In Situ and *Operando* Characterization of Lithium-ion Electrodes Using Transmission X-ray Microscopy

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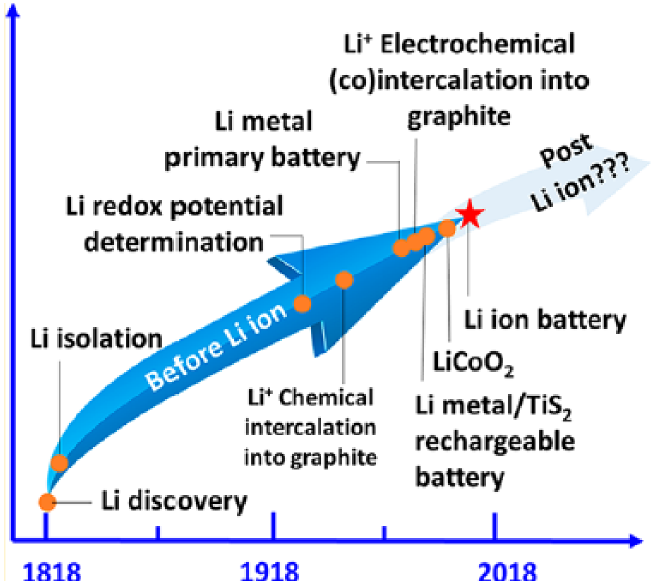
Outline

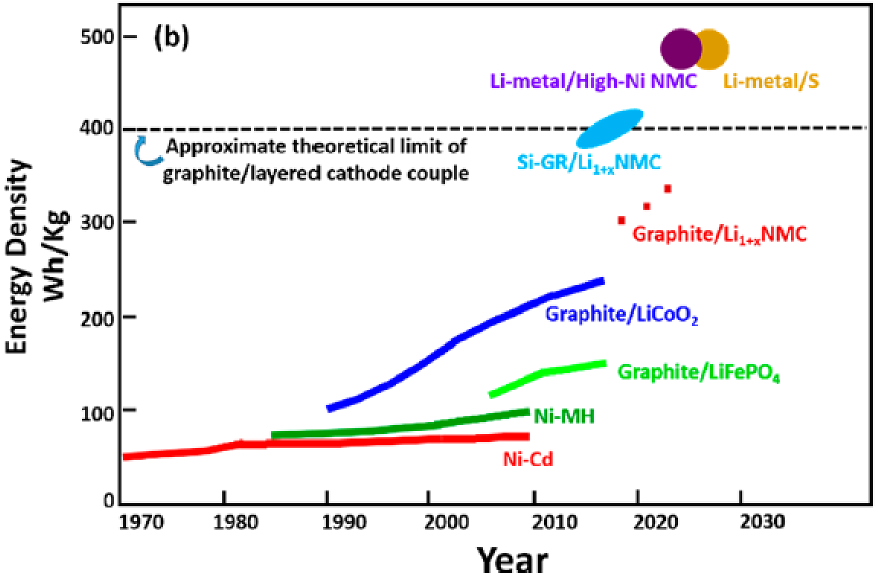
- Background and motivation
- Cathode: Lithium cobalt oxide ($LiCoO_2$)
- Anode: Tin (Sn)
- “Beyond Li-ion”
- Conclusions
- Acknowledgements

Background and motivation

- Li-ion batteries currently dominate the energy storage landscape (on Earth)
- Space applications require higher tolerance to extreme operating conditions:
  - ✓ Light weight & compact
  - ✓ Gravity
  - ✓ Operate under extreme temperatures (–120°C to 475°C)
  - ✓ Long calendar life
  - ✓ Tolerance to high levels of radiation
  - ✓ Safe



Winter et al., Chem. Rev., 118 (2018)



Stanford Synchrotron Radiation Lightsource (SSRL)

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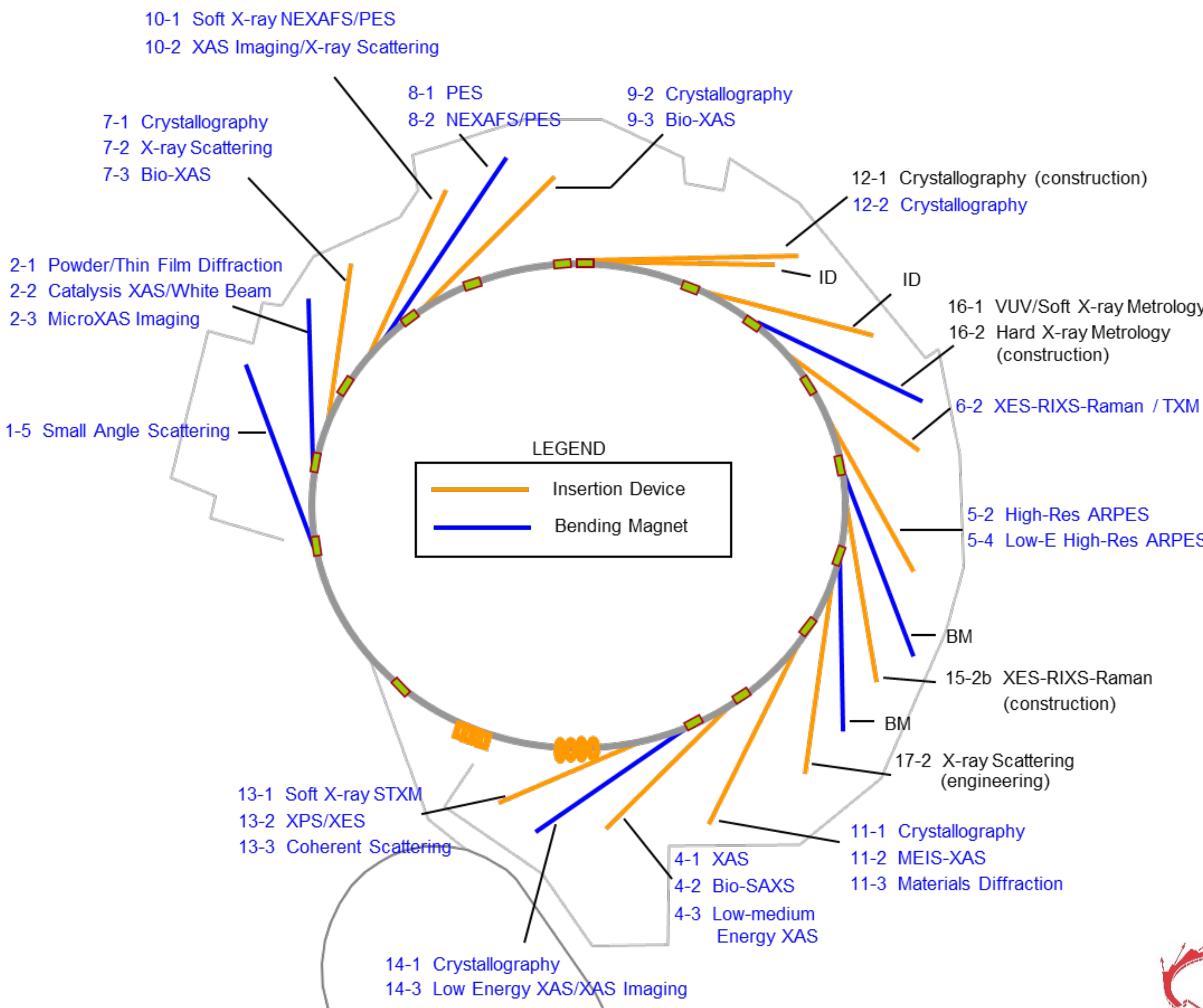

