Design and Evaluation of High Capacity Cathodes

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Argonne National Laboratory

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ES049

Vehicle Technologies Program

Overview

Timeline

- Start date: FY12
- End date: FY15
- Percent complete:

  - This is a new project

Budget

- Total project funding

  - 100% DOE
- Funding in FY12: $500K

Barriers

- Low energy density
- Cost
- Abuse tolerance limitations

Partners

- Lead PI: Michael Thackeray
- Collaborators:
  - CSE, Argonne: **Jason Croy**, Swati Pol, Roy Benedek, Donghan Kim, Kate Ryan
  - APS, Argonne: Mali Balasubramanian (XAS), Yang Ren (XRD)
  - LBNL, Vince Battaglia
  - Industry: Envia Systems, BASF, Toda, LG Chem

Objectives

- Design and synthesize high capacity, high-power and low cost cathodes for PHEVs and EVs
  - Improve the design, composition and electrochemical performance of Mn-based composite cathode structures
  - Explore processing routes to enhance surface and bulk stability of electrodes at high electrochemical potentials
  - Use atomic-scale modeling as a guide to identify, design and understand the structural features and electrochemical properties of cathode materials

Milestones (FY12)

- Evaluate a new processing route to fabricate stabilized $xLi_2MnO_3\bullet(1-x)LiMO_2$ (‘layered-layered’) electrode structures using Li_2MnO_3 as a precursor
- Exploit sonication and atomic layer deposition to stabilize the surface of ‘layered-layered’ electrode particles at high charging potentials
- Conduct studies on BATT materials at Argonne’s Advanced Photon Source (APS) to complement EFRC projects in the Center for Electrical Energy Storage - *Tailored Interfaces* (Argonne - Northwestern University - University of Illinois at Urbana-Champaign)
- Model surface structures and electrochemical phenomena in lithium transition metal oxide electrodes

Approach

- Exploit the concept of using Li_2MnO_3 as a precursor to synthesize stabilized high capacity 'composite' electrodes structures, particularly
  - 'layered-layered' $xLi_2MnO_3 \bullet (1-x)LiMO_2$
  - 'layered-layered-spinel' $y\{xLi_2MnO_3 \bullet (1-x)LiMO_2\} \bullet (1-y)LiM_2O_4$
  - 'layered-layered-rocksalt' $y\{xLi_2MnO_3 \bullet (1-x)LiMO_2\} \bullet (1-y)MO$

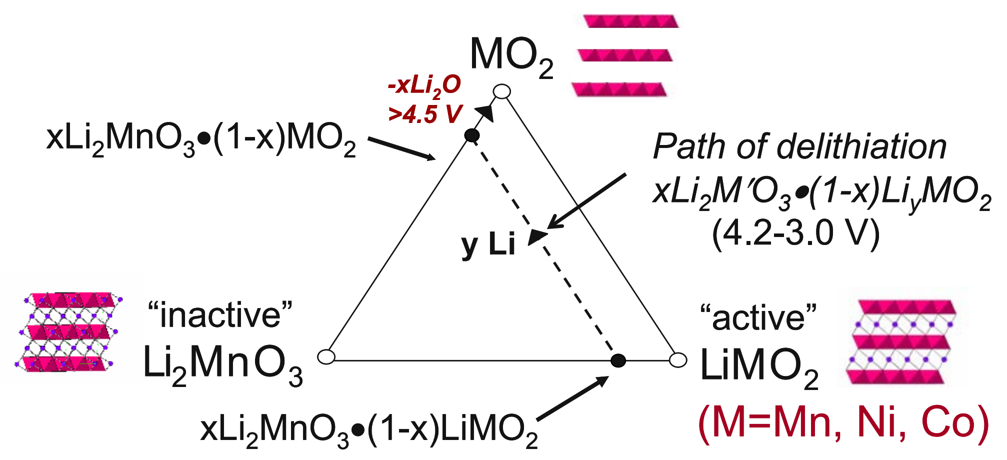
  in which M is typically Mn, Ni, and/or Co;

- Exploit sonication and atomic layer deposition methods to design effective *surface structures* to protect the underlying metal oxide particles from the electrolyte and to improve their rate capability when charged (delithiated) at high potentials;

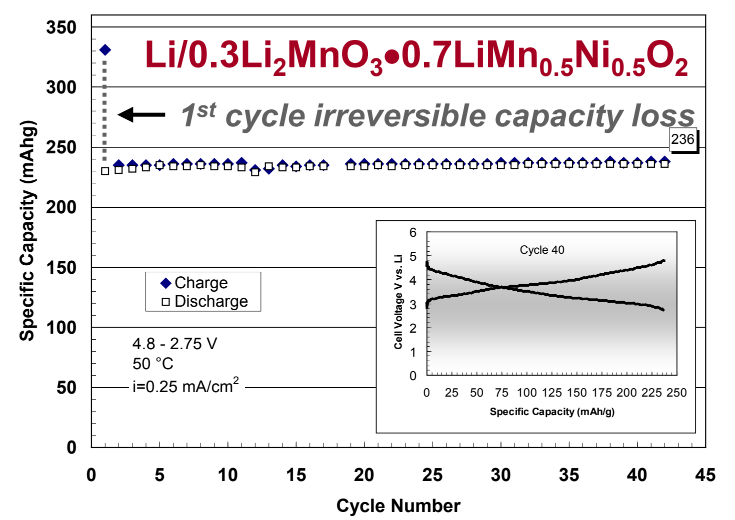
- Use *first principles modeling* and perform detailed characterization studies to aid the design of bulk and surface cathode structures and understand electrochemical phenomena.

‘Layered-Layered’ $xLi_2MnO_3 \bullet (1-x)LiMO_2$ Electrodes

Strategy: Embed inactive Li_2MnO_3 component within $LiMO_2$ structure to stabilize the electrode at high potentials (reduce oxygen activity at surface)



U.S. Pat. 6,677,082 (2004); U.S. Pat. 6,680,143 (2004)

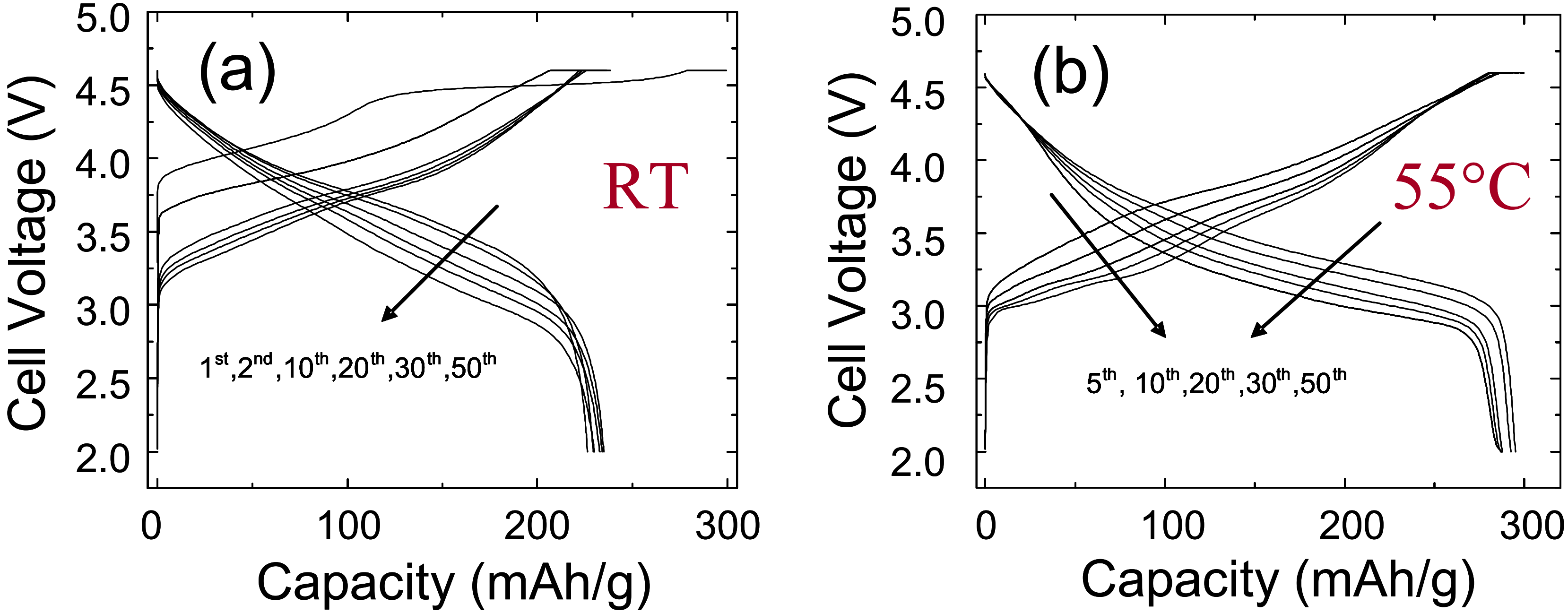


Recap of typical performance:

- 200-250 mAh/g at C/3 rate (50 °C)
- Lower capacity at RT
- *Charging to high potential (>4.4 V) damages the electrode surface, reducing the rate capability, and inducing phase transitions in bulk.*

The Voltage Decay Phenomenon

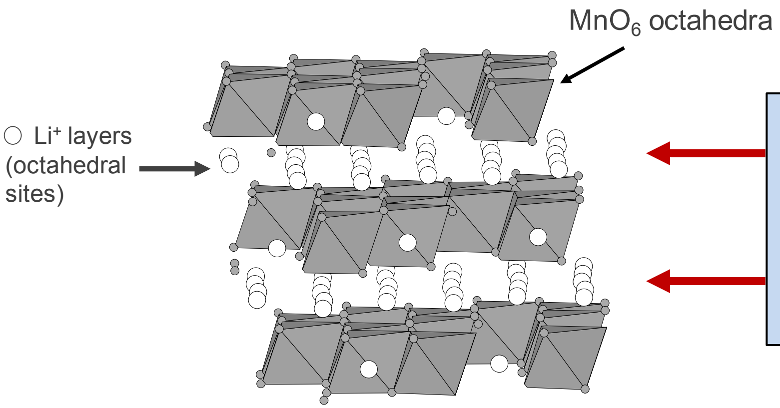
$Li/0.5Li_2MnO_3 \bullet 0.5LiNi_{0.44}Co_{0.25}Mn_{0.31}O_2$ Cells



- Voltage profile decays on cycling, reducing energy output
- Phase transition to spinel-like regions in bulk structure?

Stabilization of Composite Bulk Structures

- Voltage decay due to internal phase transitions - migration of transition metal ions into Li layers that provides ‘spinel-like’ character
- Hypothesis: Phase transitions may be arrested by introducing and controlling the number of stabilizing ions in Li layer via a Li_2MnO_3 precursor
- Stabilizing cations and anions for surface protection can be added to the solution – one shot process, e.g., Li_2MnO_3 + Ni-*X* (X = F, Al, Co, Li_3PO_4)

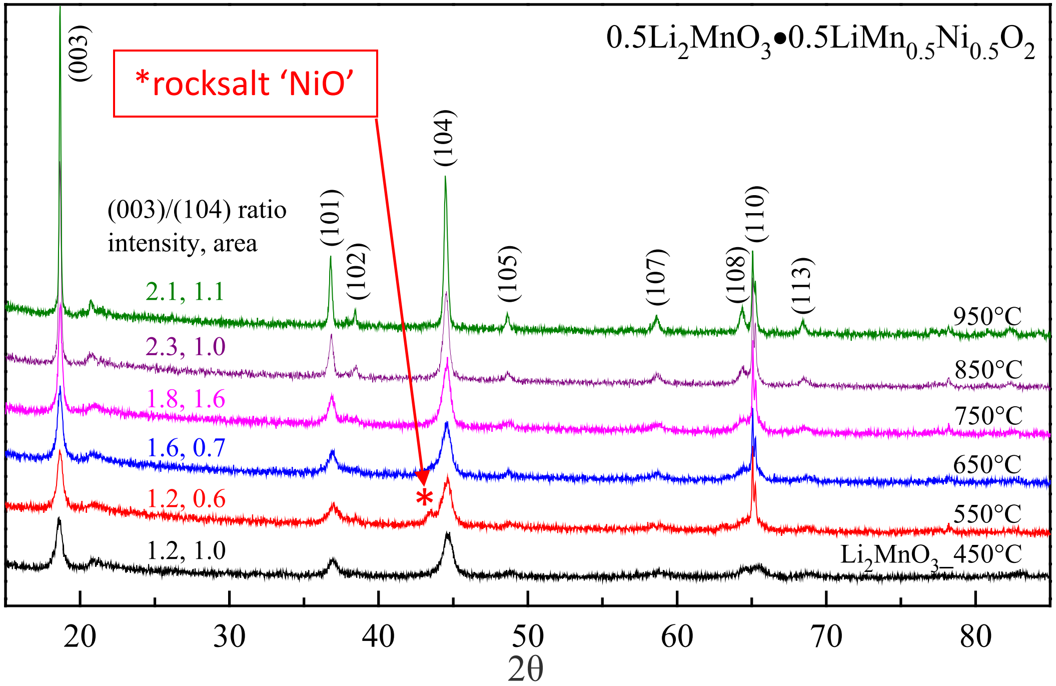


$Li^+/M^+/H^+$-ion exchange during acid treatment, followed by annealing step to complete M^+ diffusion into the lithium and transition metal layers

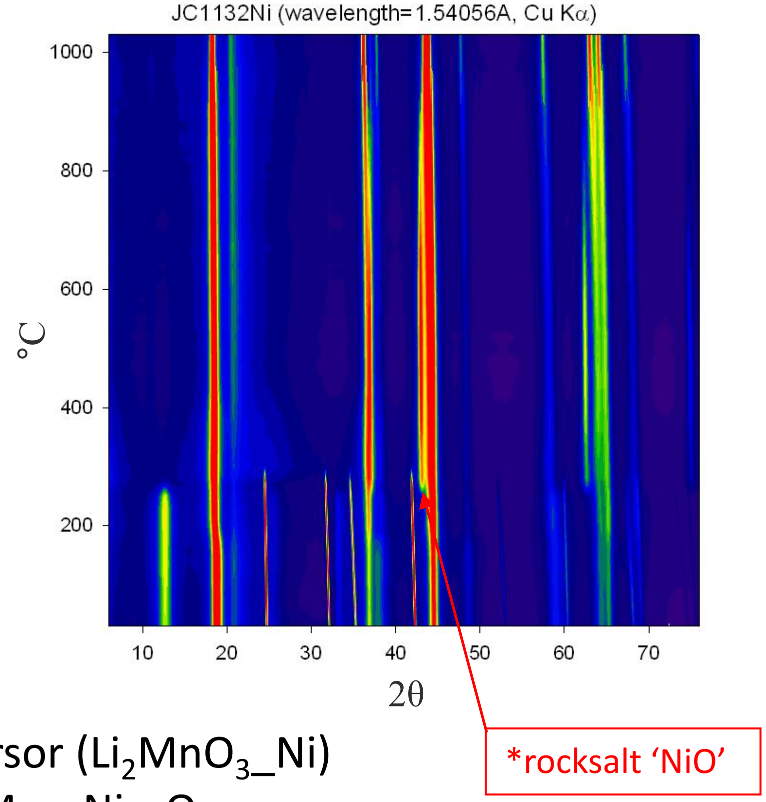
- Ideal ‘layered-layered’: No transition metal ions in Li layers
- Ideal ‘layered-layered-spinel’: 25% transition metal ions in Li layers of spinel domains & vice-versa
- Ideal ‘layered-layered-rocksalt’: No Li layers in rocksalt domains

