Optimization of Ion Transport in High Energy Composite Cathodes

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University of California San Diego
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Project ID ES216

Overview

Timeline

- April 1st, 2013
- March 31st, 2017
- Percent complete: 25%

Barriers

- Barriers addressed
  - Low rate
  - Poor voltage stability

Budget

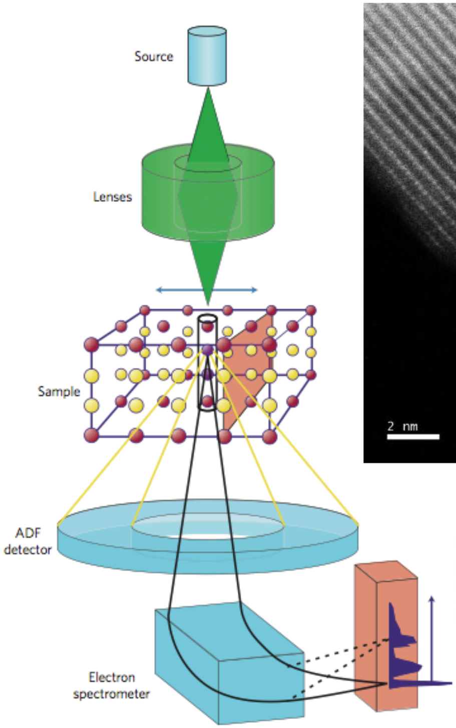
- Total project funding
  - US$ 899,999
- Funding received in FY13
  - US$ 225,000
- Funding for FY14
  - US$ 225,000

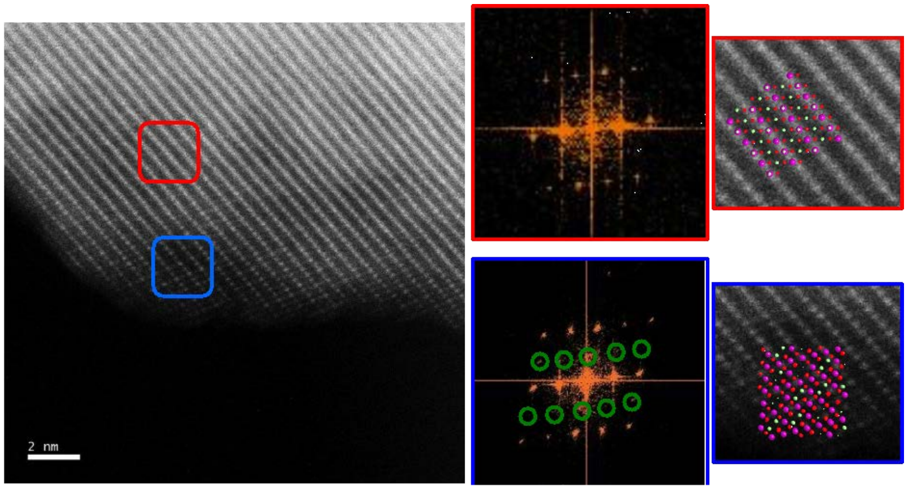
Partners

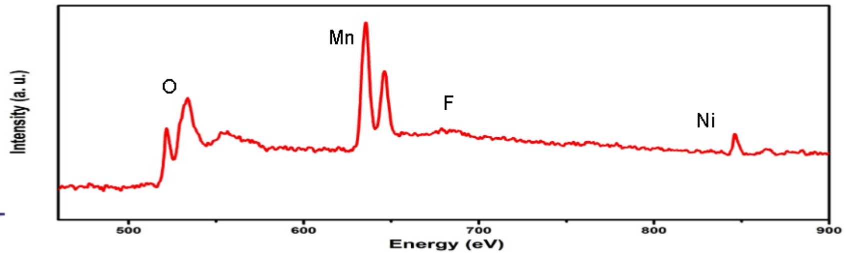
- Interactions/ collaborations
  - Envia Systems
  - Oak Ridge National Lab
- BATT team: Jordi Cabana, Robert Kostecki and Kristin Persson

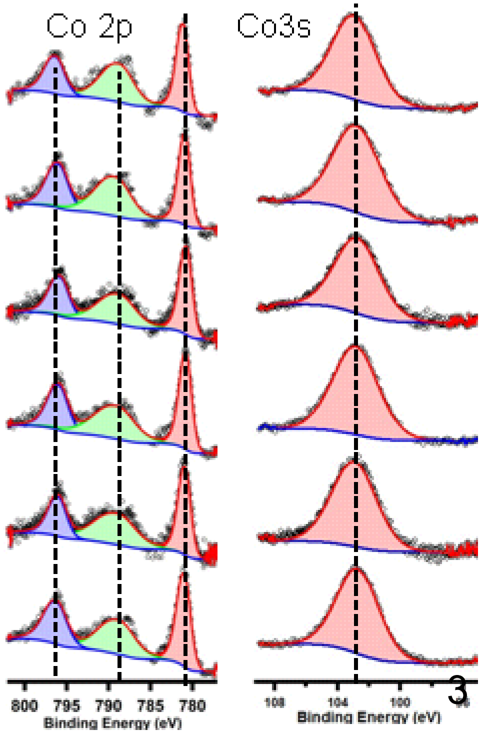
Objectives

- Probe and control the atomic-level kinetic process that govern the rate and stability in high energy (high voltage) cathode materials
- Establish quantitative diagnosis methods to determine the optimum bulk composition and surface characteristics for high rate and long life









Milestones

- Q1 Establish the initial suite of surface and interface characterization tools, including STEM/EELS, XPS and FP computation (12/31/13 ***- completed*)**
- Q2 Identify the surface coated materials (AlF_3 and Li_3PO_4) electrochemical performance matrices, including first cycle irreversible capacity, discharge energy density, voltage stability upon cycling and rate capabilities (3/31/14 ***- completed***)

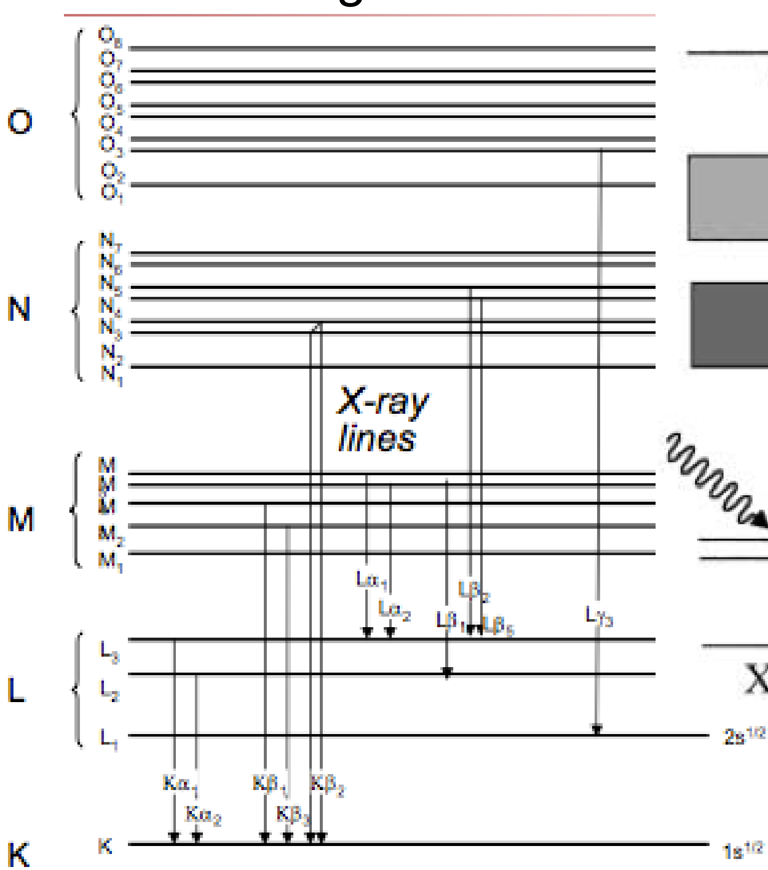
Go-No Go: Stop and change the coating materials if the improvements for rate capability and voltage stability are not significant (3/31/14)

