Oak Ridge National Laboratory | SPALLATION NEUTRON SOURCE

In situ and *operando* neutron diffraction (II)

Jue Liu

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Oak Ridge National Laboratory

U.S. DEPARTMENT OF ENERGY

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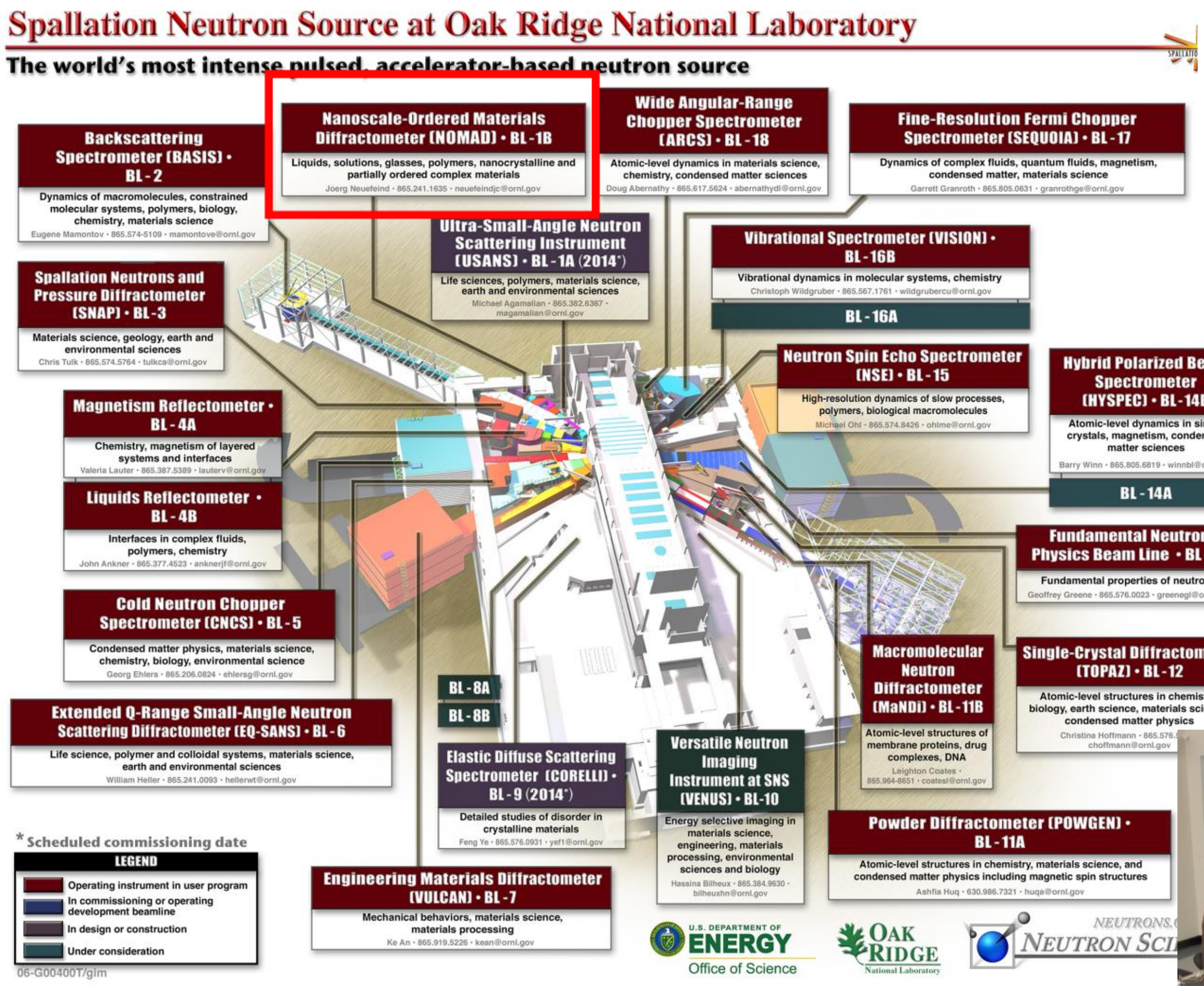
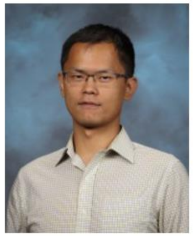
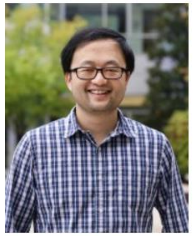


Joerg C. Neuefeind
Instrument Scientist



Cheng Li
Instrument Scientist



Jue Liu
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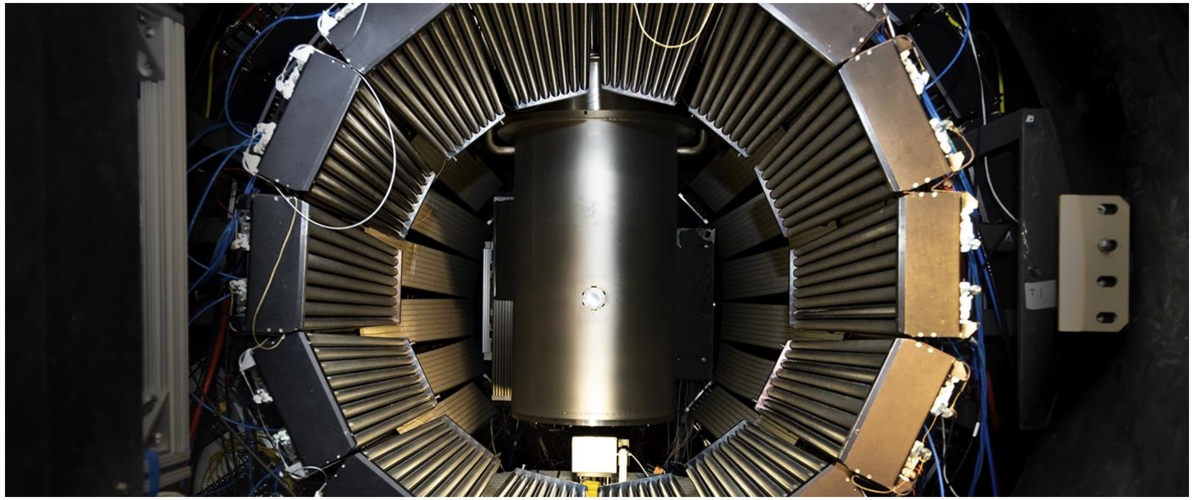
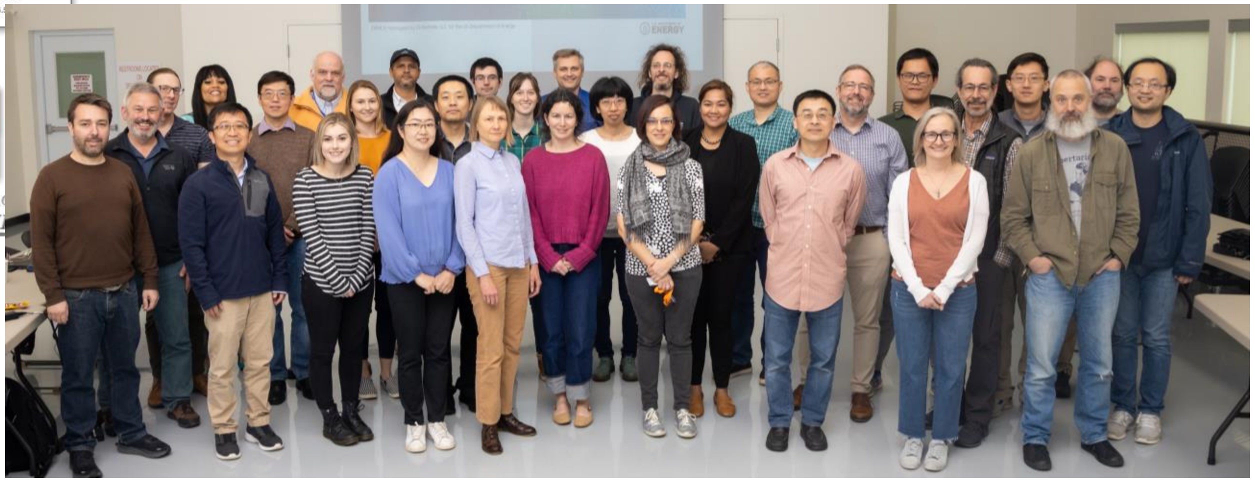
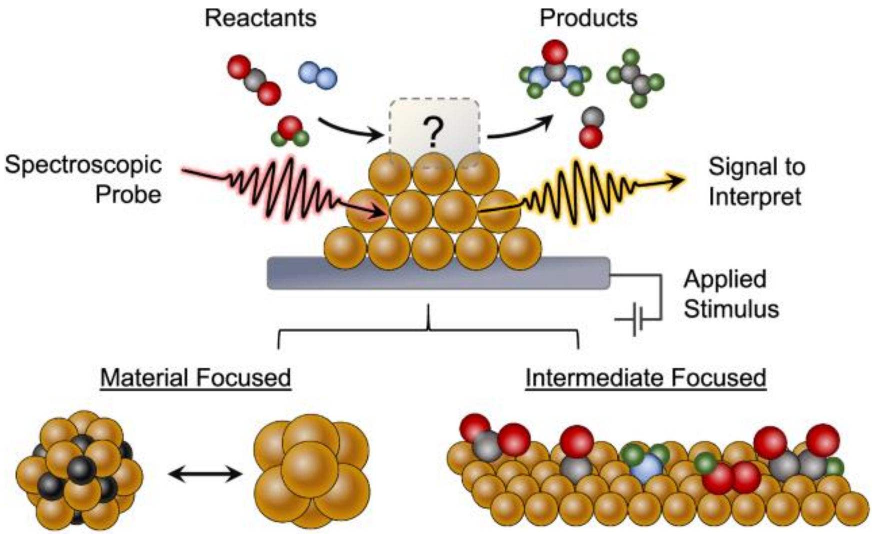




in situ and *operando* characterization of functioning materials

In situ
The examination or occurrence of a process within its original context, without relocation.

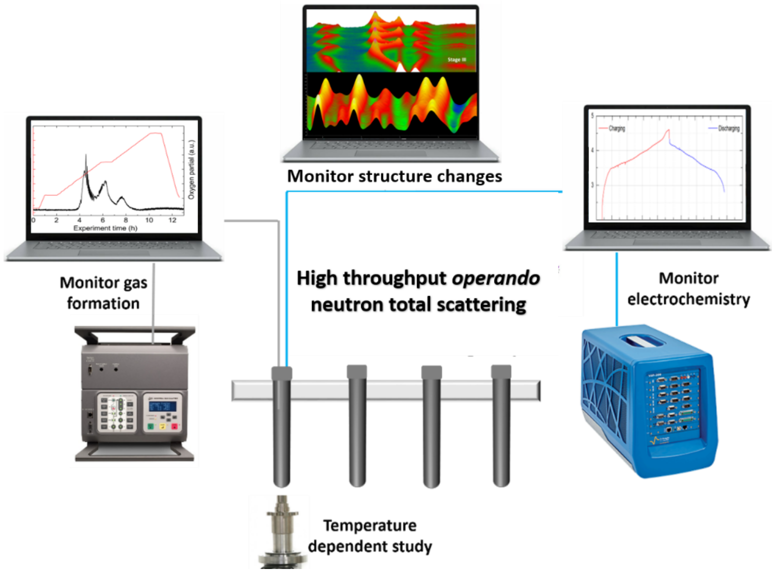
Catalytic/chemical reaction, phase transition etc.

