Lithium Ion Battery Cathode Research at LBNL

Marca M. Doeff and Feng Lin

The CalCharge Experience

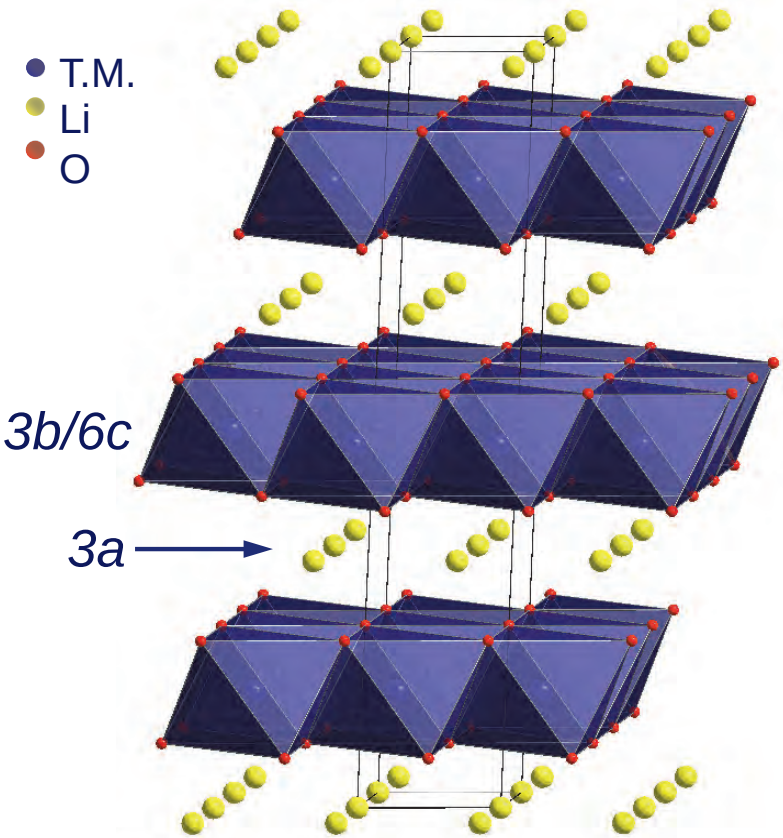
•"Working with LBNL gives you a great opportunity to work with an intelligent network and teamwork of the people from LBNL together with SLAC to discover and to understand some tricky problems from the battery world. The excellent experience of LBNL and also the network between LBNL and SLAC give you so many possibilities to answer your questions or solve your problems."

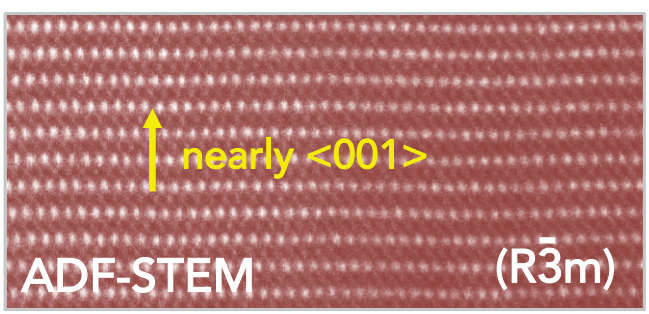
- VW embed at LBNL (Mirko Herrmann to Michel Fouré

- "If you want to stay relevant it's really nice to be able to talk to somebody from industry who can say, these are the problems we're having."

- Marca Doeff to Julie Chao, LBNL public information department, Today at Berkeley Lab, Feb. 12, 2015

NMC cathodes

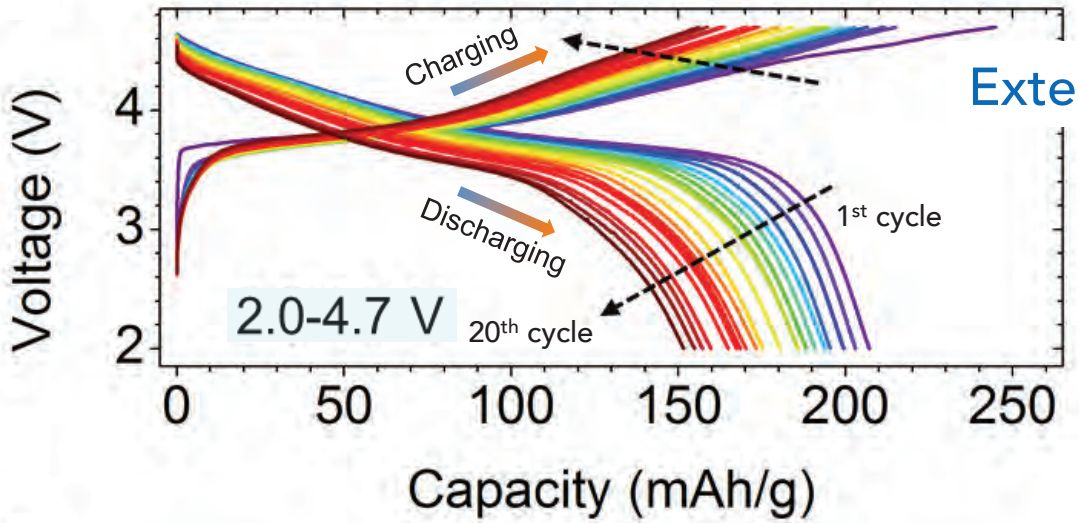




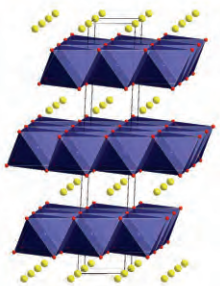
Lin *et al.* Scientific Reports 4, 5694 (2014)

- $Li[Ni_xMn_xCo_{1-2x}]O_2$, NMC (R3m)
  - x most commonly 1/3 (333)
  - Other compositions possible (e.g., 442)
  - Less Co means lower cost
  - Mn is inactive, there for structure
  - Ni is 2+, Mn is 4+, Co is 3+ in pristine materials
  - Ni and Co change oxidation states during electrochemical reactions
  - Practical capacity is somewhat higher than for traditional $LiCoO_2$ ~160 mAh/g
  - Theoretical capacity is ~280 mAh/g
  - Can we increase energy density by cycling more lithium in the structure?