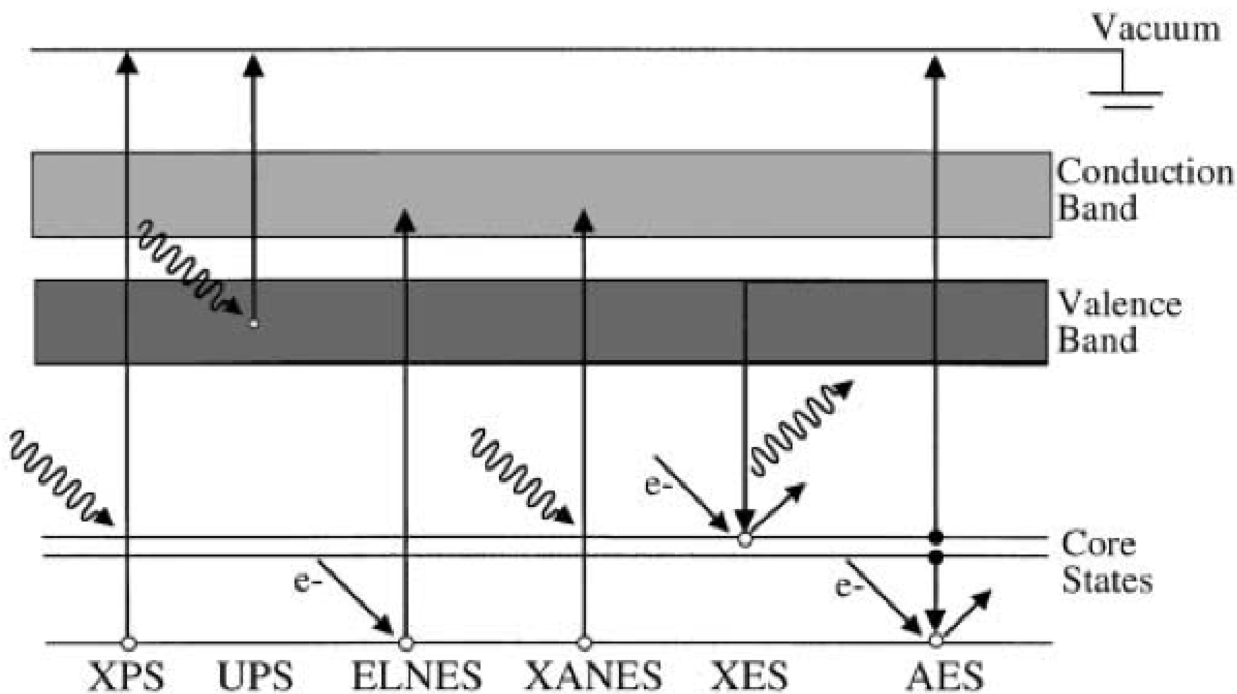
Milestones

- Q3 Characterize coated samples - coating thickness, compositions and morphology before, during and after cycling. (6/30/14 ***- completed***)
- Q4 Identify ways to extend the STEM/EELS, XAS and XPS techniques for anode materials, such as silicon anode. (9/30/14 – ***on going***)

Approaches

Combines atomic resolution scanning transmission electron microscopy (a-STEM) & Electron energy loss spectroscopy (EELS), X-ray photoelectron spectroscopy (XPS), X-ray absorption spectroscopy (XAS) and first principles(FP) computation to elucidate the dynamic changes of the bulk and surface changes





Only EELS and XAS probe the conduction band
EELS --- local DOS
XAS --- averaged DOS

Approaches

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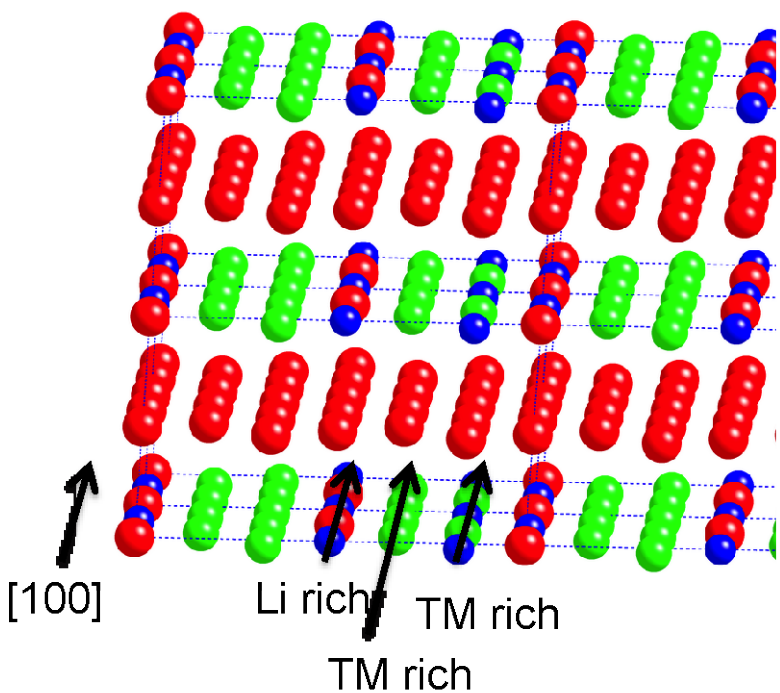
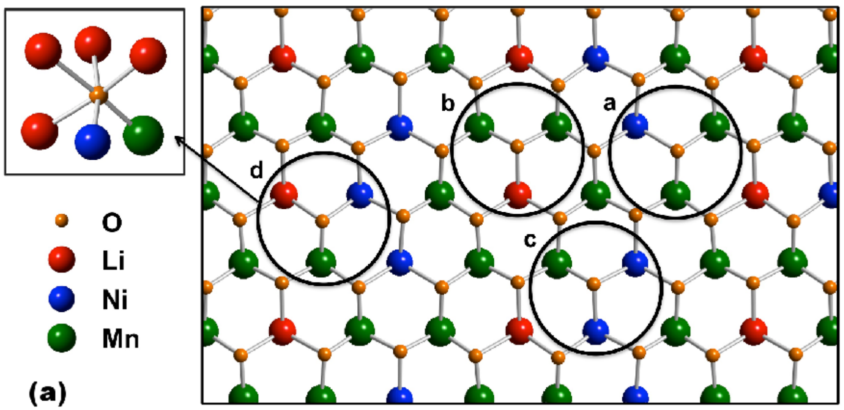
Dilute O vacancy calculation, a 96 atom unit cell

