Search for New Anode Materials

John B. Goodenough and Youngsik Kim

Texas Materials Institute
The University of Texas at Austin

DOE Vehicle Technologies Annual Merit Review Meeting

May 20, 2009

Project ID #: **es_29_goodenough**

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

- $Li_4Ti_5O_{12}$: 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

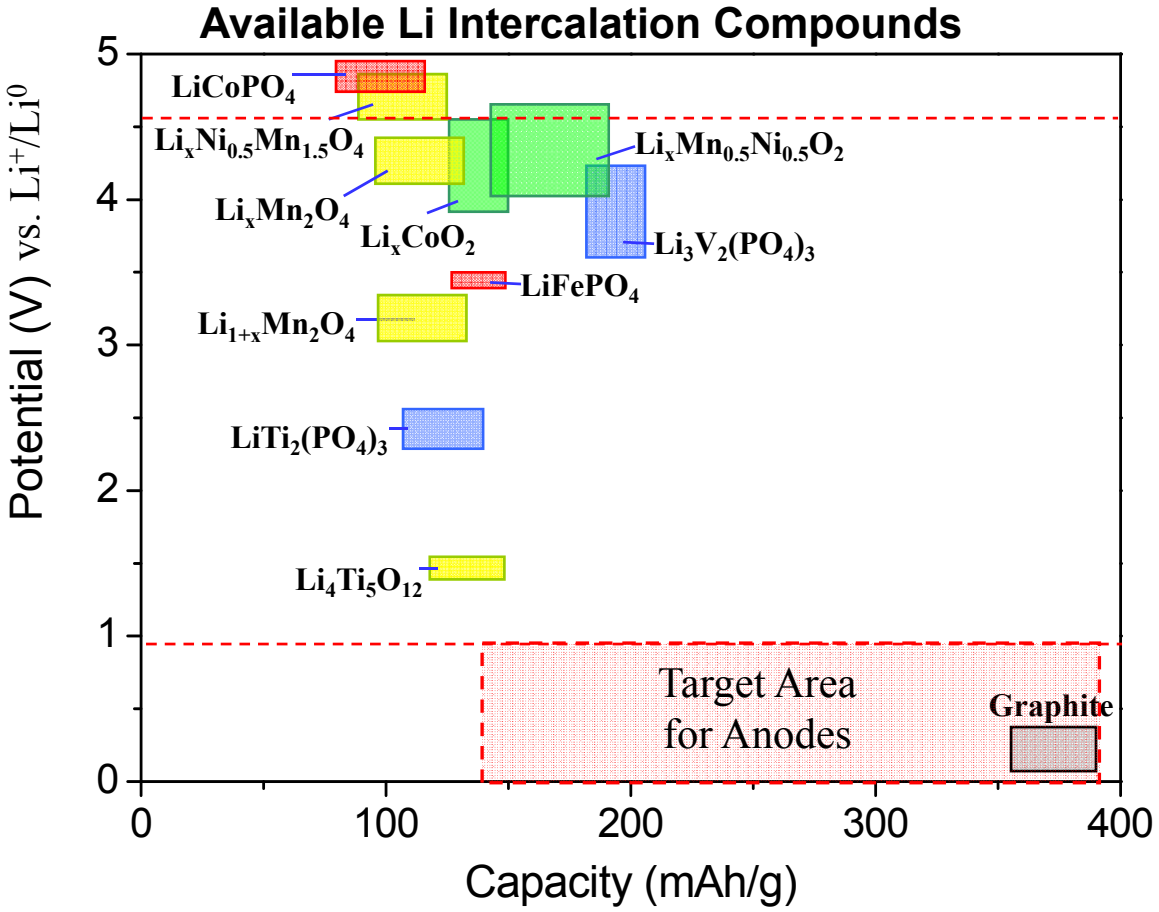
- Funding received in FY08 – $220K
- Funding received in FY09 – $315K

Partners

- Karim Zaghib of Hydro Quebec

Objectives:

Search for New Intercalation Compounds as Anodes

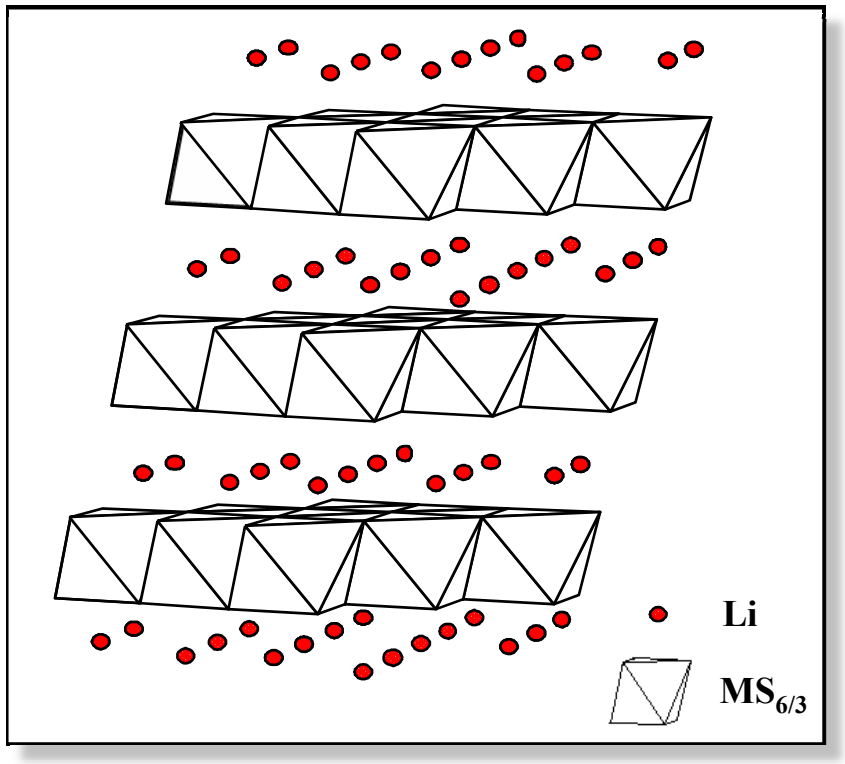


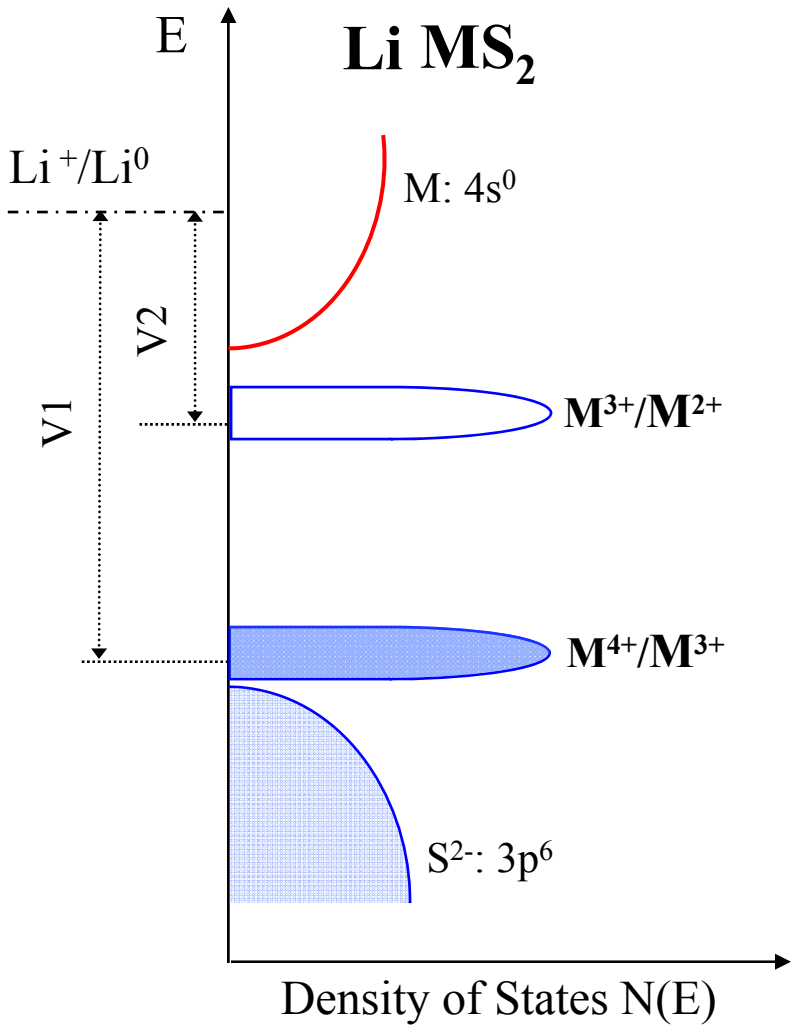
- Many cathode materials are available for commercial applications, but only two anode materials are available: $Li_4Ti_5O_{12}$ and Graphite
- Search for new inorganic intercalation compounds for anode materials, giving a voltage below 1 V vs. Li^+/Li^0.

