

Design and Evaluation of Novel High Capacity Cathode Materials

*PI: Michael Thackeray
Chemical Sciences and Engineering Division, Argonne*

*Annual Merit Review
DOE Vehicle Technologies Program*

*Washington, D.C.
May 10, 2011*

ES049

Overview

Timeline

- Start date: FY10
- End date: FY11
- Percent complete:
 - project on-going

Budget

- Total project funding
 - 100% DOE
- FY10: \$300K
- FY11: \$300K

Barriers Addressed

- Low energy
- Cost
- Abuse tolerance limitations

Partners

- Co-investigators:
 - S.-H. Kang, J. Croy, K. Gallagher, D. Kim, S. Pol, V. Pol, R. Benedek (ANL)
- Collaborators:
 - Y. Shao-Horn, C. Carlton (MIT)
 - M. Balasubramanian (APS- ANL)
 - R. Nuzzo, J. Goldman, S. Sanchez (UIUC)
 - V. Battaglia (LBNL)



Objectives

- Design high capacity, high-power and low cost cathodes for PHEVs and EVs
 - Improve the design, composition and electrochemical performance of Mn-based cathodes
 - Explore new processing routes to prepare advanced electrodes with new architectural designs
 - Use atomic-scale modeling as a guide to identify, design and understand the structural features and electrochemical properties of cathode materials

Milestones (FY10-11)

- Engineer, improve and evaluate the electrochemical properties and surface stability of composite electrode structures with a high Mn content – *on-going*
- Evaluate autogenic processes for coating metal oxide cathode particles with carbon and for fabricating stabilized surfaces with metal oxide and/or phosphate layers – *on-going*
- Model coatings and interfacial phenomena at the surface of LiMn_2O_4 electrodes – *on-going*
- Establish collaborative interactions with EFRC – Center for Electrical Energy Storage - *Tailored Interfaces* (Argonne-Northwestern University-University of Illinois (Urbana-Champaign) – *collaborations established*.
 - X-ray absorption studies on BATT materials at Argonne's Advanced Photon Source (APS) complement EFRC projects.



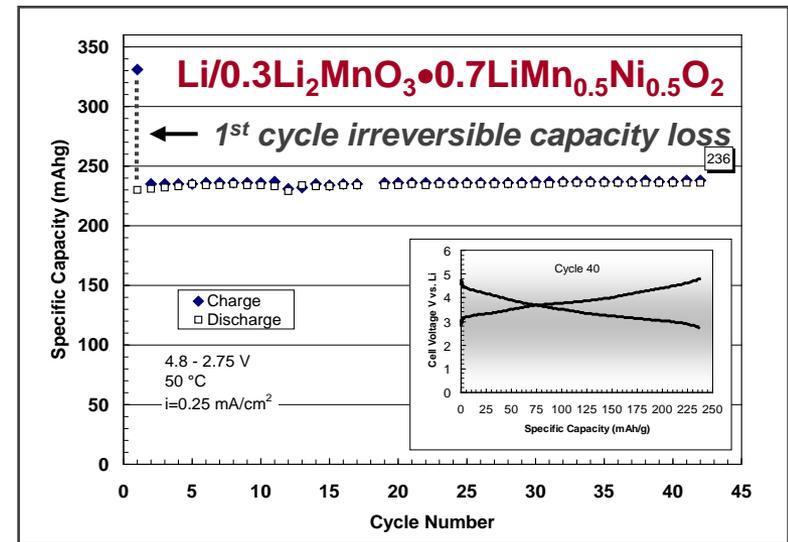
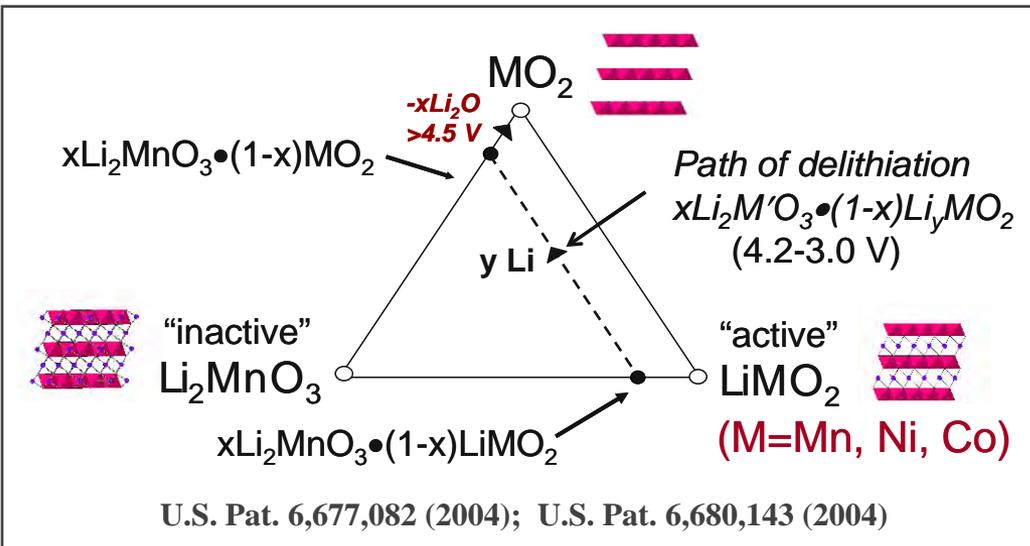
Approach

- Exploit the concept and optimize the performance of *integrated ('composite') electrodes structures*, particularly
 - (1) 'layered-layered' $x\text{Li}_2\text{MnO}_3 \bullet (1-x)\text{LiMO}_2$ (M=Mn, Ni, Co)
 - (2) 'layered-rock salt' $x\text{Li}_2\text{MnO}_3 \bullet (1-x)\text{MO}$ - **NEW**
- 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
- Explore alternative *synthesis techniques* to synthesize advanced electrode materials and surface structures and architectures
 - (1) Autogenic reactions
 - (2) Sonication - **NEW**
- Use *first principles modeling* to aid the design of bulk and surface cathode structures and to understand electrochemical phenomena



'Composite' $x\text{Li}_2\text{MnO}_3 \bullet (1-x)\text{LiMO}_2$ Electrodes

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

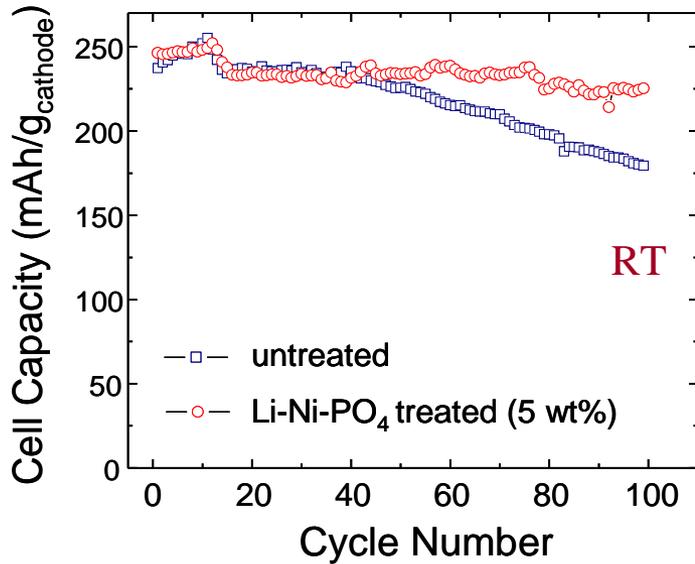


Recap of typical performance:

- 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.