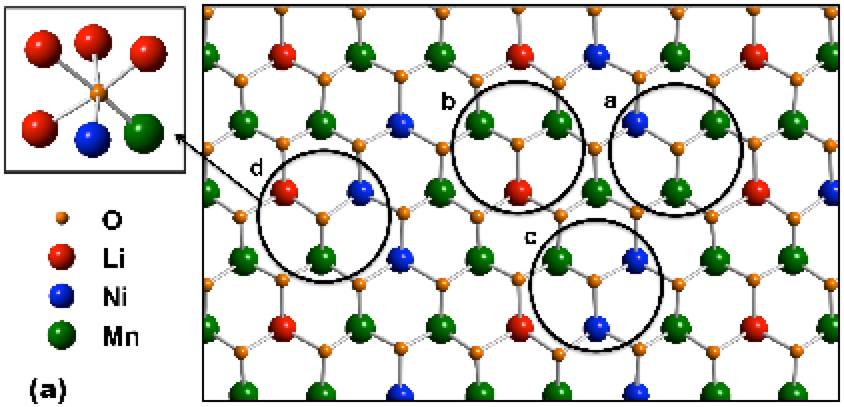


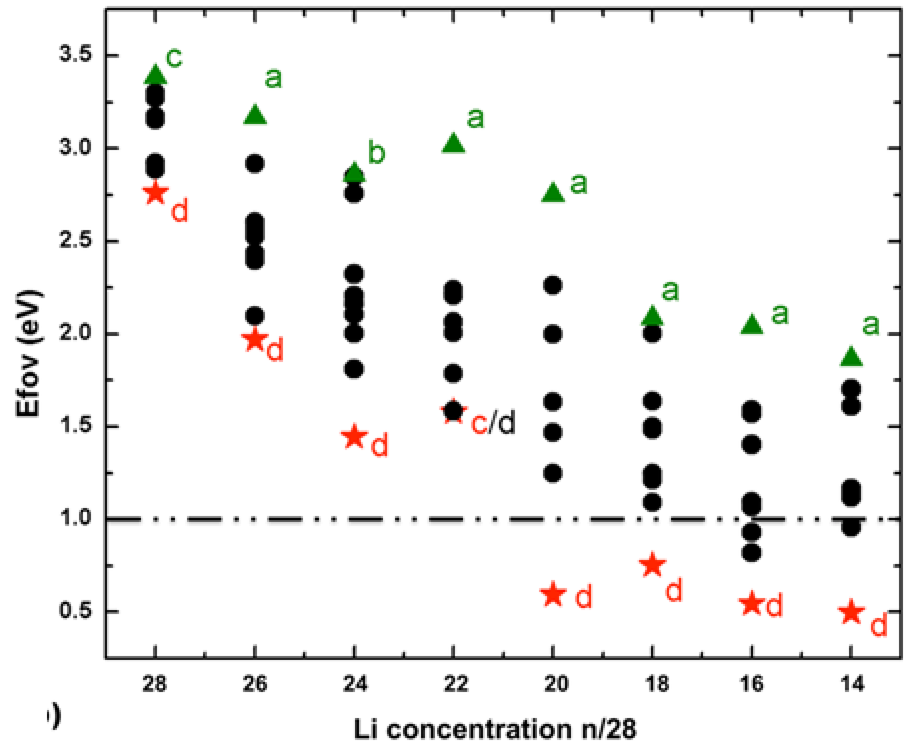


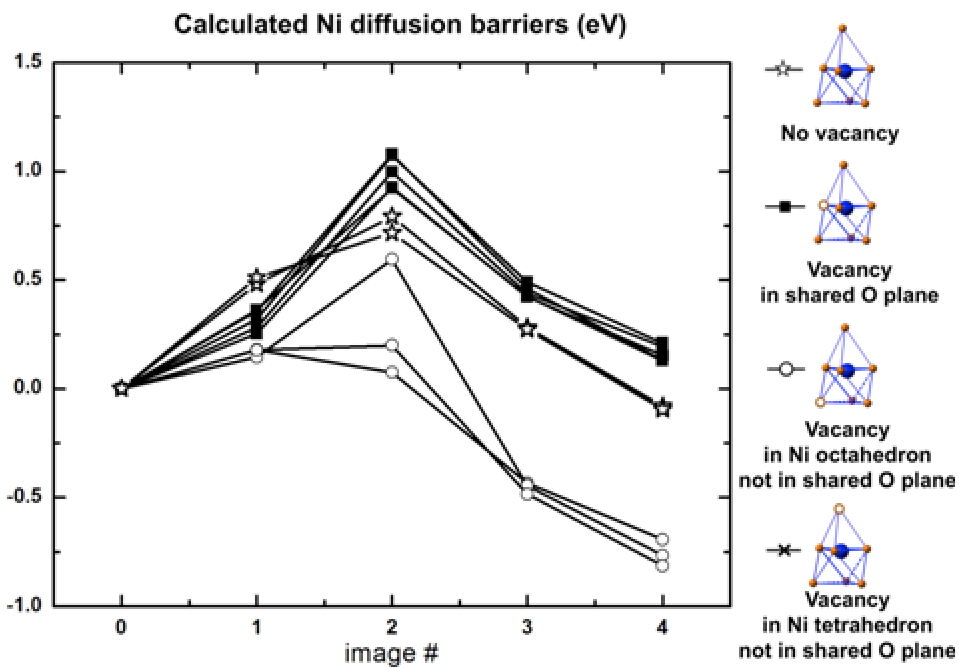
- 4 different types of local environment :

✓8 of type a: 2Mn1Ni3Li
✓10 of type b: 2Mn 4Li
✓4 of type c: 1Mn2Ni3Li
✓2 of type d: 1Mn1Ni 4Li

