*Design of High Performance, High Energy Cathode Materials

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es052

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Overview

Timeline

- Project start date 10/1/2011
- Project end date 9/30/2015
- Percent complete 60%

Budget

- Total project funding
  - DOE share $475/yr ($1900k total)
- Funding received in FY13
- $475k
- Funding for FY14 $475k

Barriers

- Barriers addressed
  - ○ Energy Density
  - ○ Cost
  - ○ Cycle Life

Partners

- Interactions/ collaborations
  - LBNL, SSRL, UCB
- Project lead= LBNL

Relevance/Objectives

- Objectives
  - Develop high energy, high performance cathode materials including composites and coated powders: emphasis on modified high capacity NMCs
  - Optimize low-cost spray pyrolysis methods for preparation of materials
  - Understand effect of Ti-substitution on high capacity NMCs
- Relevance
  - Improving NMCs to increase capacity by cycling to higher voltages is the fastest route to the higher energy density batteries needed for vehicle applications
    - Ti-substituted NMCs show improved practical capacity (up to 225 mAh/g) and better high voltage cycling than baseline materials
    - Ti-substituted NMCs are structurally stable and do not exhibit voltage fade like layered-layered composites
  - Spray pyrolysis is an attractive, one-step method for preparation of spherical particles (good for processing). Coated and composite materials can be made in either one or two steps
  - Higher energy, simpler processing= lower costs per kWh

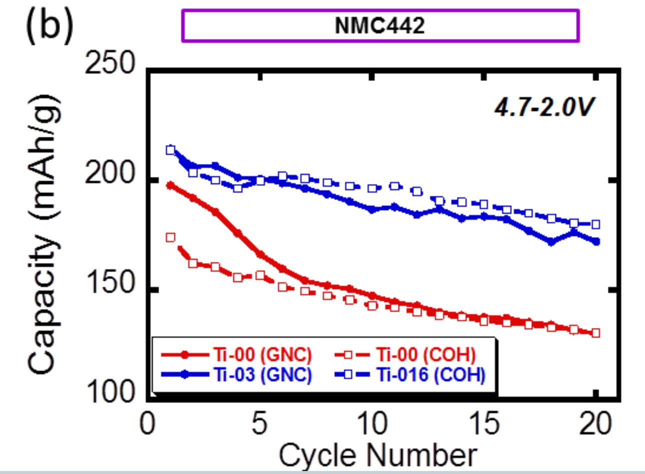
* Milestones

- Complete optimization of Ti-NMC synthesis with $TiOSO_4$ precursor (Dec-13)
  - **Discontinued. This effort has been transferred to the ABR program**
- Go/No-Go decision on infiltration of $LiFePO_4$ into LNMO (Mar.-14).
  - Criteria: A "no go" decision will be made if attempts to prevent reaction of LiFePO4 with LNMO during processing fail (Mar-14)
  - **No go decision made. Effort will be redirected towards composites with spray pyrolyzed NMCs.**
- Complete soft XAS experiments on Ti-NMCs (Jun-14).
  - **Completed ahead of schedule**
  - **Paper published in Nature Communications**
- Go/No-Go decision on spray pyrolysis of NMCs (Sept.-14)
  - Criteria: A "no go" decision will be made if the electrochemical performance of the spray-pyrolyzed material does not equal that of the material made by co-precipitation.
  - Spray pyrolyzed materials appear to have superior performance
  - **On schedule to make a "go" decision**

Approach/Strategy

- Use soft XAS and other synchrotron techniques to understand effects of high voltage cycling on NMCs and Ti-substituted NMCs
  - Goal is higher capacity without sacrificing performance
  - What is origin of improved performance in Ti-substituted samples?
  - Paper published in Nature Communications
- Synthesize NMCs by spray pyrolysis techniques
  - Simple one-step process, potentially very low cost
  - Good control of morphologies (uniform spherical particles)
  - Can make solid, porous, or hollow particles by controlling residence time
  - Can make composites with hollow particles (fill with a second phase by infiltration)
  - Can make coated materials in one step by exploiting different melting points of precursors
  - Demonstrated that hollow NMC particles made by spray pyrolysis have superior performance to those made by co-precipitation

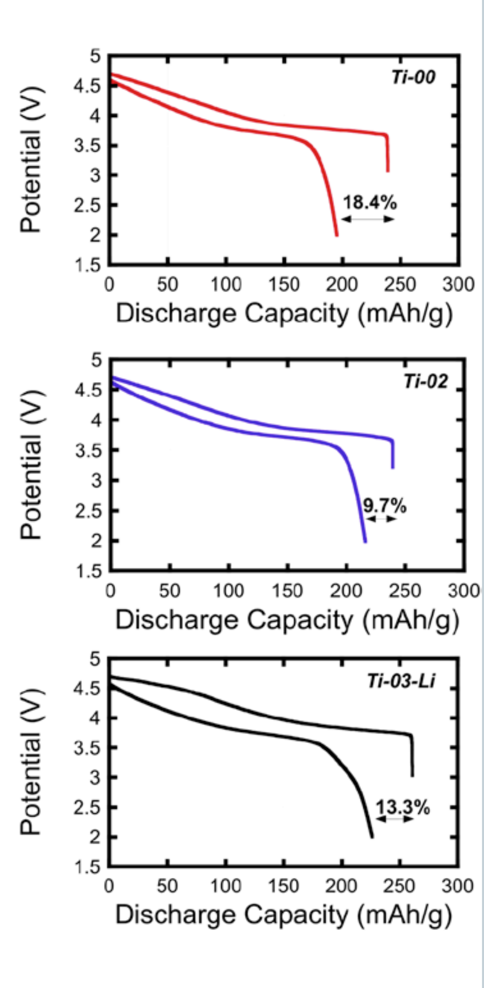
Technical Accomplishments/Progress



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

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

Previous work (reported in 2013)



