Improved Methods for Making Intermetallic Anodes

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Project ID #: ES022

Objectives

- Make electrodes based on intermetallic alloys such as 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.

Overview

Timeline

- Start: October 2008
- Finish: September 2014
- ~25% Complete

Budget

- Total project funding
  - 100% DOE
- $300K FY09 (ABR)
- $300K FY10 (ABR)

Barriers

- Development of a safe cost-effective PHEV battery with a 40 mile all electric range that meets or exceeds all performance goals
  - Intermetallic alloys have the potential to be high capacity anode materials, but the their large volume expansion must be addressed

Partners

- Dileep Singh (ANL-NE)
- Wildcat Discovery Technologies
- Binder vendors

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	September, 2009

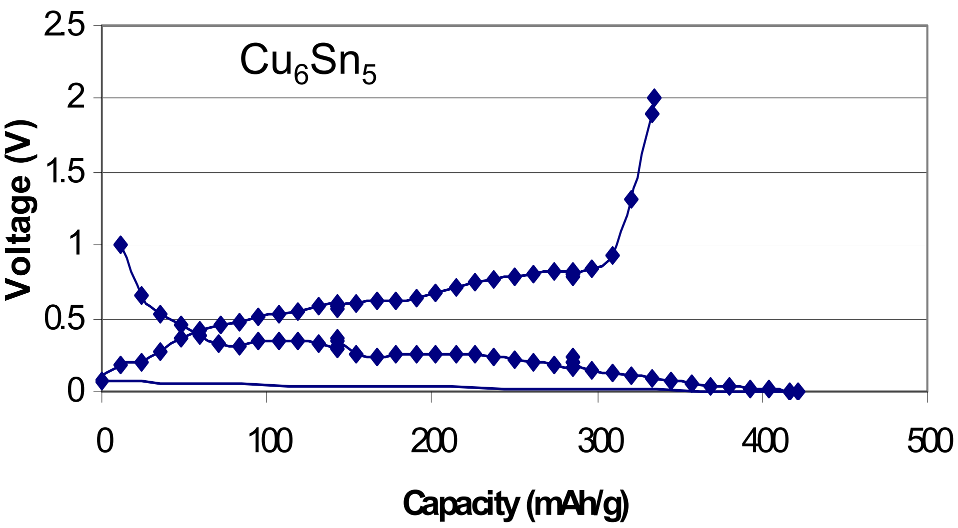
Approach

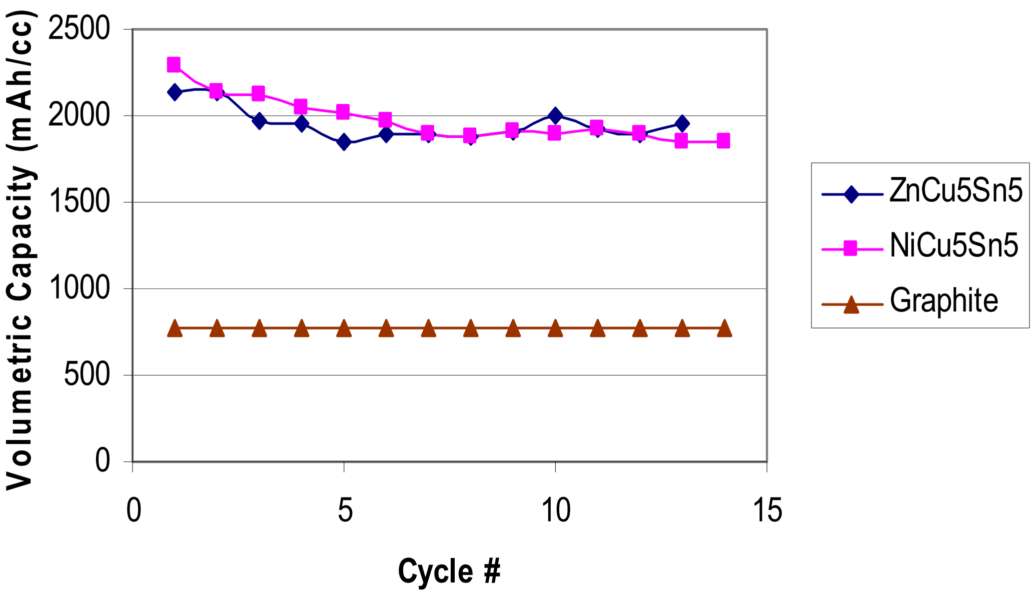
- The general approach in this subtask will be to explore alternative methods of making electrodes based on intermetallic alloys such as Cu_6Sn_5. The goal is not to create new classes of active materials but rather, to employ materials already being developed in the BATT Program.

