Design and Evaluation of High Capacity Cathodes

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Argonne National Laboratory

Annual Merit Review
DOE Vehicle Technologies Program
Arlington, VA
May 16, 2013

ES049

Overview

Timeline

- Start date: FY12
- End date: FY15
- Percent complete:
  - 25%

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, Vilas Pol, Donghan Kim, Brandon Long
  - APS, Argonne: Mali Balasubramanian (XAS), Yang Ren (XRD)
  - ES, Argonne: Greg Krumdick, Young-Ho Shin
  - ABR 'Voltage fade' team
  - Industry: Envia, BASF, Toda, LG Chem

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 and surfaces with stable architectural designs
  - Use atomic-scale modeling as a guide to identify, design and understand the structural features and electrochemical properties of cathode materials

Milestones (FY12)

- Engineer, improve and evaluate the electrochemical properties and surface stability of composite electrode structures with a high Mn content – *on going*
- Evaluate processes for fabricating metal oxide cathode particles with stabilized surfaces – *on going*
- Model coatings and interfacial phenomena at the surface of lithium-metal-oxide electrodes – *on going*
- Continue collaborative interactions with EFRC – Center for Electrical Energy Storage - *Tailored Interfaces* (Argonne-Northwestern University-University of Illinois (Urbana-Champaign) – *on going.*
  - 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 *structurally-integrated ('composite') electrodes structures*, particularly 'layered-layered' $xLi_2MnO_3 \bullet (1-x)LiMO_2$ (M=Mn, Ni, Co) materials

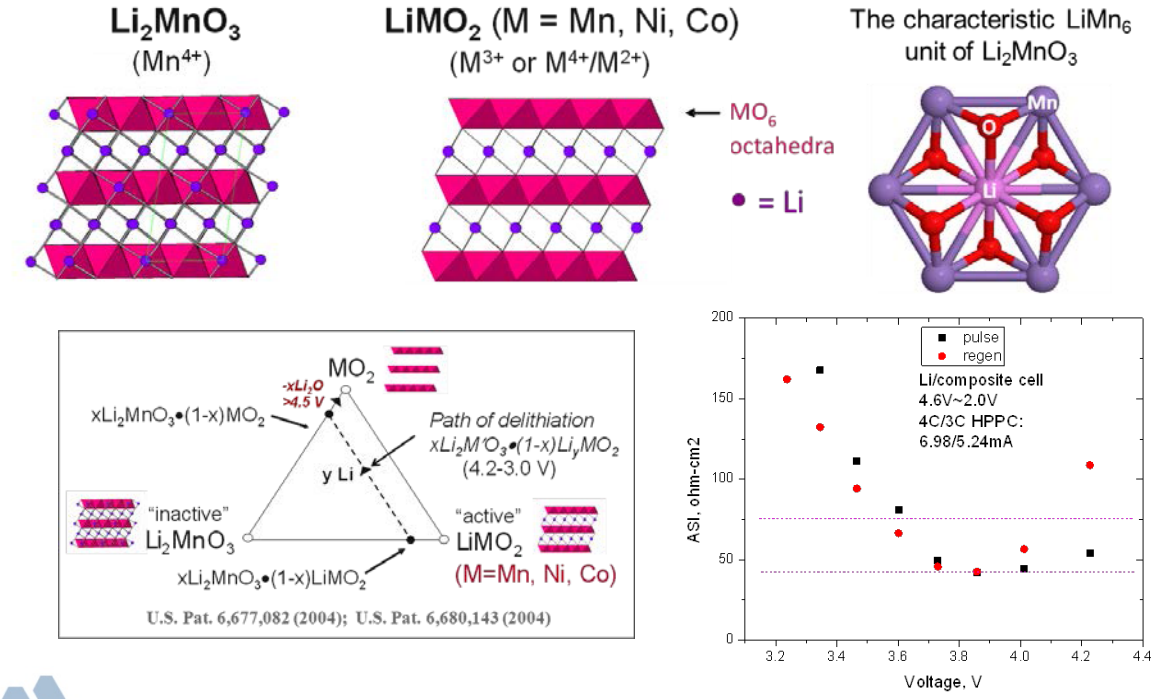
- Design effective *surface structures* to protect the underlying metal oxide particles from the electrolyte and to their improve rate capability when charged (delithiated) at high potentials

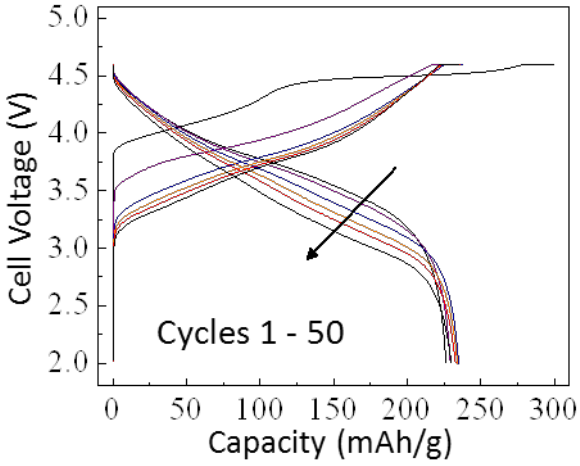
- Explore *synthesis techniques* to synthesize advanced electrode materials and surface structures and architectures, notably by sonication

- Use *first principles modeling* to aid the design of bulk and surface cathode structures and to understand electrochemical phenomena

