Develop Improved Methods for Making Intermetallic Anodes

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Project ID: ES022

Overview

Timeline

- Start: October 2008
- Finish: September 2014
- ~44% Complete

Budget

- Total project funding
  - 100% DOE
- $300K FY10 (ABR)
- $300K FY11 (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 their large volume expansion must be addressed

Partners

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

Objectives

- Make electrodes based on intermetallic alloys 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.

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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

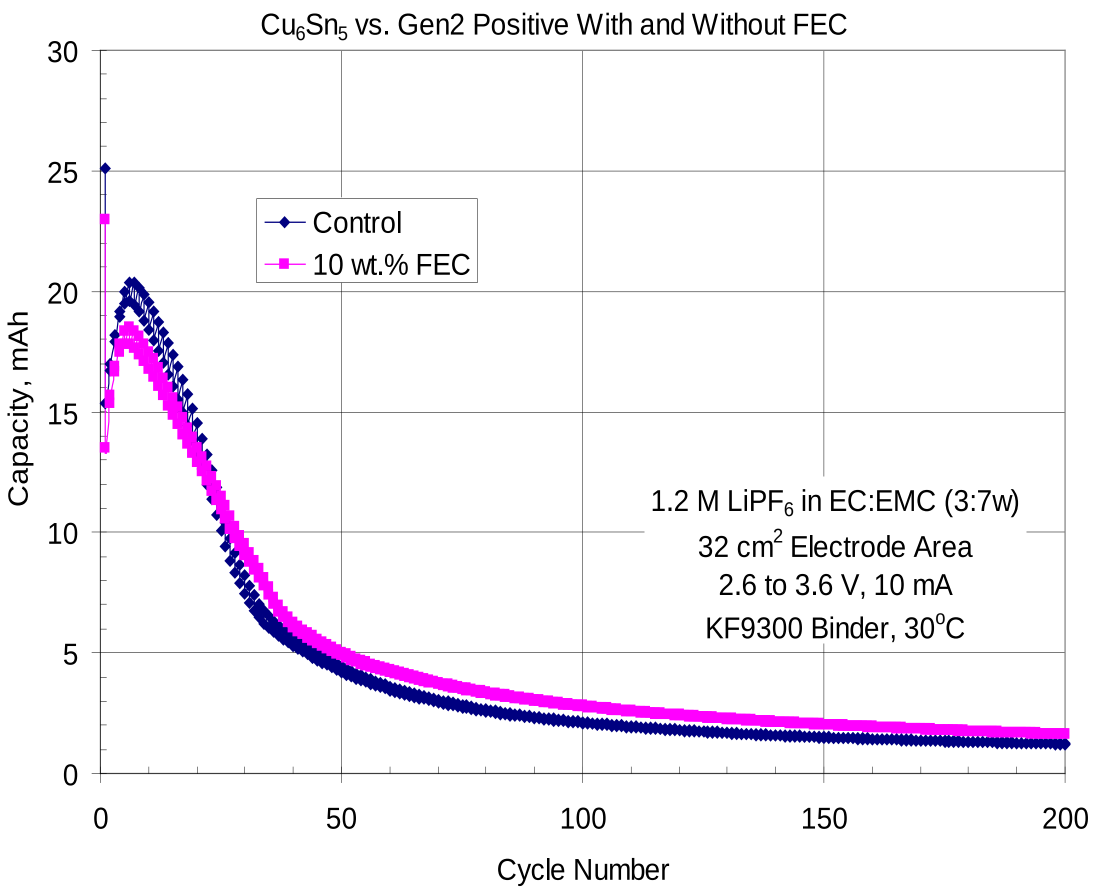
Approach

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

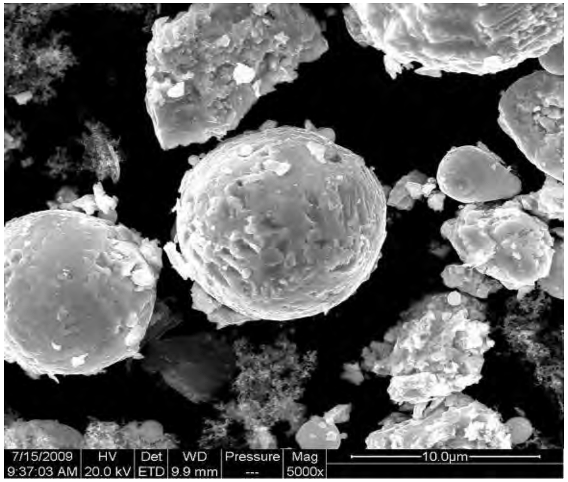
- Success will be achieved upon development of an electrode that can accommodate the large volume expansion and contraction during deep discharge cycling, and can prevent the excluded metal (such as copper) from agglomerating during cycling.

- 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.

Electrolyte Additive (FEC) Not Enough in This Case



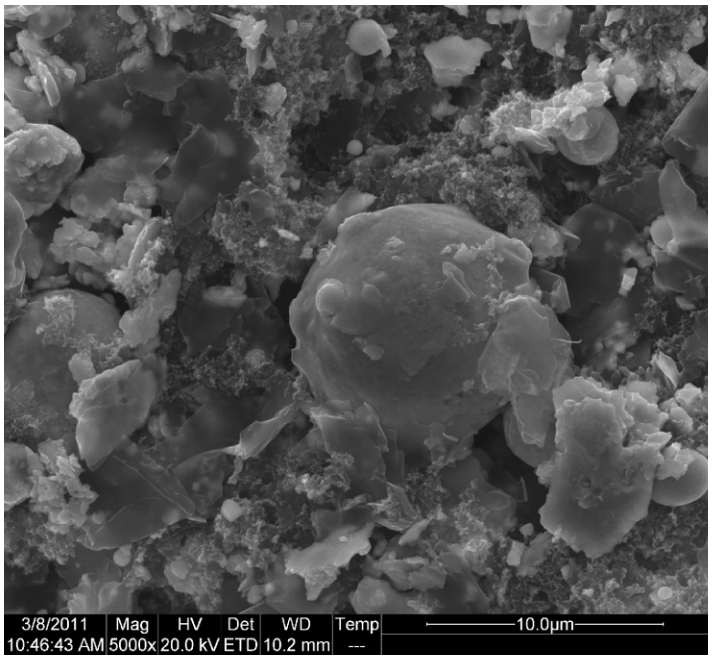
- FEC was shown to be effective in other intermetallic efforts at Argonne, but not for this particular Cu_6Sn_5 morphology or size.
- Open cell for diagnostic study



