Design of High-Performance High-Energy Cathode Materials

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Project ID #
BAT052

+ Overview

Timeline

- Project start date 10/1/2015
- Project end date 9/30/2018
- Percent complete 90%

Budget

- Total project funding
  - DOE share 100%
  - Contractor share N/A
- Funding for FY 2017 $625k
- Funding for 2018 $625k

Barriers

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

Partners

- LBNL, SSRL
- Project lead: LBNL

+ Relevance

- To reach energy density goals, practical capacities of NMCs need to be increased.
- Some ways to do this is increase Ni content (Ni-rich NMCs) and cycle to higher potentials.
  - 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).
- Both higher Ni content and higher potentials currently result in shortened cycle life. Higher Ni content compromises thermal stability (safety) at high states-of-charge. We need to understand these effects and develop strategies to counteract them.
- Some strategies (Ti-substitution, ALD coatings) appear to improve high voltage cycling behavior-understanding these effects will allow us to design better cathode materials.

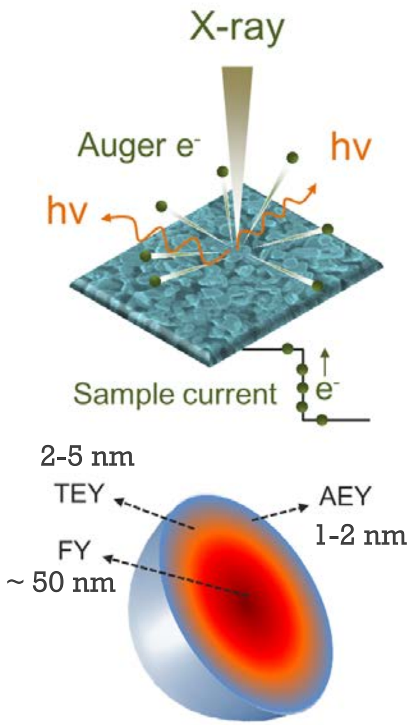
+ Objectives

- To develop high energy, high performance cathode materials, with an emphasis on designing NMCs for better performance.
- First, experiments are carried out to understand high voltage and thermal behavior of NMCs. Both commercial materials and those synthesized in-house are studied. Synthesis methods used include co-precipitation and spray pyrolysis.
- Some variants of materials are studied (e.g., Ti-substituted, those with graded compositions made by spray pyrolysis).
- Information obtained from these experiments can be used to design more robust materials.

Milestones-FY17 and FY18

Milestone	Date	Status
Synthesize baseline NMC-523 and 622 and Ti-substituted variants	12/31/16	Completed. Decision made to emphasize NMC-622 in FY2017, rather than NMC-523.
Complete surface characterization of pristine materials by synchrotron XAS and XPS	3/31/17	Completed for NMC-622.
Complete soft XAS experiments of electrodes cycled to high potentials.	6/30/17	Completed study of NMC-622. Two papers published.
Go/no go decision on core-shell composites made by spray pyrolysis	9/30/17	No go decision made. Metal segregation occurs naturally in spray-pyrolyzed samples, so that particle surfaces are already Ni-poor. This one-step process is less complicated and more effective than infiltrating hollow particles and refiring to make core-shell composites.
Complete thermal characterization of candidate NMCs by TXM and X-ray Raman	12/31/17	Data collection complete for NMC-622, and on-going for NMC-811. Analysis completed for NMC-622 and on-going for NMC-811.
Synthesize NMC-811 by spray pyrolysis and conventional methods	3/31/18	Completed
Complete surface characterization of pristine and cycled NMC-811	6/30/18	Under way
Go/no go decision on Ti-substitution of NMC-811	9/30/18	Initial experiments carried out. Discontinue if solid solutions are not formed or Ti-substitution does not benefit electrochemistry.

+ Approach/Strategy

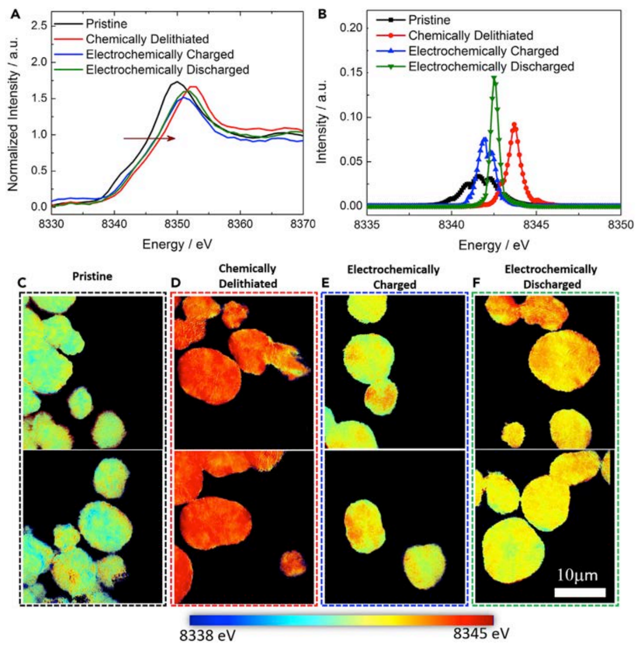


AEY- Auger Electron Yield
TEY- Total Electron Yield
FY- Fluorescence Yield

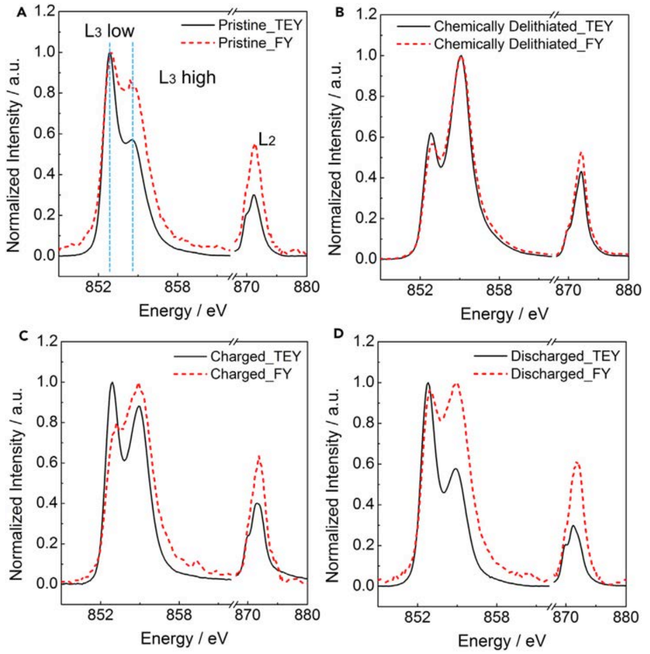
Different modes in soft XAS probe different sample depths

- Use synchrotron techniques (soft XAS, XPS, X-ray Raman, TXM) and microscopy (STEM-EELS) to understand thermal and high voltage cycling behavior of NMCs.
- Use this information to develop strategies to improve behavior (e.g., aliovalent Ti-substitution, graded compositions, coatings) and understand their effects.
- Explore alternative synthesis approaches (e.g., spray pyrolysis) that result in less Ni on surfaces of NMCs.

+Prior Year’s work



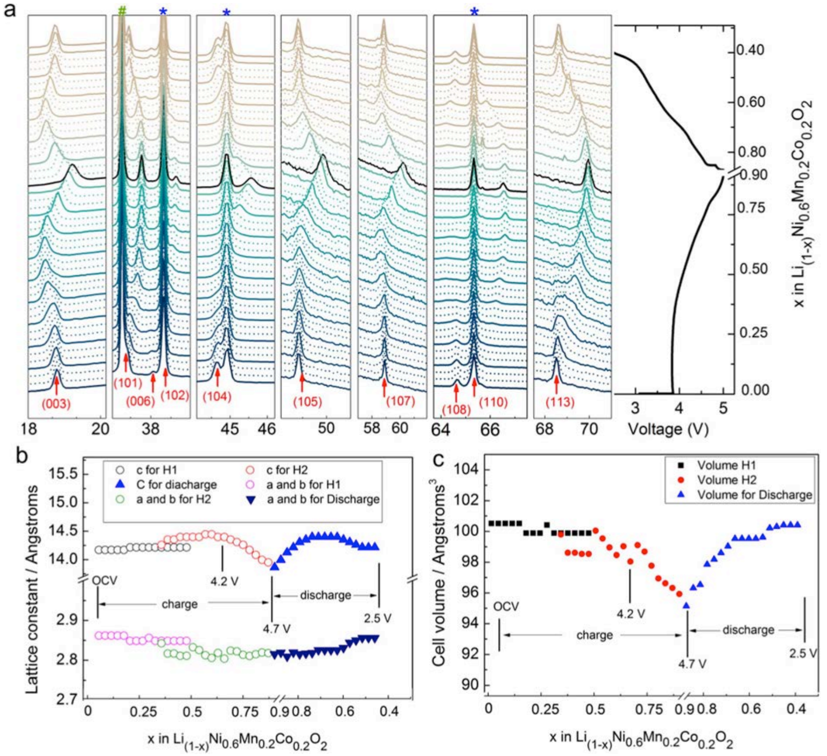
TXM 2D Ni oxidation state mapping of NMC-622 samples