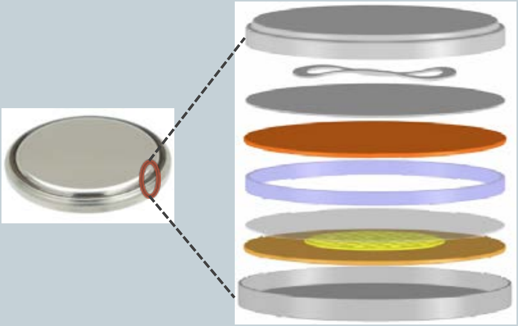
Background

- Partial Ti-substitution of NMCs increases practical capacities
- 1st cycle inefficiencies are decreased
- Improved cycling to high voltages is observed

Impetus for FY14 work

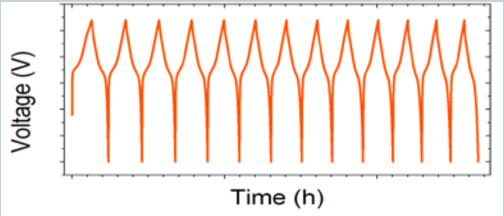
- Understand source of 1st cycle inefficiency
- Surface effect? Use depth-resolved soft XAS to investigate
- How does Ti-substitution improve performance?

Methods


Counter electrode (lithium)

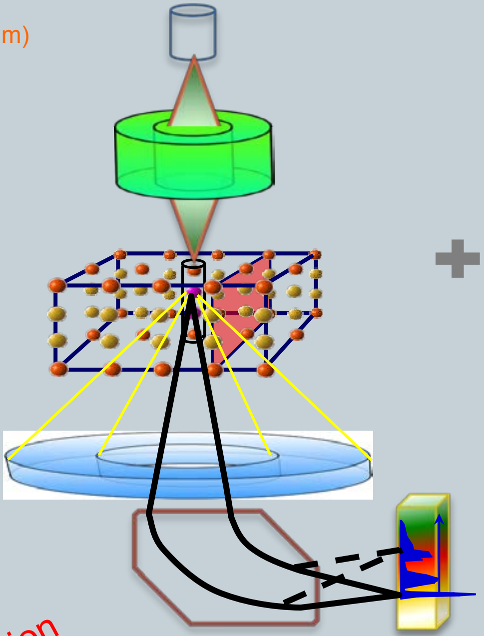
Working electrode

electrochemistry

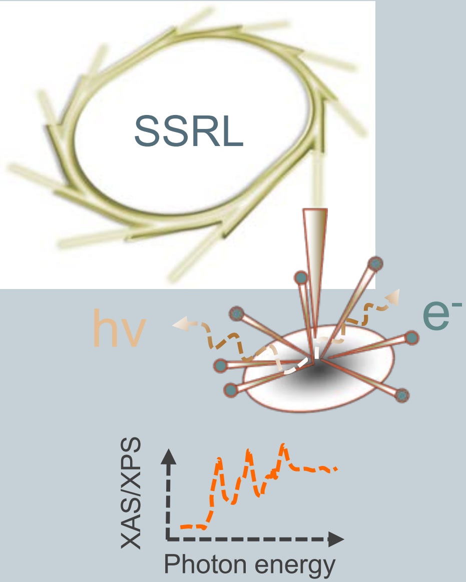


characterization

Electron microscope


Muller (Cornel)

