FAST CHARGING OF LITHIUM-ION CELLS: PITFALLS AND POSSIBILITIES

DANIEL ABRAHAM

Battery Safety Science Webinar Series
Underwriters Laboratories Inc.
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Acknowledgments
DOE-EERE
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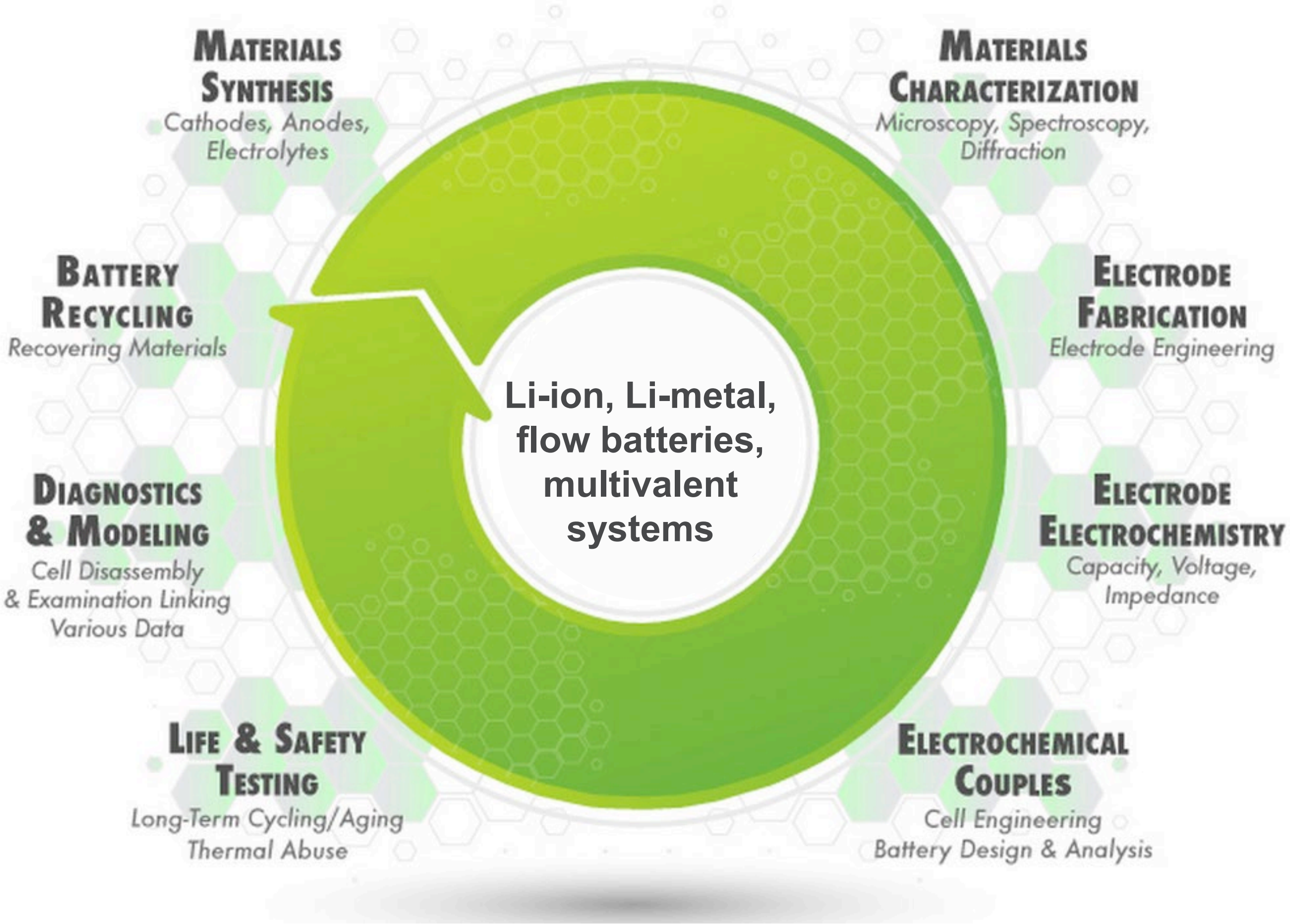
Argonne colleagues

Batteries at Argonne: Lithium-ion & Beyond



Li-ion, Li-metal, flow batteries, multivalent systems

Materials Synthesis
Cathodes, Anodes, Electrolytes

Materials Characterization
Microscopy, Spectroscopy, Diffraction

Electrode Fabrication
Electrode Engineering

Electrode Electrochemistry
Capacity, Voltage, Impedance

Electrochemical Couples
Cell Engineering
Battery Design & Analysis

Life & Safety Testing
Long-Term Cycling/Aging
Thermal Abuse

Diagnostics & Modeling
Cell Disassembly & Examination Linking Various Data

Battery Recycling
Recovering Materials

Batteries at Argonne: Funding from Government & Industry

ReCell
ADVANCED
BATTERY RECYCLING

BatPaC

EverBatt

JCESR | Joint Center for Energy Storage Research

Cell Analysis, Modeling, and Prototyping (CAMP) Facility

https://access.anl.gov/

https://www.anl.gov/manufacturing

https://www.jcesr.org/

Our research portfolio includes some key challenges facing Li-ion batteries for transportation

lower cost cathodes

- synthesize low-cobalt oxide cathodes
- examine performance & aging modes
- evaluate oxide coatings & new electrolytes

high energy-density anodes

- develop silicon-containing anodes
- accelerated tests to probe cell stability
- modeling on cell and pack level

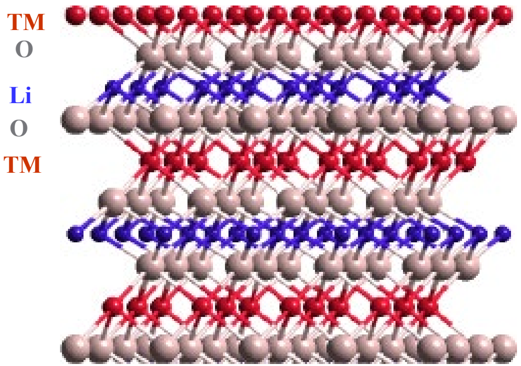
extreme fast charging

- understanding and modeling of high-rate phenomena
- effect of temperature on fast charging
- detection of Li plating
- cell aging due to high currents
- development of charging protocols

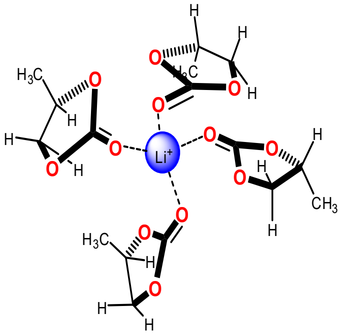
Enable fast-charge while maintaining cell performance

Can we lower battery charging time – full charge in 10 minutes?

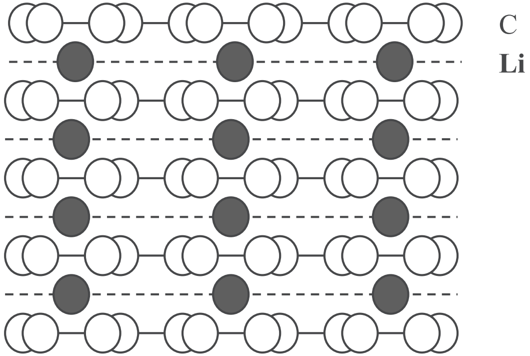
Layered oxide



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?