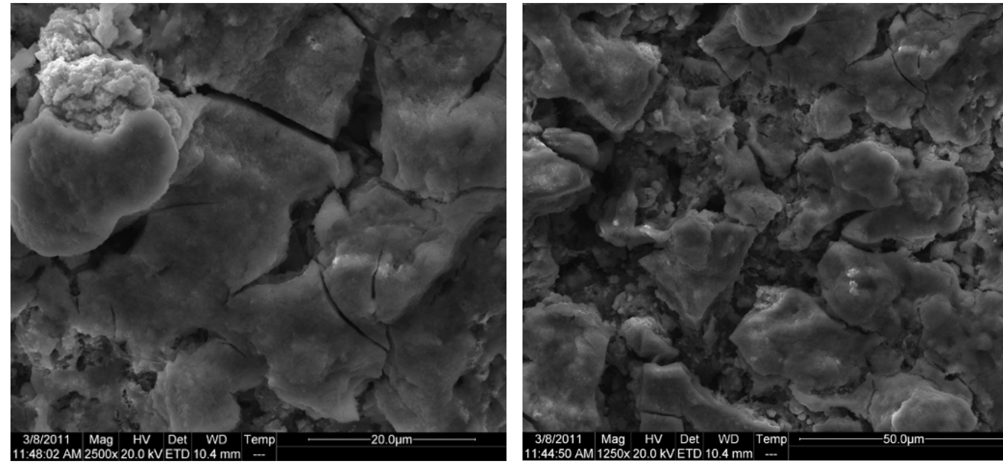
Cu_6Sn_5 powder with AB carbon and SFG-6 graphite.

Particle/Film Cracking Observed on Large Particles

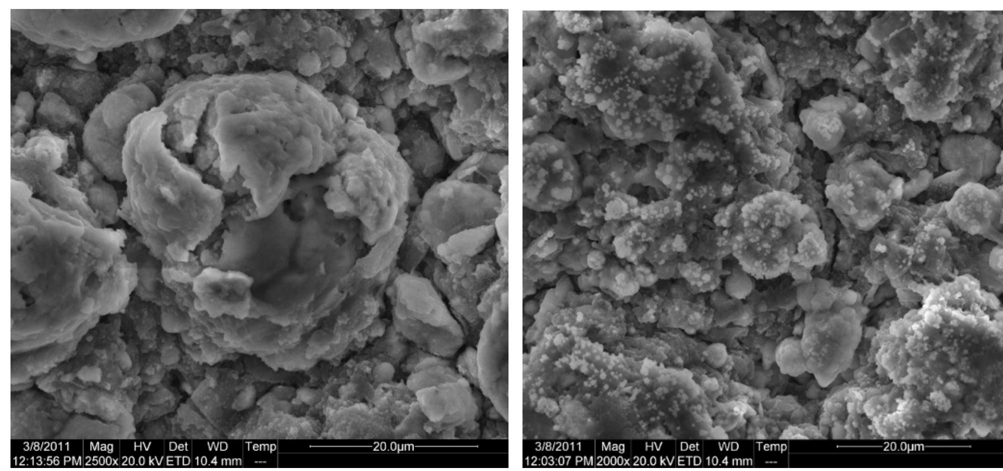
Note the relatively larger film covering the electrode and the large cracks on its surface. These film sheets are over twice as large as the original particle.



Fresh electrode of Cu_6Sn_5 with AB carbon and SFG-6 graphite.



Harvested baseline electrode after washing with DMC/DEC.

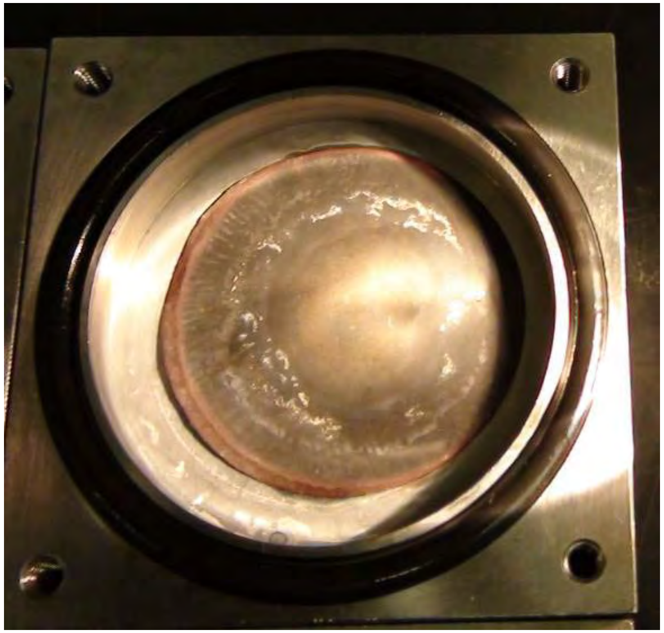


Harvested electrode (FEC) after washing with DMC/DEC. FEC has a strong influence on surface morphology.

