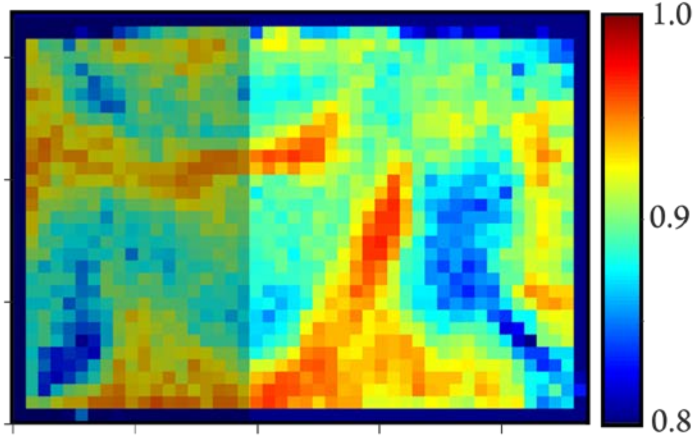
PROJECT ID: BAT461

QUANTIFYING HETEROGENEITIES/ DEGRADATION DURING FAST CHARGE

ANDREW COLCLASURE
National Renewable Energy Laboratory



Lateral variation in anode intercalation fraction after 6C charge

DOE Vehicle Technologies Program
2021 Annual Merit Review and Peer Evaluation Meeting

OVERVIEW

Timeline

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

Barriers

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

Budget

- Funding for FY 2020: $5,600,000

Partners

- Argonne National Laboratory (ANL)
- Idaho National Laboratory (INL)
- Lawrence Berkeley National Laboratory (LBNL)
- National Renewable Energy Laboratory (NREL)
- SLAC National Accelerator Laboratory
- Oak Ridge National Laboratory (ORNL)

RELEVANCE

- Lithium plating and cell degradation during fast charge are often driven by local heterogeneities in both in-depth and lateral direction across length scales ranging from cm to microns
- Goal: Detect/quantify underlying causes of observed heterogeneities to determine what needs to be improved
  - Electrolytes with better transport and wetting properties
  - Electrodes with more uniform microstructure properties
  - More uniform application of pressure
- Developing better physical understanding/models of mechanism for graphite lithiation at very high rates.

Length scale

1 cm

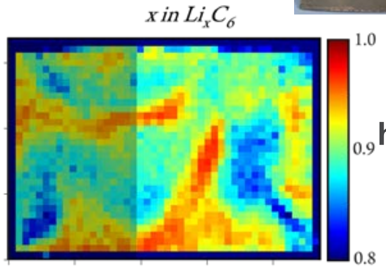
1 mm

100 µm

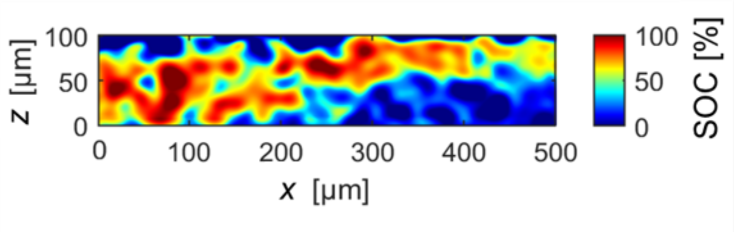
10 µm

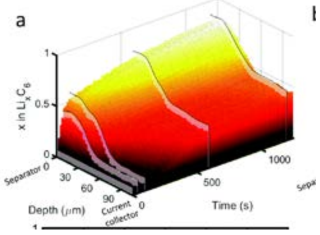
Lithium ring on coin cell electrode

Lithium plating pattern in pouch cell



Lateral heterogeneity pouch cell





Depth profile in anode during 6C charging

XCEL eXtreme Fast Charge Cell Evaluation of Lithium-ion Batteries

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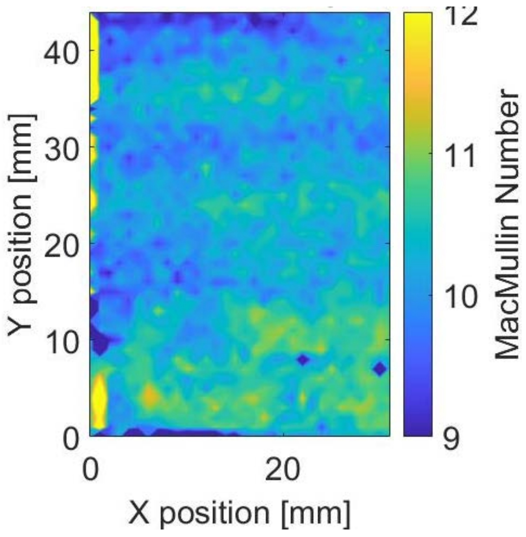
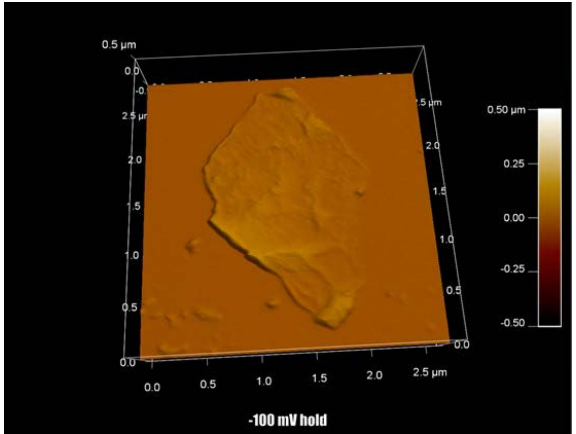
APPROACH

- Multi-lab and university team is quantifying heterogeneity during extreme fast charging (XFC) at several length scales through both experimentation and computational modeling.
- Specific activities include:
  - Mapping of local state of charge (SOC), cyclable lithium, and plated lithium using high-energy X-ray diffraction (XRD), including operando
  - Mapping of local electrode microstructure properties
  - Modeling and measurement of electrolyte wetting process
  - Development of high-order kinetic lithium plating model
  - Detailed characterization of graphite lithiation mechanism using idealized architectures: Highly oriented pyrolytic graphite (HOPG) and nano-platelets
  - In situ X-ray tomography to map SOC/plating
- Team is working to understand the underlying cause of heterogeneity observed at different length scales.