$0.5Li_2MnO_3•0.5LiMn_{0.5}Ni_{0.5}O_2$ from ‘Li_2MnO_3_Ni’
Structural Evolution

Ex-situ XRD (Bruker diffractometer)

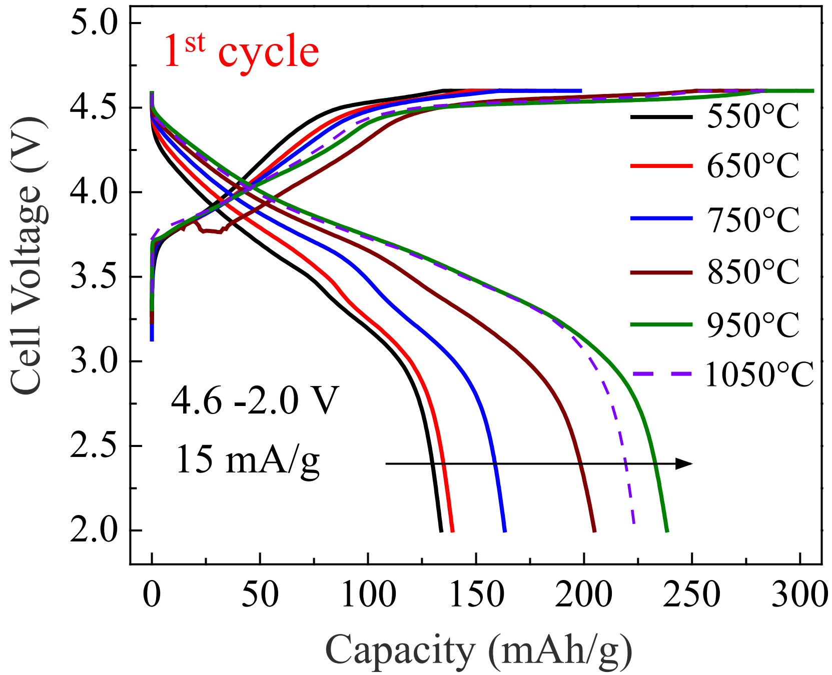

*rocksalt ‘NiO’

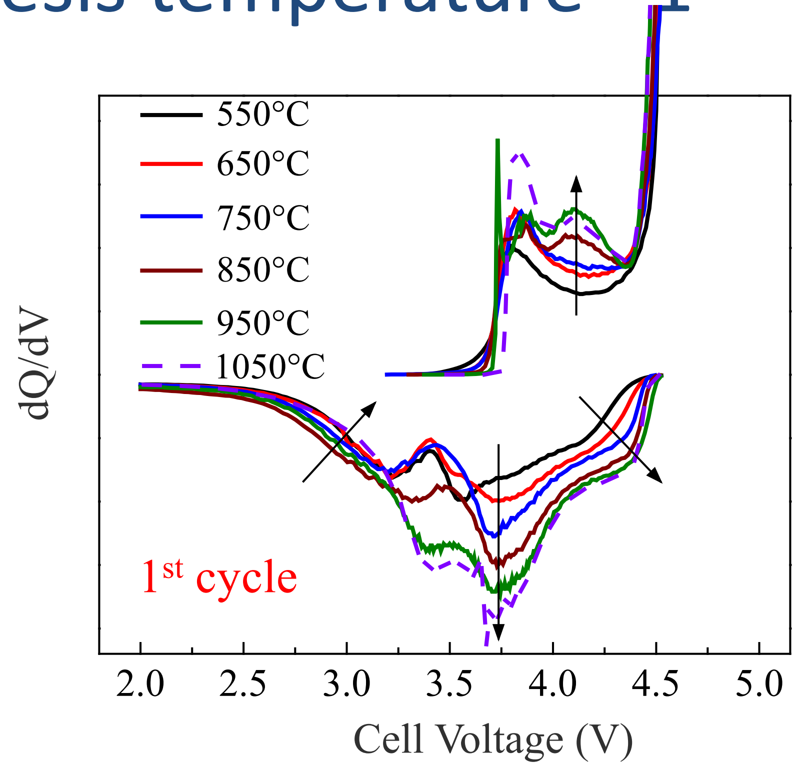
In-situ HR-XRD (APS)


*rocksalt ‘NiO’

- $NiNO_3$ in solution added to Li_2MnO_3 precursor (Li_2MnO_3_Ni)
- Targeted composition = $0.5Li_2MnO_3•0.5LiMn_{0.5}Ni_{0.5}O_2$
- Slurry dried and annealed between 450 and 1000 °C
- Comparison of *ex-situ* and *in-situ* XRD shows the evolution of a rocksalt-containing composite structure towards ‘layered-layered’ $0.5Li_2MnO_3•0.5LiMn_{0.5}Ni_{0.5}O_2$ with increasing annealing temperature.

Electrochemistry of ‘$0.5Li_2MnO_3$_Ni’ as a function of synthesis temperature - 1

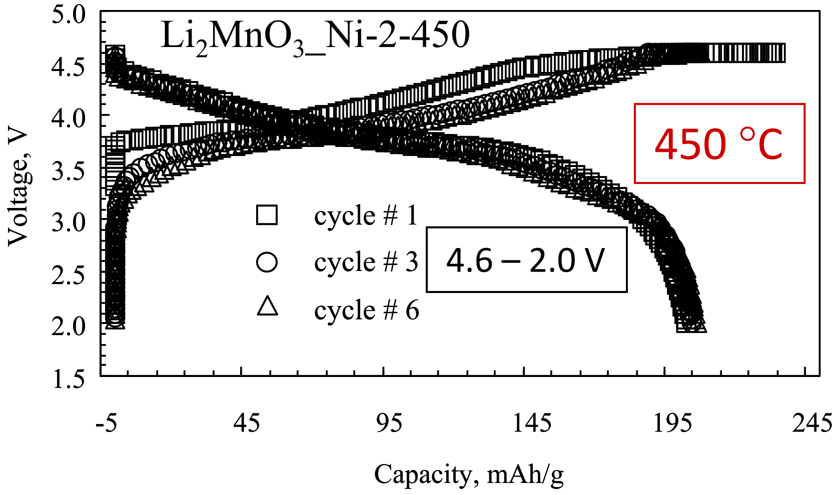


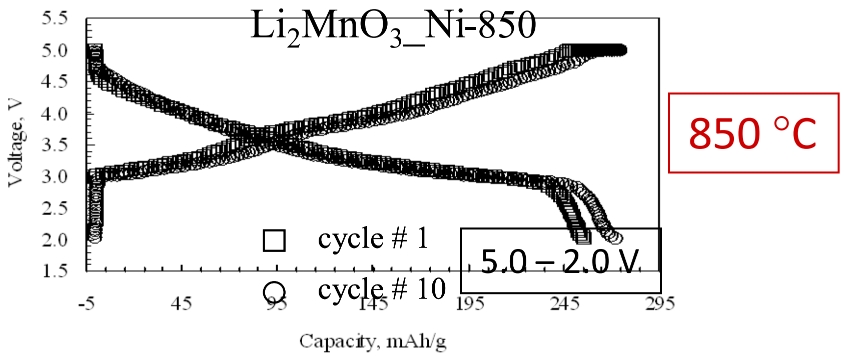


- Increased capacity on first charge and the evolution of dQ/dV peaks indicate:
  - a continuous rocksalt to layered transition consistent with the XRD data
  - an annealing temperature of ~950°C is required to access the maximum capacity from both Li_2MnO_3 and $LiMO_2$ components.

