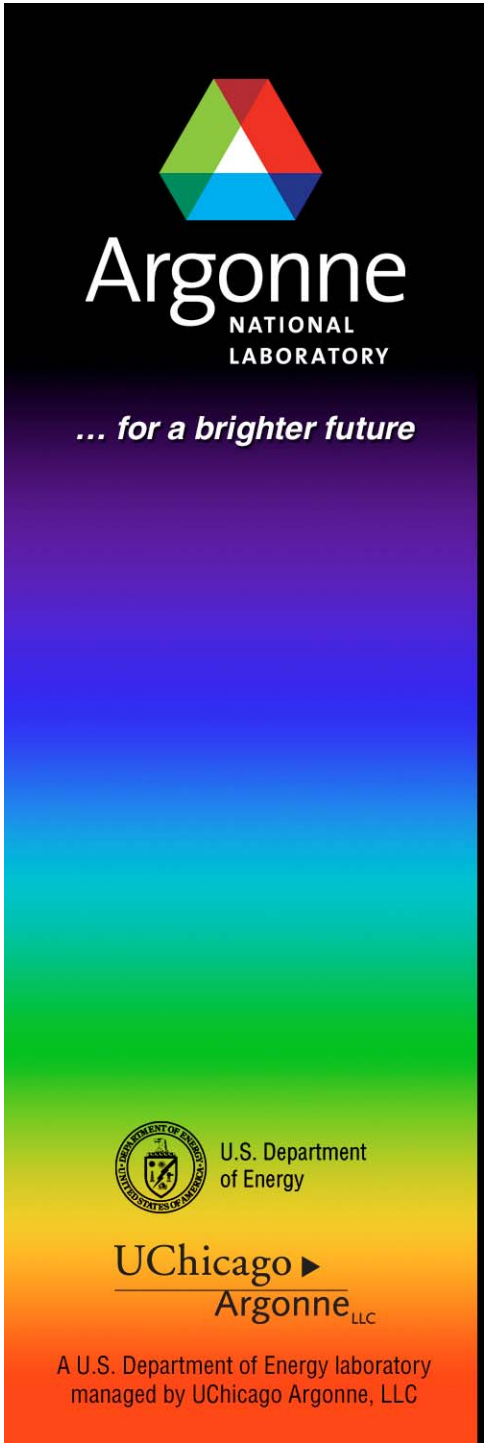

High Energy Materials for PHEVs: Cathodes (New Project)

presented by

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This presentation does not contain any proprietary or confidential information.

Purpose, Barriers and Goals, Approach, Collaborators

Purpose of Work

- Design and develop new high capacity cathodes for PHEVs

Barriers

- Vehicle range (40 miles), lithium battery energy density

Goals

- Initial technical target: >200 mAh/g for 100 cycles between 4.5 and 2.0 V without compromising power

Approach

- Use high potential (>4 V) electrochemical reactions to design new cathode materials and to use surplus lithium in precursor structures to load thin film metal- or metal-alloy anode substrates.

