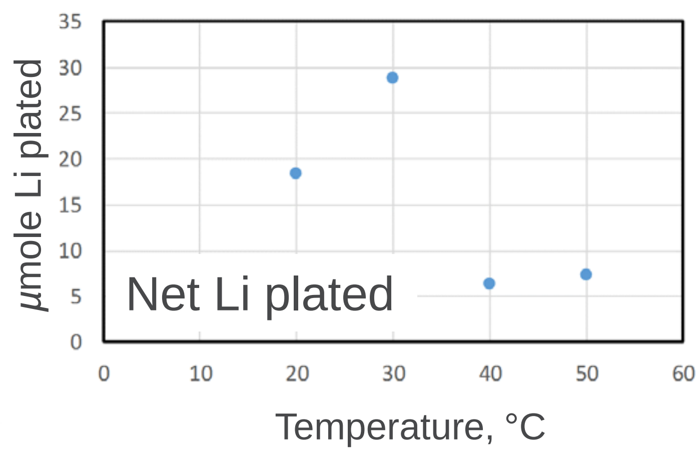
- Coin cells using "Round 2" (3 mAh/cm²) anodes vs. NMC532 cathodes
- A total of five, 6-C charge/0.5-C discharge cycles were used, and compared to cells from 1-C charge/0.5-C discharge cycling at 20, 30, 40, and 50°C
  - Cells were dismantled in glove box and washed two times with excess DMC



DETERMINE NET QUANTIFY OF PLATED LITHIUM

- Washed anodes were placed in HPLC-grade water to dissolve Li-bearing salts and react with plated lithium
- Aqueous solutions were analyzed using ICP-MS and an ion-selective electrode for Li and F (in triplicate), respectively
  - Baseline (1C) lithium subtracted from 6C lithium (corrected for LiF content, not shown)
  - Amount of Li plated follows as expected - decreasing with increasing temperature

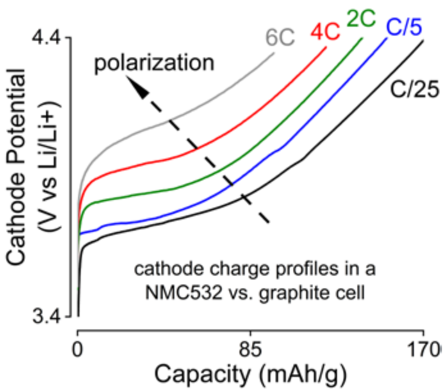




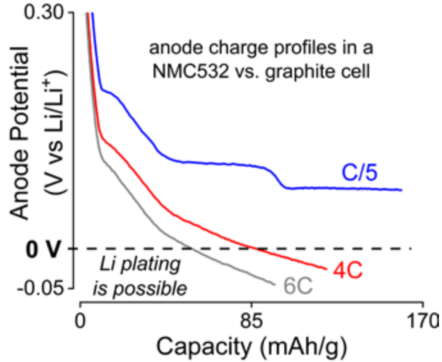
REFERENCE ELECTRODE STUDIES

REFERENCE ELECTRODE STUDY SHOWS CONDITIONS FOR Li PLATING

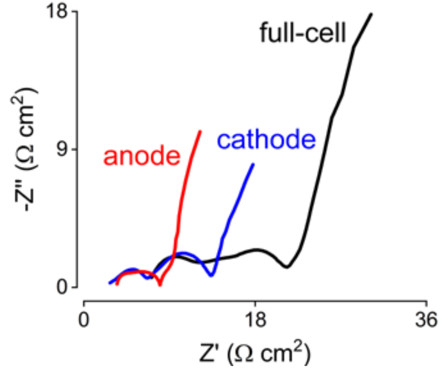
Unique information becomes accessible with a reference electrode



