Stan Whittingham
SUNY at Binghamton

The Synthesis and Characterization of Substituted Olivines and Layered Manganese Oxides

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Project ID #
ES050

Overview

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Timeline

- Project start date: 06-01-2008
- Project end date: 12-31-2011
- Percent complete: Continuing

Barriers

- Barriers addressed
  - Lower-cost,
  - Higher power,
  - Higher capacity and
  - Abuse-tolerant safer cathodes

Budget

- Total project funding
  - DOE share: 100% $
  - Contractor share: Personnel
- Funding received
  - FY09: 265k$
  - FT10: 294k$
- Funding requested
  - FY11: 340k$

Partners

- SUNY Stony Brook, LBNL, BNL, NREL, ORNL, Georgia Tech.
- Primet, and other companies

Objectives of Work

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- The primary objectives of our work are to find:
  - Lower-cost and higher capacity cathodes, exceeding **200 Ah/kg** (lab theoretical).
  - High rate PHEV compatible cathodes
  - Both of the above are to be based on environmentally benign materials

Milestones

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a) Determine the optimum composition of $LiNi_yMn_yCo_{1-2y}O_2$ for PHEV applications. (extended to Sep. 10)

- **Go**

b) Evaluate phosphate structures with varying morphologies and dopants, containing Fe and/or Mn, and compare with optimum $LiFePO_4$. (Sep. 10)

- **Go**

c) Identify materials that can undergo more than one electron per redox center. (Sep. 10)

- **New Project getting underway**

Approach to Improved Cathodes

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- Place emphasis on low cost materials,
  - Synthesize by practical approaches
  - Structurally characterize, including defects and morphology
  - Electrochemically evaluate in a range of cell configurations

  - Modified layered dioxides
    - What is role of other transition metals?
    - Minimize expensive components, such as cobalt.

  - Modified transition metal phosphates
    - Determine role of substituent cation on morphology and capacity in olivines
    - Find new classes of phosphates with a higher storage capacity

Technical Accomplishments: Barriers being Addressed

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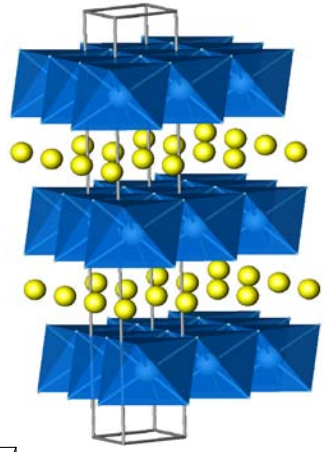
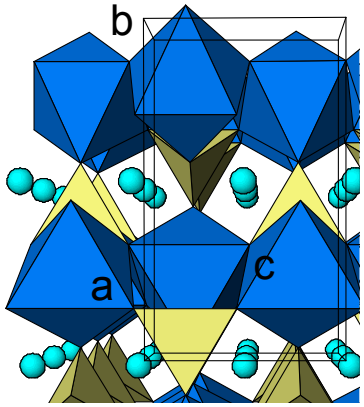
Lower-cost, higher power, higher-capacity and abuse-tolerant safer cathodes



- Ultimate capability of the MnO_2 and NiO_2 lattice
  - What is optimum $Li(MnNiCo)O_2$ **composition**
    - **Is 442 superior to 333?**
  - Need to increase **capacity** to 200 Ah/kg at C rate
    - Must cell voltage be reduced to increase capacity?
  - Need to increase rate **capability**
    - Is it really lower than Olivine phase?



- Beyond Olivines
  - Ideal olivine particle size and morphology
    - **Is a nanostructure, like the SONY tin anode, the answer? – Yes – 2009**
    - Exact reason for role of 5 % substitution of Mg or V not understood
  - > 200 Ah/kg from phosphate-type structures
    - Must vanadium be involved?

Optimum Composition in $LiMO_2$

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- What is maximum Mn in $Li(Ni_yMn_zCo_{1-y-z})O_2$?
  - Prior year results showed that
    - Maximum Mn is 0.5 in lithium stoichiometric material
      - Electrochemistry is good, but
        - Lower rate and capacity than $LiNi_{0.4}Mn_{0.4}Co_{0.2}O_2$
        - Similar capacity to $LiNi_{0.45}Mn_{0.45}Co_{0.1}O_2$
  - Rate suffers for Mn > 0.5 in lithium-rich materials
- What is "theoretical" capacity for $LiNi_yMn_yCo_{1-2y}O_2$?
  - Can 200 Ah/kg be achieved with present electrolytes?

What is Theoretical Capacity of $LiNi_yMn_yCo_{1-2y}O_2$?

