First Principles Calculations of Existing and Novel Electrode Material

Gerbrand Ceder

Principal Investigator, Project ID ES054

Massachusetts Institute of Technology

June 11, 2015

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Overview

Timeline

- Start Date Jan 2013
- End Date: Dec 2016

Barriers Addressed

- Inadequate Li-ion battery energy density, cycle life and rate
- High cost of electrode materials

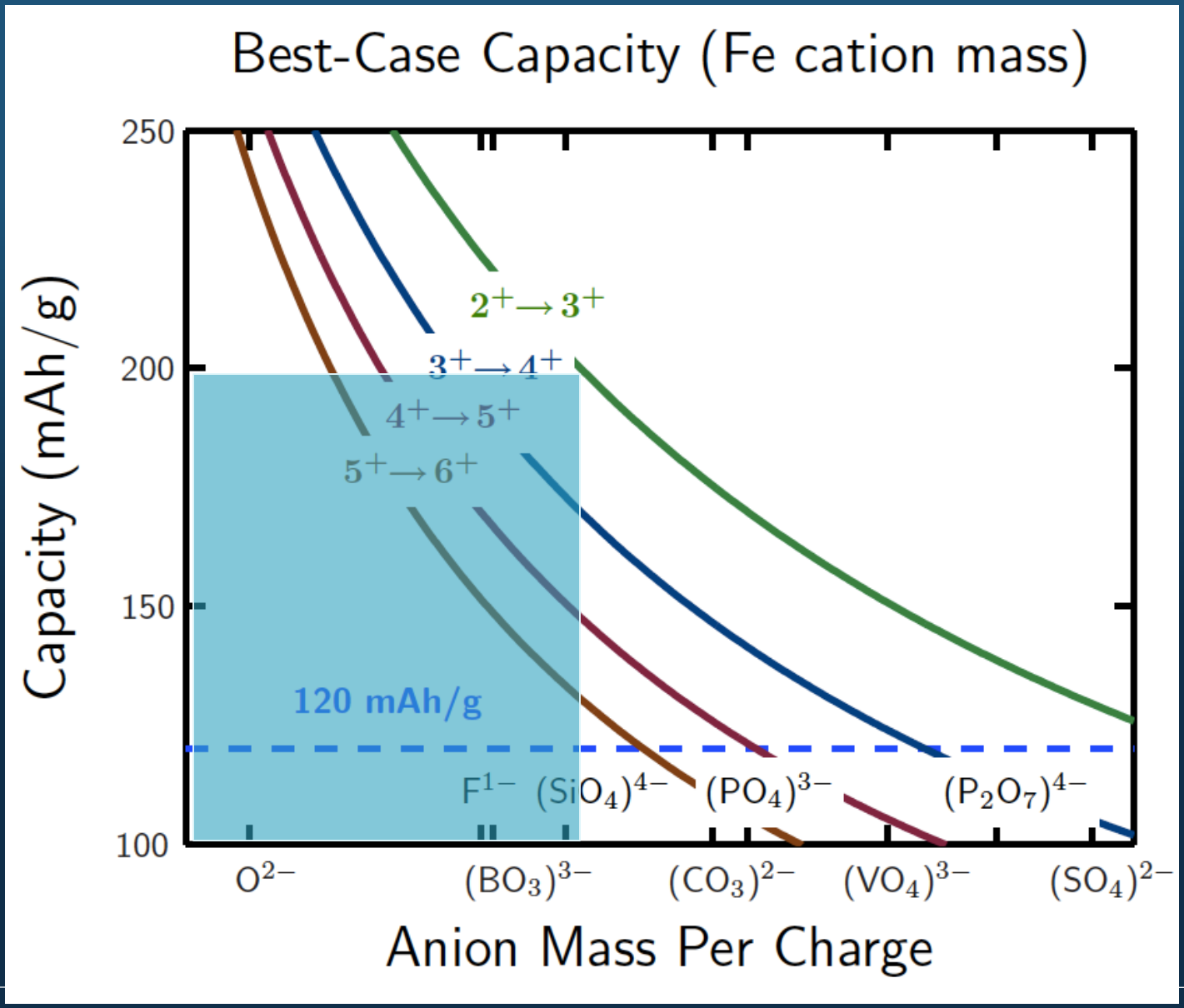
Budget

- Total budget (4 years): $930,667
- FY13 funding $221, FY14 funding $229

Partners/Collaborations within the VT program

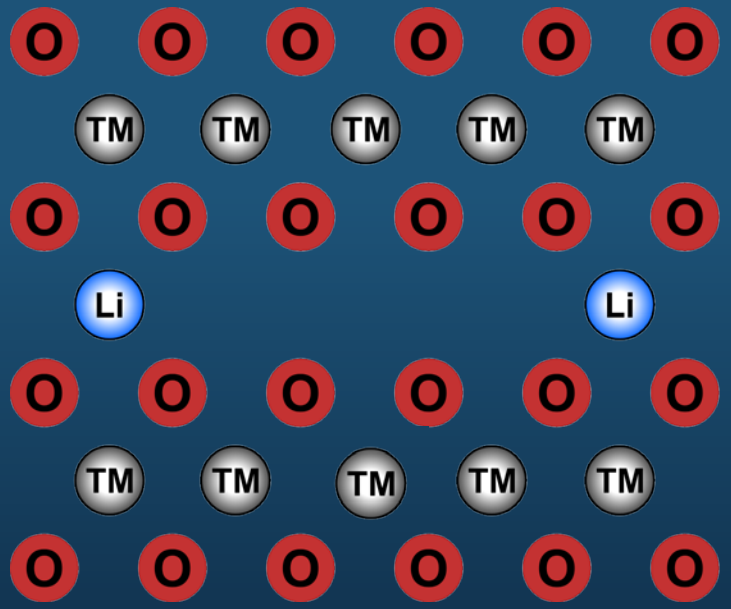
- Kristin Persson(LBNL), Venkat Shrinivasan (LBNL), Tony Burrell (ANL), Mali Balasubramanian (ANL), Dong Su (Brookhaven), Feng Wang (Brookhaven)

Master specific capacity plots (one electron)

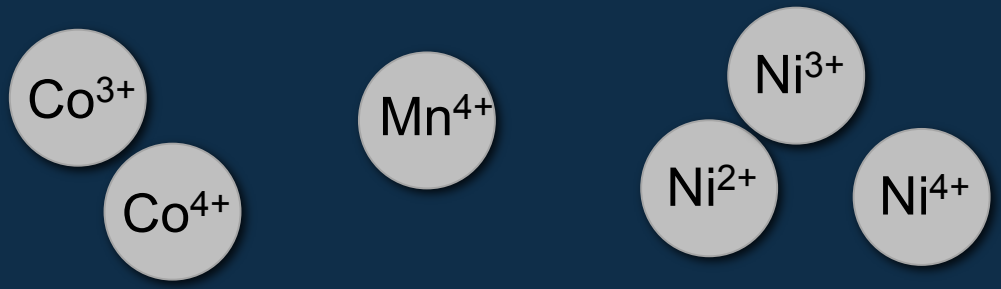


Relevance

- Layered cathodes have the highest theoretical energy densities of any cathode class. But they remain sub-optimal, reaching only about 2/3 of their theoretical capacity
- Currently limited chemistry to work with: Co, Mn, Ni … Other chemistries lead to disorder upon cycling
- Many new high capacity materials are Li-excess. Why ?



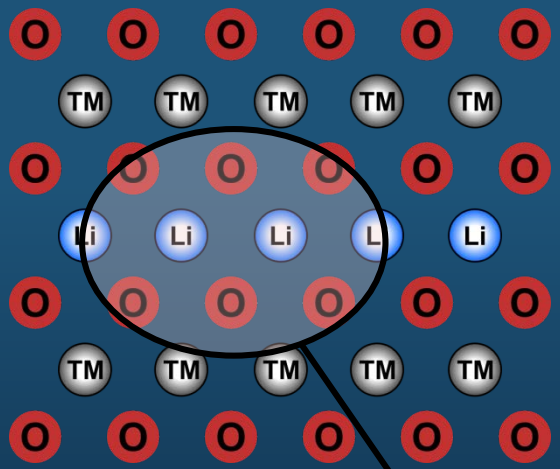
Our best materials: LCO, NCA, NCM, LRNCM

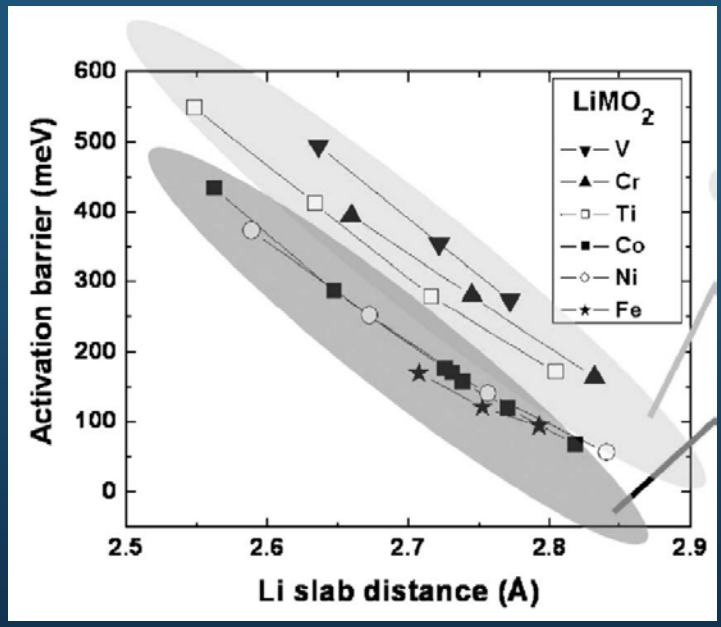


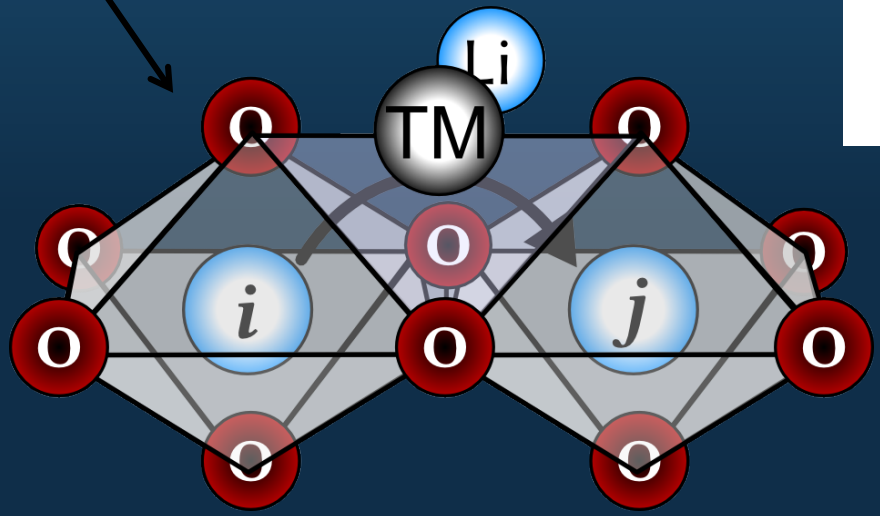
Project objectives

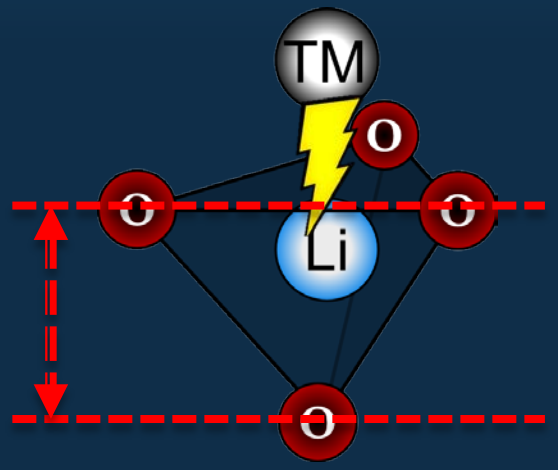
- Identify the **structure of layered cathodes** that leads to high capacity.
- Understand the role of disorder on capacity and rate
- Give insight into the role of **Li-excess**
- Develop predictive modeling of **oxygen charge transfer** and oxygen loss.
- Develop very **high capacity layered cathodes** with high structural stability (> 250 mAh/g).