electrode contributions to cell polarization

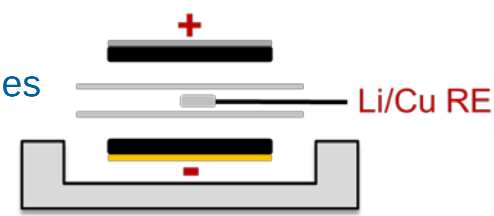


onset of Li plating conditions



individual electrode impedances

3-electrode cell
Round 1 electrodes

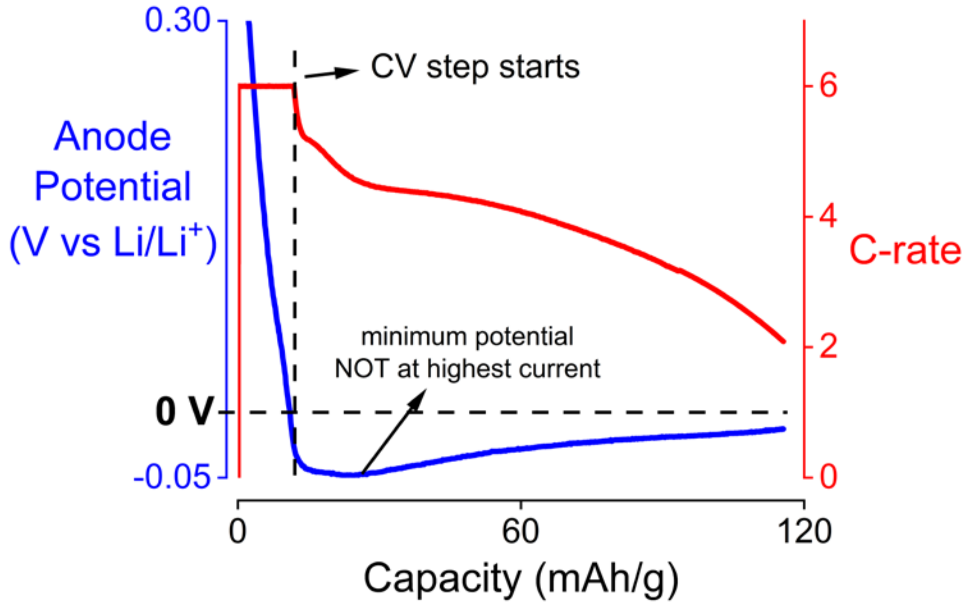


$20.3\ cm^2$ electrodes
25 µm reference wire

EVALUATION OF FAST CHARGE PROTOCOLS SHOW ANODE POTENTIAL CAN DIP IN CV ZONE

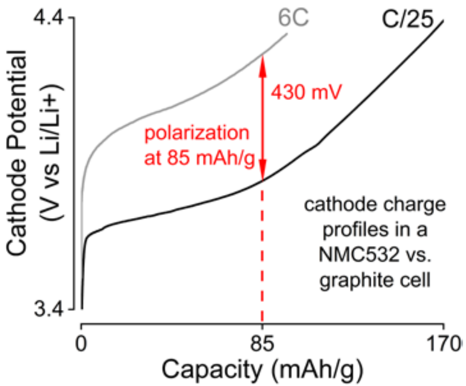
Example: constant current constant voltage, 6C 4.1 V (~16 minutes)

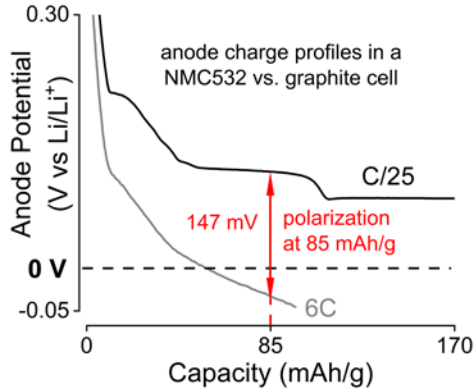
Li plating is possible in Round 2 cells



Similar experiments can assist in validating protocols developed within the XCEL program

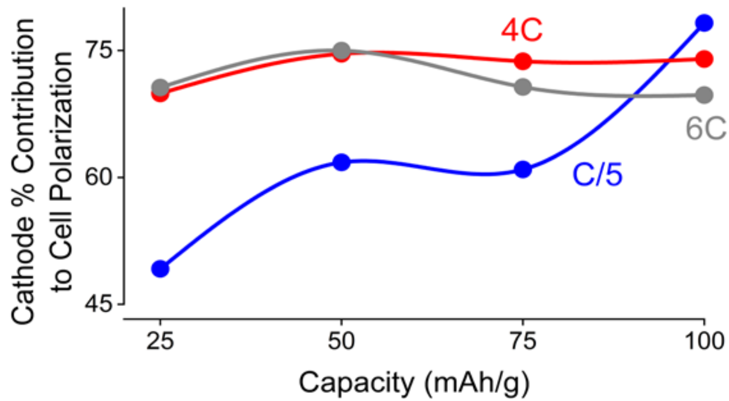
ELECTRODE POLARIZATION IS LARGER FOR THE CATHODE DURING FAST CHARGING





Relative polarization for each electrode measured from reference electrode data (Round 1)

