Develop Improved Methods of Making Intermetallic Anodes

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Vehicle Technologies Program

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Overview

Timeline

- Start: October 2008
- Finish: September 2014
- ~8% Complete

Budget

- ~$200K FY09

Barriers

- PHEV's need a high energy density battery to meet the 40 mile range target in 120 kg (80 L) battery size. Intermetallic alloys have the potential to be high capacity anode materials, but the following issues must be addressed
  - Low cycle life
  - Large volume expansion

Partners

- Fine metals supplier
- Binder vendors

Objectives

- Make electrodes based on Cu_6Sn_5 using a wide selection of binders with a particular emphasis on binders that are able to accommodate relatively large volume expansions.
- Develop methods to determine and control the optimum particle size, composition, and morphology of Cu_6Sn_5 based intermetallic alloys.

Milestones

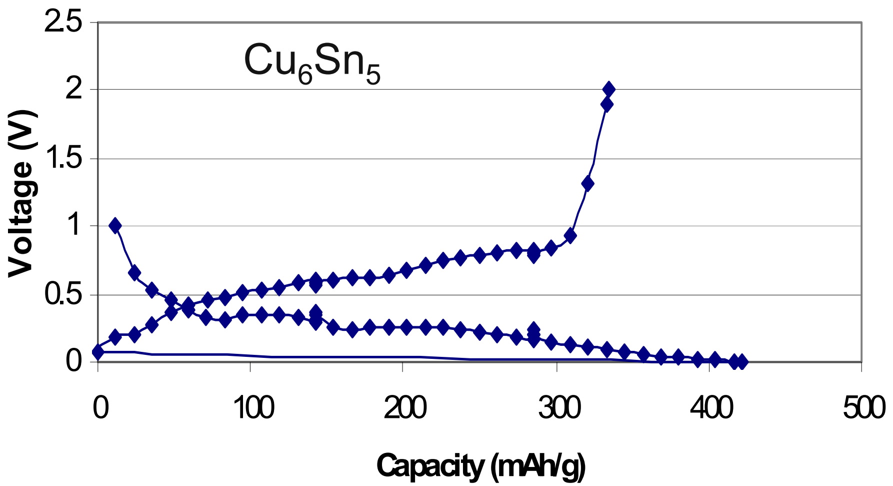
Determine influence of binder on Cu_6Sn_5 cycle life	March, 2009
Explore methods of controlling particle size and morphology	May, 2009
Produce an intermetallic electrode with 200 cycles and 80 % capacity retention	Sept., 2009

Approach

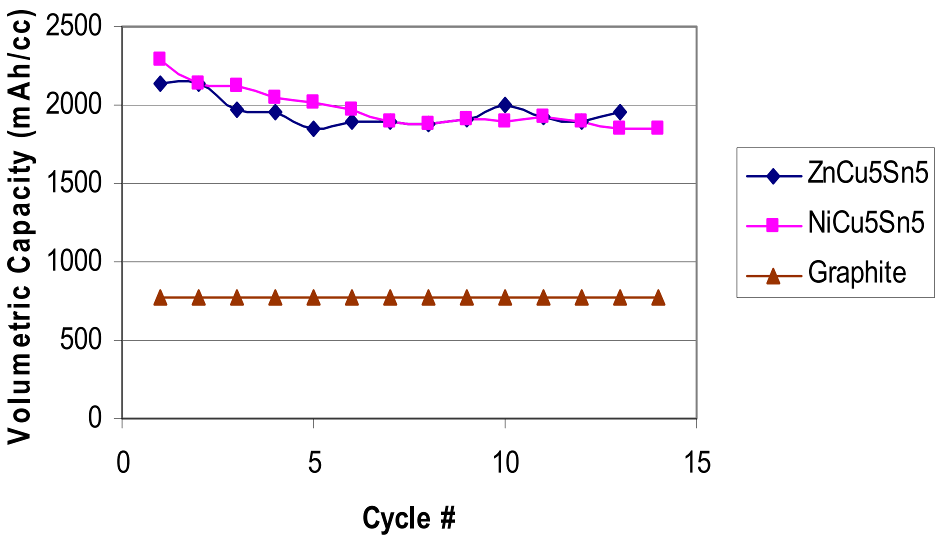
- The general approach in this subtask will be to explore alternative methods of making electrodes based on intermetallic alloys such as Cu_6Sn_5. The goal is not necessarily to develop new classes of active materials but rather, to employ materials already being developed in the BATT Program.