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

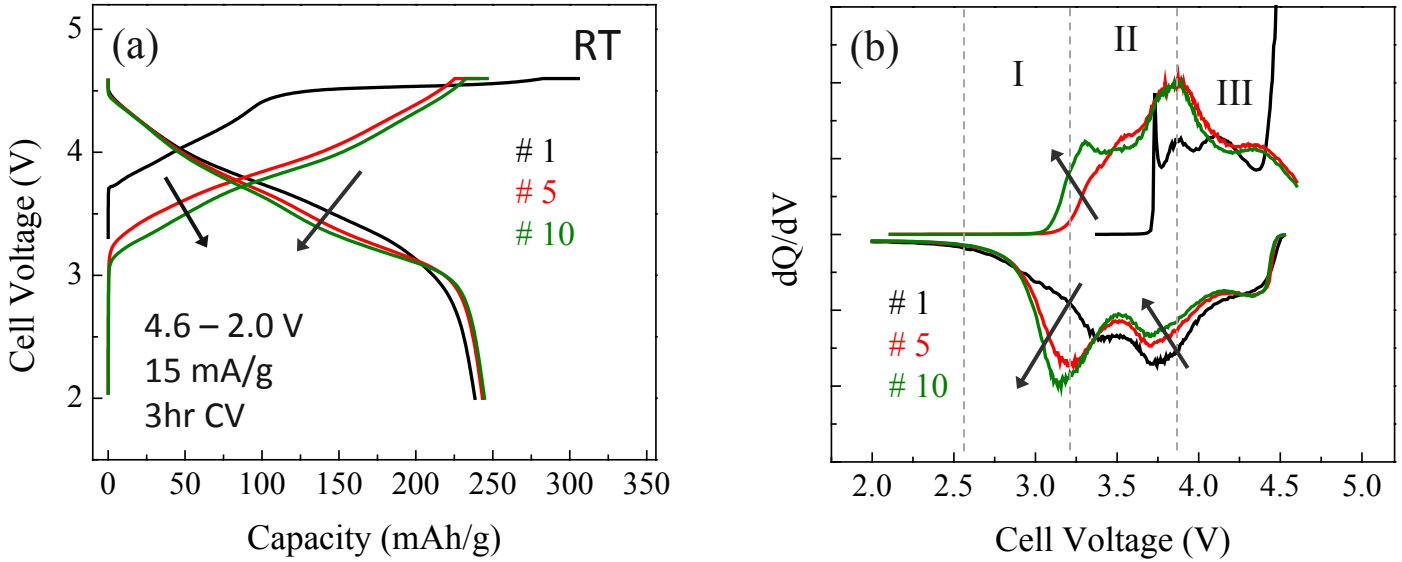
- Voltage fade – reduced energy output, system management
- Surface stabilization– poor rate performance, side reactions, dissolution
- Hysteresis – energy efficiency, system management
- Impedance – at low and high states of charge





Clues about Voltage Fade from Electrochemistry

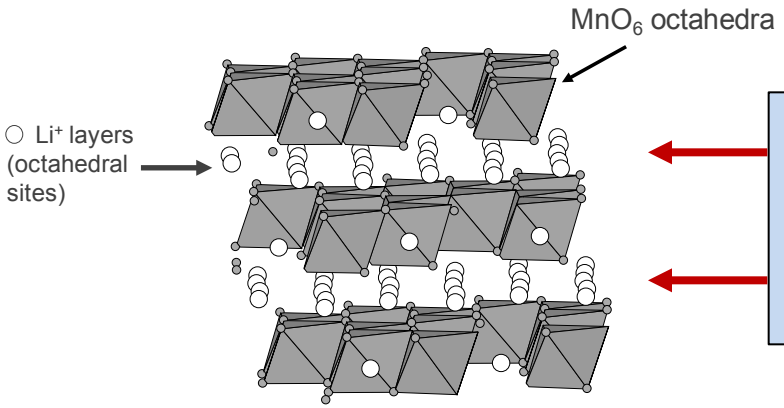
$Li/0.5Li_2MnO_3 \bullet 0.5LiMn_{0.5}Ni_{0.5}O_2$ half cells



- dQ/dV peaks relate to site energies as well as specific transition metal redox states
  ⇒ complicates interpretation of electrochemical processes in complex structures
- Redox peaks in region II vary inconsistently on charge and discharge
- Redox peaks in region I grow in magnitude with increasing Li_2MnO_3 content and with a gradual shift to lower potentials
  ⇒ Mn and its local environment play a major role in voltage fade

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



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

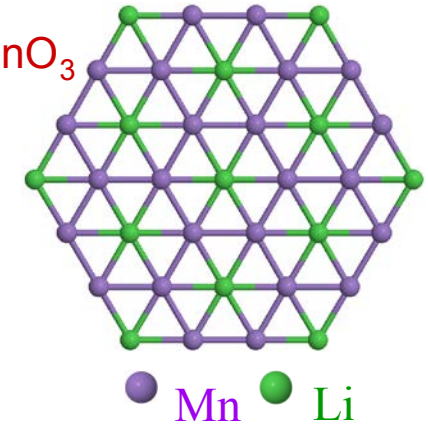
- Ideal 'layered-layered': No transition metal ions in Li layers
- Ideal 'layered-layered-spinel': 25% transition metal ions in Li layers of spinel domains & vice-versa
- Ideal 'layered-layered-rocksalt': No Li layers in rocksalt domains

Croy et al., JES 2012

The $LiMn_6$ Unit in Idealized Cathode Structures

Li_2MnO_3

$CN_{Mn\text{-}Mn} = 3$
$CN_{Mn\text{-}Li} = 3$
$CN_{Li\text{-}Mn} = 6$



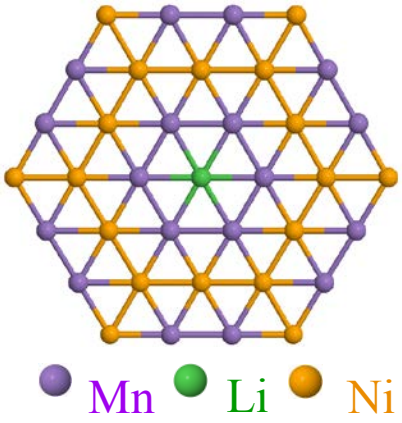
- The $LiMn_6$ unit is the characteristic building block of Li_2MnO_3
- The $LiMn_6$ unit provides a reservoir of Li to stabilize the cathode at high states of charge

$LiMn_{0.5}Ni_{0.5}O_2$

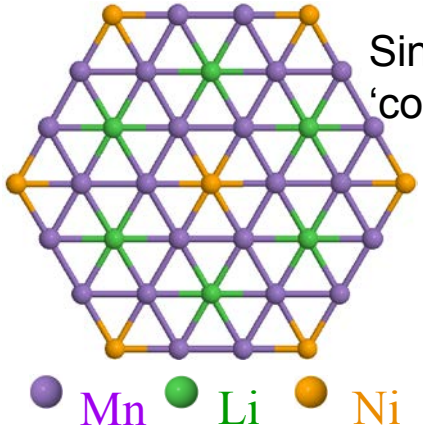
Ideal 'flower' pattern

Van der Ven et al. (2004)

