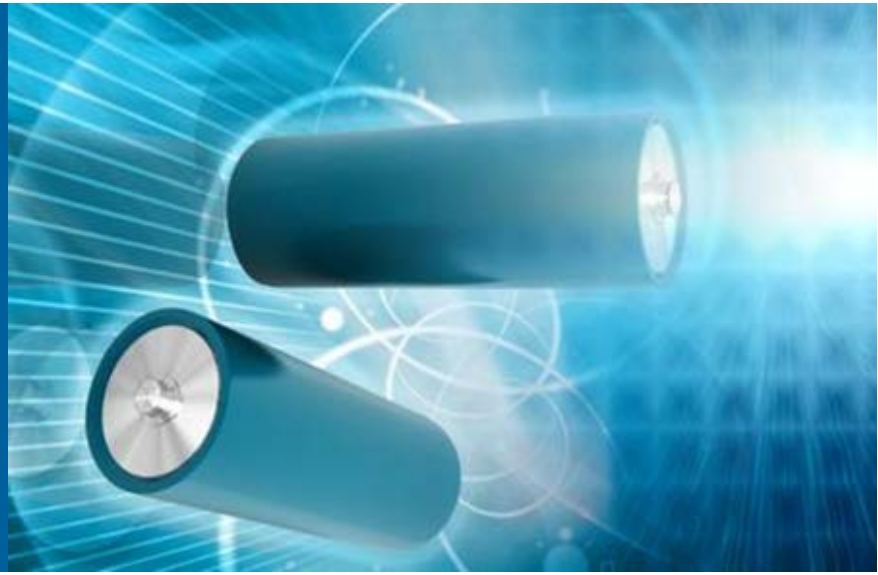
ELECTRODE BEHAVIOR DURING FAST CHARGING OF LITHIUM-ION CELLS



DANIEL ABRAHAM

35th Swiss Electrochemistry Symposium
Aarau, Switzerland

May 22, 2019

ACKNOWLEDGEMENTS
DOE-EERE
Marco Rodrigues
Kaushik Kalaga
Pierre Yao
Ilya Shkrob
Vic Maroni

ARGONNE: THE FIRST U.S. NATIONAL LABORATORY

- Located 25 miles from the Chicago Loop
- Operated by the University of Chicago for the U.S. Department of Energy
- About 3,000 employees and an annual operating budget of about $800 million
- Major research missions include basic science, environmental management, and advanced energy technologies

http://www.anl.gov/

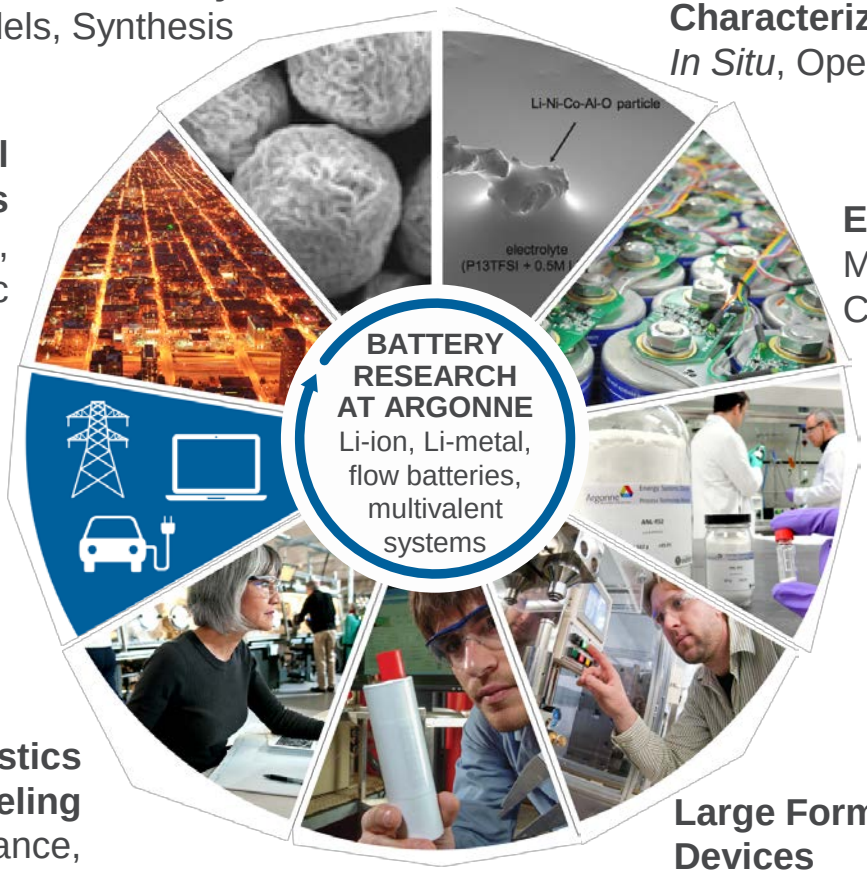
Battery R&D at Argonne – Lithium-ion and beyond

Material Discovery
Models, Synthesis

Chemistry Characterization
In Situ, Operando

System-level Analysis
Vehicle, Grid, Techno-Economic

Electrode and Cells
Modeling, Characterization



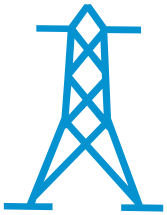
Recycling
Life Cycle, Processing

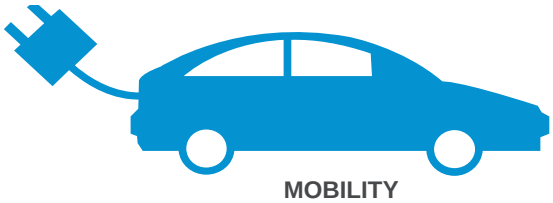
Material Process R&D and Scale Up
Organic, Inorganic

Cell Diagnostics and Modeling
Performance, Degradation

Standardized Testing
Large format, test protocols

Large Format Devices
Pouch, 18650



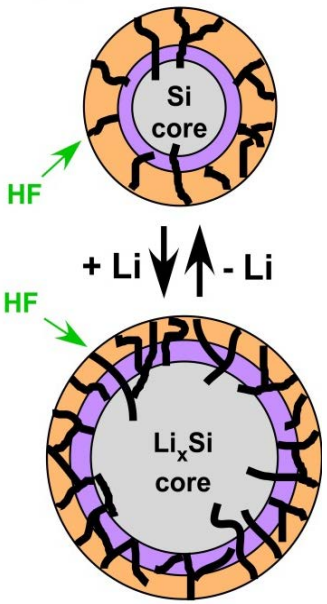


Research funding from both government and industry

Argonne NATIONAL LABORATORY

Key Challenges for Transportation

- **Lower battery cost**
  - Lower Co content in the positive electrode oxide
    - Structural stability of oxide degrades over time
- **Increase energy density**
  - Operate cells at higher voltages
    - Increased side-reactions at the positive electrode
  - Use Si in the negative electrode
    - Volume changes/fracture in Si degrades performance
- **Lessen likelihood of battery fires**
  - Use solid (ceramics, polymer) electrolytes
    - Limitations include low ionic conductivity, material cracking
- **Improve Low T (< 0 °C) Performance**
  - Modify electrolyte compositions
    - Poor performance at higher temperatures

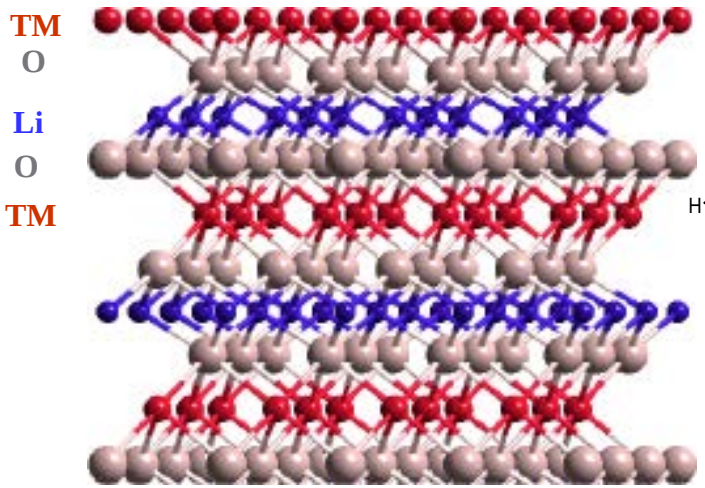


Key Challenges for Transportation

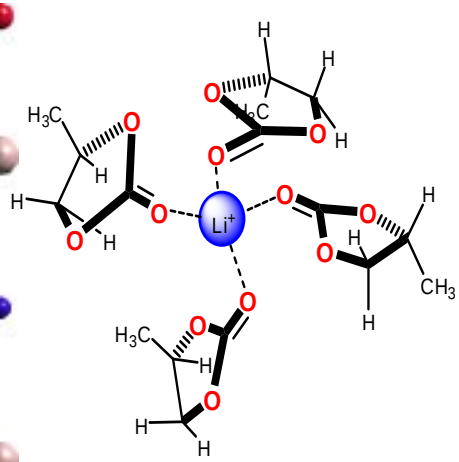
Enable fast-charge while maintaining cell performance

- Could we lower battery charging time from 1 h to 10 minutes?

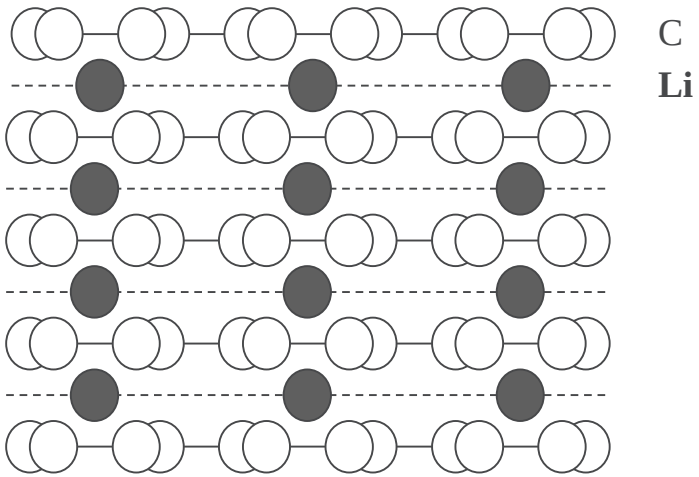
Layered oxide



Electrolyte



Graphite



Concerns

- Oxide particle fracture
- Crystal structure changes

Concerns

- Lithium plating on particles
- Graphite damage/disorder

At what rate does the performance degradation set in?

