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Intermetallic Anodes

presented by

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Overview

Timeline

- Start date: FY08
- End date: On-going
- Percent complete:
  - $LaSn_3$ project, 100%
  - Remainder on-going

Budget

- Total project funding
  - 100% DOE
- FY08: $300K
- FY09: $300K
- FY10: $400K

Barriers

- Barriers addressed:
  - Low energy
  - poor low temperature operation
  - abuse tolerance limitations

Partners

- Co-investigators:
  - J. Vaughey, L. Trahey, V. Pol
- Collaborators:
  - C. Wolverton, D. Shin (NU)
  - K. Edstrom (Uppsala Univ.)
  - Primet Precision Materials

Objectives

- Design high capacity metal, semi-metal or intermetallic anodes that will provide electrochemical couples to meet the 40-mile range requirement of PHEVs
  - *Improve the design and performance of tin-based intermetallic electrodes*
  - *Use theoretical modeling as a guide to identify, design and understand the electrochemical properties of novel intermetallic electrode systems*
  - *Initiate studies of Si-based electrodes*

Milestones (FY08-09)

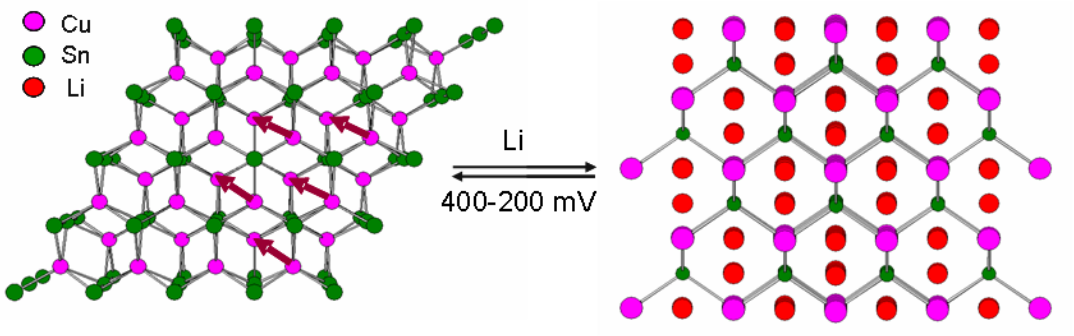
- Synthesize, design and characterize Sn- and Si-based electrode materials and architectures – *on going*
- Determine electrochemical properties in lithium half cells and full cells – *on going*
- Investigate SEI layers – *on going with Uppsala University (data collected)*
- Model and predict the structural and electrochemical behavior of intermetallic electrodes – *on going*

Approach

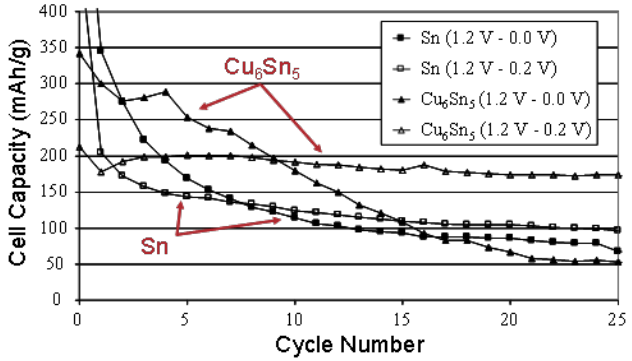
- Search for, and design, inexpensive intermetallic electrode materials that provide an electrochemical potential several hundred mV above Li^0, notably Sn-based materials, and a capacity of at least 400 mAh/g.
  - *use high surface area copper foam current collectors and electrodeposited Cu_6Sn_5 and Sn*
- Focus on compounds in which there is a strong structural relationship between the parent and product to minimize lithium diffusion distances.
- Use computational modeling to aid the design of electrode structures and understanding of electrochemical properties
  - *e.g., $LaSn_3$ that has a high Sn content.*

