In situ/Operando studies of Energy storage Materials using Neutrons

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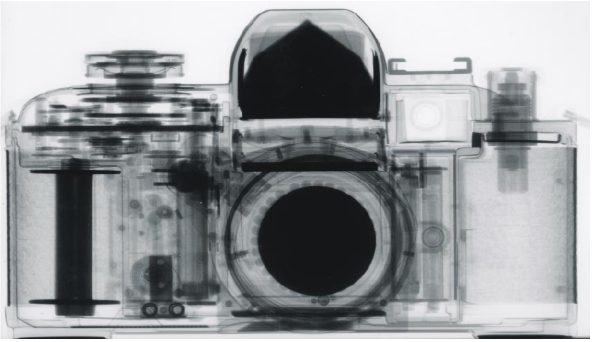
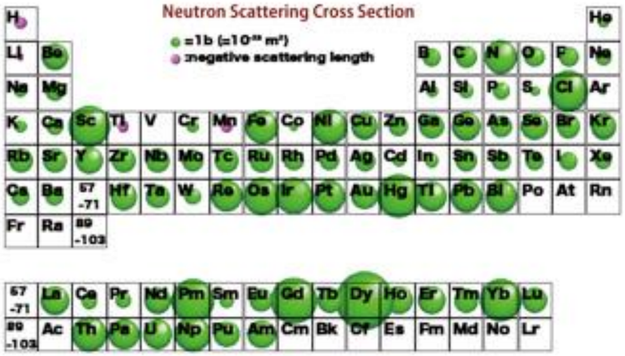
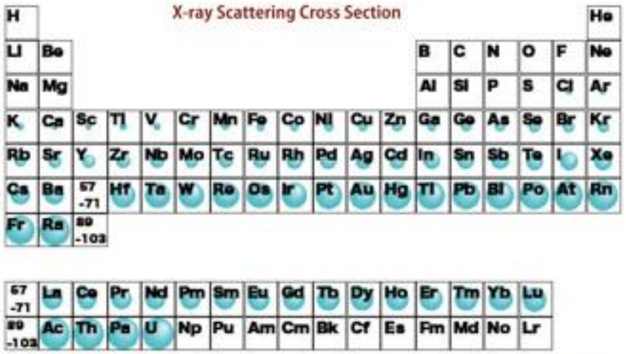
BESAC 07/14/2022

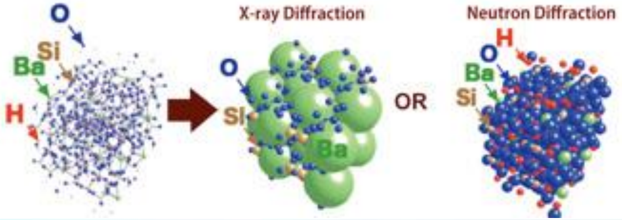
Why Neutrons?



- Detects light atoms even in the presence of heavy atoms: “Li,O,D”
- Distinguishes atoms adjacent in Periodic table and even isotopes of the same element. “TM” & “Li”
  - Natural Li b = -1.9, Abs XS = 70.5
  - ^{7}Li b = -2.2, Abs XS = 0.045
  - ^{6}Li b = ~2.0, Abs XS = 940
- Electrically neutral; penetrates centimeters of bulk material (allows non-destructive bulk analysis). Ease of *in-situ* experiments, e.g. variable temperature, pressure, magnetic field, chemical reaction etc. “In-situ electrochemistry”

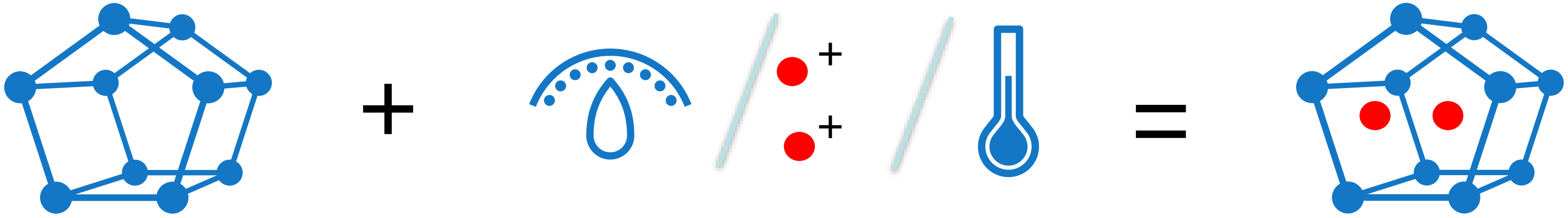






Advancing our understanding of Mechanisms

Functional materials are RESPONSIVE: External stimuli & compositional CHANGE



Characterize structure & response → Understand origin of useful properties

What do we need?

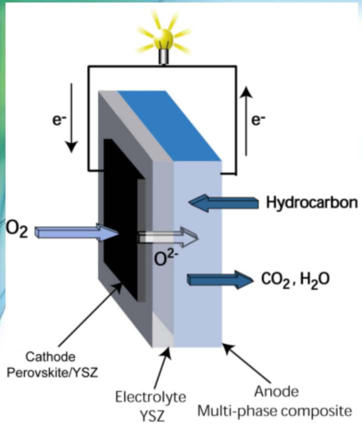
- Fast spectrometer
- Sample environment to emulate process
- Data analysis (often large amounts)
- Modeling (theory)

Some applications

- Fundamental working principles and mechanism driving operation
- Performance improvement
- Process Development
- Failure analysis

Ultimately innovation of more energy efficient technology

Solid Oxide Fuel Cell (SOFC)



- Oxygen from the air is reduced at the cathode.

$$O_2 + 4e^- \rightarrow 2O^{2-}$$

- Oxidation of fuel at the anode.

