Positive and negative electrodes: new and optimized materials

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ES070

Overview

Timeline

- PI joined BATT and LBNL in FY09
- Project start Sep '09
- Project end Aug '11
- 40% complete

Budget

- Funding FY09: $420k
- Funding FY10: $440k

Barriers

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

Partners

- Persson, Doeff, Richardson, Chen, Kostecki, Battaglia (LBNL), Grey (SUNY-SB)
- D. Milliron (MF, LBNL), A. Mehta, J. A. Hayter (SSRL, Stanford), M. Casas-Cabanas (Caen, France), M.R. Palacin (ICMAB, Spain)
- Project lead: John Newman

Relevance - Objectives

- To achieve cycle life and energy density targets using high voltage (>4.5 V) spinel electrode materials.
  - barriers: *energy density, cycle life, safety*

- To assess the viability of materials that react through conversion reactions as high capacity electrodes.
  - barriers: *energy density, cycle life*

- To investigate new phases with more than one electron per transition metal available for electrochemical reactivity.
  - barriers: *energy density*

Milestones

May 09	Set up research lab and hire a postdoctoral researcher.
Apr. 09	Evaluate the stability of the spinel framework upon copper extrusion and re-injection in $CuMn_2O_4$.
Sep. 09	Characterize $LiNi_{1/2}Mn_{3/2}O_4$ prepared using different synthesis methods. Evaluate the energy/power density and cycle life characteristics.
Mar. 10	Report the cycling performance of $LiNi_{1/2}Mn_{3/2}O_4$ made solvothermally .
Jul. 10	Choose promising Cu-M-O (M=transition metal, Al, P, Si) phases and test them.
Sep. 10	Report the characterization of cycled NiO electrodes by NMR, XAS and TEM.
Sep. 10	Synthesize Sn-based nanoalloys with controlled microstructure and report their performance as electrodes.

Approach/Strategy

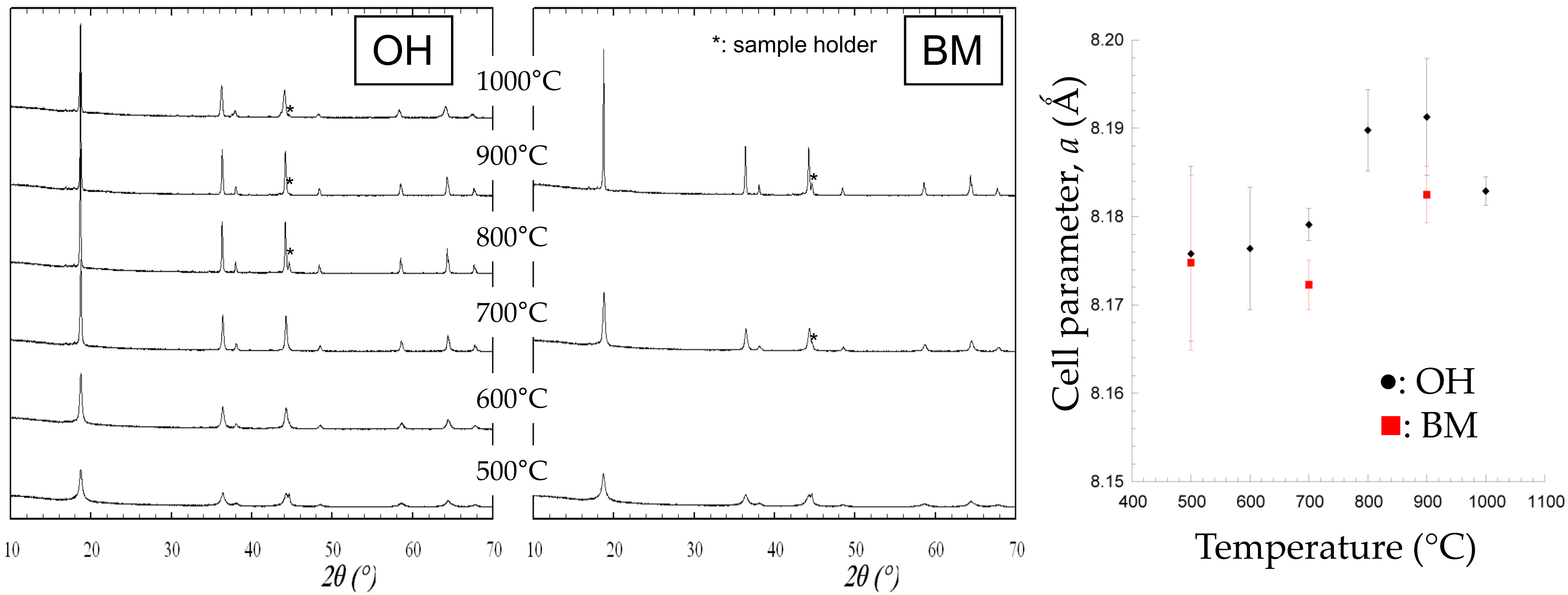
- Understand the correlation between crystal structure, nanostructure, composition and electrochemical performance in $LiNi_{1/2}Mn_{3/2}O_4$.
  - Synthesize samples with controlled particle sizes and shapes.
  - Study changes in structural order with synthesis conditions.
  - Evaluate performance at moderate and high rates.

- Get a complete picture of the interactions that govern activity of materials that react through conversion reactions.
  - Combine spectroscopic, imaging and electroanalytical techniques.
  - Assess the origin of the large voltage hysteresis observed.