$0.5\text{Li}_2\text{MnO}_3 \bullet 0.5\text{LiNi}_{0.44}\text{Co}_{0.25}\text{Mn}_{0.31}\text{O}_2$ Electrodes

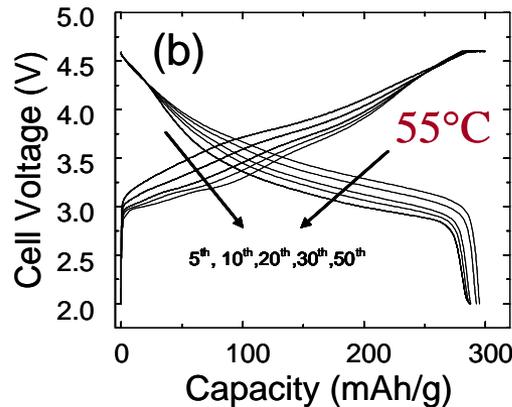
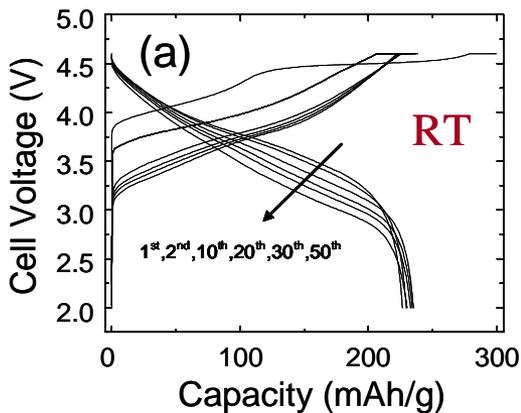


Previous approach:

- Use Li-Ni-PO_4 as a solid electrolyte below 5.0 V to protect the electrode surface at high potentials ($4.2 < V < 4.8$)
- Surface coating enhances cycling stability (4.6 – 2.0 V, 0.1 mA/cm²)
- 200 mAh/g achieved at C/1 rate

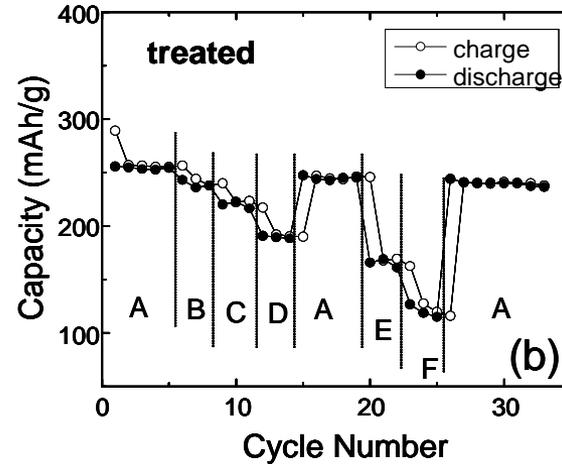
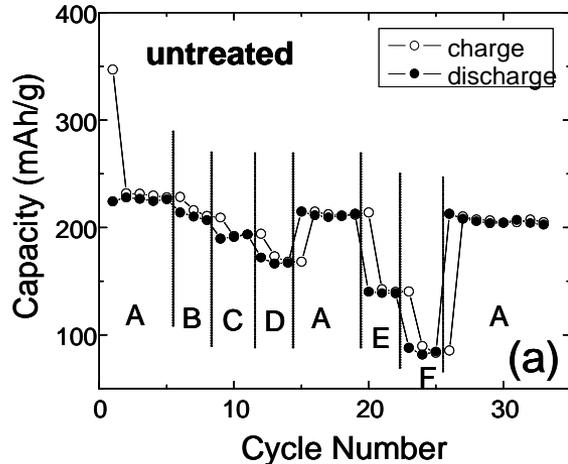
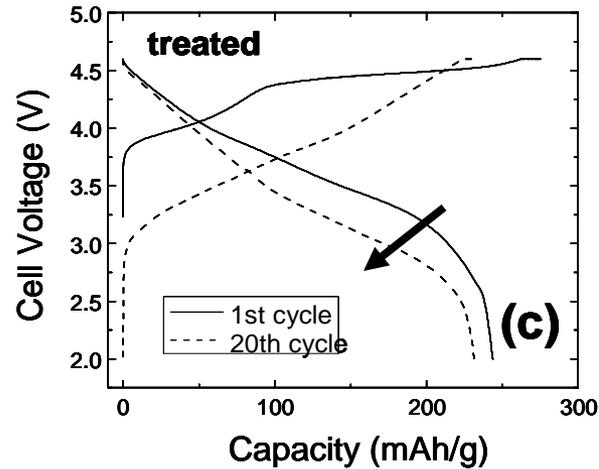
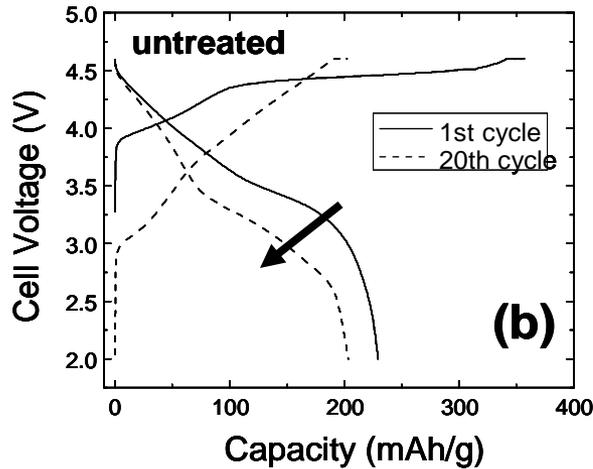
BUT

Untreated Electrodes



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

$0.5\text{Li}_2\text{MnO}_3 \bullet 0.5\text{LiCoO}_2$ Electrodes



A: 15 mA/g
B: 30 mA/g
C: 75 mA/g
D: 150 mA/g
E: 300 mA/g
F: 750 mA/g

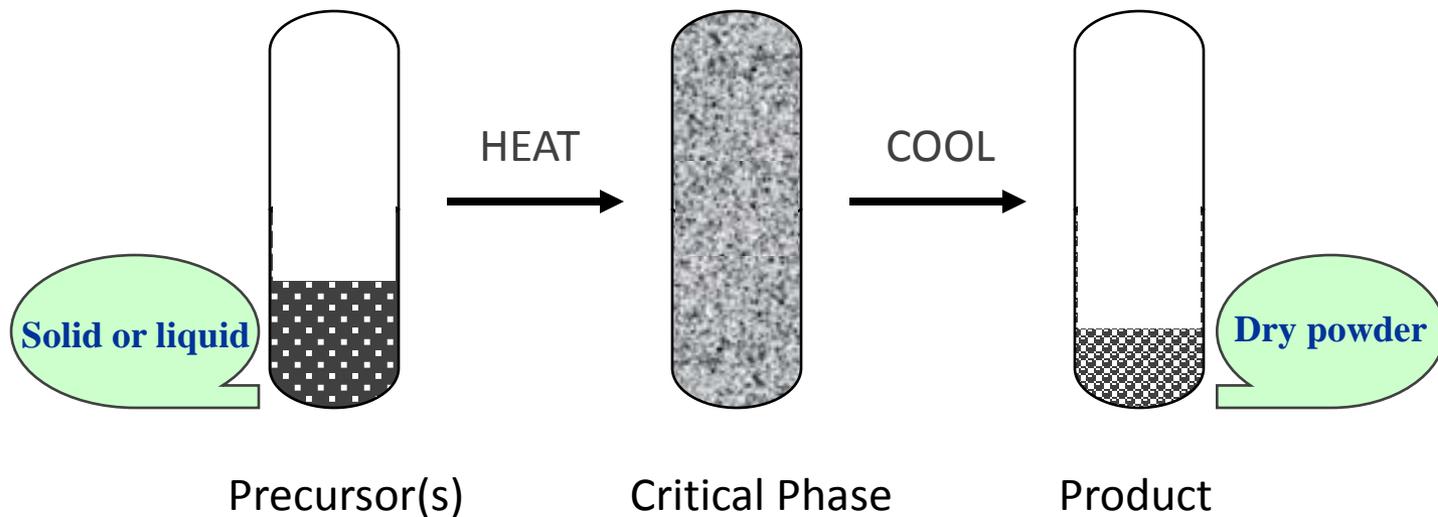
- Li-Ni-PO_4 surface treatment improves rate capability and suppresses the voltage decay - but not adequately