Accomplishment (1) Li diffusion mechanism in "rocksalts"







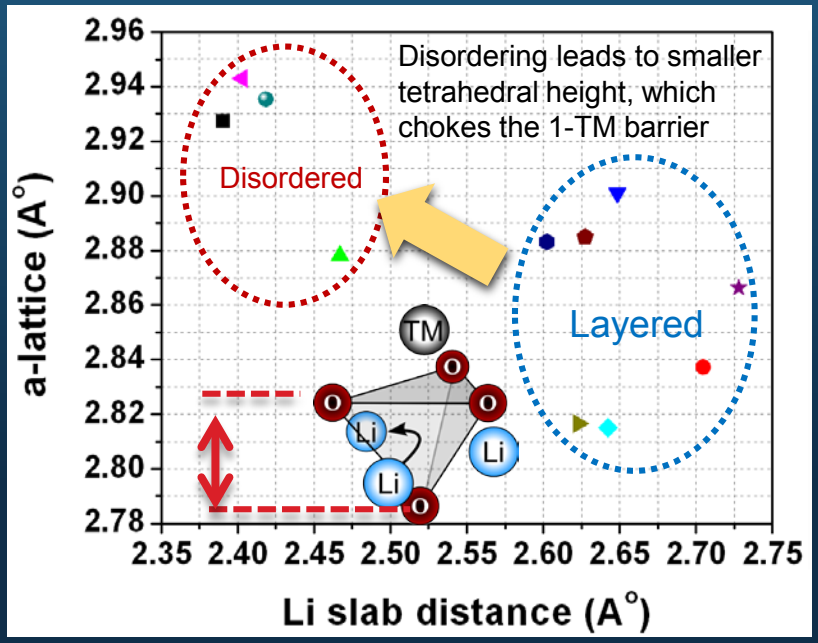


Li hopping from oct to oct site through tetrahedral site

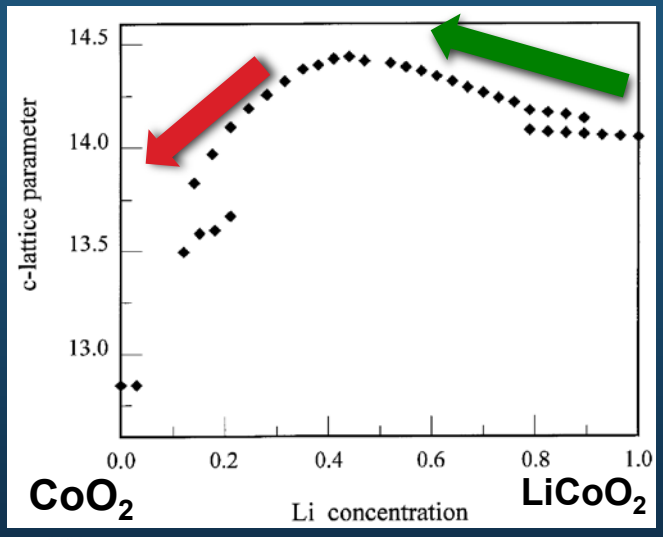
Tetrahedral site is approximately the activated state

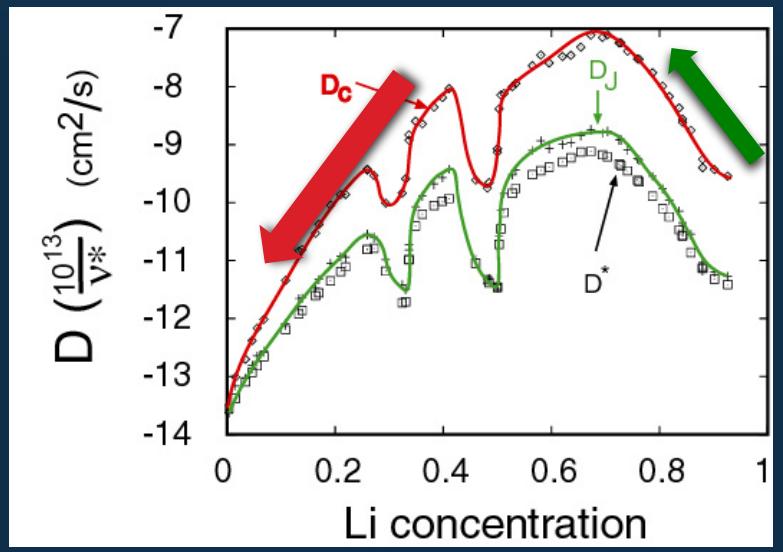
Disorder and high delithiation both cause slab distance to reduce thereby killing Li mobility

Disorder



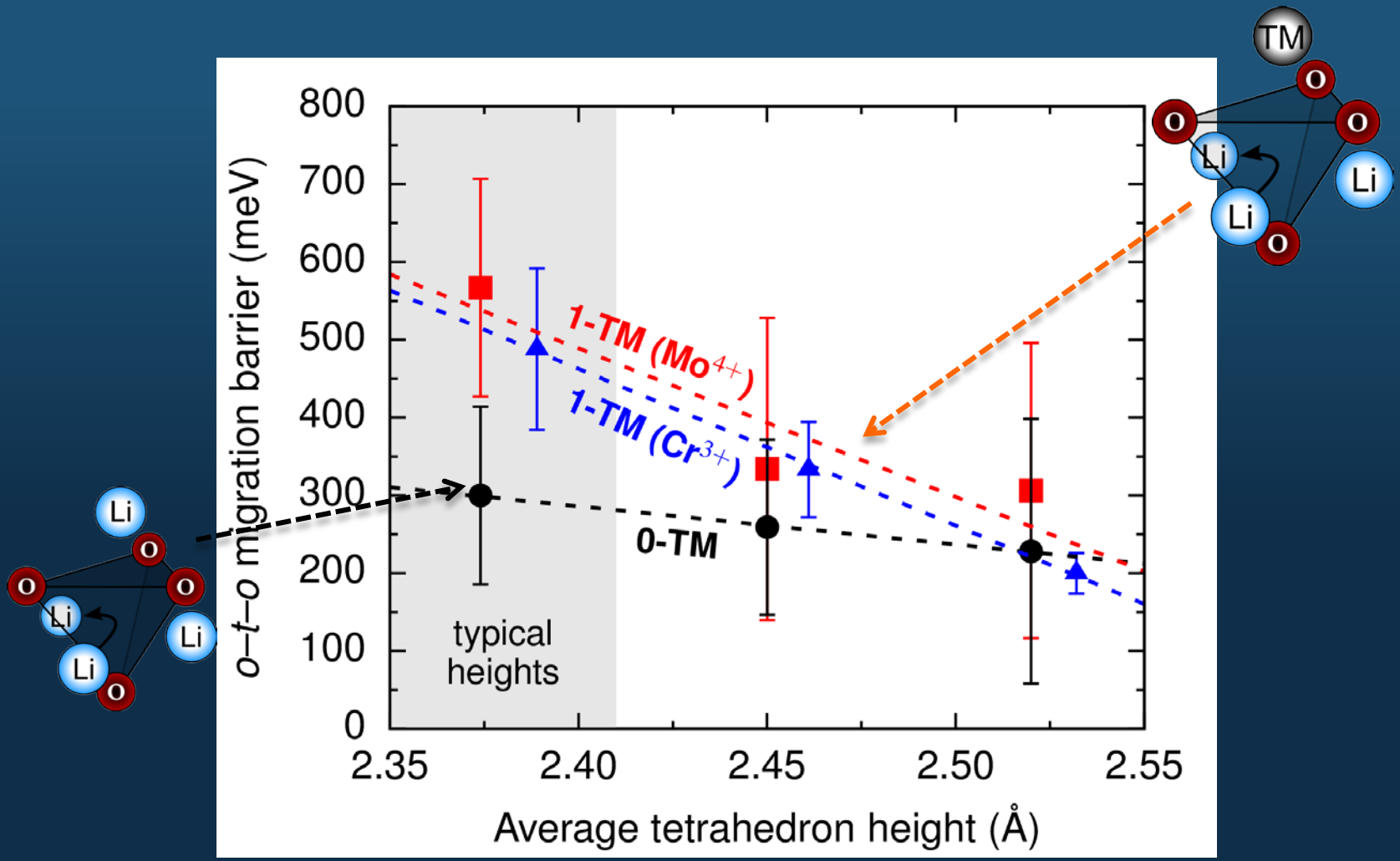
Delithiation





If we can design structures that tolerate disorder we will also solve the top of charge mobility problem

Approach (1): Use diffusion mechanism that is less tolerant to lattice parameter: Calculations show that 0-TM channels are much less sensitive to lattice parameter

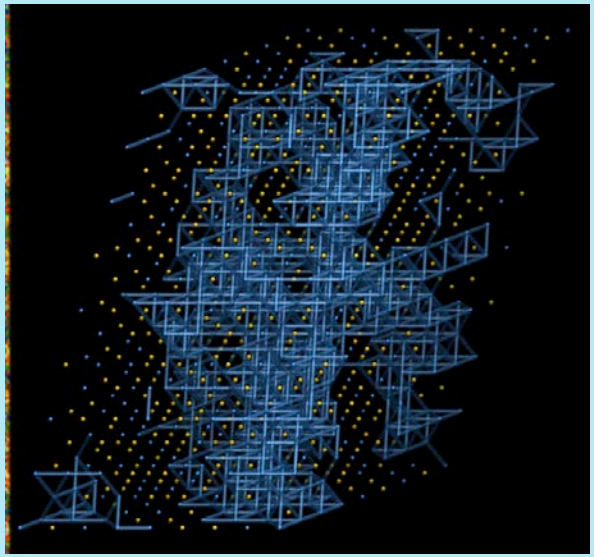


Approach (2) Monte Carlo simulations to understand percolation of good diffusion channels in partially disordered structures