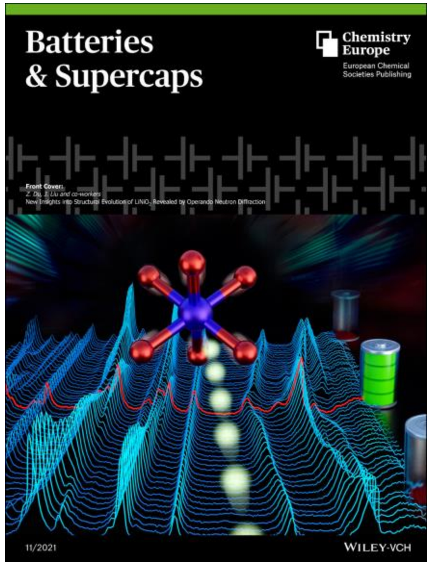


Nat Commun 16, 2593 (2025)

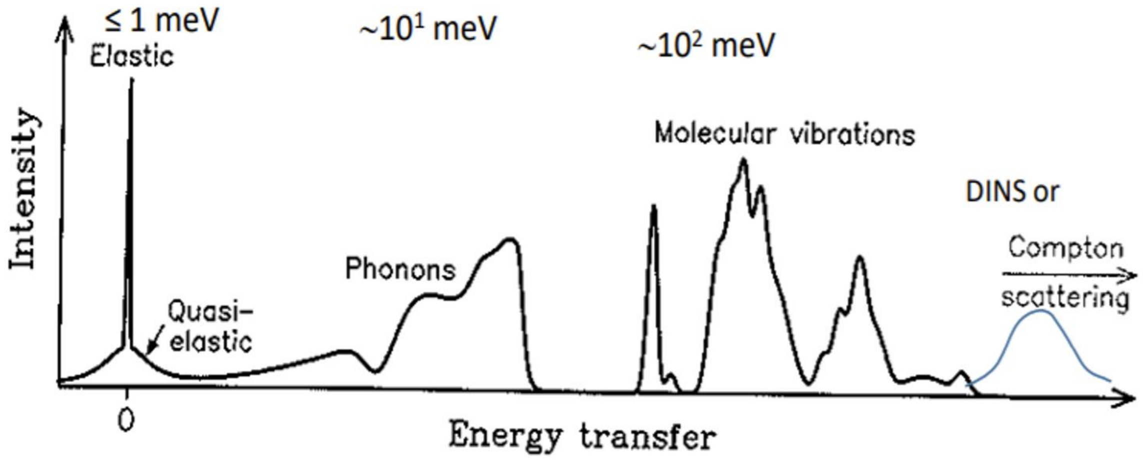
Operando
In the act of "working" or "during operation". It describes a method or technique where a device or system is observed and analyzed while it is actively functioning or performing its intended task.

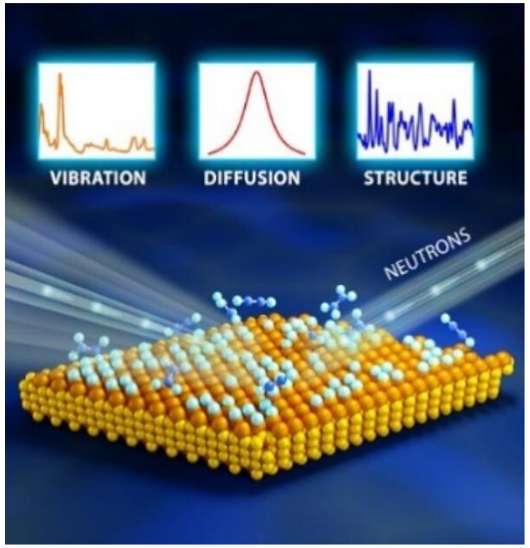
Batteries, fuel cells, engines…



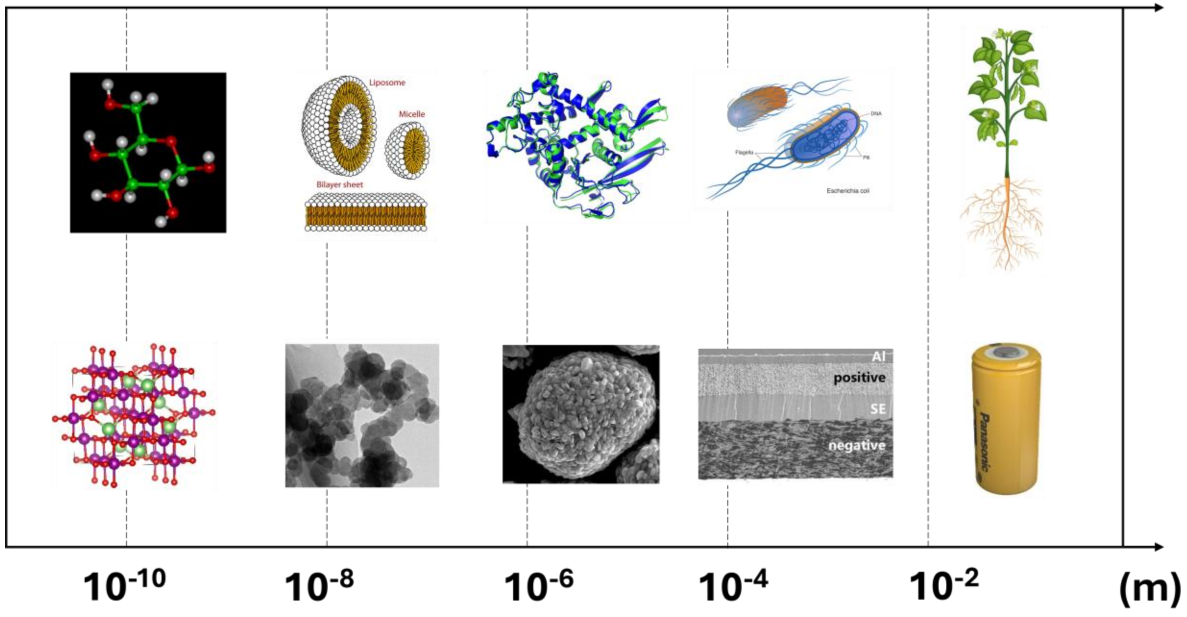


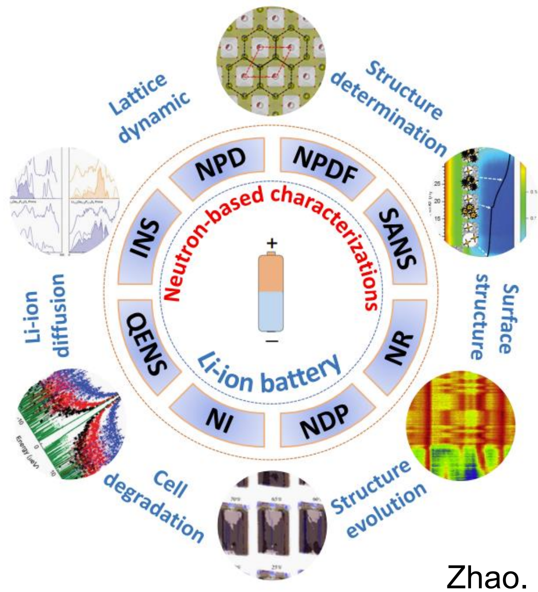
Advantages of neutron scattering for in situ/operando studies





Chem. Rev. 2023, 123, 13, 8638–8700

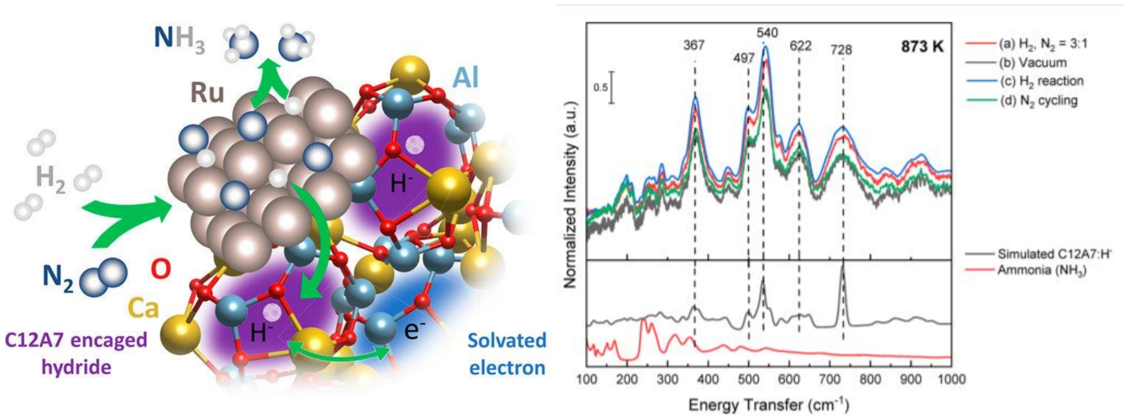




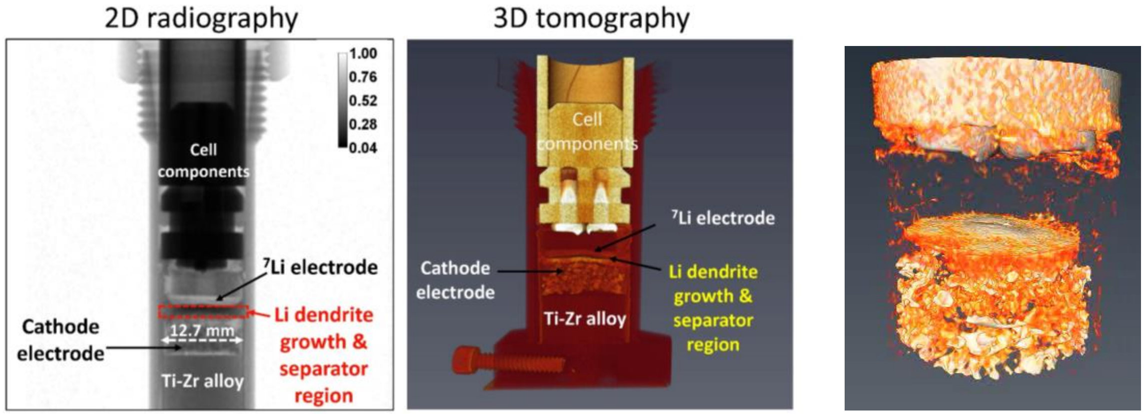
Zhao. et al. *Chinese Phys. B* 29 018201, 2020

- Neutron scattering covers a broad energy (time) and length scales for many relevant phenomena