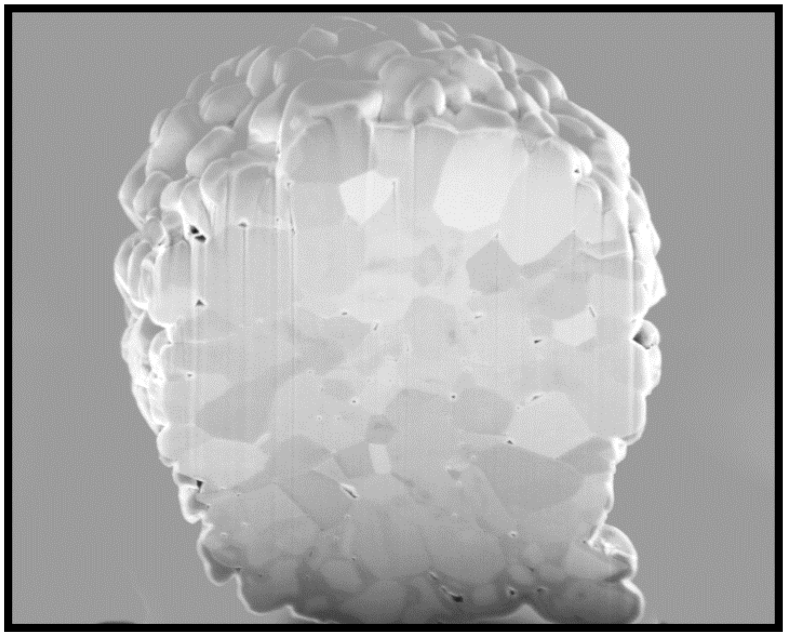
Baseline Cell Chemistry

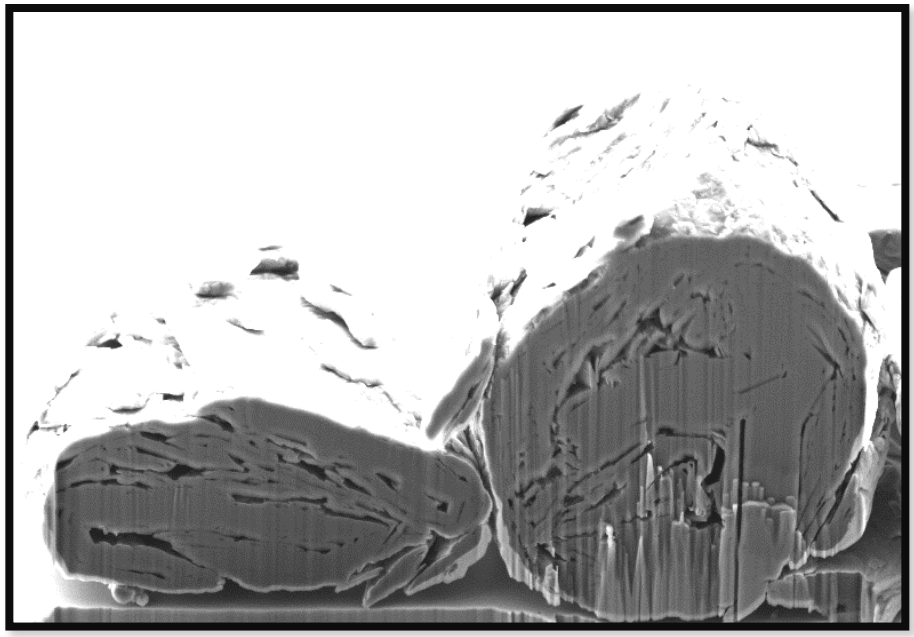
FIB-SEM cross-sections of particles

Baseline Electrolyte

- 1.2 M $LiPF_6$ in EC/EMC (3:7)

NCM523 = $Li(Ni_{0.5}Co_{0.2}Mn_{0.3})O_2$





Positive Electrode

- 90 wt% NCM523 Oxide
- 5 wt% C45 carbon
- 5 wt% PVdF binder
- 34 - 110 μm thk coating

Negative Electrode

- 92 wt% A12 Graphite
- 2 wt% C45 carbon
- 6 wt% PVdF binder
- 44 - 120 μm thk coating

Electrodes fabricated at Argonne's CAMP facility

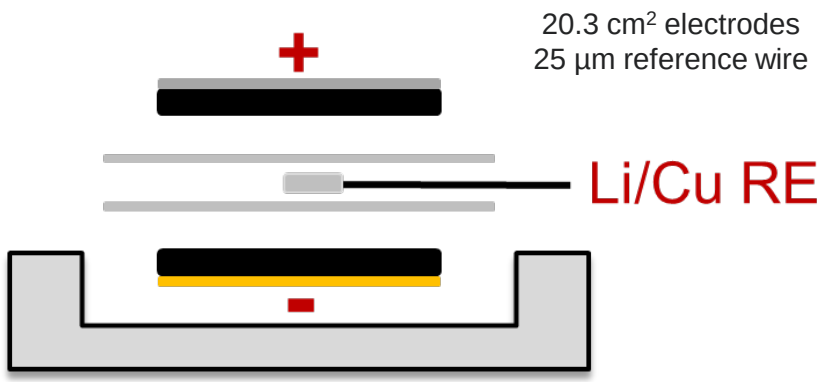
REFERENCE ELECTRODE TECHNIQUE

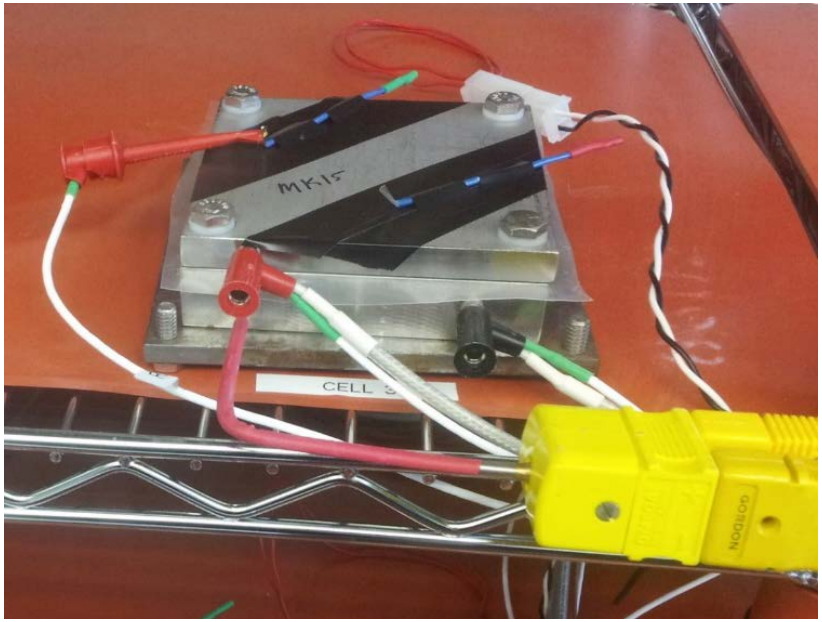
Objectives

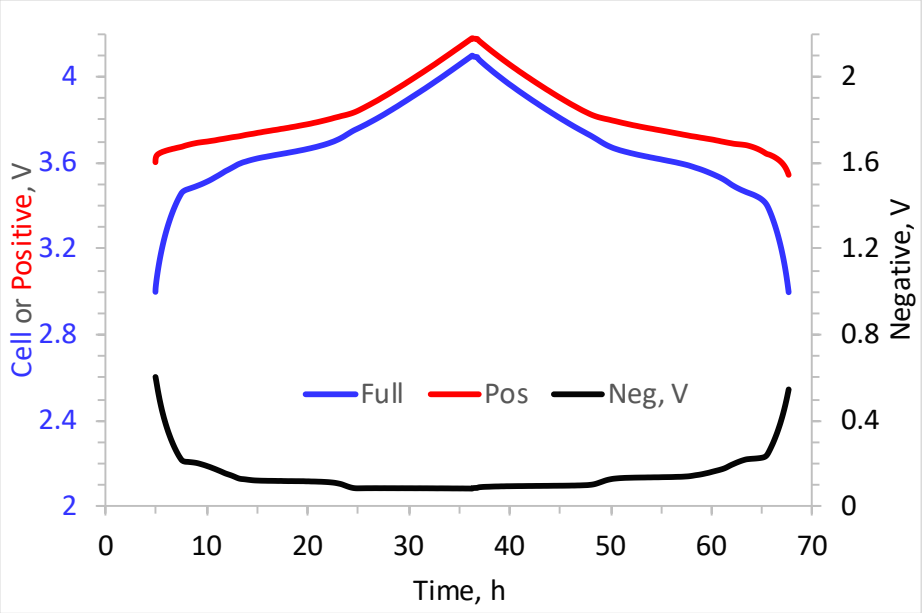
To determine cycling conditions under which Li-plating could occur

To examine electrode impedance changes that result from fast charge

Reference Electrode cells







Using a *reference electrode* allows the measurement of electrode potentials

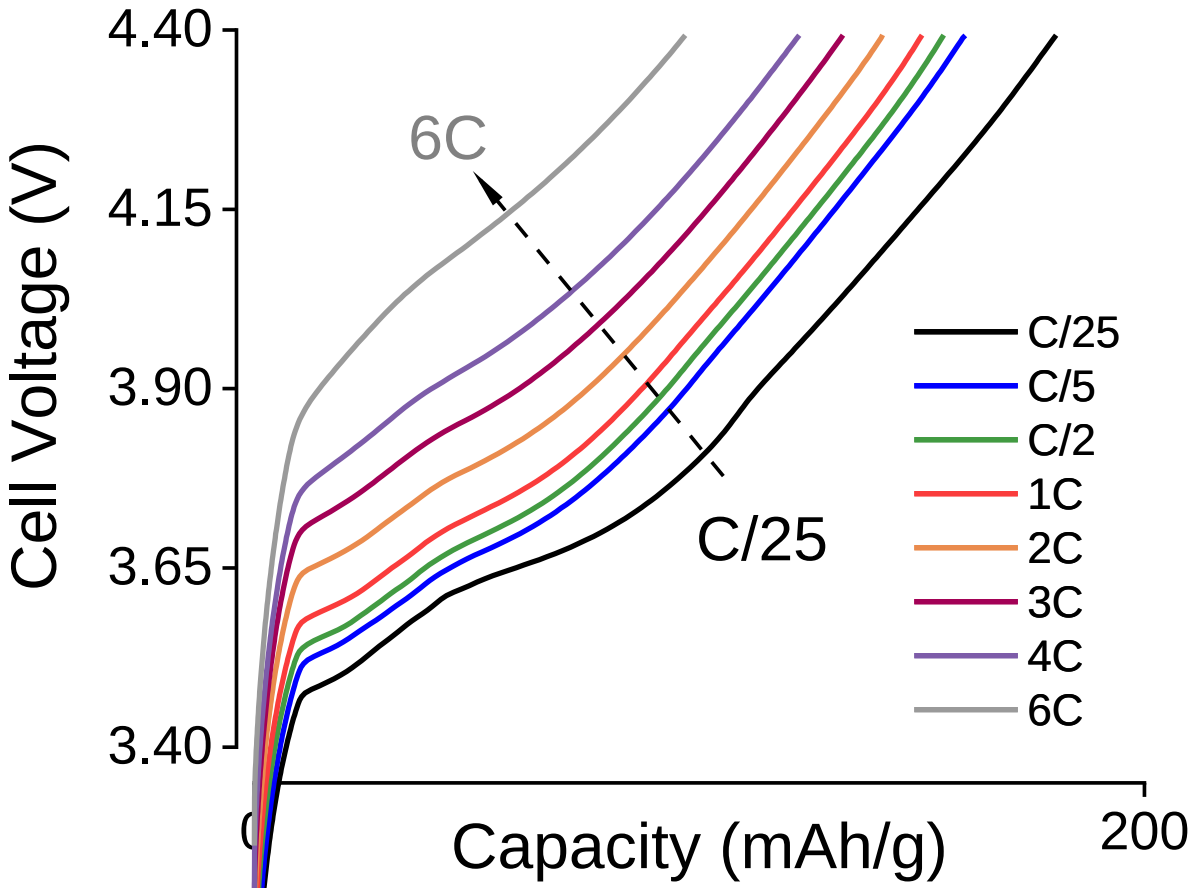
More info on Reference Electrode cells in

