DESIGN OF HIGH PERFORMANCE, HIGH ENERGY CATHODE MATERIALS

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Project id: es052

Overview

Timeline

- Project start date: 10/1/2011
- Project end date: 9/30/2015
- Percent complete: 100%

Barriers

- Barriers addressed
  - Energy Density
  - Cost
  - Cycle Life

Budget

- Total project funding
  - DOE share ($1900k)
  - Contractor share-none
- Funding received in FY 2015: $500k
- Funding for FY 2016: new multi-investigator project started: $1.7M (5 PIs)

Partners

- Interactions/ collaborations
  - LBNL, BNL, SSRL, UCB, UCSD, NREL
- Project lead: LBNL

Relevance

- To reach energy density goals, practical capacities of NMCs need to be increased.
- This is probably the fastest route to increasing energy densities. However…
  - This will require cycling to higher potentials vs. Li^+/Li
  - e.g., to reach or exceed 250 Wh/kg in a full cell, a Ni-rich NMC (622 or 811) should be cycled to 4.35V (instead of 4.2V). For 622, an advanced anode is also required (e.g., Si-C).
- We need to understand what limits the high voltage cycling behavior of NMCs.
- Some strategies (Ti-substitution, ALD coatings) appear to improve high voltage cycling behavior-understanding these effects will allow us to design better cathode materials.

Objectives

- To develop high energy, high performance cathode materials, with an emphasis on designing NMCs for better high voltage performance.
- First, experiments are carried out to understand high voltage behavior of NMCs made by conventional and novel synthetic procedures.
- Results are used to guide the design of better-performing materials (e.g., metal-segregated NMCs that are Ni-poor on particle surfaces).

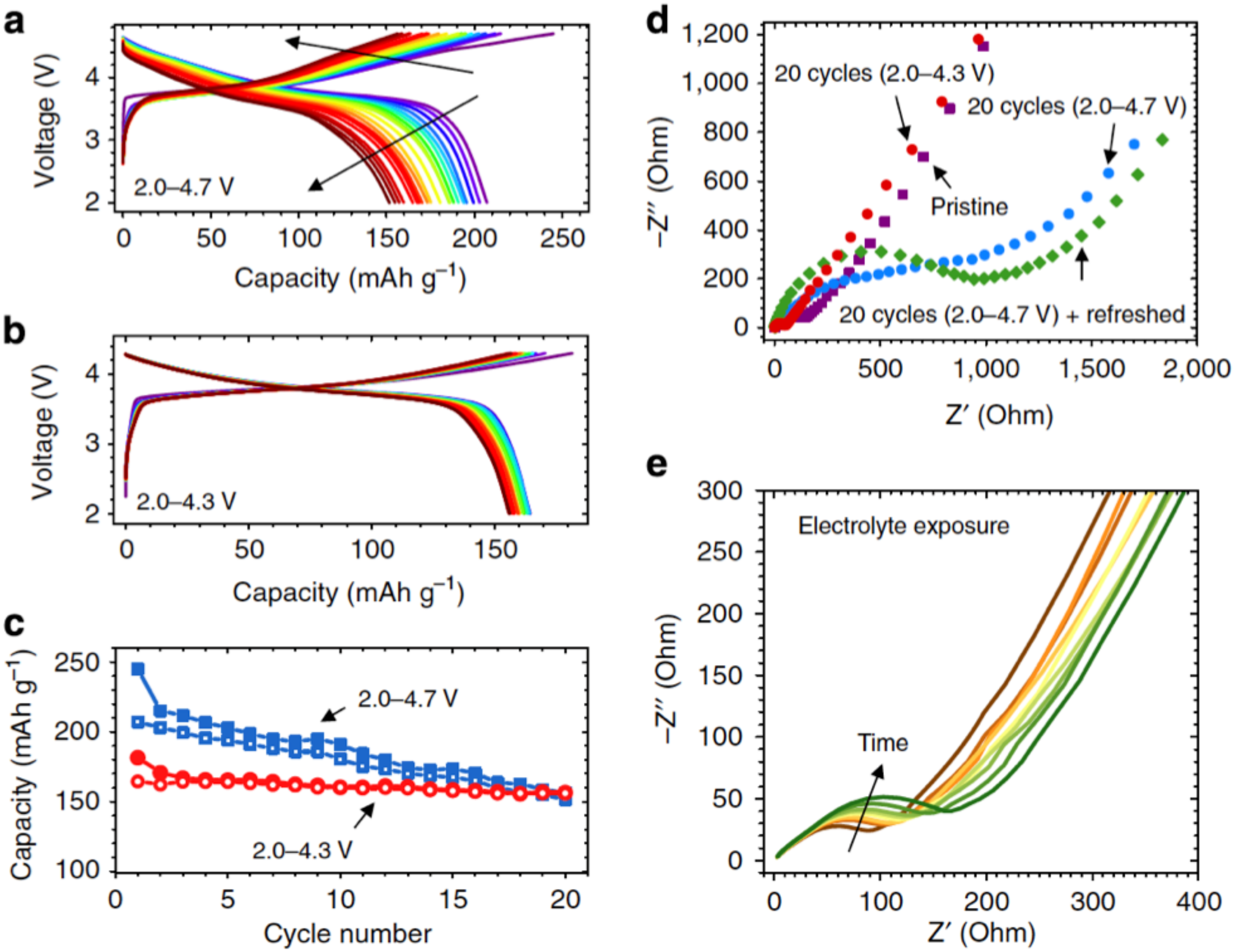
Milestones-FY 15 and FY16

Milestone	Date	Status
Complete synchrotron X-ray Raman experiments on NMC-442 and substituted NMC-442.	12/31/14	Completed.
Finish survey of composites made with spray pyrolyzed NMC hollow particles.	3/31/15	Postponed due to equipment and space issues.
Go/no go decision of feasibility of coating processes using spray pyrolysis or molecular layer deposition.	6/30/15	Decision is go, based on promising initial results.
Select best-performing materials for further study.	9/30/15 New Project	Ni-rich NMCs are selected for further study.
Synthesize baseline NMC-523 and 622 and Ti-substituted variants.	12/31/15	Completed.
Complete surface characterization of pristine materials by synchrotron XAS and XPS.	3/31/16	Completed.
Complete soft XAS experiments on electrodes cycled to high potentials.	6/30/16	On track.
Go/no go decision on core-shell composites made by spray pyrolysis.	9/30/16	On track.

Approach/Strategy

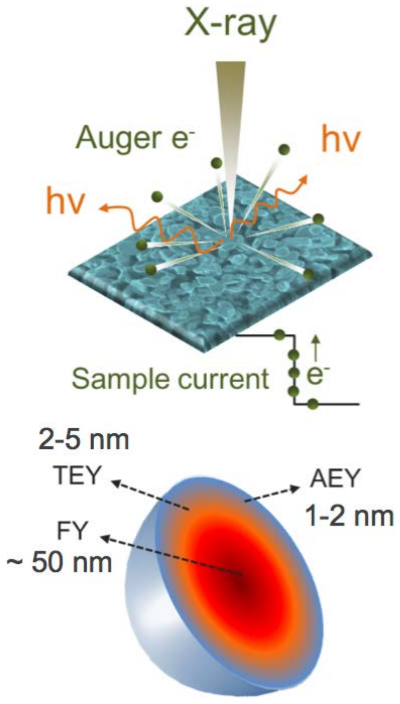
- Use synchrotron techniques (soft XAS, XPS, X-ray Raman, TXM) and microscopy (STEM-EELS) to understand thermal and high voltage cycling behavior of NMCs.
- Develop strategies to improve behavior (e.g., aliovalent Ti-substitution, graded compositions, coatings).
- The new multi-investigator project starting 10/1/15 focuses on Ni-rich NMCs. Previous work was directed towards NMCs with lower Ni contents (333, 442, etc.)
- We will use our experience with the NMC-333 and 442 systems to help guide the work on the Ni-rich systems (e.g., will Ti-substitution improve high V cycling?)