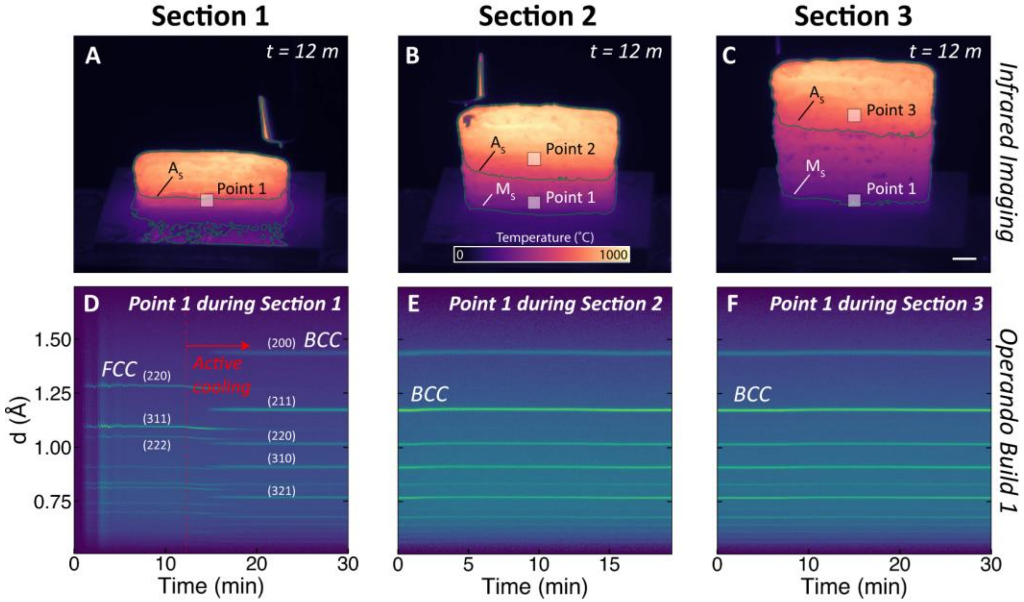
Advantages of neutron scattering for in situ/operando studies

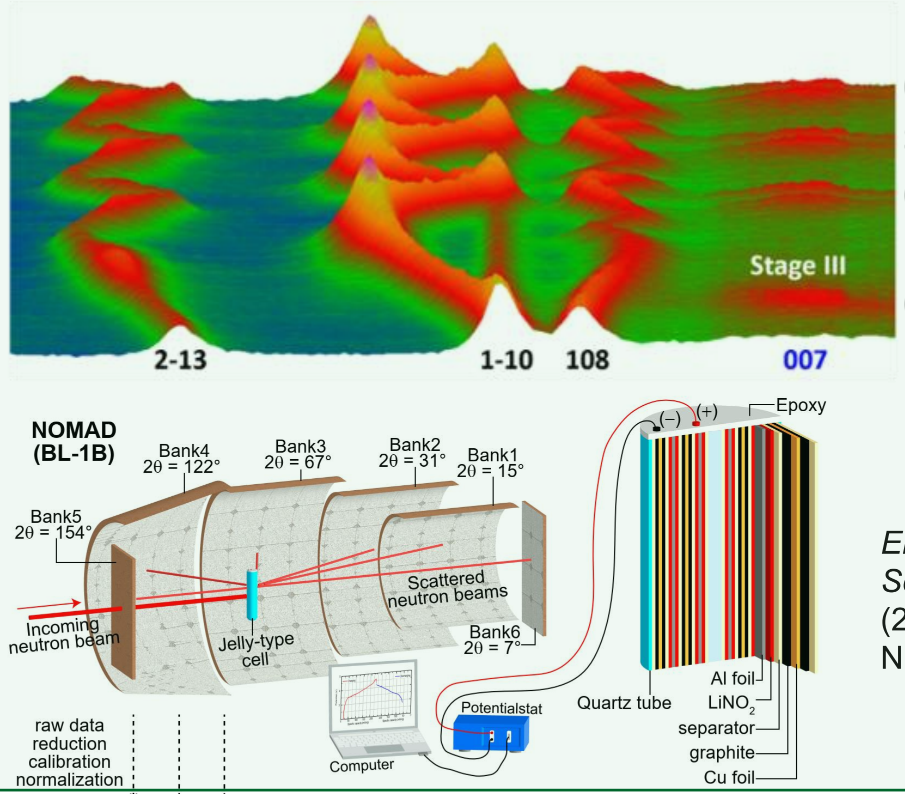


JACS, 142, 7655 (2020). Data from VISION



ACS Energy Lett. 4, 10, 2402–2408 (2019). Data from MARS





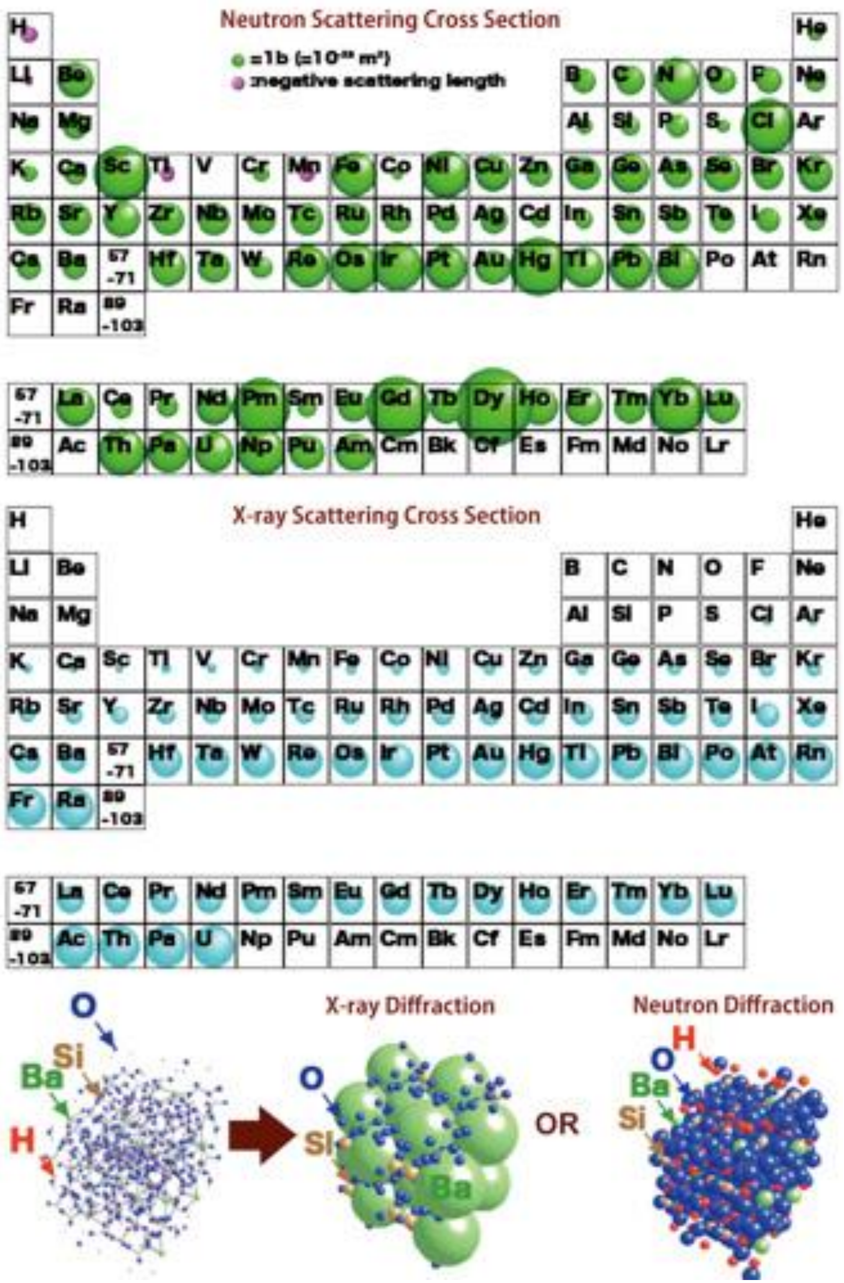
Energy & Environmental Science 14, 6441-6454 (2021). Data from NOMAD

Oak Ridge National Laboratory

Nat Commun 14, 4950 (2023). Data from VULCAN

Operando neutron diffraction for battery research

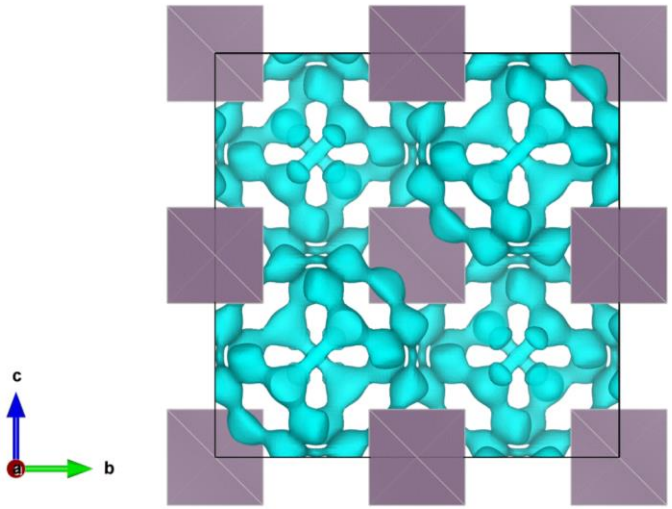
Advantages of neutron diffraction for battery research

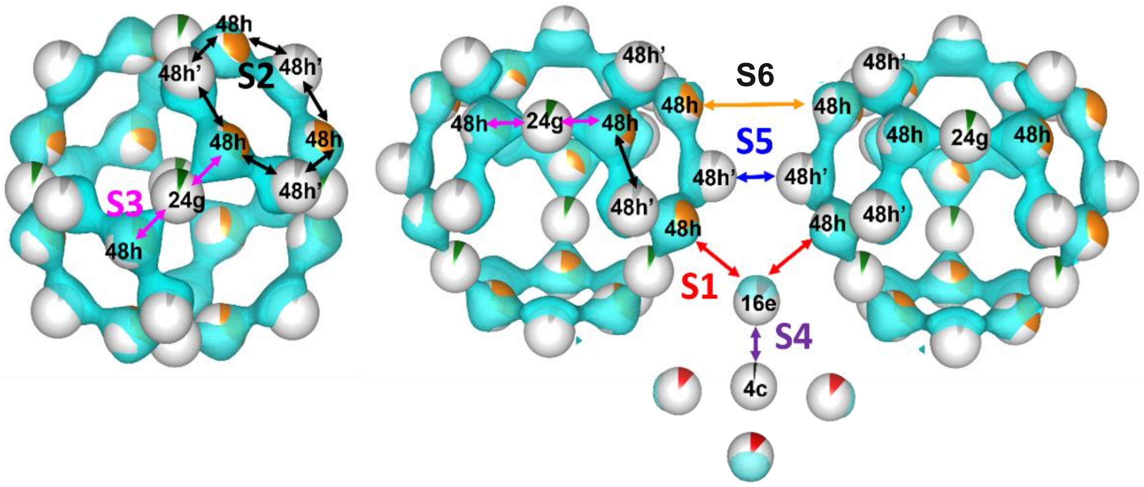


- Detects light atoms even in the presence of heavy atoms (H, Li, C and O)
- Distinguishes adjacent atoms and even isotopes of the same element (neighboring transition metal ions, e.g. Mn, Fe, Co and Ni etc.)
- With neutrons, negative scattering lengths are possible (e.g. Mn, Ti, Li, H)
- Strong penetration of the neutrons, non-destructive, no disturb of the electrochemical reactions (in situ)

