IMPACT OF FAST CHARGE ON LITHIUM-ION CELL DESIGN

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Acknowledgments
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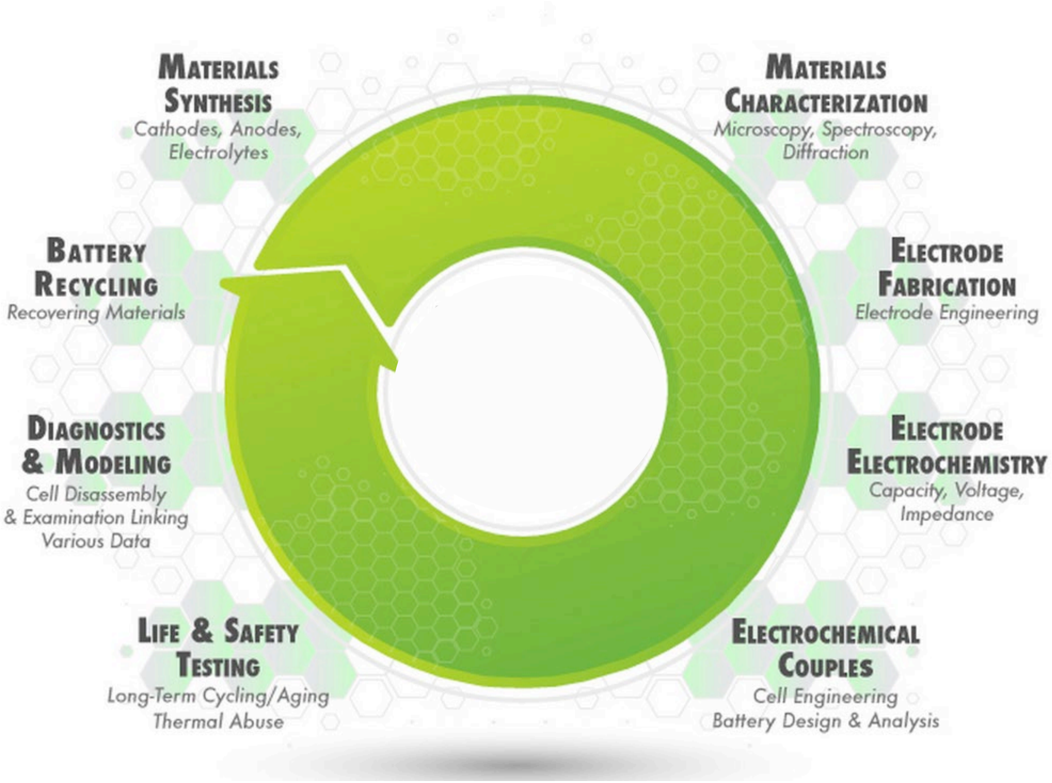
LITHIUM-ION BATTERY RESEARCH AT ARGONNE



https://access.anl.gov/

Key Challenges for Transportation

Lower Battery Cost

- Lower Co content in oxide electrode while maintaining structural stability

Increase Energy Density

- Operate cells a higher voltages
- Use Si in the negative electrode

Improve Safety

- Use solid (ceramic, etc.) electrolytes

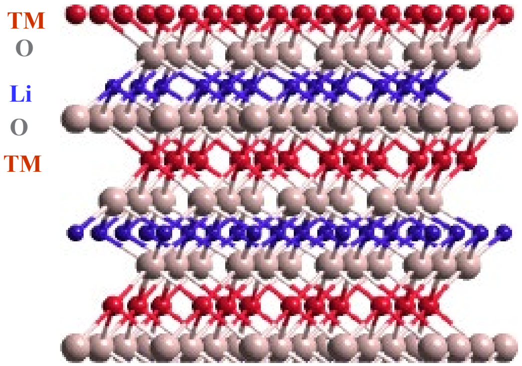
Improve Low T (<0 °C) performance

- Modify electrolyte compositions

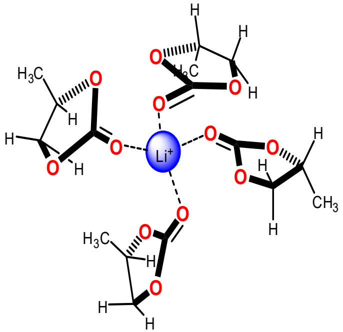
Enable fast-charge while maintaining cell performance

