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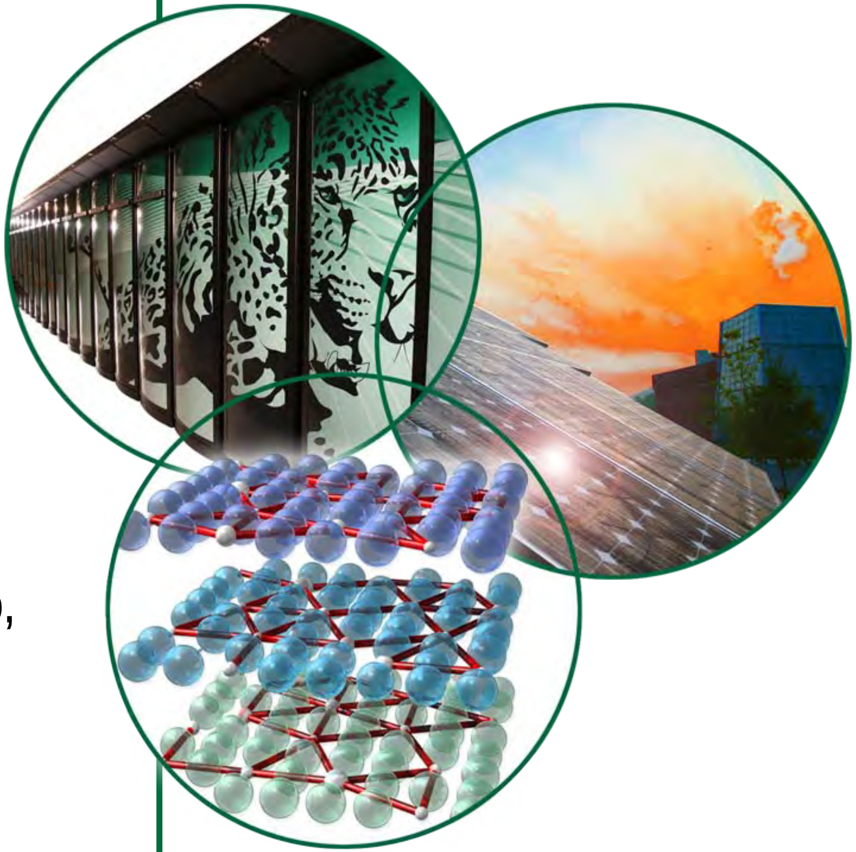
Project ID #ES093

Intercalation Kinetics and Ion Mobility in Electrode Materials for Advanced Lithium Ion Batteries