Rodrigues et al., J. Electrochem. Soc. 166 (2019) A996

Klett et al., J. Electrochem. Soc. 163 (2016) A875-A887

Abraham et al., Electrochimica Acta 49 (2004) p. 4763

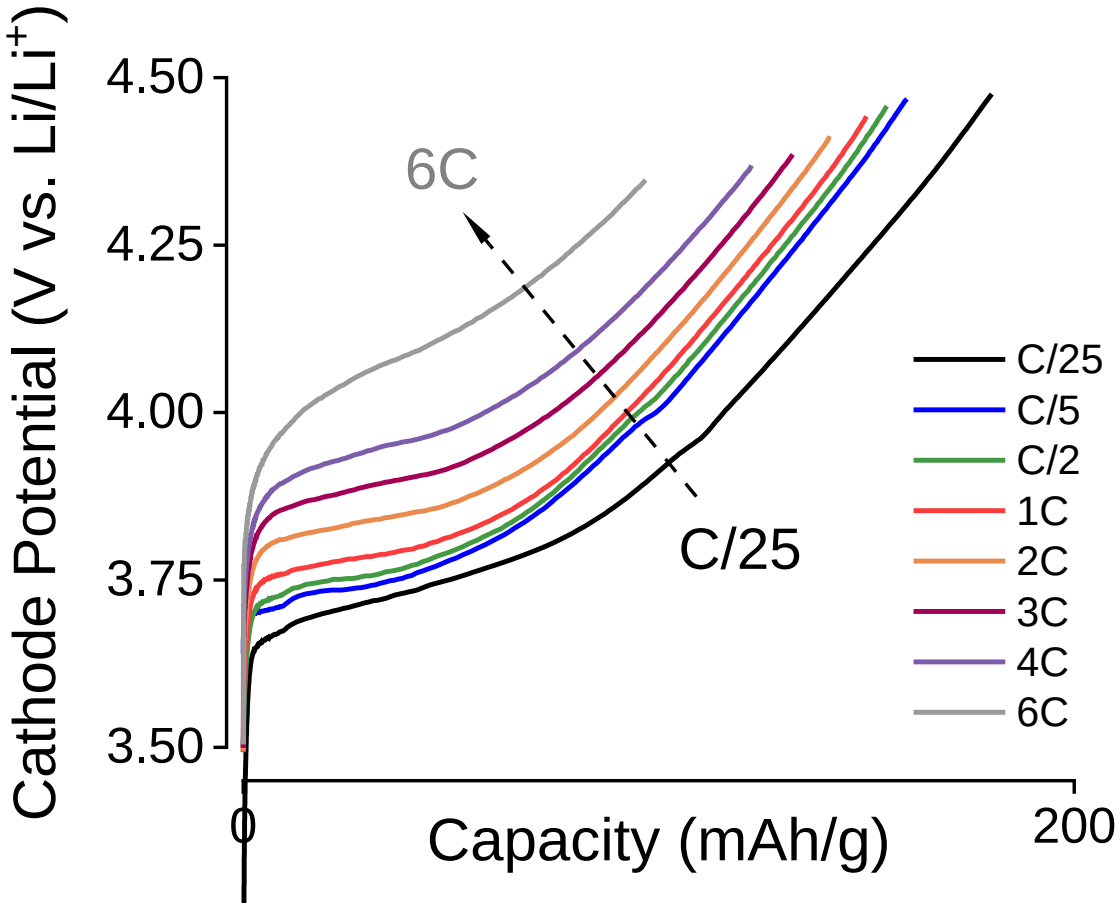
Cell voltage during cycling at various rates 3.0 – 4.39 V, 30 °C



Voltage polarization increases with rate

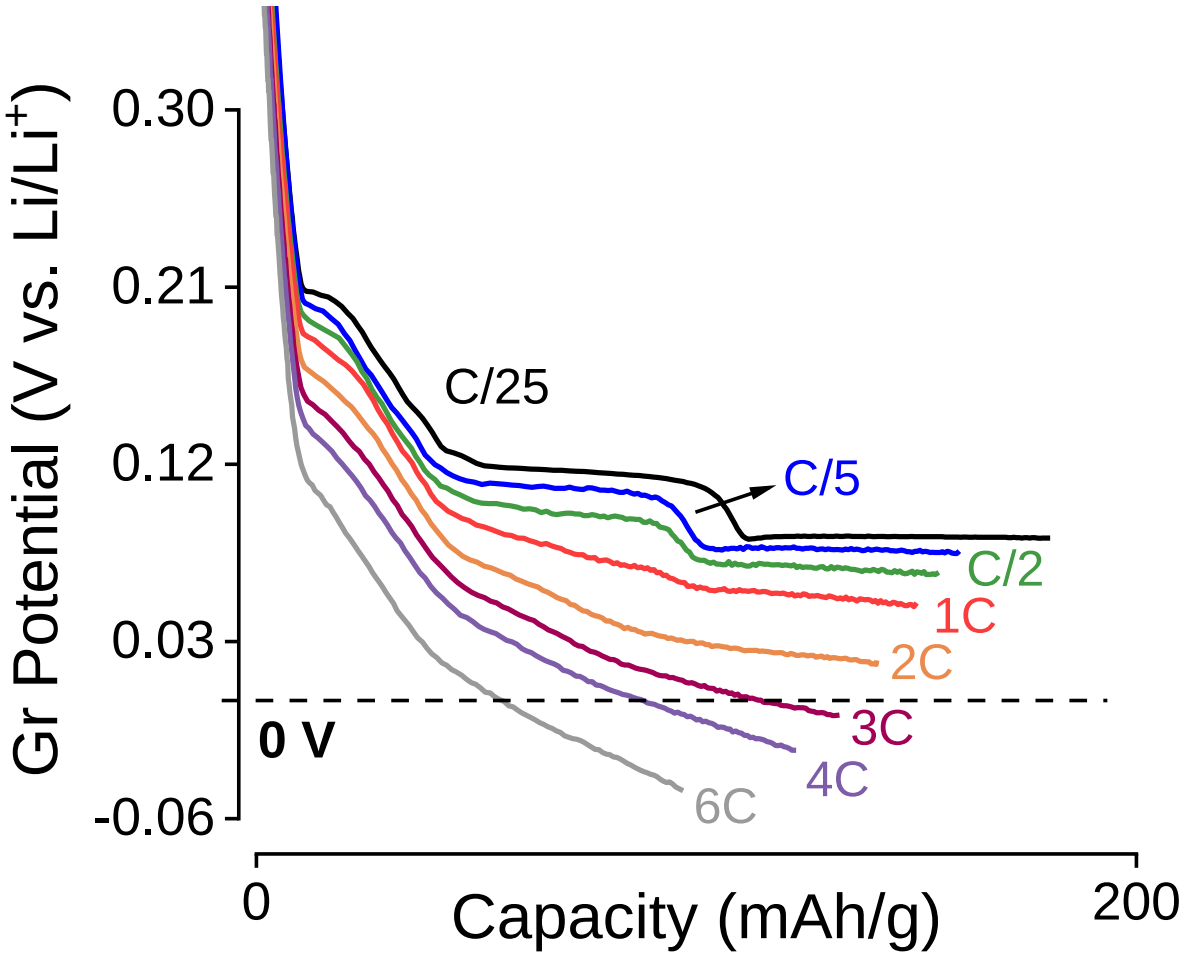
Capacity achieved decreases with rate

Positive electrode potential at various rates
Cell voltage: 3.0 – 4.39 V, 30 °C



As C-rate increases, the cell UCV is reached at progressively lower capacity because of positive electrode polarization

Negative electrode potential at various rates
Cell voltage: 3.0 – 4.39 V, 30 °C



Li-plating condition is met at rates ≥ 3C

Lowering the anode potential to ≤ 0.0 V vs Li/Li^+ creates the "Li plating condition" (LPC)

- Direct deposition of Li is thermodynamically favorable under LPC, so only *kinetic* barriers can prevent Li^0 nucleation

But does Li plating actually occur?

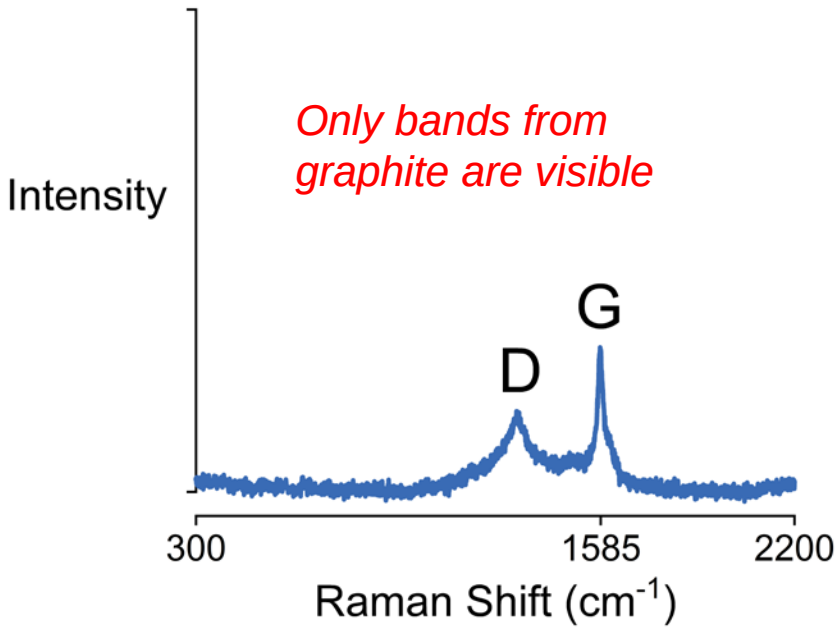
- As the high current system operates far from the thermodynamic equilibrium, LPC and Li plating are related, but distinct conditions

RAMAN SPECTROSCOPY

An accessible and sensitive tool to detect Li plating

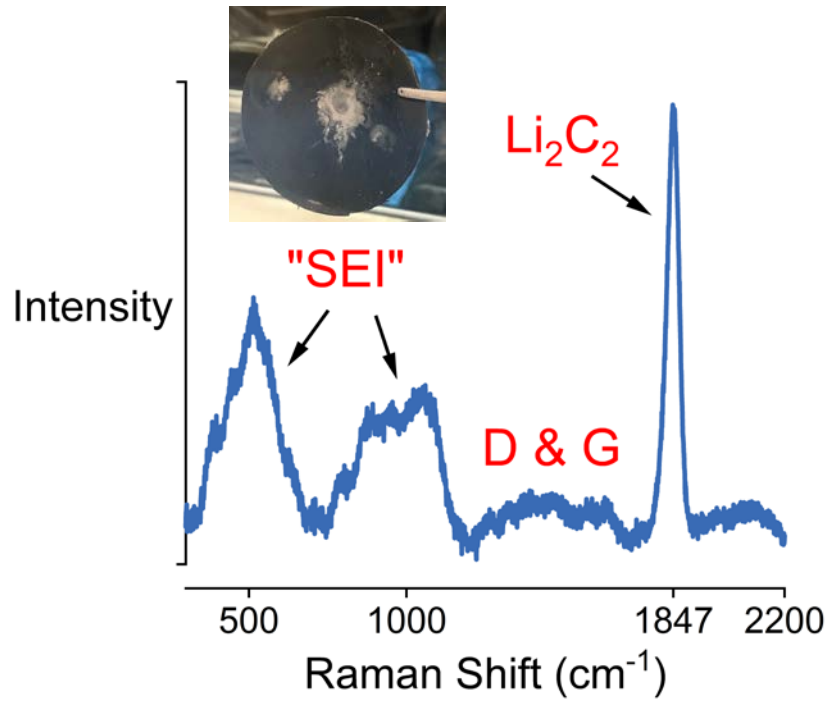
Raman Spectroscopy of graphite electrodes

