Cathodes

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Annual Merit Review
DOE Vehicle Technologies Program

Washington, D.C.
June 7, 2010

ES049

Overview

Timeline

- Start date: FY09
- End date: On-going
- Percent complete:

  - project on-going

Budget

- Total project funding

  - 100% DOE
- FY09: $300K
- FY10: $300K

Barriers Addressed

- Low energy
- Cost
- Abuse tolerance limitations

Partners

- Co-investigators:
  - S.-H. Kang, R. Benedek, V. G. Pol, C. Johnson, J. T. Vaughey (ANL)
- Collaborators:
  - Y. Shao-Horn, C. Carlton (MIT)
  - M. Balasubramanian (APS- ANL)
  - V. Battaglia (LBNL), Jose M. Calderon-Moreno (Romanian Academy)

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 (FY09-10)

- Synthesize, evaluate and optimize high capacity Mn-based cathodes (>200 mAh/g, >3 V) – *on going*
- Engineer and evaluate the electrochemical effects of protective coatings on composite electrode structures with a high Mn content at high potentials (>4.2 V) – *on going*
- Model interfacial structures and dissolution phenomena – *complete for $LiMn_2O_4$ electrodes*
- Evaluate single-step, autogenic processes for synthesizing new (or improved) materials, cathode coatings and architectures – *studies initiated*
- Establish collaborative interactions with EFRC – Center for Electrical Energy Storage - *Tailored Interfaces* (Argonne-Northwestern University-University of Illinois (Urbana-Champaign) – *collaborations initiated*

Approach

- Exploit the concept and optimize the performance of structurally-integrated, high-capacity electrodes, particularly 'layered-layered' $xLi_2MnO_3 \bullet (1-x)LiMO_2$ (M=Mn, Ni, Co) electrodes (Task 1)

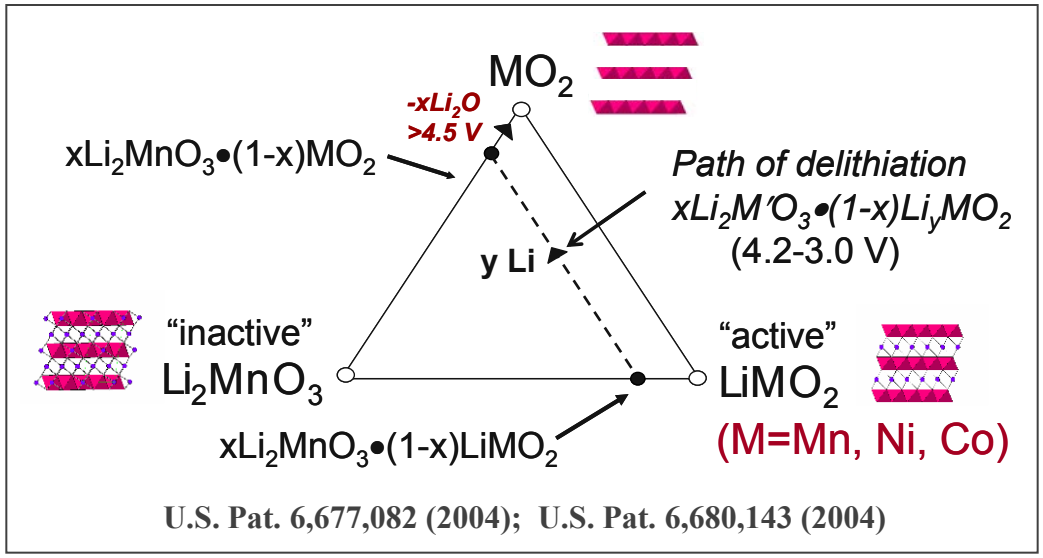
- Design effective surface structures to protect the underlying metal oxide particles from the electrolyte and to their improve rate capability when charged (delithiated) at high potentials (Task 1)

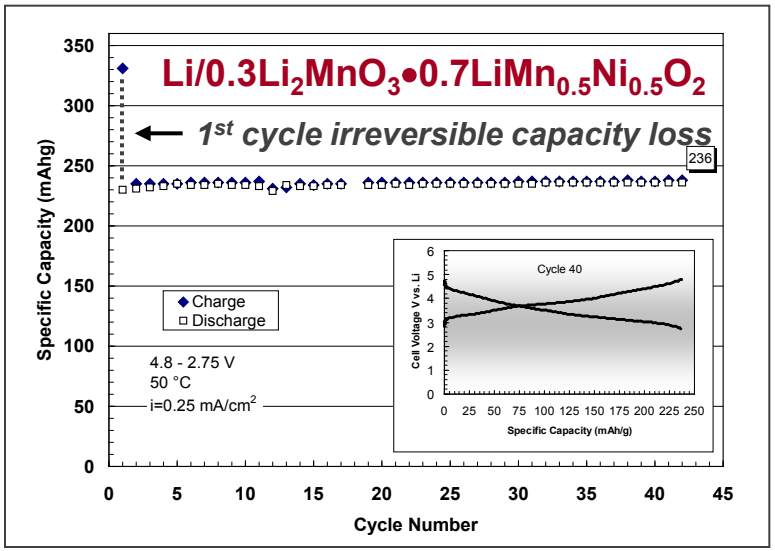
- Explore autogenic (i.e., high pressure, solventless) reactions to synthesize advanced electrode materials and surface structures with new architectural designs (Task 2)

- Use first principles modeling to aid the design of bulk and surface cathode structures and to understand electrochemical phenomena (Task 3)

1. $xLi_2MnO_3 \bullet (1\text{-}x)LiMO_2$ Electrodes

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





Recap of typical performance:

- 200-250 mAh/g achieved at C/3 rate (50 °C)
- Lower capacity at RT
- Charging electrodes to high potential (>4.4 V) damages the electrode surface and reduces their rate capability

