Novel and Optimized Materials for High Energy Density Batteries

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ES070

Overview

Timeline

- Project start Jan 2012
- Project end Sep 2015
- 25% complete

Budget

- Funding FY12: $450
- Funding FY13: $450

Barriers

- Barriers addressed
  - Gravimetric and volumetric Energy Density
  - Cycle life
  - Safety

Partners

- BATT NiMn Spinel Focus Group.
- Battaglia, Srinivasan, Kostecki, Persson, Chan (LBNL), Beamline scientists at SSRL and ALS, Grey (CU), Casas-Cabanas (CIC)

Relevance - Objectives

- To achieve cycle life and energy density targets using high capacity, high voltage electrode materials.
  - Establish chemistry-structure-properties correlations and assess origins of inefficiencies to aid in the design of better materials.
  - Discover new materials with improved chemical and electrochemical stability.
  - barriers: *energy density, cycle life, safety*

- To understand the correlation between chemistry, phase transformations and electrode performance.
  - Develop methods to couple parameters at multiple length scales.
  - Provide inputs for electrode design and modeling teams to enable battery engineering improvements and life predictions.
  - barriers: *energy density, cycle life*

Milestones

Mar. 12	Complete the crystal-chemical characterization of annealed $LiNi_{1/2}Mn_{3/2}O_4$ and identify its role on electrochemical performance. **Completed**
Sep. 12	Synthesize and physico-chemically characterize at least two different new phases showing an oxyfluoride network, containing lithium and a light transition metal. **Delayed to FY13**
Sep. 12	Identify the influence of oxide additives on the extent of electrolyte-electrode side reactions in spinel electrodes. **Completed**
Mar. 13	Complete in operando X-ray diffraction study of at least 4 samples of $LiNi_{1/2}Mn_{3/2}O_4$ with different degrees of order/disorder. **Completed**
Apr.. 13	Develop a synthetic protocol for the extensive fluorination of Li-M-O (M=Mn, Fe, Cu) using low temperature treatments. **On schedule**
Sep. 13	Synthesize at least two new Li-M-O-F (M=Mn, Fe, Cu) using direct high temperature methods. **On schedule**
Sep. 13	Determine changes during cycling of the surface chemistry of $LiNi_{1/2}Mn_{3/2}O_4$ depending on coatings and doping, in coordination with the Spinel Focus Group. **On schedule**

Approach/Strategy

- Establish composition-structure-electrochemical properties correlations in $LiNi_{1/2}Mn_{3/2}O_4$.
  - Synthesize samples with controlled microstructure, composition, ordering to define the role of crystal chemical parameters.
  - Establish the role of electrode surface chemistry on in-cycle efficiencies.
  - Ultimate goal: 100% utilization at 2C rate, 85% 1st cycle efficiency and 99.99% steady-state efficiency at C/2 rate.

- Discover new electrode materials that overcome barriers of high voltage and capacity.
  - Leverage knowledge created with $LiNi_{1/2}Mn_{3/2}O_4$.
  - Explore Li-M-O-F space (M=Fe, Mn, Cu) in search for completely new phases. Synergy with Materials Prediction teams in BATT.

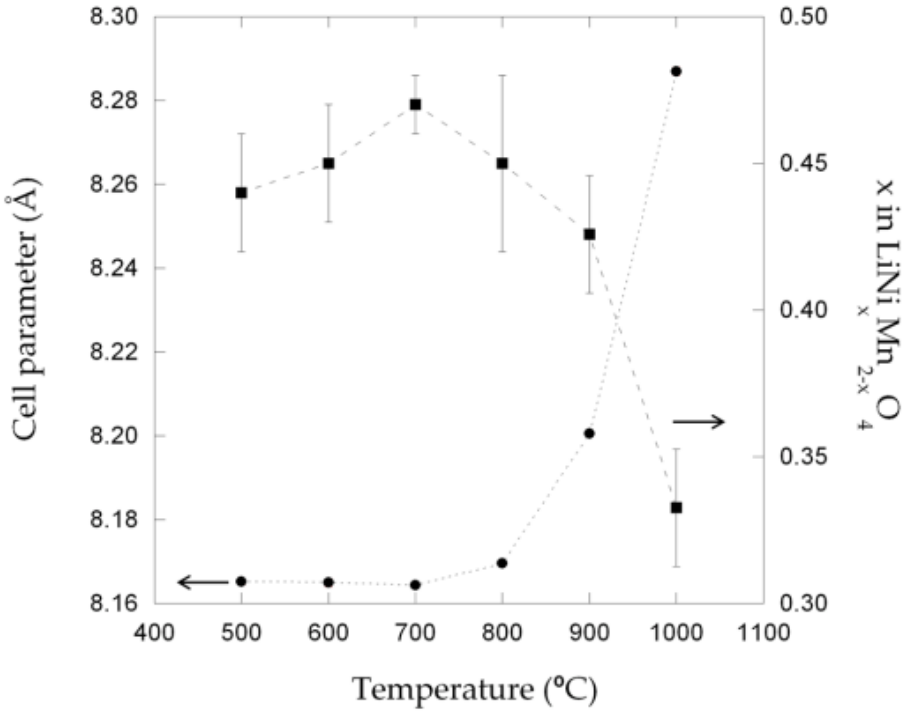
- Use synchrotron radiation to characterize electrode materials at multiple length scales.
  - Combination of diffraction, spectroscopy and imaging to evaluate inhomogeneities at nano, meso and macro scale.
  - Create a body of knowledge of electrode function that can be leveraged by electrode engineering and modeling teams in BATT.