Local Ionic Resistance





MILESTONES

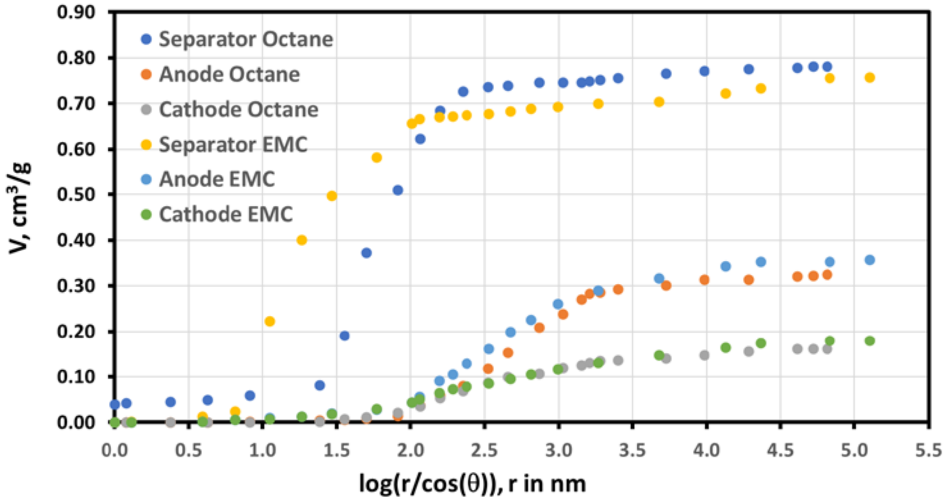
Quarter	Milestone
Q1	Kinetics of lithium plating, stripping, and influence of solid-electrolyte interphase (SEI) film will be developed and validated with the experimental data
Q1	Microstructure maps compared to XRD maps for SOC/Li plating
Q2	Correlate observed lithium plating patterns in cells to nonuniform electrolyte saturation using wetting and electrochemical models with improved electrode and separator wetting characteristics
Q3	Perform detailed ex situ, beamline studies of areas of interest in R1 and R2 cells
Q4	2D XRD mapping of hero cell

TECHNICAL ACCOMPLISHMENTS: IMPROVING THE ELECTROLYTE WETTING PARAMETERS

- **Original studies based on standard two-phase flow model with electrolyte parameters provided by Kevin Gering's Advanced Electrolyte Model (AEM) and cell component wetting parameters obtained from Standard Contact Porosimetry studies.**
- **Original porosimetry studies conducted with octane, considered a universal solvent**
- **New porosimetry studies on components conducted with ethyl methyl carbonate (EMC) as solvent, electrolyte solvent mixture is 70% by weight EMC.**

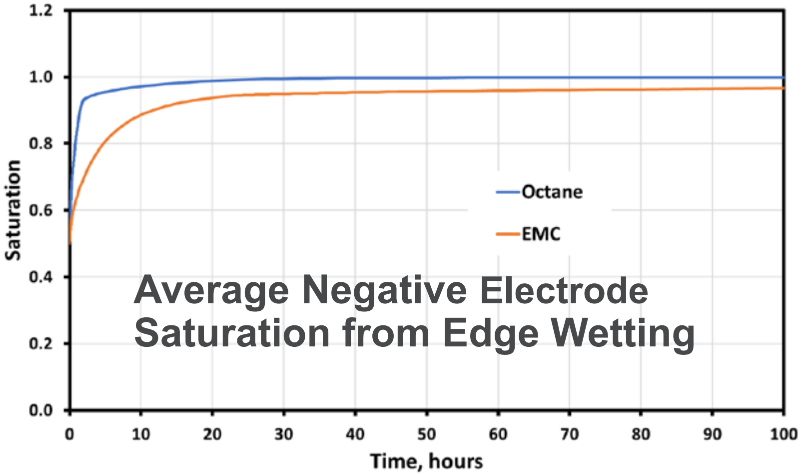
- *V* is the specific solvent volume soaked into each component as a function of pore size, *r* (θ is the average contact angle, zero for octane).
- Electrode binders are known to absorb carbonate solvents as exhibited by higher maximum volume of EMC.
- Swelling binders from EMC absorption affects the electrode pore size distribution and significantly reduces the electrode permeabilities as estimated by the Kozeny-Carman equation.

Standard Contact Porosimetry Studies

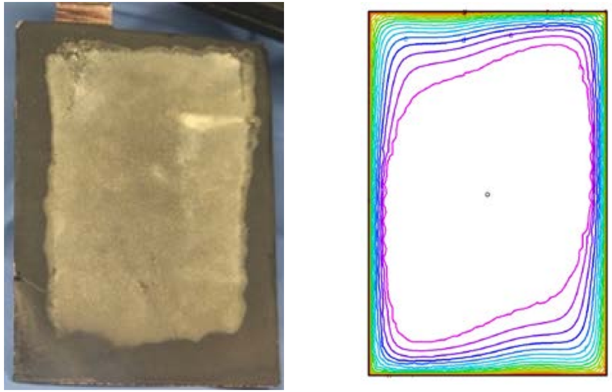


LOWER PERMEABILITY SLOWS POUCH CELL WETTING

Electrode permeabilities based on EMC studies are a factor of five lower for the anode and a factor of seven lower for the cathode compared to the octane-derived values, which significantly slows all pouch cell wetting processes.



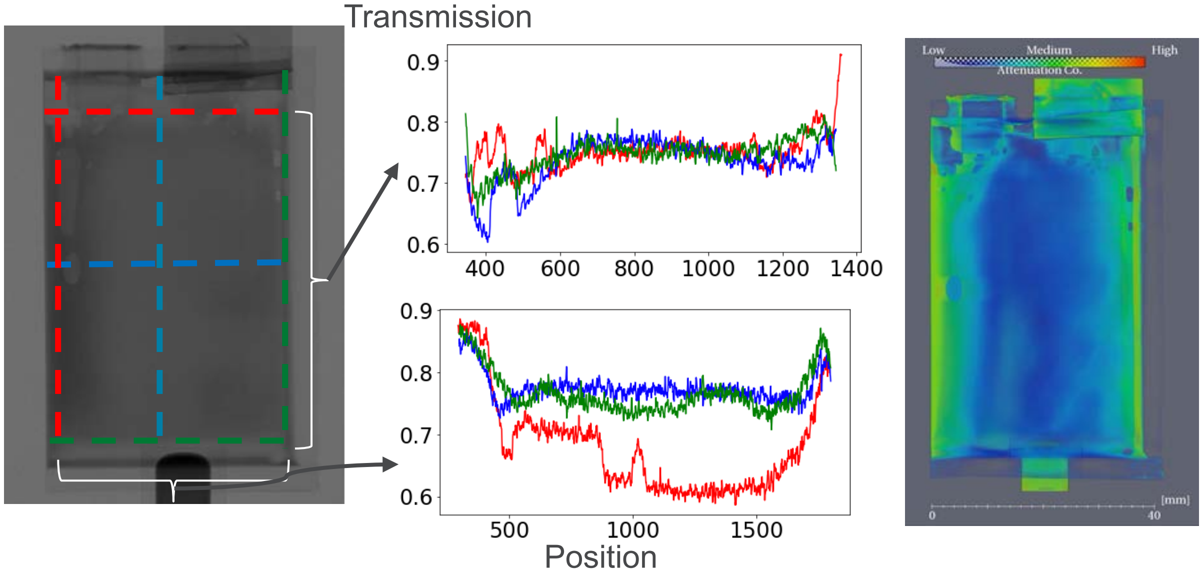
Negative Electrode and Saturation Distribution



1.0 (red > orange > yellow > green > blue > indigo > violet) 0.94

- Initial portion of the pouch cell wetting process is slower, but still very quick (i.e., tenths of seconds).
- Edge wetting process of cell components slowed by more than a factor of seven to get to 90% saturation, and full wetting can extend long past the formation process.
- All the wetting studies conducted with EMC parameters were very similar to the earlier octane-based studies, except everything occurs significantly slower.
- Many of the patterns of lithium plating observed on the face of the negative electrodes can be explained by nonuniform saturation of the electrodes.

