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Stabilization of Layered Metal Oxides

presented by

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Annual Merit Review

DOE Vehicle Technologies Program

Bethesda, Maryland

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Vehicle Technologies Program

Purpose, Barriers and Goals, Approach, Collaborators

Purpose of Work

- Design and develop low cost, high capacity, high power Mn-based cathodes

Barriers

- Low energy, cost, cycle life and abuse tolerance limitations

Approach

- Exploit structurally-integrated electrode materials, such as ‘layered-layered’ $xLi_2MnO_3 \bullet (1-x)LiMO_2$ and ‘layered-spinel’ $xLi_2MnO_3 \bullet (1-x)LiM_2O_4$ (M=Mn, Ni, Co) to access their intrinsic high capacity.

Collaborators

- Co-investigators: S.-H. Kang, C. Johnson, J. Vaughey, R. Benedek
- C. Grey, J. Cabana (SUNY, Stony Brook)
- X. Yang, W. Yoon (BNL)
- P. Bruce (St. Andrews University, UK)
- P. Novak (Paul Scherrer Institute, Switzerland)
- Primet Precision Materials (Ithaca, NY)

Reviewers' Comments on Previous Work

- Relevance to DOE/FCVT Goal and BATT Objectives
  - *"Reviewers found the work to be relevant"*

- Specific Recommendations:
  - *"This work should be not only supported, but also extended, if possible. Continue, high priority."*

  - *"Focus on implementation into batteries project. Try to find an experienced cell maker that can implement this material."*
    Commercialization of this material is in progress.

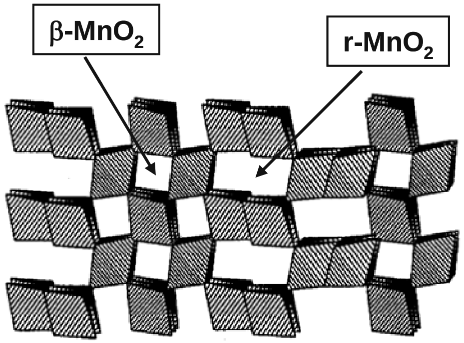
  - *"Focus on electrolyte and/or additives would likely pay off."*
  - *"Concerns about electrolyte stability at 4.6 V expressed."*
    Fluoride-stabilization techniques have been implemented.

Topics

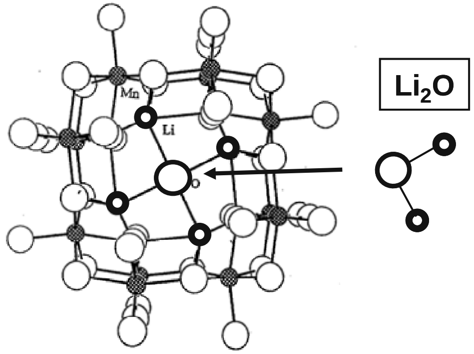
- Strategy behind using integrated electrode structures such as $xLi_2MnO_3 \bullet (1-x)LiMO_2$ (M=Mn, Ni, Co)
- Stabilization of electrode surfaces at high potential (>4.4 V vs. Li^0)
- Anomalous capacity from Mn-rich $xLi_2MnO_3 \bullet (1-x)LiMO_2$ electrodes
- Theoretical modeling: Dissolution vs. H^+ ion-exchange in reactions in metal oxide electrodes

Strategy: Use Structural Units (instead of ion dopants) to Stabilize Electrochemically–Active Materials