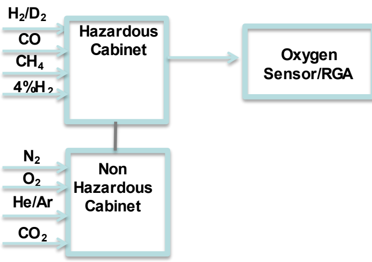
$$H_2 + O^{2-} \rightarrow H_2O + 2e^-$$

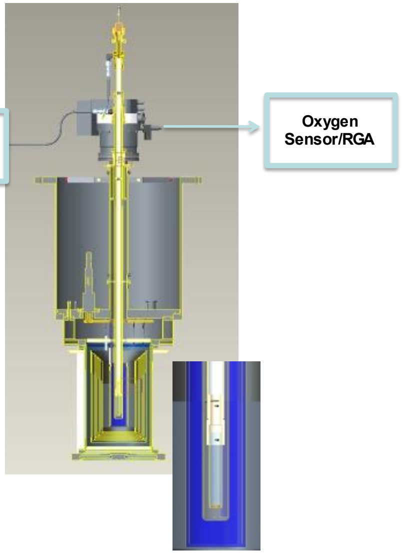
- Current cells have a reformer to generate CO/H_2 fuels from hydrocarbons.

$$CO + O^{2-} \rightarrow CO_2 + 2e^-$$

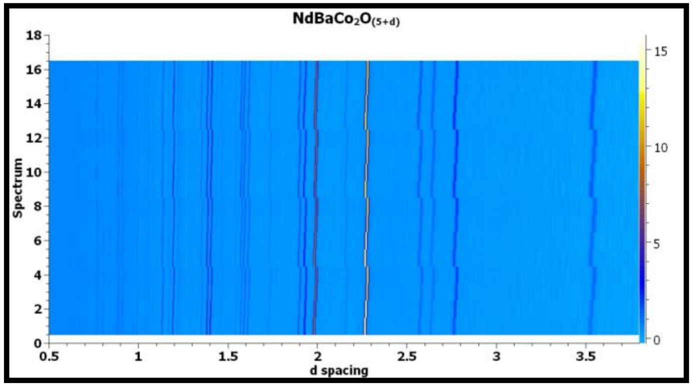
- Ideally we can utilize hydrocarbons directly:

$$CH_4 + 4O^{2-} \rightarrow CO_2 + 2H_2O + 8e^-$$





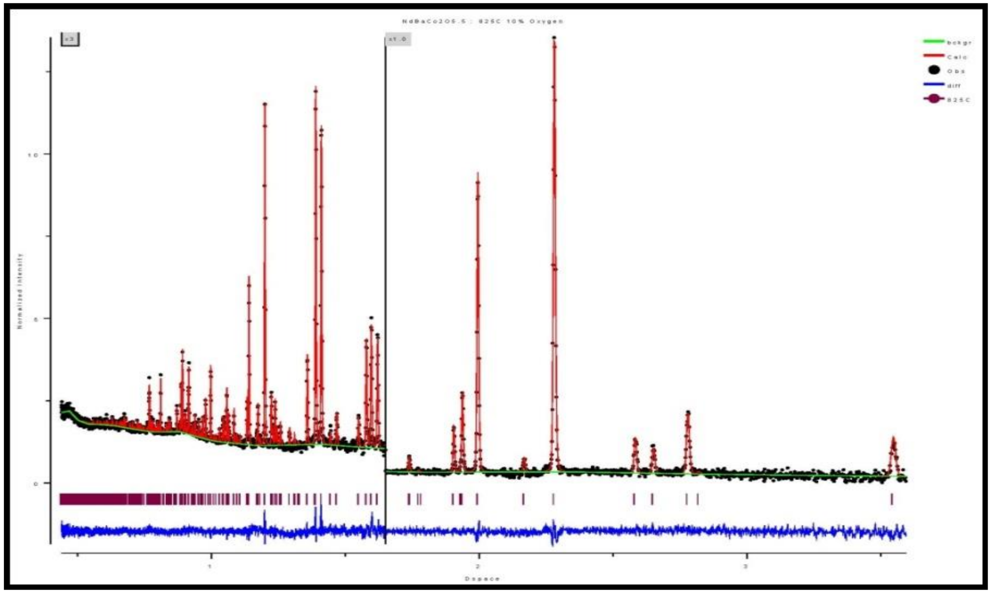
An integrated sample environment that includes a high temperature furnace, a gas flow insert, a pO_2 sensor and Residual Gas Analyzer (RGA) makes it possible to study Solid Oxide Fuel Cell (SOFC) materials among other things under operational condition. (Developed with 2009 LDRD)

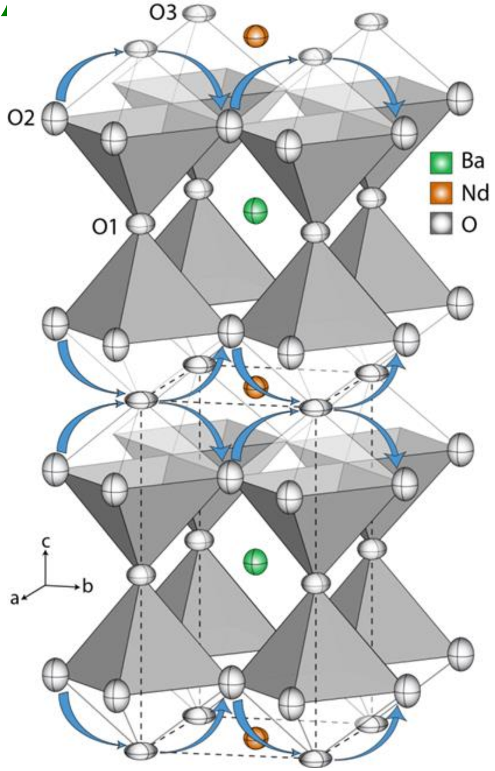


- Samples of (Nd and Pr)$BaCo_2O_{5\pm d}$ were measured @ four different pO_2 and four different temperature at each pO_2
- Equilibrium state was achieved by measuring the lattice parameter. Once the lattice parameter stopped changing, longer data was collected.
- Temperature of the sample was calibrated using a standard powder under identical condition.

Neutrons show Oxygen transport pathway in Double Perovskite ($Nd/Pr\ BaCo_2O_{5\pm\delta}$)

R.A. Cox-Galhotra, A. Huq, J.P. Hodges, J.H. Kim, C. Yu, X. Wang, A. J. Jacobson, S. McIntosh, “Visualizing oxygen anion transport pathways in $NdBaCo_2O_{5+d}$ by in situ neutron diffraction”, *J. of Mater. Chem. A 1*, 3091 (2013)





- ➢ **High Q data allows refinement of anisotropic thermal parameters and oxygen vacancy. Combined with near neighbor distances, it allows us to directly visualize the oxygen diffusion pathway.**

- ➢ **The structure is Tetragonal and not Orthorhombic as previously suggested in these pO_2 values.**

- ➢ **O3 site exhibits the largest vacancy and anisotropic motion. Motion of O2 is also very anisotropic which can hop to the near neighbor in the vacancy rich NdO plane. Fully Occupied O1 site has very small displacement and hence limited motion.**

All Solid State Battery

Samsung, the South Korean conglomerate, blamed battery manufacturing problems and design flaws for the embarrassing and costly failure of its Galaxy Note 7 smartphone and apologized to its customers and suppliers.

