Search for New Anode Materials

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This presentation does not contain any proprietary or confidential information.
Overview

Timeline
- Start – April 2003
- Task #1 Cathodes - started on Oct. 30, 2007 completed on Sept. 30, 2008, 100 % complete
- Task #2 Anodes - started on Oct. 30, 2007 completed on Sept. 30, 2008, 80 % complete

Barriers
- Li$_4$Ti$_5$O$_{12}$: Safe, but High voltage and Low capacity
- Graphite (C6): Low voltage and High capacity, but not safe at a high charge/discharge rate in carbonate electrolyte

Budget
- Funding received in FY08 – $220K
- Funding received in FY09 – $315K

Partners
- Karim Zaghib of Hydro Quebec
Many cathode materials are available for commercial applications, but only two anode materials are available: Li₄Ti₅O₁₂ and Graphite.

- Search for new inorganic intercalation compounds for anode materials, giving a voltage below 1 V vs. Li⁺/Li⁰.
Milestones

- Complete investigation of electrochemical co-deposition of polyaniline (PAn) and -LiFePO₄. (Dec. 07) Complete
- Prepare and test nanowires of PAn for chemical attachment to C-LiFePO₄. (Jun. 08) Complete
- Develop novel soft-chemical routes of patterned composites containing nanoparticles and polymers. (Sep. 08) Complete
- Exploration of Ti³⁺/Ti²⁺ and V³⁺/V²⁺ redox couples in sulfides and sulfochlorides. (Jan. 09). Complete
- Structural and electrochemical characterization of Li₁₊ₓVS₂ nanoparticles without/with substitutions for V and S (Sept. 08). Complete
- Exploration of alternative oxides as anode materials (Dec. 08). On track
- Exploration of cathode frameworks containing polyanions (Mar. 09). On track
- $M^{4+}/M^{3+}$ ($M = \text{Ti, V}$) redox couple in sulfides gives a voltage of $\sim 2.2$ V vs. $\text{Li}^+/\text{Li}^0$.

- $M^{3+}/M^{2+}$ redox couple in sulfides can give a lower voltage?
Displacement reaction (2Li + MS $\rightarrow$ M + Li$_2$S) occurs at an increasing voltage from Ti to Ni. 
$\rightarrow$ The bottom of the M 4s band decreases with increasing atomic number

$\rightarrow$ The 4s bands for Ti, V, and Cr are located below 1.0 eV vs. Li$^+$/Li$^0$.
$\rightarrow$ Ti$^{3+}$/Ti$^{2+}$, V$^{3+}$/V$^{2+}$, and Cr$^{3+}$/Cr$^{2+}$ couples are possibly accessible at target voltages.

Access to $M^{3+}/M^{2+}$ Couple in Layered LiMS$_2$ ($M = Ti, V, Cr$)

The prepared samples in this work are $Li_{0.8}TiS_2, Li_{0.8}VS_2, LiCrS_2$

High-temperature synthesis commonly gives a ratio $Li/M < 1.0$

These compounds show the possibility of reversible access to $M^{3+}/M^{2+}$ in a suitable electrolyte.

Li insertion into Li$_{0.8}$VS$_2$

Accomplishments:

- Reversible access to V$^{3+}$/V$^{2+}$ redox couple at a voltage of $\sim$ 1.0 V vs. Li$^+$/Li$^0$. 

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Accomplishments:

**Reversibility of Li Insertion into Li$_{0.8+x}$VS$_2$**

**Capacity fading on cycling**

1) ~ 30 % of the volume change on insertion of Li into LiVS$_2$

2) Carbonate electrolytes are not stable at voltages below 1.0 V vs. Li/Li$^+$.  
   → need to find more stable electrolyte
Li insertion into LiCrS$_2$

\[ \text{LiCrS}_2 \xrightarrow{x} \text{Cr + Li}_2\text{S} \]

- Not possible to access to Cr$^{3+}$/Cr$^{2+}$ redox couple that overlaps with 4s band
Li insertion into Li$_{0.8}$TiS$_2$

Accomplishments:

- Reversible access to Ti$^{3+}$/Ti$^{2+}$ redox couple at a voltage of $\sim$ 0.5 V vs. Li$^+$/Li$^0$. 

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Electrolytes are reduced as the negative electrode potential lowers until a passivating SEI layer is formed.

This layer is permeable to Li$^{+}$ ions so that it allows further Li exchange, but impermeable to other electrolyte components.
Instability of Li$_{0.8+x}$TiS$_2$ with Electrolytes

- Capacity fading on cycling
  - Stable SEI layer can improve the cyclability
- When the SEI layer is not permeable to Li$^+$ ions, the SEI layer blocks further insertion or extraction of Lithium.
Accomplishments:

Instability of VS$_2$ Cathode with Electrolytes


Introduction of M (Ti, Cr, Fe) in LiV$_{1-y}$M$_y$S$_2$ eliminates the formation of interdediate phases, which improve the capacity and the rates of charge/discharge.

Accomplishments:

V$_{1-y}$M$_y$S$_2$ (M = Ti, Cr, Fe) Electrode Materials

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Formation of an SEI layer in carbonate electrolytes limits safe anodes to $V < 1.0$ V versus Li$^+$/Li$^0$. 
Future Work

- Exploration of new oxide anodes

- New cathodes in new electrolytes permitting higher voltage versus Li\(^+\)/Li\(^0\).

- New oxides that can be used as both anode and cathode for electrochemical capacitors.