Investigation of critical parameters in Li-ion battery electrodes

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ES70_Cabana

Overview

Timeline

- PI joined BATT and LBNL in FY09
- Project start Sep ‘09
- Project end Aug ‘11
- 80% complete

Budget

- Funding FY09: $420k
- Funding FY10: $440k
- Funding FY11: $630k

Barriers

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

Partners

- Persson, Doeff, Richardson, Chen, Kostecki, Battaglia (LBNL), Grey (SUNY-SB), Whittingham (SUNY-B)
- A. Mehta, (SSRL, Stanford), M. Casas-Cabanas (Caen, France), M.R. Palacin (ICMAB, Spain), A. Dong (MF, LBNL), M.A. Marcus (ALS, LBNL)

Relevance - Objectives

- To achieve cycle life and energy density targets using high voltage (>4.5 V) electrode materials.
  - Synthesize materials with controlled crystal-chemistry and microstructure
  - Establish chemistry-structure-properties correlations that aid in the design of better materials.
  - Assess origins of in-cycle and cycling inefficiencies.
  - barriers: *energy density, cycle life, safety*

- To understand impact of materials and electrode design on performance.
  - Develop methods to couple electrode performance and transformations at multiple length scales.
  - barriers: *energy density, cycle life*

Milestones

Mar. 10	Report the cycling performance of $LiNi_{1/2}Mn_{3/2}O_4$ made solvothermally . **Completed**
Jul. 10	Choose promising Cu-M-O (M=transition metal, Al, P, Si) phases and test them. **Completed**
Sep. 10	Report the characterization of cycled NiO electrodes by NMR, XAS and TEM. **Completed**
Sep. 10	Synthesize Sn-based nanoalloys with controlled microstructure and report their performance as electrodes. **Postponed to FY11**
Mar. 11	Report the thermal analysis of cycled $LiNi_{1/2}Mn_{3/2}O_4$ electrodes and the results of annealing using different treatments. **Ongoing**
Sep. 11	Report the analysis of Sn nanoparticles at different stages of cycling. **On schedule**
Sep. 11	Report the electrochemical response of NiO when cycled at high temperatures. **On schedule**

Approach/Strategy

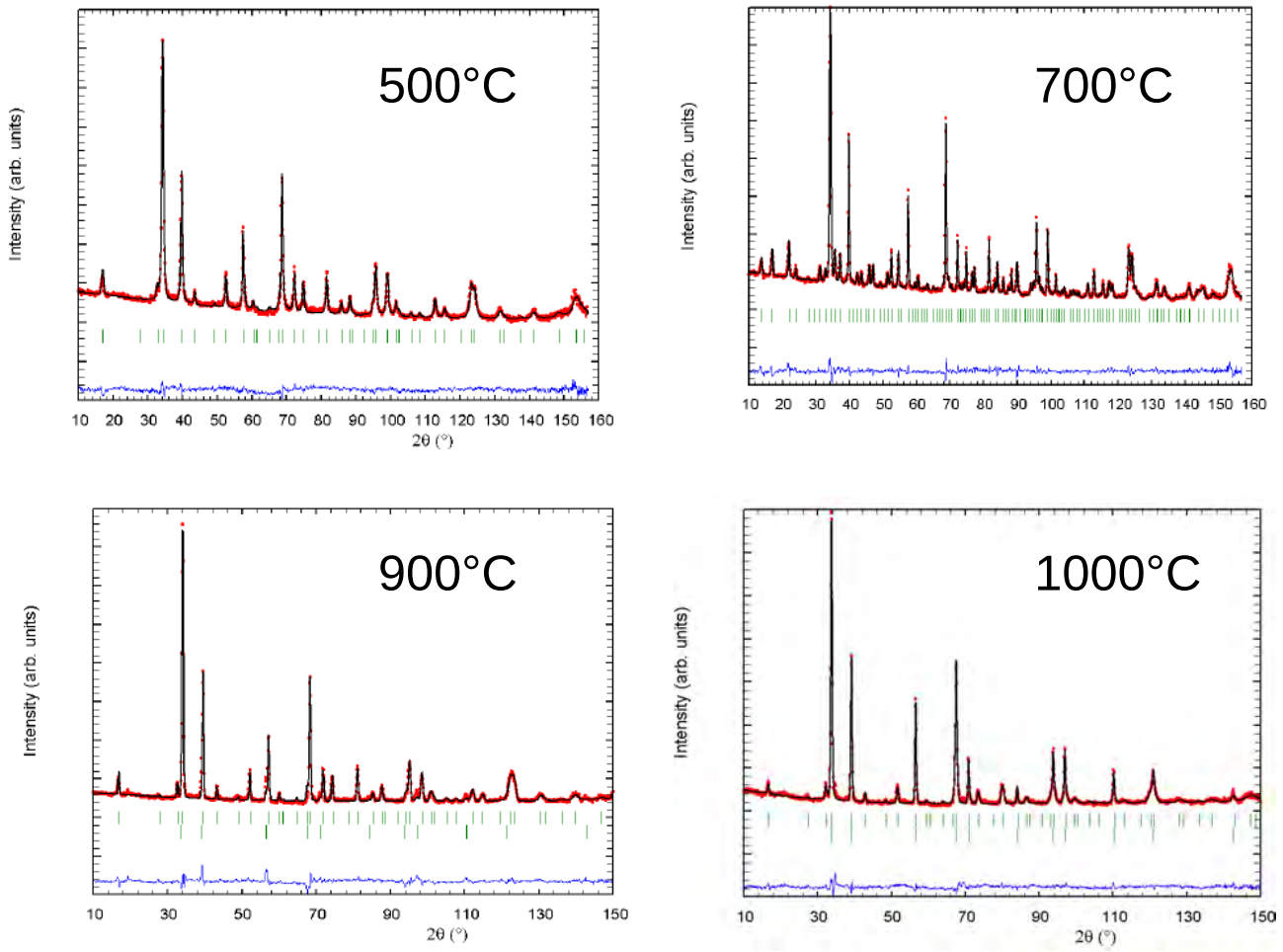
- Understand the correlation between crystal structure, microstructure, composition and electrochemical performance in $LiNi_{1/2}Mn_{3/2}O_4$.
  - Synthesize samples with controlled microstructure, composition, ordering.
  - Study changes in structural order and composition with synthesis conditions using a variety of characterization techniques.
  - Evaluate performance at moderate and high rates. Ultimate goal: 100% utilization at 2C rate, 85% 1st cycle efficiency and 99.99% steady-state efficiency at C/2 rate.

- Analyze inefficiencies of high voltage $LiNi_{1/2}Mn_{3/2}O_4$.
  - Study existence of irreversibility in the lithium intercalation reaction in high voltage materials and surface layer formation.
  - Understand the effect of surface modifications.

- Use synchrotron radiation to characterize electrode materials at multiple length scales.
  - Spectroscopy to analyze chemical changes at interfaces, surface and bulk of materials.
  - Combination of spectroscopy and imaging to evaluate inhomogeneities at nano as well as macro scale.