- Success will be achieved upon development of an electrode that can accommodate the large volume expansion and contraction during deep discharge cycling, and can prevent the excluded metal (such as copper) from agglomerating into an inert mass during cycling. Likely solutions to these problems will involve the proper choice of binders and methods of controlling the particle size and morphology during production, and during repeated cycling.

Why the Interest in Intermetallic Alloys



Previous work from the BATT program has shown that doped-Cu_6Sn_5 materials have reversible capacities similar to graphite. When their high density is taken into account the volumetric capacities are nearly 3X that of an optimized graphite based electrode.



Recent reports on the Li_xSi system by 3M have shown that using binders more appropriate for the volume expansion of the Li_xSi system can greatly enhance cycle life.

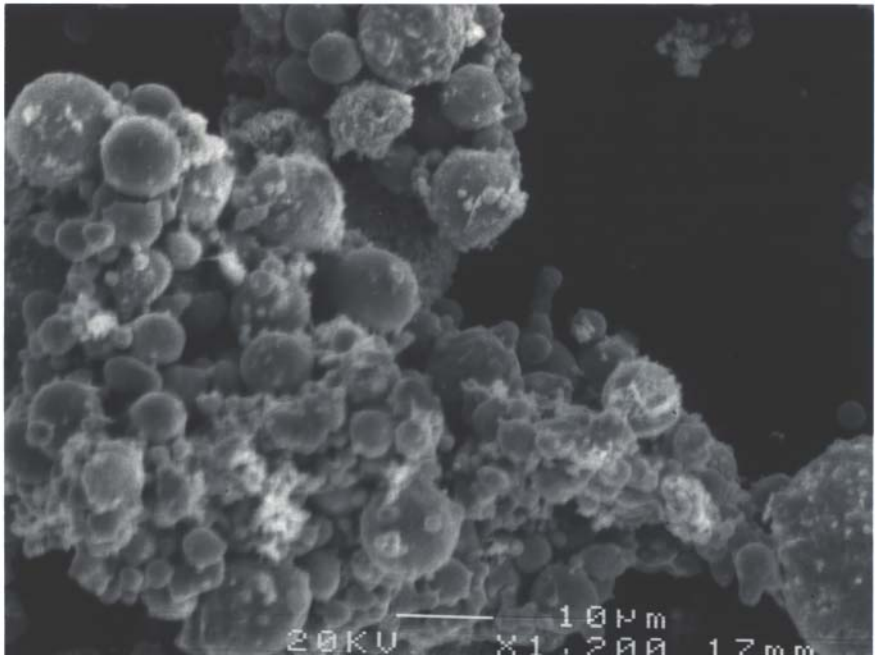
Metal Alloys Provide an Advantage in Calculated PHEV Battery Designs