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ANL: Daniel Abraham

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U.S. DEPARTMENT OF ENERGY

OAK RIDGE NATIONAL LABORATORY

MANAGED BY UT-BATTELLE FOR THE DEPARTMENT OF ENERGY

Overview

Timeline

- Start: fiscal year 2009
- End: fiscal year 2011
- 85% complete

Budget

- Total project funding
  - $1.5M
- Funding for FY11
  - $300K

Barriers

- Poor cycle life
- Low state of charge power

Goals

- Cycle life: 5000 cycles
- Calendar life: 15 years

Partners

- Argonne National Laboratory
- Center for Nanophase Materials Science

Objectives

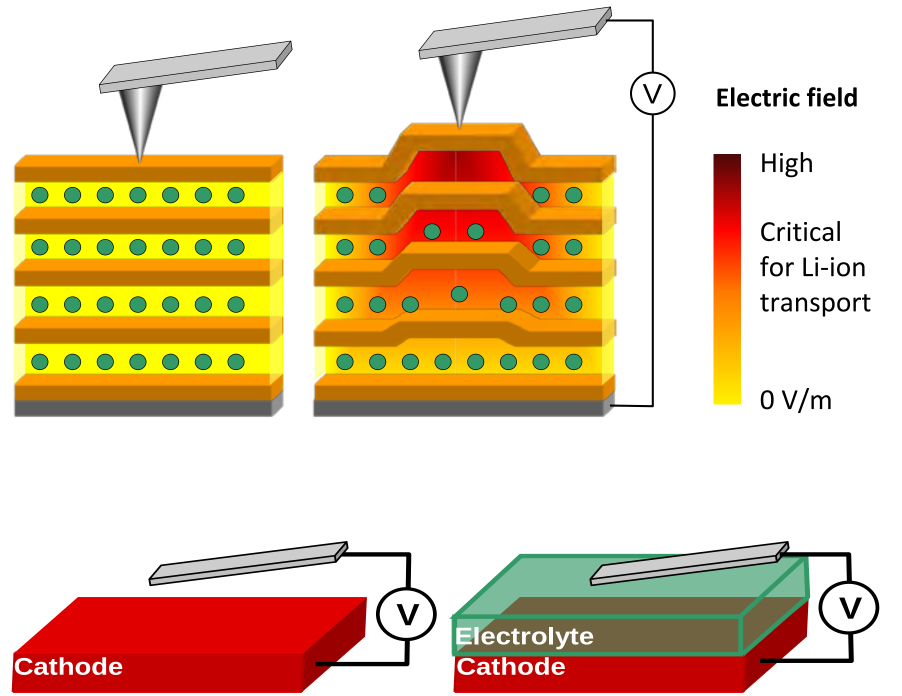
- Understanding of Li ion kinetics as a function of crystallographic features and defects in active electrode materials.
- Investigation of ion transport through solid-electrolyte interface (SEI layer).
- Investigation of effect of mechanical damage on Li ion mobility.
- Guidance for processing methods of existing materials in order to enhance low state of charge power.

Milestones

Month/Year	Milestone or Go/No-Go Decision
Oct 09	Preparation of thin film samples and subsequent FIB milling Preliminary FE modeling of micro-machined samples
Apr 10	Optimizing samples for AFM studies with non-conductive tip Successful charge/discharge of micro-electrodes
Sept 10	Successful *in situ* AFM and ESM of FIB micro-machined samples. Model predictions are verified against experimental data. Understanding diffusion kinetics and ion mobility on micrometer scale.
Sept 11	•Intercalation kinetics in by means of Electrochemical Strain Microscopy (ESM) – 85% complete •Understanding and verified modeling of stress-strain relationship and intercalation kinetics – 60% complete

Kinetic approach

- At low state of charge, lithium occupying cathode intercalation sites is reducing diffusion rates in randomly oriented electrode particles and inhibits high power delivery
- Thus, lowest state of charge allowed in traditional materials is 30%
- Mapping capability allows to study ionic transport in electrodes, across interfaces and its correlation with defects
- Knowledge allows for development of processing methods to increase defects of interest and increase diffusion rates and lithium mobility



Deformation approach

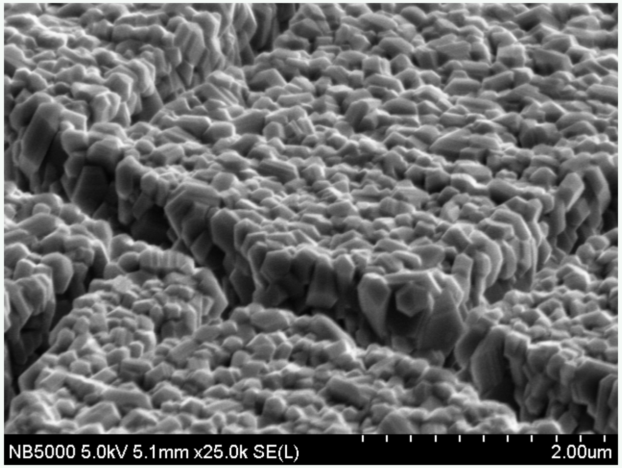
- Composites are typically calendered before cell assembly
- Calendering introduces high density of mechanical defects which changes electrochemical activity and decreases porosity and electrolyte transport
- A quantitative understanding of the influence of mechanical defects to electrochemical activity allows for a targeted processing procedure
- Optimized mechanical deformation with minimal impact on porosity decrease allows for higher power batteries

- Thin film indentation
  - Determination of basic mechanical properties for thin films of electrode materials.
  - Mechanical properties are crucial for diffusion-strain modeling and assessment of electrode degradation.
  - Evaluation of the influence of mechanical pre-straining on subsequent behavior of the material.
- Micro-pillar indentation
  - FIB micro-machined samples can be considered as representative volume elements of cathode material.
  - Known pre-defined geometry.
  - Known boundary conditions.
  - Experimental data can be used in simulations

Technical Accomplishments

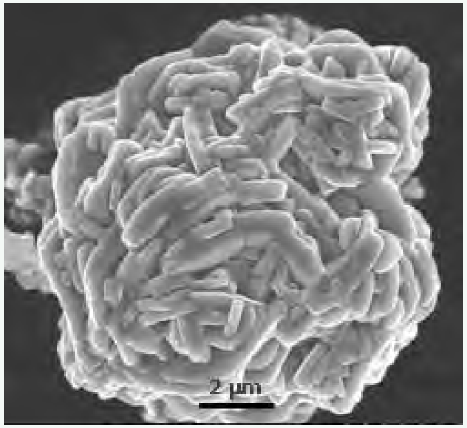
Thin Film Approach

- Thin films of $LiCoO_2$ (LCO) on Al_2O_3 substrates.
- Polishing of substrates to surface roughness of 500 Angstrom eliminates the need for Tungsten deposition.