NONUNIFORM ELECTROLYTE SATURATION



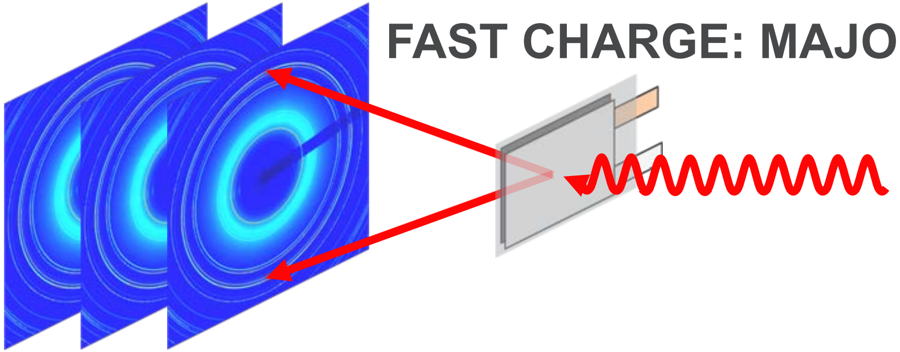
In Situ Neutron Radiography and Tomography Results

- Partial saturation of electrodes by electrolyte can contribute to the lithium plating during extreme fast-charging conditions.
- Electrolyte saturation along the edges could cause gases to be trapped in the electrode layers, causing patterns.
- Neutron radiography is used to understand the internal structure as they strongly attenuate light elements like hydrogen and lithium.
- Cells are measured as manufactured to identify nonuniform regions during electrolyte filling process or after the formation cycles to understand the regions trapped with released gases.

The attenuated beam enters the neutron sensitive detector, which digitally records the changes in neutron transmission, producing a 2D projection of the cell on the detector plane resolving the internal electrode structure

Neutron imaging experiments are conducted at Spallation Neutron Source (SNS)/ORNL with the cells from the Cell Analysis, Modeling, and Prototyping (CAMP) facility

FAST CHARGE: MAJOR CAUSE OF LATERAL HETEROGENEITY

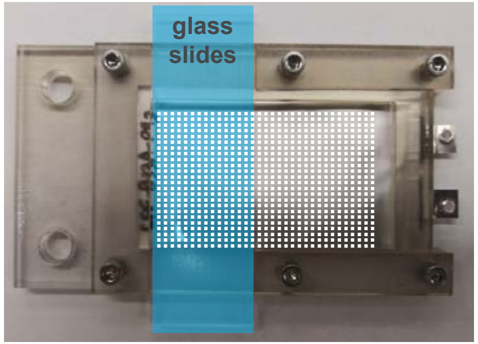


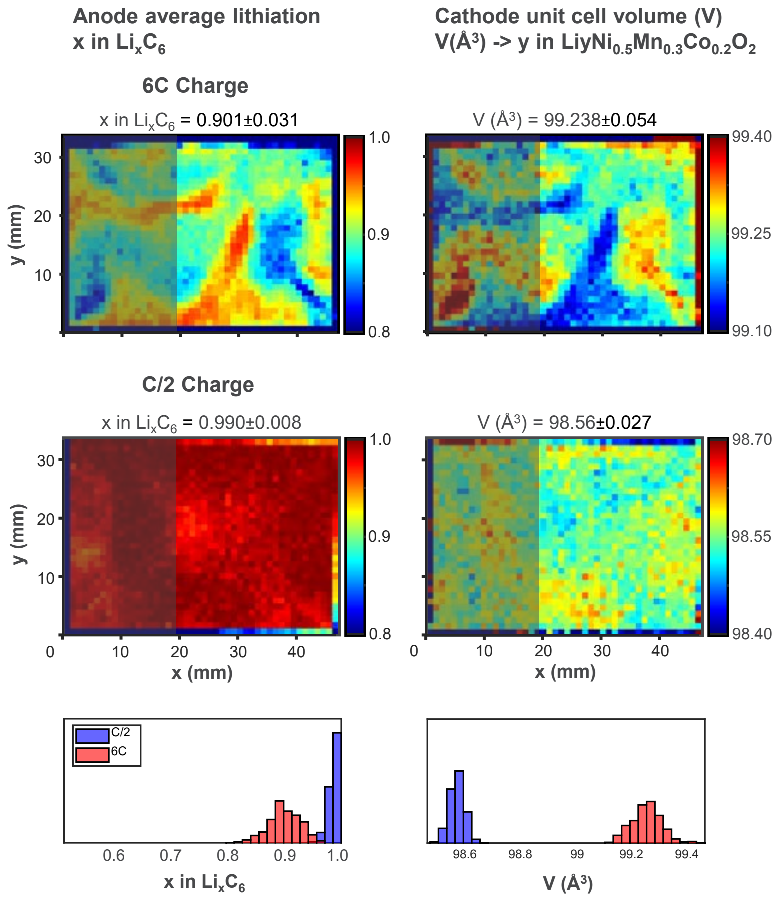
Experimental setup

- Graphite anode (R1), NMC532 cathode (R1), Celgard 2320 separator, Gen2 electrolyte.
- Charging protocol: 6C or C/2 charge, C/2 discharge, 3–4.4 V, 25 cycles. Is there an effect of rate?
- Part of cell under few psi pressure: Is there a pressure effect?

Key findings

- **Fast charge** causes significant **lateral heterogeneity** in the anode and cathode.
- **Uneven pressure** (~4 psi) **not a significant cause** of heterogeneity.





XCEL eXtreme Fast Charge Cell Evaluation of Lithium-ion Batteries

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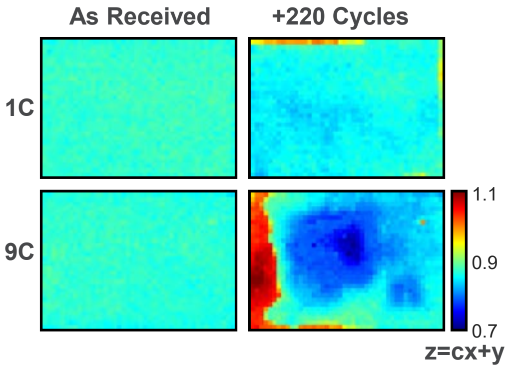
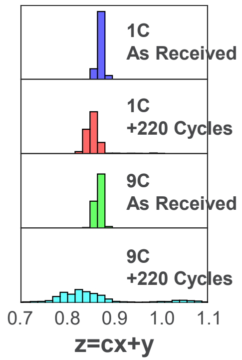
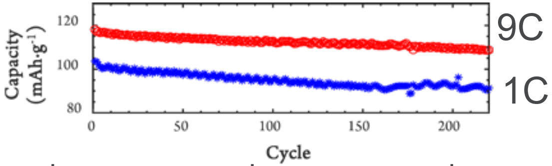
LITHIUM MOVES LATERALLY DURING EXTENDED FAST-CHARGE CYCLING BUT EQUILIBRATES WITH EXTENDED REST