Technical accomplishments:

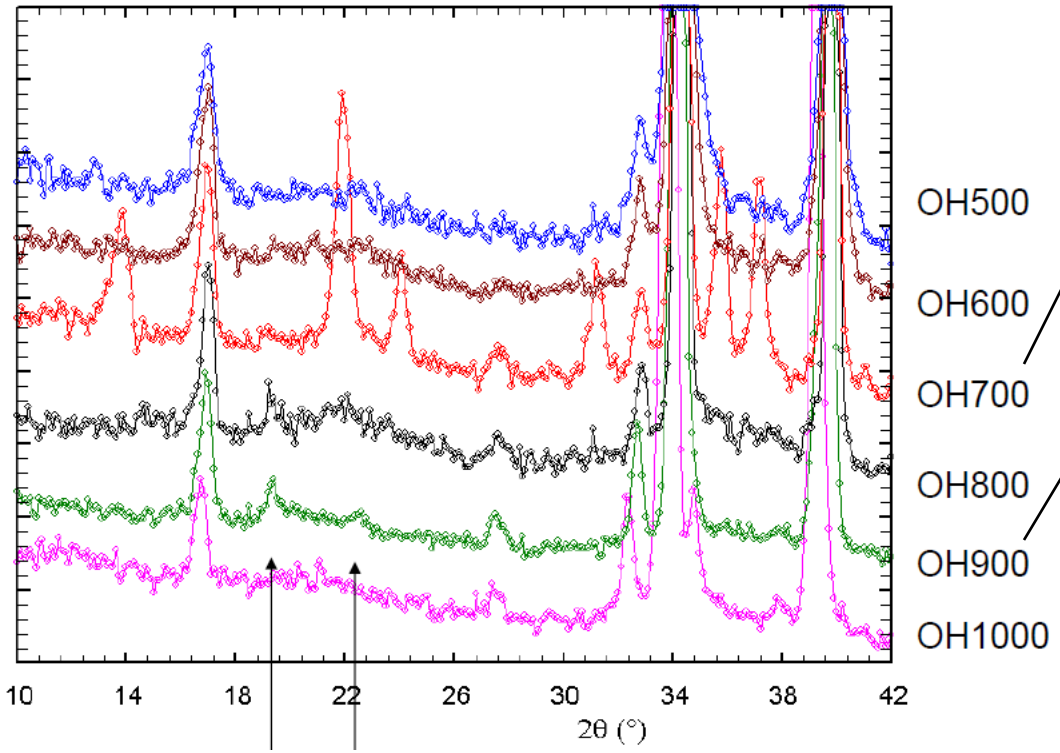
$LiNi_{1/2}Mn_{3/2}O_4$, Neutron Diffraction



- Rietveld-refined neutron diffraction data.
- Samples synthesized from hydroxide precursors at 500°C≤T≤1000°C for 12 h.

Technical accomplishments:

$LiNi_{1/2}Mn_{3/2}O_4$, Ni-Mn ordering

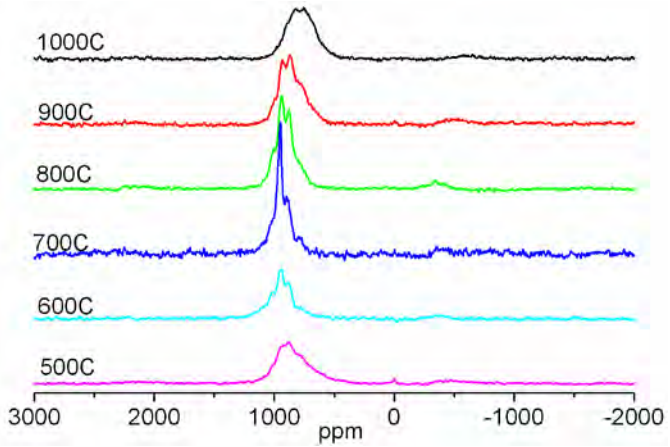


$LiMn_{1.53}Ni_{0.47}O_4 = Li[Mn_{1.42}Ni_{0.08}]_{12d}[Ni_{0.39}Mn_{0.11}]_{4b}O_4$

Name	x	y	z	B	occ.	Mult
O2	0.14710(34)	0.85841(26)	0.12579(32)	0.610(26)	1.000(0)	24
O1	0.38664(32)	0.38664(32)	0.38664(32)	0.236(49)	0.333(0)	8
Li	0.00603(136)	0.00603(136)	0.00603(136)	0.805(147)	0.333(0)	8
Mn1	0.12500(0)	0.38042(84)	0.86907(84)	0.532(83)	0.474(1)	12
Ni1	0.12500(0)	0.38042(84)	0.86907(84)	0.532(83)	0.026(1)	12
Ni2	0.62500(0)	0.62500(0)	0.62500(0)	0.568(72)	0.132(0)	4
Mn2	0.62500(0)	0.62500(0)	0.62500(0)	0.568(72)	0.035(0)	4

$LiMn_{1.55}Ni_{0.45}O_4$

Name	x	y	z	B	occ.	Mult
O1	0.26316(8)	0.26316(8)	0.26316(8)	0.837(24)	1.000(0)	32
Li	0.12500(0)	0.12500(0)	0.12500(0)	0.966(176)	0.250(0)	8
Mn	0.50000(0)	0.50000(0)	0.50000(0)	1.773(522)	0.388(1)	16
Ni	0.50000(0)	0.50000(0)	0.50000(0)	1.773(522)	0.112(1)	16

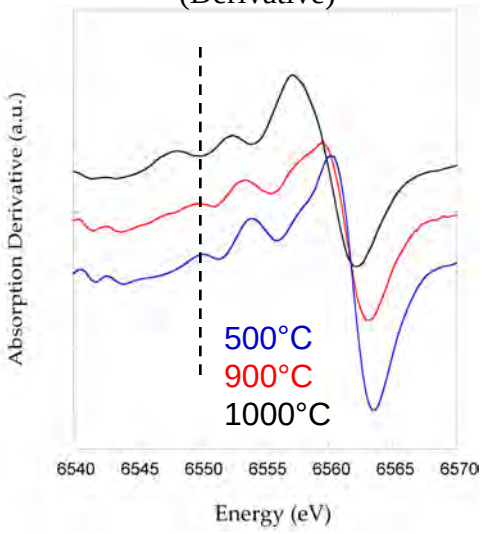


- Clear **Ni-Mn ordering transition at 700°C**. Diffuse scattering at 600°C and 800°C denotes partial ordering.
- Patterns at T ≠700°C were refined with disordered cell (Fd-3m). Pattern at T=700°C was refined with ordered supercell ($P4_332$): detected partial Ni-Mn exchange.
- Consistent with ordering schemes revealed by ^6Li MAS NMR.

Technical accomplishments:

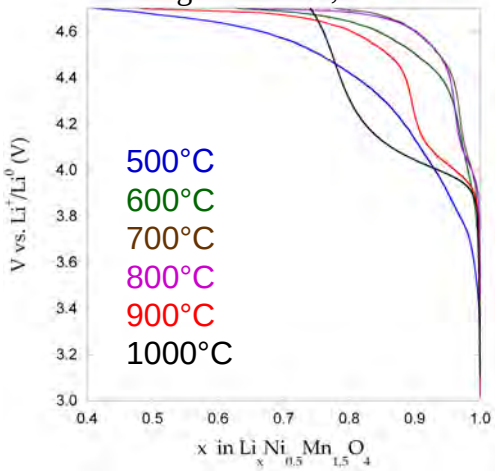
$LiNi_{1/2}Mn_{3/2}O_4$, Chemical composition

Mn K edge XANES
(Derivative)



Sample	Spinel		Rock salt	
	composition	Cell parameter	composition	Cell parameter
OH500	$LiMn_{1.56}Ni_{0.44}O_4$	a=8.1652(1)		
OH600	$LiMn_{1.55}Ni_{0.45}O_4$	a=8.1646(1)		
OH700	$LiMn_{1.53}Ni_{0.47}O_4$	a=8.16439(8) $P4_332$		
OH800	$LiMn_{1.55}Ni_{0.45}O_4$	a=8.1696(1)	$Li_{0.4}Mn_{0.4}Ni_{0.2}$	a=4.151(2)
OH900	$LiMn_{1.57}Ni_{0.43}O_4$	a=8.2006(8)	$Li_{0.4}Mn_{0.4}Ni_{0.2}$	a=4.142(2)
OH1000 *both phases strongly correlated	$LiMn_{1.67}Ni_{0.33}O_4$	a=8.2866(1)	$Li_{0.4}Mn_{0.36}Ni_{0.24}$	a=4.1473(2)