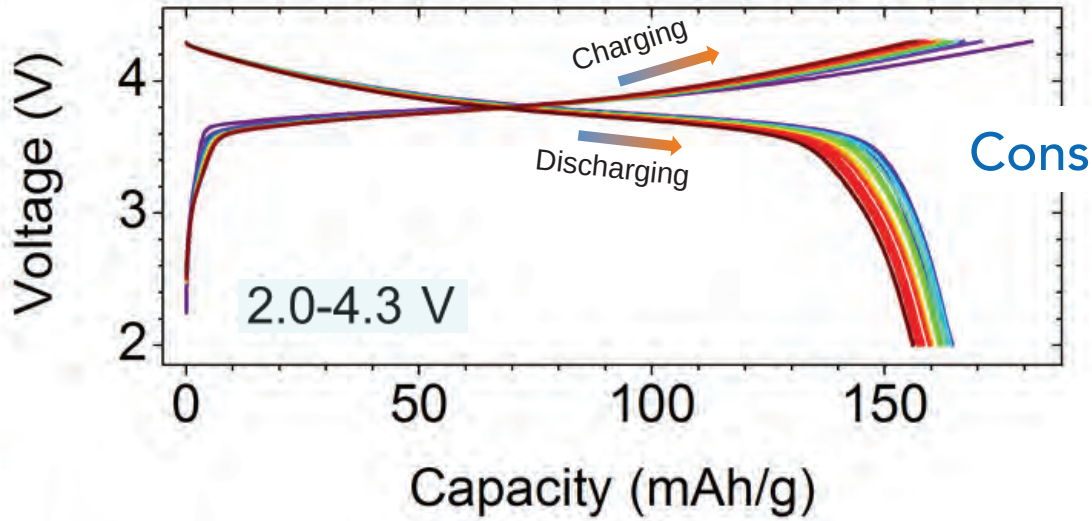
Electrochemistry of NMC cathodes



Extended lithium removal



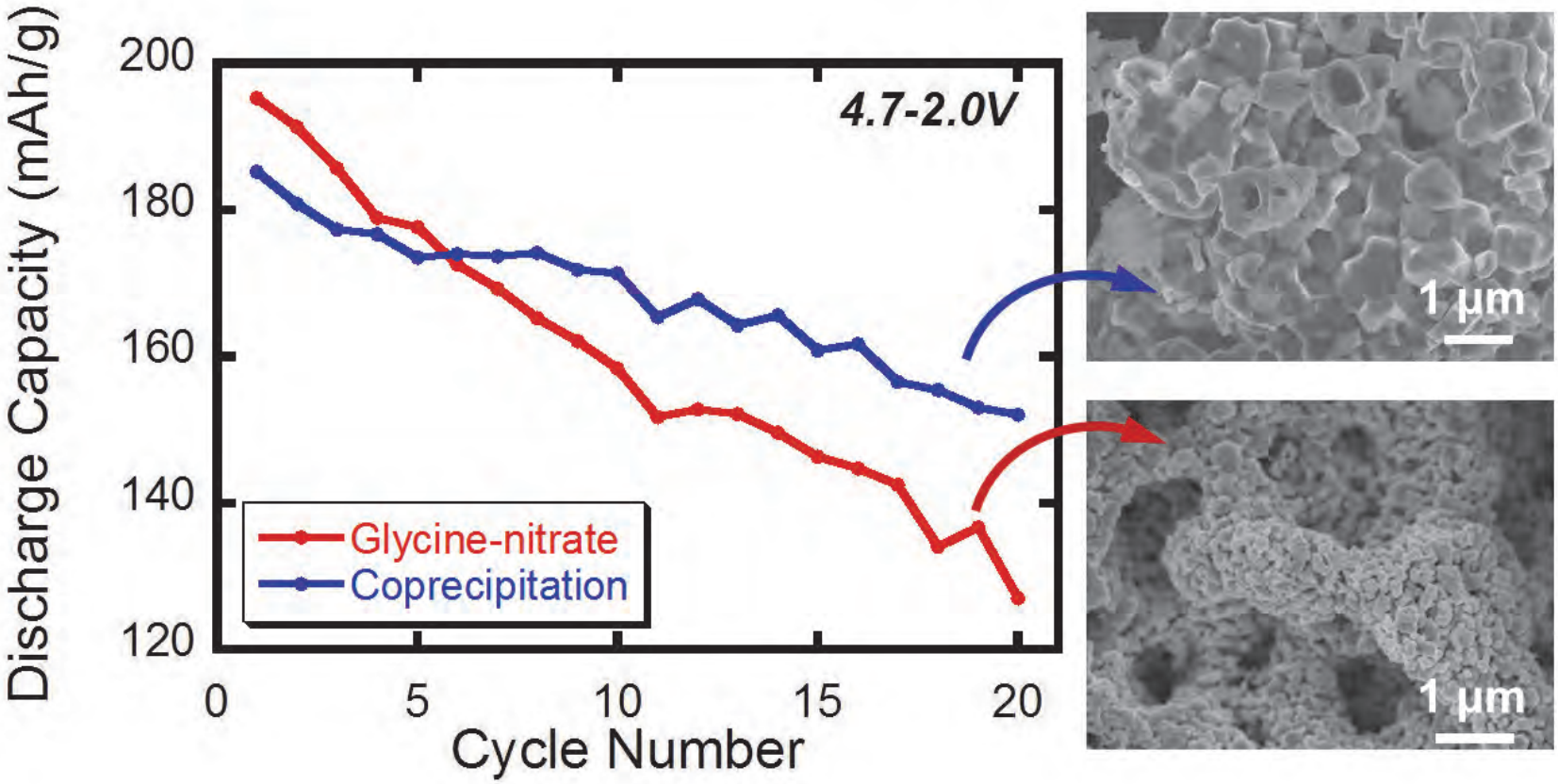
$Li_{1-x}Ni_{0.4}Mn_{0.4}Co_{0.2}O_2$



Conservative lithium removal

Lin *et al.* Nat. Commun. 5, 3529 (2014)

Does nanostructuring help?