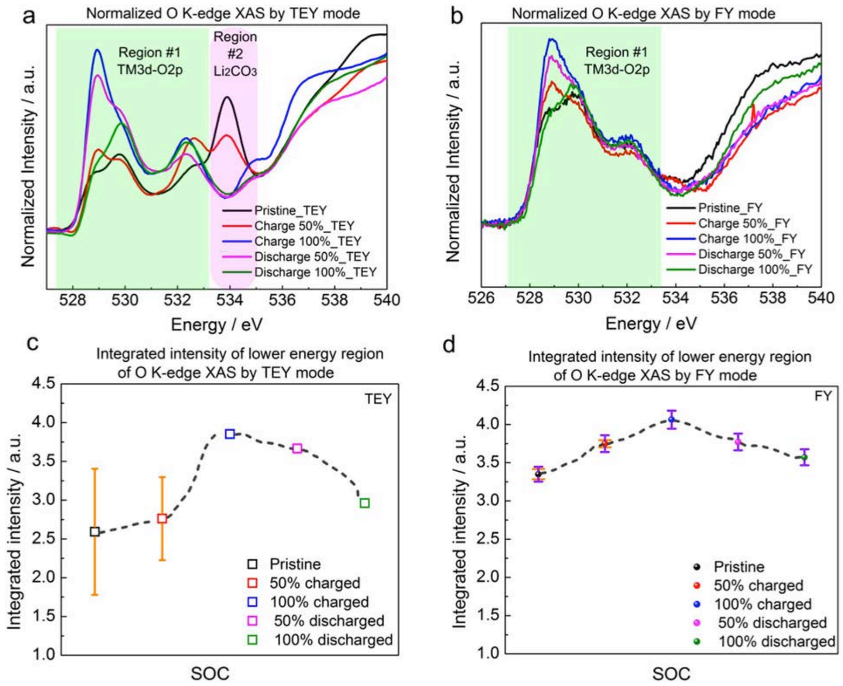
Ni L-edge XAS of NMC-622 samples at different probing depths (TEY mode ~ 5nm, FY mode ~50 nm)

Chemically and electrochemically delithiated samples were compared to see if chemically delithiated samples are a good model system for the electrochemically delithiated ones. TXM revealed that both types of samples show similar heterogeneities in terms of metal redox states. Soft XAS showed that chemically delithiated samples show less surface reconstruction than electrochemically delithiated ones, suggesting that interaction with electrolytic solutions plays an important role in this phenomenon. *Joule* 2, 464 (2018).

Prior Year’s work



In situ XRD of NMC-622 undergoing electrochemical cycling

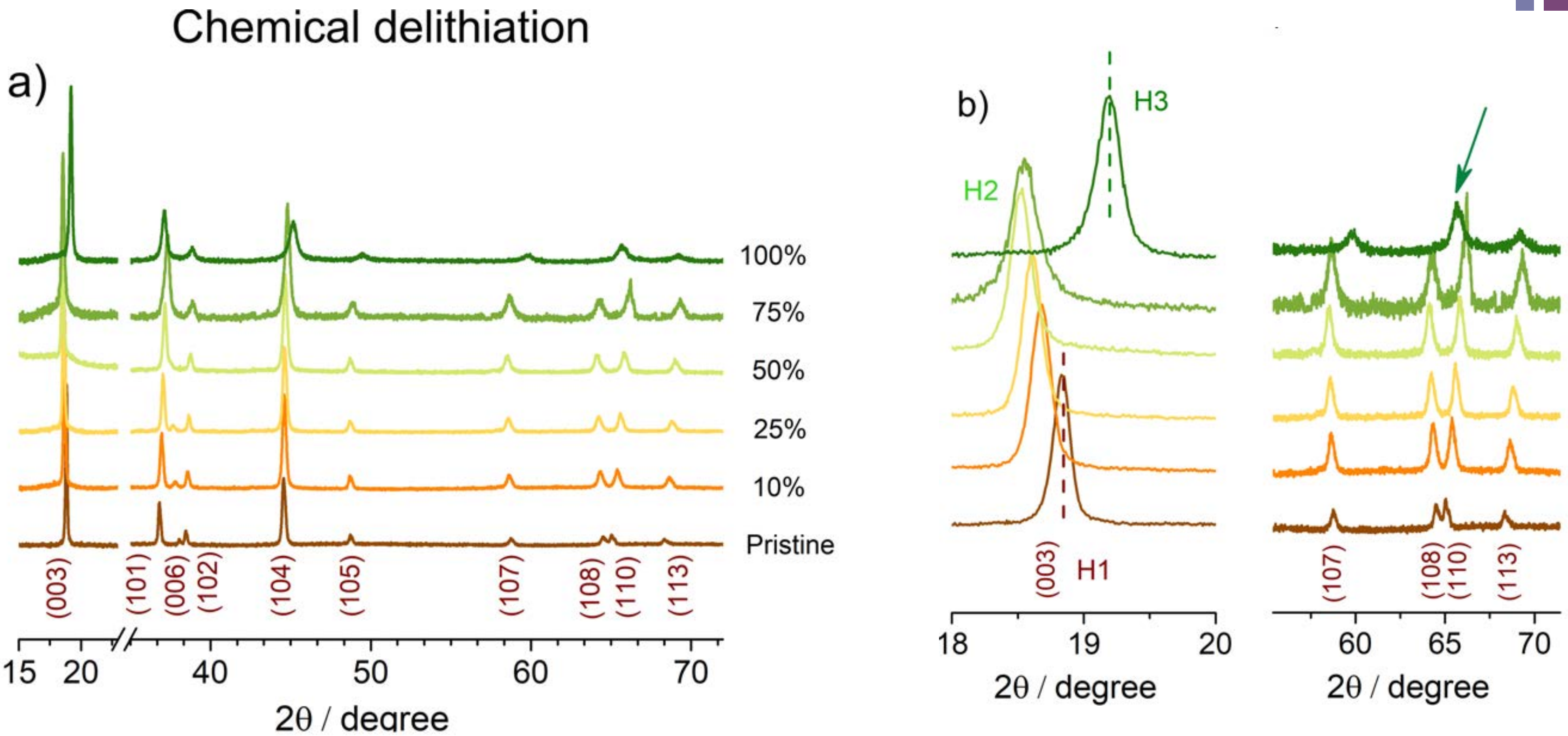


O K-edge XAS at different probing depths (TEY mode ~ 5 nm and FY mode ~ 50 nm).
Differences between changes in surface and bulk O redox states are shown in (c) and (d).

NMC-622 was characterized as a function of state-of-charge in terms of bulk and surface processes. Structural changes are highly reversible, with little volume change. Changes in Ni and O redox states differ between the surface and bulk and could be quantified. The higher activity of surface O drives the surface reconstruction process and contribute to reactions between particle surfaces and electrolyte.
J. Electrochem. Soc. 165 A696 (2018).

Technical Accomplishments and Progress

NMC-622

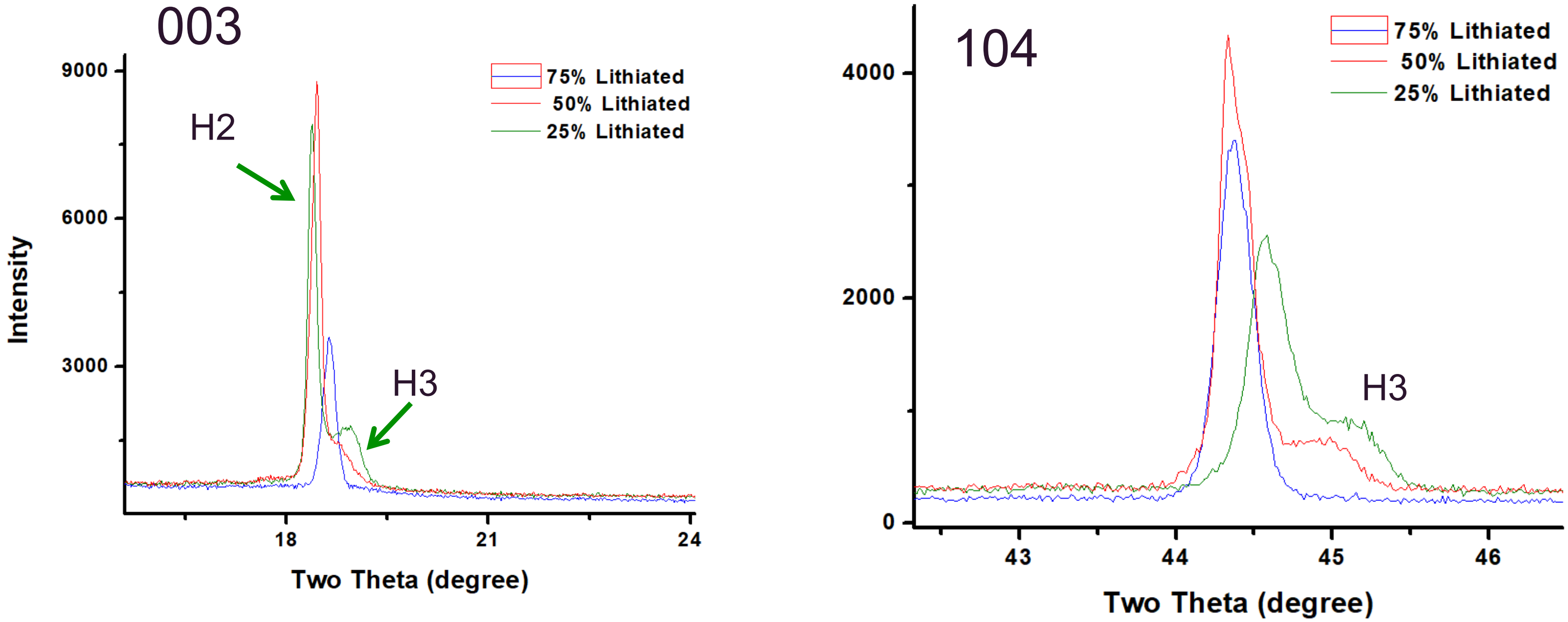


Chemical delithiation of NMC-622 yields products that retain the expected layered structure with the exception of the 100% delithiated sample (proton exchange/insertion also occurs). Several phases H1, H2, and H3 are observed, similar to what is seen during the electrochemical process, but all samples appear single phase.