Technical Achievements





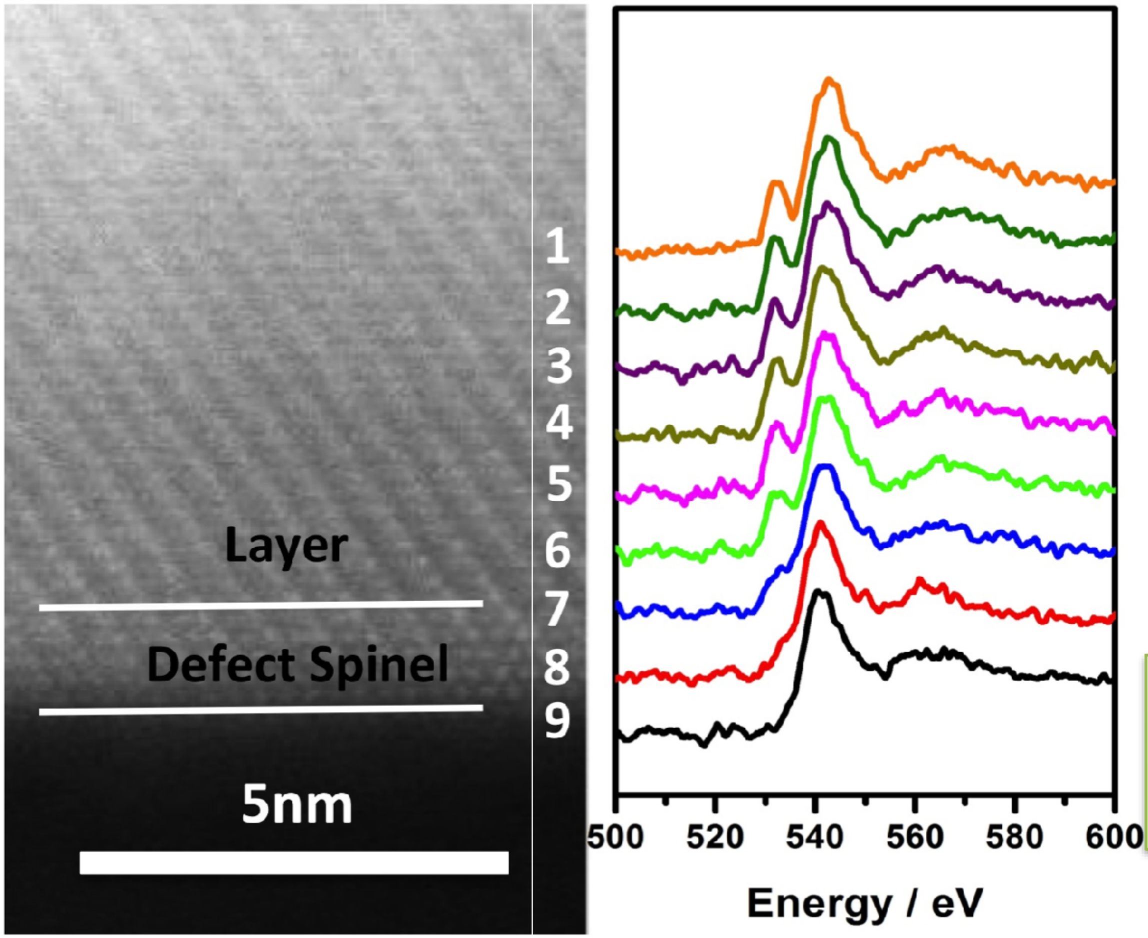


At the presence of O vacancy, both Ni and Mn migrate to Li layer

D.Qian et.al submitted, 2014

Technical Achievements

EELS was taken ~0.6nm per step
from surface to bulk



Surface phase transformation in Li-excess materials

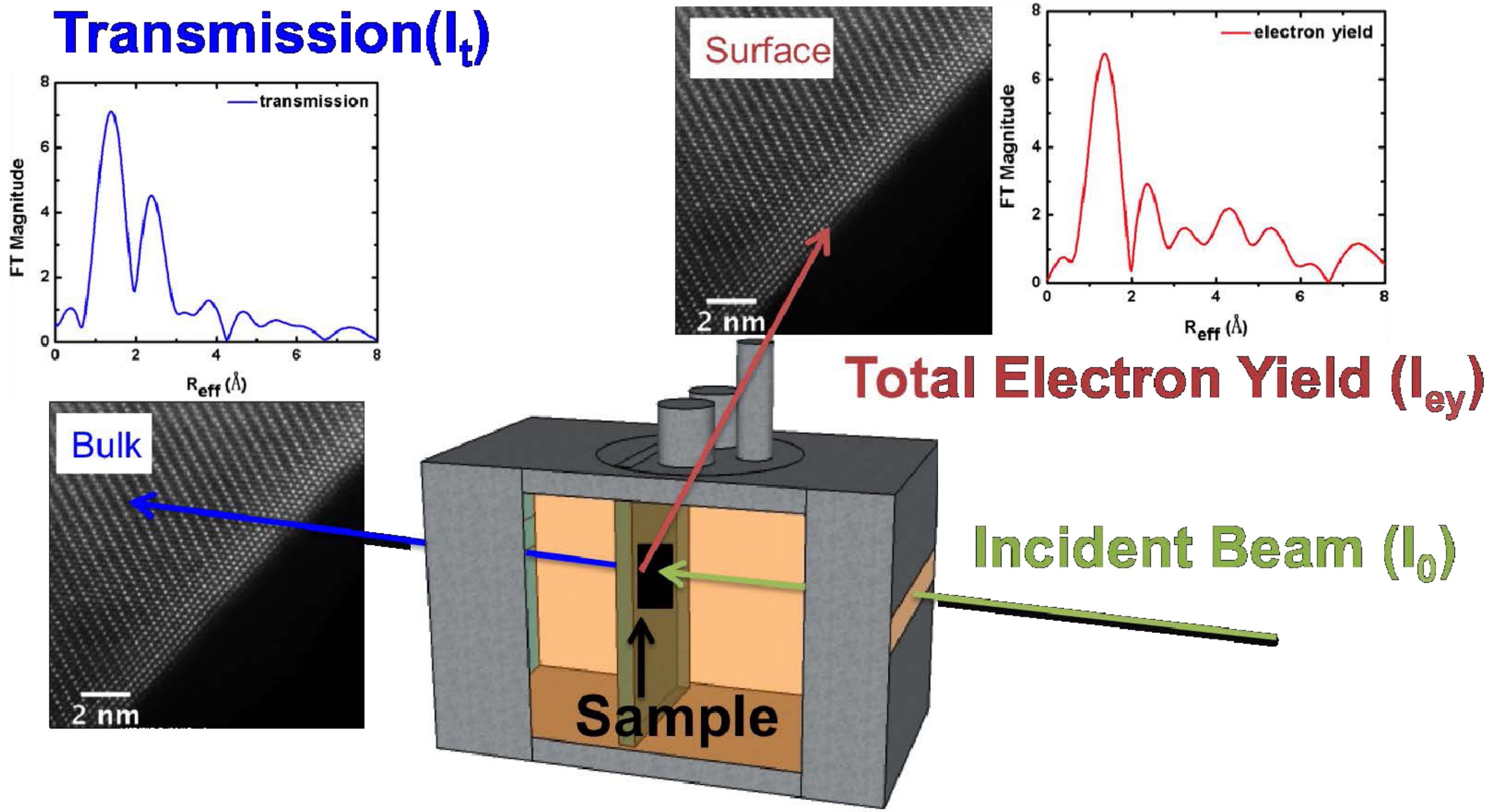
Defect spinel phase

Pre-peak disappearance:
1. the neighbour TM being reduced
2. oxygen vacancy formation