- Investigation of new Cu-M-O phases that can react via a copper extrusion mechanism.
  - Study of the stability of the framework upon Cu extrusion/re-insertion. M-O framework may remain stable (no conversion), leading to enhanced life.
  - Evaluation of the effect of the framework on the voltage at which extrusion takes place.

Technical accomplishments:

$LiNi_{1/2}Mn_{3/2}O_4$, synthesis, XRD

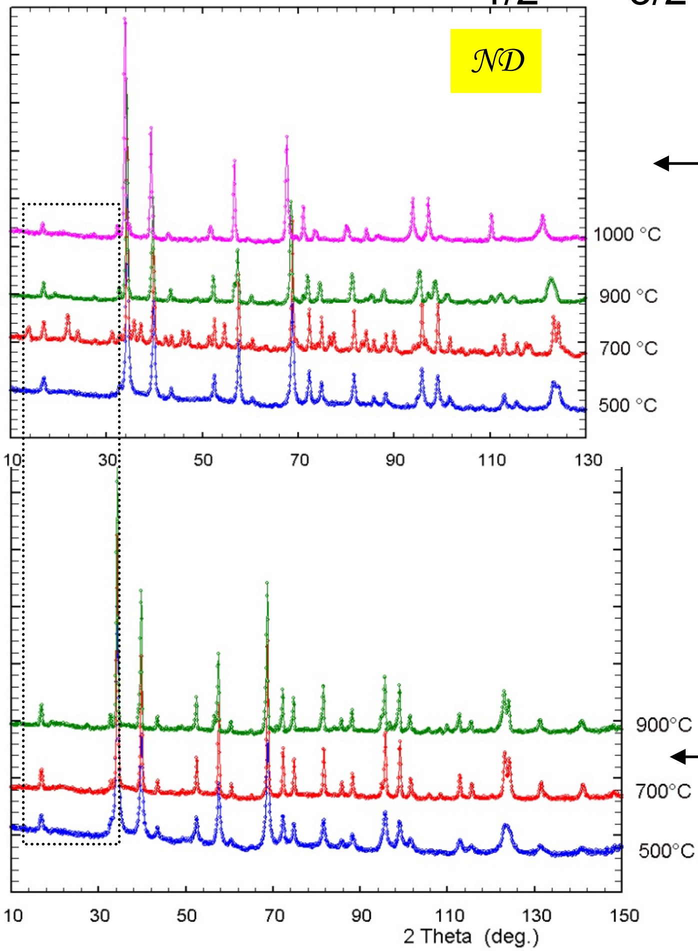


• Samples synthesized from hydroxide precursors: direct calcination for 12 h (OH, black), milling+calcination for 1-2 h (BM, red).

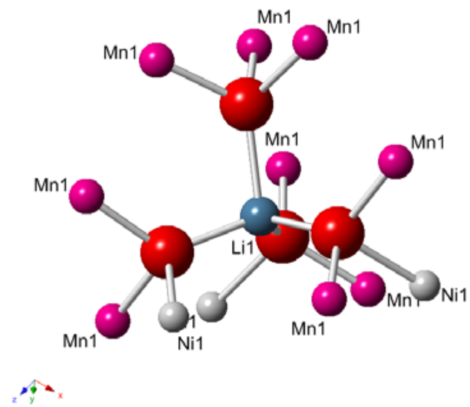
• Cell parameter depends on **synthesis temperature**.

Technical accomplishments:

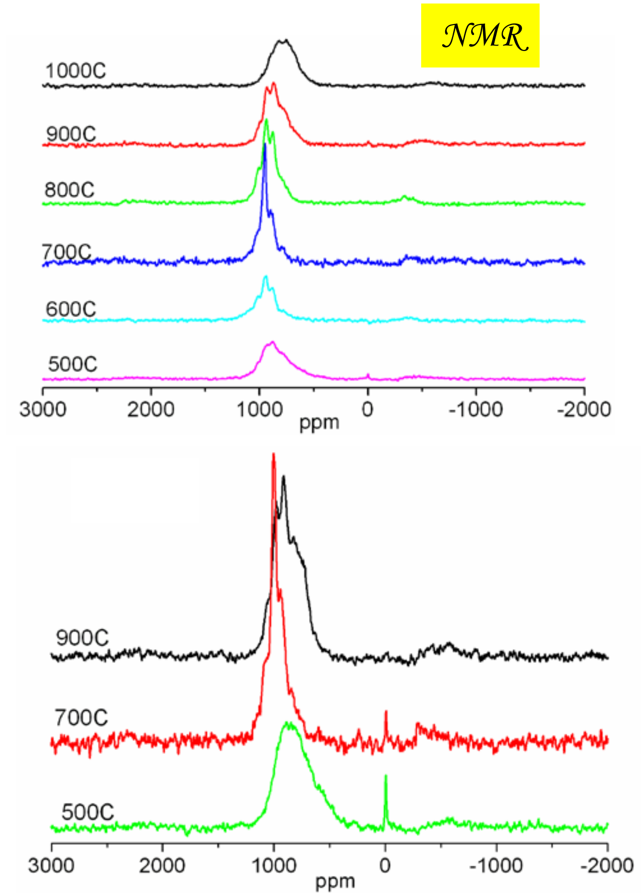
$LiNi_{1/2}Mn_{3/2}O_4$, order-disorder transition



OH



BM



*: diamagnetic impurity

- Neutron diffraction (ND): peaks between 10-30° denote <u>Ni-Mn ordering</u>.
- Nuclear Magnetic Resonance (NMR): presence of multiple, broad peaks denotes <u>disorder</u>.
- **Disorder-order-disorder transition upon heating**. Different degrees of ordering exist.