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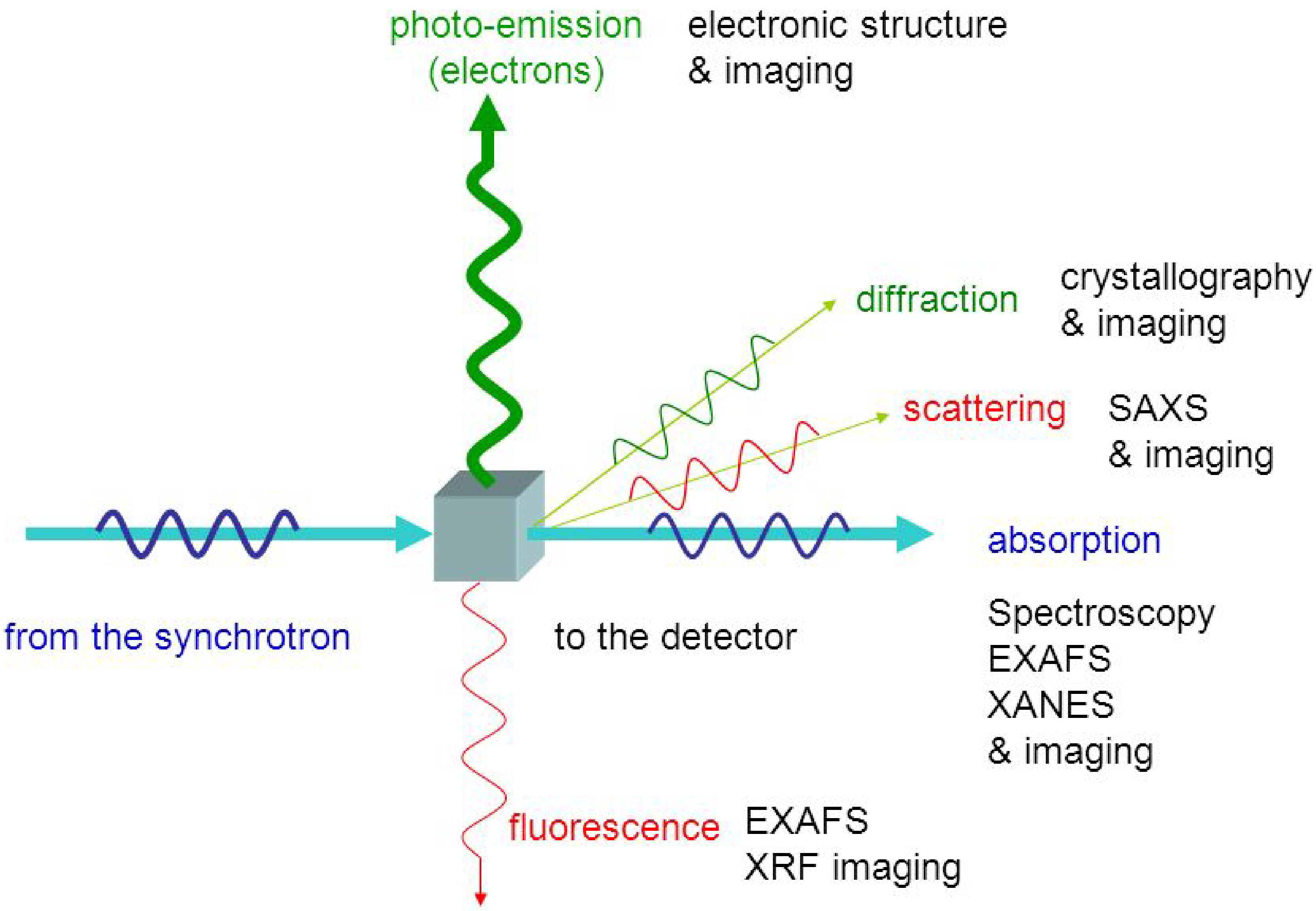
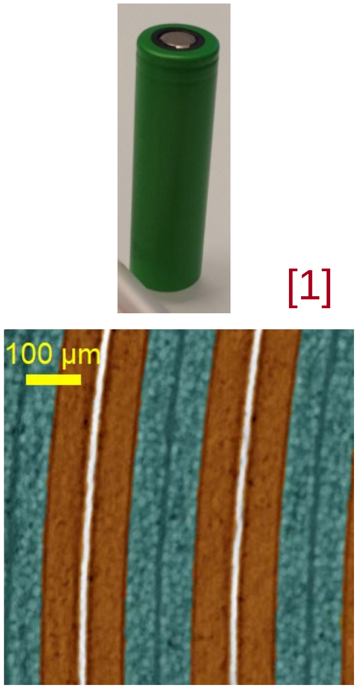
X-ray interactions with matter



Characterization across multiple length scales

full cell level — electrode level — particle level — atomic level

[1]



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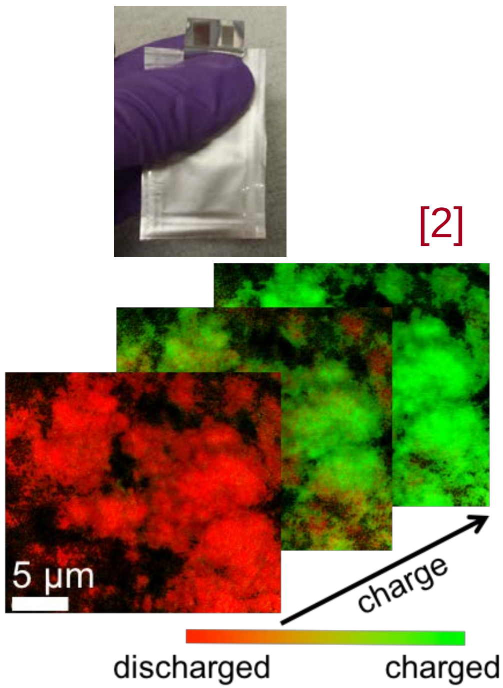
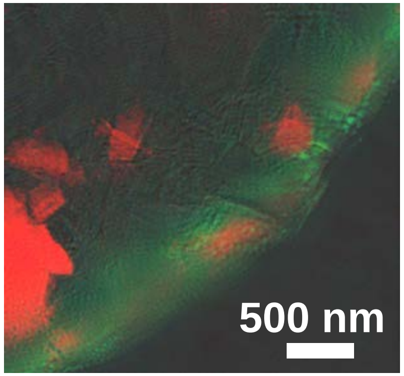
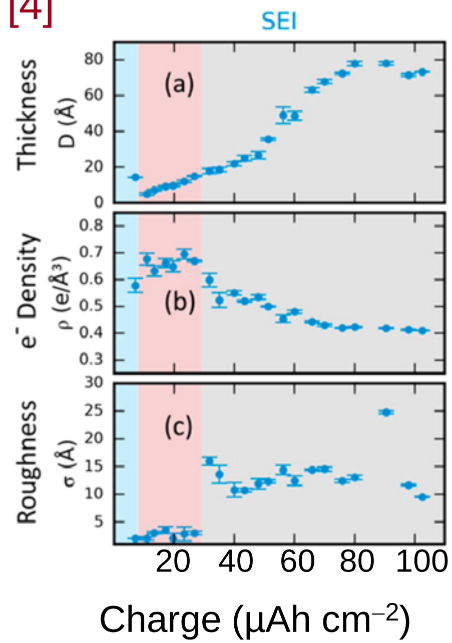


[3]



(industrial catalyst)

[4]