Courtesy of S. Whittingham (Li dendrite growth)

In 2016 Boeing grounded its entire fleet of the next-generation of 787 Dreamliners after the lithium batteries on two of the aircraft caught fire

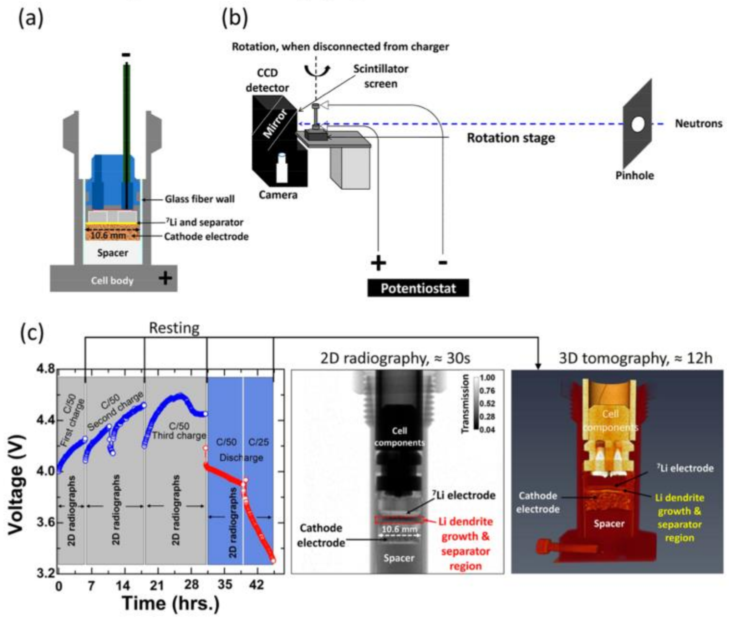
Typically for the Li-ion battery the electrolyte is a solution of lithium salts and organic solvents.

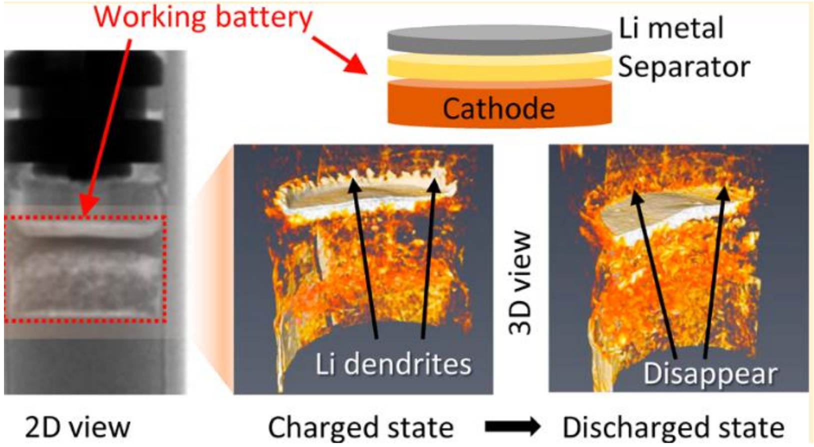
Recharging the cell gives a mossy Li deposit on the anode, and on repeated cycles, a dendrite growth from the anode across the electrolyte can short-circuit the cell with explosive or incendiary consequences.

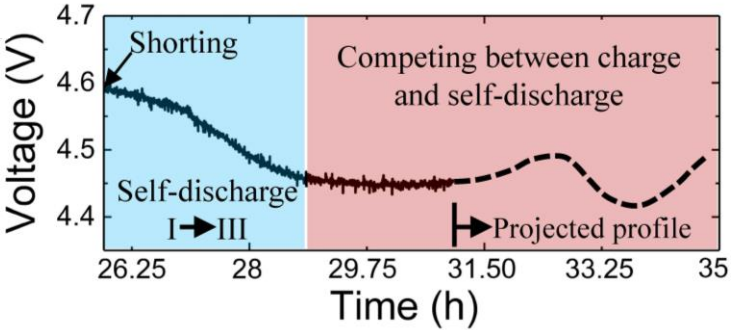
Tesla, a maker of electric cars performed a remote software update to its Model S luxury cars after two fires, which were blamed on road debris damaging the under tray containing the vehicles' lithium batteries.

Li dendrite growth visualized by *in operando* neutron imaging

Scheme 1. Schematics of the Operando Neutron Imaging Experiment[a]





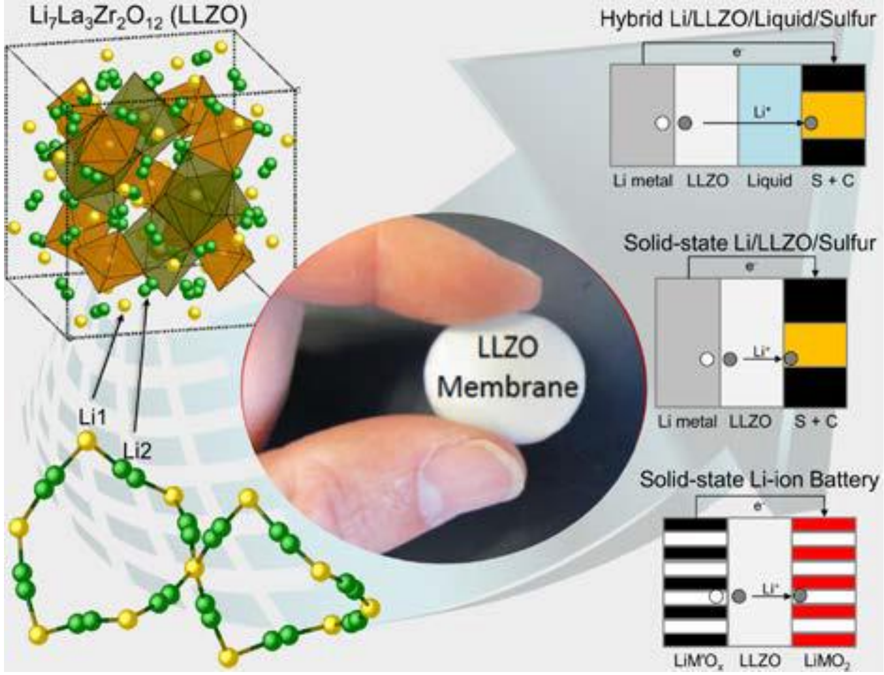


- A specially-designed electrochemical cell was used to study the Li dendrite growth in real-time using neutron imaging.
- A dynamic distribution of Li flowing from anode to cathode during charge, induced by the internal short-circuit due to the Li dendrite growth, has been observed.
- A competing mechanism after battery shorting between the short-induced self-discharge and charge is proposed to explain the voltage drop/rise during the extended charging time.