Graphite electrode from a highly aged cell (360, C/3 cycles, **no Li plating**)



Extensive SEI growth does not produce Raman signals

Graphite electrode after fast charging (6C charge, **Li plating**)



Very intense SEI and acetylide (Li_2C_2) bands are visible in the Raman spectra

Rodrigues et al. ACS Appl. Energy Mater. 2019, 2, 873

Raman Spectroscopy of overlithiated graphite

graphite electrode
overlithiated by 20% at C/20

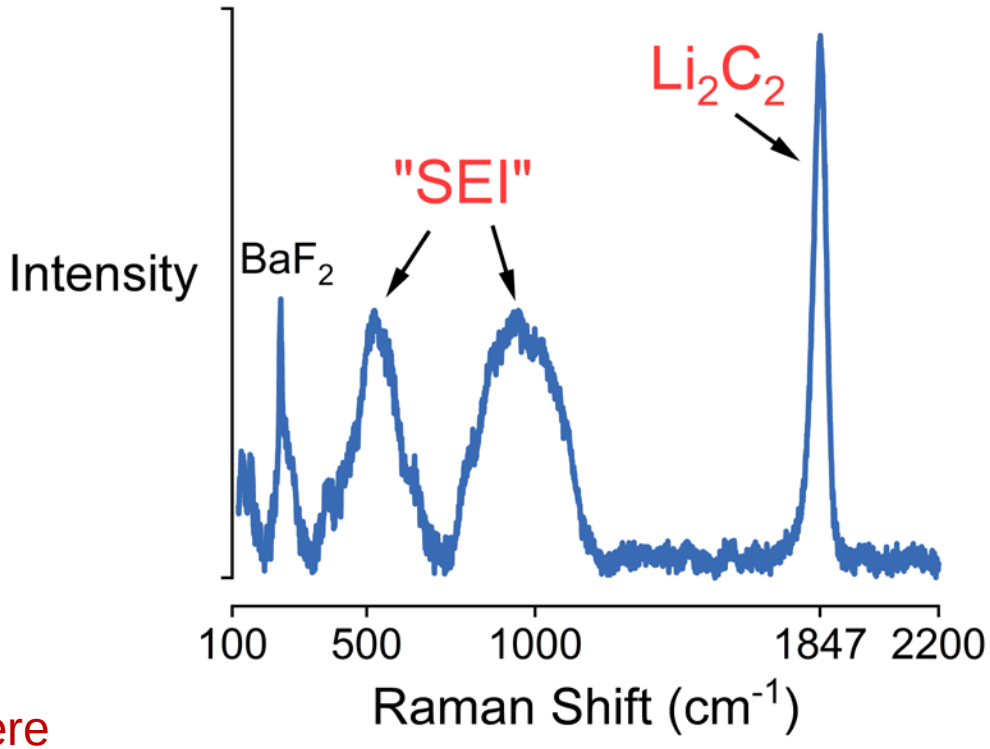
overlithiated

delithiated

coulombic efficiency = 91.8%

Li_2C_2 is detected even in regions where there is no visual indication of plating

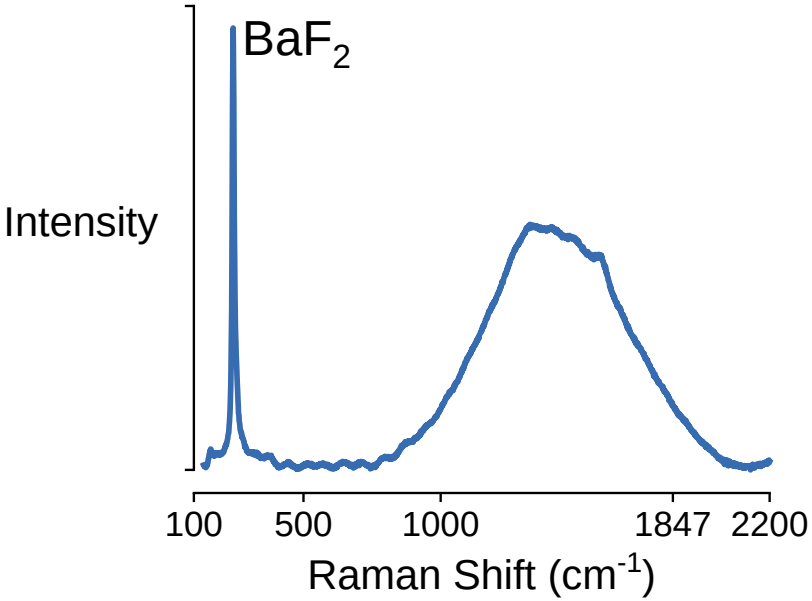
unwashed, discharged



Li_2C_2 correlates with Li plating

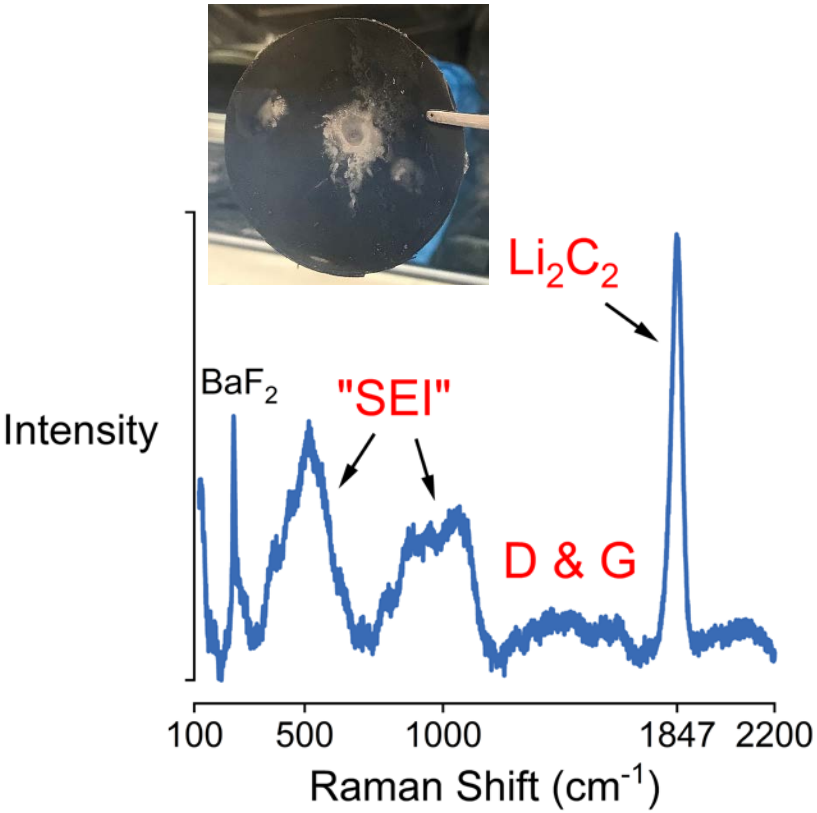
Raman Spectroscopy of lithiated graphite and graphite from fast-charged cell

unwashed lithiated graphite electrode, with no Li plating



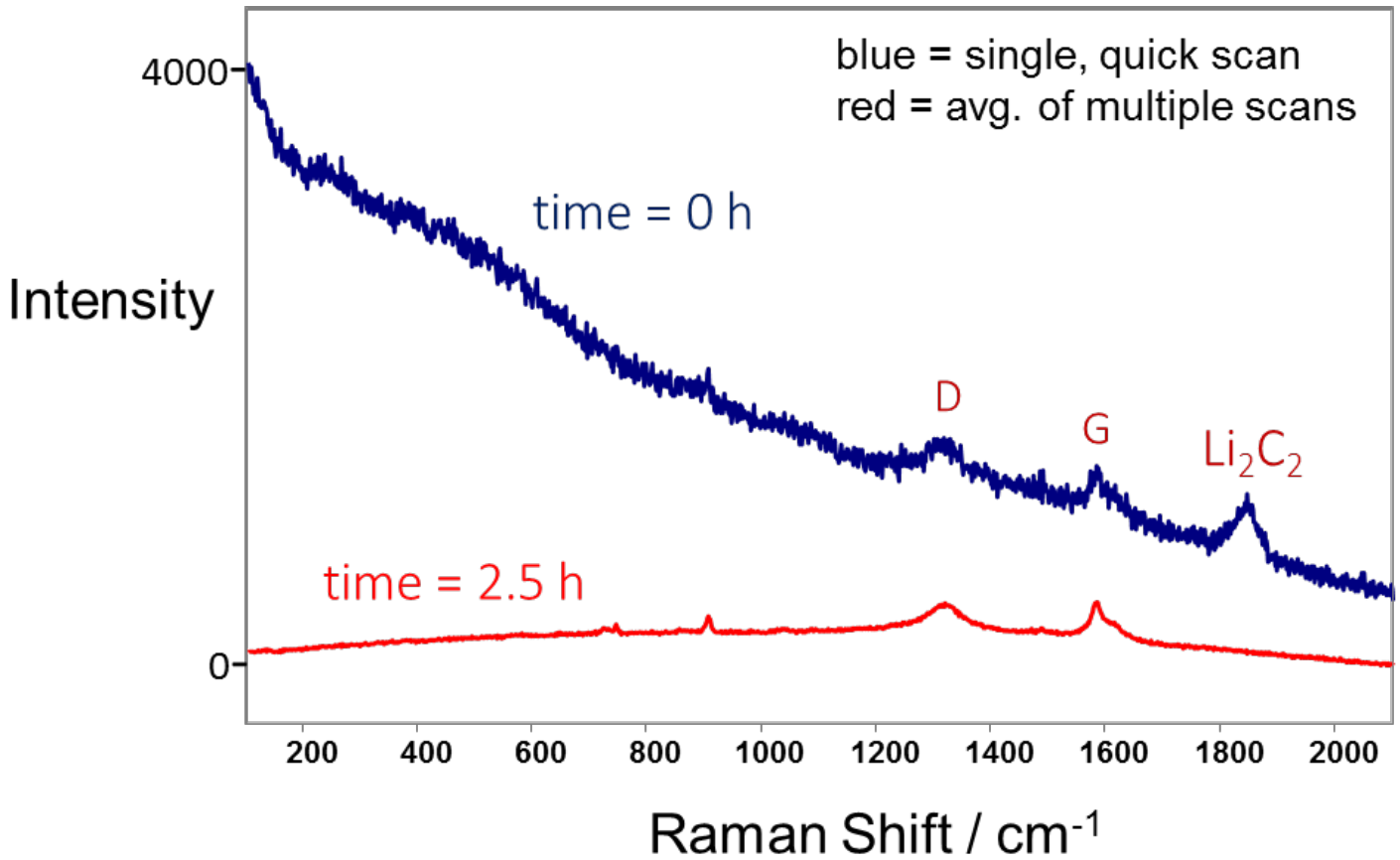
No evidence of acetylide

Graphite electrode after fast charging (6C charge, **Li plating**)



Lithium acetylide band is a spectroscopic marker for metallic lithium

Raman spectra of a (Li-plated) Gr electrode exposed to lab air



1) extremely high intensity of Li_2C_2 band

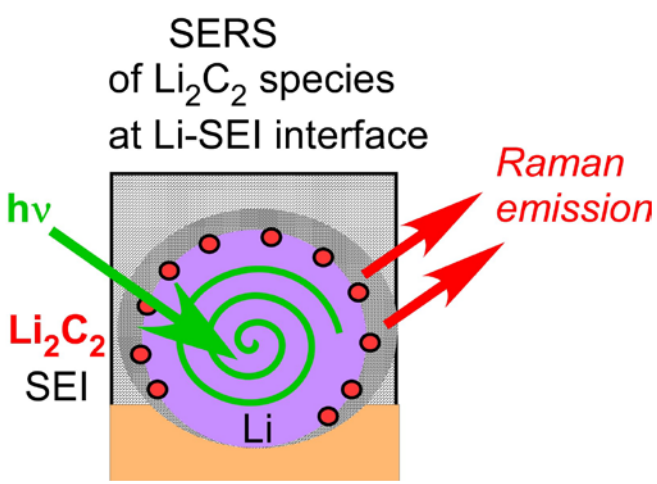
2) when Li is oxidized/hydrolyzed, only D and G bands remain

How does lithium plating enhance the acetylide (carbide) band?