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

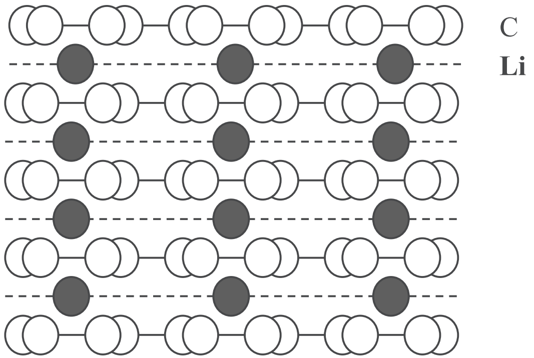
Layered oxide



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?

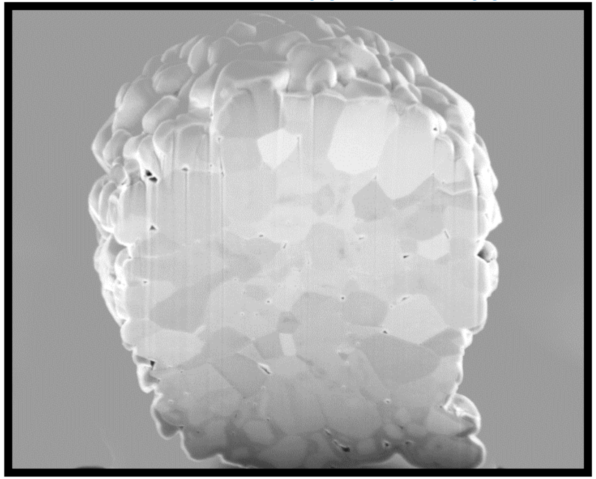
Baseline Cell Chemistry

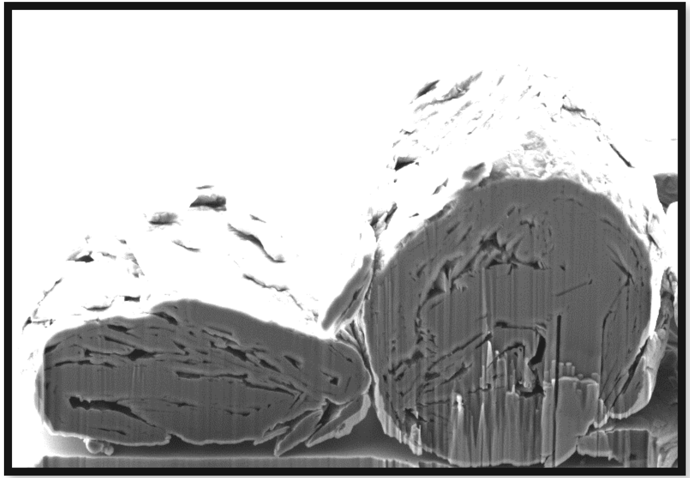
FIB-SEM cross-sections of particles

Baseline Electrolyte

- 1.2 M $LiPF_6$ in EC/EMC (3:7 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% A12 Graphite
- 2 wt% C45 carbon
- 6 wt% PVdF binder
- 44 - 120 μm thk coating

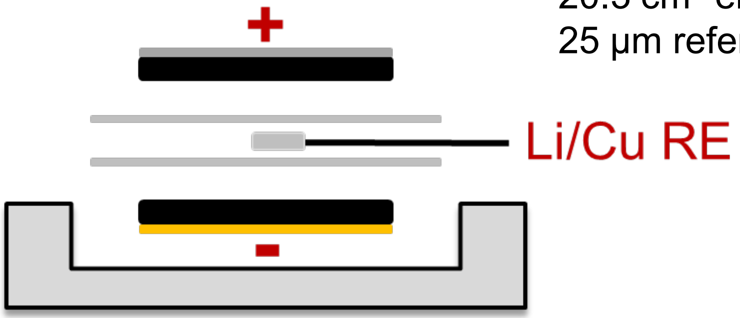
Electrodes fabricated at Argonne's CAMP facility