Collaborators

- Co-investigators: Sun-Ho Kang, Chris Johnson

Example: Electrochemical Activation of Li_2MnO_3

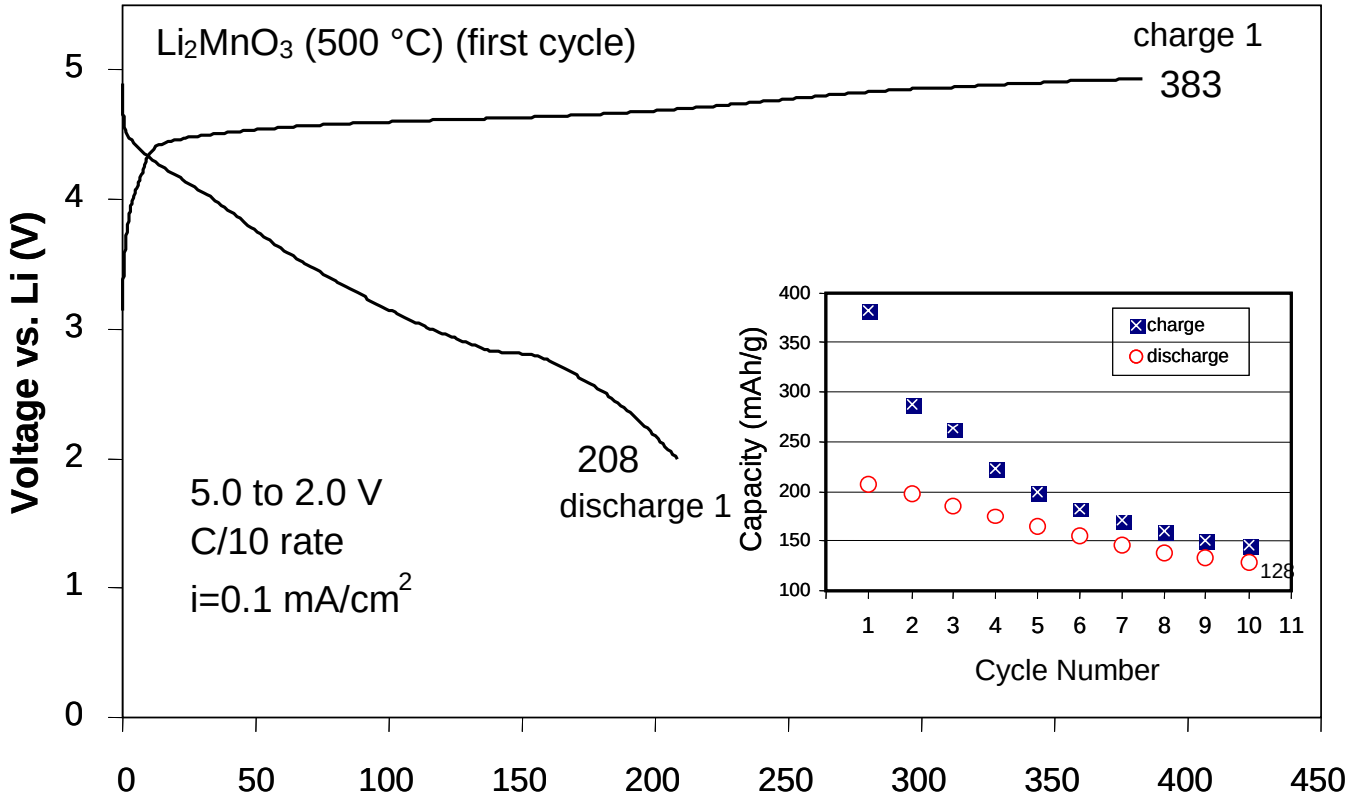
$$Li_2MnO_3\ (Li_2O{\bullet}MnO_2) \xrightarrow{4.5\text{-}4.8\ V} MnO_2 + 2\ Li + \tfrac{1}{2}\ O_2$$

- Net loss is Li_2O
- Two Li^+ ions removed during electrochemical activation (charge)
- One Li^+ ion reinserted into residual MnO_2 component:

$$Li + MnO_2 \rightarrow LiMnO_2$$

- Use surplus Li to load anode: C_6, metals or even bare substrate (Li metal)
- Complementary to lithium metal project (Vaughey and Dees)
- Use Li_2MnO_3 precursor in combination with high capacity charged cathodes, particularly where two-electron transfer reactions are possible, e.g., V_2O_5 (442 mAh/g), LiV_3O_8 (372 mAh/g)
- Blended electrodes or integrated (layered) structures?