Origin: small carbide clusters form by reduction of SEI species by plated Li, becoming part of its SEI

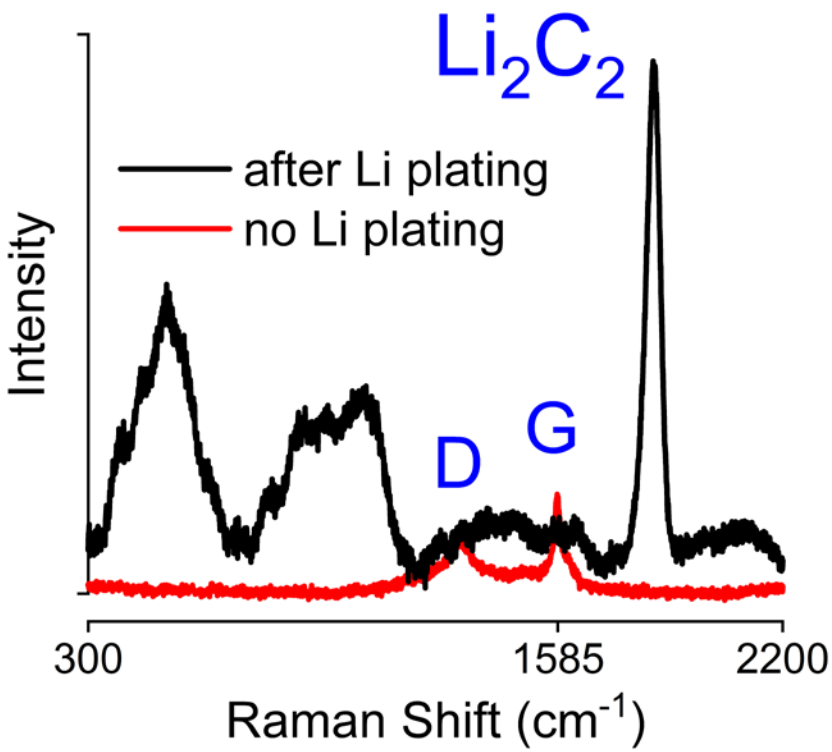
$$\text{SEI or electrolyte} + Li_{(s)} \rightarrow Li_2C_2$$

Mechanism: plated Li enhances the signal from its immediate SEI through surface-enhanced Raman scattering (SERS)

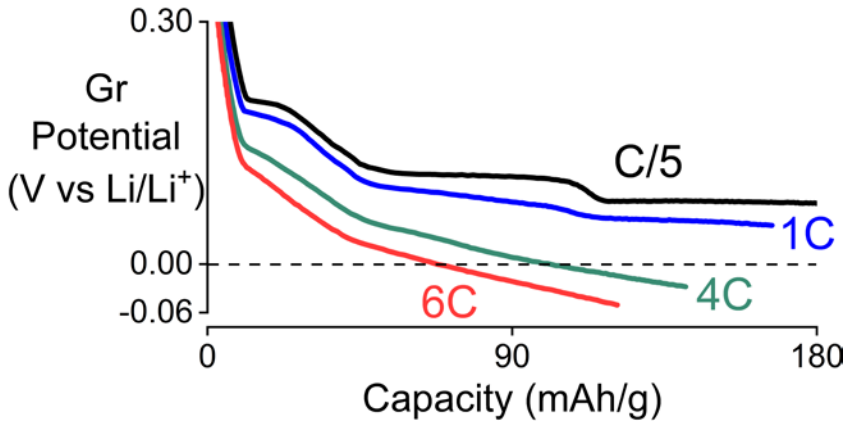


Result: Li_2C_2 band is only detected when metallic Li is present

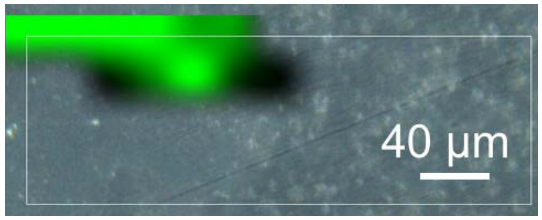
Sensitive and specific to Li



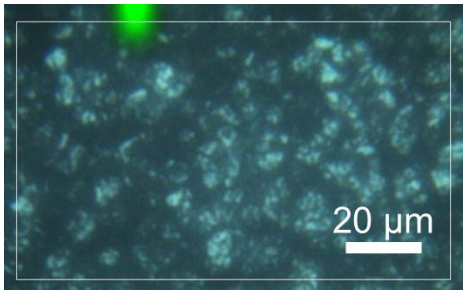
Spatially-resolved Li_2C_2 detection even after a single fast charge



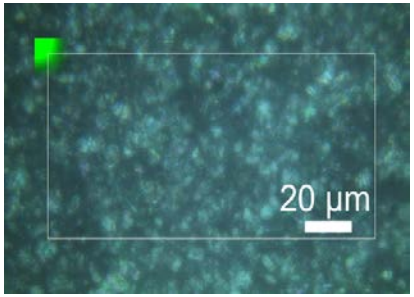
graphite electrode after 7 cycles at 6C



after 1 cycle at 6C



after 1 cycle at 4C



Potential for **operando** studies of Li nucleation

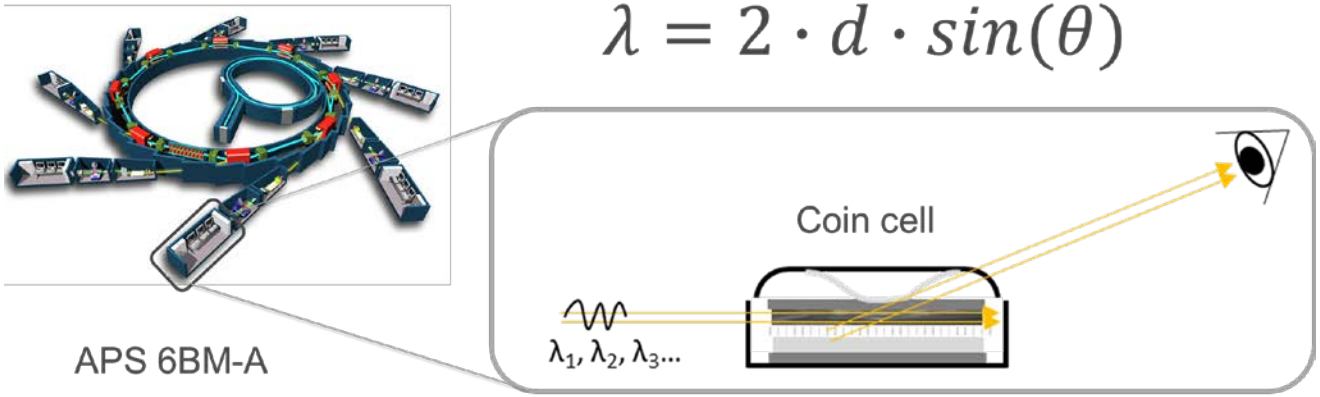
OPERANDO X-RAY DIFFRACTION

To examine lithium concentration gradients that are generated along the electrode cross-section during fast charging

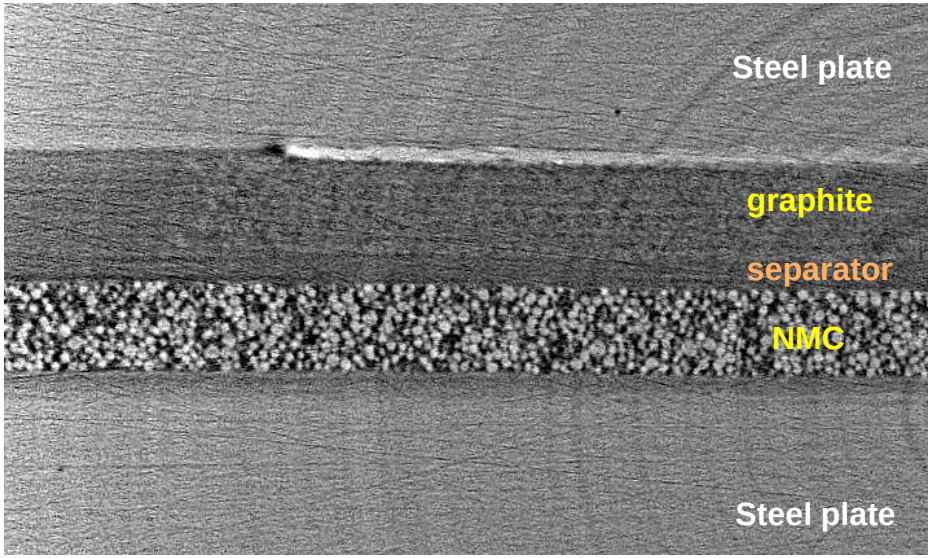
Persistence of these concentration gradients can result in non-uniform aging of the electrodes, making it difficult to predict cell life

Energy Dispersive X-Ray Diffraction

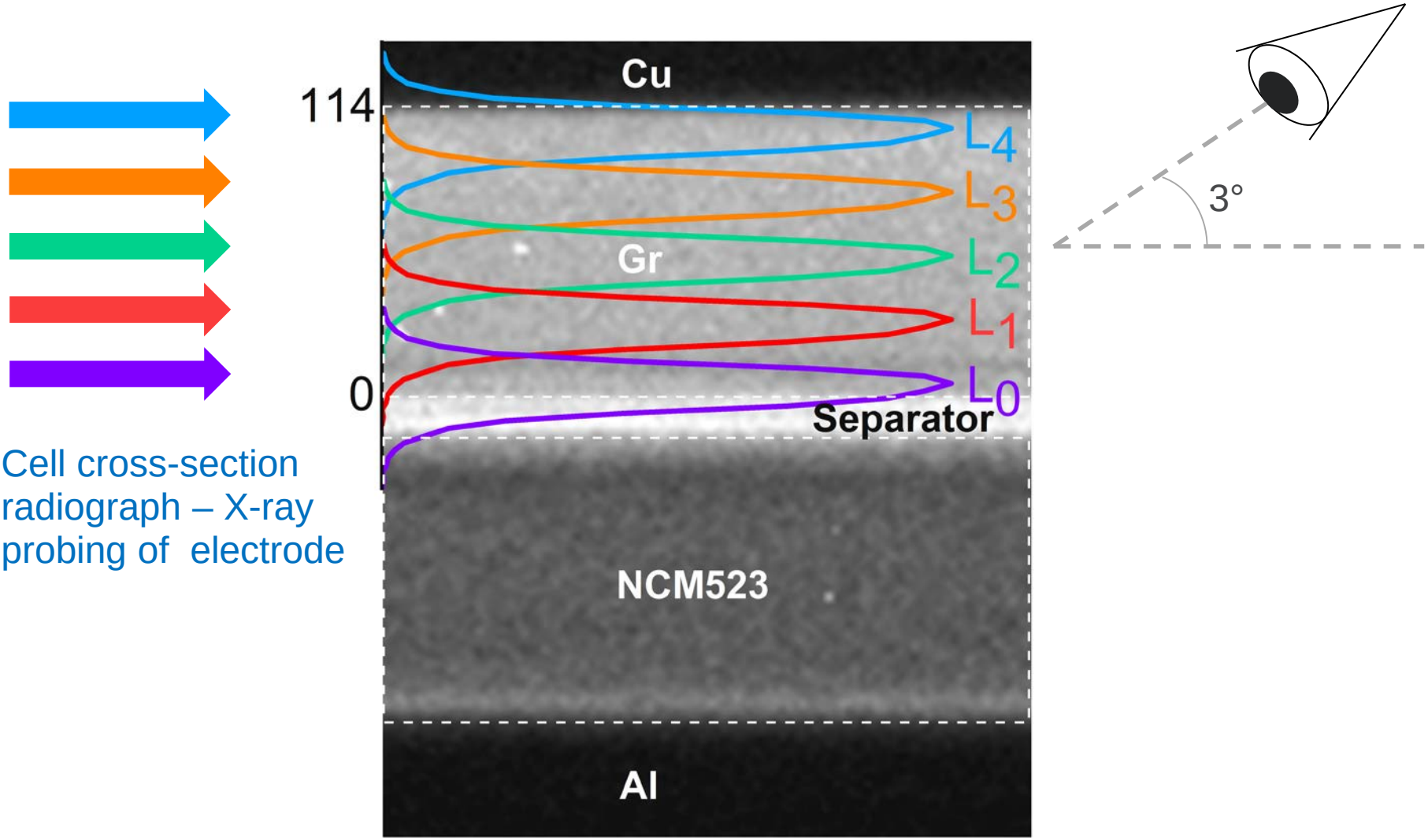
$$\lambda = 2 \cdot d \cdot sin(\theta)$$