3 V Electrodes

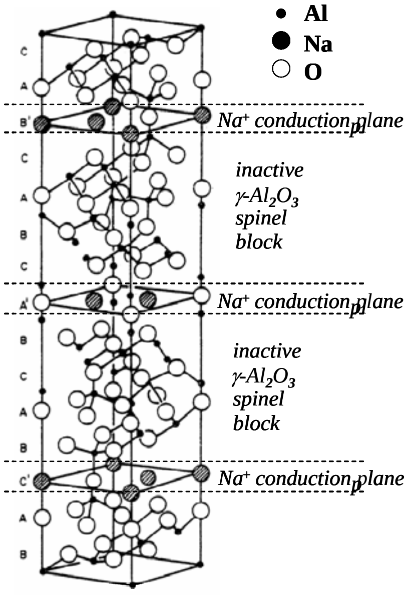


γ-MnO$_2$: Intergrowth of β-MnO$_2$ and ramsdellite-MnO$_2$

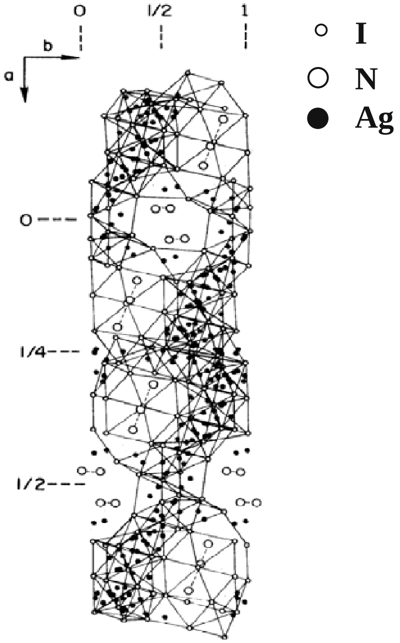


Li$_2$O-stabilized α-MnO$_2$: 0.15Li$_2$O•MnO$_2$

Solid Electrolytes



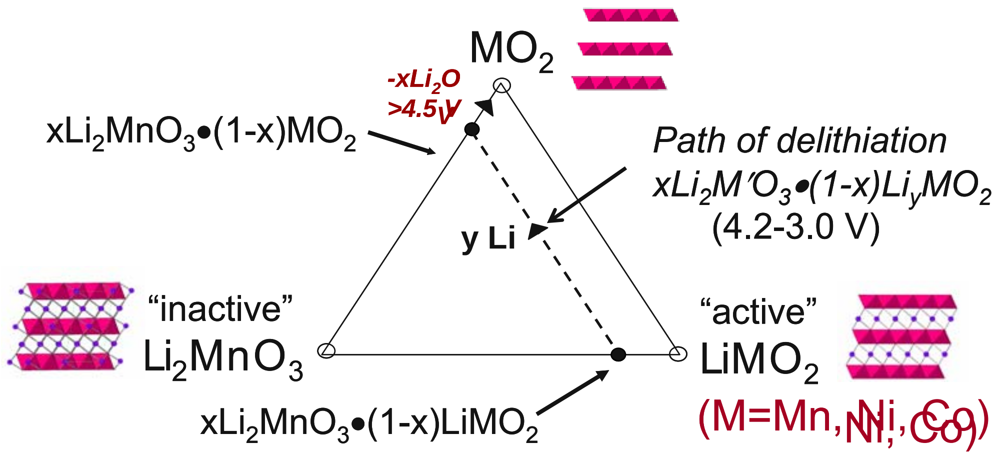
β-alumina, Na$_2$O•11Al$_2$O$_3$



44AgI•3(C$_{11}$H$_{22}$N$_3$)I$_3$

xLi_2MnO_3•(1-x)$LiMO_2$ Electrodes (Recap)

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



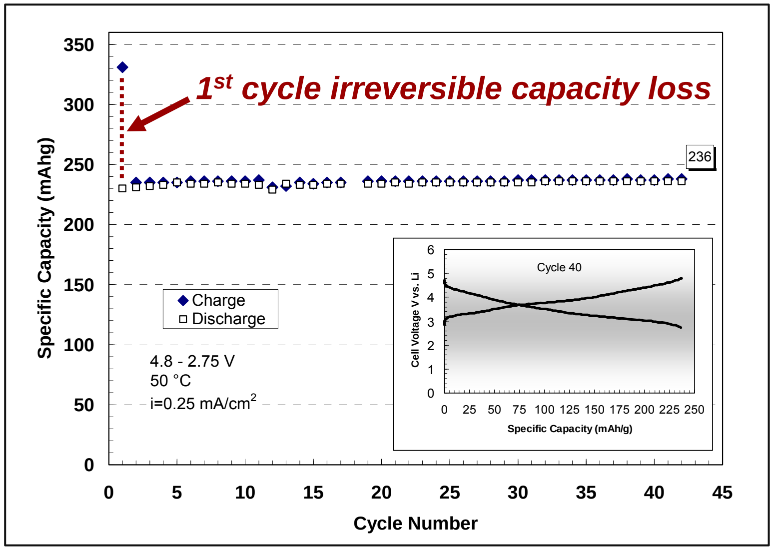
U.S. Pat. 6,677,082 (2004); U.S. Pat. 6,680,143 (2004)

⇐ *Keep Li_2MnO_3 content as low as possible to maximize capacity*

200-250 mAh/g achievable from high Mn-content electrodes (no cobalt) ⇒

Large irreversible capacity loss on initial cycle (Li_2O removal from Li_2MnO_3) ⇒