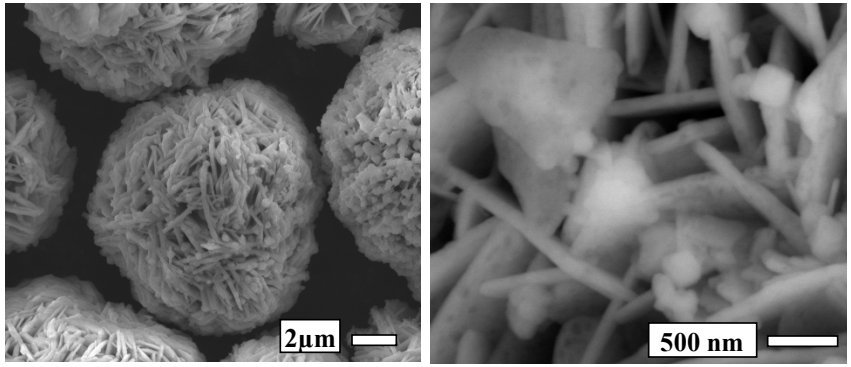
Li-Ni-PO_4 Treatment

($0.5Li_2MnO_3 \bullet 0.5LiNi_{0.44}Co_{0.25}Mn_{0.31}O_2$ Electrodes)

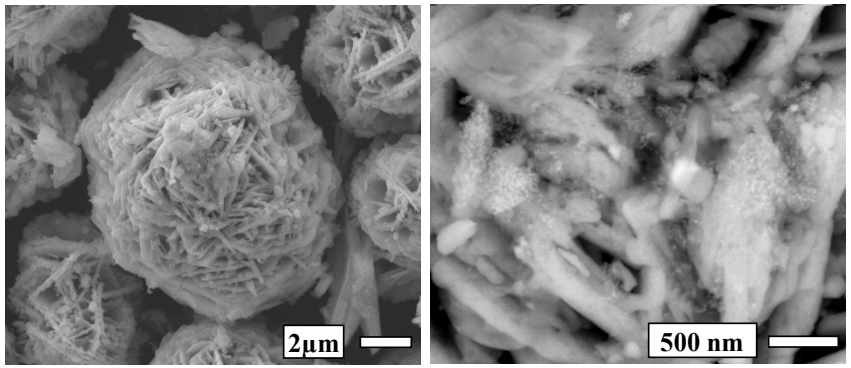
- Concept: Use Li-Ni-PO_4 as a solid electrolyte below 5.0 V to protect the $xLi_2MnO_3 \bullet (1\text{-}x)LiMO_2$ electrode surface at high potentials and to improve rate capability

- Sol-gel technique (pH<4) used to etch and coat the electrode

- Theoretical modeling discounts the possibility of a defect $Li_{3-2x}Ni_xPO_4$ (Li_3PO_4-type) surface structure (EFRC interaction – Shin, Wolverton, Northwestern University)