Milestones

- Complete investigation of electrochemical co-deposition of polyaniline (PAn) and -$LiFePO_4$. (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 Ti^{3+}/Ti^{2+} and V^{3+}/V^{2+} redox couples in sulfides and sulfochlorides. (Jan. 09). **Complete**
- Structural and electrochemical characterization of $Li_{1+x}VS_2$ 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**

Access to M^{3+}/M^{2+} Couple

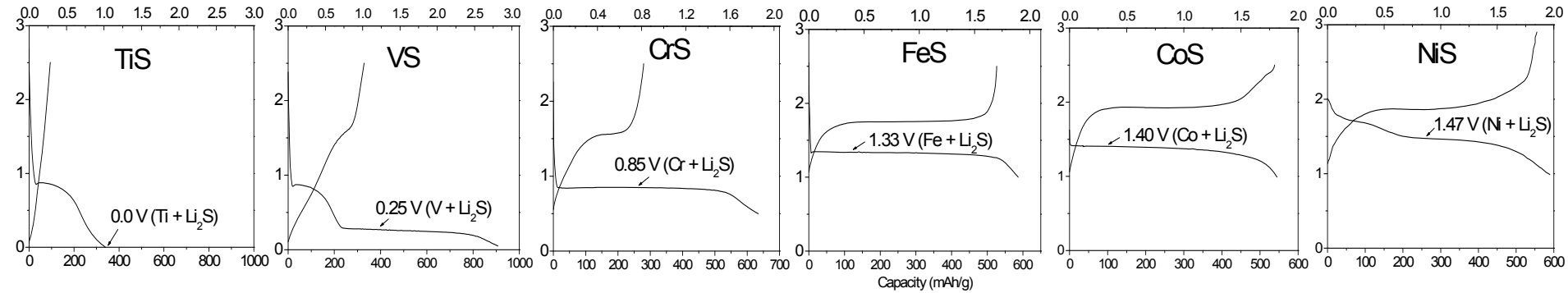


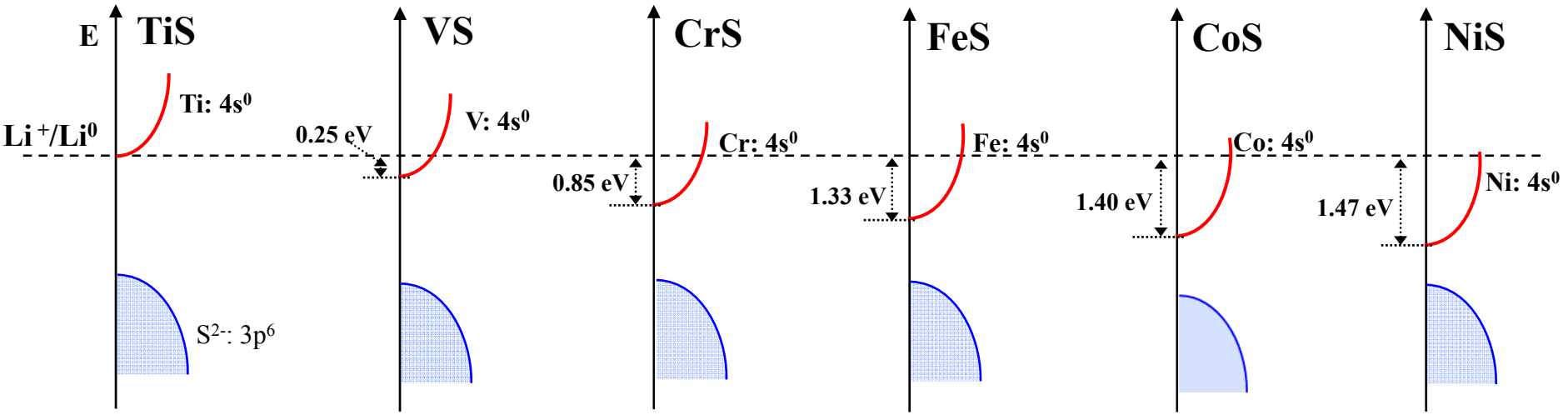


- M^{4+}/M^{3+} (M = Ti, V) redox couple in sulfides gives a voltage of ~ 2.2 V vs. Li^{+}/Li^{0}.
- M^{3+}/M^{2+} redox couple in sulfides can give a lower voltage ?

Accomplishments:

Position of Metal 4s Band in MS (M = Ti, V, Cr, Fe, Co, Ni)





- Displacement reaction ($2Li + MS \rightarrow M + Li_2S$) occurs at an increasing voltage from Ti to Ni.
  → The bottom of the M 4s band decreases with increasing atomic number
- The 4s bands for Ti, V, and Cr are located below 1.0 eV vs. Li^+/Li^0.
  → Ti^{3+}/Ti^{2+}, V^{3+}/V^{2+}, and Cr^{3+}/Cr^{2+} couples are possibly accessible at target voltages.

Y. Kim, J.B. Goodenough, *J. Phys. Chem.C* 112 (2008) 15060.

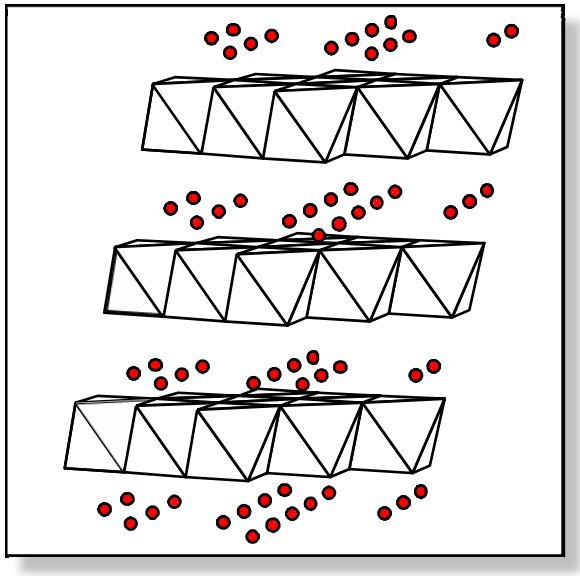
Accomplishments:

Access to M^{3+}/M^{2+} Couple in Layered $LiMS_2$ (M = Ti, V, Cr)

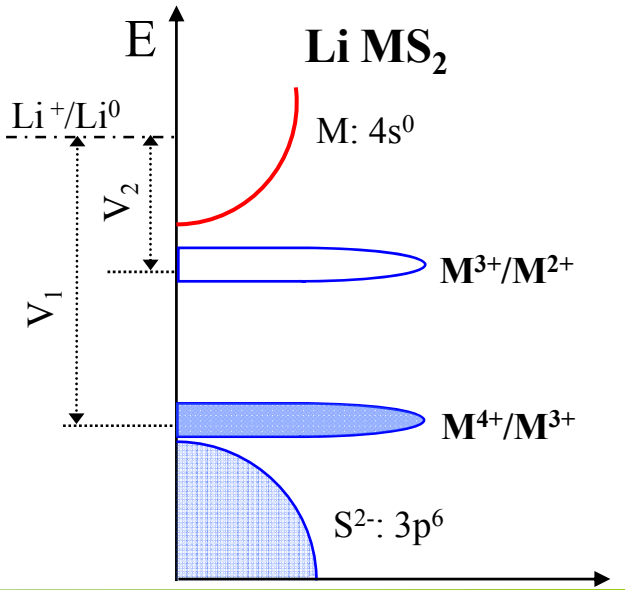
D.W. Murphy, J.N. Carides, *J. Electrochem. Soc.* 126 (1979) 349.