Most polarization arise from the **cathode**: vital knowledge for thermal management and calorimetric analysis



OPERANDO XRD ANALYSIS DURING CHARGE

OPERANDO CELL AND FAST CHARGE PERFORMANCE

Diagnosing fast-charge heterogeneities using extra thick electrodes

Negative electrode after 100 cycles

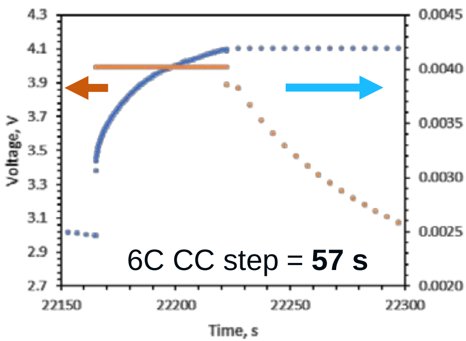
Negative electrode:
- CAMP LN3174-29-3
- 91.83 wt% Superior graphite SLC1520P
- 2 wt% Timcal C45
- 6 wt% Kureha 9300 PVDF Binder
- Cu foil: 15 μm thick
- **Coating thickness: 101 μm**
- Porosity: 36.2 %
- Loading: 13.97 mg/cm^2
- Coating density: 1.38 g/cm^3

Positive electrode:
- CAMP LN3174-25-4
- 90 wt% ECOPRO NMC622
- 5 wt% Timcal C45
- 5 wt% Solvay 5130 PVDF
- Al foil: 20 μm thick
- **Coating thickness: 112 μm**
- Porosity: 34 %
- Loading: 30.24 mg/cm^2
- Coating density: 2.70 g/cm^3
- Areal Capacity: 4.60 mAh/cm^2

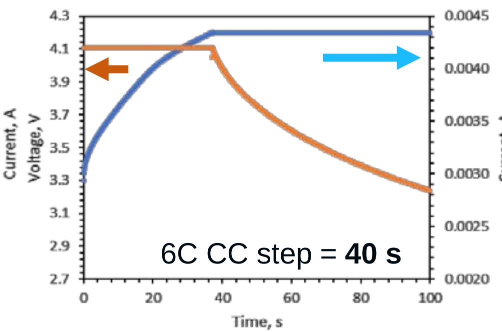
Cycling conditions:
- 6C CC/CV charge to 4.1 V
- 2C CC discharge to 2.8 V

'Micro' coin cell:
- Pos. diameter: 4.76 mm
- Neg. diameter: 3.97 mm
- Measured capacity: ~ 0.72 mAh
- Separator: Celgard 2320
- Electrolyte: Gen2 flooded

Cycling at NREL



Cycling at The European Synchrotron (during X-ray exposure)



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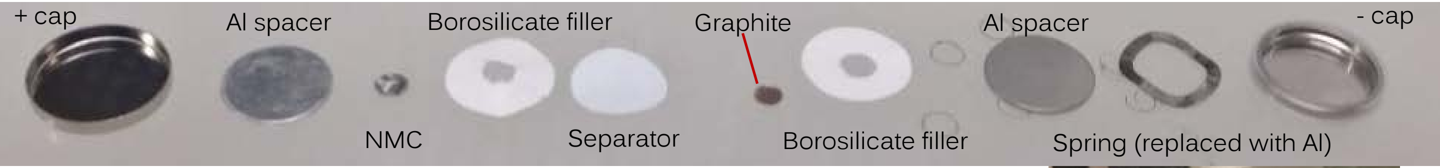
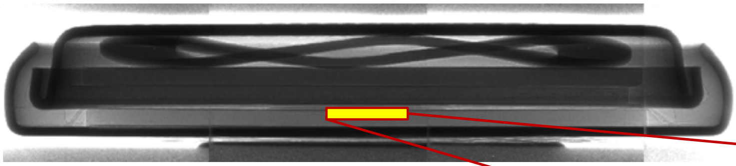
OPERANDO XRD EXPERIMENT OVERVIEW