	x in Li_xC_6		y in $Li_yNi_{0.5}Mn_{0.3}Co_{0.2}O_2$		z (cx+y) c = lattice n:p ratio		Capacity	Capacity Fade
	$\bar{x}$	σ_x	$\bar{y}$	σ_y	$\bar{z}$	σ_z	($mAh \cdot g^{-1}$)	($mAh \cdot g^{-1}$)
1C (as received)	0.0080	0.0010	0.8644	0.0058	0.8706	0.0066	118.2	-9.5
1C (+220 cycles)	0.0199	0.0280	0.8409	0.0107	0.8561	0.0322	108.7	
9C (as received)	0.0050	0.0026	0.8628	0.0063	0.8667	0.0083	103.6	-12.7
9C (+220 cycles)	0.0391	0.0653	0.8223	0.0407	0.8523	0.0907	90.9	

Round 1 (40 µm) single-layer pouch cells, $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$ (NMC532) cathode, graphite anode cycled 600 times (1C and 9C charge, C/2 discharge), (3–4.1 V)

Cells mapped after extended rest period in cold storage
- **Lateral heterogeneity equilibrates during extended rest**

Fast-charge and slow-charge cells had the same starting lithium inventory
- **Heterogeneity when lithium plating is absent does not deplete lithium inventory**

Fast charge caused significant heterogeneity after further 220 cycles; left region (near electrodes) higher lithium than start
- **Heterogeneity caused by lateral Li migration**

Extra capacity fade of fast charge (12.7 mAh/g vs. 8.02 mAh/g) caused by heterogeneity (depletion of Li from central region)
- **Heterogeneity causes reversible capacity fade.**

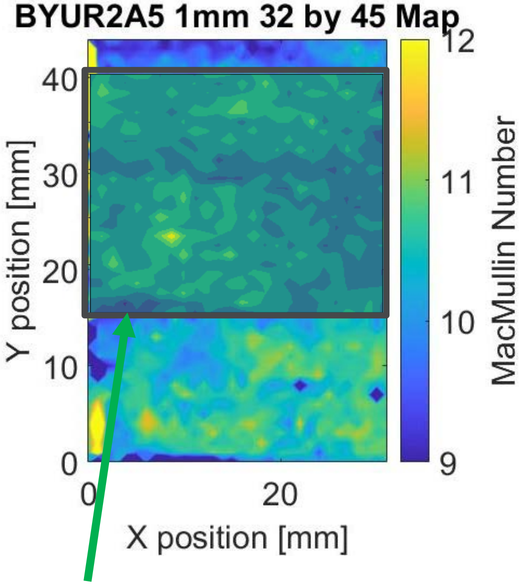
LOCAL MAPPING OF ELECTRODE ION TRANSPORT PROPERTIES

DEAN WHEELER, BRIGHAM YOUNG UNIVERSITY

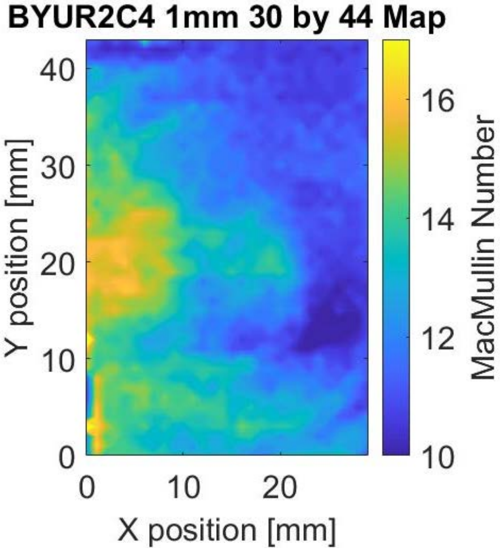
The blocking electrolyte method [1] is applied locally with a scanning probe to do electrochemical impedance spectroscopy at multiple locations across an electrode film (1-mm spacing) to make a map of MacMullin number.

The mapped electrodes were sent to CAMP for cell assembly and cycling.

Harry Charalambous (Advanced Photon Source - APS) then used XRD to map the SOC of the electrodes after cycling.



Overlay of partial map of electronic conductivity, showing correlation to heterogeneity in ionic transport

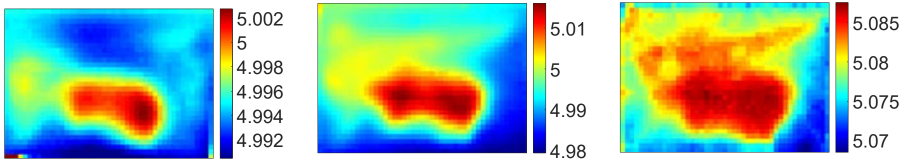


[1] Pouraghajan et al. *J. Electrochem. Soc.* 165, A2644 (2018).

INITIAL COMPARISON DOES NOT SUGGEST CORRELATION BETWEEN SOC AND MICROSTRUCTURE VARIATION

Discharge Cycle 10 | Discharge Cycle 452 | Charge Cycle 453

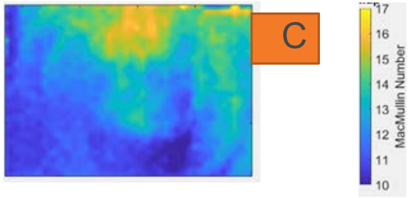
Cathode: c/a lattice ratio – increasing heterogeneity
Cathode SOC (red = less Li)

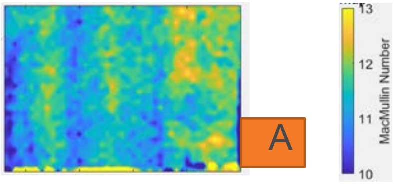


c/a = 4.9951±0.0033 | c/a = 4.9962±0.0084 | c/a = 5.0797±0.0042

Anode: x in Li_xC_6 – low heterogeneity

BYU mapping of ionic resistance, reoriented to same as APS mapping (anode facing up and cathode facing down)



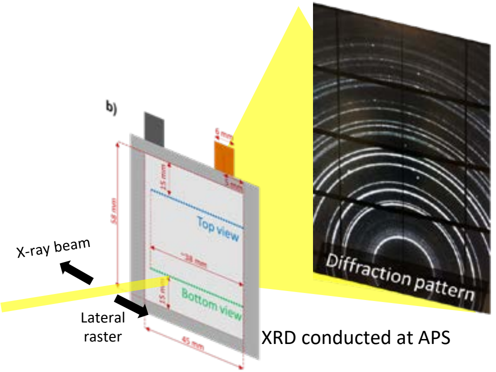


A second round of testing with new electrodes is in progress.