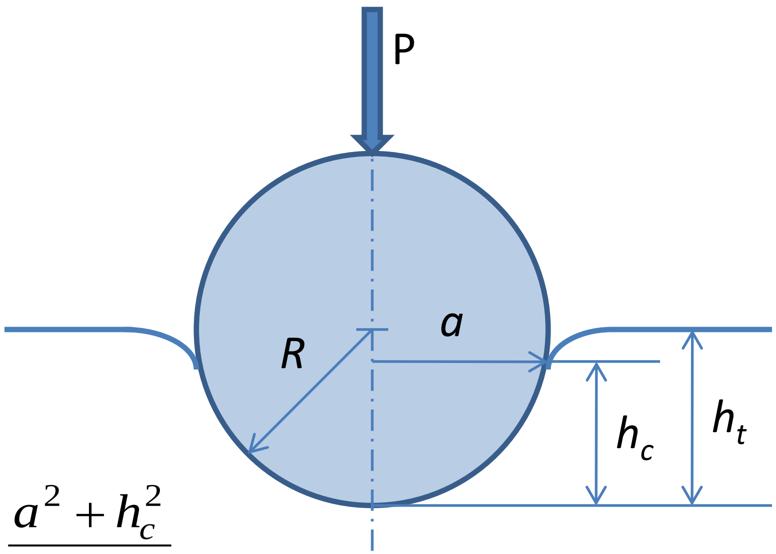
Powder Approach

- $Li_{1.05}(Ni_{1/3}Co_{1/3}Mn_{1/3})_{0.95}O_2$ (NCM) and $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA) on aluminum foil with PVDF/Carbon black