- 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.

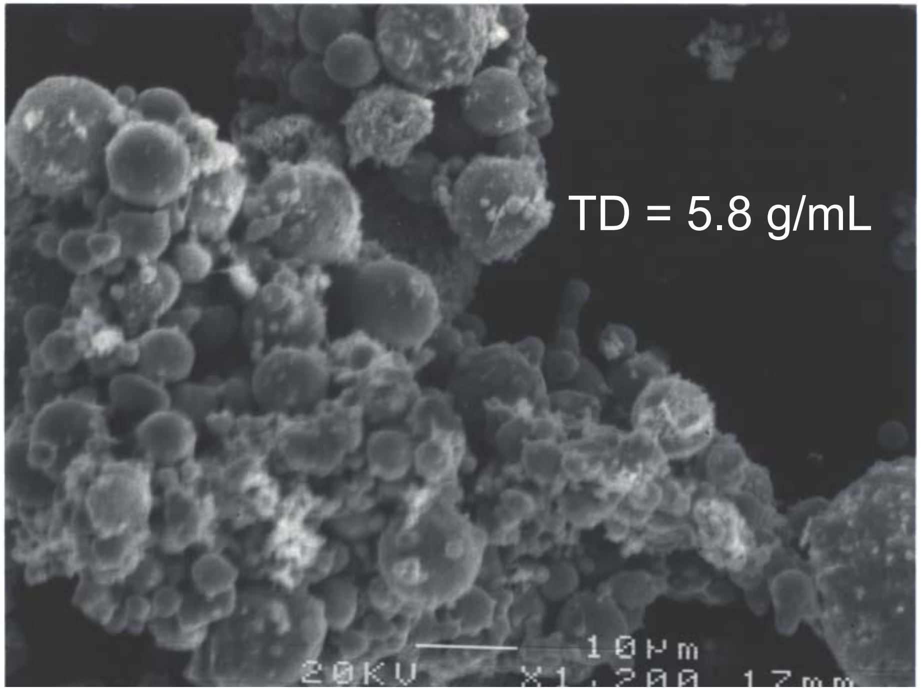
Metal Alloys Provide an Advantage in Calculated PHEV Battery Designs

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/cm^2	28.4 mg/cm^2
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/cm^2	18.3 mg/cm^2

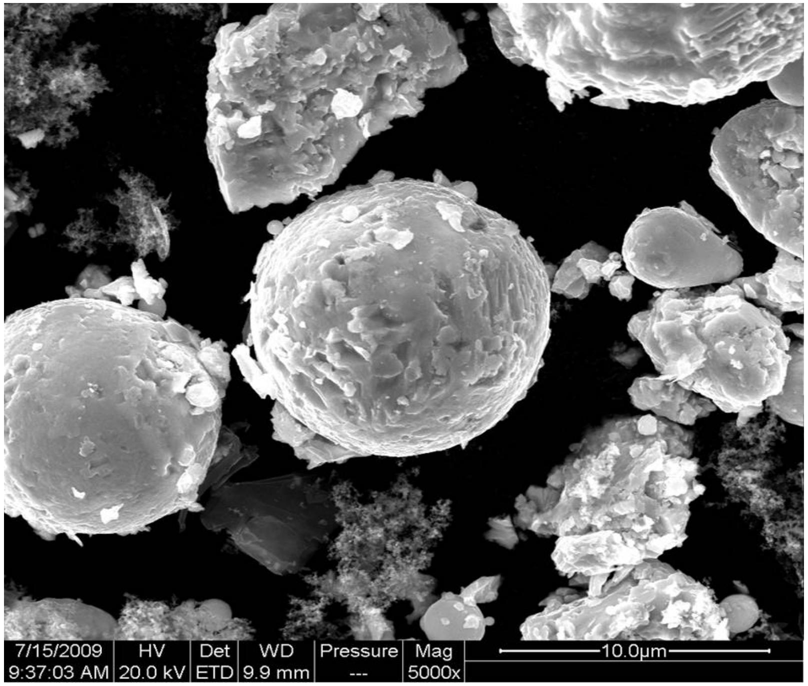
Cell Couple	Graphite vs. NCM	Cu_6Sn_5 vs. NCM
Battery Power	45 kW	45 kW
Battery Weight	111 kg	104 kg
Battery Volume	69 L	54 L
Battery Energy	15.5 kWh	15.5 kWh
C/3 Capacity	46.8 Ah	53.5 Ah
Number of Modules	8	8
Cells per Battery	96	96
Battery Voltage	336 V	298 V
Vehicle Range	40 miles	40 miles