Surface Treatment Using Aggressive Reactions

Li-Ni-PO_4 -treated $0.5\text{Li}_2\text{MnO}_3 \bullet 0.5\text{LiNi}_{0.44}\text{Co}_{0.25}\text{Mn}_{0.31}\text{O}_2$ (NMC)

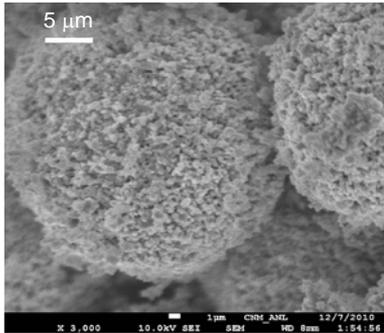
1. Autogenic Reactions: Self-generating reactions that occur within an enclosed vessel typically at high pressure and temperature



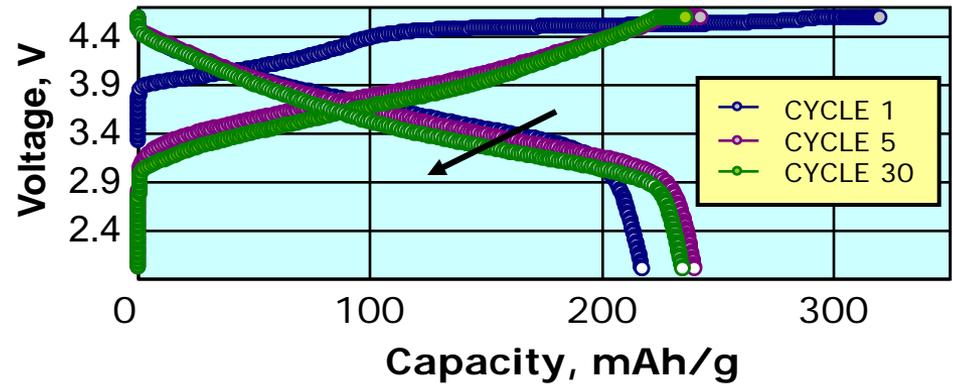
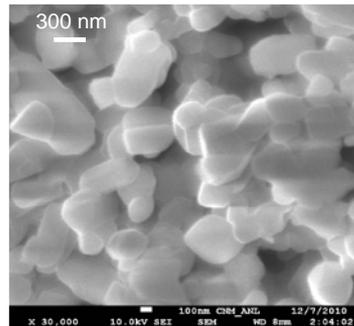
- Proven technique for producing carbon coatings, e.g. C-TiO₂
- $0.5\text{Li}_2\text{MnO}_3 \bullet 0.5\text{LiNi}_{0.44}\text{Co}_{0.25}\text{Mn}_{0.31}\text{O}_2$ reacted with LiH_2PO_4 and Ni-acetate tetrahydrate (1:1 ratio, 5 wt%) in autogenic reactor
- Ar atmosphere, 700 °C, 20 min (low pressure)

Surface Treatment Using Aggressive Reactions

SEM

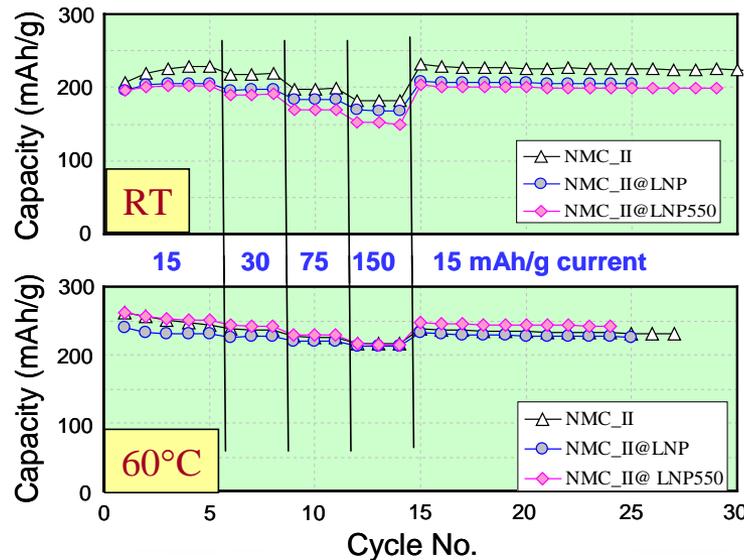
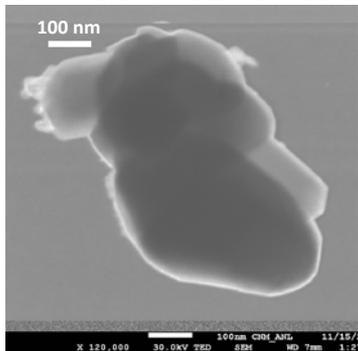