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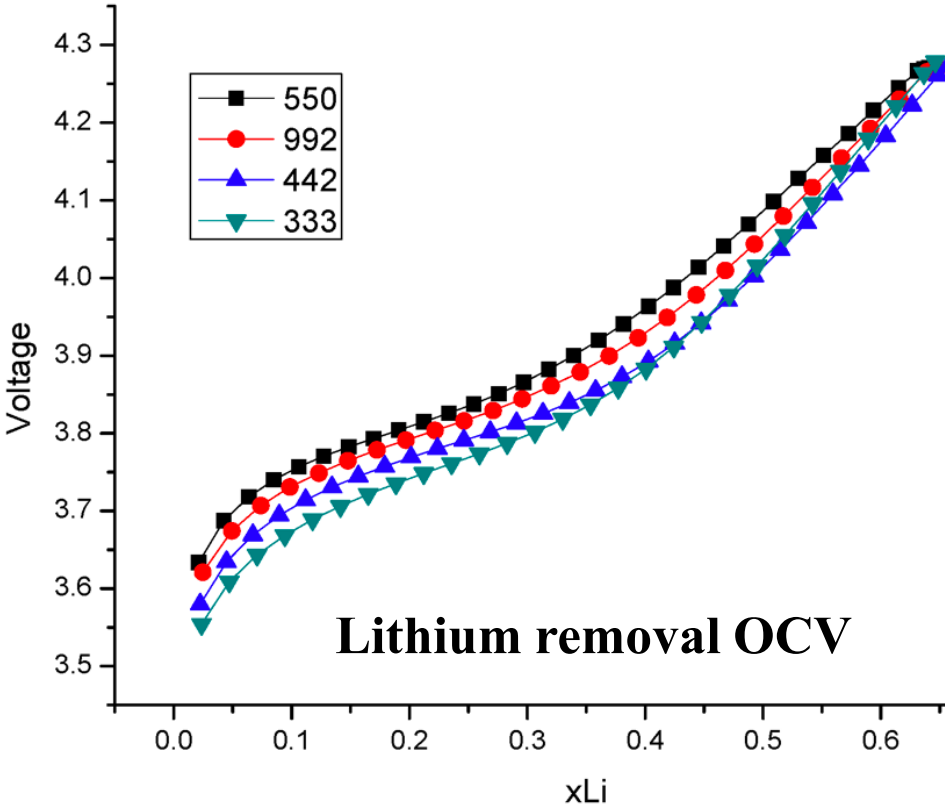
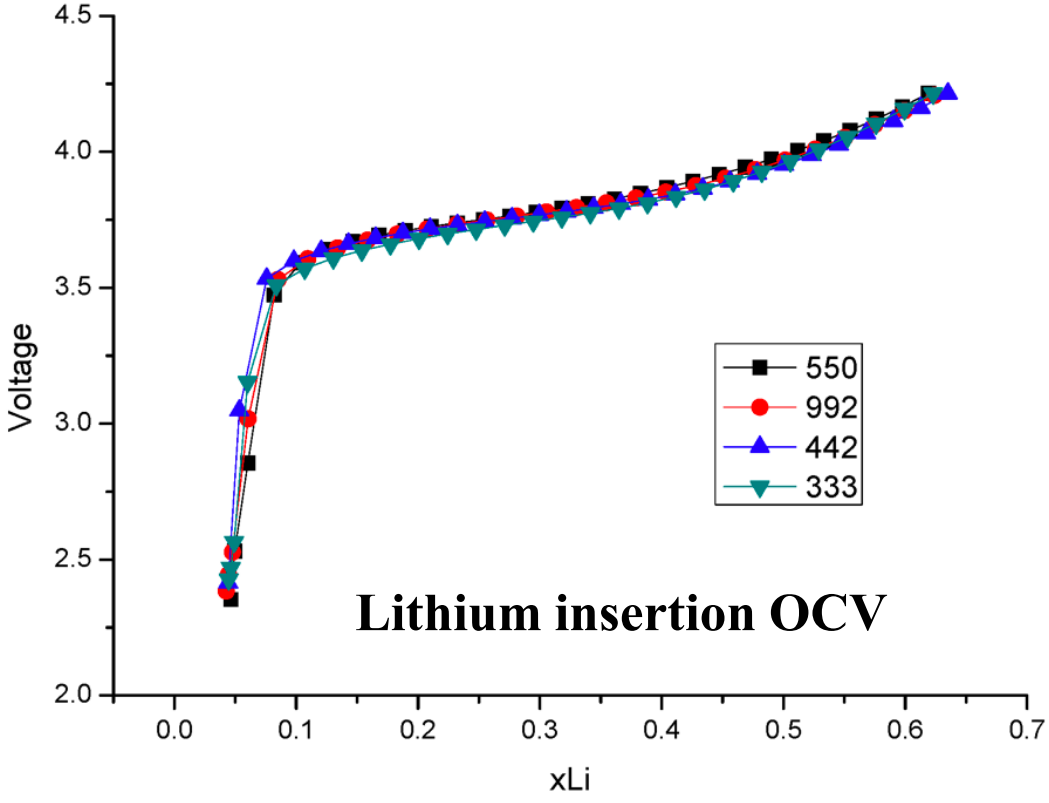
- Maximum capacity is:
  - 180 Ah/kg for a 4.3 volt cut-off on charging
  - 200 Ah/kg for a 4.4 volt cut-off on charging
    - But, all cells show a 1st cycle loss of 10-15 Ah/kg
    - Thus, theoretical capacity of over 220 Ah/kg needed for 200 Ah/kg practical
  - Need higher voltage electrolyte, or higher nickel content to lower voltage





What is Power Capability of $LiNi_yMn_yCo_{1-2y}O_2$?