VS_2, $LiVS_2$, Li_2VS_2

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



MS_2 (M^{4+}) ⇆ **$LiMS_2$ (M^{3+})** ⇆ **Li_2MS_2 (M^{2+})**

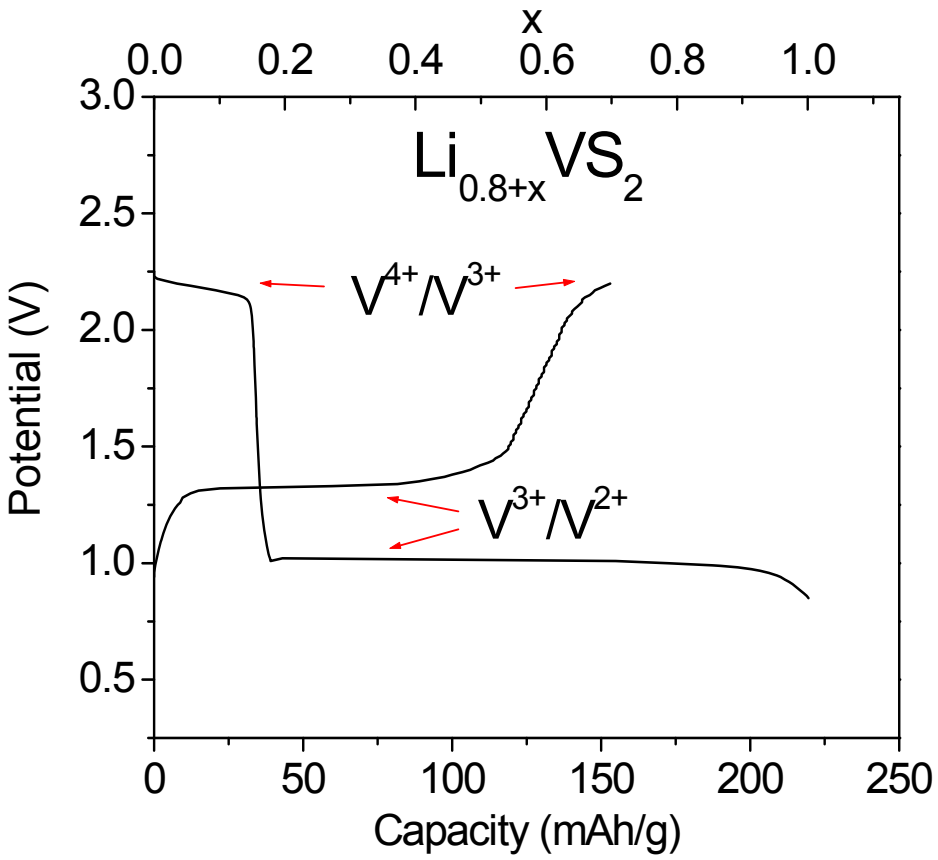


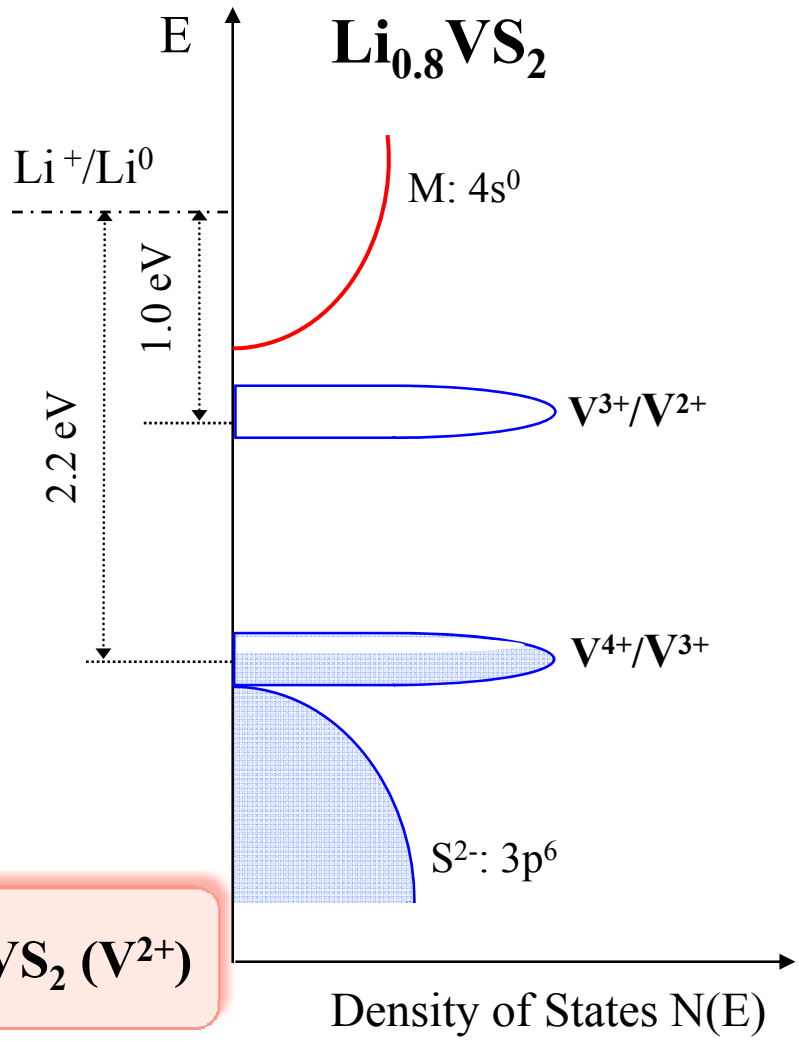
The prepared samples in this work are

$Li_{0.8}TiS_2$, $Li_{0.8}VS_2$, $LiCrS_2$

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

Li insertion into $Li_{0.8}VS_2$

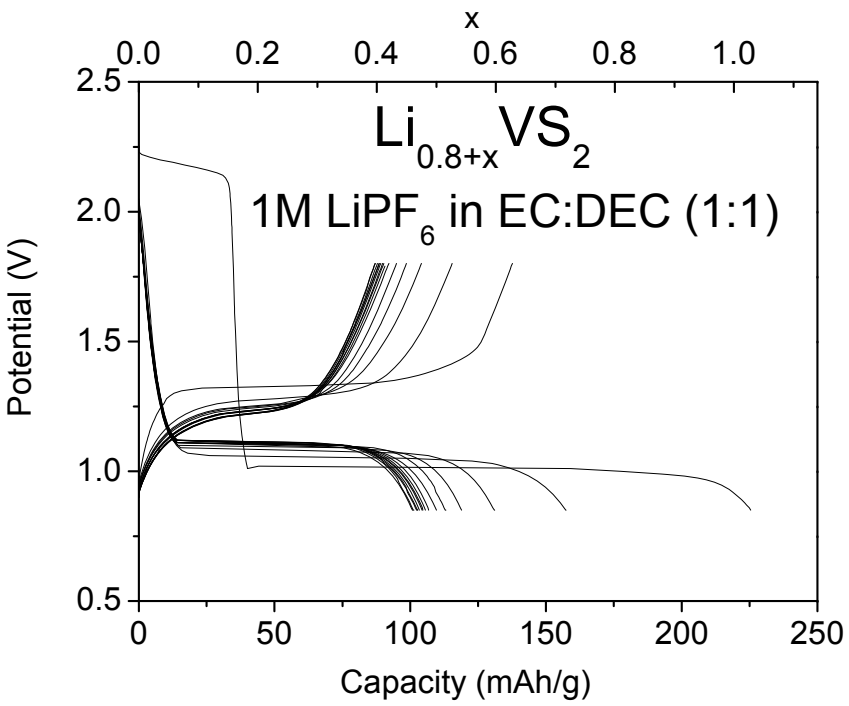


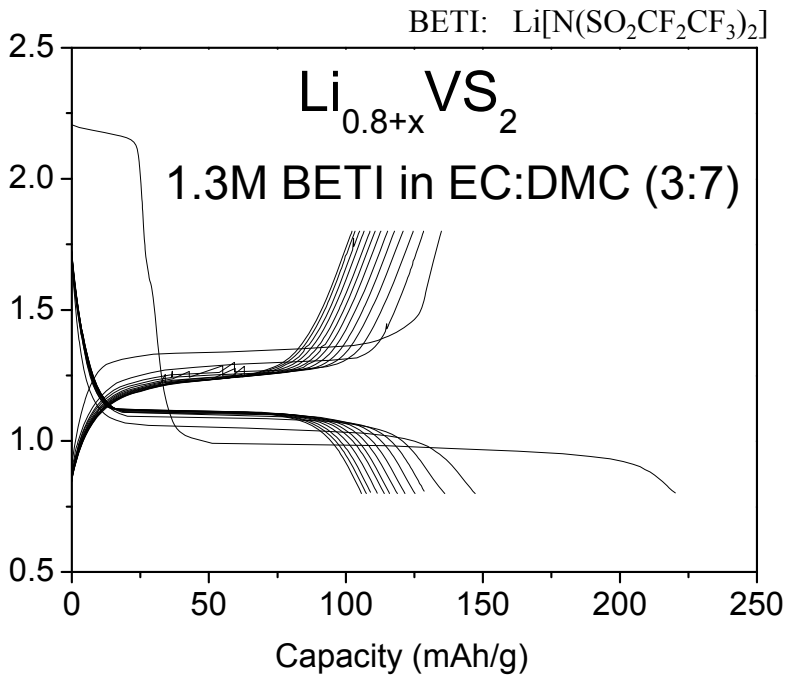


$Li_{0.8}VS_2$ (V^{4+}/V^{3+}) ⇨ Li_1VS_2 (V^{3+}) ⇨ Li_2VS_2 (V^{2+})

