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Plug-In Electric Vehicle R&D on High Energy Materials

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Tuesday, February 26th, 2008

DOE Vehicle Technologies Program
Annual Merit Review, FY2008
Hybrid Electric Systems
Energy Storage / Applied Battery Research

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U.S. Department of Energy

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Purpose of Work

- This new project (Summer, 2007) was established to advance the commercialization of a lithium metal anode through the development of methods, techniques, and models designed to improve electrode safety and life. The high energy density of the lithium metal anode would allow for a significant increase in the fuel economy of a hybrid electric or plug-in hybrid electric vehicle.

- Tasks

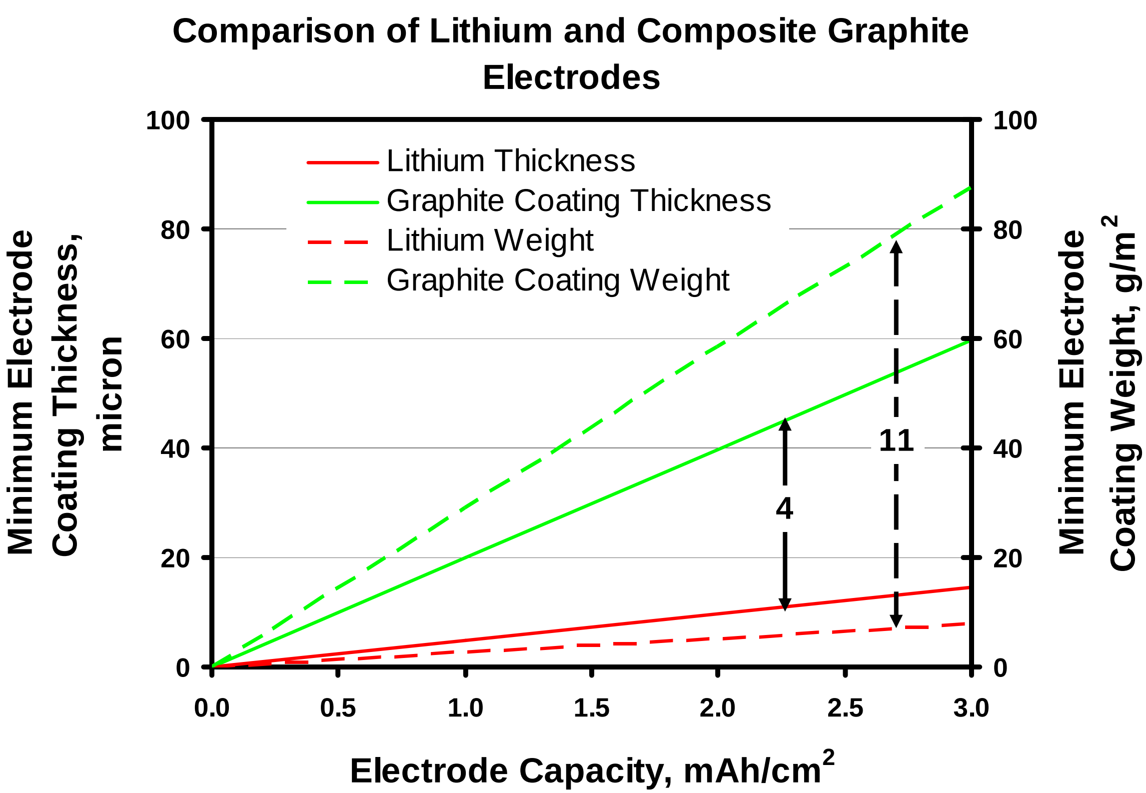
  – Perform literature review and evaluation of lithium anode technologies

  – Initiate experimental efforts based on results

Technical Barriers

- Lithium metal anodes have many materials-related issues:
  - Dendrite formation
    - *Mechanism of formation understood based on distribution of current density during electro-deposition*
    - *Leads to high surface area lithium that tends to be more reactive to the electrolyte*
    - *Dendrite formation and growth can lead to cell shorts*
  - SEI stability
    - *Cycling can cause cracks in the SEI layer – exposing fresh Li to the electrolyte*