Untreated NMC particles and electrochemistry



Li-Ni-PO₄-treated NMC particles and electrochemistry

TEM

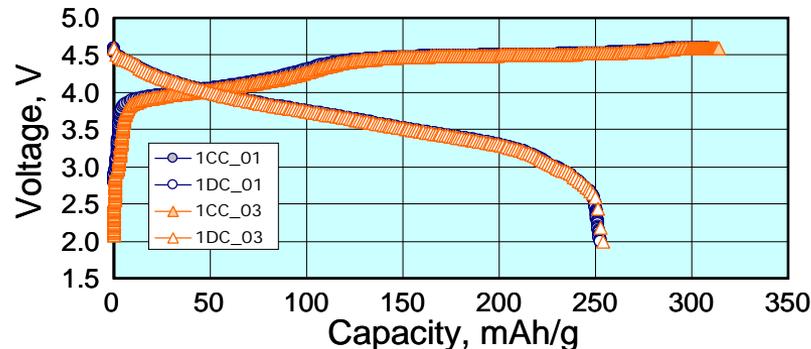
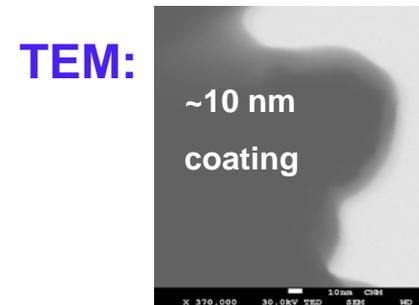
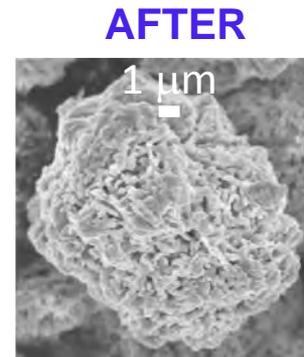
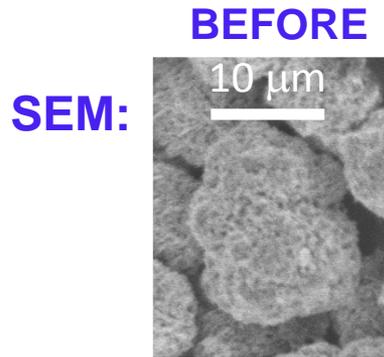
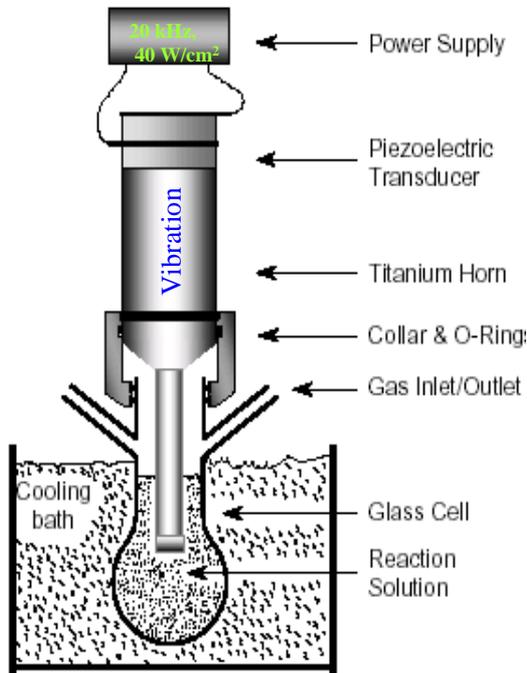
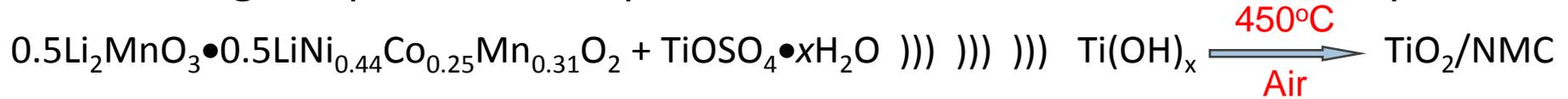


- NMC particle morphology unaffected by treatment
- No significant impact on electrochemical behavior observed using autogenic coating reactions
- Investigations of surface in progress

Surface Treatment Using Aggressive Reactions



2. Sonication: Formation \rightarrow growth \rightarrow implosive collapse of bubbles, locally increasing temperature and pressure. Can it be used to coat nanoparticles ?

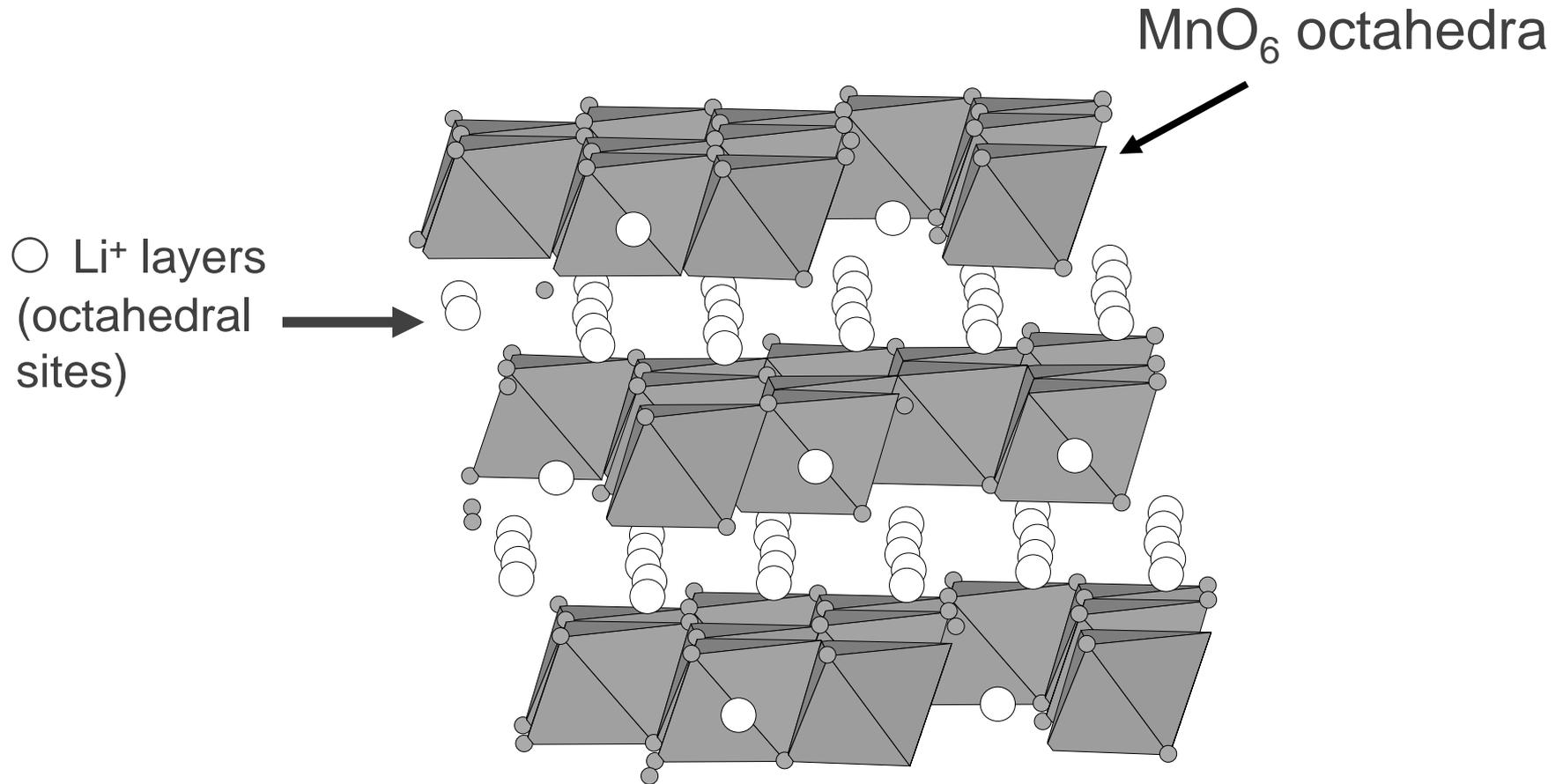


- Promising initial data (duplicate)

Stabilization of Composite Bulk Structures

- Exploration of new ion-exchange approach to fabricate Li_2MnO_3 -stabilized composite electrode structures
- Ion-exchange reactions with Na precursors well known:
 - Delmas, Bruce – Layered LiMnO_2 from NaMnO_2 (transforms to spinel)
 - Ceder – Layered $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ from $\text{NaMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$
 - Johnson – ‘Layered-spinel’ from $\text{Na}_{1-x}\text{Li}_y\text{Mn}_{0.75}\text{Ni}_{0.25}\text{O}_2$
 - Non-aqueous medium used
- Alternative strategy:
 - Use Li_2MnO_3 as the precursor
 - Effect M^+ ion-exchange reactions in an acidic environment, followed by a heat-treatment step to form composite electrode structures.
 - Versatile, simple and inexpensive approach – can target ‘layered-layered’, ‘layered-spinel’ and new ‘layered-rocksalt’ compositions, $x\text{Li}_2\text{MnO}_3 \bullet (1-x)\text{MO}$ (e.g., $\text{M}=\text{Ni}, \text{Co}$)