+ NMC-811 Chemical Delithiation

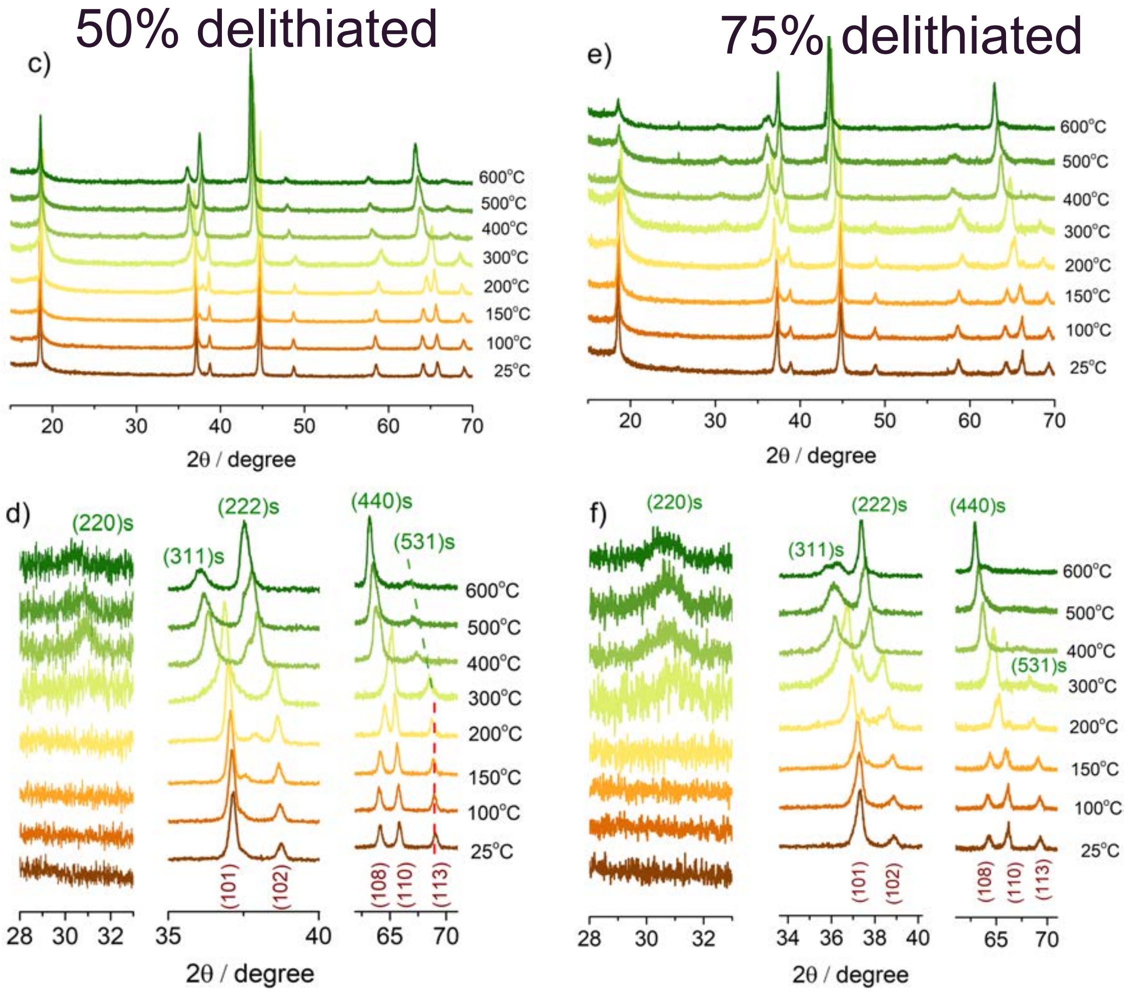
NMC-811

Chemical delithiation



Chemical delithiation of NMC-811 to the same degree as some of the NMC-622 samples results in several two-phase mixtures, but, otherwise, samples exhibit the expected layered structure. This implies that two-phase regions exist over broader composition ranges than in NMC-622. *In situ* XRD experiments on cells containing NMC-811 are being planned to compare the electrochemistry to these results.

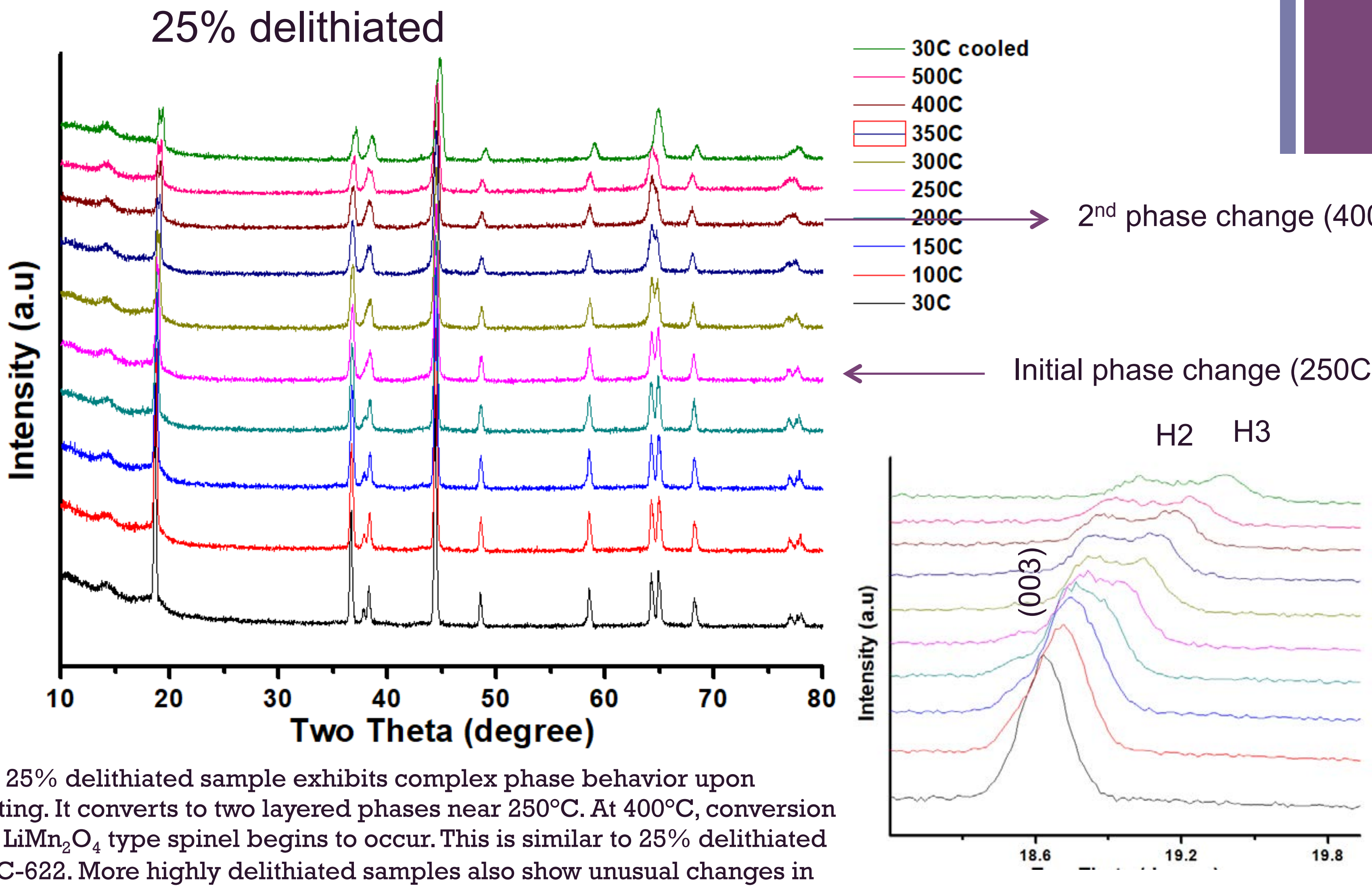
+ NMC-622 *in situ* heating experiments



As samples are heated, bulk structural changes occur. Thermal stability decreases as lithium is removed. In 10 and 25% delithiated samples (not shown), disordering occurs near 300°C and partial conversion to a $LiMn_2O_4$ type spinel occurs at higher temperatures, which requires no oxygen loss. For the 50% delithiated sample, disordering occurs near 200°C, with formation of a $LiMn_2O_4$-type spinel above this temperature, followed by further decomposition to a M_3O_4 type spinel near 400°C, implying loss of oxygen. These changes occur at lower temperatures for the 75% delithiated material, with formation of some rock salt (MO) at 300°C, with further loss of oxygen as well. The completely delithiated sample undergoes these changes at even lower temperatures; by about 300°C, complete conversion to M_3O_4 and MO has occurred.