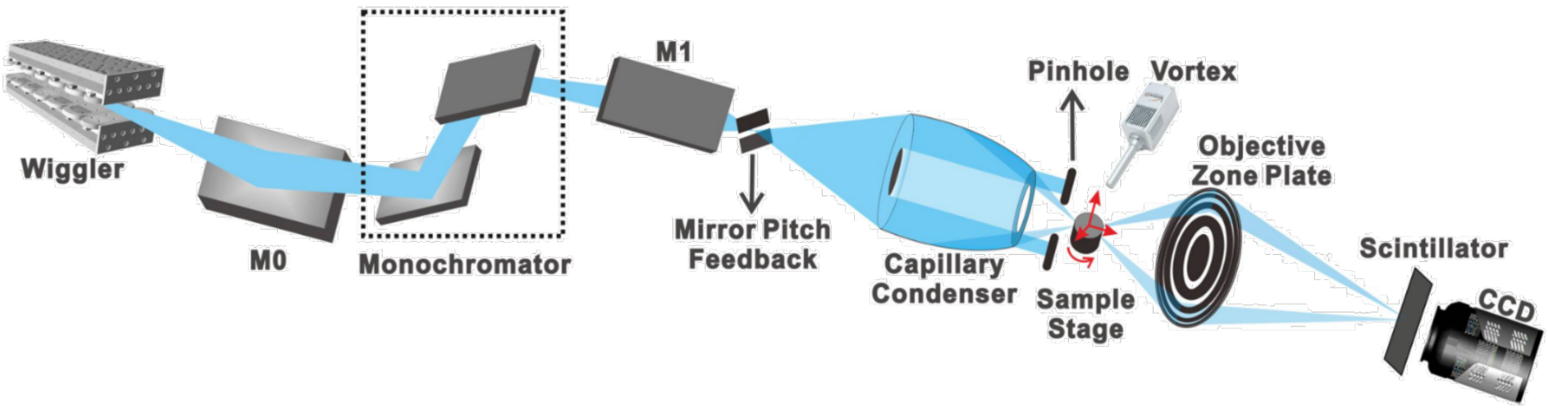


µCT — TXM — ptychography — scattering spectroscopy

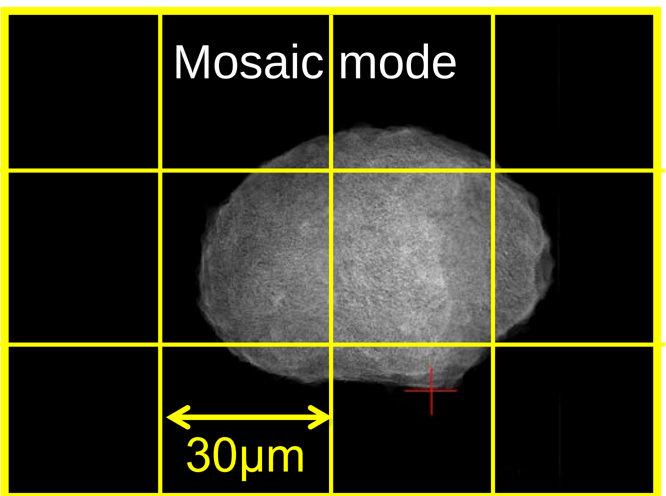
1. *Unpublished results from APS on an 18650 cell*
2. *Nelson Weker et al, ChemElectroChem, 2 (2015)*
3. *Wise et al. ACS Catal., 6 (2016)*
4. *Cao et al, Nano Lett.,16 (2016)*

Transmission X-ray microscopy @ BL6-2c

X-ray microscopy provides nondestructive, high resolution X-ray images

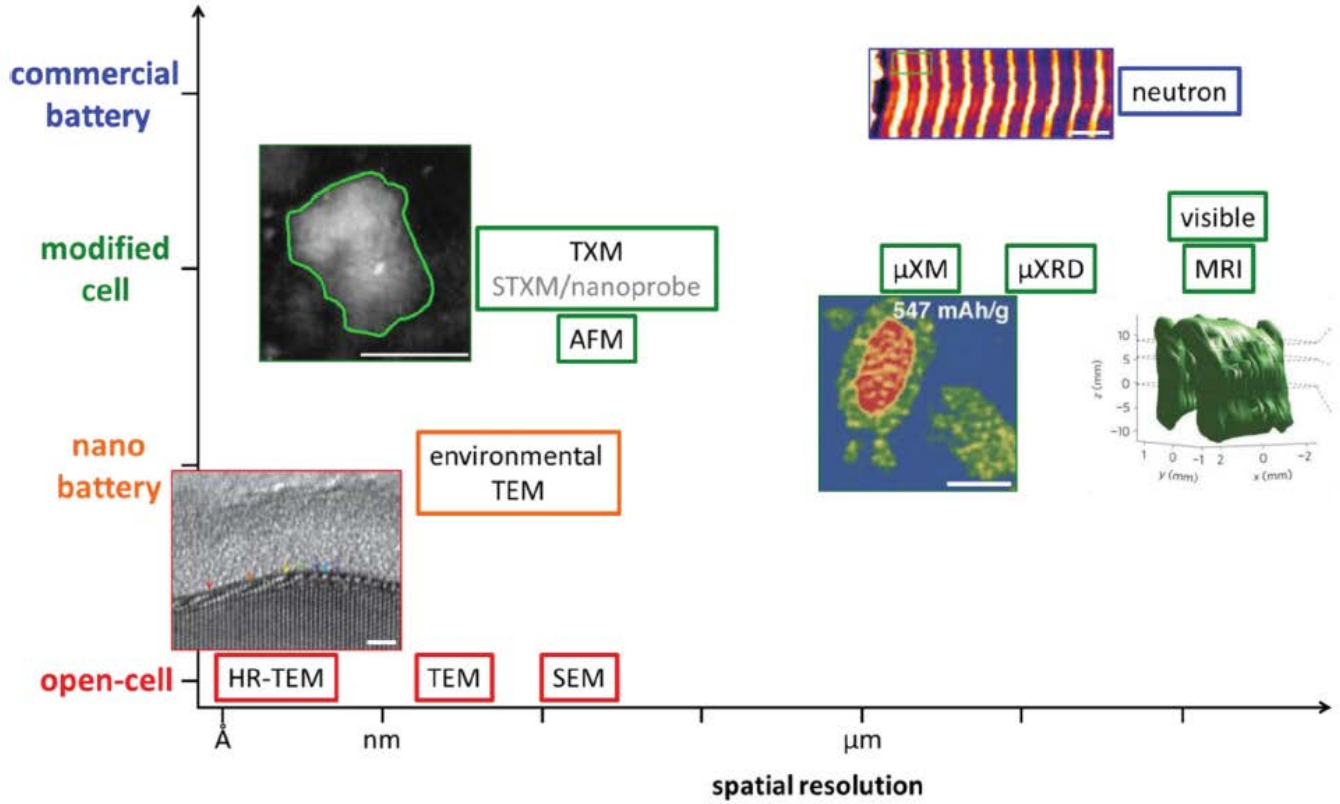


- Fast: ½ sec imaging
- ~30 nm resolution imaging
- ~30 µm field of view (mosaic mode)
- thick samples → *in situ* samples
- elemental/chemical mapping (~5 – ~13 keV)
    - Ni, Mn, Co, Fe, and Zn
- tomography (~50 nm resolution)



Comparison to other complementary techniques

Plot of various *in situ* imaging techniques for energy storage and type of cells.