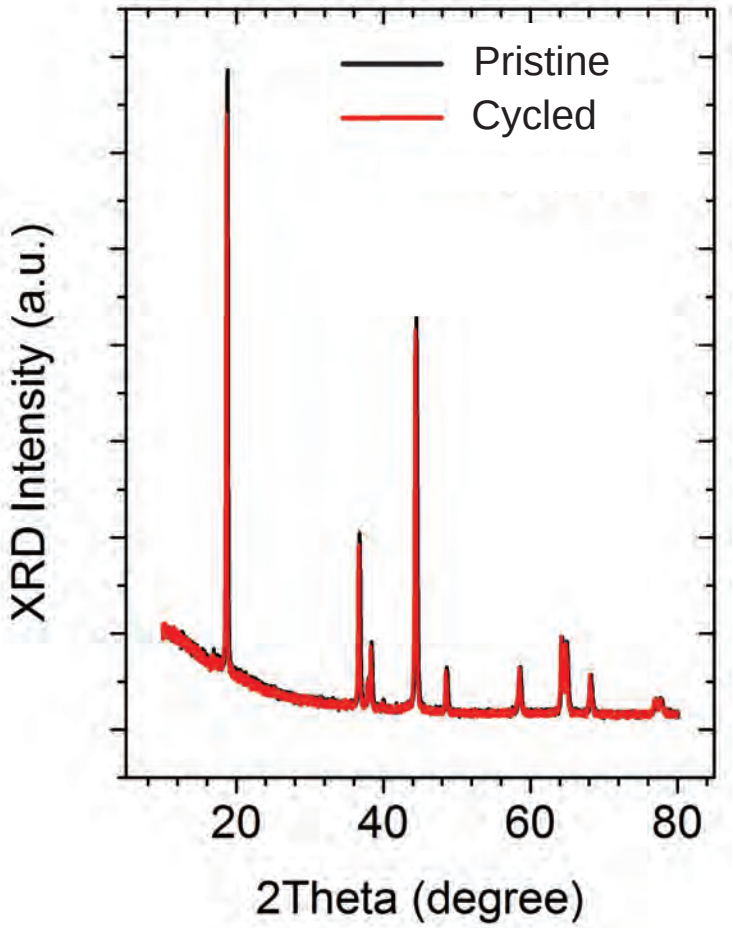


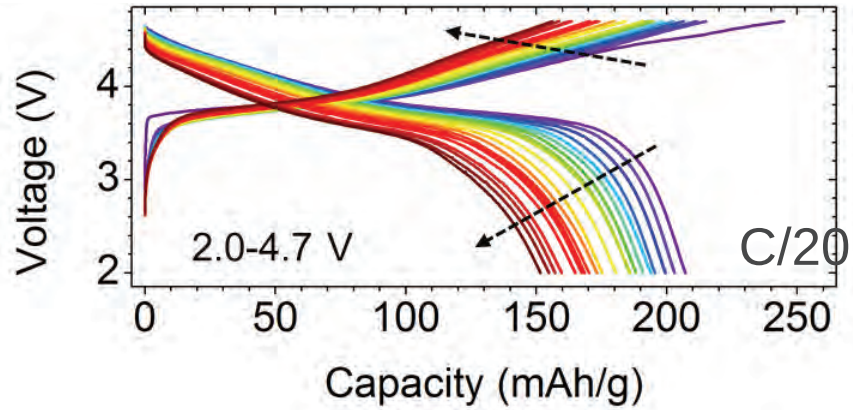
Cycling to a high potential results in higher practical capacities, at the expense of capacity retention. It's worse when particles are small (surface areas are high).

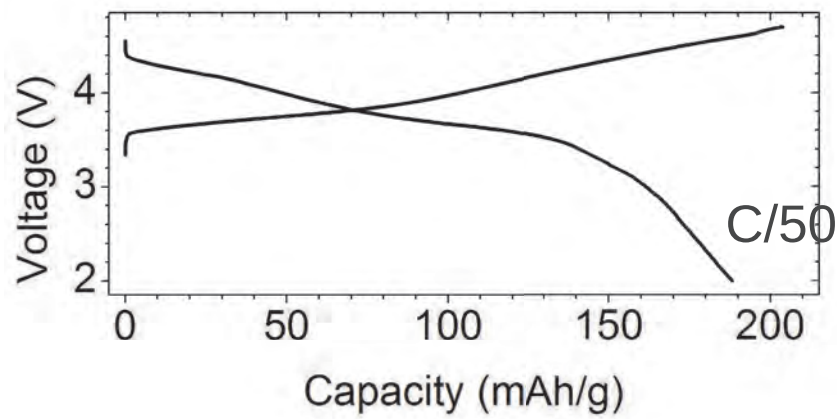
Kinson C. Kam and Marca M. Doeff, *Materials Matters, Aldrich Materials Science*, 7(4), 56 (2012).

What causes capacity fading ?