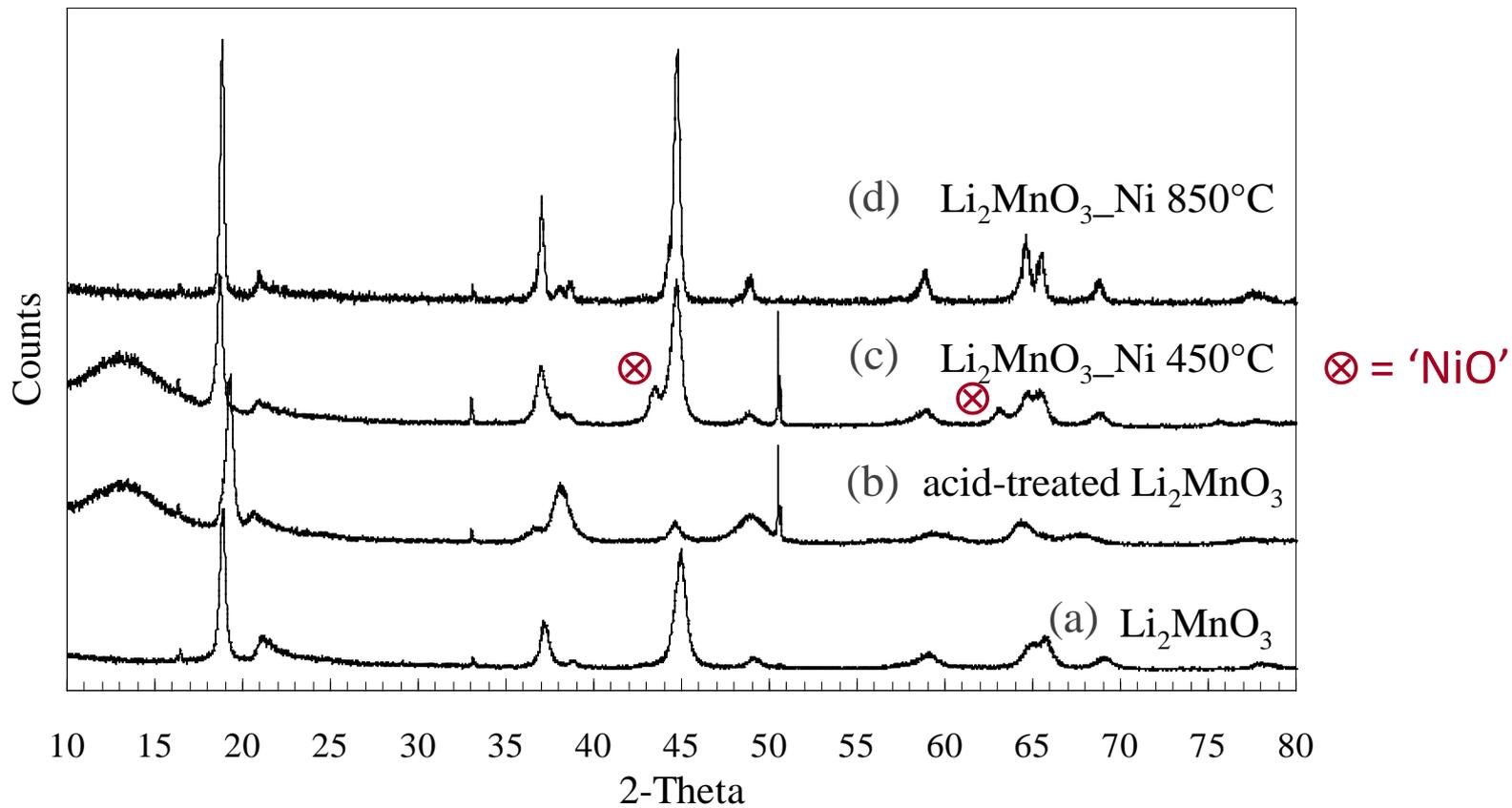
The Li_2MnO_3 ($\text{Li}[\text{Li}_{1/3}\text{Mn}_{2/3}]\text{O}_2$) Structure



- M^{2+} -ion exchange into Li^+ sites of transition metal layers seems possible
- Extent of ion-exchange controls the structure/composition of the product

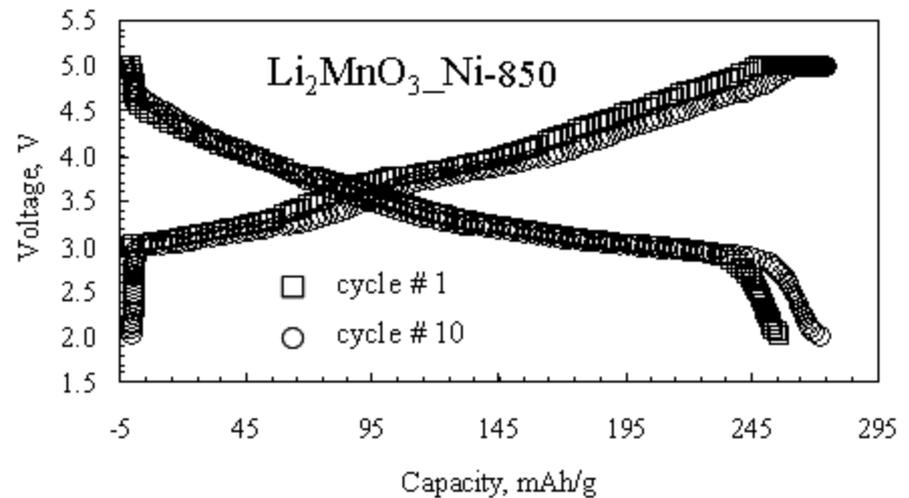
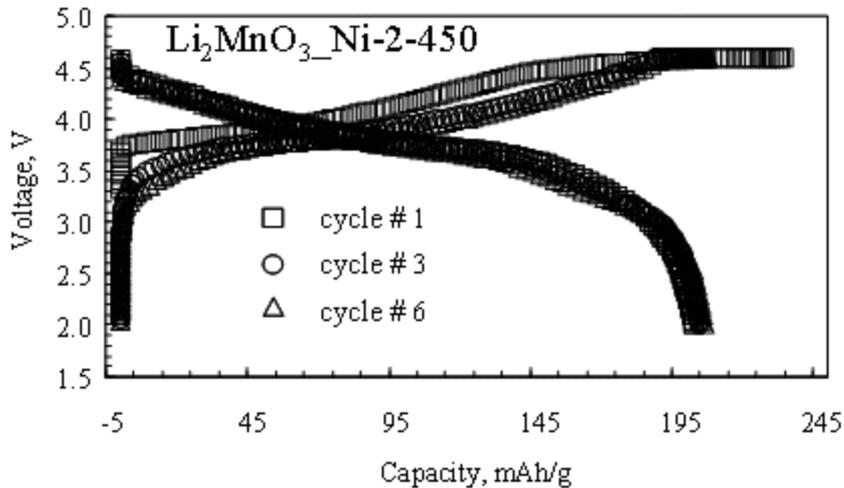