As imaging resolution is improved to study finer structures, the required modifications to the *in situ* cell take it further from a realistic commercial battery architecture

Nelson Weker et al., Adv. Funct. Mater., 25 (2015)

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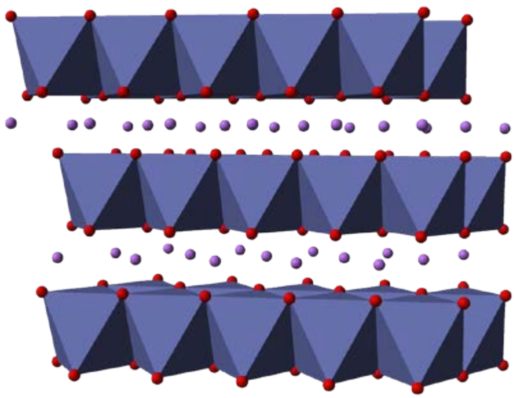
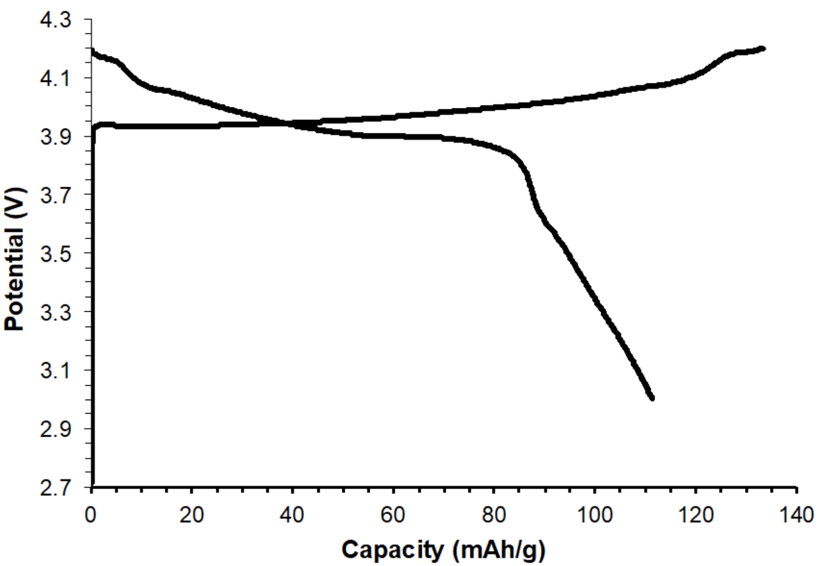
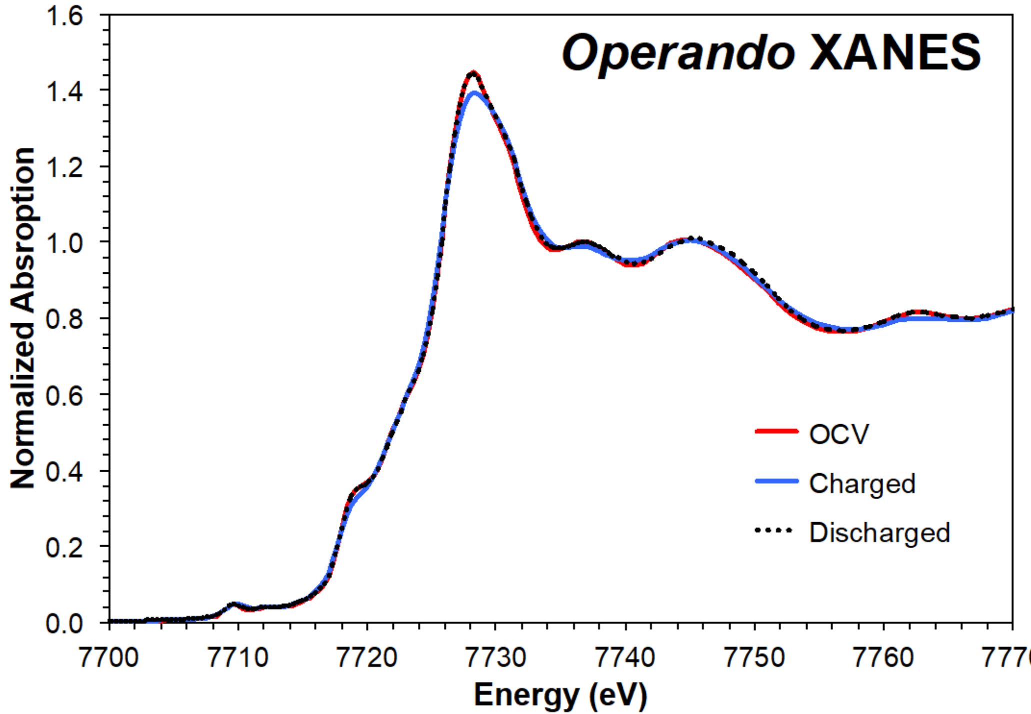
Commercial cathode material: $LiCoO_2$

$$LiCoO_2 \underset{discharge}{\overset{charge}{\rightleftarrows}} Li_{1-x}CoO_2 + x\,Li^+ + x\,e^- \quad (x \leq 0.5)$$

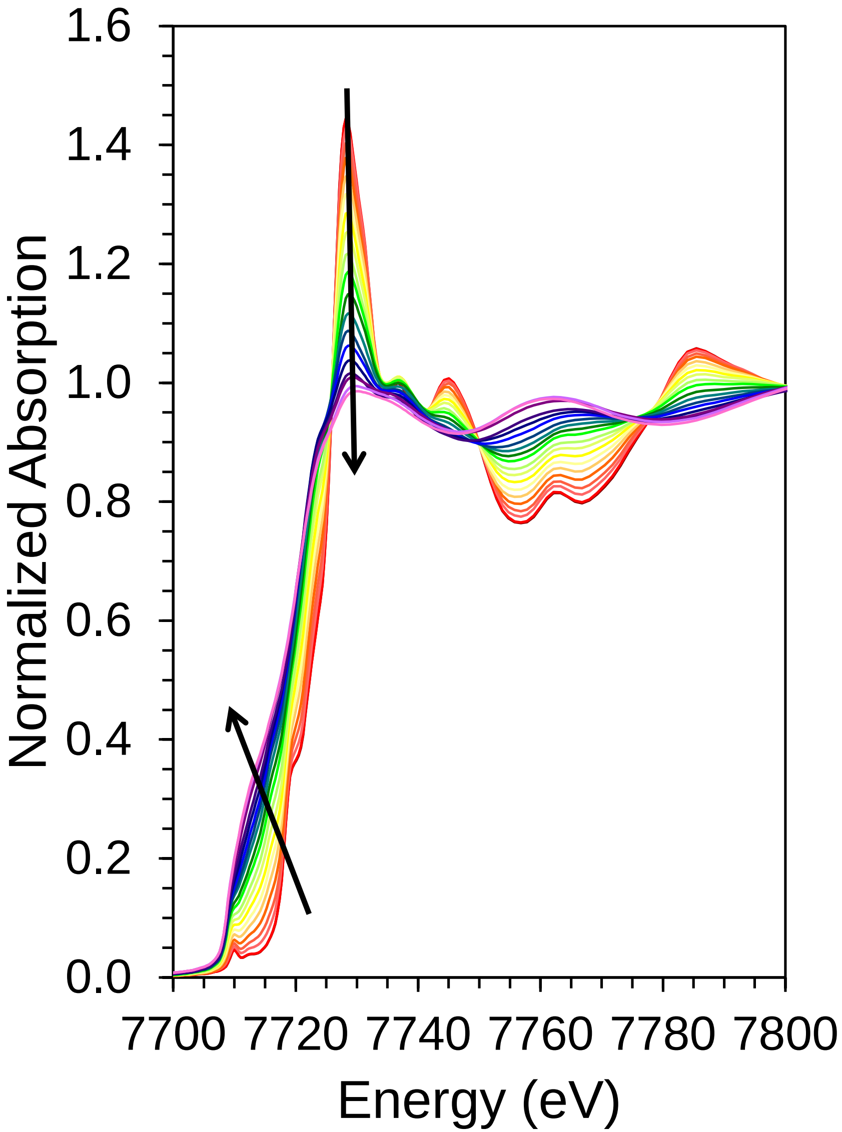
~135 mAh g^{-1} reversible capacity (~0.5 Li^+)