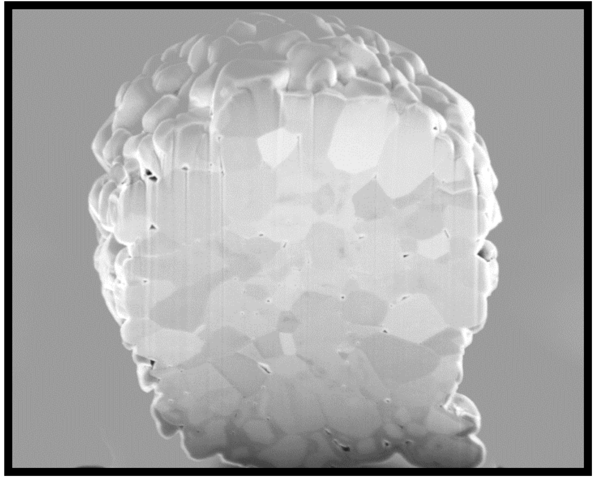
Baseline Cell Chemistry

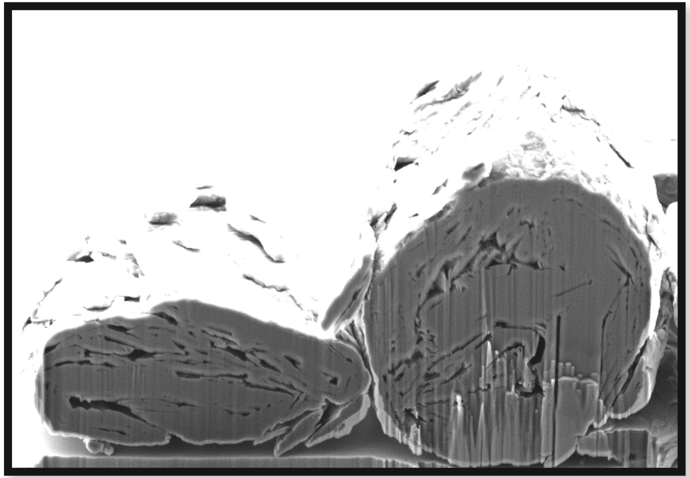
FIB-SEM cross-sections of particles

Baseline Electrolyte

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

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

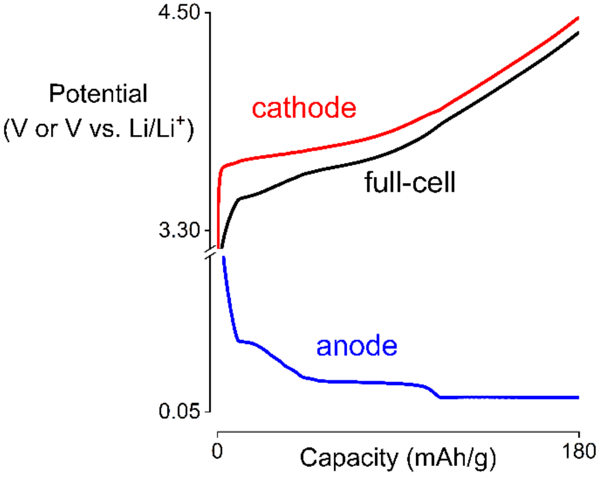
Negative Electrode

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

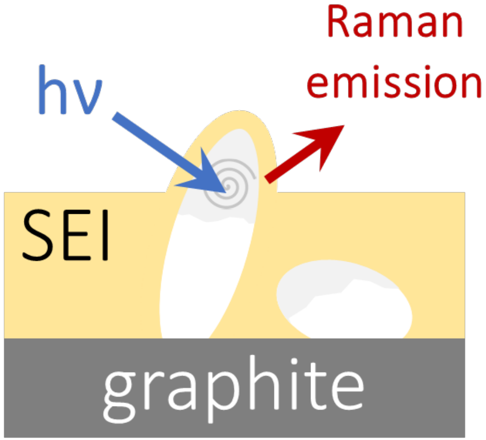
Electrodes fabricated at Argonne's CAMP facility

Argonne NATIONAL LABORATORY

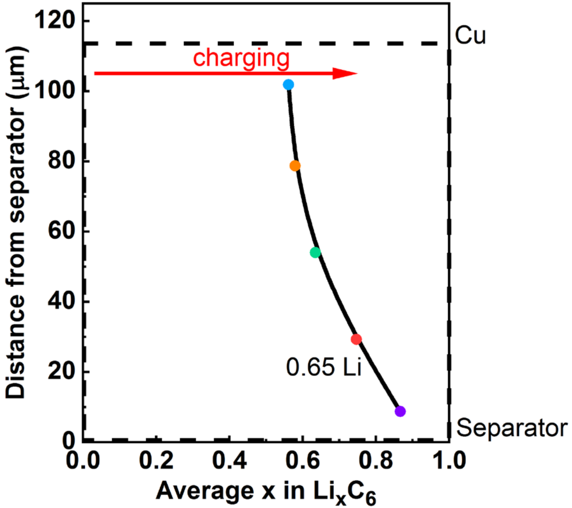
How to study fast-charge?



Experiments using a reference electrode



Li detection using Raman spectroscopy



Electrode heterogeneity studies using X-rays

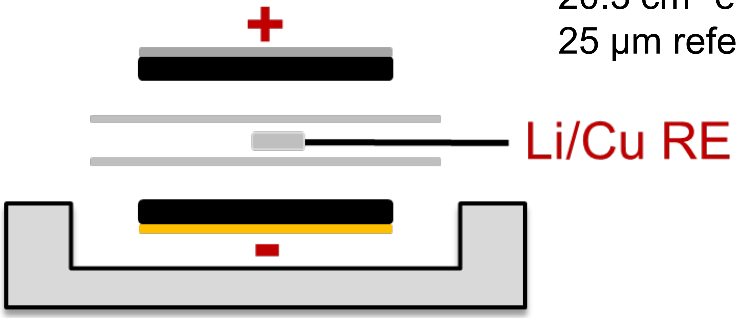
Experimental studies feed electrochemical models which are then used to develop fast charge protocols

Rodrigues et al. J. Electrochem. Soc., 2019, 166, A996
Shkrob et al. J. Electrochem. Soc., 2019, 166, A3305
Shkrob et al. J. Electrochem. Soc., 2019, 166, A4168
Rodrigues et al., J. Electrochem. Soc. , 2020, 167, 130508

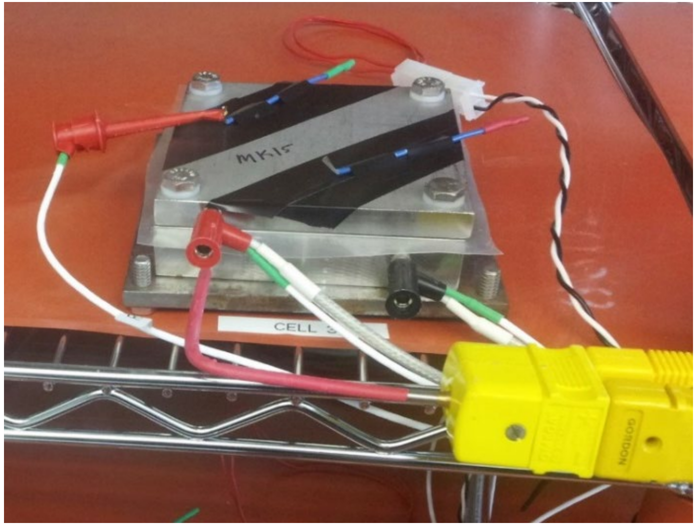
REFERENCE ELECTRODE CELLS

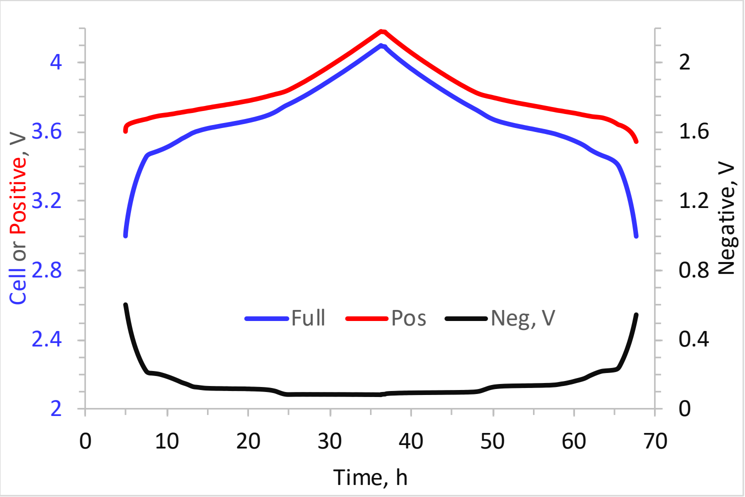
- **Cycling conditions under which Li-plating could occur**
- **Effect of temperature**
- **Effect of electrolyte**