Daniel Abraham, ANL

Technical Accomplishments
Mechanical Behavior of LCO



$$\tilde{R} = \frac{a^2 + h_c^2}{2h_c}$$

$$h_c = h_t - \frac{\xi P}{S}$$

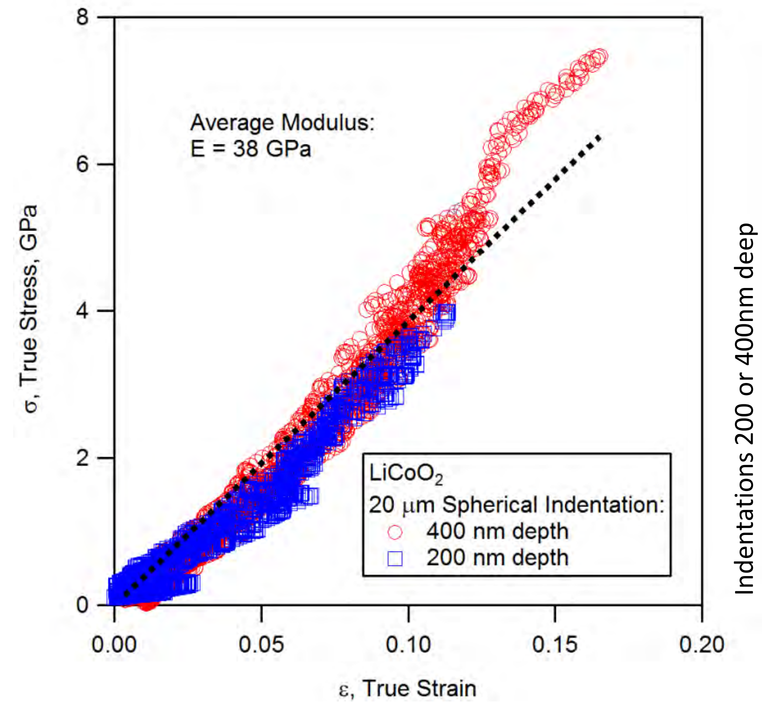
$$\rho = \frac{h_t}{h_c} - 1$$

$$a = \sqrt{\frac{1}{\pi}\sum_{n=0}^{N} C_n h_c^{2/2^n}}$$

True stress: $\sigma = \frac{0.9P}{\pi a^2}\rho$

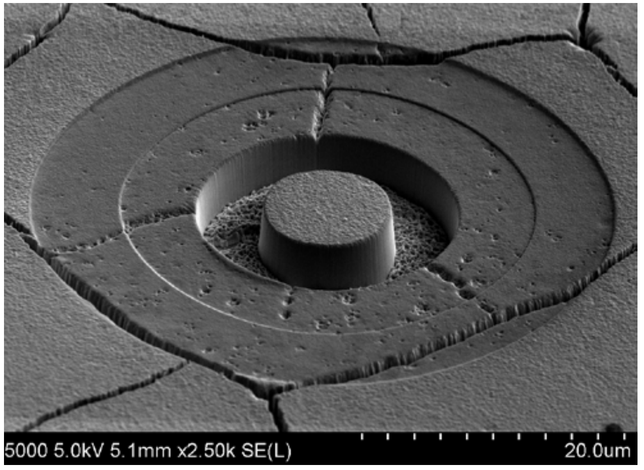
True strain:

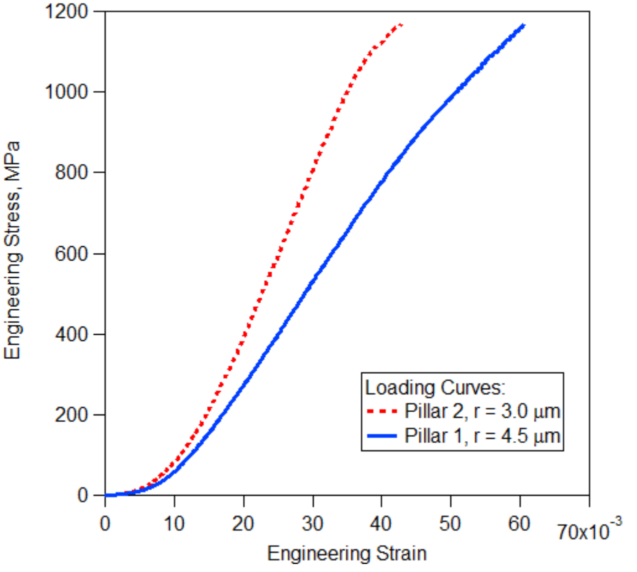
$$\varepsilon = \frac{0.9P\rho}{\pi a^2\left(1-\nu^2\right)}\left\{\frac{4}{2.7P\rho}\left[2\left(h_t - h_c\right)\tilde{R}^{1/3}\right]^{3/2} - \frac{1-\nu_i^2}{E_i}\right\}$$



Technical Accomplishments
Mechanical Behavior of LCO

Micro-pillar compression confirms indentation result



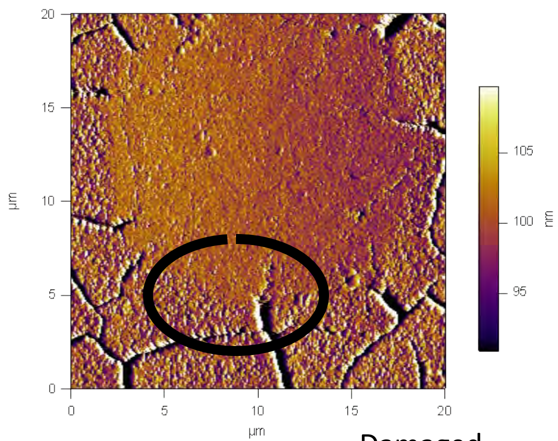


Micro-Indentation of Pillars:

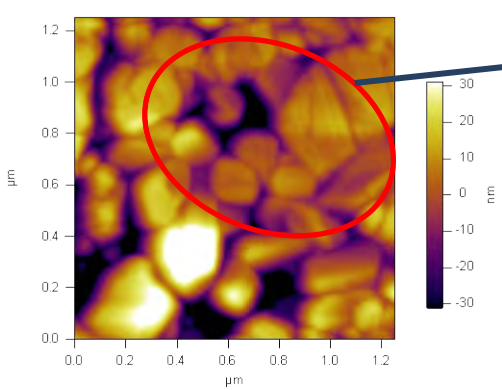
- MTS Nano-Indenter XP. 20 µm dia flat tip indenter
- Strain rate $\dot{\varepsilon} = 5 \cdot 10^{-4}$
- Average Young's Modulus $E = 32\,GPa$