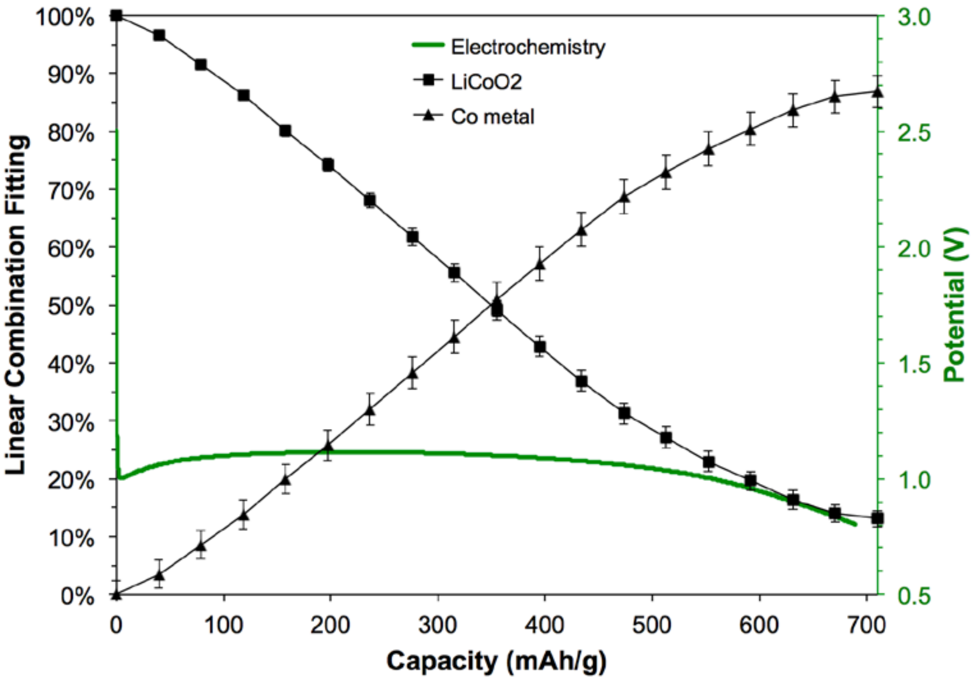






Operando XANES of deep discharge of $LiCoO_2$





- $LiCoO_2 + 3Li^+ + 3e^- \xrightarrow{discharge} Co + 2Li_2O$
- Agrees with capacity (~2.6 Li^+) and *operando* X-ray diffraction

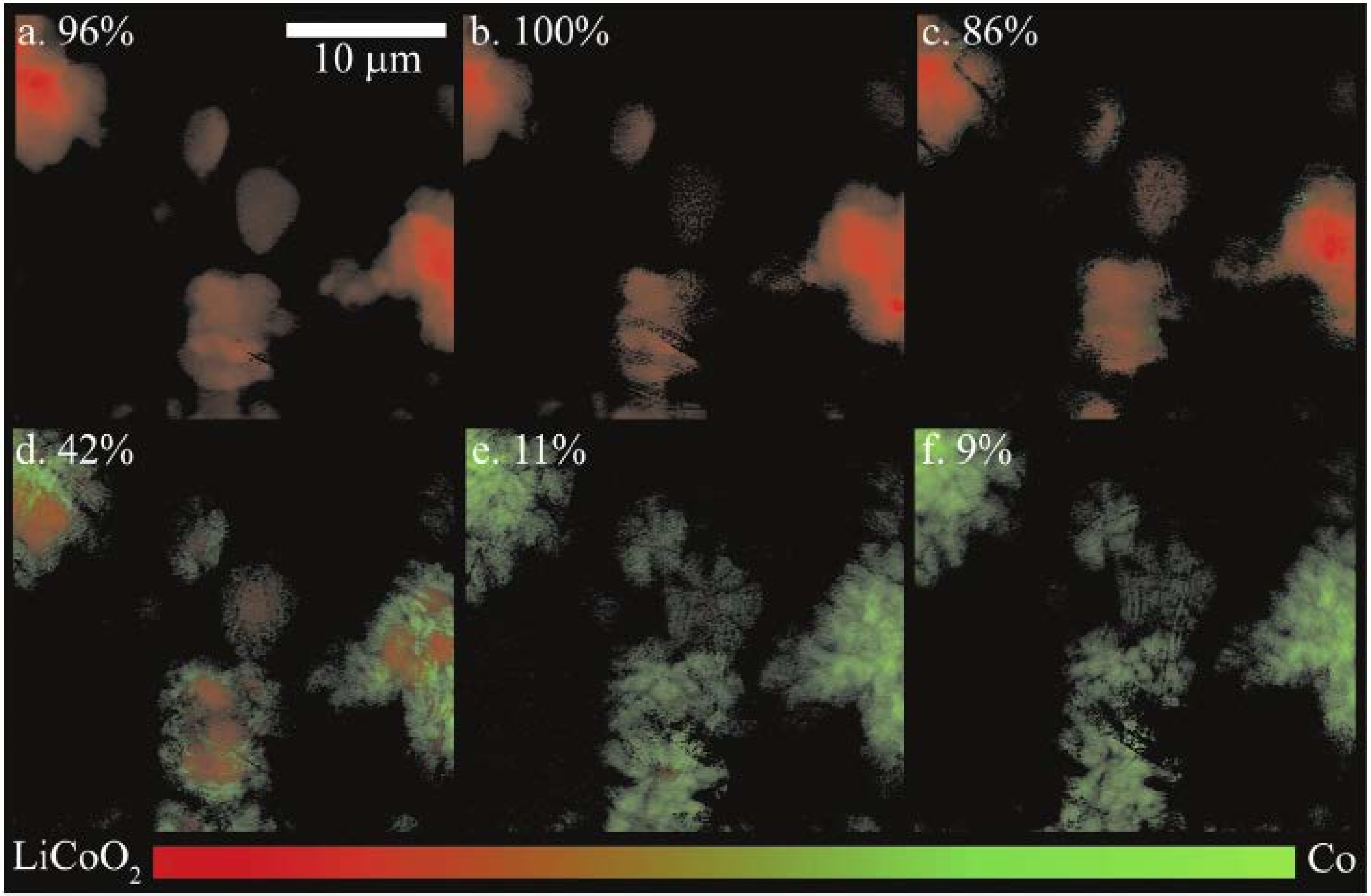
Nelson Weker et al., Electrochim. Acta, 247 (2017)

Deep discharge of $LiCoO_2$

Nelson Weker et al., Electrochim. Acta, 247 (2017)

Incomplete transformation to Co metal:

- Core/shell: Core remains $LiCoO_2$
- Disconnected particles remain $LiCoO_2$



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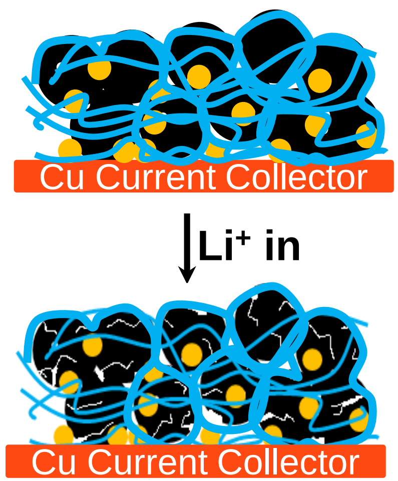
Porous anodes for high capacity and high cycle life

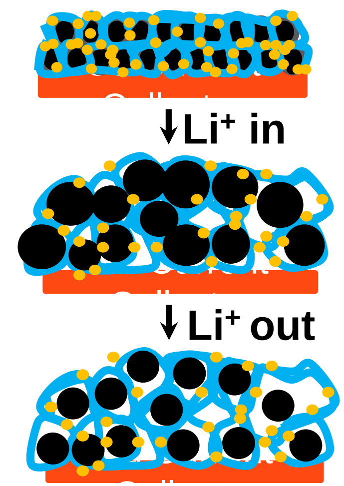
Mechanism	Pros	Cons	Example (Specific Capacity)
Intercalation	Maintains Structure	Low Capacity	Graphite (372 mAh g^{-1})
Alloy	High Capacity	Volume Expansion	Tin (960 mAh g^{-1})