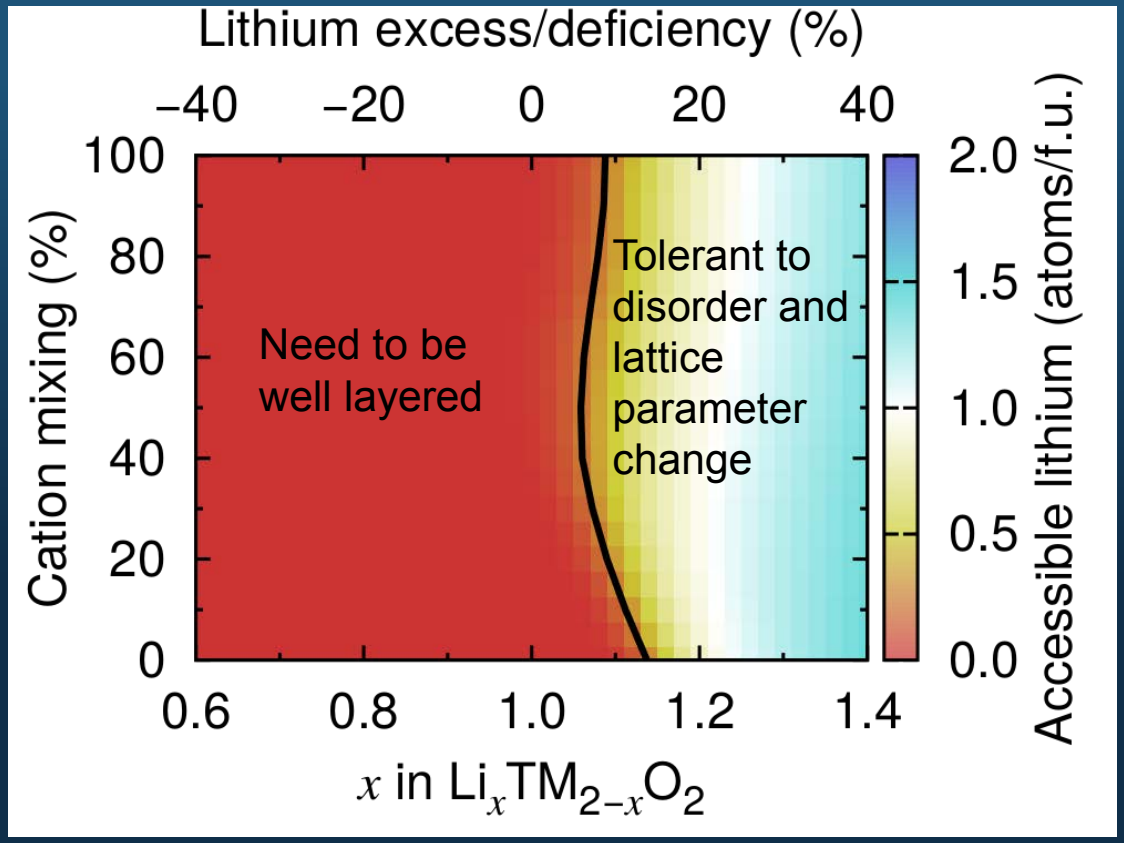
In other words:
When do 0-TM channels form a **percolating network**?

APPROACH

Monte Carlo simulation to find percolation thresholds for 0-TM diffusion channels

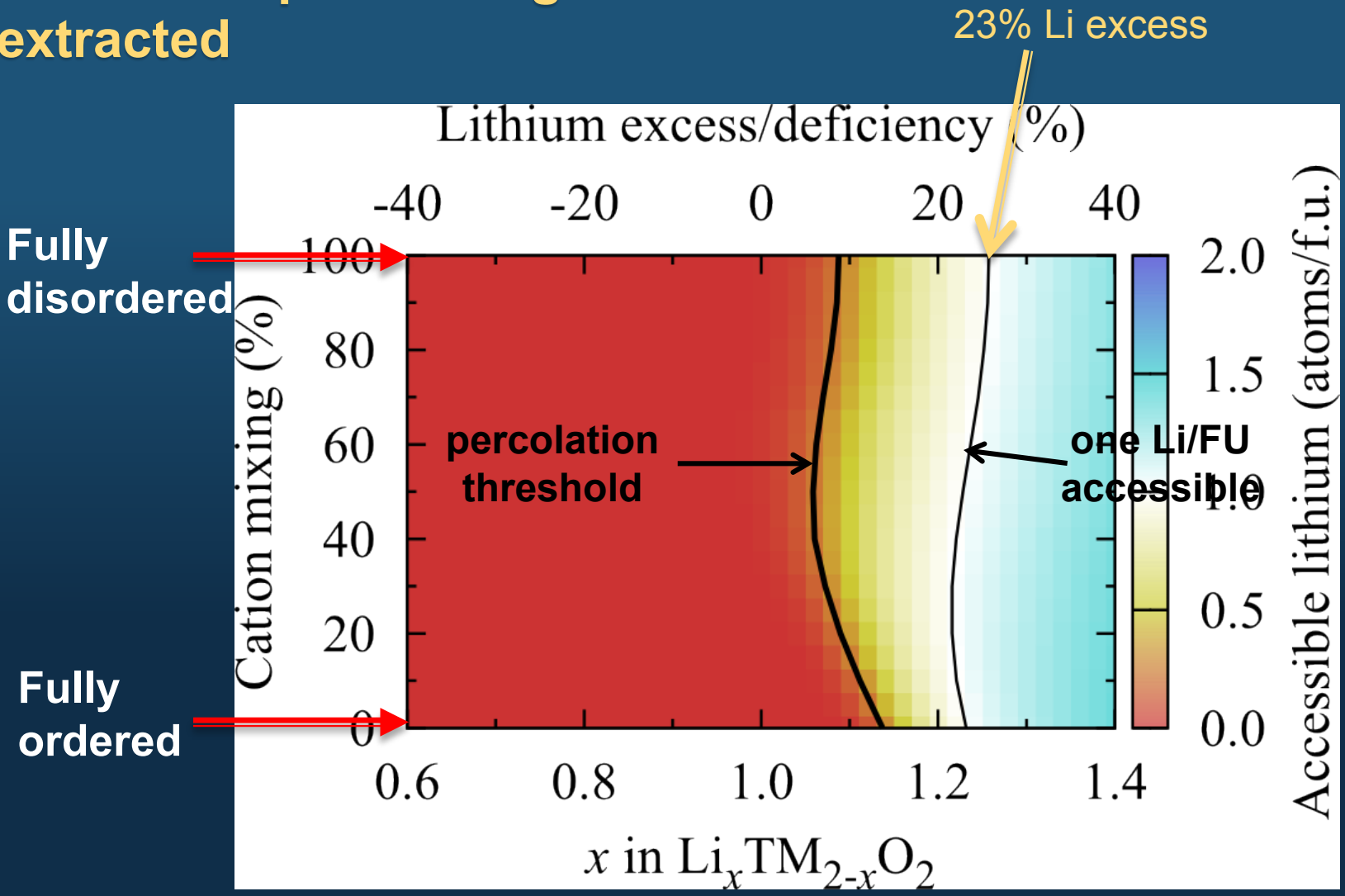


Accomplishment (2): Percolation map for 0-TM shows which compositions will be tolerant to disorder and lattice parameter reduction

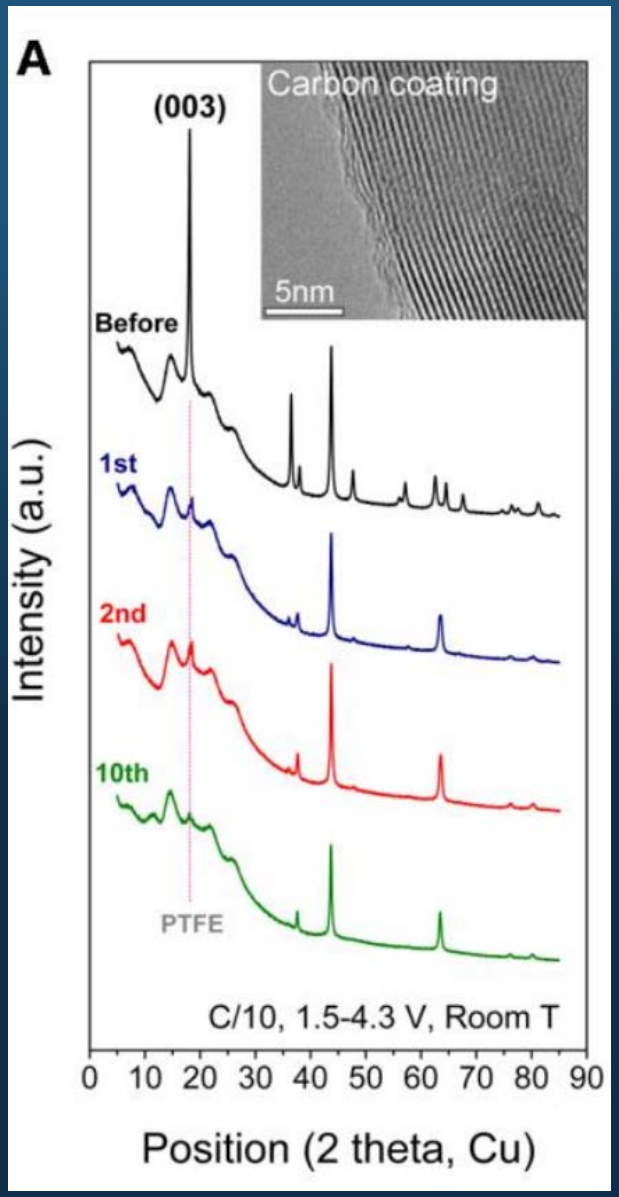


- By adding Li excess > 10% the material achieves an additional Li diffusion mechanism which is insensitive to lattice parameter

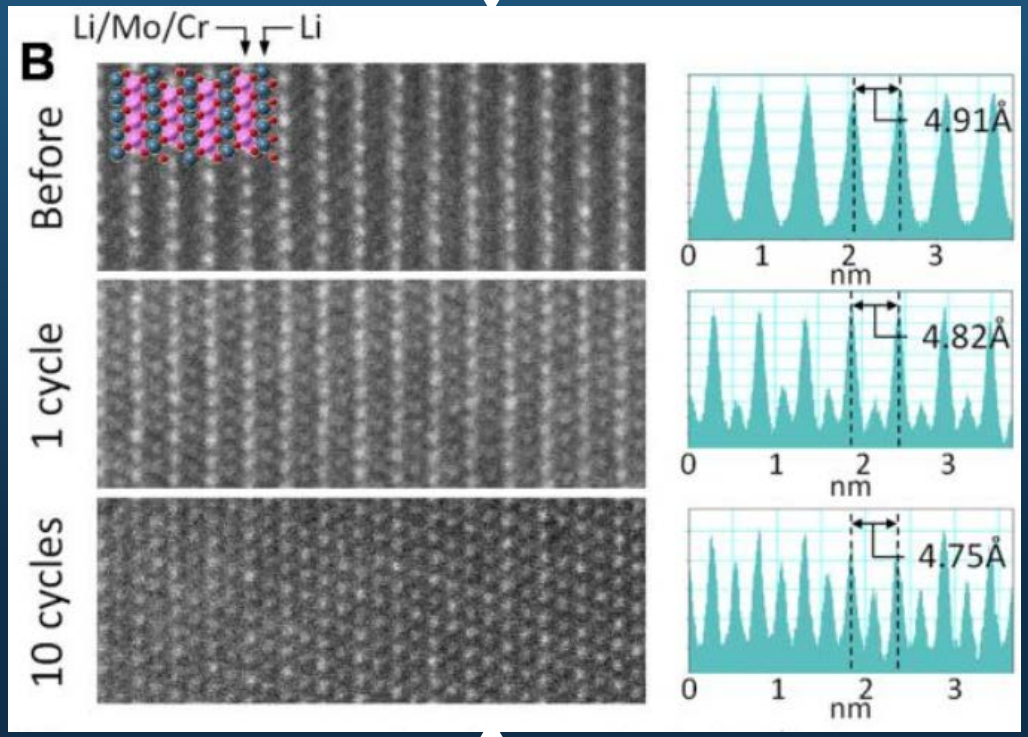
Accomplishment (4): Model for practical capacity. Amount of Li in the percolating cluster is the amount that can be extracted