Reference Electrode cells & Typical Data



20.3 cm^2 electrodes
25 µm reference wire



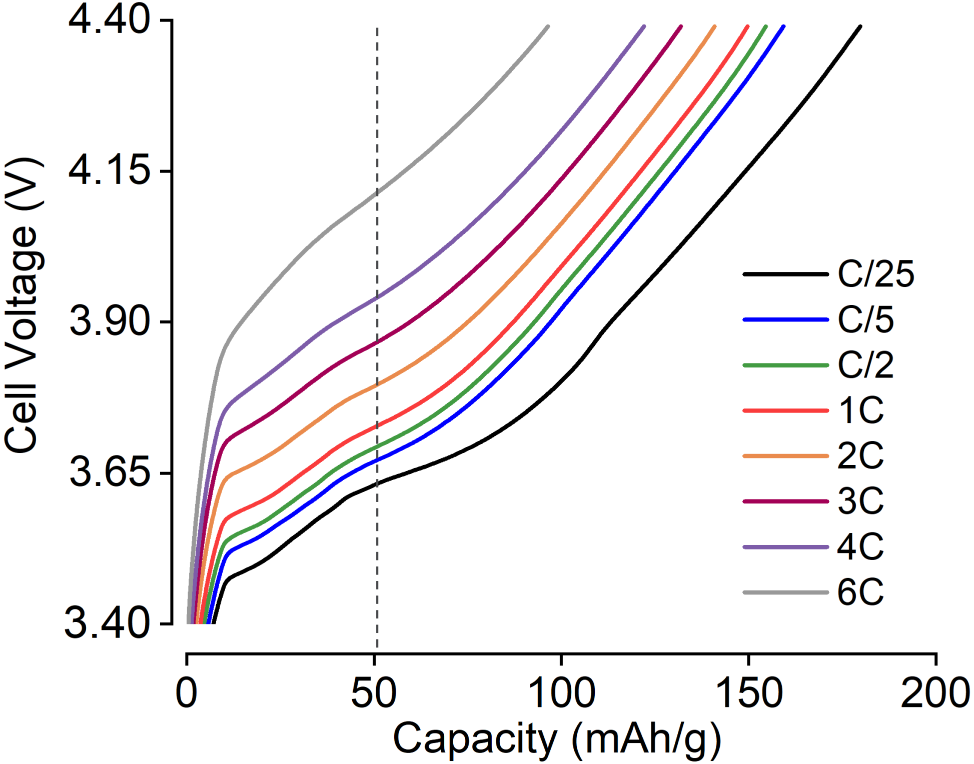


Using a *reference electrode* allows the measurement of electrode potentials along with the cell voltage

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

Cell voltage & capacity at various cycling rates

3.0 – 4.4 V, 30 °C



As Charge Rate Increases

Voltage Polarization Increases

- For example at 50 mAh/g, cell voltages are 3.62 V and 4.09 V at C/25 and 6C rates, a difference of 470 mV

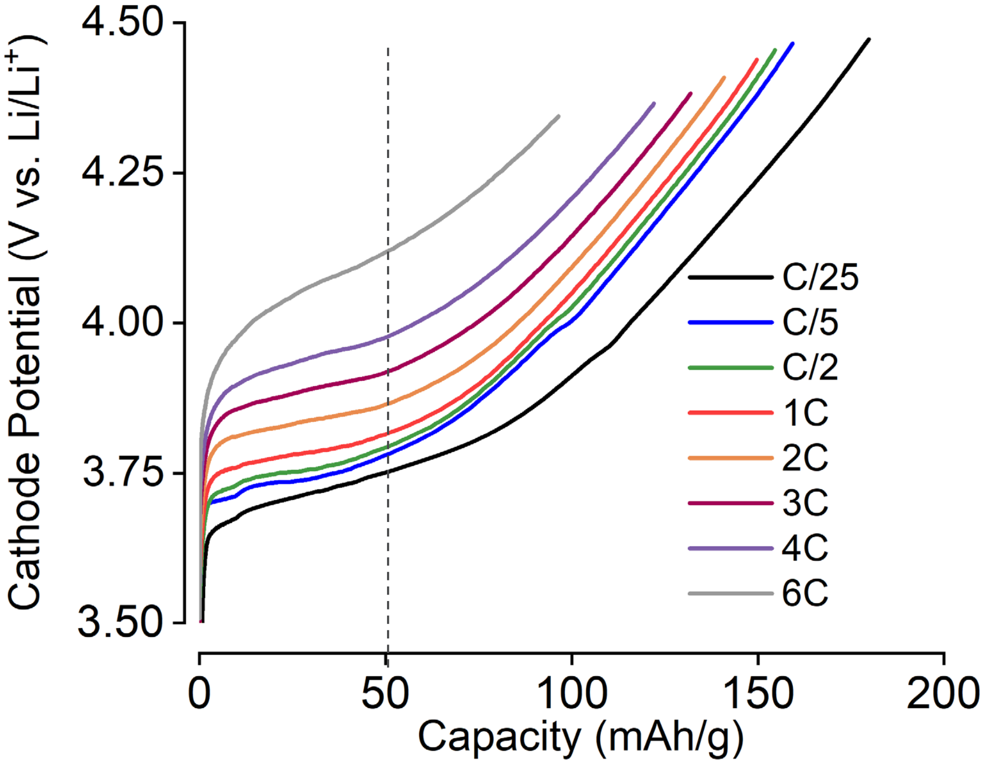
Charge capacity decreases

- For example, charge capacities are 180 and 97 mAh/g at C/25 and 6C rates a difference of 83 mAh/g

~40 μm thick electrodes

Positive electrode potential at various cycling rates

Cell cycling range: 3.0 – 4.4 V, 30 °C



Potential Polarization

- Of the 470 mV polarization at 50 mAh/g seen for the full cell, 360 mV is from the oxide electrode. This *iR* polarization would heat up the electrode, requiring effect heat dissipation in the cell