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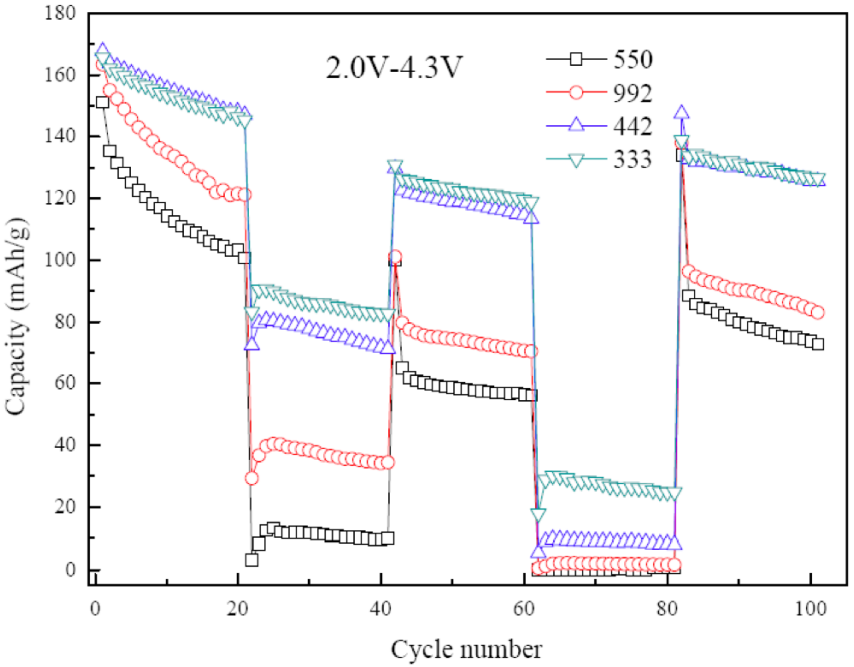
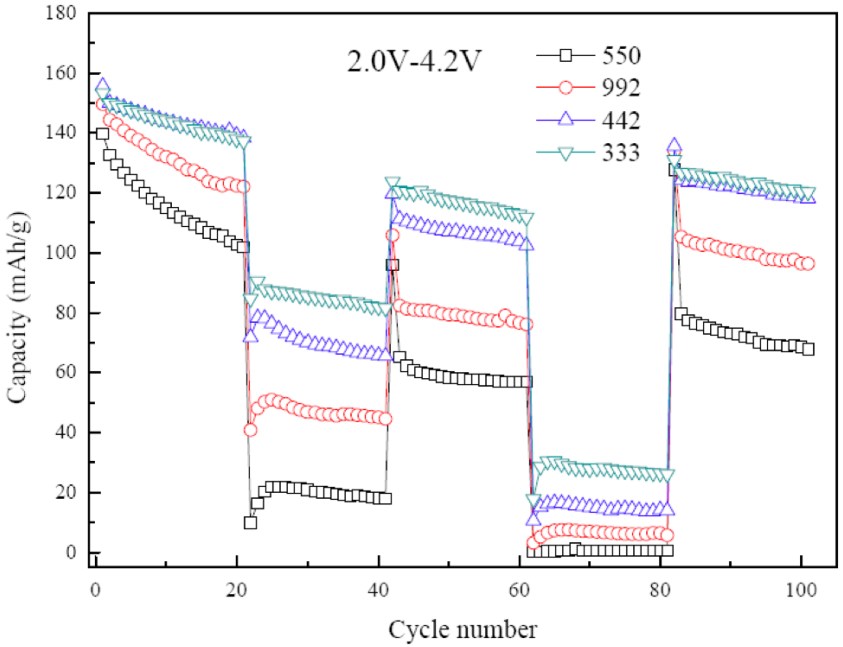
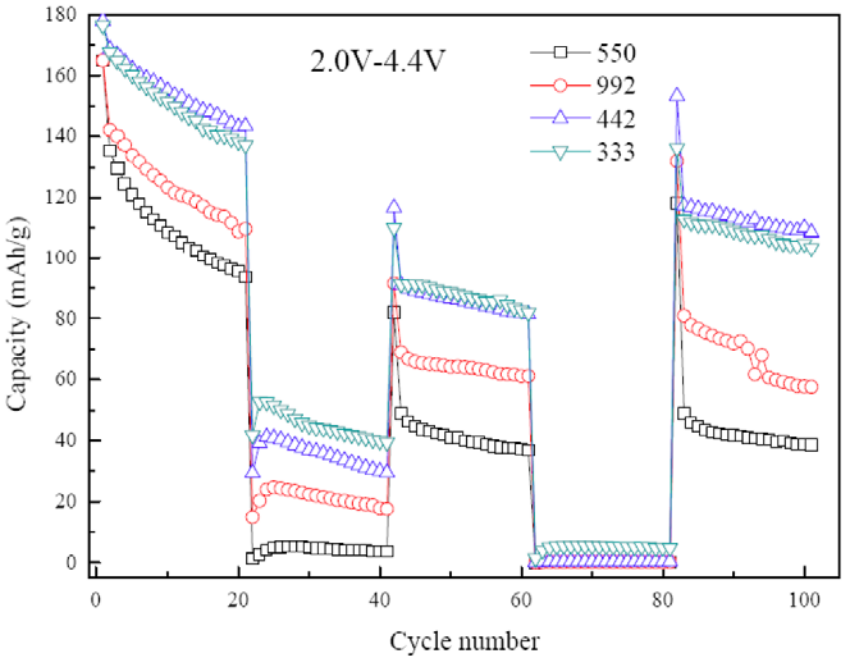
- 442 and 333 have comparable power
  - 550 and 992 significantly lower
- Capacity increases with charging voltage
  - Fade rate increases with charging voltage
- Can power capability be improved?
  - Initial tests at NREL say yes