+ NMC-811 *in situ* heating experiments

25% delithiated



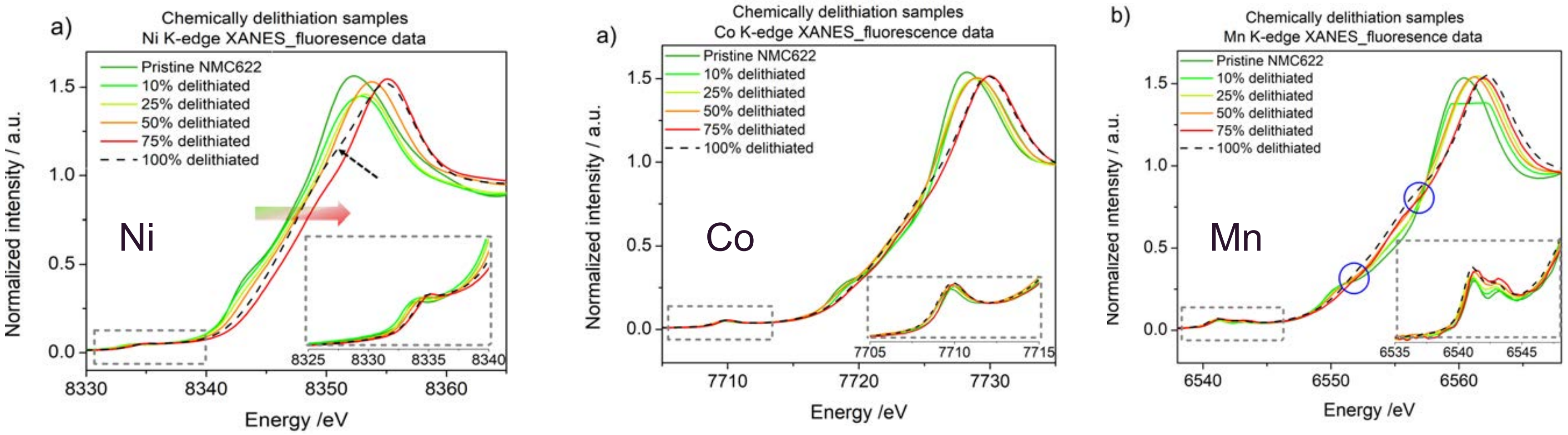
The 25% delithiated sample exhibits complex phase behavior upon heating. It converts to two layered phases near 250°C. At 400°C, conversion to a $LiMn_2O_4$ type spinel begins to occur. This is similar to 25% delithiated NMC-622. More highly delithiated samples also show unusual changes in two-phase behavior. Partial conversion to spinel begins as low as 120°C for the 75% delithiated sample (200°C for 50% delithiated), followed by rock salt formation, with no apparent intermediate M_3O_4 formation.

+ Comparison of bulk thermal stabilities

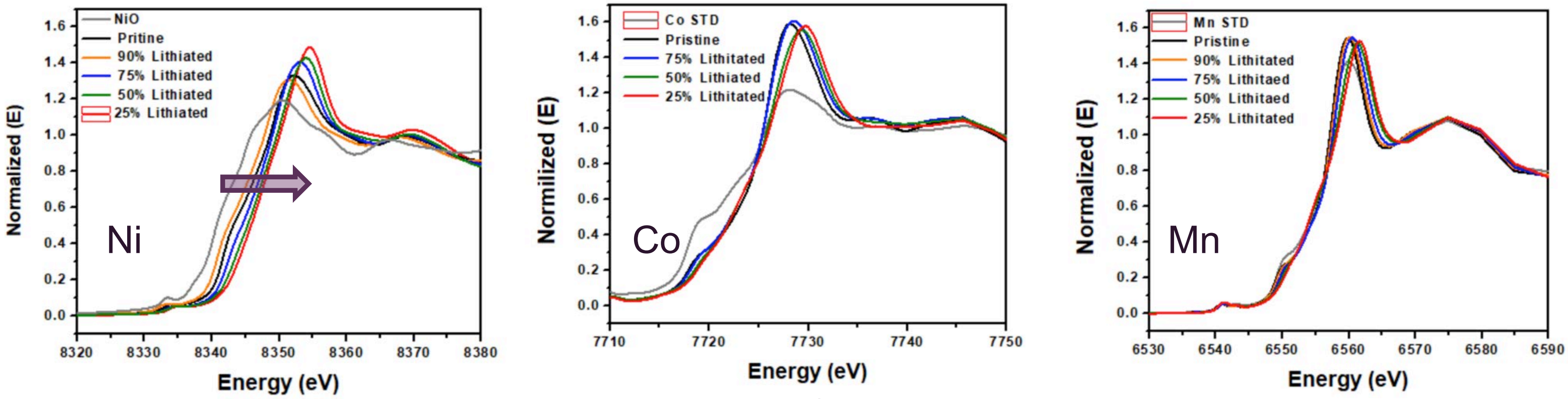
Chemical Delithiation %	Onset temp of phase change NMC811	Onset temp of phase change NMC622
25	Room Temp (1 layered) 250°C (2 layered) 400°C (spinel)	300°C (disordering) 400°C (spinel)
50	Room Temp (2 layered) 200°C (1 layered, spinel) 400°C (spinel, MO*)	200°C (spinel) 300°C (M_3O_4*)
75	Room Temp (2 layered) 120°C (1 layered, spinel) 150°C, 200°C, 350°C (layered to spinel to MO*)	150°C (spinel) 300° C (M_3O_4*, MO*)
100	N/A	150°C (disorder) 200°C (MO*, M_3O_4*)

*= implies O_2 loss

Hard XAS characterization of delithiated samples before heating



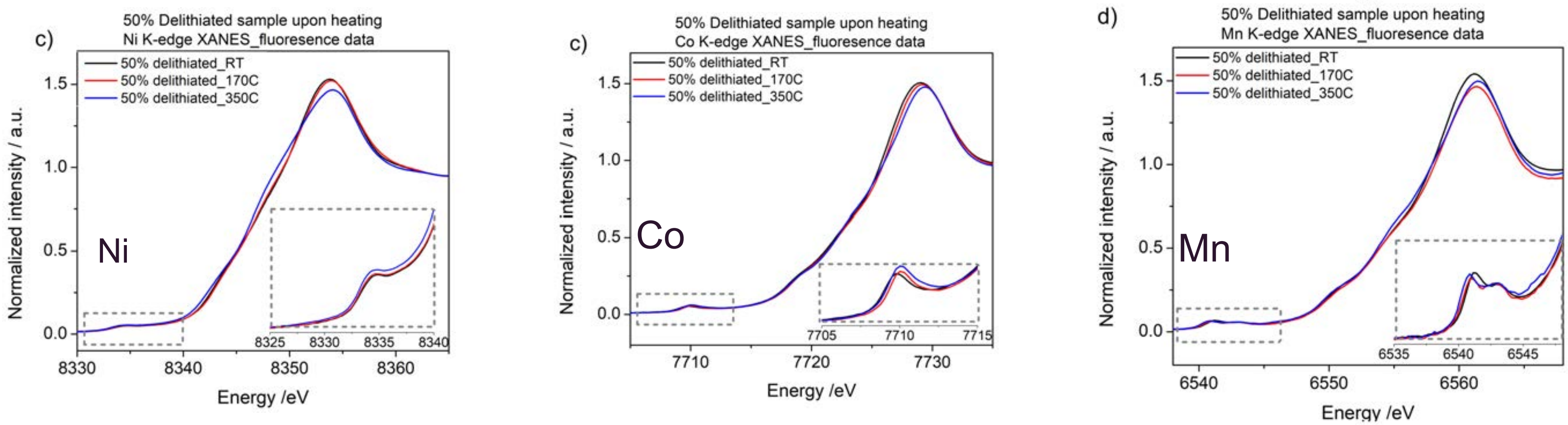
NMC-622



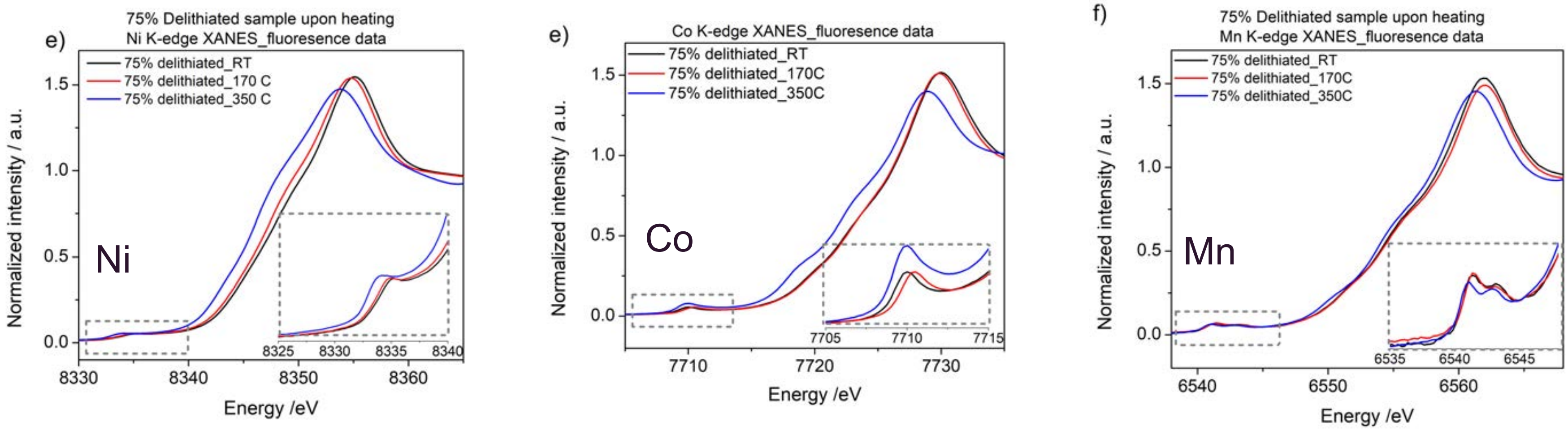
NMC-811

Hard XAS probes the bulk. Ni and Co K edges shift to higher energies as lithium is removed, consistent with oxidation. (The exception is the fully delithiated NMC-622, which may have undergone proton exchange/insertion). Mn does not undergo oxidation, but minor shifts in the edge energies occur due to changes in bondlengths. Results are similar to that of electrochemically delithiated samples (not shown).