Electrochemistry of ‘$0.5Li_2MnO_3$_Ni’ as a function of synthesis temperature – 2

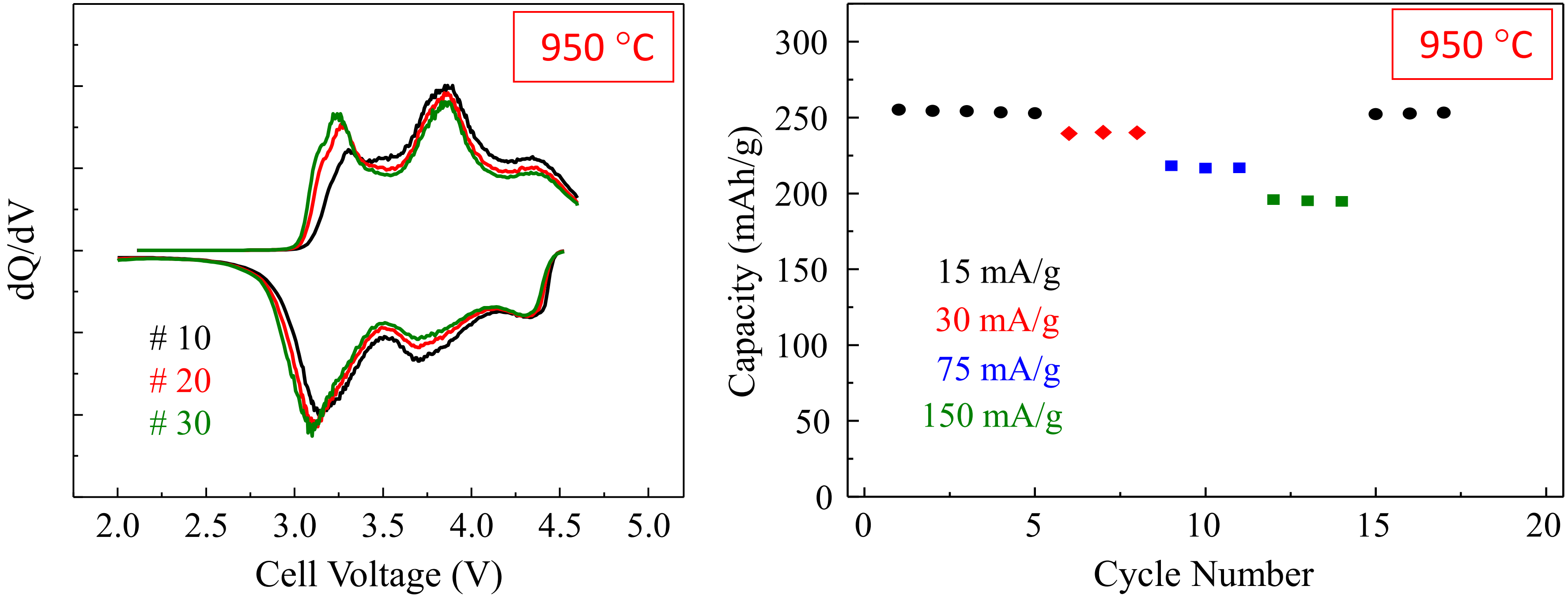
Targeted Composition: $0.5Li_2MnO_3 \bullet 0.5LiMn_{0.5}Ni_{0.5}O_2$





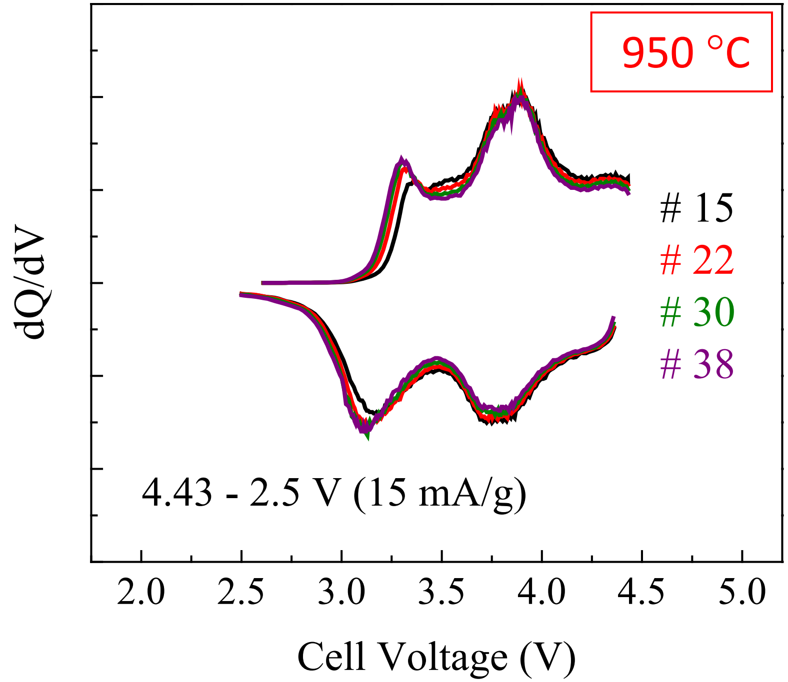
- Li_2MnO_3_Ni-2-450 electrodes with a stabilizing MO component appear to enhance the voltage stability of composite electrode structures when activated at high potentials
- Average discharge potential of ‘layered-layered’ Li_2MnO_3_Ni-850 is lower than that of ‘layered-layered-rocksalt’ Li_2MnO_3_Ni-2-450
- Extent to which NiO domains convert to $LiMn_{1-x}Ni_xO_2$ is T dependent

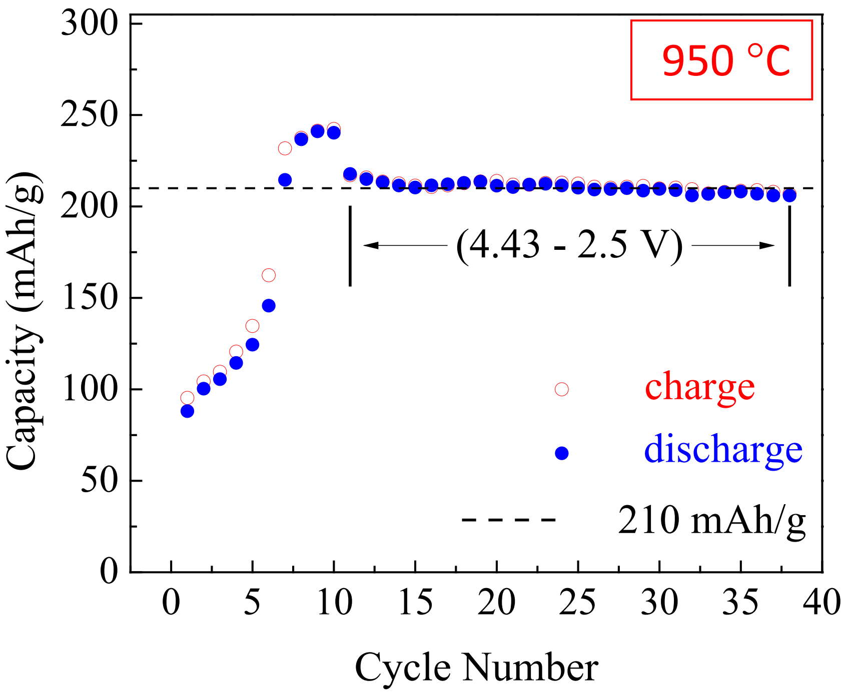
$0.5Li_2MnO_3 \bullet 0.5LiMn_{0.5}Ni_{0.5}O_2$ from Li_2MnO_3: Stability and Rate Performance



- Electrodes synthesized from Li_2MnO_3 rapidly reach 'stable' configuration
- Good capacity and rate capability achieved:
  - ~240 mAh/g at ~C/8 rate (30 mA/g)
  - ~200 mAh/g at ~C/1.3 rate (150 mA/g)