Synchrotron Lightsource

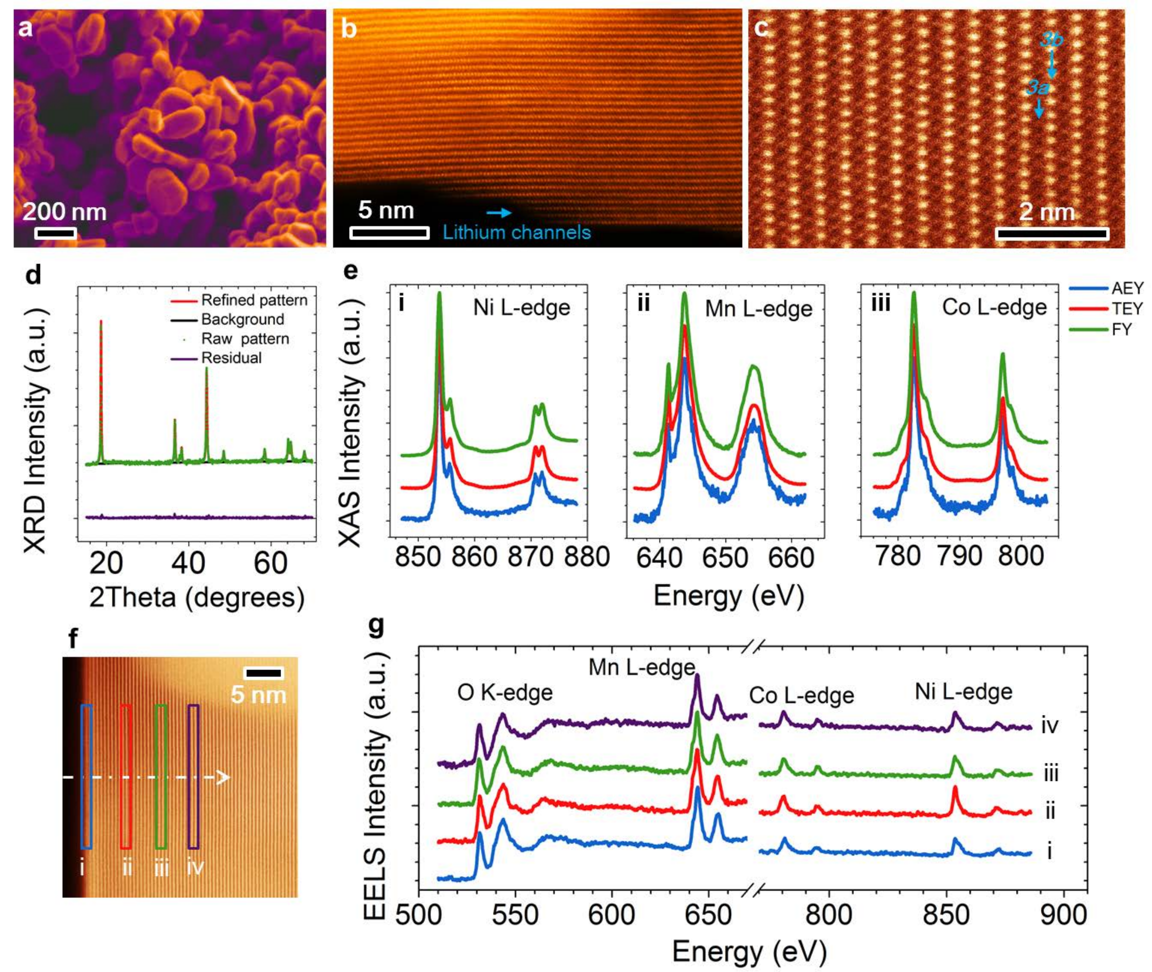


Core-level spectroscopies
EELS, XAS & XPS

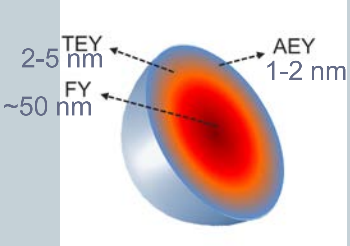
- ○ Spatially resolved (Å / EM)
- ○ Ensemble-averaged (mm^2 / XAS)
- ○ Surface sensitive probing (nm / EM, XPS and XAS/AEY-TEY)
- ○ Correlation between crystal/electronic structures and battery performance