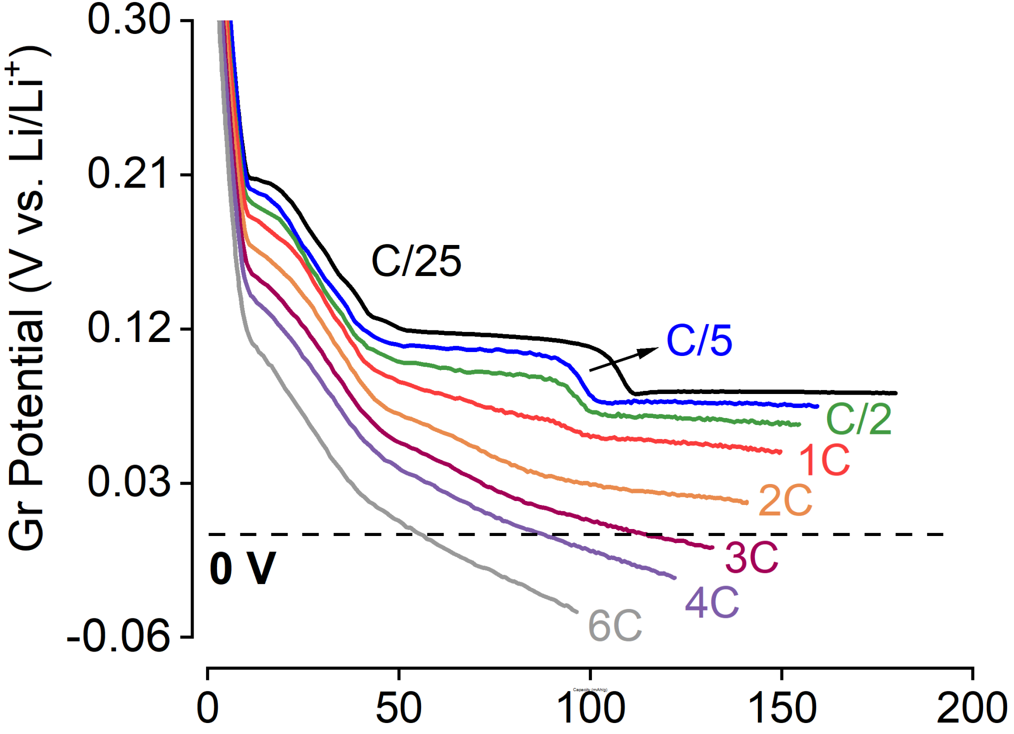
Charge capacity

- Positive electrode polarization causes the cell to reach the UCV sooner, which explains the lower capacities at higher rates

~40 μm thick electrodes

Negative electrode potential at various cycling rates

Cell cycling range: 3.0 – 4.4 V, 30 °C



Potential Polarization

- 110 mV (~23%) of the full cell polarization is from the anode

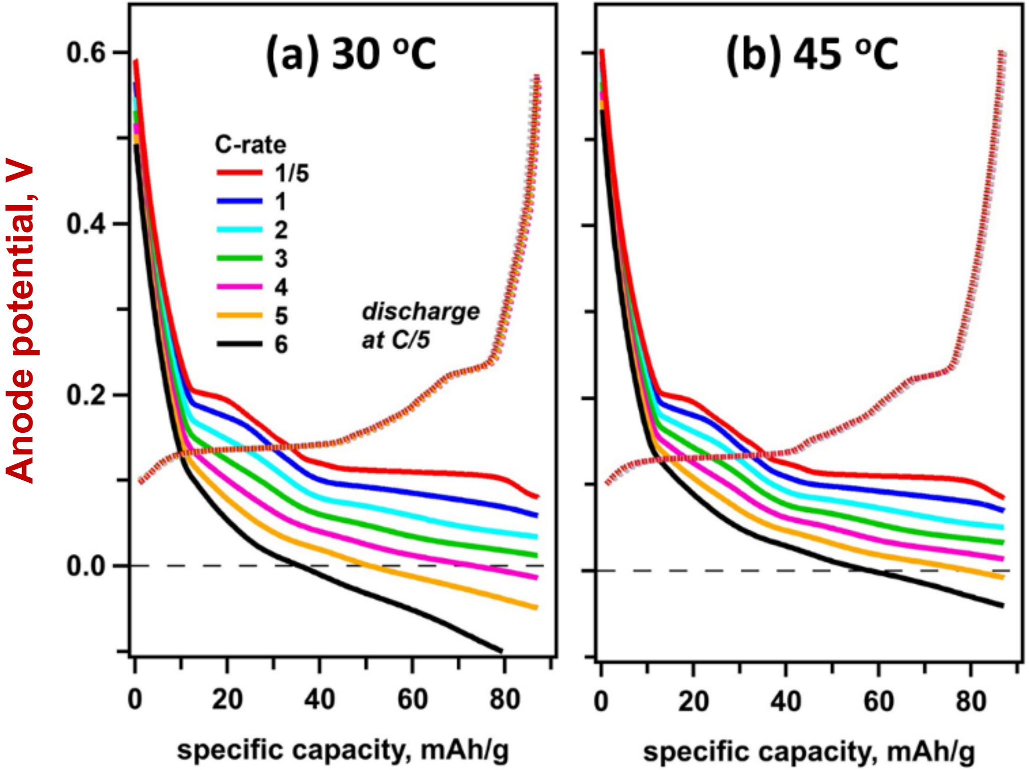
Li-plating condition (LPC)

- Met at rates ≥ 3C
- Li-plating also depends on
  - quantity of charge moved
  - cell temperature

~40 µm thick electrodes

Effect of temperature on anode potentials

30 °C and 45 °C, C/5 to 6C rates, capacity-limited charge



Potential Polarization

- Lower at higher temperature for both electrodes

Li-plating condition (LPC)

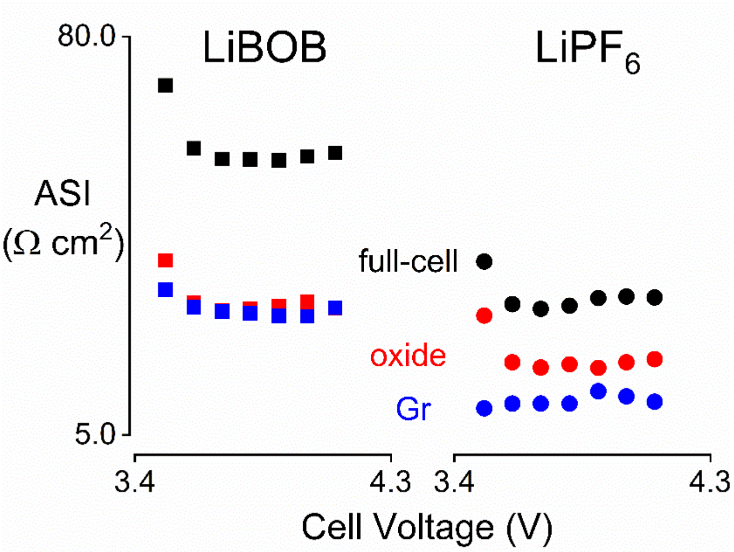
- Plating expected at 3.4C for 30 °C and 4.6C at 45 °C

~70 µm thick electrodes

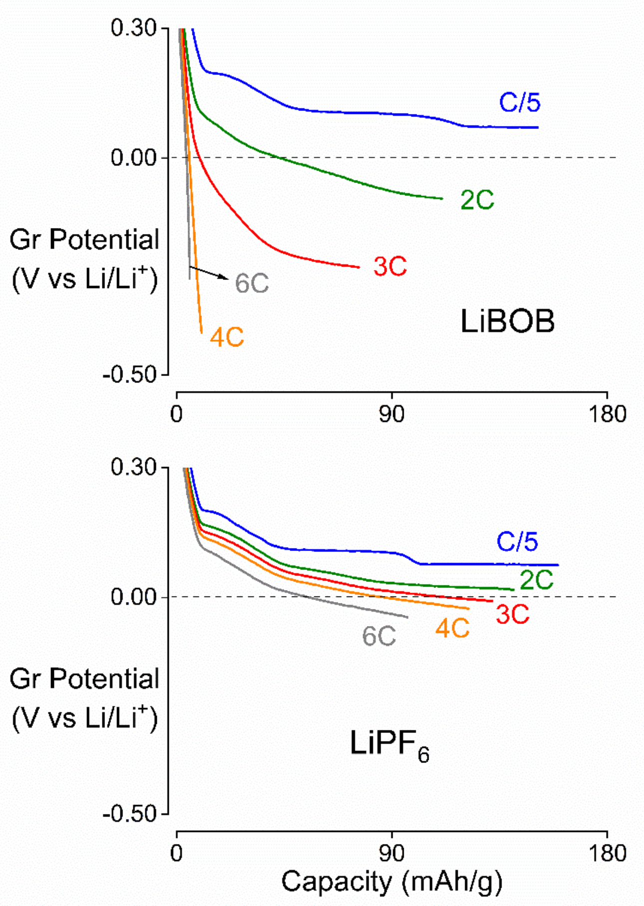
Rodrigues et al., J. Electrochem. Soc. , 2020, 167, 130508