Radiography
&
Tomography



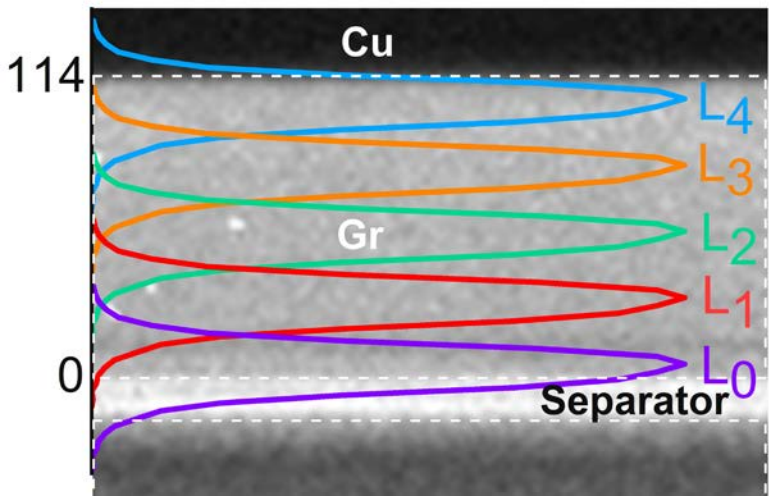
Examining electrode cross-sections using operando energy dispersive X-ray diffraction

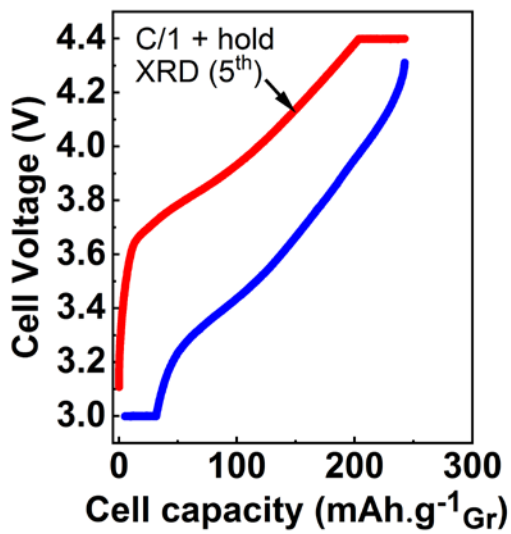


Cell cross-section radiograph – X-ray probing of electrode

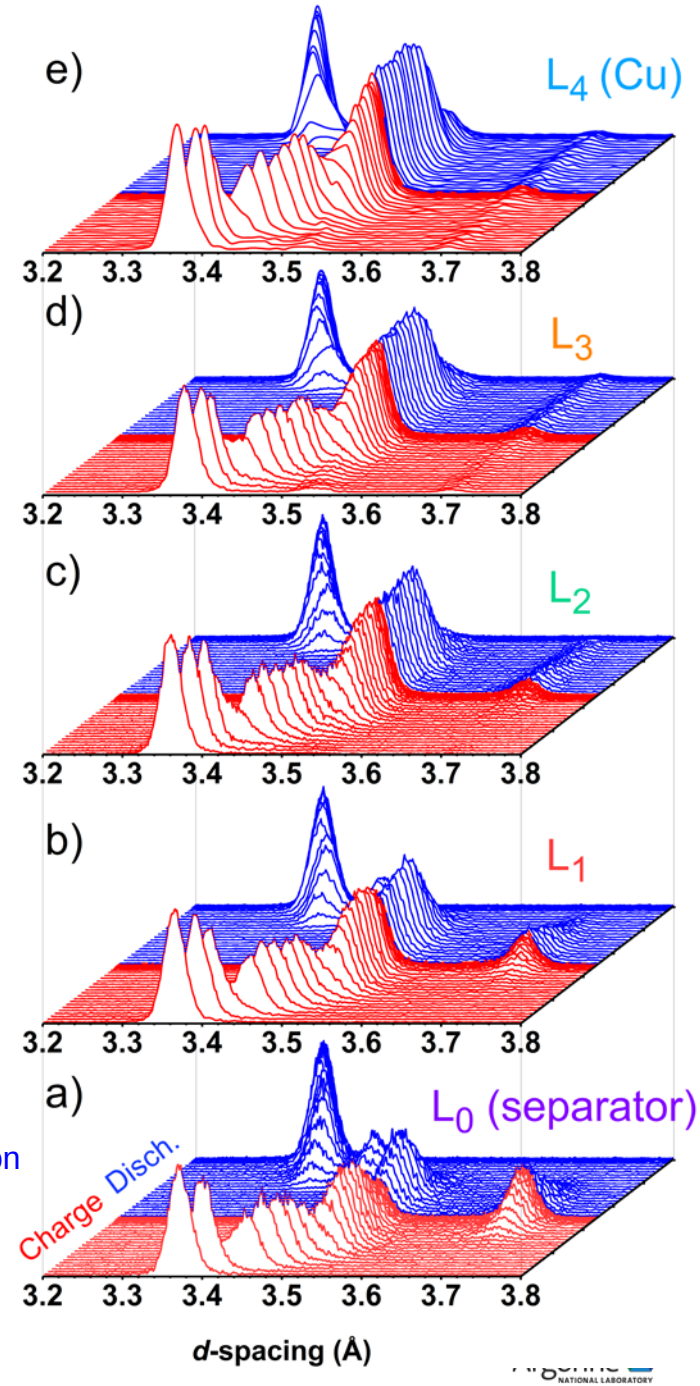
Yao et al. Energy Environ. Sci., 2019,12, 656

XRD spectra of Gr anode during 1C cycling (after formation)





3-4.4 V, 1C



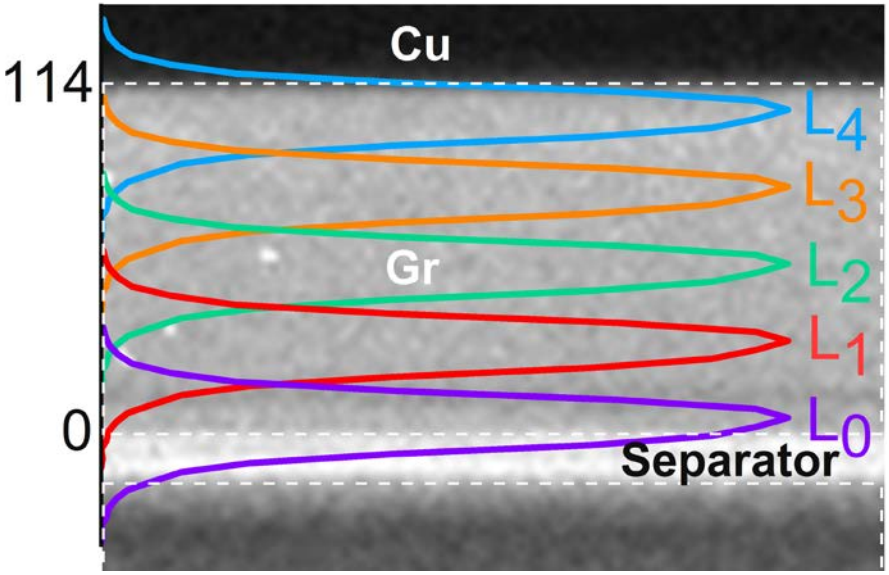
Gr DeLithiation

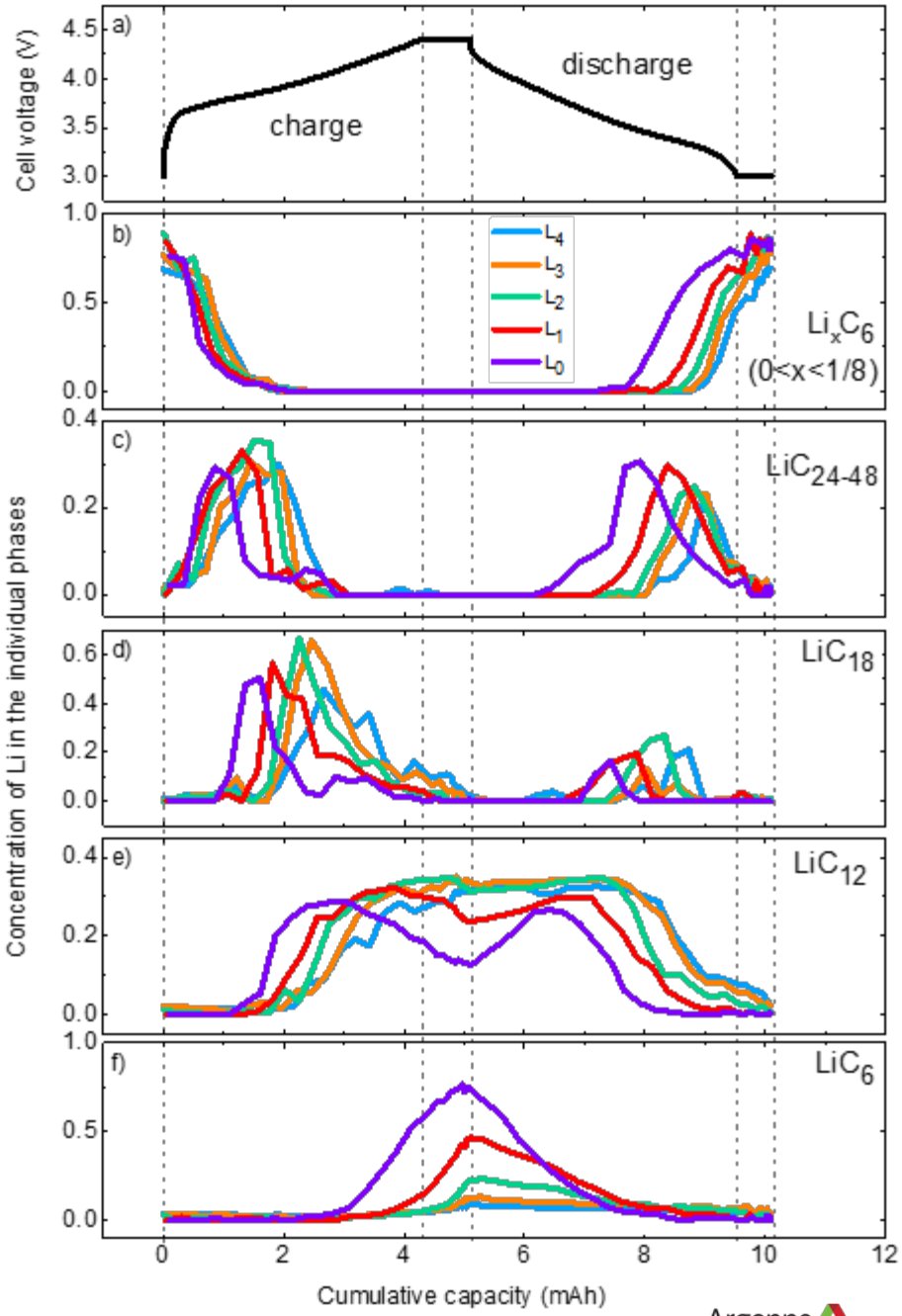
Gr Lithiation

Charge Disch.