REFERENCE ELECTRODE TECHNIQUE

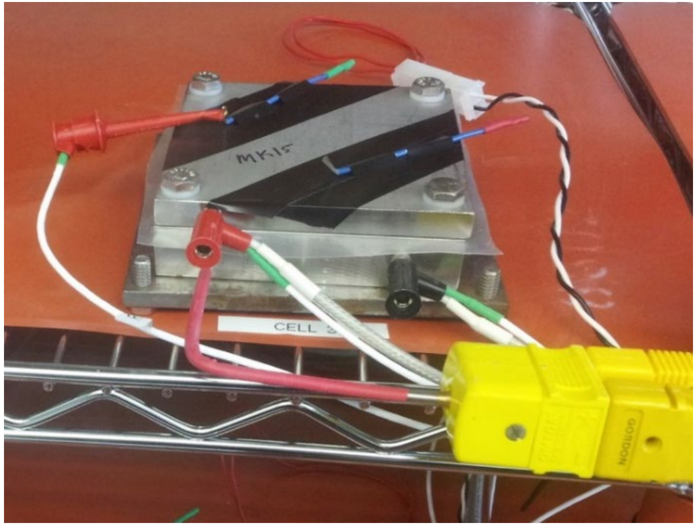
- **Cycling conditions under which Li-plating could occur**
- **Electrode impedance changes that result from fast charge**
- **Effect of electrolytes**

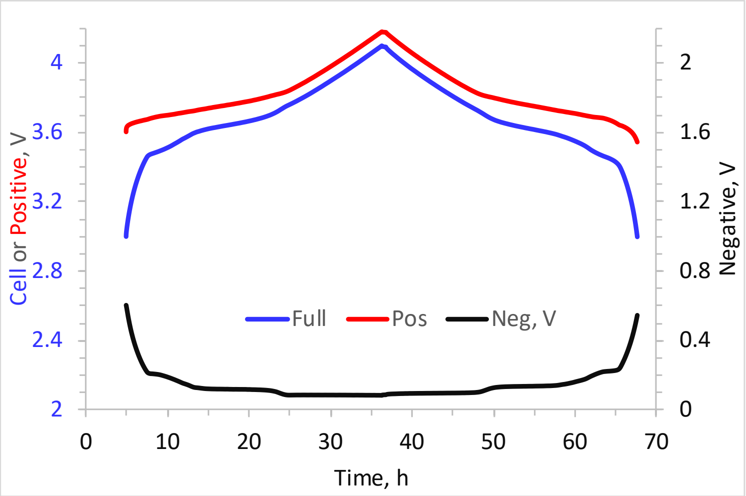
Rodrigues et al. J. Electrochem. Soc., 2019, 166, A996
Shkrob et al. J. Electrochem. Soc., 2019, 166, A3305
Shkrob et al. J. Electrochem. Soc., 2019, 166, A4168

Reference Electrode cells & typical data



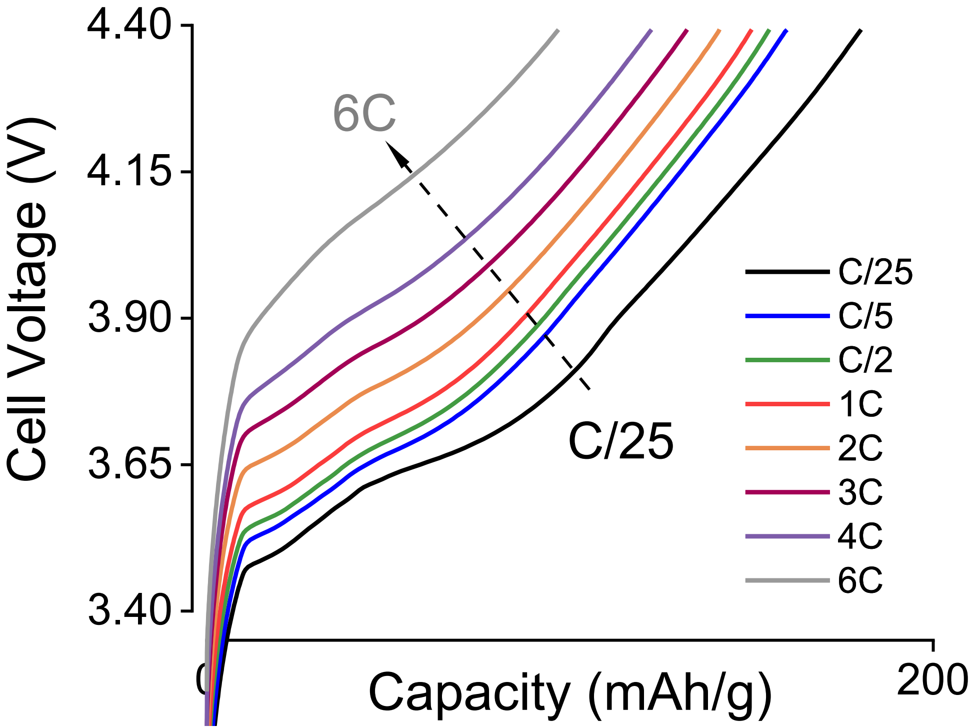
20.3 cm^2 electrodes
25 µm reference wire





