Energy Materials Science

SSRL 50th Anniversary Celebration

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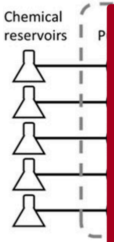
April 20, 2023

U.S. DEPARTMENT OF ENERGY | Stanford University

SLAC NATIONAL ACCELERATOR LABORATORY

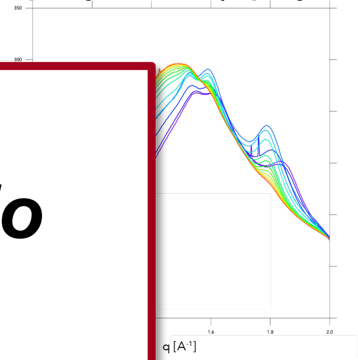
In situ & *operando* hard X-rays characterization

SAXS + synthesis to optimize atomically precises catalysts



Fong et al. J. Chem.

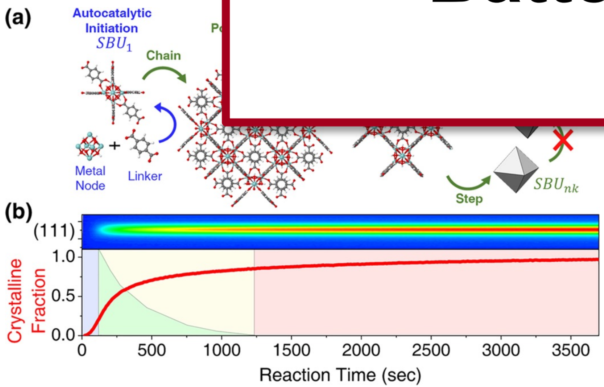
SAXS + deconstruction of polymers (upcycling)



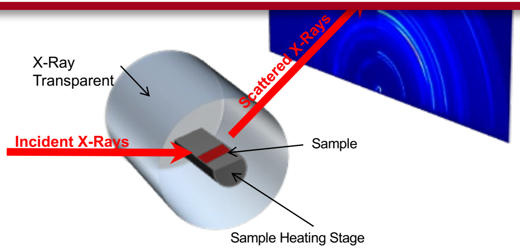
Theme: Multimodal & *operando*

Batteries as example case

XRD + synthes

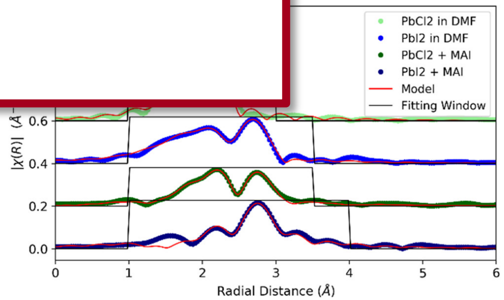


Dighe et al, JACS Au, 2, 2, 453–462 (2022)



Stone et al., Nat. Commun. **9**, 3458 (2018).

ovskite PV



Thampy & Stone, Inorg. Chem. **49**, 18, 13364 (2020).

Motivation: Green energy needs green storage

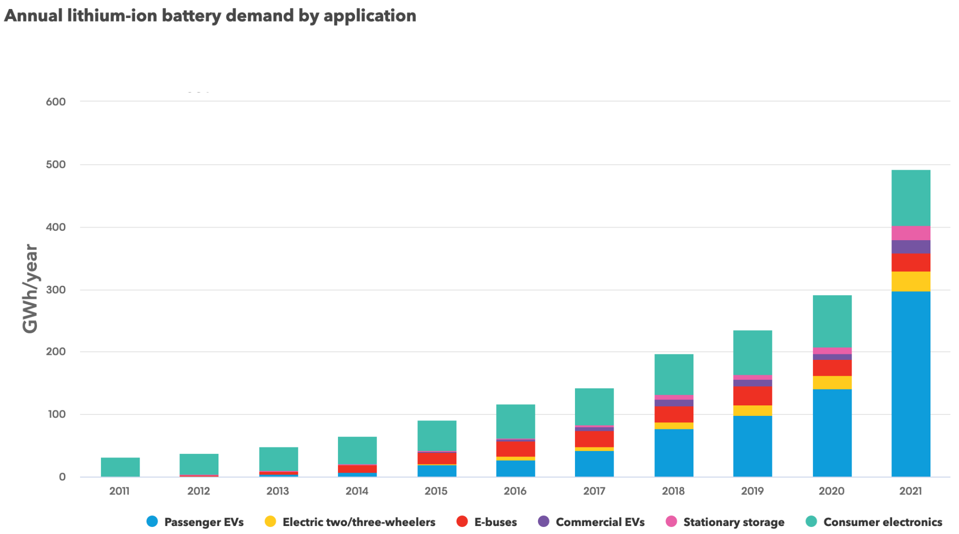
- Energy storage using Li-ion battery was driven by consumer electronics
- Now dominated by EVs (& grid in the future)
- EVs & stationary storage require **better batteries**
- Higher demand requires **greener batteries**

How can batteries hold more charge?

How can they last longer?

How can we use "greener", cheaper materials?

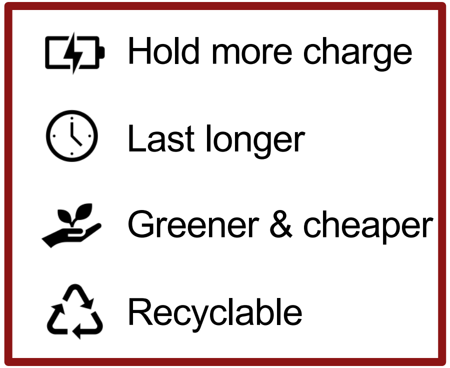
How can we recycle them?

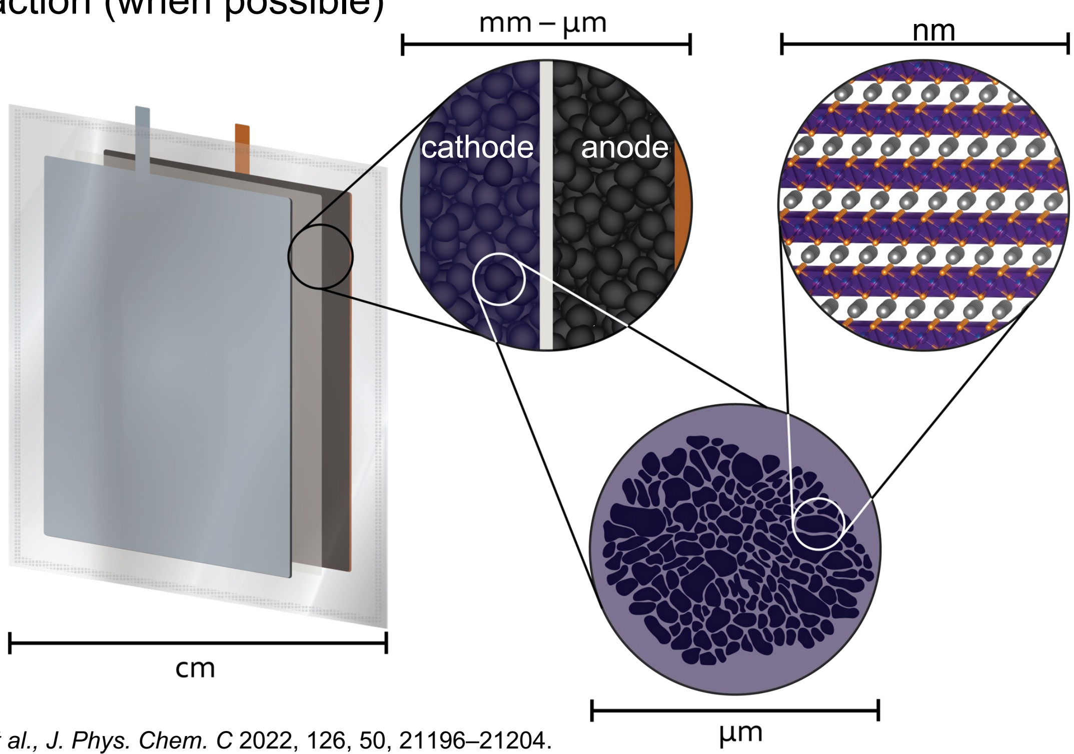


Bloomberg New Energy Finance

Need to understand batteries at many length scales

- Batteries operate (and fail) at many length scales
- Need to characterize batteries across the whole range of length scales
- Need to characterize the system in action (when possible)

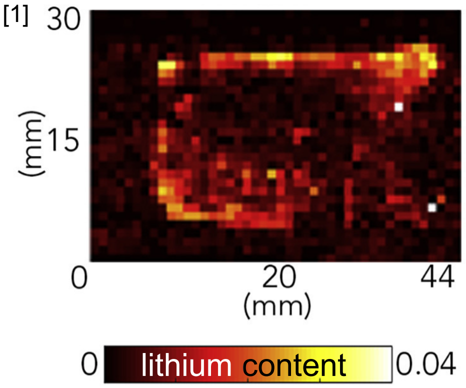


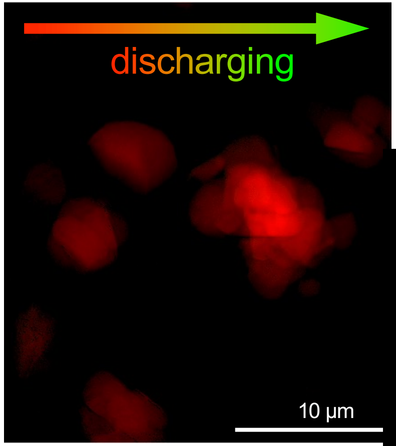


Preefer *et al.*, *J. Phys. Chem. C* 2022, 126, 50, 21196–21204.

