The Role of Surface Chemistry and Bulk Properties on the Cycling and Rate Capability of Lithium Positive Electrode Materials

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Project ID ES084

Overview

Timeline

- Start date: March 2008
- End date: June 2010 - renewing
- Percent complete:

  - project on-going

Barriers

- High cost
- Low energy density
- Poor cycle and calendar life
- Abuse tolerance limitations

Budget

- Total Project Funding: $520K
- FY09 funding: $315K
- FY08funding: $205K

Partners

- Lead PI: Yang Shao-Horn
- Co-PI: Azzam Mansour (NSWC)
- Collaborators: Michael M. Thackeray (ANL)

Research Objectives:

- To develop fundamental understanding of surface chemistry and bulk cation distributions on cycling performance and rate capability

- To design positive electrodes with stable electrode-electrolyte interface with improved cycling performance and rate capability

Research Approaches:

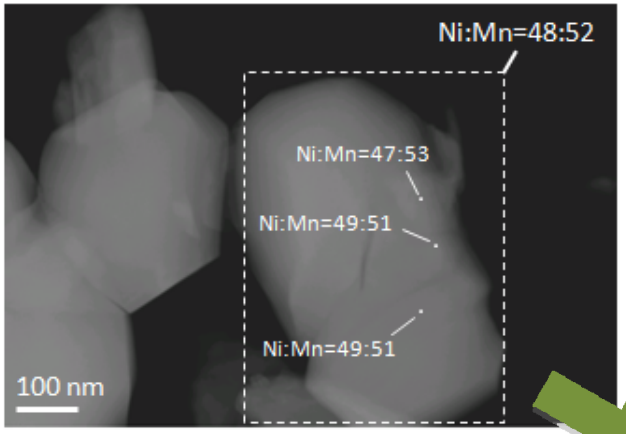
- Probing the ***surface chemistry*** of positive electrode materials before and after cycling using surface-sensitive electron microscopy, X-ray photoelectron spectroscopy and electron-yield X-ray adsorption spectroscopy.

- Studying the ***bulk structure*** of positive electrode materials before and after cycling using synchrotron X-ray diffraction and transmission X-ray absorption spectroscopy.

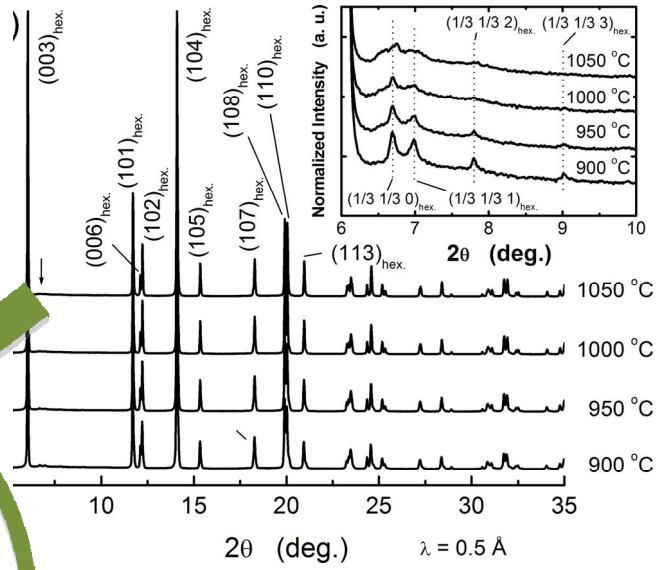
- Correlating surface chemistry and bulk structure information with ***electrochemical performance characteristics*** such as capacity retention and rate capability to determine the origin of surface instability.

Research Approach Overview

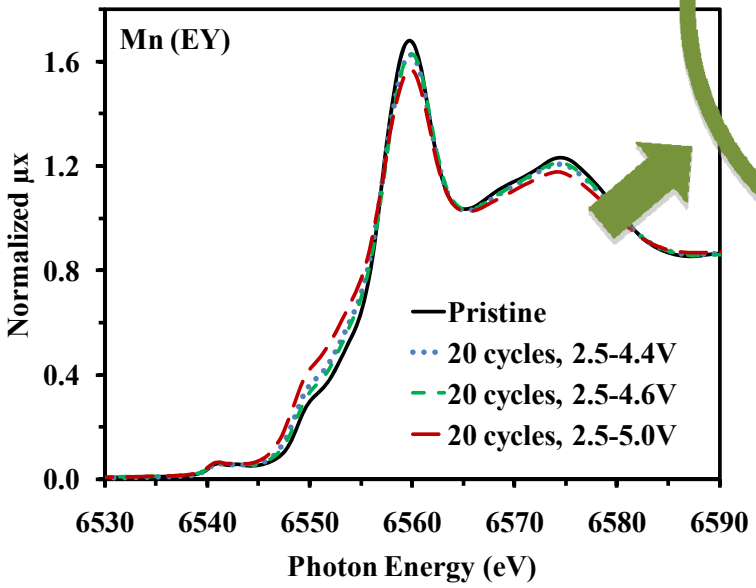
Surface and Bulk Chemistry: **Electron microscopy**



Bulk Structure: **Synchrotron X-ray diffraction & X-ray absorption spectroscopy (transmission)**



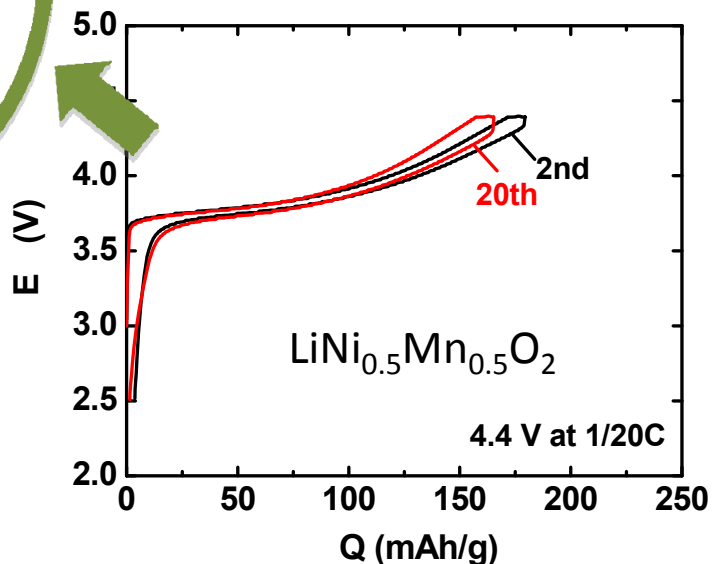
Surface Chemistry:
X-ray photoelectron spectroscopy (XPS)
X-ray absorption spectroscopy (electron yield)



Determine the origin of surface instability & bulk degradation

Design materials with improved cycling and rate capability

Electrochemical Reactivity:



Milestones FY10

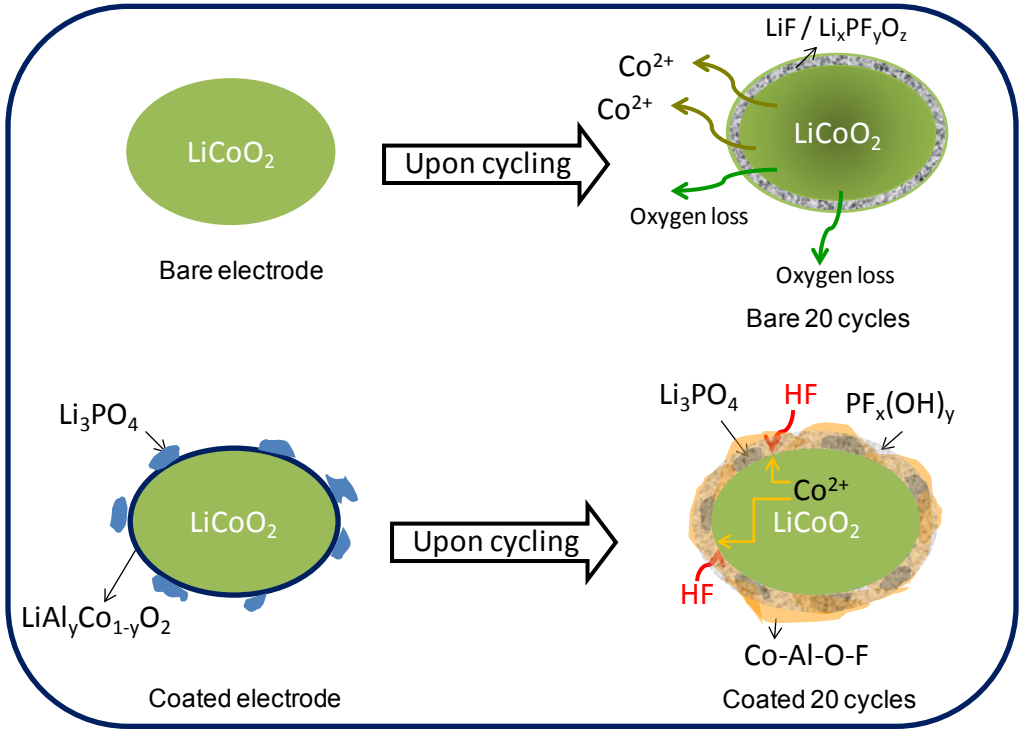
Develop fundamental understanding in the relationship between the surface chemistry of $LiNi_{0.5}Mn_{0.5}O_2$ (ref. $LiCoO_2$) and rate/cycle characteristics - ongoing

Apply the fundamental understanding to design and develop stable surfaces of cycled high-energy cathodes – initiated

Develop angle resolved X-ray photoelectron spectroscopy (ARXPS) to study the surface chemistry of $LiNi_{0.5}Mn_{0.5}O_2$ and $LiCoO_2$ as a function of depth from surface - ongoing