Hard XAS on heated NMC-622 samples



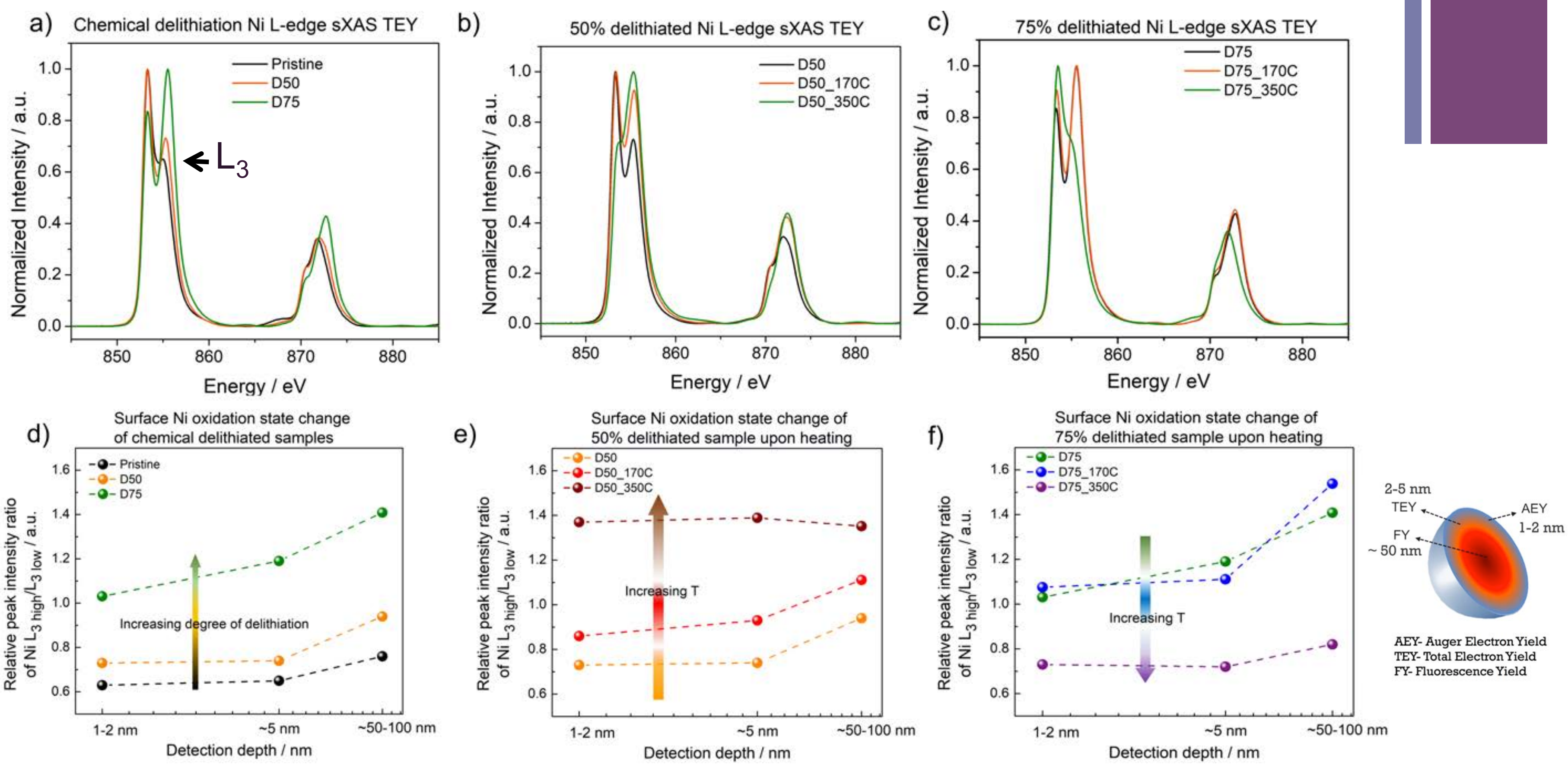
50% delithiated



75% delithiated

For the 50% delithiated sample, changes in metal oxidation state upon heating to 170 or 350°C are minimal and are consistent with XRD results, implying little to no oxygen loss from the bulk. For the 75% delithiated sample, reduction of Ni,Co, and Mn are obvious in the sample heated to 350°C. This is consistent with decomposition to reduced metal oxides (M_3O_4, MO) at higher temperatures, as observed in the XRD data.

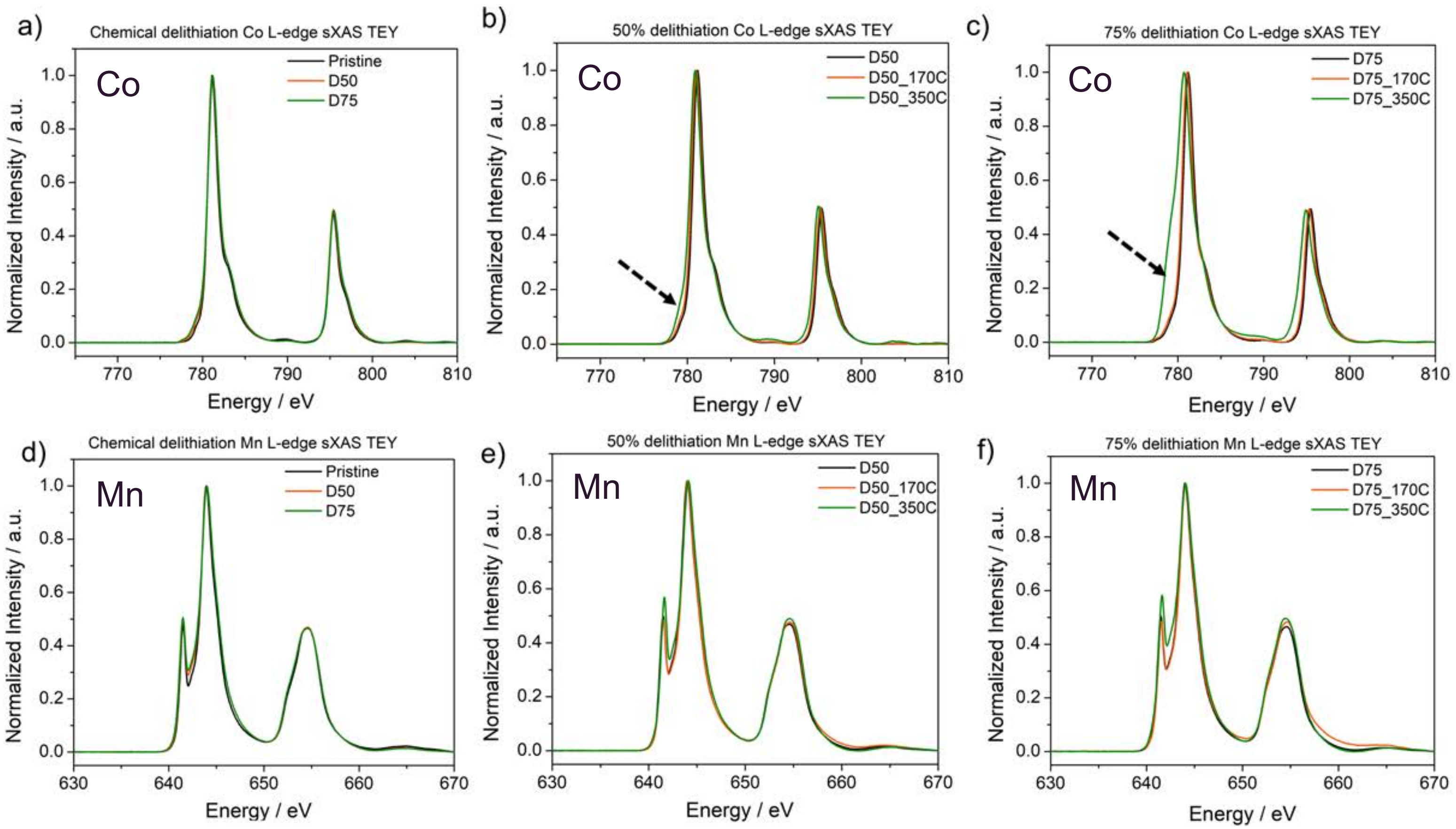
+ Ni L-edge soft XAS on NMC-622



Soft XAS is a surface characterization and depth profiling technique (AEY mode ~1-2 nm, TEY mode ~5 nm, FY mode ~50 nm). The ratios of the L_{3high} and L_{3low} peaks give information about the relative Ni oxidation states (a). Discrepancies between surface and bulk Ni oxidation states in the delithiated samples (d) imply surface reconstruction to a rock salt phase. For the 50% delithiated sample, the relationship is maintained upon heating to 170°C although the sample is somewhat oxidized overall. The sample becomes more homogenous at 350°C and the Ni is oxidized on the surface to a depth of at least ~50-100 nm (b, e). For the 75% delithiated sample, heating to 170°C causes some reduction close to the surface (probably associated with loss of oxygen), but slight oxidation occurs deeper in the sample(c, f). Heating to 350°C results in dramatic reduction of both surface and bulk Ni and homogenization of oxidation states.