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

Reversibility of Li Insertion into $Li_{0.8+x}VS_2$



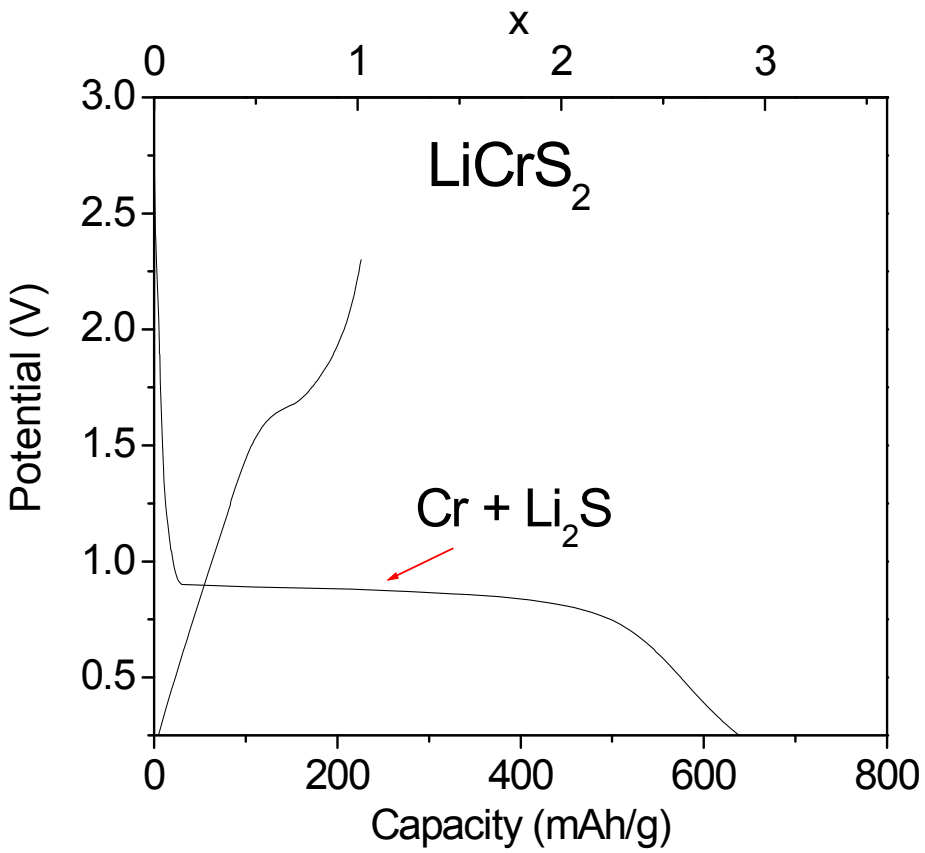


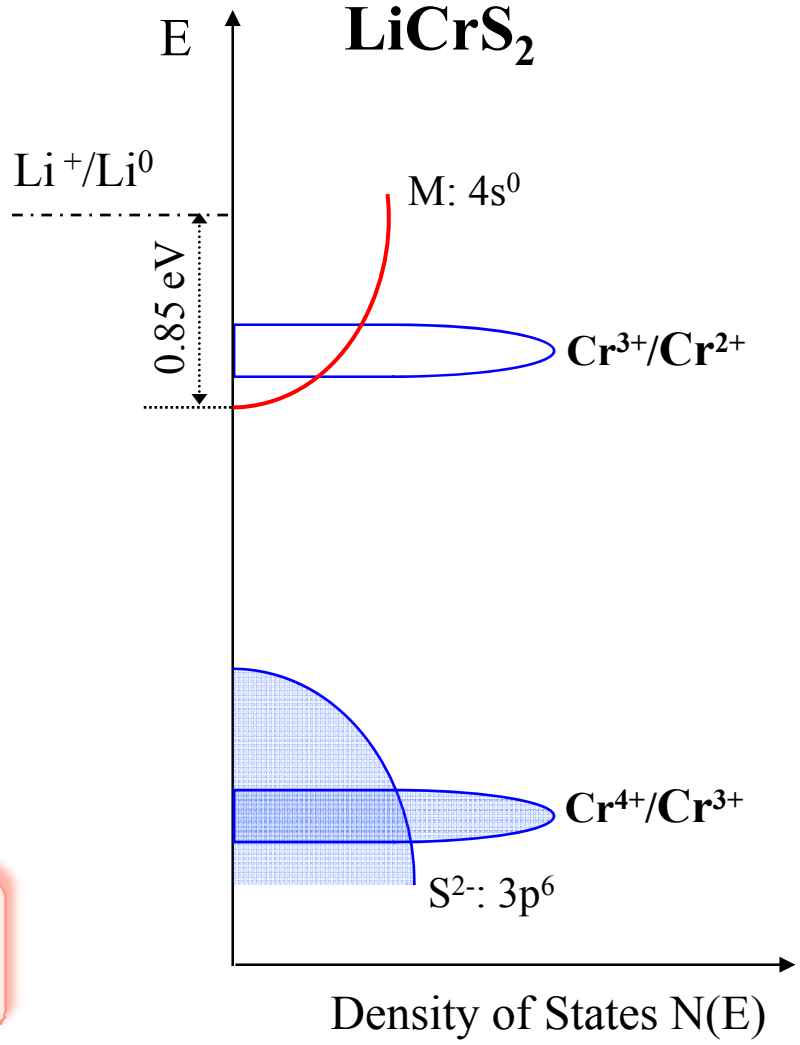
Capacity fading on cycling