TM ion migration happens most in the region where the oxygen vacancy presented

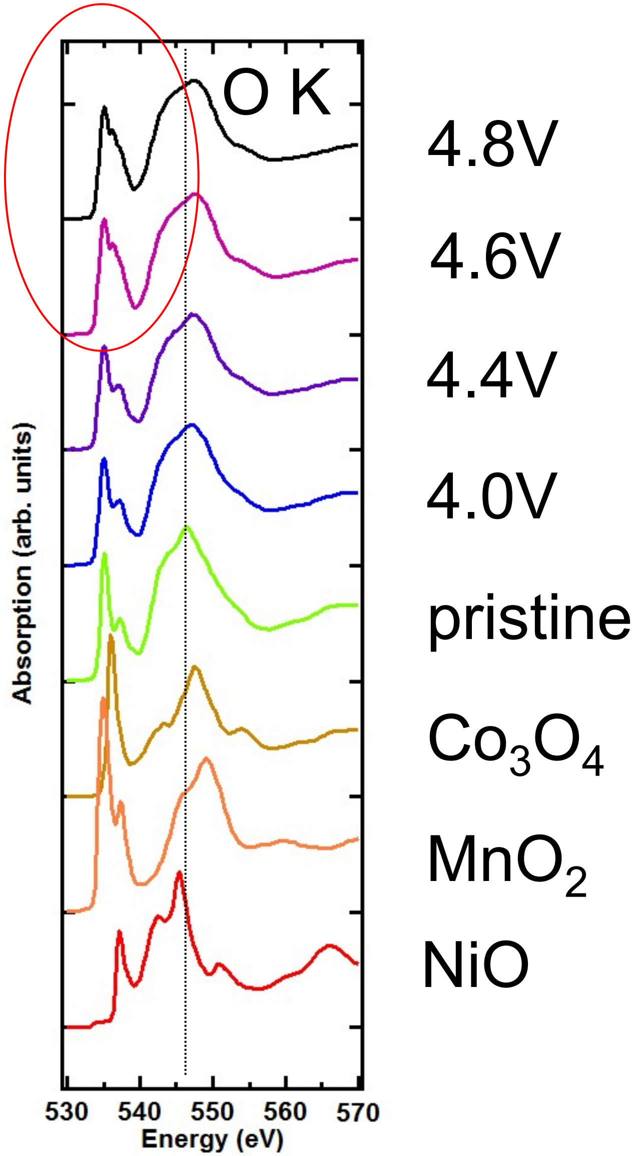
D.Qian et.al submitted, 2014

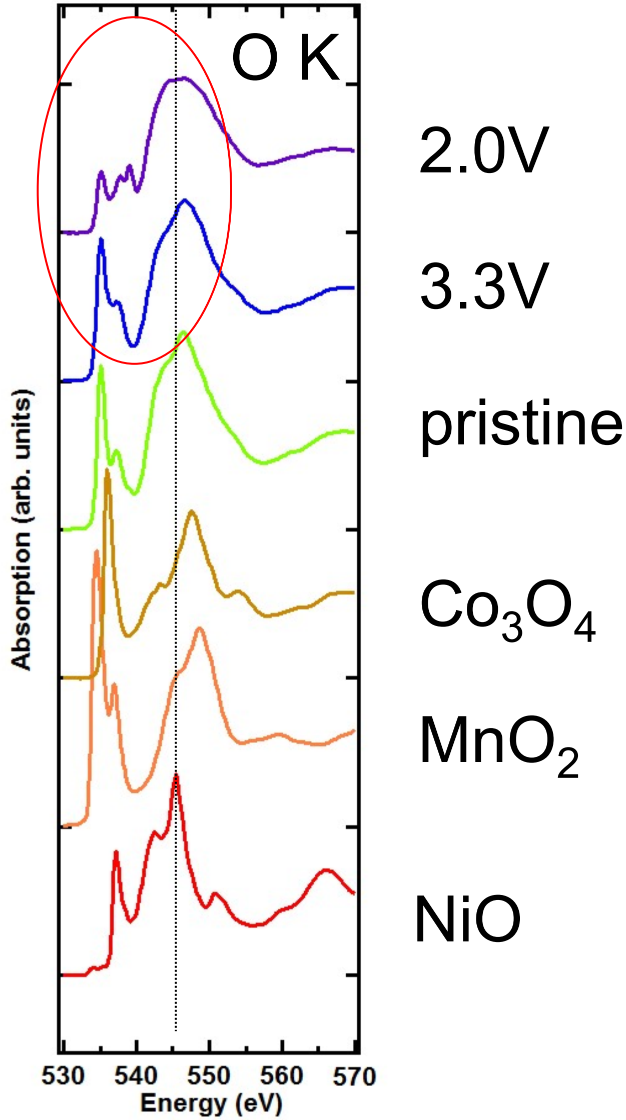
Depth Resolved Spectroscopy



Kyler Carroll etc. PCCP, 2013

Soft XAS

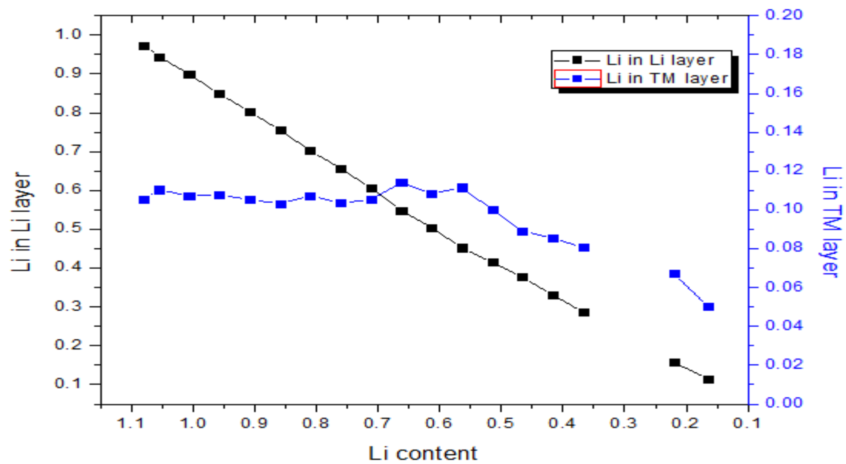


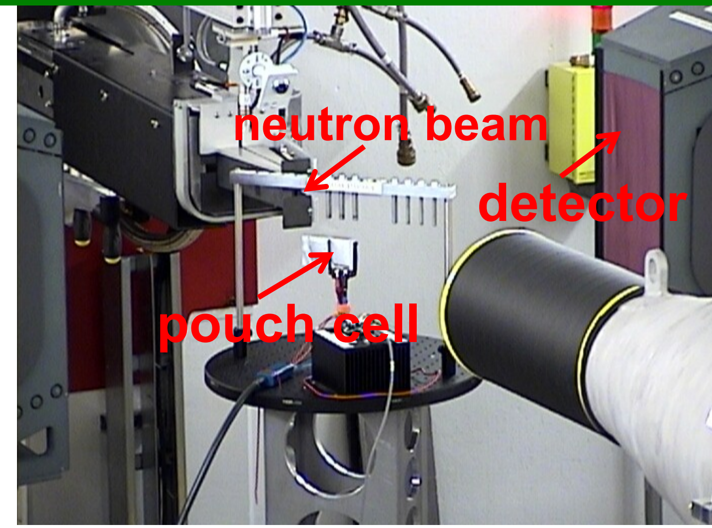


Surface O environment definitely changed after 1 cycle

Most significant changes occur at discharge

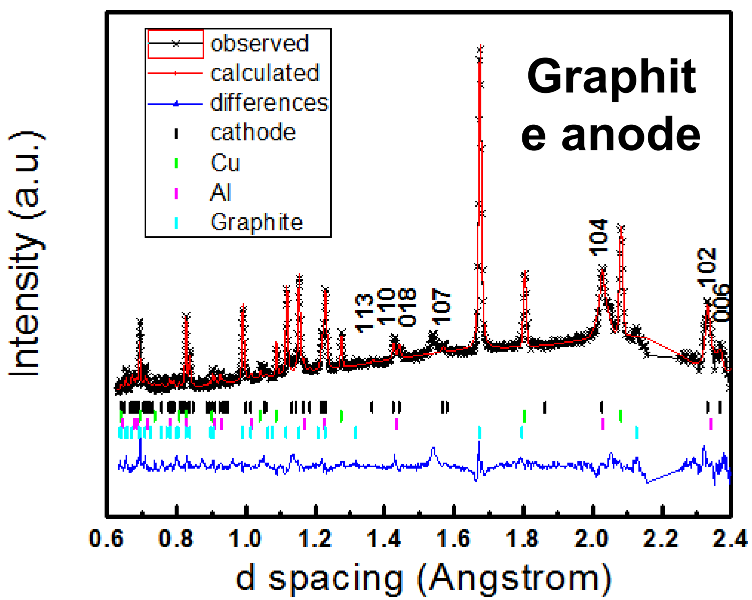
In Situ Neutron Diffraction

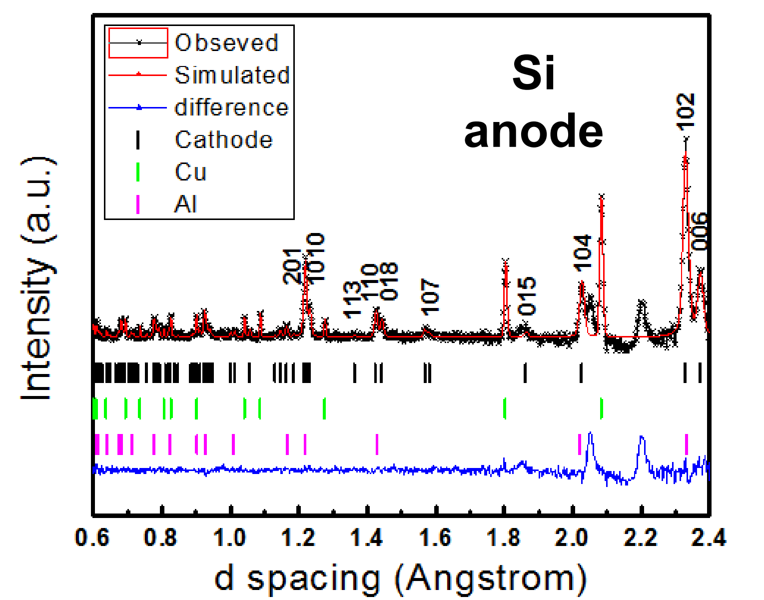




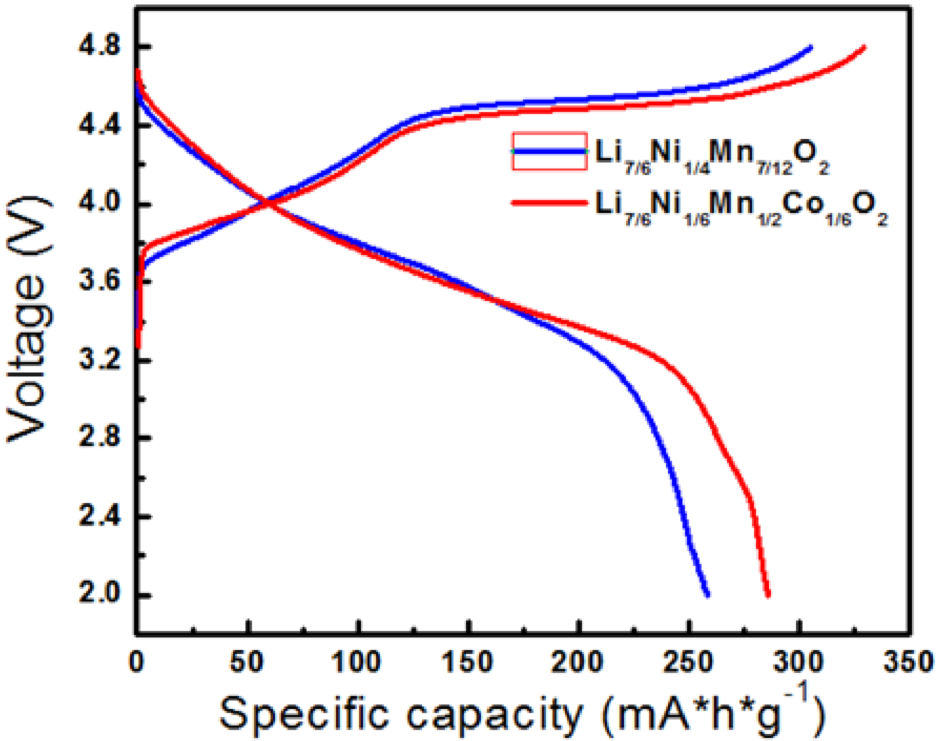
R_{F2} = 11.81% R_{wp} = 1.2% Chi^2 = 1.702