Need characterization across length scales

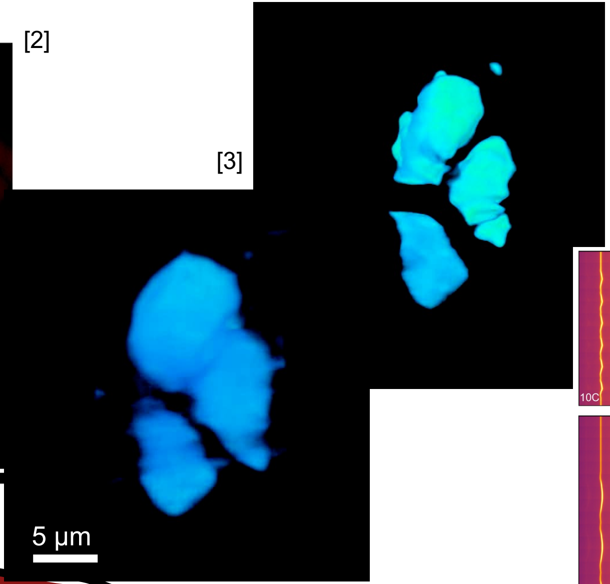
[1]



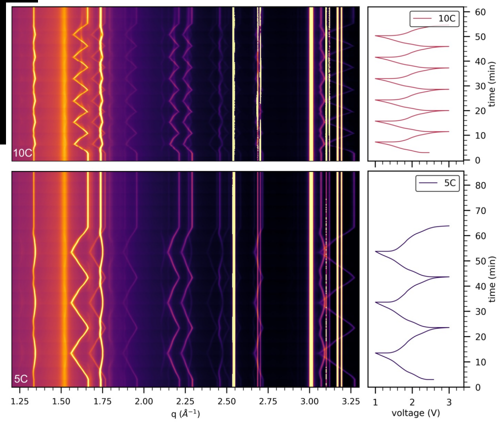


[2]

[3]



[4]



battery level

electrode level

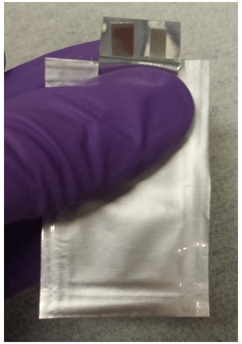
particle level

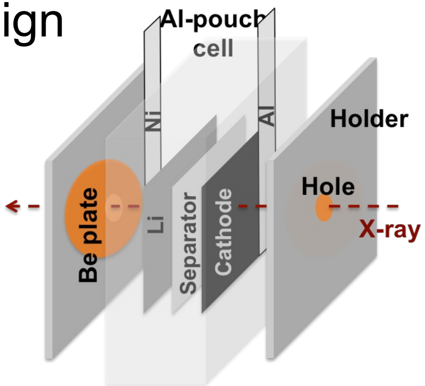
atomic level

1. Tanim, Paul, *et al*. Cell Reports Physical Sciences, 1:7, 100114 (2020).
2. Nelson Weker *et al.* Electrochimica Acta 247, 977-982 (2017).
3. Nelson Weker *et al.* Energy & Environmental Science 2014, 7, 2771-2777.
4. Preefer *et al. in preparation* diffraction during extreme fast cycling

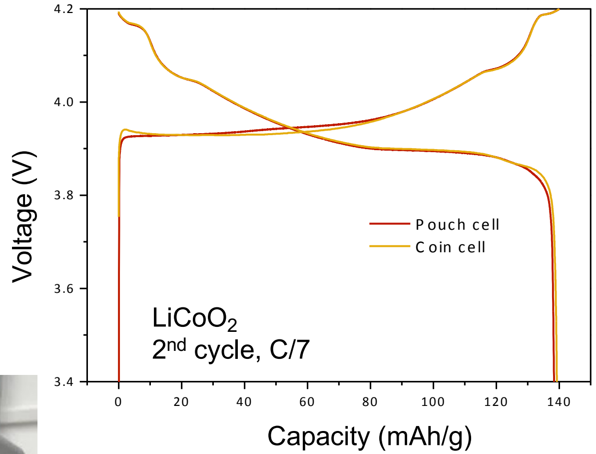
Multimodal *operando* X-ray characterization suite at SSRL