A Metallic Lithium Negative Electrode Offers many Significant Advances over Graphitic Negative Electrodes



- Fast kinetics with no lithium diffusion allow for a planar electrode geometry
- More than an order-of-magnitude reduction in coating weight
- Factor of 4 reduction in coating volume
- Opens up the use and development of much higher capacity positive electrode materials

Approach

- ***Coating the lithium metal with a Li conductive film***

  – Previous methods used to prevent/control dendrite growth have included –

    - Electrolyte additives – *addition of organic molecule to the electrolyte that polymerizes at some voltage to coat the Li (anode) surface.*
    - Varying electrolyte solvents and salts – *changes the SEI layer*
    - Polymer or Gel Electrolytes – *inhibits dendrite growth*

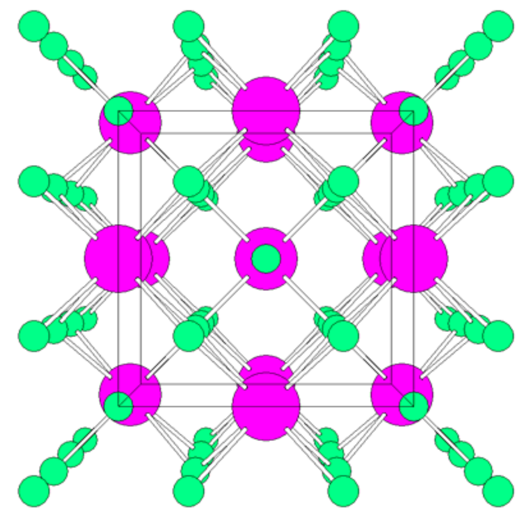
  – We have started to look at *ex-situ methods* to coat lithium.

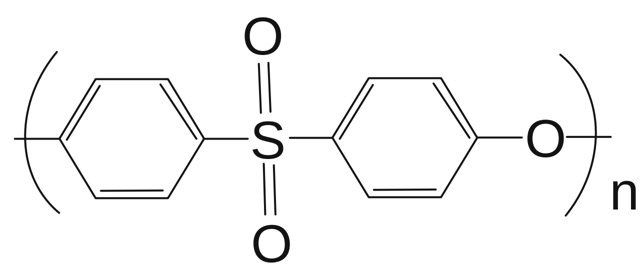
    - *Organic*
    - *Inorganic*

Performance Measures and Accomplishments

- Completed literature study of current technologies

- The baseline cell for our studies is the Li / $Li_4Ti_5O_{12}$ half cell.
- Uncoated Li Cells
  – Dendrite formation as early as 12th cycle
- Lithium metal coated with an inorganic lithium ion conductor
  – Li_3Sb ~ 2 x 10^{-4} S/cm*
  – $Li_{2-x}(AlGe)_2(PO_4)_3$ >10^{-4} S/cm**
  – LiPON ~10^{-6} S/cm
- Organic polymers
  – PES – polyethersulfone





*Weppner, Huggins JES 1977; ** Kobayashi, et. al., JES 2005

Literature Review

- Lithium Anodes are used in several industries:
  - Primary battery manufacturers
    - *Standard for medical battery industry (Greatbatch, Medtronic)*
    - *Implantable Defibrillators, pacemakers, and drug pumps*
  - Secondary battery manufacturers
    - *Polymer electrolyte batteries (e.g. HQ)*
    - *Sulfur batteries (Polyplus, Sion)*

- Literature studies
  - Several groups (notably D. Aurbach) have performed detailed studies of the effect of changing electrolyte solvents, salts, and temperature.
  - Electrolyte additives
  - Continuing studies on new electrolyte materials, including polymers and ionic liquids

