The Synthesis and Characterization of Substituted Olivines and Layered Manganese Oxides

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Project ID #
es_22_whittingham

Overview

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Timeline

- Project start date: 06-01-2007
- Project end date: 05-31-2010
- Percent complete: Continuing

Budget

- Total project funding
  - DOE share: 100% $
  - Contractor share: Personnel
- Funding received
  - FY08: 188k$
  - FT09: 265k$
- Funding requested
  - FY10: 280k$

Barriers

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

Partners

- SUNY Stony Brook, LBNL, BNL, U. Maryland
- Primet, and other companies

Objectives of Work

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

Milestones

a) Characterize the electronically stabilized manganese oxide, determine the rate capability *vs.* Co content, determine the role of Ni and understand its disorder to obtain a stable high rate abuse tolerant cathode (including application to HEVs), determine the optimum composition and compare the best samples with the base case cathodes. (Sep. 09) .

- **Go**

b) Determine feasibility of aliovalent doping of olivine, $LiMPO_4$, determine optimum particle size and evaluate other phosphate structures containing Fe and Mn and compare them with high temperature $LiFePO_4$. (Sept. 09)

- **Go – doping allows nanostructure and higher capacity**

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

- **New project just getting underway**

Approach to Improved Cathodes

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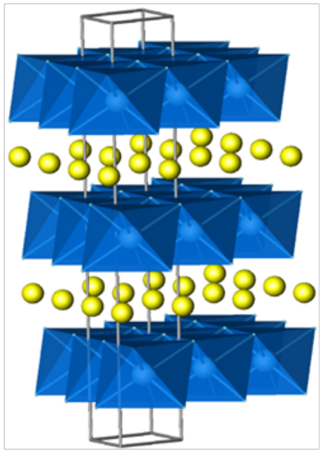
- Place emphasis on layered manganese dioxides, modified with other transition metal compounds
  - Minimizing the use of cobalt; go to 20 or 10 %
  - Determine structure, stability and electrochemical behavior
    - Understand the atomic disorder, and relate to electrochemical behavior
      - Emphasis on role of Ni, and its tendency to migrate during cycling
      - Understand the impact of moving to Li-rich compounds

- Place emphasis on the low cost safe transition metal phosphates
  - Understand their synthesis and structure, including disorder
    - Determine solubility ranges for isovalent mixed metals, $Li(MnMgFeCu\ldots.)PO_4$
    - Determine aliovalent and isovalent substitution for range of metals
    - Search for new phosphate structures with a higher storage capacity

Technical Accomplishments: Barriers being Addressed

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

- The long-term **stability** of the MnO_2 and NiO_2 lattice
  - – $LiMnO_2$ converts to spinel on charging, losing 50% capacity
  - – $LiNiO_2$ unsafe on charging, oxygen evolution
  - – $LiCoO_2$ low capacity and too expensive
  - – **Determine optimum Li(MnNiCo)O_2 composition**
    - **Is 442 superior to 333?**

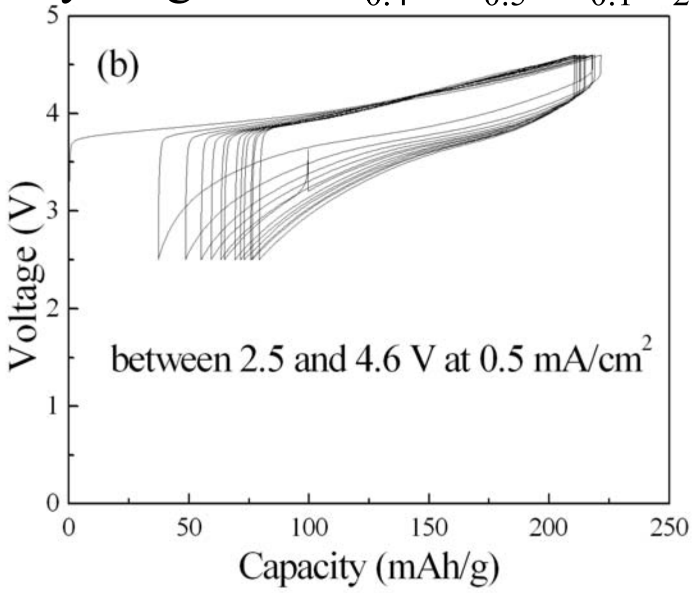


- **Capacity** (volumetric) and rate of Olivines, $LiFePO_4$
  - – A low cost synthesis/manufacturing process for $LiFePO_4$
    - **Low cost material needs low cost process – GO last year**
  - – The high electrical resistivity of $LiFePO_4$
    - **Can substitution work?**
  - – Ideal particle size and morphology for reaction mechanism
    - **Is a nanostructure, like the SONY tin anode, the answer?**