Bulk



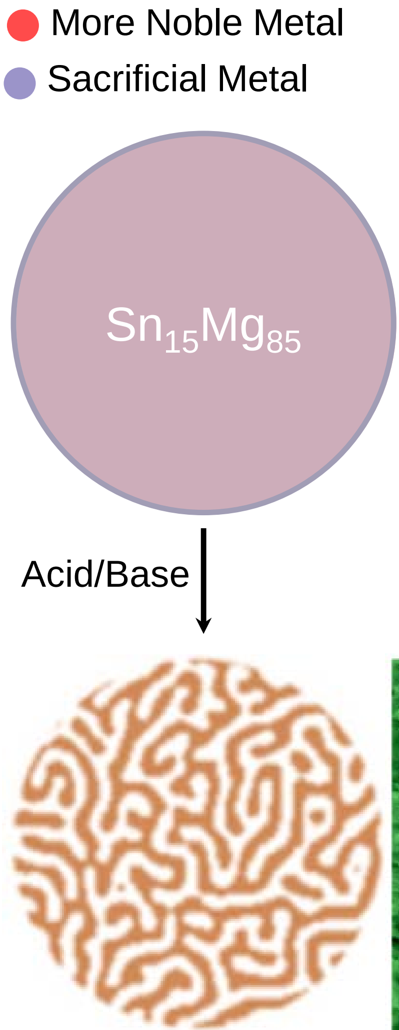
Cracking and Pulverization

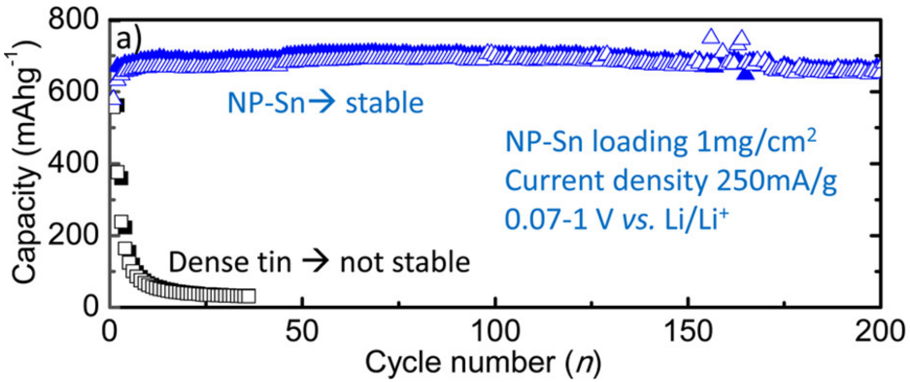
Nanoparticles



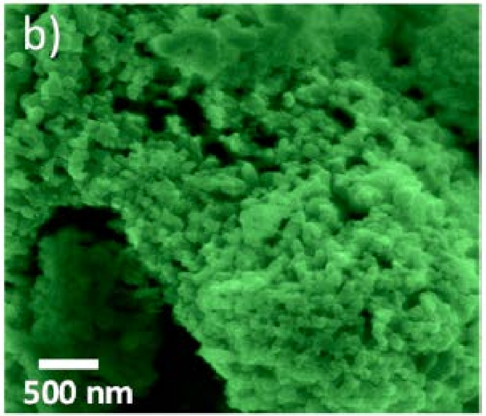
Lose contact with conductive matrix and current collector