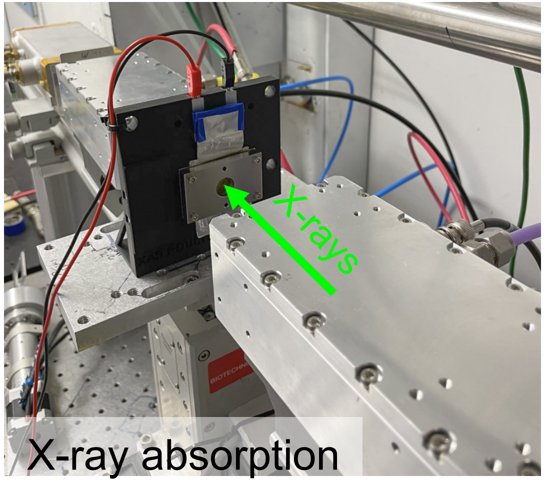
Cross platform pouch cell design



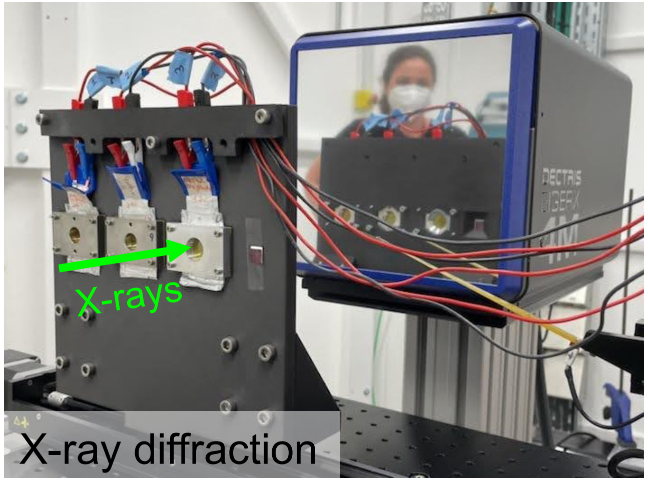


Identical cycling on & off the beamline

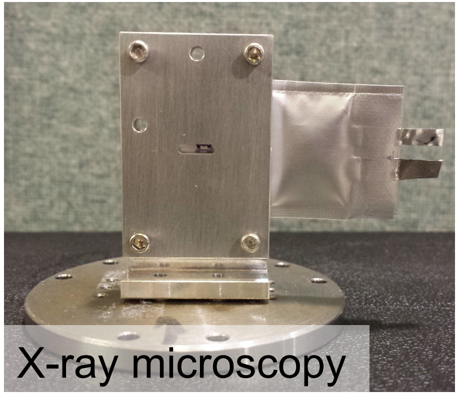




X-ray absorption



X-ray diffraction



X-ray microscopy

Basic science to industry relevant problems

Accelerating basic scientific understanding and battery commercialization

JCESR Joint Center for Energy Storage Research

DRX+

Applied Materials®

Battery 500 Consortium

Bosch

SCALAR

envia systems

XCEL

eXtreme Fast Charge Cell Evaluation of Lithium-ion Batteries

Sony

Xerion Advanced Battery Corp

muRata Innovator in Electronics

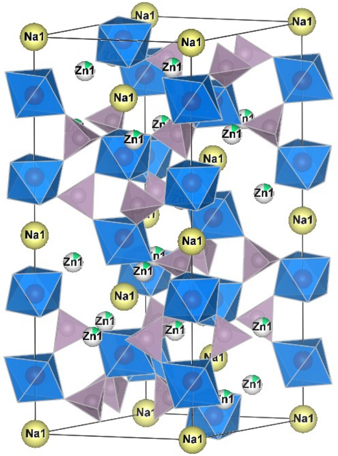
CNGMD Incorporating Metastability

EaCAM

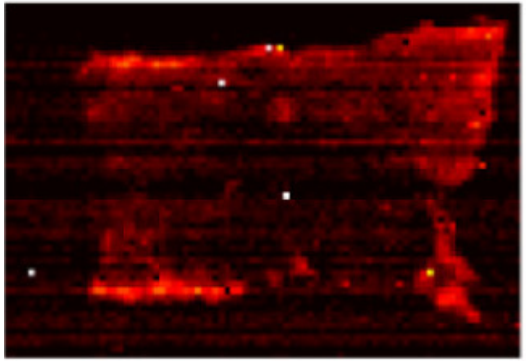
Lucid

3 vignettes of multimodal, *operando* characterization

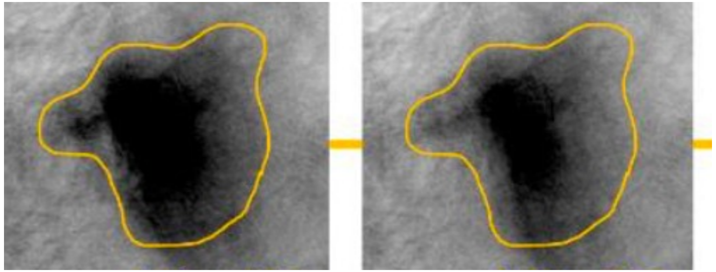
Zn batteries cathode



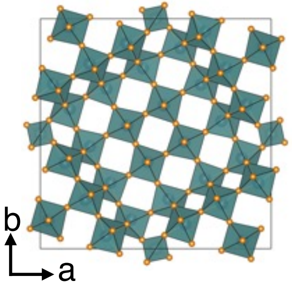
Li metal mapping



Mg-S cathode dissolution



Sneak peak of ongoing work!



$Mo_3Nb_{14}O_{44}$

Multivalent (MV) energy storage: 2 electrons per ion!

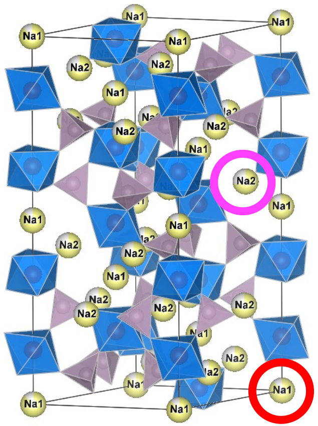
- MV metal anode support high volumetric capacity
  - 2 electrons per metal ion!
  - Zn has highest
- Can use aqueous electrolyte (safer & cheaper)
- Need cathode material to reversibly intercalate Zn^{2+}

Element	Standard Potential (vs. SHE)	Specific Capacity (mAh g^{-1})	Volumetric Capacity (mAh cm^{-3})	Ionic Radius (Å)	Hydrated Ionic Radius (Å)
Li	-3.04	3860	2061	0.76	3.40 – 3.82
Mg	-2.36	2206	3834	0.72	3.00 – 4.70
Ca	-2.84	1337	2072	1.00	4.12 – 4.20
Zn	-0.76	820	5855	0.75	4.04 – 4.30

NASICON $Na_3V_2(PO_4)_3$ — Potential cathode for Zn^{2+}

Goal: Can we get 2x the storage by inserting Zn^{2+} instead of Na^+?

$Na_3V_2(PO_4)_3$

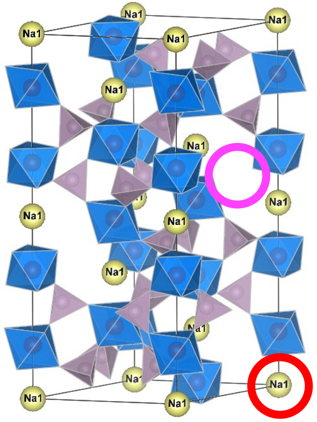


6b site – Na1

18e site – Na2

Charge

$NaV_2(PO_4)_3$

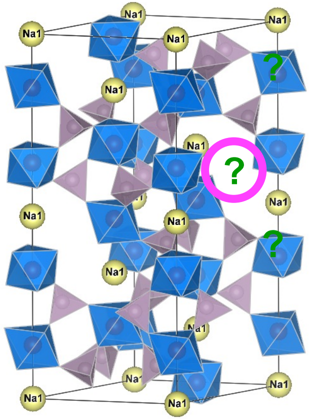


6b site – Na1

18e site – empty

Discharge

$(?)NaV_2(PO_4)_3$



Can Zn^{2+} occupy empty 18e sites?

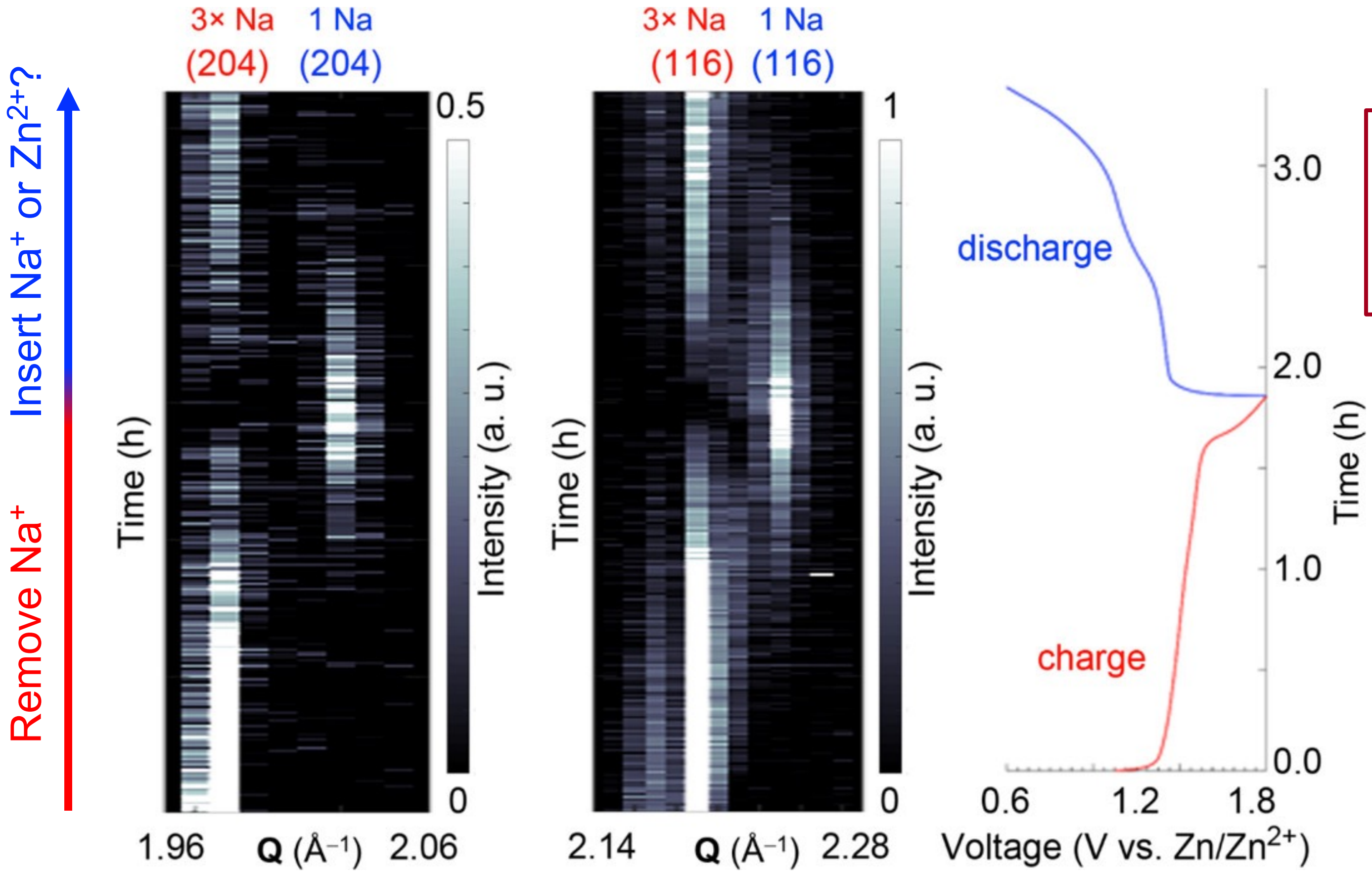
Jesse S.-W. Ko

NASICON = Na Super Ionic CONductor

JCESR Joint Center for Energy Storage Research

Ko et al., *Chemistry of Materials* 32, 7, 3028-3035 (2020).