Background and Previous Work



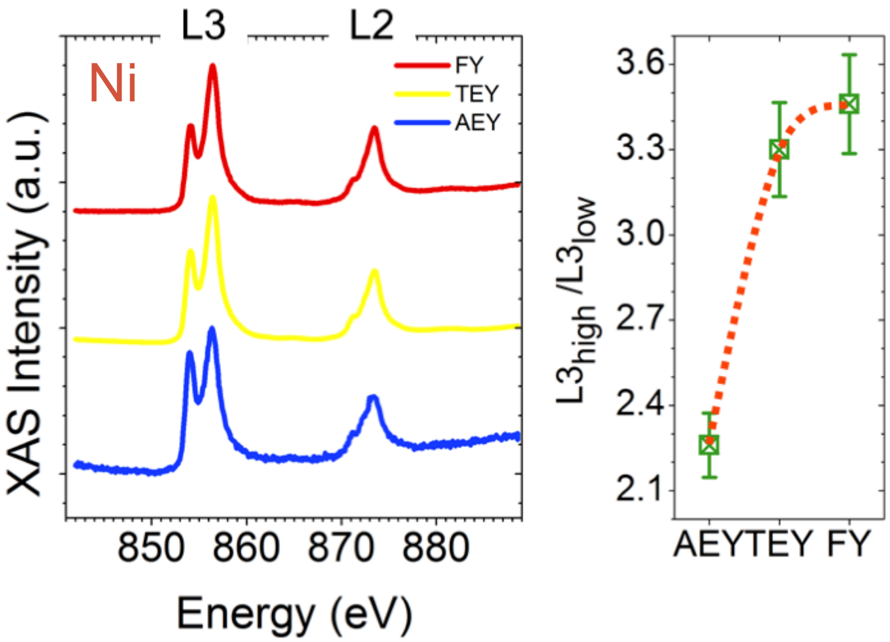
High V cycling of NMC-442 results in impedance rise and rapid capacity loss. Lin *et al.* Nat. Commun. 5, 3529 (2014)

Background and Previous Work



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

Charged (4.7 V vs Li+/Li)

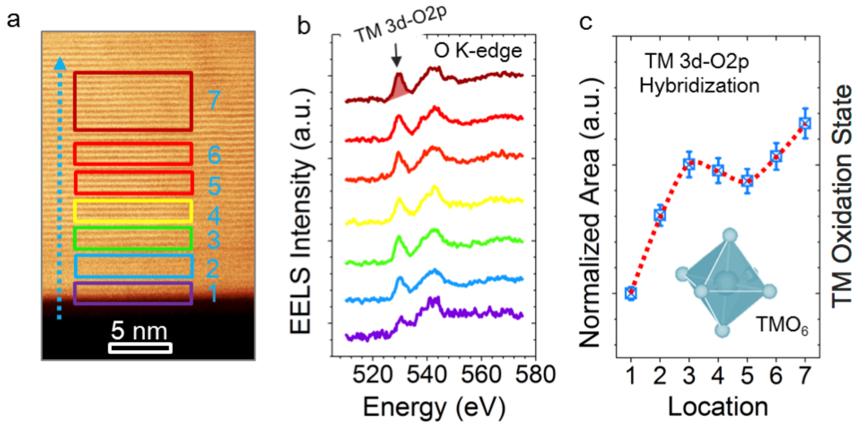


Profiling of a charged NMC-442 electrode shows that there is an oxidation state gradient for Ni going from the surface to the bulk, with reduced Ni on the surface. The same is true for Co and Mn.

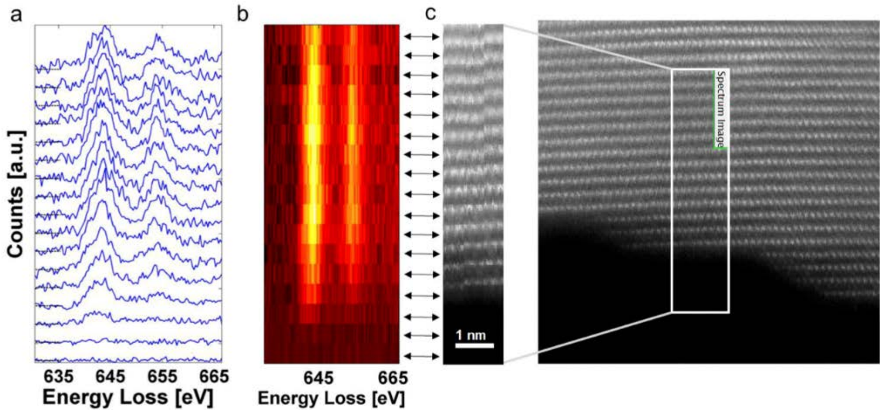
Soft XAS is a depth profiling technique. Results are ensemble-averaged (probe many particles) and give information about average oxidation states of metals.

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

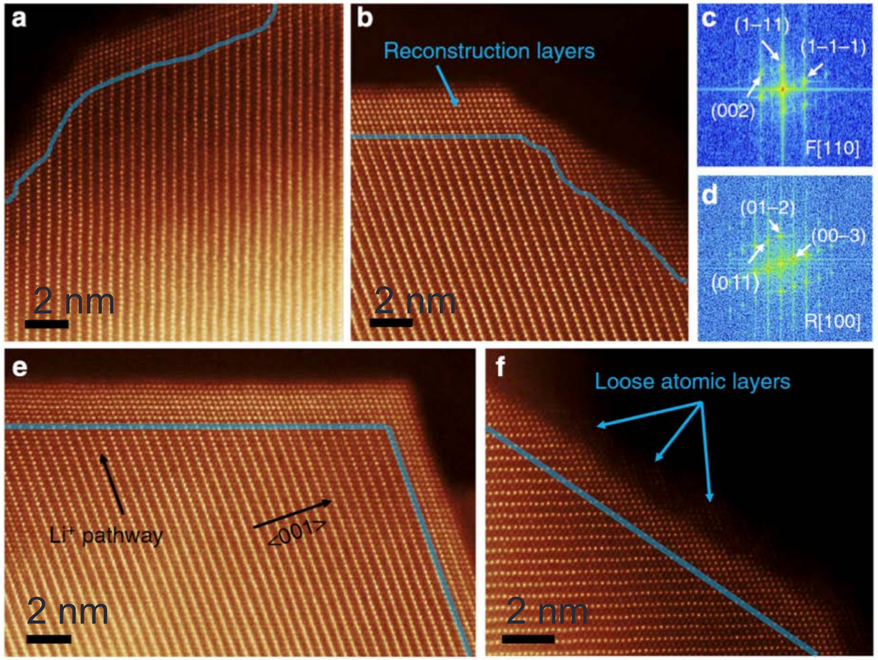
Background and Previous Work



STEM-EELS on a single charged particle (4.7V) shows oxidation state gradient



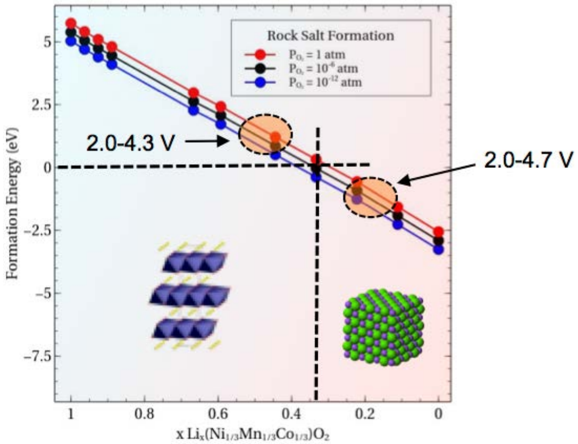
No oxidation state gradient or rock salt on surfaces of pristine powder