Bulk

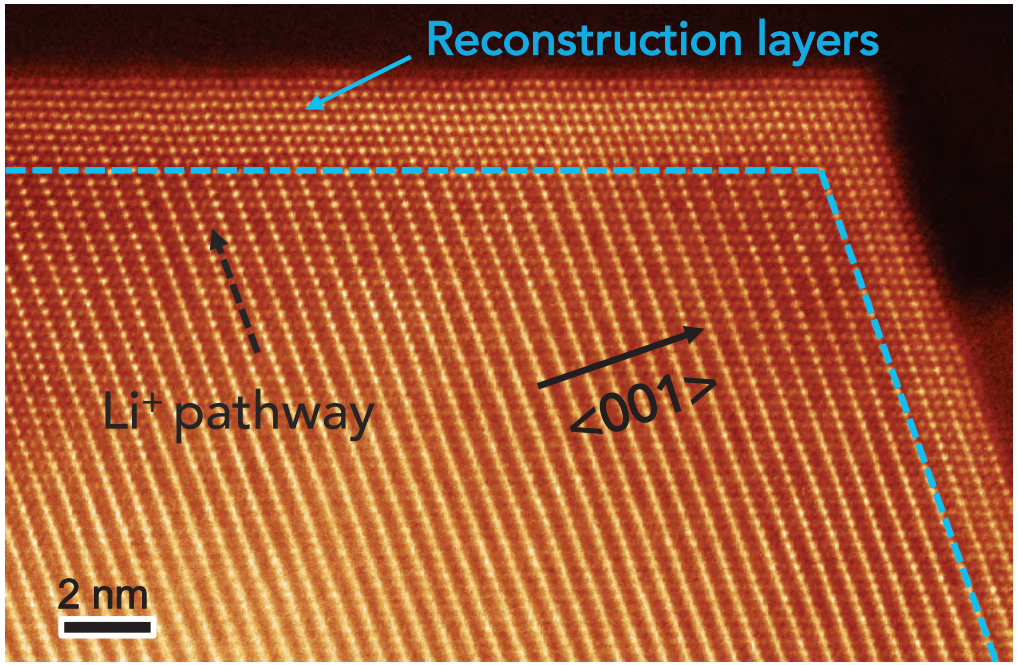


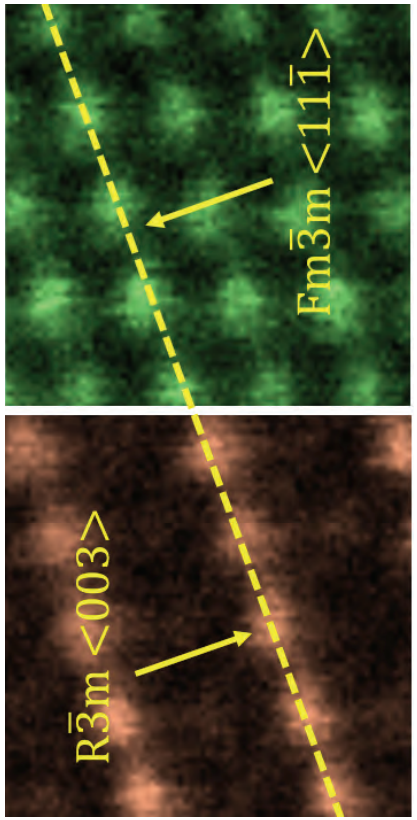




No structural changes to the bulk, capacity can be recovered after 20 cycles

Surface Reconstruction



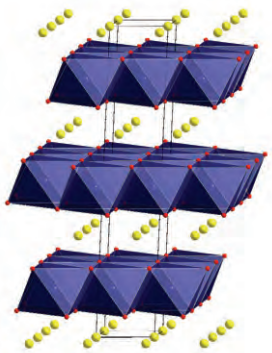


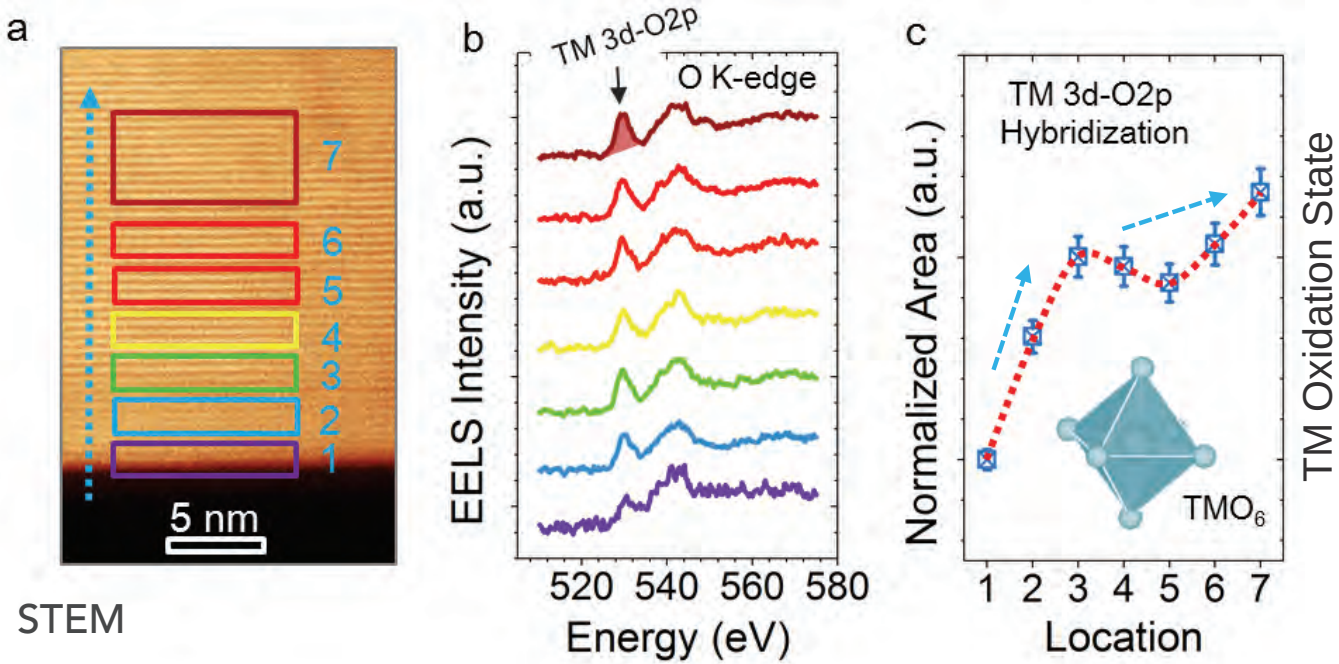
* Epitaxial growth (minimal lattice mismatch) * Anisotropic

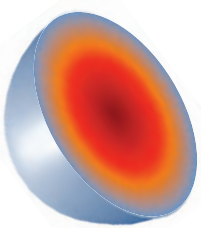
Lithium transportation "highway" is blocked by transition metals

Lin *et al.* Nat. Commun. 5, 3529 (2014)

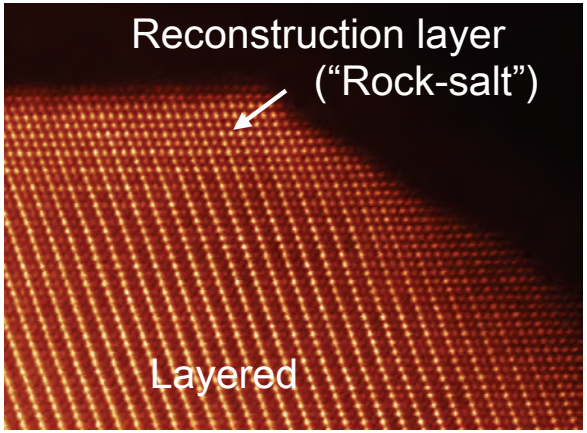
Oxidation State Gradient in Charged NMC Particles







The gradient distribution of oxidation states is confirmed by spatially resolved STEM-EELS in individual NMC particles.

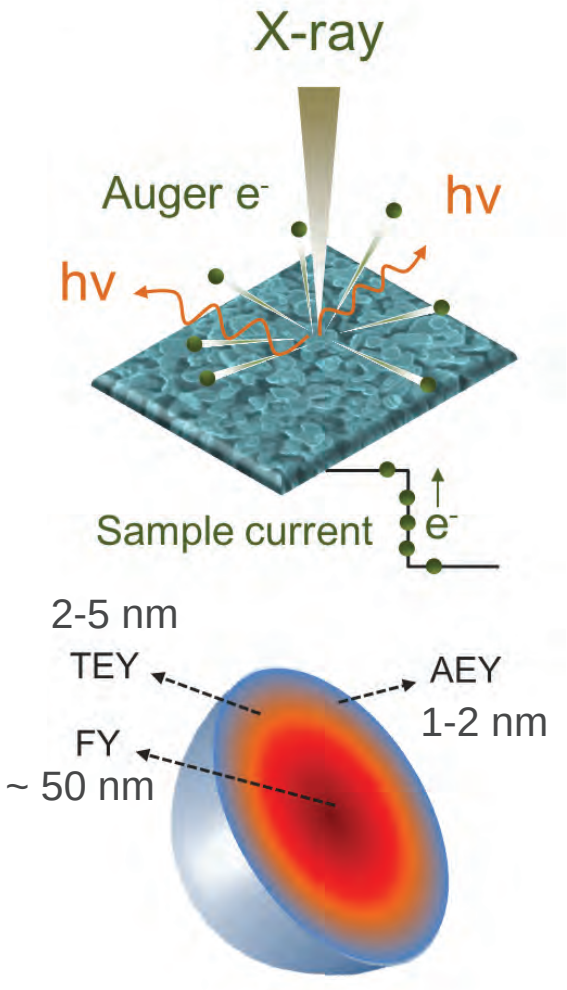


STEM: Scanning Transmission Electron Microscopy
EELS: Electron Energy Loss Spectroscopy

Lin *et al.* Energy Environ. Sci 7, 3077 (2014).