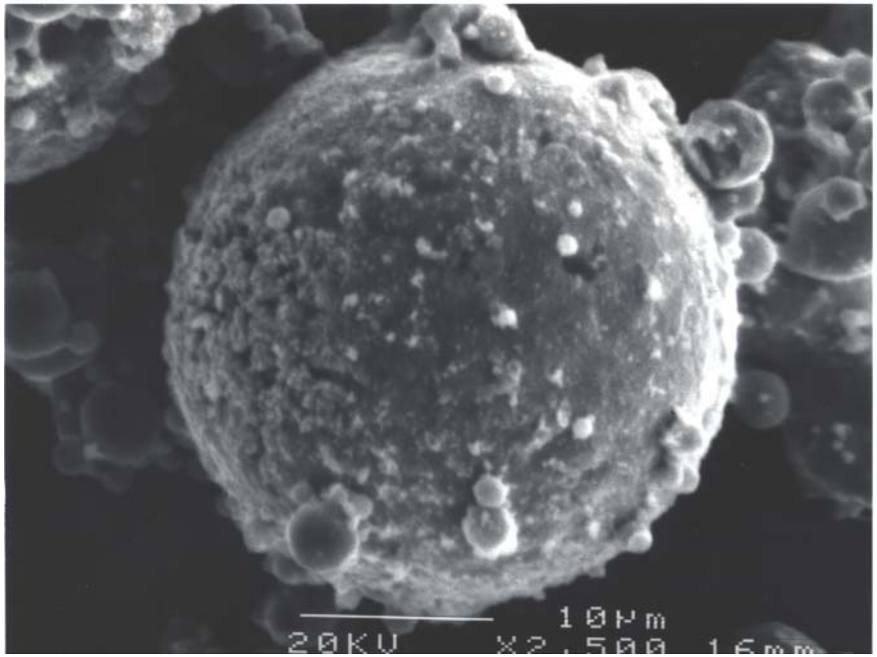
Cell Couple	Graphite vs. NCM	Cu_6Sn_5 vs. NCM
Positive Electrode (32 % porosity)		
Material Capacity	200 mAh/g	200 mAh/g
Active Loading	84 %	84 %
Coating Thickness	72 µm	100 µm
Coating Loading	18.4 mg/cm²	28.4 mg/cm²
Negative Electrode (34 % porosity)		
Material Capacity	290 mAh/g	400 mAh/g
Active Loading	92 %	84 %
Coating Thickness	100 µm	67 µm
Coating Loading	14.9 mg/cm²	18.3 mg/cm²

Cell Couple	Graphite vs. NCM	Cu_6Sn_5 vs. NCM
Battery Power	45 kW	45 kW
Battery Weight	111 kg	104 kg
Battery Volume	69 L	54 L
Battery Energy	15.5 kWh	15.5 kWh
C/3 Capacity	46.8 Ah	53.5 Ah
Number of Modules	8	8
Cells per Battery	96	96
Battery Voltage	336 V	298 V
Vehicle Range	40 miles	40 miles

- Calculations based on Paul Nelson's Battery Design Model (Argonne).