- Calculations based on Paul Nelson’s Battery Design Model (Argonne)
- No 30% power margin was used in these predictions

Obtained Cu_6Sn_5 Sample from Vendor



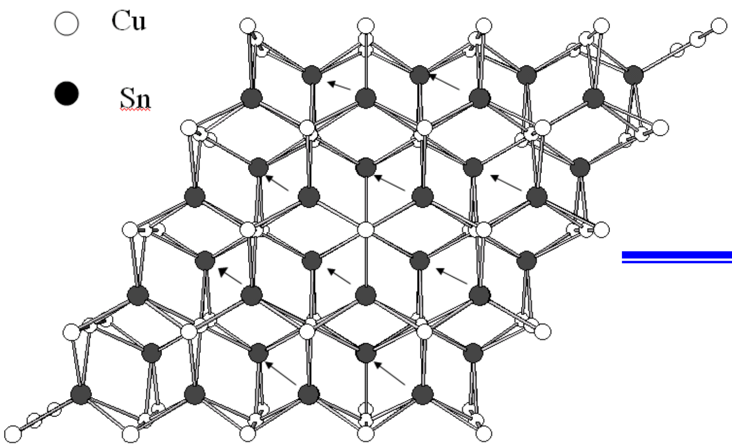
SEM photo of Cu_6Sn_5 powder as received.



SEM photo of Cu_6Sn_5 powder blended on roller mill with acetylene black carbon and SFG-6 graphite.

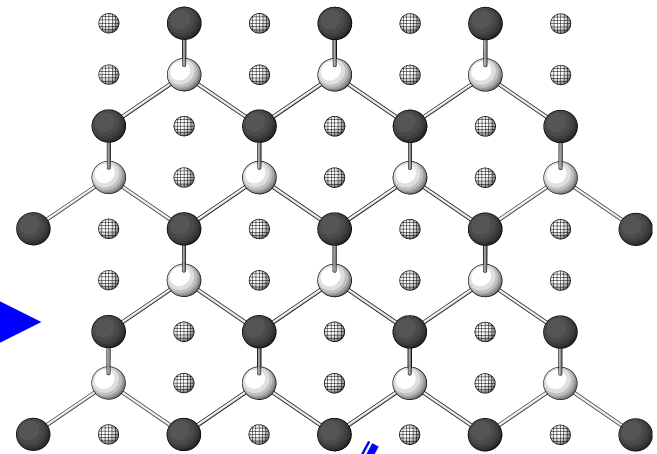
- Study was initiated with this sample due to its high tap density.

