The Synthesis and Characterization of Substituted Olivines and Layered Manganese Oxides

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Overview

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

• 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

a) Determine the optimum composition of LiNi$_{y}$Mn$_{y}$Co$_{1-2y}$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

• 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

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

• Ultimate capability of the MnO₂ and NiO₂ lattice
  – What is optimum Li(MnNiCo)O₂ 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$_2$

- **What is maximum Mn in Li(Ni$_y$Mn$_z$Co$_{1-y-z}$)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$_y$Mn$_y$Co$_{1-2y}$O$_2$?**
  - Can 200 Ah/kg be achieved with present electrolytes?
What is Theoretical Capacity of LiNi$_y$Mn$_y$Co$_{1-2y}$O$_2$?

- 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 1$^{st}$ 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$_y$Mn$_y$Co$_{1-2y}$O$_2$?

- 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$_{y}$Mn$_{y}$Co$_{1-2y}$O$_2$ Have Power Capability - Yes

- 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

2.35mg (90% 442, at least 10%PCNT)
Solid Solution Behavior of LiFePO$_4$ gives higher capacity and rate

- Substituting LiFePO$_4$ gives nanostructure
  - LiFeP$_{1-y}$V$_y$O$_4$ 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

3 µm with 50 nm crystallites
200 Ah/kg Capacity Cathodes: >1 Li/M

- 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

- Mn and Fe pyrophosphates
  - $\text{Li}_2(\text{FeMn})\text{P}_2\text{O}_7$ 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. $\text{Mn}^{4+}\text{P}_2\text{O}_7$)
Higher Capacity Cathodes: >1 Li/M

- Attempted formation of \( \text{Li}_2(\text{MnFeV})\text{P}_2\text{O}_7 \)
  - Electrochemical evaluation of “\( \text{Li}_2\text{VP}_2\text{O}_7 \)” underway
  - Two lithium can be cycled
  - X-rays at 1, 2, 3 and 4 show crystalline material
Collaboration and Coordination with other Institutions

• The layered oxides
  – C. Grey (SUNY Stony Brook) Ion ordering in LiMO₂
  – M. Doeff (LBNL) Al substitution in LiMO₂
  – A. Dillon (NREL) High rate evaluation of LiNi₀.₄Mn₀.₄Co₀.₂O₂
  – S. V. Kalinin (ORNL) Scanning probe microscopy of LiₓMO₂
  – F. Alamgir (Georgia Tech.) in-situ XAS of LiₓMO₂ at BNL

• The olivines
  – C. S. Wang (U. Maryland) Synthesis of single-phase LiFeP₁₋₇V₇PO₄
  – G. Ceder (MIT) Mechanism of olivine reaction
  – Primet (Ithaca) Electrochemical evaluation of nano-scissored material
Future Work

• **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$_y$PO$_4$
  - Understand role of substituents on reaction rate

• **2-Electron Materials**
  - Find materials that can reach 200 – 250 Ah/kg at 1C rate
Summary

- **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
    - 1$^{st}$ 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