Cu_6Sn_5 (Recap)

Cu_6Sn_5 to Li_2CuSn transition



Electrochemistry: Cu_6Sn_5 vs. Sn

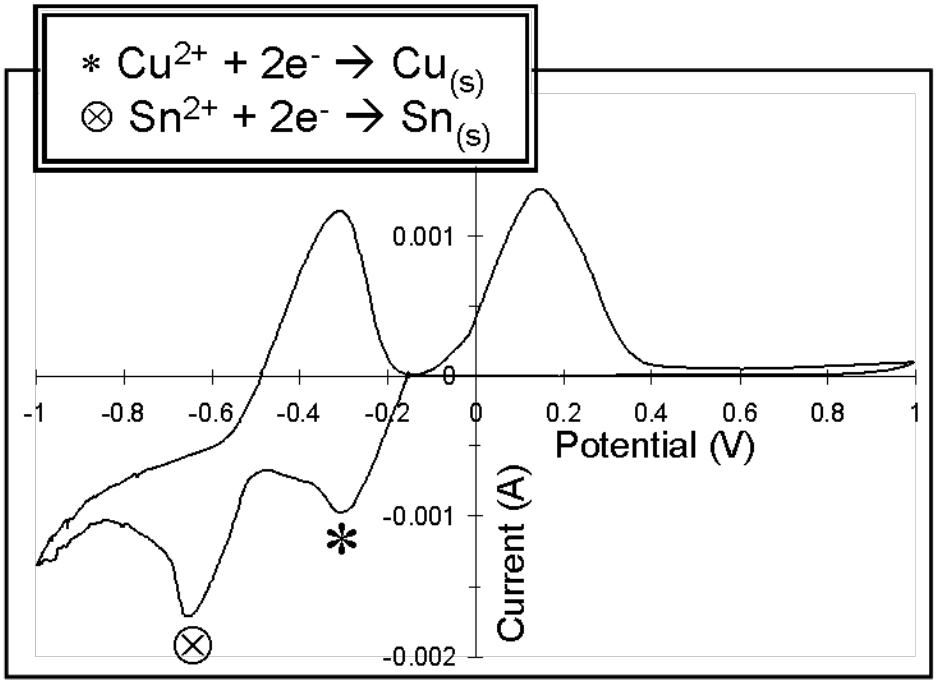


$$21.25\ Li + Cu_6Sn_5 \rightarrow 5\ Li_{2+x}Cu_{1-x}Sn + (1+5x)\ Cu \rightarrow 6\ Cu + 5\ Li_{4.25}Sn$$

- Strong structural relationship between Cu_6Sn_5, Li_2CuSn and "Li_3Sn" (x=1) exists.
- Li insertion/Cu displacement reaction: Th. Cap. ≈600 mAh/g; Pr. Cap. ≈200 mAh/g
- Mimics Na/$NiCl_2$ reaction (100% efficient): $2\ Na + NiCl_2 \rightarrow 2\ NaCl + Ni$.
  - Cells assembled in discharged state; NaCl powder in porous Ni substrate.
- Volume expansion problem.