Song B., Dhiman I., Carothers J.C., Veith G.M., Liu J., Bilheux H.Z., Huq A., "Dynamic Lithium Distribution upon Dendrite Growth and Shorting Revealed by Operando Neutron Imaging", *ACS Energy Letters,* **4,** 2402-2408 (2019).

Current solid state synthesis of $Li_7La_3Zr_2O_{12}$ (Li_2CO_3+Al_2O_3+$La(OH)_3$+ZrO_2)

- Synthesis at ~1273 K
- Lithium loss, compensated by 5-20% excess
- Lithium gradient formed
  - Excess lithium → Tetragonal LLZO → interior of pellet or powder
  - Lithium deficient → Pyrochlore → pellet surface or powder



Why is there lithium loss?

- Li_2O is not volatile at 1073 - 1273 K
- Li_2O is volatile in 10 ppm water >1073 K, exceeding 10^{-6} atm
- Controlling options limited
    - Add excess lithium
    - Limit water vapor << 10 ppm
    - Limit temperature > 1073 K

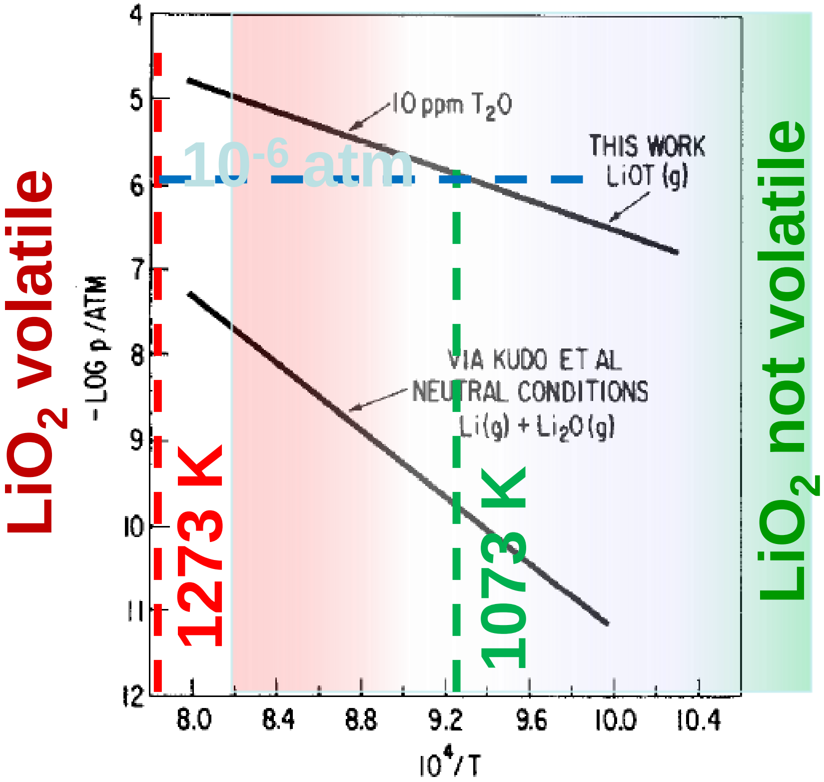
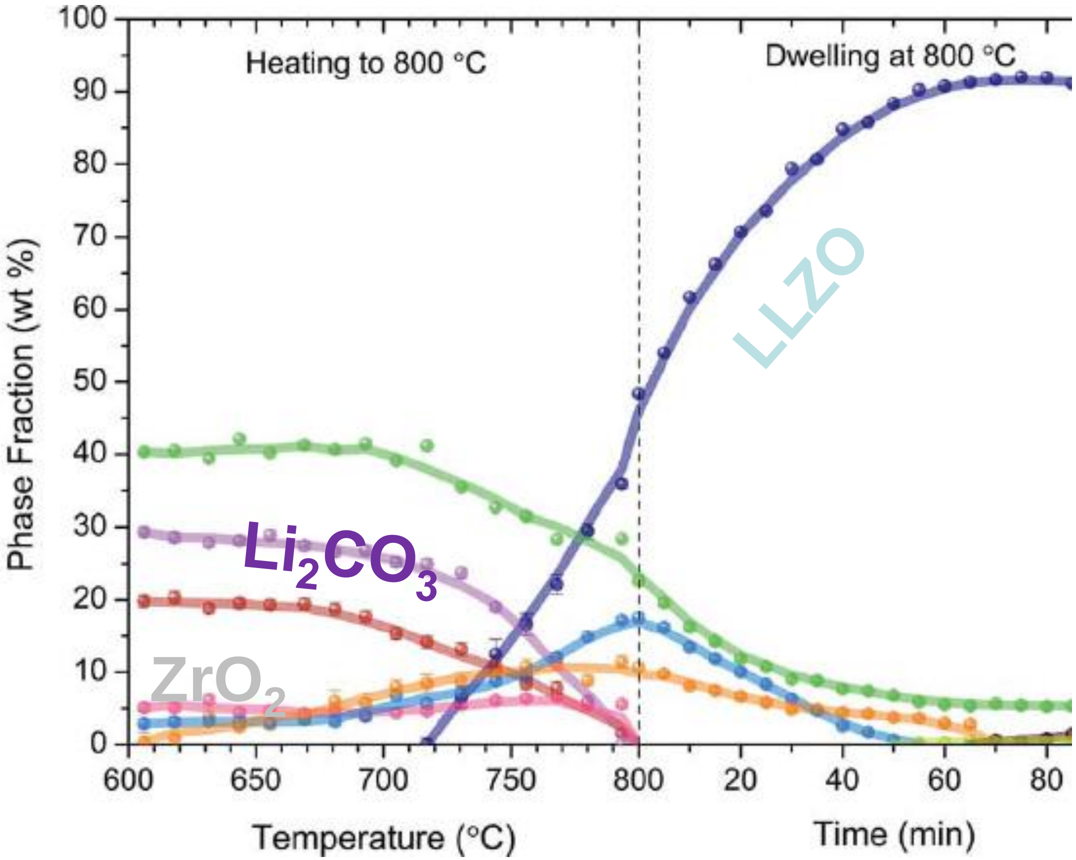


Fig. 2. Effect of 10 ppm T_2O pressure in helium purge stream on vaporization of Li bearing species from Li_2O(s).