Obtained Cu_6Sn_5 Sample from Vendor



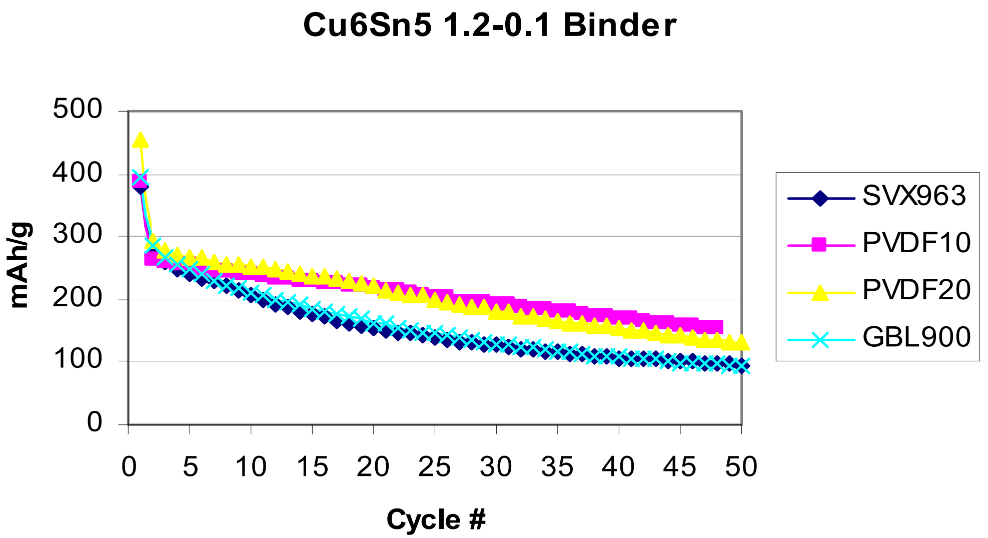


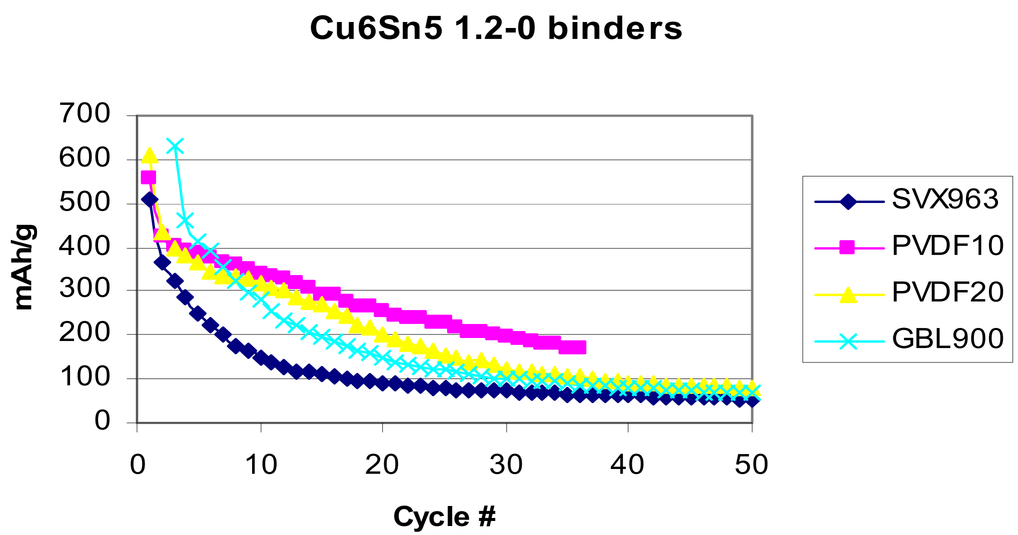
- Study has been initiated with this sample.
- Samples with varying particle size and dopants are being sourced.

Elastic Binders Are Needed

- Whereas binders and electrode recipes have been optimized for graphite, little effort has been applied to the intermetallic anode materials.
- The binder typically used in anode systems was developed with Li/graphite (~10 % volume expansion) in mind.
- Part of the capacity fade of intermetallic anodes is related to the binder not holding the electrode together as the volume fluctuates by as much as 450 %.
- Recent evidence suggests that the binder is an important variable that must be optimized for these new anode systems.
- Several classes of commercial binders have been identified and are being sourced for evaluation in the $Li_xM_yCu_5Sn_5$ system.

Previous Work Showed Better Performance with PVDF as the Binder for Cu_6Sn_5





Even with different levels of lithiation and Cu extrusion, the Cu_6Sn_5 system shows that the binder does matter in altering capacity fade – especially at higher volume expansion. SVX963 and GBL900 work almost as well as PVDF down to 0.1 V but have higher fade when 0.0 is the low end cutoff.