Technical accomplishments:

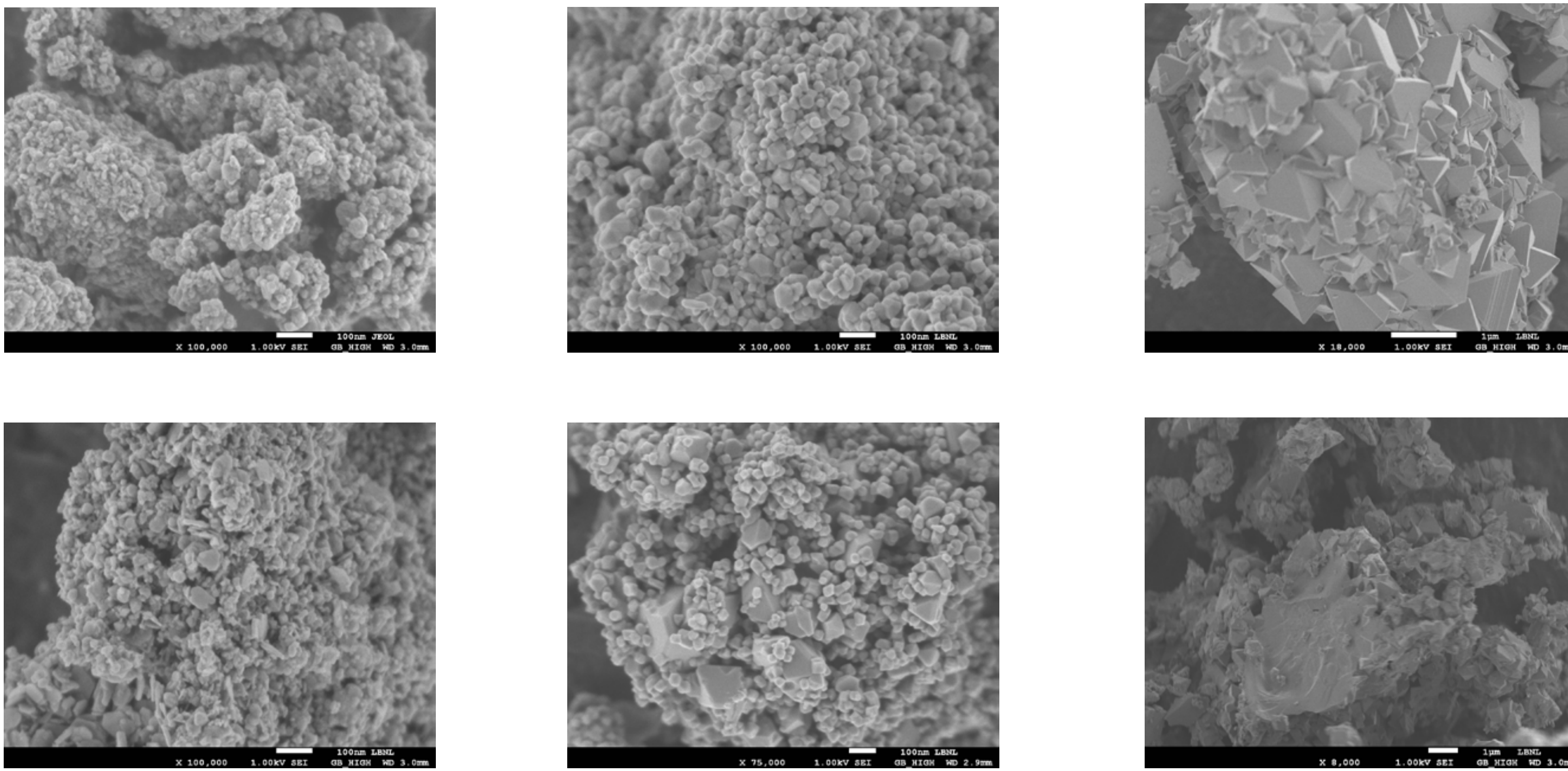
$LiNi_{1/2}Mn_{3/2}O_4$, microstructure

SEM

500 C — 700 C — 900 C

BM

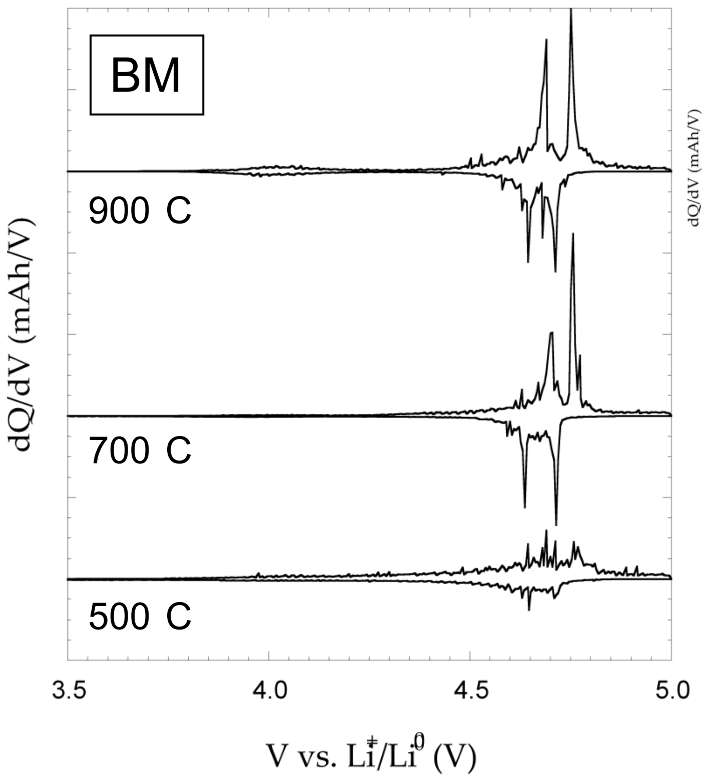
OH

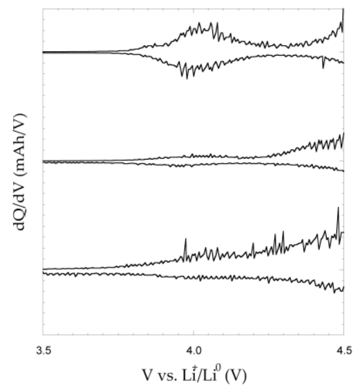