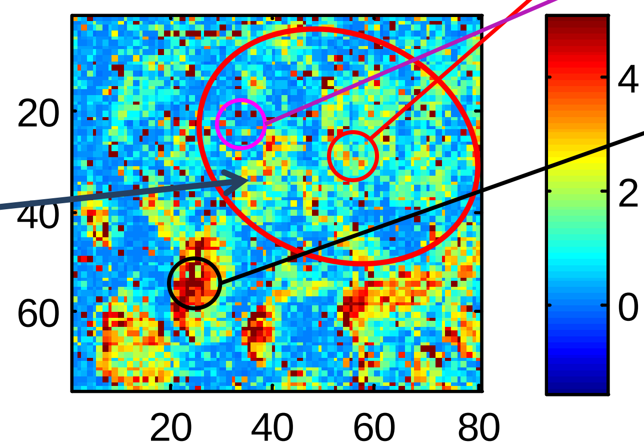
Technical Accomplishments
Electrochemical activity of deformed regions reduced

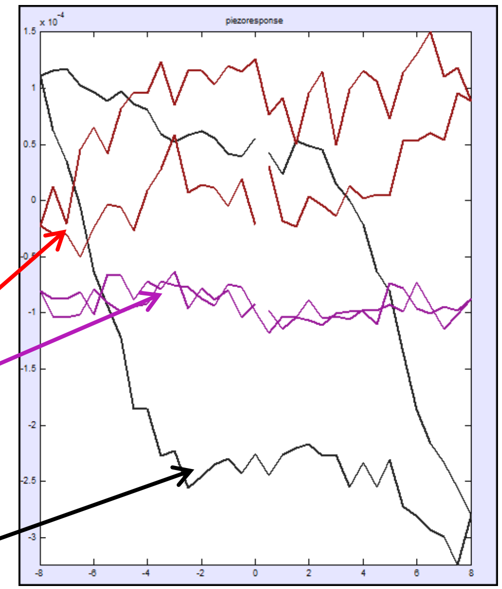
Indented areas show weaker response indicating that lithium mobility is suppressed by compressive mechanical damage