SVX – rubber/latex

GBL – PVdF/polymer additive

Obtained Range of PVDF Binders

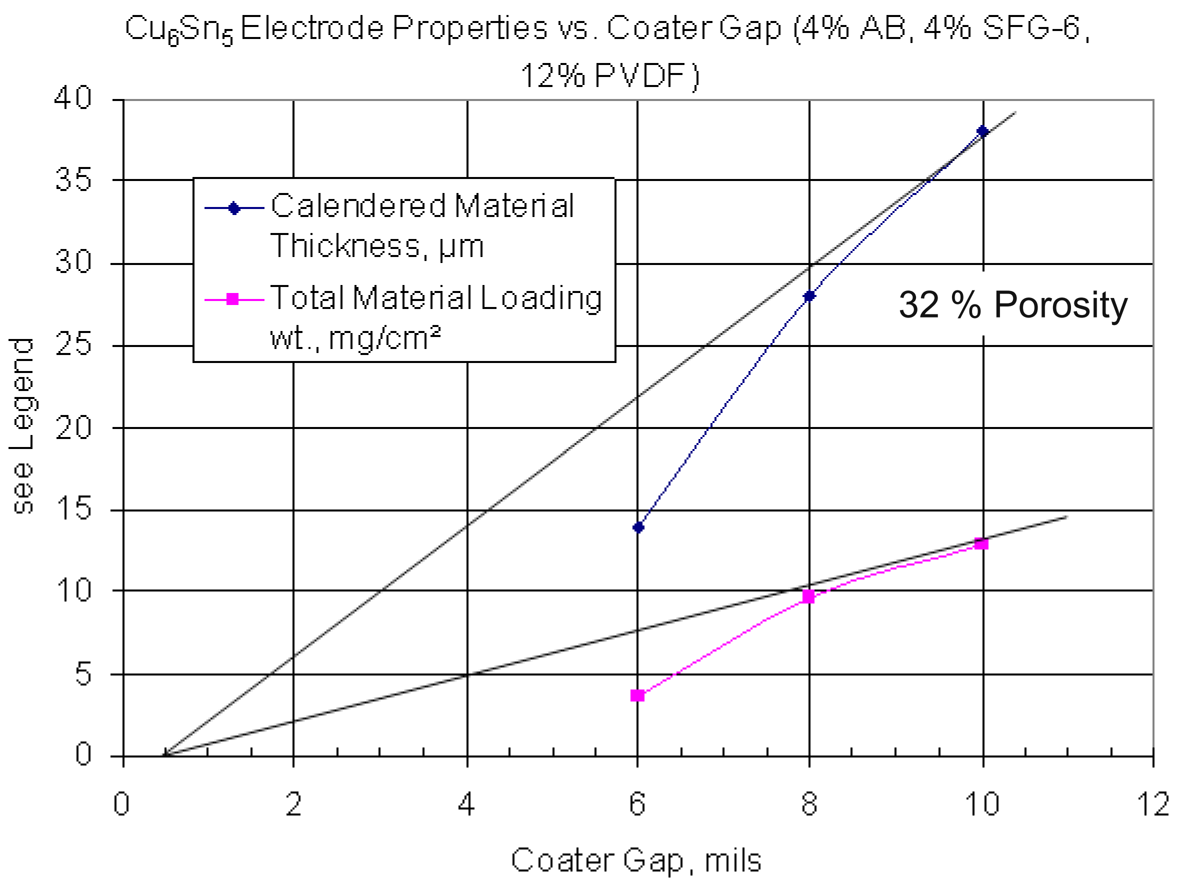
KF Polymers (PVDF) from Kureha Chemical Ind.

Molecular Weight	About 280,000	About 350,000	About 500,000	About 630,000	About 1million
For Cathode	W#1100	W#1300	W#1700	W#7200	W#7300
	L#1120(12%)	L#1320(12%)	L#1710(10%)	L#7208(8%)	L#7305(5%)
For Anode	W#9100		W#9200		W#9300
	L#9130(13%)		L#9210(10%)		L#9305(5%)

( ) of L series shows the powder content.