Technical Accomplishment – Identify the working principles of surface coatings

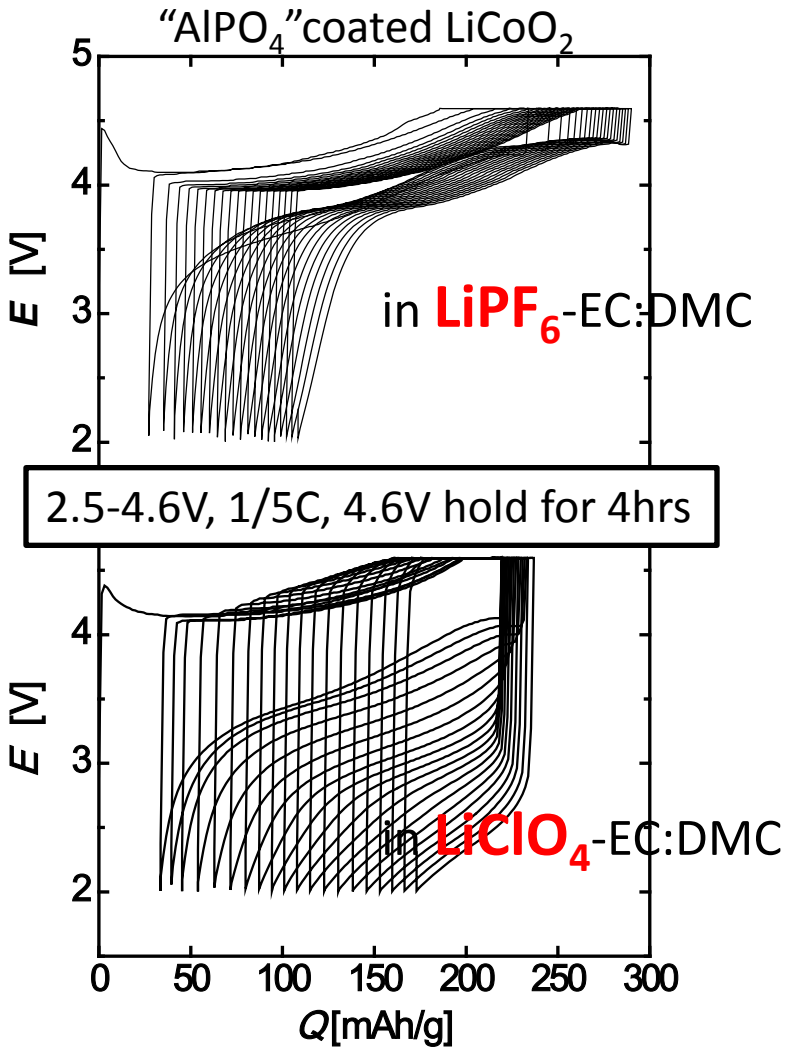
Recap:



Shao-Horn et al, CM 2009

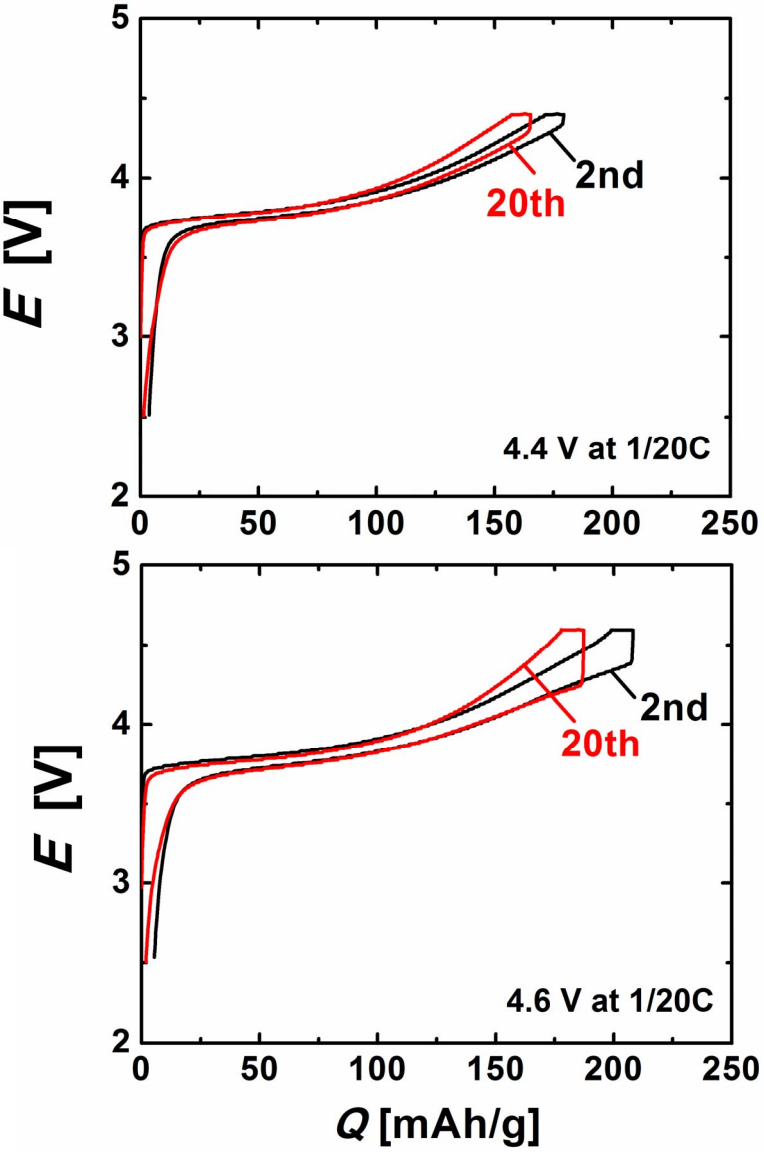
- **Formation of Metal fluorides/oxyfluorides at the interface is key to achieve long cycle life and high efficiency**
- **Coating does not enhance capacity retention in $LiClO_4$-based electrolyte**

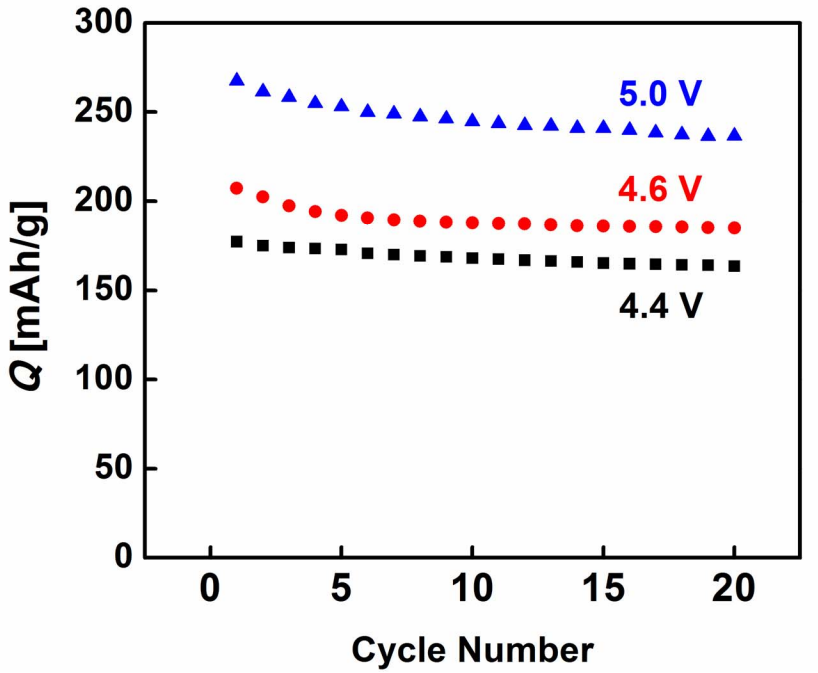
Further evidence



High-voltage cycling test of low-cost and high-energy cathode

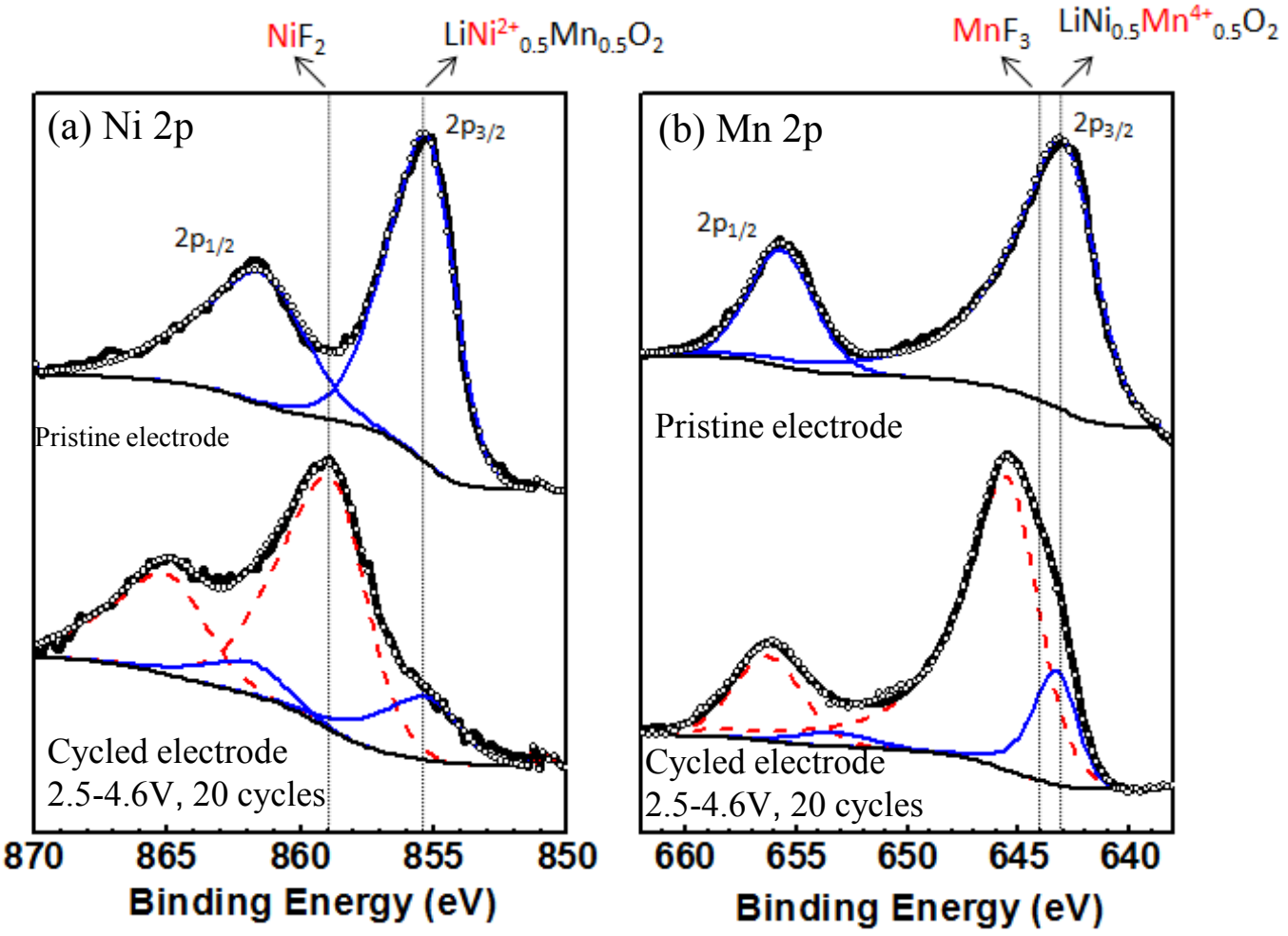
- Results: cycling performance of annealed $LiNi_{0.5}Mn_{0.5}O_2$





- Small capacity loss~ 90% after 20 cycles
- High round-trip efficiency > 90% after 20 cycles

Surface chemistry changes after cycling
- XPS Results of cycled annealed $LiNi_{0.5}Mn_{0.5}O_2$ electrodes