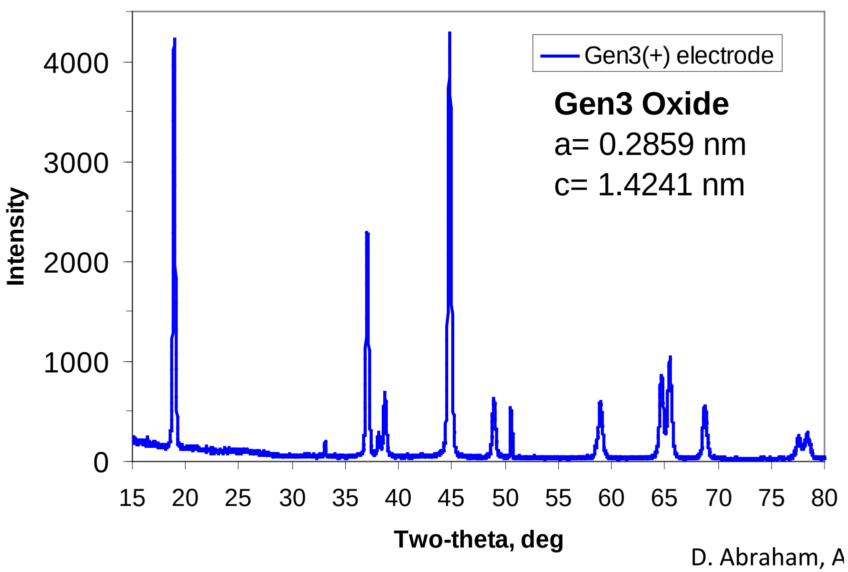
Damaged Area

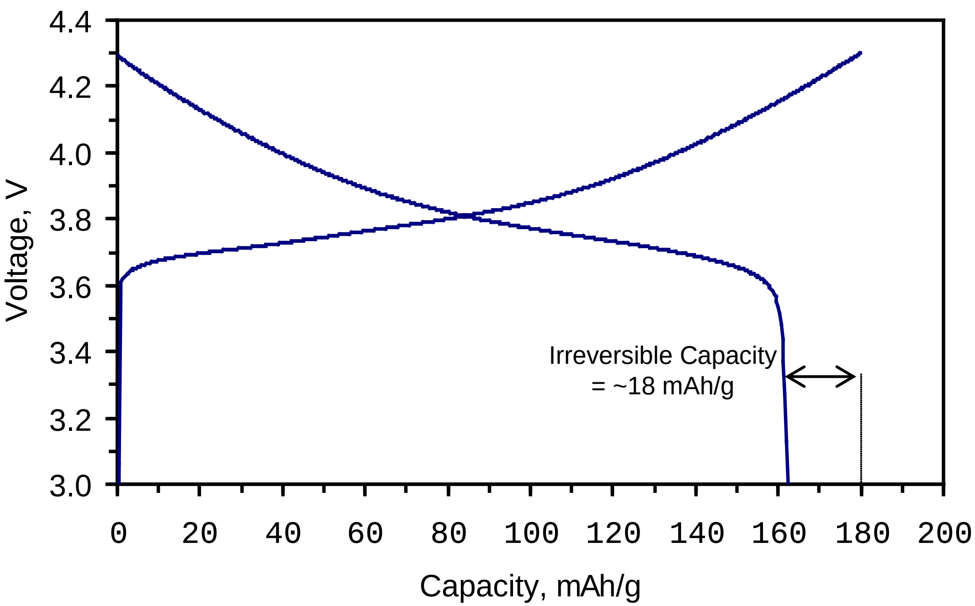






Technical Accomplishments
NCM electrodes

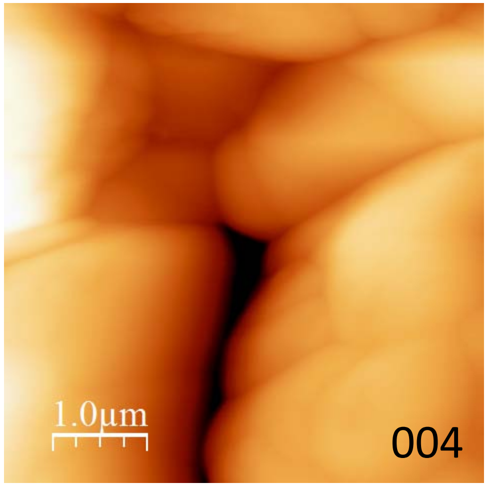




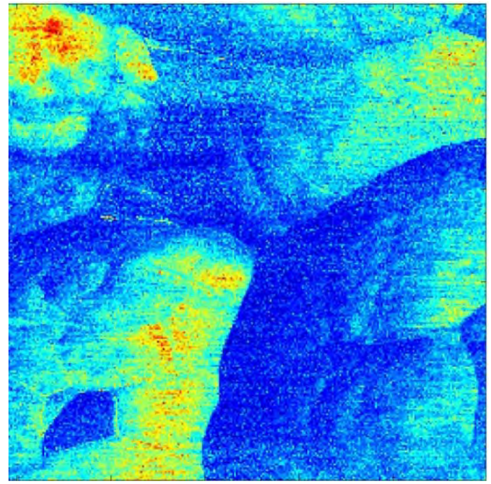
First cycle 30°C data from a Gen3(+)/Li cell obtained with a 3.9 mA/g current (~C/40) in the 3-4.3V range.