Electrolyte composition effect on anode potentials

EC:EMC (3:7 w/w);
1M $LiPF_6$ or 0.7M LiBOB



LiBOB cells have ~2x the impedance of $LiPF_6$ cells



Higher impedance leads to greater Gr polarization for LiBOB increasing likelihood of Li-plating

Electrolytes with high Li^+ conductivity are under development

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

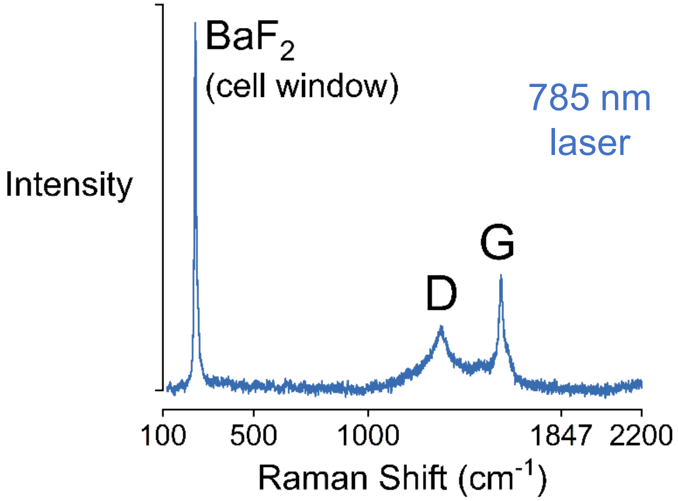
RAMAN SPECTROSCOPY

- **An accessible and sensitive tool to detect Li plating**

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

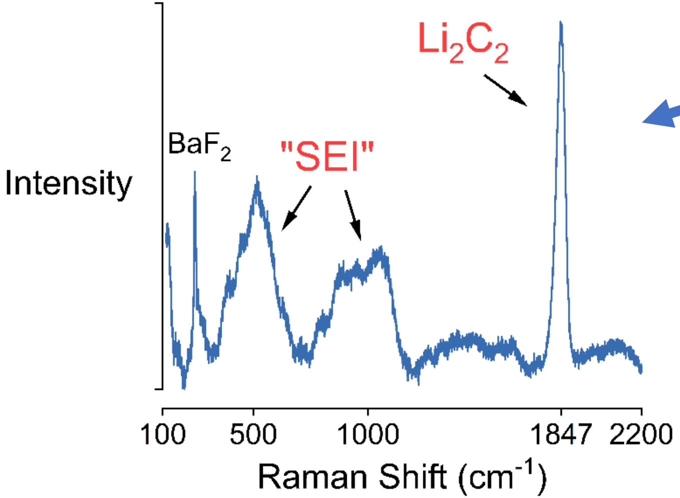
Raman bands from SEI compounds become intense after Li plating

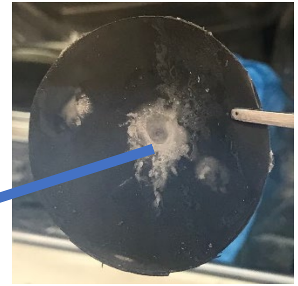
unwashed graphite electrode after 360 aging cycles (**no Li plating**)



Extensive SEI growth does not produce Raman signals

unwashed graphite electrode after **fast charging**

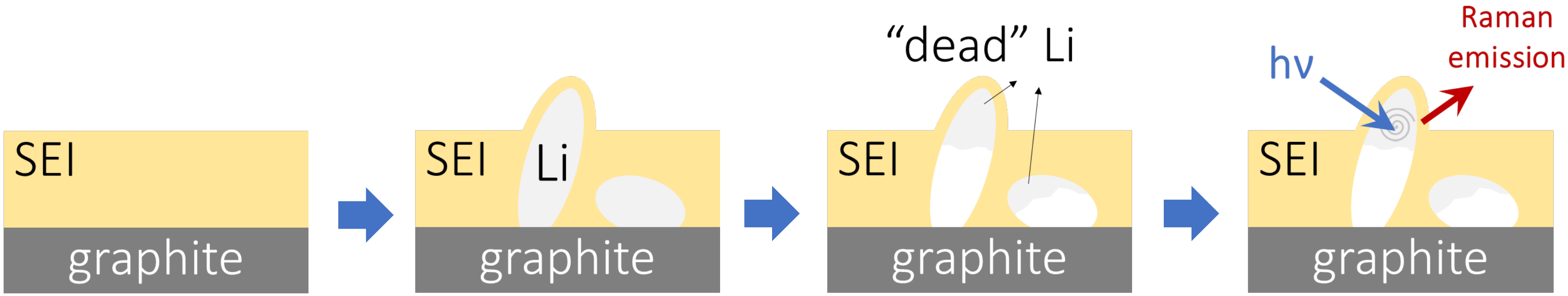




Intense SEI and acetylide bands seen in the Raman spectra

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

Plated Li enhances Raman scattering from SEI compounds in its vicinity



SEI forms due to electrolyte reduction

Li plates and forms its own SEI

a fraction of Li plates irreversibly

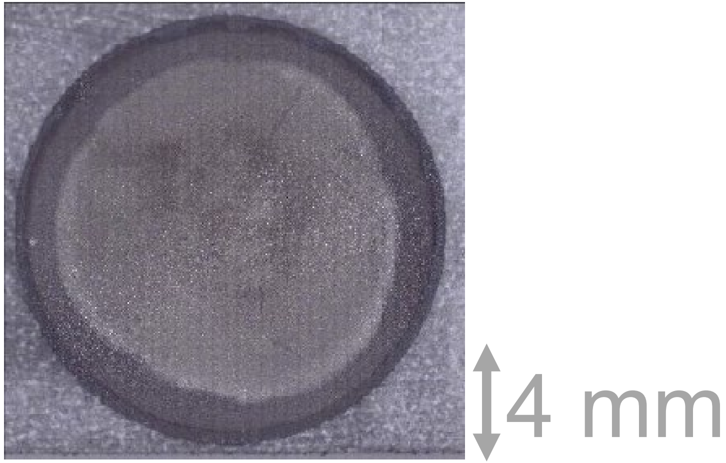
dead Li intensifies SEI bands through SERS mechanism

SERS = surface enhanced Raman scattering

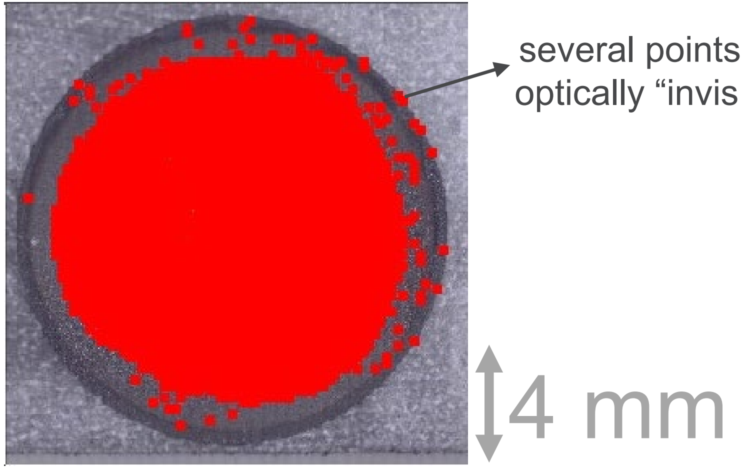
Li plating detected in “overhang” regions