Electrochemical Activation of Li_2MnO_3

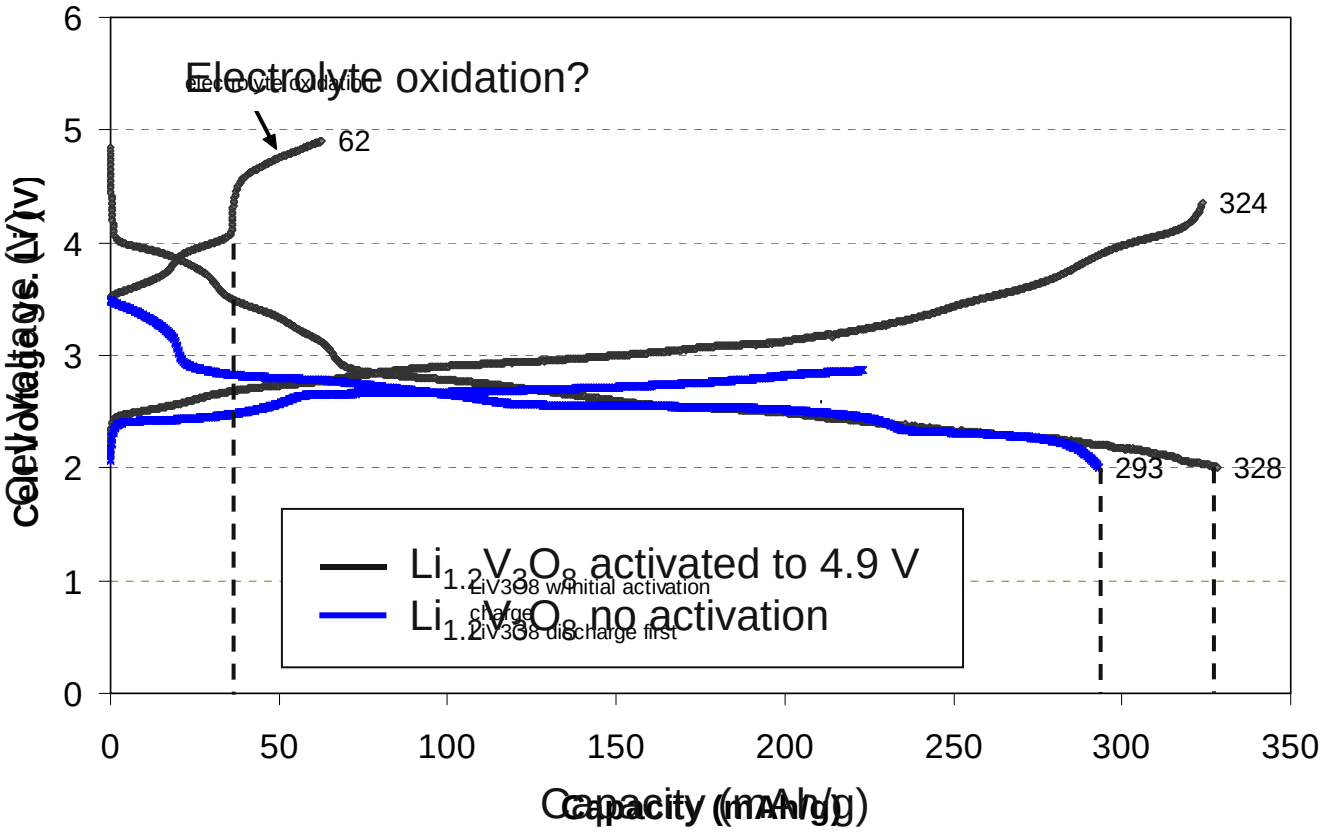


- Theoretical capacity of initial charge is 459 mAh/g
- Practical capacity: 383 mAh/g (charge) and 208 mAh/g (discharge) (~2:1 ratio)
- Pure Li_2MnO_3 does not cycle well over wide voltage window