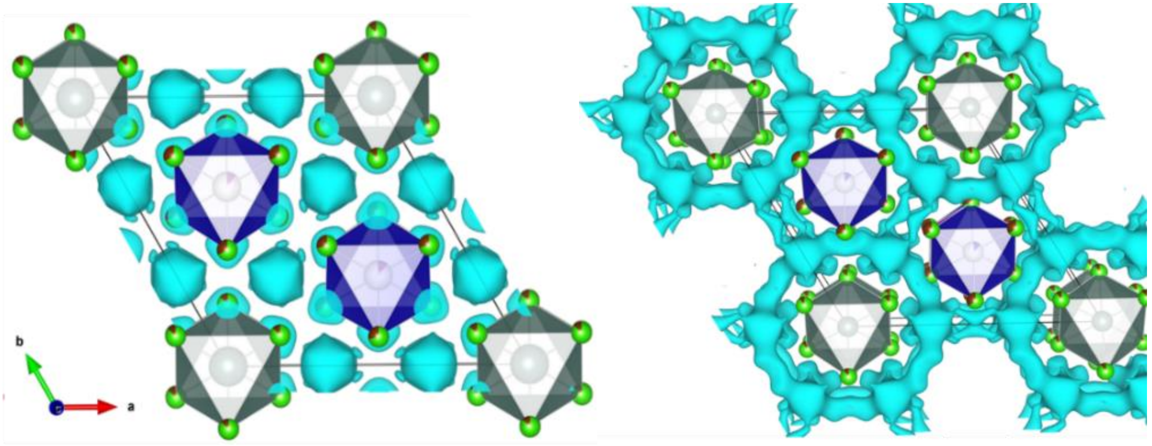
Identifying Li^+ positions in battery electrode/electrolyte materials

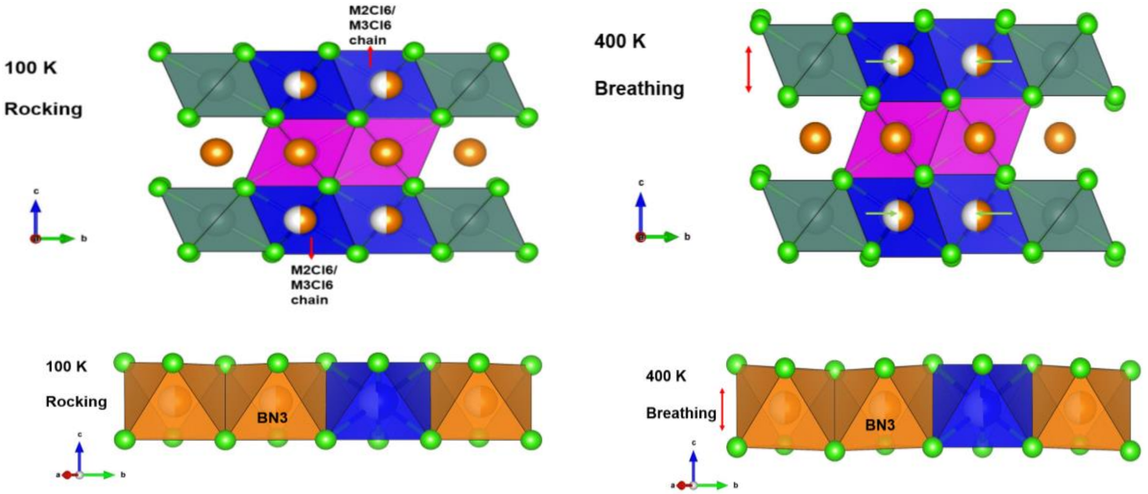
Li sublattice in argyrodite Li_6PS_5Cl





Superionic transition in Li_3YCl_6



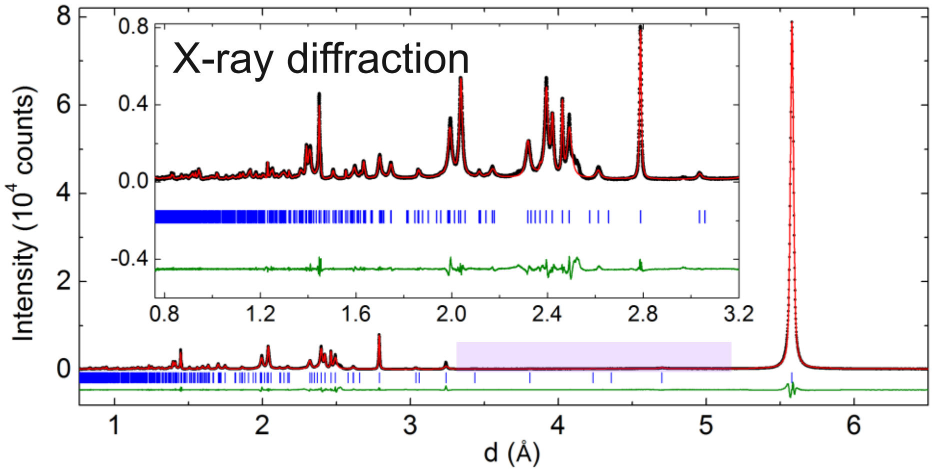


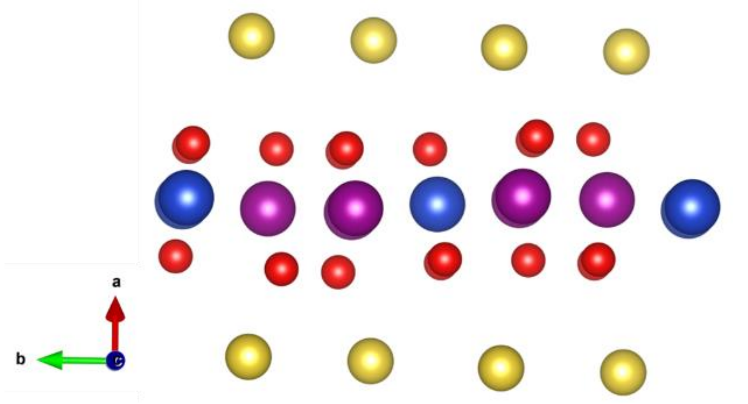
Chien et al. *Chem. Mater.* 2024, 36, 1, 382–393

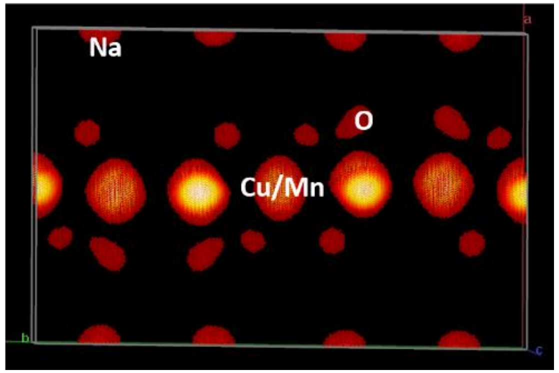
Liu, Z. et al *Nat. Chem.* 2024, 16, 1584–1591

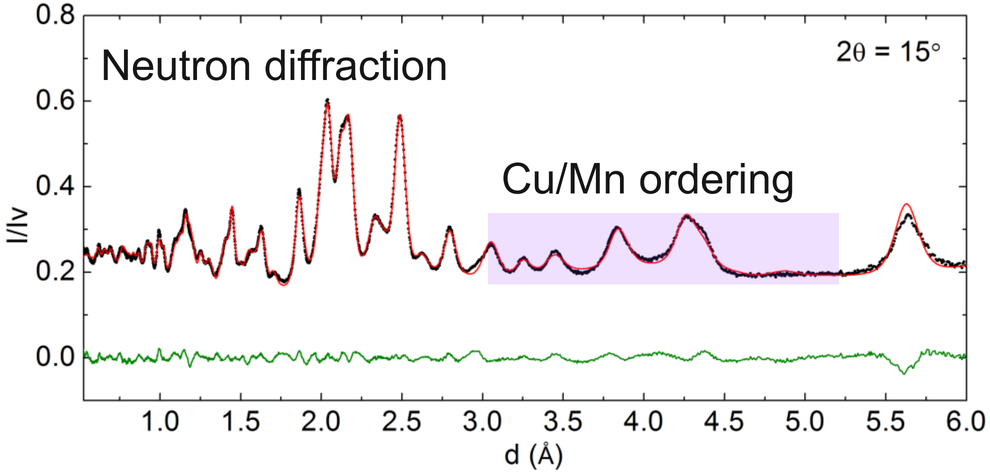
Distinguishing neighboring transition metal cations

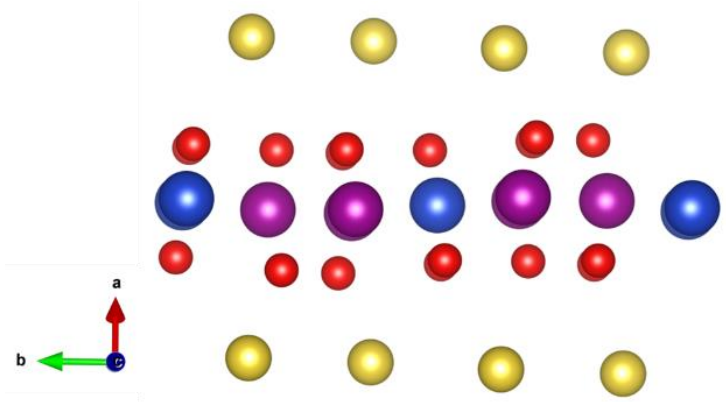
P3-type layered $Na_{2/3}Cu_{1/3}Mn_{2/3}O_2$