Technical Accomplishments/Progress

Pristine NMC442-2%Ti

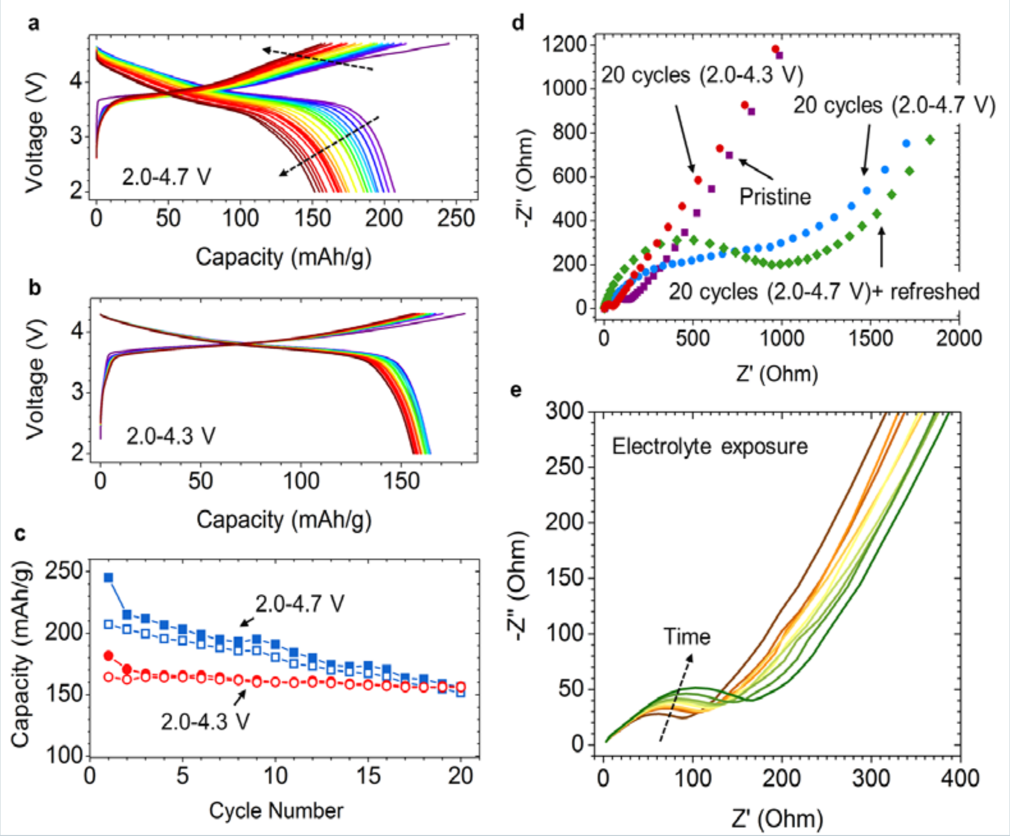


(**a**) SEM image. (**b**) High-resolution Z-contrast ADF/STEM image. (**c**) Atomic resolution Z-contrast ADF/STEM image along the [100] zone axis, with the R3m *3a* and *3b* sites indicated in the image. (**d**) XRD pattern with Rietveld refinement (**e**) XAS spectra of Ni L-edge (i), Mn L-edge (ii) and Co L-edge using Auger electron yield (blue), total electron yield (red) and fluorescence yield (green) modes. (**f** and **g**) EELS spectra integrated from areas (i), (ii), (iii) and (iv).



Technical Accomplishments/Progress

Li/NMC442-2%Ti half cells

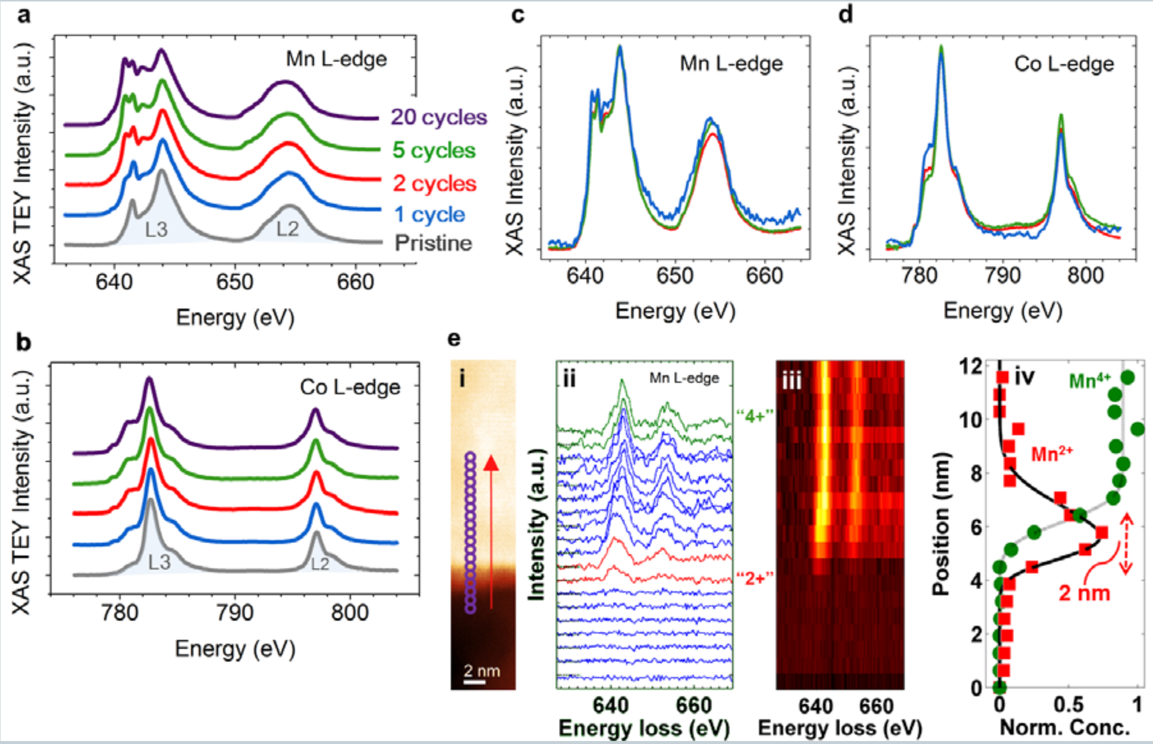


- Stable cycling to 4.3V with little change in impedance
- Capacity loss upon cycling to 4.7V with increased impedance
- Exposure to electrolyte (no electrochemistry) causes an increase in impedance (7 days total time)
- Similar results seen for undoped materials

Feng Lin, Isaac Markus, Dennis Nordlund, Tsu-Chien Weng, Mark Asta, Huolin L. Xin, and Marca M. Doeff, **Nature Commun.** 5:3529, DOI: 10.1038/ncomms4529 (2014).