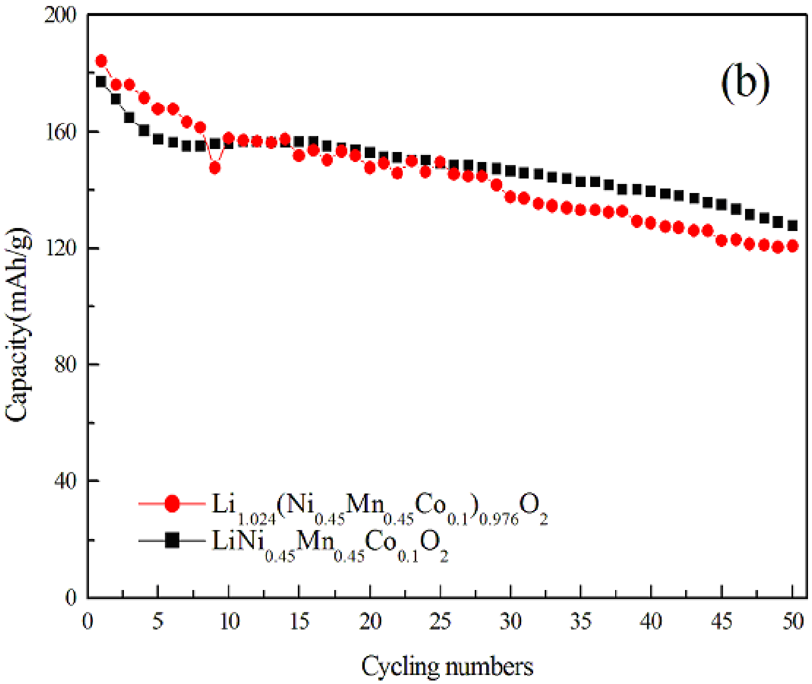
Optimum Composition in $LiMO_2$

- What is maximum Mn in $Li(Ni_yMn_zCo_{1-y-z})O_2$?
  - Mn is lowest cost and least likely to evolve O_2 on charging (safest)
  - Maximum Mn is 0.5 in lithium stoichiometric material
  - Rate suffers for Mn > 0.5 in lithium-rich materials
- The electrochemistry of $LiNi_{0.4}Mn_{0.5}Co_{0.1}O_2$ is good
  - Similar to $LiNi_{0.45}Mn_{0.45}Co_{0.1}O_2$; but note fading issue.

Cycling of $LiNi_{0.4}Mn_{0.5}Co_{0.1}O_2$



Cycling at 0.5 mA/cm², 2.5 to 4.6 volts



What is Optimum Composition in $LiNi_yMn_yCo_{1-2y}O_2$ for Energy and Power?