Copper Deposits Seen after Cycling on These Electrodes

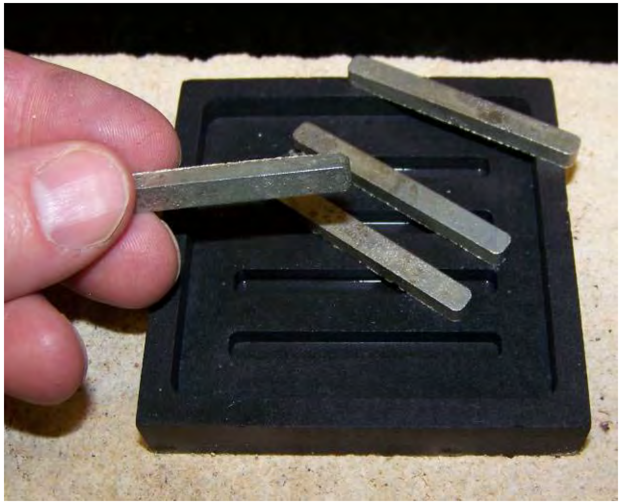
- Copper color observed on electrodes after cycling indicate that copper displacement is a problem. Remains to be seen if it exists for smaller particle sizes
- Copper foil appears unaffected underneath
- See if this problem exists with smaller particles from Wildcat Discovery Technologies

Baseline



10% FEC

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)	Biaxial Modulus (GPa)	Fracture Toughness (MPa $m^{0.5}$)
Cu_6Sn_5	71±18	54±12	2.19±0.54
$NiCu_5Sn_5$	44.4±2.7	79.1±4.1	1.32±0.13
$ZnCu_5Sn_5$	104.2±3.1	55.3±4.4	2.56±0.23
$FeCu_5Sn_5$	88.0±6.5	74.3±2.8	2.38±0.15
Cu_5Sn_6	73.9±2.7	54.0±7.8	2.56±0.40
$Li_5Cu_6Sn_5$	23.7±9.3	54±19	0.95±0.39

Lithiation lowers the fracture toughness and strength, but does not affect the modulus.

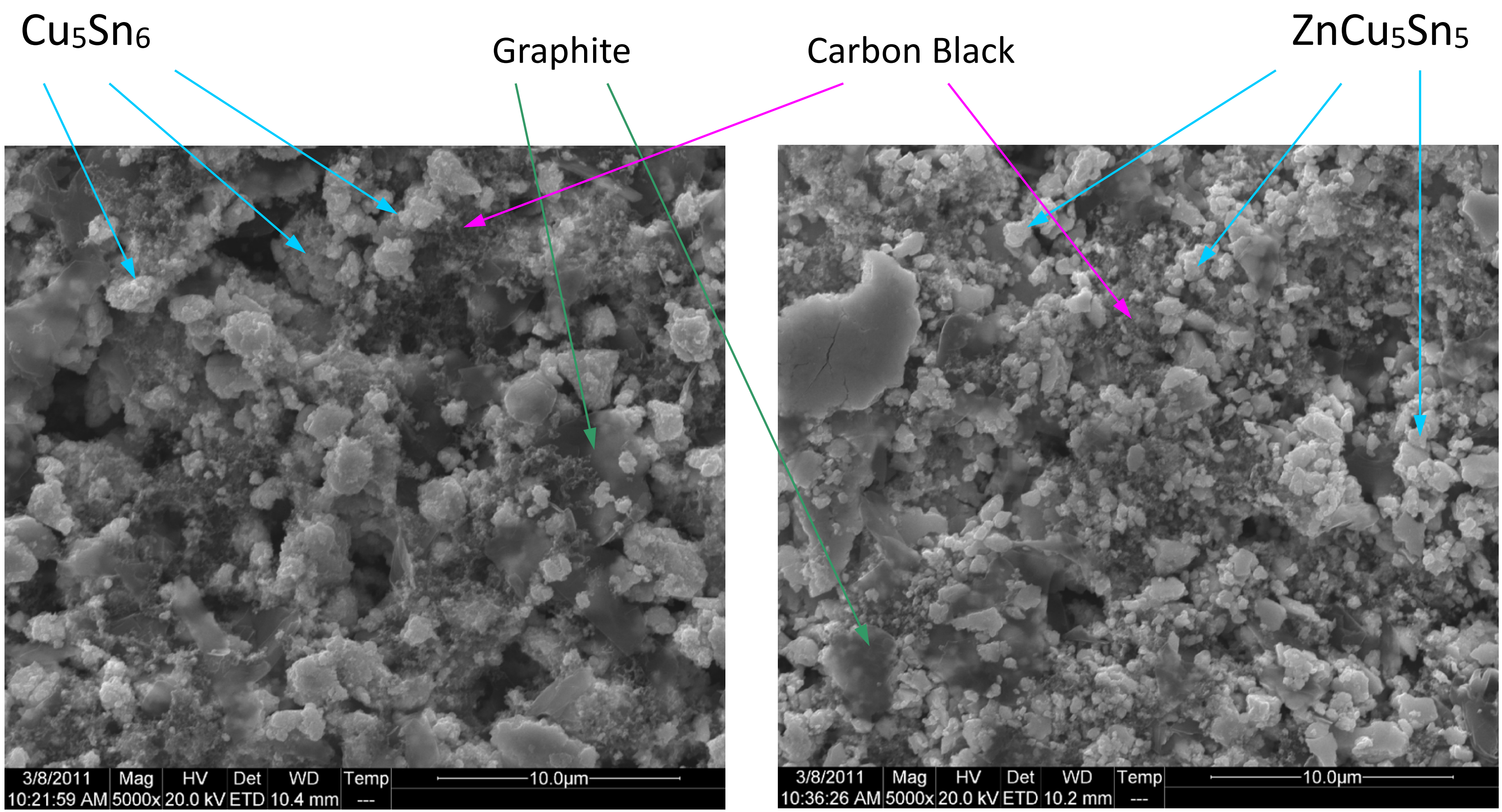
Strength: four-point bend test
Elastic modulus: four-point bend test
Fracture toughness: notched samples tested in 3-point bend

