Plan for Customized Cells

- Task # 1: Establish ***background signal*** from non-active cell components for *in-situ* neutron diffraction setup
- Task # 2: Characterize ***inhomogeneities and material degradation*** during formation cycle and long term cycling
  - Age cells with USABC DST_{620} cycling protocol for 1000 cycles
- Task # 3: Characterize ***effect of electrode defects***
  - Manufacture electrodes with areal solid loading gradient
- Task # 4: ***Effect of formation cycle*** current on material degradation
  - Use 20% higher current density than ANL formation protocol
- Task # 5: Compare material degradation in electrodes manufactured via ***different processing methods***
  - Aqueous processing

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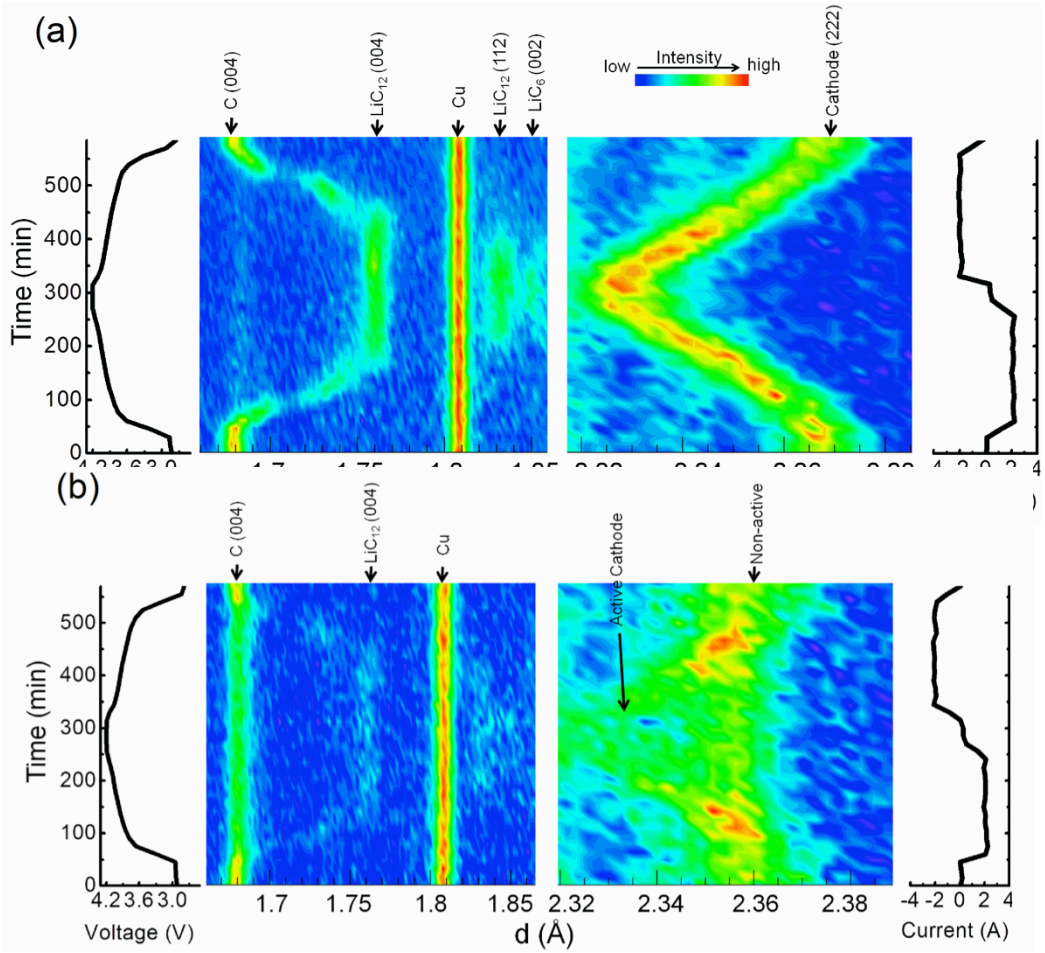
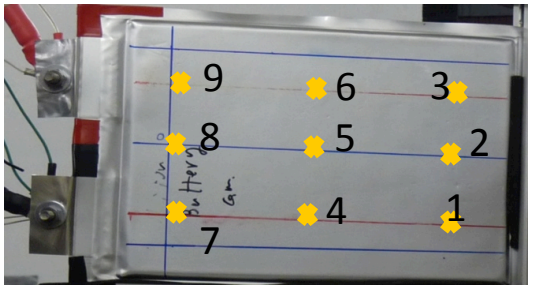
In-situ Neutron and Synchrotron Diffraction Mapping of Large Format Li-ion Batteries

- Overall capacity reduced to 60% of the fresh





A good spot where the local capacity is still at nearly 100%.