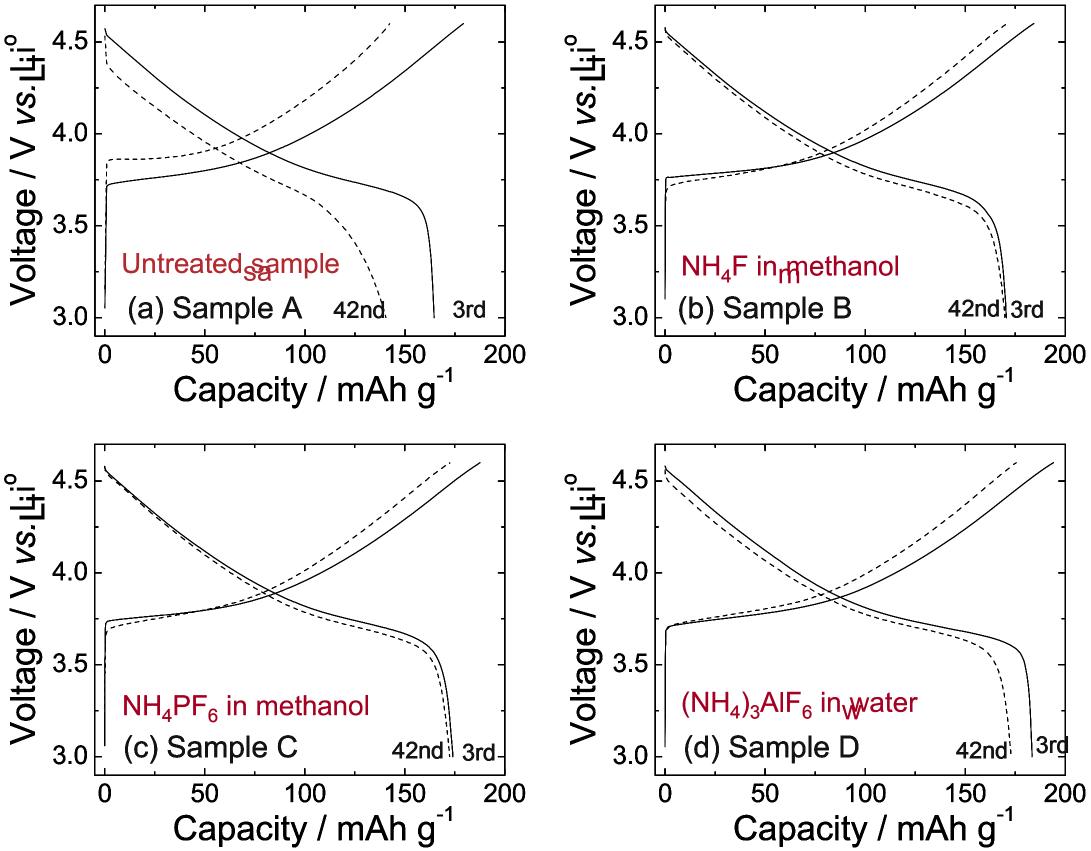
Li/0.3Li_2MnO_3•0.7$LiMn_{0.5}Ni_{0.5}O_2$ (50 °C)



Fluorinated Electrodes

- Charging $LiMO_2$ and $xLi_2MnO_3 \bullet (1-x)LiMO_2$ electrodes to high potential (>4.4 V) damages the electrode surface
- Fluorination of spinel $LiMn_2O_4$ and layered $xLi_2MnO_3 \bullet (1-x)LiMO_2$ electrodes is known to improve capacity and cycling stability
- Robust oxy-fluoride surface?
- Approach: Use mildly acidic fluorinated solutions to wet and passivate $xLi_2MnO_3 \bullet (1-x)LiMO_2$ particles completely without severely damaging or corroding the surface – mild etch
  - soluble salts with stabilizing cations and anions
  - $(NH_4)_3AlF_6$; NH_4PF_6; NH_4BF_4 in water, methanol, etc
  - molarity of solutions ~2.5×10^{-3} M
  - pH $\approx$ 6.0 - 6.5
- Composition used: $0.1Li_2MnO_3 \bullet 0.9LiMn_{0.256}Co_{0.372}Ni_{0.372}O_2$ [alternatively, $Li_{1.048}(Mn_{0.333}Ni_{0.333}Co_{0.333})_{0.952}O_2$]