Technical Accomplishments
Li ion kinetics in NCM

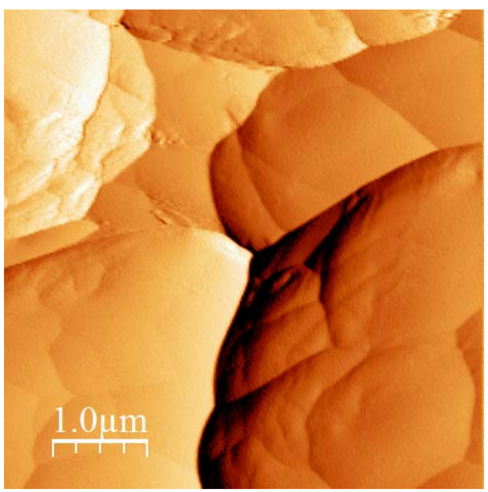
Topo



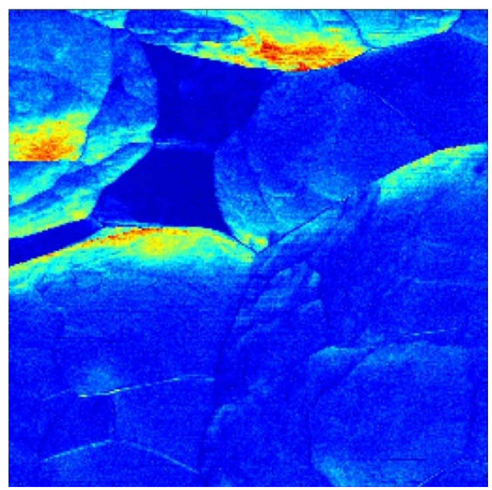
OP Amplitude



Deflection



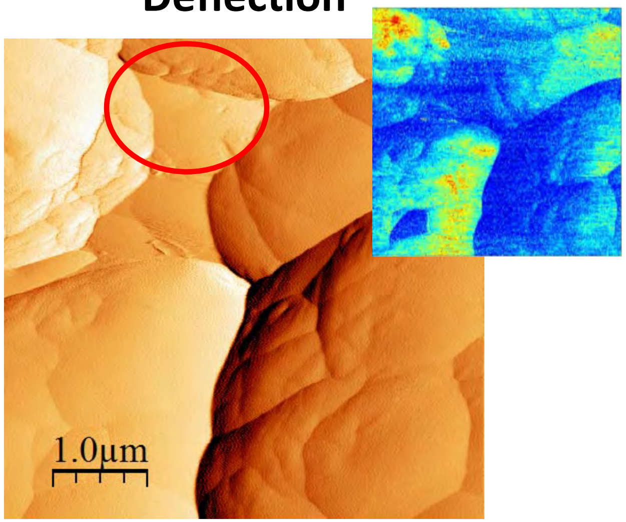
IP Amplitude



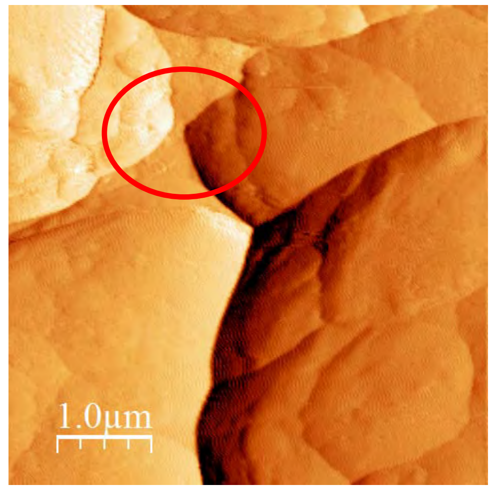
In-plane (IP) and Out-of-Plane (OP) signals are different. Grains show “hot spots” of ion motion as seen on ESM amplitude maps.

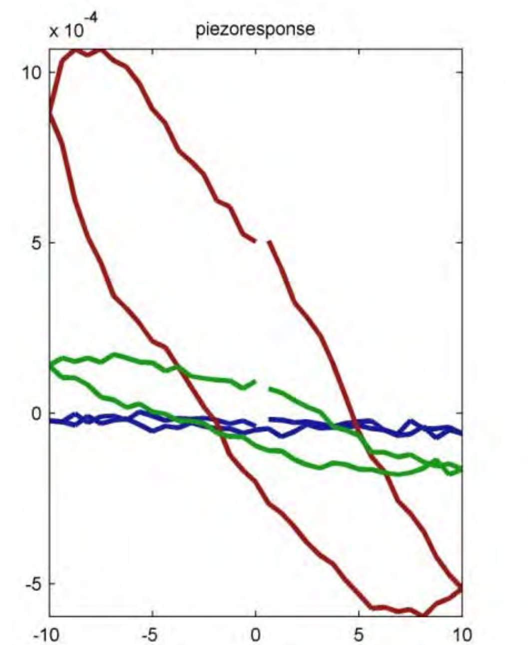
Technical Accomplishments
Li ion kinetics in NCM