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

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



<u>As Charge Rate Increases</u>

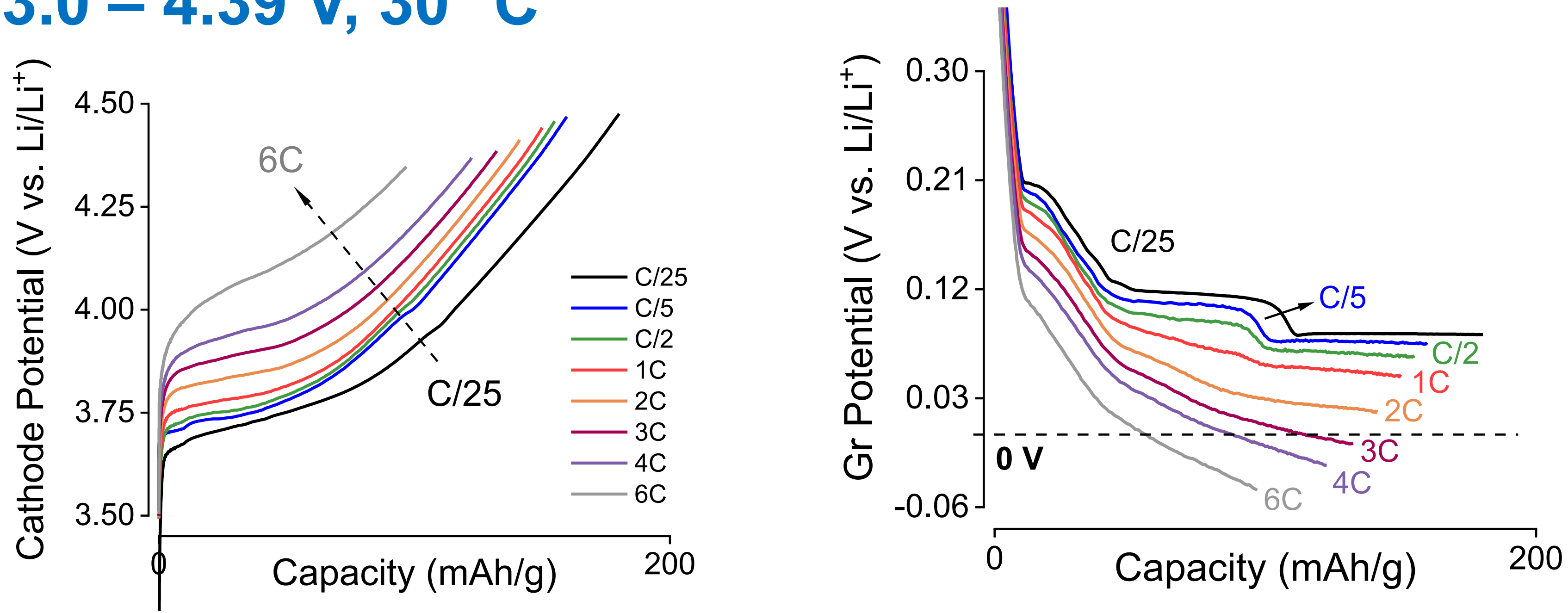
Voltage Polarization Increases

- For example at 45 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

Electrodode potentials at various cycling rates
3.0 – 4.39 V, 30 °C



- **Li-plating condition is met at rates ≥ 3C**
- Of the 470 mV polarization at 45 mAh/g, 360 mV is from the oxide electrode and 110 mV is from the graphite electrode
- Positive electrode polarization causes the cell to reach the UCV at progressively lower capacities