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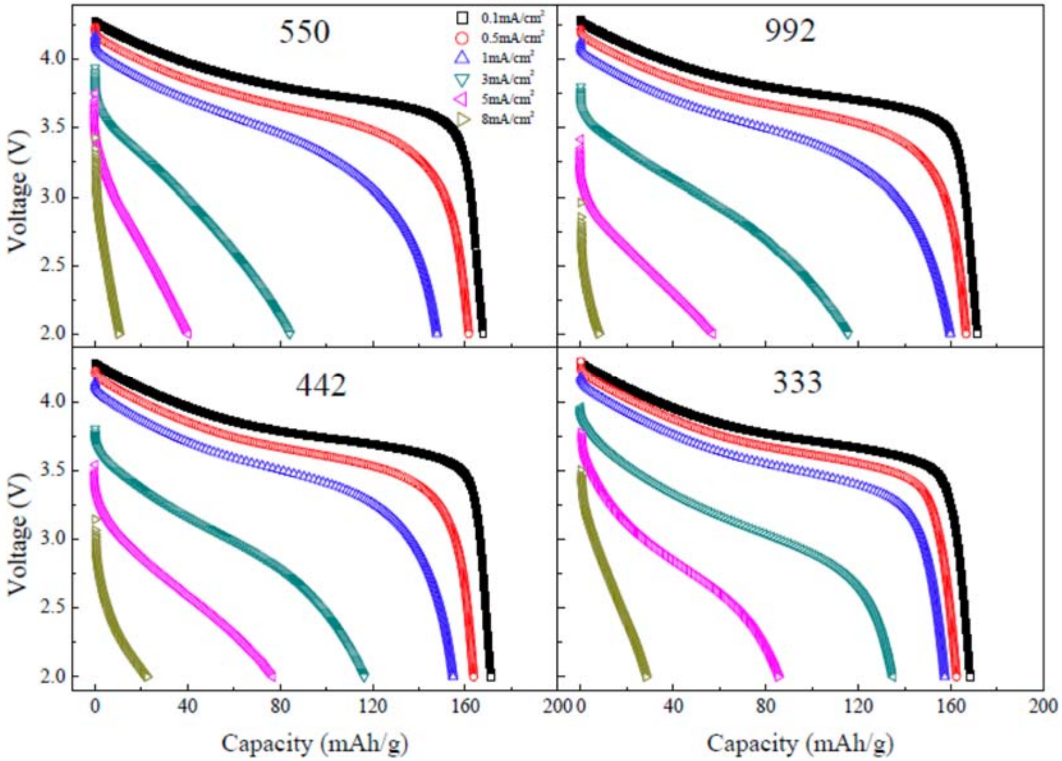
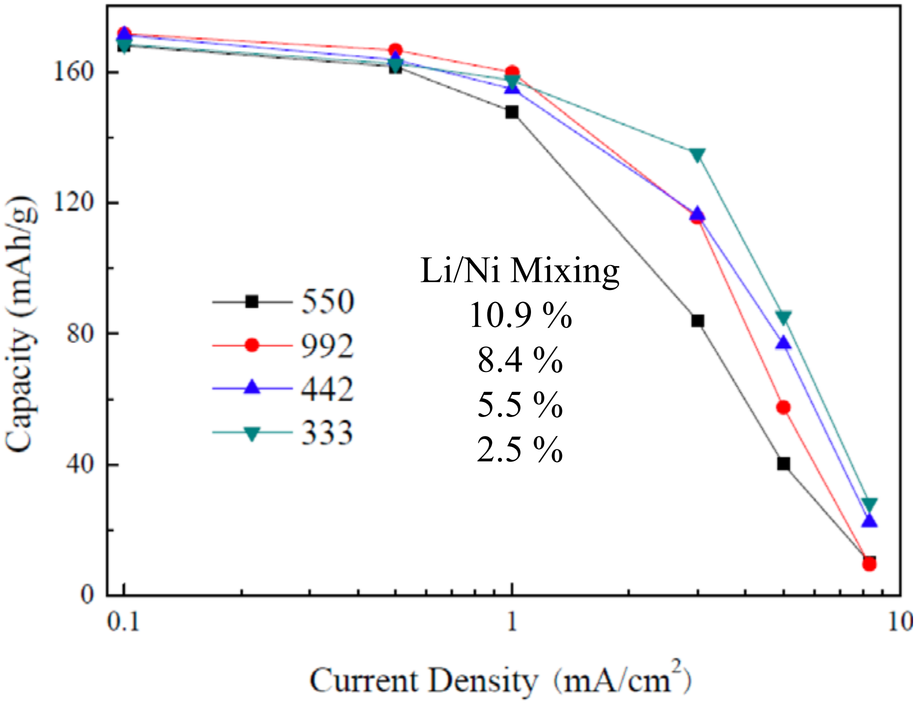
- What is optimum value of y?
  - 550, 991, 442 and 333
    - **Low charging rate of 0.1 mA/cm^2**
      - **Highest cobalt gives best capacity at higher rates**
      - **But 10% cobalt gives highest capacity at intermediate rates**





What is Optimum Composition in $LiNi_yMn_yCo_{1-2y}O_2$ for Energy and Power?