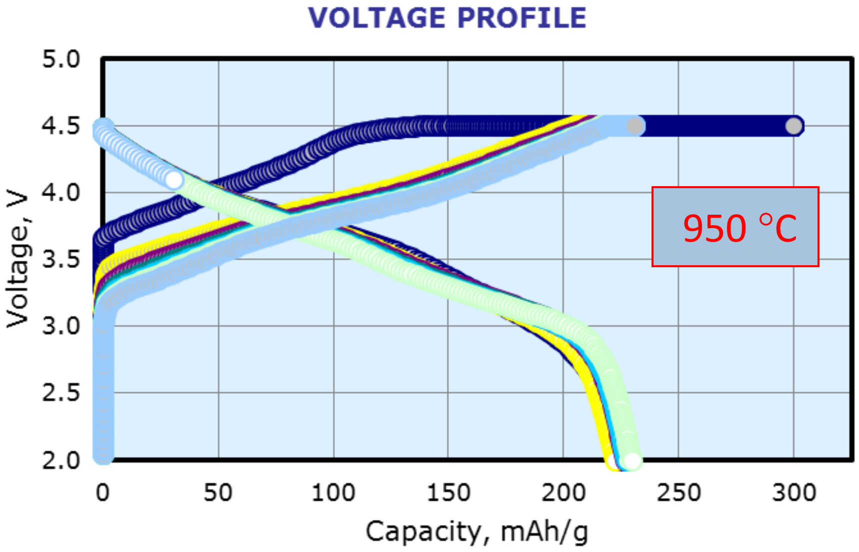
$0.5Li_2MnO_3 \bullet 0.5LiMn_{0.5}Ni_{0.5}O_2$ from Li_2MnO_3: Voltage dependence





- Activation of all but ~15% of the Li_2MnO_3 component combined with a reduced voltage window (4.43 – 2.5 V) produces a relatively stable charge/discharge profile and a high capacity (210 mAh/g)

$0.5Li_2MnO_3 \bullet 0.5LiMn_{0.5}Ni_{0.5}O_2$ from Li_2MnO_3: Activation dependence

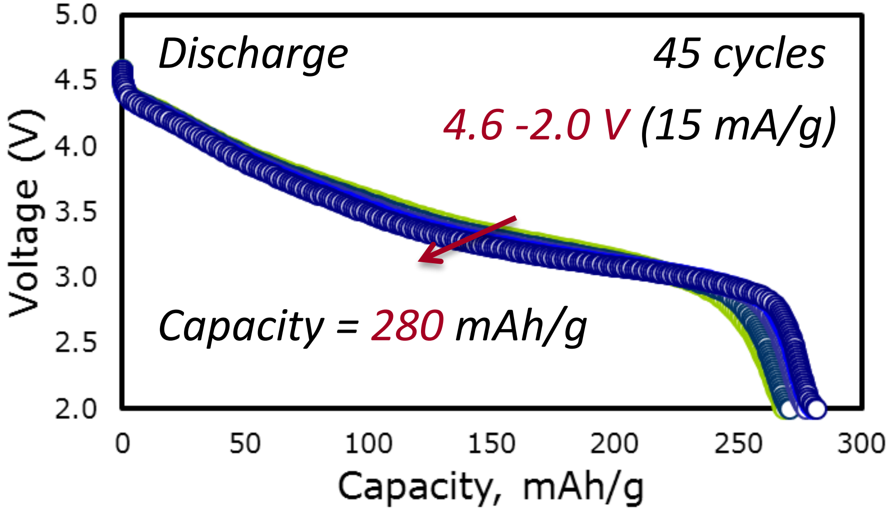


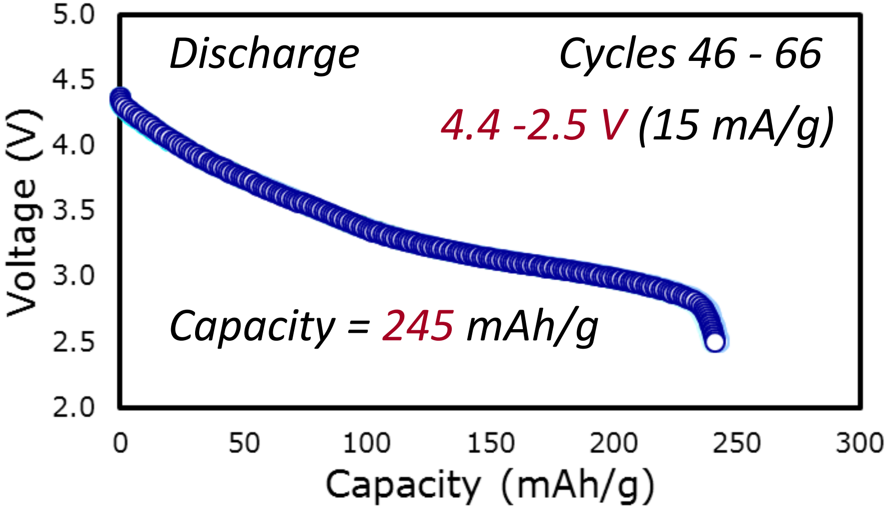
- Slow ‘break-in’ to 300 mAh/g at 4.5 V (15 mA/g) followed by cycling between 4.5 – 2.0 V gives a relatively stable charge/discharge profile over the first 15 cycles, relative to cycling to between 4.6 – 2.0 V
- This protocol yields ~230 mAh/g (at 15 mA/g) even at 4.5 V for a calculated ~15% unactivated Li_2MnO_3

‘Layered-layered’ Electrodes from Li_2MnO_3 – 850 °C

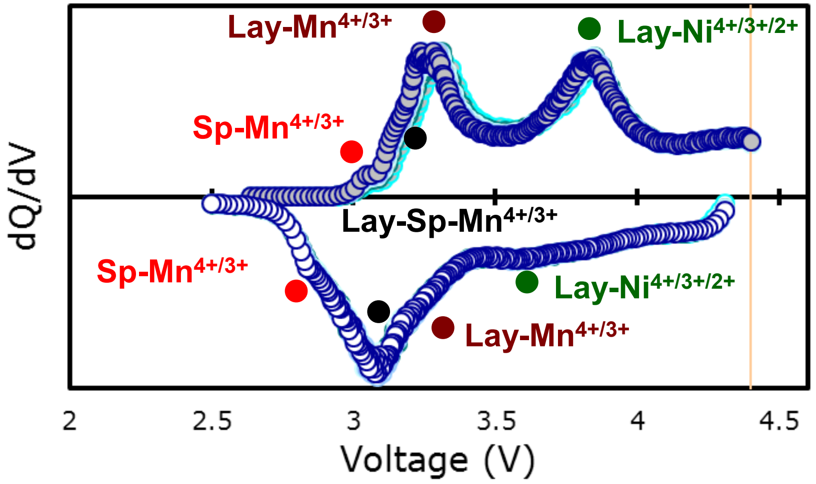
Targeted Composition: $0.5Li_2MnO_3 \bullet 0.5LiMn_{0.5}Ni_{0.5}O_2$