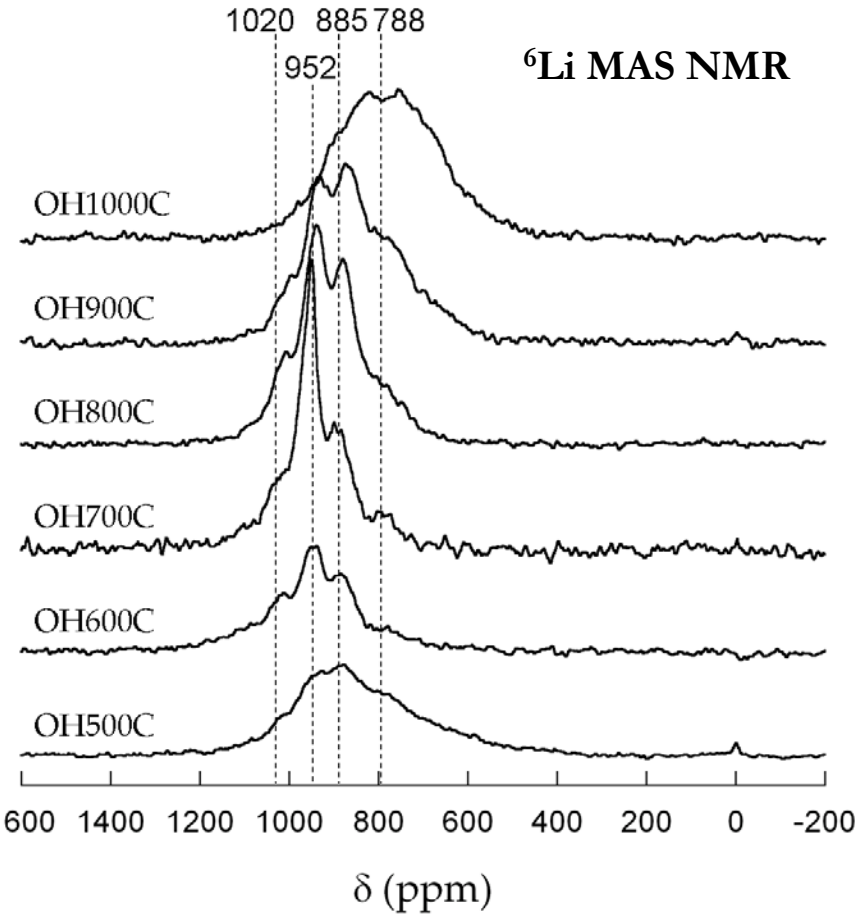
Technical accomplishments:

$LiNi_{1/2}Mn_{3/2}O_4$: a material with rich crystal chemistry

Cabana *et al.*, *Chem. Mater.* 24 (2012) 2952
Cabana *et al.*, *J. Electrochem. Soc.* 158 (2011) A997

Neutron Diffraction

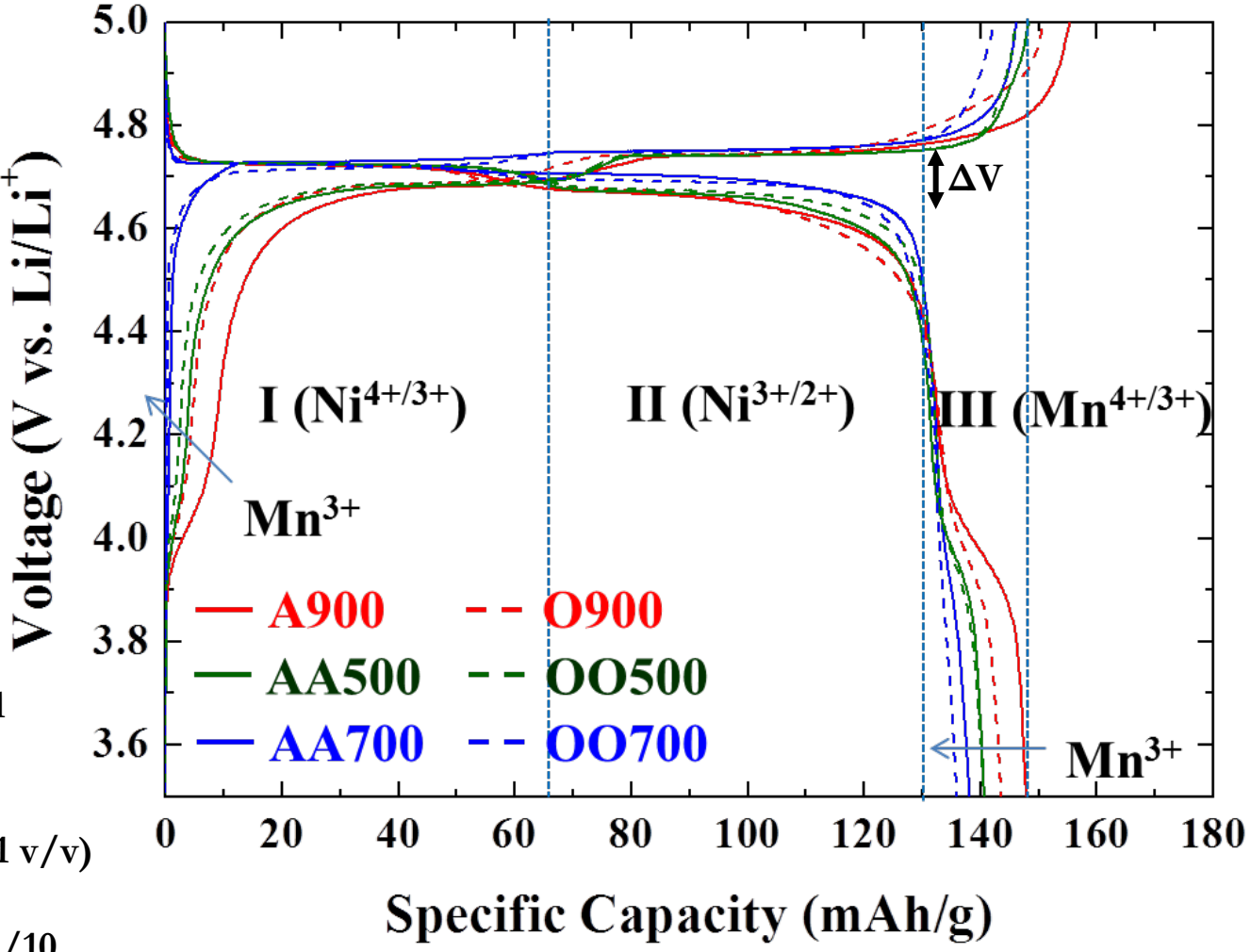




- Samples synthesized from hydroxide precursors at 500°C≤T≤1000°C for 12 h.
- Clear Ni-Mn ordering transition at 700°C. Generation of Mn^{3+} at high temperature.
- NMR: Different Ni-Mn ordering schemes are possible.