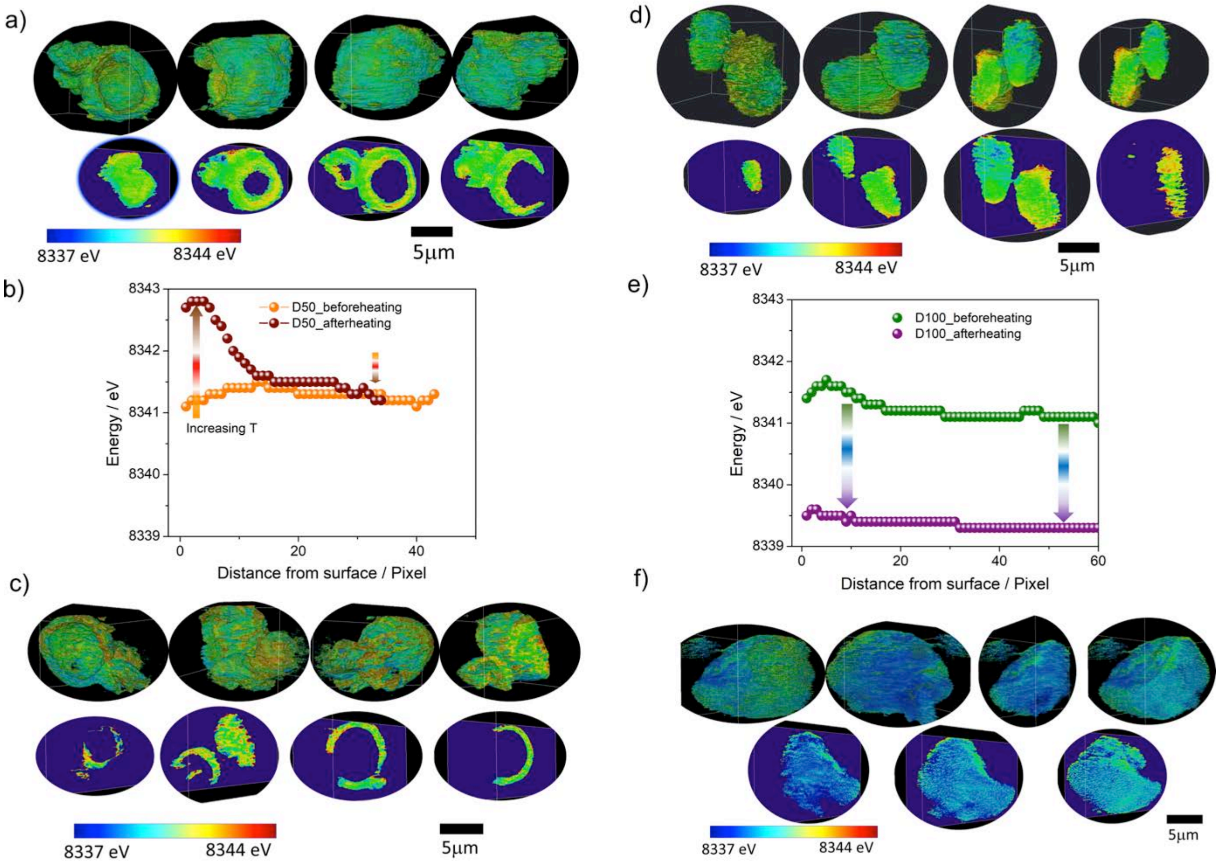
+ Co and Mn L-edge soft XAS on NMC-622

50% 75%



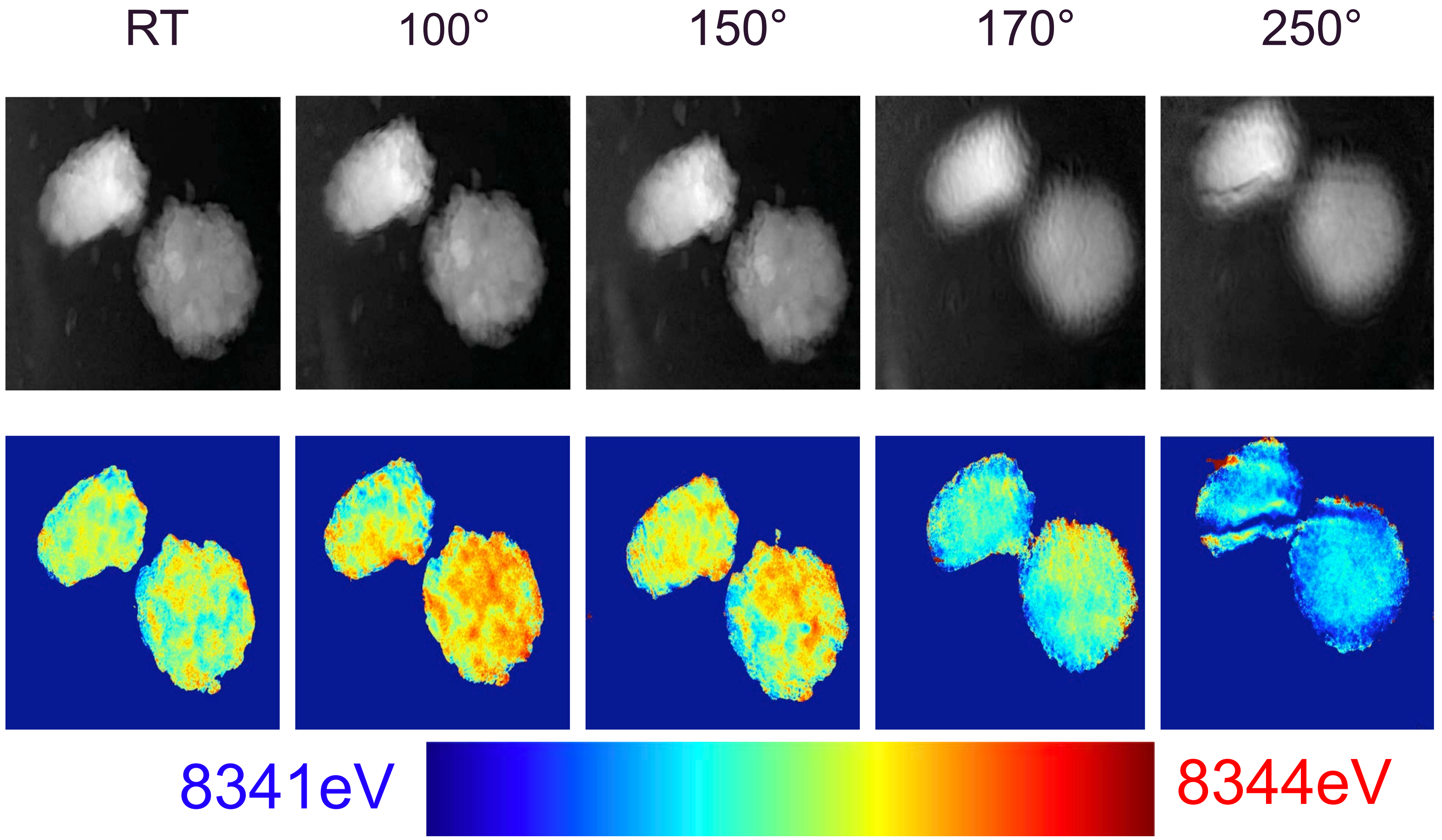
Co and Mn L-edge soft XAS was carried out in TEY mode, probing to a depth of about 5 nm. The surface is somewhat reduced compared to the bulk because of surface reconstruction. Heating to 170°C has little effect on oxidation states for Co and Mn for either sample, but there is evidence of reduction of Co at 350°C, particularly in the 75% delithiated sample. This suggests that Co is present in reduced phases on the particle surfaces. Surprisingly, Mn shows little change in oxidation state upon heating.