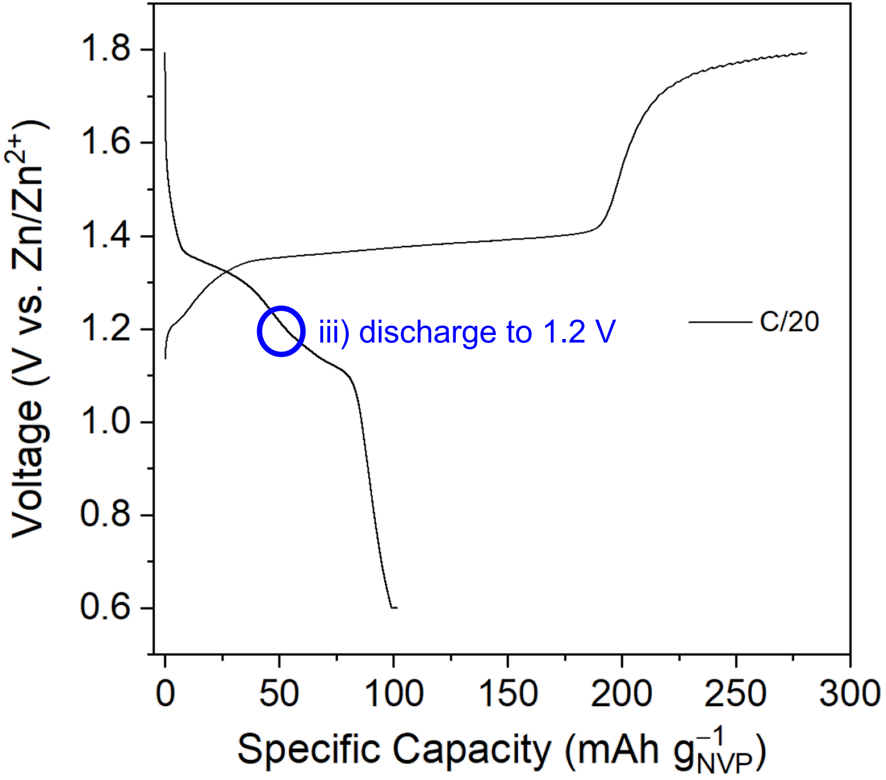
Qualitative changes with *operando* X-ray diffraction



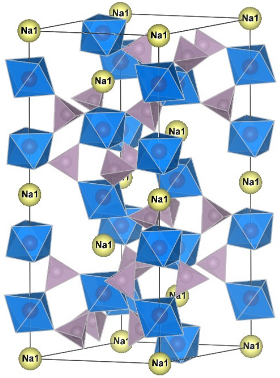
Not sensitive enough to see Na^+ vs. Zn^{2+} insertion

Ko et al., *Chemistry of Materials* 32, 7, 3028-3035 (2020).

Both Na^+ & Zn^{2+} insertion with discharge to 1.2 V



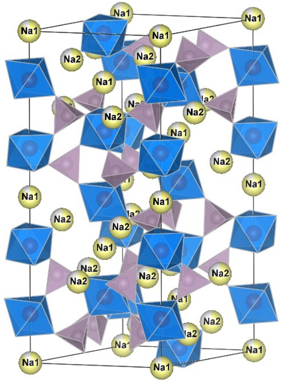
$NaV_2(PO_4)_3$
34.92%



6b site – Na1
18e site – empty

Na1 occ: 1.0

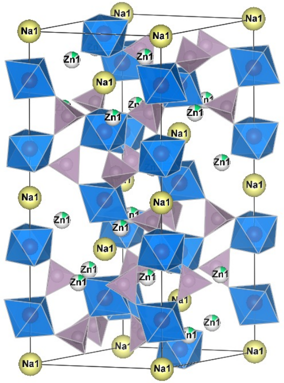
$Na_3V_2(PO_4)_3$
42.27%



6b site – Na1
18e site – Na2

Na1 occ: 0.87
Na2 occ: 0.72

$Zn_{0.25}NaV_2(PO_4)_3$
22.81%

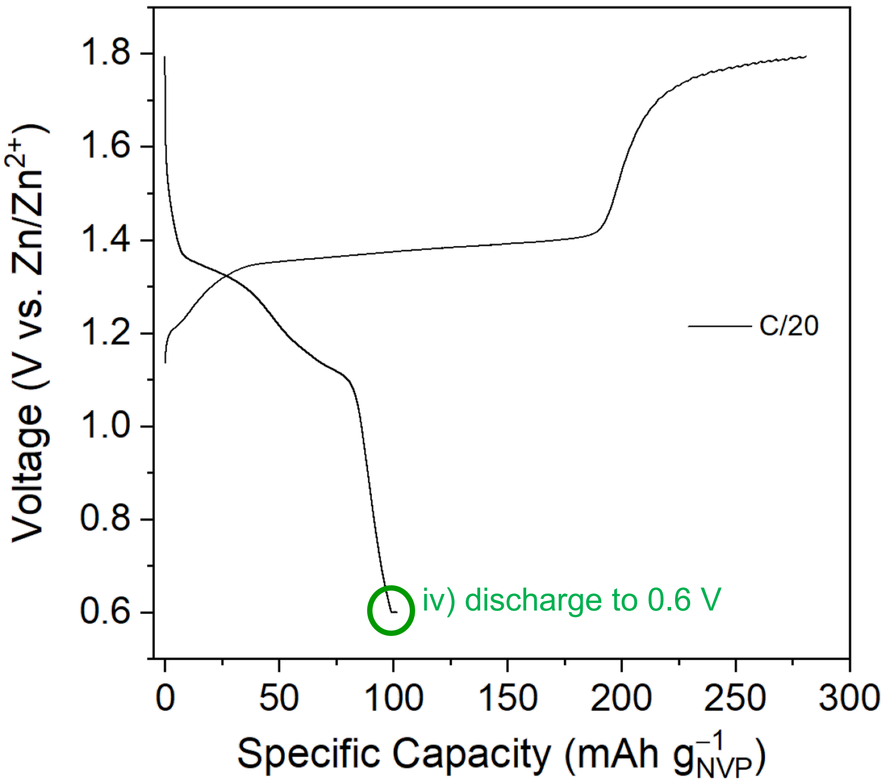


6b site – Na1
18e site – Zn

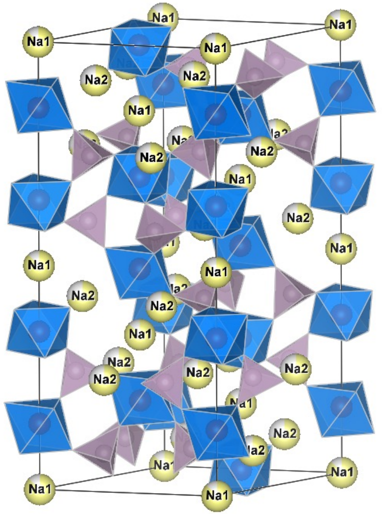
Na1 occ: 1.0
Zn occ: 0.12

Ko et al., *Chemistry of Materials* 32, 7, 3028-3035 (2020).