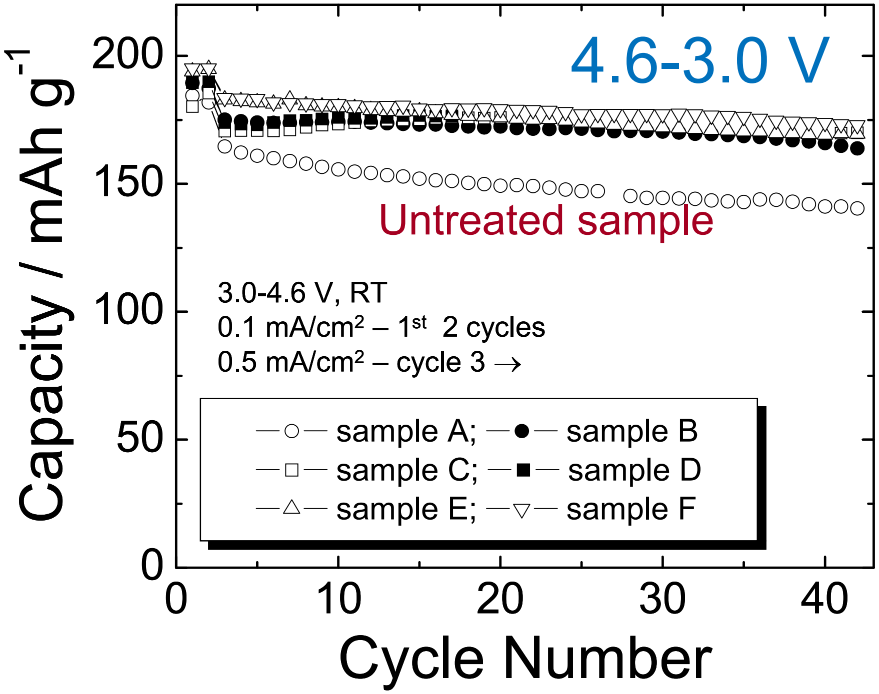
Electrochemical Behavior of Surface-treated $xLi_2MnO_3 \bullet (1-x)LiMO_2$ Electrodes (Half Cells)



- Significantly improved cycling behavior obtained from mildly fluorinated electrodes

Relative Cycling Stability: Li half cells

$Li/0.1Li_2MnO_3 \bullet 0.9LiMn_{0.256}Ni_{0.372}Co_{0.372}O_2$



Sample A: untreated sample

Sample B: NH_4F in methanol

Sample C: NH_4PF_6 in methanol

Sample D: $(NH_4)_3AlF_6$ in water

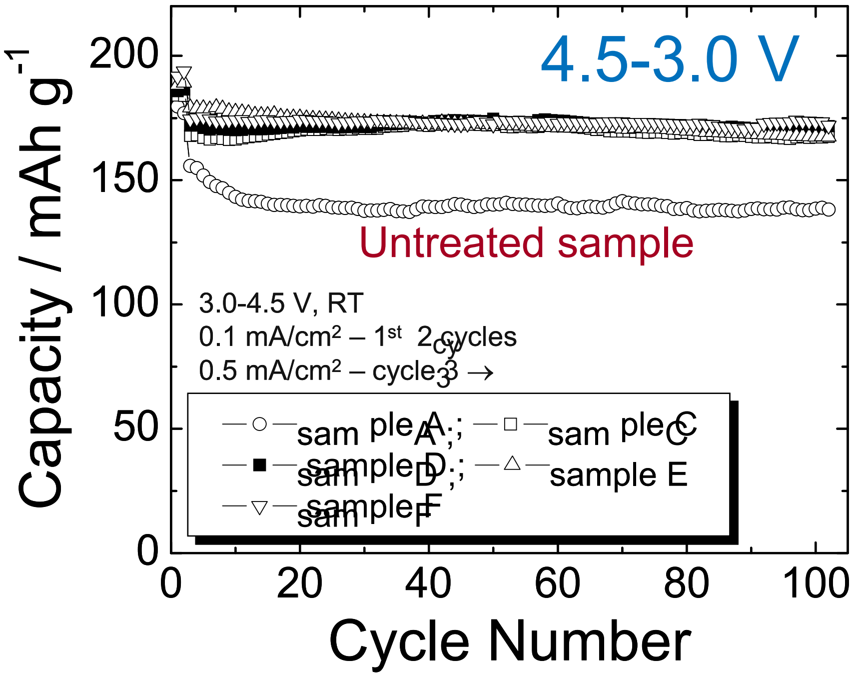
Sample E: H_3PO_4 + NH_4PF_6 in methanol

Sample F: NH_4BF_4 in methanol

- Surface-protected electrodes show enhanced capacity and greater cycling stability
- Reduced oxygen activity and greater surface stability of electrode` at high potentials? – less O_2 lost? – less damage to electrode surface?