Accomplishment (5): $Li_{1.211}Mo_{0.467}Cr_{0.3}O_2$: a fully disordered material that cycles with high capacity



well-separated
Li and TM layers

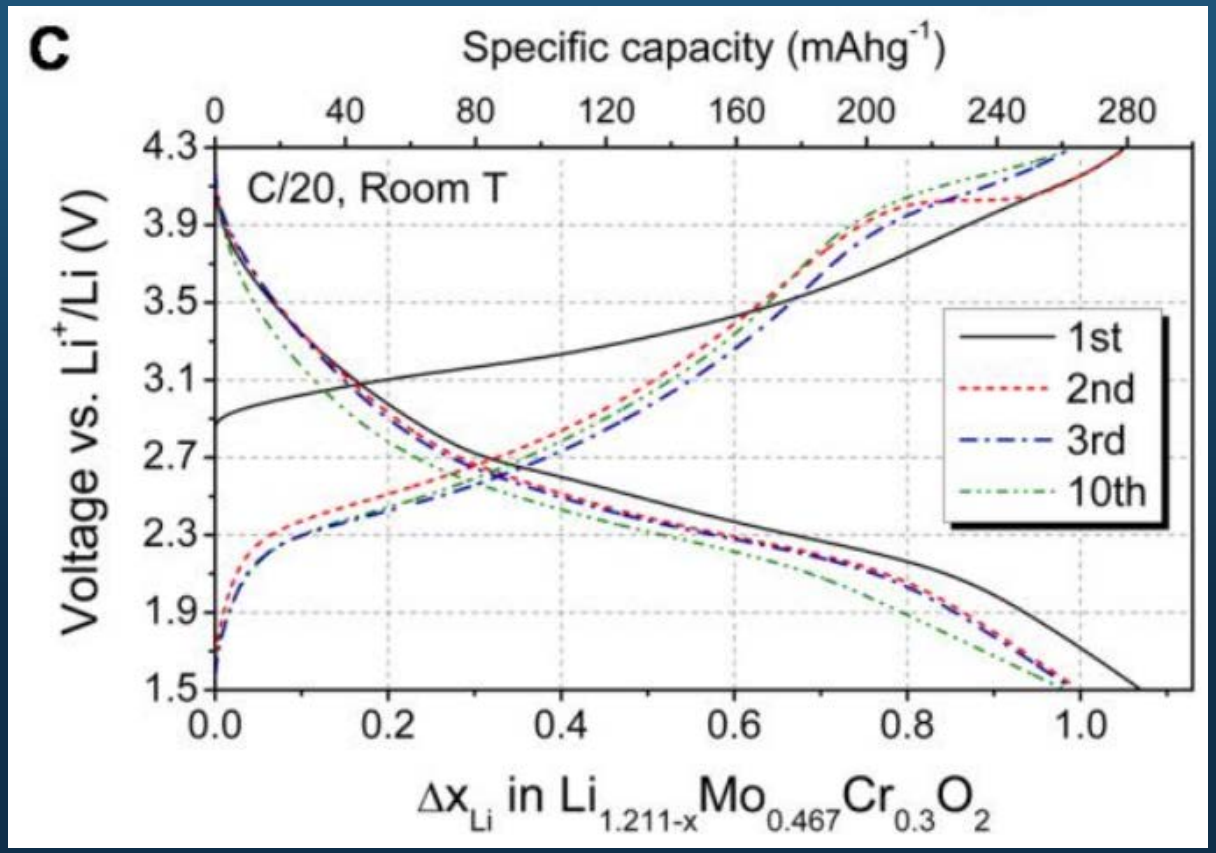


intense
cation mixing

$Li_{1.211}Mo_{0.467}Cr_{0.3}O_2$ (LMCO): A Material with near theoretical capacity