$CN_{Mn\text{-}M} = 5$
$CN_{Ni\text{-}M} = 6$
$CN_{Li\text{-}Mn} = 6$



$0.5Li_2MnO_3 \bullet 0.5LiMn_{0.5}Ni_{0.5}O_2$



Single-phase 'composite' structure

Ordered distribution of $NiMn_6$ units ($LiMO_2$) and $LiMn_6$ units (Li_2MnO_3)

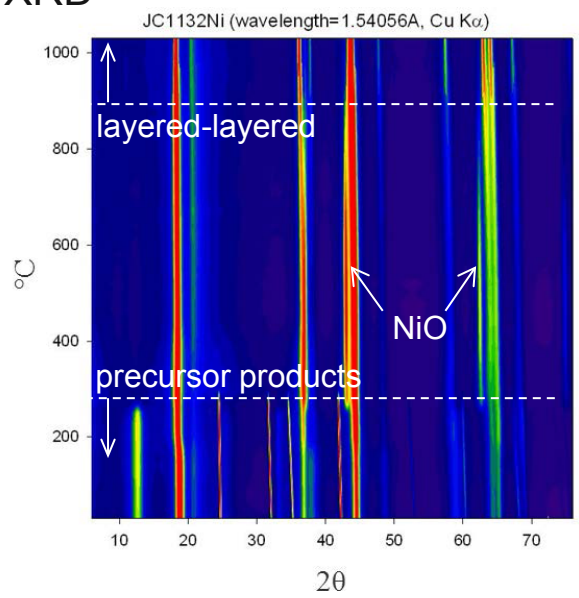
Jarvis et al. Chem. Mater. 2011

$CN_{Mn\text{-}M} = 4$
$CN_{Ni\text{-}Mn} = 6$
$CN_{Li\text{-}Mn} = 6$

Structural Evolution During Synthesis

$0.5Li_2MnO_3 \cdot 0.5LiMn_{0.5}Ni_{0.5}O_2$

In-situ XRD



450ÁC:

- Ni-M coordination ~9, consistent with NiO-like regions
- (CN=12 in NiO); Mn coordination ~3 (as in Li_2MnO_3)

450 – 800ÁC:

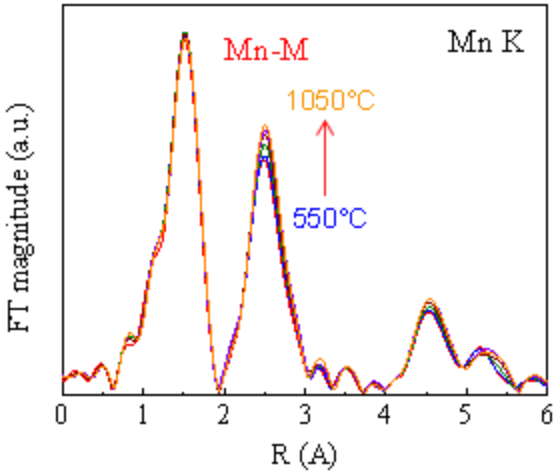
- Mn CN increases to ~4; Ni CN decreases to ~6

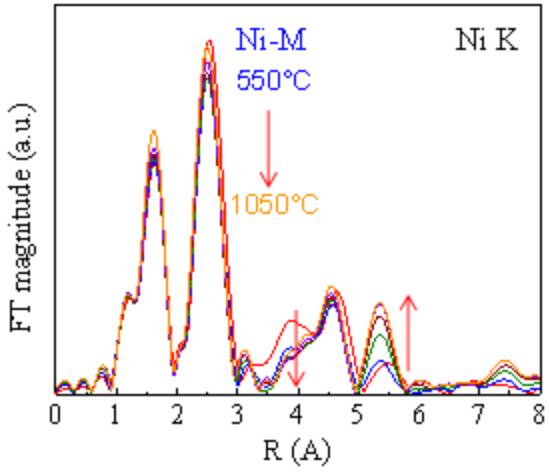
  ⇒ decomposition of NiO regions and the migration of Ni into the transition-metal rich layers.

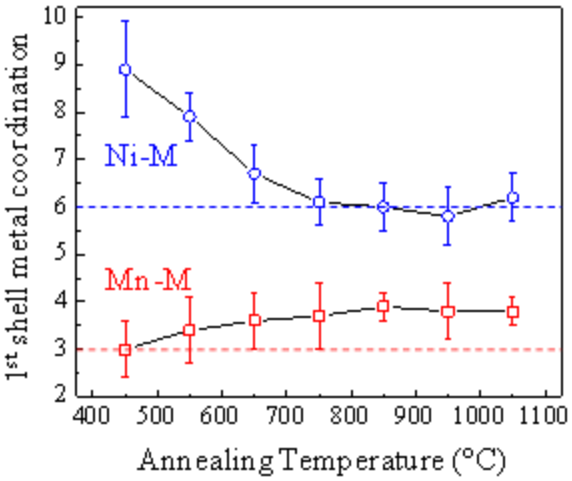
800ÁC and above:

- Layered composite structure, with Mn under-coordinated relative to Ni, close to 'single-phase' arrangement with characteristic $LiMn_6$ units of Li_2MnO_3