Gr stages identified from spectral deconvolution

Dilute stage **I'**	$LiC_{\infty-48}$
stage **IV/III**	LiC_{48-24}
Stage **IIL**	LiC_{18}
Stage **II**	LiC_{12}
Stage **I**	LiC_6





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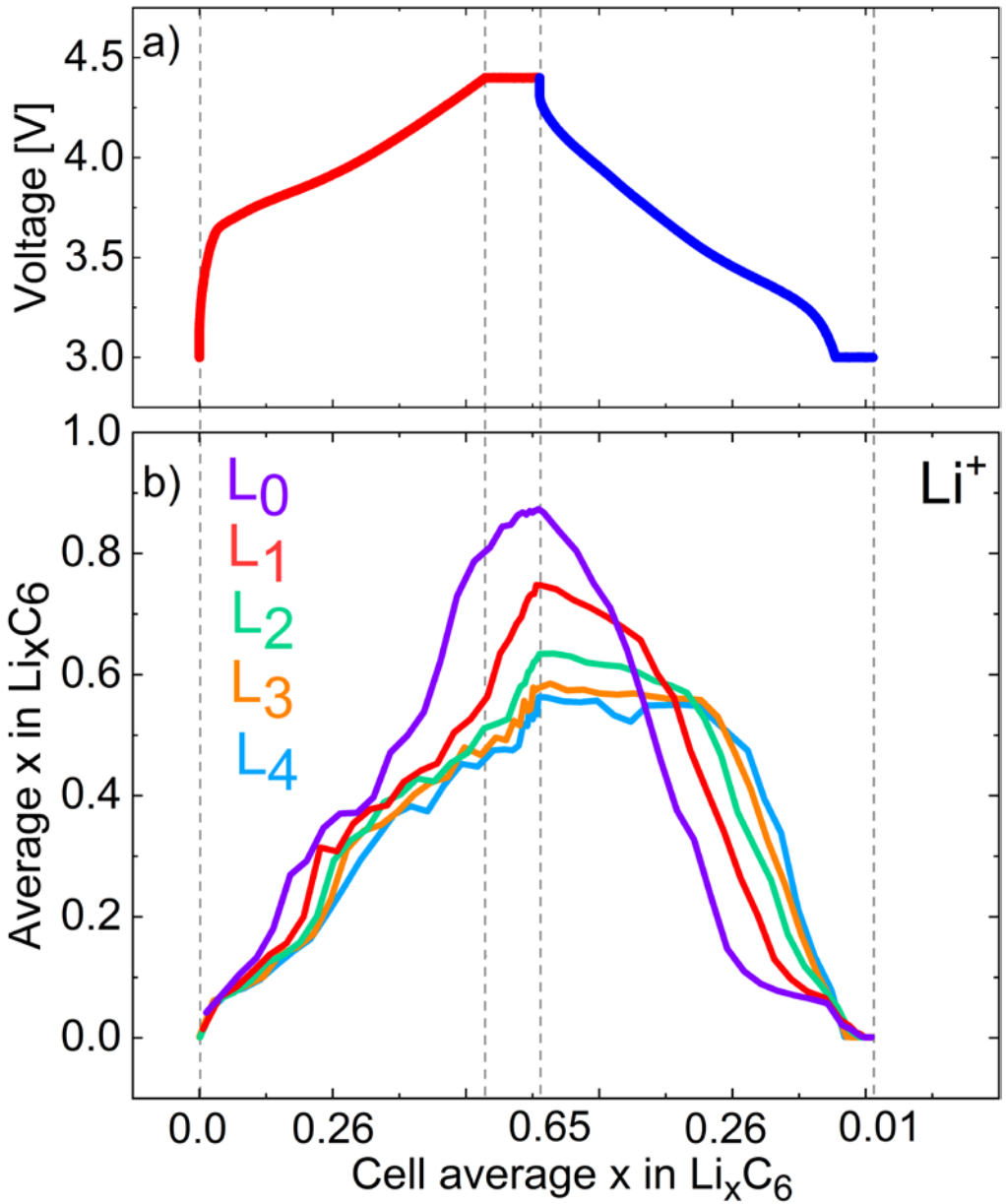
Average Li content of various layers

L_0: Separator

L_4: Cu Current collector



Inhomogeneous insertion/extraction of Li^+ observed even at a 1C rate

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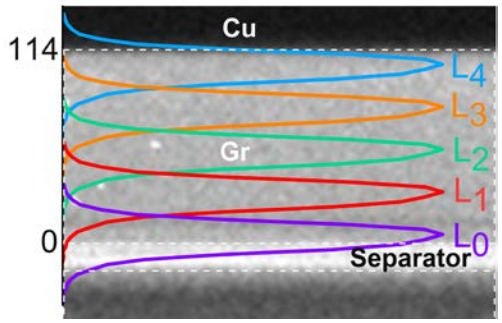
Average Li content of various layers during cycling at 1C rate