Charge in Li cell, C/10

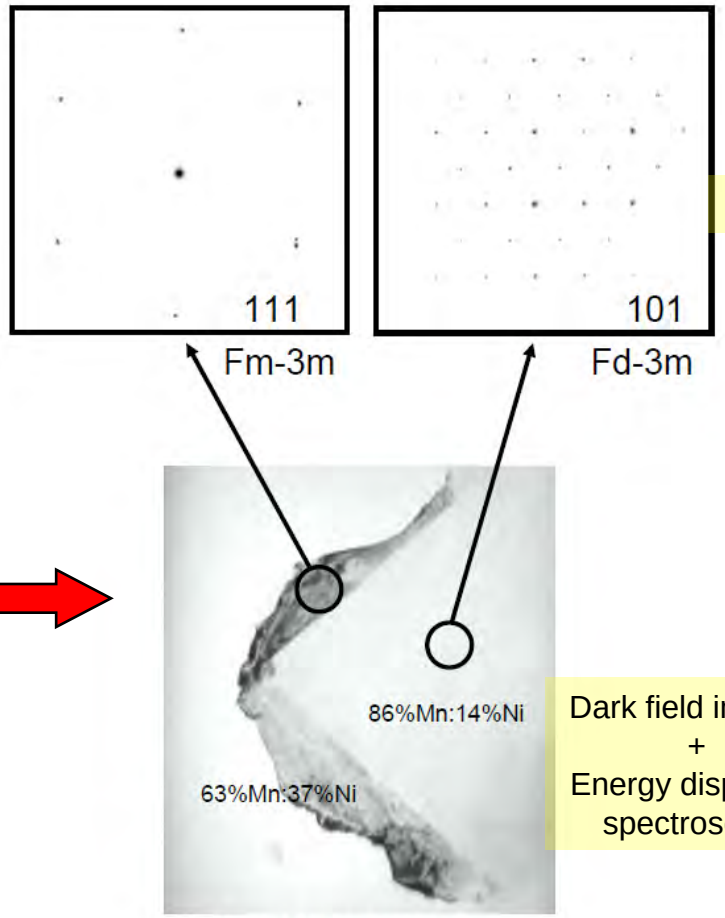


- Increase in Mn/Ni ratio upon heating ⇒ **increase in Mn^{3+}** + unit cell parameter.
- Increase in Mn^{3+} correlates with electrochemical activity around 4.0 V. Washed out profile for OH500C could be due to defective/poorly crystallized particles.
- **No evidence for O vacancies** found. Mn enriching is due to segregation of Ni in a rocksalt impurity.

Technical accomplishments:

$LiNi_{1/2}Mn_{3/2}O_4$, Chemical composition (II)

Sample	Spinel			Rock salt		
		Mn	Ni		Mn	Ni
OH800 89% spinel 11% rock salt	Mean	76	24	Mean	66	34
	Max	84	29	Max	67	35
	Min	71	16	Min	65	33
	$LiMn_{1.52}Ni_{0.48}O_4$			$Li_{0.4}Mn_{0.4}Ni_{0.2}$		
		Mn	Ni		Mn	Ni
OH900 78% spinel 22% rock salt	Mean	78	22	Mean	66	34
	Max	83	30	Max	69	37
	Min	70	17	Min	63	31
	$LiMn_{1.56}Ni_{0.44}O_4$			$Li_{0.4}Mn_{0.4}Ni_{0.2}$		
		Mn	Ni		Mn	Ni
OH1000 30% spinel 60% rock salt	Mean	85	15	Mean	63	37
	Max	87	28	Max	68	41
	Min	72	13	Min	59	32
	$LiMn_{1.7}Ni_{0.3}O_4$			$Li_{0.39}Mn_{0.38}Ni_{0.23}$		



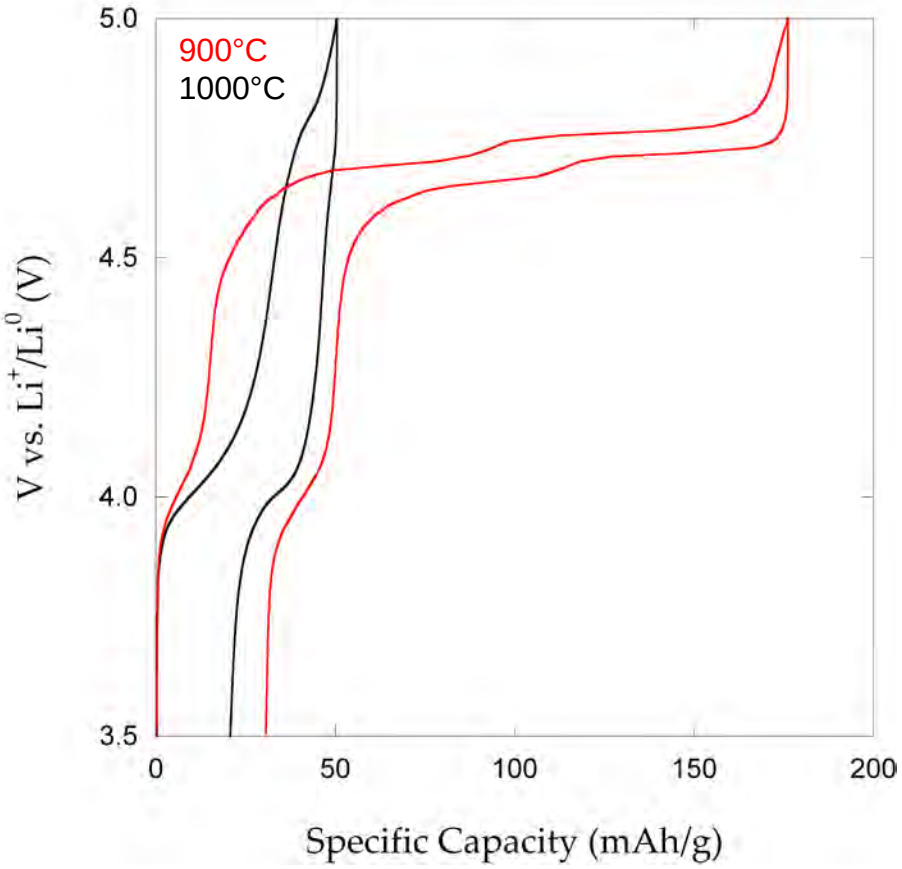
Electron diffraction

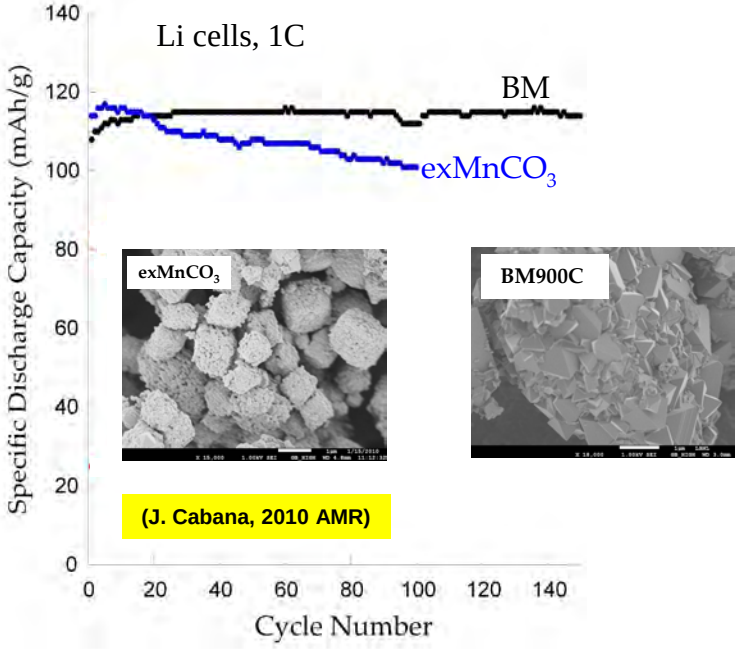
Dark field imaging
+
Energy dispersive spectroscopy

- Composition by EDS-TEM analysis from ~30 particles.
- Rocksalt-type impurity **can segregate to the surface of the particles**. <u>It contains Mn</u> (not $Li_{1-x}Ni_xO$), probably in +3 state (deduced from XANES).
- The process is exacerbated <u>as the calcination temperature is increased</u>.