M. Tetenbaum and C. E. Johnson,
J. Nucl. Mater., 1984, **120**, 213–216.

Can the synthesis temperature be reduced?

- LLZO does not begin to form until ~1023 K, requires long dwell
- Li_2CO_3 remains until ~ 1023 K
- Substituting less stable form of lithium may reduce synthesis temperature



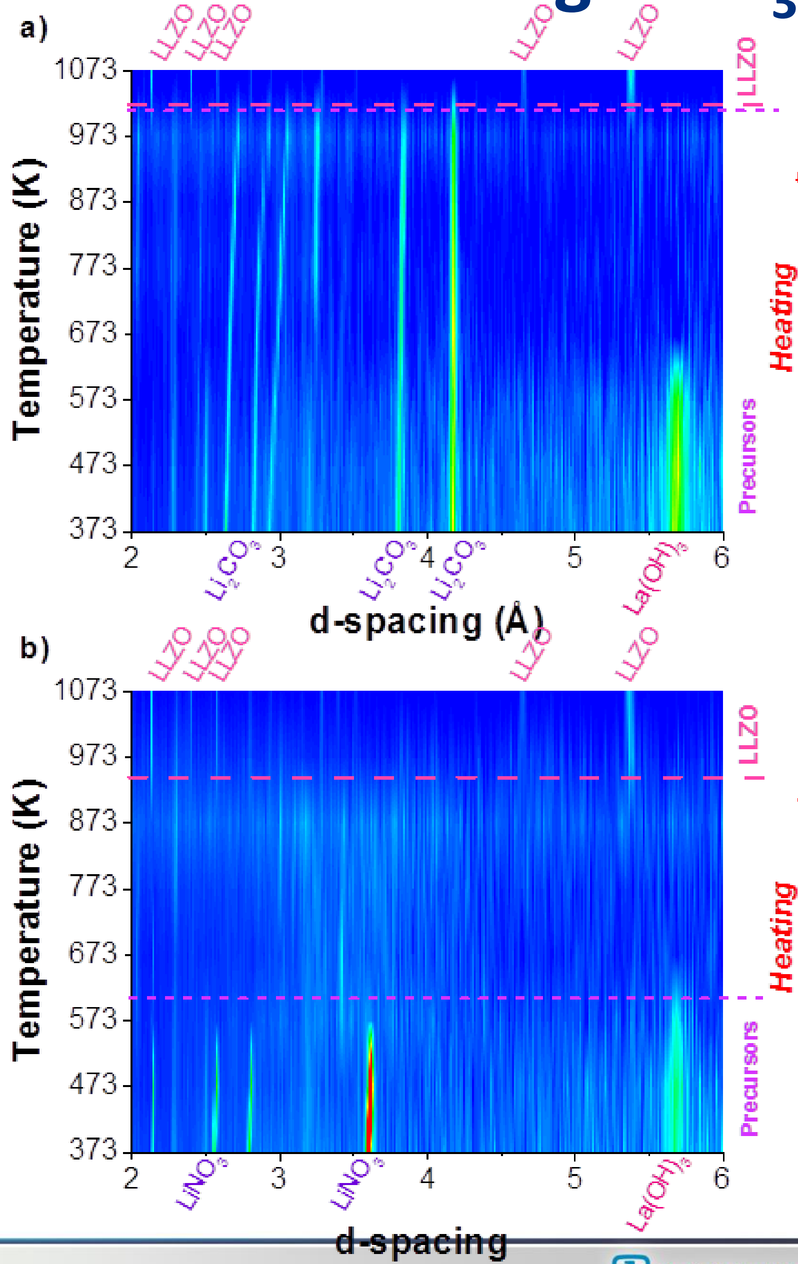
Y. Chen, E. Rangasamy, C. R. dela Cruz, C. Liang and K. An, *J. Mater. Chem. A*, 2015, **3**, 22868–22876.

Experimental Procedure

- Stoichiometric mix of precursors +6 wt% excess lithium milled
  - $La(OH)_3$
  - ZrO_2
  - Al_2O_3
  - Li_2CO_3 or $LiNO_3$
- Pressed into ¼” pellets
- Heated in alumina-lined flow cell with flowing dry air
  - 373 K -1073 K in 100 K increments
  - 2 h hold for ND at POWGEN
- Repeated heating, monitoring gas with mass spec.

LLZO forms at lower temperature when using $LiNO_3$

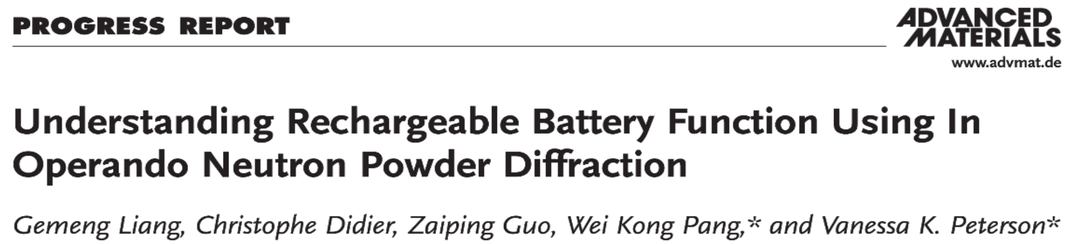
- LLZO first observed at different temperature
  - Li_2CO_3: First observed at 1073 K
  - $LiNO_3$: First observed at 973 K
- ND indicates $LiNO_3$ is not observed after 473 K



Conclusions

- Li_2CO_3 as the lithium precursor
  - $La_2O_2(CO_3)$ is majority phase at 773 – 973 K
  - LLZO is not observed until 1073 K
- $LiNO_3$ as the lithium precursor
  - $La_2O_2(CO_3)$ limited to carbon from ZrO_2 surface
  - LLZO is the majority phase observed at 973 K
- Calcining temperature ↓ 100 K
  - Reduce energy usage
  - Reduce lithium loss
- ZrO_2 likely limiting reduction of temperature
  - ZrO_2 surface carbonates → carbonate intermediates