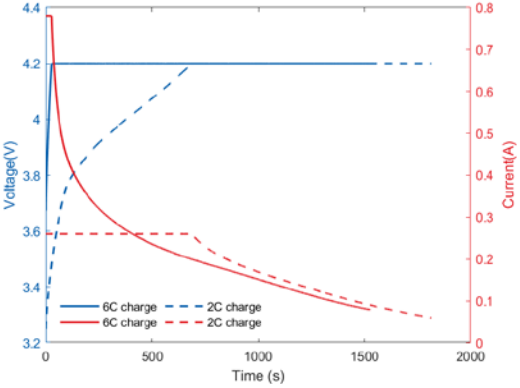
Quantifying heterogeneous graphite lithiation and current density inside fast-charging pouch cells with operando XRD

Experiment:

- Lateral operando X-ray diffraction during 6C charge
- 39 points per line, 0.5 s per point, 1-mm spacing, 0.2 x 0.2-mm beam



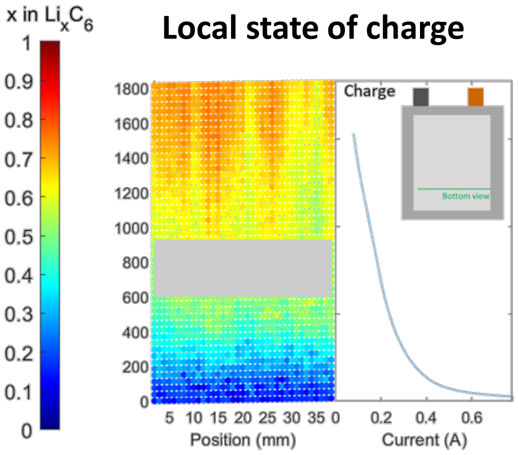
XRD conducted at APS



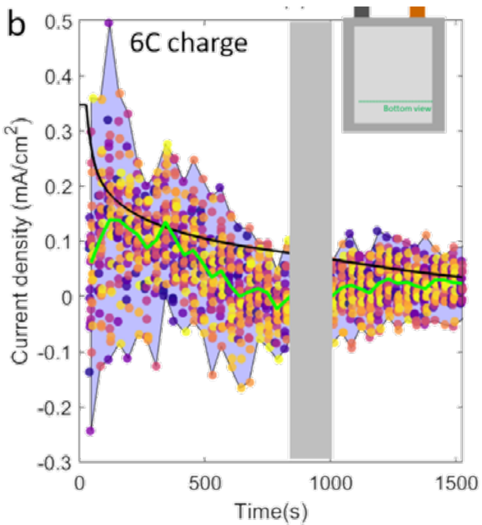
Results:

- Current density widely varied within the cell, sometimes reaching twice the average predicted
- Intercalation fraction difference up to 0.1 that could drive lithium plating

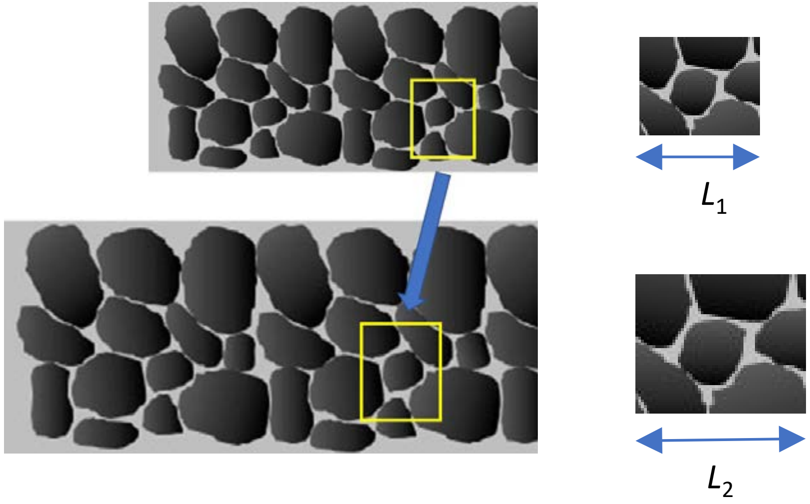
Local state of charge



Local current density



Effect of Lithium Plating on Graphite Lithiation

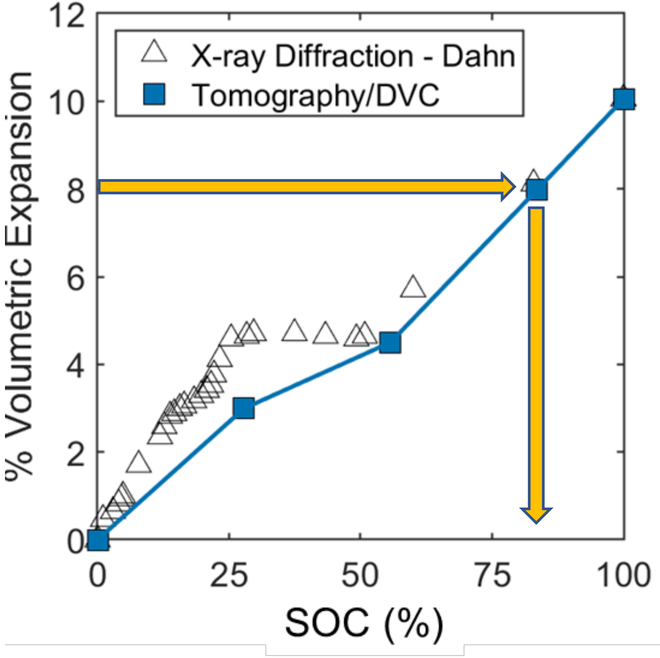


Digital Volume Correlation (DVC):

Divide pristine electrode into small 3D boxes

Identify the same box in the lithiated state using cross-correlations

Compare box sizes to get local % expansion = $100 \times ((L_2 - L_1)/L_1)^3$

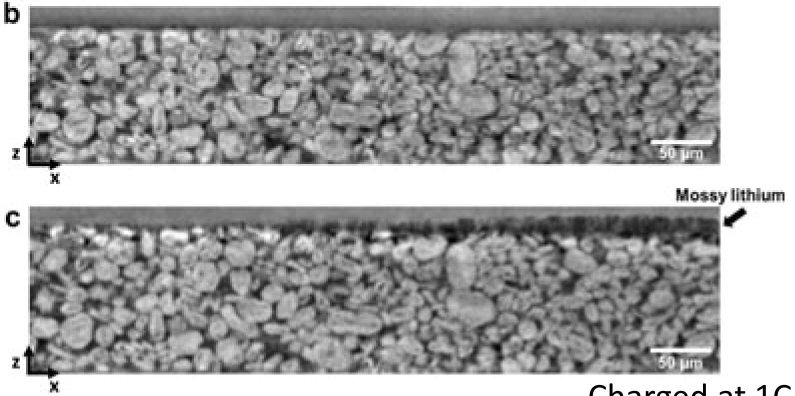


Use calibration to get local lithiation.