Technical accomplishments:

$LiNi_{1/2}Mn_{3/2}O_4$, Impurity *vs.* performance



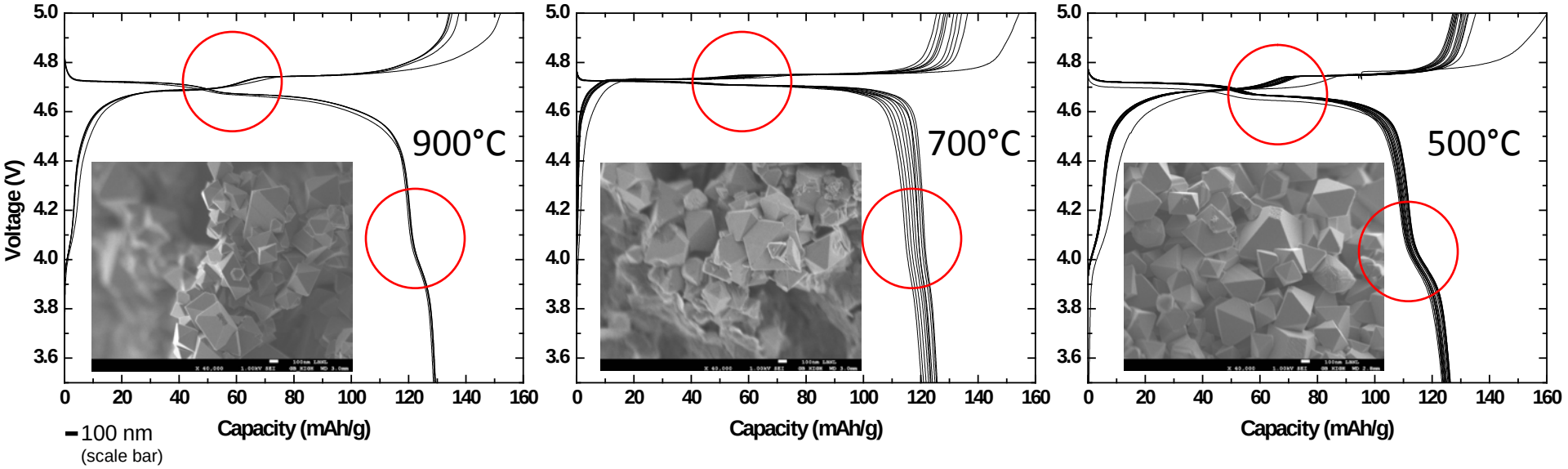


- **Li extraction is not possible from rocksalt impurity** ⇒ cripples performance, especially if it accumulates on the surface of spinel particles.
- Minimization is desirable. Important implications when annealing is used to increase particle size, which is needed for better performance.

Technical accomplishments:

$LiNi_{1/2}Mn_{3/2}O_4$, Effect of annealing

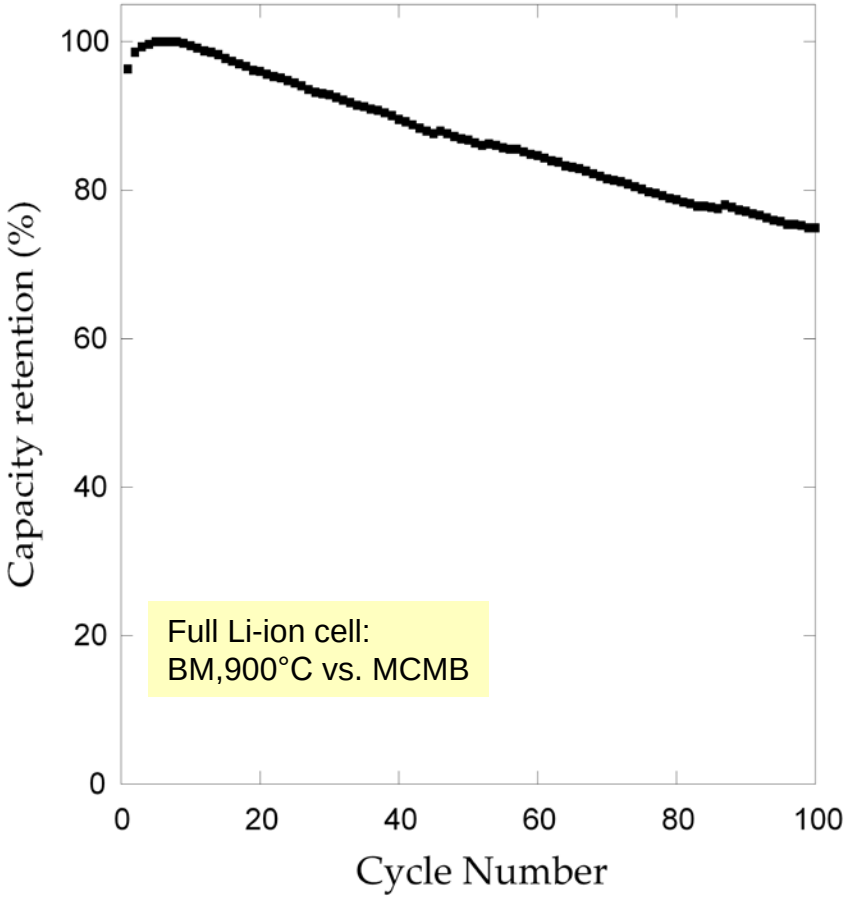
Li cells, C/10

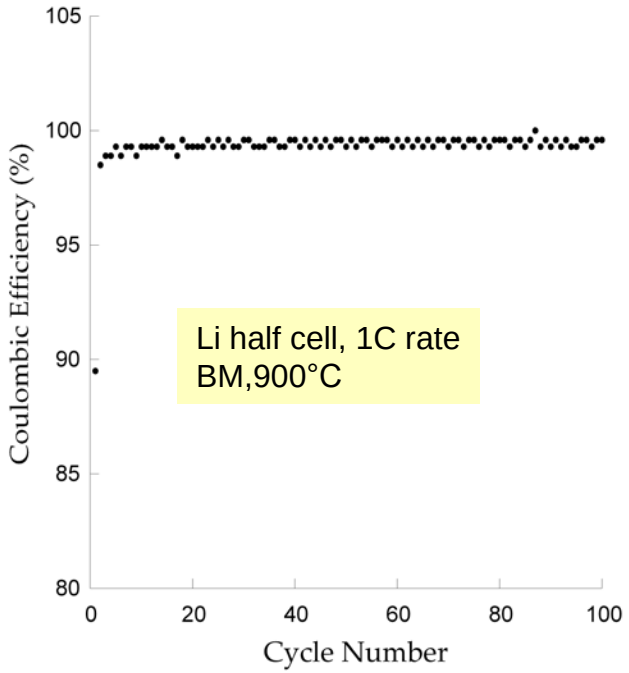


- Samples synthesized from hydroxide precursors: heated in air at 900°C, 1 h + 12 h at 500 or 700°C.
- No notable changes in particle size/morphology observed (consistent with absence of major coarsening below 800°C, *vid. J. Cabana – 2010 AMR*)
- Annealing at 700°C: mechanism of **ordered spinel**. Smaller Mn^{3+} signal.
- Annealing at 500°C: mechanism of **disordered spinel**. Similar Mn^{3+} signal.
- Decouple microstructure from crystal-chemistry: higher capacity/efficiencies at 900°C (under study).