Technical accomplishments:

Identification of electrochemical proxies



2032 coin cell

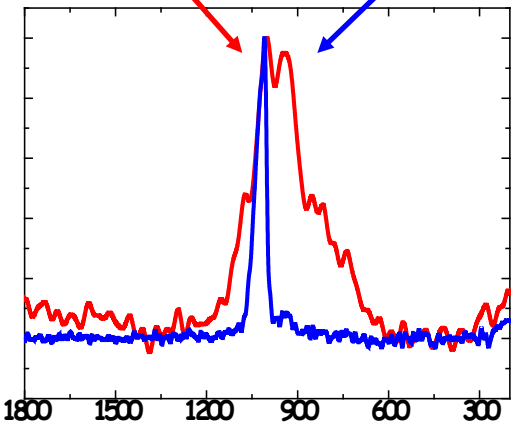
1M $LiPF_6$ in EC/DEC (1:1 v/v)

3.5 – 5 V at C/10 (C = 147 mA/g)

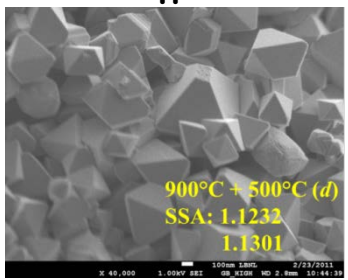
Technical accomplishments:

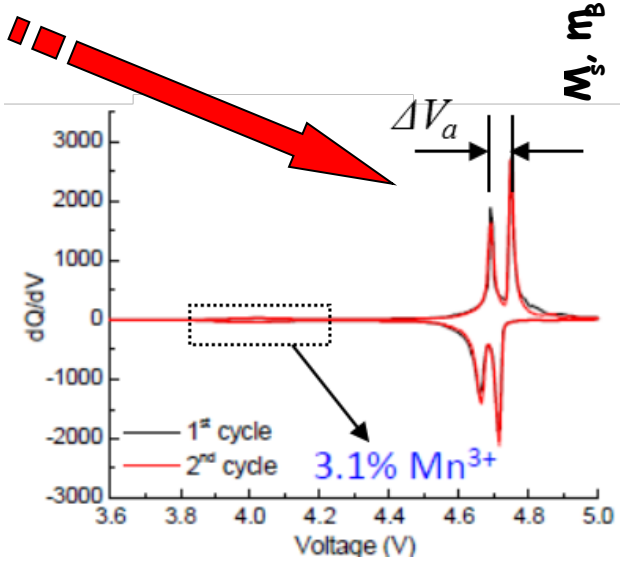
Decoupled chemical parameters by sample annealing

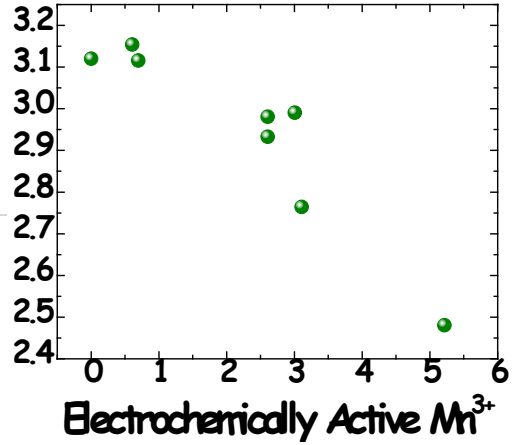
	900C air	500C air	700C air	900C O_2	500C O_2	670C O_2	700C O_2	730C O_2	500C air + O_2	700C air + O_2	900C air 12hrs
ΔV_a (1st cycle)	67	58	24	67	67	52	32	23	58	38	67
BET	1.14	1.12	1.13	1.11	1.13	1.22	1.19	1.24	1.08	1.21	0.87
Mn^{3+}	5.2%	2.6%	0.7%	3.1%	2.6%	1.2%	0.0%	0.4%	3.0%	0.6%	5.0%



^{6}Li MAS NMR



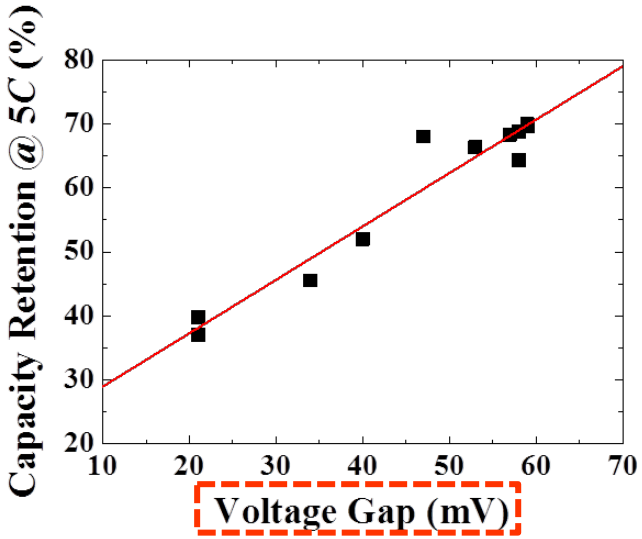




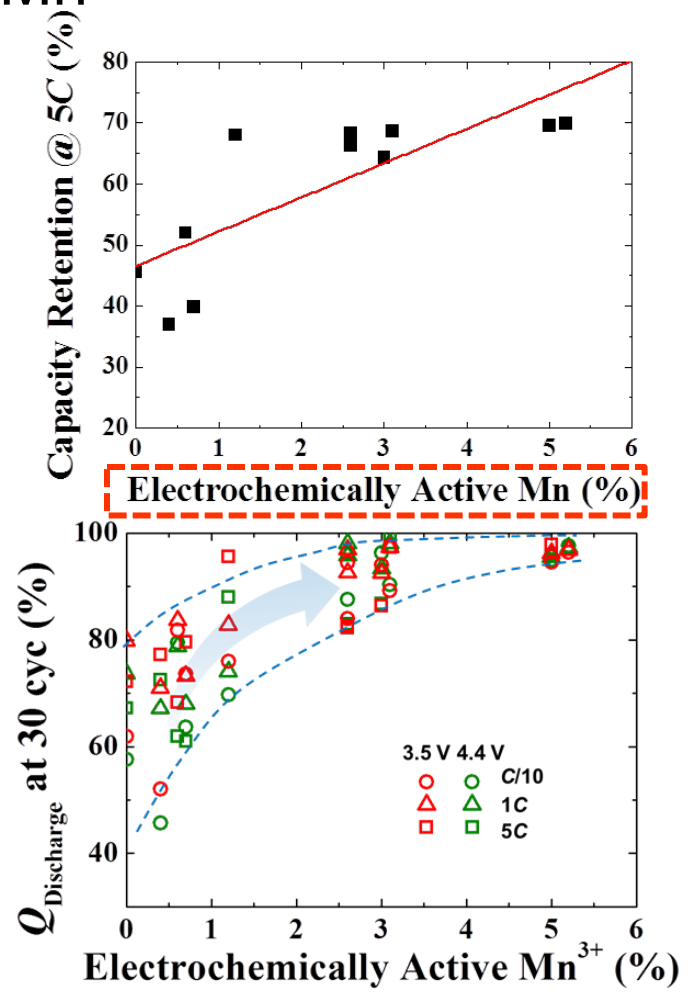
Magnetic Susceptibility

Technical accomplishments:

Electrochemistry-ordering correlations are much stronger than with Mn^{3+}



vs.