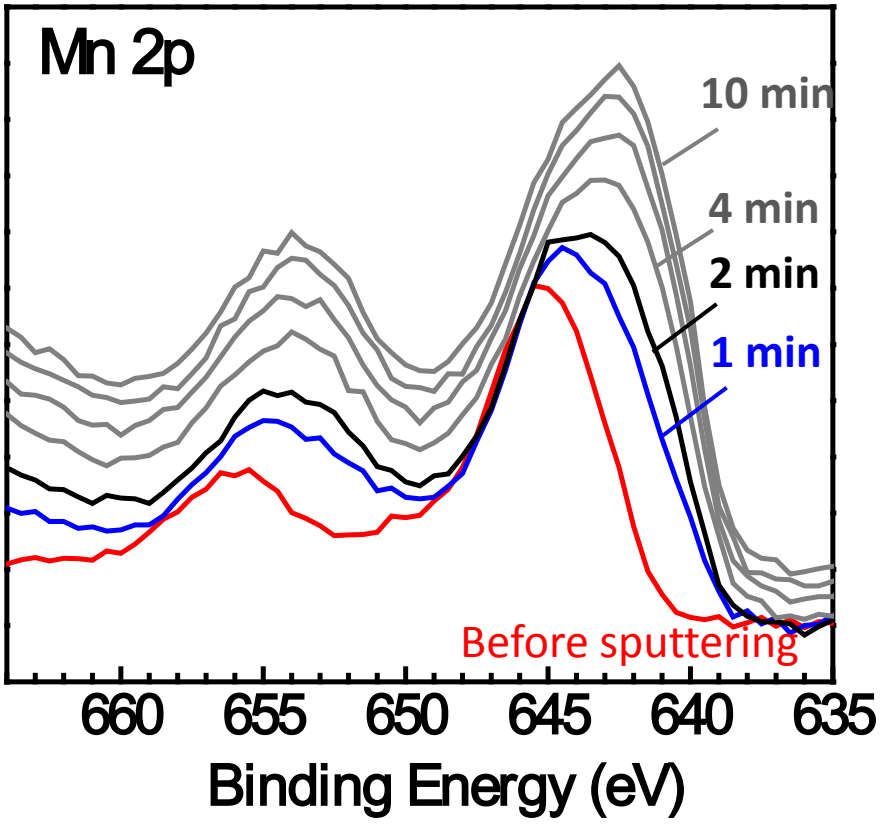


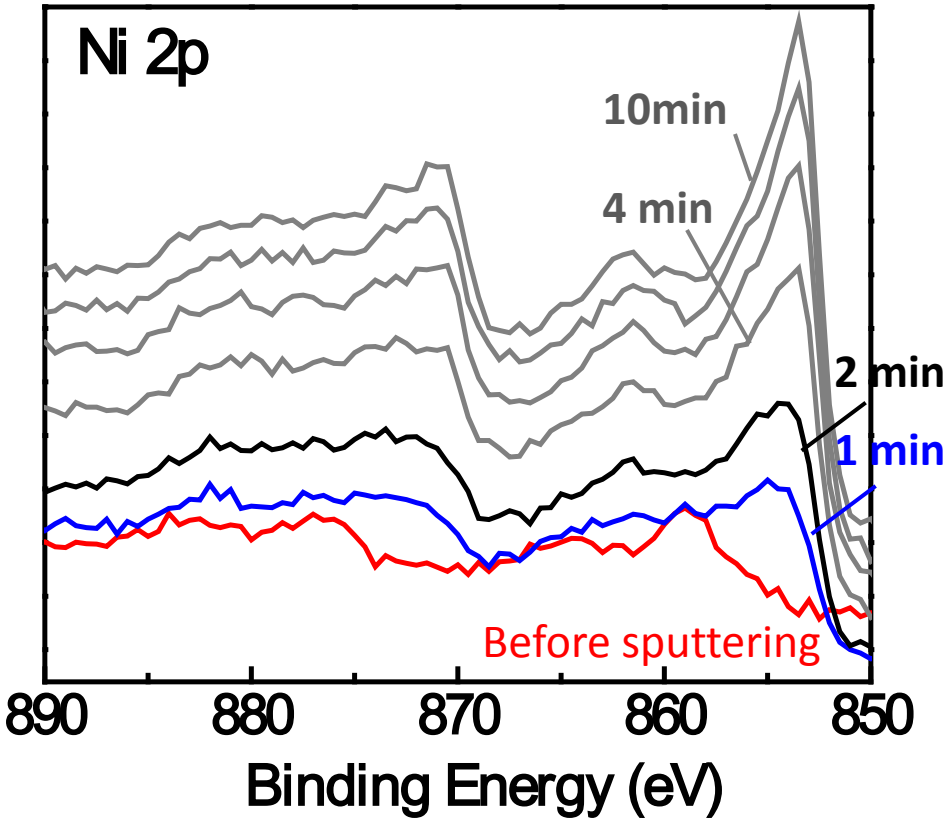
Formation of nickel and manganese fluorides in the surface region is confirmed; appears to be critical for good cycle life

Surface chemistry as a function of depth thickness

XPS – Ar-Sputtered Depth Profile of annealed $LiNi_{0.5}Mn_{0.5}O_2$

20 cycles, 2.5-4.6 V



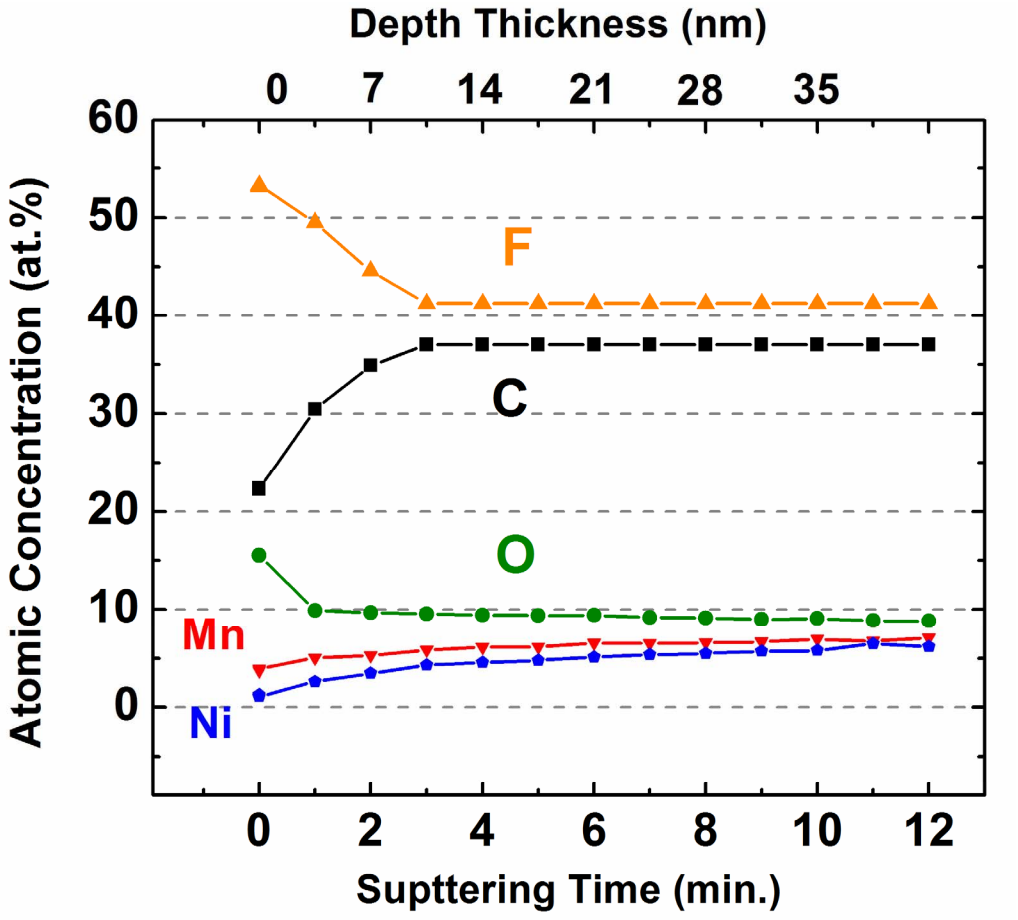


- The surface region with metal fluorides is about 7nm thick
- The sputtering rate is estimated to be ~ 35 Å/min of SiO_2

Surface chemistry as a function of depth thickness

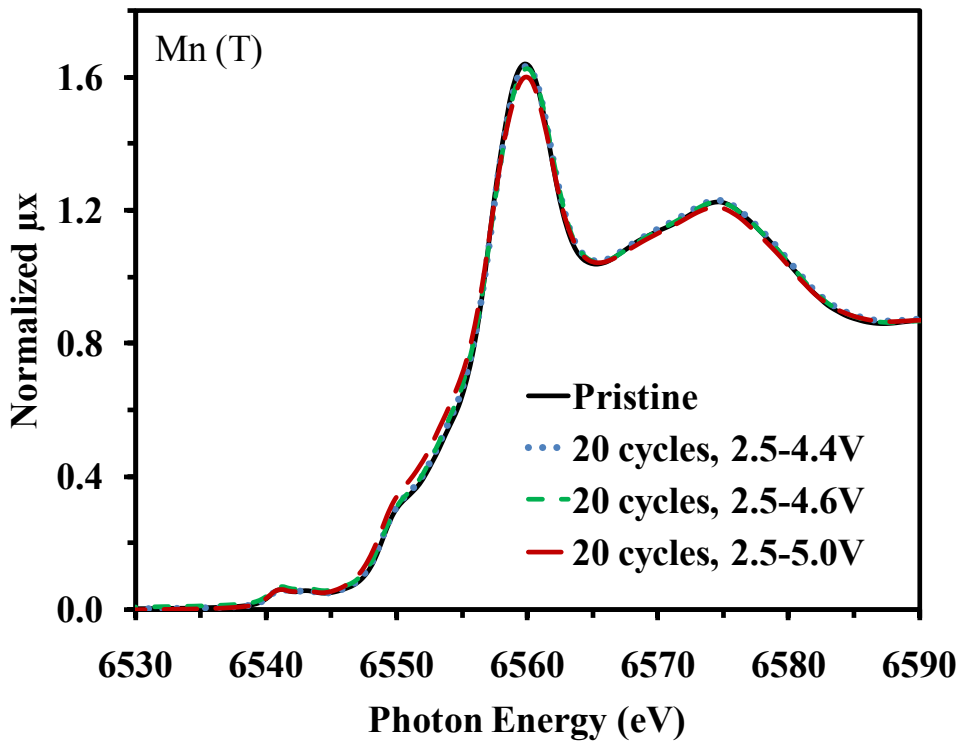
XPS – Ar-Sputtered Depth Profile of annealed $LiNi_{0.5}Mn_{0.5}O_2$