Raman map of coin cell electrode (spectrometer inside glovebox)

optical image



Map of Li_2C_2 band



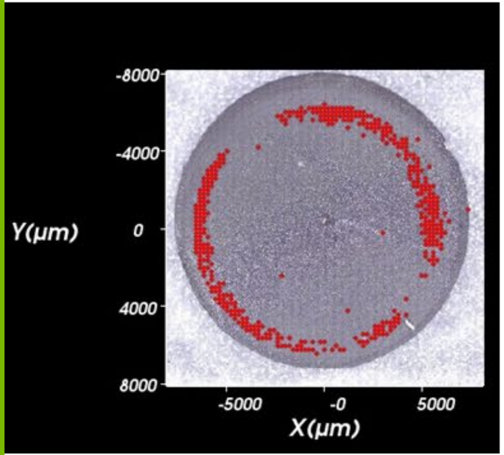
several points are optically “invisible”

mapping: 785 nm laser, single 5-s acquisition every 200 μm

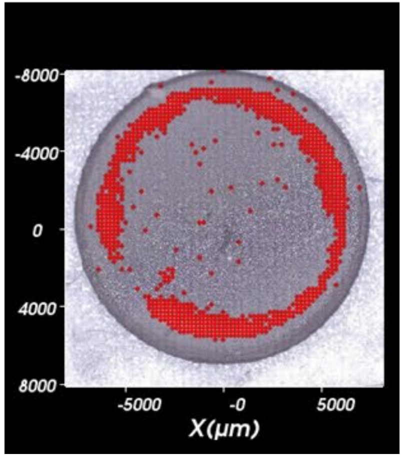
Raman (Li_2C_2) map of coin cell electrodes

6C charge, C/2 discharge, 3-4.1 V; cell in discharged state

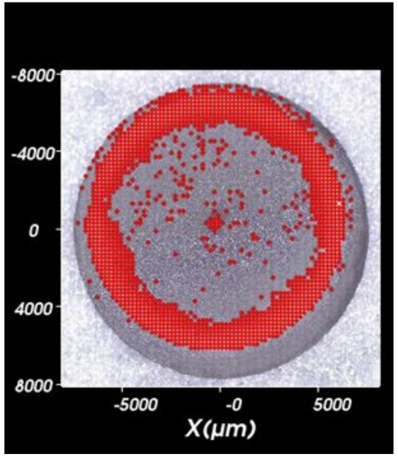
1 fast charge



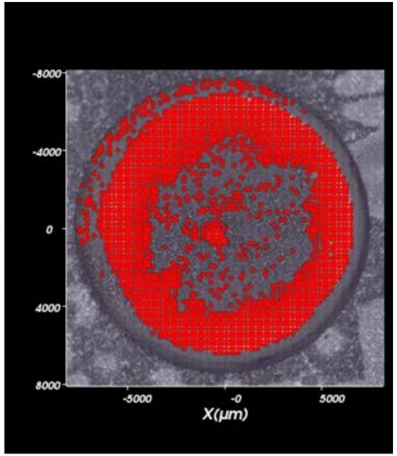
3 fast charge



5 fast charge



20 fast charge



Li plating is non-uniform

Indicates non-homogeneous electrode behavior

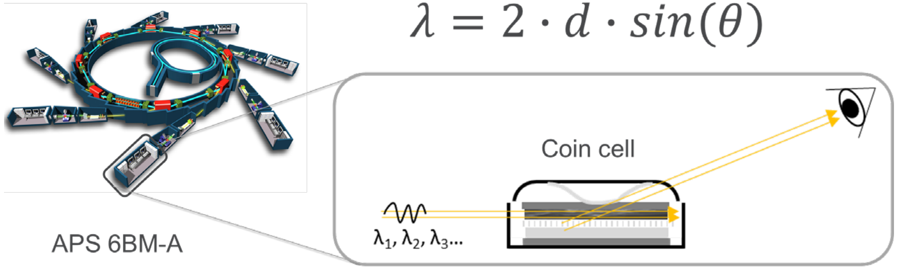
Okasinski et al., Phys. Chem. Chem. Phys. 22, 21977 (2020)

STUDYING ELECTRODE HETEROGENEITY

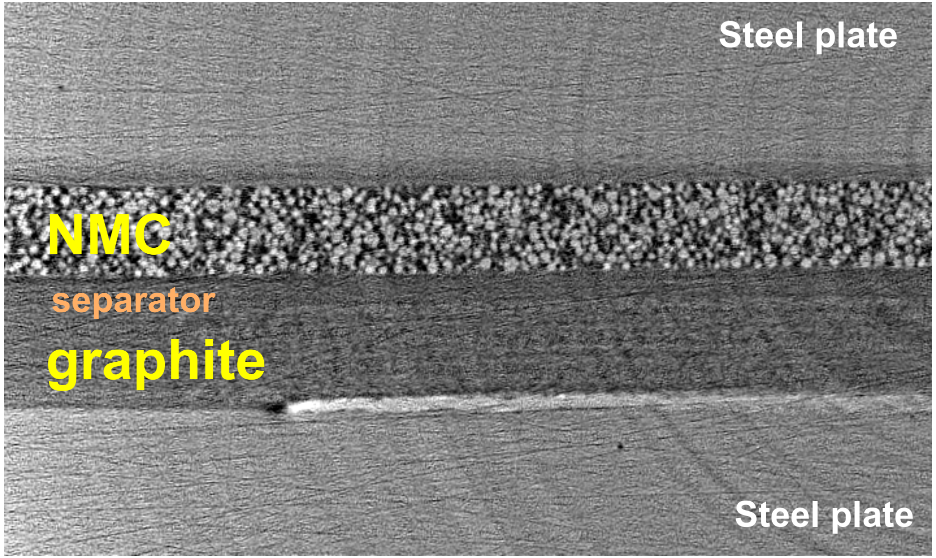
- **Lithium concentration gradients are generated along the electrode cross-section during fast charging**