High Voltage Cycles → *Low Voltage Cycles*

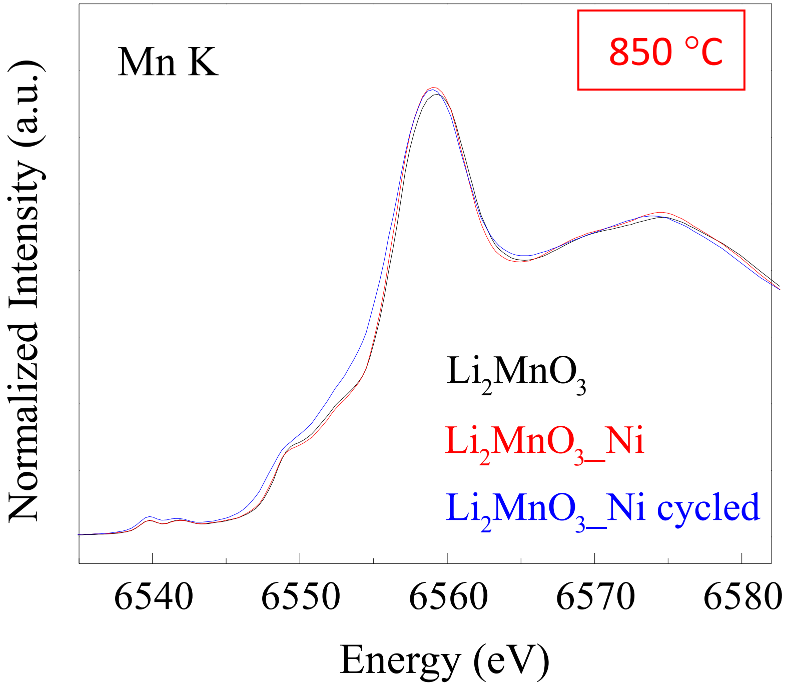


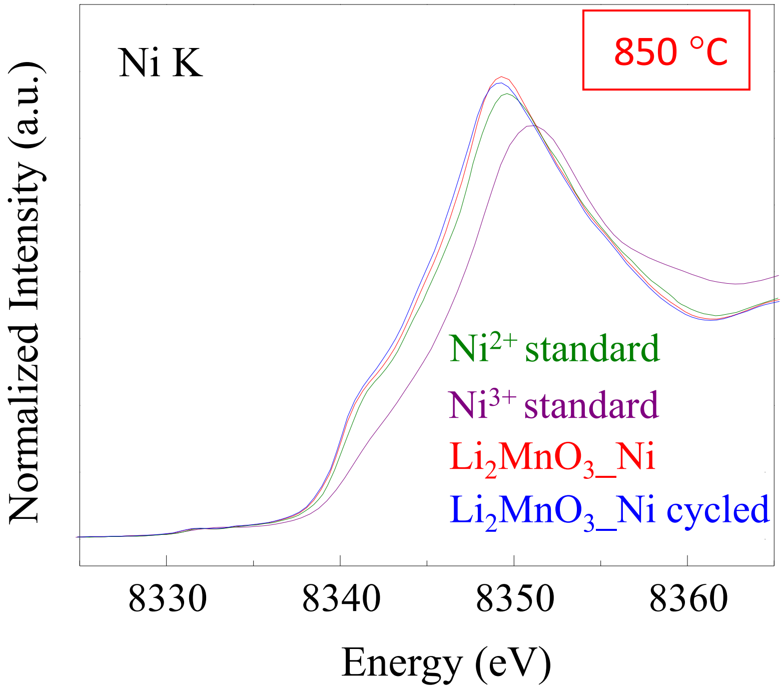


- Electrode performance is dependent on synthesis conditions, e.g., pH, leaching and annealing times/temp, stabilizing ions, composition, precursor synthesis
- Excellent cycling capacity (245 mAh/g) and stability obtained when the electrode is initially activated between 4.6-2.0 V, then narrowing the voltage window to 4.4-2.5 V



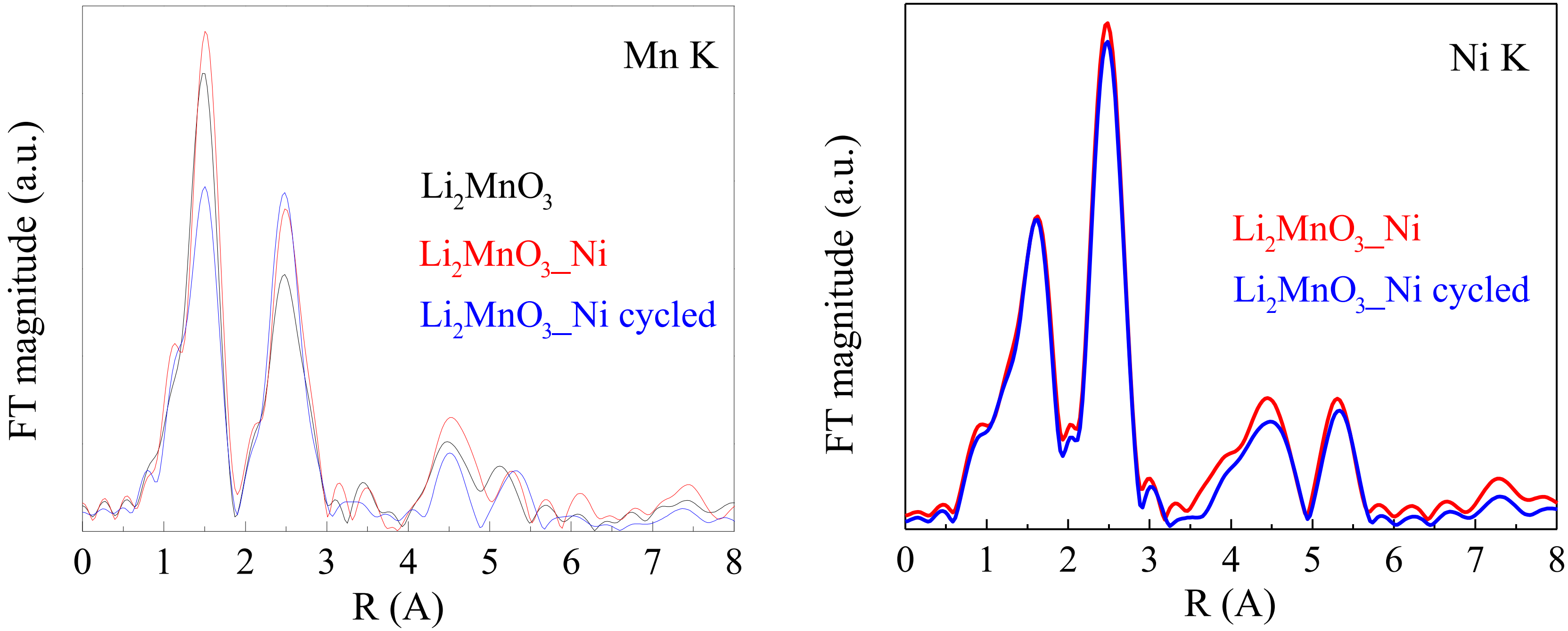
$0.5Li_2MnO_3 \bullet 0.5LiMn_{0.5}Ni_{0.5}O_2$ from Li_2MnO_3: X-ray Absorption Spectroscopy (XANES)





- XANES data show a slight reduction of manganese after 50 cycles between 4.6 – 2.0 V (15 mA/g)
- Nickel exists as Ni^{2+} in both the fresh and cycled electrodes (data collected in the discharged state, 2.0 V)

$0.5Li_2MnO_3$•$0.5LiMn_{0.5}Ni_{0.5}O_2$ from Li_2MnO_3:
X-ray Absorption Spectroscopy (EXAFS)



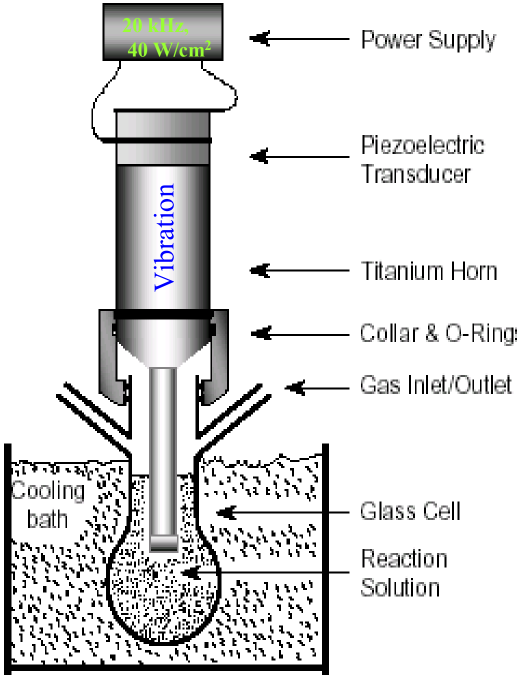
- EXAFS data show that structural degradation and thus the resultant voltage decay are likely due to significant changes in the manganese environment that occur during activation of the parent electrode.
- The improved electrochemical stability of $0.5Li_2MnO_3$•$0.5LiMn_{0.5}Ni_{0.5}O_2$ electrode structures from Li_2MnO_3 is tentatively attributed to the synthesis method that allows stable nickel-manganese configurations to form that reduce the size and concentration of damaging manganese-rich regions.