Significant Lattice Changes Occur Upon Lithiation



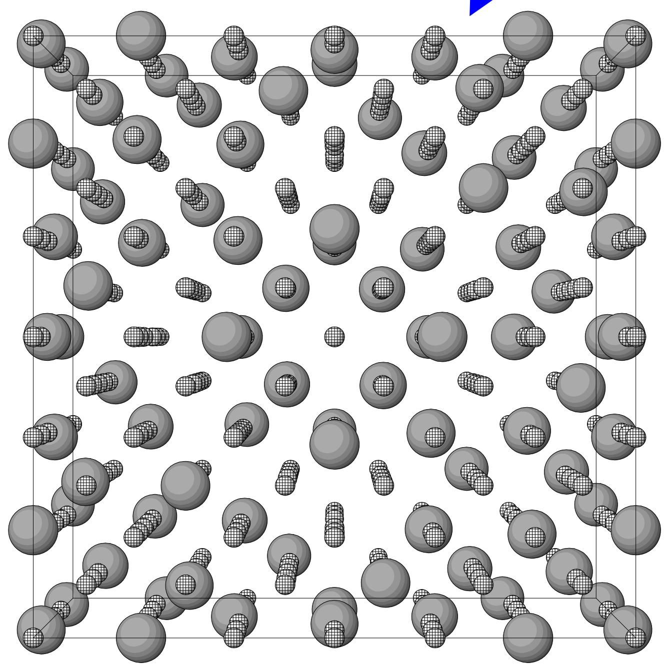
Cu_6Sn_5

Atoms	Length
Sn-Sn	5.12 Å
Cu-Cu	2.52 Å
Cu-Sn	2.82 Å



Li_2CuSn
+ 1 Cu for every 5 Sn

Atoms	Length
Sn-Sn	4.44 Å
Cu-Cu	4.44 Å
Cu-Sn	2.72 Å



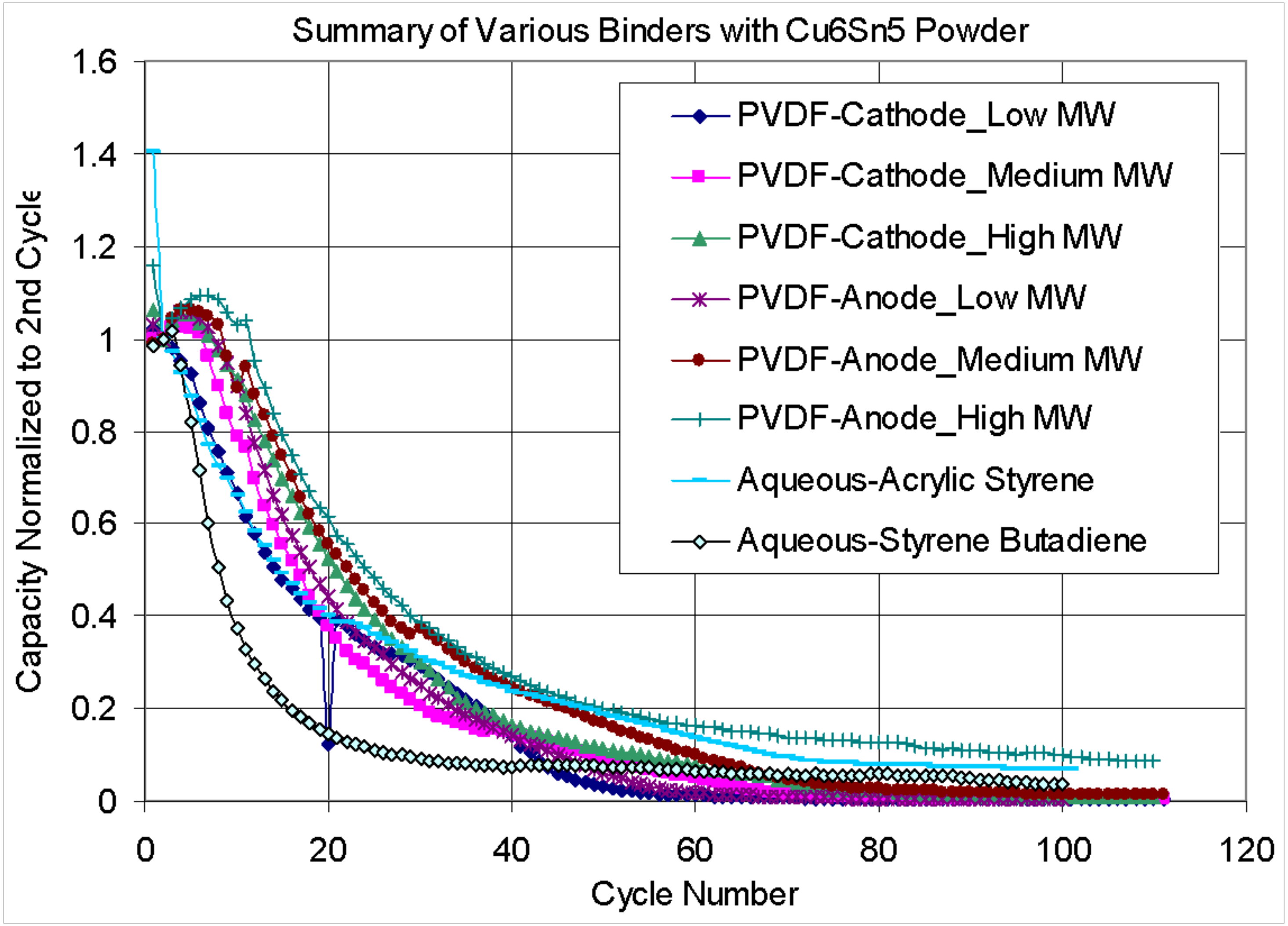
$Li_{17}Sn_4$
+ 6 Cu for every 5 Sn

Atoms	Length
Sn-Sn	5.0 Å

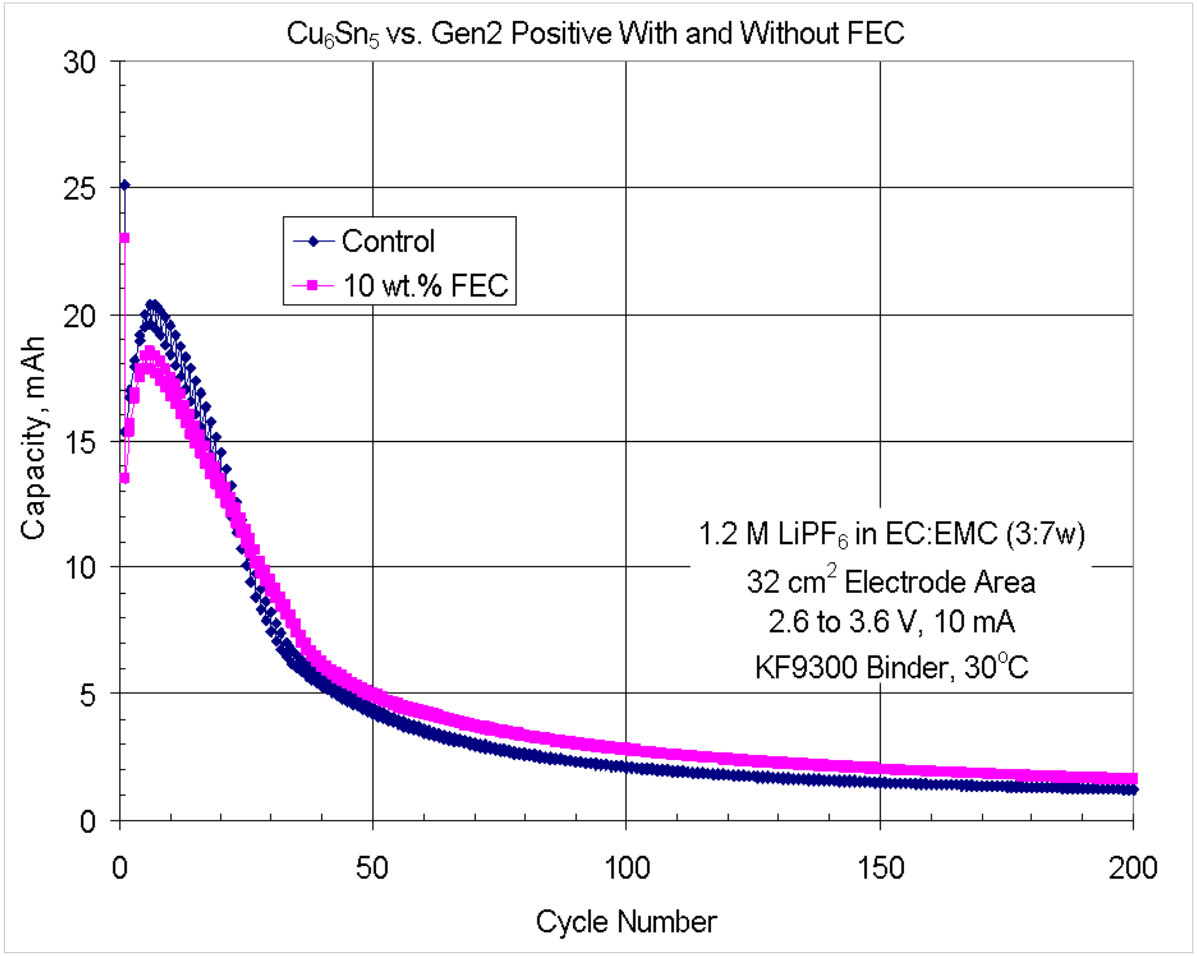
Elastic Binders Are Needed

- Binder and electrode recipes have been optimized for graphite, which has ~10% volume expansion upon lithiation
- Little effort has been applied to the intermetallic anode materials where the volume fluctuates by nearly 200%
- Several classes of commercial binders were identified and evaluated with the sourced Cu_6Sn_5 powder
- Solid anode additives (alumina, magnesia, and graphite) were also explored to see if they impeded the agglomeration of displaced copper

Choice of Binders Did Not Enhance Capacity Retention (for this powder sample)



Electrolyte Additive (FEC) Not Enough in This Case



- FEC was shown to be effective in other intermetallic efforts at Argonne
- This particular Cu_6Sn_5 morphology or size may not be suitable for battery electrodes