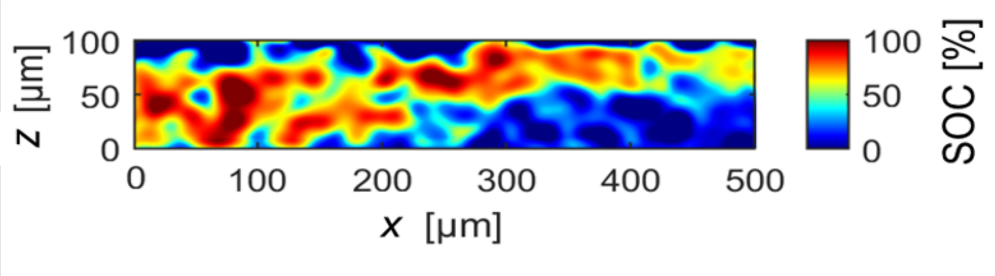
Ho, Parkinson, Finegan, Trask, Jansen, Tong, and Balsara. *ACS Nano*, submitted.

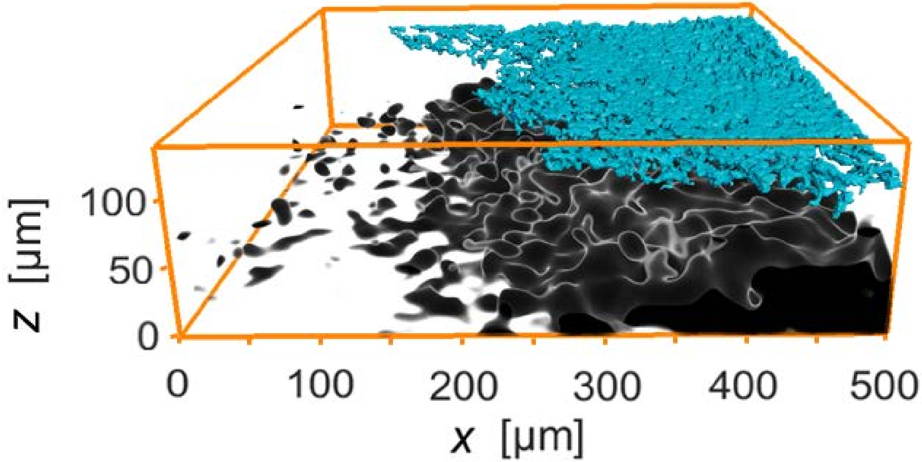
X-ray Tomography Data and the Shadow Effect

Discharged



Charged at 1C



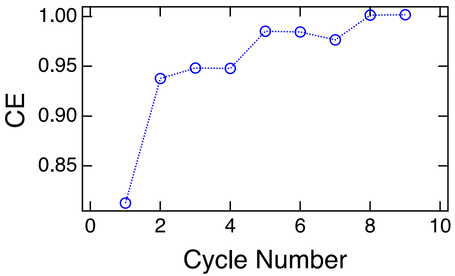


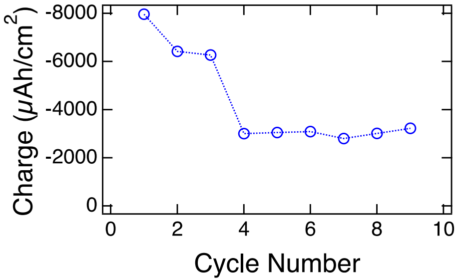
Graphite electrode pixels with less than 30% SOC colored black.

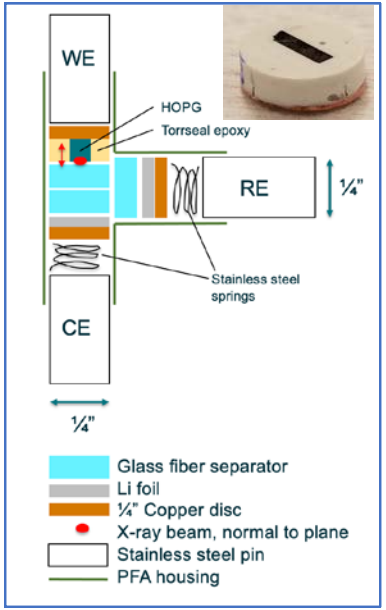
Takeaway: Explicit 3D Newman modeling is needed to understand the nature of the transport bottleneck that leads to the "Shadow Effect."

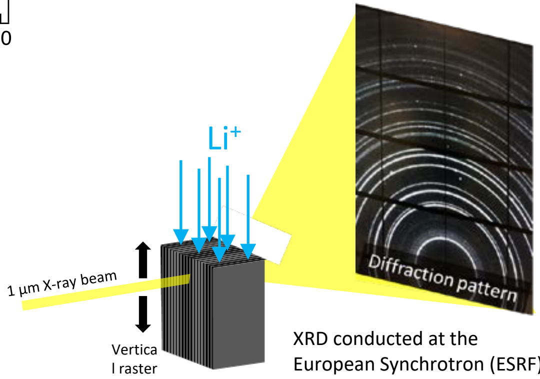
High-Speed XRD Depth Profiling of HOPG During Fast Lithiation and Li Plating

Objectives:
- Understand the response of graphite during fast charging and Li plating
- Use understanding of graphite behavior to inform fast-charging models and protocols



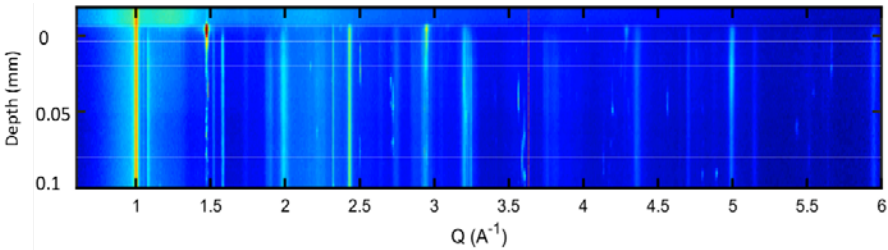


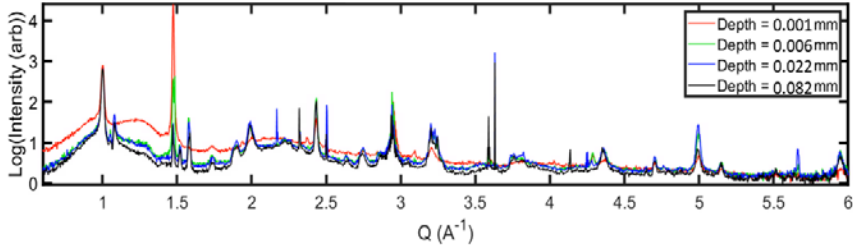




XRD conducted at the European Synchrotron (ESRF)