Technical accomplishments:

$LiNi_{1/2}Mn_{3/2}O_4$, Full Li-ion cells

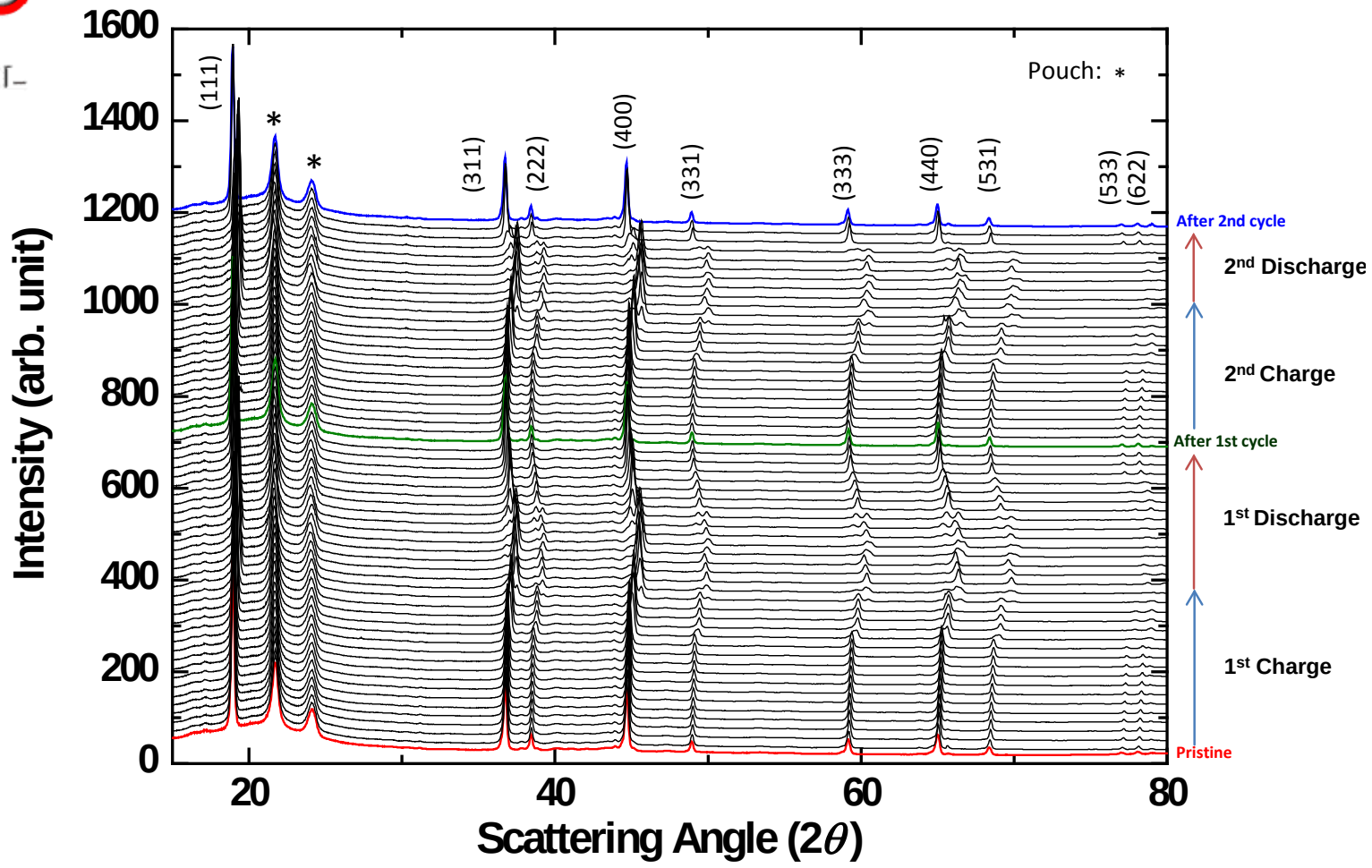




- **Unacceptable capacity loss** of 75% in Li-ion cell after 100 cycles.
- The low coulombic efficiencies observed (~99.5%) even upon extended cycling likely produce losses in the negative electrode that cripple the lifetime of the battery.
- Coulombic efficiency appears to be a **pressing issue**.

Technical accomplishments:

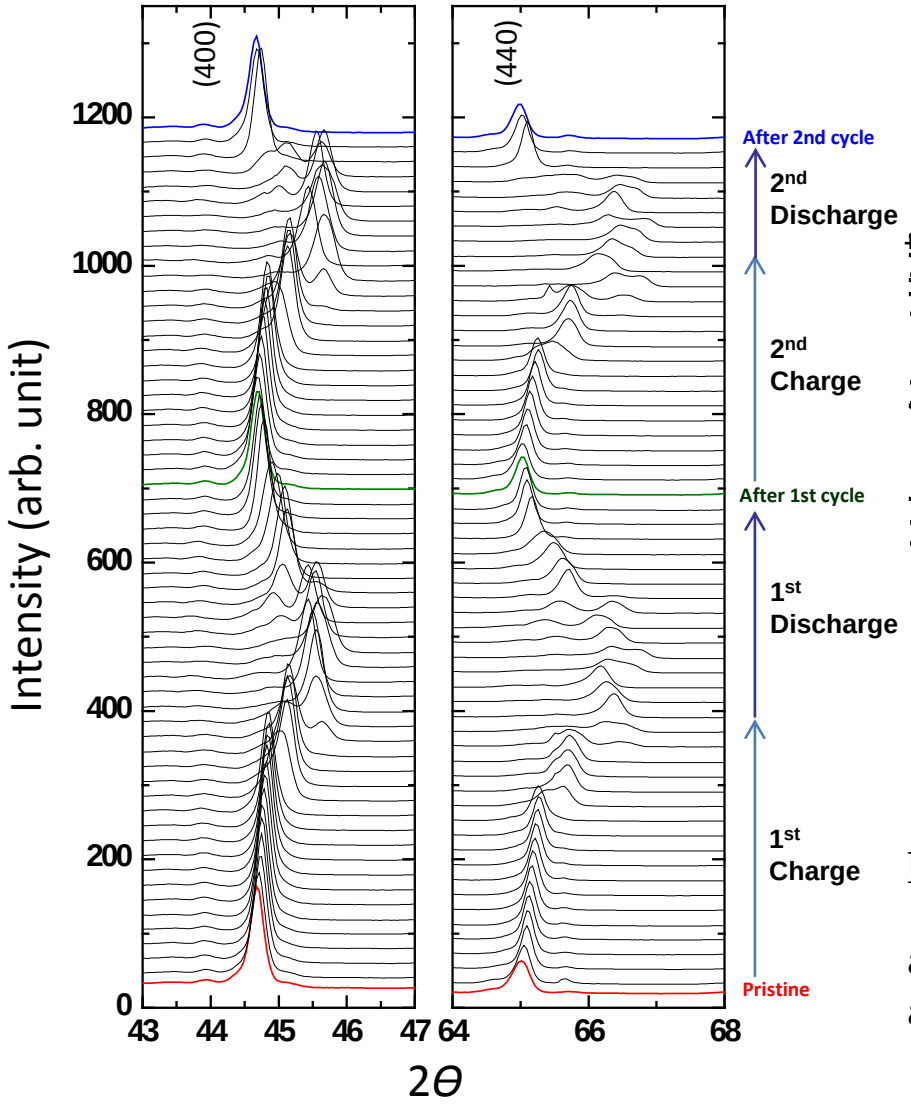
$LiNi_{1/2}Mn_{3/2}O_4$, Electrochemical reversibility