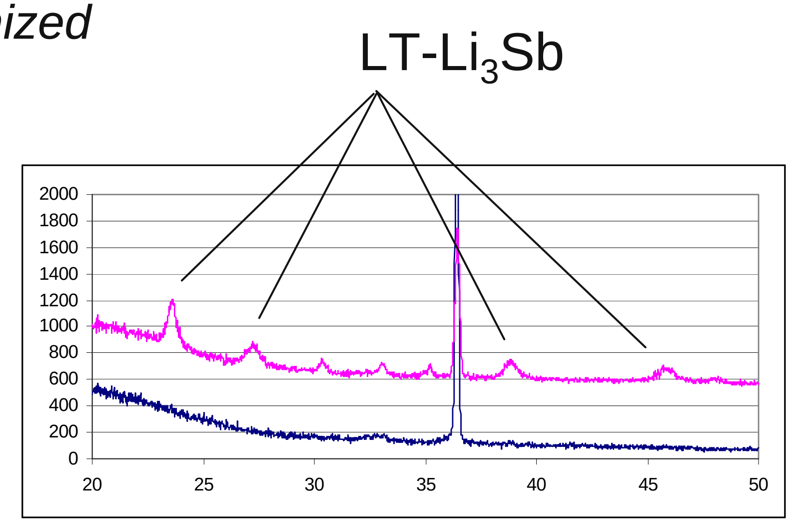
Inorganic Coatings

- Various solvents were evaluated for solubility of appropriate metals salts and stability towards Li metal.
  - DMC, DEC, NMP, DMF, THF, AN
  - $SnCl_2$ ($Li_{4.4}Sn$), $SbCl_3$ (Li_3Sb), $AgNO_3$ ($Li_{15}Ag_4$)
    - *Coatings choice derived form previous work on non-graphitic anodes*
    - *Since material stays in fully lithiated state, the major problem of Zintl-based alloys - volume expansion and contraction on cycling causing electrode pulverization - is minimized*

–Films initially made by dip-coating.

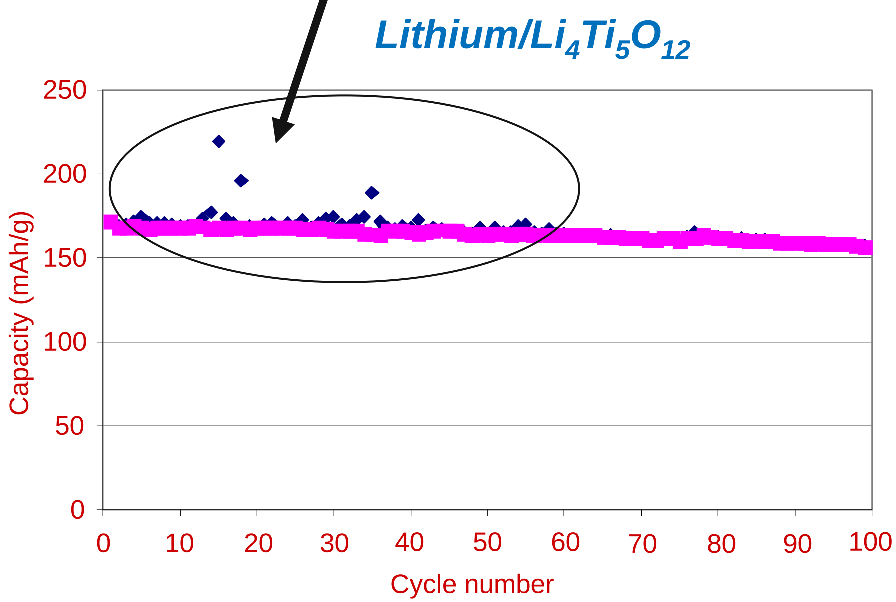
•*Contact with Li surface reduces the salt to the desired Zintl salt.*