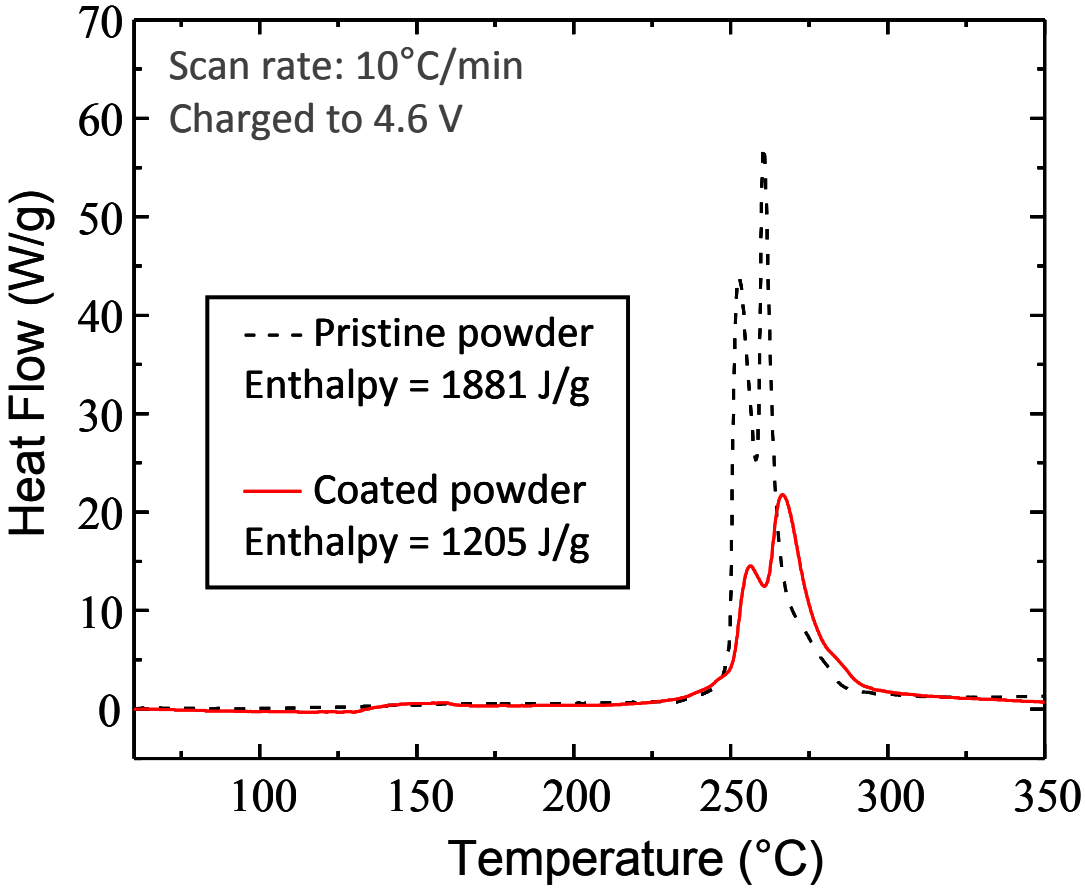


untreated



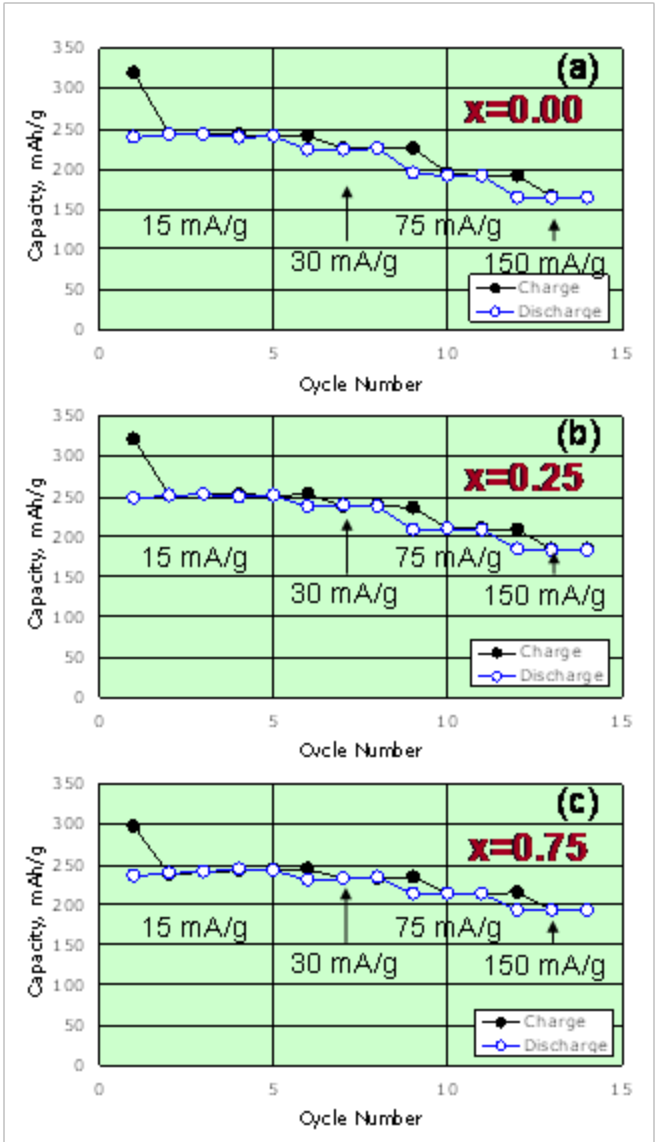
treated

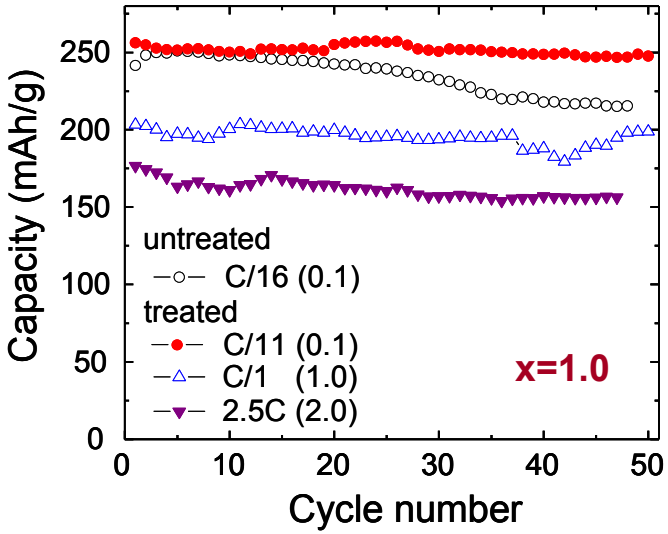
Thermal Stability of Untreated and Li-Ni-PO_4 Treated $0.5Li_2MnO_3 \bullet 0.5LiNi_{0.44}Co_{0.25}Mn_{0.31}O_2$ Electrodes



- DSC data show that surface-protected electrodes, charged to 4.6 V, are more tolerant to temperature excursions in the electrolyte (1.2 M $LiPF_6$ in EC:EMC)

Rate capability of $Li_{3-2x}Ni_xPO_4$-treated electrodes





- The rate capability increases as a function with increasing Ni content, x
- Li_3PO_4 (x=0) provides the most resistive layer at 150 mA/g (~C/1 rate)
- All $Li_{3-2x}Ni_xPO_4$-treated electrodes cycle with near 100% cycling efficiency, unlike the parent, untreated electrode (98.7%)
- Electrodes (x=1) meet the 200 mAh/g, C/1 rate, 3.5 V average, capacity/power yardstick for a 20-40 mile range PHEV at room temperature

$xLi_2MnO_3 \bullet (1-x)LiMO_2$ Electrodes

Evaluation against $Li_4Ti_5O_{12}$ and TiO_2 Anodes for Safe Li-Ion Cells

Opportunity:

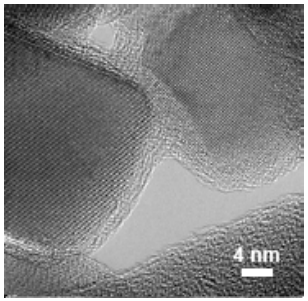
TiO_2 electrodes offer a significantly higher theoretical capacity (335 mAh/g) compared to $Li_4Ti_5O_{12}$ (175 mAh/g)

$Li_4Ti_5O_{12}$ (LTO) Cells

- Two sets of $0.5Li_2MnO_3 \bullet 0.5LiNi_{0.44}Co_{0.25}Mn_{0.31}O_2$ electrodes with loadings of 2.1 and 3.1 mg/cm^2 were prepared with 100-µm and 125-µm blades (ANLCC100 and ANLCC125, respectively).
- LTO/ANLCC125 – anode limited
- LTO/ANLCC100 – cathode limited

Carbon-coated TiO_2 (TiO_2-C) Cells

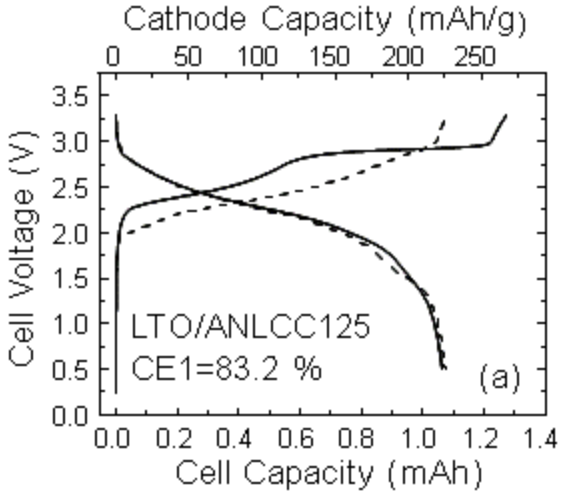
- Carbon-encapsulated anatase (TiO_2-C) product synthesized by an autogenic process (EFRC interaction)
- TiO_2-C product evaluated against ANLCC100 and ANLCC125, as above
- TiO_2-C/ANLCC125 – anode limited; TiO_2-C/ANLCC100 – cathode limited