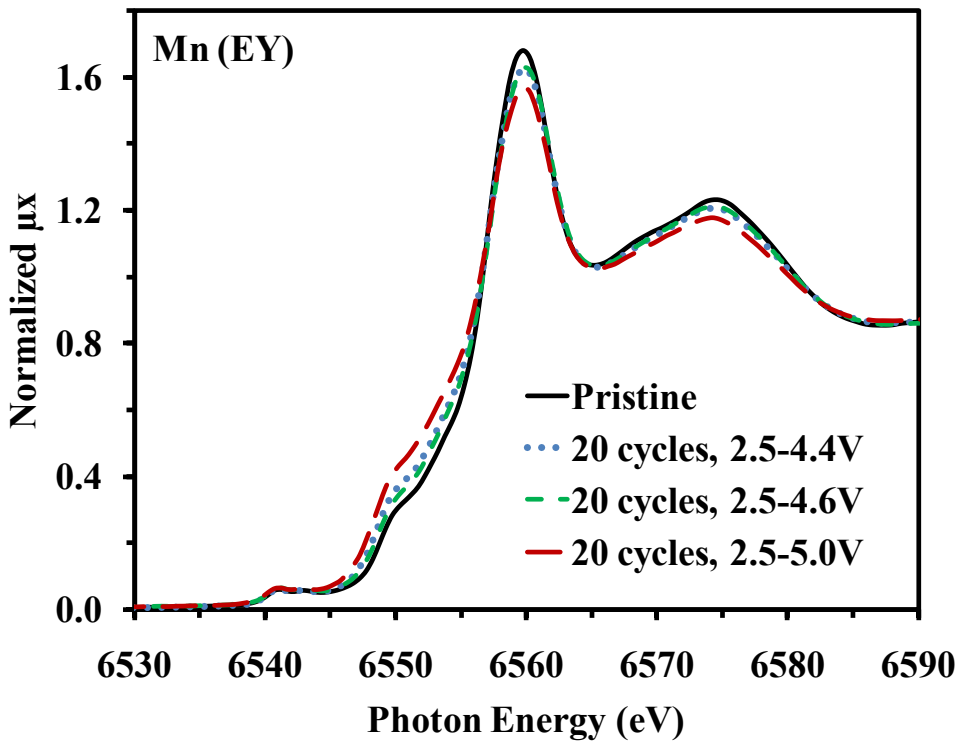
20 cycles, 2.5-4.6 V



The surface of cycled electrodes is rich in Mn relative to Ni (~10 nm), which is not the case for pristine electrode with has similar amounts of Ni and Mn.

Mn K-edge Transmission (T) and Electron Yield (EY) XANES of Cycled Annealed $LNi_{0.5}Mn_{0.5}O_2$ Electrodes

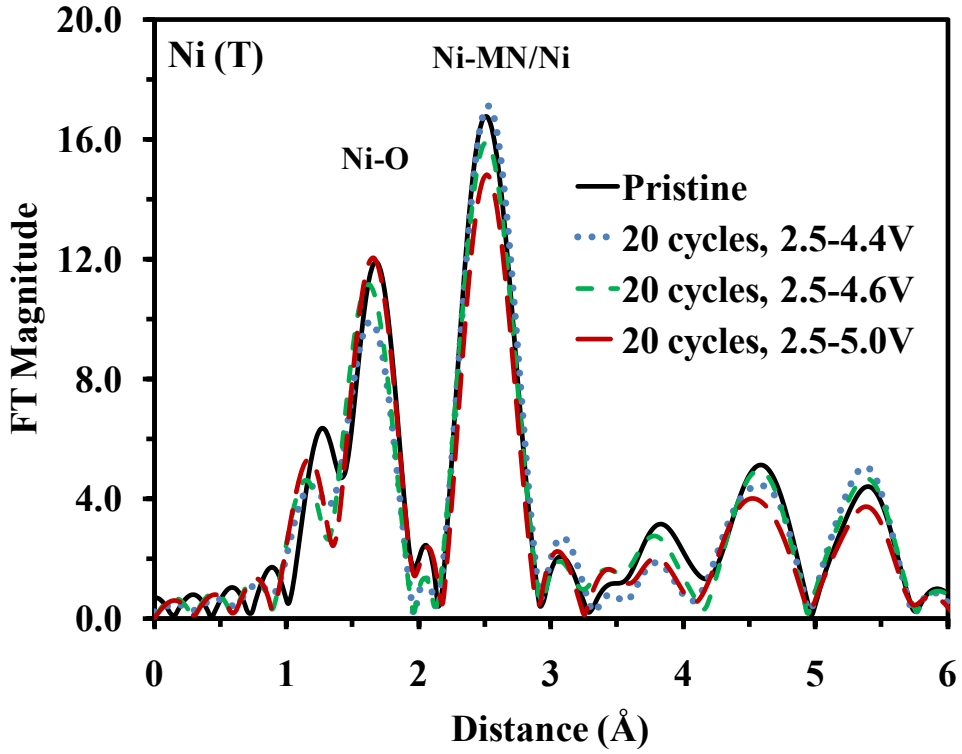


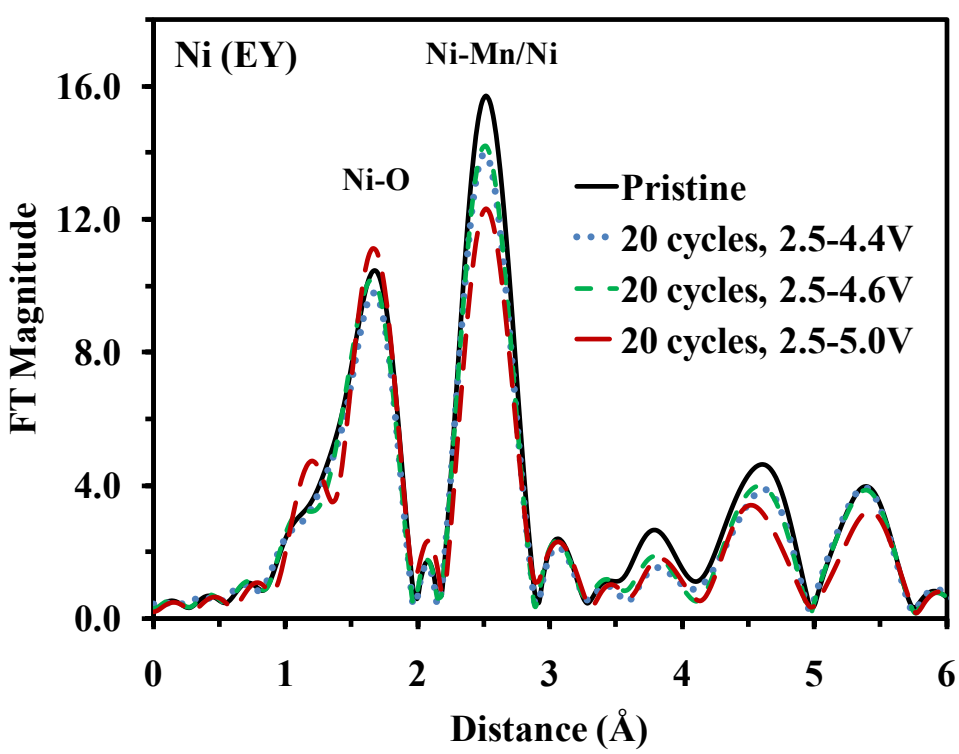


At the bulk level (transmission): no noticeable changes in the Mn oxidation state

At the surface level (electron yield): lowered Mn oxidation state, which was pronounced after cycling to 5.0 V. This observation is consistent with metal fluoride formation by XPS.

Ni K-edge Transmission (T) and Electron Yield (EY) Fourier Transforms of Cycled Annealed $LNi_{0.5}Mn_{0.5}O_2$ Electrodes

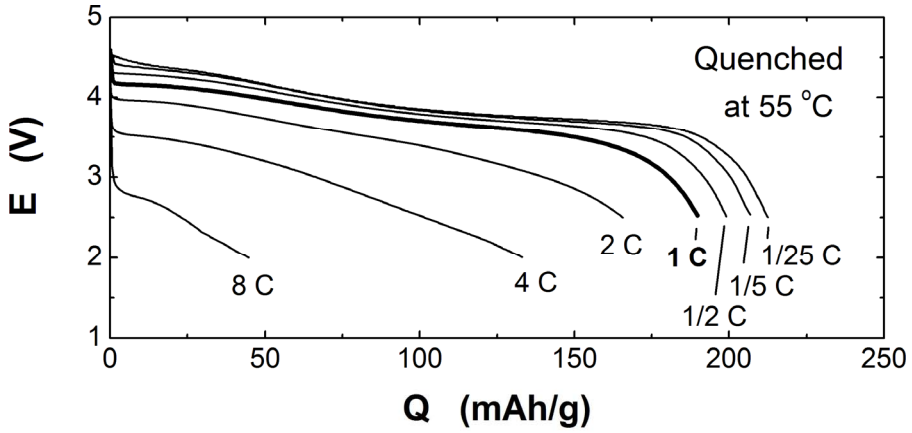


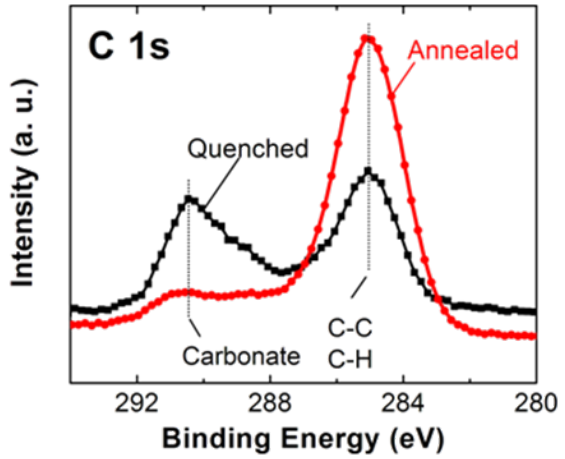


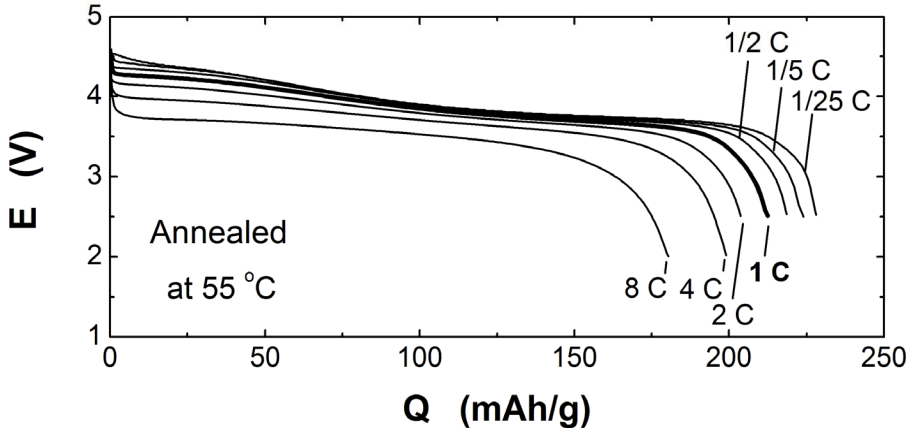
The bulk: no changes to 4.6 V but more layered upon cycling to 5.0 V

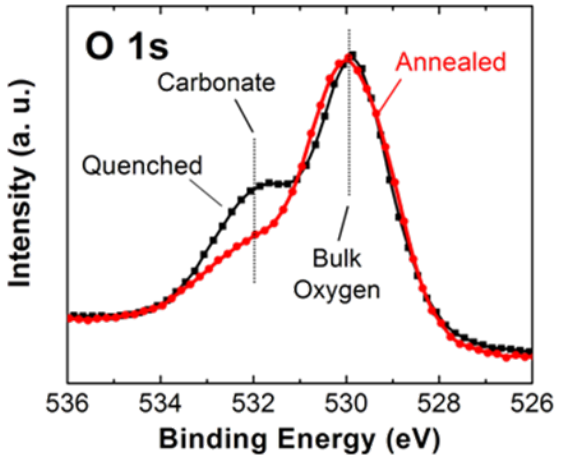
The surface: the formation of surface Ni fluorides. which was suggested by XPS.