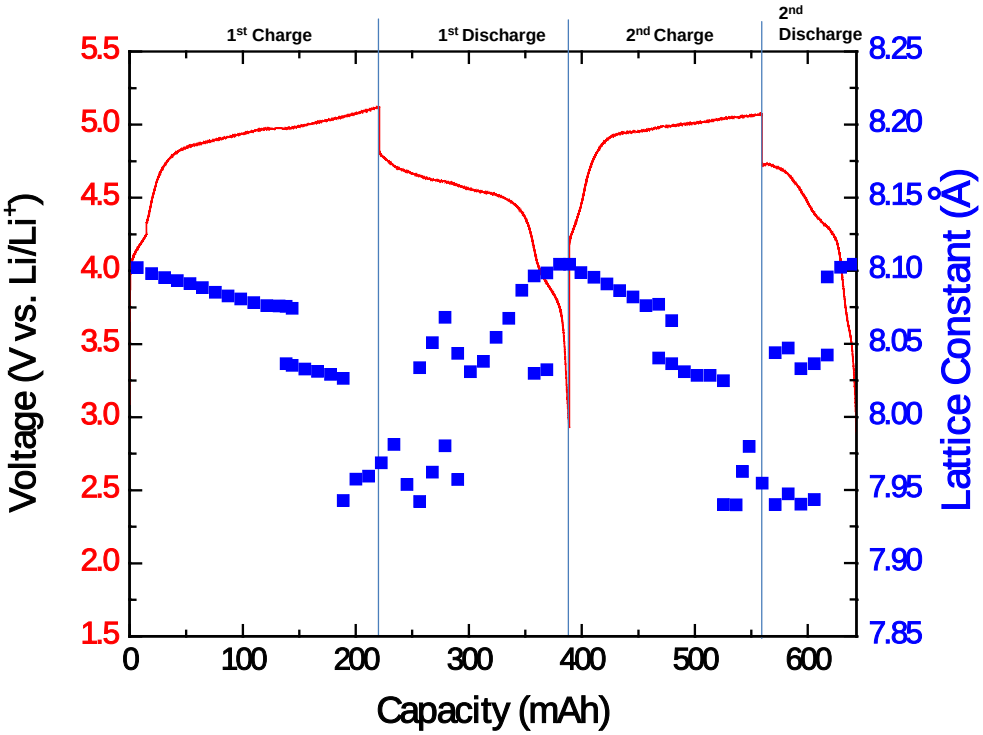


- Synchrotron XRD patterns (referenced to Cu Kα) collected during 2 cycles of Li/$LiNi_{0.5}Mn_{1.5}O_4$ at 900°C.
- Multiple processes are observed during lithium extraction/reinsertion.

Technical accomplishments:

$LiNi_{1/2}Mn_{3/2}O_4$, Electrochemical reversibility (II)

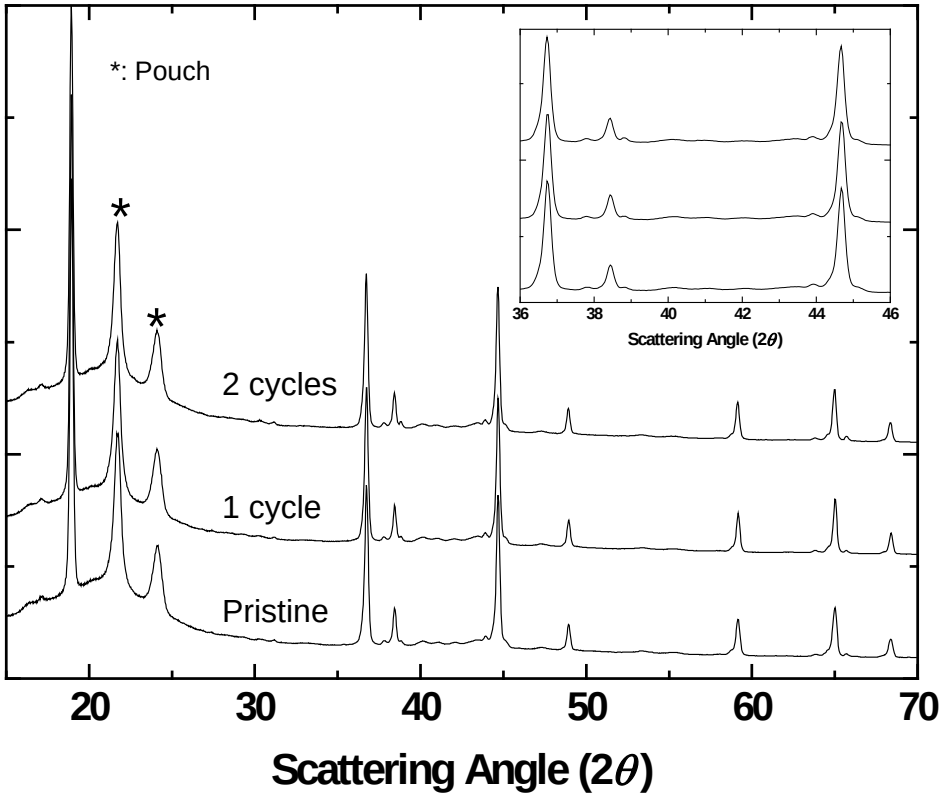


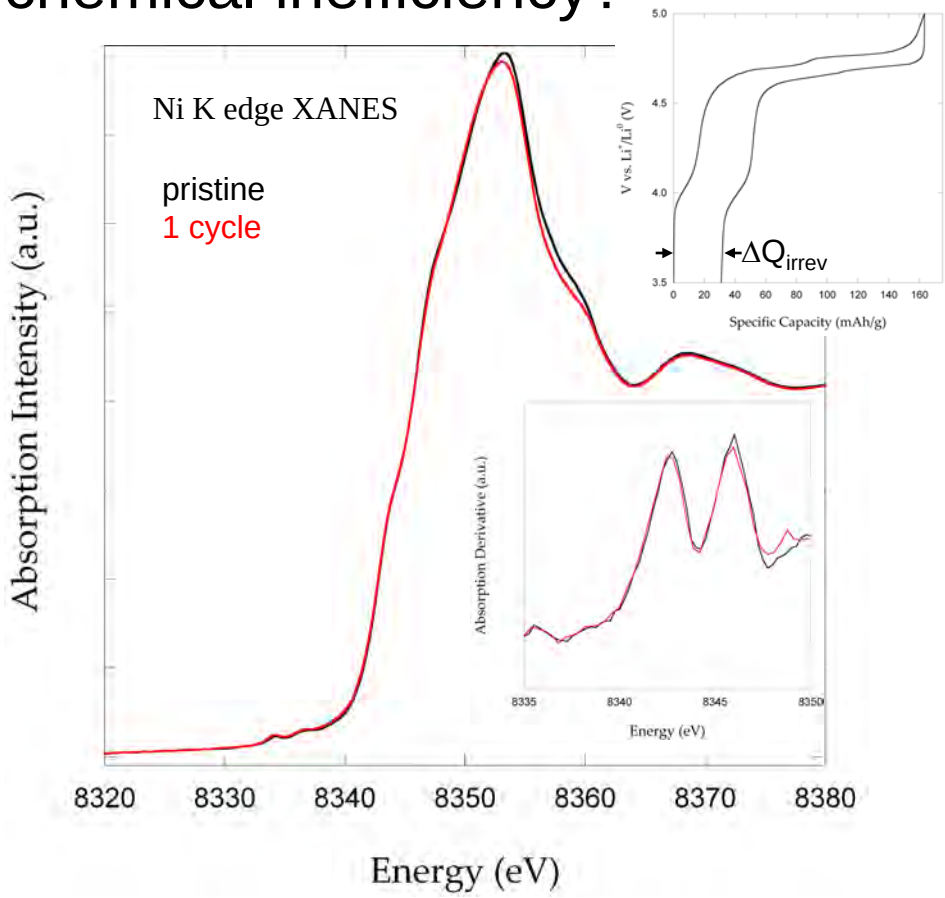


- Single phase - 2 phase - single phase - 2 phase processes on charge. Reversible on discharge.
- Changes in cell parameter (~2% volume change) and phase distribution are **largely reversible** even after 2 cycles.

Technical accomplishments:

$LiNi_{1/2}Mn_{3/2}O_4$, Crystal-chemical inefficiency?