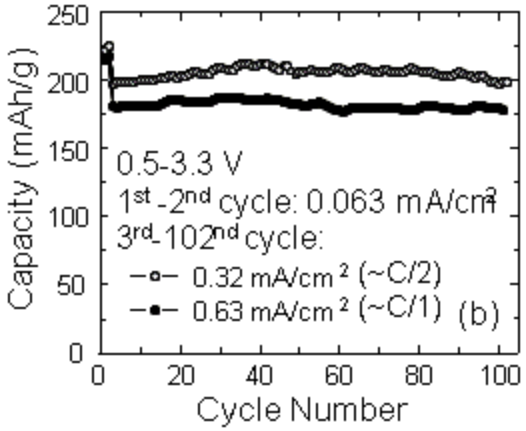


Electronically-interconnected TiO_2-C nanoparticles

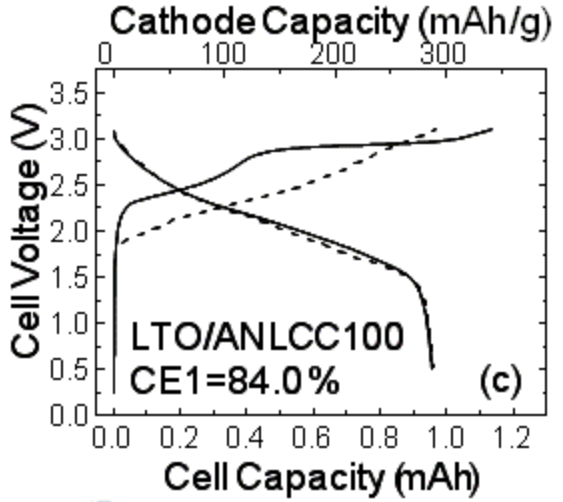
$Li_4Ti_5O_{12}/xLi_2MnO_3 \bullet (1-x)LiMO_2$ Cells