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	0.27	257	0.033	507
$NiCu_5Sn_5$	0.046	258	0.0057	510
$ZnCu_5Sn_5$	0.36	256	0.044	507
$FeCu_5Sn_5$	0.17	259	0.021	511
Cu_5Sn_6	0.37	~244	0.046	566
$Li_5Cu_6Sn_5$	0.051	-	0.0063	-

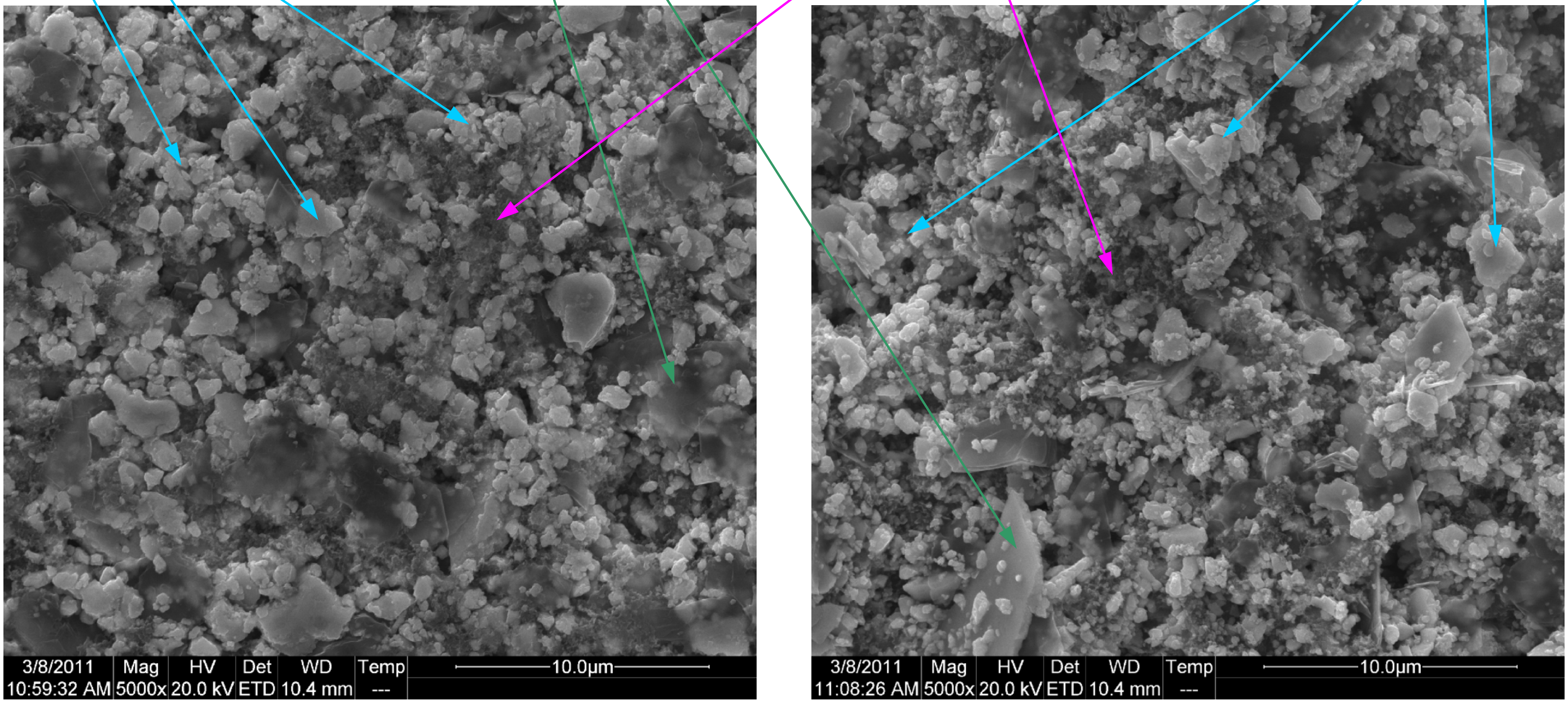
Critical particle size based on Huggins' decrepitation model (*Ionics* 6 (2000) p. 57-63).

Calendered Electrodes Made with Alloys Synthesized by Wildcat Discovery Technologies