Surface Stabilization by Sonication

e.g., TiO_2-coated $0.5Li_2MnO_3 \bullet 0.5LiNi_{0.44}Co_{0.25}Mn_{0.31}O_2$ (NMC)

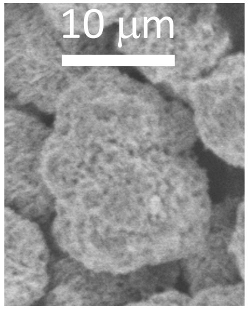
- Sonication: Formation → growth → implosive collapse of bubbles, that locally increases temperature and pressure.
- Use high energy process to simultaneously clean surface and coat nanoparticles

$$0.5Li_2MnO_3 \bullet 0.5LiNi_{0.44}Co_{0.25}Mn_{0.31}O_2 + TiOSO_4 \bullet xH_2O \;\;))) \;\;))) \;\;))) \;\; Ti(OH)_x \xrightarrow[\text{Air}]{450^{o}C} TiO_2/NMC$$

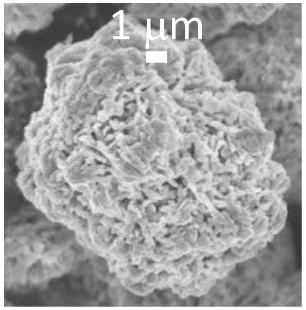


SEM:

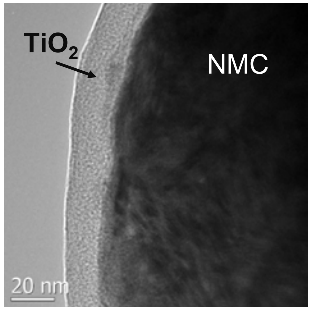
BEFORE



AFTER

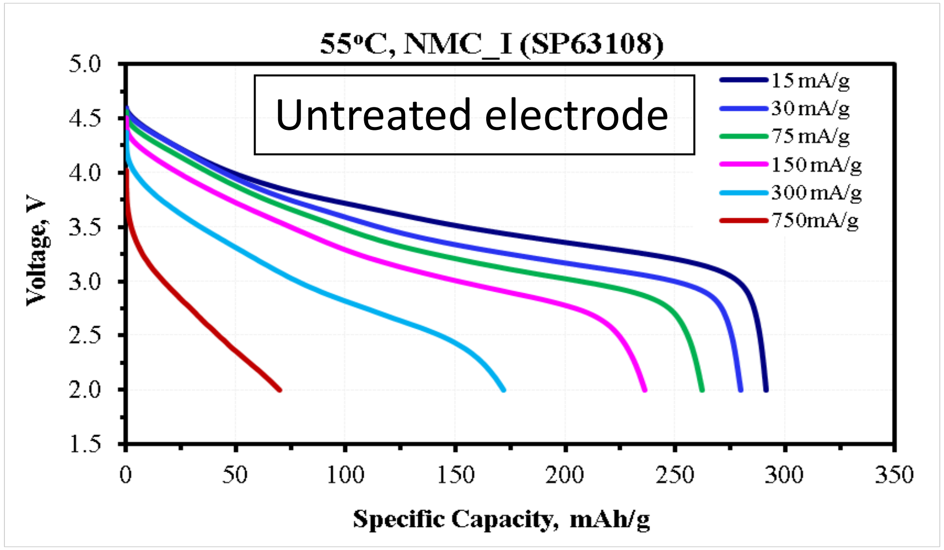


HRTEM

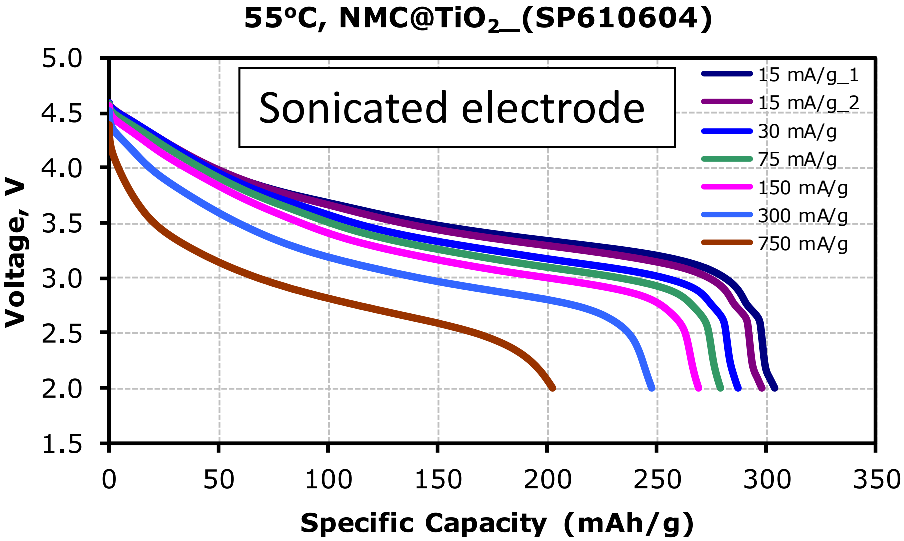


- Successfully demonstrated for TiO_2, $Li_4Ti_5O_{12}$, ZrO_2, Li_2ZrO_3
- NMC particles uniformly coated
- Electrochemical data show that the coatings significantly enhance the rate capability, notably at high temperature (55 °C) - see next two slides

Electrochemical Data of Untreated and Sonicated NMC Electrodes (TiO_2) at 55 °C

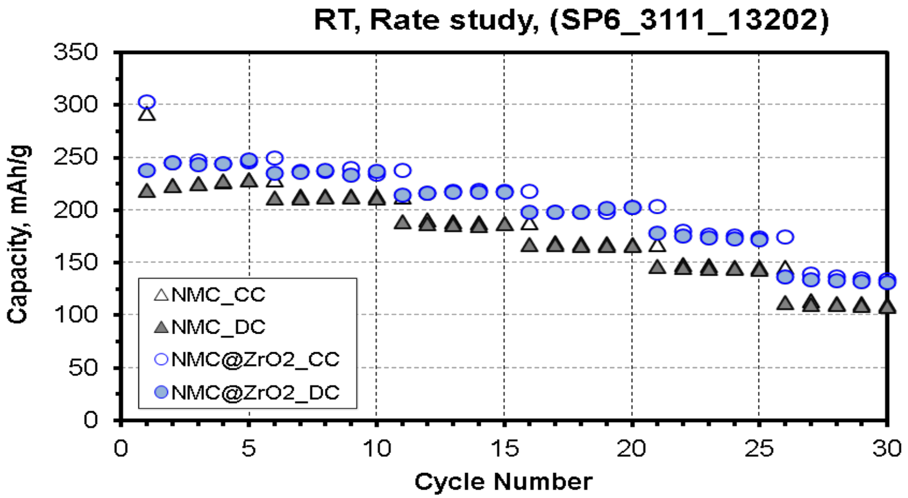


Current i (mA/g)	Avg Cap (mAh/g)	Ah Eff %
15	1^{st}: 291	**88.8**
	286.7	98.8
30	279.5	99.1
75	262.0	98.9
150	236.0	98.4
300	171.9	91.3
750	50.5	78.0