Both Na^+ & Zn^{2+} (& H^+) insertion with discharge to 0.6 V



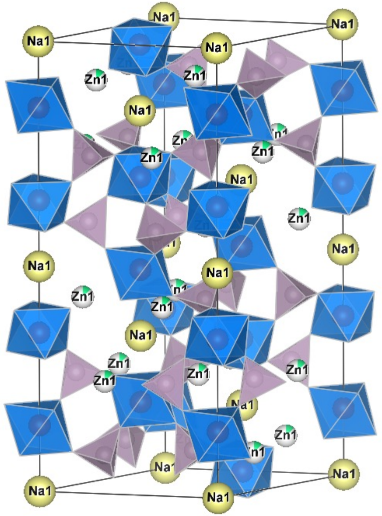
$Na_3V_2(PO_4)_3$
57.38%



6b site – Na1
18e site – Na2

Na1 occ: 0.87
Na2 occ: 0.72

$Zn_{0.25}NaV_2(PO_4)_3$
42.64%

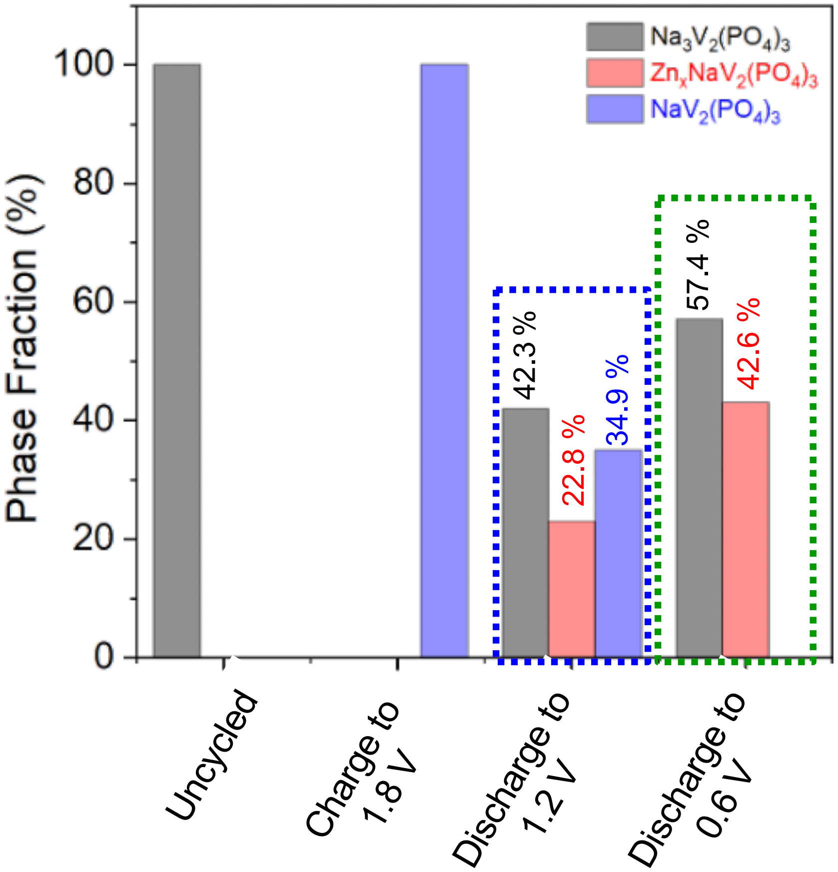


6b site – Na1
18e site – Zn

Na1 occ: 1.0
Zn occ: 0.12

Ko et al., *Chemistry of Materials* 32, 7, 3028-3035 (2020).

Ex situ X-ray diffraction: Summary



Discharge to 1.2 V

- Results in three phases ($NaV_2(PO_4)_3$, $Na_3V_2(PO_4)_3$, and $Zn_xNaV_2(PO_4)_3$)
- Unreacted $NaV_2(PO_4)_3$ still present at 1.2 V

Discharge to 0.6 V

- Two phases present ($Na_3V_2(PO_4)_3$ and $Zn_xNaV_2(PO_4)_3$)
- Zn occupancy in $Zn_xNaV_2(PO_4)_3$) only 12%

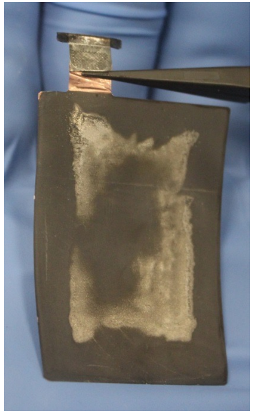
H^+ insertion into Zn site!

Fast charging: >15 min charging (>4C)

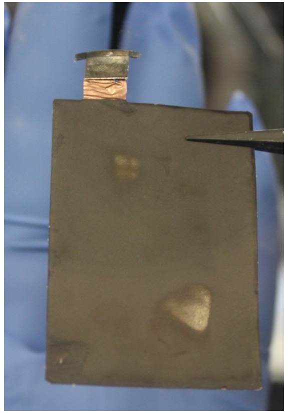
- How do we design batteries that also work well for fast charging?
- Li metal plating can dominate degradation & reduce capacity with loss of inventory
- Can we quantify Li plating and connect to capacity loss?

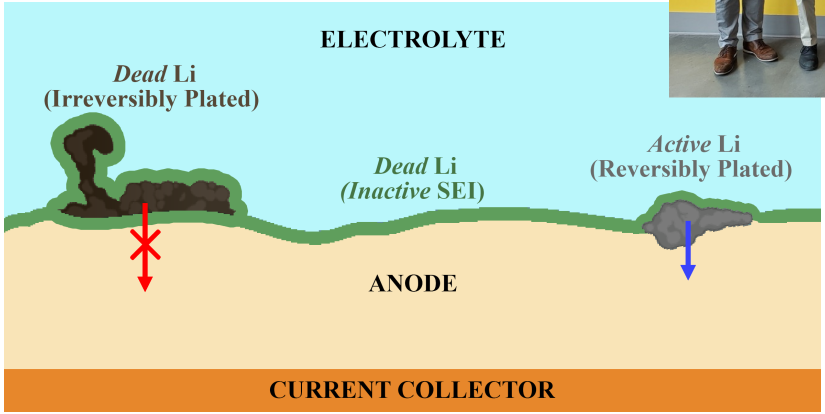
Li visibly plated onto graphite anode

10 min charging



15 min charging

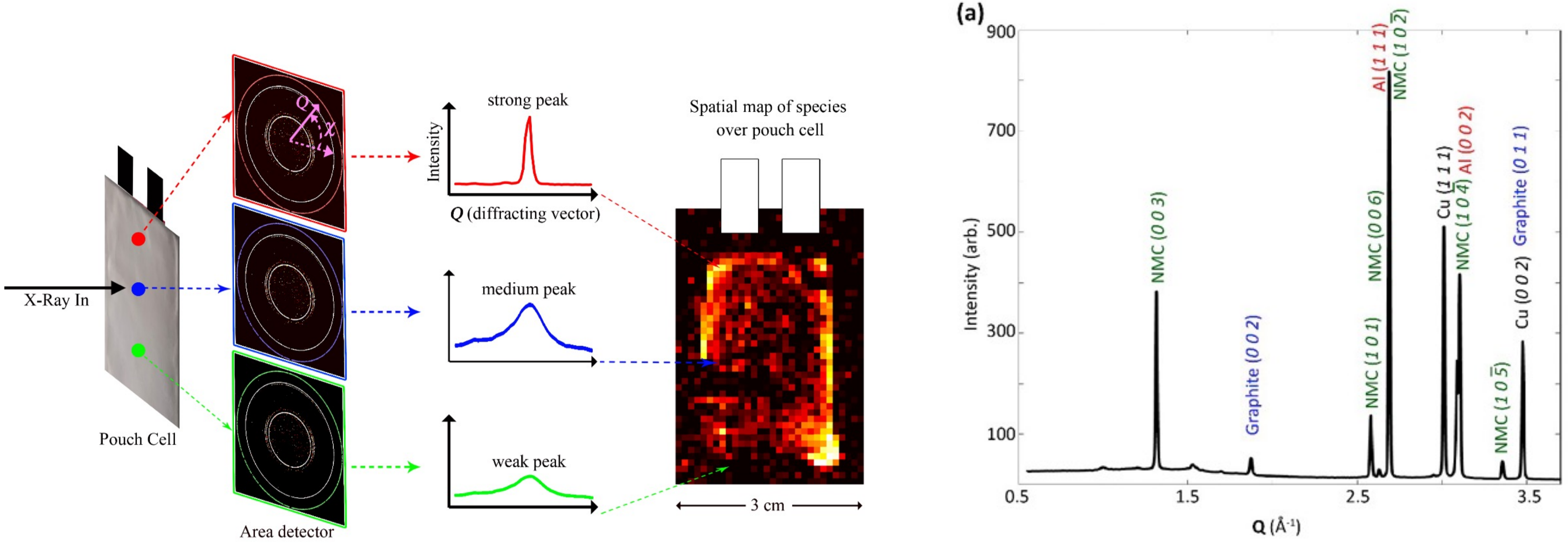




Paul, *et al.*, *Advanced Energy Materials*, 2100372 (2021).

eXtreme Fast Charge Cell Evaluation of Lithium-ion Batteries

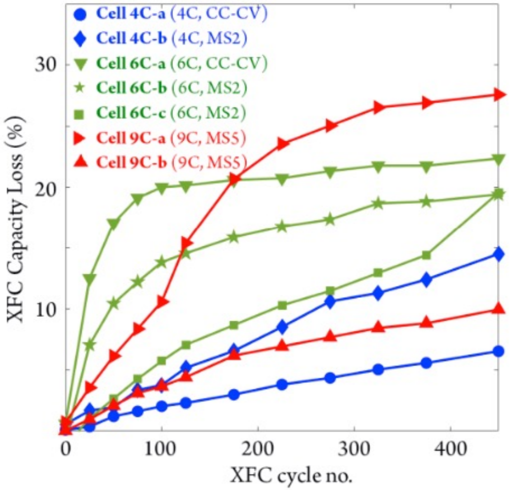
X-ray diffraction to map Li plating



- Correlate spatial distribution of all crystalline phases: Li metal, graphite staging, cathode ($LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$ = NMC)
- Performed *in situ* (non-distructive)
- More quantitative than visual inspection

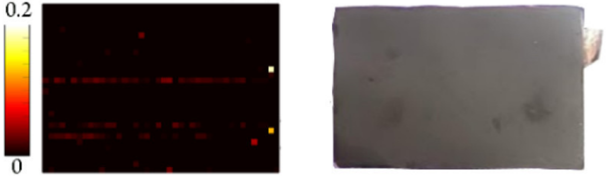
Paul, et al. *Energy & Environmental Science,* 14, 4979-4988 (2021).