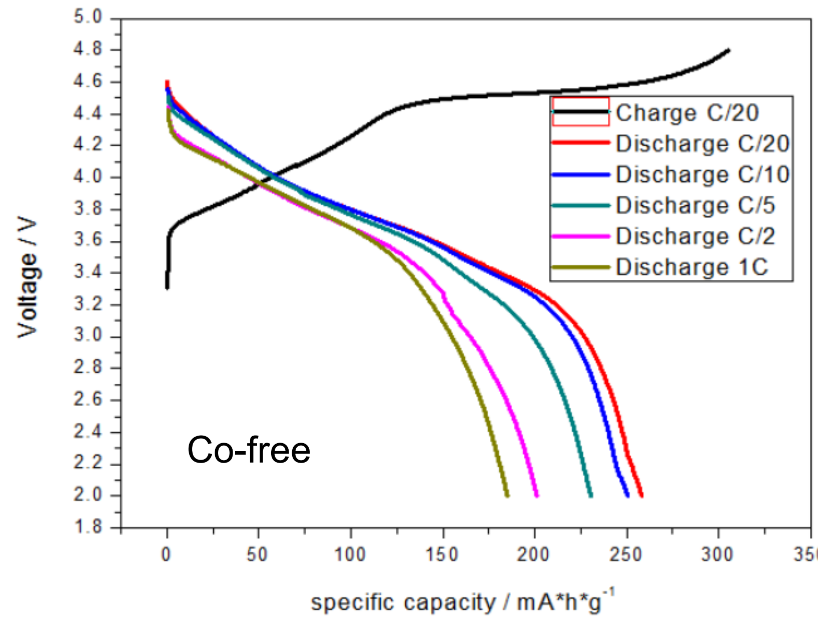
R_{F2} = 9.27% R_{wp} = 1.16% Chi^2 = 1.358