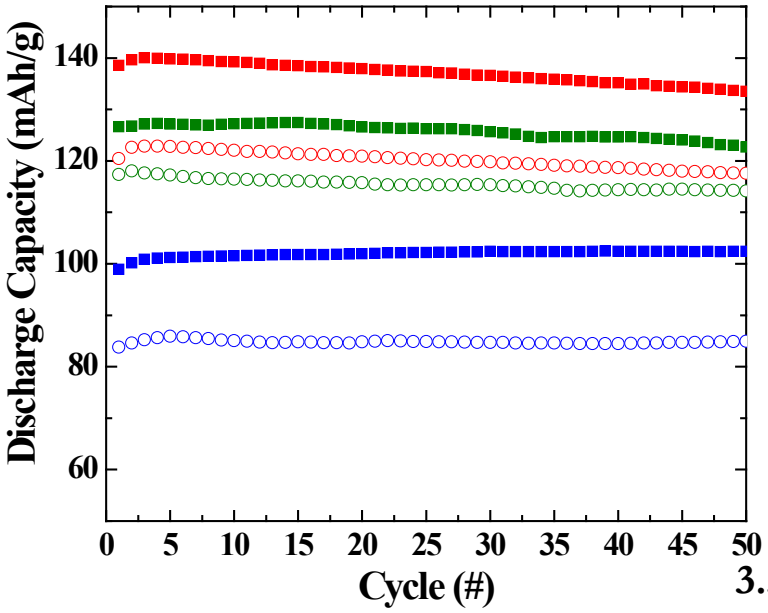
- Correlation between disorder and better retention at higher rates.
- Variability in Mn^{3+} contents within disorder (2.6-5.2%) does not produce substantial differences.

Kim *et al.*, *Submitted for publication*

Technical accomplishments:

Restricting voltage window offers other clues

A900

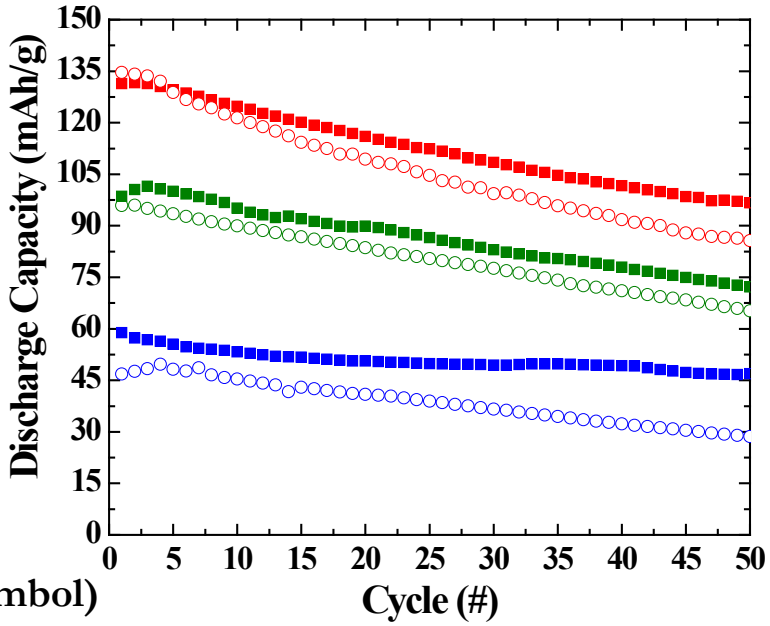


Red: @ C/10

Green: @ C

Blue: @ 5C

AA700



3.5 – 5 V (closed symbol)

4.4 – 5 V (open symbol)

Rate (C)	Retention @ 4.4 V	Retention @ 3.5 V
1/10	97.63 %	96.35 %
1	97.25 %	96.86 %
5	101.35 %	103.51 %

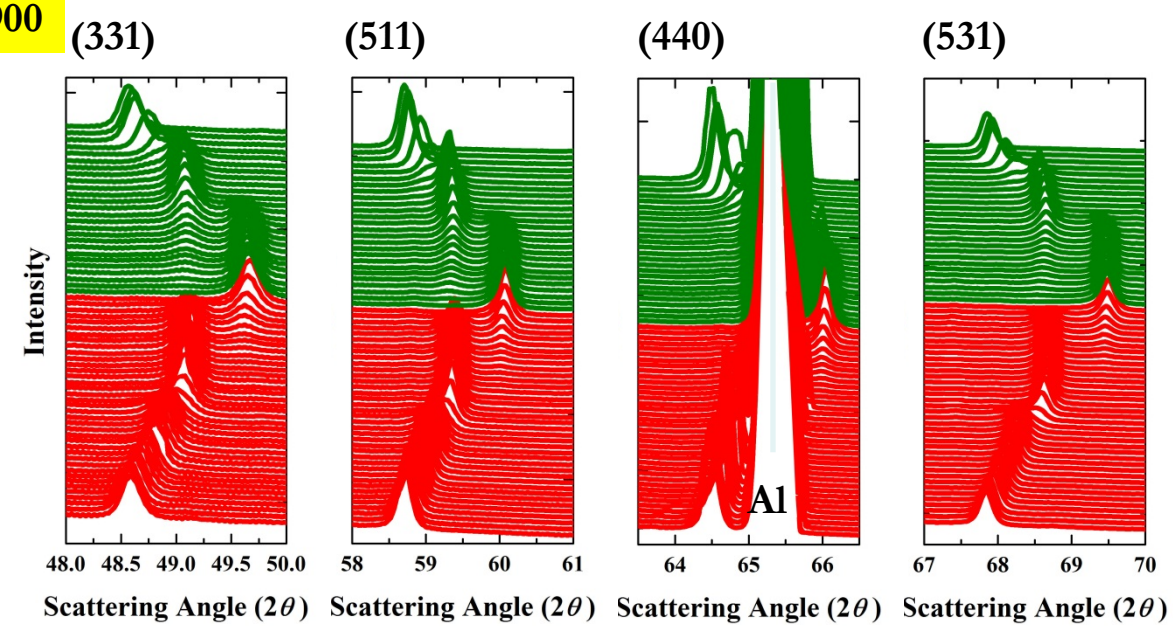
Rate (C)	Retention @ 4.4 V	Retention @ 3.5 V
1/10	63.64 %	73.57 %
1	68.01 %	73.26 %
5	61.02 %	79.65 %

- Disordered samples: No significant change found when cycling at restricted windows ⇒ presence of Mn^{3+} has a modest effect on rate performance (=transport).
- Ordered samples: Worse retention in restricted window ⇒ is a very small amount of Mn^{3+} desirable?