A bad spot where the local charging capacity is greatly reduced and both the anode and cathode lost their charging capacity

Cai, L., Ke, A., Feng, Z., Liang, C., Harris, S. *J. Power Source*, v236 p163-168 (2013)

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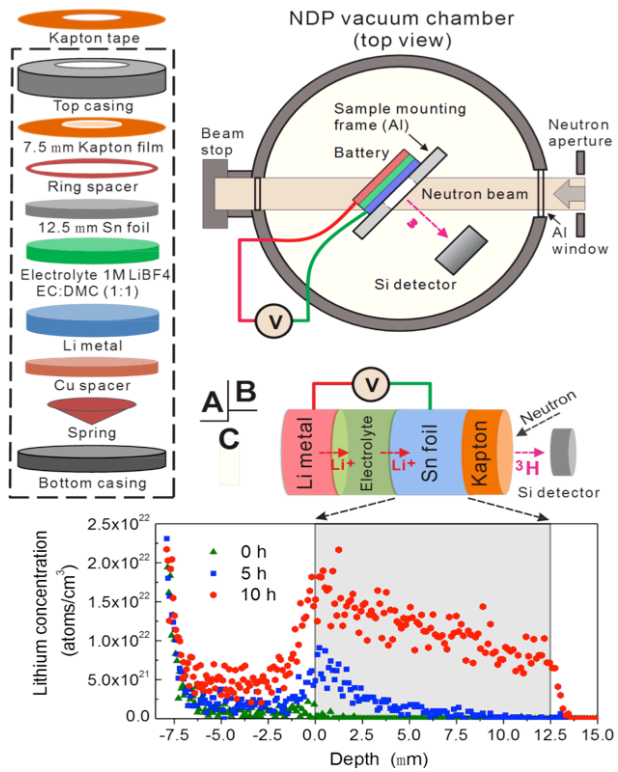
In Situ Quantification and Visualization of Lithium Transport



(A) *In situ* cell; (B) setup; (C) snap shots of *in situ* Li data

Work performed at the Ohio State University and National Institute of Standards and Technology

THE OHIO STATE UNIVERSITY

Co, Canova, and Cao et al, *In Situ Quantification and Visualization of Lithium Transport with Neutrons*, Angewandte Chemie, **53**, 1-6, (2014).

Scientific Achievement

Developed framework to perform *in situ* quantitative measurement of Li concentration in surface region of electrodes.

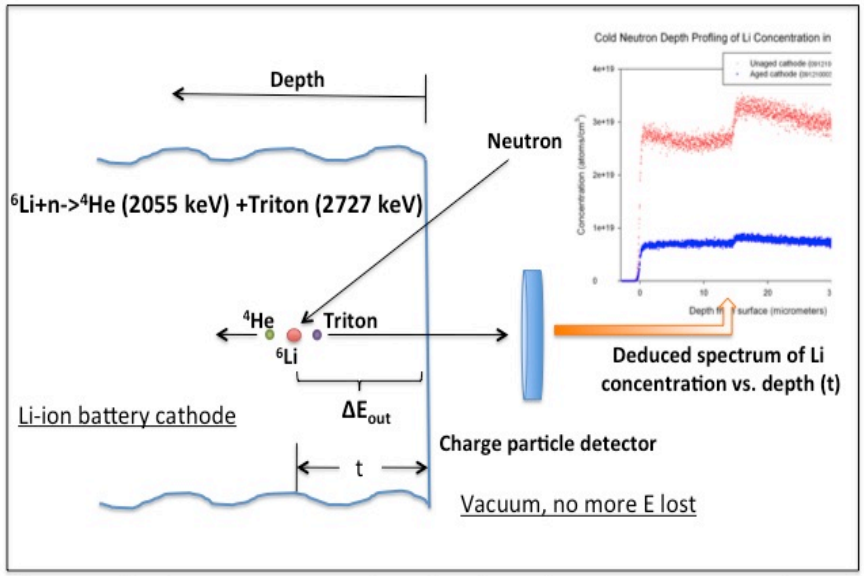
Significance and Impact

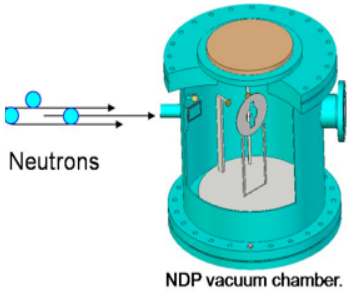
Demonstrated *in situ* NDP as a valuable method that complements the existing methods for battery studies and gives important additional insight into the transport mechanisms occurring in Li batteries.