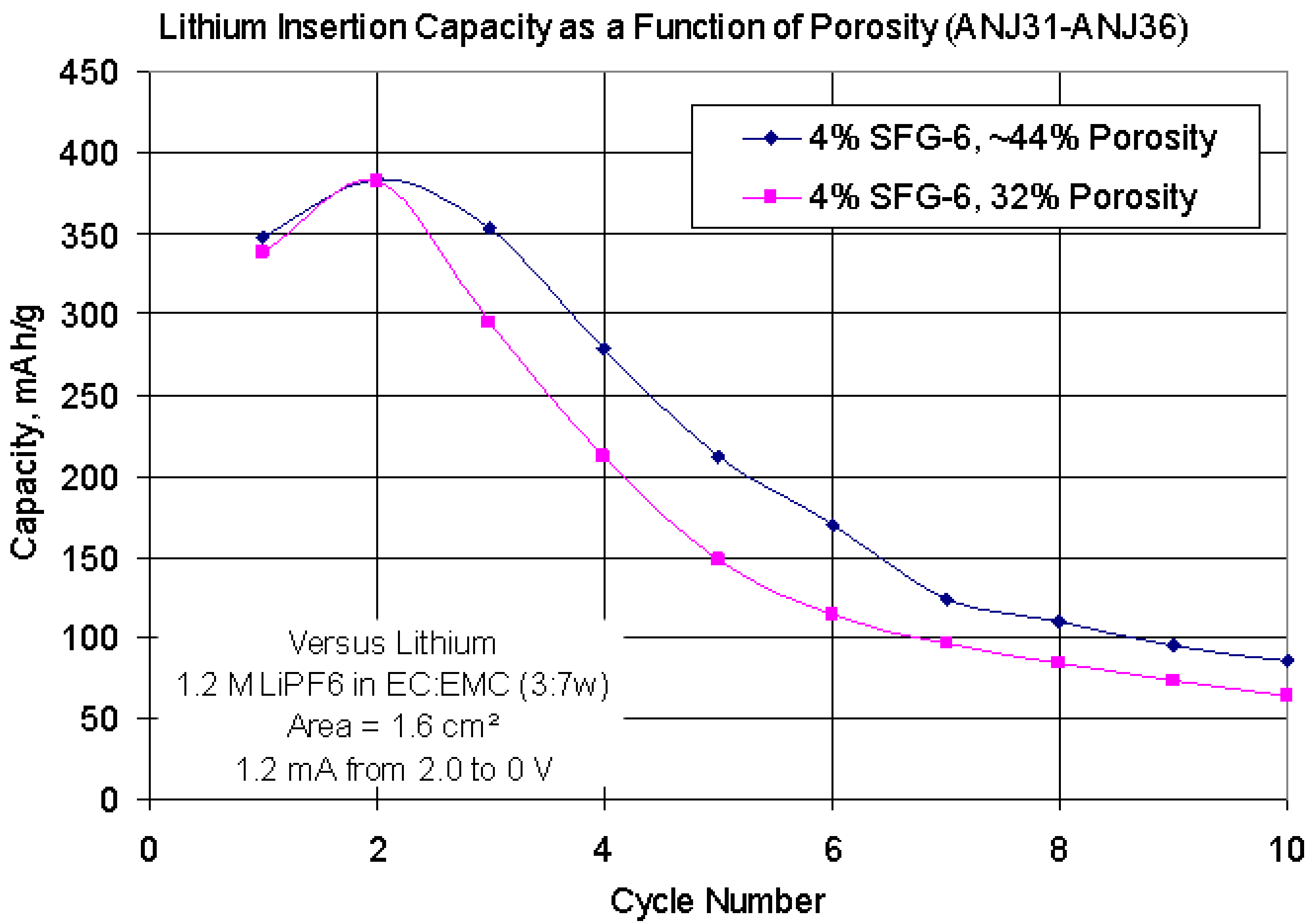
- A study has been initiated with these binders to determine the influence of the binder's molecular weight and functional groups (positive vs. negative).

Initiated Engineering Studies of Cu_6Sn_5 Electrode Loading



Electrodes made with Argonne's minicoater.

Electrode Porosity May Affect Capacity Fade



- Capacity fade is severe for both of these thick electrode designs and may indicate that alternative electrode processing methods are needed.

Volume Expansion Is a Concern

- Full lithiation of Cu_6Sn_5 may not be practical due to the extra volume of the extruded copper.
  - Can this volume expansion be designed into the particle and/or electrode?

Phase*	Volume per Sn Atom, Å³
Sn	34.2
LiSn	41.1
Li_7Sn_3	61.2
Li_5Sn_2	64.3
$Li_{13}Sn_5$	65.5
Li_7Sn_2	80.3
$Li_{17}Sn_4$	95.4

*Adapted from R.A. Huggins and W.D. Nix, *Ionics* **6** (2000) p. 57-63.

Phase	Unit Cell(s)	Volume of Unit Cell, Å³	Volume per Sn Atom, Å³
Cu_6Sn_5	$Cu_{24}Sn_{20}$	782	39.1
Li_2CuSn + Cu	$Li_8Cu_4Sn_4$ + 0.8Cu	245 +0.8(11.75)	63.6
$Li_{17}Sn_4$ + Cu	$Li_{340}Sn_{80}$ + 96Cu	7634 +96(11.75)	109.5