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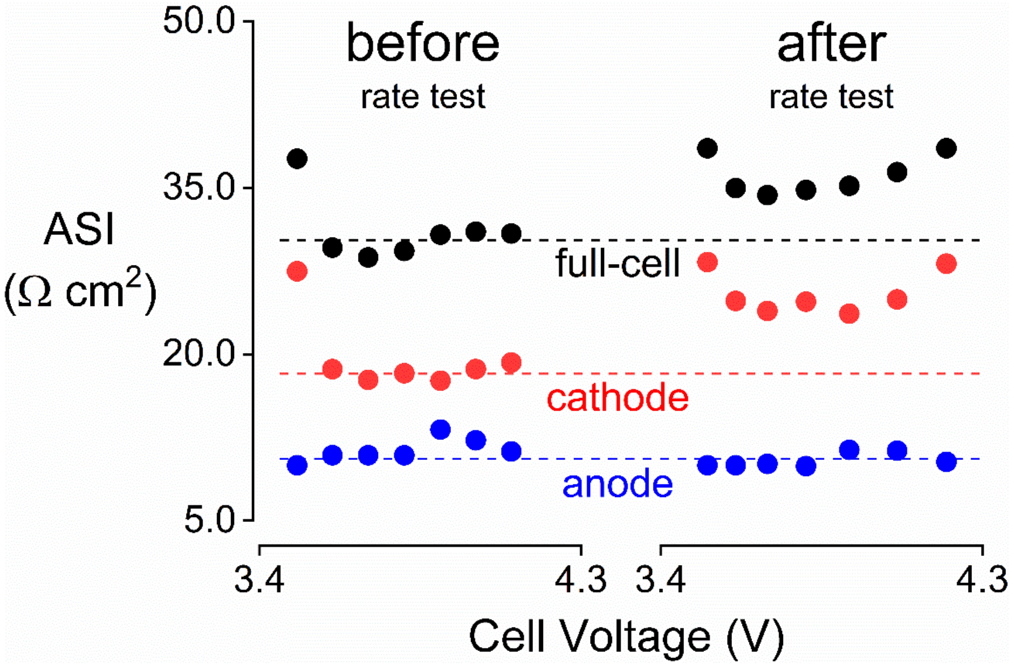
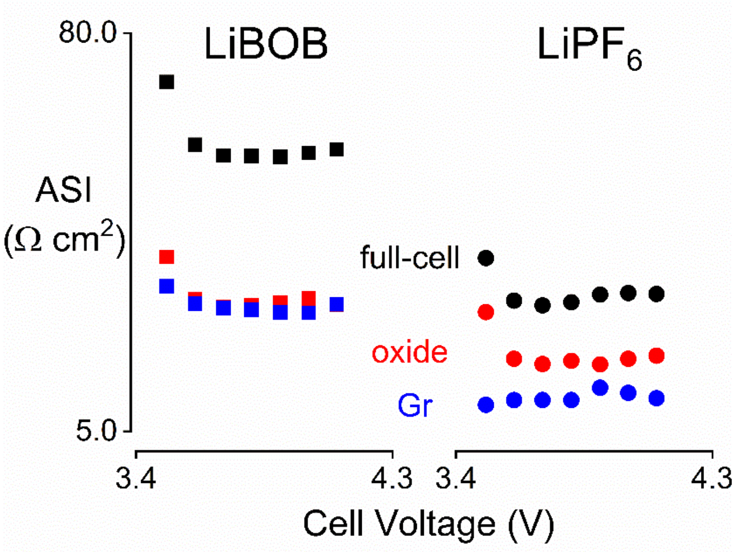
Impedance measurements before and after a series of fast charge cycles (up to 6C)