Real Time Battery Cycling



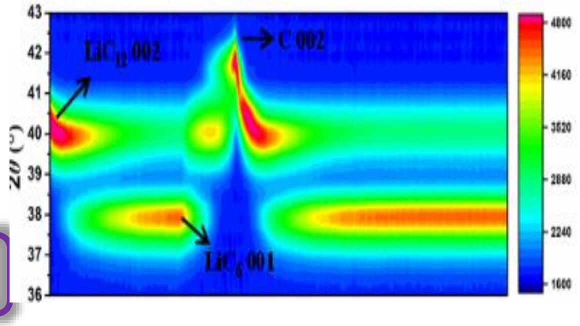
PROGRESS REPORT

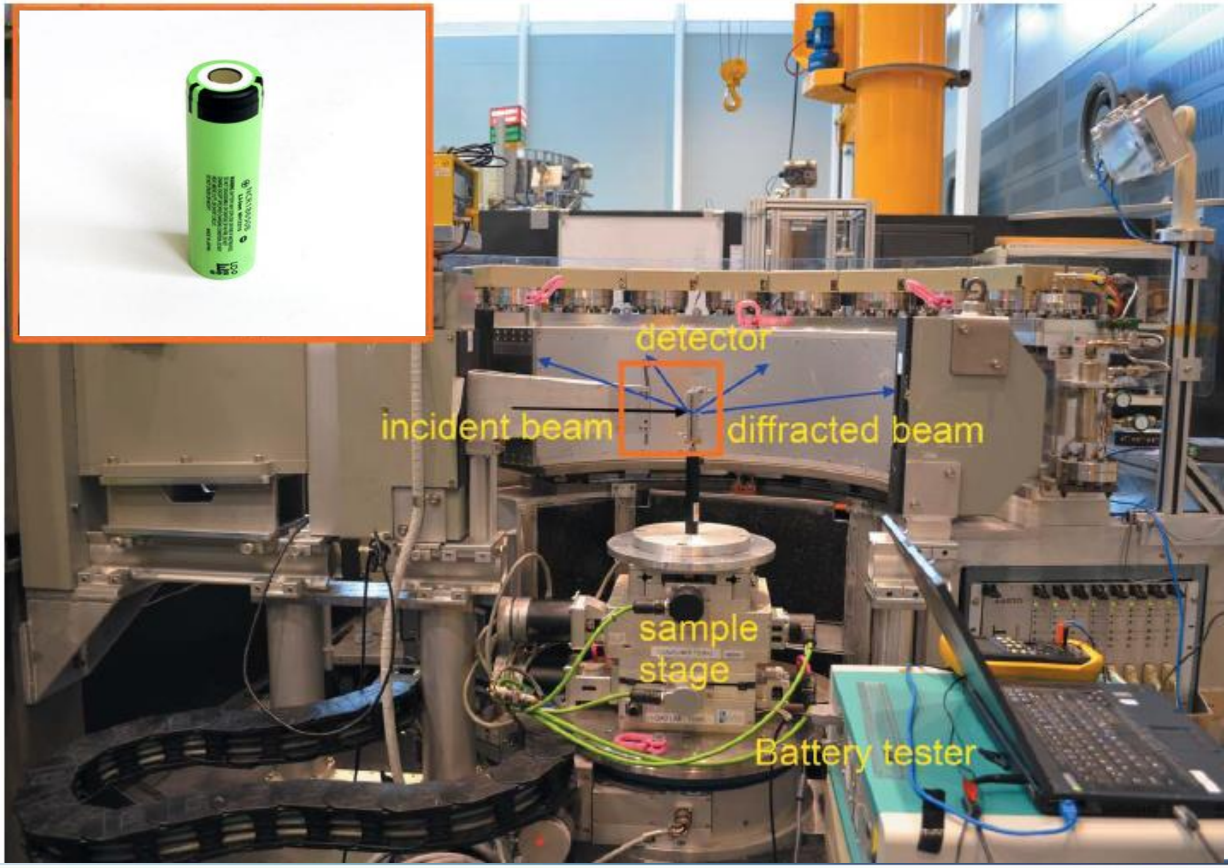
ADVANCED MATERIALS
www.advmat.de

Understanding Rechargeable Battery Function Using In Operando Neutron Powder Diffraction

Gemeng Liang, Christophe Didier, Zaiping Guo, Wei Kong Pang, and Vanessa K. Peterson**

Fastest real time measurements 2020: **10 s (Wombat, ANSTO)**





18650 Panasonic CGR18650CE
- Graphitized carbon as Meso-Carbon MicroBeads (MCMB)
- $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (NMC)

Operation
- As-received
- Cycled 3.0-4.2 V at 75 mA (C/30)