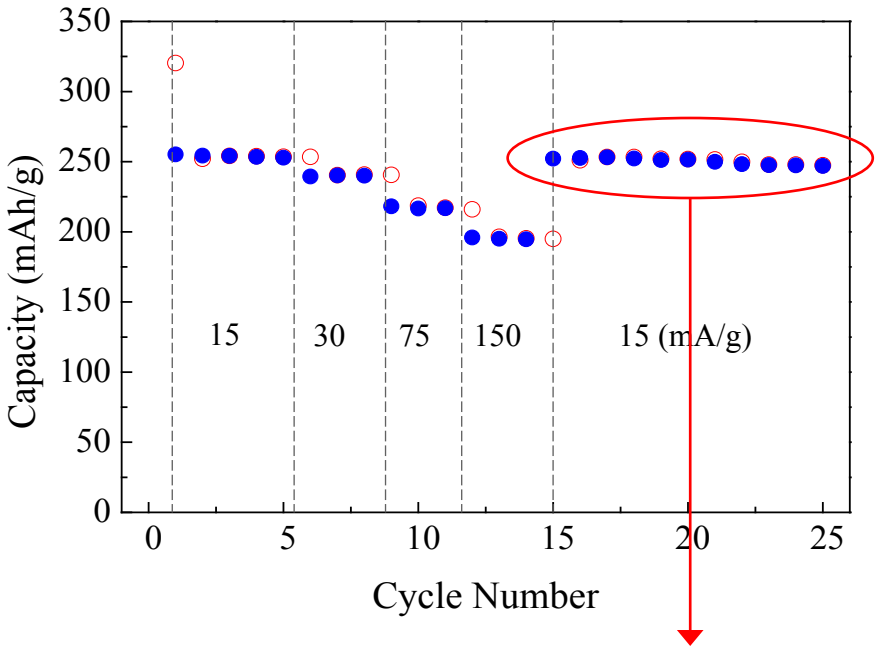
EXAFS



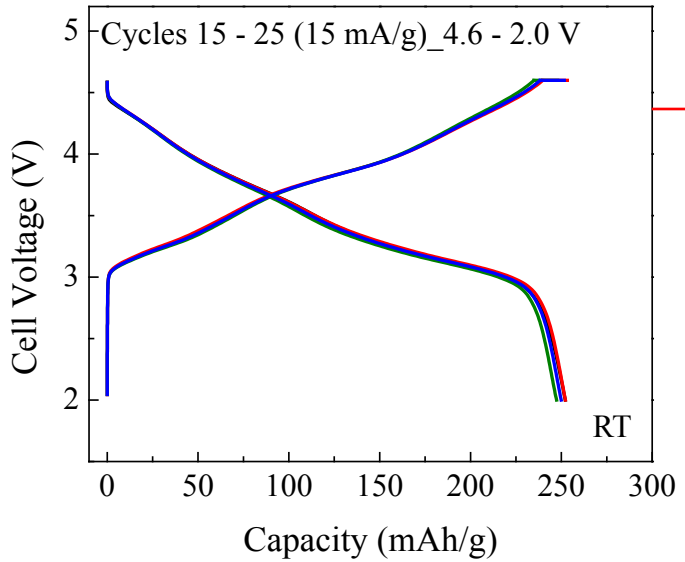


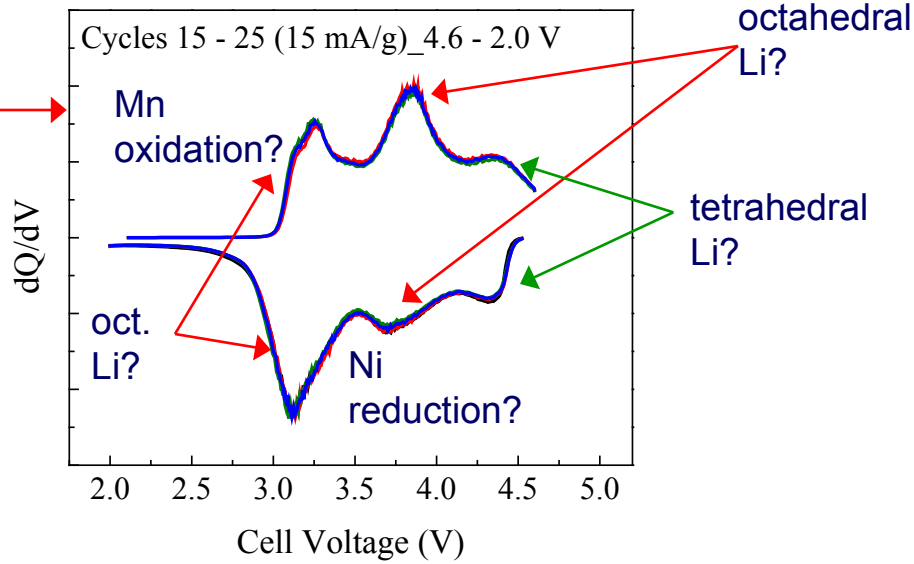


$Li/0.5Li_2MnO_3 \bullet 0.5LiMn_{0.5}Ni_{0.5}O_2$ Half Cells

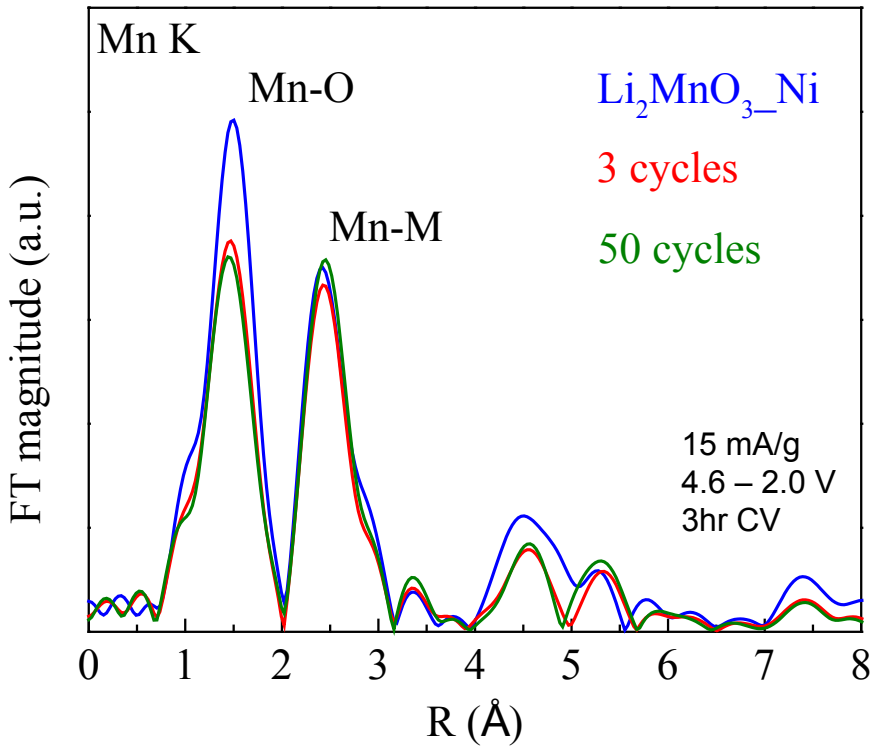


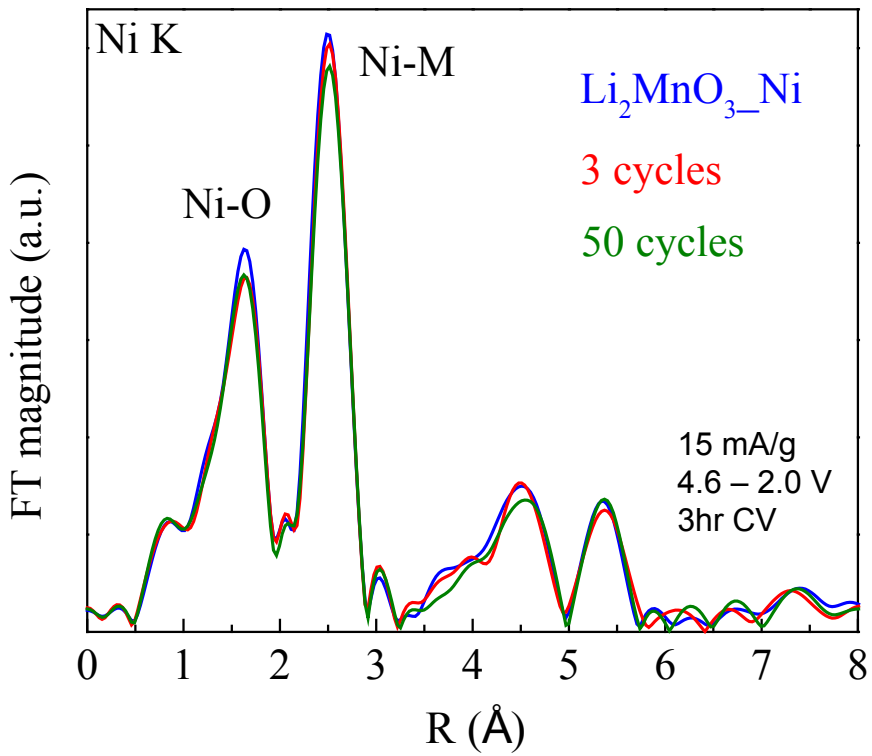
- High capacity above 3 V (~225 mAh/g)
- Activation/break-in cycles required
- 'Stable' profile and dQ/dV plot after ~10 cycles
- 'Reversible' reaction
- Discharge different to charge process
  ⇒ cation migration affects reaction routes?
- Redox dependent on Mn-Ni interactions?
- Composition of a fully activated discharged electrode is $LiMn_{0.75}Ni_{0.25}O_2$ or $Li_2Mn_{1.5}Ni_{0.5}O_4$, but profile more 'layered-like' than 'spinel'.