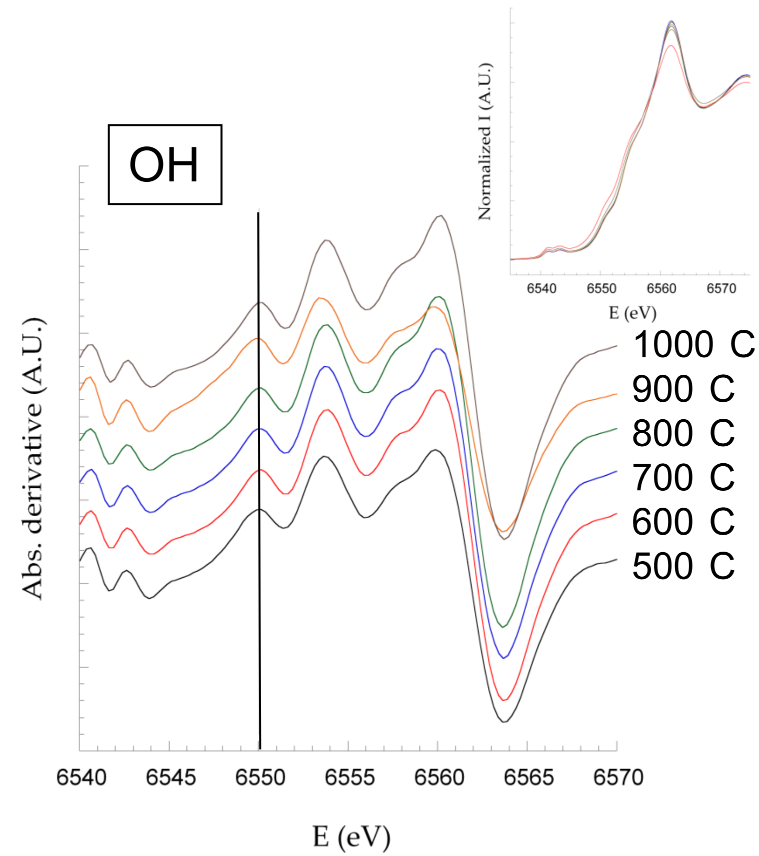
- Notable <u>increase in particle size</u> occurs **above 700°C**.
- Particle <u>size, shape</u> distribution is **more homogeneous for BM** (shorter calcination t, no pellet is made).

Technical accomplishments:

$LiNi_{1/2}Mn_{3/2}O_4$, Mn^{3+} content





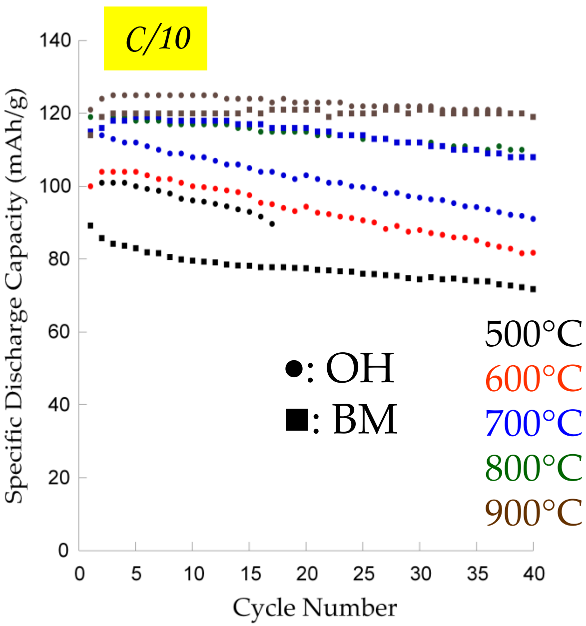


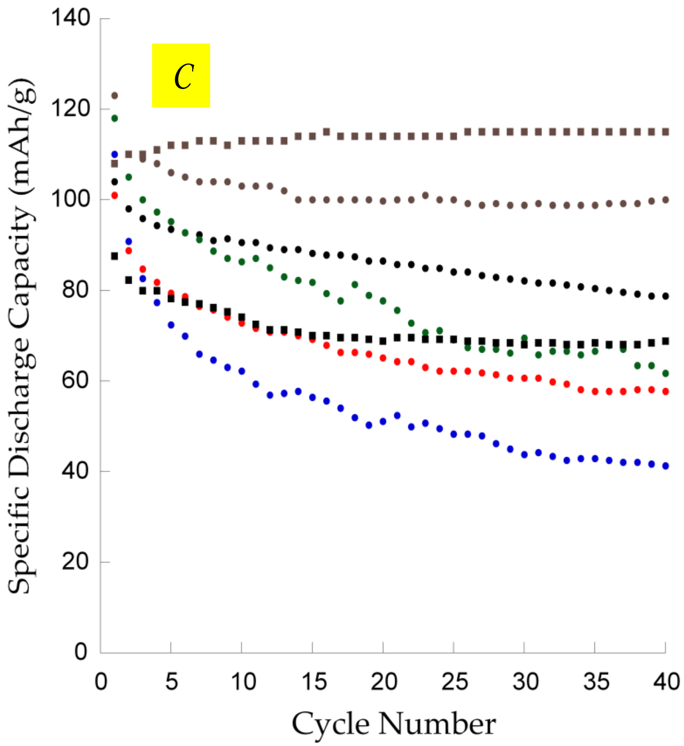
- Capacity at 4 V suggests presence of <u>different amounts of Mn^{3+}</u>, depending on synthesis temperature.
- XANES data indicates differences in Mn^{3+} are **very small**.

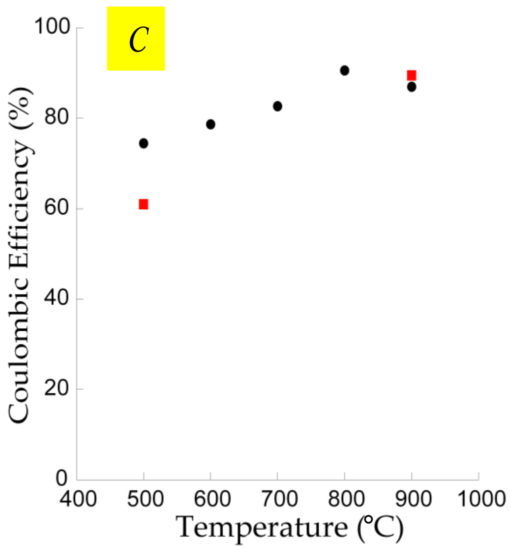
[Results are equivalent between BM and OH]

Technical accomplishments:

$LiNi_{1/2}Mn_{3/2}O_4$, electrode properties



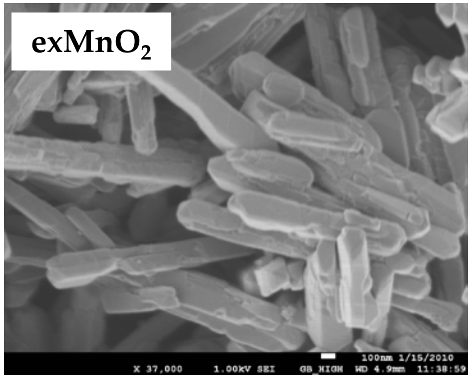


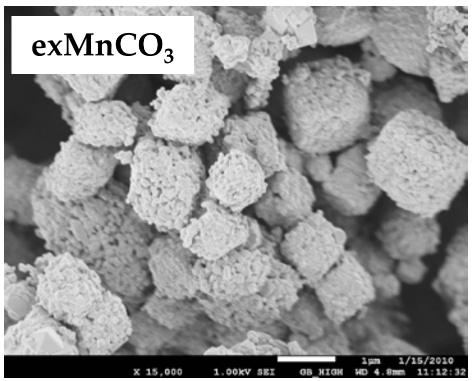


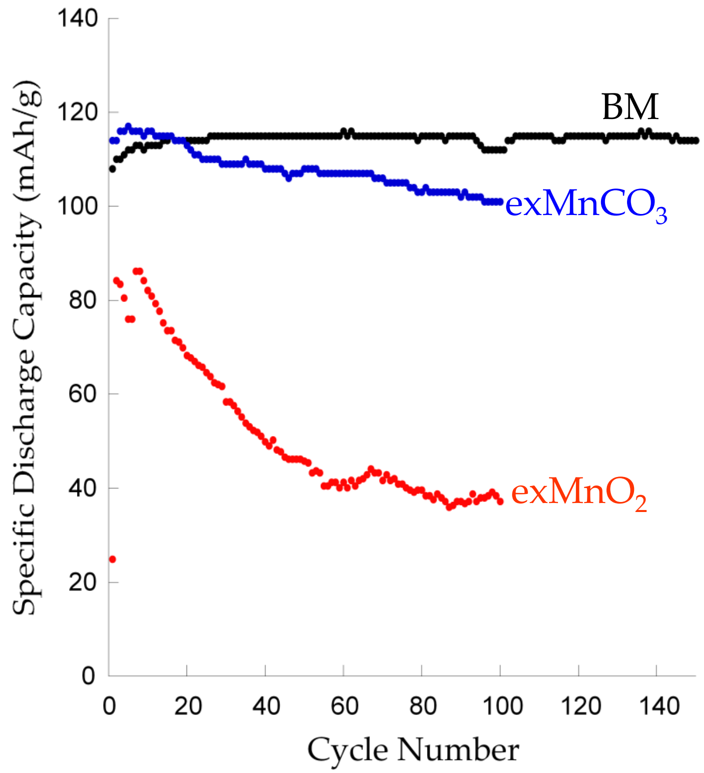
- Performance at moderate and high rates improves with synthesis temperature. Particle size seems to be **more critical** than order-disorder or capacity at 4 V (Mn^{3+} content).
- 1st cycle coulombic efficiency improves with synthesis temperature ⇒ bigger particle sizes **are better** to avoid side reactions.
- **No need to go nano** to get high rate performance for $LiNi_{1/2}Mn_{3/2}O_4$.
- BM, 900°C: 120 mAh/g (C/10), 115 mAh/g (C) after 40 cycles. **Best performance**.