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

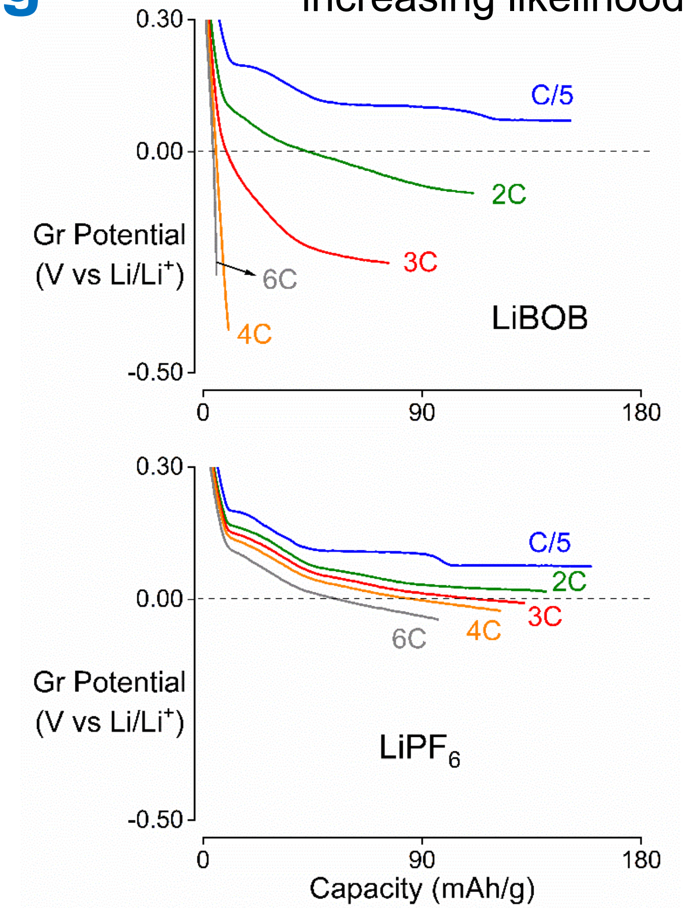
Electrolyte composition affects the likelihood of Li-plating

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 electrode polarization for LiBOB increasing likelihood of Li-plating



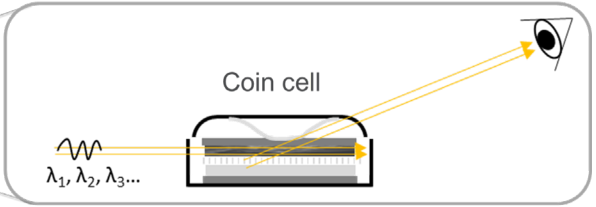
STUDYING ELECTRODE HETEROGENEITY

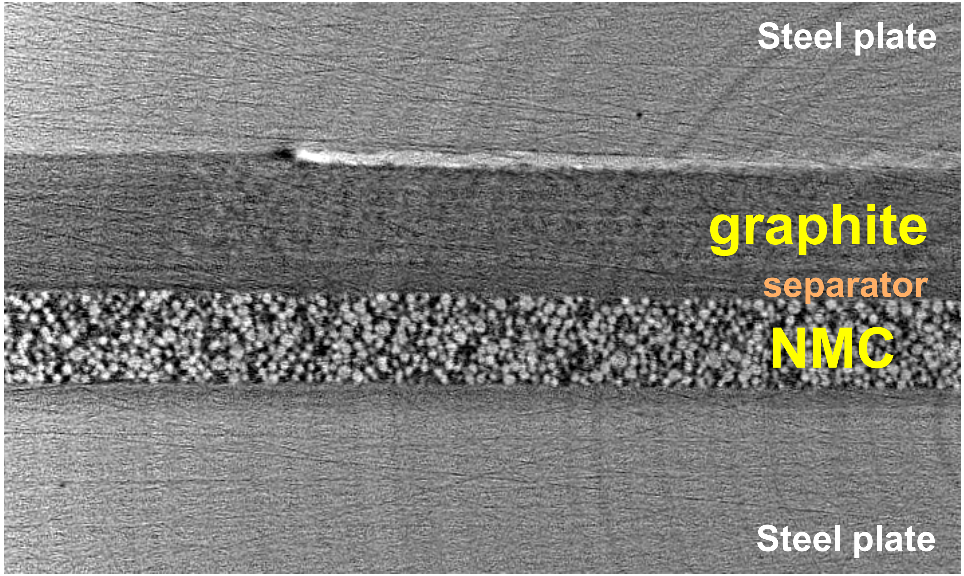
- **Lithium concentration gradients are generated along the electrode cross-section during fast charging**
- **Persistence of these concentration gradients can result in non-uniform aging of the electrodes, making it difficult to predict cell life**

Yao et al. Energy Environ. Sci. 2019,12, 656
Rodrigues et al. Appl. Energy Mater. 2019, 2, 873