Technical Accomplishments/Progress

Surface Reconstruction and Chemical Evolution After Cycling (2.0-4.7V)

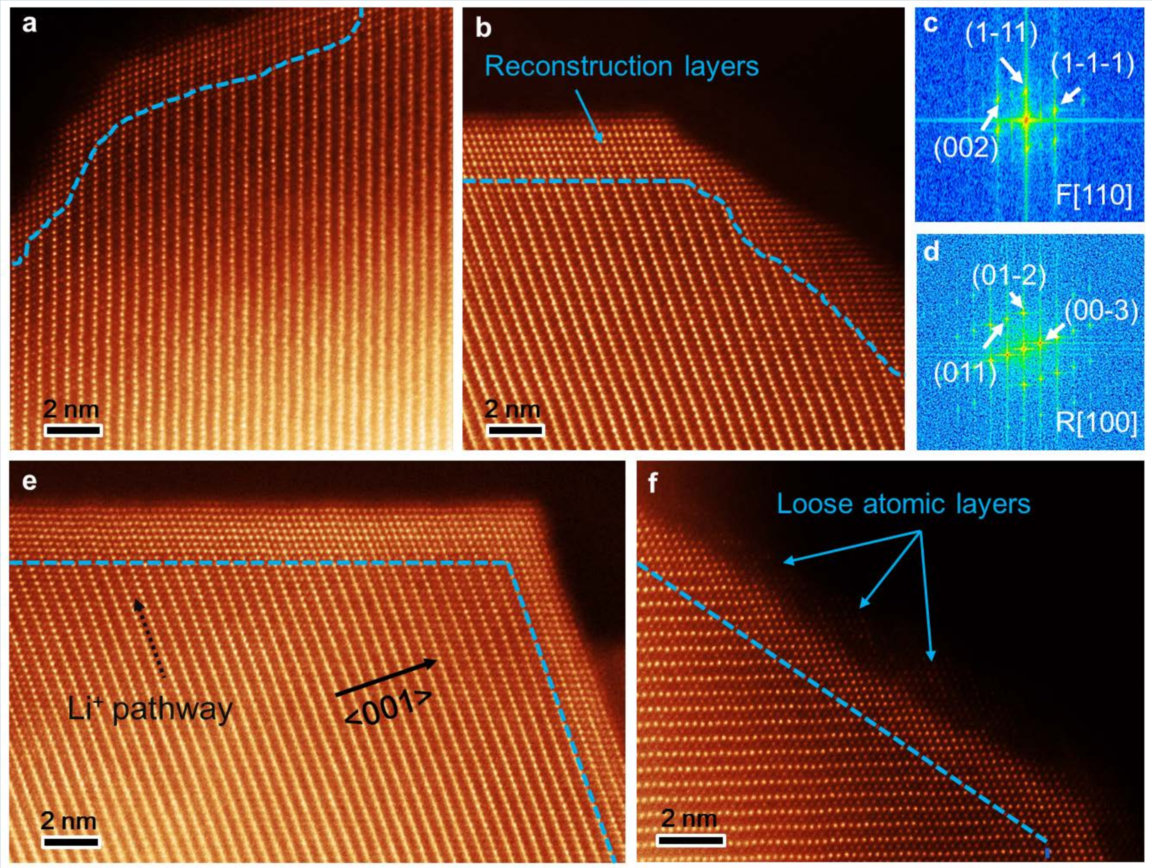


Surface transition metals are in the reduced state after cycling to high voltages

(**a**) Mn L-edge XAS/TEY spectra and **(b)** Co L-edge XAS/TEY spectra after the designated number of cycles. (**c**) Mn L-edge XAS spectra and (**d**) Co L-edge XAS spectra for an electrode after 2 charge-discharge cycles in the AEY (blue), TEY (red) and FY (green) modes. (**e**) EELS line scan profile for an NMC particle along the <001> direction after 5 cycles: (i) STEM image for the scanning pathway, (ii) Mn L-edge EELS spectra along the scanning pathway, (iii) 2D EELS map visualizing the peak shift, and (iv) concentration profiles for Mn^{2+} and Mn^{4+} obtained from the data using a linear combination method. All the measurements were performed on electrodes in the fully discharged state.