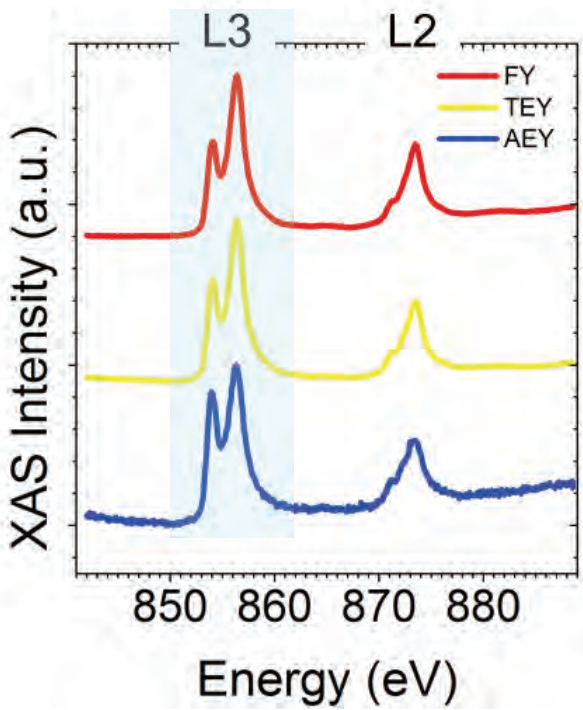
Soft XAS experiments at SSRL

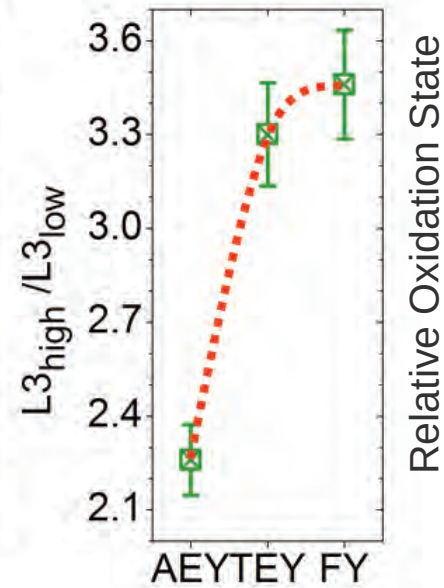
Oxidation State Gradient in Charged NMC Particles



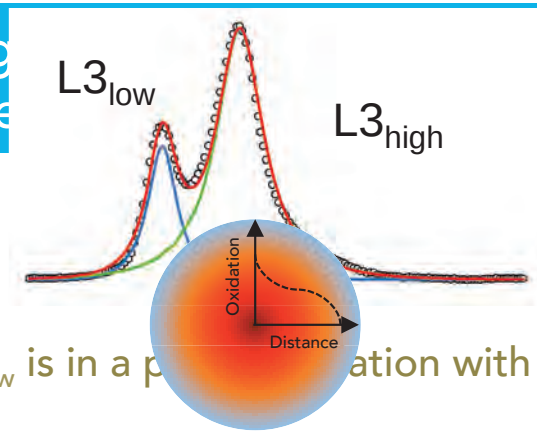
AEY- Auger Electron Yield
TEY- Total Electron Yield
FY- Fluorescence Yield

Charged (4.7 V *vs* Li^+/Li)





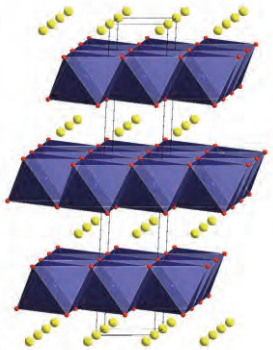
Oxidation state g IC particles observed by ense

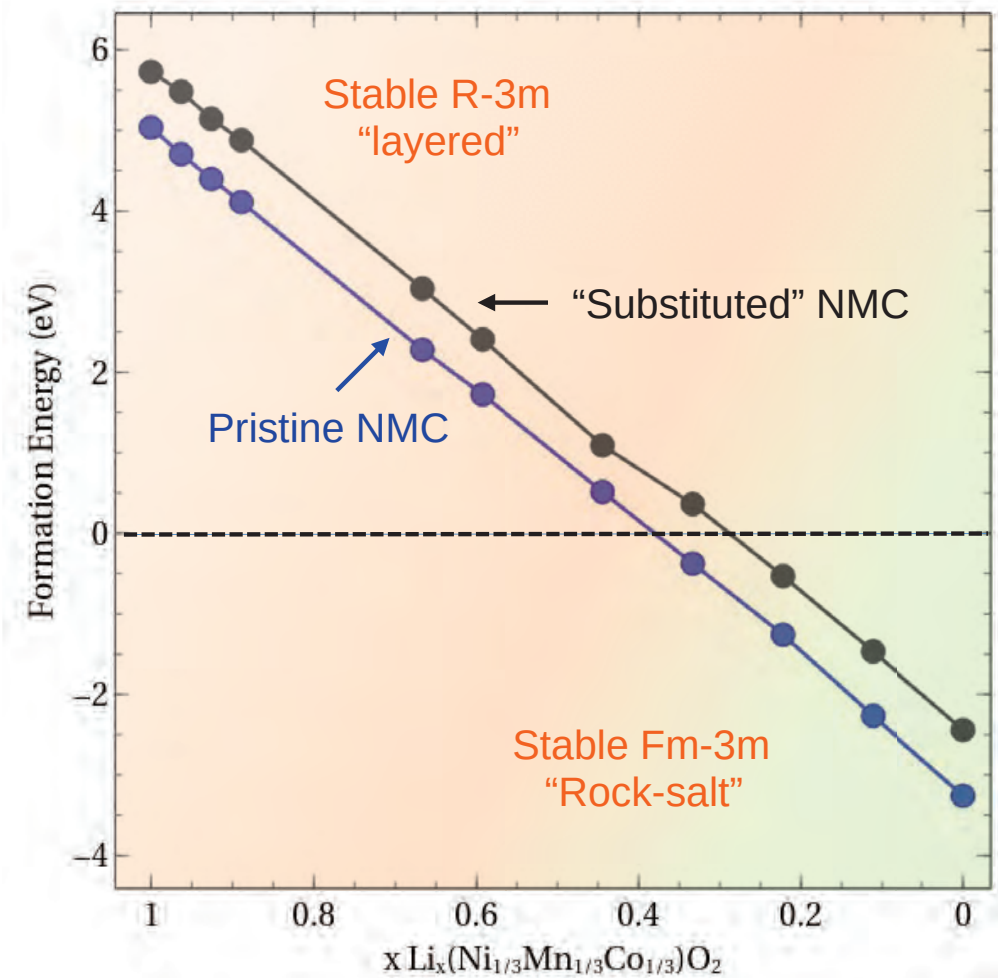


Note: $L3_{high}/L3_{low}$ is in a p ation with oxidation states

Lin *et al.* Energy Environ. Sci 7, 3077 (2014).