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 $LiCrS_2$

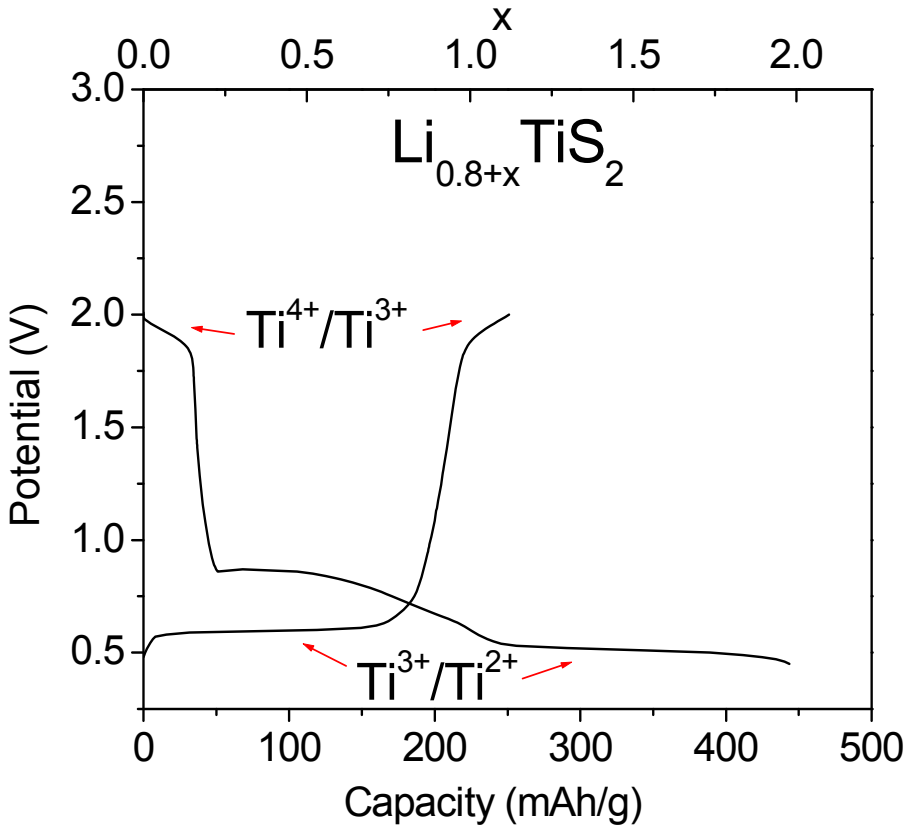


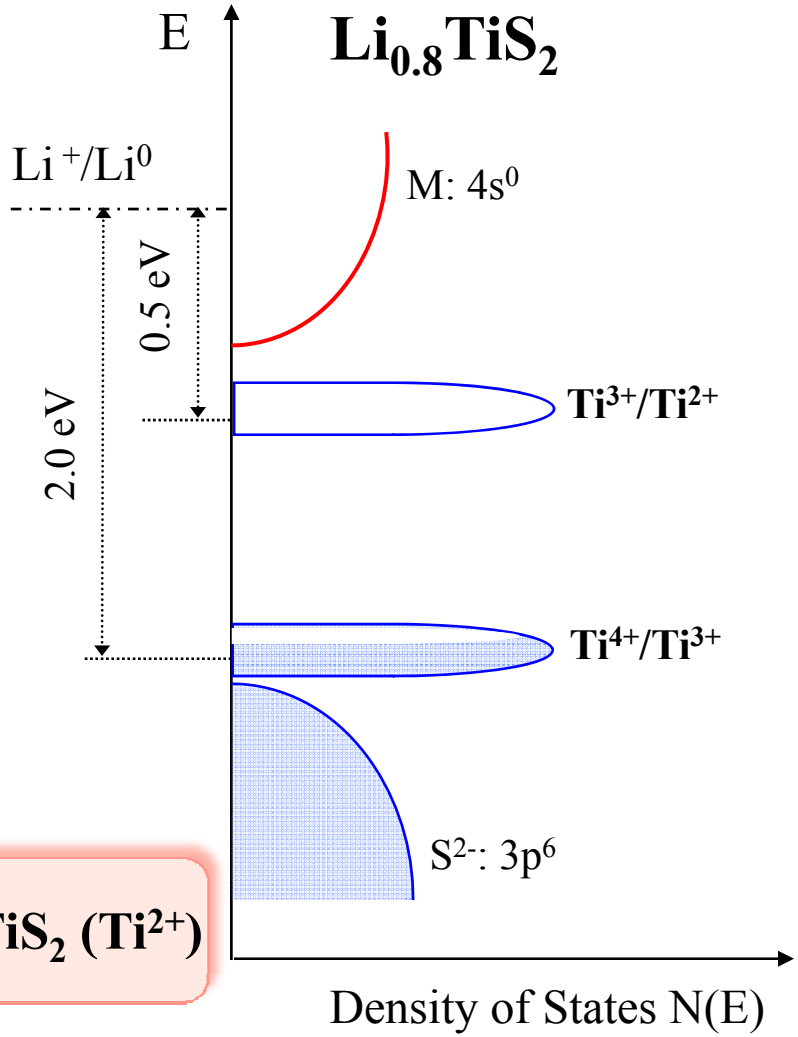


$LiCrS_2$ (Cr^{3+}) ⇨ **$Cr + Li_2S$**

- Not possible to access to Cr^{3+}/Cr^{2+} redox couple that overlaps with 4s band