Volume Expansion Is a Concern

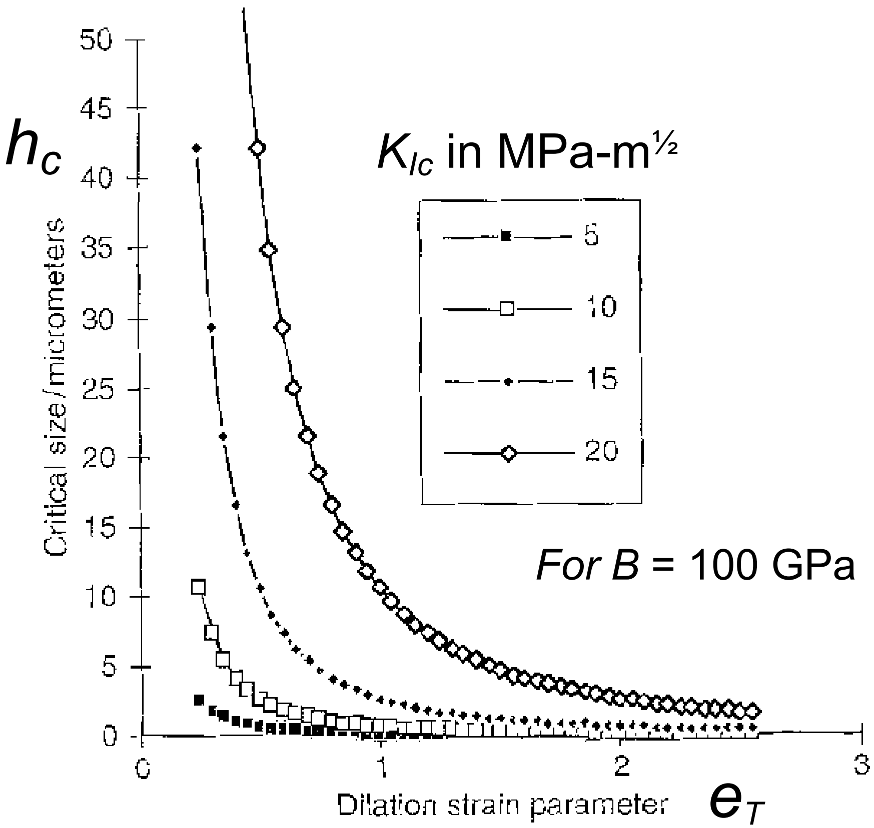
- Full lithiation of Cu_6Sn_5 may not be practical due to the large volume change.
  - Can this volume fluctuation be designed into the particle and/or electrode?

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

Huggins' Critical Particle Size Model



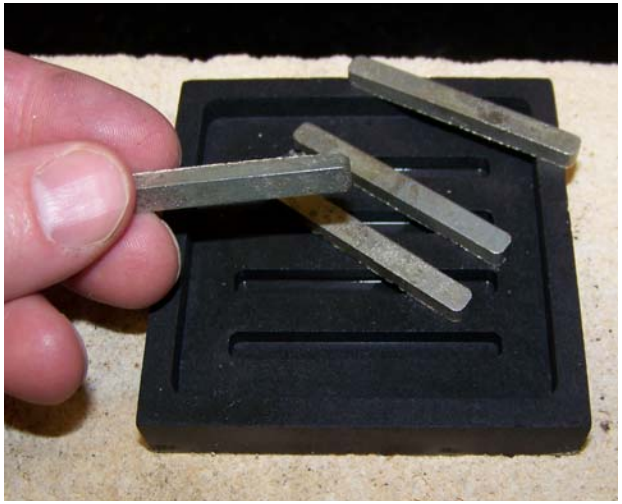
R.A. Huggins and W.D. Nix, "Decrepitation Model For Capacity Loss During Cycling of Alloys in Rechargeable Electrochemical Systems", *Ionics* **6** (2000) p. 57-63.

- 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 ($\Delta V/V$)

Determine Mechanical Properties of Intermetallic Alloys



Elastic modulus (Universal Materials Testing Machine (Instron))

- Measurements were made from stress strain plots obtained during four-point-bend tests using rectangular bars of the test material
- Outer fiber stress and associated strain were obtained from standard elastic beam theory
- Slope of the stress vs. strain plot gave the elastic modulus of the material

Fracture toughness (Single Edged Notched Bend (SENB))

- Single-edged notched beam test was used for fracture toughness evaluations
- Thin wafering blade was used to notch the samples such that the notch depth to sample thickness was ~0.5
- Samples were tested in three-point bend loading configuration at a constant displacement rate
- Fracture toughness was determined from the peak load at failure, sample dimensions, and a standard fracture mechanics relationship

Results of Mechanical Testing on Cast Bars

Alloy	Strength (MPa)	Modulus (GPa)	Fracture Toughness (MPa $m^{0.5}$)
Cu_6Sn_5	79±14	41.1±4.4	2.19±0.54
$NiCu_5Sn_5$	41.0±7.5	65.9±8.5	1.32±0.13
$ZnCu_5Sn_5$	93.0±8.9	46.0±6.2	2.56±0.23
$FeCu_5Sn_5$	78.9±7.0	52.19±0.89	2.38±0.15
Cu_6Sn_6			
Li_2CuSn			