+ TXM on NMC-622 samples



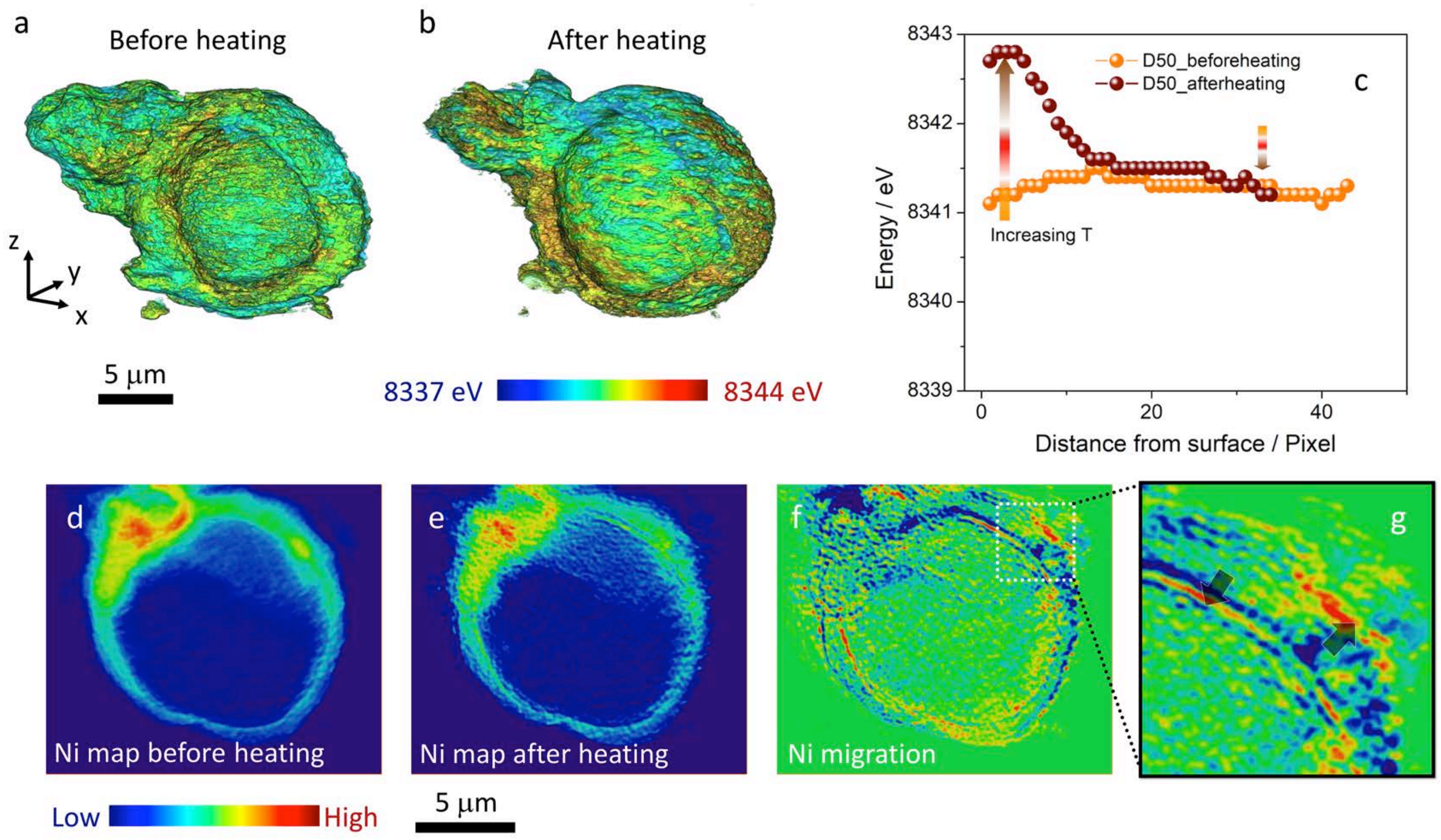
Transmission X-ray Microscopy (TXM aka nanotomography) was carried out on delithiated NMC-622 samples, before and after heating to 350°C. 2D Ni oxidation state mapping is presented for the 50% delithiated sample before (a) and after (c) heating. The average energy of the edge (an indicator of oxidation state) is plotted as a function of depth (1 pixel=32.5 nm) in (b). While Ni is slightly reduced on the surface in the unheated material (evidence of some surface reconstruction), the sample is fairly homogeneous (on average). After heating, a large oxidation state gradient exists, with more oxidized Ni on the surface. In contrast, the same experiment on the 100% delithiated sample before (d) and after (f) heating shows a dramatic reduction of Ni, no matter what the depth.

In situ heating/TXM experiment on 75% delithiated NMC-811



75% delithiated NMC-811 was heated in the TXM beam-line under Ar. These 2D color maps of average Ni oxidation states show that the Ni oxidation state first rises at temperatures as low as 100-150°C, but then decreases above this temperature.

TXM mapping of Ni content in 50% delithiated NMC-622



In addition to changes in Ni oxidation states that develop upon heating to 350°C (a, b, and c), there are changes in the distribution of Ni (d, e) throughout the particle. As-made spray pyrolyzed particles have a natural gradient in Ni content, with more Ni on particle surfaces than in the bulk (Nature Energy 1, 15004 (2016).). As the particle is heated, Ni migrates (f, g).

Responses to Previous Year Reviewers' Comments

"The first question pertained to oxidized Ni ions, which are very sensitive to the surrounding environment, e.g., air exposure. The reviewer asked how much impact the PIs think the handling process (opening the cell, preparing the XAS sample, etc.) has on the surface nitrogen and oxygen state, and asked if there are any plans to do the XAS study in situ."

- Samples are handled in inert atmosphere gloveboxes and transferred in sealed containers to beam lines, where they are examined under vacuum (or inert atmosphere, depending on experiment). They are never exposed to air. Because of the shallow penetration depth of soft XAS experiments (1-100 nm, depending on detector) and the requirement for high vacuum, *in situ* work is not practical. However, we do *in situ* experiments for XRD, TXM and hard XAS (bulk techniques) when there is a reason to do so. Note that beam time is limited and *in situ* experiments are very time-intensive, so we cannot do everything *in situ.*

"NMC622 does not appear to show "excellent reversibility" because there is a high capacity loss in the first cycle."

- All NMCs show first cycle inefficiencies, with the amount depending on the sample, voltage limits, current density, etc. This is probably related to the surface reconstruction phenomenon. Reversibility is excellent on subsequent cycles when normal cycling conditions are used.

"The reviewer said that it is difficult to believe that Mn is inactive in the voltage range of 2.5 - 4.7V. The reviewer asked about collecting more unambiguous Mn K-edge data using hard X-rays. While it is likely true that the surface Ni is less oxidized than the bulk Ni, the data do not support such a view because the spectra show the Ni3+ peak in the bulk looks larger than the surface Ni3+. In addition, Ni3+ has a peak at the same position as the carbonate peak."

- There have been many hard XAS studies performed on NMCs by many groups (including mine) over a period of many years, showing that Mn is not redox-active under normal conditions (an exception are the LMR-NMCs after electrochemical activation, which are not a subject of study here). In soft XAS, the L_{3high}/L_{3low} ratios are in a positive relationship with Ni oxidation state, but absolute values cannot be assigned, only relative ones. Note that it is the ratio that is important, not the intensity of any one peak. Finally, XAS is element-specific, and carbonate species will not be detected at energies used to probe Ni oxidation states. In O K-edge experiments, peaks due to both T.M.-O and CO_3^{2-} appear, but do not overlap.

"The reviewer recommended that a commercial partner supply samples for benchmarking"

- Note that we do use commercial materials for some of our studies. However, these materials vary considerably in quality, and factors such as storage and transport are out of our control, and can affect surface properties. To be sure we are studying the right composition and a material unaffected by aging or exposure to unknown conditions, we also synthesize our own materials using co-precipitation and other processes.

Collaboration and Coordination with Other Institutions

- We work closely with beam line scientists at Stanford Synchrotron Radiation Lightsource (SSRL) and publish with them regularly
  - Apurva Mehta (hard XAS and XRD)
  - Dennis Nordlund, Dimosthenes Sokaras (soft XAS)
  - Yijin Liu (TXM)
- We work closely with a microscopist from Brookhaven National Laboratory (Huolin Xin)
- We also collaborate with several scientists at LBNL and publish with them
  - Dr. Guoying Chen
  - Dr. Wei Tong
- Our invited review article "Synchrotron X-ray Techniques for Studying Materials Electrochemistry in Rechargeable Batteries" published recently in Chem. Rev., was a joint effort with beam line scientists at SSRL (Yijin Liu, Dennis Nordlund), Brookhaven National Lab (Qiao-Xing Yang, Xiqian Yu), the Advanced Light Source at LBNL (Nobumichi Tamura, Wanli Yang) and scientists from Virginia Tech (Prof. Feng Lin and Dr. Chixia Tian), UC San Diego (Prof. Shirley Meng and Prof. Oleg Shpyrko) and the Center for High Pressure Science and Technology Advanced Research in Shanghai (Tsu-Chien Weng)
- We have hosted students, postdocs, and scientists from the following institutions recently and are actively collaborating with them.
  - University of Eastern Finland (Dr. Anna Lahde, spray pyrolysis)
  - Virginia Tech (Prof. Gordon Yee, Na-ion batteries)
  - Technical University of Munich (Jennifer Ludwig, hydrothermal synthesis)

Remaining Challenges and Barriers

- Synchrotron beam time is limited and is scheduled and allocated to users depending on demand and scores on general user proposals. Our scores are near the top, so that we are awarded a fair number of shifts. However, sometimes factors beyond our control, such as instrument issues, mean that planned experiments have to be postponed, incurring delays.
- While *in situ* experiments are the "gold standard", they are very time-intensive. For this reason, it often makes sense to do *ex situ* experiments first in order to get a general sense of what is happening. *In situ* experiments are then selected carefully after analysis of this data to make the best use of scarce time.
- Some experiments generate large amounts of data (e.g., TXM). It takes considerable time and effort to analyze this data.
- Because of time constraints, it can take many months to fully characterize and understand a material or phenomenon. We have finished collecting data on NMC-622 and have nearly completed data analysis and are preparing a publication. We are still collecting data on NMC-811, and analysis should be complete by the end of this fiscal year with caveats as listed above.
- Not all of the data that we collected last year could be presented here due to space constraints. We tried to select the most interesting and representative results.