Can We Inhibit Rock-Salt Formation?

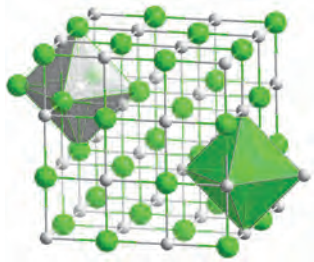




$LiNi_{0.4}Mn_{0.4}Co_{0.2}O_2$

Ti

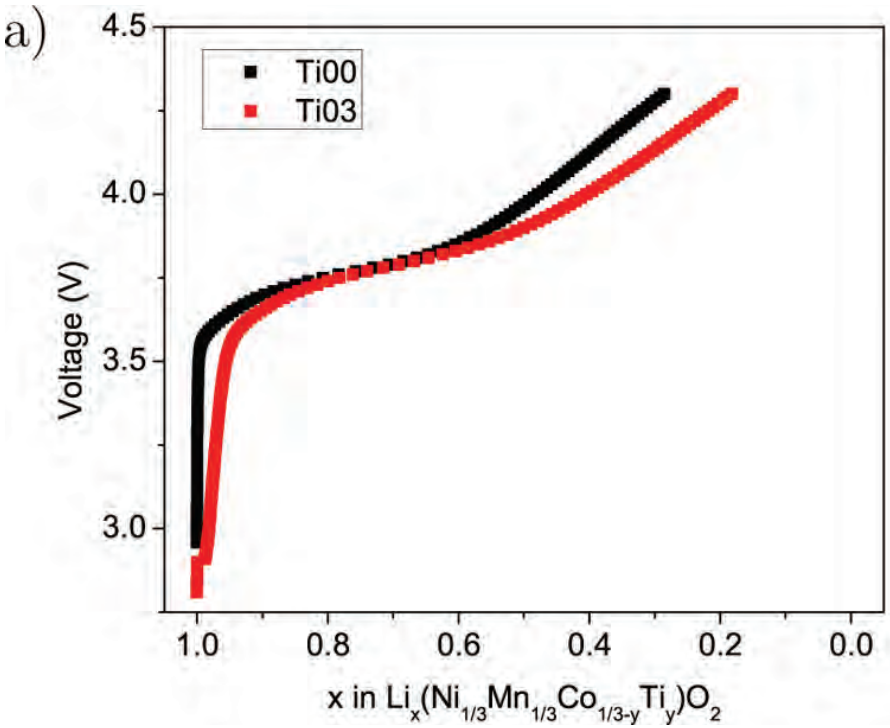
Partial substitution



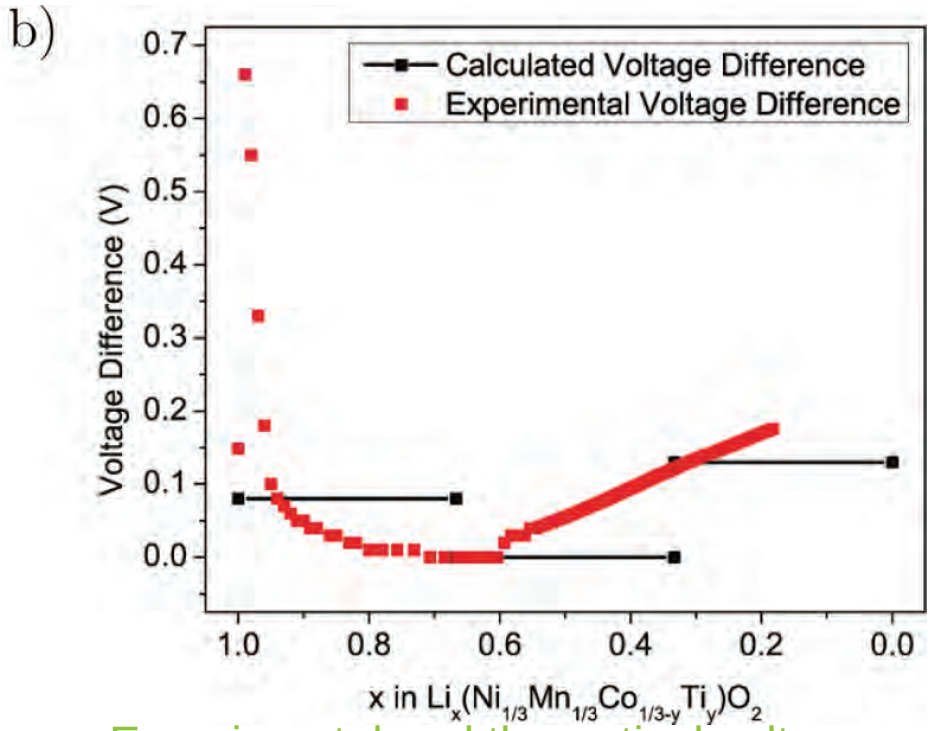
Inhibit rock-salt formation using Ti-substituted NMC materials to enable high-voltage operation

Markus, Lin, Kam, Asta & Doeff J. Phys. Chem. Lett. 5, 3649 (2014).

Additional Benefits of Ti Substitution



Data from slow stepped potential experiments (close to equilibrium)



Experimental and theoretical voltage differences between Ti-substituted and baseline electrodes

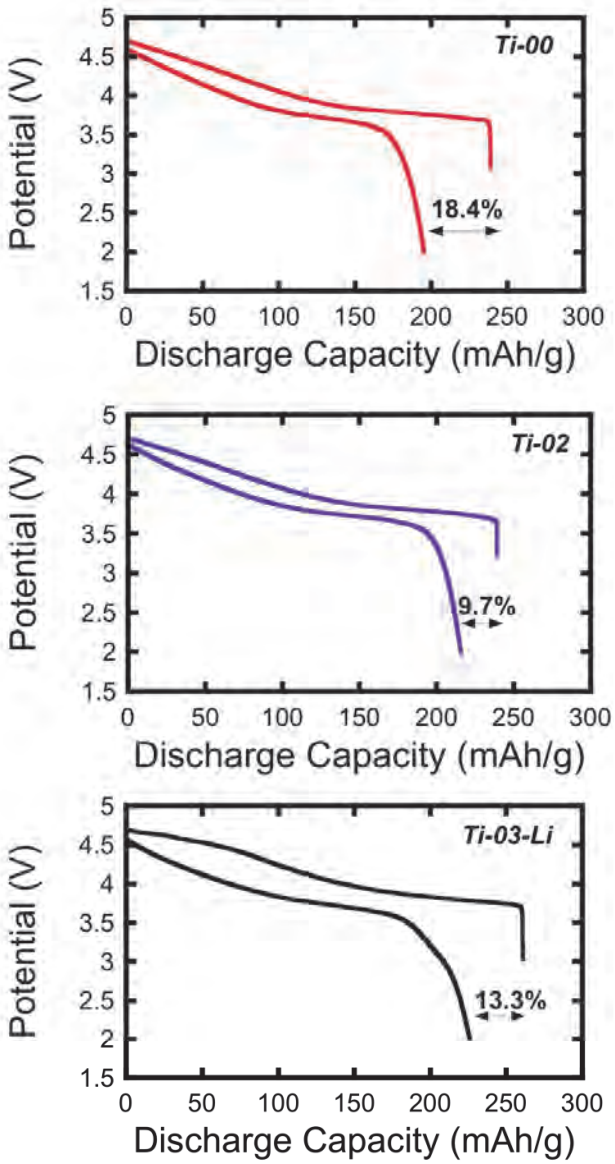
Ti-substitution changes the voltage profile, so that more Li can be extracted at practical voltage limits. This is predicted by theory.