280mAh/g

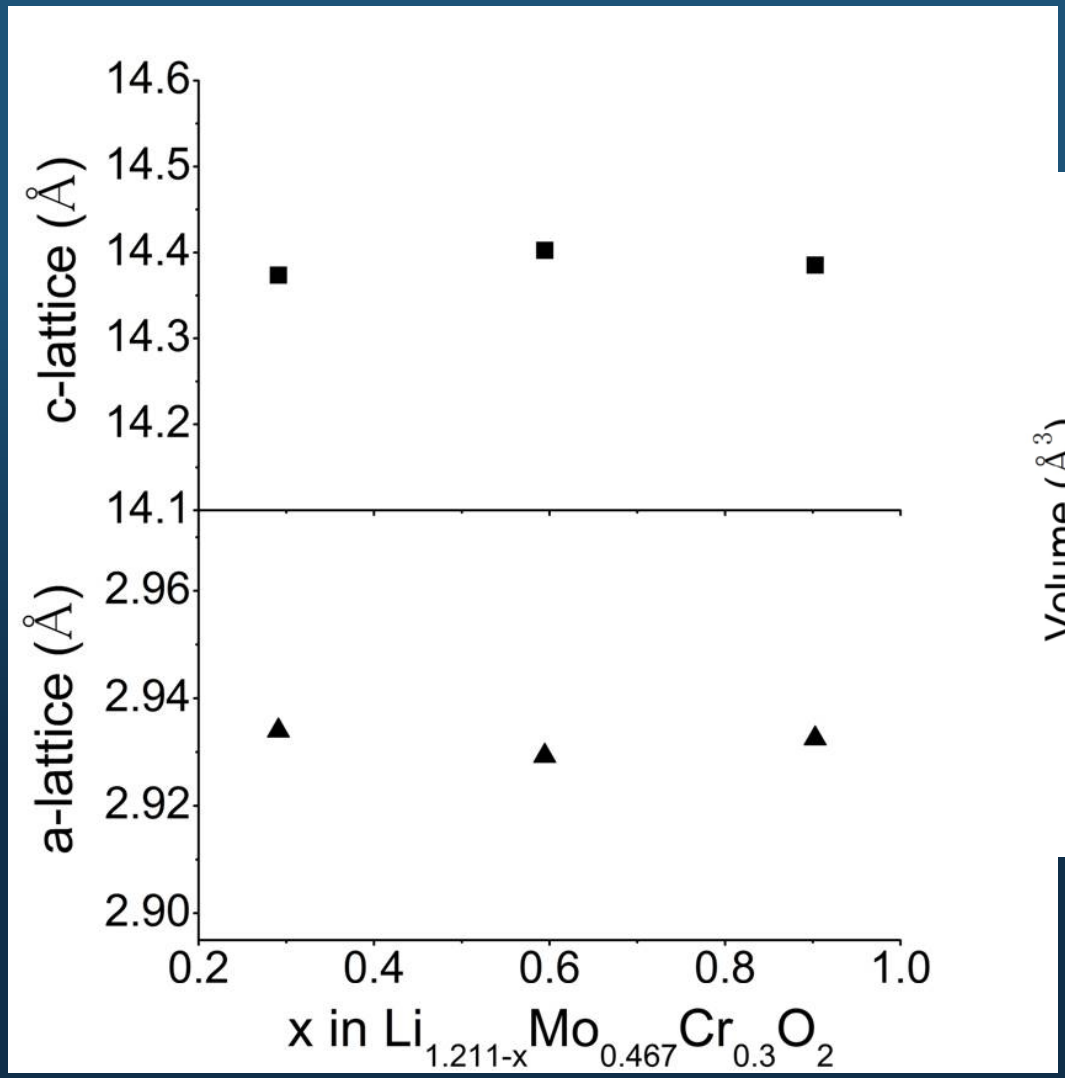
$LiMO_2$ ⟵ MO_2

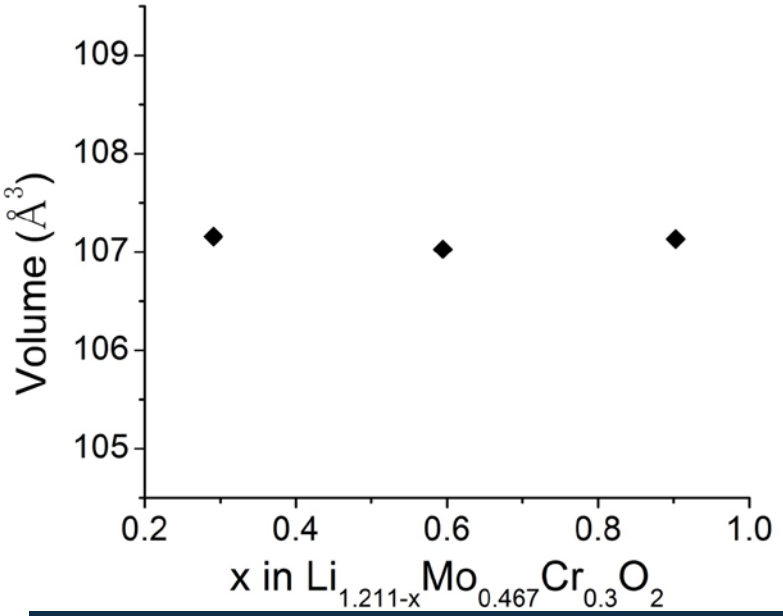


712 Wh/kg
3350 Wh/l
Density = 4.7

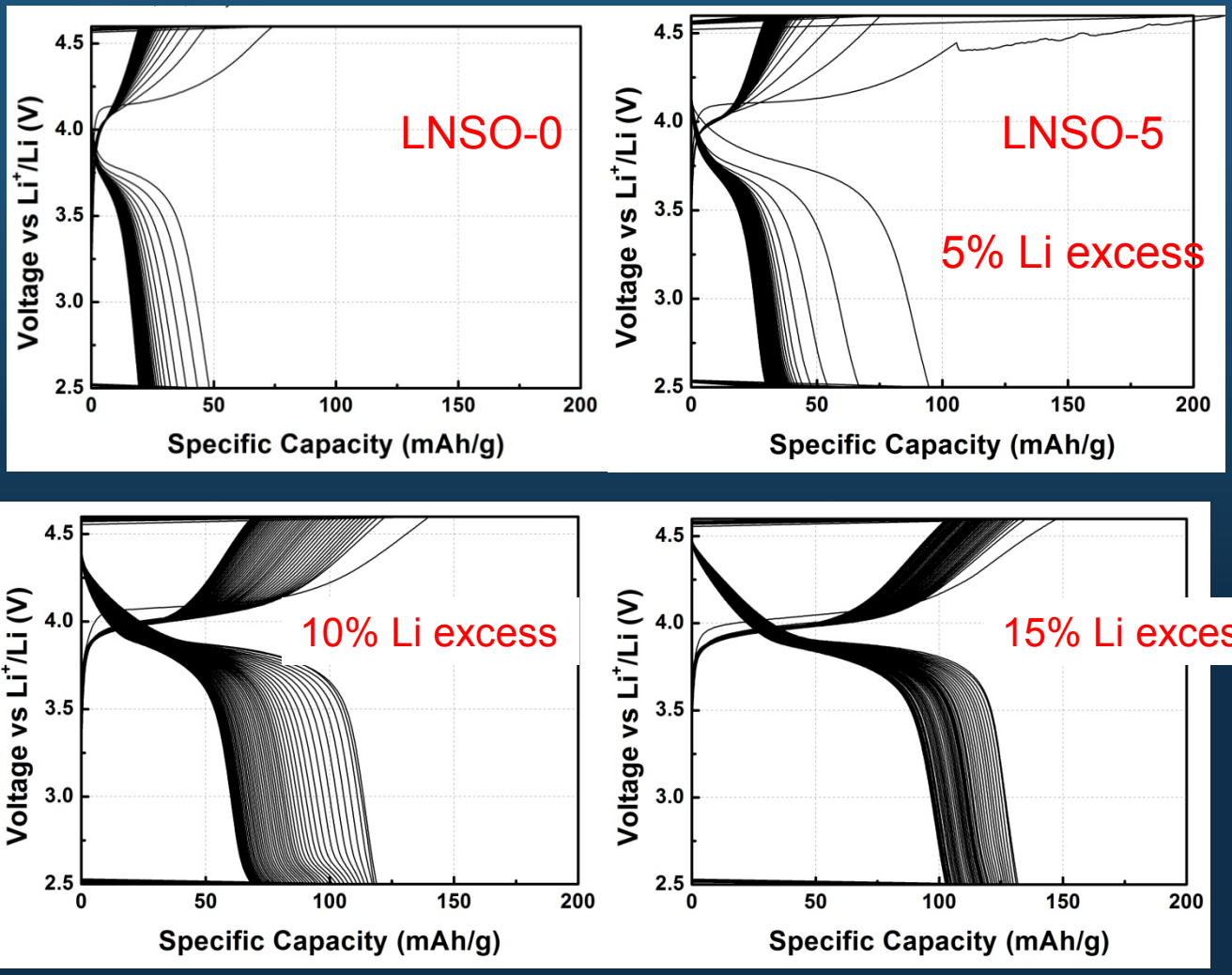
J. Lee, A. Urban, X. Li, D. Su, G. Hautier, G. Ceder, *Unlocking the Potential of Cation-Disordered Oxides for Rechargeable Lithium Batteries,* Science, 343 (6170), 519-522 (2014)

Accomlishment (6): First zero strain cathode !





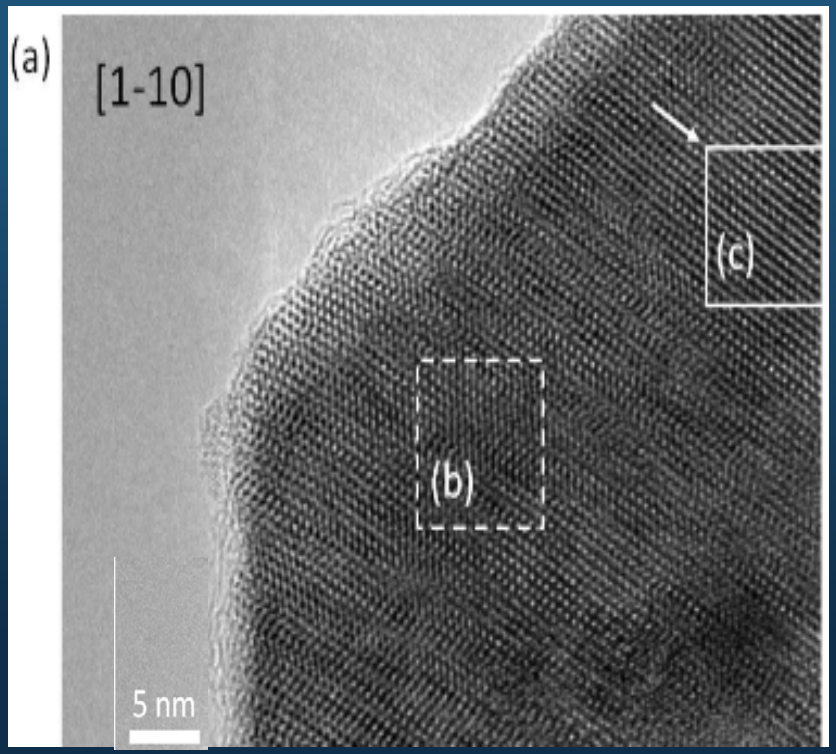
Accomplishment (8): Improve $Li(Ni_{2/3}Sb_{1/3})O_2$ by adding lithium excess?

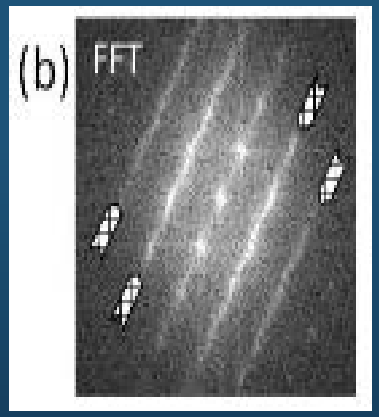


X. Ma, et al., J. Power Sources (2007)

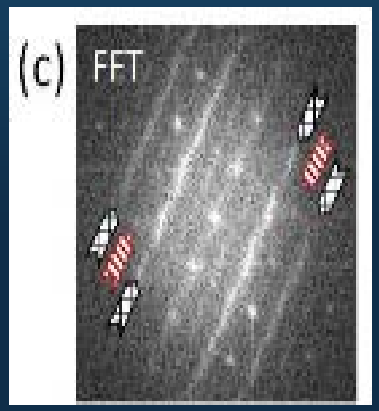
N. Twu et al. NanoLetters (2015)

Within a single particle of $Li_{1.15}Ni_{0.47}Sb_{0.38}O_2$, there are two domains with different superstructures





Fourier transform inside dashed box

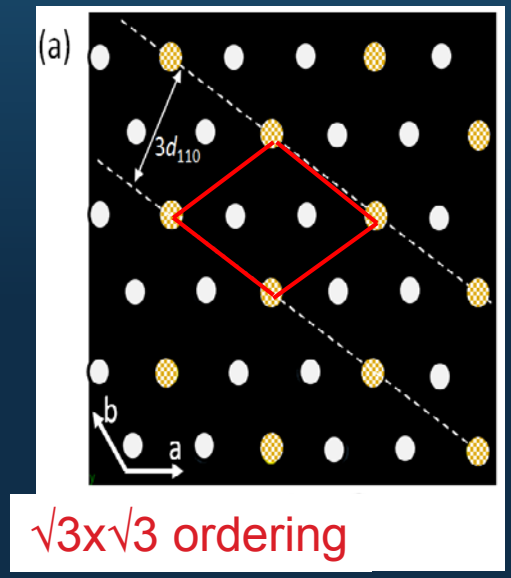


Fourier transform inside solid box

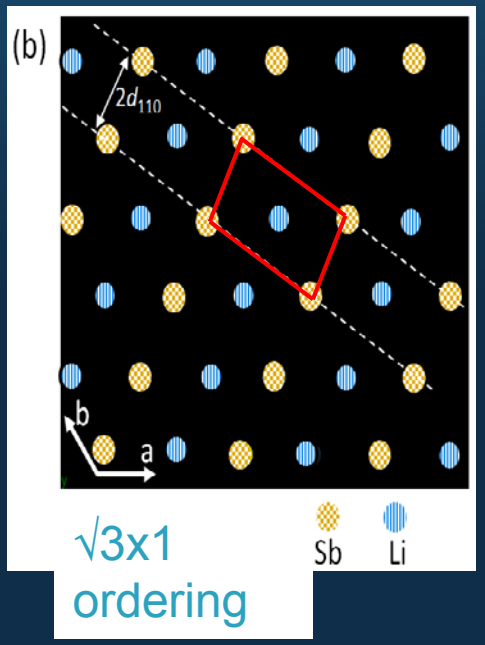
N. Twu et al. NanoLetters (2014)

We identified one domain to be √3x√3 Ni-Sb, and propose a 2nd domain of √3x1 Li-Sb

$Li[Ni_{2/3}Sb_{1/3}]O_2$ domain with √3x√3 honeycomb ordering



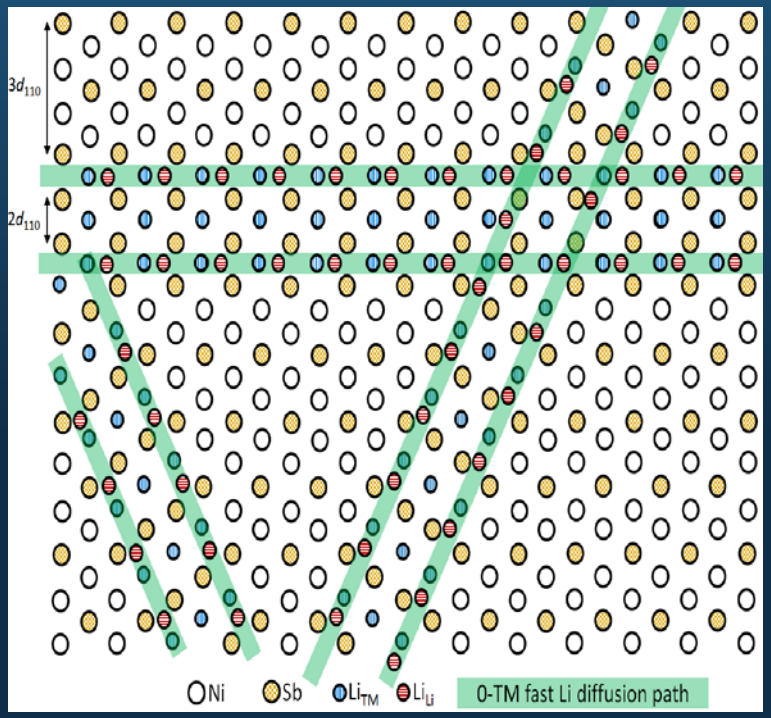
$Li[Li_{0.5}Sb_{0.5}]O_2$ domain with √3x 1 honeycomb ordering



N. Twu et al. NanoLetters (2014)

Implications of a two domain microstructure

In the transition metal layer, excess Li segregates into 1D Li-Sb stripe domains within bulk domains of Ni-Sb. **The interface of the two domains forms 0-TM diffusion channels**.