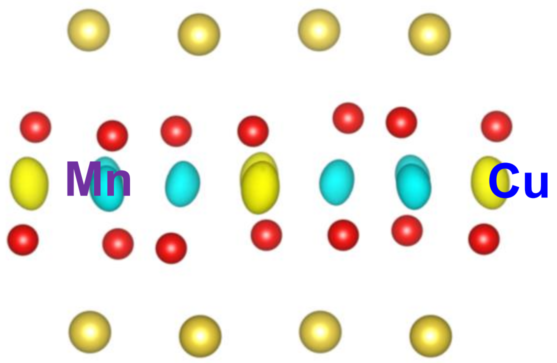










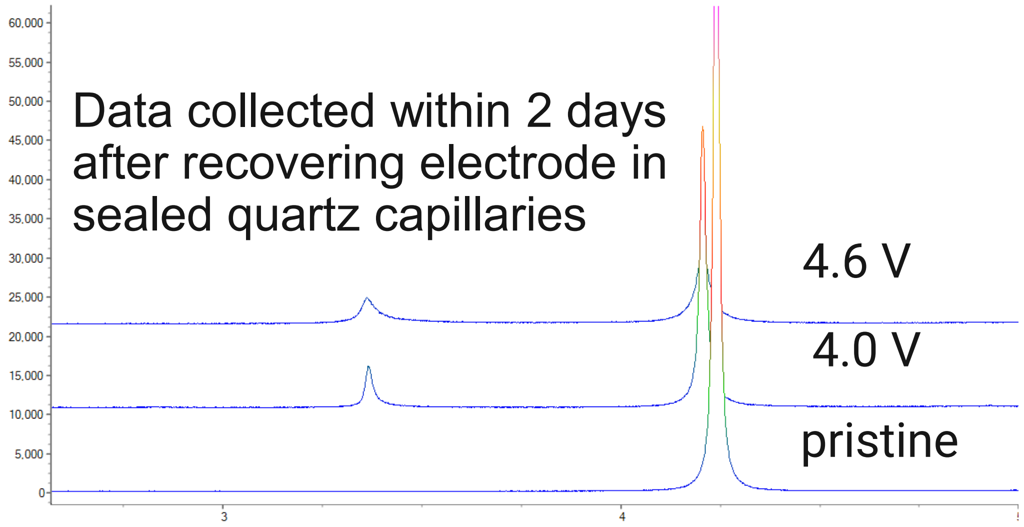


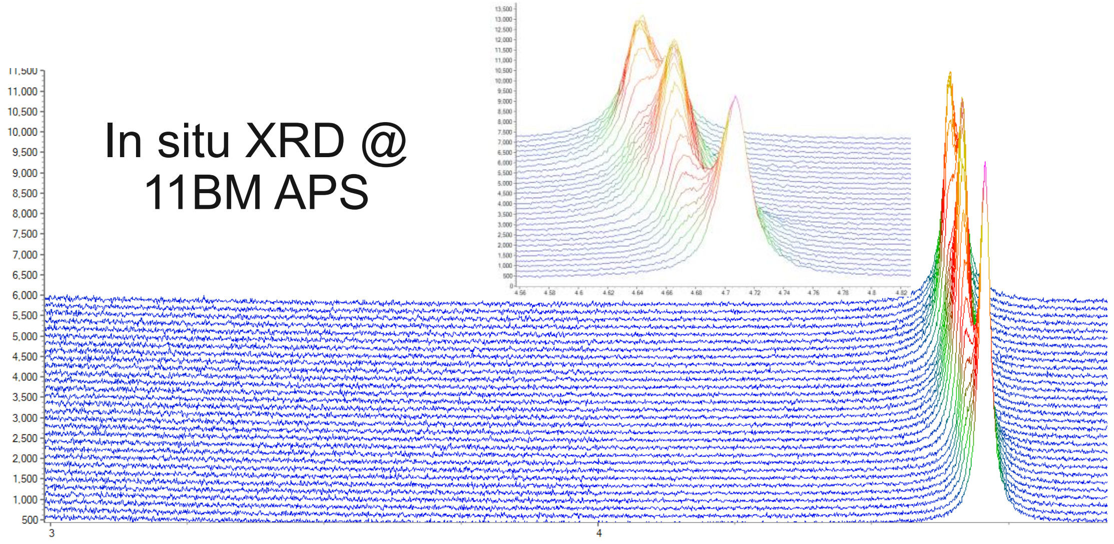
S.G. $P2_1/c$, a = 6.6027(2) Å, b = 8.7137(2) Å, c =5.0085(1) Å and β = 122.360(1)°

Wang X. et. al. *Nat. Comm.* 2023, 14, 7665.

Why do we need *operando* (neutron) diffraction?

$Na_{2/3}Cu_{1/3}Mn_{2/3}O_2$

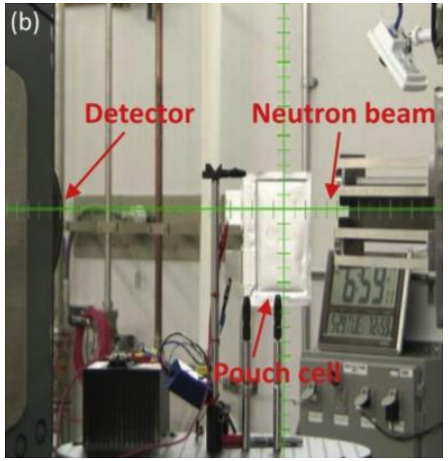




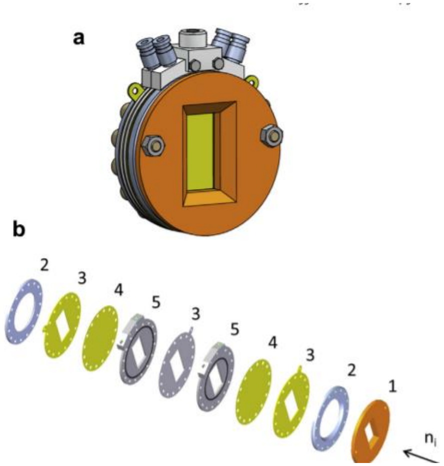
- Many intermediate phases are metastable
- Sensitive to light elements and excellent contrast for neighboring cations
- Non-destructive and not disturbing the electrochemical reaction
- Neutron diffraction is a flux limited technique

Challenges of *operando* neutron diffraction study of batteries?

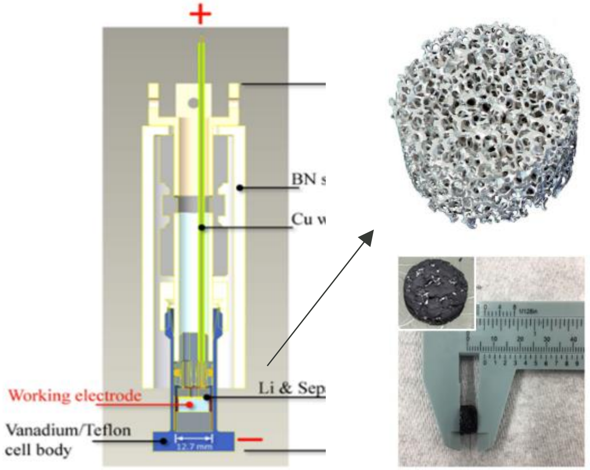
Pouch cell



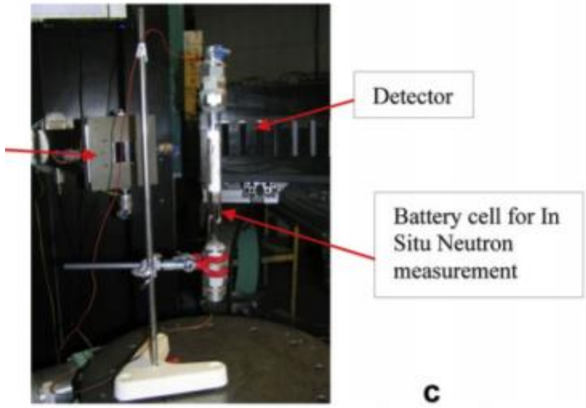
Coin cell



Cylindrical cell



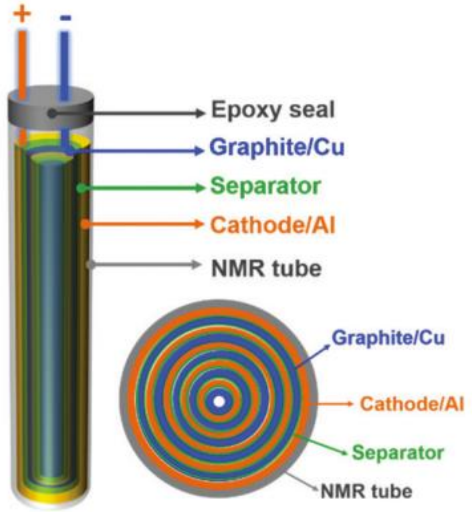
Jelly roll cell

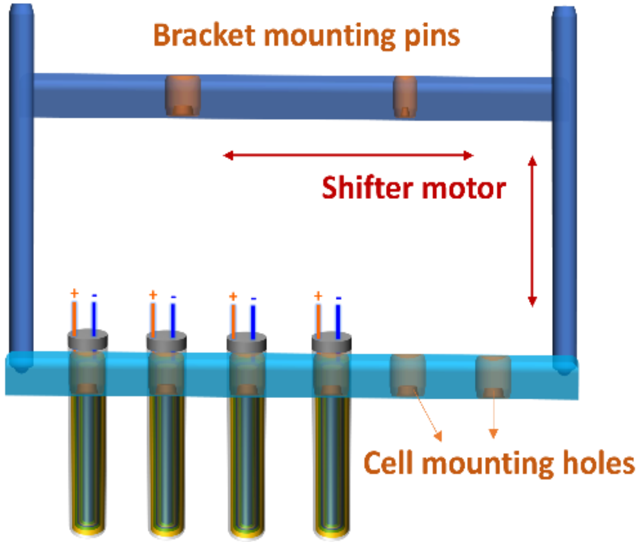


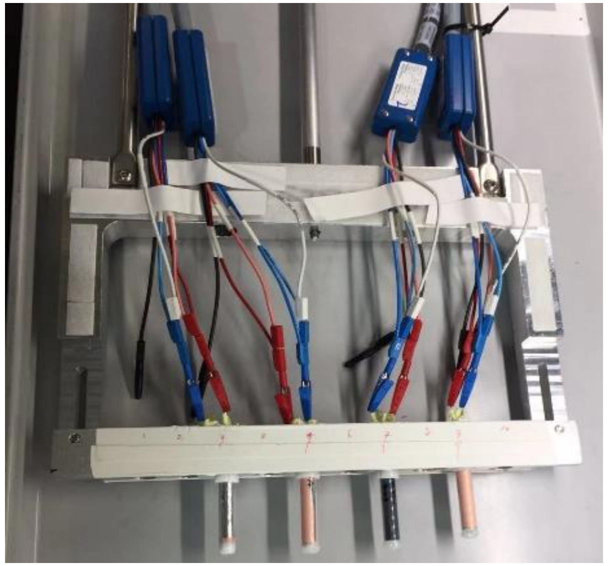
- New in situ cells with low background and reproducible electrochemistry
- High throughput measurements, fast data acquisition (minutes or sub-minute) of quantitatively refinable data

J. Power Sources 226, 249-255, 2013
Adv. Mater. 32.18 (2020): 1904528.
J. Power Sources , 248, 900-904,2014
Chem. Mater., 31, 124-134, 2018