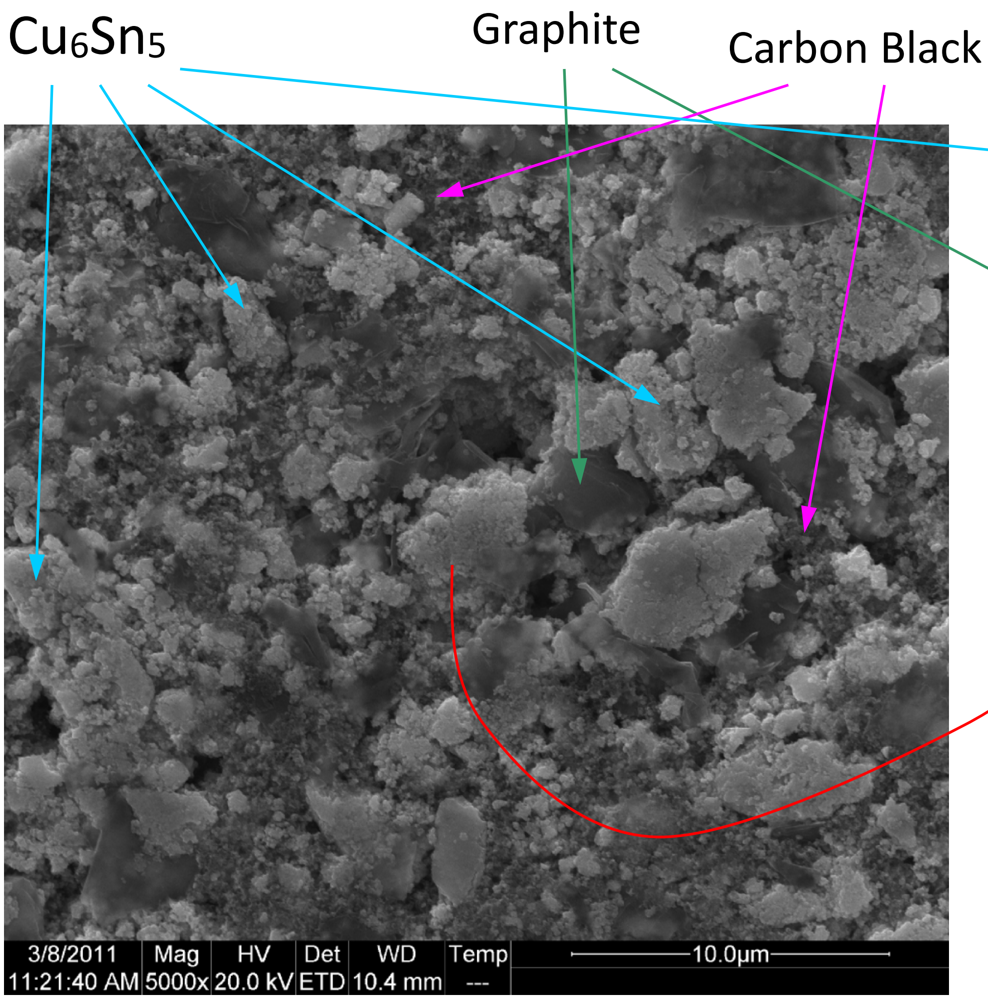


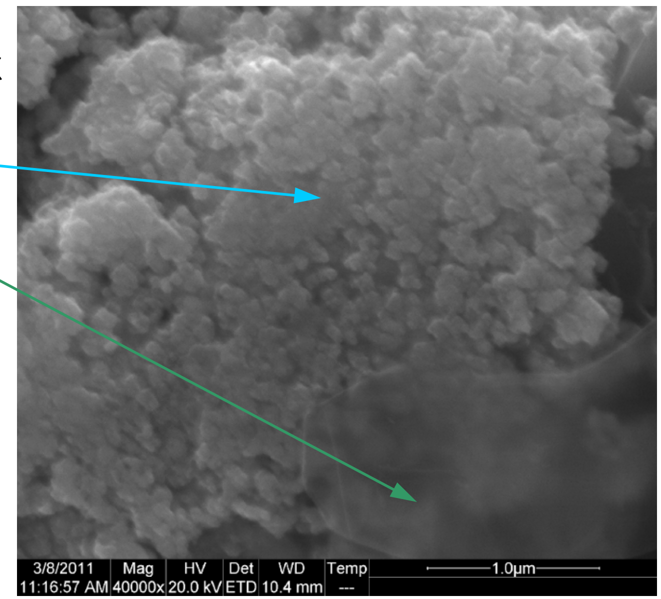
Calendered Electrodes Made with Alloys Synthesized by Wildcat Discovery Technologies

$FeCu_5Sn_5$ Graphite Carbon Black $NiCu_5Sn_5$



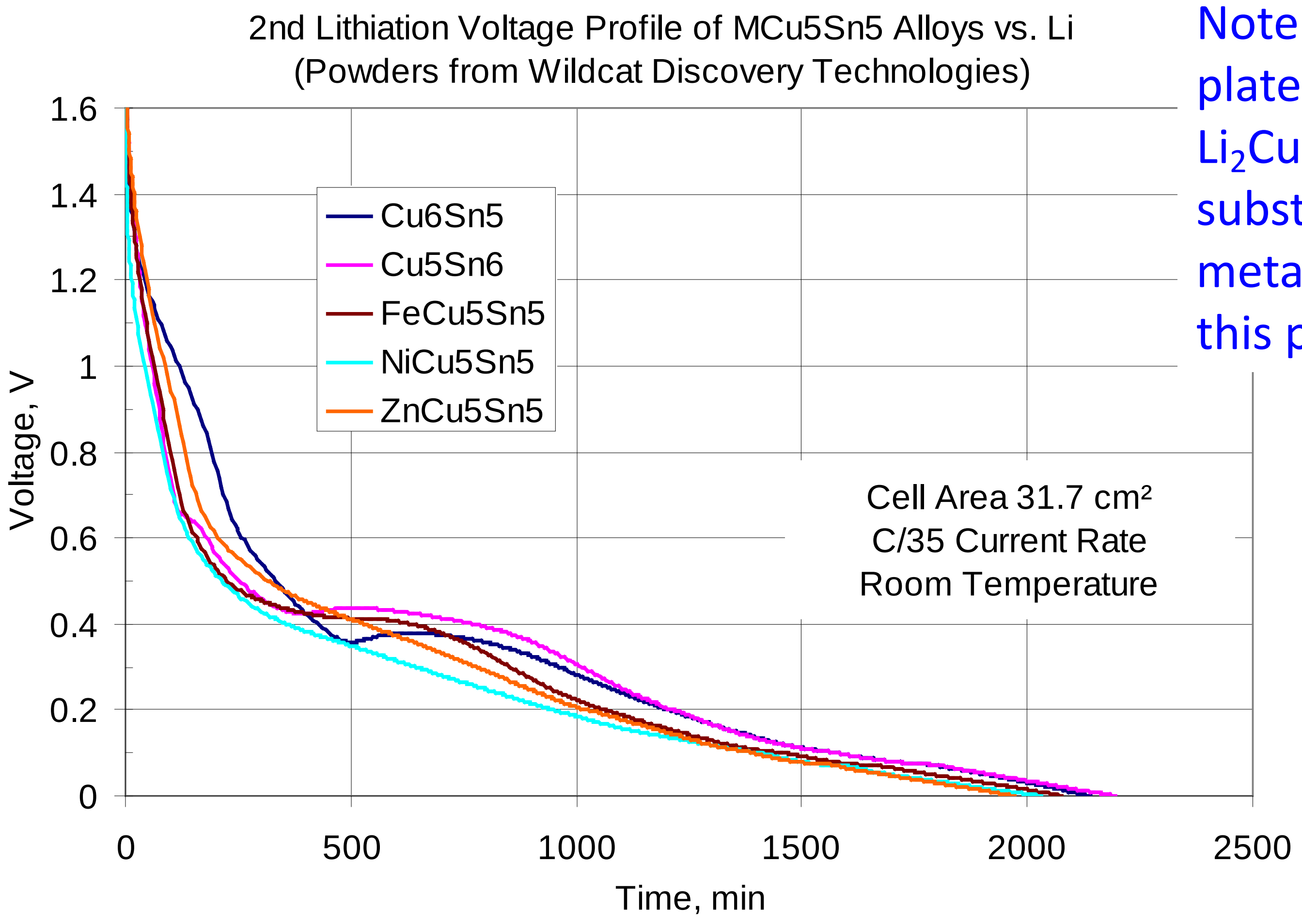
Calendered Electrodes Made with Alloys Synthesized by Wildcat Discovery Technologies