$Li_{1.2}V_3O_8$ Selected for Proof of Concept

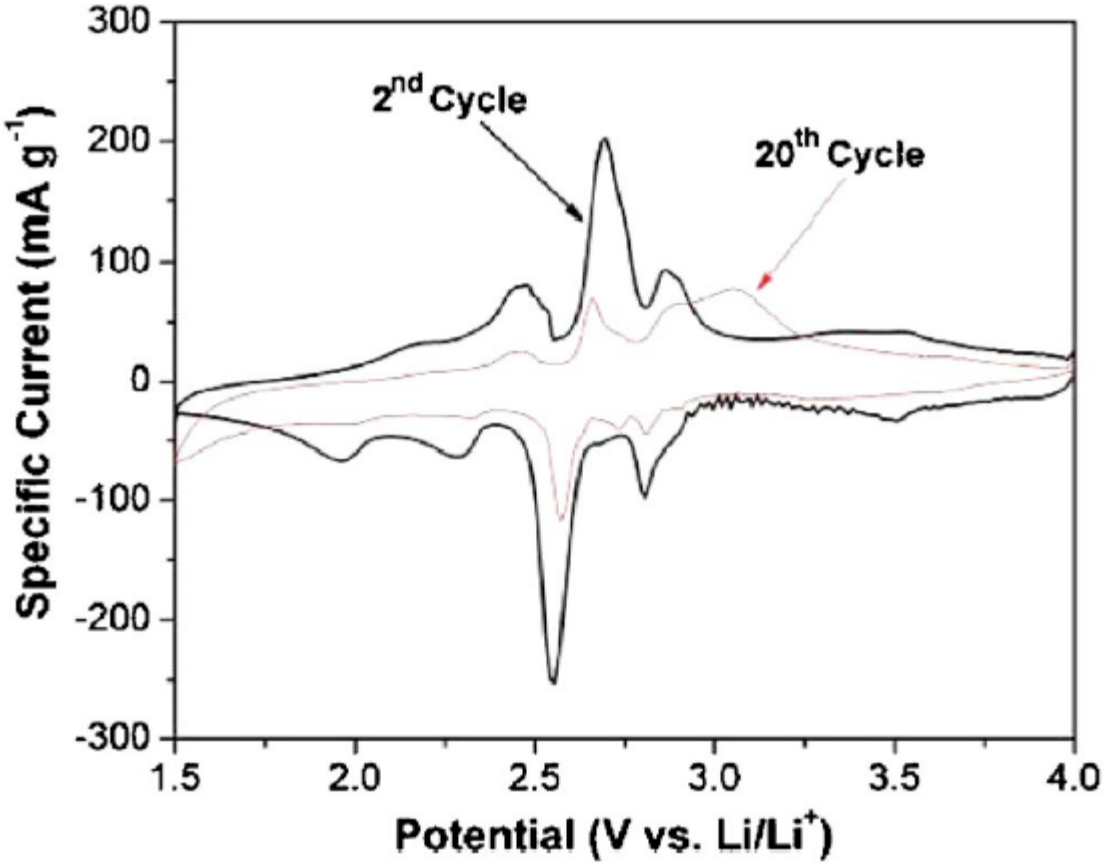
- $Li_{1.2}V_3O_8$ and Li_2MnO_3 both have Li_2O-stabilized layered structures ($LiV_3O_8 = Li_2O•3V_2O_5$ and $Li_2O•MnO_2$)
- $Li_{1.2}V_3O_8$ used in Li-polymer batteries
- Selected Composition: $0.26Li_{1.2}V_3O_8•0.74Li_2MnO_3$
- Balanced electrode: 1.48 Li^+ (max) extracted from Li_2MnO_3 during charge and 0.74 Li^+ inserted into each of $Li_{1.2}V_3O_8$ and MnO_2 components
- Preparation:
  - $Li_{1.2}V_3O_8$ prepared from Li_2CO_3 and NH_4VO_3 at 450 °C in air
  - Li_2MnO_3 prepared from Li_2CO_3 and $MnCO_3$ at 450 °C in air
  - $Li_{1.2}V_3O_8$ and Li_2MnO_3 components mixed and fired at 300 °C in air.