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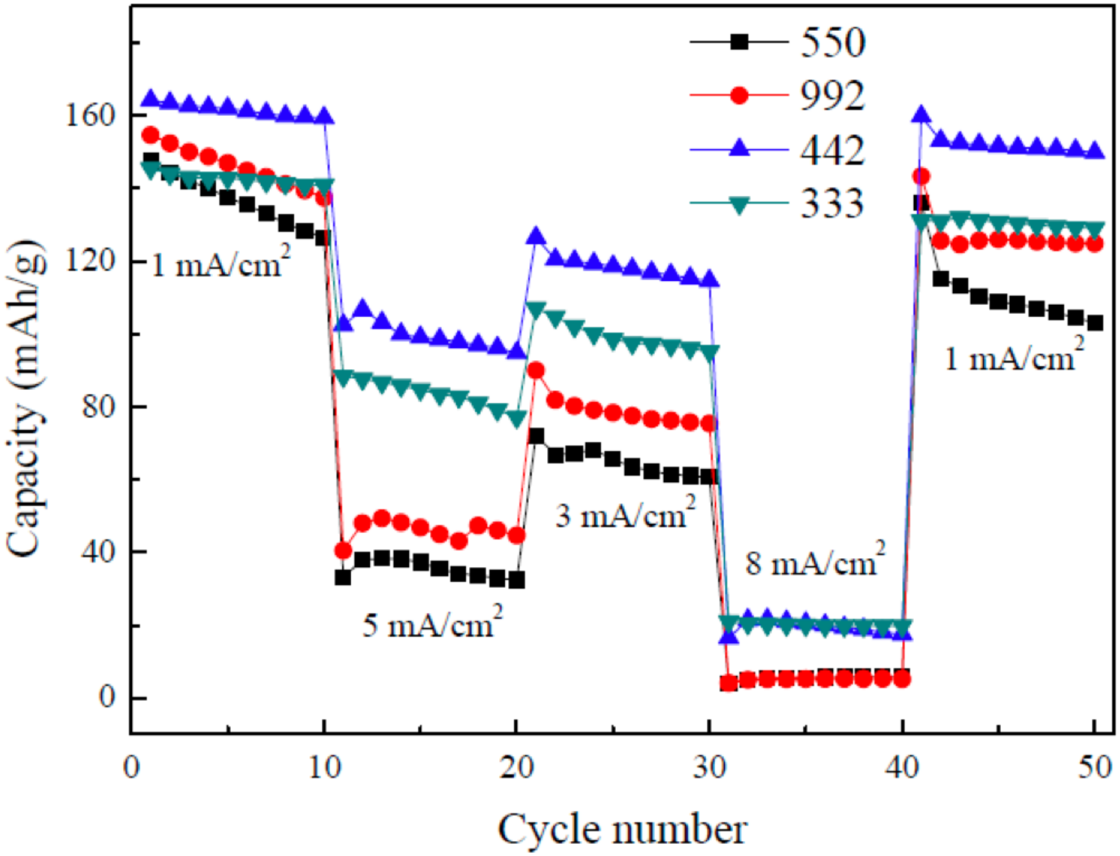
- What is optimum value of y?
  - 550, 991, 442 and 333
    - **Equal charging and discharging rates**
      - $LiNi_{0.4}Mn_{0.4}Co_{0.2}O_2$ gives highest capacities
        - Suggests this phase has highest charge capabilities



Conclusion:
442 appears to show the best charging capability

Solid Solution Behavior of $LiFePO_4$

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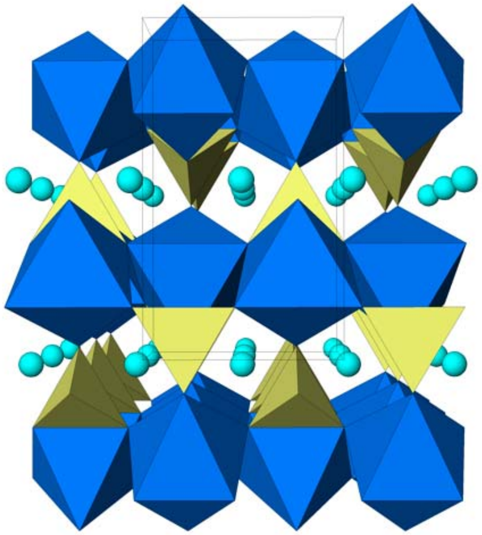
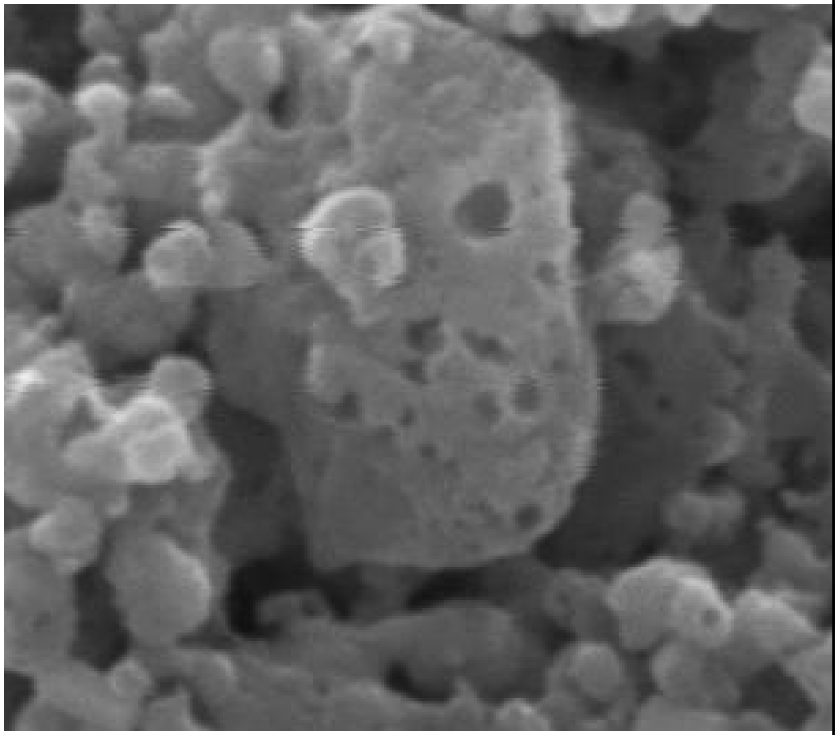
- $LiFePO_4$ can be substituted on both Fe and P sites
  - Vanadium substitution occurs on P site: $LiFeP_{1-y}V_yO_4$
    - Gives a **nanostructured** material
      - 50 nm crystallites in micron-sized particles
    - Leads to higher density
      - Higher capacity
        - Weight and volume basis