Li insertion into $Li_{0.8}TiS_2$

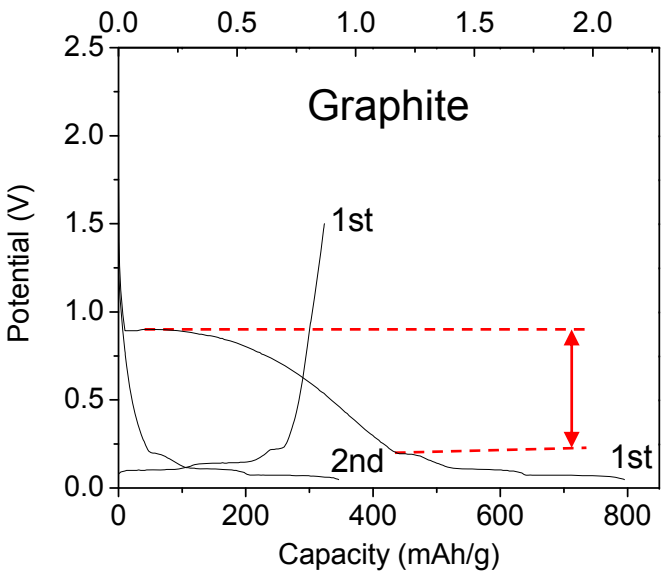


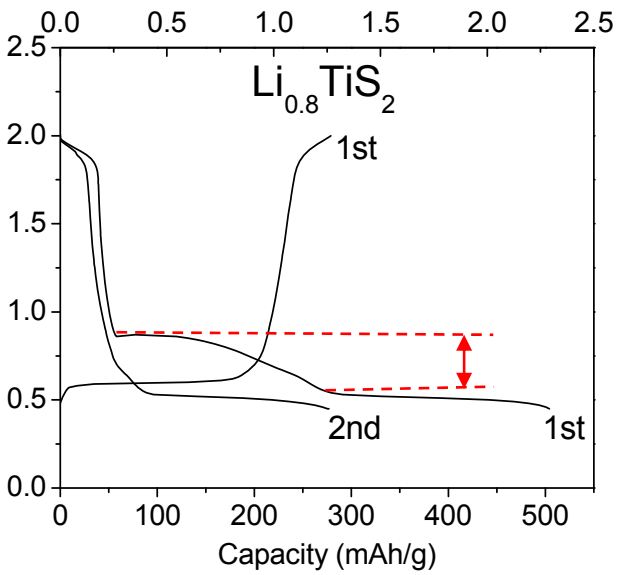


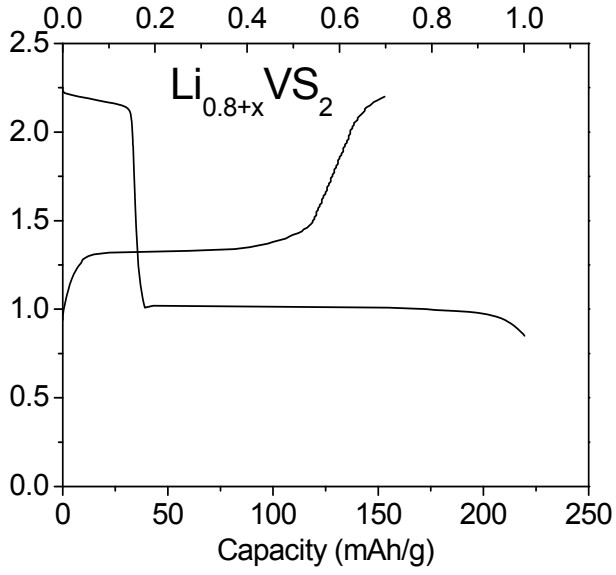
$Li_{0.8}TiS_2$ (Ti^{4+}/Ti^{3+}) ⇨ Li_1TiS_2 (Ti^{3+}) ⇨ Li_2TiS_2 (Ti^{2+})

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

Accomplishments:
Solid-Electrolyte-Interface (SEI) Layer

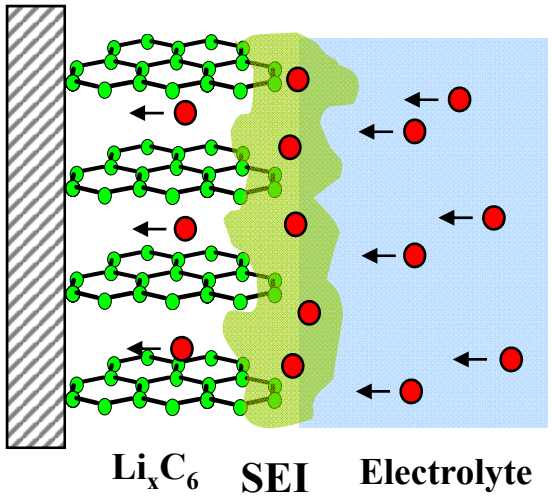


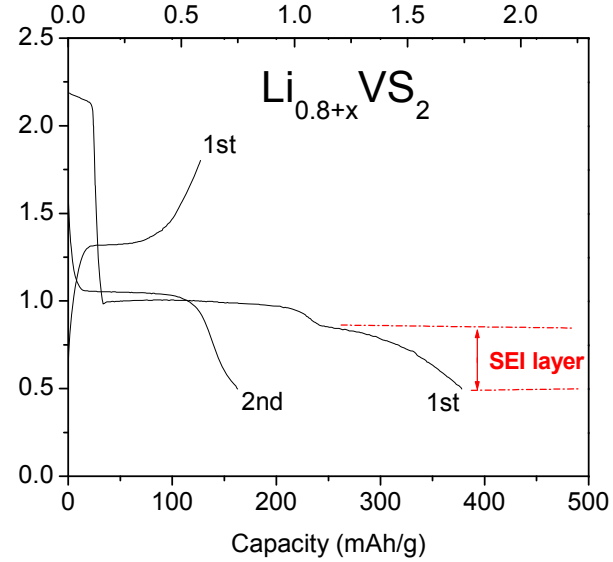




- Electrolytes are reduced as the negative electrode potential lowers until a passivating SEI layer is formed.

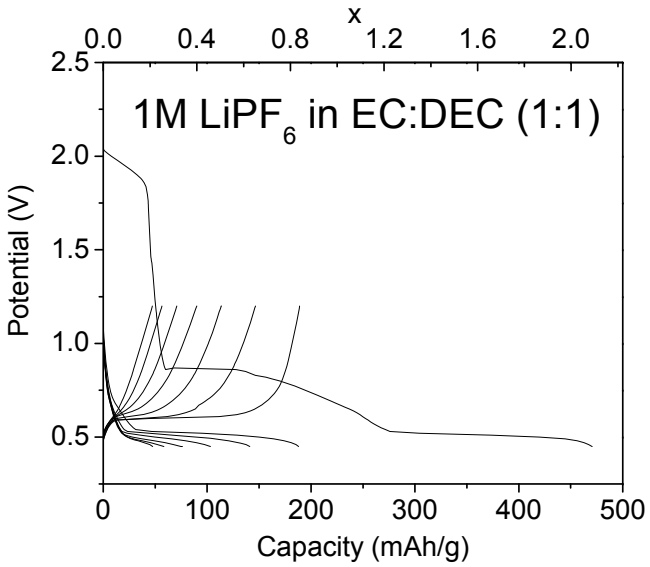
- This layer is permeable to Li^+ ions so that it allows further Li exchange, but impermeable to other electrolyte components.

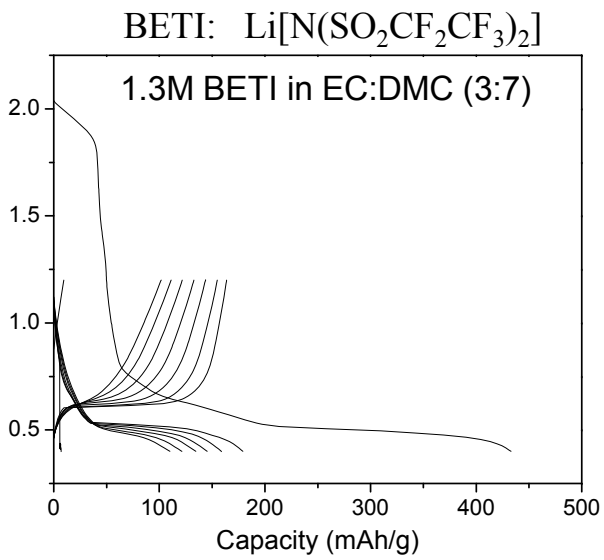


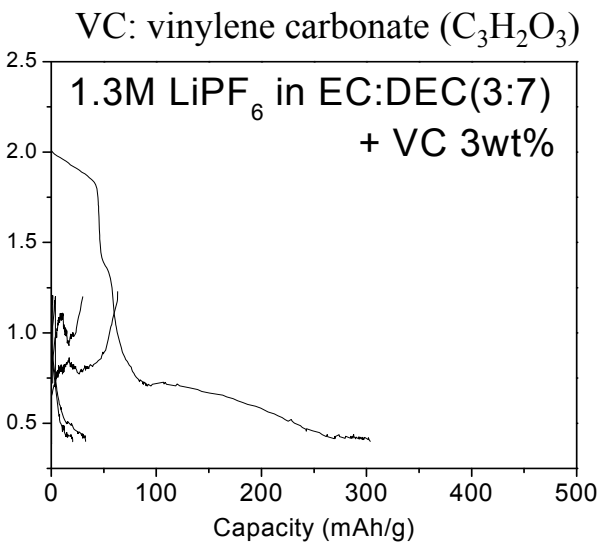


Accomplishments:

Instability of $Li_{0.8+x}TiS_2$ with Electrolytes

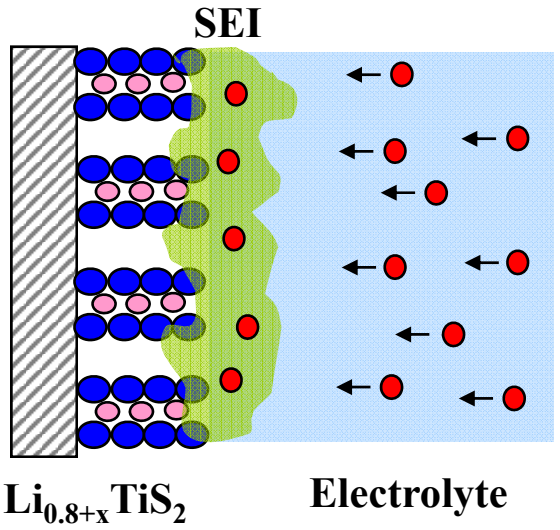






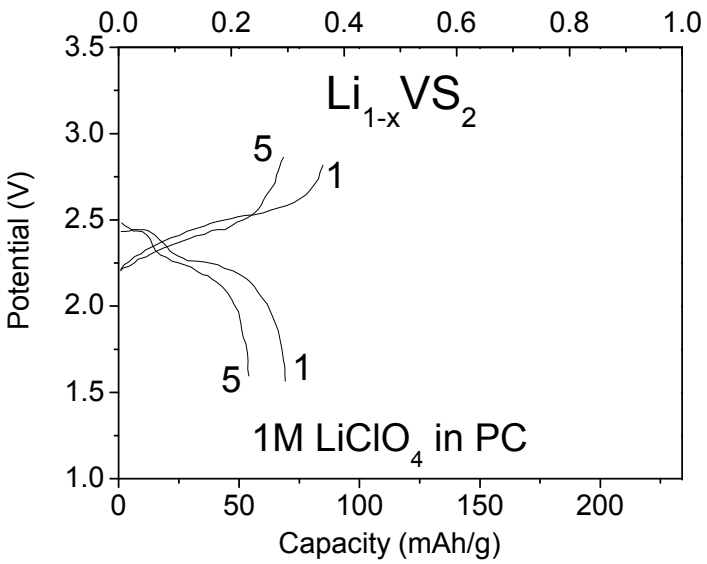
- Capacity fading on cycling
  Stable SEI layer can improve the cyclability

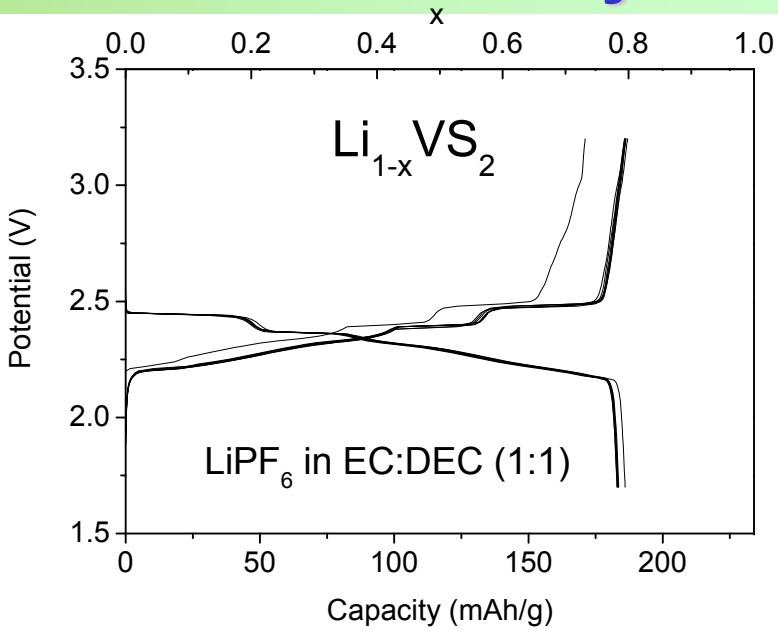
- When the SEI layer is not permeable to Li^+ ions, the SEI layer blocks further insertion or extraction of Lithium.

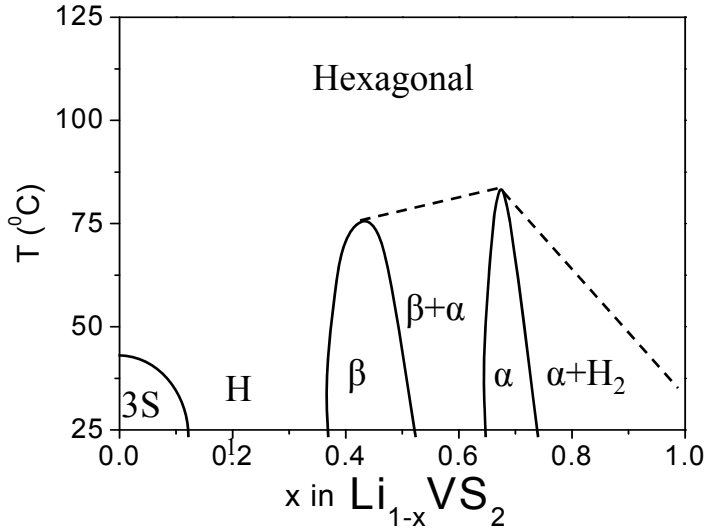


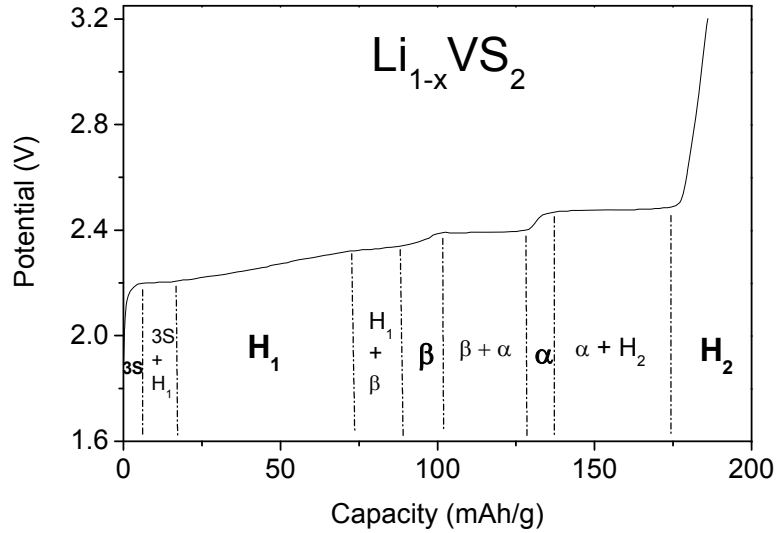
Accomplishments:

Instability of VS_2 Cathode with Electrolytes







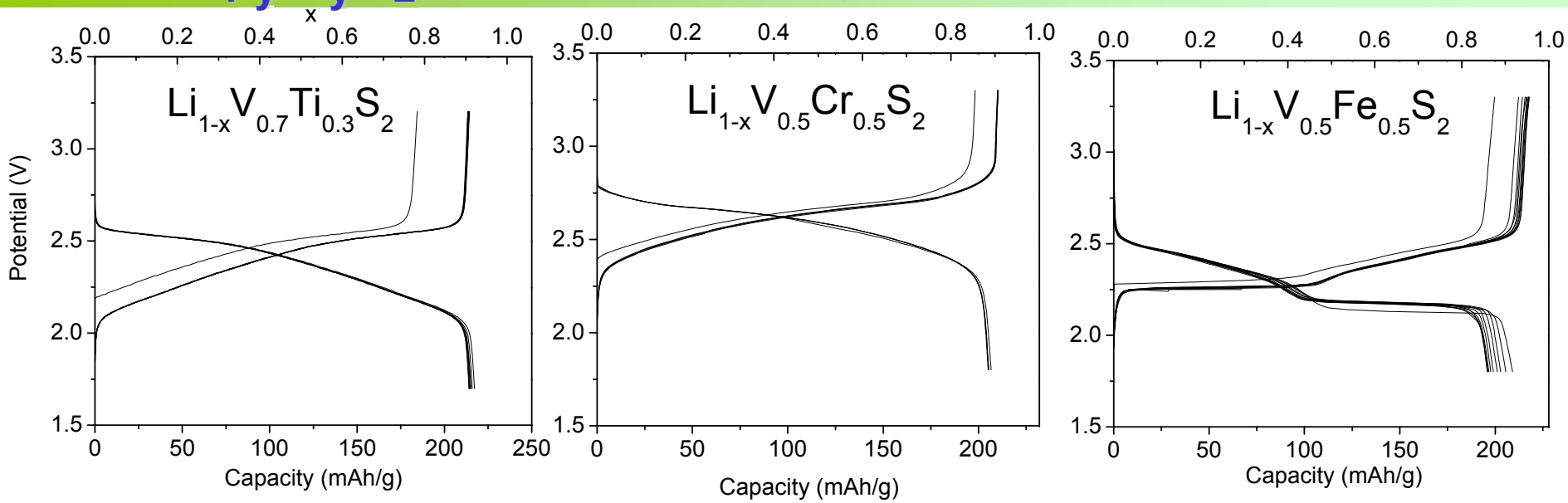


Murphy, D.W. et. al. *Inorg. Chem.* 16 (**1977**) 3027.

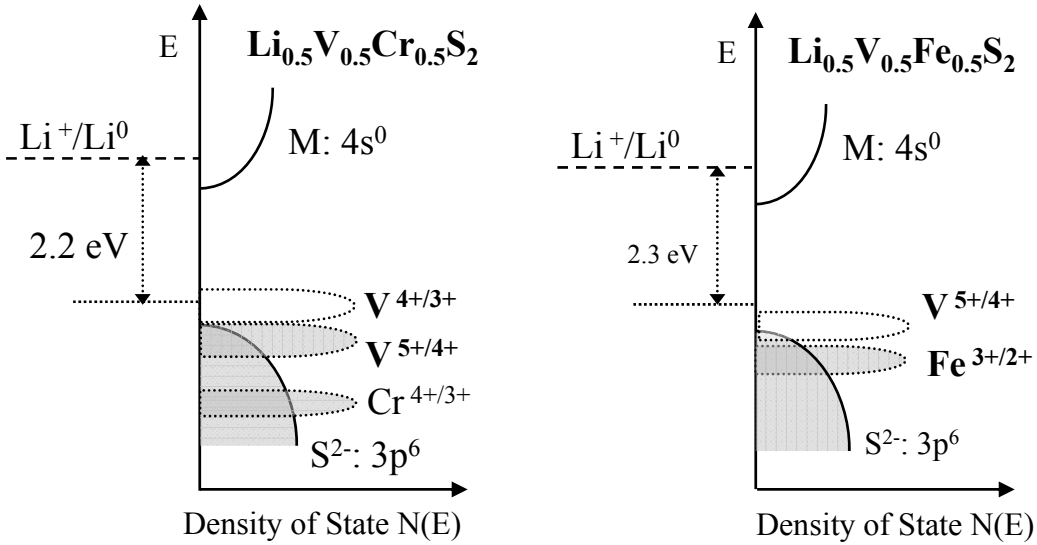
Y. Kim, J.B. Goodenough, *Electrochem. Solid-State Lett. 12* (**2009**) A73

Accomplishments:

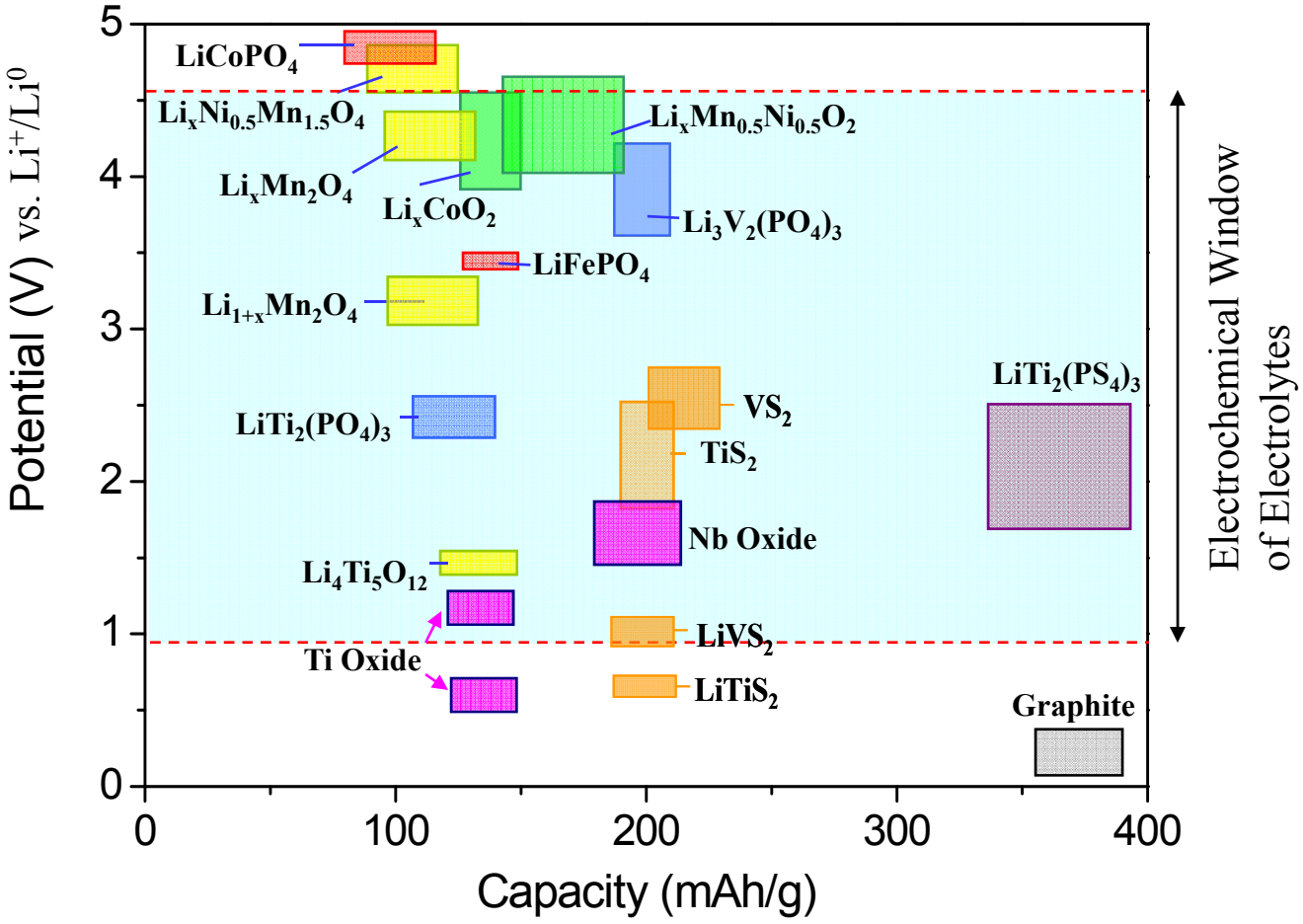
$V_{1-y}M_yS_2$ (M = Ti, Cr, Fe) Electrode Materials



- Introduction of M (Ti, Cr, Fe) in $LiV_{1-y}M_yS_2$ eliminates the formation of interdediate phases, which improve the capacity and the rates of charge/discharge.



Summary



- 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.