Developing neutron diffraction friendly *in situ* cells and sample environment



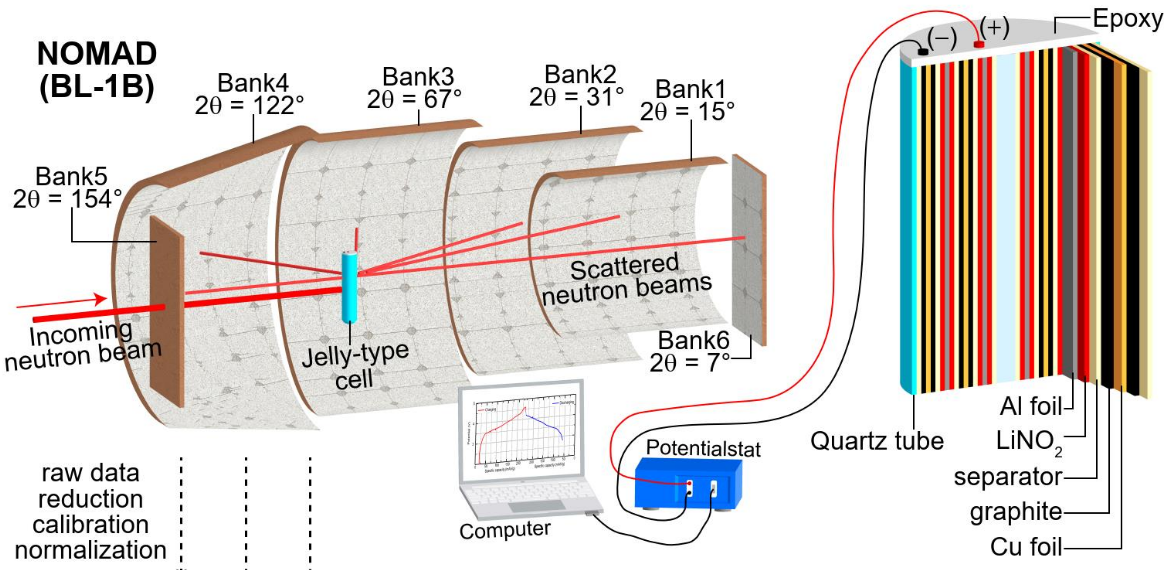


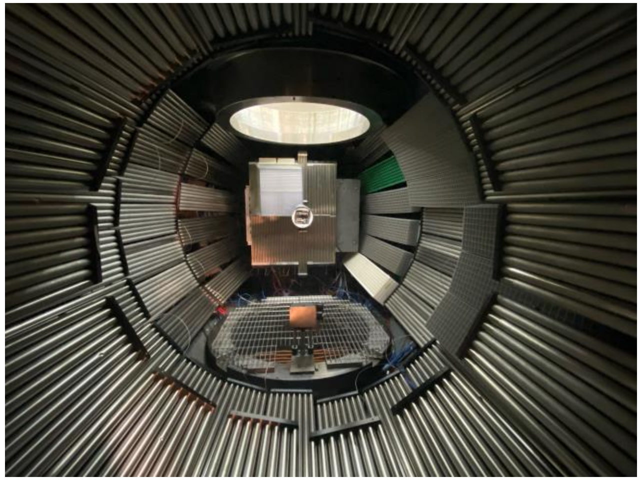


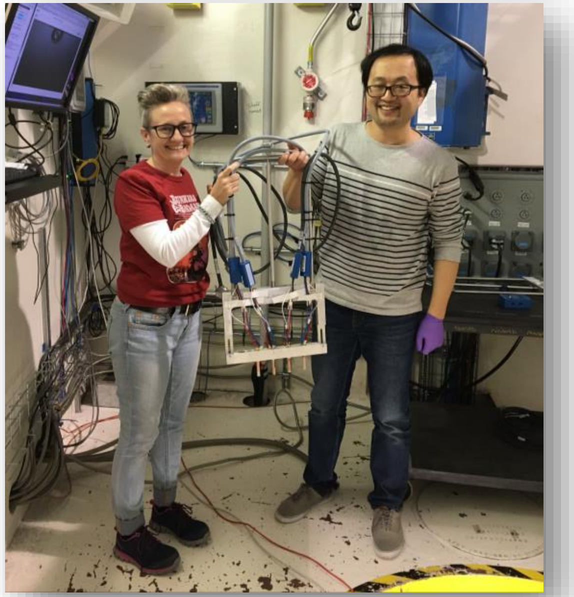
- Easy electrode alignment (transparent) and prevent internal short circuit (insulating)
- Reproducible electrochemistry
- Easy fabrication of large amounts of customized *in situ* cells (high throughput)
- Minimizes the amounts of illuminated electrolytes and significantly reduces the parasitic/incoherent scattering signal

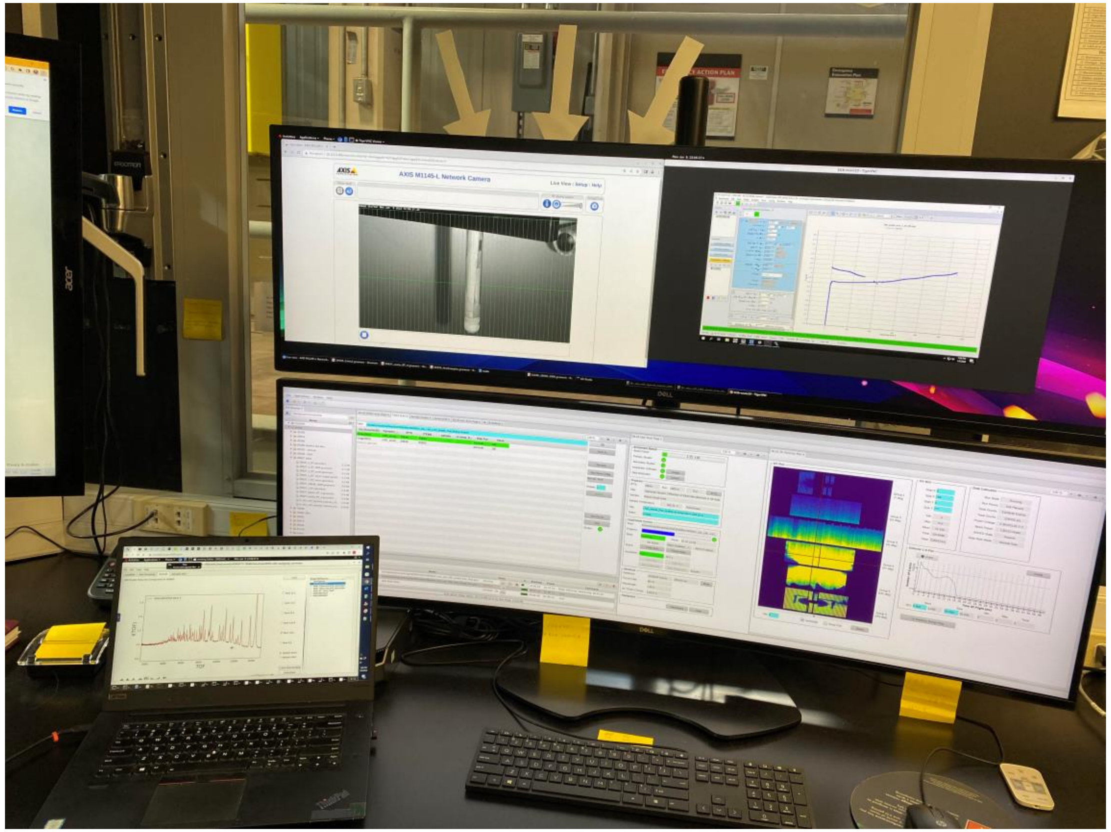
Energy & Environmental Science 2021, 14, 6441-6454 *Advanced Science* 2021, 8 , 2102318

Experiment set up and data collection









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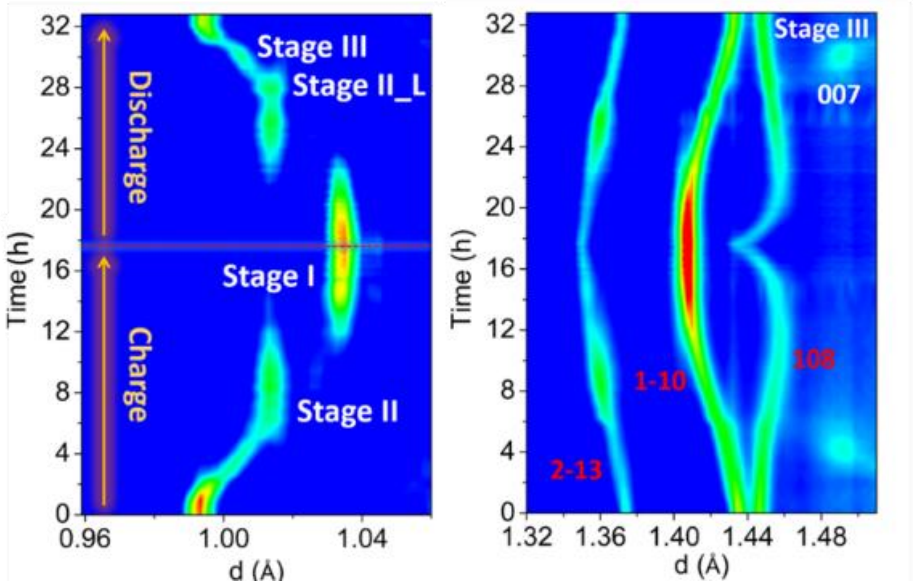
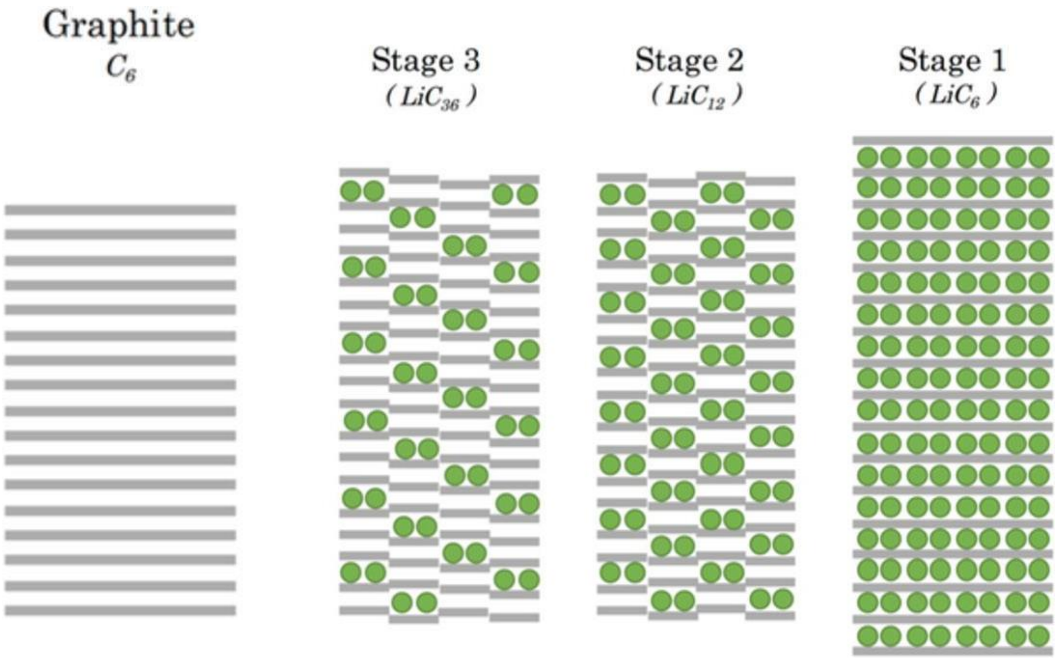
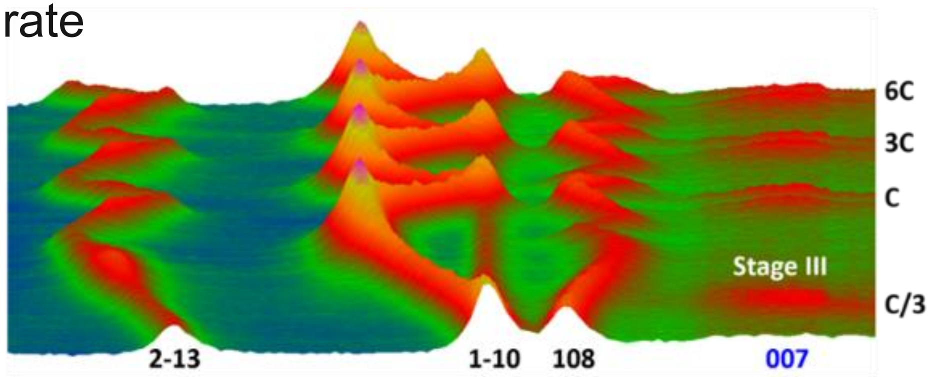
Data quality assessment