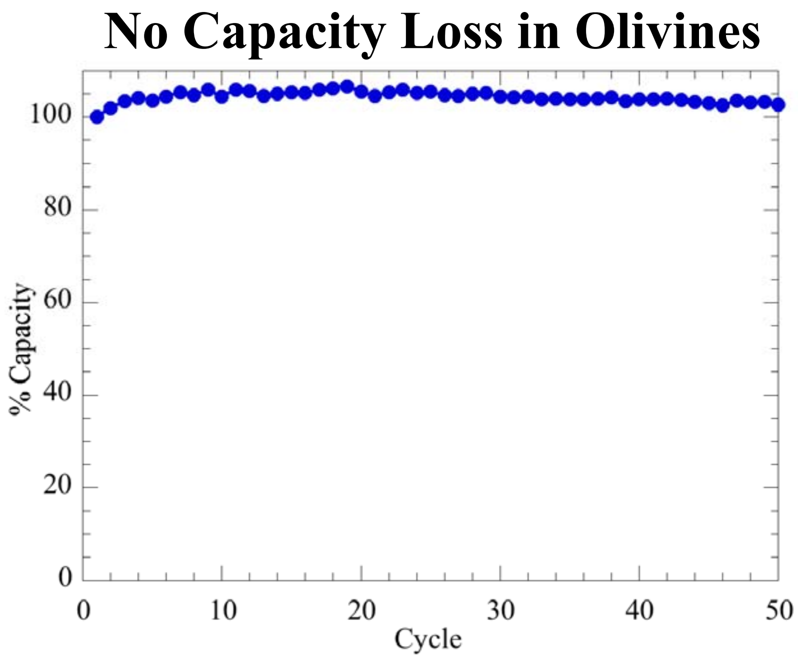
Collaboration with C-S Wang at U. Maryland

3 µm with 50 nm crystallites



Substituted $LiFePO_4$ shows high rate

- $LiFeP_{1-y}V_yO_4$ for y about 5%
  - Formed by firing samples ground in acetone
  - Needs much less carbon than nanopowders



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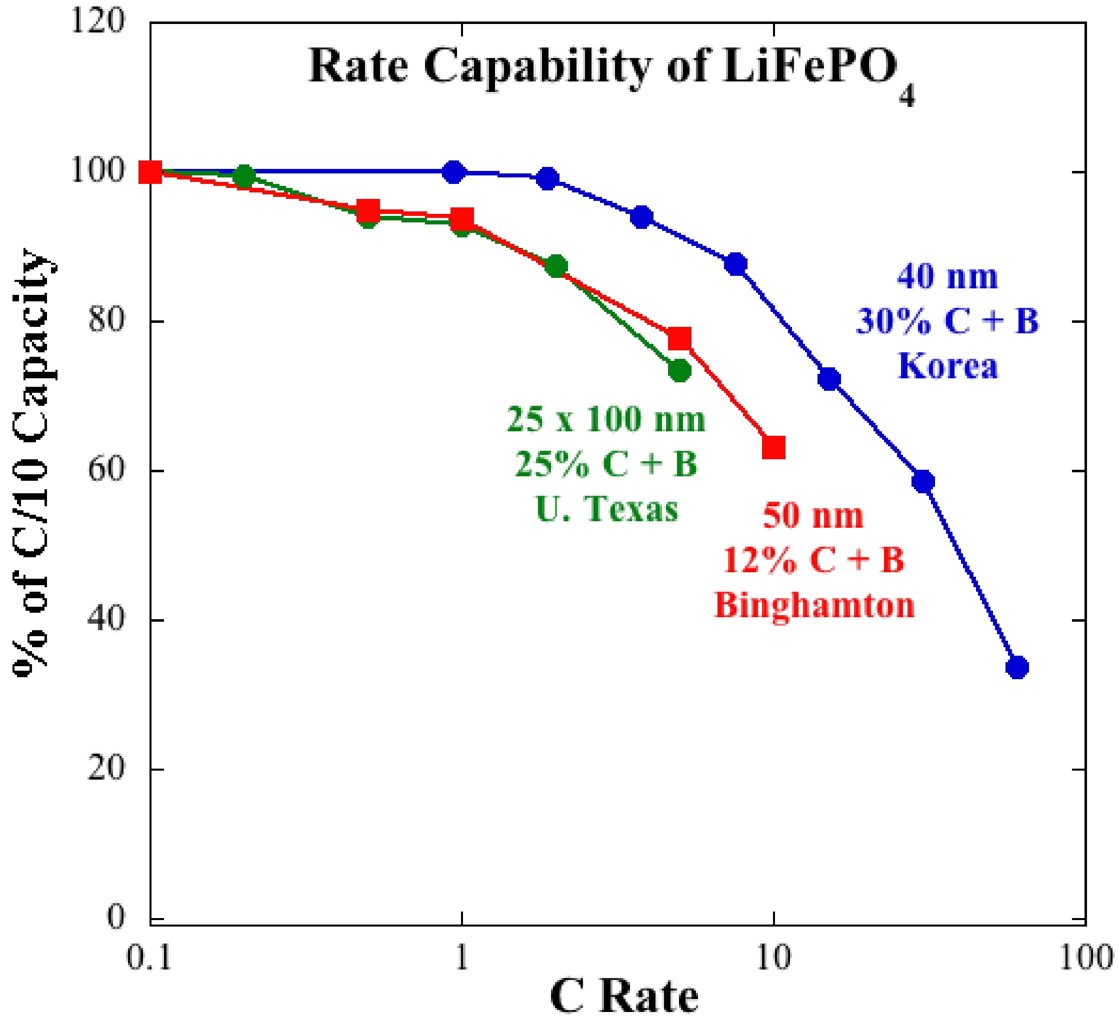