C rate: 0.33 2.0 0.67 3.3 0.33





Does $LiNi_yMn_yCo_{1-2y}O_2$ Have Power Capability - Yes

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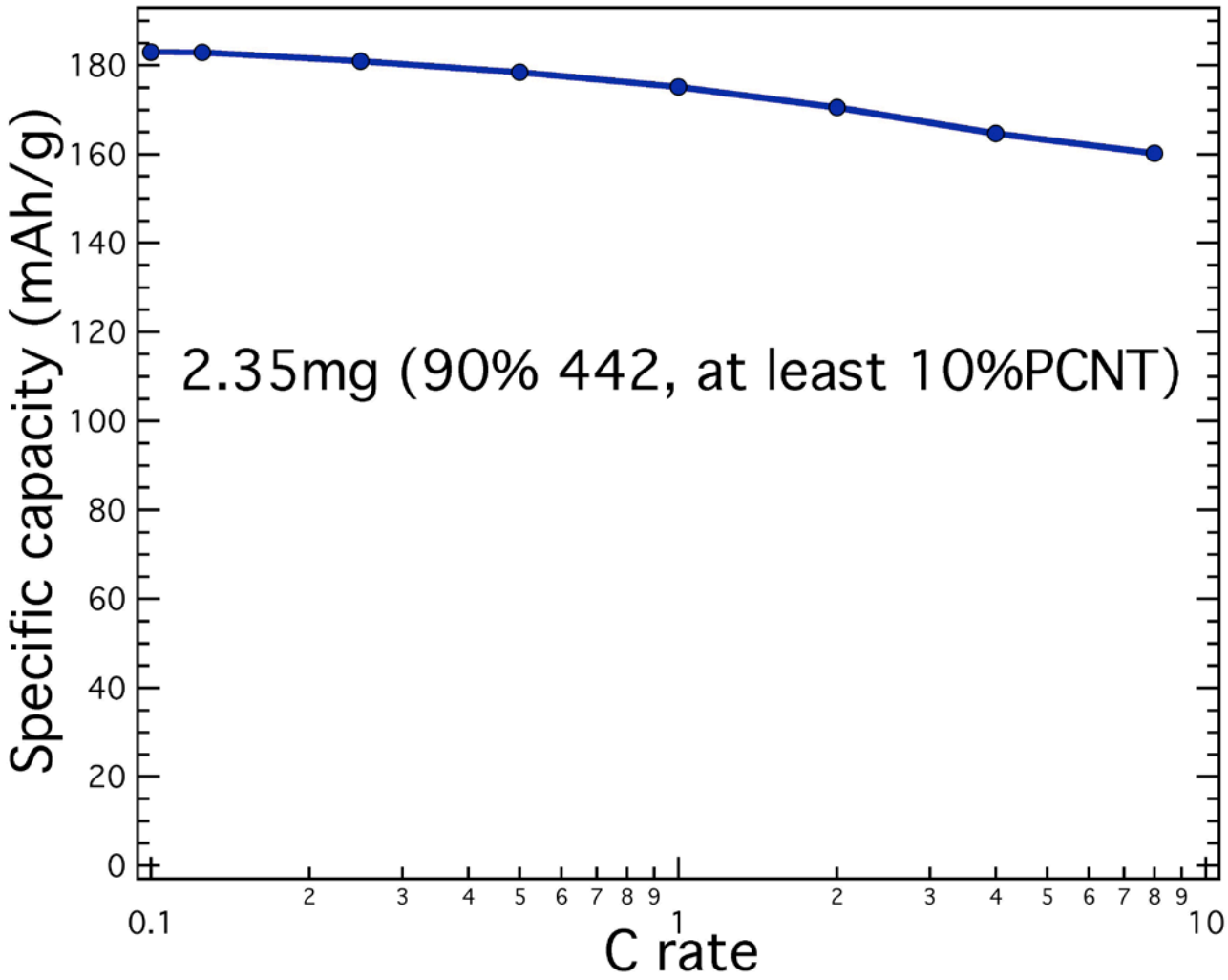
- Binder-free test of $LiNi_{0.4}Mn_{0.4}Co_{0.2}O_2$
  - Shows high rate capability
- Thus, material has inherent power capability