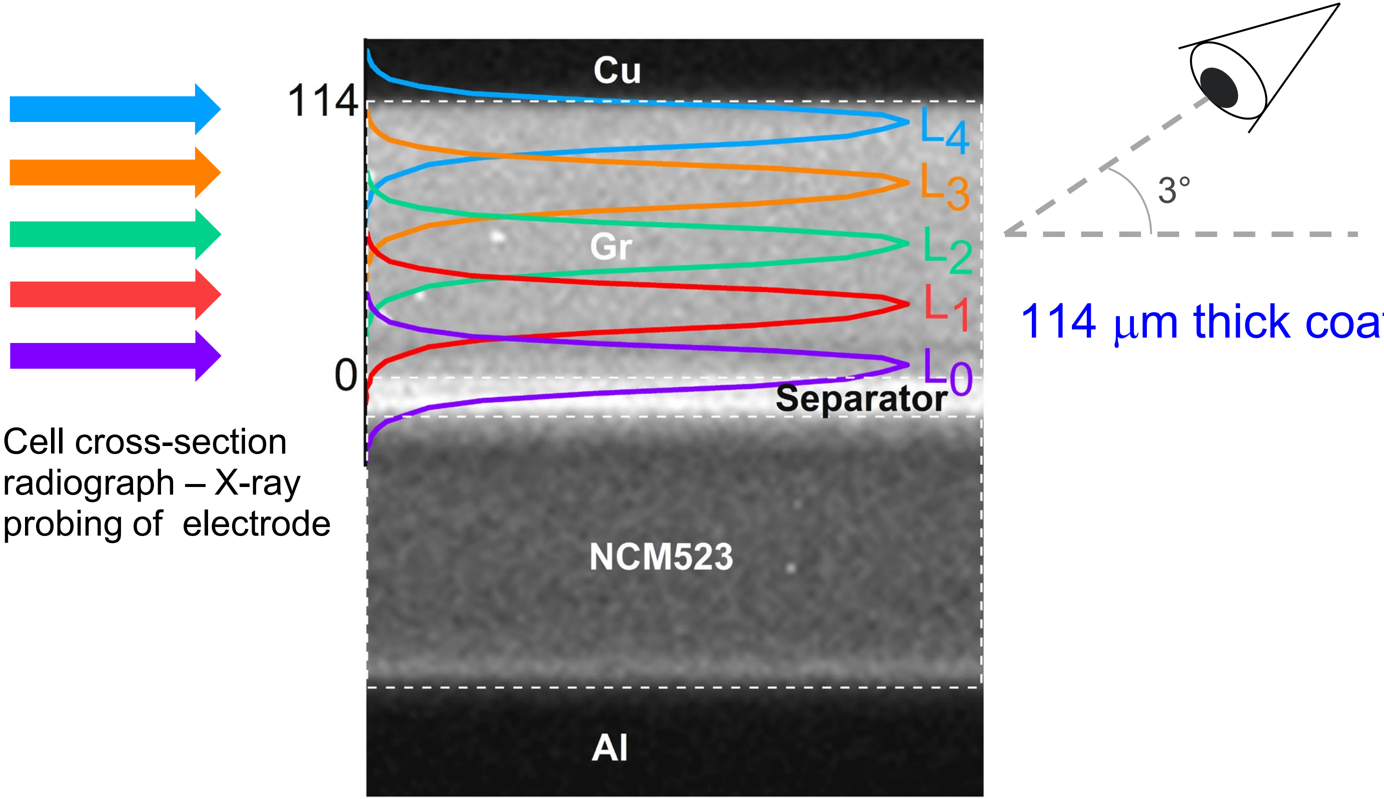
Radiography, Tomography & Energy Dispersive X-ray Diffraction

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



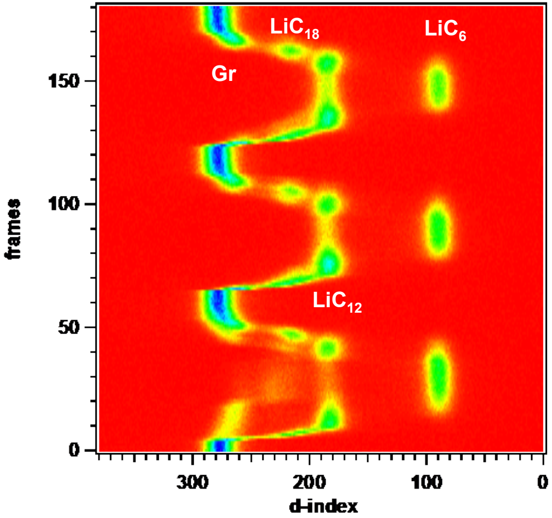


Examining electrode cross-sections using operando energy dispersive X-ray diffraction at 1C rate