Deflection



Deflection after BEPS

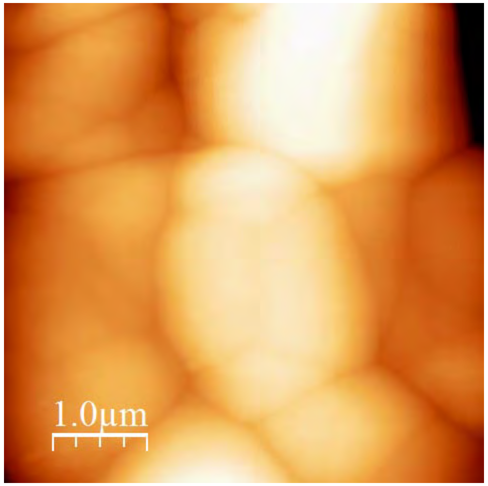




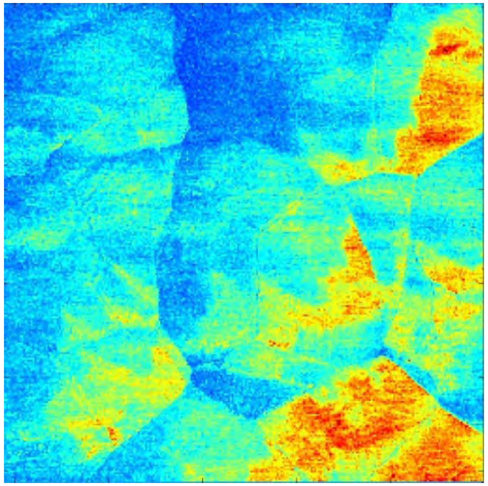
Due to ion movement, grain topography is changed during measurement
Effect can be quantified

Technical Accomplishments
Li ion kinetics in NCM

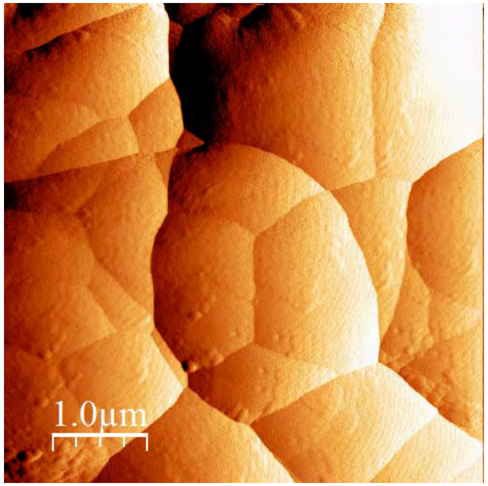
Topo



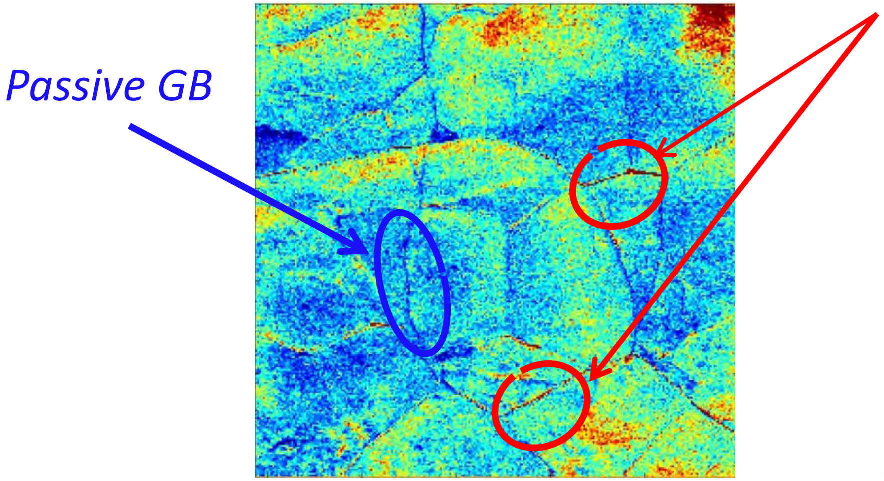
OP Amplitude



Deflection



IP Amplitude



Collaborations

Partners

- Argonne National Laboratory: Daniel Abraham
- Center for Nanophase Materials Sciences: Sergei Kalinin, Nina Balke, Senli Guo
- Materials Science and Technology Division: Hongbin Bei

Summary

- First quantitative measurement of mechanical behavior of cathode materials on scale of electrochemical activity
- Understanding of deformation on electrochemical activity
- Quantification of grain boundaries and other defect's influence on electrochemical activity

Proposed Future Work

- Effect of surface coatings
- ESM in liquid electrolyte
- Using indentation to monitor change in mechanical properties during charge/discharge
- Process development to change activity and influence low state of charge power