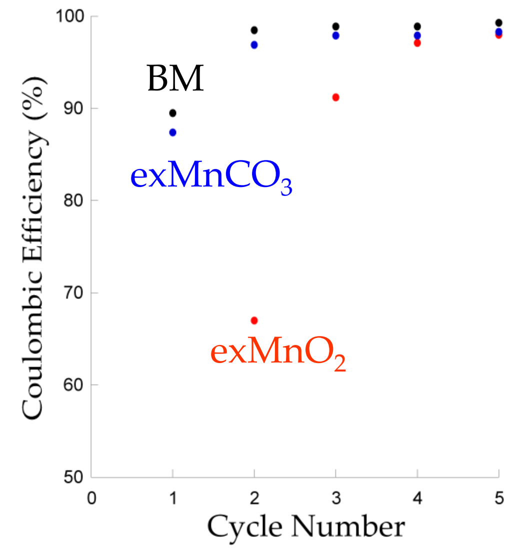
Technical accomplishments:

$LiNi_{1/2}Mn_{3/2}O_4$, influence of particle morphology







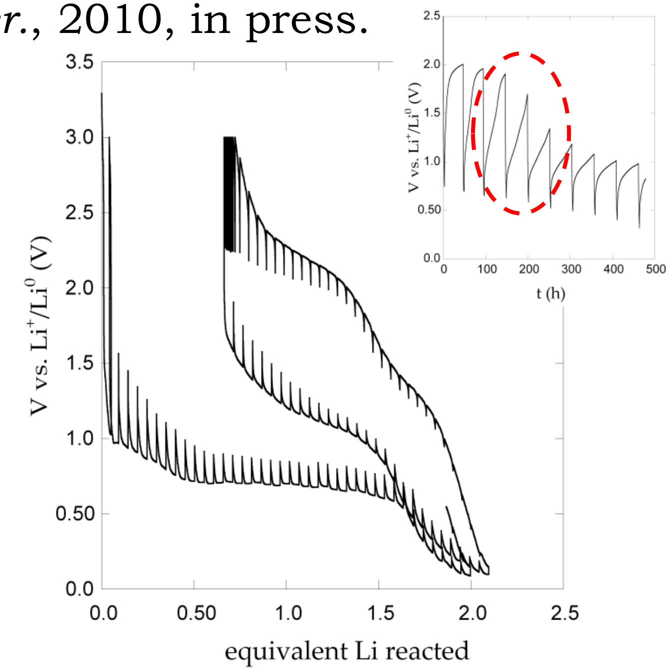


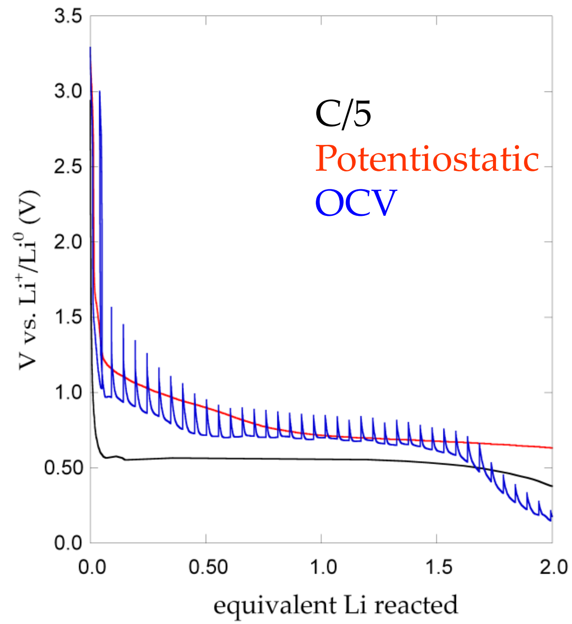
- exMnO_2/ex$MnCO_3$: made from solvothermal MnO_2/$MnCO_3$ at 750°C.
- BM, 900°C: **Best performance**, 114 mAh/g after 150 cycles at C rate.
- **Nanostructuring does not appear to produce an advantage** even at high rates.
- New collaboration with V. Battaglia (BATT): advanced battery testing of *BM, 900°C*.

Technical accomplishments:

Mechanism of conversion reactions, NiO: case example

- Conversion reactions result in very high capacities.
- Main obstacle is low energy efficiency due to voltage hysteresis.
  - State-of-the-art and challenges recently reviewed (w/ M.R. Palacin, ICMAB): *Adv. Mater.*, 2010, in press.