Electrochemical Activation of $Li_{1.2}V_3O_8$



- 0.2 Li is extracted from $Li_{1.2}V_3O_8$ between 3.5 and 4.0 V
- It is difficult to extract Li_2O from remaining LiV_3O_8, at least below 5.0 V
- Delivered capacity >300 mAh/g after activation to 5.0 V

Cyclic Voltammogram of $Li_{1.2}V_3O_8$ Electrode

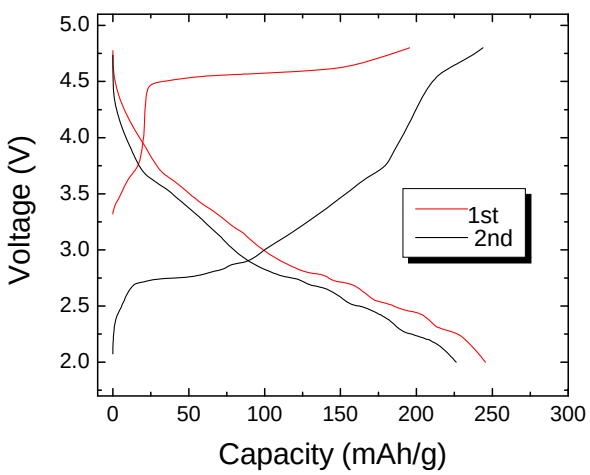


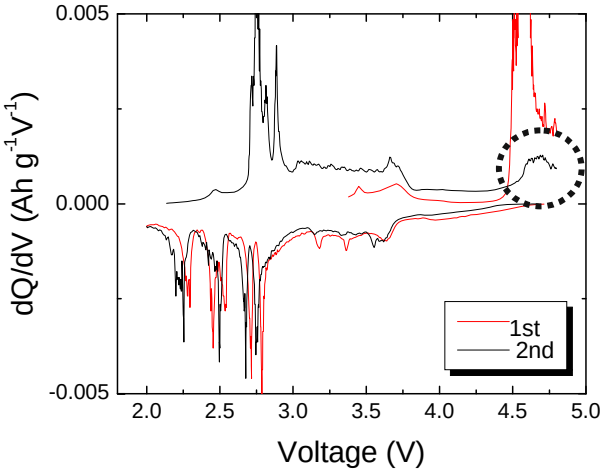
- $Li_{1.2}V_3O_8$ fingerprint: major reduction peak at 2.55 V and minor peaks at 3.50, 2.80, 2.30 and 1.95 V

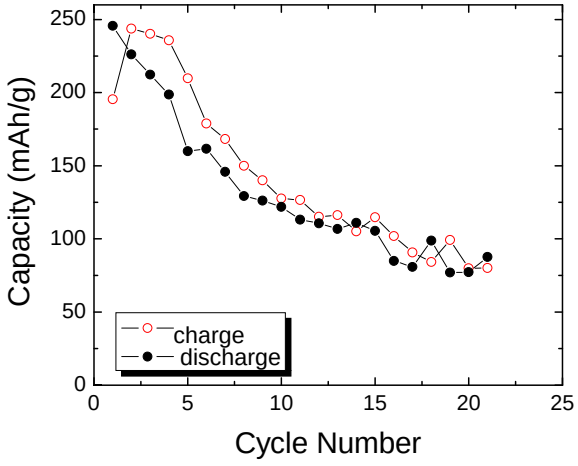
T. J. Patey et al., Electrochemical and Solid-State Letters, **11**, A46 (2008)