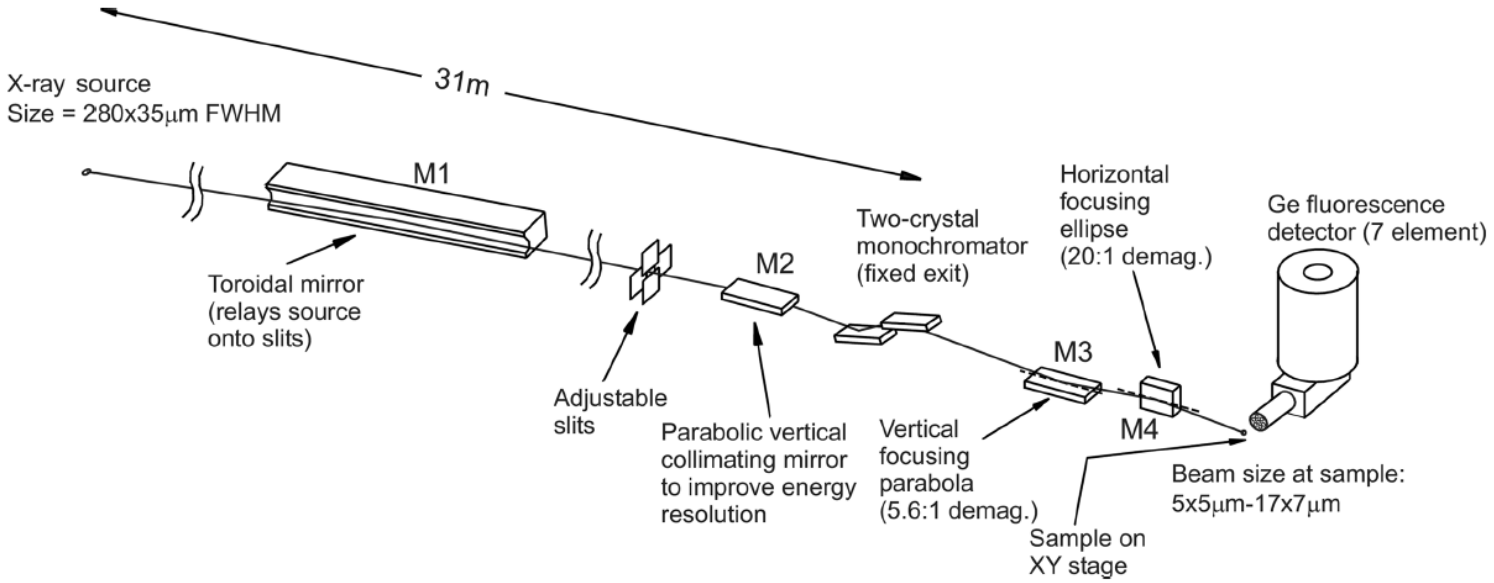




- **ΔQ_{irrev} is not related** to crystallographic or chemical inefficiencies: structure and Ni^{2+} content recovered after 1 cycle.
- ~130 mAh/g discharge capacity ⇒ ~88% theoretical capacity. Is Li completely removed upon charge?

Technical accomplishments:

μ-XAS as a technique to study electrode inhomogeneities



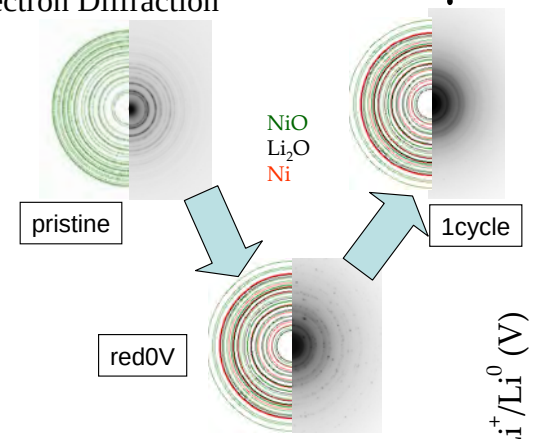
• Small (down to 1x1 μm) spot size on the sample allows collection of multiple X-ray absorption spectra with spatial resolution ⇒ good for complex inhomogeneous samples.

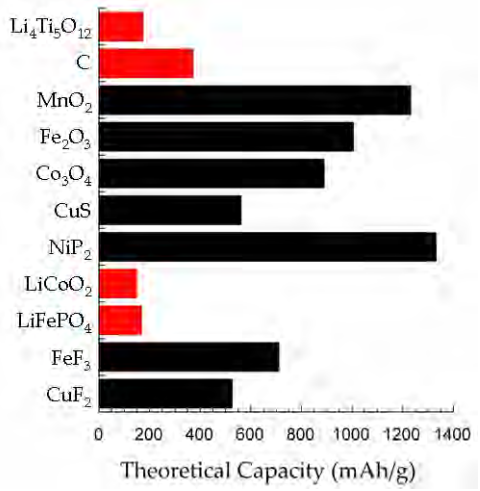
• Three detectors available: total electron yield (probes ~10 nm), fluorescence yield (<1 μm), transmission (through sample).

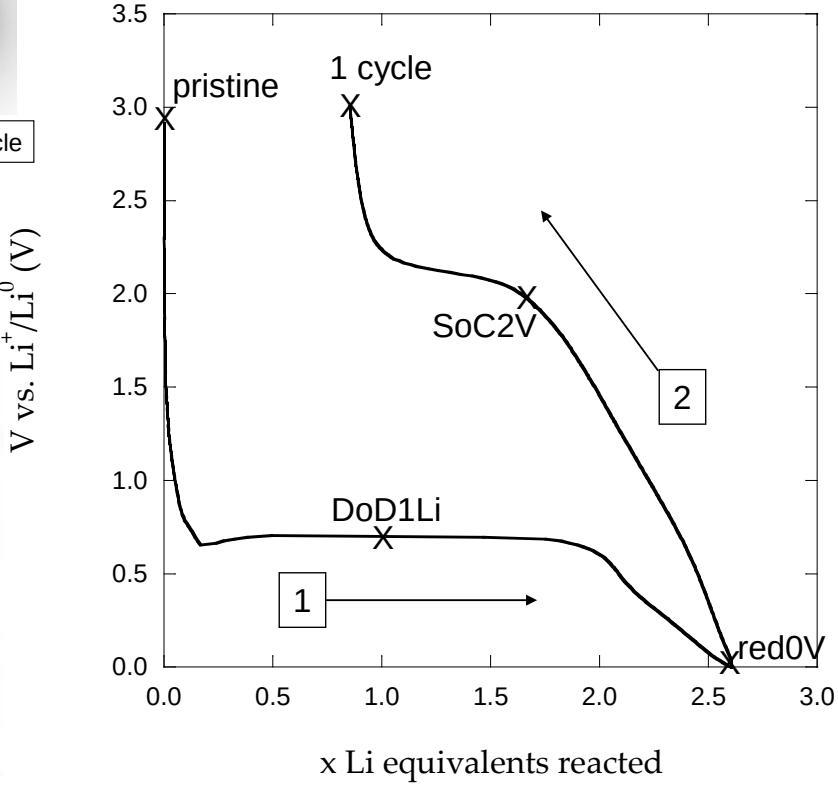
Technical accomplishments:

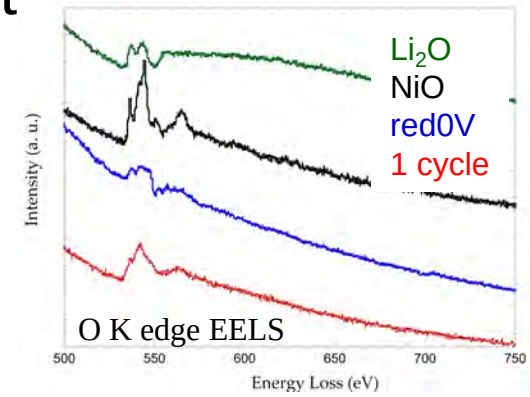
μ-XAS, NiO as proof of concept

Electron Diffraction

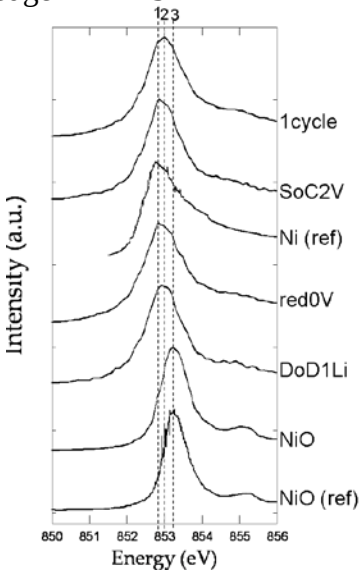








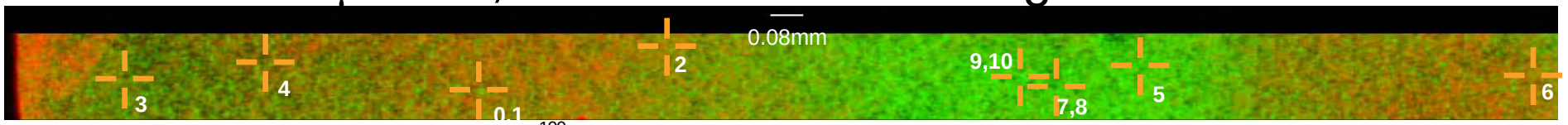
Ni $L_{II,III}$ edge XANES



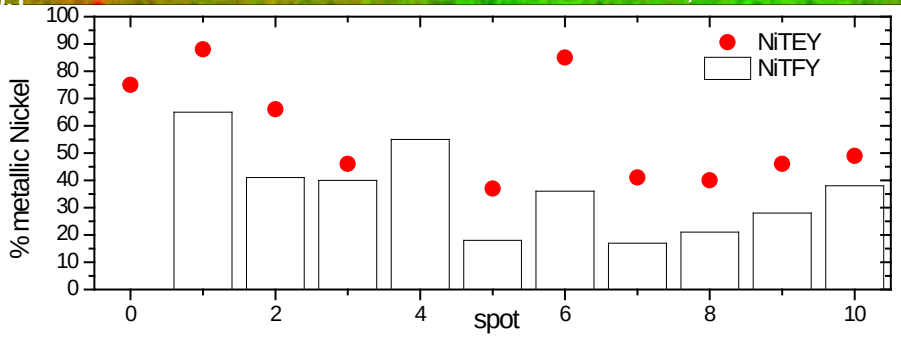
- $NiO + 2Li \leftrightarrow Ni + Li_2O \Rightarrow$ reversible conversion reaction that leads to high storage capacity.
- Ni species involved are easily resolvable $\Rightarrow$ <u>good model system</u> to test the efficacy of the technique.

Technical accomplishments:

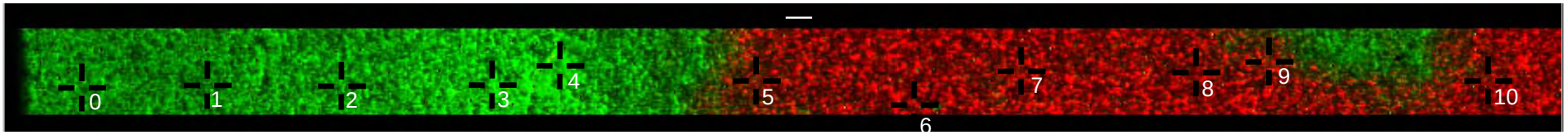
μ-XAS, Identification of homogeneities



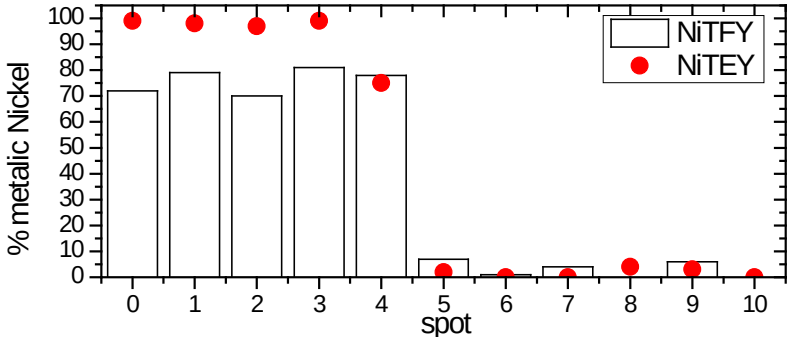
73% NiO+15% CB+12% PVDF
Discharged halfway, C/20



NiO
Ni



73% NiO+15% CB+12% PVDF
Discharged halfway, 1C



Ni
NiO

- **Inhomogeneities in the phase transformation** identified at mm scale. Aggravated as rate is increased ⇒ risk of capacity losses, overdischarge, localized heat.
- Methodology can be extended to other systems (including those showing amorphous phases) → generate input for electrode design.

Collaboration and Coordination with Other Institutions

- Within BATT:
  - Dr. V. Battaglia (LBNL): testing of spinel electrodes in Li-ion cells.
  - Dr. M. M. Doeff (LBNL): XAS and XRD of electrode materials.
  - Dr. R. Kostecki (LBNL): understanding surface reactivity in cathode materials.
  - Prof. C.P. Grey (SUNY-SB): MAS-NMR of electrode materials.
  - Prof. Whittingham (SUNY-Binghamton): magnetic susceptibility of spinels.

- Outside BATT:
  - Dr. M. Casas-Cabanas (ENSICaen, France): neutron diffraction and electron microscopy of electrode materials.
  - Dr. A. Mehta (SSRL): XAS and XRD of electrode materials.
  - Dr. M.A. Marcus (LBNL): μ-XAS of electrode materials.
  - Dr. A. Dong (LBNL): synthesis of materials with controlled nanostructures.

Future Work

- Continue to understand parameters that control performance of $LiNi_{1/2}Mn_{3/2}O_4$ (within BATT Focus Group):
  - Continue using NMR (with Grey group) as core technique for analysis of ordering.
  - Collaboration has been established with Whittingham group to analyze Mn^{3+} content using magnetic susceptibility.
  - Establish sensitivity of XANES to small amounts of Mn^{3+}.
  - Analyze role of crystal-chemistry on electrode performance in samples where microstructure effects are decoupled.
- Continue to investigate sources of coulombic inefficiency in $LiNi_{1/2}Mn_{3/2}O_4$ (within BATT Focus Group):
  - Samples at full charge: Is there Li^+ left? Is there Ni^{4+}? Are holes created into O 2p bands? What is the composition of electrolyte decomposition layers on surface of electrode? Use combination of soft and hard XAS.
  - Analyze the effect of simply adding inorganic additives to electrode on coulombic efficiency. Compare to traditional coatings.
- Extend μ-XAS method to commercially relevant systems (alloys, intercalation).

Summary

- $LiNi_{1/2}Mn_{3/2}O_4$ crystallizes in a variety of patterns of with different Ni/Mn ordering. Ni/Mn mixing can be found in samples showing unit cell superstructures.
- All samples made in this study show Mn over-stoichiometry, but no evidence of O^{2-} vacancies. Mn^{3+} is due to a preferential segregation of Ni in a rock salt impurity, which also contains Mn.
- Amounts of impurity and Mn^{3+} increase with synthesis temperature. Impurity is detrimental to performance; needs to be minimized during material preparation.
- Annealing of samples prepared at high temperature leads to decoupling of microstructure from ordering/composition.
- Poor performance of $LiNi_{1/2}Mn_{3/2}O_4$ in Li-ion cell, most likely due to coulombic inefficiencies. These are not related to crystal-chemical irreversibilities.
- Developed a μ-XAS method to evaluate charge distribution with high spatial resolution. Analyzed discharge inefficiency dependence on rate for conversion model system.