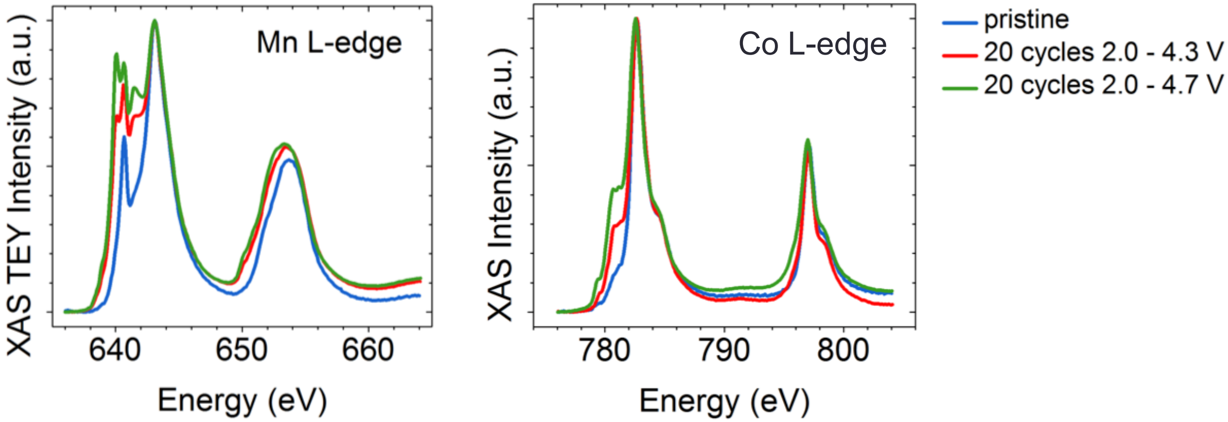
a) 30 hrs exposure to electrolyte,
b-f) 1 cycle to 4.7V (end of discharge)

Surface reconstruction to a disordered rock salt occurs upon exposure to electrolyte and cycling under a variety of conditions. This results in lower average oxidation states for metals on particle surfaces compared to the bulk. A cathode/electrolyte interface layer containing LiF, Li_2CO_3, and other species also forms upon charge to high potentials. This causes a rise in impedance.

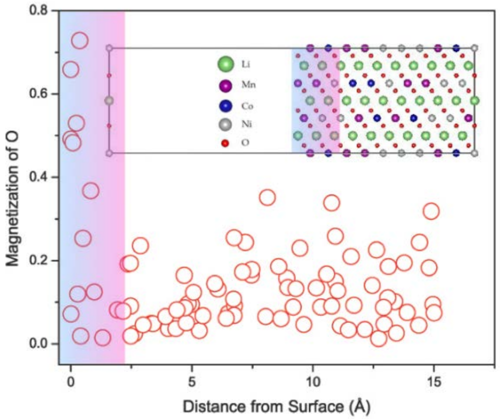
Background and Previous Work



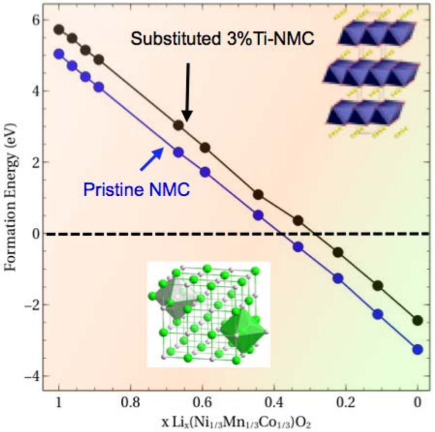
Theory predicts formation of disordered rock salt from layered structure at high states-of-charge



Soft XAS results show that surface reconstruction is more severe after cycling to 4.7V, but still occurs during cycling to 4.3V.



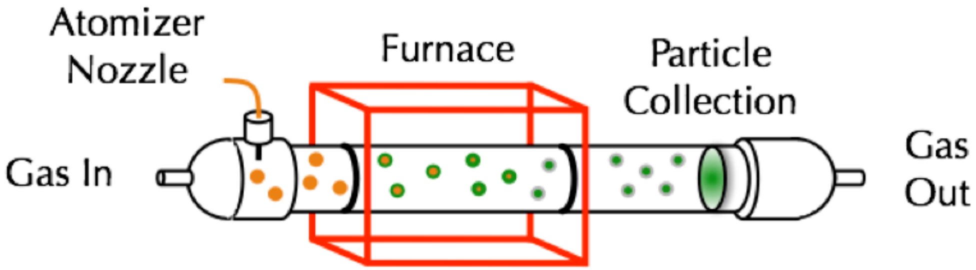
Oxygen at surface is higher energy and more likely to leave.

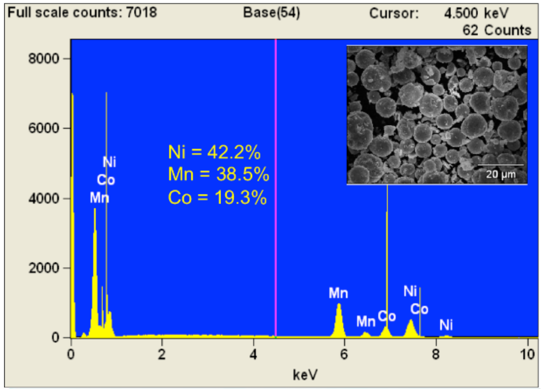


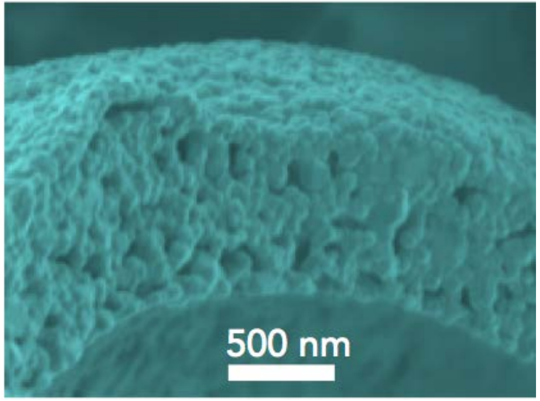
Ti-substituted NMCs are more stable w.r.t. formation of rock salt in a delithiated state. Our experimental work shows that better high voltage cycling is achieved with Ti-NMCs, and surface reconstruction is less severe.