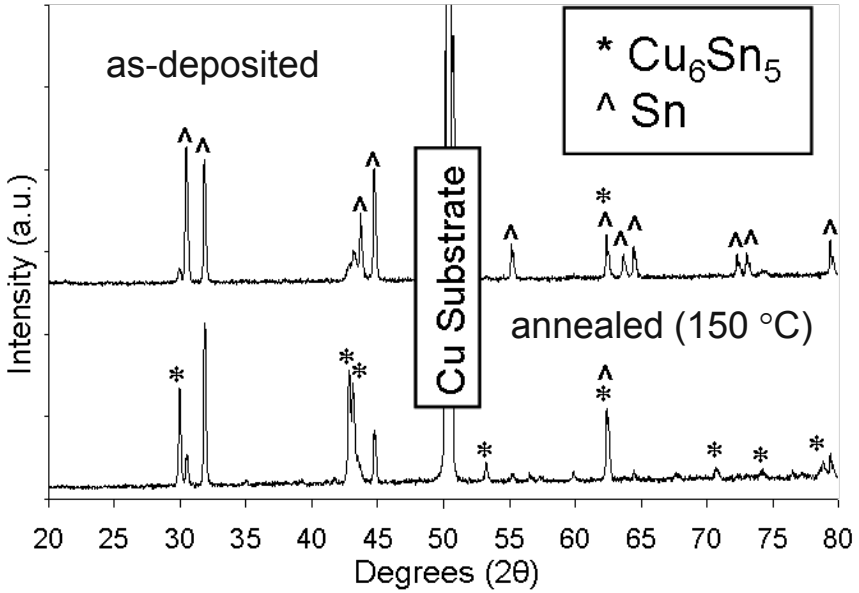
New approach to electrode design and current collection is required

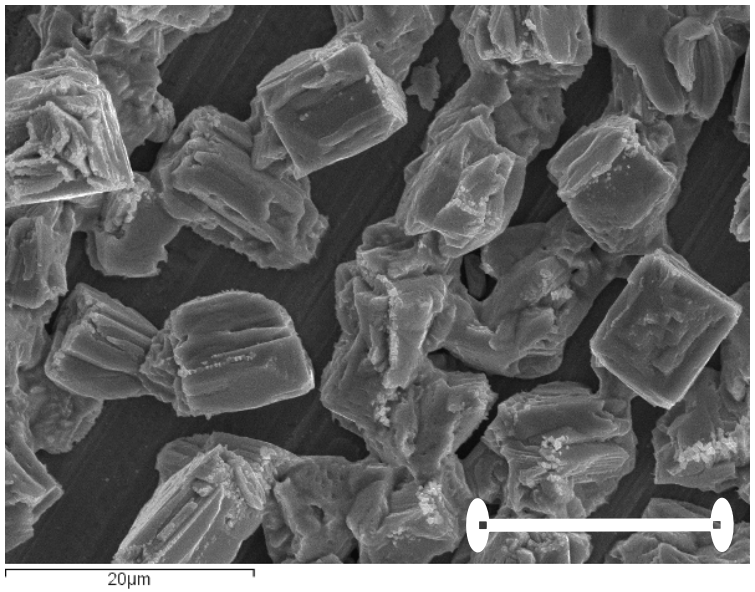
Cu_6Sn_5/Sn Fabrication by Electrodeposition



- 0.002 M $CuCl_2$ and 0.2 M $SnCl_2$ in HCl solutions used.
- Control of Cu and Sn concentrations critically important to fabricate Cu_6Sn_5.
- Cu_6Sn_5 and Sn deposited at -600 mV vs. SCE reference electrode (pulsed).
- <500 mV produces Cu_4Sn; >-600 mV produces dendritic structures.