Binghamton Material

Tested at NREL by C. Ban and A. Dillon



Solid Solution Behavior of $LiFePO_4$ gives higher capacity and rate

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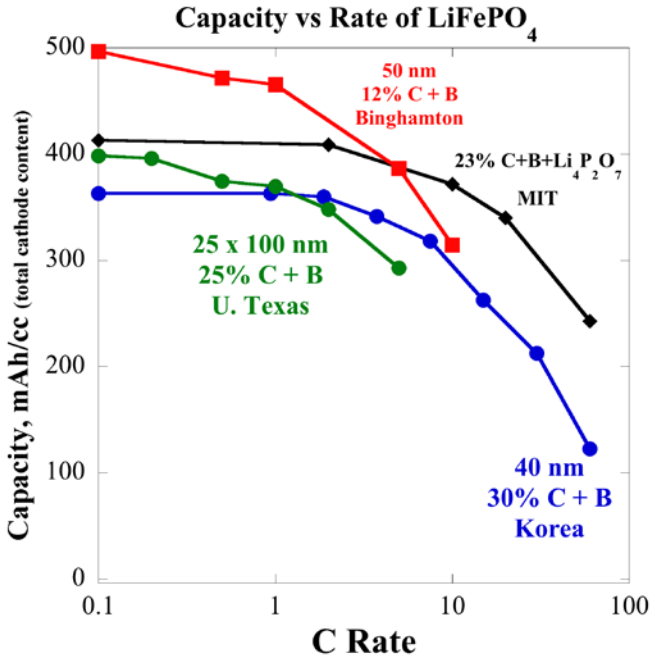
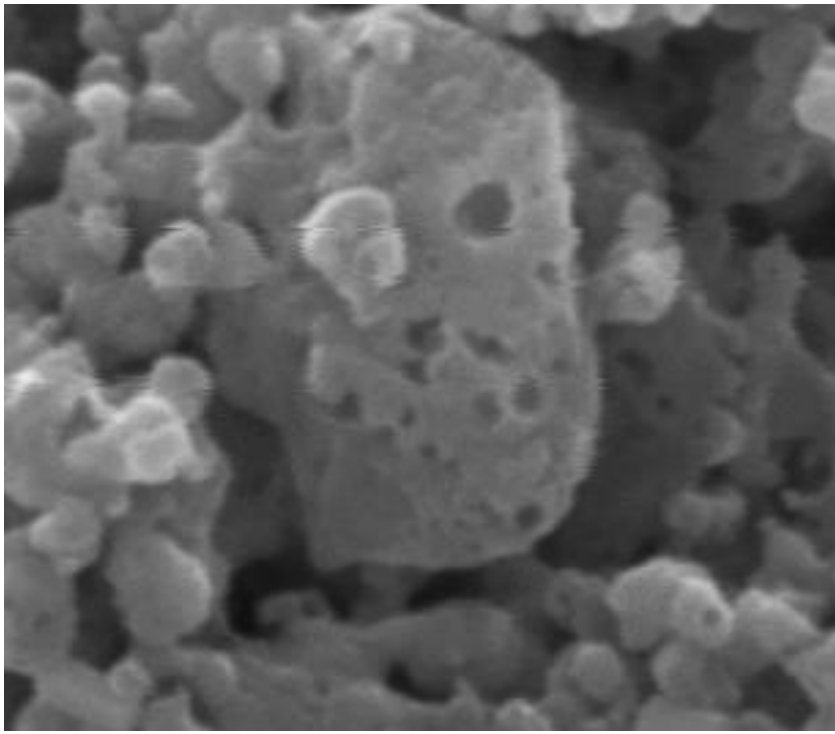
- Substituting $LiFePO_4$ gives nanostructure
  - $LiFeP_{1-y}V_yO_4$ has highest capacity at PHEV rates (2009 data)
- Study underway to determine how substitution impacts properties
  - Morphology vs defects (strain); optimum substitution level
    - Initial data suggest substitution on Li, Fe and P sites possible