Research Details

- Higher rates of lithiation (de-lithiation) at the near surface (~1μm) vs. bulk (~10μm)
- Driving force for lithium movement is purely diffusion due to concentration gradient
- High diffusion coefficient (ca. 2 – 5 x 10-7 cm^2/s) during the initial charge reaching consistent diffusion coefficient values (ca. 0.8 – 2 x 10-7 cm^2/s) after 300 min
- Lithiation of Sn does not occur in uniform increments
- Significant parasitic losses during first 230 minutes

Neutron Depth Profiling: Operating Principles





- Sample is bombarded with a low energy neutrons (~ 0.025 eV);
- Difference between the residual energy of the particle emerging from the surface and energy of the particle at its origin is measured;
- Relate to the depth of the reacting lithium atom and Li concentration.

Advantages:

- Li cross-section for NDP is 940 barn (1 barn = 10^{-24} cm^2), one of the largest among the light elements.
- This method allows for **direct quantitative measurement** of lithium concentration vs. depth.
- Depth resolution of 100 nm possible.
- Non-destructive, sample extraction not necessary.
- Technique is well known and largely applied to static samples with recent interest in *ex-situ* characterization of Li-ion cells.

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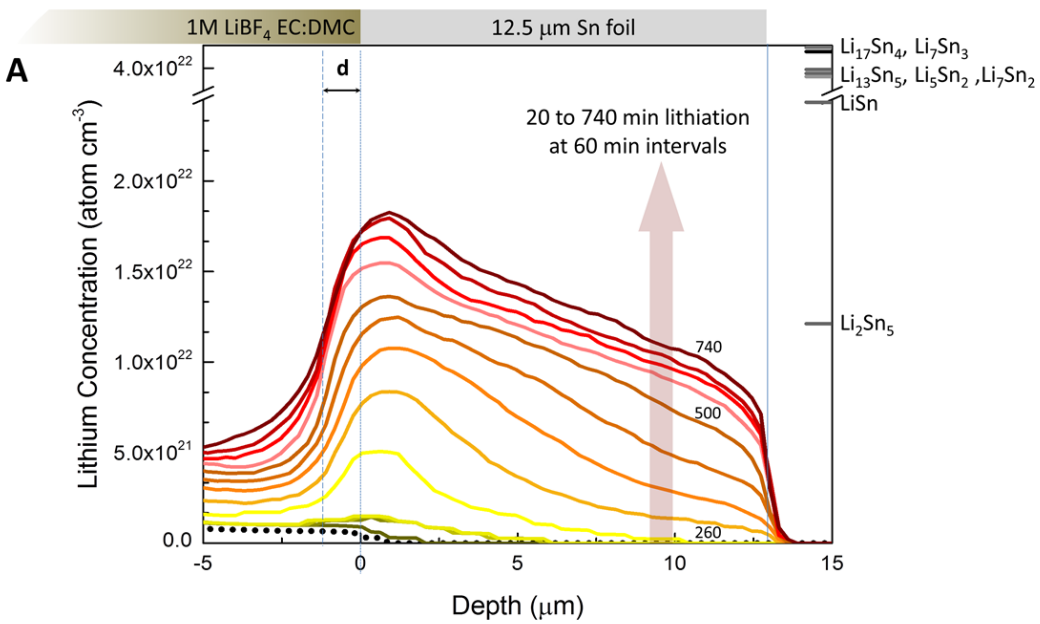
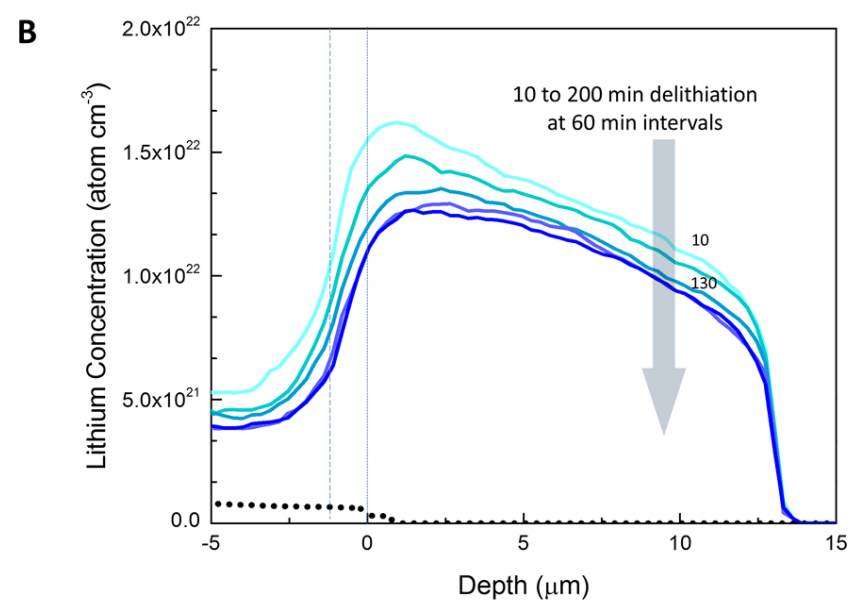
In-situ NDP Results