Technical Accomplishments/Progress

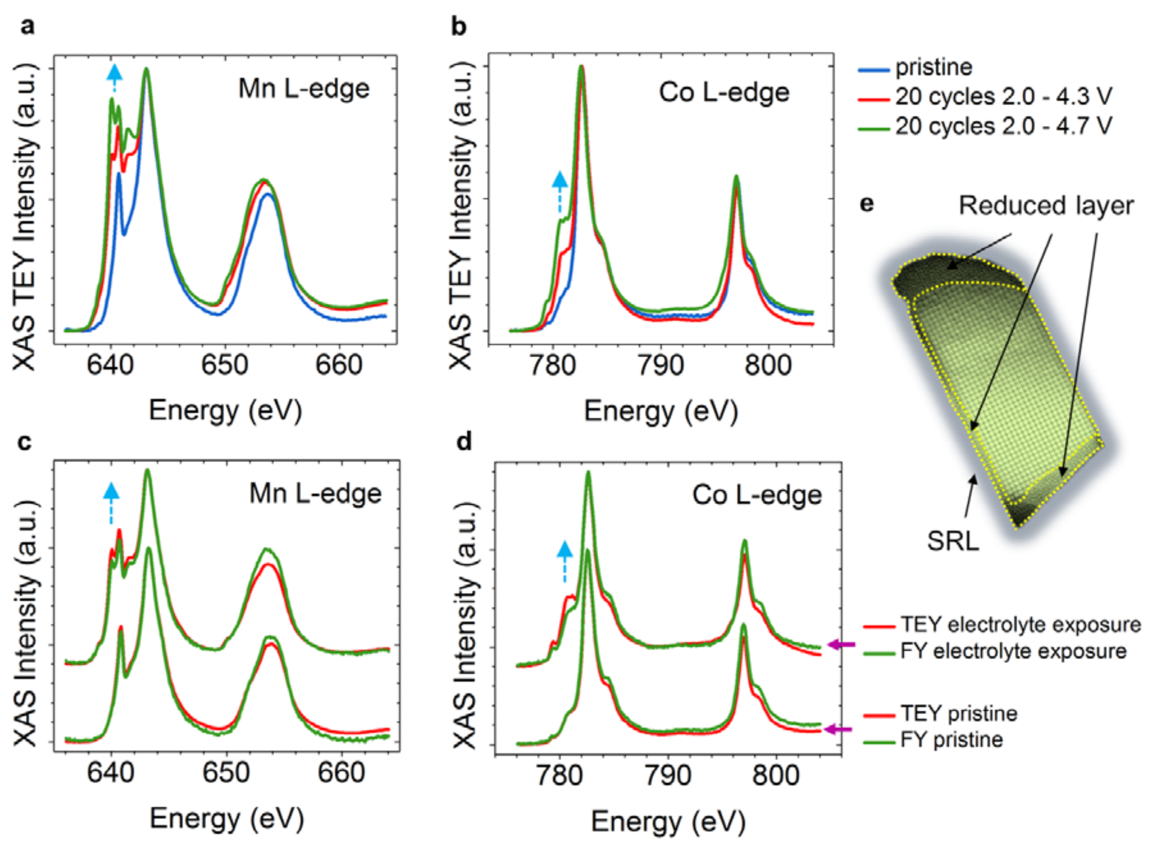
Atomic Resolution ADF-STEM Images of Particles



(**a**) After 30 hours electrolyte exposure (**b**) After 1 cycle (2.0-4.7 V) (**c** and **d**) FFT results showing the surface reconstruction layer ($Fm\bar{3}m$ [110] zone axis) and the NMC layered structure ($R\bar{3}m$ [100] zone axis) respectively in (**b**). (**e**) Showing variation of the surface reconstruction layer thickness on orientation after 1 cycle (2.0-4.7 V). (**f**) Image showing loose atomic layers on an NMC particle, after 1 cycle (2.0-4.7 V).

Technical Accomplishments/Progress

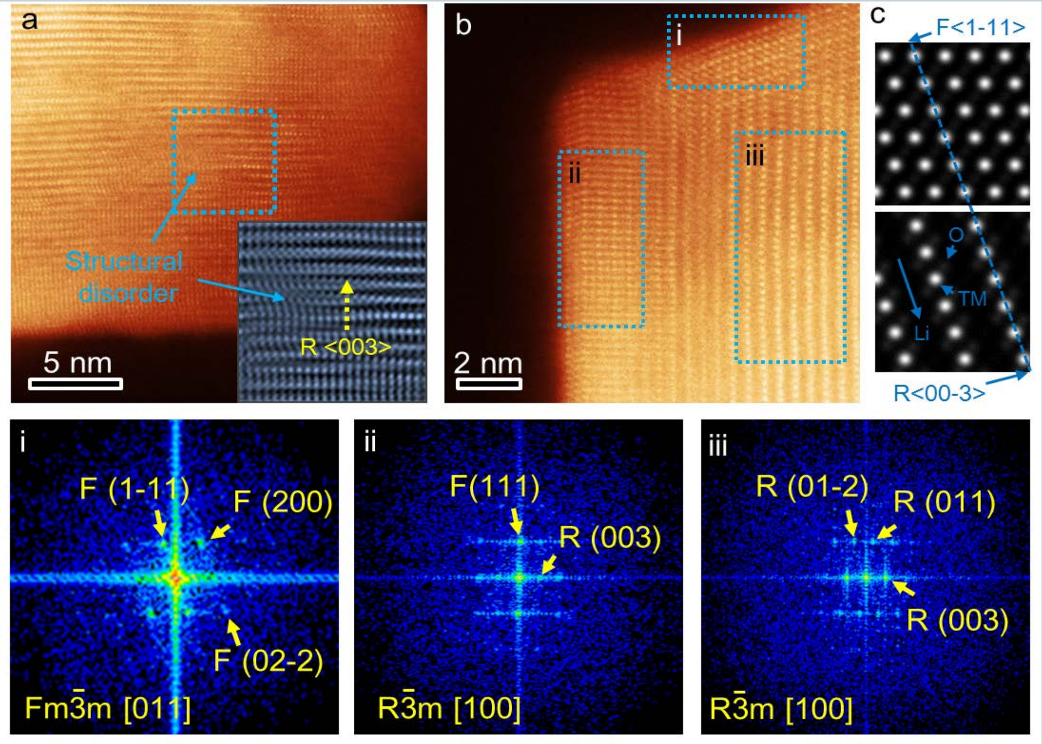
Dependence of Surface Reduced Layer on Voltages and Electrolyte Exposure



(**a**) Mn L-edge XAS/TEY spectra and (**b**) Co L-edge XAS/TEY spectra of pristine and cycled electrodes (20 cycles). (**c**) Mn L-edge XAS/TEY/ FY spectra and (**d**) Co L-edge XAS/TEY/FY spectra of a pristine electrode and one exposed to electrolytic solution for 7 days. The blue dashed arrows in (**a**-**d**) indicate the increase of transition metals having low oxidation states. (**e**) Schematic model of a NMC particle with a surface reduced layer and a surface reaction layer (SRL).