Collaboration with C-S. Wang at U. Maryland

3 μm with 50 nm crystallites



200 Ah/kg Capacity Cathodes: >1 Li/M

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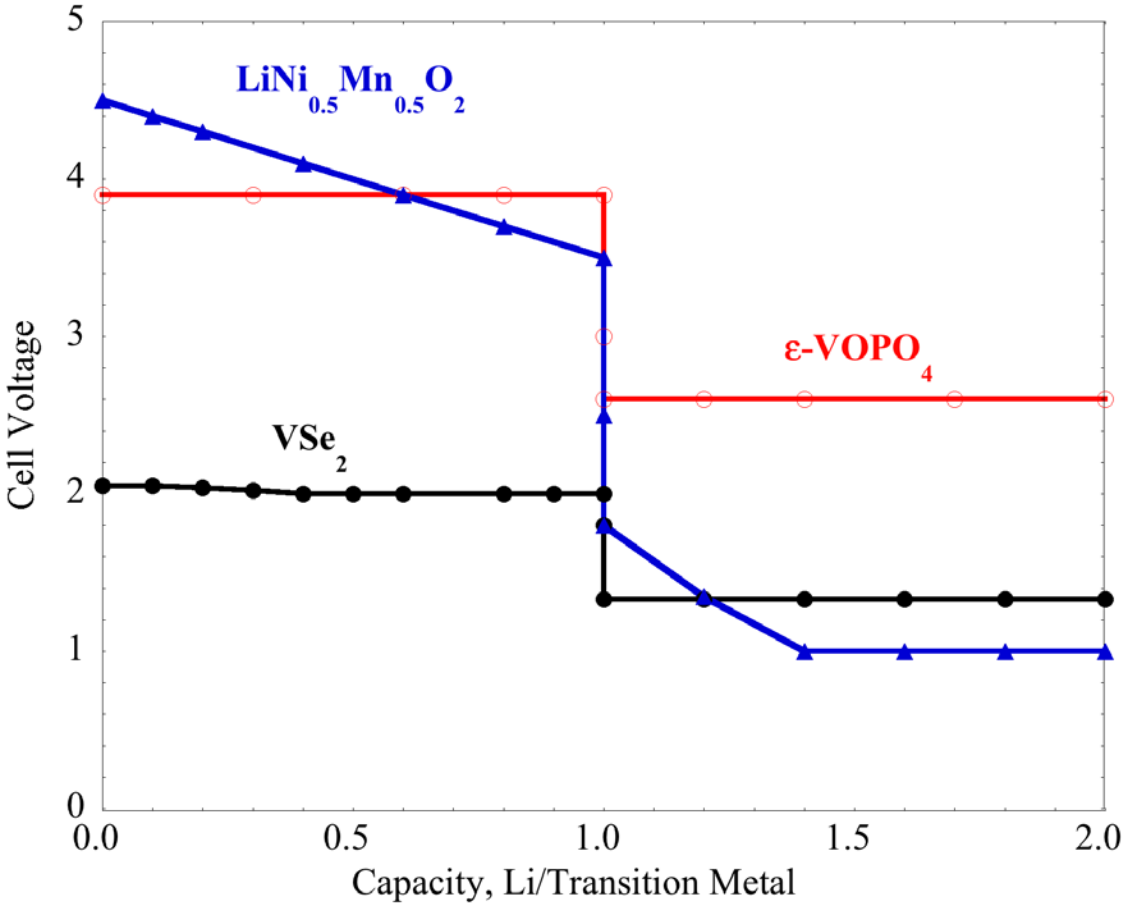
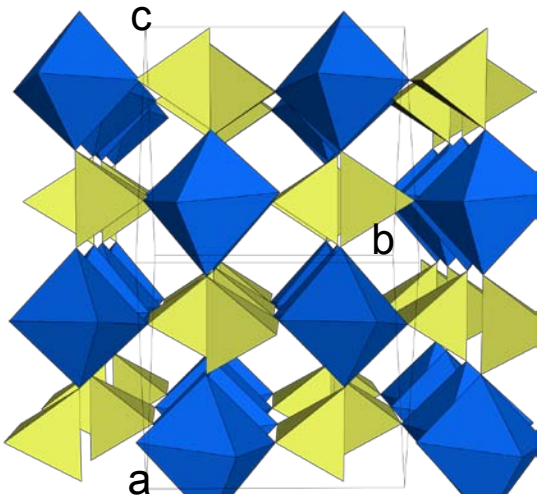
- Several materials known to react with more than 1 lithium
  - Dc to dc converters can handle voltage differences
- Search for new structures