Technical accomplishments:

Why are ordered and disordered samples different?

A900

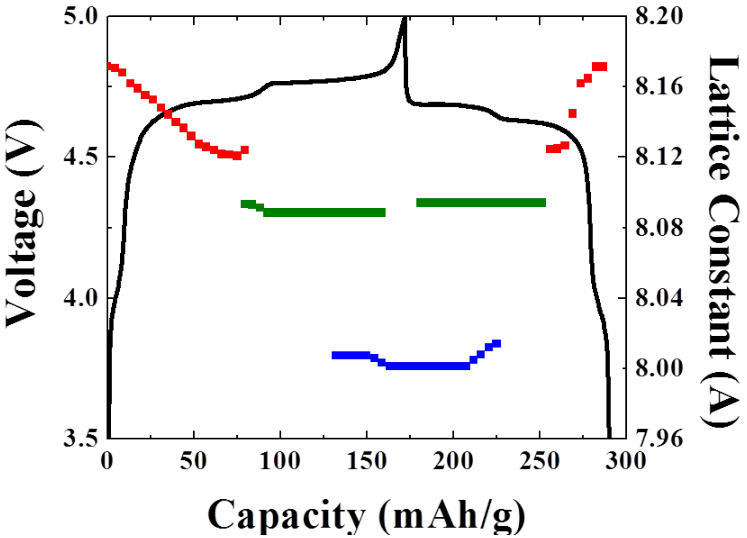


SSRL

BL11-3

Discharge

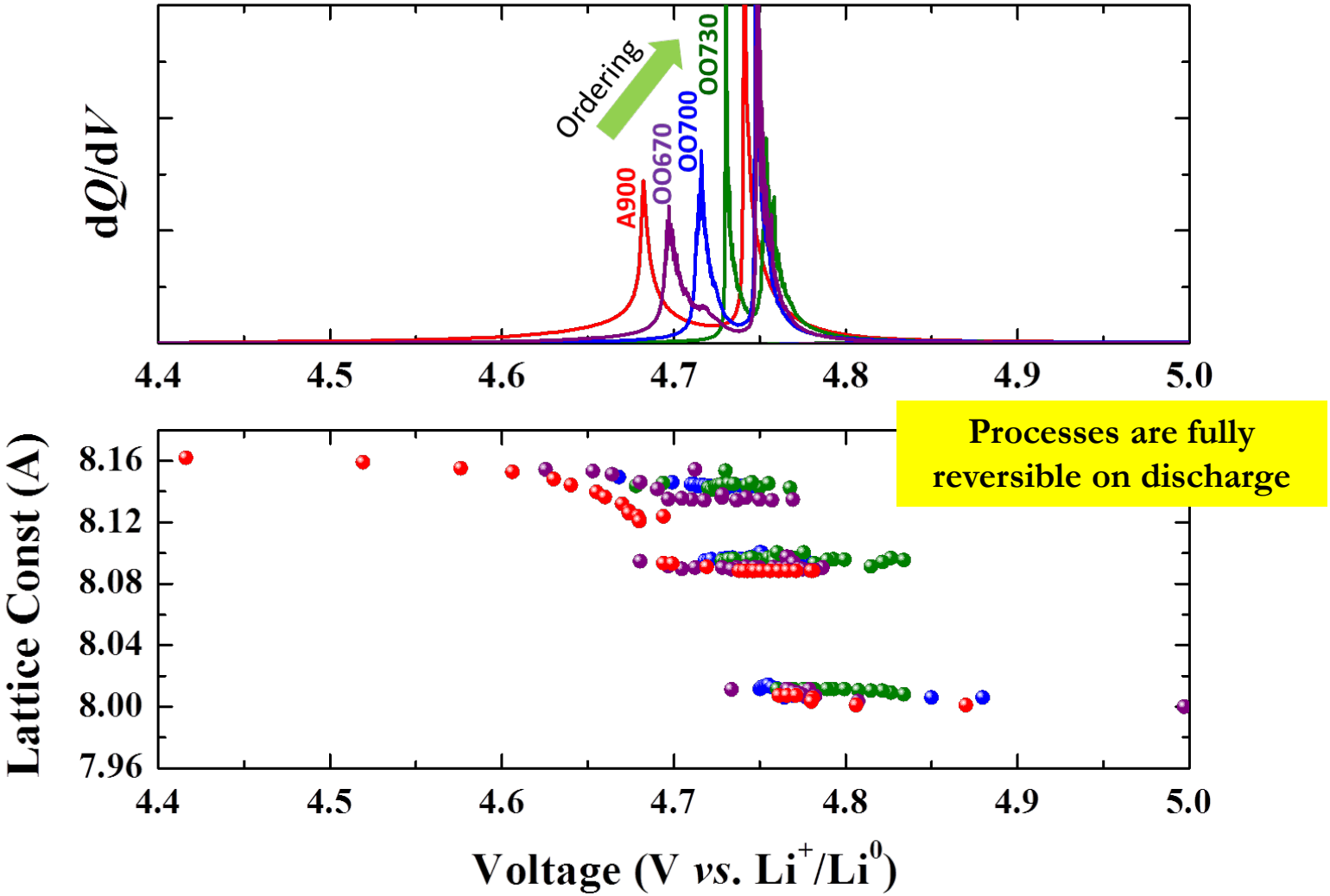
Charge



Solid solution reaction (a to a') →
Two phase reaction (a' and b) →
Two phase reaction (b and c)

Technical accomplishments:

Formation of solid solutions favors high rate performance

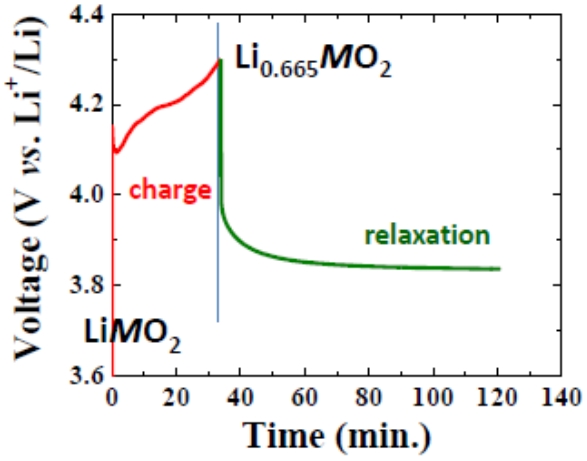


Processes are fully reversible on discharge

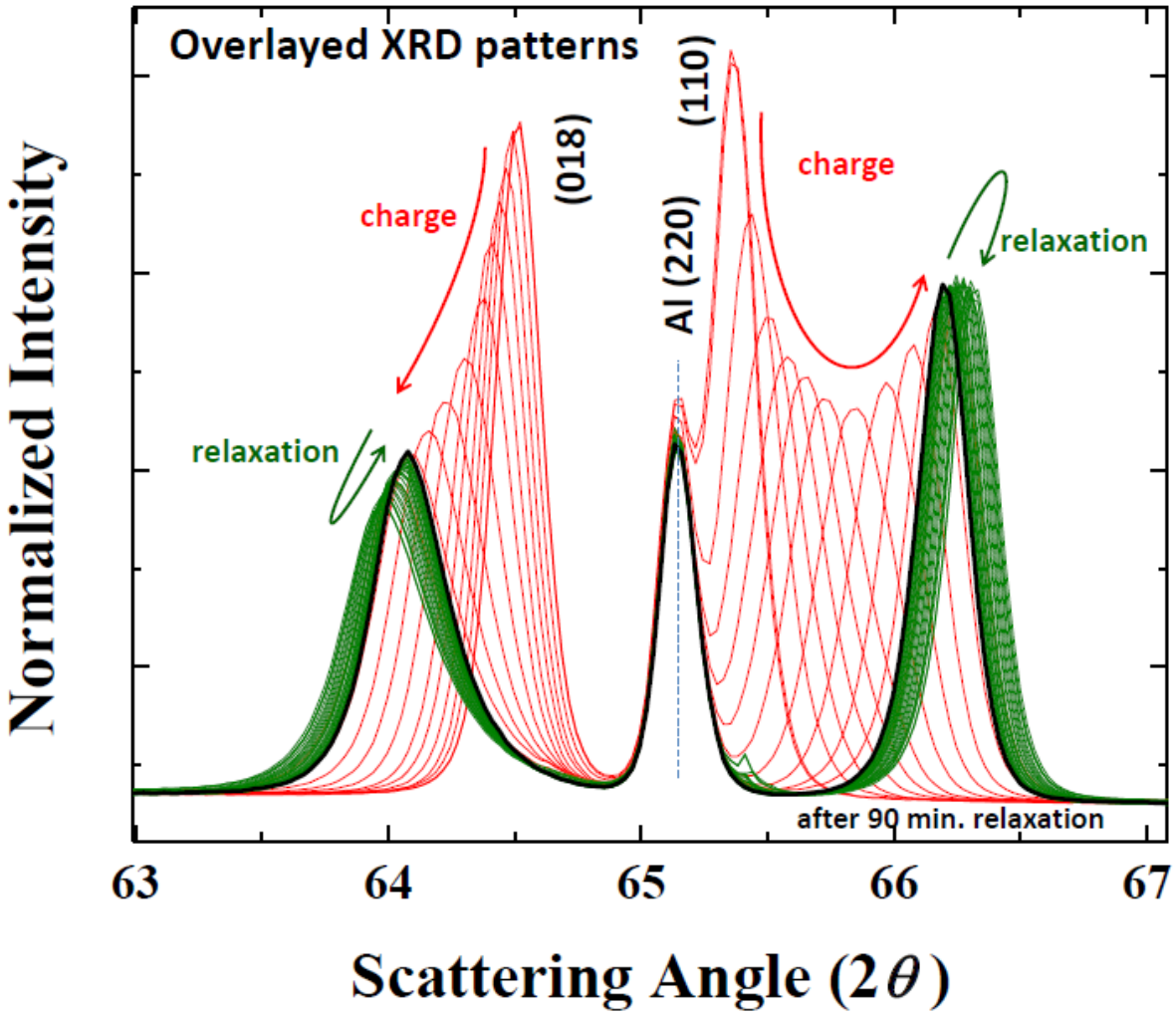
• Cutting voltage at 4.4 V in ordered samples leads to domains that are still two-phase ⇒ phase transformation hysteresis?

Technical accomplishments:

Phase transformation inhomogeneity in thick NMC electrodes

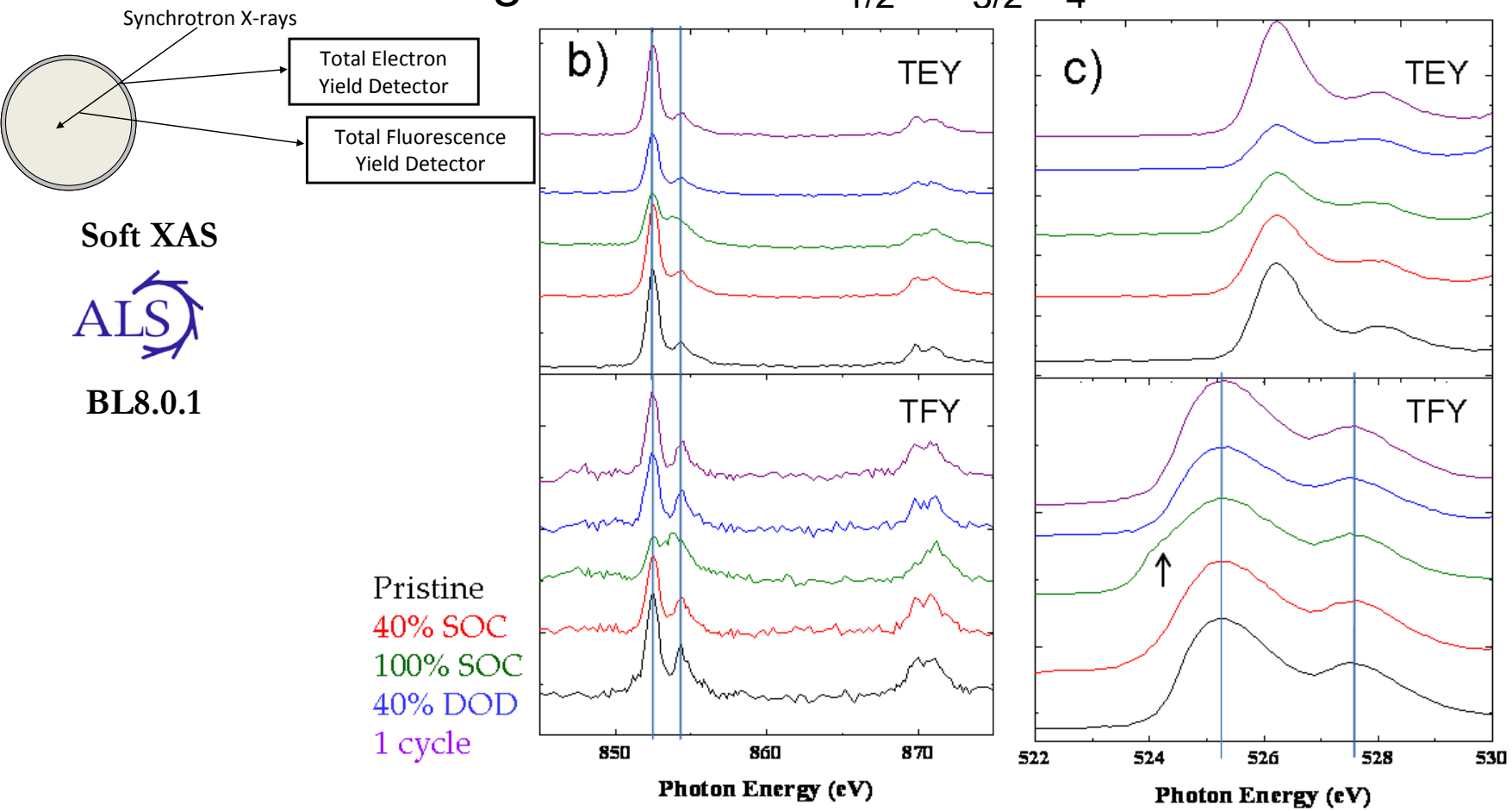


- 150 μm thick NMC333 electrodes supply by Battaglia group.
- Charged to 1C + Relax.
- Collected XRD in transmission (averaged through electrode depth)
- Peak evolution during relaxation suggests changes in composition + built-in inhomogeneities.



Technical accomplishments:

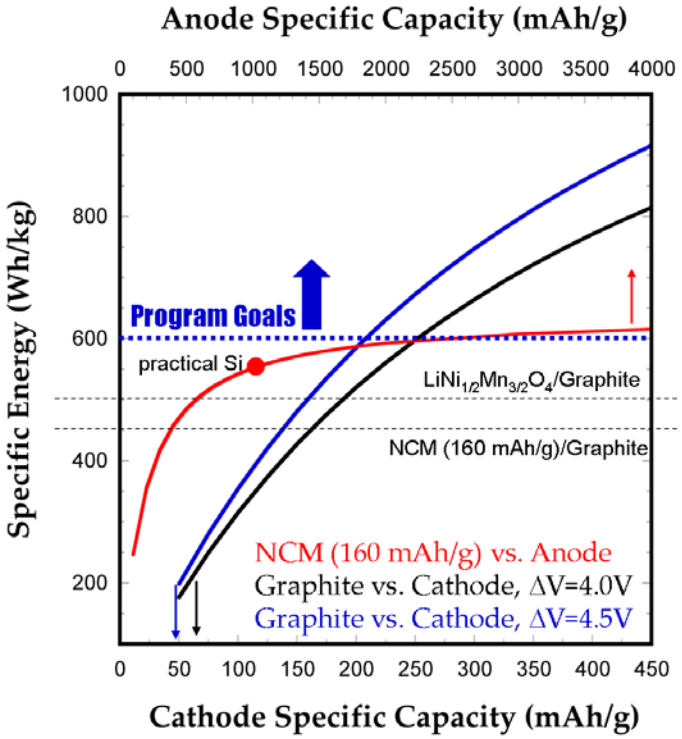
Chemical changes at the $LiNi_{1/2}Mn_{3/2}O_4$ electrode surface

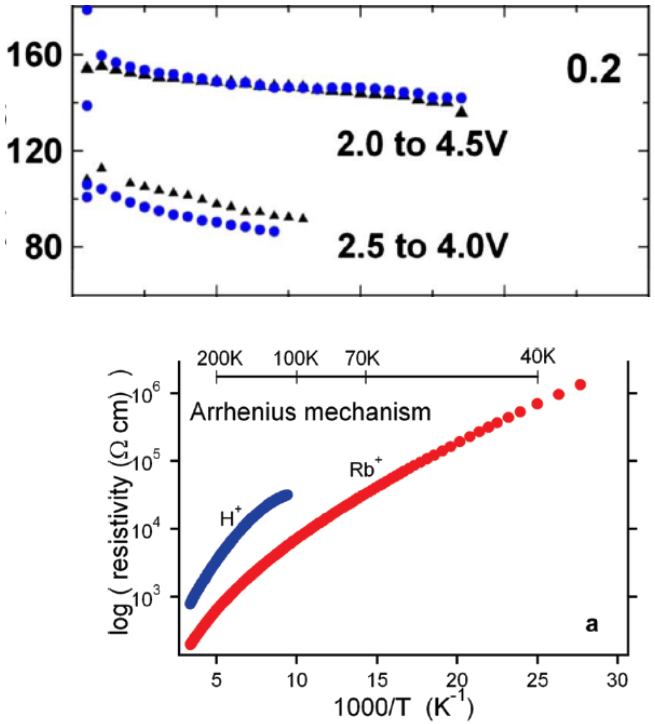


- Line shape changes for Ni ⇒ oxidation of Ni^{2+}.
- Small shoulder develops at O pre-edge ⇒ Ni-O bond nature is changing.
- Significant differences between TEY and TFY ⇒ surface is less oxidized?
  - Proposed mechanism: material has active participation in electrolyte decomposition; oxidized (acidic) Ni(-O) attacks electrolyte molecules.