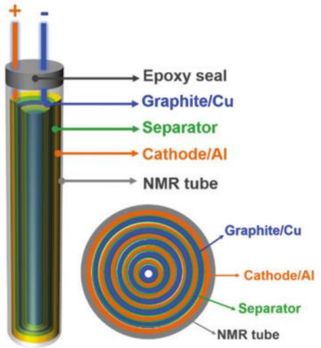
Slow rate





Fast rate



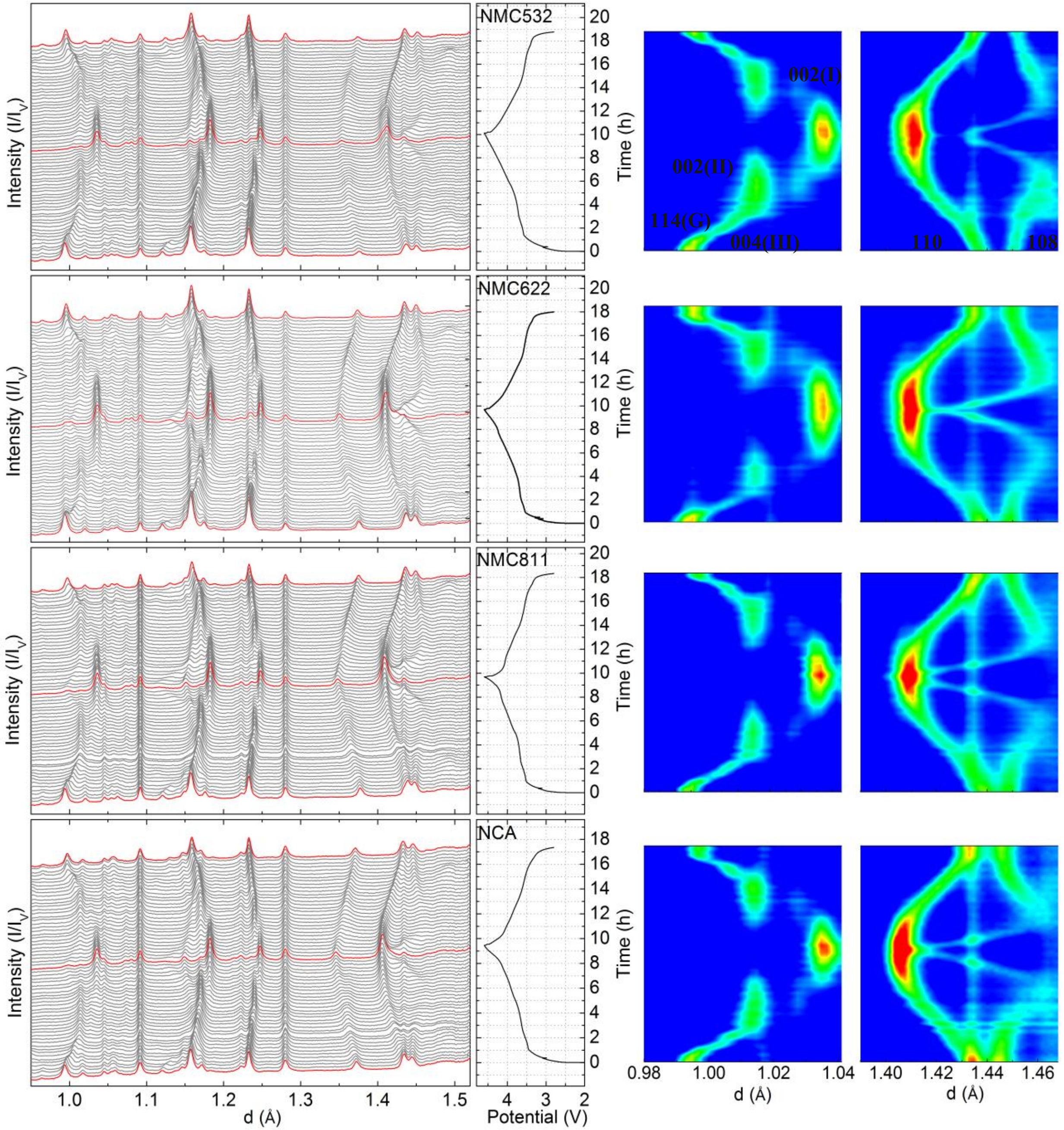


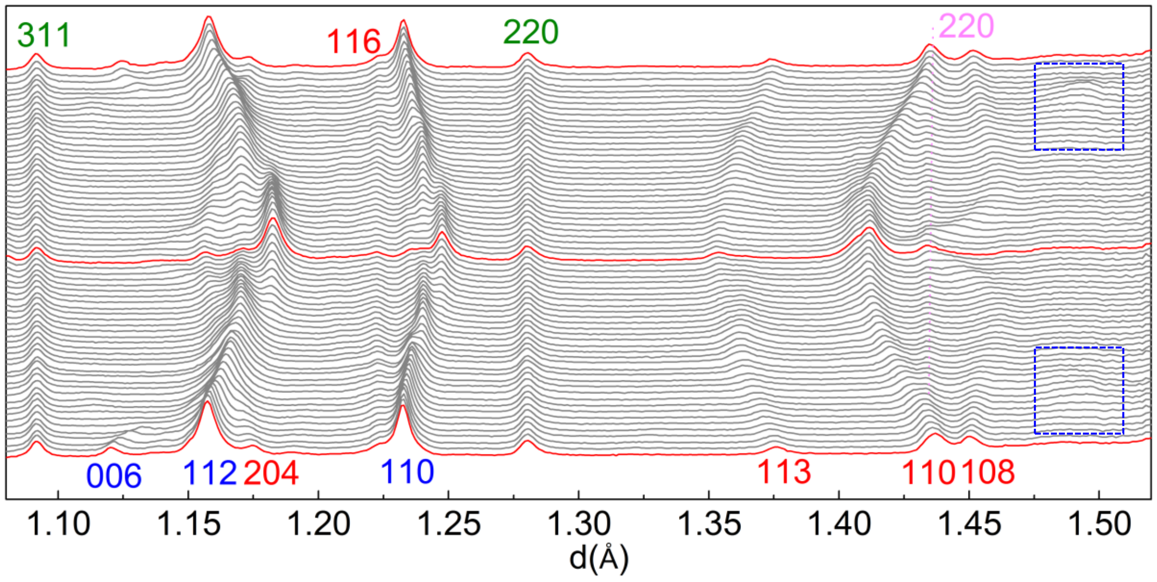
- Can be operated in either high throughput or high-rate mode
- Good quality data can be obtained for both cathode and anode electrode materials

Advanced Science 2021, 8 , 2102318

Energy & Environmental Science 2021, 14, 6441-6454

Data quality assessment: qualitative analysis





- Four different phases: cathode, graphite, Al and Cu.
- Graphite lithiation follows staging phase transitions (stage III phase is a solid solution phase)
- NMC/NCA follows solid solution reaction path

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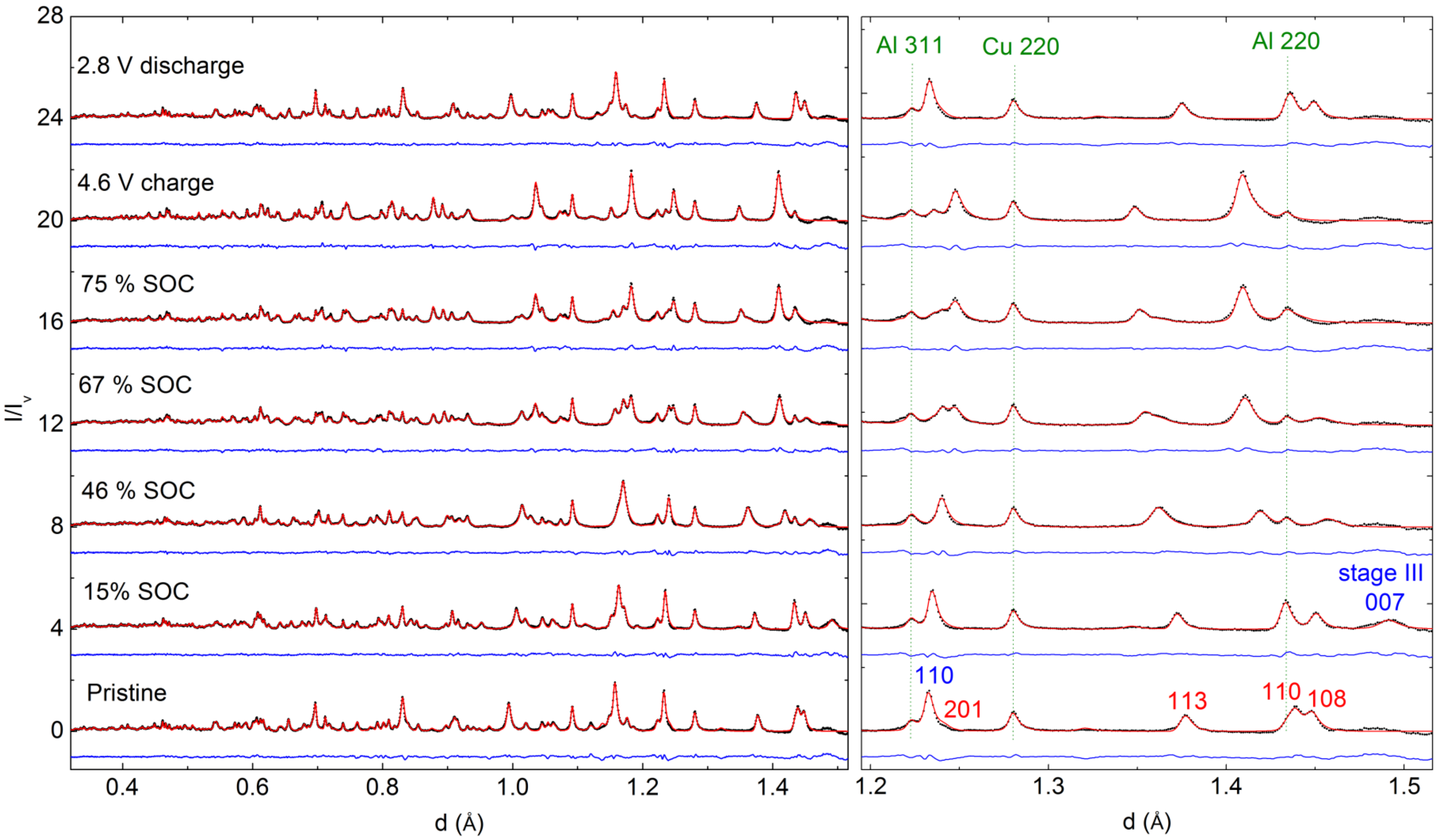
Parametric structure refinements