Additional, more energetic, processing steps are required to break these large secondary particles into primary particles

Some Differences in Voltage Profile



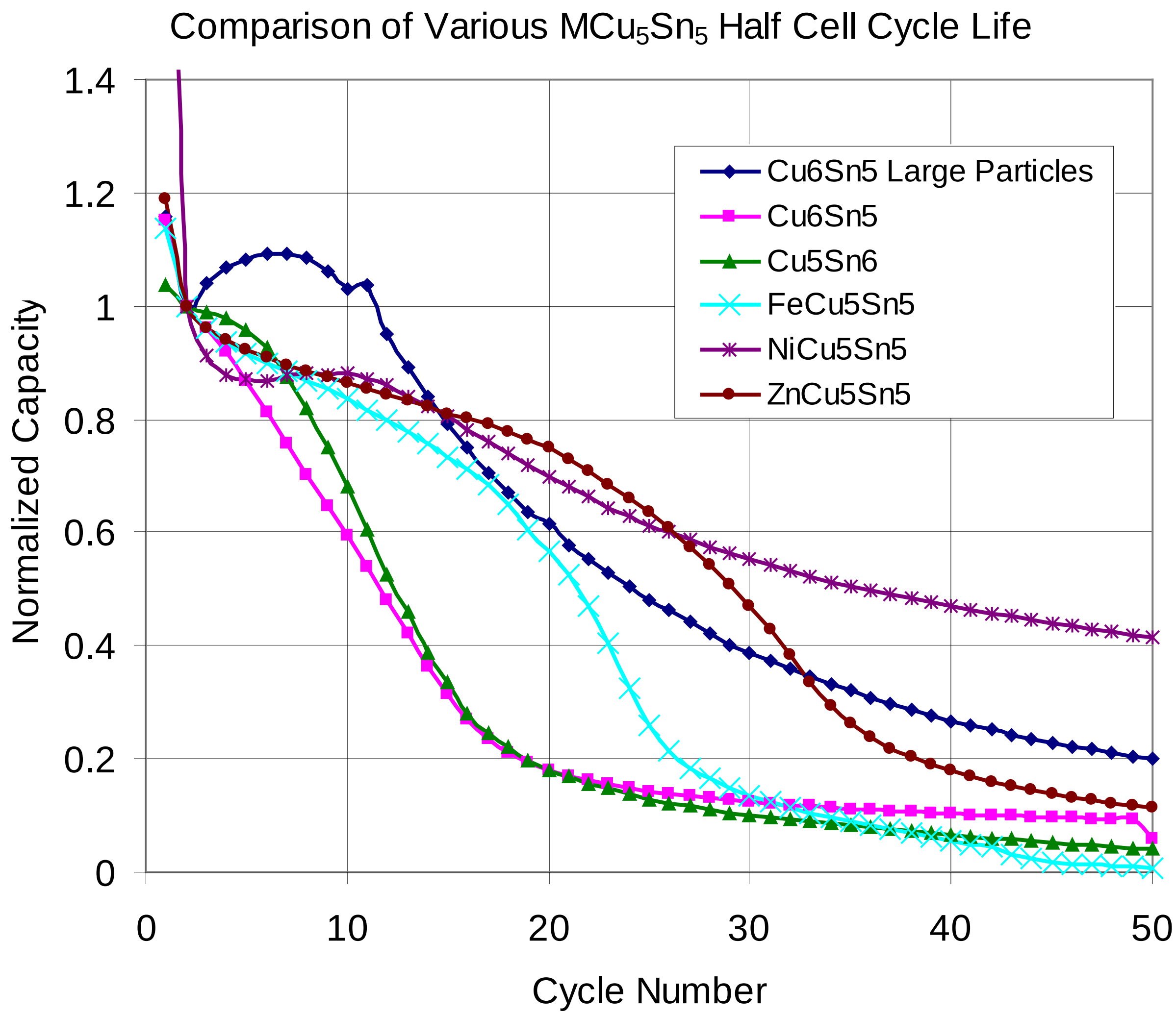
Note the lack of the 0.4 volt plateau corresponding to Li_2CuSn for the Ni and Zn substituted alloys. These metals may interfere with this phase formation.