$0.26Li_{1.2}V_3O_8 \bullet 0.74Li_2MnO_3$ Electrodes

- Half cell data
- Cells cycled between 4.8 and 2.0 V at 0.05 mA/cm^2





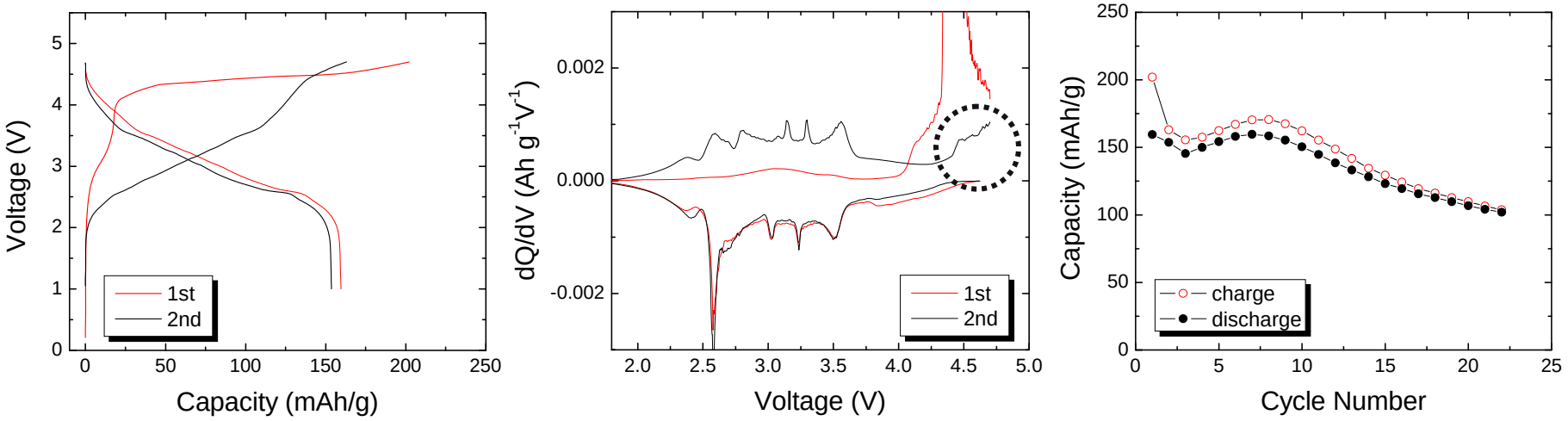


- >200 mAh/g achieved during early cycles with contributions from both $Li_{1.2}V_3O_8$ and Li_2MnO_3 components
- Irreversible oxidation process at 4.5 V
- Poor cycling stability – resembles pure Li_2MnO_3

  $\Rightarrow$ Li_2MnO_3 content too high

$0.26Li_{1.2}V_3O_8 \bullet 0.74Li_2MnO_3$ Electrodes

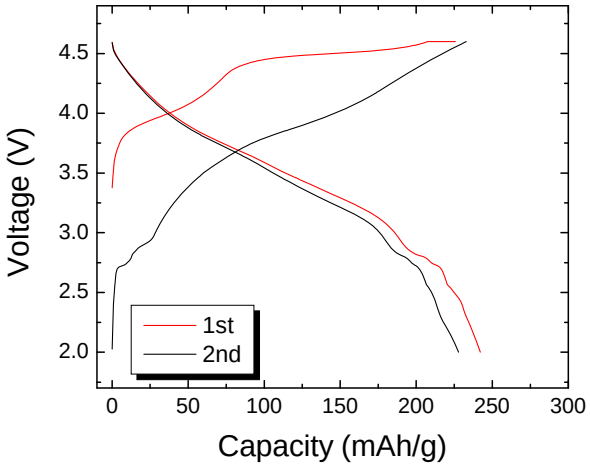
- Full cell data (MCMB 10-28 anode)
- Cathode limited
- Cells cycled between 4.7 and 1.0 V at 0.05 mA/cm^2 (1st 2 cycles) and thereafter between 4.7 and 2.0 V at 0.10 mA/cm^2