Markus, Lin, Kam, Asta & Doeff. J Phys. Chem. Lett. 5, 3649 (2014)
Kam, Mehta, Heron & Doeff. J. Electrochem. Soc. 159, A1383 (2012)

Ti-substitution in NMCs

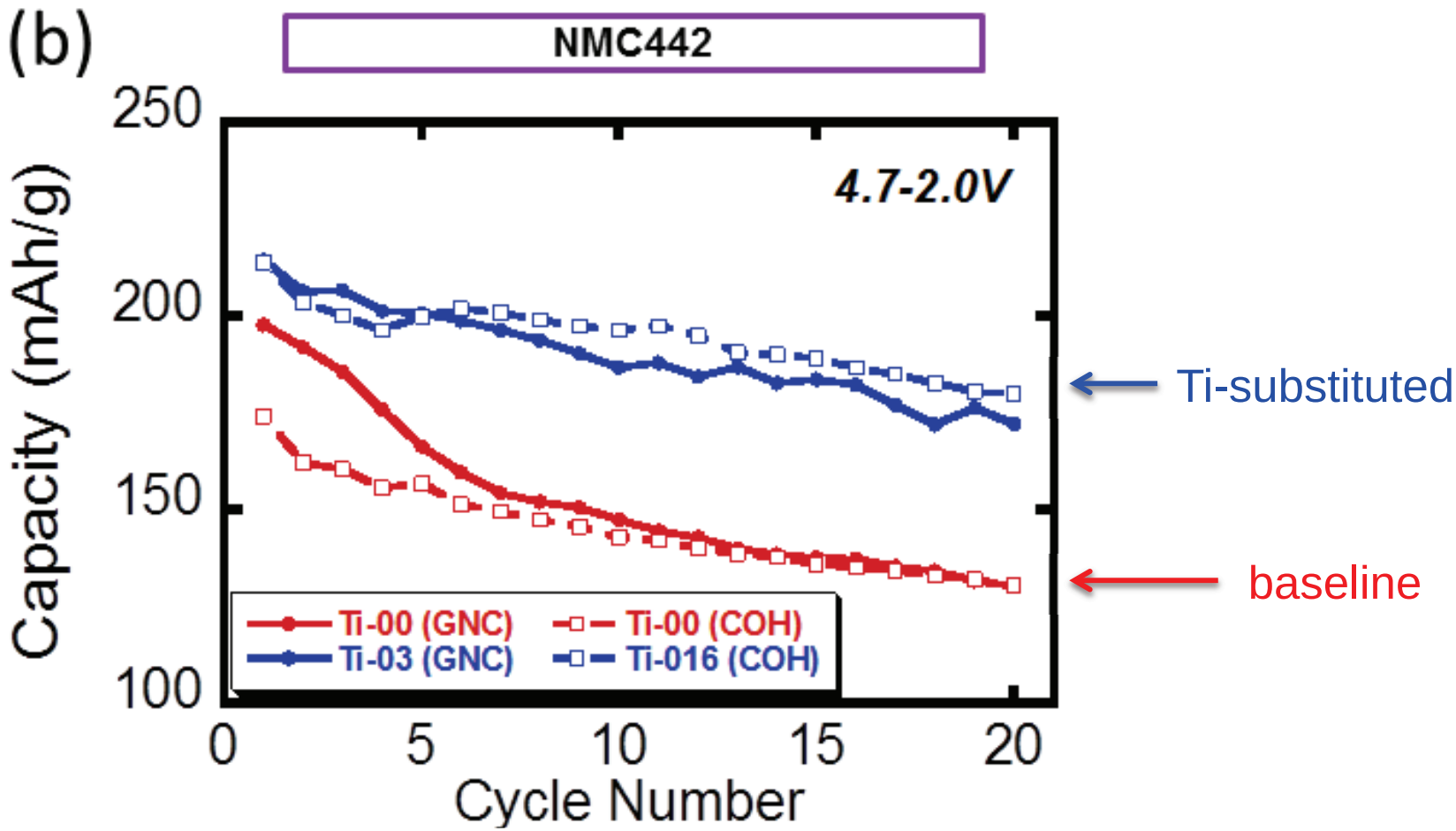
- **Partial Ti-substitution for Co in NMCs increases practical capacity**
- **Improvement is also due to better first cycle efficiencies**

Kinson Kam and Marca M. Doeff, J. Mater. Chem., 21, 9991 (2011).