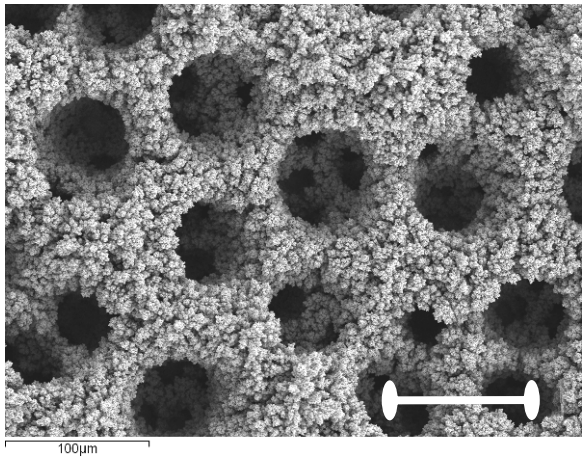
XRD patterns and SEM images



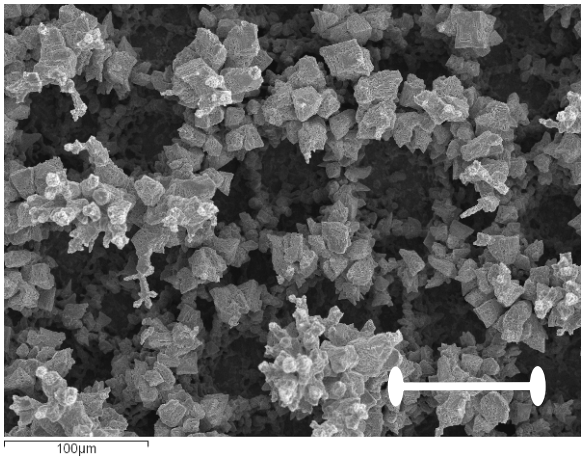


- XRD pattern of as-deposited product shows predominantly Sn, trace Cu_6Sn_5.
- XRD pattern of annealed product reveals Cu_6Sn_5 and Sn.
- EDS analysis shows average composition of product as being ~90 at.% Sn and ~10 at% Cu.

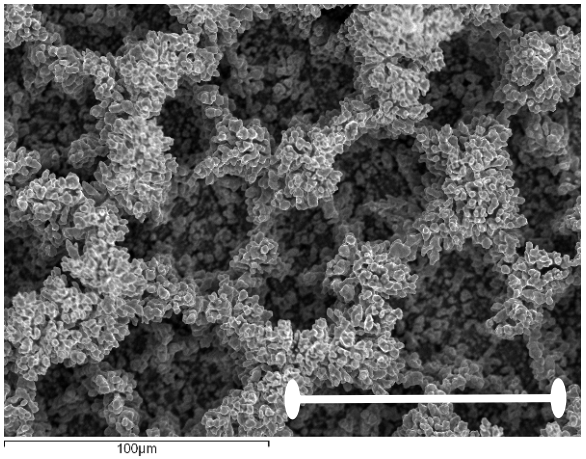
Electrodeposited Cu_6Sn_5/Sn on Cu Foam Electrodes



1. As-deposited Cu foam



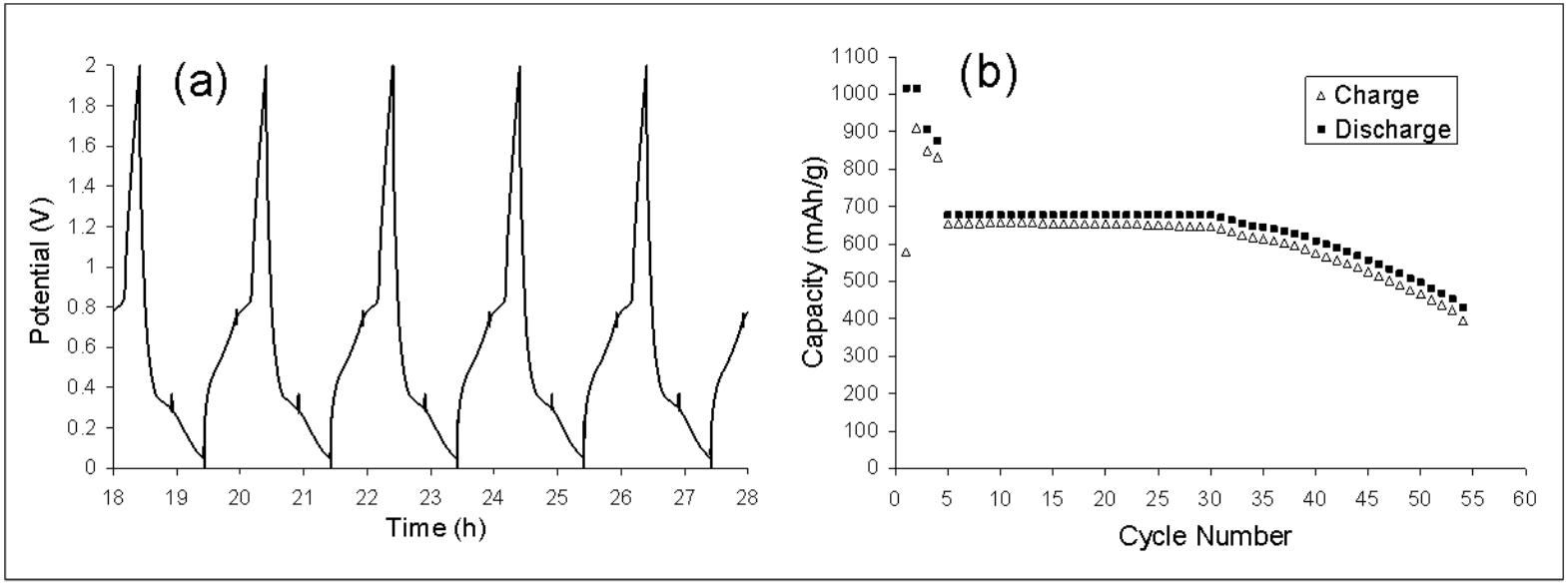
2. Annealed Cu foam (500 °C)