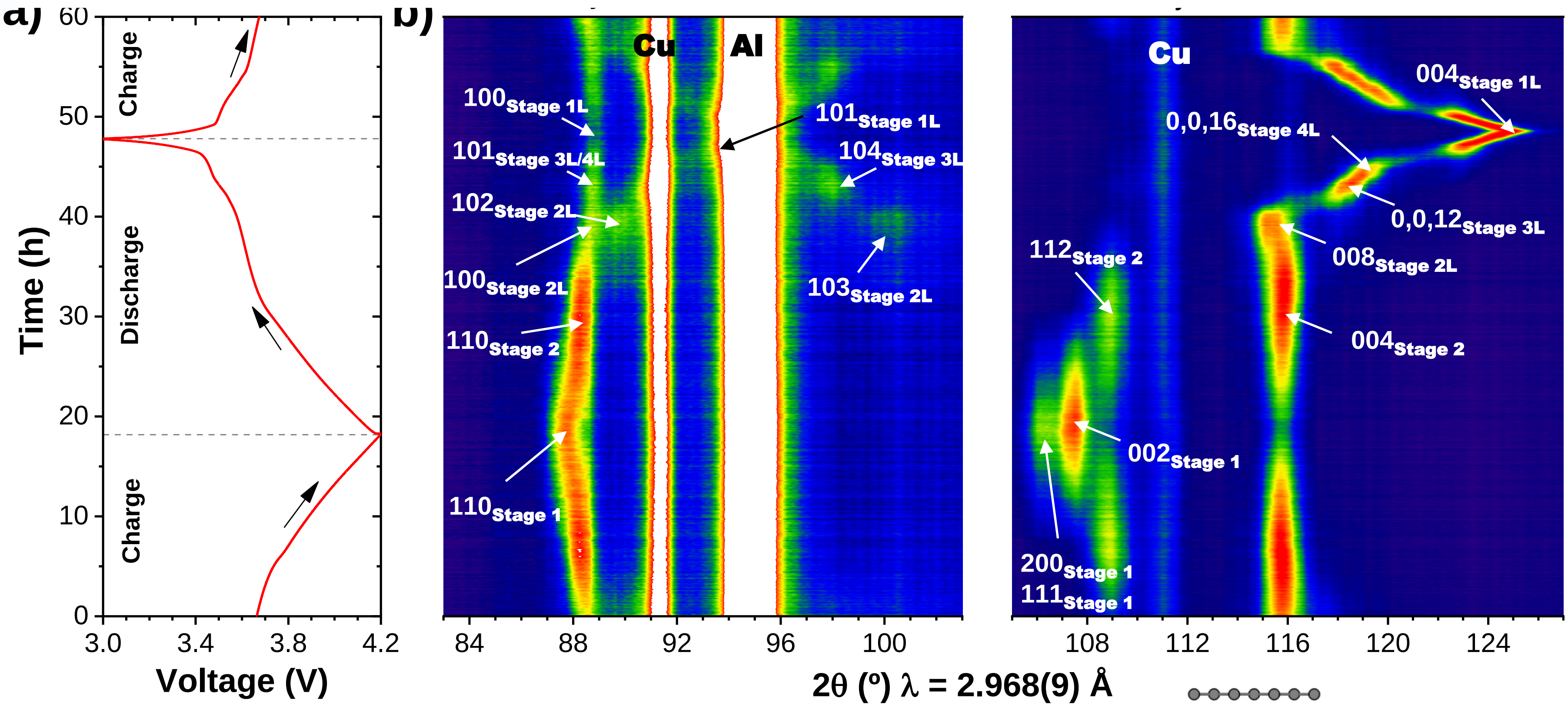
1 min data (& 10 s measurements)
- Li_xC_6 with $0.5 > x > 0.04$
- $< 5 \times 10^{-4}$ Li per measurement

G. Liang, C. Didier, Z. Guo, W. K. Pang, V. K. Peterson*, Adv. Mat. (2020)
C. Didier, W. K. Pang, Z. Guo, S. Schmid, V. K. Peterson*, Chem. Mat. (2020)

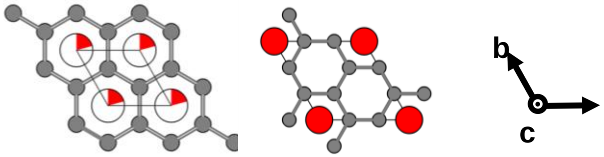
Revisiting Li Intercalated Graphite Phase Evolution

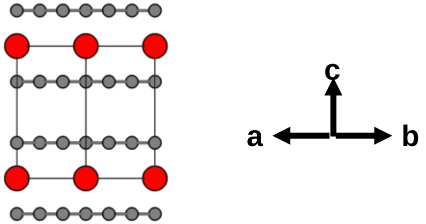
Ordering in the (110) plane
LIG 10*l* & 110 reflections

Ordering along [001]
LIG 00*l* reflections

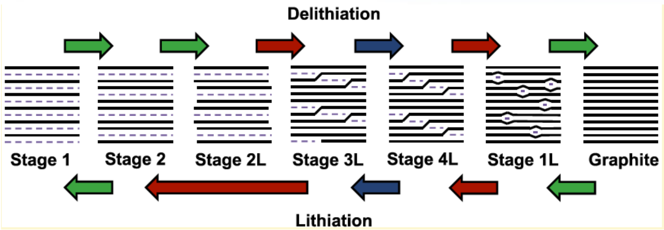


Carbon
Lithium

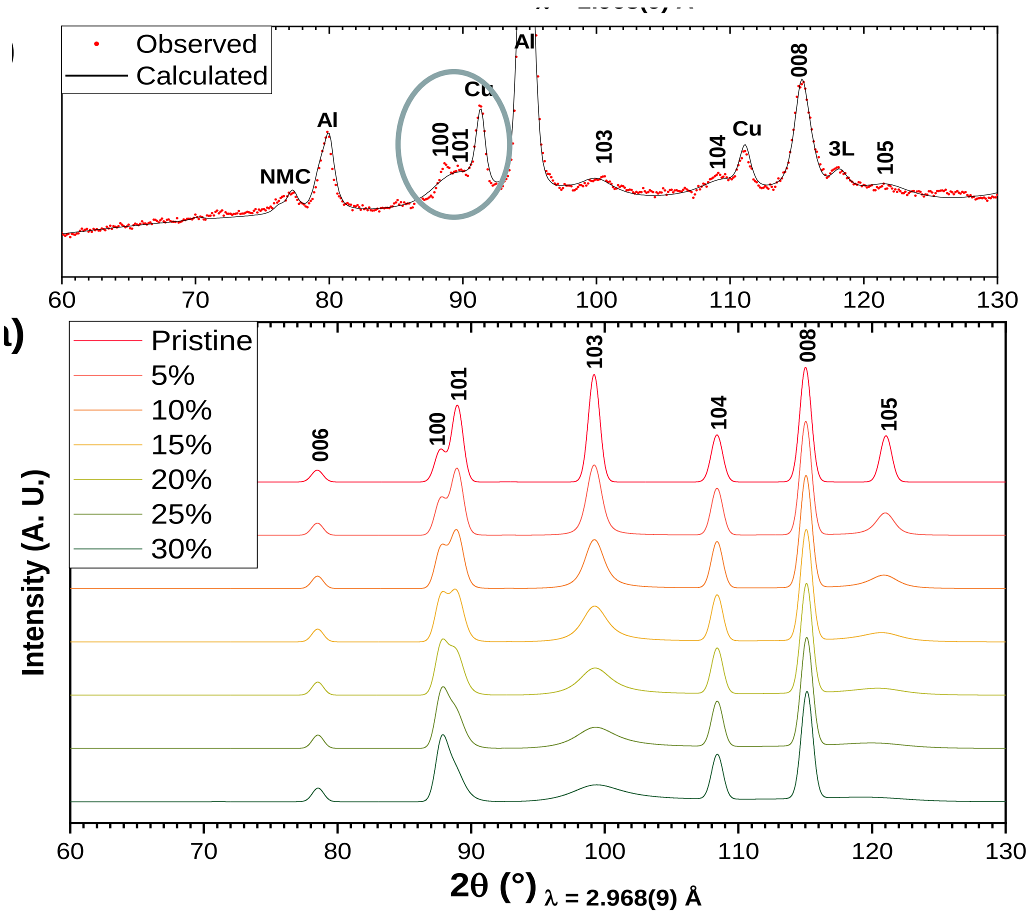




The Stage 2 & 2L Phase Structure



Stage 2L: Disordered “liquid” state, no Li ordering in the *(a, b)* plane; /AB/BA/ stacking



Stage 2L & 2 co-exist.