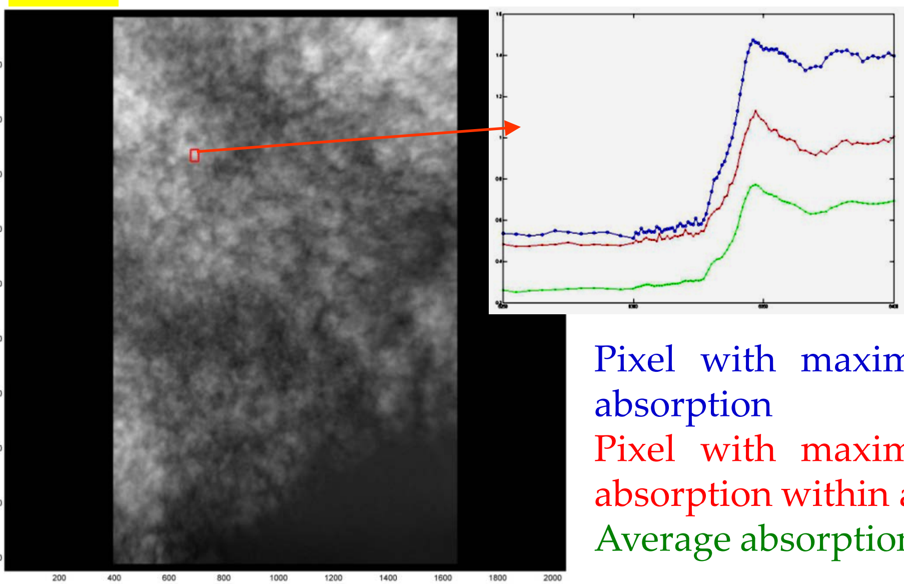


- NiO taken as case example.
- Hyteresis changes with cycle number.
- Different "equilibrium" potential values obtained with potentiostatic and OCV experiments. Side processes during relaxation (circled area).

Technical accomplishments:

Mechanism of conversion reactions, NiO: case example

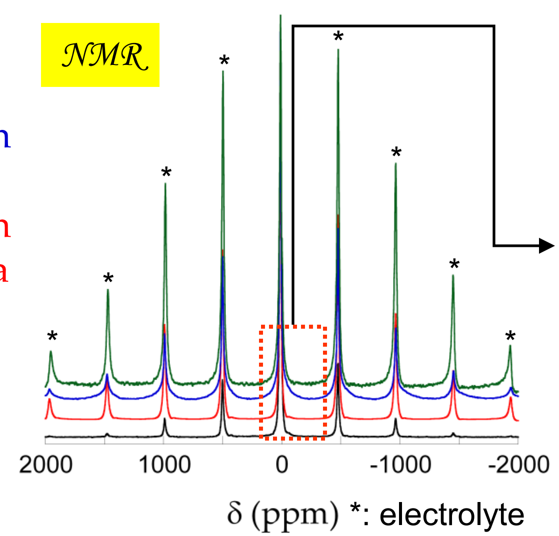
TXM

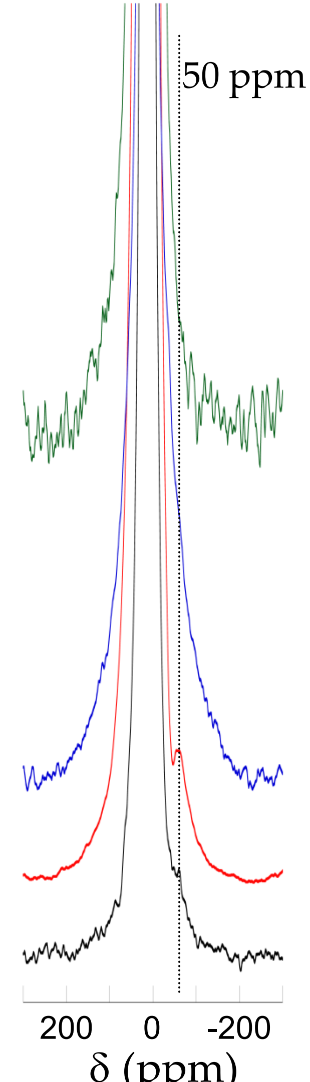


Pixel with maximum absorption
Pixel with maximum absorption within area
Average absorption

<u>Discharge</u>:
0.1 equivalent Li
1 equivalent Li
DoD 0 V
<u>Charge:</u>
SoC 2 V