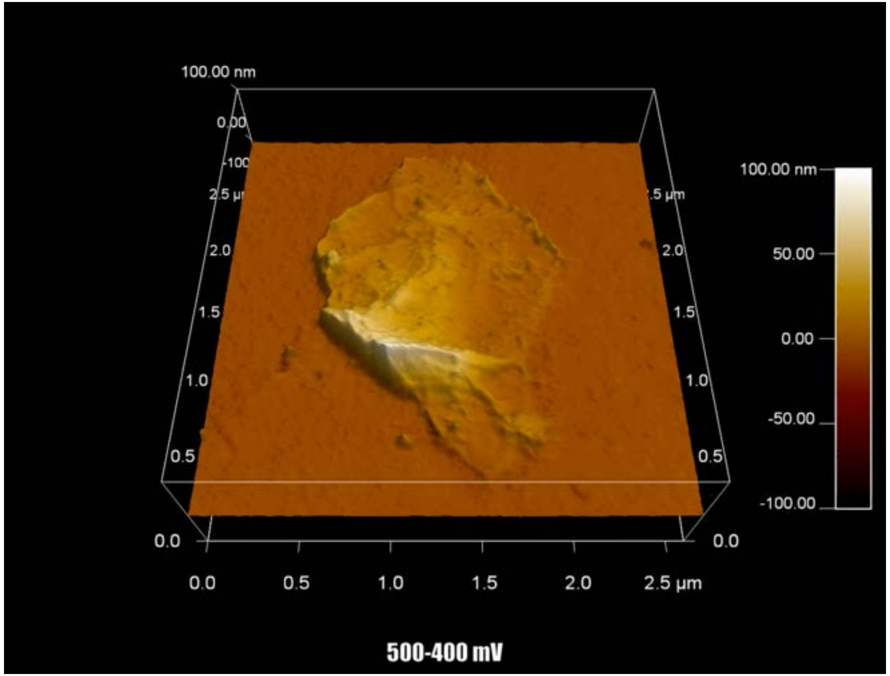
Experiment Overview:
- 1-µm vertical step size (resolution)
- Full line scan to 100-µm depth every 2 s
- Currents of 2, 4, and 8 mA cm^{-2} applied
- Li plating intentionally induced
- Depth profiling data collected



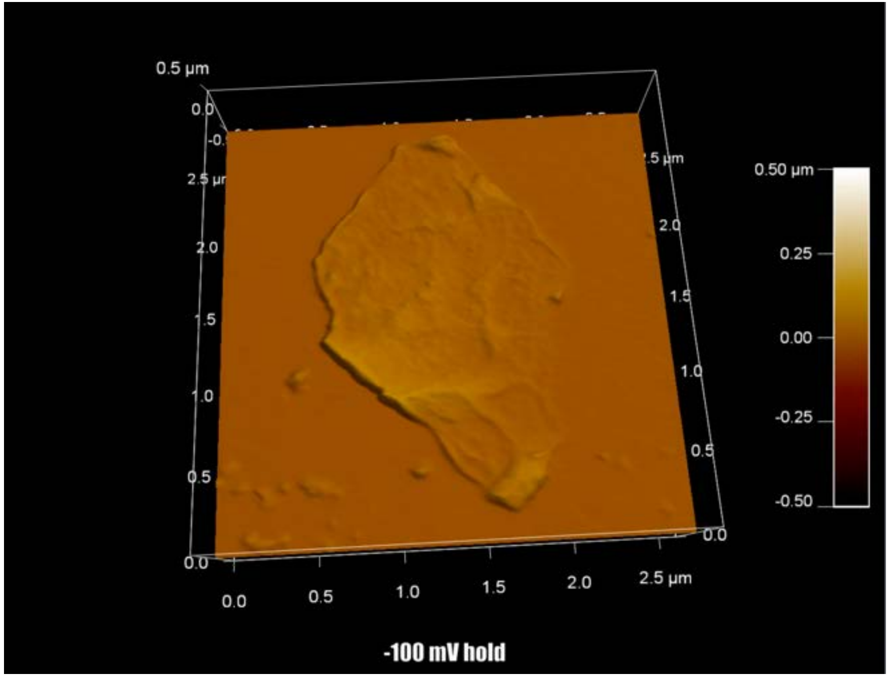


LITHIUM PLATING ON GRAPHITE NANOPLATELETS

SEI growth and Li intercalation



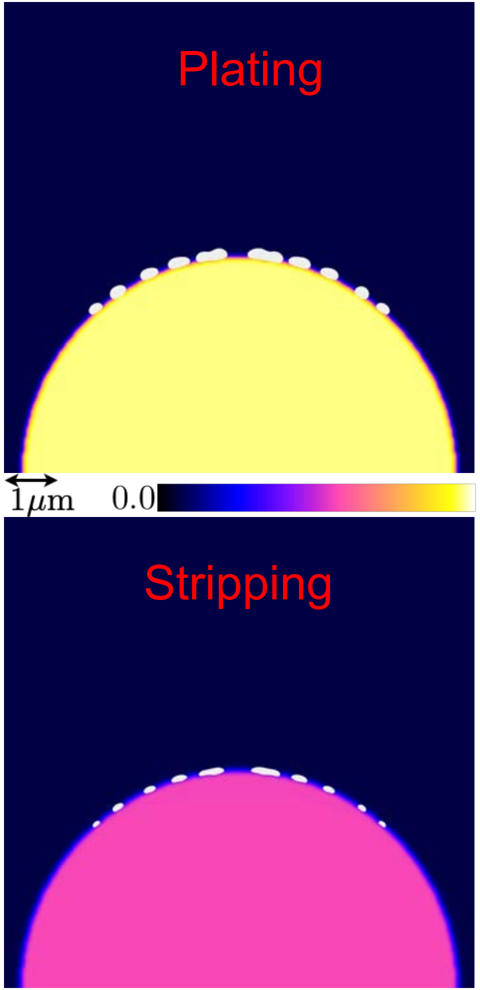
Li plating and stripping



- SEI growth and Li intercalation starts at the edge planes and defects on graphite
- Lithium plating is not fully reversible and stripping of large lithium causes graphite exfoliation.