- High quality data collected for composition dependent Ni-rich cathodes
- Quantitative structure changes obtained using parametric structure refinements

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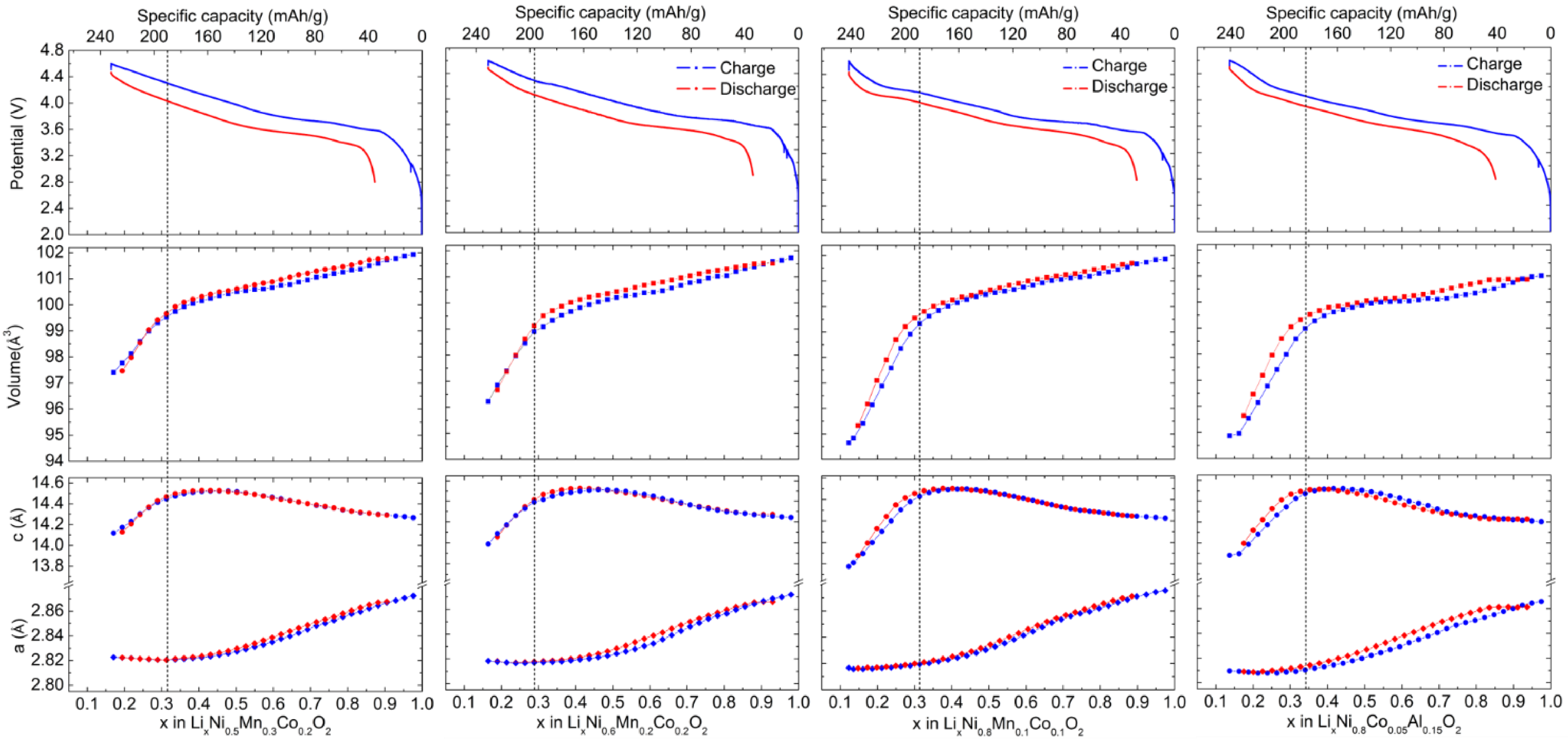
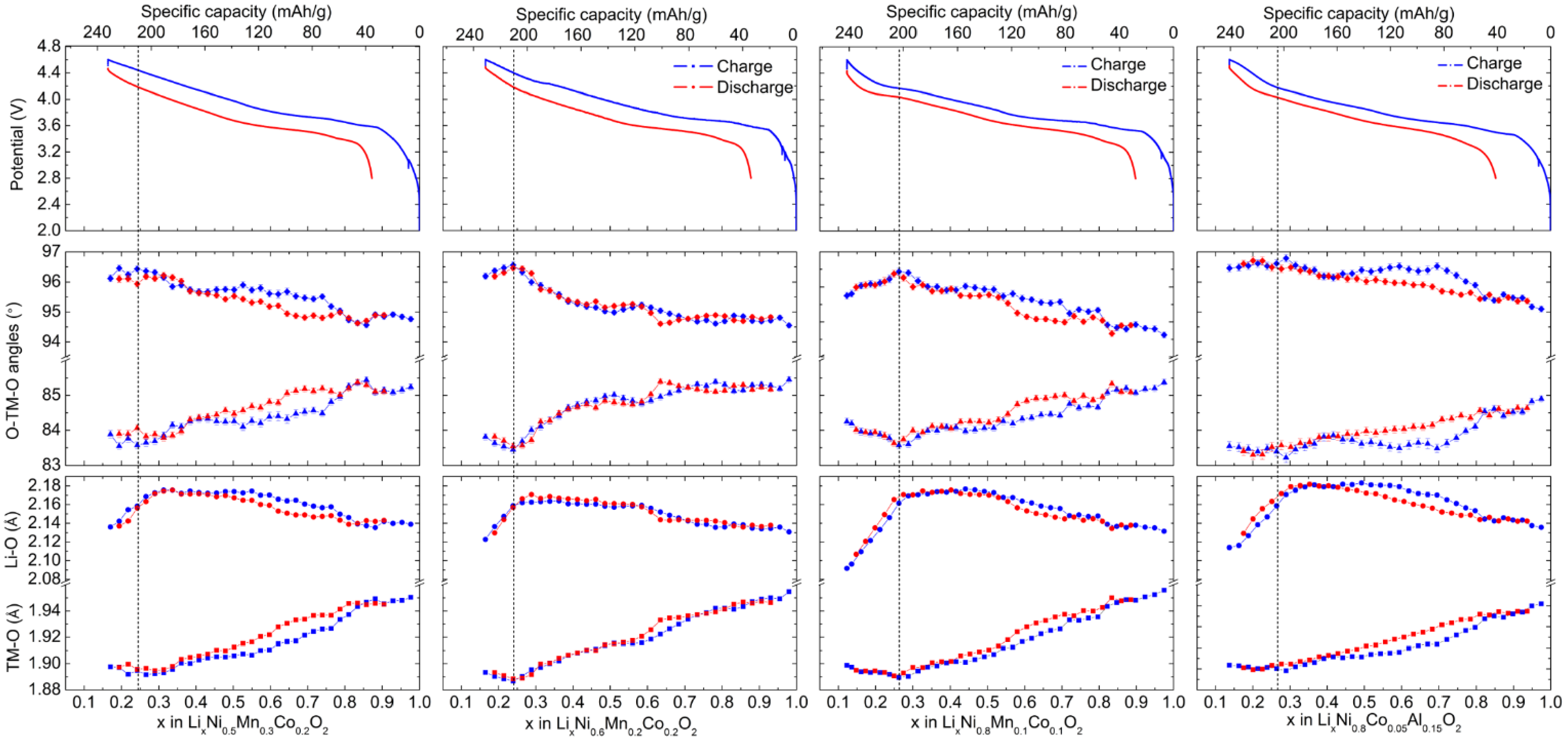
Universal structural evolution of Ni-rich cathode materials



Anomalous increase of average TM-O bond lengths above ~75% SOC



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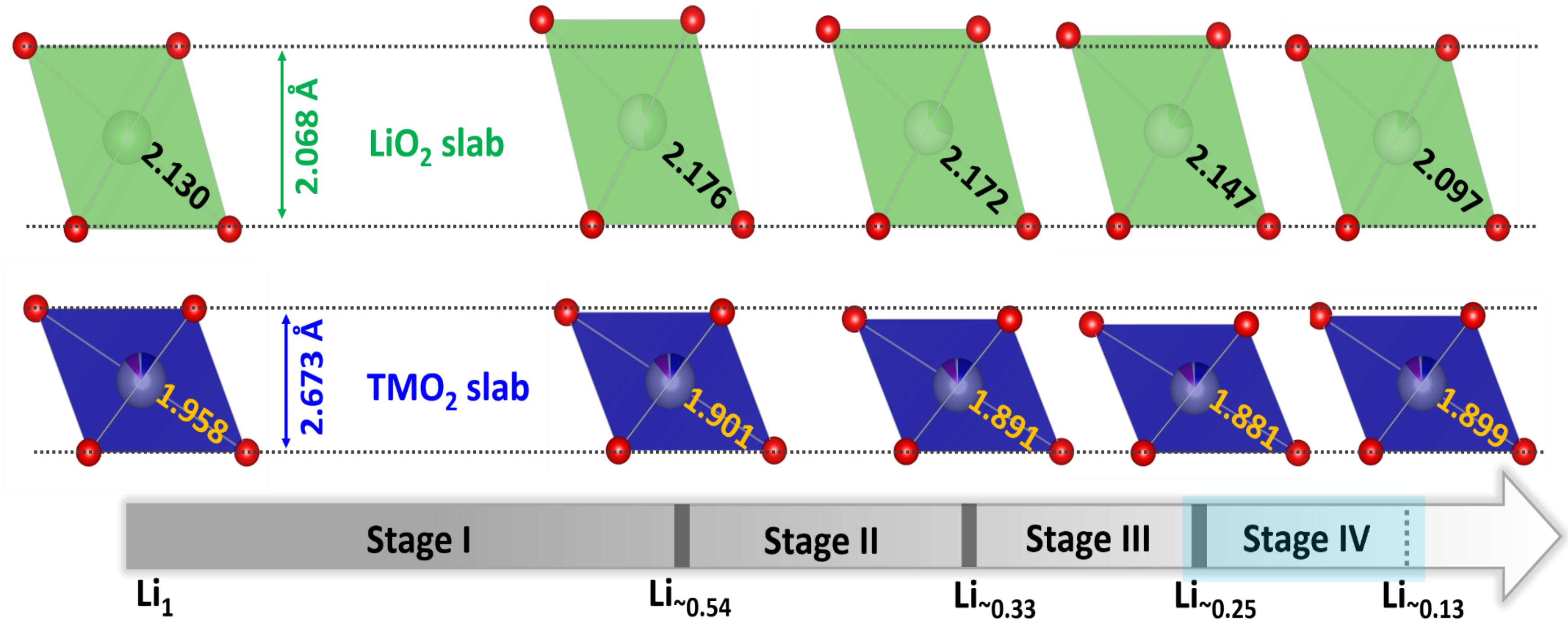
Universal structural evolution of Ni-rich cathode materials



- Classical model explains structural transitions in stage I and II: competition between the decrease of screening effects and the increase of TM-O covalency
- More complex mechanisms for structural evolution in stages III and IV
- The abnormal increase of average TM-O bond lengths in stage IV cannot be explained using the classical model

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Thank you!

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