Relative Cycling Stability: Li-ion cells

$C_6/0.1Li_2MnO_3 \bullet 0.9LiMn_{0.256}Ni_{0.372}Co_{0.372}O_2$



Sample A: untreated sample

Sample C: NH_4PF_6 in methanol

Sample D: $(NH_4)_3AlF_6$ in water

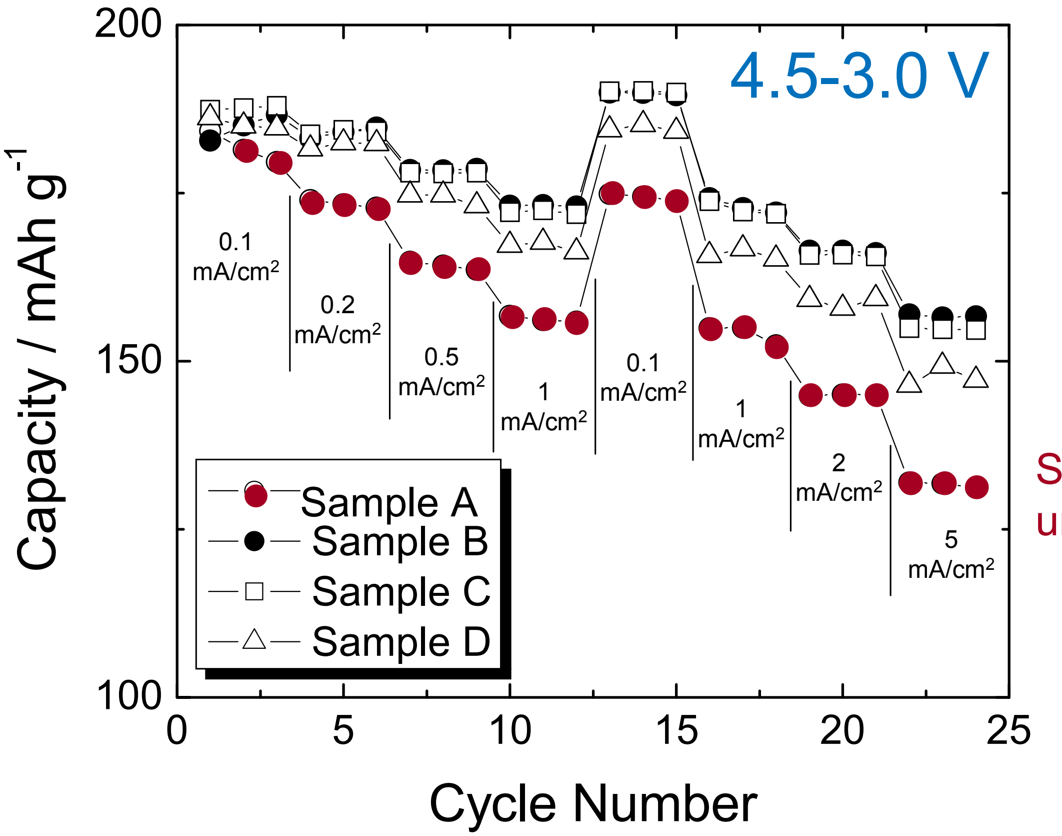
Sample E: $H_3PO_4 + NH_4PF_6$ in methanol

Sample F: NH_4BF_4 in methanol

- Surface-protected electrodes show excellent cycling stability and lower impedance when repeatedly charged to 4.5 V in Li-ion cells (MCMB 1028 graphite anode) at moderately high rate (0.5 mA/cm^2; >C rate)

Relative Rate Capability: Li-ion cells

$C_6/0.1Li_2MnO_3 \bullet 0.9LiMn_{0.256}Ni_{0.372}Co_{0.372}O_2$



Sample A
untreated sample

- Fluorinated surfaces have lower impedance and a higher rate capability
- Partially reduced surface with mixed-valent cations – improved electronic conductivity?