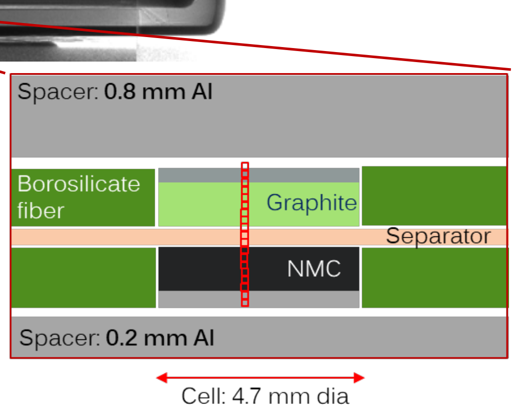
Micro-cell design

High speed and high resolution XRD:

- Maximize X-ray transparency and signal/noise ratio
- Minimize performance loss







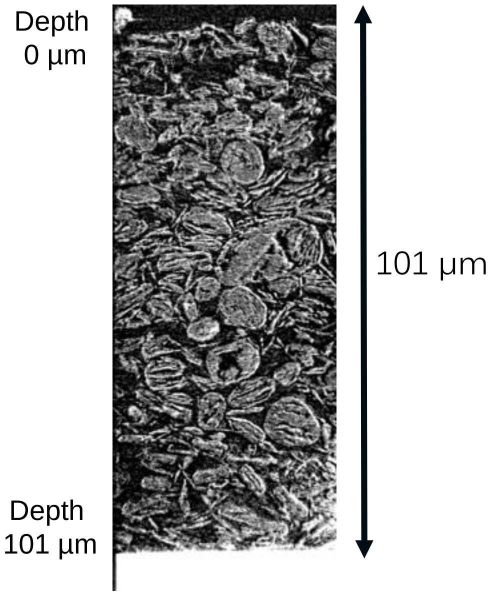
ESRF experiment conditions:

- 60 keV beam
- 0.6 µm × 0.3 µm beam
- 0.05 s exposure
- 3 µm step sizes
- 148 XRD points at 100 Hz
- 1.5 s per line scan
- 13 s between line scans

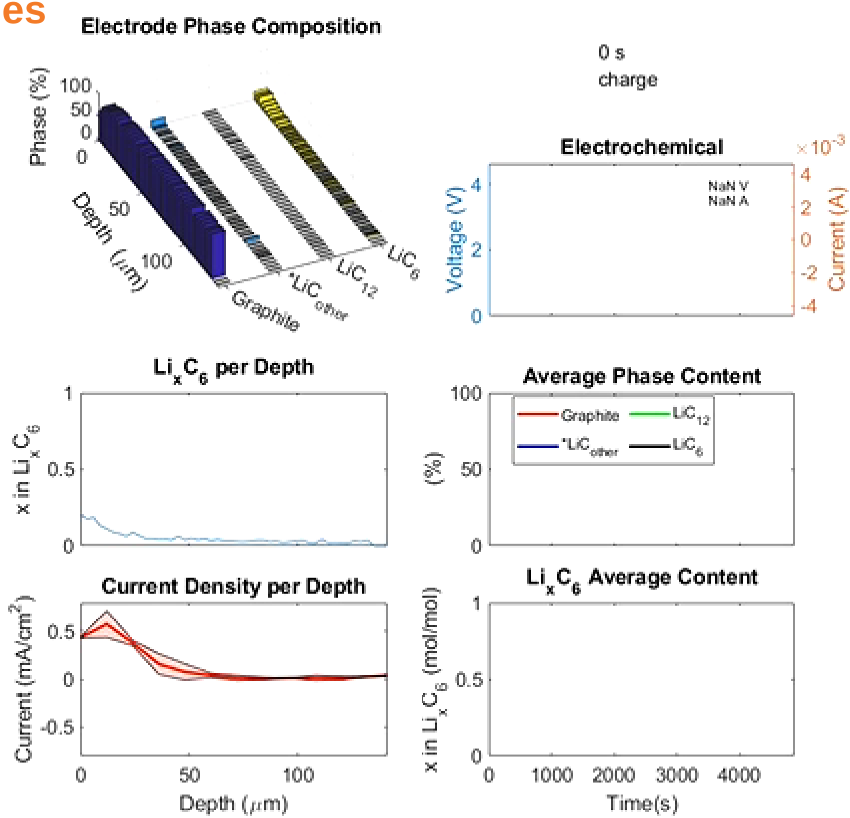
PROFILING CHARGE GRADIENTS

Fast-charge heterogeneities

High-resolution and high-speed XRD at The European Synchrotron (ESRF)