Selective dealloying – facile method to form porous networks





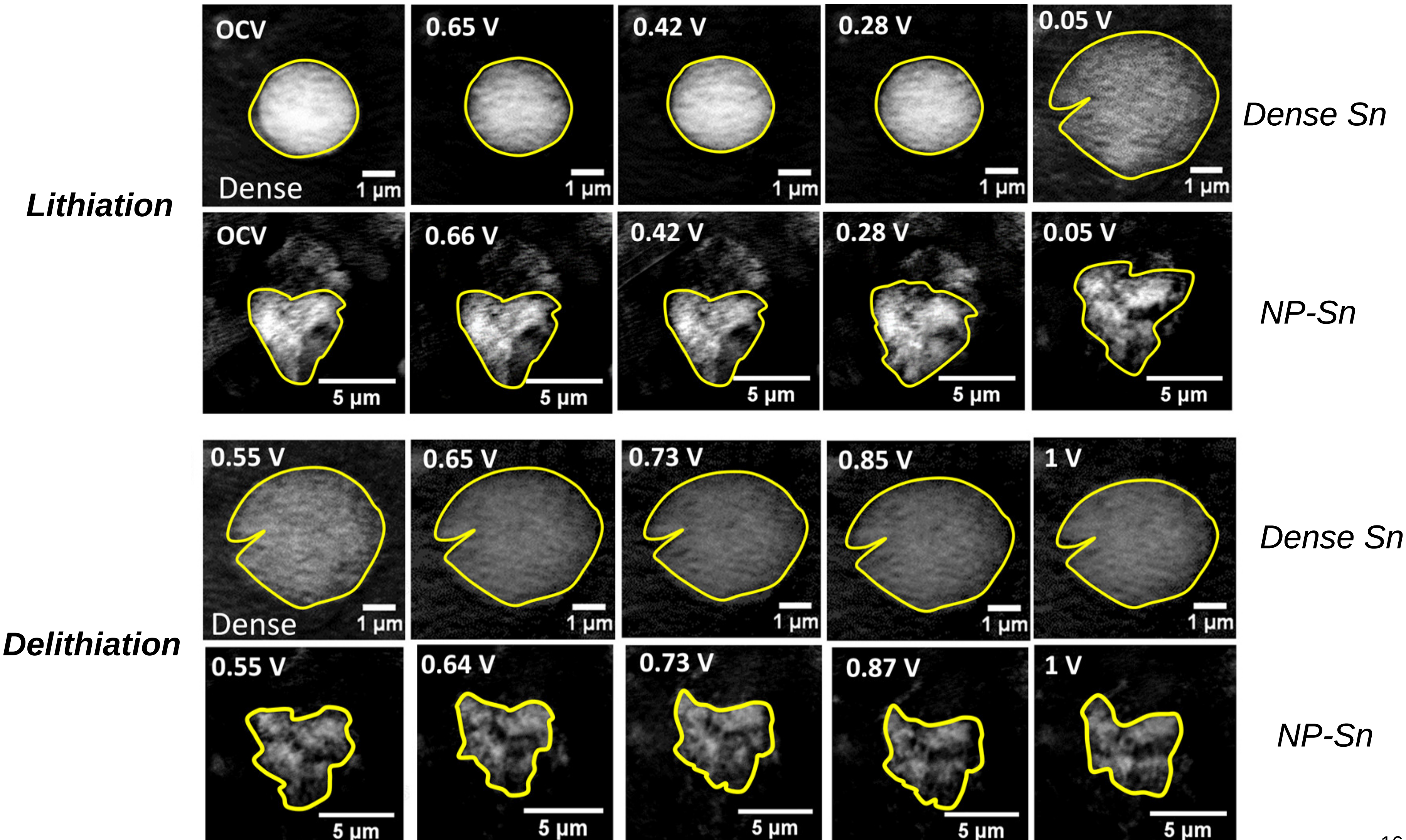
Nanoporous Sn



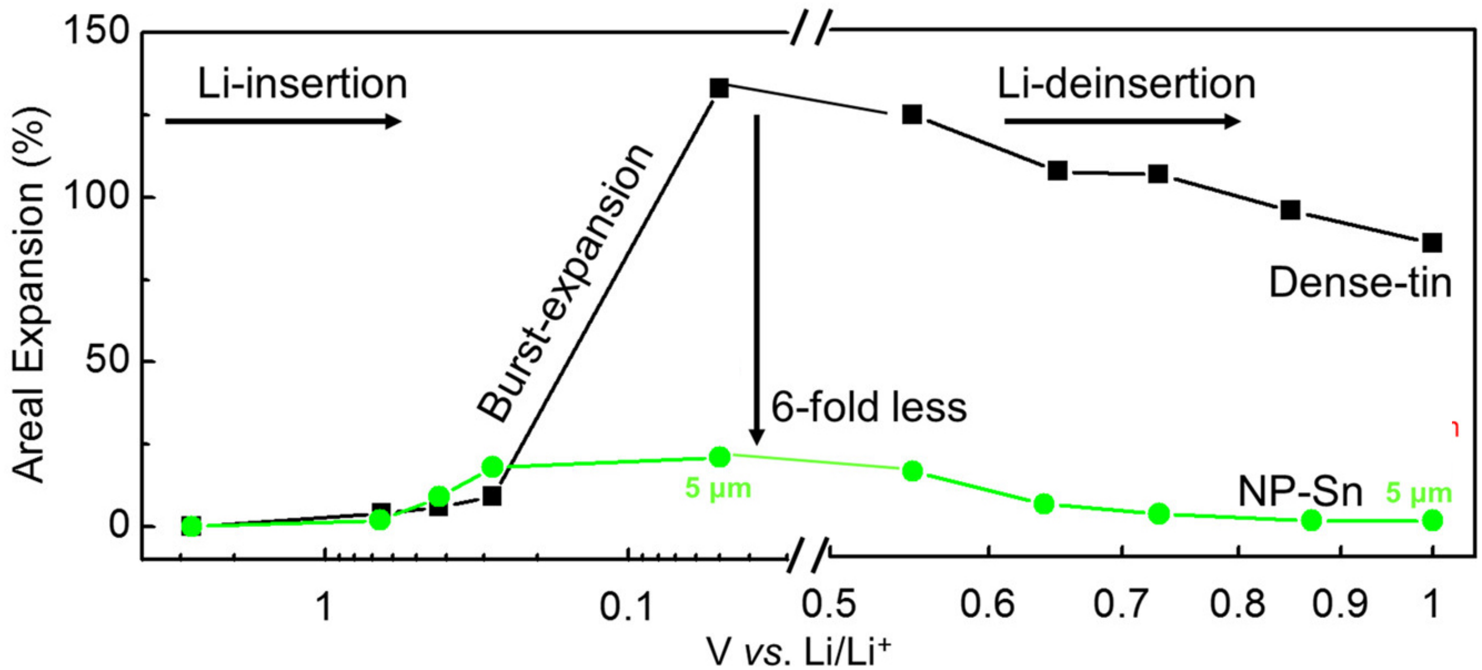
- Nanoporous Sn (NP-Sn) with ~25% internal porosity
- High capacity alloying anodes undergo large volume changes during cycling resulting in cracking/pulverization
- Nanoporosity can reduce volume changes to avoid irreversible deformation and extend battery lifetime

Erlebacher et. al., Nature, 410 (2001)

Visualizing volume changes in dense and porous Sn



Visualizing volume changes in dense and porous Sn



- End of Li^+ insertion leads to burst expansion of dense Sn
- Crack formation in dense Sn
- Porous Sn 6× smaller areal expansion

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Multivalent charge storage (Mg^{2+}, Zn^{2+}, Ca^{2+}, etc.)

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CHEMICAL REVIEWS

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Odyssey of Multivalent Cathode Materials: Open Questions and Future Challenges

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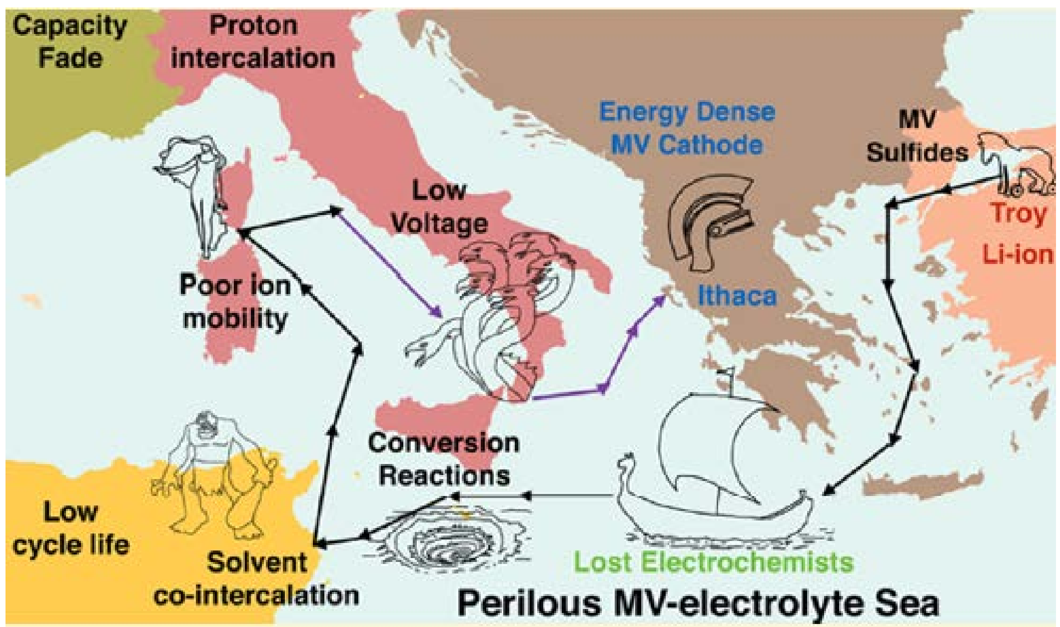

Canepa et al., Chem. Rev., 117 (2017)

X-ray diffraction measurements @ BL11-3

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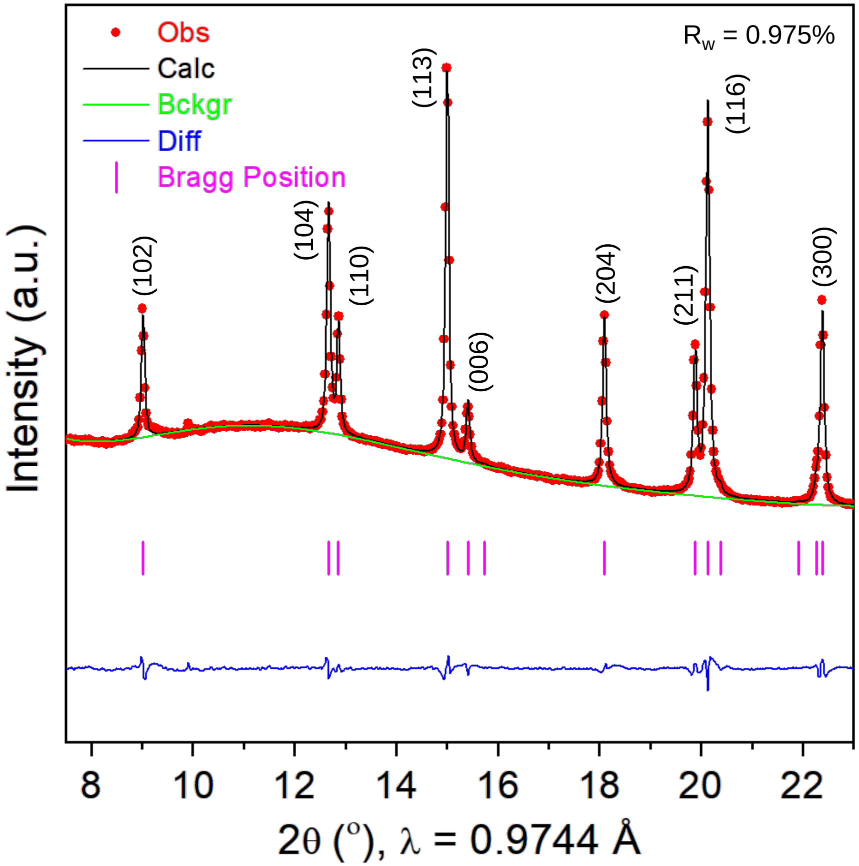
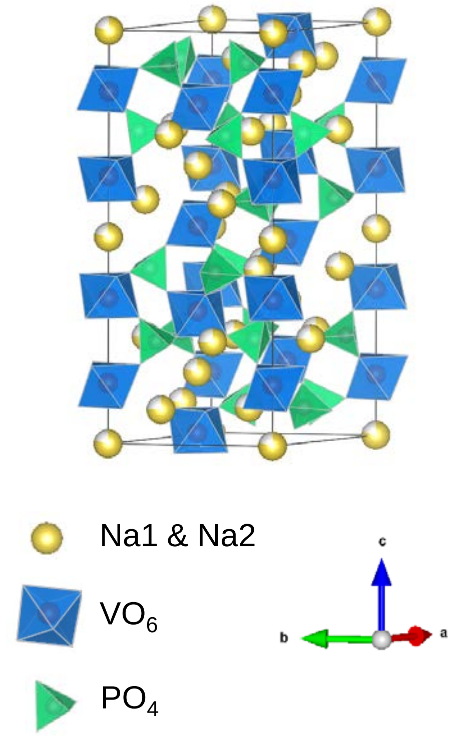
- Confirm phase-pure NVP particles @ BL11-3