Surface fluorides is important for cycling performance - What is important for rate capability?



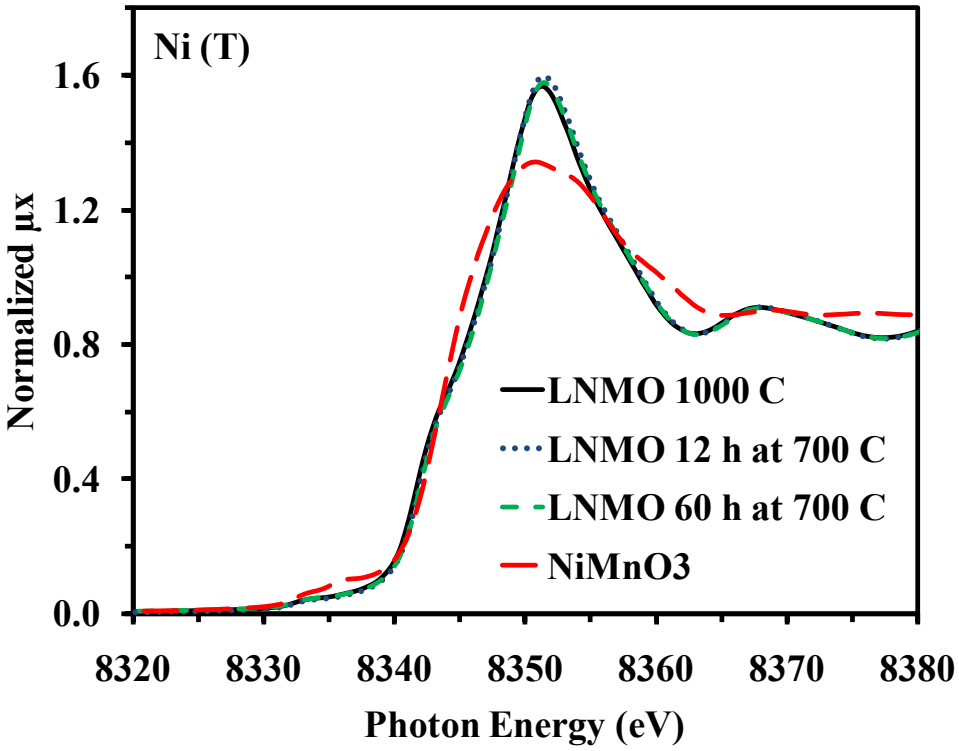


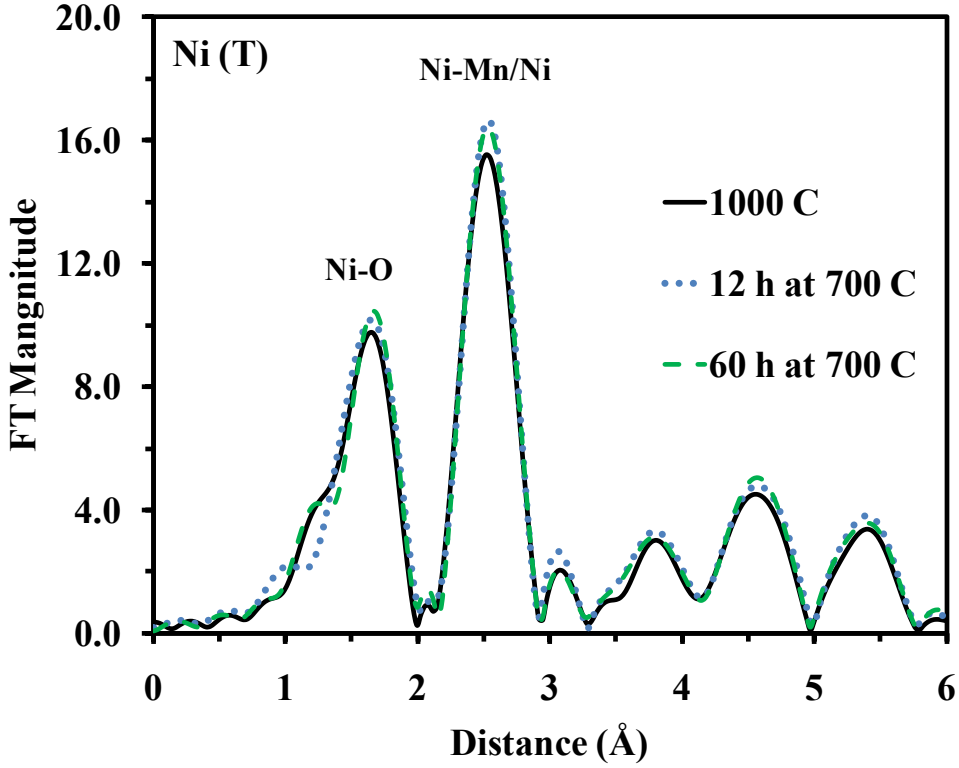




Reduction of surface carbonates upon annealing at 700 °C for 12 h improves rate capability

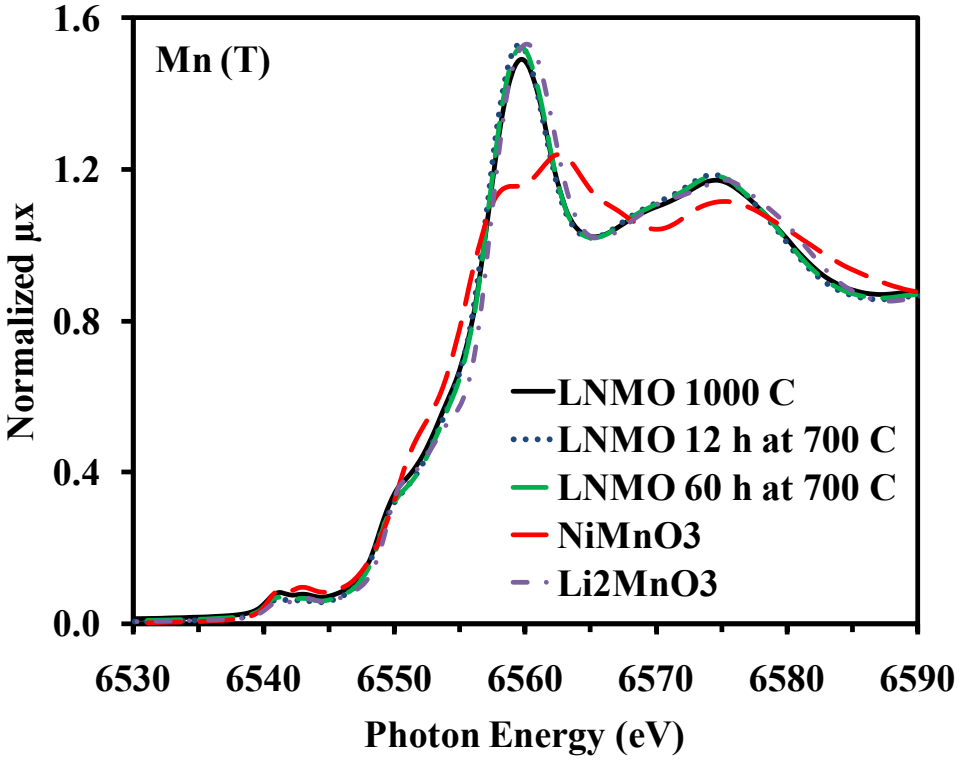
Transmission Ni K-edge XANES and Fourier Transforms of $LiNi_{0.5}Mn_{0.5}O_2$ – The Influence of Annealing

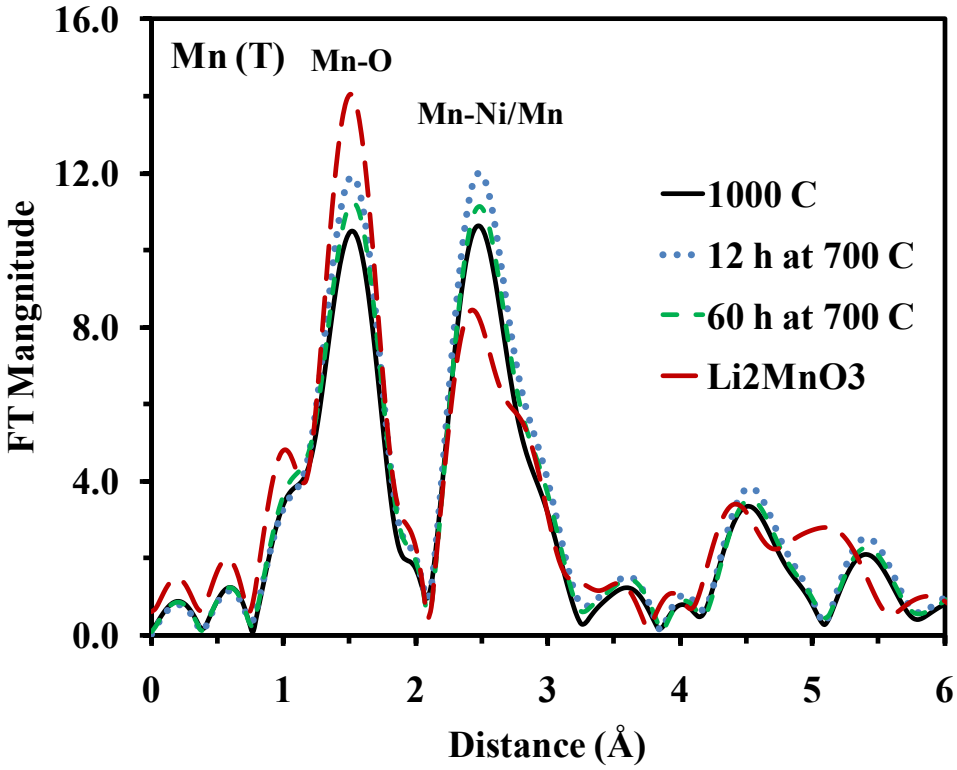




Changes in the oxidation state and local structure of Ni^{2+} as a result of annealing are small