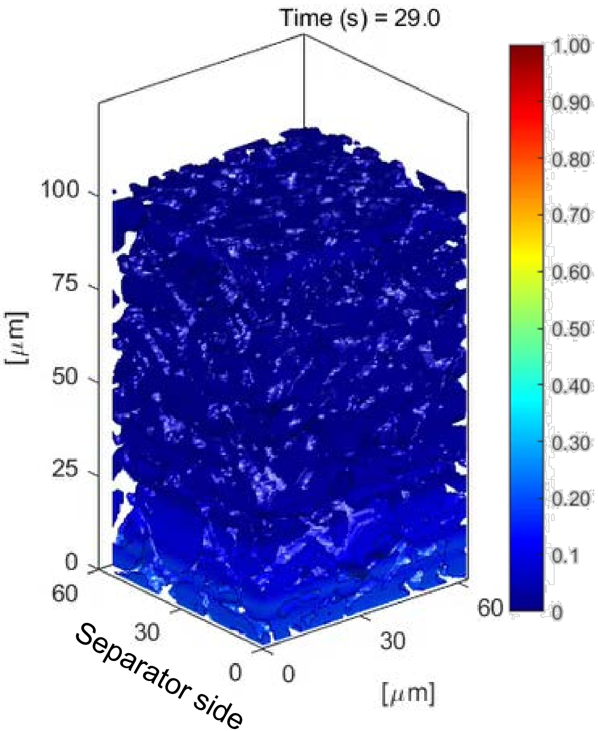
Argonne's LN3174-29-3 (SLC1520P)



PROFILING CHARGE GRADIENTS

Superimposed empirical data

Concentration of x in Li_xC_6

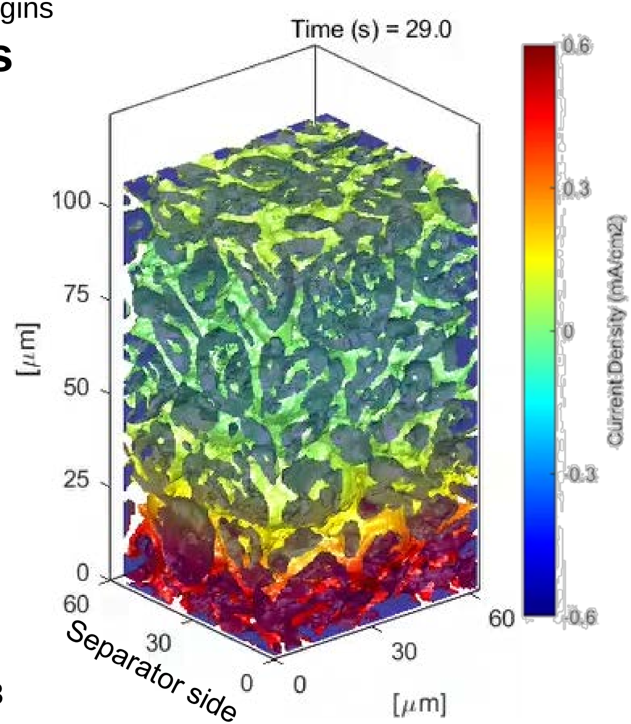


Discharge begins

1600 s

Argonne's LN3174-29-3 (SLC1520P)

Estimated current density



X-ray nano-CT carried out at UCL

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RESPONSES TO PREVIOUS YEAR REVIEWERS' COMMENTS

- This project was not reviewed last year.

COLLABORATION ACROSS LABS AND UNIVERSITIES

- Five national laboratories (Argonne, NREL, INL, SLAC, and LBNL) and three universities (Stanford, UC-Berkeley, and Princeton) have teamed to form this integrated effort focused on enabling fast charge capability.
- National User Facilities involved in this work presented include the Advanced Photon Source. International Facilities include the European Synchrotron Radiation Facility.
- This effort is part of a broad range of unified studies (BAT338, BAT339, BAT340, BAT371, BAT383, BAT384, BAT386).

REMAINING CHALLENGES AND BARRIERS

- Lowering tortuosity alone may not be enough to prevent lithium plating during fast charging
  - May require multi-prong approach including new electrolytes, higher temperatures, etc.