Mapped Li plating in 7 cells: 3 different charge rates

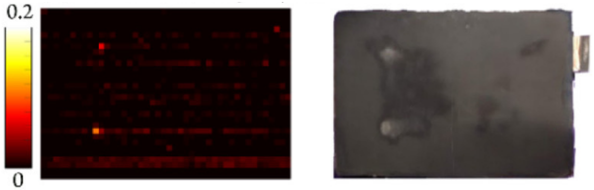


15-min. charging

Cell 4C-a: 8% capacity fade

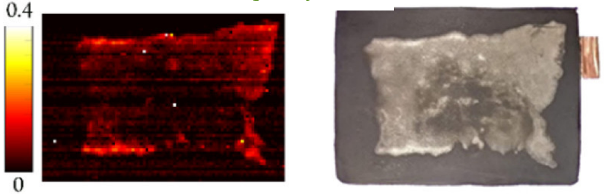


Cell 4C-b: 14% capacity fade

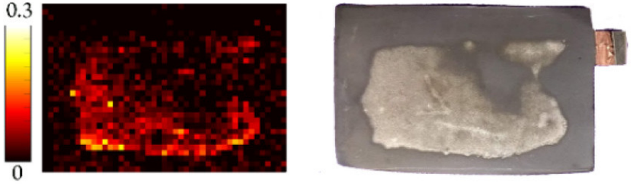


10-min. charging

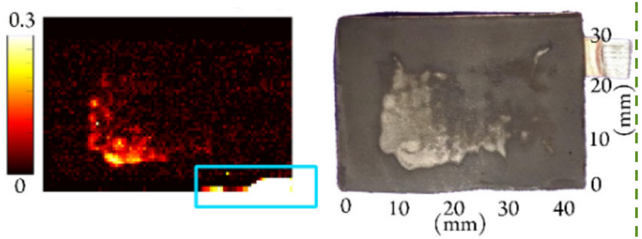
Cell 6C-a: 22% capacity fade



Cell 6C-b: 20% capacity fade

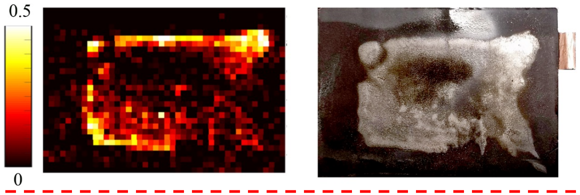


Cell 6C-c: 20% capacity fade

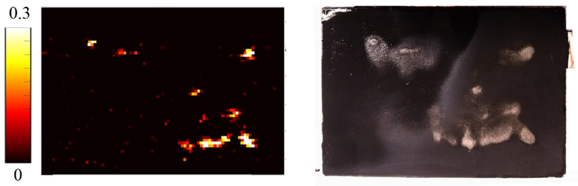


<10-min. charging

Cell 9C-a: 28% capacity fade

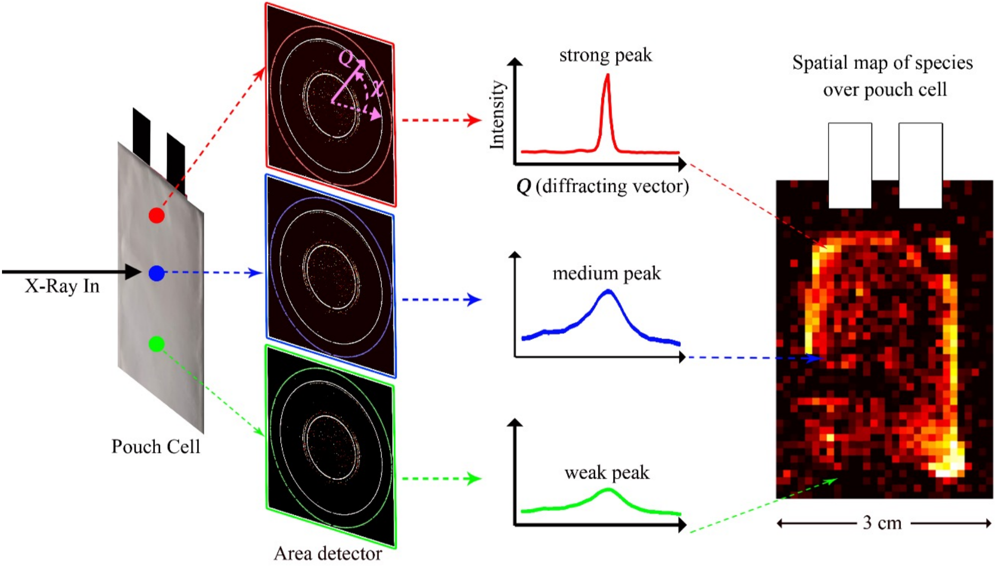


Cell 9C-b: 10% capacity fade



Paul, et al. *Energy & Environmental Science,* 14, 4979-4988 (2021).

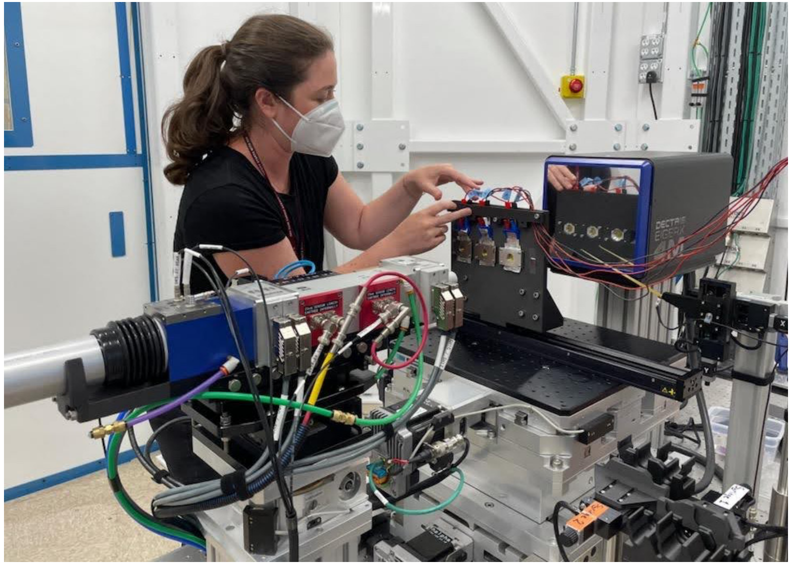
Now we can do this work at SSRL's BL17!



Paul, et al. *Energy & Environmental Science,* 14, 4979-4988 (2021).

Enables *in situ X-ray* diffraction mapping

New beamline 17



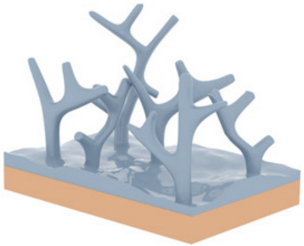
- Undulator beamline
- 6-circle diffractometer
- KB optics: 10 μm x 20 μm spot
- 5 – 20 keV

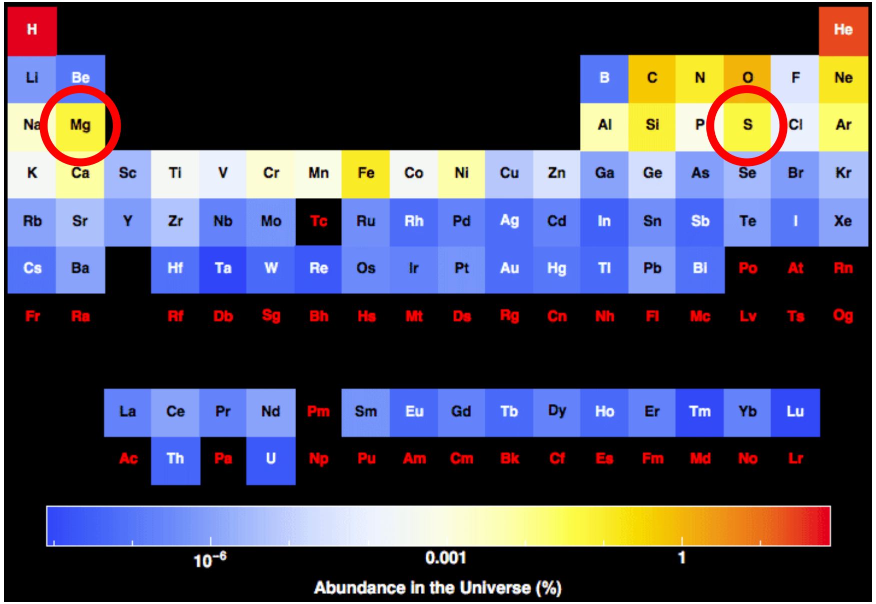
Magnesium sulfate cathode

Mg metal anode & S composite cathode

- Very high energy densities (beyond limit of Li-ion)
- S, Mg: inexpensive and abundant
- Mg metal doesn't form dendrites

muRata
INNOVATOR IN ELECTRONICS





Proposed reaction pathway:

$$S_8 – MgS_4 – MgS_2 – MgS$$

Battery architecture:

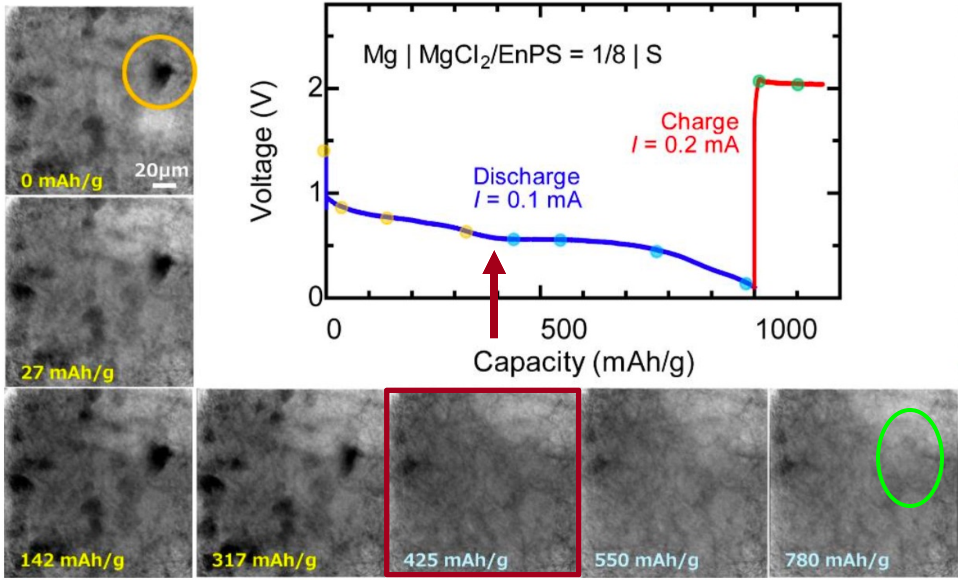
- Mg metal anode
- S/C composite cathode

Yuan *et al. Sci. Adv.*, 6, 10 (2020).

http://periodictable.com/

Operando imaging to understand irreversibility

- Mg: alternative to Li metal
- Sulfur is an inexpensive cathode material



- Nearly all sulfur particles disappear during first discharge plateau
- No particles reappear at charge → remaining particles are inactive
- Irreversible morphology change

Nakayama *et al. Chemistry of Materials*, 30(18), 6318-6324 (2018).

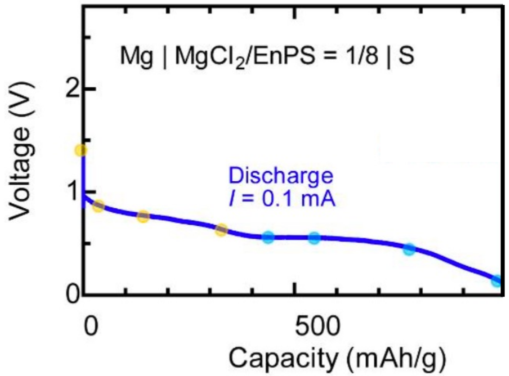
Looking closer at one particle's behavior

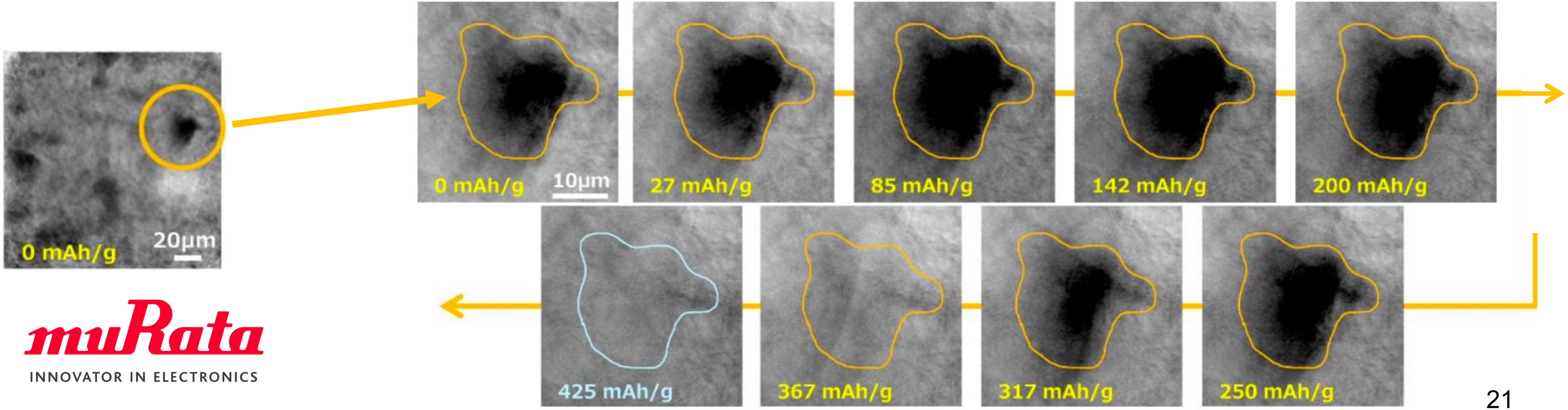
0 – 200 mAh/g: Particle expands slightly

$$Mg + S_8 \rightarrow MgS_8$$

200 – ~350 mAh/g: Particle dissolves rapidly

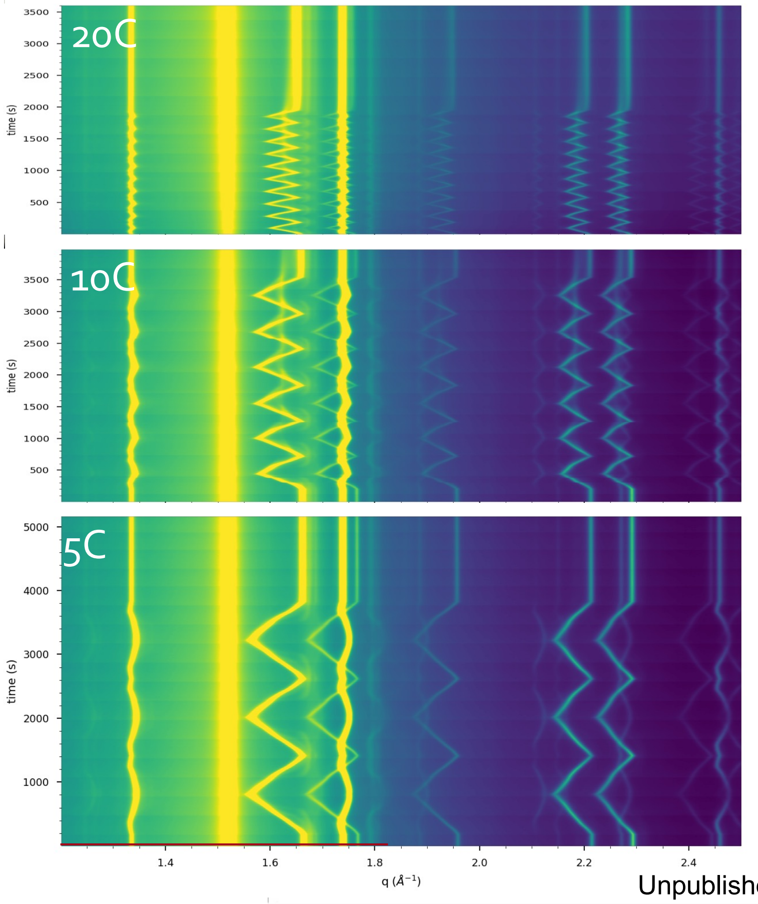
$$Mg + MgS_8 \rightarrow 2MgS_4$$





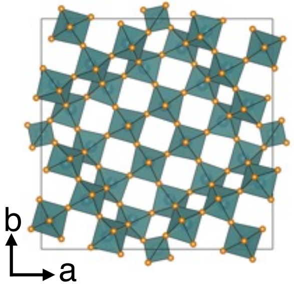
Nakayama *et al. Chemistry of Materials*, 30(18), 6318-6324 (2018).