All of the MCu_5Sn_5 Electrodes Have a High Capacity Density Compared to Graphite

Anode	Tap Density g/mL	2nd Delithiation Capacity of Alloy, mAh/g	Electrode Capacity Density mAh/cm^3
Cu_6Sn_5	2.05	472	544
$NiCu_5Sn_5$	2.90	434	513
$ZnCu_5Sn_5$	2.48	488	704
$FeCu_5Sn_5$	2.46	514	757
Cu_5Sn_6	2.51	557	816
Graphite	0.8 - 1.1	340	440

Efforts will be concentrated on these two alloys

Smaller Particle Size Did Not Improve Cycle Life



Possible reasons include:

- larger surface area (higher activity) of the smaller particles
- breakup of the secondary particles
- copper displacement
- insufficient binder
- insufficient carbon filler

Collaborations

- Wildcat Discovery Technologies proved to be of great assistance in synthesizing these small particle alloys for this task
- Dileep Singh and Kristen Pappacena of Argonne (NE Division) provided guidance in designing test bars for mechanical testing and conducted the measurements to determine the strength, toughness, and modulus
- Updates were routinely provided by several BATT colleagues regarding the latest new materials that are nearing readiness for engineering study
- Several discussions were held with binder vendors (Solvay Solexis and Kureha) regarding their material properties and applications
- The electron microscopy was accomplished at the Electron Microscopy Center for Materials Research at Argonne

Summary

- Concluded the study of critical particle size based on Huggins' decrepitation model by mechanically testing alloy casts of lithiated copper-tin
  - Results indicate that even smaller particle sizes are required upon lithiation
- Initiated testing of $M_yCu_5Sn_5$ alloys with <0.5 μm particle size from Wildcat Discovery Technologies for M = Cu, Ni, Zn, Fe, and Sn
  - High mass and volume capacity density was achieved for these alloys
  - Additional processing is needed to solve short cycle life problem
- Diagnostic investigation of Cu_6Sn_5 cell with large particle size shows evidence of cracks in large surface film and copper displacement
- Energy density of $M_yCu_5Sn_5$ electrodes are significantly higher than graphite electrodes, which warrants further consideration

Future Work

- Focus efforts on enhancing cycle life of $FeCu_5Sn_5$ and Cu_5Sn_6 by
  - Using high energy ball milling to breakup secondary particles
  - Increase binder and carbon black content
  - Revisit the influence of elastic binders, including cellulose & polyimides
- Explore increased content of Sn in alloy with Wildcat Discovery Technologies to see effects on copper displacement/retention
- Initiate electrolyte additive study to enhance SEI formation
- Consider engineering electrodes and cells using new materials from the BATT Program that show promise of outperforming graphite regarding cost and energy density
  - Conversion metal oxides like Fe_2O_3 and Li_5FeO_4
- Explore graphene-Sn composite electrode using CVD to determine upper limit of technical feasibility for Sn systems (see back-up slide)

Contributors and Acknowledgments

- Wenquan Lu (Argonne)
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- Dileep Singh (Argonne-NE)
- Junbing Yang (Argonne)
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  - Jon Jacobs

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- Kureha

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Technical Back-Up Slides

The following slides are for the use of the Peer Reviewers and general public. They may be presented as part of the oral presentation. These additional slides will be included in the copy of the presentation that will be made available to the Reviewers and the general public.

Sn-Graphene Nano-composites through Chemical Vapor Deposition

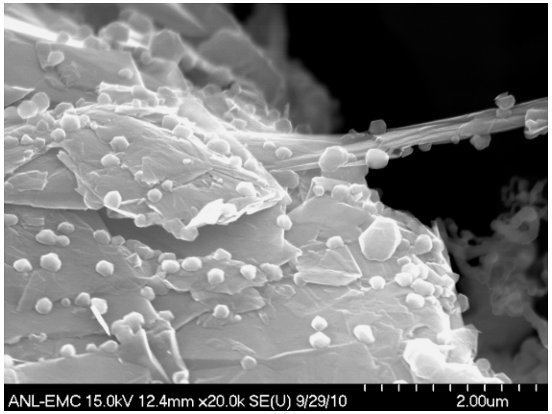
- Achieve nanoscale deposition of Sn particles on, or in between, graphene sheets through chemical vapor deposition (CVD) process

- Work Plan
  - Graphene synthesis through modified Hummel procedure with focus on structure control and cost reduction
  - Incorporation Sn nanoparticles on, or in between, graphene sheets through CVD process

- Argonne has all the equipment for the proposed work in place already

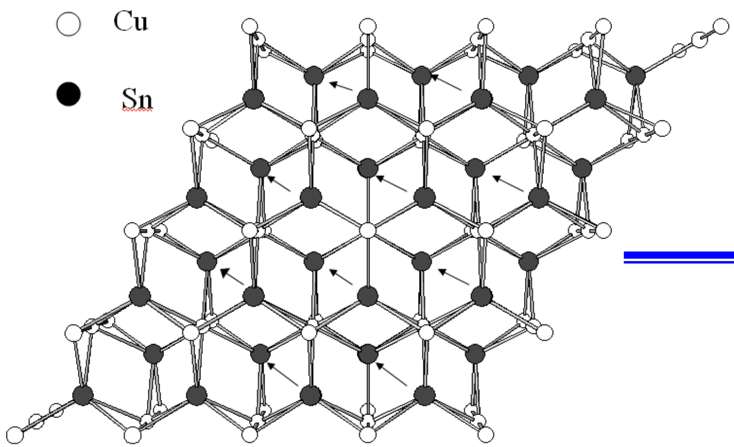
- Candidate Sn precursors for the CVD process:

  monobutyltin trichloride (MBTC), tin tetrachloride (TTC) monomethyltin trichloride (MMTC), dimethyltin dichloride (DMTC), trimethyltin chloride (TMTC), and tetramethyltin (TMT), Tetraphenyltin et al.