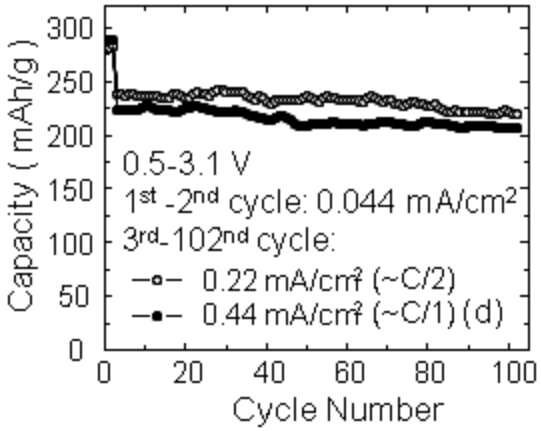
Anode-limited





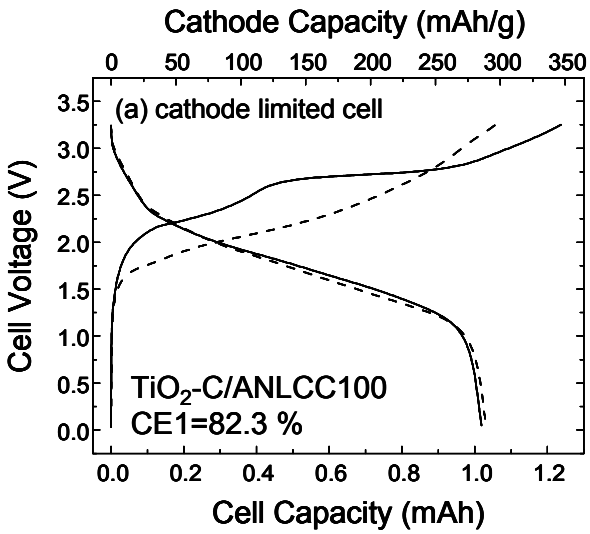
Cathode-limited

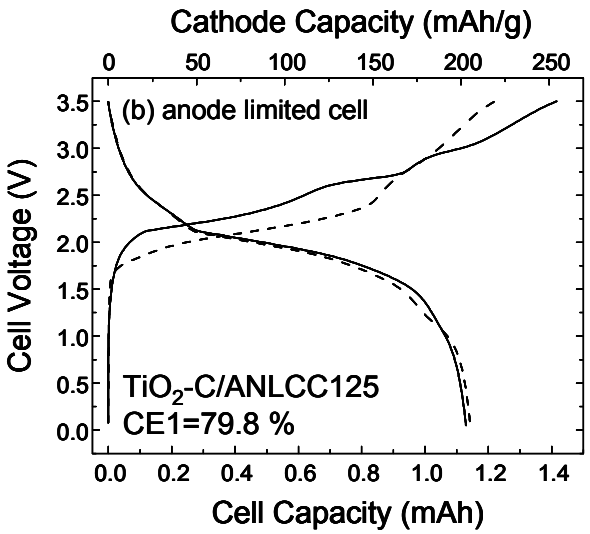


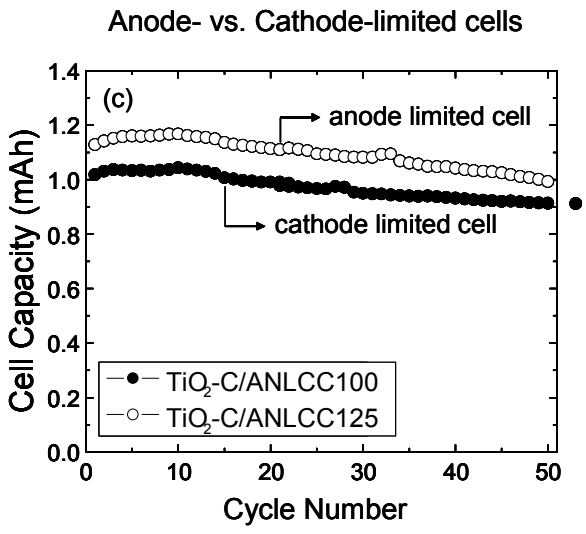


- Two formation cycles used to activate cathodes (C/11-C/16).
- Cells cycled 100 times at 8 to 16 times the formation rate.
- Anode-limited cells showed superior cycling stability. When discharged at ~C/1, the cathodes delivered ~175 mAh/g in anode-limited cells and >200 mAh/g in cathode-limited cells.
- The data bode well for developing higher energy Li-ion cells than those offered by the $Li_4Ti_5O_{12}/Li_{1+x}Mn_{2-x}O_4$ 'spinel-spinel' system, without compromising too heavily on power.

TiO_2-C/xLi_2MnO_3•(1-x)$LiMO_2$ Cells



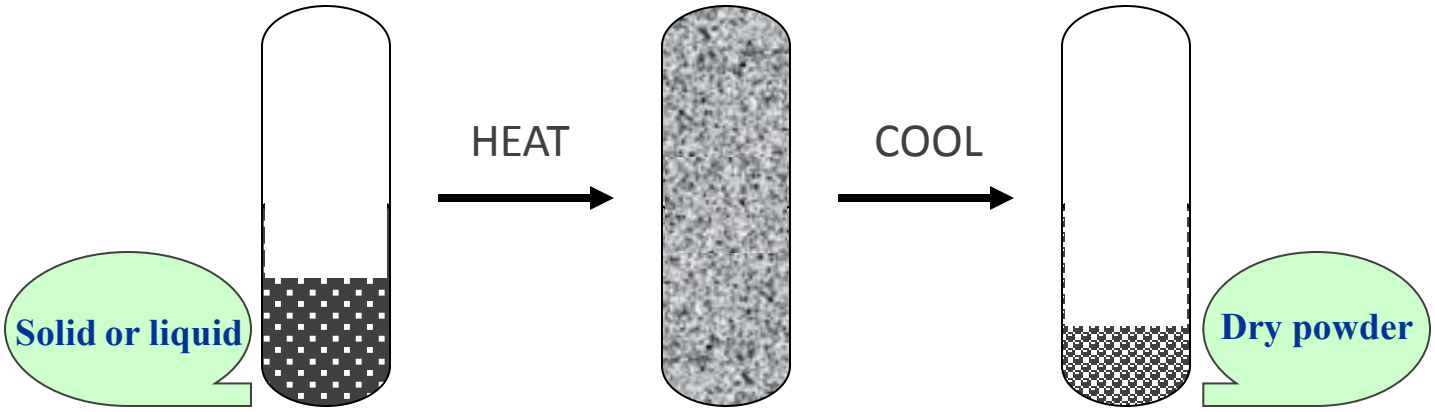




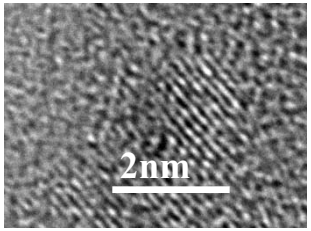
- Voltage profiles of TiO_2-C/ANL-NMC cells are similar to $Li_4Ti_5O_{12}$/ANL-NMC cells.
- TiO_2-C/ANL-NMC cells operate at slightly lower voltage because the TiO_2-C anode has a higher redox potential (~1.8 V vs. Li^0) than $Li_4Ti_5O_{12}$ (~1.55 V vs. Li^0).
- Nanoparticulate TiO_2-C anodes offer a higher rechargeable anode capacity (~200 mAh/g) compared to $Li_4Ti_5O_{12}$ cells.
- TiO_2-C/xLi_2MnO_3•(1-x)$LiMO_2$ cells show a steady capacity fade, attributed to the instability of the lithiated Li_xTiO_2 (anatase) electrode structure at high lithium loadings (x>0.5). Goal: Design improved TiO_2-based anode structures/architectures.

2. Autogenic Reactions

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



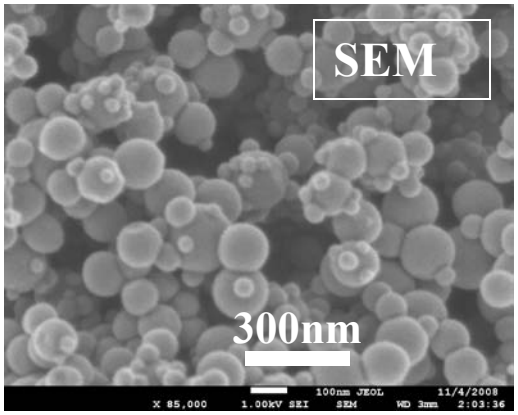
- Product highly dependent on precursor and reaction conditions
- Allyl triphenyltin [$C_{21}H_{20}Sn$] $\xrightarrow[450\ psi\ (3\ MPa)]{700\ ^oC}$ $Sn_{(s)} + C_{(s)} + H_{2\ (g)}\uparrow$