The 2L phase model does not describe the 100/101 reflection intensity

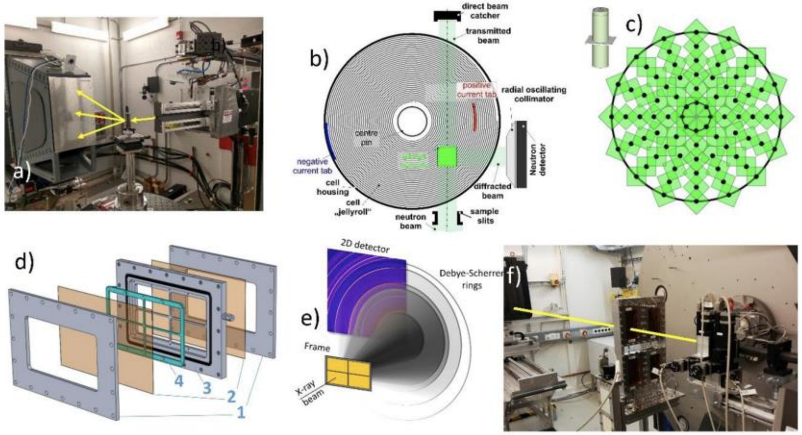
Constructed a phase model of stage 2L with stage 2 inclusions as /AA/ or /BB/ stacking faults

- Carbon layers eclipsed around Li
- Fault probability (Diffax):
  - 0% = 100% stage 2L
  - 30% = 70% stage 2L & 30% stage 2

Data support a model of stage 2L with 15-20% 2 inclusions

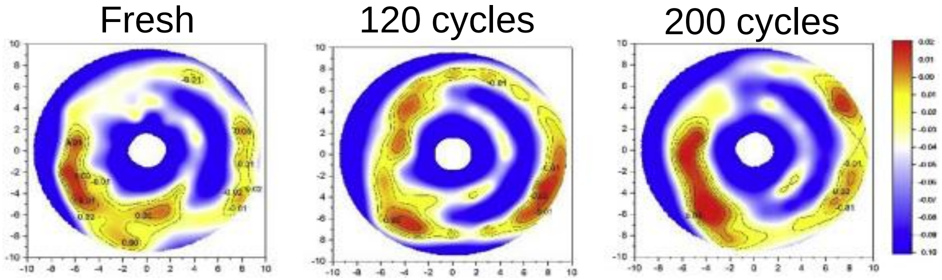
Spatially Resolved Neutron Powder Diffraction

Li distribution from graphite intercalated phase reflection intensities (structure factor)



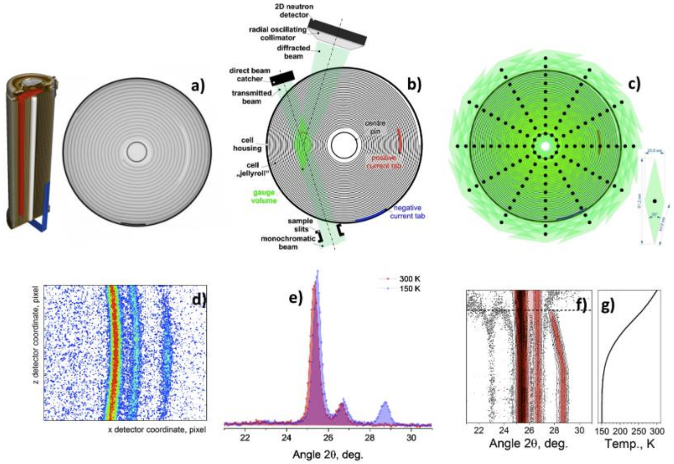
VULCAN, SNS ORNL USA

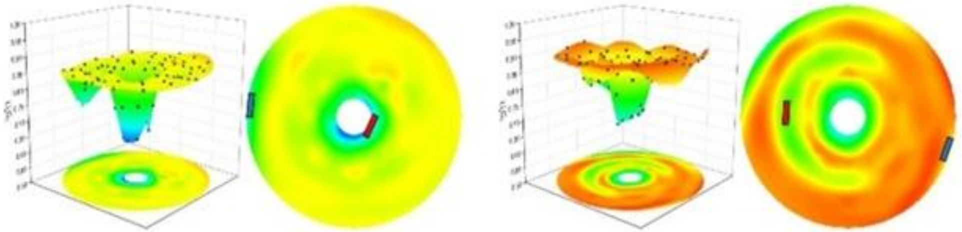
D. Petz et al, J Power Sources, 2020



STRESS-SPEC, FRMII Germany

D. Petz et al, Batteries & Supercaps, 2021.





Other techniques

- **Reflectometry:**
  - *In situ* studies of interfacial reactions
  - Sub-nanometer depth profiles of layered structures
  - Ion transport in solid electrodes and electrolytes
  - In plane roughness/morphology
  - Ordering in crystals, liquid crystals
  - Atomic structures near surfaces

- **Small Angle (SANS):**
  - SEI formation in batteries
  - Dendrite formation

- **Vibrational Spectroscopy**
  - Lattice dynamics of ionic conductors, especially proton conductors.
  - In-situ impedance spectroscopy (phonon behavior under AC electric field)
  - Characterization of solid-electrolyte interphase (SEI)

- **Quasielastic Neutron Scattering**
  - Ion diffusion (e.g. Li, Na, H, O, etc.)
  - Atomic scale understanding of the diffusion process
    - Nature of diffusion (free diffusion / jump-diffusion / presence of ion traps)
    - Geometry of the localized processes
  - Characteristic times from about picosecond to nanosecond scale
  - Diffusion coefficient
  - Energy barrier for diffusion from temperature dependent measurements