3. Cu_6Sn_5/Sn on Cu foam

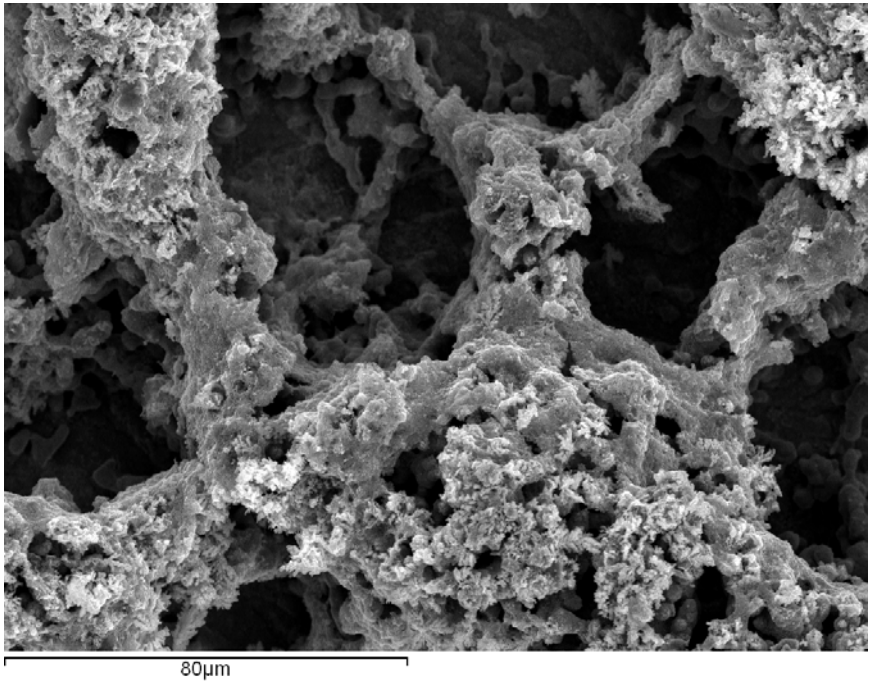
- 1. As-deposited Cu-foam is brittle and powdery.
- 2. Annealing at 500 °C strengthens Cu-foam to Cu foil contact, providing a sufficiently robust substrate for electrodeposition of Cu and Sn. Overall porosity maintained.
- 3. Morphology maintained after Cu_6Sn_5/Sn pulsed electrodeposition at -600mV vs. SCE. Sn concentration varies from ~20% within the porous electrode to ~90% at outermost surfaces.