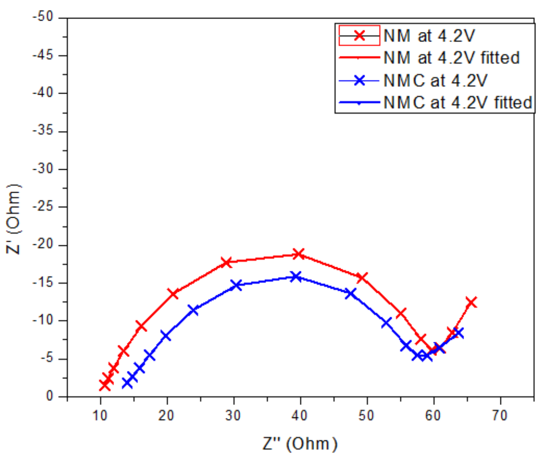


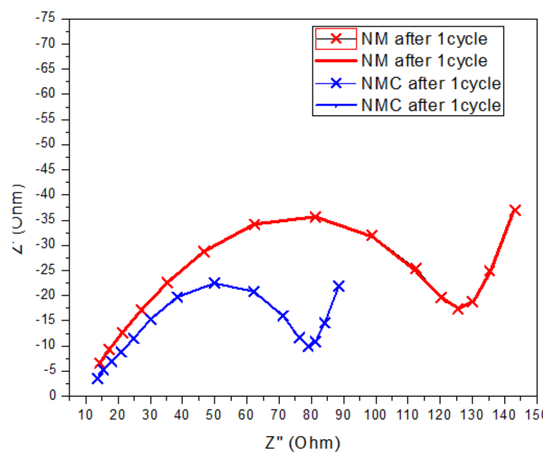


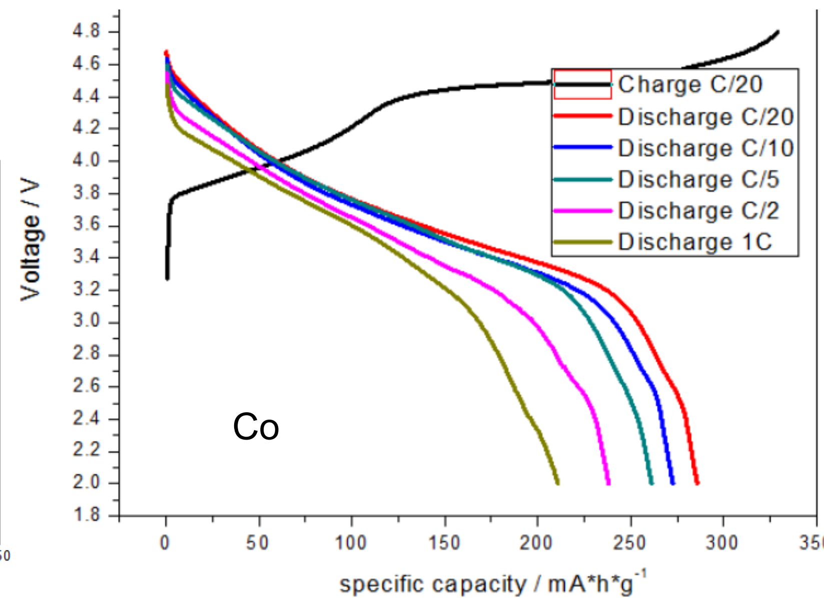
Co-Substitution



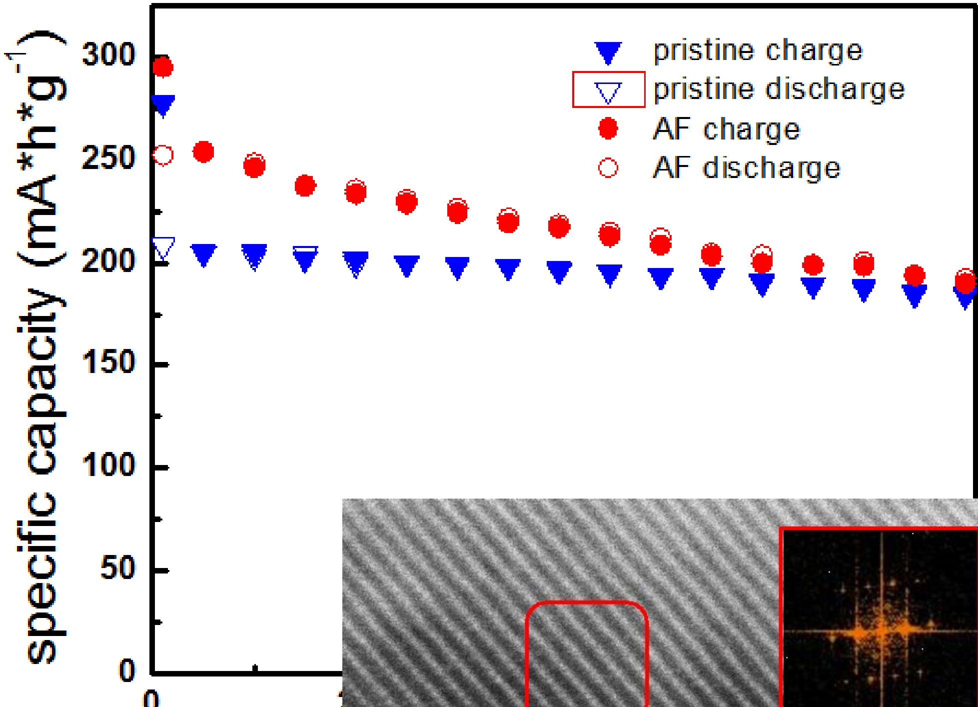


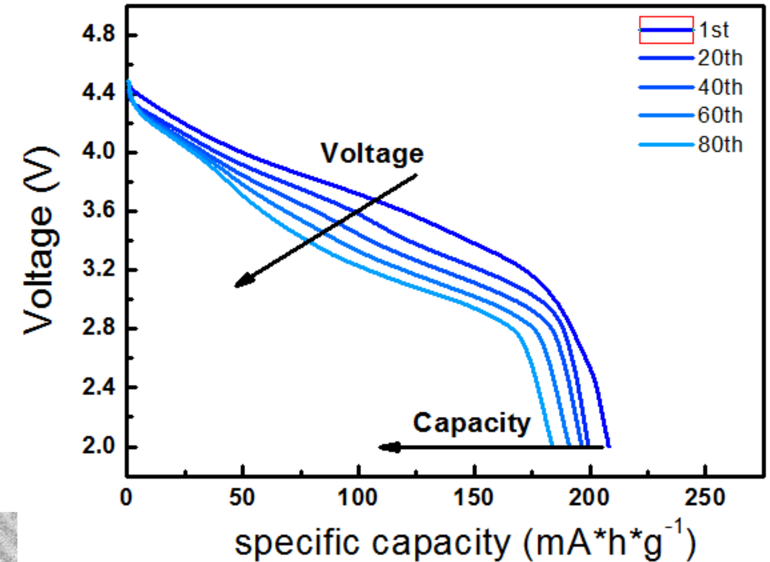


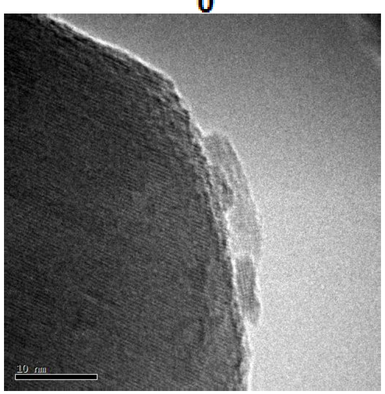


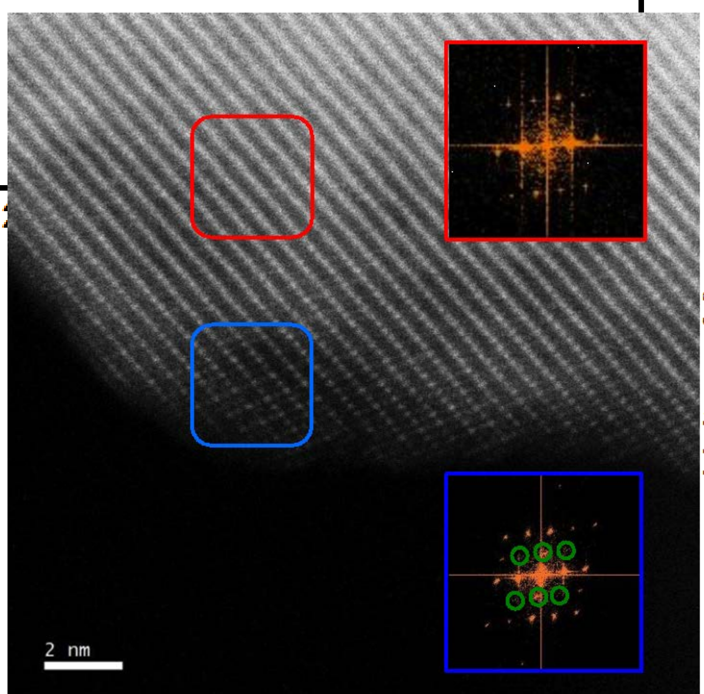


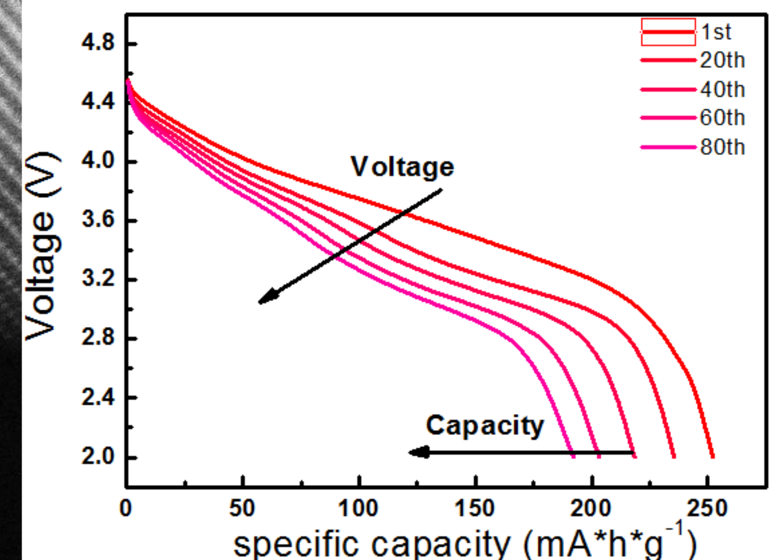
Coatings – AlF_3





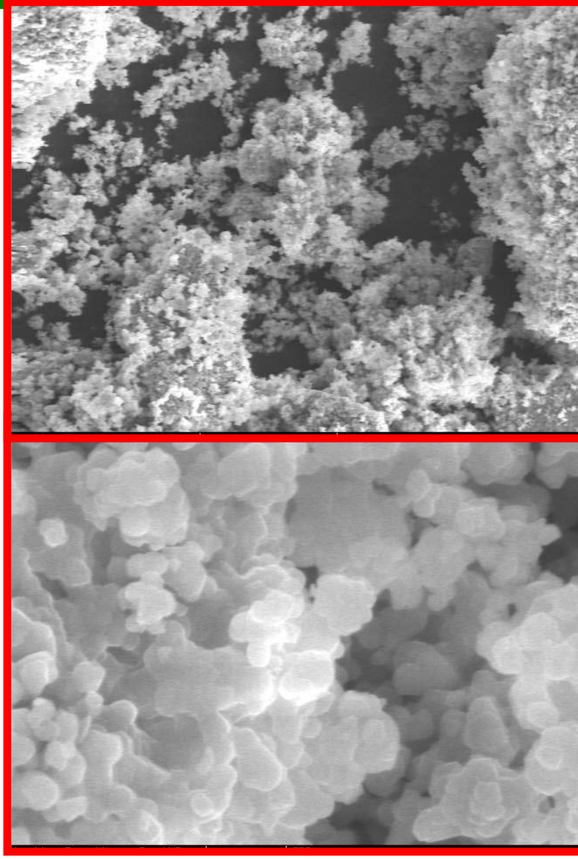


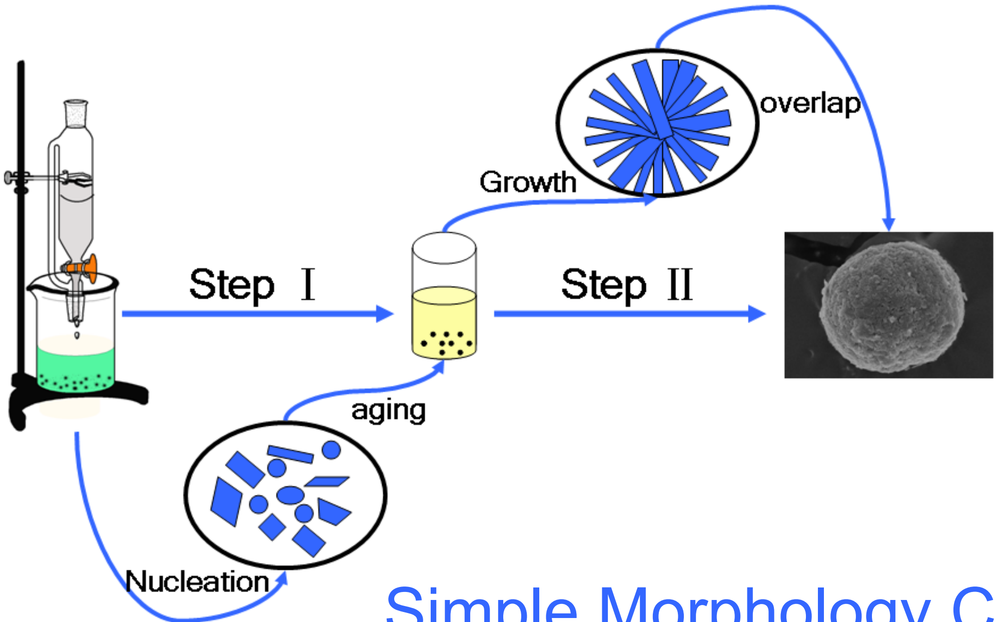




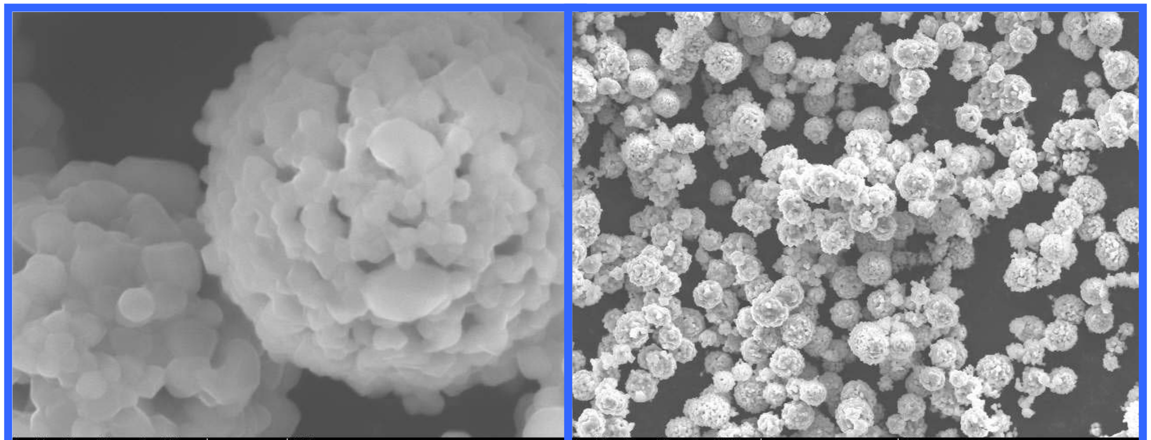
Morphology Control

Non- Morphology Control





Simple Morphology Control



Impact

A Dual Layer Complex Interphase Model

EELS/TEY/XPS(Mn3p)