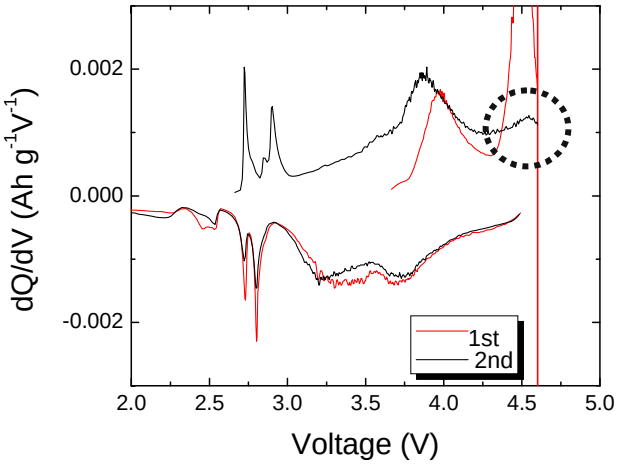


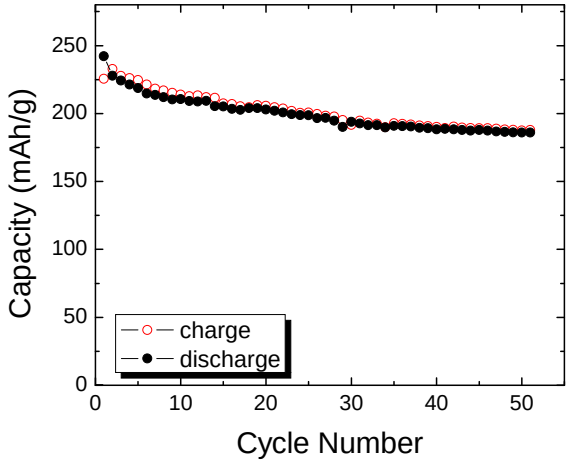
- $Li_{1.2}V_3O_8$ fingerprint evident in dQ/dV plot, confirming use of surplus lithium in parent cathode and demonstrating proof of concept.
- Low capacity utilization (150 mAh/g) attributed to excess MCMB in anode, high Li_2MnO_3 content in cathode, and irreversible oxidation at >4.4 V

$0.1Li_{1.2}V_3O_8 \bullet 0.9[0.5Li_2MnO_3 \bullet 0.5LiMO_2]$ Electrodes ($M=Ni_{0.44}Co_{0.25}Mn_{0.31}$)

- $Li_{1.2}V_3O_8$ prepared from Li_2CO_3 and NH_4VO_3 at 450°C in air
- $0.5Li_2MnO_3 \bullet 0.5LiMO_2$ from LiOH and Ni-Co-Mn hydroxide at 900°C in air
- $Li_{1.2}V_3O_8$ and $0.5Li_2MnO_3 \bullet 0.5LiMO_2$ products blended, fired at 450°C in air
- Half cell data: cells cycled between 4.6 and 2.0 V at 0.05 mA/cm^2







- Significantly improved capacity retention
- Both $Li_{1.2}V_3O_8$ and $0.5Li_2MnO_3 \bullet 0.5LiMO_2$ components used
- Irreversible oxidation process at 4.5 V – voltage window too wide.

Summary and Plans for FY2008/2009

- These initial studies have demonstrated a proof of concept in which a lithium-rich cathode precursor, such as Li_2MnO_3, is used to supply surplus lithium to the anode during an initial 'activation' charge where it can subsequently be used to lithiate not only the activated MnO_2 component, but also a 'charged' component, such as LiV_3O_8, in the parent cathode.
- The preliminary results hold promise for increasing the capacity of cathode materials above 200 mAh/g when cycled between 4.5 and 2.0 V.
- This project is in its initial stages. Further work will be conducted in FY2008/2009 to exploit this concept further with the goal of designing new electrode structures and to improve capacity and cycling stability by:
  1) optimizing the composition of the parent electrodes,
  2) balancing cells (anode and cathode capacity),
  3) tuning the voltage window of the cell,
  4) exploring other lithium-rich precursors and charged cathode components,
  5) comparing differences in electrochemical behavior between blended electrodes and structurally integrated electrodes.

Publications, Patents and Technology Transfer

- This is a new project
- No publications have been submitted
- One patent application has been filed
- It is too early to consider any technology-transfer opportunities

Acknowledgments

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