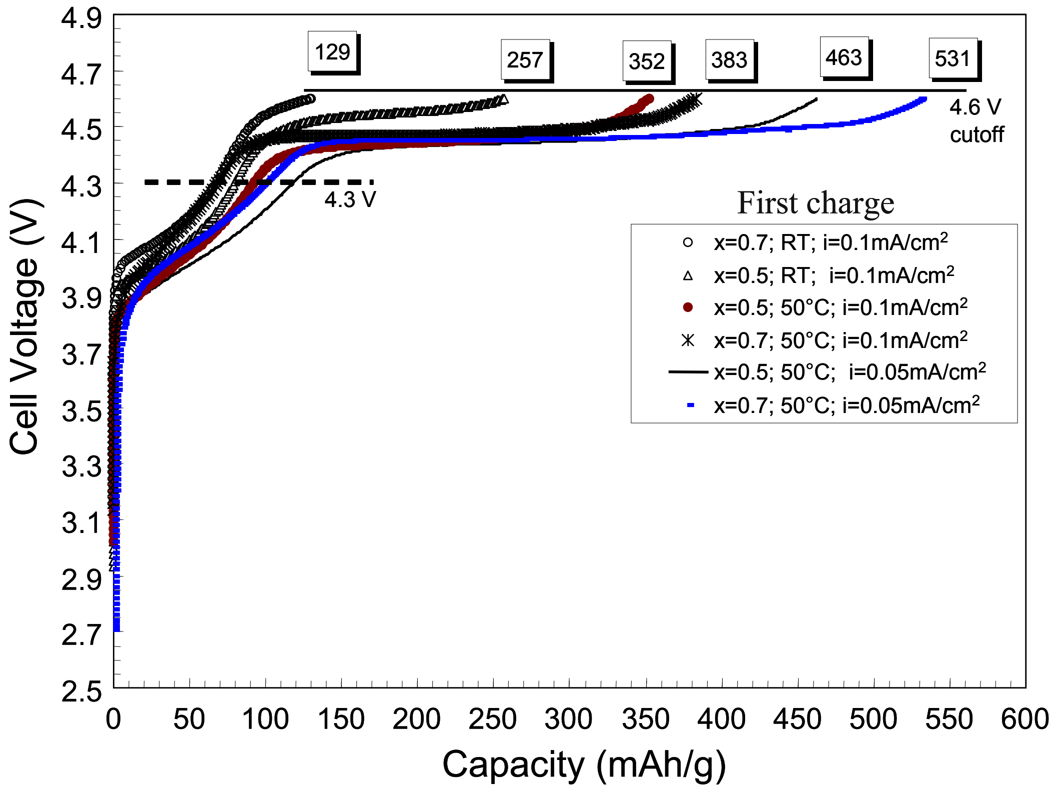
Anomalous Capacity of $0.7Li_2MnO_3 \bullet 0.3LiMn_{0.333}Ni_{0.333}Co_{0.333}O_2$ Electrodes

Charge Capacity - complete Li extraction:	412 mAh/g
Capacity from $LiMO_2$ Component:	73 mAh/g
Capacity from Li_2MnO_3 Component:	339 mAh/g

Discharge Capacity - Li insertion to rocksalt composition:	242 mAh/g
Capacity from $LiMO_2$ Component:	73 mAh/g
Capacity from MnO_2 Component:	169 mAh/g

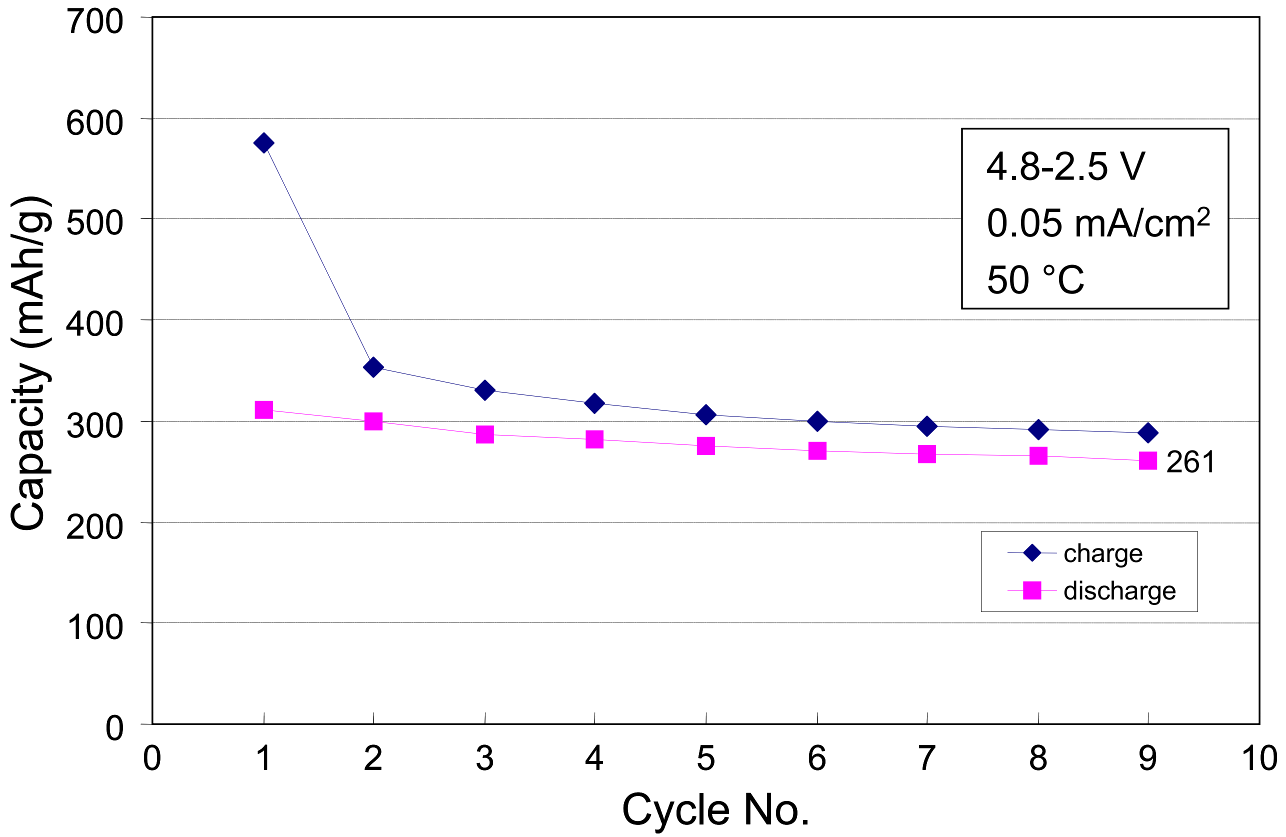
(Calculations based on the mass of electrode material initially loaded in cell)