Markus et al. J. Phys. Chem. Lett. 5, 3649 (2014).
Lin *et al.* Nat. Commun. 5, 3529 (2014)

Technical Accomplishments and Progress

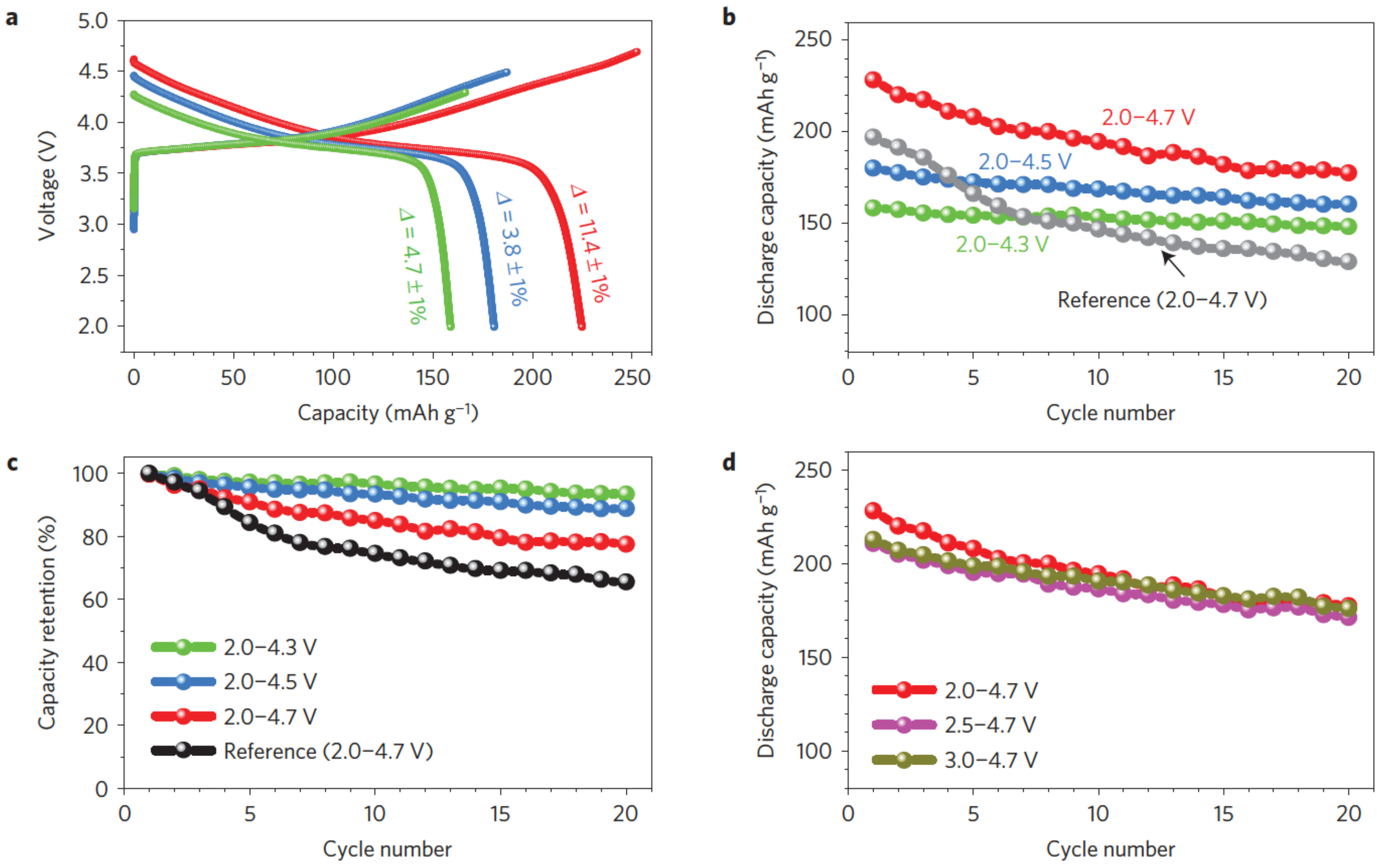






Spray pyrolysis was used to generate spherical NMC particles consisting of fused agglomerates. Because of the limitations of our home-made system, particles were hollow and required an additional annealing step. The use of a commercial system with a longer tube would circumvent the need for a second step and result in solid particles. The composition of the particles was close to the targeted value for NMC-442.

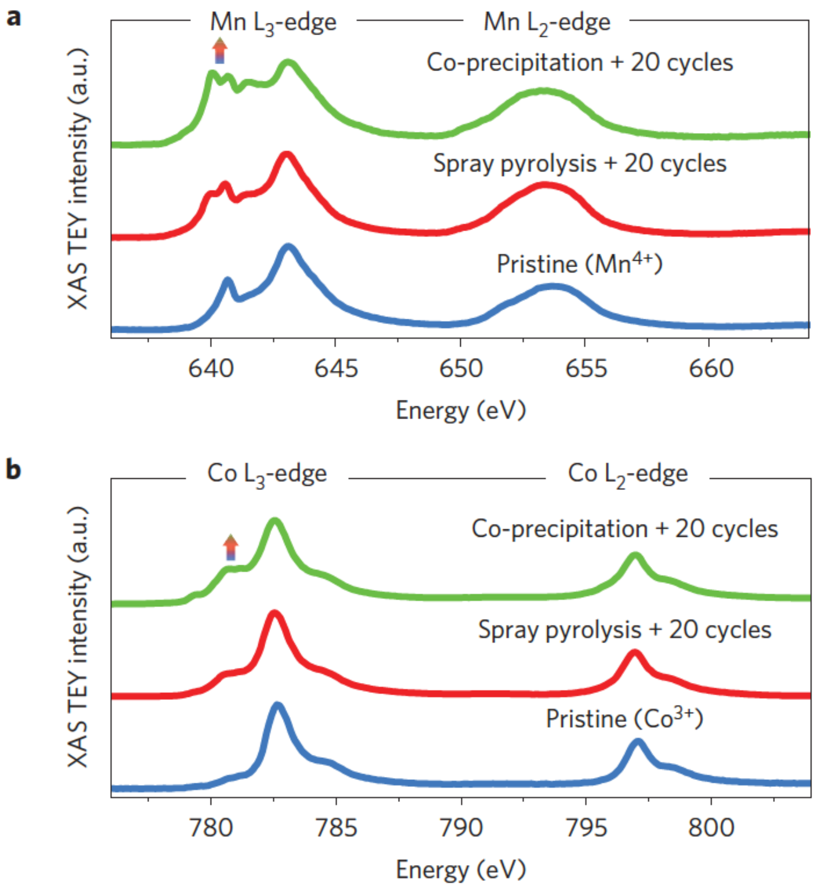
Technical Accomplishments and Progress



Galvanostatic cycling (C/20) of cells containing spray-pyrolyzed NMC-442 cathodes. The low first cycle inefficiencies (a) are striking. Capacity retention upon cycling to 4.7V is improved compared to a reference material (b and c) and initial capacities are higher as a result of the improved efficiency. Results are comparable to conventionally made Ti-NMCs, which also show improved high voltage cycling behavior.