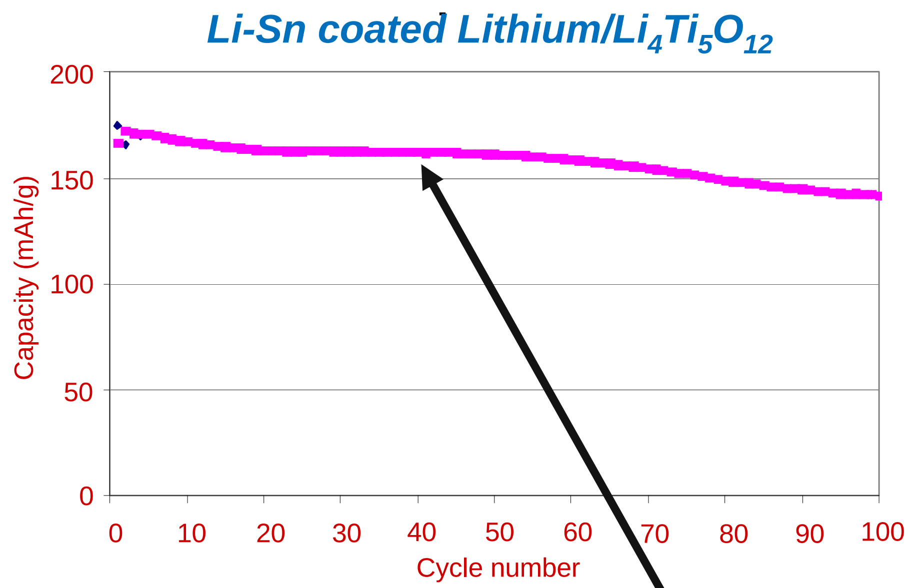
•*Coating thickness is depend**e**nt upon salt concentration and **s**urface roughness.*



Inorganic Coatings - Cycling

Evidence of dendrite formation as early as 10th cycle (baseline cell)





Little evidence for dendrite formation.

Organic Coatings

- Initial polymer chosen for study was polyethersulfone (PES) based on a survey of the open literature and US patents. It is a polymer commonly used to coat Li in the medical battery industry (one of the largest users of Li anodes).
- Evaluated solubility of PES in a variety of solvents
  - Fairly soluble in a few typically available solvents (e.g. NMP, DMF).
    - *Appears minimally soluble in typical electrolyte solvents – especially at RT.*
  - Used low weight% solution to dip coat lithium
    - *DMF/PES coating - "milky"-transparent film*
    - *NMP/PES coating - amber transparent film*
    - *Evaluating performance and properties of coated materials*
    - *Method allows for the addition of solid state Li-ion conductors or other additives to be added to the Li-interface , e.g. LiSICON's*

Technology Transfer

- Lithium metal anodes – if commercialized in secondary liquid electrolyte batteries – would increase the number of possible cathodes and battery chemistries available to manufacturers.
  - Limitation with graphite is need for Li source
  - Expands library of cathodes to include non-lithium compounds (e.g. MnO_2)

- Simple coating method would allow for commercialization of the Li anode while introducing minimal new materials into the cell and allowing more control over the coating itself.

Activities for the Next Fiscal Year

- Milestones
  - Determine role and fate of inorganic coatings
    - *Examine Li / Li_3Sb and Li_3Sb / electrolyte interfaces*
    - *Continue studies of Sn and other active metals*
  - Optimize organic coatings
    - *Examine role of inorganic additives in cell performance*
    - *Optimize polymer thickness, micro- and nano-scale morphology*
    - *Polymer-inorganic nano-composite coatings*
      - Enhance Li-ion conductivity of polymer coating
  - Engineering of SEI surface morphology
    - *Investigate effect of grain size and shape on stability of SEI during cycling*

Summary

- New project Summer 2007
- Developing and evaluating new coatings of lithium metal to try to extend the life of the Li metal anode and prevent dendrites.
  - Literature/patent searches and evaluation
  - Scoping studies
- Hired Dr. Carmen Lopez in Jan 2008
  - Studied the formation of dendrites and nano-crystal growth mechanisms in non-aqueous electrolytes.
- Attacking problems in two ways
  - Inorganic coatings derived from previous work on non-graphitic anodes
  - Starting point for organic coatings based on efforts of the medical battery industry

Acknowledgements

- Carmen M. Lopez
- Andy Jansen
- Yan Qin

Support from Tien Duong and David Howell of the U.S. Department of Energy's Office of Vehicle Technologies Program is gratefully acknowledged.