Proposed Future Research

- For the rest of FY2018, we will finish up the thermal characterization of NMC-811 and investigate the effects of Ti-substitution on phase behavior, thermal stability, and electrochemical behavior.
- This project will end on Sept. 30, 2018. New proposals for work on cathode materials and Na-ion battery materials are being prepared now.
- Na-ion work will focus on synthesis and characterization of candidate titanate anodes and will be coordinated with other PIs working on Na-ion cathodes and electrolytes at ANL, BNL and PNNL.
- Cathode work will be directed towards preparation and characterization of novel disordered rock salt phases with potential for very high capacities, and/or substitution of Ni-rich NMCs to improve thermal and electrochemical properties.
- Any proposed future work is subject to change based on funding levels

Mandatory Summary Slide

- In general, thermal stability decreases as lithium contents are lowered and nickel contents rise.

- The trend is layered →disordered→spinel→M_3O_4 spinel→MO (rock salt) as the temperature is raised. Formation of M_3O_4 and MO imply loss of oxygen, a concern for safety. Delithiated NMC-811 shows complicated phase behaviors at lower temperatures, and M_3O_4 is not always observed as an intermediate during heating to high temperatures.

- Surface sensitive techniques reveal a more complex behavior than the bulk techniques (XAS and XRD). In some cases, metals on the surface are first oxidized upon heating, and then are reduced at higher temperatures.

- TXM experiments show evidence of Ni migration during heating of delithiated NMC-622 materials. Depending on temperature and composition, surfaces may be more oxidized than the bulk after heating.

- Migration of Ni (and possibly Li) may explain some of the complexity of the thermal behavior. We are still analyzing results.

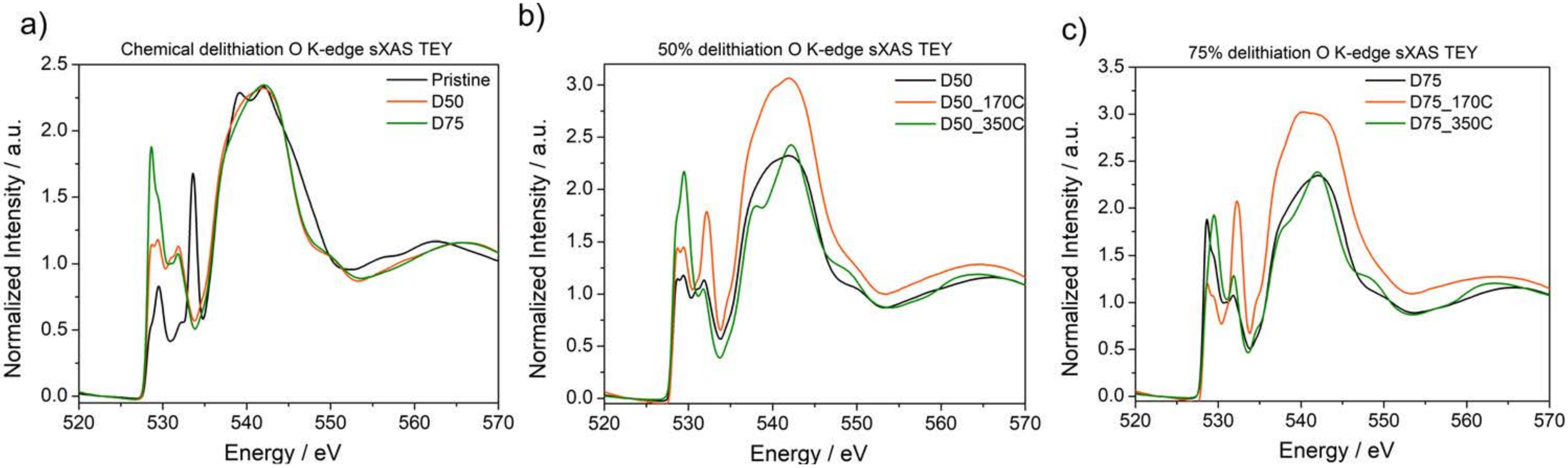
Instruction

Technical Back-Up Slides

- These slides may be printed out and posted on your assigned poster board after your main presentation (optional).

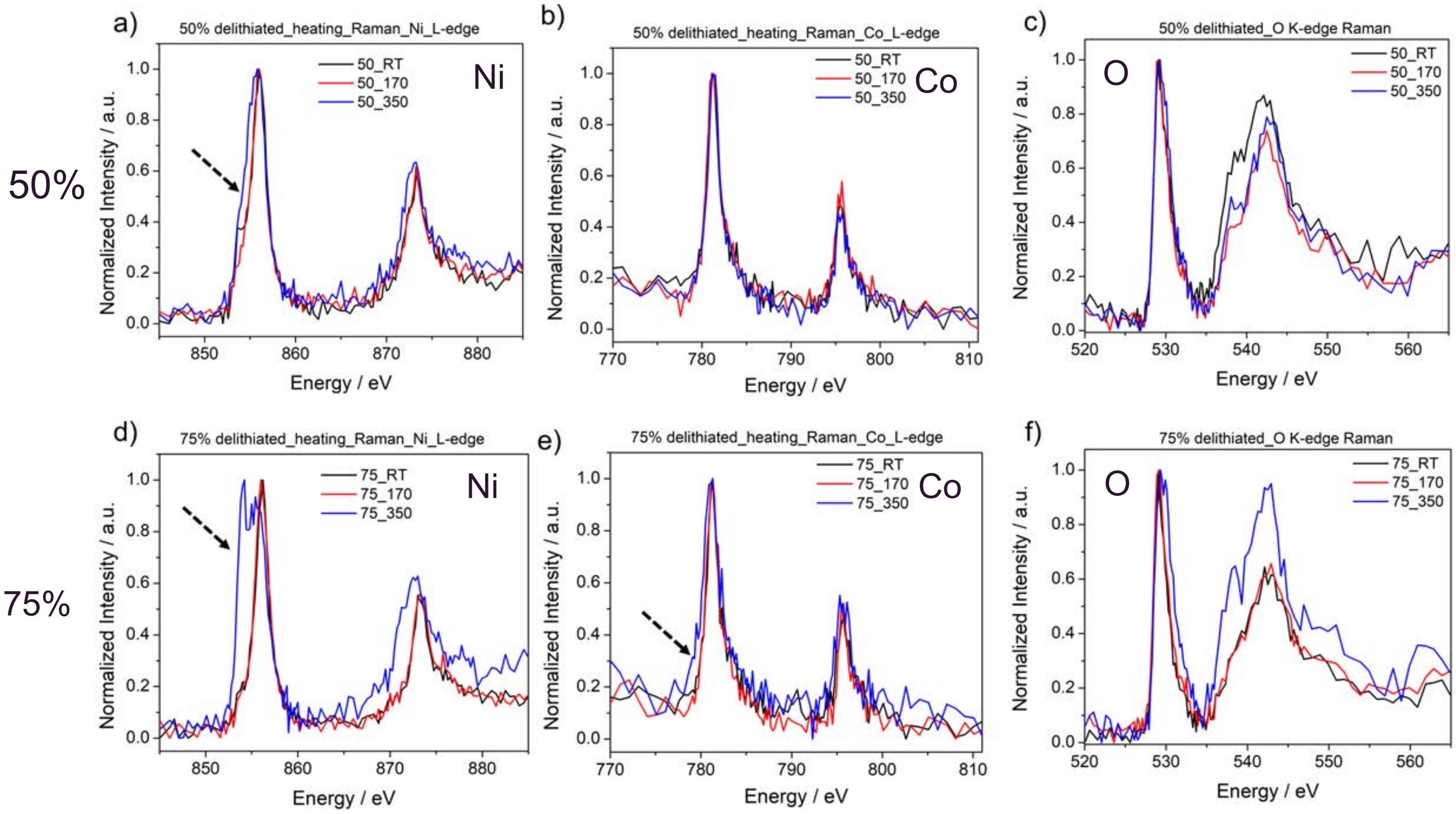
(Note: please include a “divider” slide if you are including back-up technical slides [maximum of five]. These back-up technical slides will be available for your presentation and will be included in the web PDF files released to the public.)

+ O K-edge soft XAS on NMC-622



O K-edge XAS in TEY mode (~ 5 nm probing depth) of pristine and delithiated samples is shown in (a). TM3d-O2p peaks generally are seen near 530 eV. Increased intensity is consistent with the generation of more hole states (oxidation). The results shown in (b) on the 50% delithiated sample shows evidence of oxidation upon heating, while the data in (c) for the 75% delithiated sample shows evidence of reduction at 350°C, consistent with the Ni L-edge data.

+ X-ray Raman on NMC-622



X-ray Raman is a soft X-ray technique that probes the bulk (in contrast to soft XAS). An advantage over hard XAS techniques, which also probe the bulk, is the greater sensitivity of the L-edge data to changes in metal oxidation states, compared to the K-edge data. Here, it appears that Ni is slightly reduced upon heating of the 50% delithiated sample to 350°C (compare to hard XAS results, for which this is less obvious). Little change is seen for Co or O, however. For the 75% delithiated sample, reduction of both Ni and Co are seen at 350°C, and shifts in the T.M3d-O2p band near 530 eV are consistent with this.