Transmission Mn K-edge XANES and Fourier Transforms of $LiNi_{0.5}Mn_{0.5}O_2$ – The Influence of Annealing





Changes in the oxidation state and local structure of Mn^{4+} as a result of annealing are small

Summary of local structure parameters of $LiNi_{0.5}Mn_{0.5}O_2$ – The Influence of Annealing

Quenching Temperature	X-Y pair	N	R (Å)	sigma^2 (10^{-3}Å^2)
1000 °C quench	Mn-O	6	1.904(3)	5.3(4)
	Mn-Ni/Mn	5.0(4)	2.890(3	5.1(6)
	Ni-O	6	2.054(6)	6.5(7)
	Ni-Mn/Ni	6.6(7)	2.930(5)	6.4(7)
1000 °C quench + 12 h anneal at 700 °C	Mn-O	6	1.908(3)	4.0(3)
	Mn-Ni/Mn	5.3(5)	2.893(3)	4.5(6)
	Ni-O	6	2.058(7)	5.8(8)
	Ni-Mn/Ni	6.9(8)	2.931(5)	6.3(8)
1000 °C quench + 60 h anneal at 700 °C	Mn-O	6	1.910(3)	4.5(3)
	Mn-Ni/Mn	5.2(4)	2.894(3)	5.0(5)
	Ni-O	6	2.057(3)	5.9(5)
	Ni-Mn/Ni	6.8(4)	2.932(2)	6.3(4)

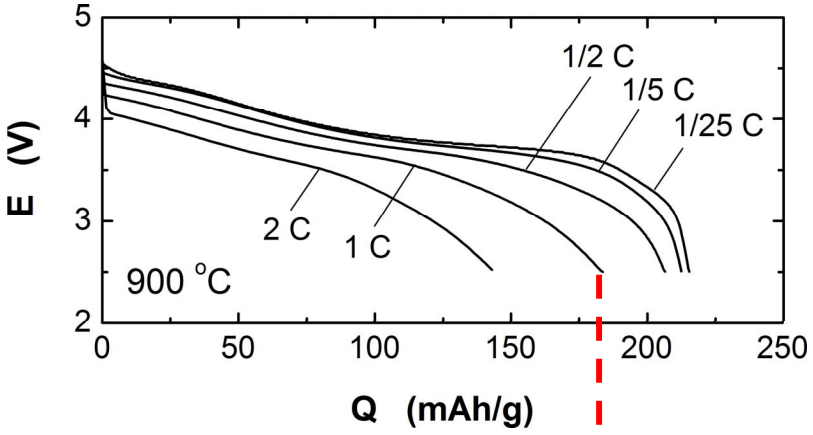
Uncertainties are given in parenthesis

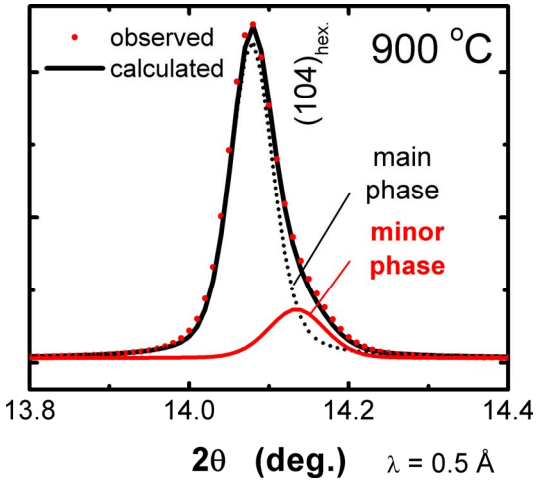
Annealing =>

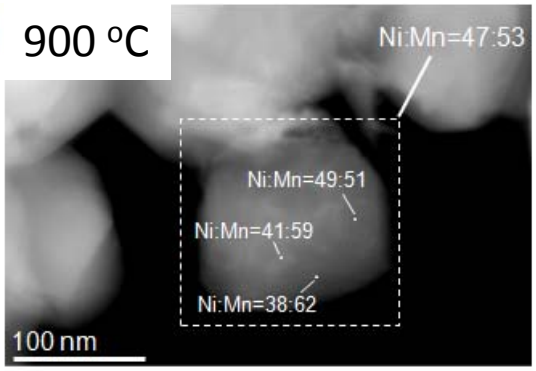
No change in the local structure

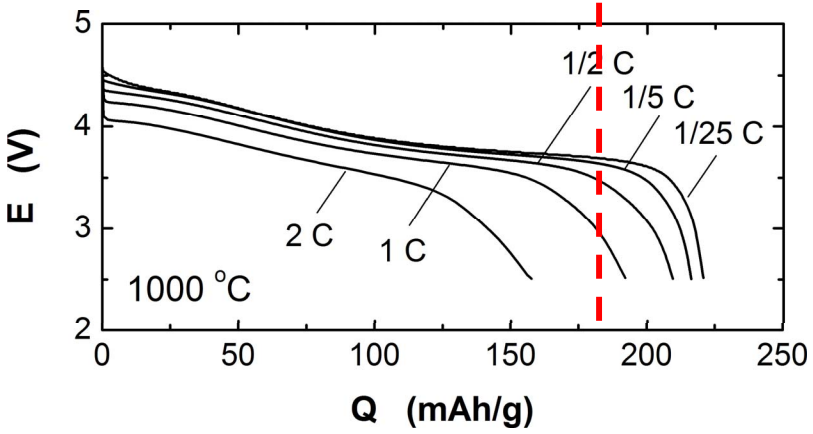
Slightly higher order for Mn-O bonds

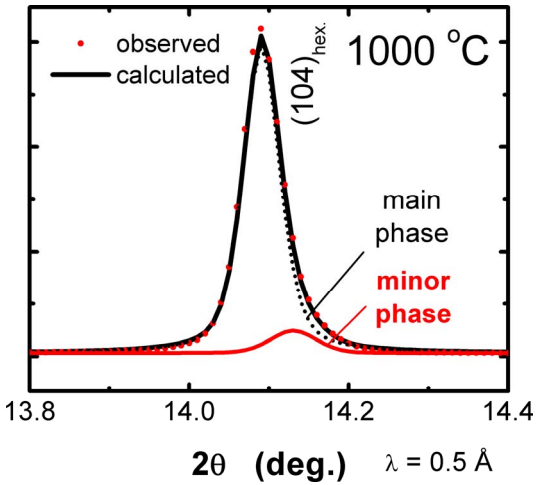
Phase segregation also influences rate performance

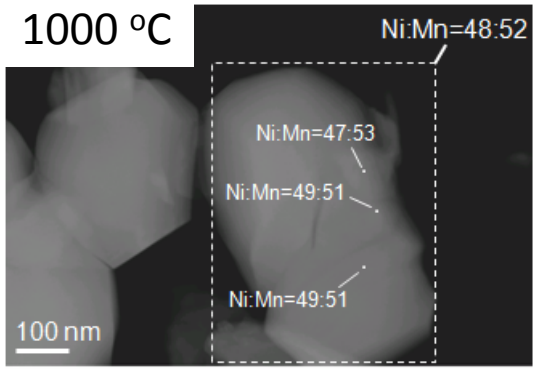










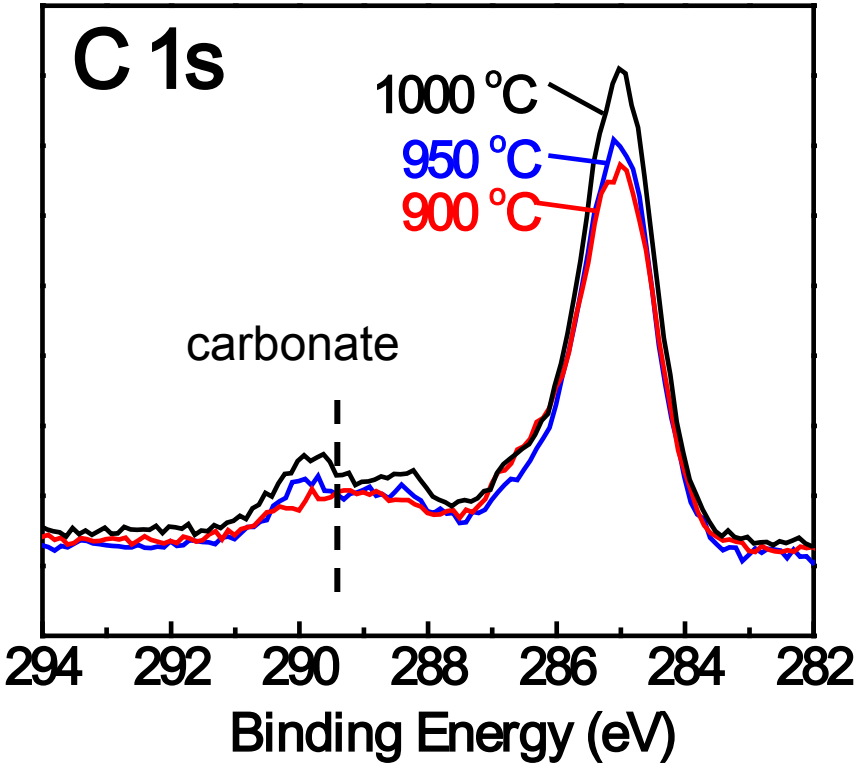


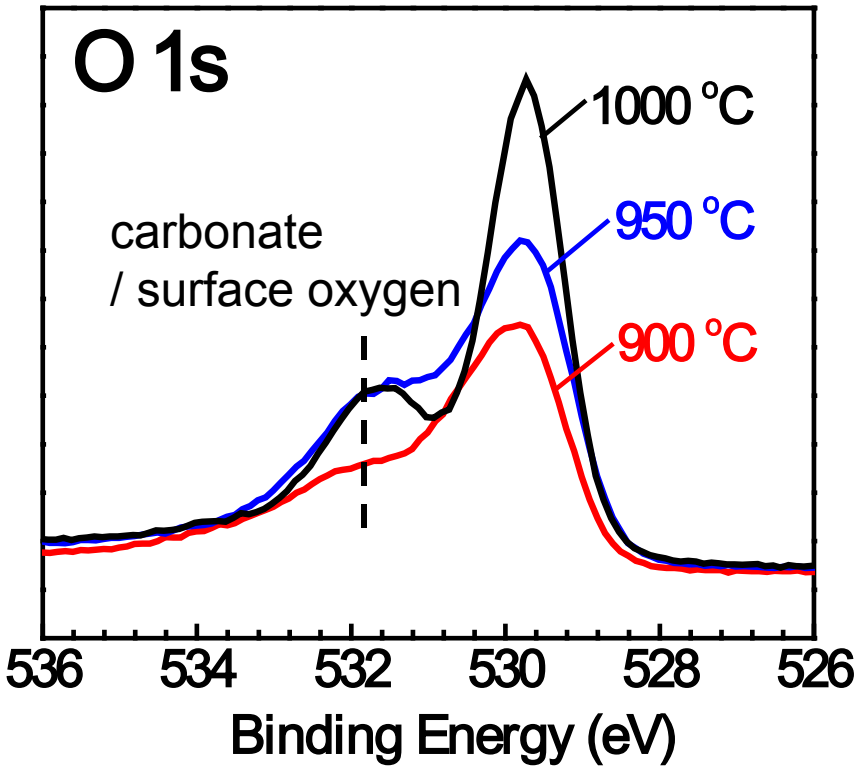
- Material segregated into a major $Ni^{2+}O$ phase and a minor Li_2MnO_3 phase; phase segregation decreased when T ↑ to 1000°C