Strength: four-point bend test
Elastic modulus: four-point bend test
Fracture toughness: notched samples tested in 3-point bend

Intermetallic Particles Must Be Sub-micron in Size

Intermetallic Alloy	$10Li + MCu_5Sn_5 \leftrightarrow 5Li_2CuSn + M$		$85Li + 4MCu_5Sn_5 \leftrightarrow 5Li_{17}Sn_4 + 20Cu + 4M$	
	Critical Particle Size, µm (eT = 0.63)	Theoretical Capacity, mAh/g	Critical Particle Size, µm (eT = 1.8)	Theoretical Capacity, mAh/g
Cu_6Sn_5	0.47	257	0.058	507
$NiCu_5Sn_5$	0.067	258	0.0082	510
$ZnCu_5Sn_5$	0.51	256	0.063	507
$FeCu_5Sn_5$	0.35	259	0.042	511
Cu_6Sn_6				
Li_2CuSn				

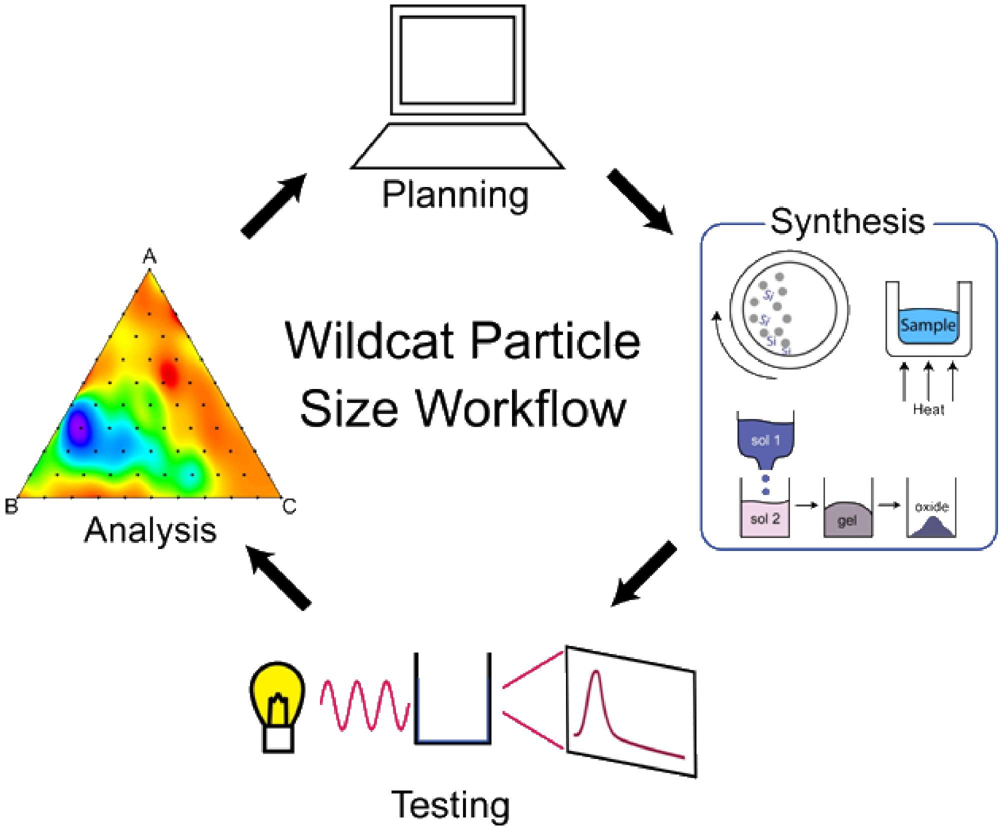
High Throughput Particle Size Control

- Contracted Wildcat Discovery Technologies to synthesize MCu_5Sn_5 samples (100 g) with controlled particle size
  - High throughput materials discovery company
  - Specialty synthesis

- Wildcat performed a high throughput screen to identify reaction conditions for target particle size