Technical accomplishments:

Li-M-O-F, toward chemically stable high voltage electrodes





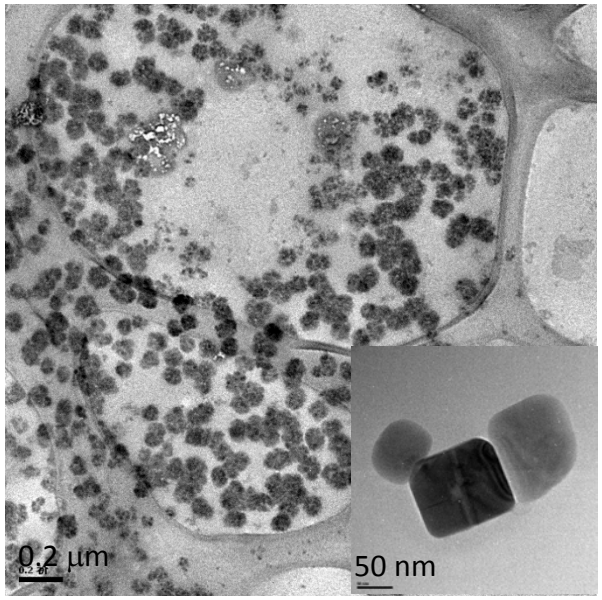
Liao *et al.*, *J. Electrochem. Soc.* 157 (2010), 19.
Kobayashi et al., *J. Am. Chem. Soc.* 131 (2009), A355.

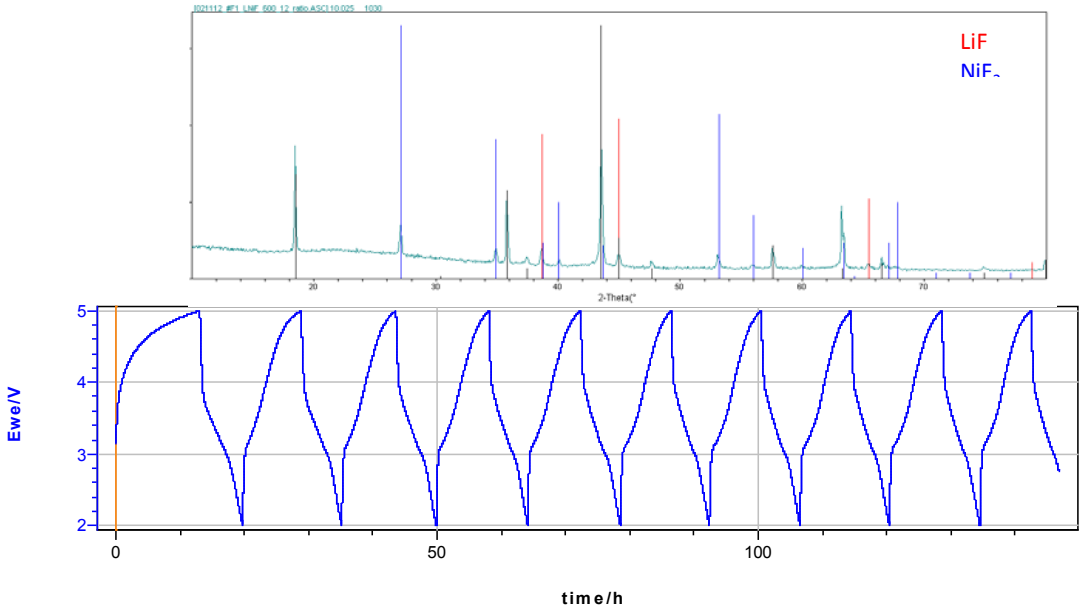
- Goal: search for new phases with 200+ mAh/g capacities ≡ 1+ e^-/total transition metal (TM) reversibly cycled.
- Needs to rely on high TM oxidation states ⇒ stabilization using F^-.
- Li-M-F: low electronic conductivity ⇒ oxyfluorides as synergistic phases. Oxyfluorides with semiconducting properties are known.

Technical accomplishments:

Exploration of new Li-M-O-F initiated in FY12

- Goal: explore Li-M-O-F space (M=Fe, Mn, Cu) in search for completely new phases with substantial amounts of F (>20% total anionic content). Synergy with Persson/Ceder (Materials Prediction).
- Synthetic strategies:
  - Classical solid state: High T treatment of mixtures of LiF/MF_x, Li_2O/MO_x, inert atmosphere.
  - Low temperature routes (<400°C):
    - Precipitation/thermolysis of precursors in high boiling point solvents.
    - Mild fluorination: Mix pre-formed Li-M-O with PVDF, heat to induce F insertion.





Collaboration and Coordination with Other Institutions

- Within BATT:
  - Members of the NiMn Spinel Focus Group.
  - Dr. V. Battaglia, V. Srinivasan (LBNL): understanding of composite electrode function.
  - Dr. R. Kostecki (LBNL): understanding surface reactivity in cathode materials.
  - Prof. C.P. Grey (SUNY-SB): MAS-NMR of electrode materials.
  - Dr. K. Persson (LBNL), Prof. G. Ceder (MIT): Discovery of new electrode materials.
  - Prof. M. S. Whittingham (SUNY-Binghamton): magnetic properties of materials.

- Outside BATT:
  - Dr. M. Casas-Cabanas (CIC Energigune, Spain): neutron diffraction of electrode materials.
  - Dr. C. Delacourt (LRCS, France): understanding of composite electrode function.
  - Dr. E. Chan (LBNL): synthesis of materials with controlled nanostructures.

Future Work

- Shift attention from bulk effects to electrode surface-electrolyte in $LiNi_{1/2}Mn_{3/2}O_4$:
  - Establish robust understanding of side reactions and their possible acid-base (electrode-electrolyte) origin.
  - Use X-ray spectroscopy to understand differences between materials with different modifications, e.g. ion substitution, coatings.
  - Develop new X-ray-based tools that increased selectivity, sensitivity and specificity.
- Continue exploration of Li-M-O-F chemical spaces:
  - In collaboration with computational teams in BATT.
  - Complete the design of synthetic methods: protocols of fluorination reactions and colloidal synthesis to produce large amounts of nanoscale Li-M-F.
  - Exploration of Li-Mn/Fe/Ni-O-F using classical solid state reactions.
- Develop a better understanding of phase transformations at the electrode level, with the goal of locating SOC inhomogeneities.

Summary

- Continued to uncover and describe the rich crystal-chemistry of $LiNi_{0.5}Mn_{1.5}O_4$:
  - Annealing was used as means to control crystal-chemistry while "freezing" microstructure.
- Strong correlation between rate capability (transport) and disorder. Weak correlation with Mn^{3+}, although small amounts may still be necessary.
- Crystal chemistry can have an impact through the phase transformations that occur during electrode operation:
  - Excellent performance of $LiNi_{0.5}Mn_{1.5}O_4$ with increasing disorder is driven by extended solid solution region.
  - Evidence of possible chemical gradients in thick NMC electrodes suggested by in situ XRD.
- Decoupling between surface and bulk oxidations states in high voltage electrodes suggests electrolyte decomposition is driven by acidic M-O surface species:
  - Increase ionicity of the bond by using new Li-M-O-F phases.