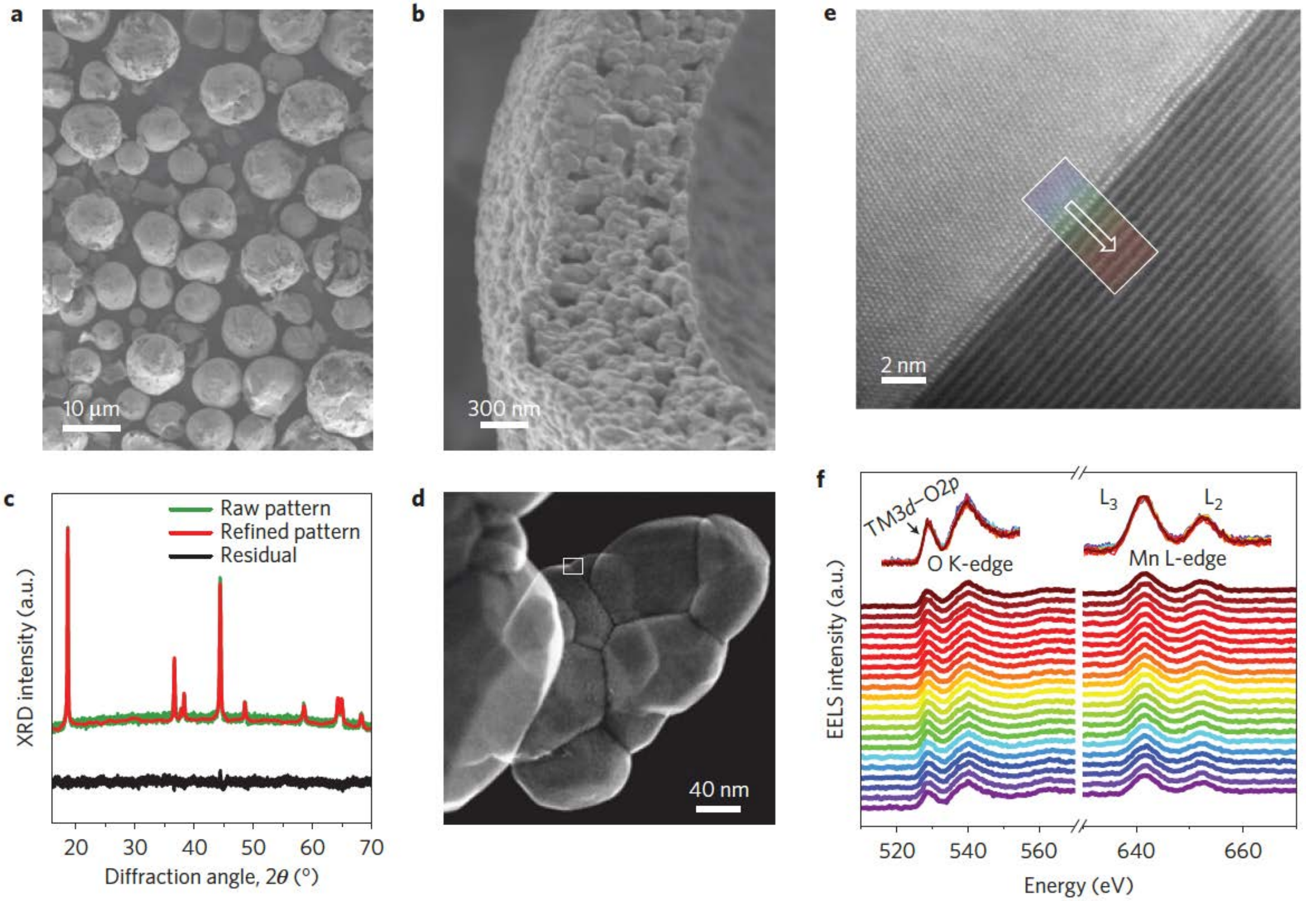
Lin et al. *Nature Energy*, 1, 1 (2016).

Technical Accomplishments and Progress



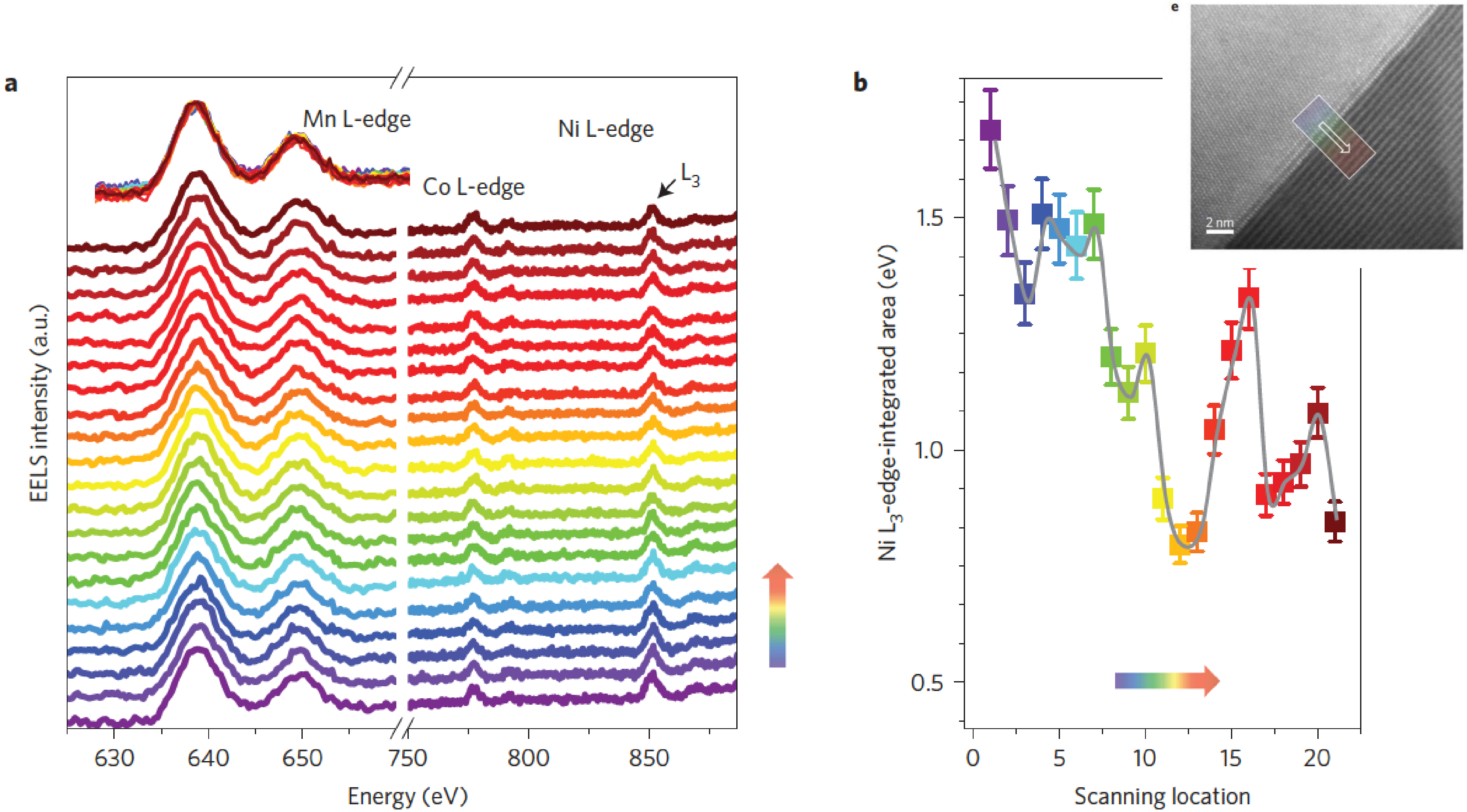
Soft XAS results on pristine electrodes and those cycled 20 times to 4.7V and stopped in the discharged state are shown at left. Both the Mn and Co L_{3low} edges are higher in magnitude for the co-precipitated NMC than they are in the spray-pyrolyzed sample after cycling, indicating that there is less surface reconstruction in the latter. Why does the spray pyrolyzed sample behave differently from the co-precipitated one?

Technical Accomplishments and Progress



The XRD pattern of the spray-pyrolyzed sample (c) is consistent with a pure single-phase NMC-442 material. The lattice parameters do not differ substantively from that of the co-precipitated sample. SEM images (a, b) show that the large secondary particles consist of tightly bound nanoparticles, suggesting that microstructure may play a role. The ADF- STEM image (d) shows a magnification of several of these grains. The enclosed white box shows the transgranular region over which O-K edge and Mn L-edge EELS was performed.