- STEM confirmed phase segregation within individual particle

✓**The rate-capability was improved by reducing phase segregation**

XPS to probe the surface carbonate – $LiNi_{0.5}Mn_{0.5}O_2$ synthesized at – 900 °C, 950 °C and 1000 °C



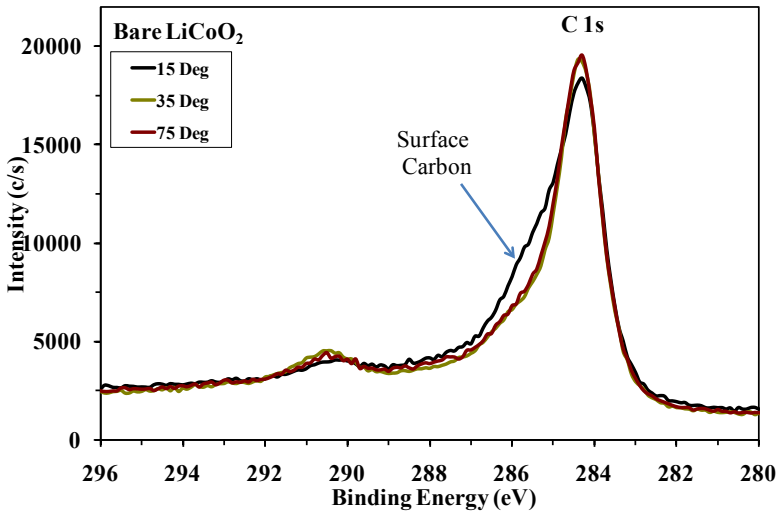


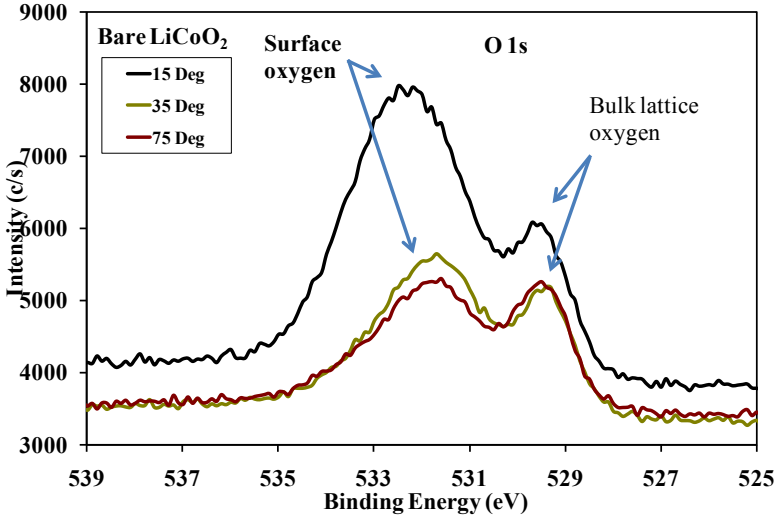
- **C 1s** : comparable amount of surface carbonate for all temperatures**.**
- **O 1s** : O lattice peak narrowing with increasing temperature

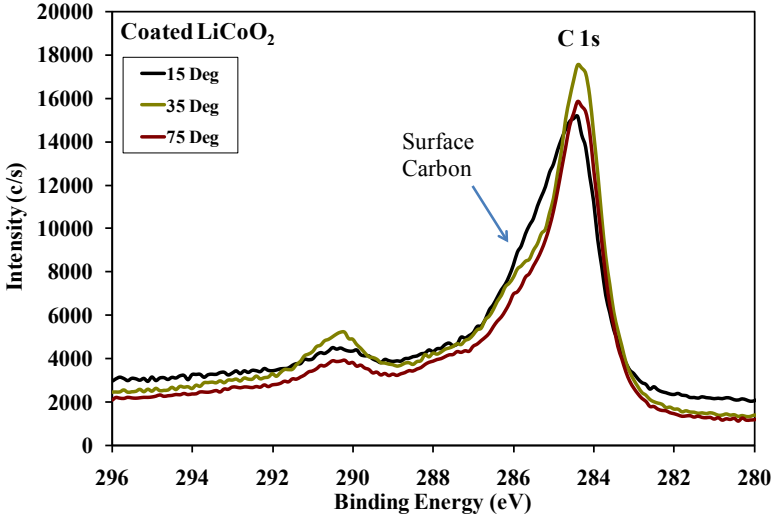
All temperatures have comparable amount of surface carbonate
=> further support that phase segregation is the dominating factor

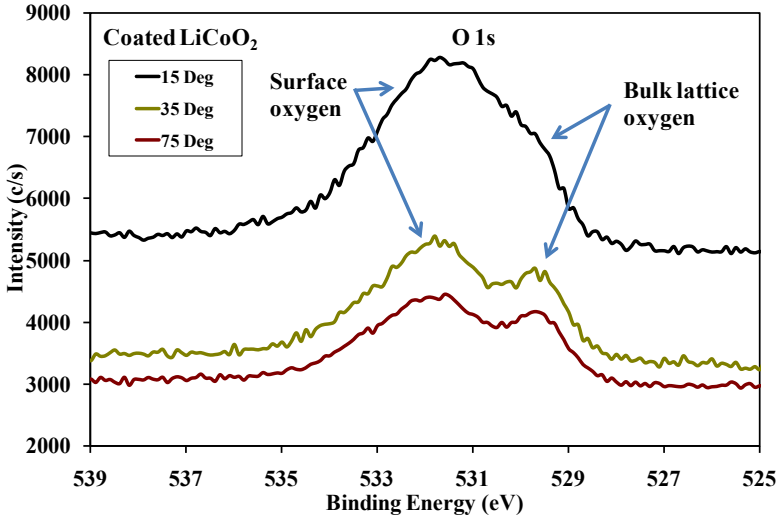
Angle Resolved-XPS to probe surface chemistry/composition

Test case, Bare $LiCoO_2$ vs. "$AlPO_4$" coated $LiCoO_2$





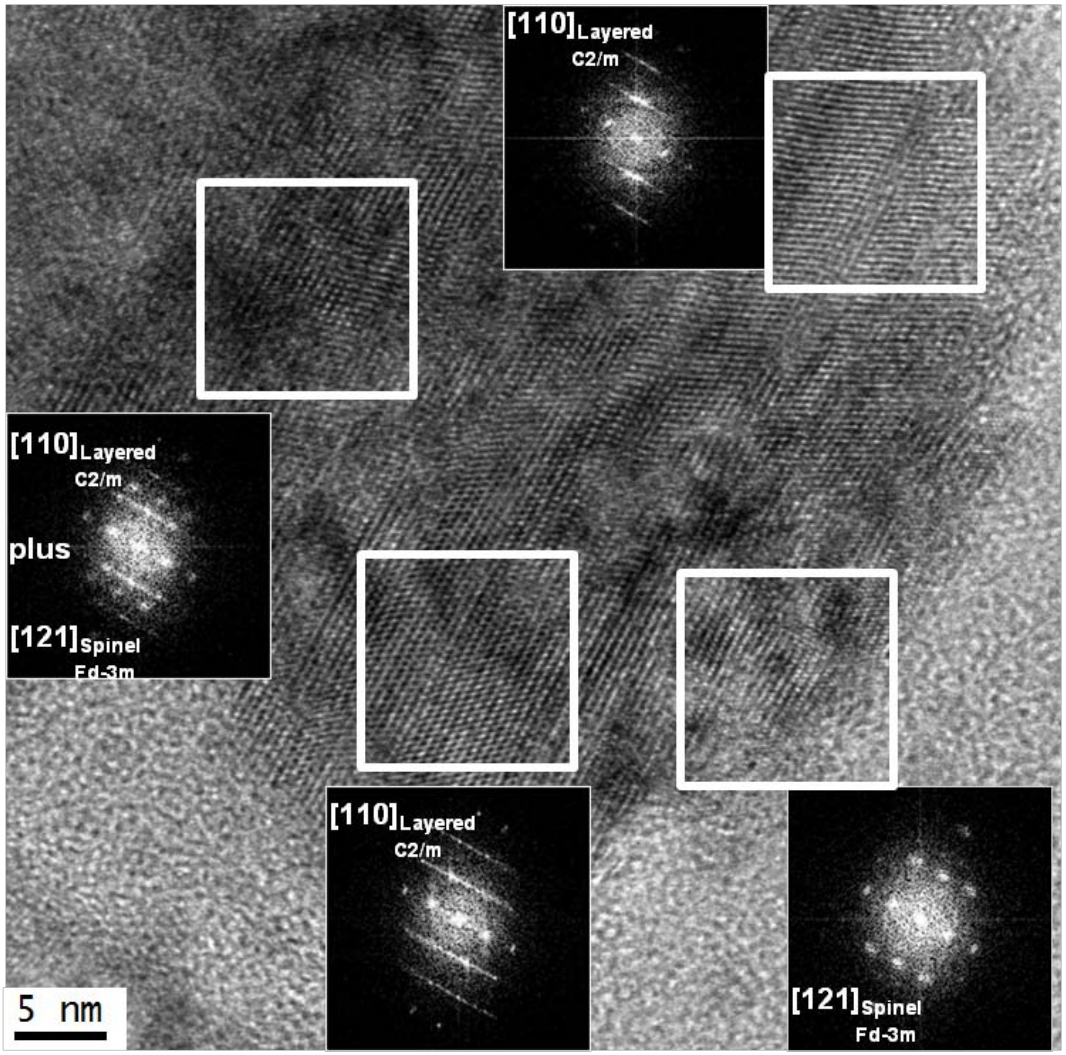




✓**Obtain chemical and composition as a function of depth from the surface without Ar-ion beam induced damage to the sample**

Collaboration with S.H. Kang and M.M. Thackeray

$Li_{1.2}Ni_{0.25}Mn_{0.75}O_y$ (900 °C)