$Mn^{2/3+}$ during charge

$Mn^{\sim 3.5+}$ discharge

EELS/XAS

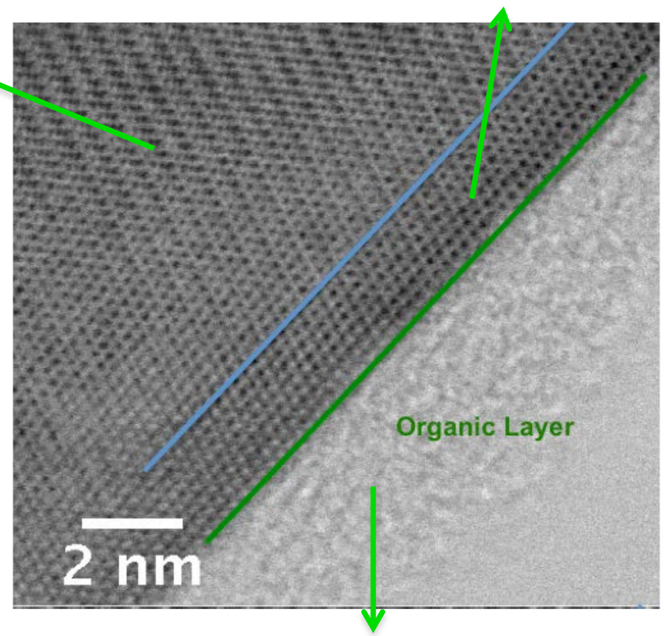
Mn^{3+} during charge

Mn^{4+} discharge

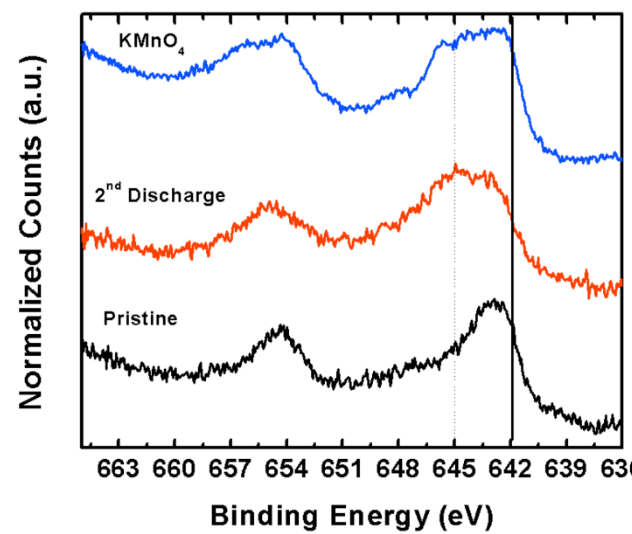
O^{2-} to O^{-} oxidation

$Ni^{2+} \rightarrow Ni^{4+}$ charge

$Ni^{4+} \rightarrow Ni^{2+}$ discharge



XPS(Mn2p)



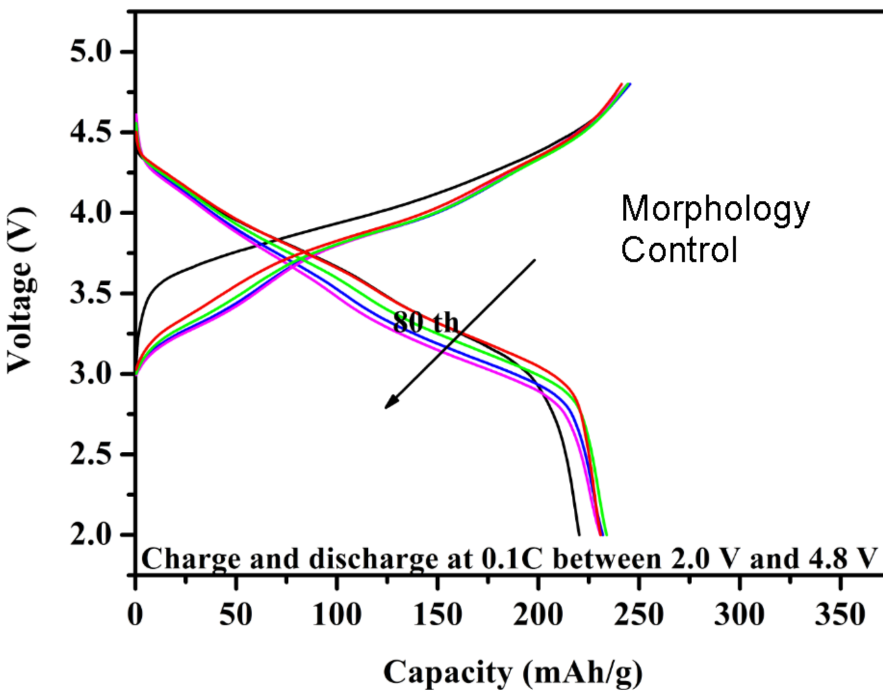
Kyler Carroll etc. PCCP, 2013

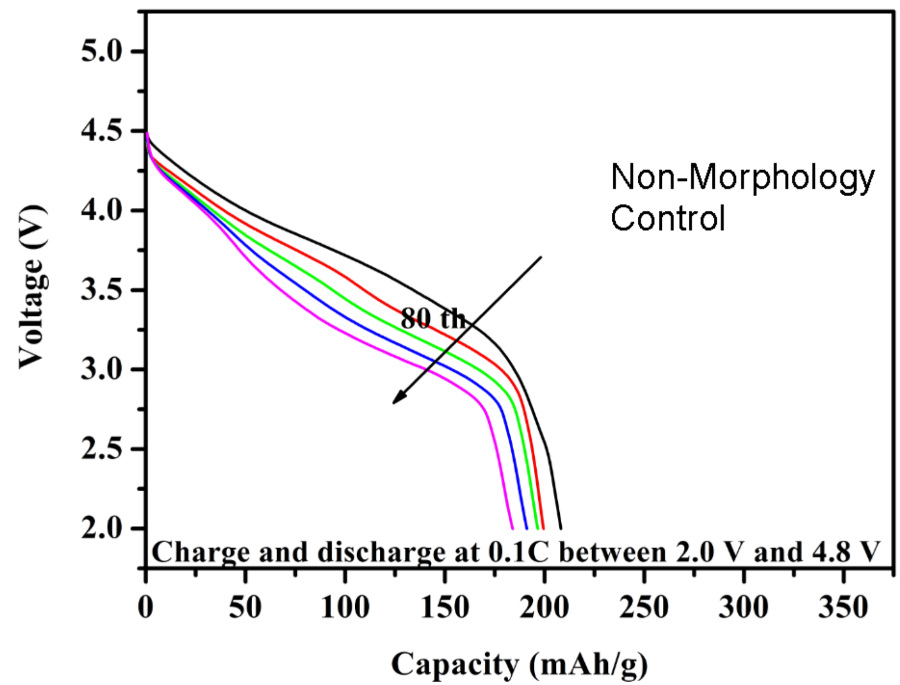
Higher Oxidation

Mn after Charge

Impact

Much Improved Voltage Stability





Collaborations

Dr. Miaofang Chi (SHaRe – STEM/EELS)
Dr. An Ke (SNS – in situ Neutron)

Multilayer in situ Neutron Cell

Future Work

- Characterize coating compositions, thickness and morphology and their effect on impedance/ion transport
- Quantitative refinement of in situ Neutron scattering experiment data
- Identify ways to extend the STEM/EELS, XPS and XAS techniques for Si based anode materials

Summary

- Our diagnostic tool suite consisting STEM/EELS, XPS, XAS and FP is effective at identifying the dynamic structural and chemical changes at the interface.
- Probing oxygen activities are possible with in-situ soft X-ray absorption spectroscopy and in-situ Neutron scattering
- Coating, substitutions and morphology control all have profound effect on the “voltage fade”. Strategies for enabling high voltage cathodes need to be optimized.

Responses to Previous Year Reviewers' Comments

NEW PROJECT FY 2013