PROPOSED FUTURE RESEARCH

- Develop methods of altering the electrode microstructure to improve tortuosity during slurry making/coating process
  - Drying process (align platey graphite perpendicular to foil - *e.g.*, magnetic fields)
  - Multi-layer coating (gradient porosity)
  - Pore formers (salt, volatile solids, etc.)
- Develop thinner anode electrodes with higher loading and low porosity (<20%) without distorting electrode
  - May require multi-modal distribution of particle sizes and morphologies

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

SUMMARY

- Fabricated, formed, and distributed Round 2 pouch cells with varying anode porosities (26%, 36%, and 47%)
- Developed method to quantify Li metal on anodes via ICP-MS
- Reference Electrode study identified point of lithium plating *in operando*
- XRD study identified lithium and current profiles *in operando* during fast charge
- Provided technical data and electrochemical results to modeling teams
- Distributed numerous graphite powders, electrode sheets, and pouch cells (over 140) to XCEL teams
  - Assisted SLAC, Argonne, and NREL teams with XRD beam times
  - Fabricate 3-tab pouch cells in support of metalized separator study (not shown)

CONTRIBUTORS AND ACKNOWLEDGEMENTS

Aashutosh Mistry
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Abhi Raj
Alison Dunlop
Andrew Colclasure
Antony Vamvakeros
Aron Saxon
Bryan McCloskey
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David Robertson
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Hakim Iddir
Hang-Georg Steinrück
Hansen Wang
Ilya Shkrob

Ira Bloom
Jiayu Wan
Johanna Nelson Weker
John Okasinski
Juan Garcia
Kamila Wiaderek
Kandler Smith
Kaushik Kalaga
Kevin Gering
Marca Doeff
Marco DiMichiel
Marco Rodrigues
Matt Keyser
Michael Evans
Michael Toney
Nancy Dietz Rago
Nitash Balsara
Partha Mukherjee
Partha Paul
Paul Shearing
Pierre Yao
Ravi Prasher
Ren Yang
Robert Kostecki
Ryan Jackman

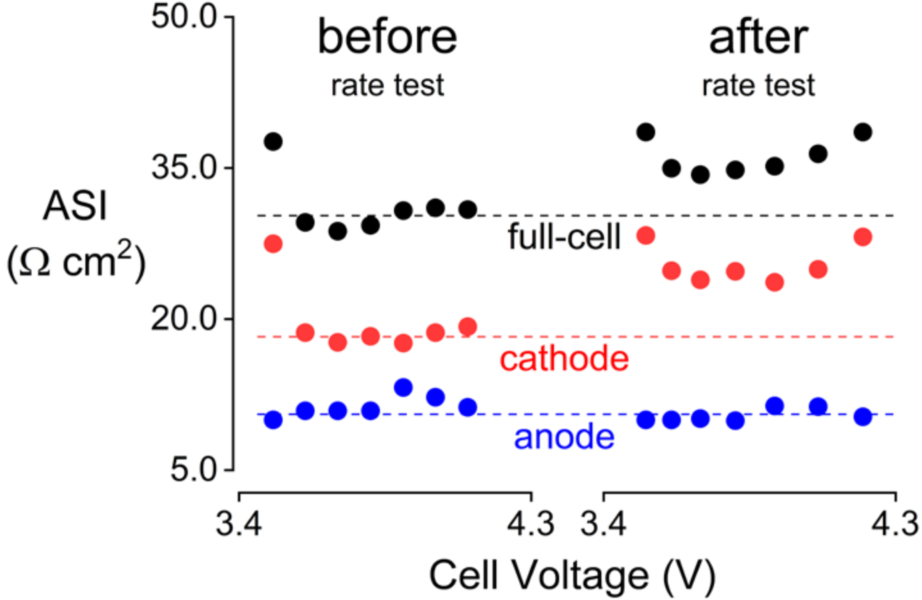
Sang Cheol Kim
Sangwook Kim
Sean Wood
Seoung-Bum Son
Shabbir Ahmed
Shriram Santhanagopalan
Steve Trask
Tanvir Tanim
Uta Ruett
Venkat Srinivasan
Victor Maroni
Vince Battaglia
Vivek Thampy
Wei Tong
Weijie Mai
Wenxiao Huang
William Huang
Yanying Zhu
Yi Cui
Zhenzhen Yang

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

TECHNICAL BACK-UP SLIDES

IMPEDANCE RISE AFTER FAST CHARGING WITH ROUND 2 ELECTRODES

Impedance measurements before and after a series of fast charge cycles (up to 6C) after which **Li plating was detected**



Li plating does not affect the anode impedance, but high charging currents can increase the cathode impedance