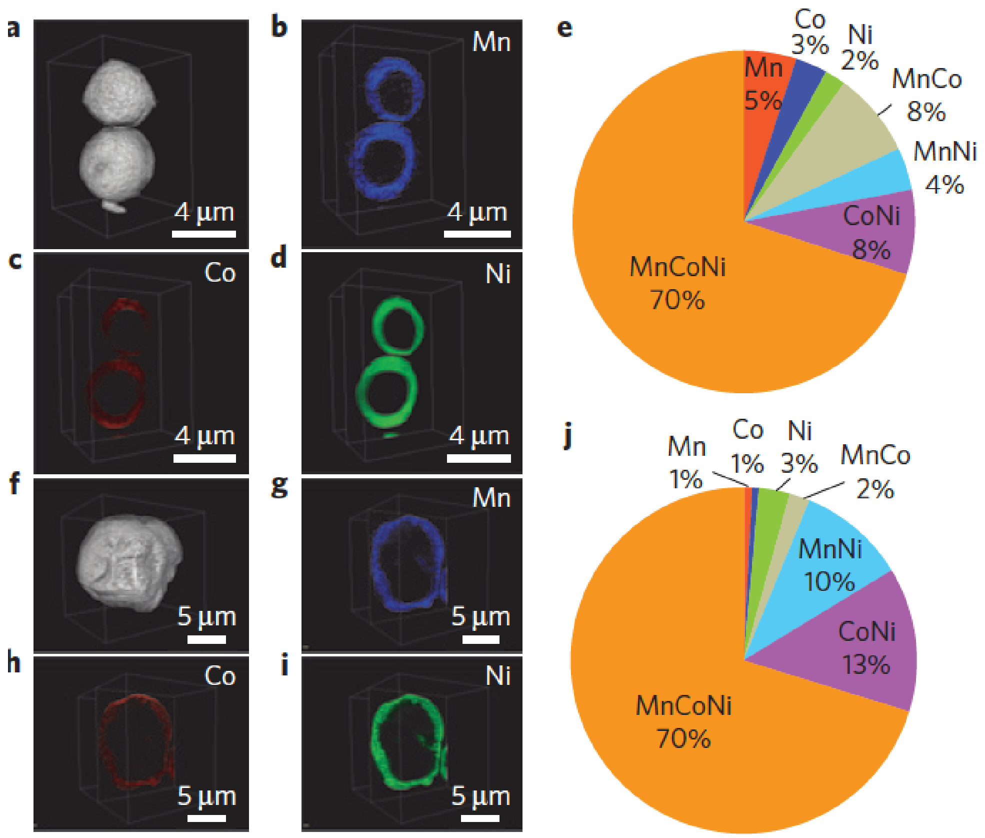
Technical Accomplishments and Progress



a) Transition metal L-edge EELS spectra along the scanning path shown in the inset. Spectra were normalized using the Mn L-edge, which shows no variation with position (top shows overlapped spectra). b) shows Ni L_3-integrated areas calculated after normalization. Multiple peak area calculations were used. These results show that the Ni-content varies across the transgranular region, with lower Ni content at the primary particle surface compared to the bulk.

Technical Accomplishments and Progress

annealed



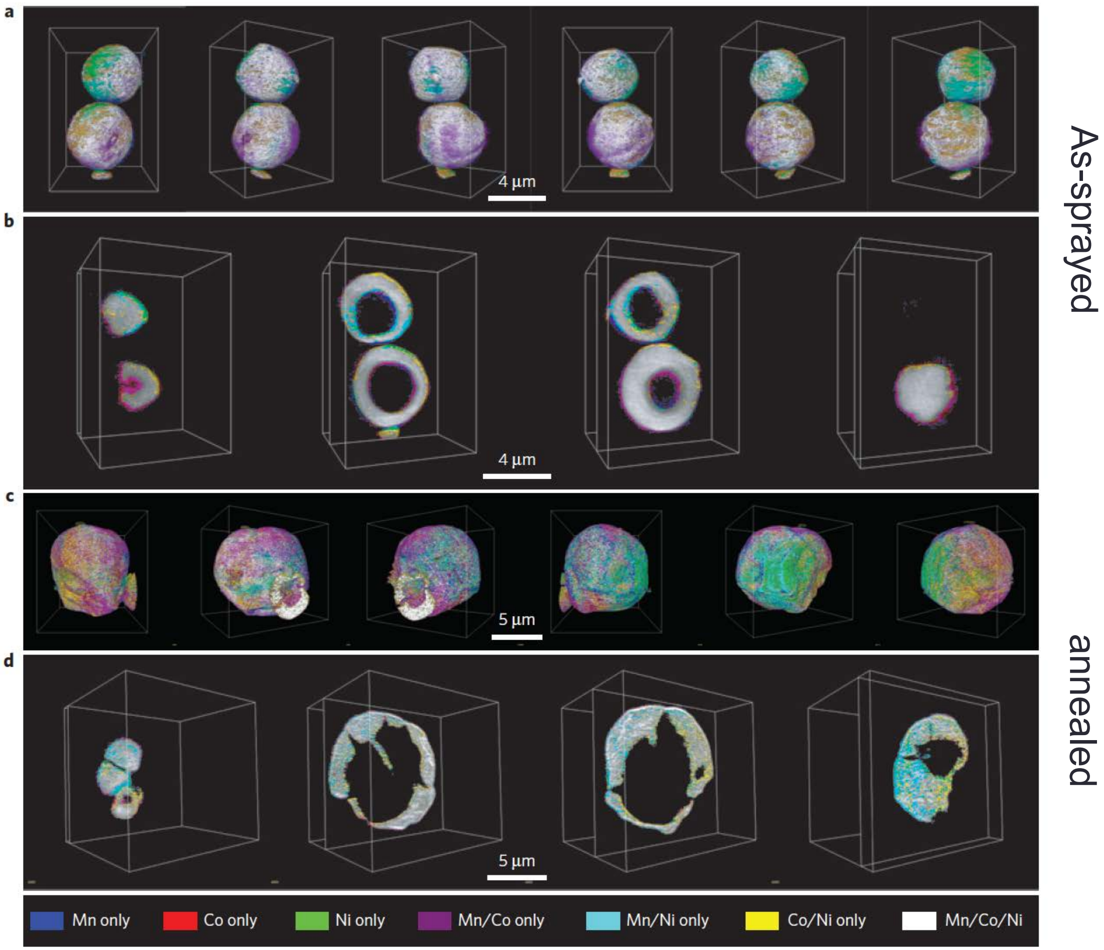
As-sprayed

Elemental mapping and association calculation using transmission X-ray tomography. a-d), 3D elemental distribution of selected NMC particles collected directly after spray pyrolysis, and f-i) after annealing at 850° C. Single energy tomography provides the 3D morphology of the particles (a, f), multi-energy tomography data with elemental sensitivity, visualized by slicing through the center of the particles, with blue, red, and green representing Mn, Co, and Ni, respectively (b-d, g-i) and the relative concentrations of 3D elemental associations calculated by using absorption correlation tomography (e, j).

1 voxel = 32.5 x 32.5 x 32.5 nm

Spray-pyrolyzed particles are surprisingly heterogeneous. Only 70% of voxels contain all 3 metals in both the as-sprayed and annealed materials.