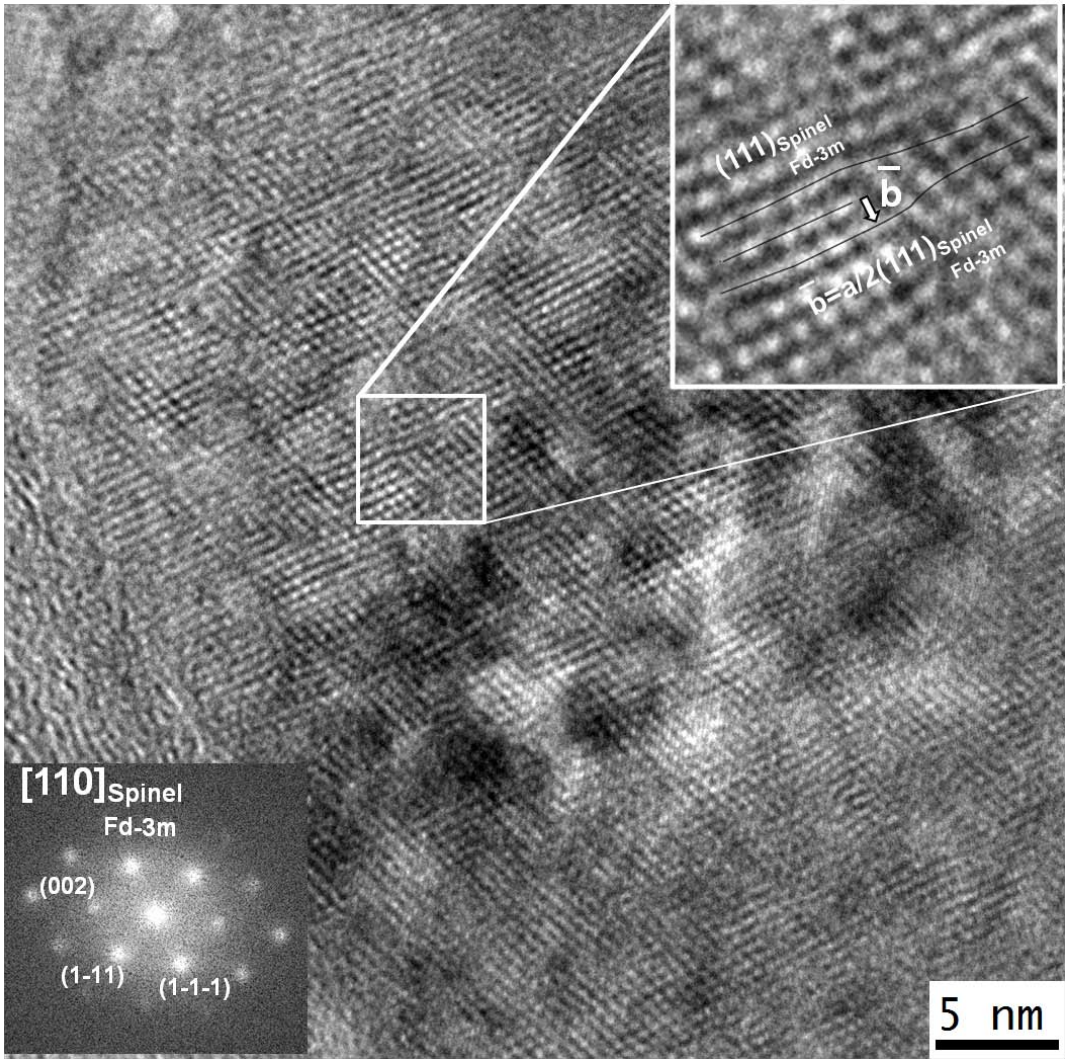
Direct evidence for the integration of spinel and layered material in the as-prepared $Li_{1.2}Ni_{0.25}Mn_{0.75}O_y$.

The fast Fourier transforms (FFTs) show the local symmetry of the material. In this case, they show that the material the micrograph consists of both Spinel Fd-3m and layered C2/m (Li_2MnO_3).

The streaks in the FFT of the Layered C2/m indicated stacking faults similar to those seen in Li_2MnO_3 by Boulineau et al. (Chem. Mater. 2009).

Collaboration with S.H. Kang and M.M. Thackeray

Cycled $Li_{1.2}Ni_{0.25}Mn_{0.75}O_y$ (900 °C) – 2.0-4.95 V – 50 cycles

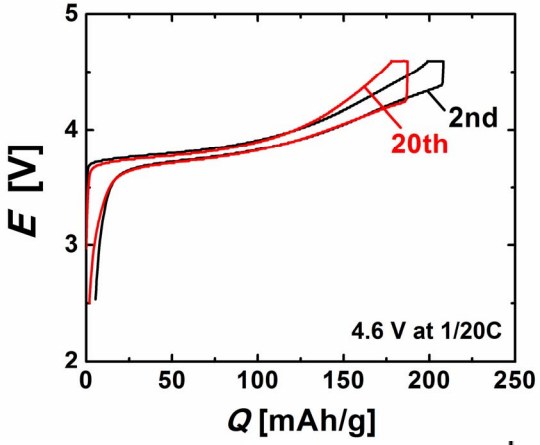


The cycled sample shows mostly the Spinel Fd-3m structure.

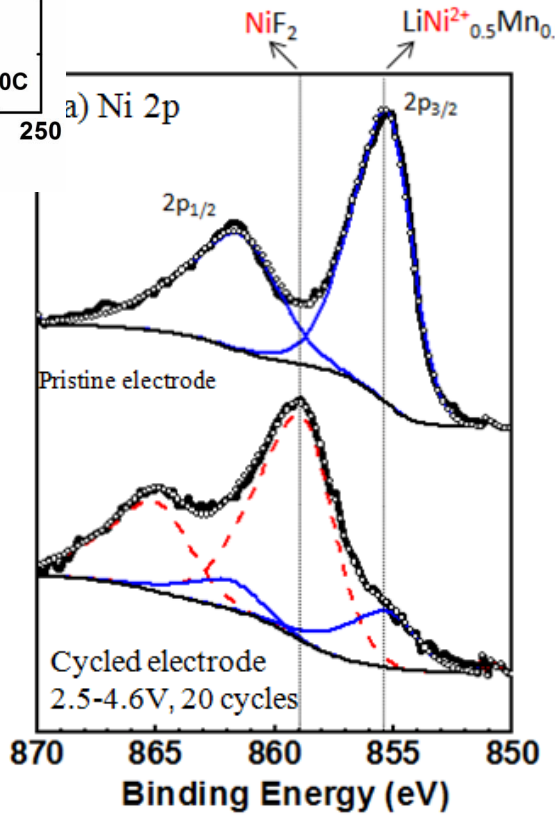
Some crystal contain dislocations. With very large Burgers vector of a/2[111]. This might be associated with oxygen loss during cycling.

Summary

Identifying the key criteria toward better cycle life upon cycling for low-cost and high-energy $LiNi_{0.5}Mn_{0.5}O_2$

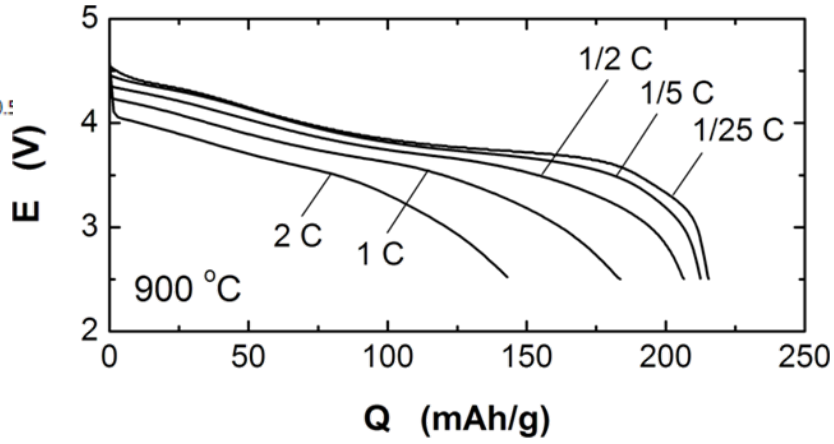


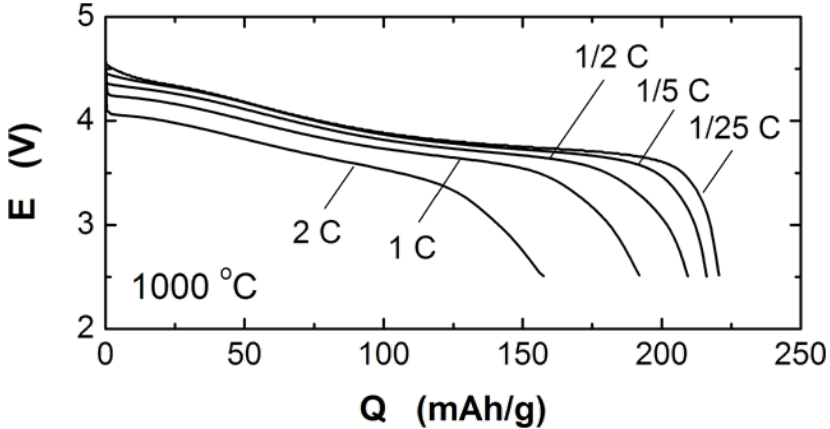
Formation of surface metal fluorides/oxyfluorides is key to achieve long cycle life and high efficiency



Probing the effects of surface chemistry and cation distribution on the rate capability of $LiNi_{0.5}Mn_{0.5}O_2$

The rate capability was improved by reducing surface carbonates and phase segregation by altering synthesis condidtions





Ongoing and Planned Activities

- **Continue to examine the role of surface chemistry on cycle life and rate capability of low cost and high energy positive electrode materials such as $LiNi_{0.5}Mn_{0.5}O_2$ using angle-resolved XPS and electron yield XAS:**
  - **Examine variations in the surface chemistry / composition of annealed $LiNi_{0.5}Mn_{0.5}O_2$ vs. quenched $LiNi_{0.5}Mn_{0.5}O_2$ powders.**
  - **Examine variations in the surface chemistry of cycled $LiNi_{0.5}Mn_{0.5}O_2$ electrodes. In this case, the electrodes will be transferred from an Ar filled glove box to the analysis chamber of the XPS system without exposure to ambient conditions.**

- **Continue to examine the bulk structure of annealed and quenched $LiNi_{0.5}Mn_{0.5}O_2$ and their cycled electrodes using transmission XAS:**
  - **We will use temperature dependent measurements in order to reduce the correlation between the disorder and the coordination number in order to reduce the uncertainties in the local structure parameters.**
  - **Explore the possibility of conducting the ARXPS measurement using hard X-rays at a synchrotron radiation facility . Using hard X-rays can increase the depth of analysis several folds relative to that when soft X-rays are used such Al and Mg K_{alpha} X-rays.**