EXAFS of $0.5Li_2MnO_3 \bullet 0.5LiMn_{0.5}Ni_{0.5}O_2$ Electrodes

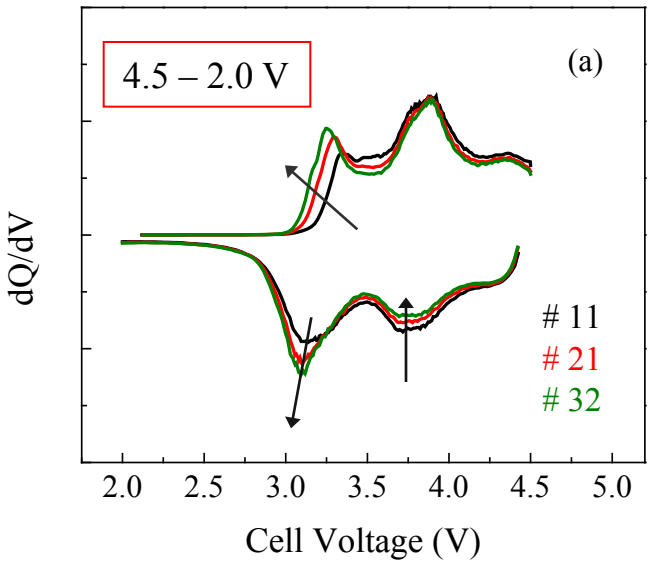


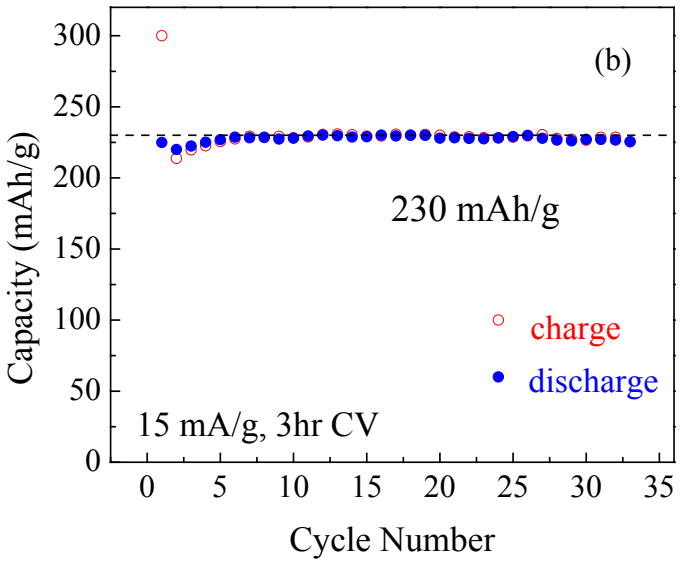


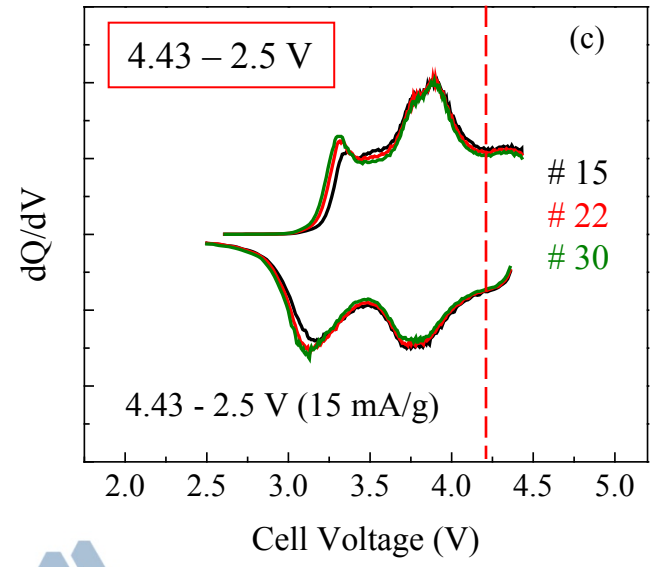
- Local Mn environment is affected immediately by electrochemical activation at 4.6 V
- Mn environment changes slowly on continued cycling
- In contrast, local Ni environment remains essentially unchanged over 50 cycles

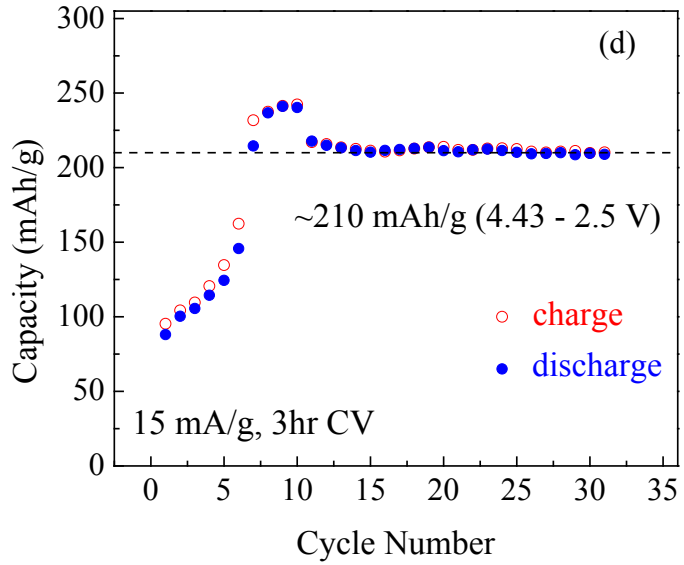
Controlling the Voltage Window and Structural Changes

$Li/0.5Li_2MnO_3 \cdot 0.5LiMn_{0.5}Ni_{0.5}O_2$ half cells



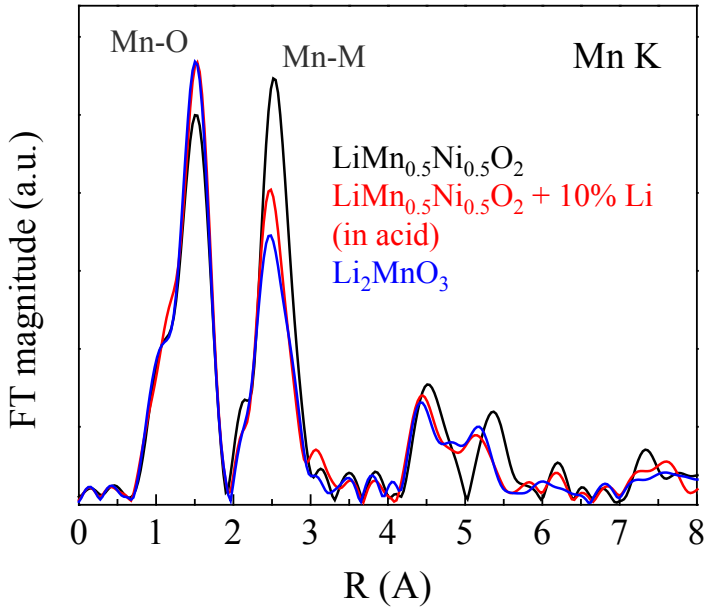






- Narrow the voltage window after activation
- Do not activate all the Li_2MnO_3!
- Keep some $LiMn_6$ regions in structure
- Maximize Mn-Ni nearest neighbors and minimize Mn-Mn nearest neighbors to enhance stability
- Optimize electrode composition
- If possible, suppress Mn/Ni migration to maintain the highest discharge potential

Precursor Materials Other Than Li_2MnO_3: $LiMn_{0.5}Ni_{0.5}O_2$?

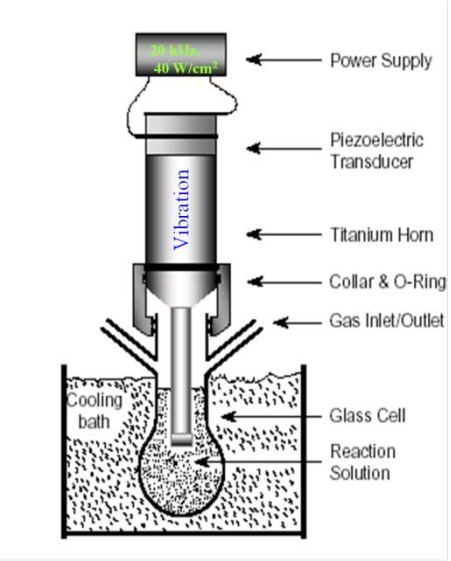


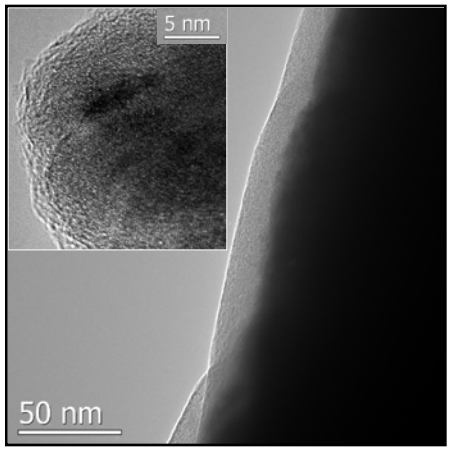
- Can other precursors be used besides Li_2MnO_3 to fabricate unique atomic arrangements?
- Can composition and domain size be carefully controlled?
- $LiNi_{0.5}Mn_{0.5}O_2$ has some Li/Ni interchange between layers providing LiM_6 units in TM layers (e.g., the ideal flower pattern)
  - $\Rightarrow$ Is it possible to introduce Li_2MnO_3 units/regions into a $LiNi_{0.5}Mn_{0.5}O_2$ precursor?
- XAS clearly shows the Mn environment going towards that of Li_2MnO_3.
- Collaborations with Greg Krumdick and Young-Ho Shin at Argonne's scale-up facility are in progress to synthesize and evaluate precursor materials.