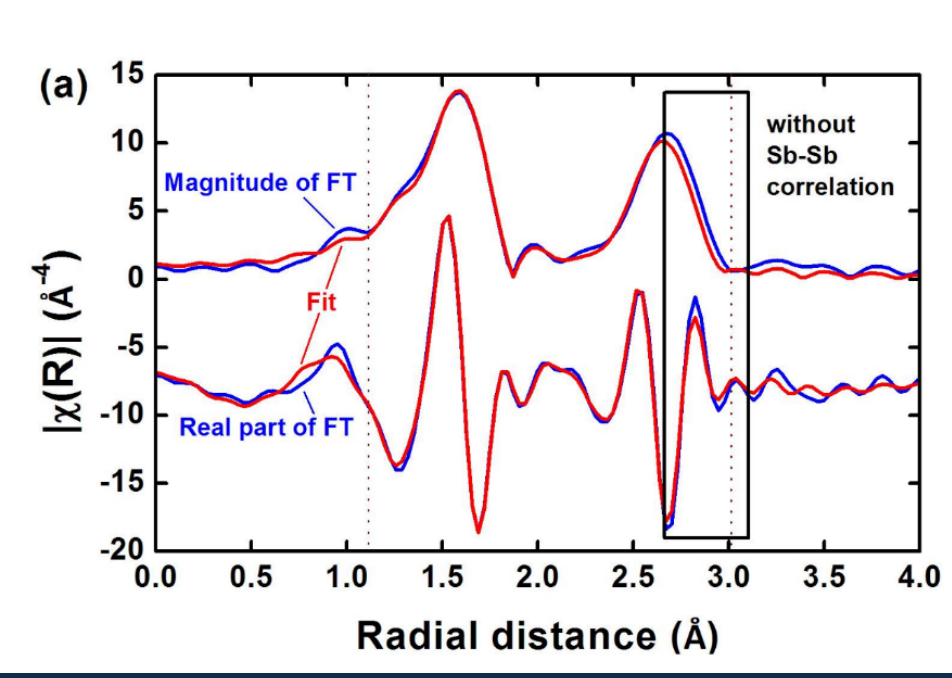


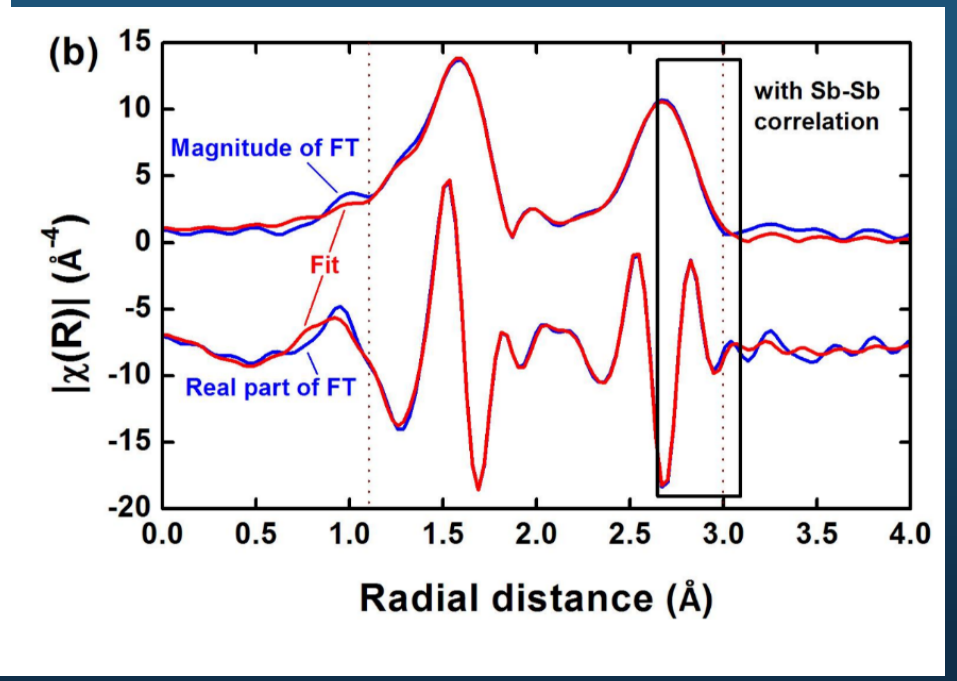
√3x1 Li-Sb stripe ordering

√3x√3 Ni-Sb honeycomb ordering

N. Twu et al. NanoLetters (2014)

EXAFS supports our structure model of Ni-Sb honeycomb divided by Li-Sb stripes





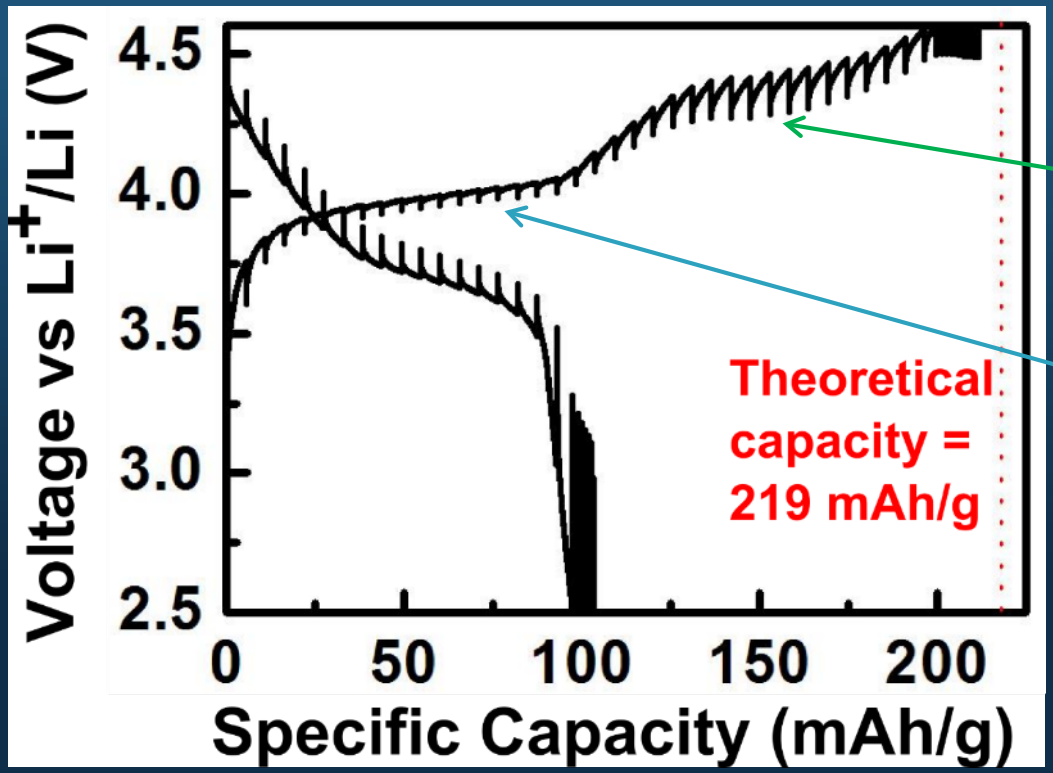
Fits improves with Sb-Sb at ~ 3.10Å

- ✓ Improvements in EXAFS fits support Sb-Sb nearest neighbors at ~ 3.10Å, which would be present in the Li-Sb stripe domain

Work performed in collaboration with Mali Subramanian (ANL)

All these materials have strong oxygen redox-activity

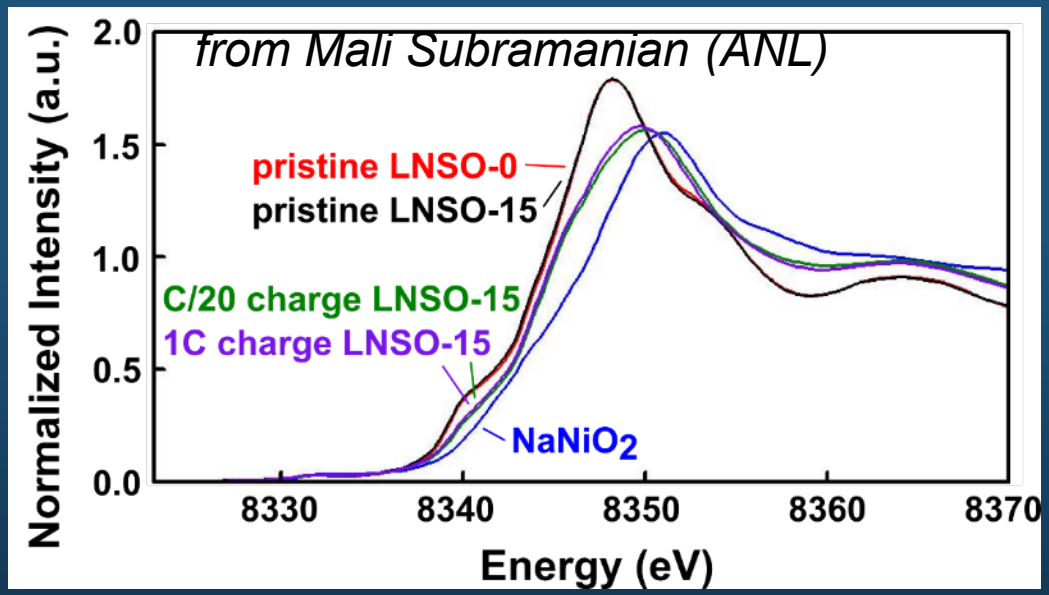
$Li_{1.15}Ni_{0.47}Sb_{0.38}O_2$ Theoretical $Ni^{2+/4+}$ is 219 mAh/g



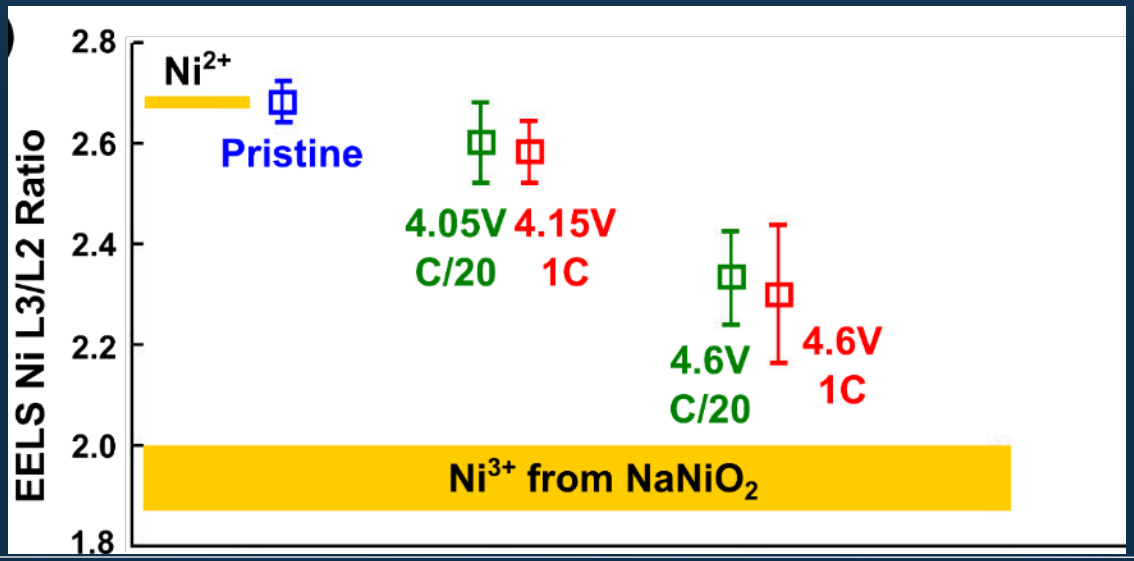
"Slow" process
Overpotential plateau at 4.45V
Equilibrium plateau at 4.25V