Substituted $LiFePO_4$ shows highest capacity based on whole cathode content

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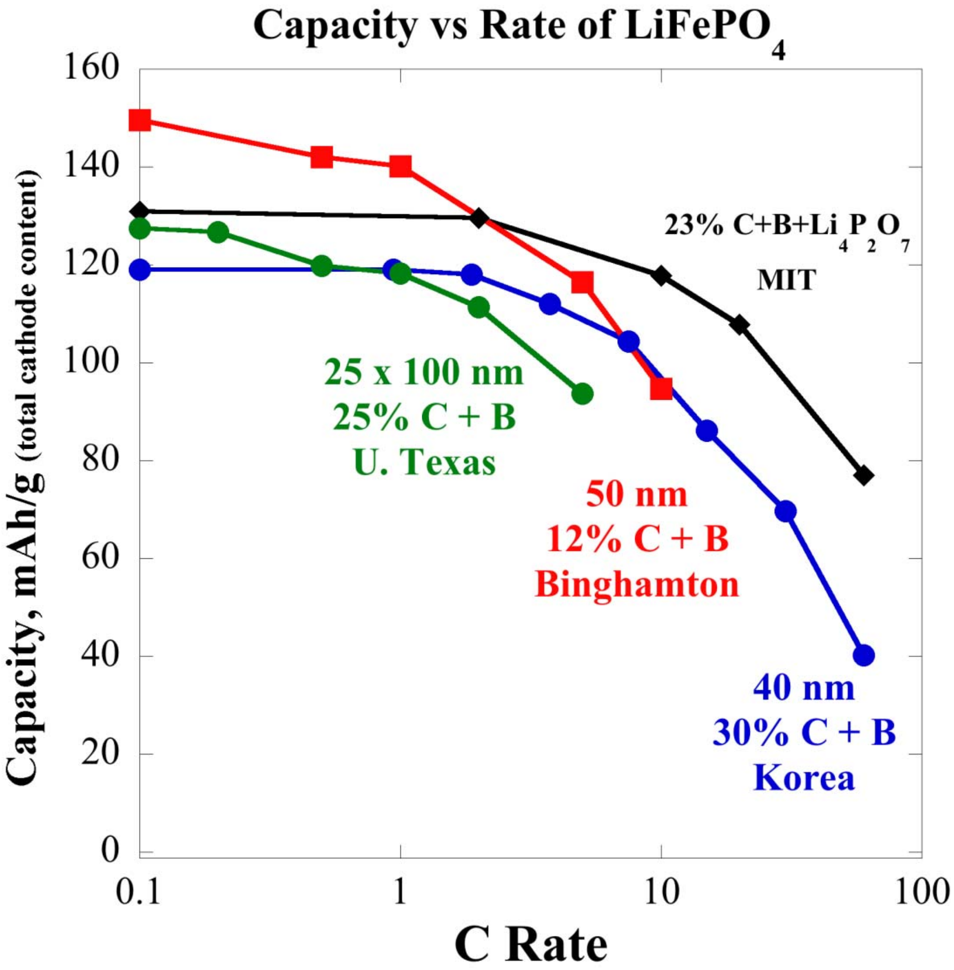
- $LiFeP_{1-y}V_yO_4$ for y about 5%
  - Formed by firing samples ground in acetone
  - Needs much less carbon than nanopowders
    - Enhanced capacity
      - Gravimetric
      - Volumetric even more