Sonochemical Coatings: Al_2O_3/ZrO_2 on $0.5Li_2MnO_3 \bullet 0.5LiMn_{0.5}Ni_{0.5}O_2$

Sonochemistry *(V. Pol, S. Pol)*

$0.5Li_2MnO_3 \bullet 0.5LiMO_2 + ZrCl_2$))))))))) $Zr(OH)_x$ → 450°C → ZrO_2-coated electrode

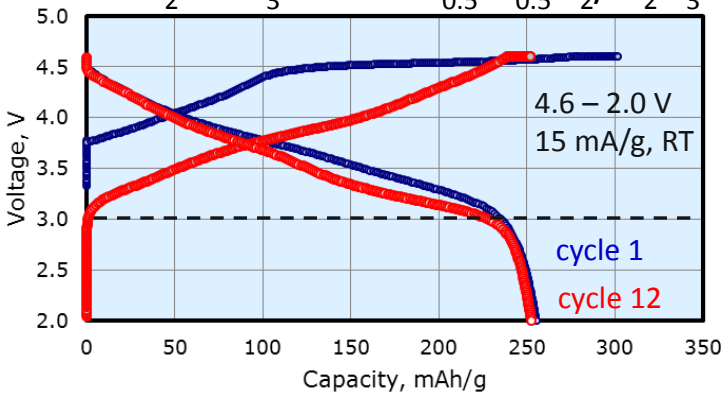


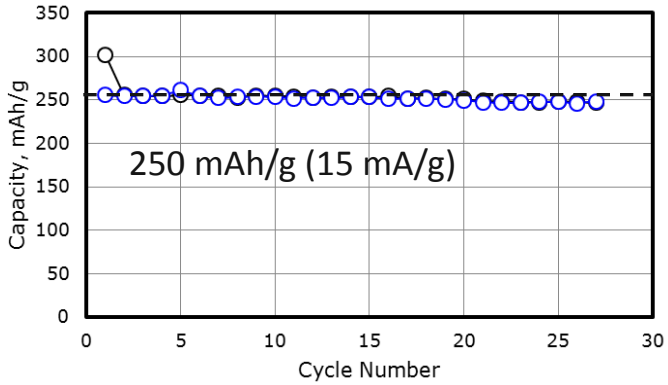


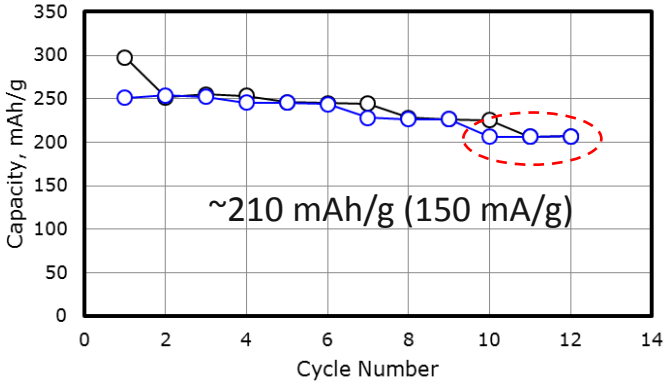
$0.5Li_2MnO_3 \bullet 0.5LiMn_{0.5}Ni_{0.5}O_2/ZrO_2$

- Sonochemical method uniformly coats particles
- High capacity (~230 mAh/g above 3.0 V)
- Good cycling stability, 85% first-cycle efficiency
- 250 mAh/g at 15 mA/g, 210 mAh/g at 150 mA/g
- Voltage fade persists on cycling, endorsing the conclusion from initial studies on TiO_2-coated electrodes that voltage fade is a bulk effect.

$0.5Li_2MnO_3 \bullet 0.5LiMn_{0.5}Ni_{0.5}O_2/Al_2O_3$







Simulations of spinel surfaces and coatings

- HF-promoted dissolution: constrained first principles MD calculations of Mn dissolution from (110), (001) surfaces of $LiMn_2O_4$ were performed. Adsorbed F^- lowers the activation barrier for Mn dissolution and facilitates reduction to Mn^{2+}

- MD simulations of Li^+ trajectories in AlF_3 and Al_2O_3 are in progress to model the maximum Li-ion current flow through $LiMn_2O_4$ protective coatings

- Theory effort on spinel surfaces and coatings temporarily redirected to address the voltage fade phenomenon in high capacity, layered lithium metal oxide electrodes (funded by ABR program)

Spin-off technology from BATT Research

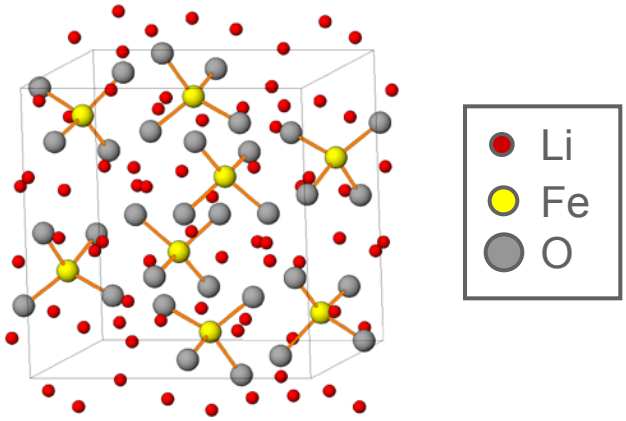
Exploitation of Li_2O-Containing Electrodes for Li-O_2 Cells

$$Li_2MnO_3\ (Li_2O{\bullet}MnO_2) \xrightarrow{4.5\text{-}4.8\ V} MnO_2 + 2\ Li + \tfrac{1}{2}\ O_2\ (459\ mAh/g)$$

- Net loss is Li_2O at 4.5 to 4.8 V – irreversible reaction
- Li_2O is the ultimate discharge product of an ideal Li - O_2 cell

  ⇒ Implications for designing dual-functioning electrodes/ electrocatalysts that form compounds with Li_2O?