"Fast" process at 4V
Low overpotential

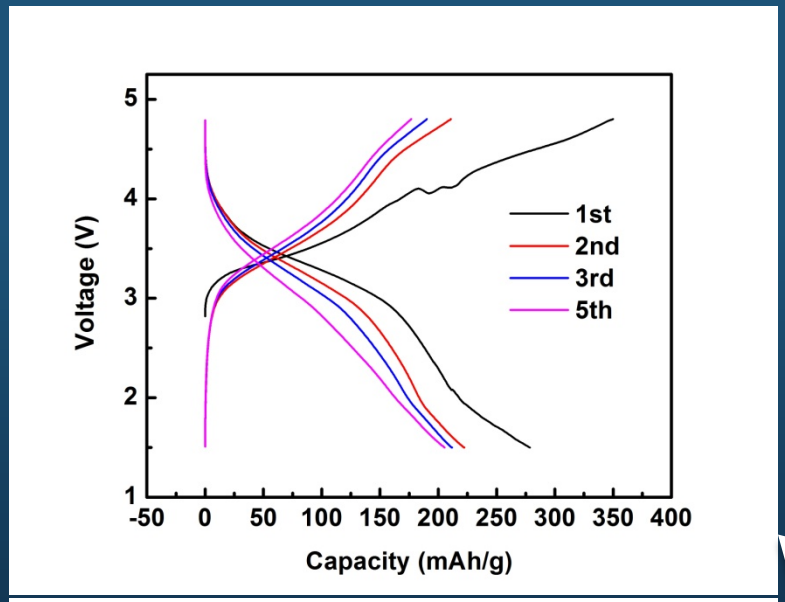
XANES and EELS both indicate Ni oxidation limited to +3

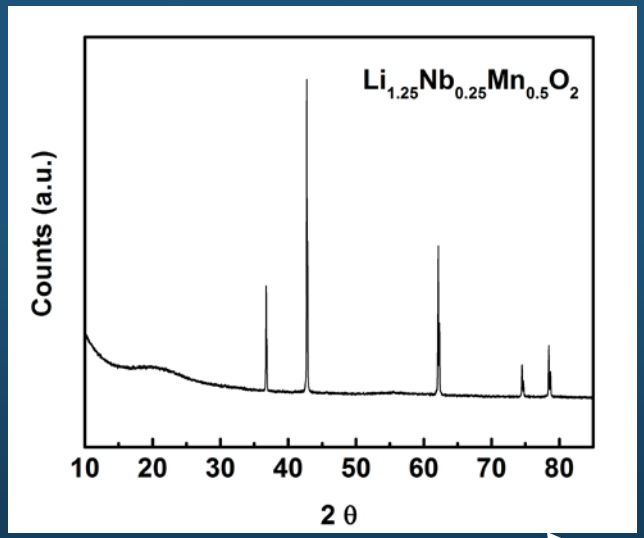


In this material oxygen redox sits below Ni^{3+}/Ni^{4+}



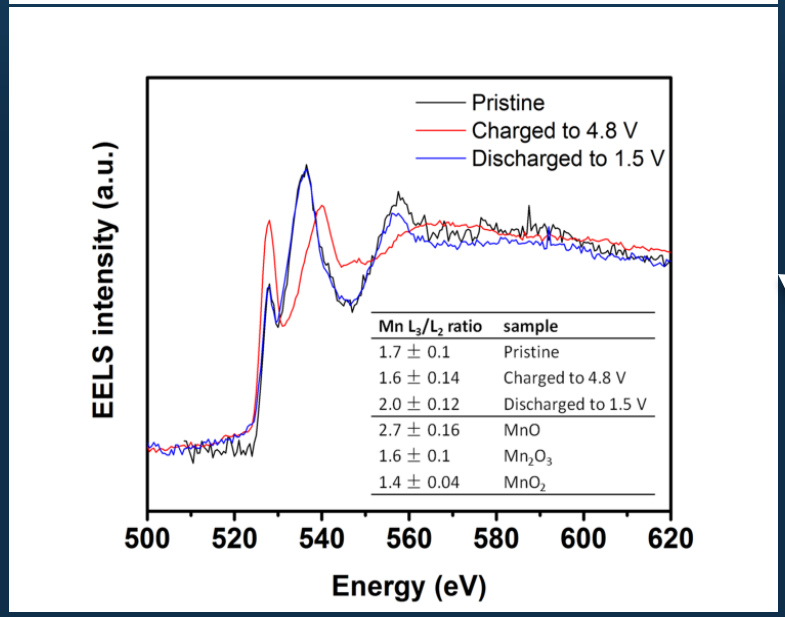
Accomplishment (7): New fully disordered materials with high capacity: $Li(Li,Mn,Nb)O_2$





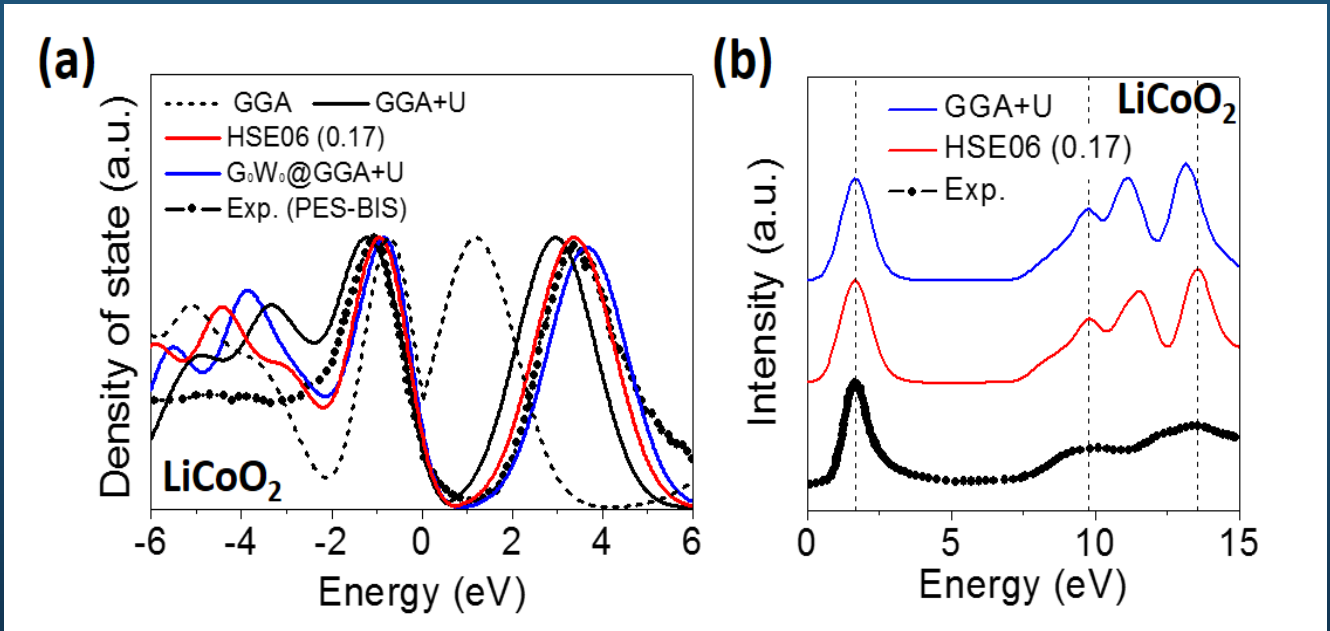
Fully disordered rocksalt

Considerably more redox capacity than expected from Mn3+/Mn4+

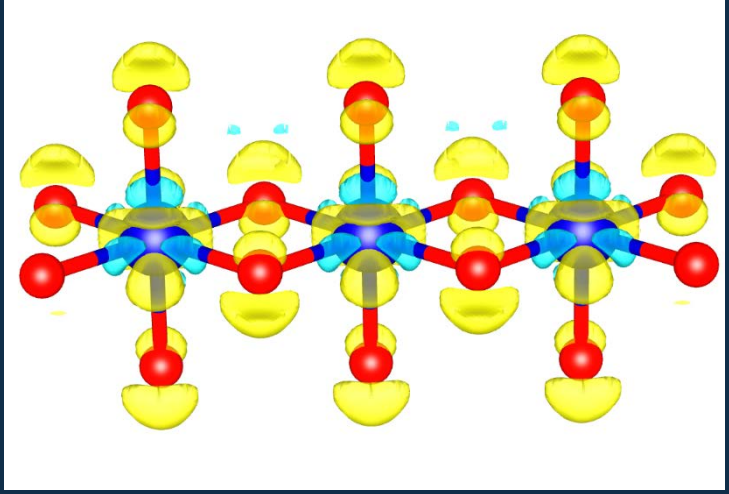


EELS shows first Mn oxidation, then reversible oxygen oxidation

Calibrate computational methods to accurately predict redox balance between TM and Oxygen



Calculated vs experimental Density of states and EELS spectrum



Calculated charge density change around Co and O upon oxidation of LiCoO2

Summary and strategy for high capacity cathodes

- Focus on well layered materials reduces chemistry options as most TM have some mobility
- Limits to achieving theoretical capacity in layered cathodes, and sensitivity to disorder come from same underlying physics: Sensitivity to bond length contraction around activated state
- Strategy to achieve theoretical capacity: percolate “0-TM” channels which are less sensitive to bond length changes
- This can be achieved with Li-excess which cause percolation of 0-TM channels
- 280 mAh/g is achievable

Future Work

- Expand research into the Li-excess disordered rocksalts for high capacity: Li(Li,Mn,Nb)O2, and Ni-Ti based systems in order to combine high capacity with high voltage.

- Model voltage slope in disordered materials. Why do some have a lot more slope than others ? Chemistry dependence ?

- Li-excess seems to bring down voltage for oxygen oxidation. Develop accurate models to predict oxygen oxidation. Relation to oxygen loss ?

Milestones

Month Year	Milestone	Status
December 2014	Demonstrate capability to accurately predict oxygen redox activity in cathode materials by comparing calculations to spectroscopic data.	Complete
March 2015	Develop model for Na-vacancy ordering in Na-intercalation compounds	Complete
June 2015	Develop model for effect of Li-excess in $Li(Li,Ni,Sb)O_2$.	Complete
September 2015	Develop model for oxygen oxidation	Ongoing

Questions ?

Collaborations

- K Persson (LBNL) on Li-excess materials
- Mali Subramanian (ANL): EXAFS and in-situ probing of electronic structure of Li excess materials
- Tony Burrell: discussions on LRNMC materials (Li-rich) and applicability of theory to voltage fade materials
- Feng Wang (Brookhaven): synthesis of materials
- Dong Su (Brookhaven): characterization (TEM)
- Venkat Shrinivasan (LBNL): modeling

COMPANIES

- Umicore: Synthesis and evaluation of materials
- Bosch: System level evaluation of materials

Response to Reviewer Comments

The reviewers generally acknowledge that seeking out fundamental mechanisms and new high capacity positive electrode materials is a huge challenging and that the PI has readily taken on these activities, and stated that this is an “important contribution”

Some reviewers asked questions about the importance of Na-ion materials, een though that field has recently seen a lot of excitement

We have been reducing the activity in this area

Some reviewers asked about whether one could include surface effects on the kinetics of these material.