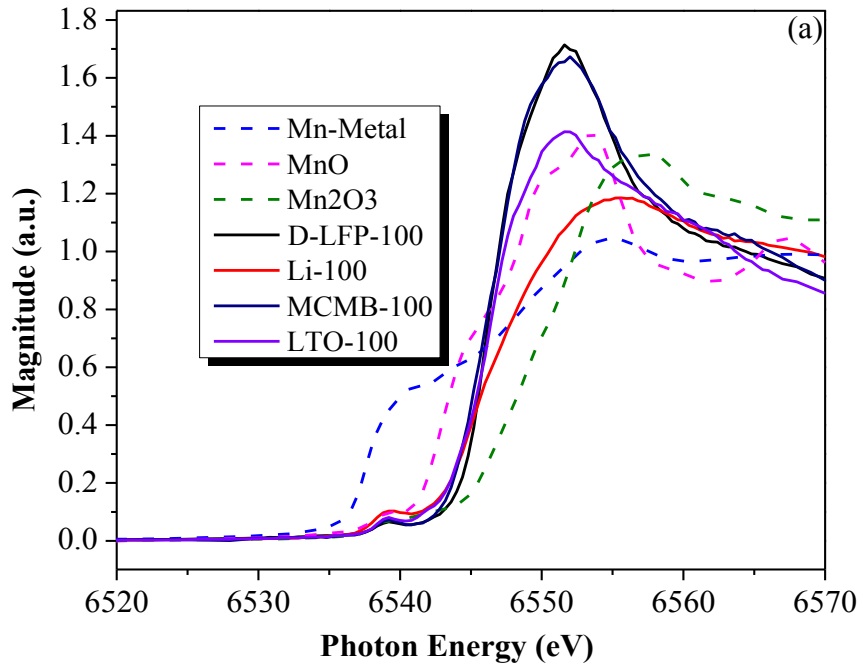
- Snap-shots track the Lithium distribution during lithiation (A) and subsequent delithiation (B);
- Three regions are considered, namely the electrolyte region (-5 to 0 μm), a "near surface" region (0 to 1 μm), and the bulk anode region (> 5 μm), where 0 μm is at the interface:
  - Prior to Lithiathion, concentration in electrolyte corresponds to equilibrium (1M $LiBF_4$);
  - Upon lithiation, it is evident that an enrichment of Li at the near surface region (up to 2 μm) of Sn is prevalent (0 to 260 min) followed by the diffusion of Li into the bulk;
  - Higher rates of lithiation (also de-lithiation) at the near surface (~1μm) vs. bulk (~10μm).

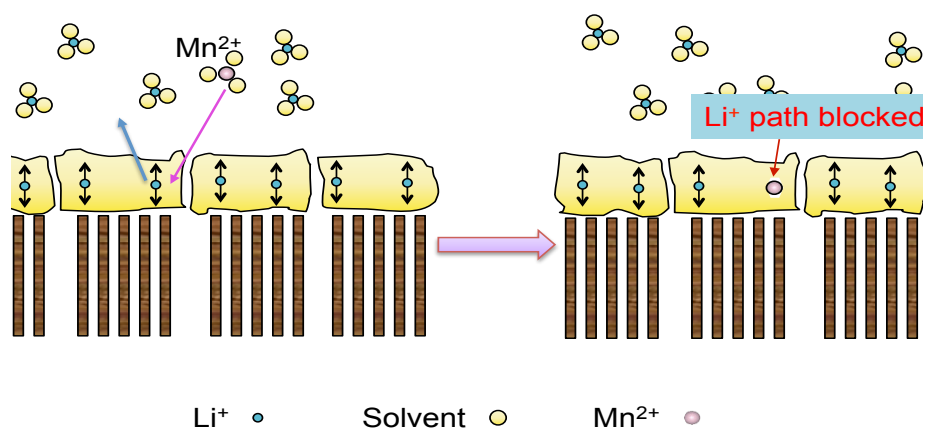




Mn dissolution-migration-deposition process

- The oxidation state of manganese deposited on the anodes is +2 by XAS and XPS analysis.
- Mn incorporation in the SEI proceeds via a metathesis reaction between Mn^{2+} and some species within the SEI.
  - Counter to conventional wisdom: a reduction reaction leads to the formation of metallic Mn^{0}.
- Capacity fading is caused by changing composition of the SEI on the graphite anode due to continuous reaction with the dissolved Mn^{2+} from the cathode.





Work conducted by THU and ANL

Nature Comm., 4, 2437 (2013).