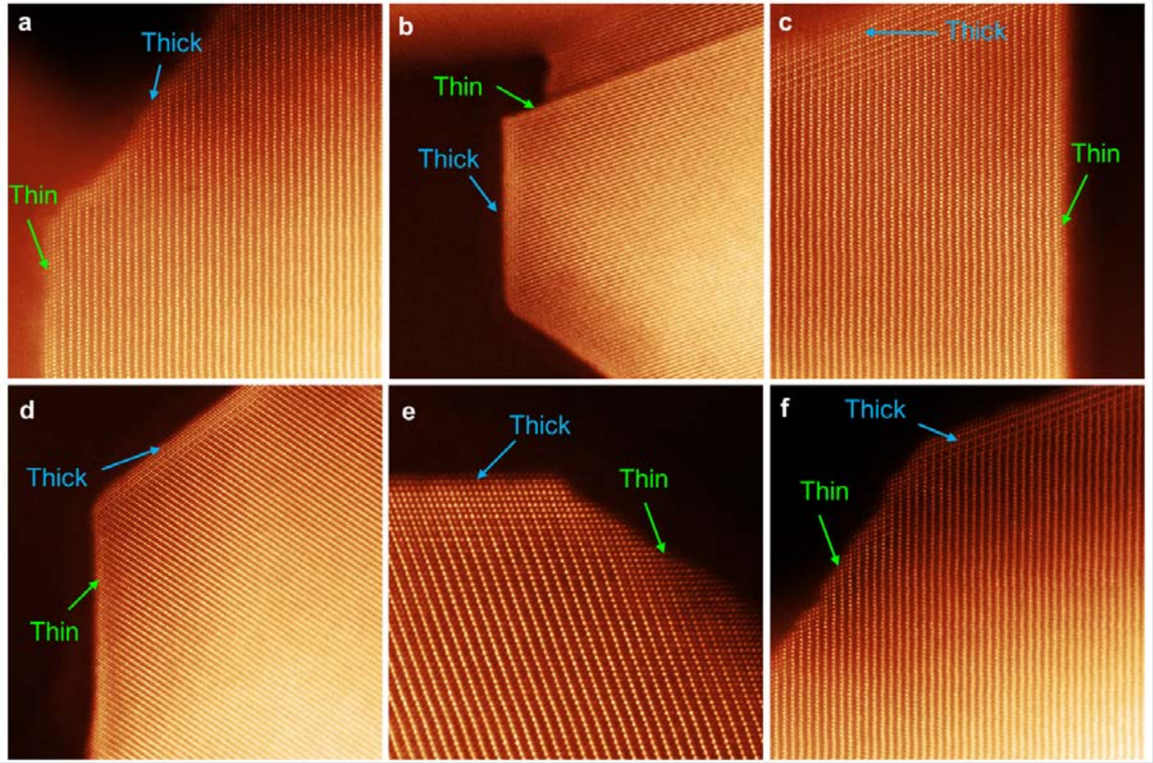
Technical Accomplishments/Progress

Charged NMC Particles



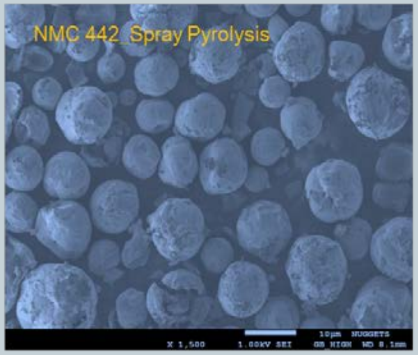
- Rock-salt structure ($Fm\bar{3}m$): TM^{2+} (electrochemically inactive for cathode)
- Charged layered structure ($R\bar{3}m$): Charged $Ni^{3+/4+}$, Mn^{4+}, Co^{3+}