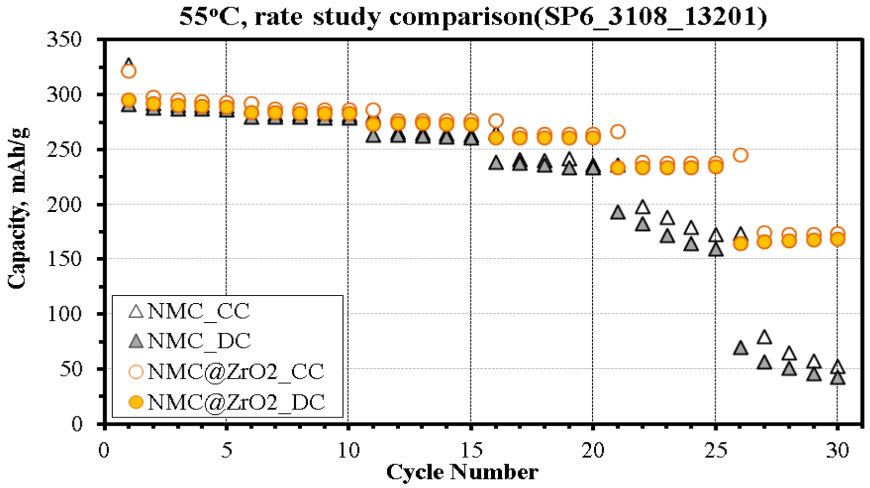


Current i (mA/g)	Avg Cap (mAh/g)	Ah Eff %
15	1^{st}: 304	**90.1**
	295.8	98.6
30	287.6	98.9
75	279.3	99.1
150	269.3	99.0
300	247.7	99.4
750	202.4	99.7

Electrochemical Data of Untreated and Sonicated NMC Electrodes (ZrO_2) at RT and 55 °C



Current (mA/g)	Cycle #	Avg Cap (mAh/g)	Ah Eff %
15	1	303-238	**78.4**
	4	244	99.7
30	7	236	99.6
75	15	217	99.8
150	18	197	99.7
300	25	172	98.9
750	29	131	97.5



Current (mA/g)	Cycle #	Avg Cap (mAh/g)	Ah Eff %
15	1	321-295	**91.9**
	3	290	98.4
30	10	283	98.9
75	15	273	98.95
150	20	260	98.8
300	25	234	98.4
750	30	168	97.3

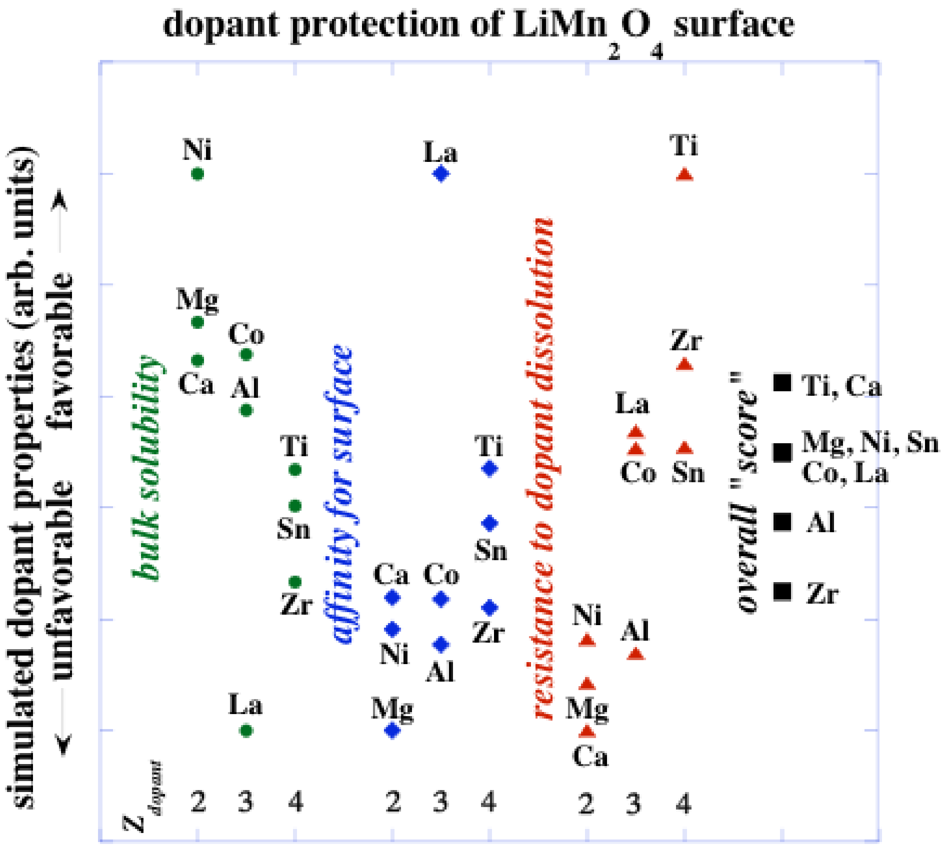
Theory: Doping and Dissolution in Lithium Transition-Metal Oxides - 1

- Because of its high crystallographic symmetry, $LiMn_2O_4$ was selected for theoretical studies of doped lithium transition-metal oxides

  Many different dopants of lithium manganate spinel have been employed in an attempt to inhibit its dissolution in acidic electrolytes, although it is still unclear which choice, if any, is optimal. First-principles simulations of doped spinel were performed to explore whether a clear preference for some dopants over others could be ascertained. Among desired properties of dopants in this context are: (a) low oxidation state, (b) reasonable bulk solubility, (c) reasonable surface affinity for the dopant, and (d) resistance to detachment and dissolution of the dopant at a spinel surface.

  Properties (b)-(d) were simulated for divalent, trivalent, and tetravalent dopants. Each property was expressed in terms of an energy, which is plotted on the abscissa scale of the figure on the following slide. An overall score was devised to compare different dopants.

Theory: Doping and Dissolution in Lithium Transition-Metal Oxides - 2



- Overall, the theoretical analysis showed a preference for tetravalent Ti as dopant

- The advantageous oxidation state of divalent dopants for bulk solubility is offset by other properties for which Ti is superior.

Future Work - FY2012/FY2013

- The concept of using Li_2MnO_3 as a precursor for fabricating composite electrodes with enhanced structural and electrochemical stability is extremely versatile and shows considerable promise; significant momentum has been gathered at Argonne on this focused topic. These efforts will therefore continue in FY2012/FY2013 with the goal of reaching/exceeding the energy and power goals required for 40-mile PHEVs and EVs.
- The stabilization of both surface and bulk structures, preferably in one step using the Li_2MnO_3 precursor approach, will be addressed. Complementary experimental and theoretical approaches will be used to understand and improve parameters that are responsible for the surface stability, rate capability and cycle life of high capacity Mn-rich oxide electrode materials.
- Approaches for fabricating stable surface architectures will be broadened by exploiting both sonication and ALD techniques.
- EFRC-related research on BATT cathode materials and interactions with the academic community and industry will be maintained.

Summary

- Efforts to stabilize the surface and bulk properties of high-capacity, Mn-based composite electrode structures using a Li_2MnO_3 precursor were undertaken. The process has the potential for controlling atomic configurations and for fabricating surface-protected electrodes in a single step.
- Significant progress was made in fabricating and stabilizing the cycling stability of $0.5Li_2MnO_3 \bullet 0.5LiMn_{0.5}Ni_{0.5}O_2$ electrodes; high-resolution XRD and XAS data provided important structural information that has contributed to understanding the complex electrochemical behavior of these materials.
- Sonication reactions were evaluated for fabricating surface-stabilized electrode particles. Data showed that sonication uniformly coats the particle at the nanometer scale, and enhances the rate capability of the electrodes.
- Simulation of doped $LiMn_2O_4$ structures was undertaken to explore whether a preference for some dopants over others could be determined. Tetravalent titanium was predicted to be a preferred dopant.

Acknowledgment

Support for this work from DOE-EERE, Office of Vehicle Technologies is gratefully acknowledged – Tien Duong, David Howell