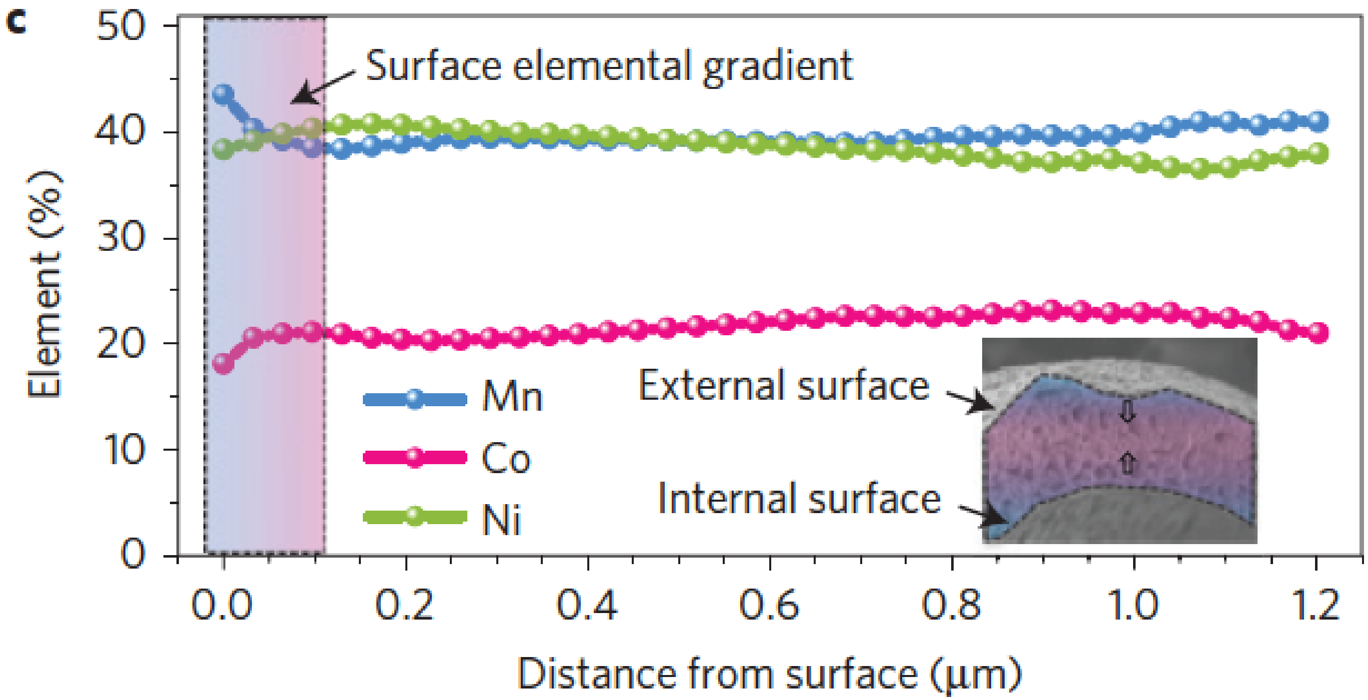
Technical Accomplishments and Progress



3D elemental association maps from the TXM experiments. A and c show elemental association viewing particles from different angles in the as-sprayed and annealed samples. B and d show 2d slices of the elemental associations cut through at different depths of the imaged particles. Movies are provided with the original Nature Energy paper.

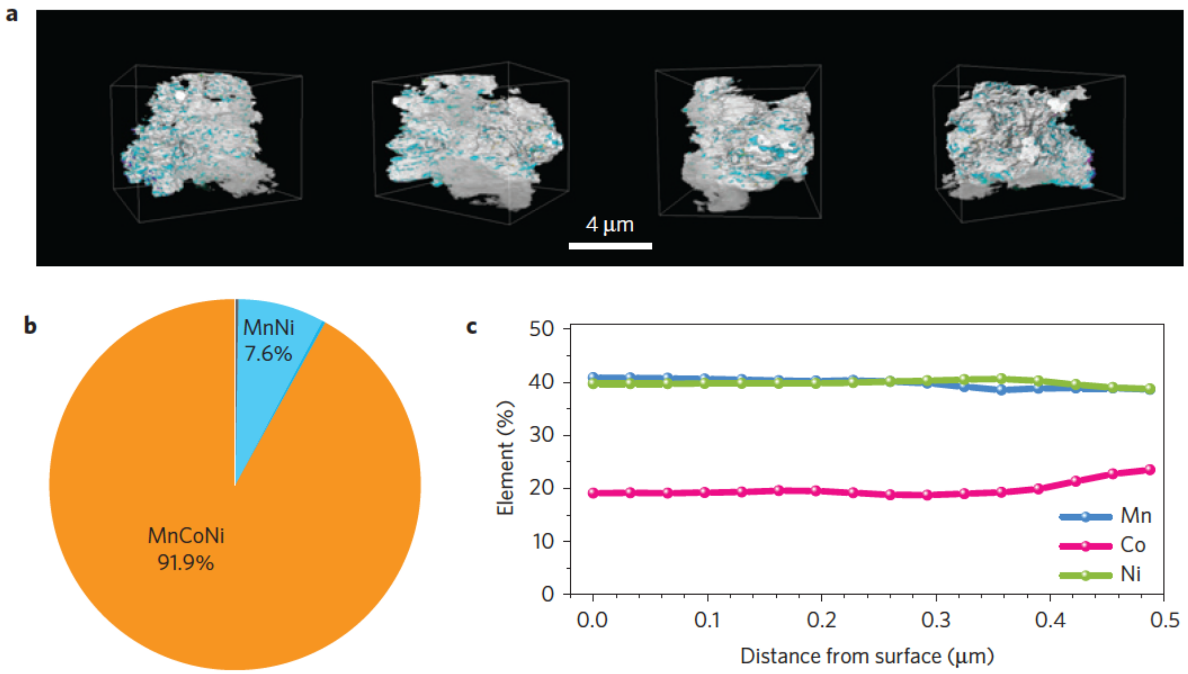
Elemental association maps suggest strongly that particle surfaces are Ni-poor (blue, red, purple).

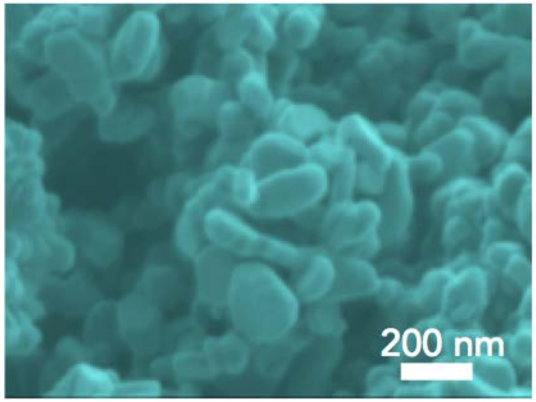
Technical Accomplishments and Progress



A quantitative analysis of the elemental association data shows that there is indeed less Ni on the surfaces of the spray-pyrolyzed samples than in the bulk. This, along with the microstructure of the particles, is probably responsible for the decreased surface reconstruction and better cycling performance. The next step is to correlate surface reconstruction and Ni content in Ni-rich NMCs to see if we can verify that Ni is the driving force for this.

Technical Accomplishments and Progress





a) TXM experiments on a co-precipitated NMC-442. b) elemental associations, and c) composition as a function of distance from the surface. On the right is a SEM image of a co-precipitated sample. While the primary particles are small, they are much less tightly agglomerated than in the spray-pyrolyzed sample. The composition of the sample is also much more homogeneous (92% of voxels contain all 3 elements) and there is no composition gradient in Ni going from the surface to the bulk. The higher surface Ni content may account for the greater degree of surface reconstruction seen in co-precipitated samples compared to spray pyrolyzed ones. This, in turn, affects the high voltage cycling behavior.