NMR

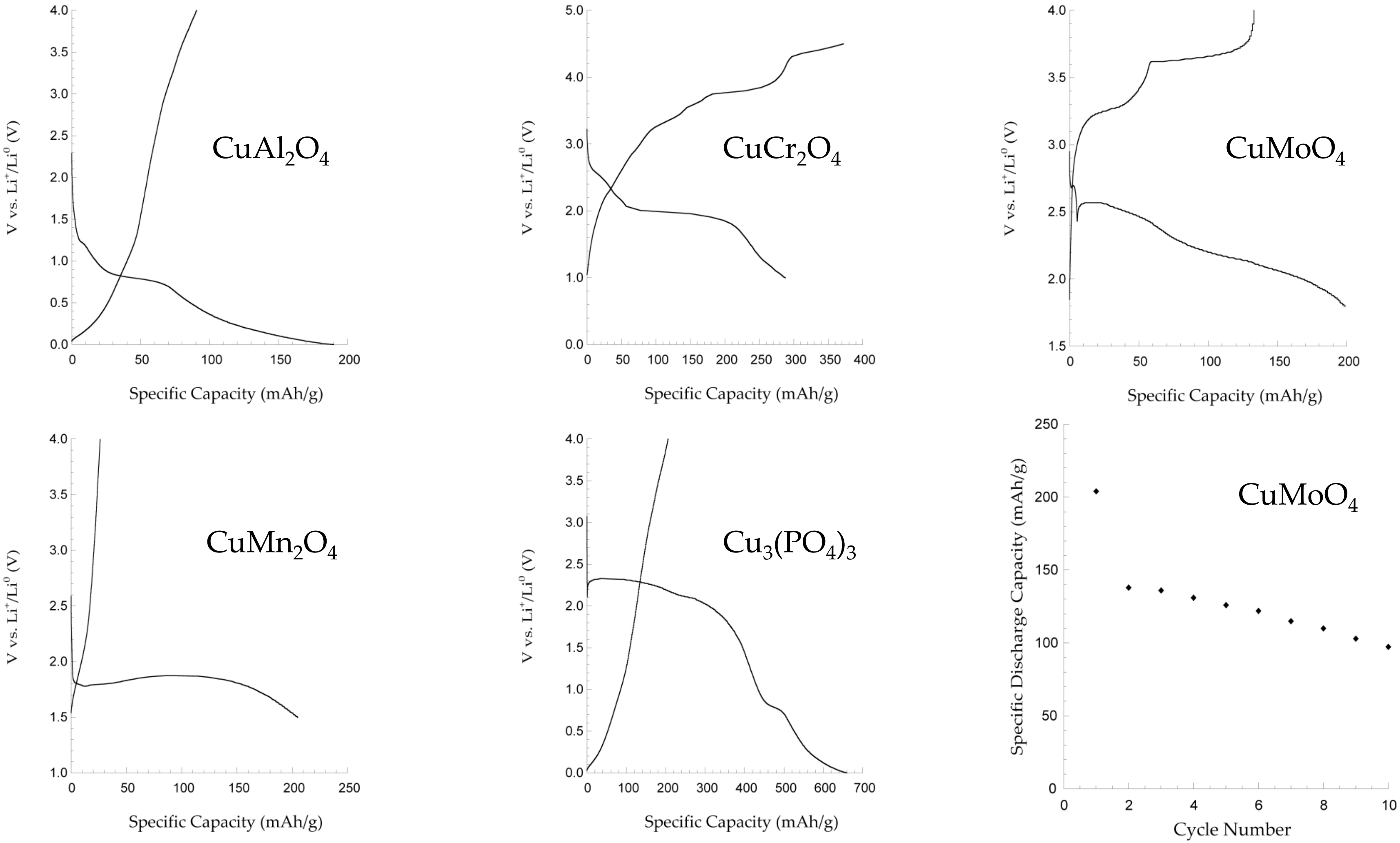




- TXM of electrodes: **chemical speciation at ~30 nm** resolution. <u>Project started</u> with J.A. Hayter (SSRL) to identify (un)converted areas.
- NMR at different Li contents (C.P. Grey, SUNY-SB):
    - ~0 ppm: electrolyte and **Li_2O**.
    - ~50 ppm: <u>unexpected</u>, **Li-O-Ni contacts** (not only Li_2O+Ni)?

Technical accomplishments:

Electrochemical testing of Cu-M-O phases



- Cu extrusion at different V. Only reversible capacity for $CuCr_2O_4$ and $CuMoO_4$.
- $CuMoO_4$: high voltage, but large hysteresis + poor retention.

Collaboration and Coordination with Other Institutions

- Within BATT:
  - Dr. K. Persson (LBNL): atomistic modeling as driver for identifying novel phases that react through Cu extrusion.
  - Dr. R. Kostecki (LBNL): understanding surface reactivity in cathode materials.
  - Dr. V. Battaglia (LBNL): advanced electrode testing of spinel electrodes.
  - Prof. C.P. Grey (SUNY-SB): MAS-NMR of electrode materials.

- Outside BATT:
  - Dr. M. Casas-Cabanas (ENSICaen, France): neutron diffraction of electrode materials.
  - Dr. M.R. Palacin (ICMAB): electroanalytical study of conversion reactions.
  - Drs. A. Mehta, J.A. Hayter (SSRL): XAS and TXM of electrode materials.

Future Work

- High voltage spinel phases:
  - Transfer *BM, 900 C* to Battaglia group for advanced battery testing (e.g., using alternative electrolytes).
  - Control Mn^{3+} contents, ordering in *BM* and solvothermal (large particle size) samples and evaluate effect.
  - Study surface side reactions (e.g., using soft X-ray spectroscopy); collaboration with Kostecki group starting to evaluate effect of coating and carbon additives. <u>Need to minimize coulombic inefficiencies</u>.
- Conversion reactions:
  - Evaluate the effect of temperature (50-150 C) on hysteresis (is it kinetic or thermodynamic?).
  - Continue study of mechanism of reaction using NMR, TEM, TXM and XAS. Relate mechanism to hysteresis (milestone set for Sep. '10).
- Cu-containing phases:
  - Study what controls the reversibility of the reaction by assessing changes upon Cu extrusion.
  - Continue screening for phases that may show high stable capacities (go/no-go decision will be made at the end of the fiscal year).

Summary

- Mn^{3+} content and Ni-Mn ordering in $LiNi_{1/2}Mn_{3/2}O_4$ are highly dependent of method and temperature of synthesis.
  - MAS-NMR: very suitable tool to detect degrees of ordering.
- Comparison of different $LiNi_{1/2}Mn_{3/2}O_4$ samples indicates particle size is a critical factor on performance. No need to use nanoparticles to get good life at high rates (C).
- Analysis of the origins of hysteresis in conversion reactions has started.
  - Preliminary results suggest the mechanism is not as simple as previously thought.
  - Advanced imaging + spectroscopic techniques to assist in the study are in process of being developed.
- Different Cu-M-O have been tested as electrodes.
  - Only $CuMoO_4$ and $CuCr_2O_4$ show reversible capacities. Large hysteresis and poor cycle life observed.