XRD Patterns: Li_2MnO_3 -Ni Composite Structures



- “ Li_2MnO_3 -Ni 450” indicative of ‘layered-rock salt’ (Li_2MnO_3 -NiO’) structure
- Structural formation likely to go through $\text{H}[\text{Li}_{1/3}\text{Mn}_{2/3}]\text{O}_2$ intermediate
- “ Li_2MnO_3 -Ni 850” indicative of ‘layered-layered’ composite structure

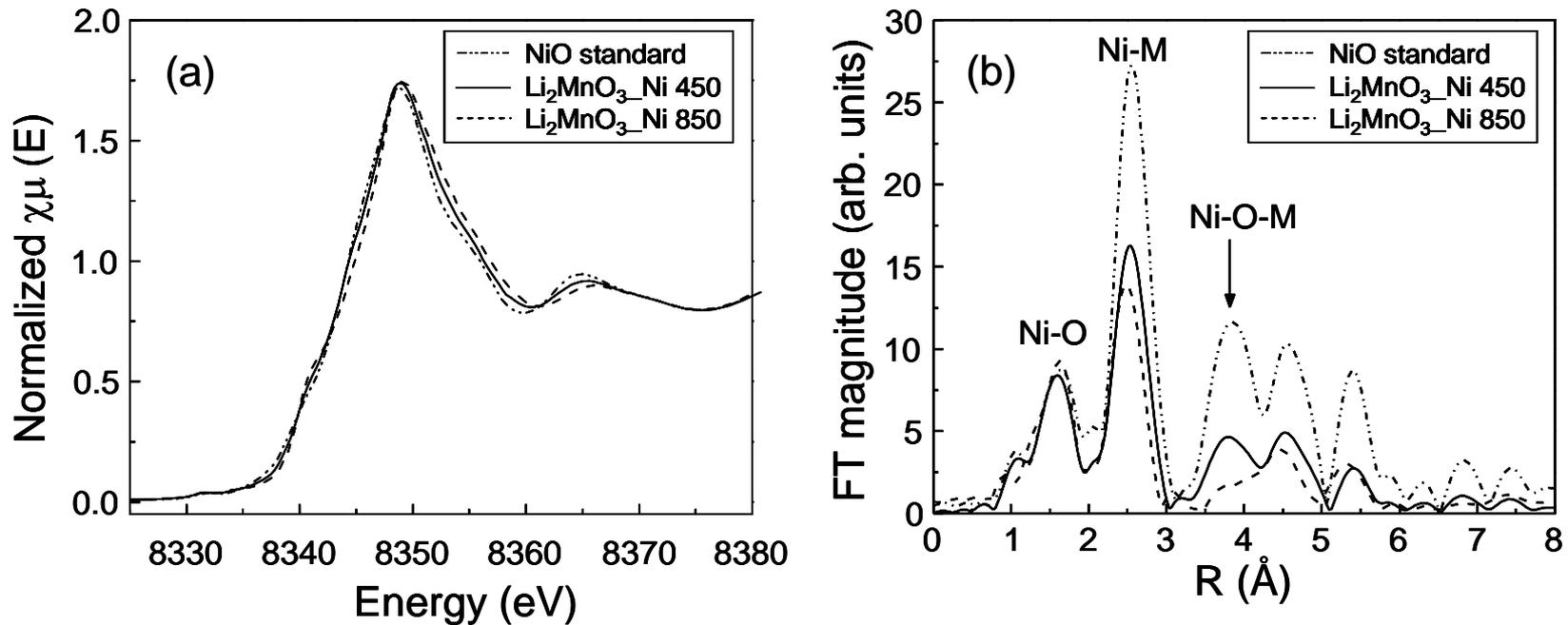
Electrochemistry: 'Li₂MnO₃_Ni' Electrodes



- Earlier indications suggest that $\text{Li}_2\text{MnO}_3\text{-Ni}$ electrodes with a stabilizing MO component may provide improved discharge voltage profile stability over conventional composite materials when activated at high potentials
- Average potential of layered-layered " $\text{Li}_2\text{MnO}_3\text{-Ni 850}$ " electrode lower than that of layered-rocksalt " $\text{Li}_2\text{MnO}_3\text{-Ni 450}$ "
- Extent to which NiO domains convert to $\text{LiMn}_{1-x}\text{Ni}_x\text{O}_2$ is T dependent

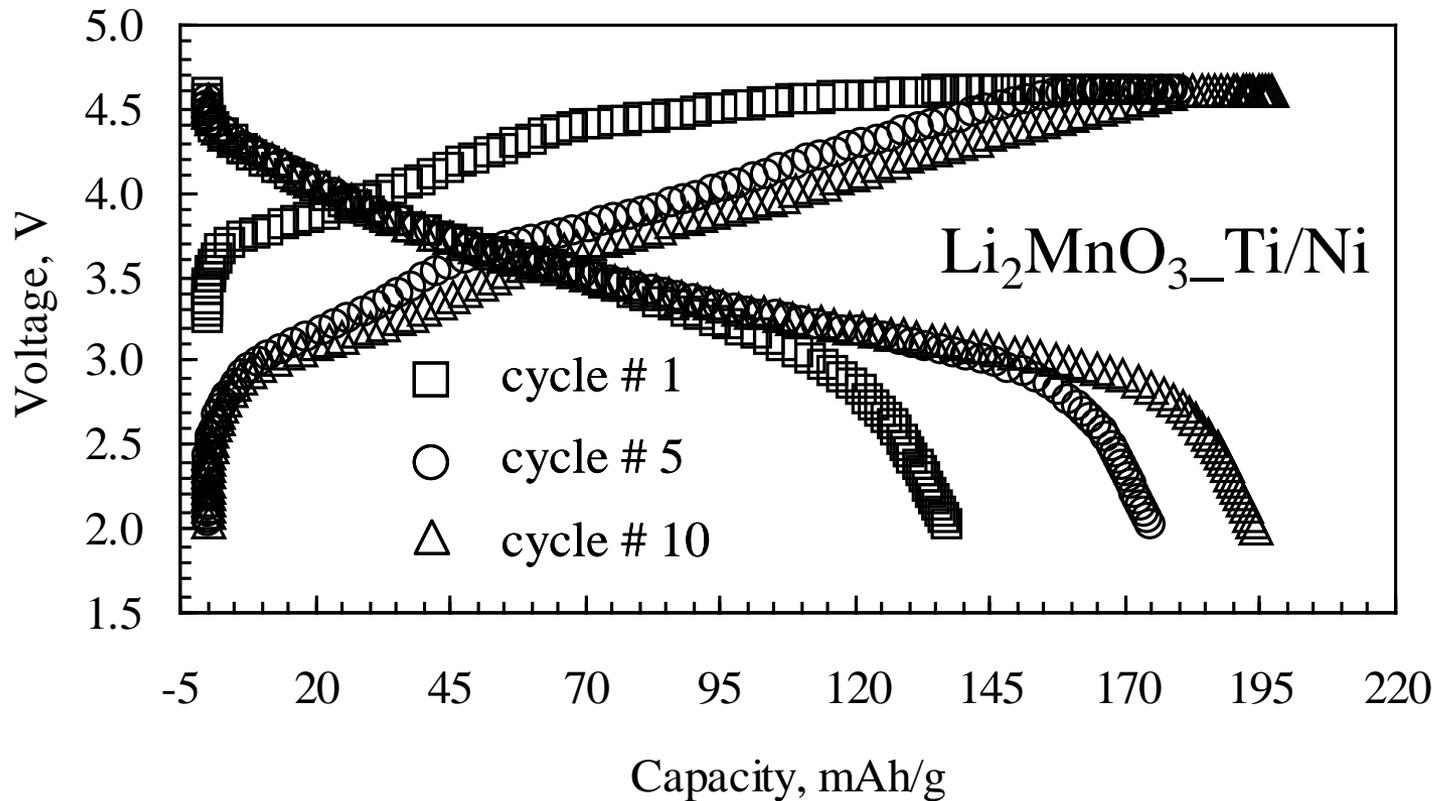


X-ray Absorption Spectroscopy: 'Li₂MnO₃_Ni'