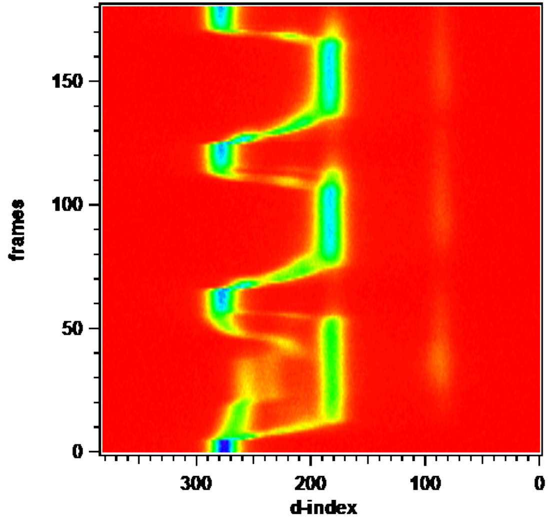


Cell cross-section radiograph – X-ray probing of electrode

114 μm thick coating

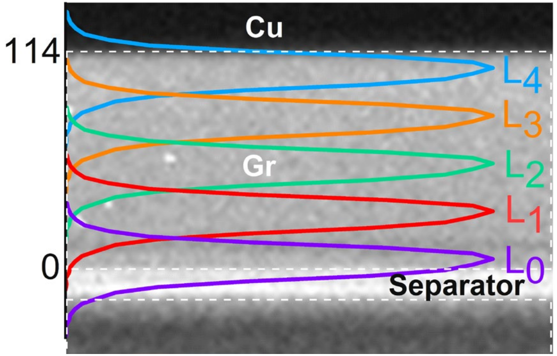


(Near separator)



(Near current collector)

Average Li content of various layers during 1C cycling



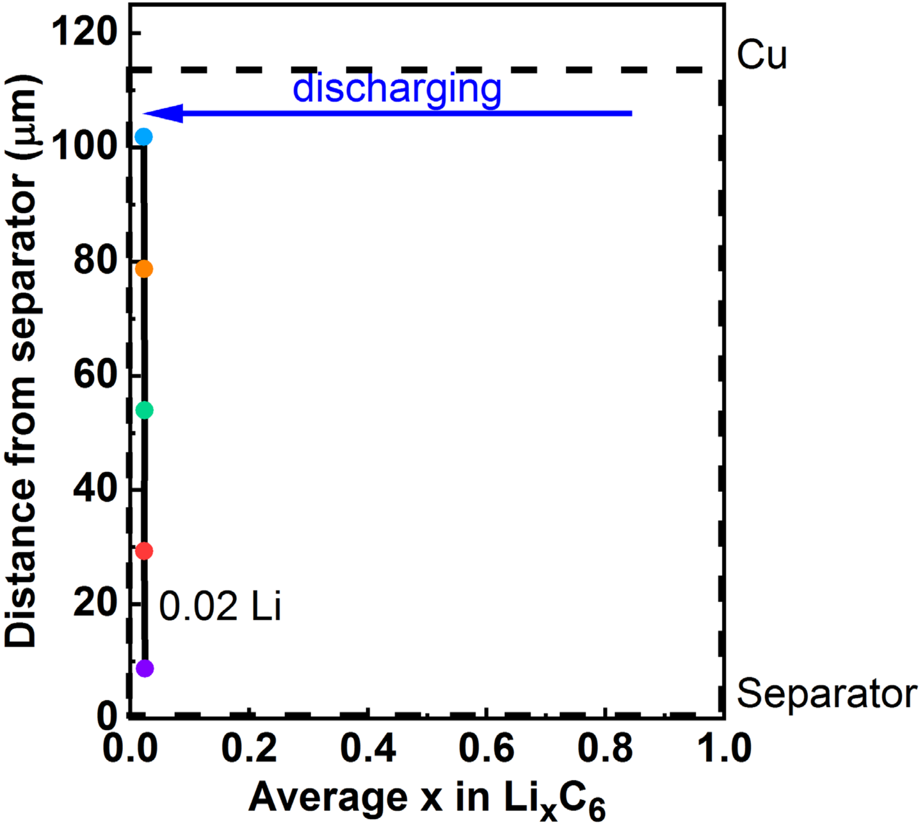
101.9 μm

78.7 μm

54.0 μm

29.3 μm

8.7 μm



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Design considerations to enable fast charging

Cycling protocols

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

Electrolyte design

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

Particle design

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

Electrode design

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

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