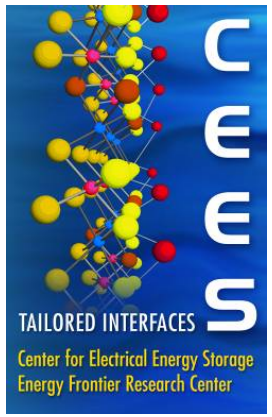
Li_5FeO_4 (Pbca)
(*a*=9.218 Å; *b*=9.213 Å; *a*=9.159 Å)



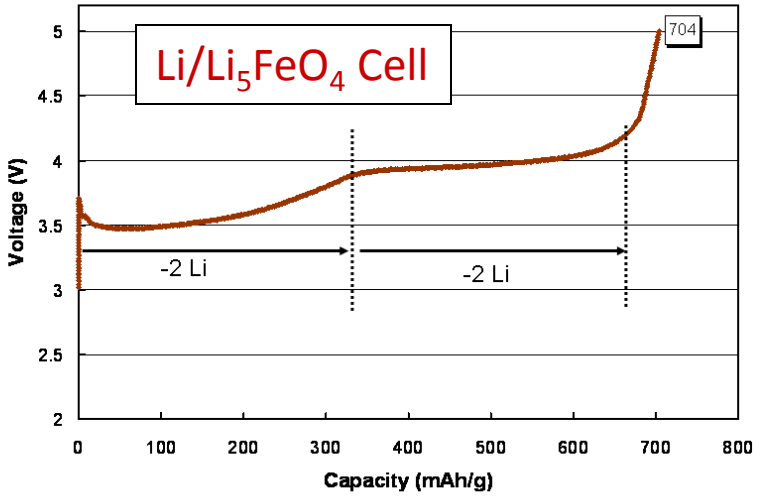
Defect antifluorite structure

$Li_5FeO_4 = 5Li_2O{\bullet}Fe_2O_3$

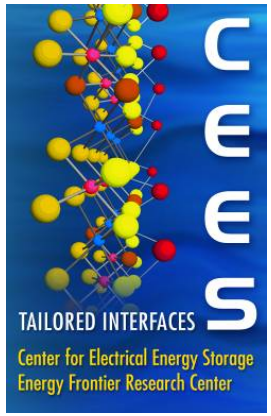
5 Li per Fe atom

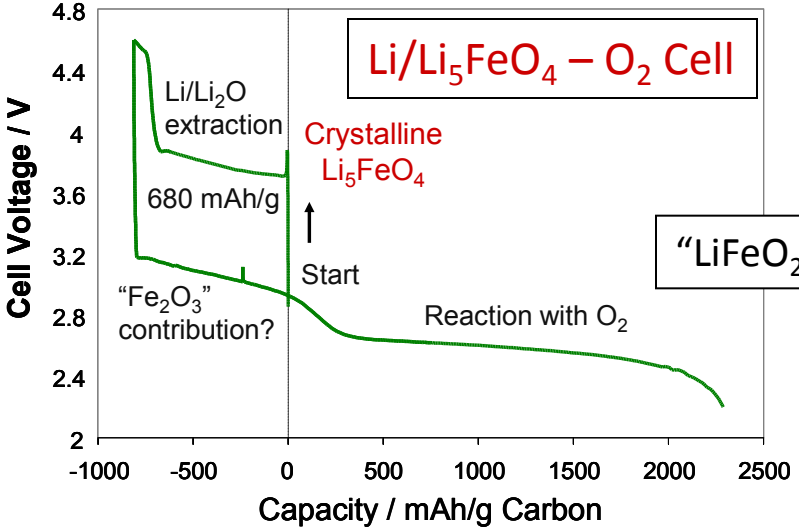


Spin-off technology from BATT Research



- XANES data show evidence of **Li_2O extraction**
- Composition of charged product = "$LiFeO_2$" ($Li_2O \bullet Fe_2O_3$)
- Capacity of Li_5FeO_4 (removal of 4 Li) = **694 mAh/g**





Li_2O removal from Li_5FeO_4:
Experiment: 3.9-3.7 V
Calculation: 3.8-3.4 V

"$LiFeO_2$" ($Li_2O \bullet Fe_2O_3$) + 4 Li + O_2 ↔ "Li_5FeO_4" ($5Li_2O \bullet Fe_2O_3$) + O_2?

'Li_2O' reaction with '$LiFeO_2$':
Experiment: 3.2-3.0 V
Calculation: 3.3 V

Theoretical energy density of a 3 V Li/Li_5FeO_4-O_2 cell = 2082 Wh/kg (4 Li)

C. S. Johnson, et al., Chem. Mater (2010); Trahey et al., Electrochem. Solid State Lett. (2011)

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 on this focused topic. These efforts will therefore continue in FY2013/FY2014 with the goal of reaching/exceeding the energy and power goals required for 40-mile PHEVs and EVs.
- Efforts to stabilize both surface and bulk structures of composite electrode materials using Li_2MnO_3 and other precursors will continue. Complementary experimental and theoretical studies will be undertaken 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.
- Efforts to fabricate stable surface architectures will be continued using sonication, which is showing considerable promise, 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 continued.
- Significant progress was made in understanding the voltage fade phenomenon and in addressing structural issues and the cycling limitations of 'layered-layered' composite electrode structures with high-resolution XRD and XAS data.
- Sonication reactions show promise for coating electrode particles. It has been demonstrated, in particular, that this technique can be used effectively to deposit stabilizing nanolayers of Al_2O_3, ZrO_2 and TiO_2 on the electrode particle surface without significantly impacting electrochemical properties of the electrodes at moderate rates.
- The theory component in this project continues to address solubility and surface stabilization of lithium metal oxide electrodes; during the past six months, this component was temporarily put on hold to direct efforts to the understanding of the voltage fade phenomenon as part of an interaction with the ABR program.
- This project has spun-off new electrode/electrocatalyst designs for Li-O_2 cells.

Acknowledgment

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