Note: different height scale between the two graphics

ADVANCED LITHIUM NUCLEATION & PLATING MODEL



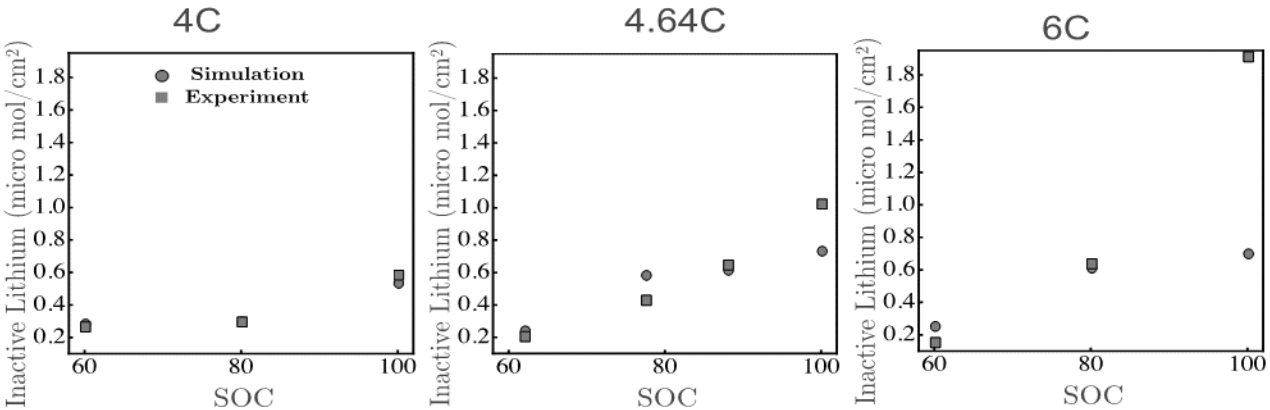
$$G[\{\xi_i\},\{c_j\},\rho;T] = \int_\Omega \left[g(\{\xi_i\}, c_j, T) + \sum_{i=l,e,g} \frac{\alpha_i^2}{2} (\nabla \xi_i)^2 + \rho\phi \right] d\Omega$$

Total free energy

Volumetric uniform free energy density

Gradient penalty energies

Electric energy density



- Lithium stripping during discharging process has been implemented in the existing formulation
- The amount of inactive lithium from plating and stripping in simulations are compared against the titration results from LBNL
- Experimental and simulation results pertaining to inactive lithium are in good agreement for 4C and 4.64C at different SOCs
- At higher C-rate (i.e., 6C), the inactive lithium from simulation results are underpredicting at 100% SOC. Further, consideration of SEI effects and other side chemical reactions can potentially improve the model.

K. S. N. Vikrant and S. Allu, "Modeling of Lithium Nucleation and Plating Kinetics Under Fast Charging Conditions," (2021) *J. Electrochem. Soc.* **168** 020536

K. S. N. Vikrant, E. McShane, A. M. Colclasure, B. D. McCloskey, and S. Allu, "Effect of Lithium Plating and Stripping Kinetics on Inactive Lithium Under Fast Charging Conditions," (in preparation).

RESPONSE TO PREVIOUS YEAR REVIEWERS' COMMENTS

- Project was 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

INL Idaho National Laboratory — Performance characterization, failure analysis, electrolyte modeling and characterization, Li detection, charging protocols

BERKELEY LAB — Li detection, electrode architecture, diagnostics

NREL NATIONAL RENEWABLE ENERGY LABORATORY — Thermal characterization, life modeling, micro- and macroscale modeling, electrolyte modeling and characterization

OAK RIDGE National Laboratory — Detailed Li plating kinetic models, SEI modeling, neutron imaging of electrolyte wetting

SLAC NATIONAL ACCELERATOR LABORATORY — Li detection, novel separators, diagnostics

REMAINING CHALLENGES AND BARRIERS

- Determine underlying cause of heterogeneity at millimeter and tens to hundreds of micron-length scale
  - Initial attempt indicates SOC maps don’t correlate with microstructure properties
- Many different heterogeneities at disparate length scales exist simultaneously, and isolating the effect of an individual heterogeneity remains challenging
- Improving electrolyte wetting is difficult and may not be improved sufficiently by prolonging formation process
- Need to determine if there is a critical level/tipping point for heterogeneity.

PROPOSED FUTURE WORK*

- Repeated XRD and microstructure mapping to test if there is a correlation between the two (post-mortem mapping)
- Microstructure characterization of tomography data to determine if local plating is tied to a microstructure property
- Tomography at higher rates: How does plating morphology/location change?
- Neutron imaging of pouch cells during fast charging to determine role wetting plays in plating
- Quantify changes in heterogeneity with “Hero-cell” builds/novel protocols
  - Changes with reduced carbon binder domain
  - Different separator
  - Different electrolyte
- More comprehensive modeling that bridges length scales/complexity.

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

SUMMARY

- Modeling indicates electrolyte wetting can take longer than standard formation process
- Quantified with high-energy XRD variations in local SOC/lithium plating with ~1-mm resolution both operando and resting
- In situ tomography shows severe lithium plating can lead to poor graphite utilization far from separator
- Team has well characterized graphite behavior at sub-micron-length scale
- Implemented lithium plating model that considers nucleation and growth effects to more accurately describe plating process than simple Butler-Volmer models
- Detailed comparison of SOC heterogeneity with local microstructure property mapping.

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PUBLICATIONS

- H. Charalambous, K. M. Wiaderek, D.P. Abraham, A.R. Dunlop, S.E. Trask, A.N. Jansen, T.R. Tanim, P.R. Chinnamc, A.M. Colclasure, W. Xu, A.A. Yakovenko, O.J. Borkiewicz, L.C. Gallington, U. Ruett, and Y. Ren. "Revealing causes of macroscale heterogeneity in lithium-ion pouch cells using synchrotron X-ray Diffraction." (Submitted).

- A.S. Ho, D.Y. Parkinson, D.P. Finegan, S.E. Trask, A.N. Jansen, W. Tong, and N.P. Balsara. "3D detection of lithiation and lithium plating in graphite anodes during fast charging." (Submitted).

- J.C. Garcia, I. Bloom, C. Johnson, D. Dees, and H. Iddir. "Graphite Lithiation under Fast Charging Conditions: Atomistic Modeling Insights." *J. Phys. Chem. C* **124**, 8162–8169 (2020).

- A. M. Colclasure, T.R. Tanim, A.N. Jansen, S.E. Trask, A.R. Dunlop, B.J. Polzin, I. Bloom, D. Robertson, L. Flores, M. Evans, E.J. Dufek, and K. Smith. "Electrode scale and electrolyte effects on extreme fast charging of lithium-ion cells." *Electrochimica Acta* **337**, 135854 (2020).

PUBLICATIONS

- Francois Usseglio-Viretta, Weijie Mai, Andrew Colclasure, and Kandler Smith. "Enabling fast charging of lithium-ion battery through Secondary/dual pore network: Part I - analytical model." *Electrochimica Acta* **342**, 136034 (2020).

- Weijie Mai, Francois Usseglio-Viretta, Andrew Colclasure, and Kandler Smith. "Enabling fast charging of lithium-ion battery through Secondary/dual pore network: Part II - numerical model." *Electrochimica Acta* **341**, 136013 (2020).

- Francois L. E. Usseglio-Viretta, Donal P. Finegan, Andrew Colclasure, Thomas M. M. Heenan, Daniel Abraham, and Kandler Smith. "Quantitative relationships between pore tortuosity, pore topology, and solid particle morphology using a novel discrete particle size algorithm." *J. Electrochem. Soc.* **167**, 100513 (2020).

- E.J. McShane, A.M. Colclasure, D.E. Brown, Z.M. Konz, K. Smith, and B.D. McCloskey. "Quantification of Inactive Lithium and SEI Species on Graphite Electrodes After Fast Charging." *ACS Energy Letters* **5**, 2045–2051 (2020).