Anomalous Capacity:
$xLi_2MnO_3 \bullet (1-x)LiMn_{0.333}Ni_{0.333}Co_{0.333}O_2$ Electrodes (x=0.5, 0.7)



- 531 mAh/g obtained from $xLi_2MnO_3 \bullet (1-x)LiMn_{0.333}Ni_{0.333}Co_{0.333}O_2$ at 0.05 mA/cm² (> theoretical, 412 mAh/g), 383 mAh/g at 0.1 mA/cm²
- More electrolyte oxidation/oxygen release at low current rates

Anomalous Capacity:
$0.7Li_2MnO_3 \bullet 0.3LiMn_{0.333}Ni_{0.333}Co_{0.333}O_2$ Electrode



- $0.7Li_2MnO_3 \bullet 0.3LiMn_{0.333}Ni_{0.333}Co_{0.333}O_2$ electrode delivers >250 mAh/g during the early cycles at 0.05 mA/cm^2 (> theoretical, 242 mAh/g)
- Reversible Li + $O_2 \leftrightarrow Li_2O_2$ reaction? How do we exploit this?

Figure 5

Modeling Dissolution Reactions of Lithium Metal Oxides

- Dissolution of $LiMn_2O_4$ spinel electrodes is a well known phenomenon that severely damages the electrochemical cycling stability of cells at elevated temperature (>40 °C).

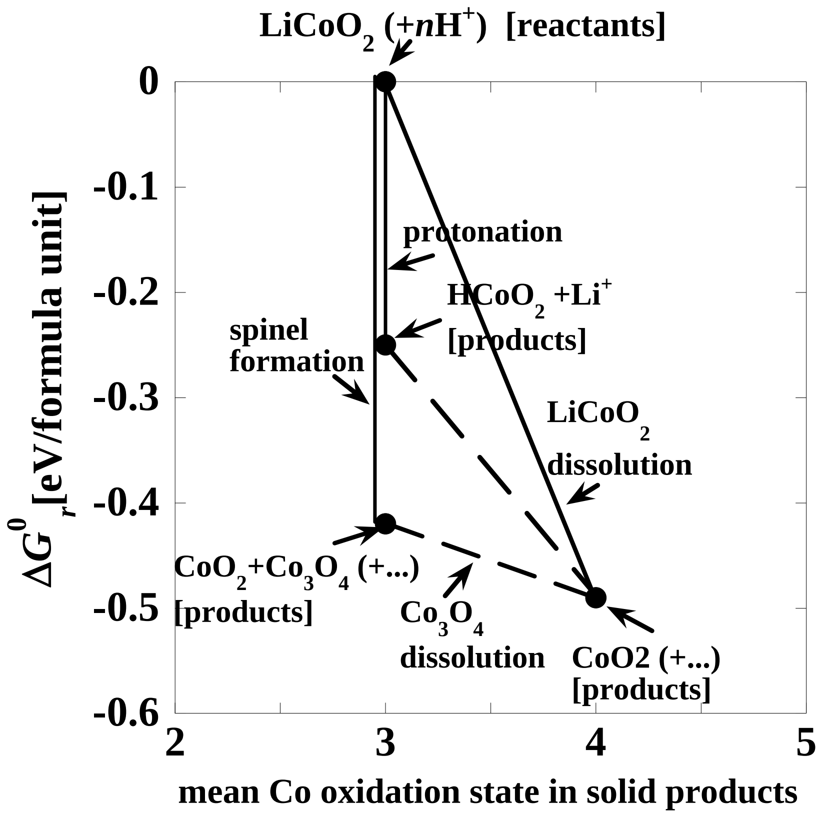
- Dissolution is also known to occur in layered $LiMO_2$ electrodes (Mn, Ni, Co)

- H^+-ion exchange can occur in Li_2MnO_3 ($Li[Li_{1/3}Mn_{2/3}]O_2$) yielding $H[Li_{1/3}Mn_{2/3}]O_2$