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Low Carbon Content critical for high capacity in $LiFePO_4$

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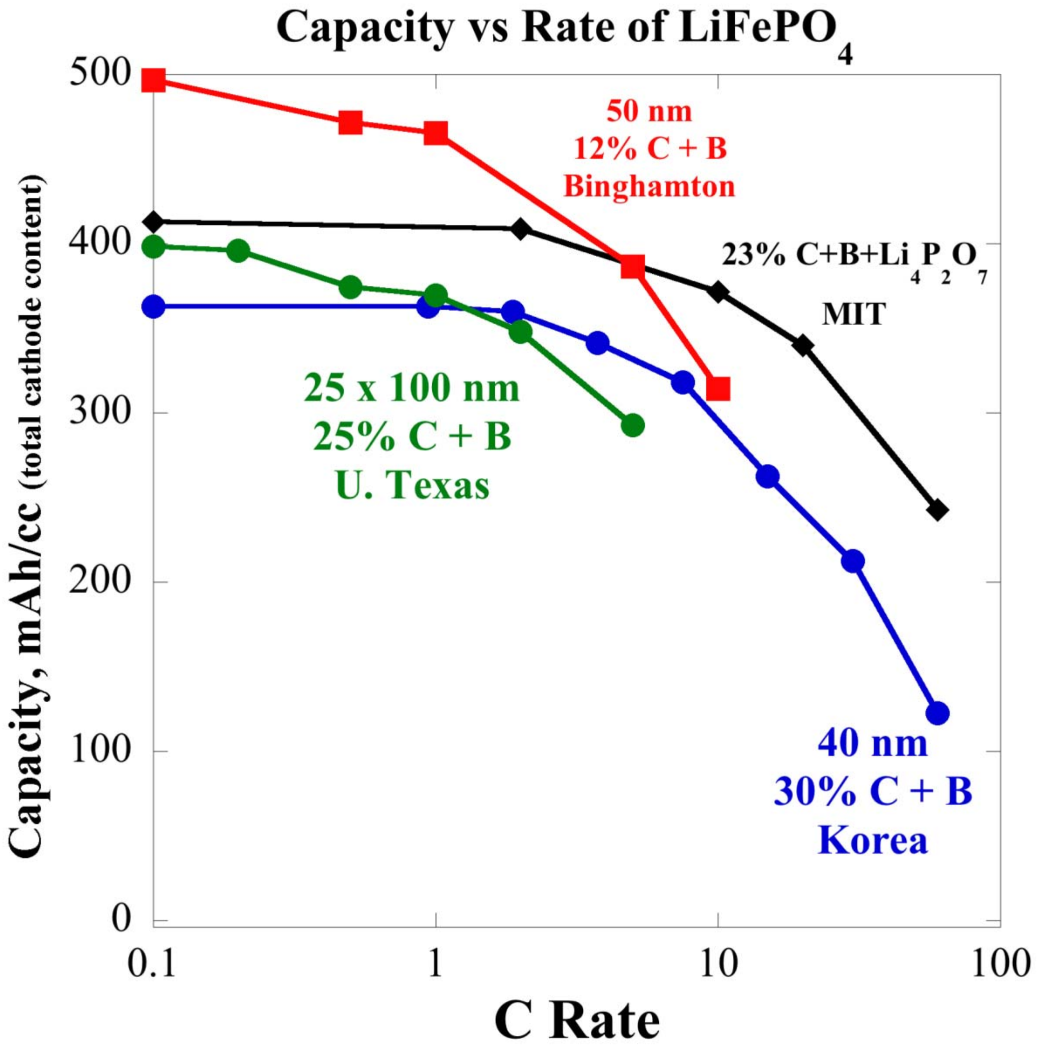
- Volumetric capacity seriously impacted by:
  - **High carbon content**
  - Nano-materials with low tap density (not incorporated into figure)