Responses to Previous Year Reviewers' Comments

- *The reviewer found the work narrowly focused on only one dopant and expressed a desire to it expanded to include series of dopants such as those of different oxidation states, for example, and evaluate their impact. The reviewer also thought the work should have included NMC of different compositions.*
  - Response: We have studied the effect of several other substituents on the performance of NMCs of various compositions in the past (Fe, Al, Ti). Results have been reported at previous Merit Reviews and in several publications (see JES 159, A1562 (2012), Chem. Mater. 24, 3307 (2012), JES 157, A1317 (2010), JES, 156, A1011 (2009)). Fe and Al substitution reduces capacity, although Al substitution improves thermal properties and rate capability. Only Ti substitution increases capacity and appears to improve high voltage cycling, when levels of delithiation are kept equal. This is why we chose to study the effects of Ti-substitution more intensively.
- *…the longevity of Ti-substitution on the surface properties has yet to be established and the cycling data presented does not support the claim that the cycle life has improved.*
  - Response: The results we reported indicated that capacity retention for Ti substituted NMCs upon cycling to high potentials is better than that for the unsubstituted baseline material, **provided that levels of delithiation upon charge are the same.** When cycling to 4.7V, more lithium is removed from the Ti-substituted structure than the baseline structure because the substitution changes the voltage profile. This means that higher capacities can be obtained in practical voltage ranges for the Ti-substituted material, although the effect on long term cycling still needs to be established. We will collaborate with the Battaglia group to assess this in the future. It is likely that several strategies need to be used to ensure reliable cycling to high potentials, including the use of high voltage electrolytes and coatings. We are collaborating with the Ban group for the latter, and are now using electrolytes from Daikin.
- *The reviewer also suggested the project team explore higher Ni content materials using dopants and study their thermal behavior – a key drawback of this group of cathode materials.*
  - Response: This will be the focus of the new project, which started Oct. 2015. We have been collecting data relevant to the thermal behavior and high voltage cycling behavior of several Ni-rich NMC compositions and should be able to report the fully analyzed results at the next Merit Review.

Collaboration and Coordination with Other Institutions

- The project ending in FY15 was a single investigator project
- The new project is a multi-investigator effort with Kostecki, Tong, McCloskey, and Ban of NREL

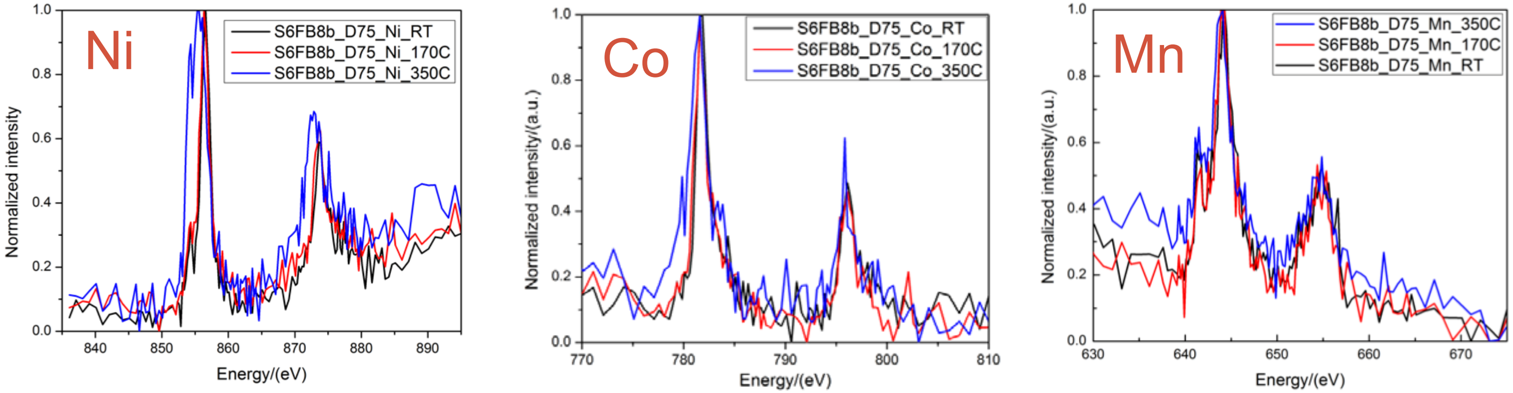
Collaborator	Institution	Nature of Collaboration
Prof. M. Asta	UC Berkeley	Computation on Ti-NMCs. Shared graduate student (Isaac Markus)
A. Mehta, D. Nordlund, T.-C. Weng, D. Sokaras, Y. Liu	SSRL	Synchrotron XRD, Raman, imaging, and XAS experiments
Huolin Xin	BNL	STEM-EELS, high resolution TEM
R. Kostecki, W. Tong, B. McCloskey	LBNL	Ni-containing cathodes, Ni-rich NMCs
C. Ban	NREL	ALD and MLD coatings on Ni-rich NMCs
G. Chen, R. Kostecki, K. Persson, M. Salmeron	LBNL	Solid electrolytes
E. Crumlin, N. Tamura	ALS/LBNL	Synchrotron studies on solid electrolytes
S. Meng	UCSD	Cathodes, synchrotron studies

Remaining Challenges and Barriers

- A full understanding of the high voltage cycling and thermal behavior of Ni-rich NMCs will require close coordination among all the PIs involved in this project.
- Synchrotron beam time is allocated based on the scores obtained on general user proposals. We have received very high scores on our proposals giving us first priority, but some beam lines are very heavily subscribed and time is limited.
- The resolution of the TXM experiment is ~30 nm. This limits the types of samples that can be studied (e.g., it's difficult to study nanometric samples).
- While Ti-substituted NMCs and spray-pyrolyzed materials perform better during high voltage cycling, there is still capacity fading. Multiple strategies will need to be pursued to ensure stable cycling to high potentials, including the use of specially designed electrolytes and ALD coatings.

Proposed Future Work

- We have started a new multi-investigator project, focusing on Ni-rich compounds, including Ni-rich NMCs and their high voltage behavior.
- Work in the upcoming year for the Doeff group involves analysis of the details of thermal behavior of Ni-rich NMCs using synchrotron techniques (transmission x-ray microscopy, x-ray Raman). Preliminary results are shown below.



X-ray Raman results on a 75% delithiated NMC-622 sample, showing that Ni is reduced when the compound is heated to 350° C but Co and Mn are not. The behavior is similar to that seen for $LiNiO_2$ and implies loss of oxygen.

- We will also use an array of techniques to determine how Ni content affects surface reconstruction and cathode electrolyte interfaces, including soft XAS, synchrotron XPS, and STEM-EELS.
- We will coordinate efforts with the Kostecki group (spectroscopic investigations of the CEI), McCloskey group (DEMS to measure gas evolution upon cycling), Tong group (Li-Ni-O phases), and Ban group (ALD coatings).
- We anticipate no difficulties achieving the milestones involving obtaining data at synchrotron or microscopy facilities. One milestone involves a decision point on synthesis of composites by spray pyrolysis. If the decision is no-go, we will emphasize the diagnostic aspects of the project to replace the synthesis task.

Summary

- Surface reconstruction and formation of a cathode/electrolyte interfacial layer on NMC particle surfaces contribute to impedance rise during high voltage cycling and result in capacity fading.
- Spray-pyrolyzed NMC-442 shows evidence of less surface reconstruction compared to co-precipitated samples after twenty high voltage cycles. Higher discharge capacities, lower first cycle coulombic inefficiencies, and better capacity retention are also observed.
- Spray-pyrolyzed NMC-442 powders are surprisingly heterogeneous in composition according to both TXM and STEM-EELS results. In particular, both the primary and secondary particle surfaces are lower in Ni content than deeper in the bulk.
- These results strongly imply that Ni is the driving factor for surface reconstruction, and that materials designed with less Ni on particle surfaces will sustain high voltage cycling better than conventional materials.
- Extension of these studies to Ni-rich compositions in the upcoming year should give us more information about the role that Ni plays in surface reconstruction.