  ⇒ provides motivation to study dissolution vs. H^+ exchange reactions in structurally-integrated $xLi_2MnO_3 \bullet (1-x)LiMO_2$ electrodes

- Start with simple system: $LiCoO_2$

Theoretical Modeling: First Principles Calculations Dissolution vs. H^+ Ion-Exchange in Li_xCoO_2



- Hybrid approach: first principles DFT calculations used to determine free energies of solid phases and tabulated empirical quantities used for aqueous species
- Free energy calculations predict cobalt dissolution favored over H^+-ion exchange in acidic (electrolyte) media, despite the instability of CoO_2.
- Calculations consistent with experiment (chemical reaction of $LiCoO_2$ with acid)

R. Benedek et al., JES – submitted (2008)

Publications

- 2007 Publications

1. S.–H. Park, S.–H. Kang, C. S. Johnson, K. Amine and M. M. Thackeray, *Lithium-Manganese-Nickel-Oxide Electrodes with Integrated Layered-Spinel Structures for Lithium Batteries*, Electrochem. Comm. **9**, 262 (2007).
2. C. S. Johnson, N. Li, C. Lefief and M. M. Thackeray, *Anomalous Capacity and Cycling Stability of* $x\mathrm{Li_2MnO_3}\bullet(1-x)\mathrm{LiMO_2}$ *Electrodes (M=Mn, Ni, Co) in Lithium Batteries at 50 °C*, Electrochem. Comm. **9**, 787 (2007).
3. S.-H. Kang, P. Kempgens, S. Greenbaum, A. J. Kropf, K. Amine and M. M. Thackeray, *Interpreting the Structural and Electrochemical Complexity of* $0.5\mathrm{Li_2MnO_3}\bullet0.5\mathrm{LiMO_2}$ *Electrodes for Lithium Batteries* $(M = \mathrm{Mn}_{0.5-x}\mathrm{Ni}_{0.5-x}\mathrm{Co}_{2x}, 0 \leq x \leq 0.5)$, J. Mater. Chem., **17**, 2069–2077 (2007).
4. M. M. Thackeray, S.-H. Kang, C. S. Johnson, J. T. Vaughey, R. Benedek, and S. A. Hackney, $\mathrm{Li_2MnO_3}$*-stabilized* $\mathrm{LiMO_2}$ *(M=Mn, Ni, Co) Electrodes for High Energy Lithium-Ion Batteries*, J. Mater. Chem., **17**, 3112 - 3125 (2007).
5. M. M. Thackeray, *The Structural Design of Electrode Materials for High Energy Lithium Batteries*, J. Chem. Eng. of Japan **40**, 1150 (2007).

Patents and Technology Transfer

- Patents from BATT Program (*with BES contributions)

  1. *M. M. Thackeray, C. S. Johnson, K. Amine and J. Kim, *Lithium Metal Oxide Electrodes for Lithium Cells and Batteries*, US Patent No. 6,677,082 (13 January, 2004).
  2. *M. M. Thackeray, C. S. Johnson, K. Amine and J. Kim, *Lithium Metal Oxide Electrodes for Lithium Cells and Batteries*, US Patent No. 6,680,143 (20 January, 2004).
  3. C. S. Johnson, M. M. Thackeray and A. J. Kahaian, *Protective Coating on Positive Lithium-Metal-Oxide Electrodes for Lithium Batteries*, US Patent No. 7,049,031 (23 May, 2006).
  4. *M. M. Thackeray, C. S. Johnson, K. Amine and J. Kim, *Lithium Metal-Oxide Electrodes for Lithium Cells and Batteries*, US Patent 7,135,252 (14 November 2006).
  5. M. M. Thackeray, C. S. Johnson and N. Li, *Manganese Oxide Composite Electrodes for Lithium Batteries*, US Patent 7,303,840 (4 December 2007).

- Technology transfer/license agreements established: Patents 1 and 2.

Future Plans

- Optimize integrated 'layered-layered' and 'layered-spinel' electrodes:
  - *optimize composition and capacity utilization (200-250 mAh/g)*
  - *improve power*
  - *design electrodes that avoid a high-potential (>4.4 V) activation step*
  - *enhance surface stability of electrodes at high potentials*
  - *investigate possibility of stabilizing nano-particulate metal oxide electrodes*
  - *explore origins of anomalous capacity and find ways to exploit it.*
- Evaluate performance parameters:
  - *electrochemical behavior in full cells*
  - *structure – electrochemical property relationships (in situ X-ray diffraction and absorption, neutron diffraction, NMR, HRTEM etc)*
- Model dissolution phenomena in spinels; initiate simulation of local structure in integrated materials and stabilized surfaces (time permitting)

Acknowledgments

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