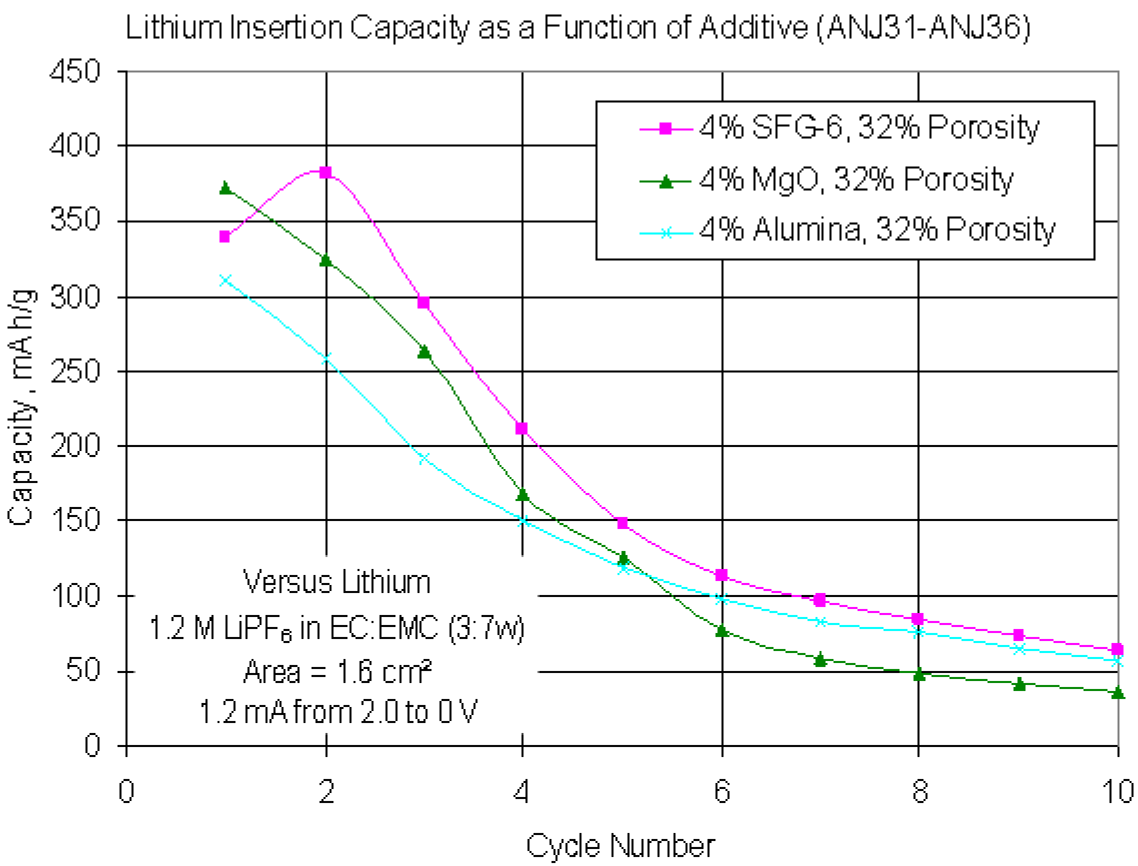
Use Inert Additives to Extend Life

The discharge mechanism for the $Li_xM_yCu_5Sn_5$ electrode materials can be related to the $Na/NiCl_2$ and $LiAl/FeS_2$ battery systems. Previous electrode optimization work on these materials has identified the main culprit in capacity fade is due in part to diffusion of the displaced metal (Cu, Ni, Al) from the reaction center. By adding high surface area secondary components to the electrode, (e.g. MgO in LiAl and S in $NiCl_2$), this diffusion can be controlled resulting in significant enhancements in performance.

Earlier studies on the $FeCu_5Sn_5$ type electrode have highlighted a similar capacity fade mechanism. Recent work on the addition of extra tin to the electrode active material mix has shown some positive results, however, it is believed this effect will be mitigated during cycling by agglomeration problems usually associated with Sn-based anodes.