• Nanostructure with low carbon content may be the answer

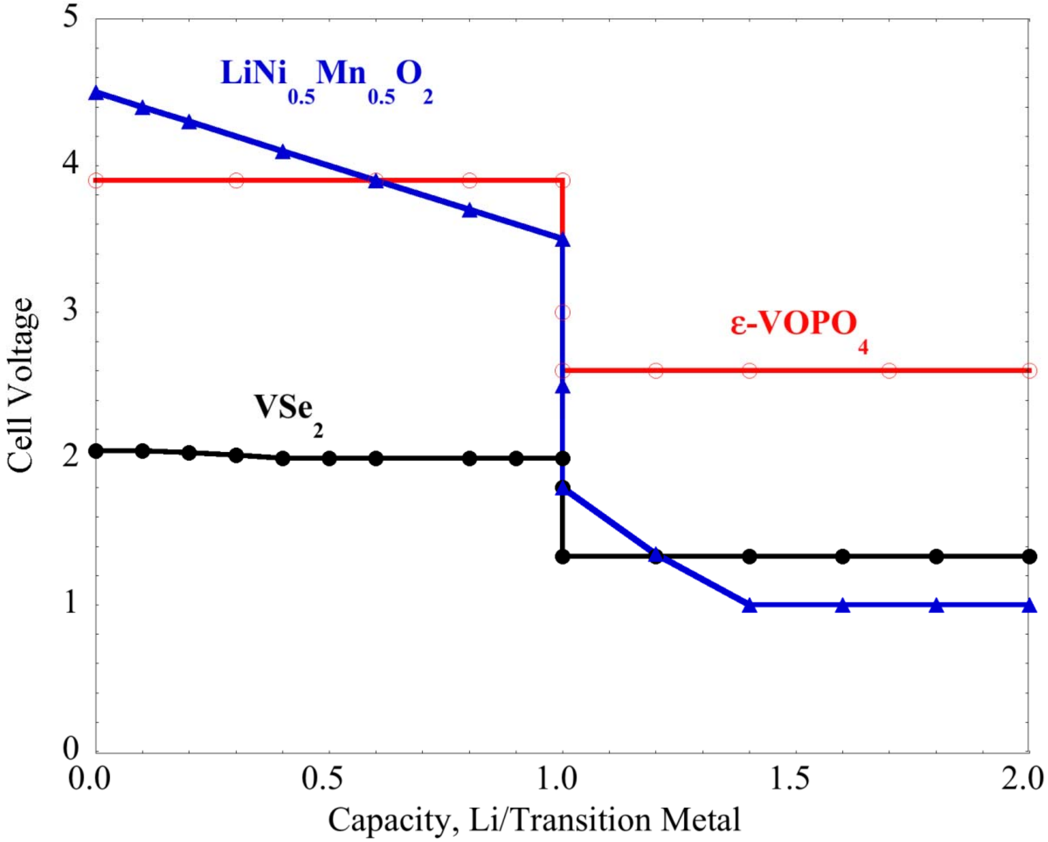
• PHEV needs around 1C to 2C constant output

- Capacity more important than power



Higher Capacity Cathodes: >1 Li/M

- Several materials react with more than 1 lithium
  - Initial studies underway to identify promising candidates
    - Vanadium oxides reviewed (with A. Dillon of NREL)
      - J. Mater. Chem., in press (2009)



Future Work

- **$LiMO_2$:**
  - Determine charge capabilities of $LiMO_2$
    - Compare 991 and 442 with 333
      - Work with C. Grey and M. Doeff to understand ion ordering
  - Understand why $LiMO_2$ capacity fades on cycling
    - Contrast $LiFePO_4$ and $Li_4Ti_5O_{12}$ where there is no fade

- **Phosphates -**
  - Determine composition range of single-phase $LiFeP_{1-y}V_yPO_4$
  - Find other iron phosphates with higher lithium contents
    - Higher capacity

- Identify materials that can undergo more than **one electron per redox center**
  - Perform extended cycling on phosphate to determine cycling loss
    - Determine reaction mechanism

Summary

- Substitution in $LiFePO_4$ shown to be feasible
  - Vanadium substitution on P site leads to nanostructure
    - Lower conductive carbon level
    - Higher capacities, particularly on a volumetric basis
  - Opens up opportunities for $LiMnPO_4$
- $LiMn_{0.33}Ni_{0.33}Co_{0.33}O_2$ composition may not be optimum
  - $LiMn_{0.4}Ni_{0.4}Co_{0.2}O_2$ may have better charging capabilities
  - $LiMn_{0.45}Ni_{0.45}Co_{0.1}O_2$ will have lowest cost
    - Need to better understand ordering in the transition-metal layer
      - Determine role of aluminum
- Technology transfer being accomplished
  - Students working with battery companies, e.g. Primet
  - Students in battery companies and at LBNL, NREL and PNNL
  - Publications to transfer knowledge
- Collaborations
  - A number of collaborations are underway and are effective
    - Industry, Academia and National Laboratories