Higher Capacity Cathodes: >1 Li/M

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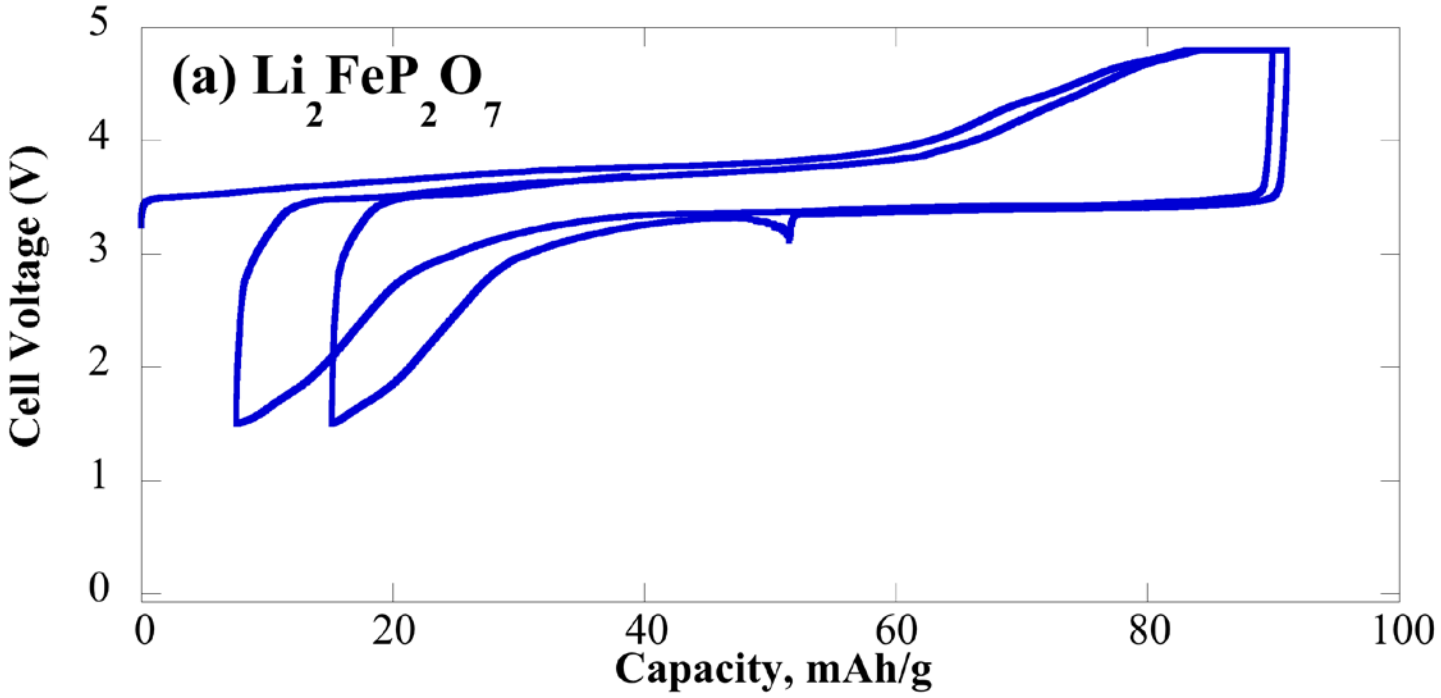
- Mn and Fe pyrophosphates
  - $Li_2(FeMn)P_2O_7$ formed for range of Fe and Mn content
    - Pure phases formed for first time
      - Capacity is directly related to Fe content
      - Not yet able to remove 2nd lithium (e.g. $Mn^{4+}P_2O_7$)