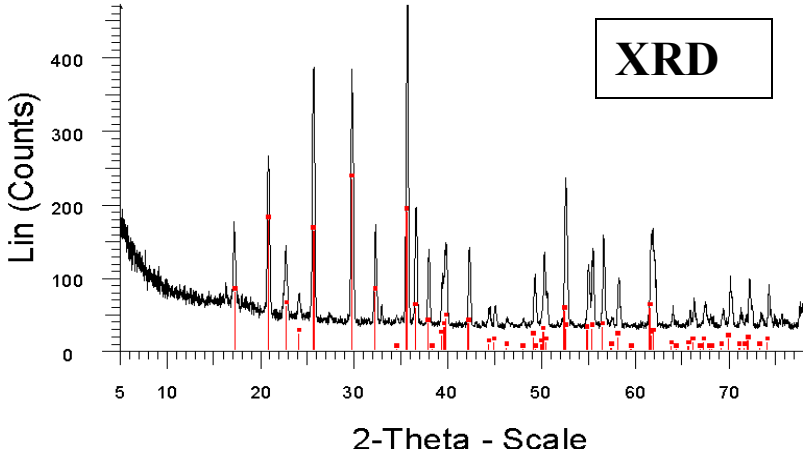


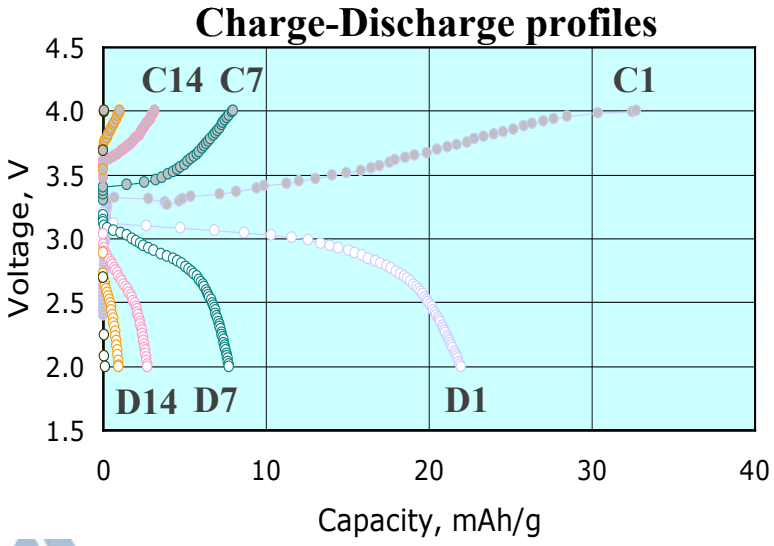
Synthesis and Properties of $LiFePO_4$

1) FeC_2O_4 precursor

$$LiH_2PO_4 + FeC_2O_4 \xrightarrow[3h]{700\ ^oC} LiFePO_4 + C + \text{gaseous product}$$





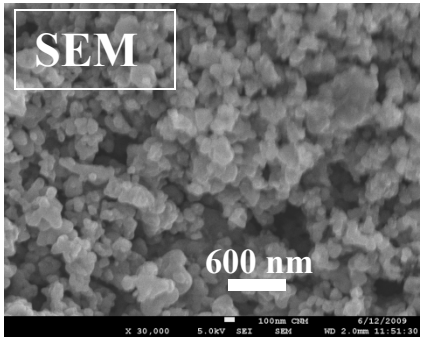


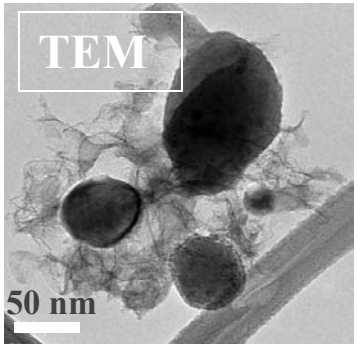
- Despite apparent single-phase, spherical character of a nano-sized $LiFePO_4$ product (containing some carbon) from a FeC_2O_4 precursor, the olivine electrode displays very poor electrochemical behavior (<20 mAh/g) at a 0.08 mA/g rate.

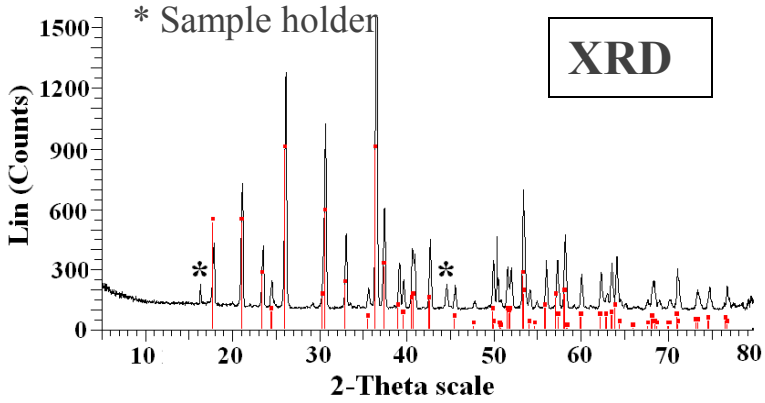
Synthesis and Properties of $LiFePO_4$

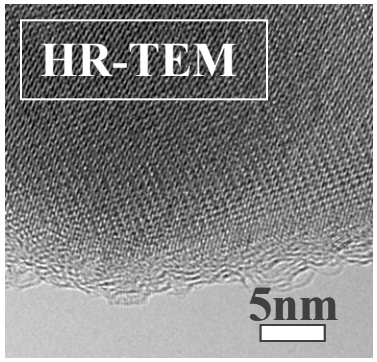
2) $FePO_4$ precursor

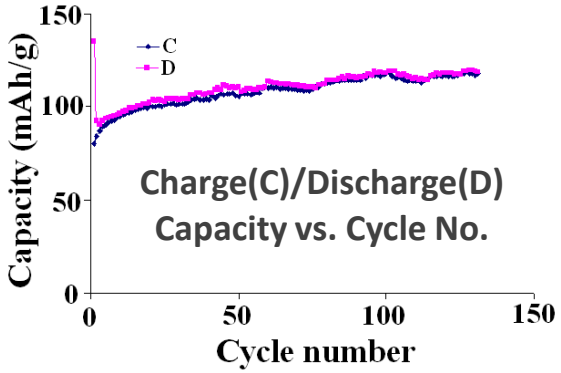
$$Li_2CO_3 + FePO_4.H_2O + C_6H_{12}O_6\ (\text{glucose}) \xrightarrow[3h]{700\ ^oC} LiFePO_4/C + \text{gaseous product}$$