- Ni-K XANES showing Ni predominantly in the 2+ state, in all compounds: NiO (standard), Li₂MnO₃_Ni 450 and Li₂MnO₃_Ni 850 in (a)
- Magnitude of the Fourier transformed Ni K-edge EXAFS, showing Ni-O, Ni-M and Ni-O-M correlations, the latter from local rocksalt-like corner-shared configurations in (b)

Electrochemistry: 'Li₂MnO₃_Ti/Ni' Electrodes

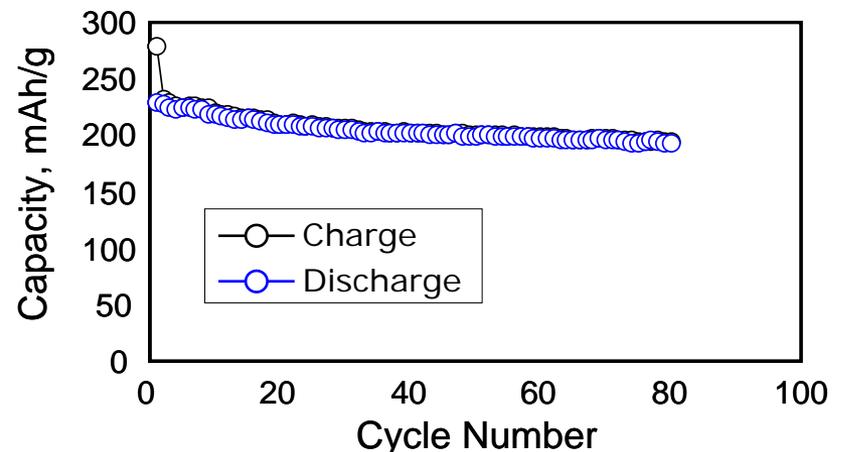
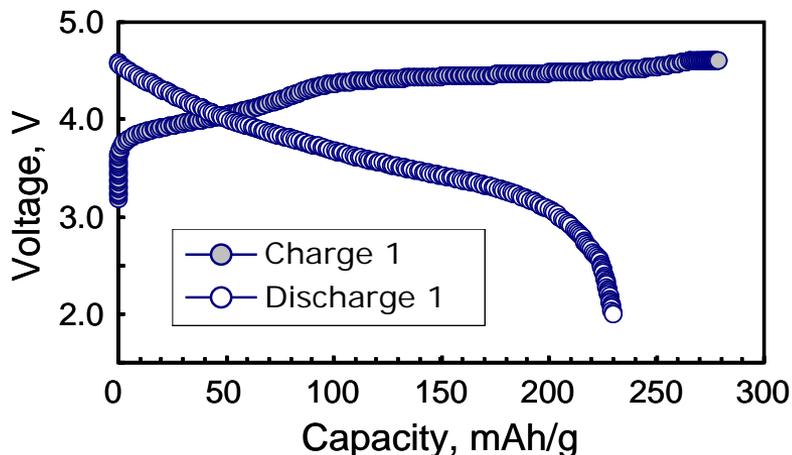


- Break-in cycles required for Ti-substituted Li_{2-x}Ti_xMnO₃-Ni 450 electrode
- Similar, stable voltage profile observed to Li₂MnO₃-Ni 450 electrode

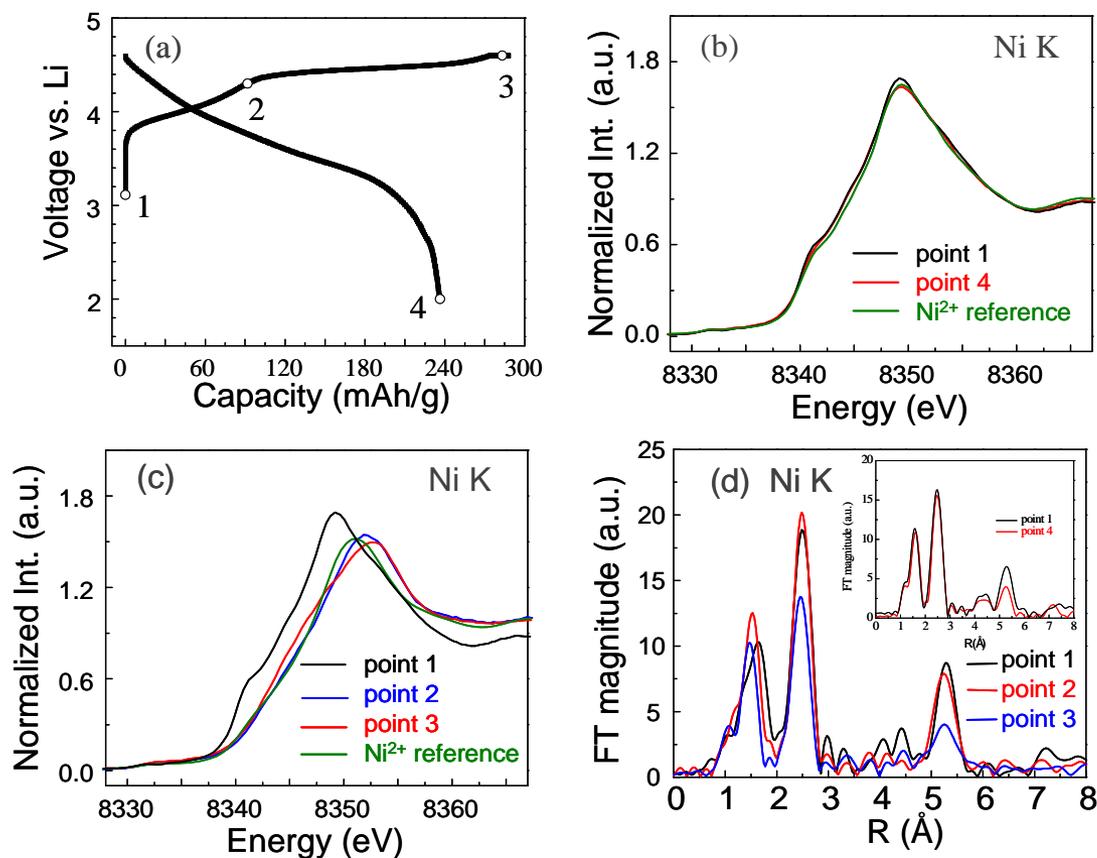


Versatility of Approach

- Stabilizing cations and anions for surface protection can be added to the solution – one shot process, e.g., $\text{Li}_2\text{MnO}_3\text{-Ni-Li}_3\text{PO}_4$
- Li_2MnO_3 precursor project forms basis for FY2012 BATT cathode proposal
- Wide scope and possibilities
- Compare with earlier coating procedures (2-step sol gel precipitation of Li-Ni-PO_4 on composite electrode structures)