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

Radiography, Tomography & Energy Dispersive X-ray Diffraction



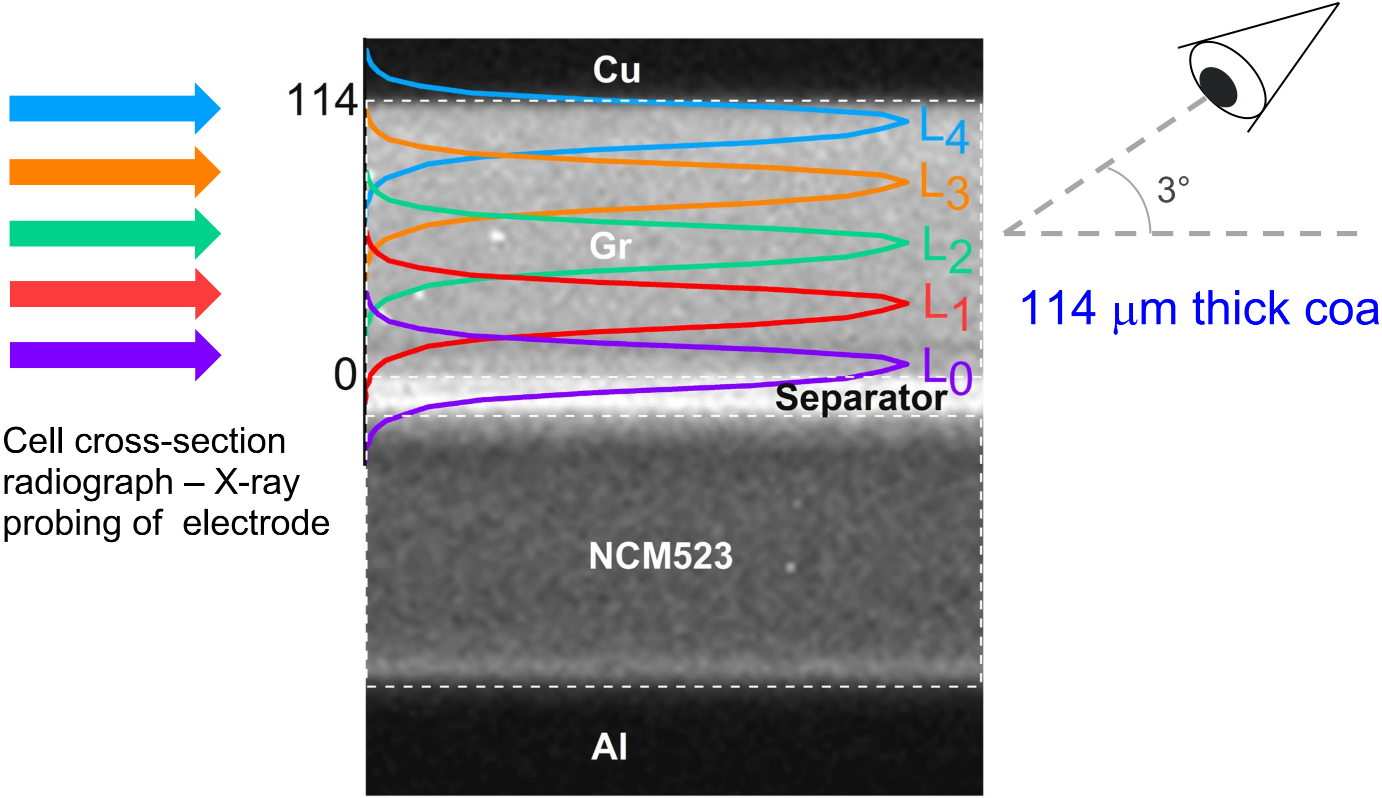
$$\lambda = 2 \cdot d \cdot sin(\theta)$$



<u>Advantage</u>: High-energy X-rays can penetrate casings of coin cells, pouch cells, etc. No special cell design needed

Okasinski et al., Phys. Chem. Chem. Phys. 22, 21977 (2020)