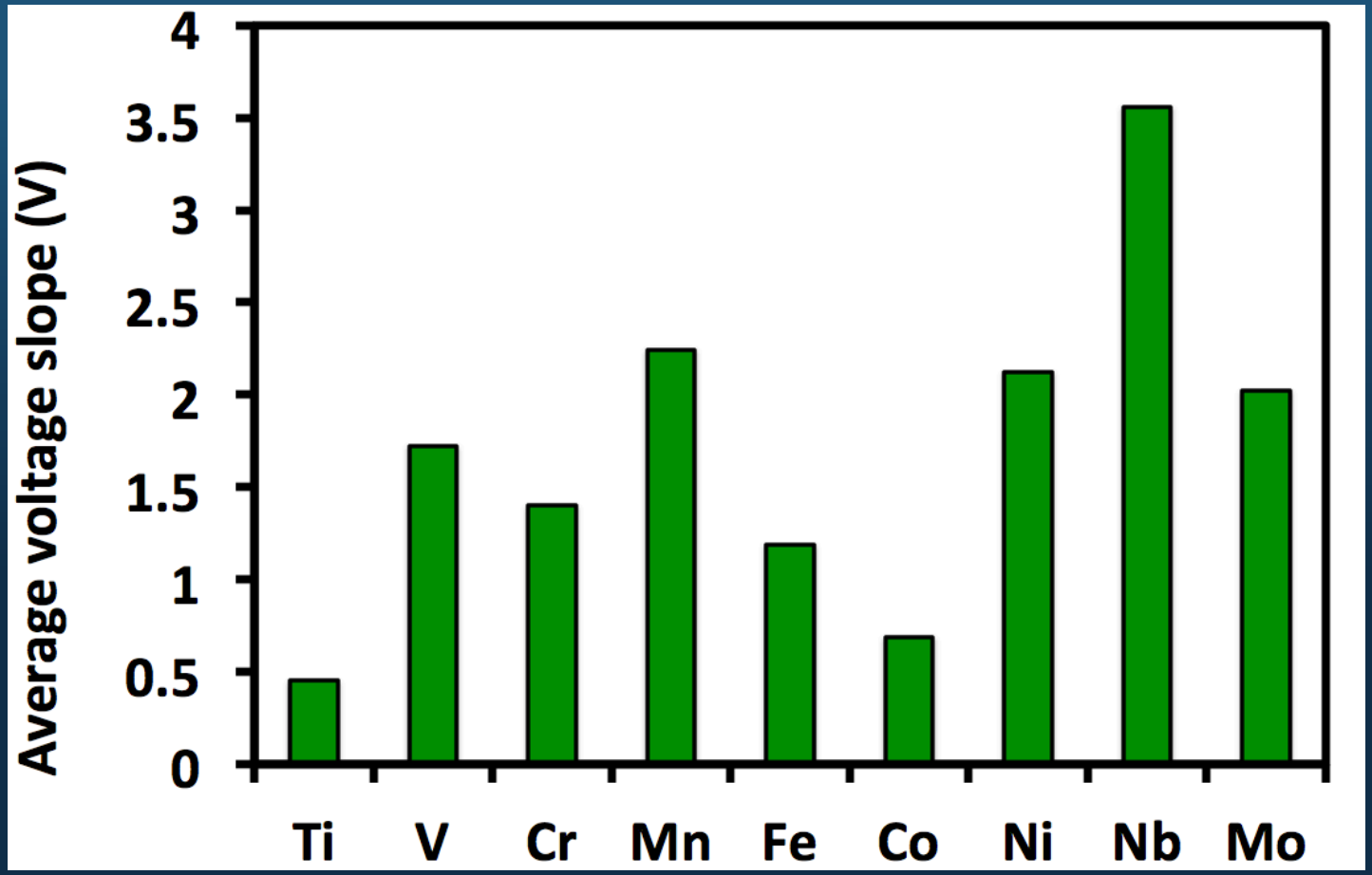
We appreciate the comment and are aware of the importance of surface regions that are distinct from the bulk. We have initiated studies to look at the surface layers on cathode materials in another program (EFRC). To retain a clear separation of programs we do not report on it at the AMR review

One reviewer asked whether the Li-excess materials are solid solution or composite in nature

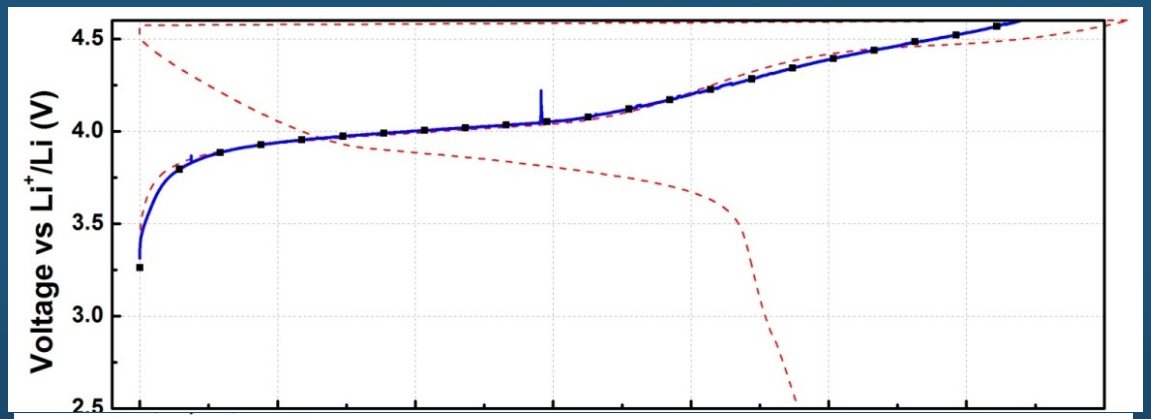
We have used TEM on several materials and find that the Ni-Sb systems contains domains with distinct compositions, the Mo-Cr and other novel materials do not

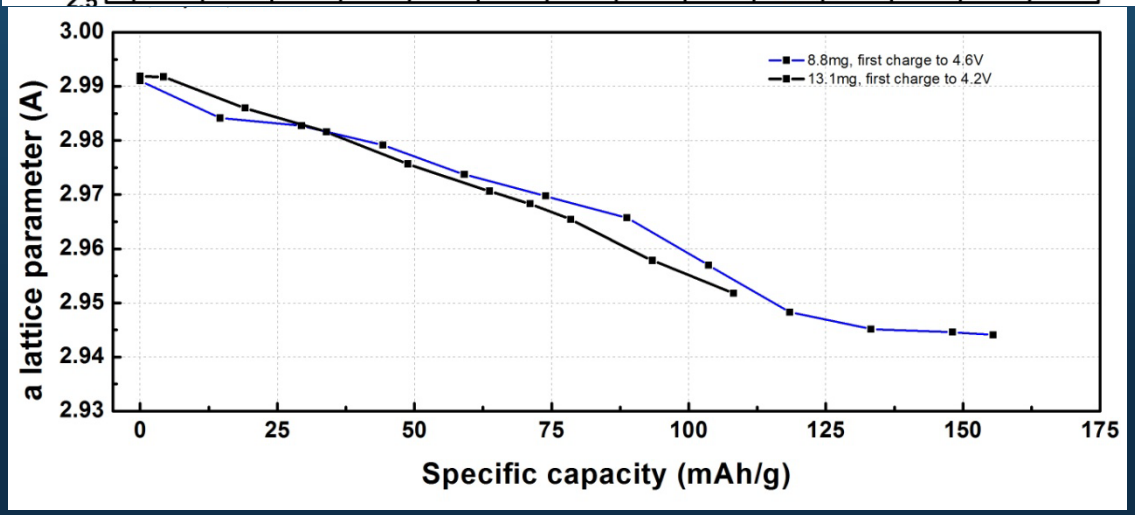
Back-up slides

A theoretical investigation into the slope of hypothetically disordered materials



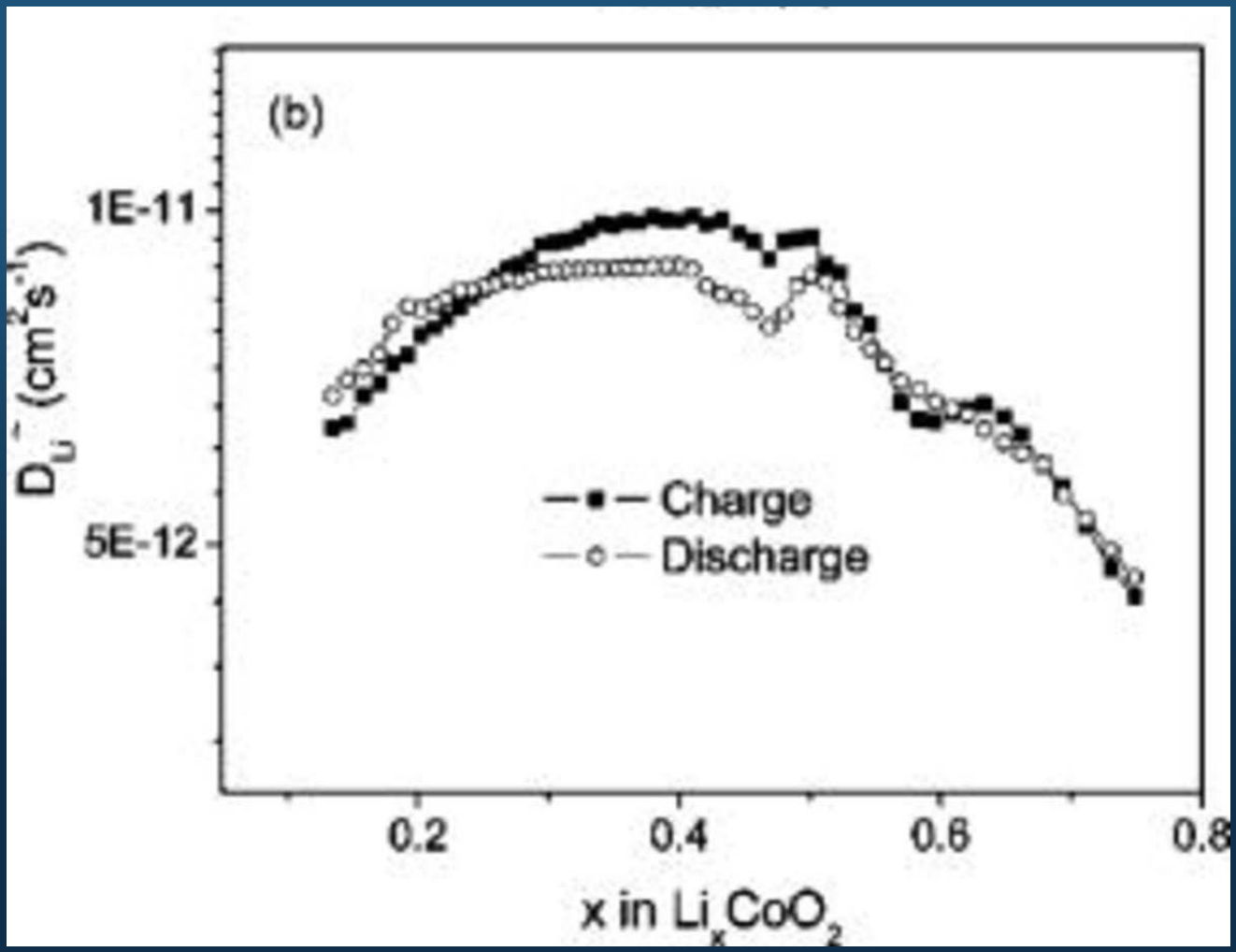
Oxygen versus metal redox activity ? $Li(Li_xNi_{2-4x/3}Sb_{x/3})O_2$





Can Ni be oxidized to Ni^{4+} in Li-rich materials ???

Chemical diffusion coefficient of Li in Li_xCoO_2 as obtained with PITT.



Xia H et al. J. Electrochem. Soc. 2007;154:A337-A342

Electronic structure determines Tet/Oct preference