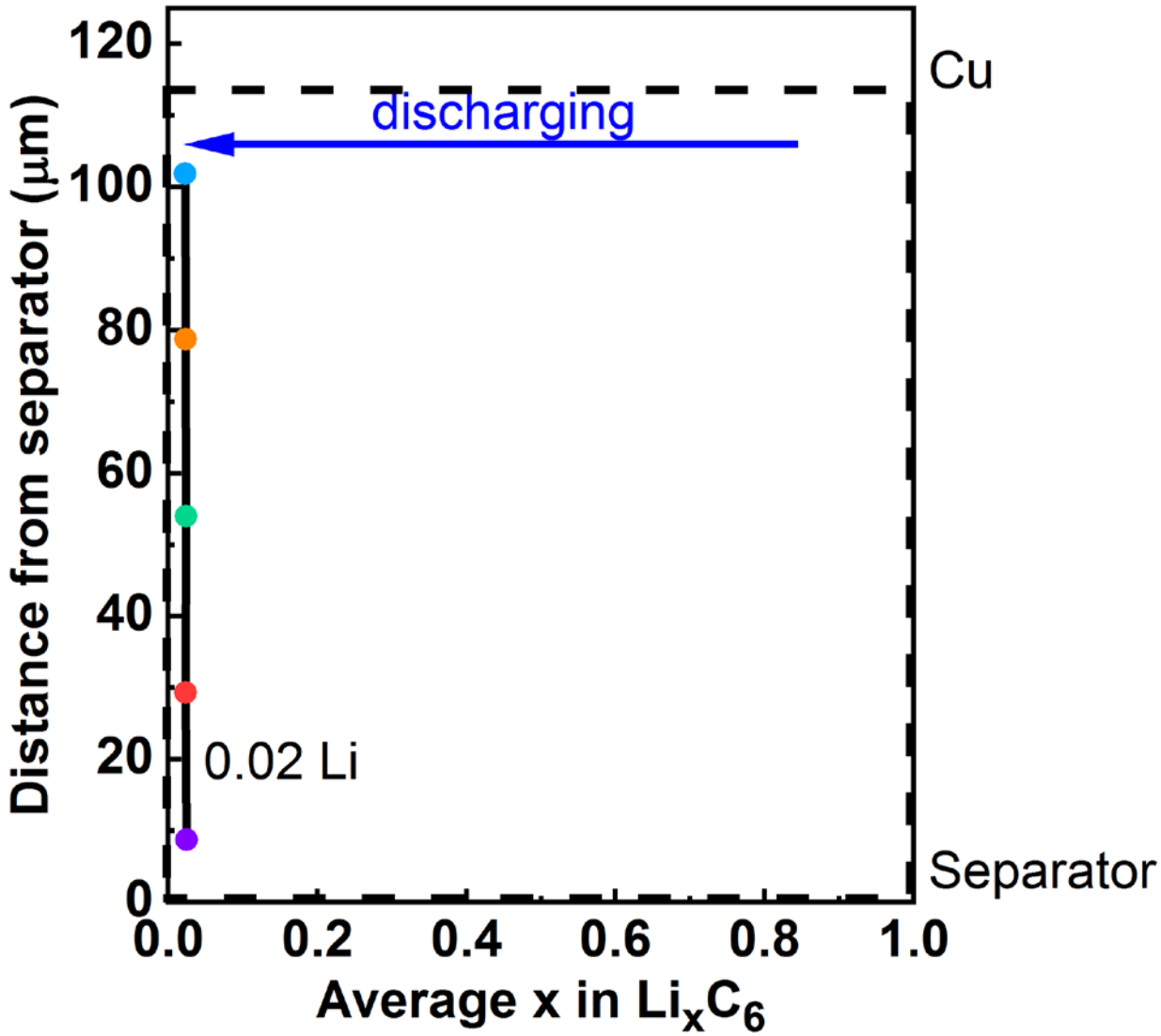
101.9 μm

78.7 μm

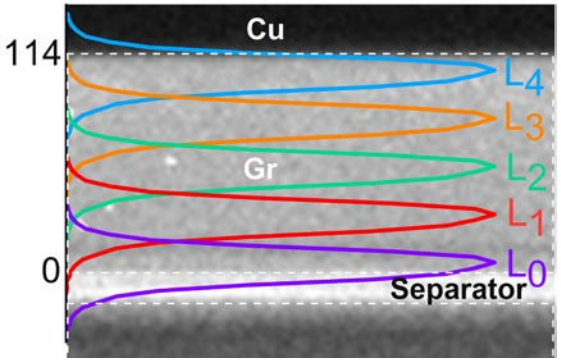
54.0 μm

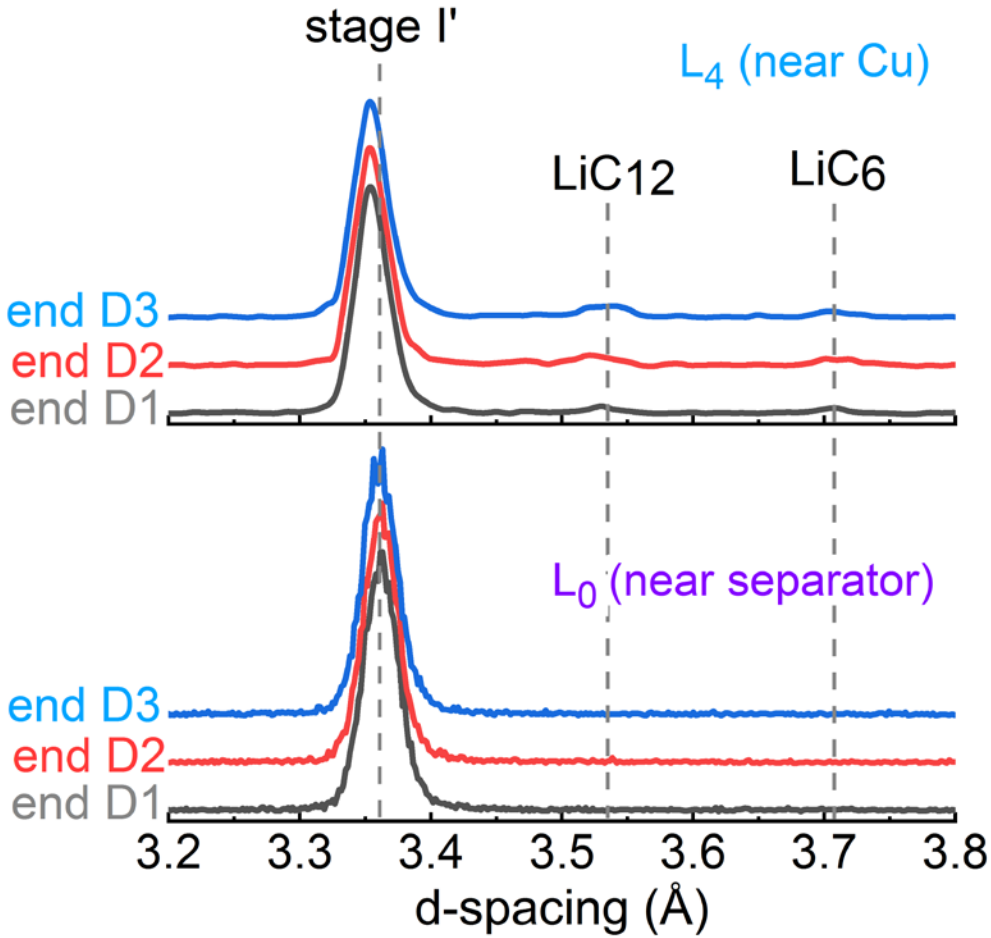
29.3 μm

8.7 μm



Residual LiC_6 and LiC_{12} in deep layers over 3 fast-discharges = CE << 99.999% (not necessarily SEI)





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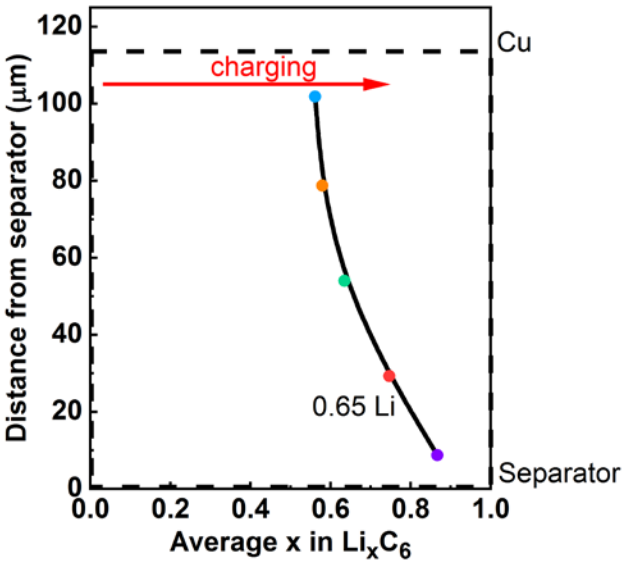
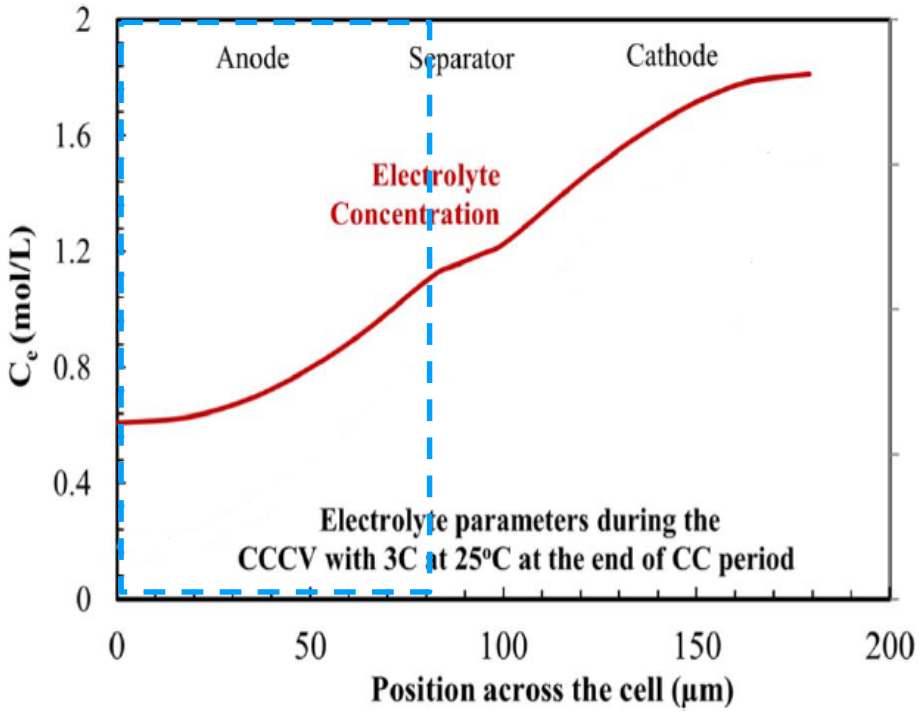
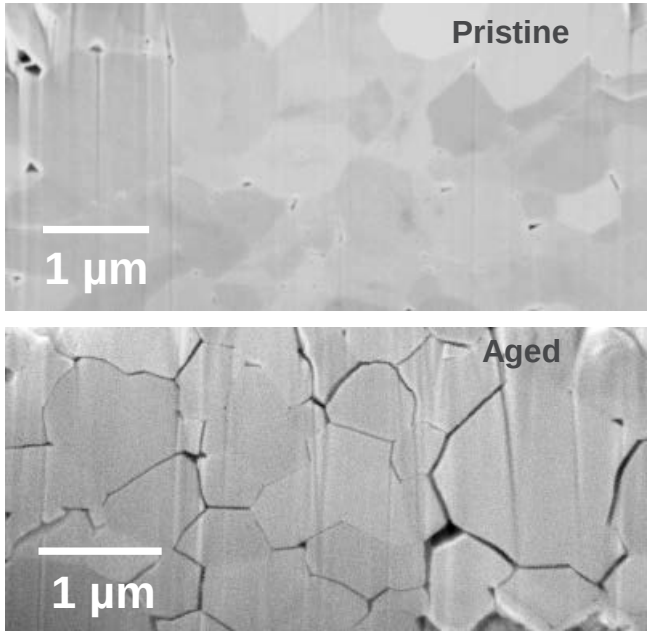
Comparing data with electrochemical models



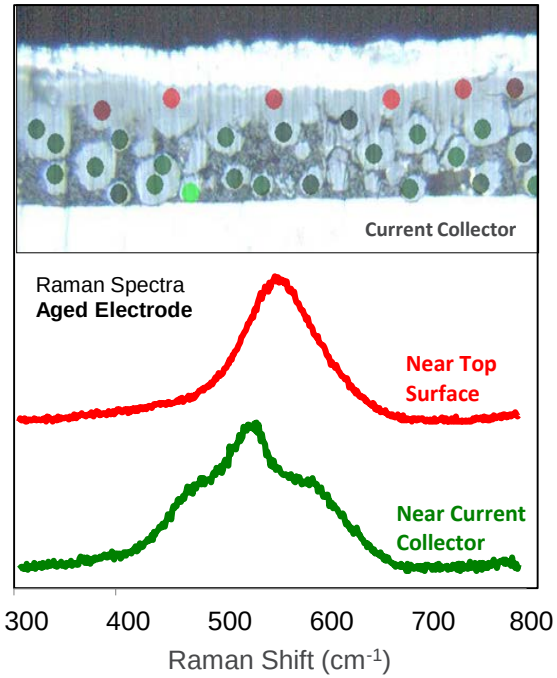


Fast charging also degrades performance of the positive (oxide) electrode

Li^+ gradients also present in oxide electrode



FIB/SEM
Primary particle separation (cracking) evident in oxides



Raman Spectroscopy
Oxide particles near electrolyte interface have higher impedance

Gilbert et al. , Adv. Mater. Interfaces 2018, *1701447*

Approaches to enable fast charging

Electrolyte design

- Maximize Li^+ ion conductivity to minimize concentration gradients
- Minimize SEI impedance for rapid Li^+ ion diffusion into graphite

Electrode design

- Align pores to minimize tortuosity & speed up Li^+ ion diffusion
- Porosity gradients (more porous near separator)

Particle design

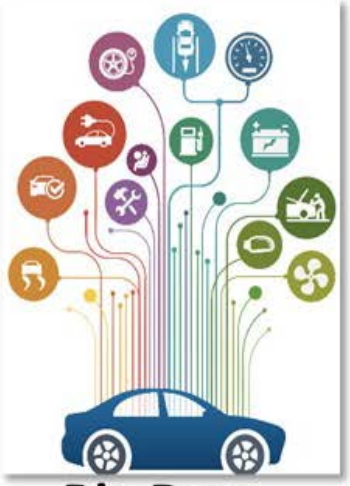
- Optimize graphite morphology/size for rapid Li^+ ion diffusion
- Optimize other cell components (oxide, separator)

Cycling protocols

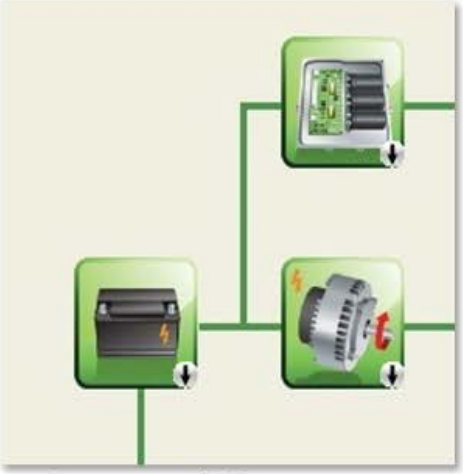
- High temperature charging speeds up Li^+ ion diffusion in electrode
- Pulsed/intermittent charging allows time for Li^+ ion diffusion into graphite

The Transportation Revolution

A. Schlenker, ANL (2017)



Big Data



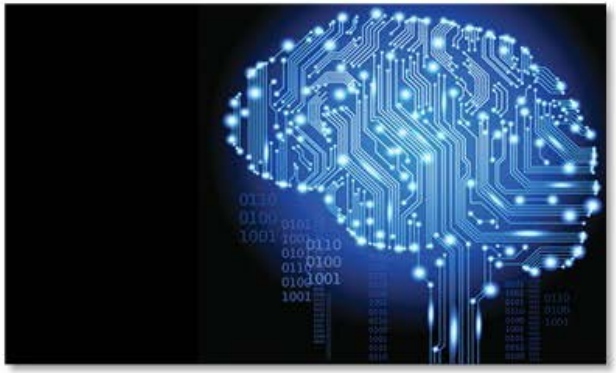
Control Systems

Vehicle Design

Lightweighting

Powertrain Optimization

Advanced Sensors



AI/Machine Learning

Source: ‘Energy Efficient Mobility Systems’. DOE/Michael Berube. 2016