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

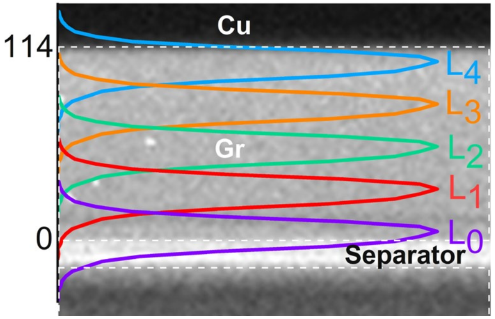


Cell cross-section radiograph – X-ray probing of electrode

114 µm thick coating

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

Average Li content of various layers – cycle at 1C rate



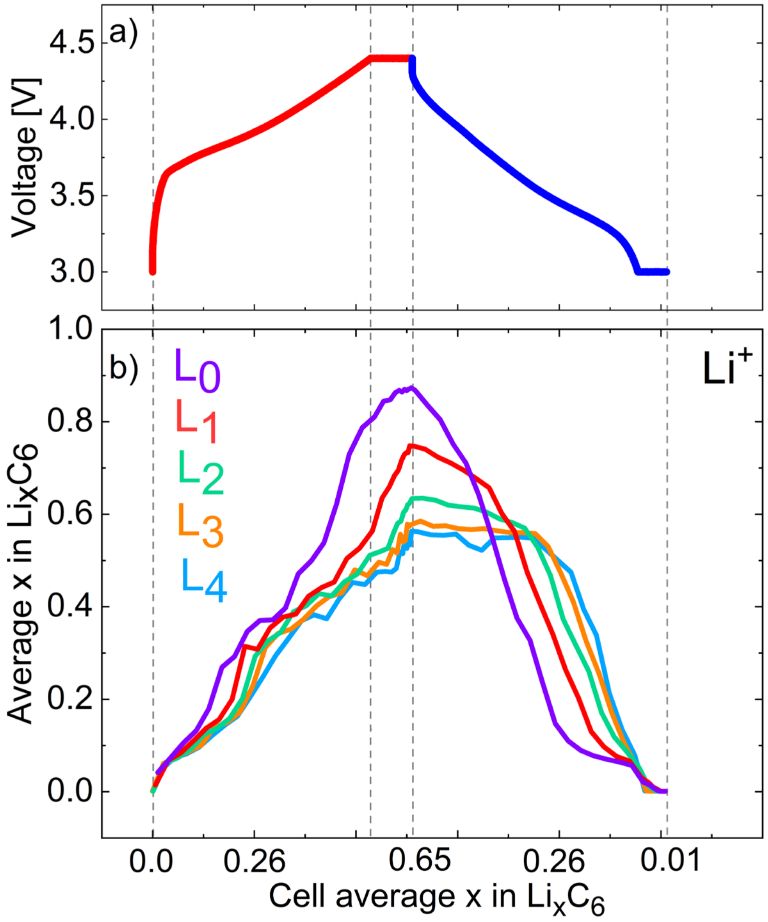
101.9 μm

78.7 μm

54.0 μm

29.3 μm

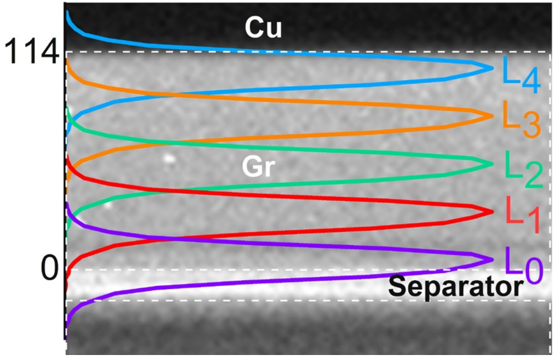
8.7 μm



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

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

Average Li content of various layers during 1C cycling



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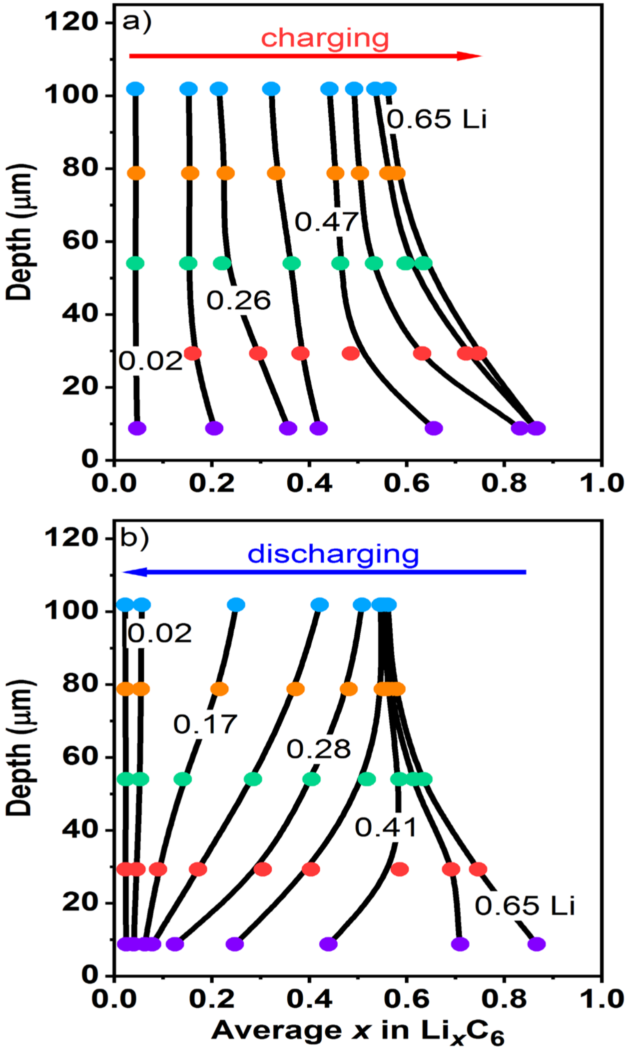
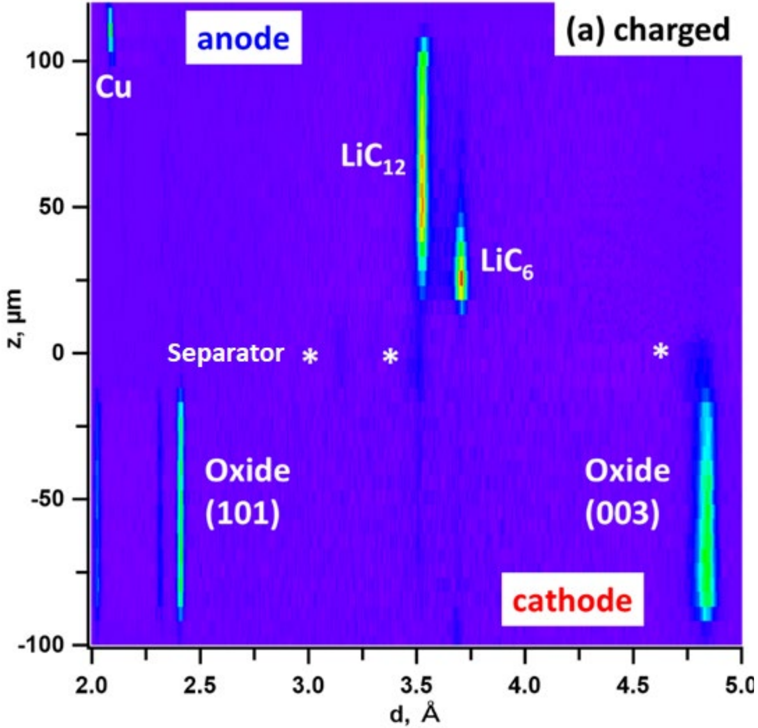


Yao et al. Energy Environ. Sci. 2019,12, 656

Takeaways

Lateral (*in plane*) and transverse (*along thickness*) heterogeneity in the electrodes during cycling can be studied using X-ray techniques.



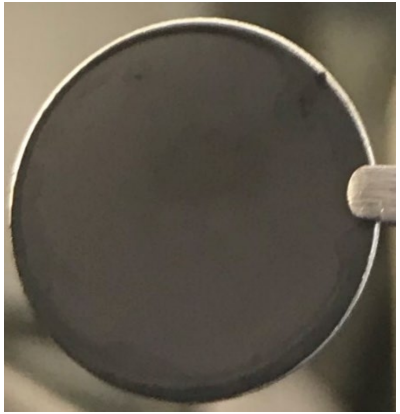
Persistent heterogeneity in the electrodes causes non-uniform aging, making it difficult to predict cell life

Okasinski et al., Phys. Chem. Chem. Phys. 22, 21977 (2020)

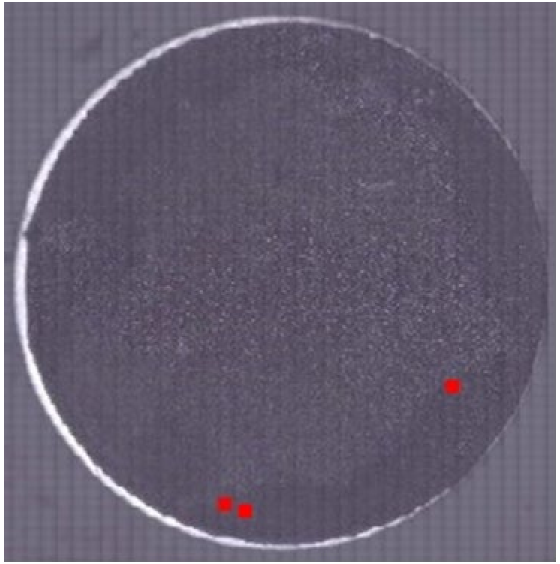
Takeaways

Raman spectroscopy can help identify Li plating, even when it is not clearly visible in optical images.

Optical image



map of Li_2C_2 band

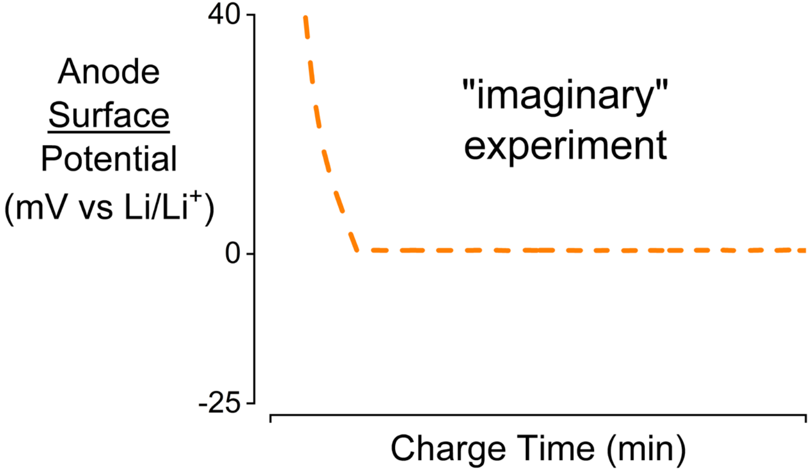


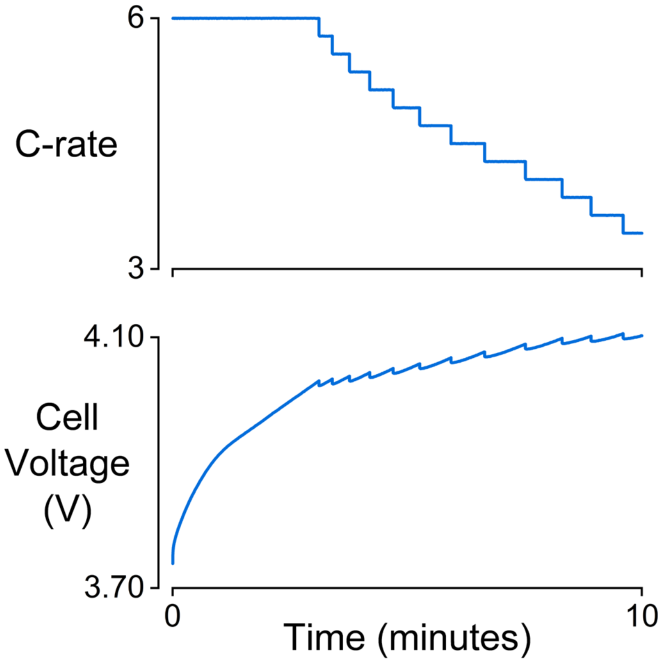
Raman imaging showed Li presence in only **3 of 5000+ spots** after 5 "seesaw cycles" with 6C charge

Graphite morphologies that allow rapid Li^+ ion diffusion are needed to mitigate Li plating

Takeaways

Data from reference electrode cells can help identify cycling conditions that cause Li-plating. With this information, fast charge protocols that mitigate Li-plating in two-electrode cells are being designed.





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