XAS Studies: Li-Ni-PO_4 coated $\text{Li}_2\text{MnO}_3 \bullet \text{LiCoO}_2$



- XAS data collected ex situ at 4 points on charge-discharge curve (a)
- XANES data show Ni^{2+} at the start of charge and end of discharge (b)
- XANES data show oxidation of Ni^{2+} to Ni^{3+} during charge
- FT data show that Ni^{2+} ions are incorporated in the transition metal layers during the coating process

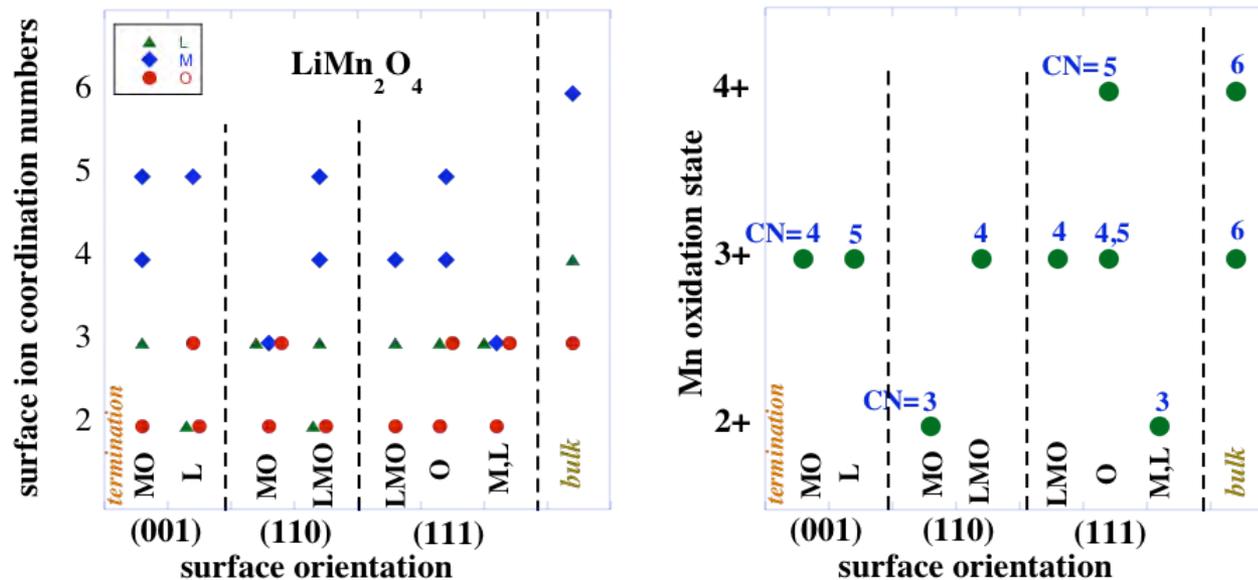
- 550 °C coating is not present as LiNiPO_4 : Li_3PO_4 or substituted derivative?



Theory: Surface Structure of LiMn_2O_4

Influence on chemical and electrochemical properties

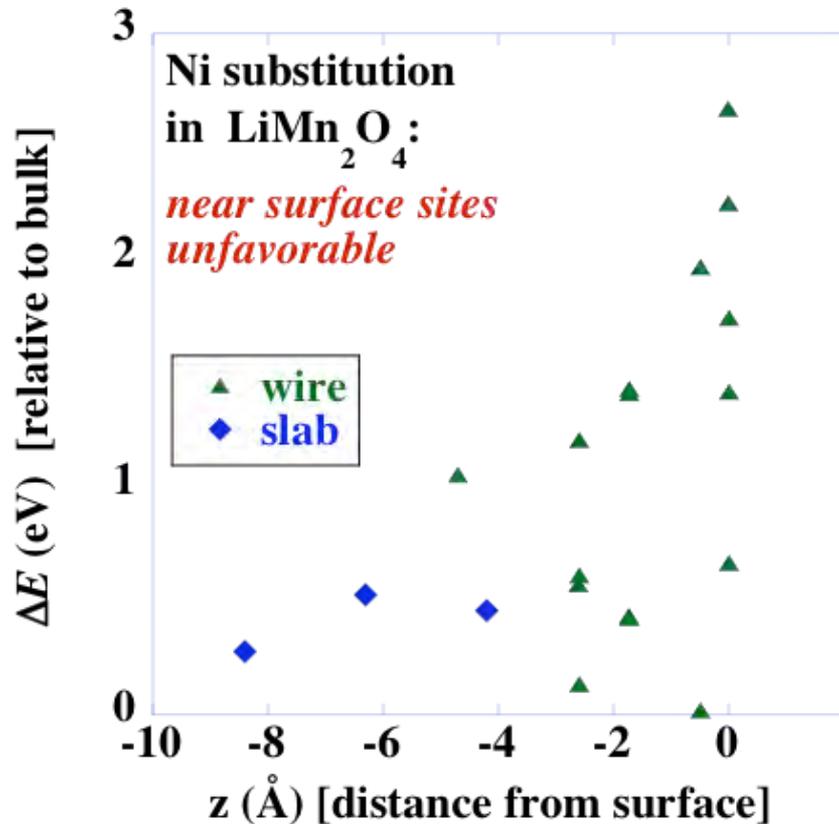
- Simulations of LiMn_2O_4 surfaces, both pristine and Ni-doped



- Left: Surface ion coordination numbers as a function of surface orientation, relative to the bulk.
- Right: Lower coordination numbers yield lower Mn oxidation states
- Most Mn ions near surface are trivalent, enhancing solubility

Theory: Surface Structure of LiMn_2O_4

Influence on chemical and electrochemical properties



- Energy of Ni-ion substitution for Mn at surface relative to the bulk
- In bulk, Ni^{2+} charge is compensated by Mn^{4+}
- Near surface, Mn prefers trivalent state, making substitution unfavorable, explaining the positive substitution energies at the surface
- Erosion of the Mn-rich layer to expose Ni-rich regions would be expected to provide some protection to further dissolution

Future Work - FY2011/FY2012

- Continue to exploit and optimize various composite electrode structures (composition and performance) with the goal of reaching/exceeding the energy and power goals required for 40-mile PHEVs and EVs. Exploit new $x\text{Li}_2\text{MnO}_3 \bullet (1-x)\text{MO}$ systems.
- Focus on the stabilization of both surface and bulk structures. Use complementary experimental and theoretical approaches to improve the surface stability, rate capability and cycle life of high capacity Mn-rich oxide electrodes at high potentials.
- Further explore sonication to fabricate and evaluate stable surface architectures.
- Continue EFRC-related work and interact with energy storage Centers.



Summary

- Efforts were continued to stabilize the surface and bulk properties of high-capacity, composite electrode structures.
- A new route to processing composite electrode structures using a Li_2MnO_3 precursor and ion-exchange reactions was demonstrated. The process has the potential for fabricating surface-protected electrodes in a single step.
- A new family of 'layered-rock salt' $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{MO}$ electrode structures (e.g., $\text{M}=\text{Mn}, \text{Ni}, \text{Co}$) that show potential for providing enhanced structural and electrochemical stability was identified and evaluated.
- Autogenic and sonication reactions were evaluated for fabricating surface-stabilized electrode particles. Initial data showed that the latter technique, in particular, has the potential for significantly impacting and advancing the surface properties of metal oxide electrodes.
- Simulation of Ni-substituted LiMn_2O_4 structures has provided valuable insight into surface ion coordination and Mn oxidation states that impact solubility.

Acknowledgment

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