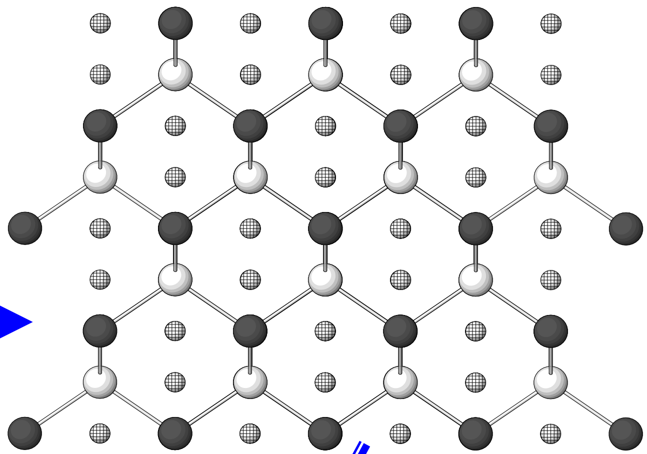
Si-Graphene nano-composites synthesized at CSE (J. Yang)

Significant Lattice Changes Occur Upon Lithiation



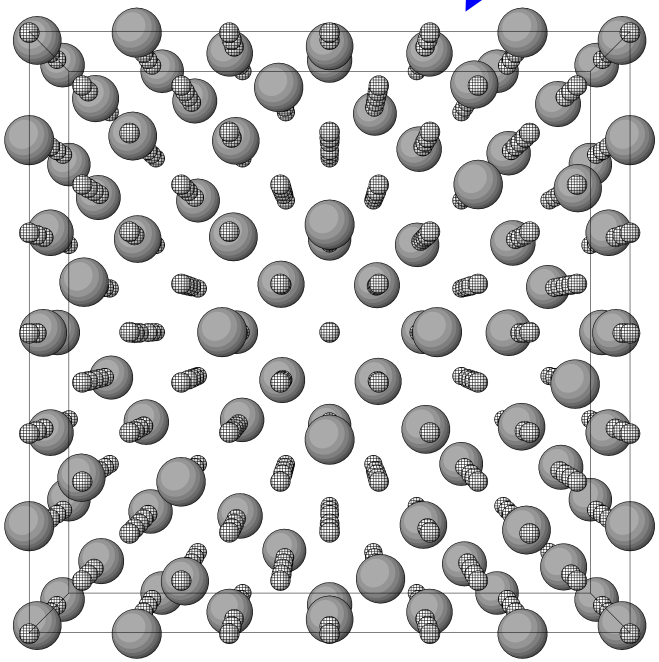
Cu_6Sn_5

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

Volume Expansion Is a Concern

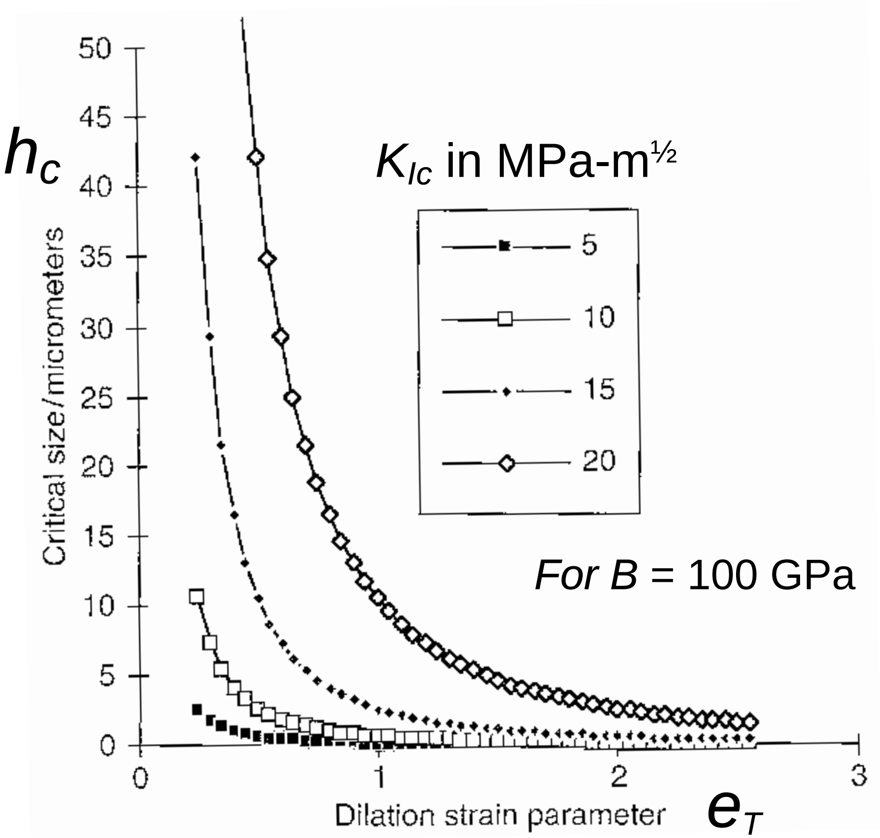
- Full lithiation of Cu_6Sn_5 may not be practical due to the large volume change.
  - Can this volume fluctuation be designed into the particle and/or electrode?

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

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

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

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 ($\Delta V/V$)