Pushing *operando* and multimodal into the future



›th/Bronze Phases†: Class of
›t cycle ***very fast*** (1 min/charge)

›80



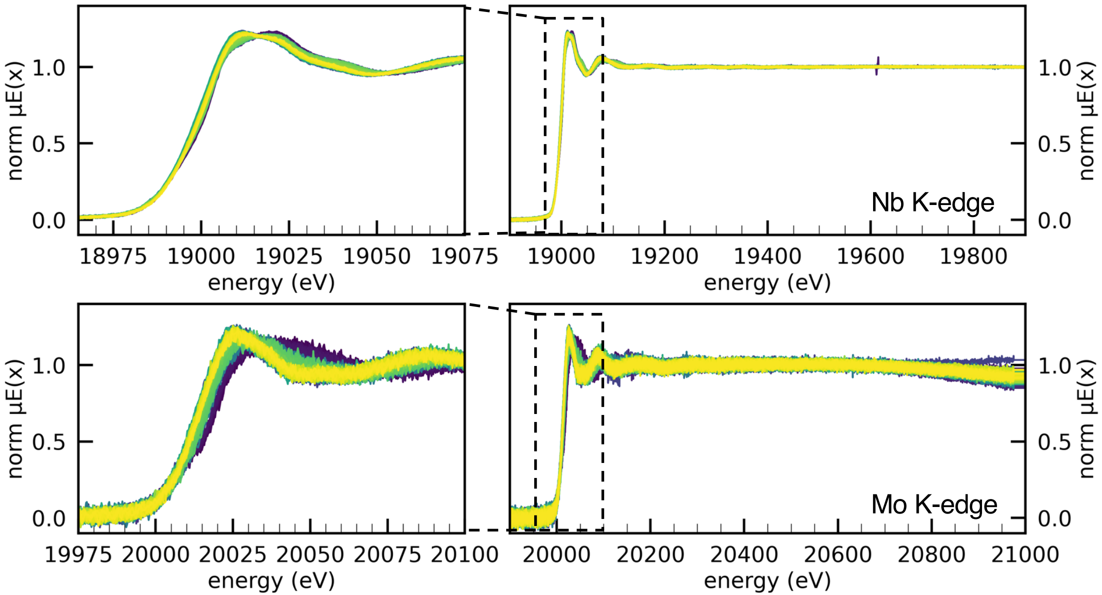
$Mo_3Nb_{14}O_{44}$

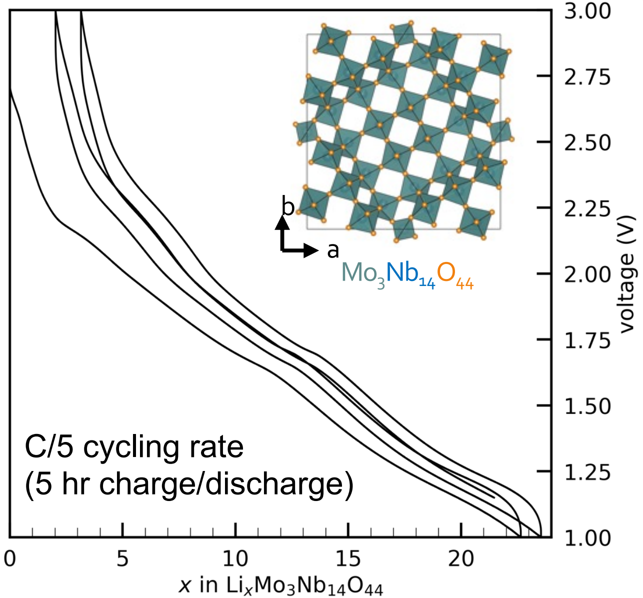
- BL 17 can capture fast structural changes
- Lattice expansion and contraction primarily along the c-axis
- Amount of lattice changes correlates with capacity being stored (faster charging stores less charge)

Unpublished results by Preefer *et al.*

† *J. Am. Chem. Soc.* 2016, 138, 28, 8888–8899

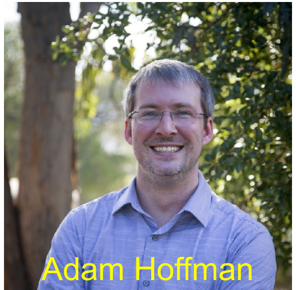
Pushing *operando* and multimodal into the future



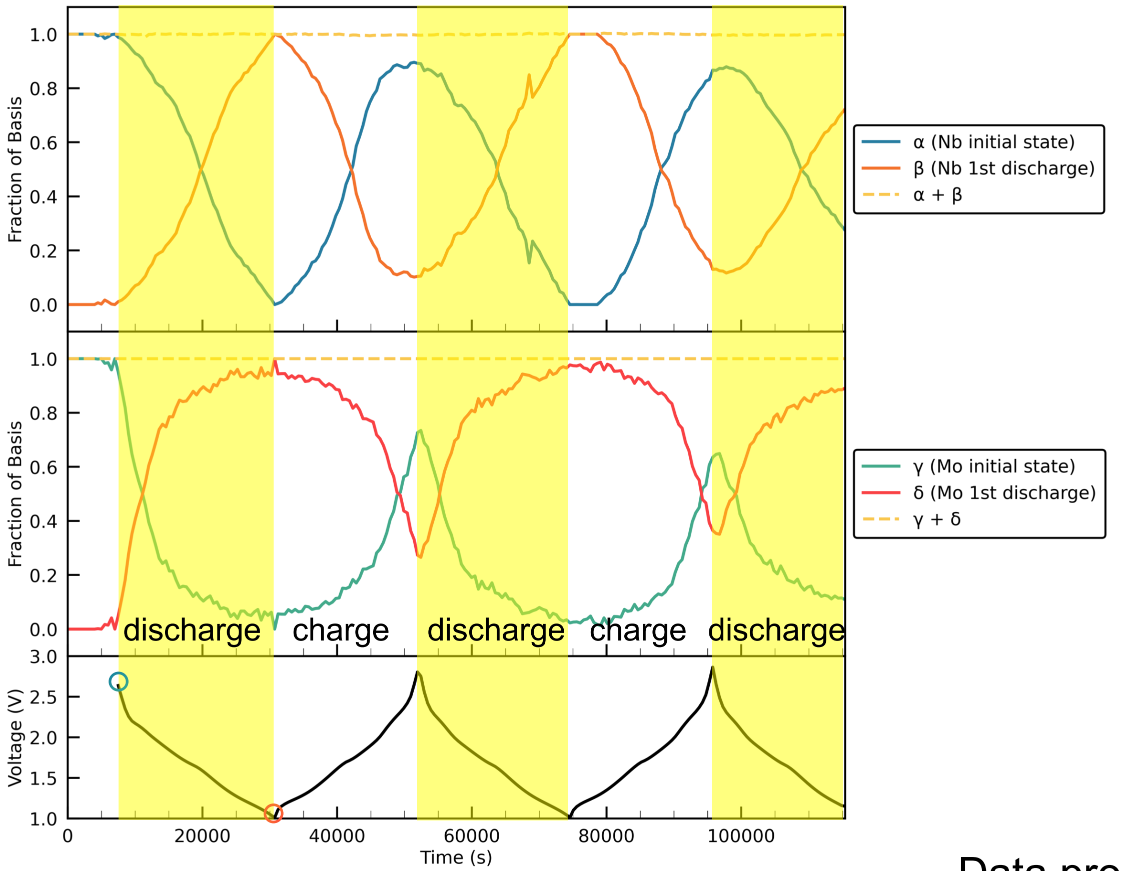


- XAS at BL 9-3 in continuous scanning mode
- Collected up to 20C (3 min charge/discharge)
- 90 s sweep per edge, Nb and Mo K-edges swept in succession (pseudo-simultaneously)

Unpublished results by Preefer *et al.*



Discharge chemistry not reversable



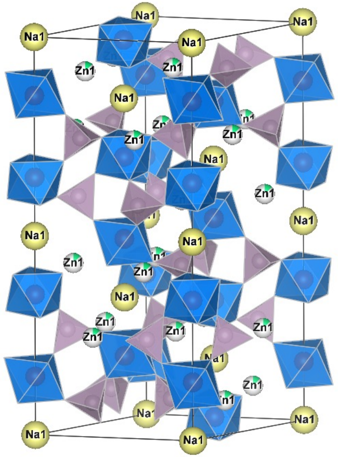
Unpublished results by Preefer *et al.*

- Linear combination using initial state (before current is applied) and 1st discharge
- Mo and Nb reduce/oxidize simultaneously
- But Mo reduces/oxidizes earlier & faster
- Irreversibility upon charge, and to a greater extent in Mo

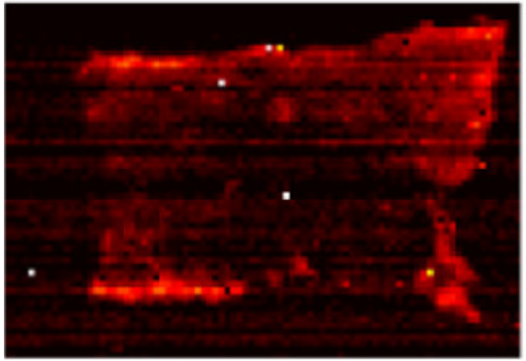
Data processing & fits using catXAS

Multimodal, *operando* X-ray characterization

Zn batteries cathode



Li metal mapping



Mg-S cathode dissolution