NVP powder X-ray diffraction pattern



$Na_3V_2(PO_4)_3$

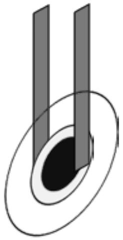
Rhombohedral $R\bar{3}c$ space group
$a = b = 8.7$ Å
$c = 21.8$ Å



Operando XRD (@ SSRL BL11-3) shows qualitative changes during charge/discharge

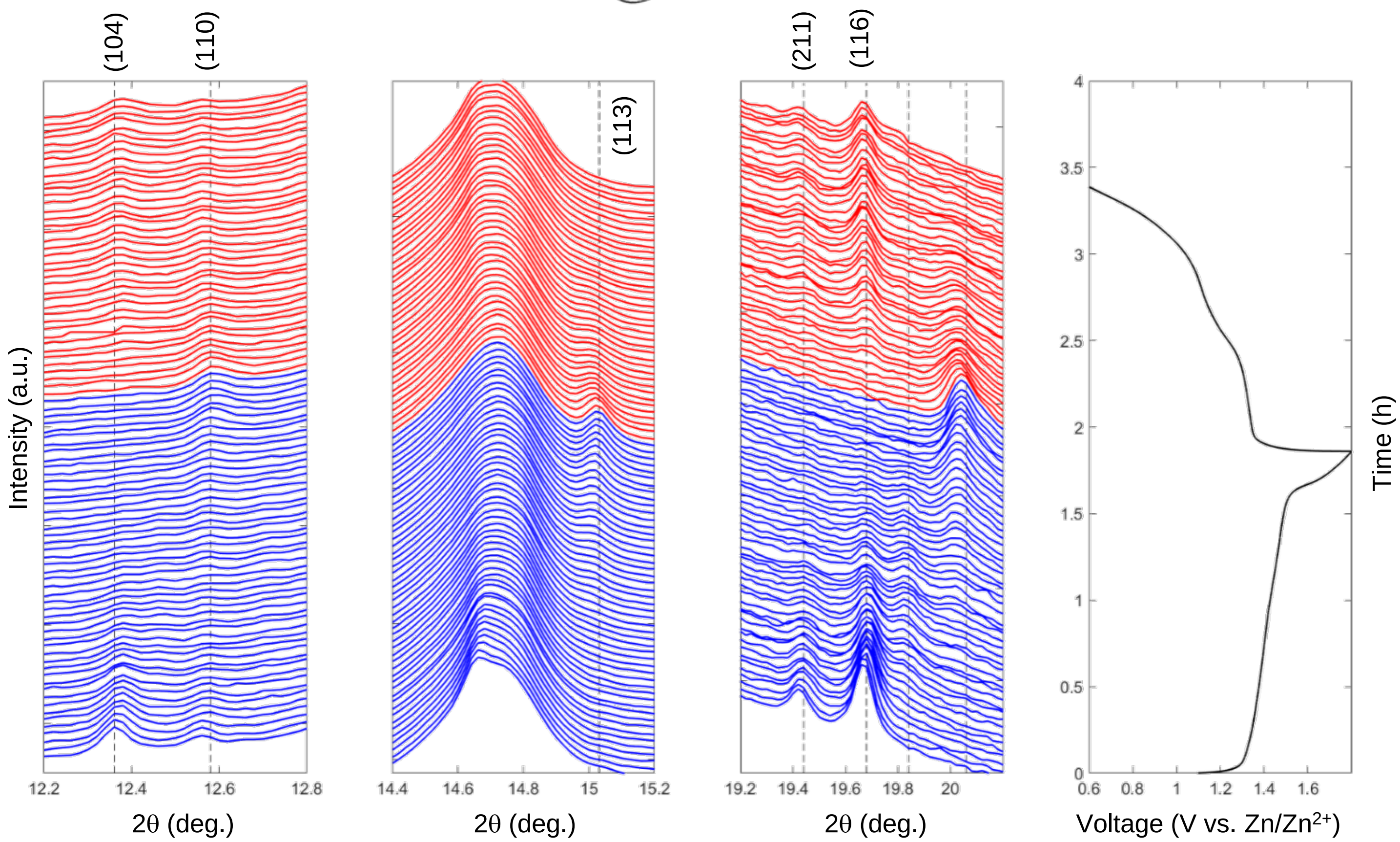
Electrolyte:
0.5 M Zn Acetate

Counter:
Zn foil (0.25 mm)/4 mm hole in center



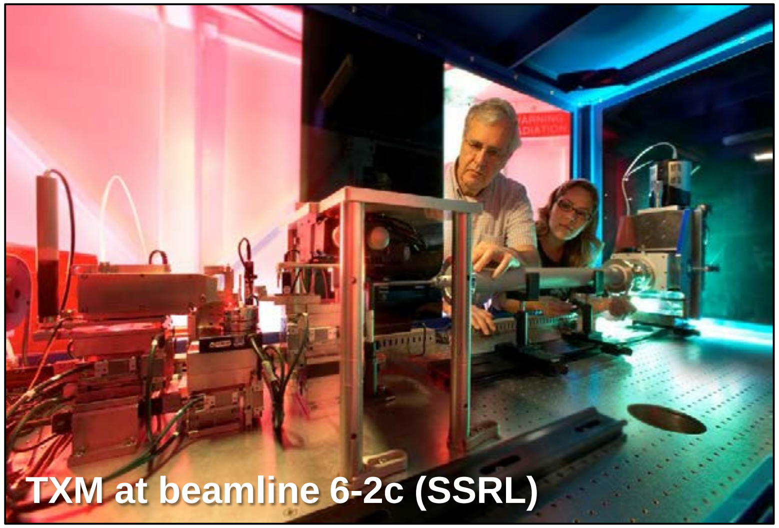
Separator:
Whatman
glass fiber

Electrode (70/20/10):
NVP/SuperP/PVDF
coated on Al foil
mass loading: 1 mg cm^{-2}



Conclusions

- Transmission X-ray microscopy enables high resolution *operando* visualization of battery materials nondestructively
- Tracked the chemistry of $LiCoO_2$ particles by mapping Co oxidation states when cycled outside standard operating conditions
- Understood the benefits of 3D porous morphology on volume expansion anode material (Sn)
- Investigating multivalent charge storage based on Zn^{2+} insertion/de-insertion of $Na_3V_2(PO_4)_3$


TXM at beamline 6-2c (SSRL)

Acknowledgements

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Thank you for your attention and time

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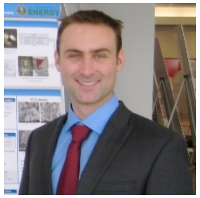
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