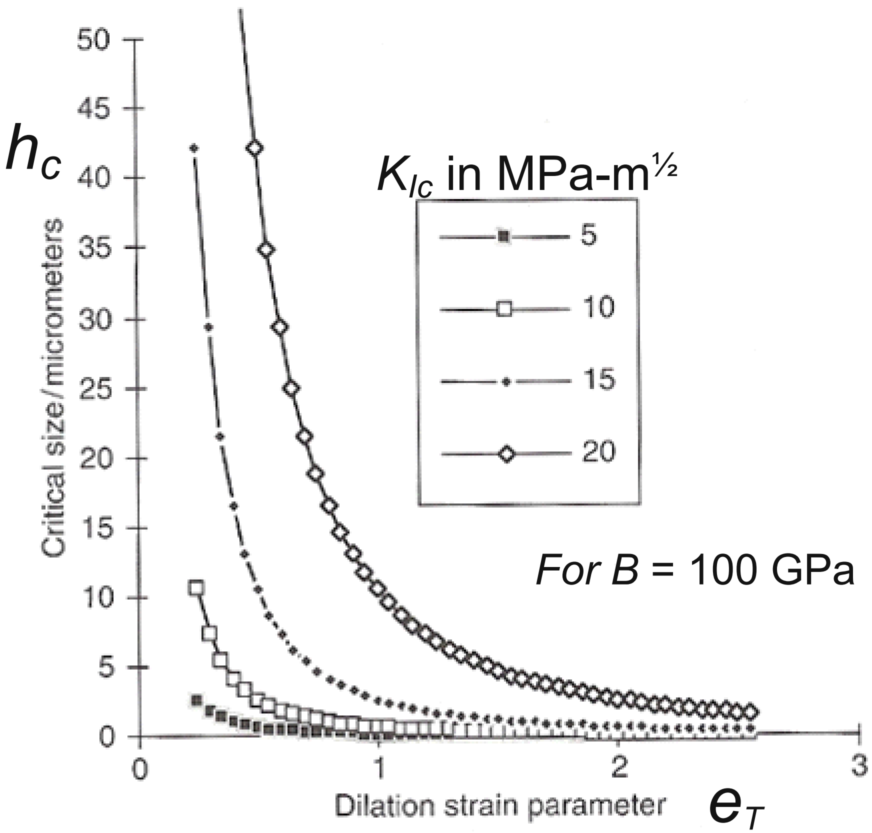
We plan to study the controlled addition of inactive secondary phases to the electrode to help control the metal (Fe, Cu) diffusion. Since Cu_6Sn_5-based electrode have such high volumetric capacities, additions of even 20% inert phases would still represent a significant enhancement in cell capacity.

Metal Oxide Bulk Additives Did Not Enhance Capacity Retention



- The addition of metal oxide additives to the bulk electrode does not appear to prevent capacity fade in these thick electrode designs.
- New electrode processing methods are being explored such as particle size reduction, binder selection, and oxide coatings on the particle (instead of the bulk).

Huggins' Critical Particle Size Model



R.A. Huggins and W.D. Nix, "Decrepitation Model For Capacity Loss During Cycling of Alloys in Rechargeable Electrochemical Systems", *Ionics* **6** (2000) p. 57-63.

- The model work of Huggins suggests a particle size of 0.2 μm is preferred for pure Sn as a starting material.
- Intermetallic alloys provide an opportunity to increase the fracture toughness and decrease the elastic modulus of metal anodes through alloying with additional metals and phases.

$$h_c \approx \frac{23}{\pi}\left(\frac{3K_{Ic}}{Be_T}\right)^2$$

h_c is critical size in μm
K_{Ic} is fracture toughness in MPa-m½
B is elastic modulus in GPa
e_T is strain dilation ($\Delta V/V$)

Future Work

- Continue investigation of elastic binders for intermetallics.
- Obtain and study vendor made samples of Cu_6Sn_5 samples made with varying particle size.
- Obtain and study vendor made samples of substituted metal species in the $Li_xM_yCu_5Sn_5$ system.
  - Copper rich Cu_6Sn_5
  - Partial iron substitution of copper
- Explore the subject of critical particle size based on Huggins work by making alloy casts of lithiated intermetallic alloys and evaluating their mechanical properties
  - Universal Materials Testing Machine (Instron) tension testing for modulus
  - Single Edged Notched Bend (SENB) testing for fracture toughness
- Continue search for additives that promote copper retention at the particle level and electrode level.
- Initiate electrolyte additive study to enhance SEI formation for intermetallic electrodes.

Summary

- Developed coating process to make electrodes with varying thickness of Cu_6Sn_5 to establish baseline.
- Identified metals supplier to help in development of intermetallic alloys of varying particle size and morphology.
- Evaluated the influence of conductive and resistive additives to electrode powder mix in an attempt to minimize copper migration.
- Expanded Argonne's Battery Design Model to assess the benefit of using intermetallic alloys in PHEV batteries.
- Obtained numerous samples of electrode binders for binder optimization study.

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