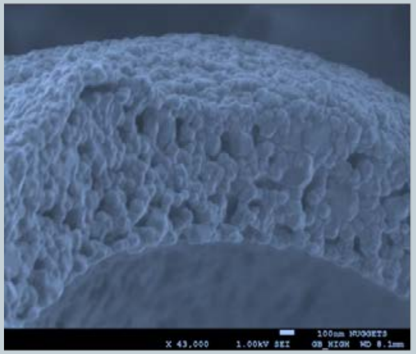
Technical Accomplishments/Progress

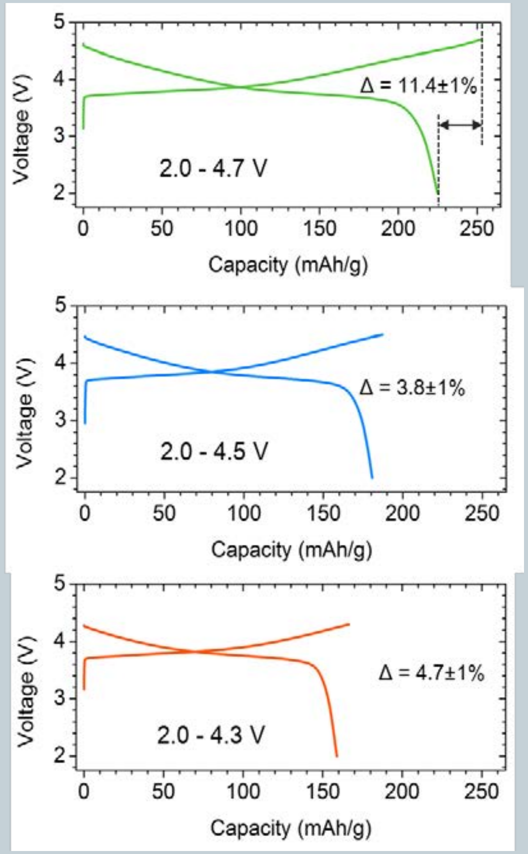


Surface Reconstruction is Crystal Orientation Dependent

Technical Accomplishments/Progress







- Uniform hollow spheres ~ 10 µm made up of nanoparticles
- Hierarchical structuring results in good electrochemical performance
- Longer residence times should result in solid particles
- Hollow particles useful for making composites via infiltration

NMC442 made by spray pyrolysis

Responses to Previous Year Reviewers' Comments

- Several reviewers suggested coordinating Ti-NMC work with groups working on high voltage electrolytes
- One reviewer asked for more cycling data

Response: *The practical Ti-NMC work has been transferred to an ABR project with Farasis, Inc., which includes a high voltage electrolyte developer (DuPont). Materials will be tested in full cell configurations at different rates and cycled more extensively, using specially developed electrolytes. Work on Ti-NMCs under BATT is now solely focused on diagnostics directed towards understanding high voltage performance.*

- Two reviewers expressed concern that Ti-substitution in NMCs was not a new concept; one suggested a literature and patent search.

Response: *There are examples in the literature where* Ti^{4+} *has been substituted for* Mn^{4+} *(**isovalent** substitution) in NMCs. Note that our work involves substitution of* Ti^{4+} *for* Co^{3+} *(**aliovalent** substitution), which has not been reported in the literature until now. **Isovalent** substitution of* Ti^{4+} *degrades performance, while **aliovalent** substitution improves performance.*

Collaboration and Coordination with Other Institutions

- Soft XAS experiments performed at Stanford Synchrotron Radiation Lightsource (SSRL) with Dr. Dennis Nordlund and Dr. Tsu-Chien Weng. (outside VT program).
- Synchrotron XRD and hard XAS experiments with Dr. Thomas Richardson (retired) and Dr. Guoying Chen of LBNL (inside VT program) and Dr. Apurva Mehta of SSRL (outside VT program)
- Synchrotron XPS experiments underway with Dr. Phil Ross (retired) and Dr. Ethan Crumlin of LBNL (outside VT program)
- TEM experiments with Dr. Huolin Xin, previously at LBNL, now at Brookhaven National Lab. (outside VT program)
- Computational work underway with Professor Mark Asta, Materials Sciences and Engineering Department, U. C. Berkeley (outside VT program)
- Cathode synthesis work with Professor T. Rojo of the University of the Basque Country and CICenergigune, Spain (outside VT program)
- Cathode synthesis work and synchrotron experiments with Dr. Jordi Cabana, previously at LBNL, now at the U. of Illinois at Chicago (previously in VT program, now in JCESR)

Remaining Challenges and Barriers

- Achieving higher capacity in NMCs probably requires cycling to higher voltages. Surface rock salt formation is accelerated under these conditions, causing losses upon cycling.
  - Ti substitution ameliorates this to some extent, but it still occurs
  - Can we continue to improve materials, either by substitution or by other means?
  - An encouraging example is high voltage $LiCoO_2$
  - This is worth trying-probably quickest route to higher energy density
- Spray pyrolysis synthesis of NMCs results in hollow spheres, not good for energy density
  - Can we make solid particles by lengthening residence time?
  - Can we make dense composite materials by infiltrating hollow particles?

Proposed Future Work

- *Note that synthesis and full cell characterization (including extended cycling) of Ti-NMCs has been transferred to an ABR project with Farasis, Inc.*
- Synchrotron X-ray Raman experiments will be carried out to improve understanding of rock salt formation in NMC materials (milestone planned)
- Spray pyrolysis/infiltration will be used to make composite materials with hollow NMC spheres. Infiltrates may include $LiNi_{0.5}Mn_{0.5}O_2$, $LiNi_{0.5}Mn_{1.5}O_4$, and NMCs with higher Ni content (go/no go decisions on various combinations)
- Coated particles will be made by spray pyrolysis and tested (coatings include Al_2O_3, ZnO, etc.) to improve high voltage performance. (go/no go decisions on processing)

Summary

- A rock salt structure is formed on NMC particle surfaces during cycling and upon electrolyte exposure.
- The thickness of the rock salt layer depends on particle surface facet, length of electrolyte exposure, and cycling regime
- The rock salt layer contains reduced Ni, Co, and Mn
- Capacity losses during high voltage cycling are due primarily to impedance rise (low rate discharge recoups most of the capacity)
- Ti-substitution may modify composition of rock salt layer, making it more conductive
- Spray pyrolysis is a simple one-step process for making NMCs with spherical particle morphologies and excellent electrochemical properties
- Hollow particles may be useful for preparation of composites, solid particles can be made by lengthening residence time.