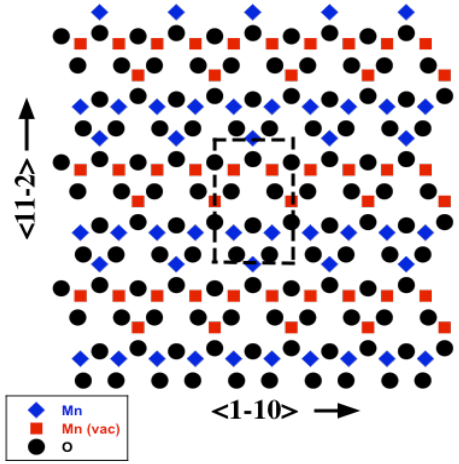
- Significantly improved electrochemical behavior obtained from single-phase, nano-sized $LiFePO_4$ particles from a $FePO_4$ and glucose precursors, the carbon-coated product delivering 100-120 mAh/g at a 0.08 mA/g rate.
- <u>Autogenic reactions to be pursued further in the search for advanced electrode materials and architectures</u>

3. Simulation of Atomic Structure and Properties of $LiMn_2O_4$ Surfaces

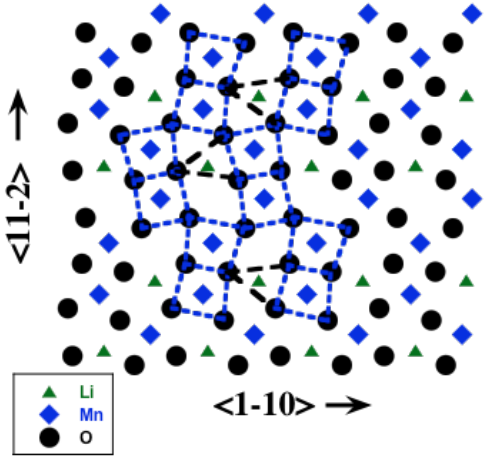
- Study motivated by the necessity to understand the surface stability of metal oxide cathodes at high potentials and implications for solubility
- Chemical and electrochemical reactions are sensitive to surface atomic structure, particularly coordination
- Focus on simulation of surface structure of $LiMn_2O_4$ ('GGA + U' level of density functional theory using VASP code)
- Consideration given to Mn- and MnO-terminated surfaces
- Classical-potential simulations of $MgAl_2O_4$ spinel have shown that the (001) surface is lowest in energy, followed by (110) and (111)
- Radical reconstruction is predicted for Mn-terminated (111) surface, in which the top layers mix to form a stoichiometric Li-Mn-O termination layer
- Surface reconstruction of (111) minimizes under-coordination of surface Mn, O
- Surface Mn ions are reduced
- Despite under-coordination of flat surfaces (terraces), dissolution may require additional defects, such as non-bridging O

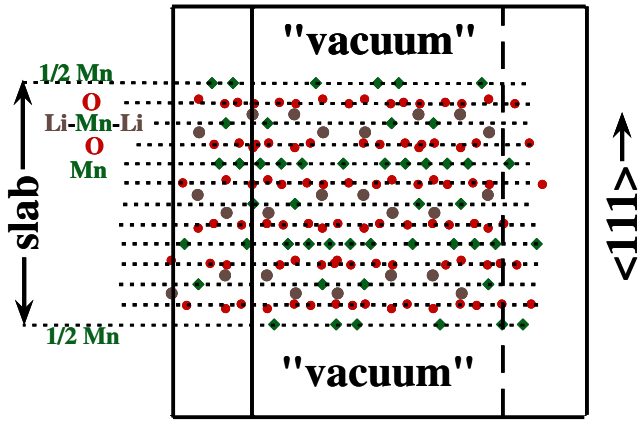
Unreconstructed and Reconstructed (111) Surfaces