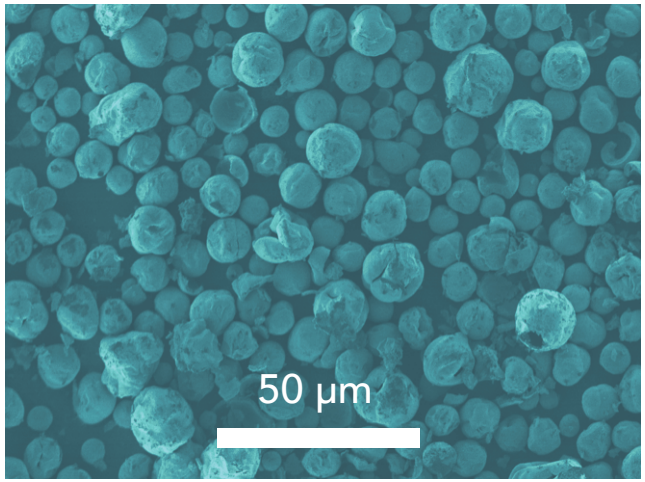
Li/NMC-333 series cells

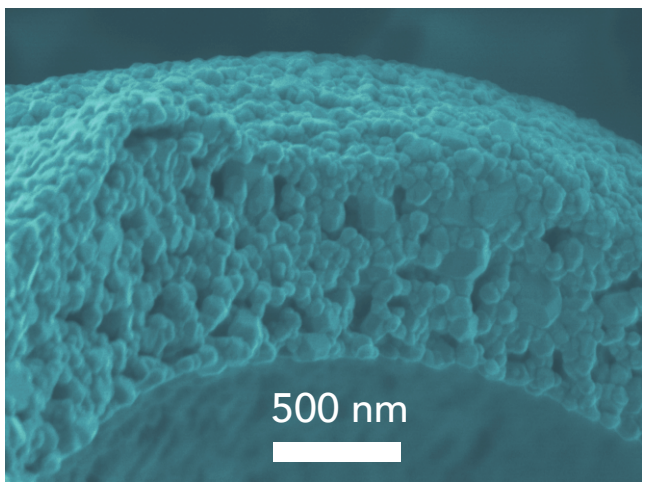
Improved high voltage cycling

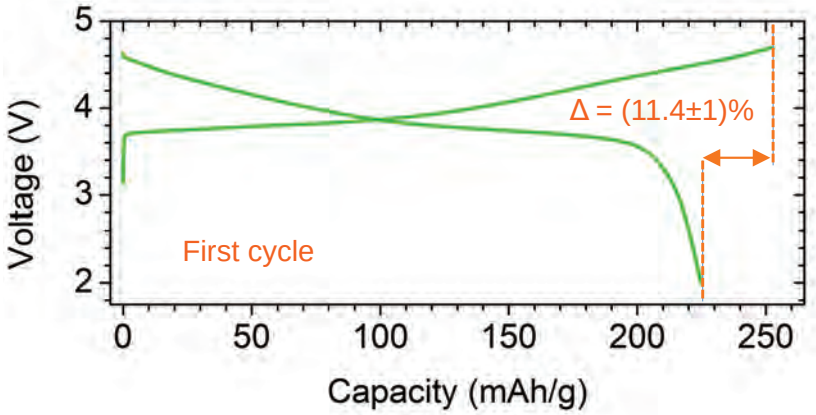


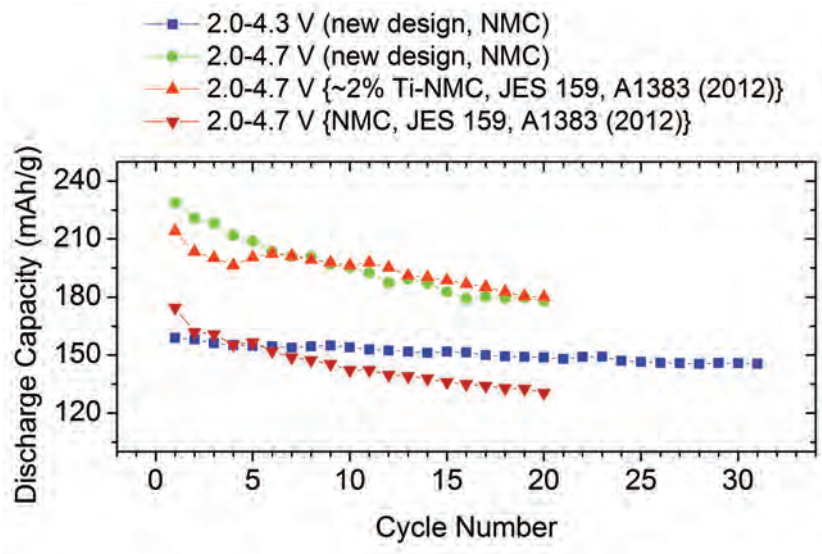
Kinson C. Kam, Apurva Mehta, John T. Heron, and Marca M. Doeff, **J. Electrochem. Soc.** 159, A1383 (2012).

Spray Pyrolysis Synthesis







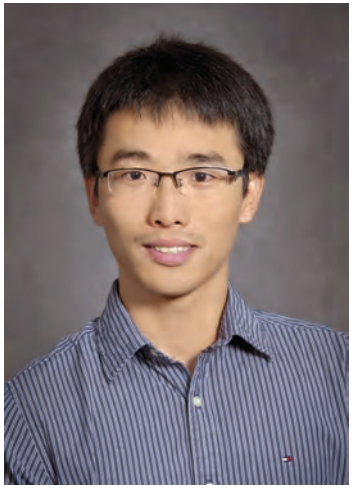


Spray pyrolysis synthesis gives results as good as Ti-substitution, why?
Pristine surface chemistry, particle morphologies?

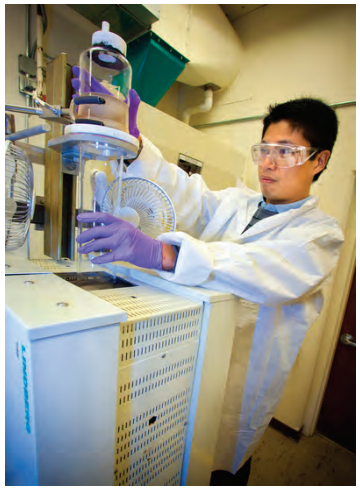
Conclusions and Future Work

- Increasing the amount of lithium extraction from NMCs (charging to higher potentials) is a possible route to higher energy density in Li ion cells
- Pathways to improving performance include synthesis optimization and substitutional chemistry to delay rock salt formation during delithiation reactions
- We still see capacity fading-this may be due to side-reactions with the electrolytic solution
- Multiple strategies are needed to counter capacity fading during high potential cycling
  - Electrolyte optimization
  - Use of additives (see Jeff Dahn's recent work)
  - Coatings

NMC project contributors

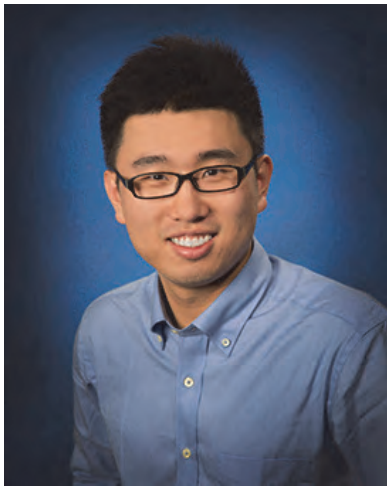


Dr. Feng Lin



Dr. Kinson Kam
(Haldor Topsoe)

Isaac Markus
PhD student, UCB



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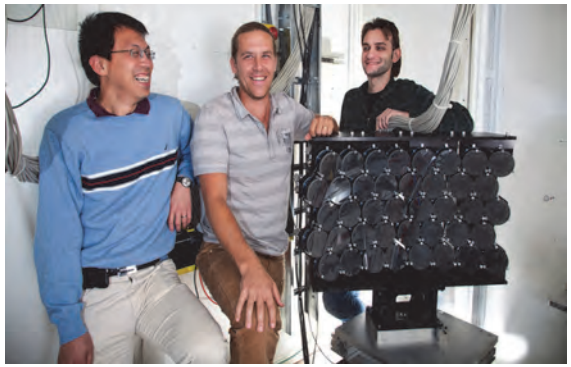

Dr. Tsu-Chen Weng Dr. Dennis Nordlund Dr. Dimosthenis Sokaras

Prof. Mark Asta, UCB

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