- In 2 weeks, ran ~150 reactions

- Tested
  - Milling conditions
  - Process control agents
  - Reagents



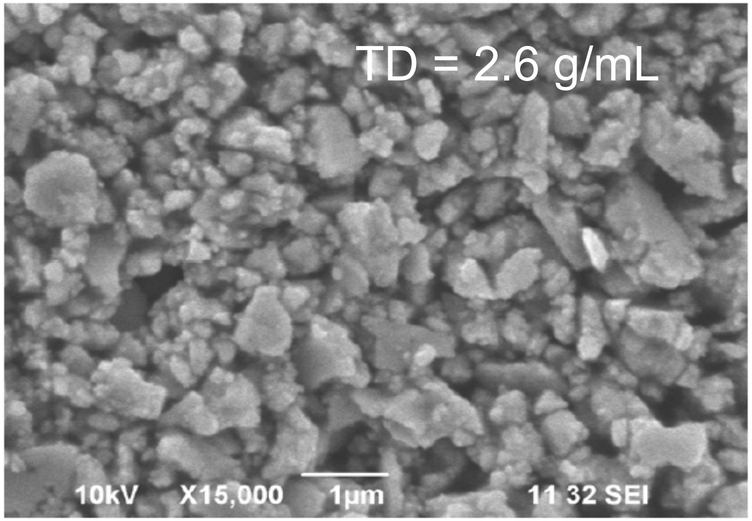
Materials Successfully Synthesized by Wildcat Discovery Technologies

Wildcat Discovery Technologies

Variety of morphologies induced

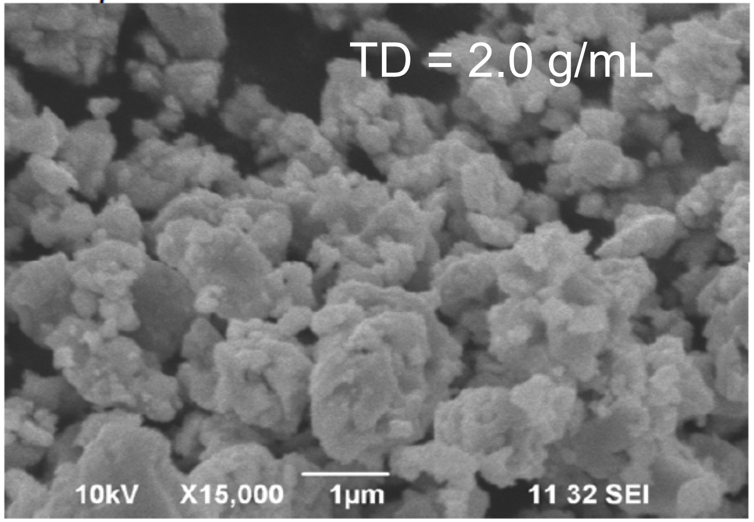
- Primary particle size (<100 nm to micron)
- Porous and dense structures

Sample 4

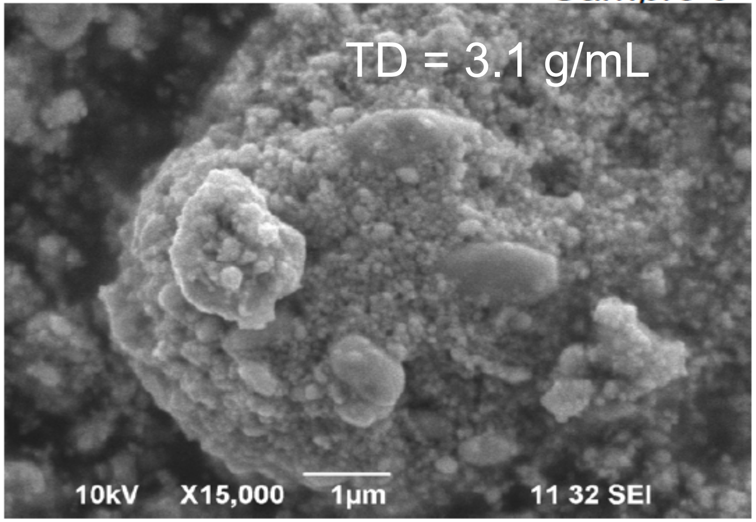


Selected Method #4 for its primary particle size and separation

Sample 1



Sample 6



Future Work

- Now in the process of testing $M_yCu_5Sn_5$ alloys with 0.5 μm particle size from Wildcat Discovery Technologies for M = Cu, Ni, Zn, Fe, and Sn
- Revisit the influence of elastic binders with new smaller intermetallic alloys
- Explore the subject of critical particle size based on Huggins work by making alloy casts of lithiated intermetallic alloys and evaluating their mechanical properties
- Continue search for additives that promote copper retention at the particle level and electrode level
  - Influence of grain size
- Revisit electrolyte additive study to enhance SEI formation on new smaller intermetallic electrodes
- Monitor energy density of final electrode design to compare against graphite/carbon electrodes

Summary

- Explored the subject of critical particle size based on Huggins work by making alloy casts of intermetallic alloys and evaluating their mechanical properties
- 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

Contributors and Acknowledgments

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