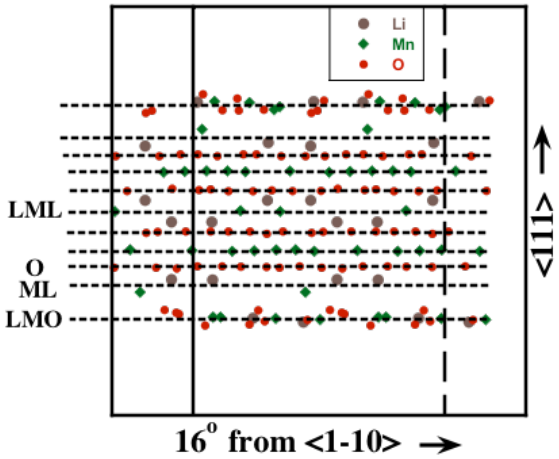
Unreconstructed



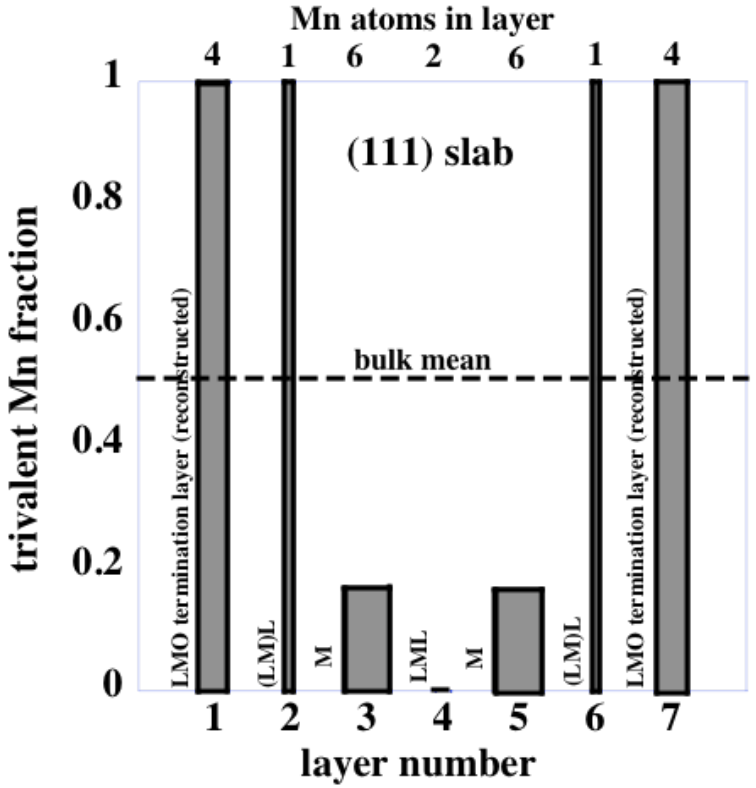
Reconstructed







Features of Reconstructed $LiMn_2O_4$ Surfaces



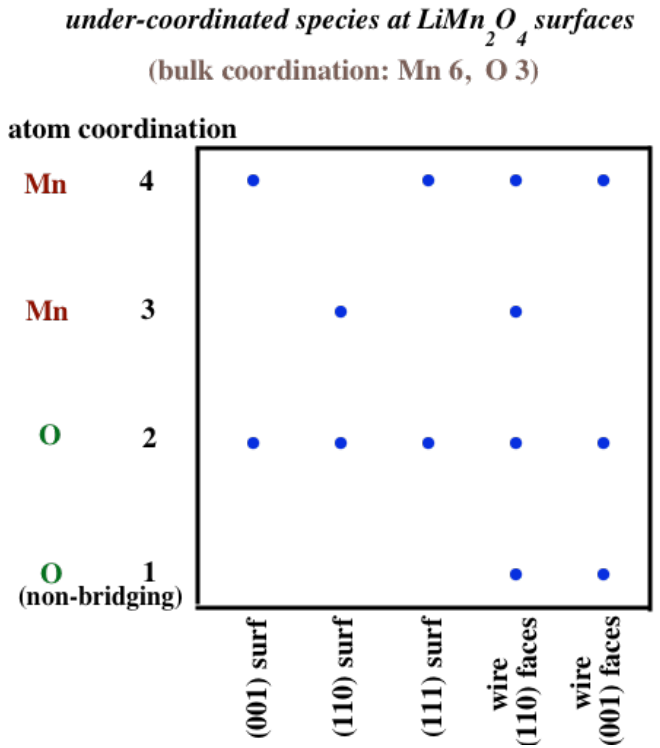
- Under-coordination results in reduction of surface Mn ions, relative to bulk (see figure for reconstructed (111) slab)
- 3-fold coordinated Mn divalent at (110) surfaces

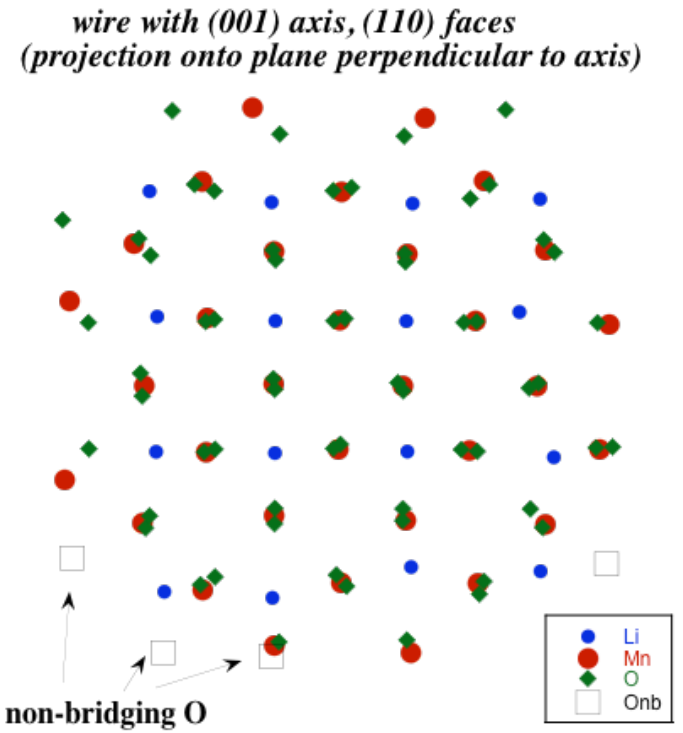
Significance of Surface Coordination for Dissolution

- The presence of non-bridging oxygen greatly increases driving force for dissolution, i.e., energy gain for acid promoted dissolution reactions

$$LiMn_2O_4 + 2H^+ \rightarrow \{LiMn_2O_4\text{-}[MnO]\} + Mn^{2+} + H_2O \quad (1)$$

$$\{LiMn_2O_4\text{-}[MnO]\} + 2H^+ \rightarrow \{LiMn_2O_4\text{-}[MnO, Li_2O]\} + 2Li^+ + H_2O \quad (2)$$





Future Work - FY2010/FY2011

- Continue to exploit and optimize $xLi_2MnO_3 \bullet (1-x)LiMO_2$ electrodes (composition and performance) with the particular goal of reaching or exceeding the energy and power goals required for 40-mile PHEVs and EVs.
- Focus on surface studies: phosphates and fluorides – 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.
- Exploit highly versatile, autogenic synthesis technique to fabricate and evaluate novel electrode materials and coating architectures, e.g., high capacity TiO_2 anodes coupled to high capacity Mn-based cathodes for safe Li-ion cells.
- Pursue interactions with energy storage EFRCs.

Summary

- Further progress was made to stabilize the surface, and improve the rate capability and cycle life of high-capacity $xLi_2MnO_3 \bullet (1-x)LiMO_2$ electrodes (M=Mn, Ni, Co) when charged to high potentials (>4.5 V).
- $xLi_2MnO_3 \bullet (1-x)LiMO_2$ electrode materials have the attention of industry – collaborations are in place with materials manufacturers worldwide.
- $Li_{3-2x}Ni_xPO_4$ coatings ($0<x\leq1$) improve the rate capability (200 mAh/g at C/1) and cycling efficiency (~100%) at room temperature; charged, coated electrodes generate less heat when reacted with electrolyte at elevated temperature.
- Autogenic reactions have been used to prepare carbon-coated electrodes in a single step – this versatile technique holds promise for fabricating electrode advanced materials (cathodes and anodes) with modified morphologies and electrochemical properties.
- Simulation of Mn- and MnO terminated surface structures of $LiMn_2O_4$ has provided insight into atomic coordination and Mn oxidation state that impact solubility.

Acknowledgment

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