Higher Capacity Cathodes: >1 Li/M

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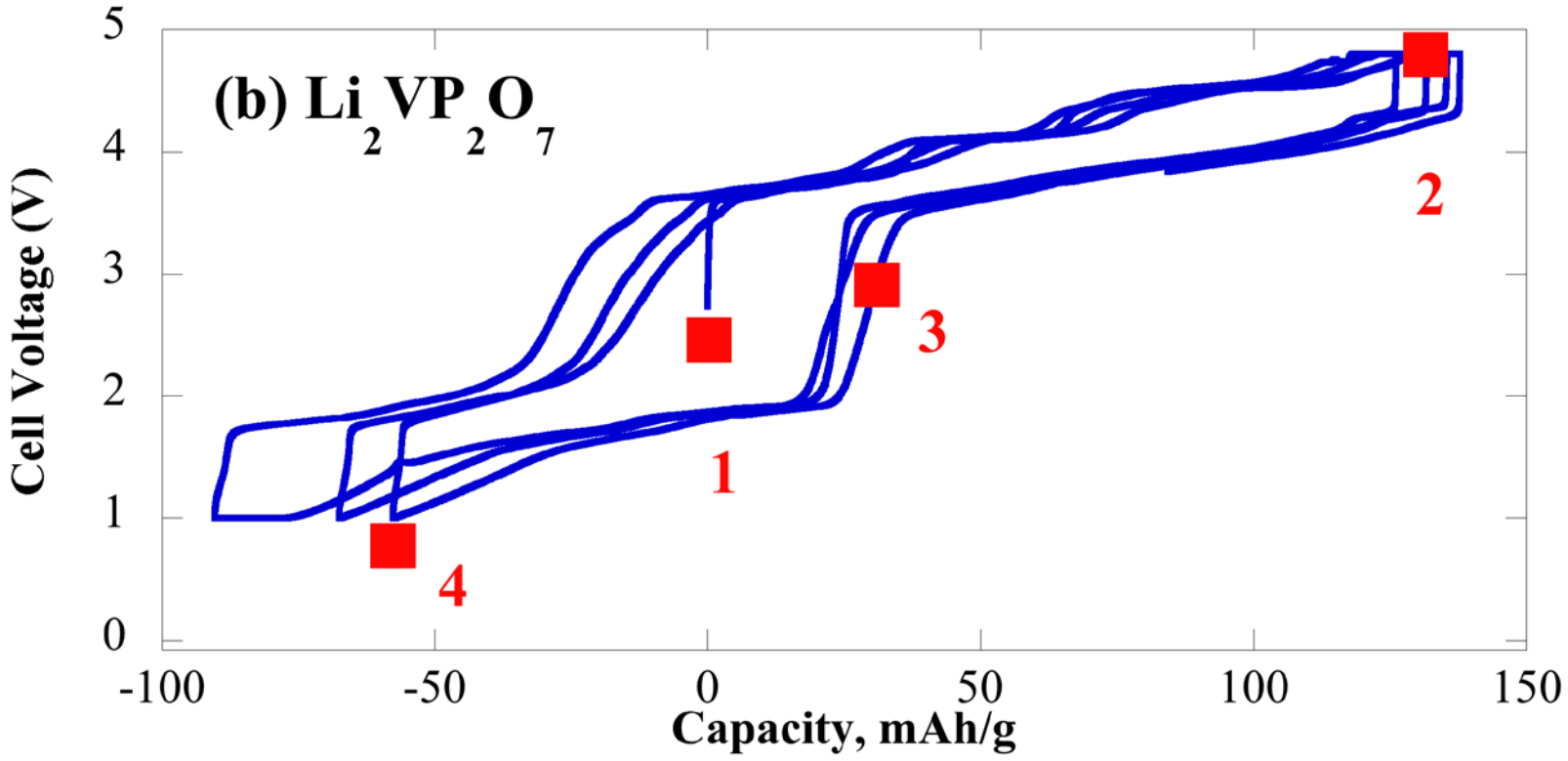
- Attempted formation of $Li_2(MnFeV)P_2O_7$
  - Electrochemical evaluation of "$Li_2VP_2O_7$" underway
    - Two lithium can be cycled
      - X-rays at 1, 2, 3 and 4 show crystalline material



Collaboration and Coordination with other Institutions

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- **The layered oxides**
  - C. Grey (SUNY Stony Brook) Ion ordering in $LiMO_2$
  - M. Doeff (LBNL) Al substitution in $LiMO_2$
  - A. Dillon (NREL) High rate evaluation of $LiNi_{0.4}Mn_{0.4}Co_{0.2}O_2$
  - S. V. Kalinin (ORNL) Scanning probe microscopy of Li_xMO_2
  - F. Alamgir (Georgia Tech.) in-situ XAS of Li_xMO_2 at BNL
- **The olivines**
  - C. S. Wang (U. Maryland) Synthesis of single-phase $LiFeP_{1-y}V_yPO_4$
  - G. Ceder (MIT) Mechanism of olivine reaction
  - Primet (Ithaca) Electrochemical evaluation of nano-scissored material

Future Work

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- **$LiMO_2$**
  - Determine inherent rate capability of $LiMO_2$
    - Work with A. Dillon and C. Ban of NREL
  - Understand what controls voltage of $LiMO_2$
    - Reduce by say 0.1 volts to increase capacity and stability/lifetime
    - 200 Ah/kg goal at 1C rate
- **Phosphates**
  - Determine composition range of single-phase $LiFeP_{1-y}V_yPO_4$
  - Understand role of substituents on reaction rate
- **2-Electron Materials**
  - Find materials that can reach 200 – 250 Ah/kg at 1C rate

Summary

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- **$LiMO_2$** - $LiMn_{0.40}Ni_{0.40}Co_{0.20}O_2$ may be optimum composition
  - 200 Ah/kg can be obtained for charging voltages over 4.4 volts
    - 1st cycle loss will dictate higher charging voltage
  - Need to modify voltage profile to attain 200 Ah/kg with present electrolytes
  - Collaborative work with NREL shows that $LiMO_2$ has inherent high rate
- Olivine – $LiFePO_4$
  - Work underway to understand positive role of substituents
  - Will be used as model for optimizing other materials
- New compounds identified with greater than 1e per redox center
  - Vanadium compounds showing most promise
    - Will be used to show proof of concept
- Technology transfer underway
  - Students in battery companies and at BNL, NREL and PNNL
  - Publications to transfer knowledge