Electrochemistry: Cu_6Sn_5/Sn on Cu Foam Electrodes



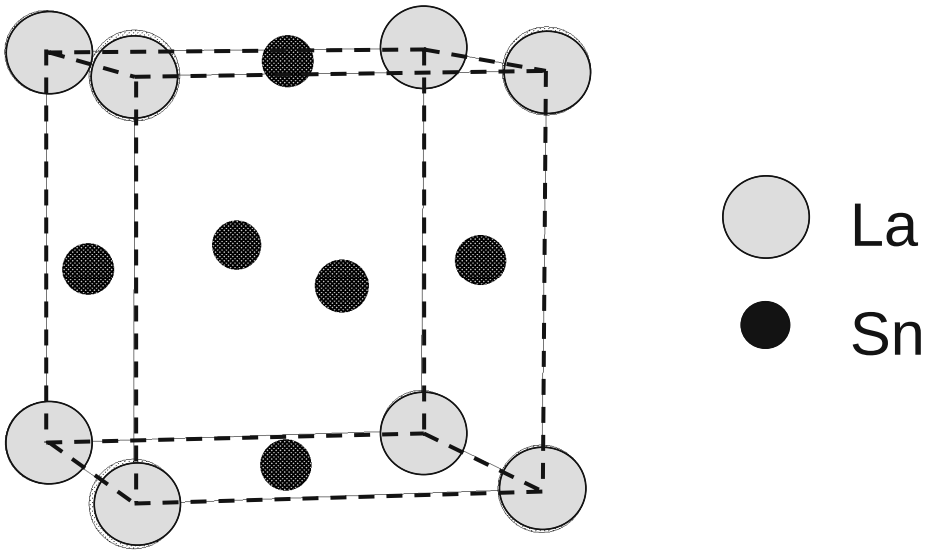
- Significant improvement in reversible capacity achieved (650 mAh/g vs. 200 mAh/g for ball-milled Cu_6Sn_5 samples).
- Results suggest excellent cycling of Sn within a copper-tin matrix electrode.
- Large irreversible capacity drop during early cycles attributed to electrolyte reactions with high surface area electrode to form passivation layer.
- Abrupt onset of capacity fade after 30 cycles unknown - Li electrode or Cu_6Sn_5/Sn electrode?

SEM Image of Cycled Cu_6Sn_5/Sn/Cu Electrode



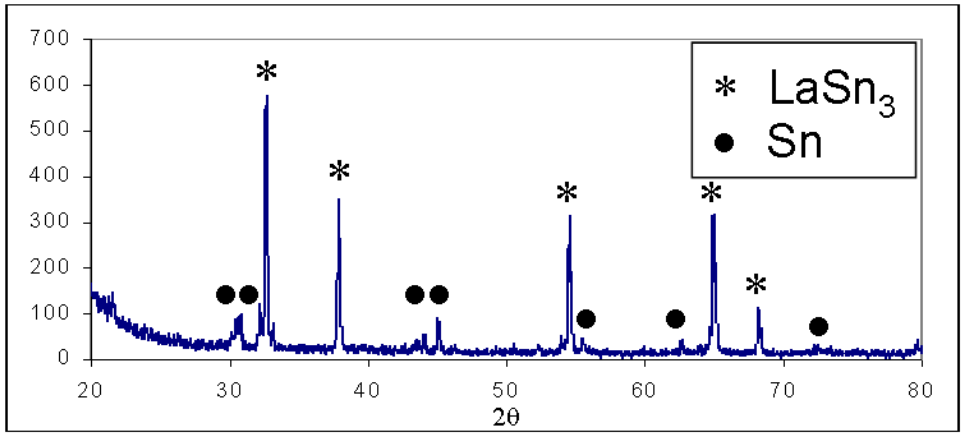
- Cu-foam network still intact.
- Rounded morphology evident of repeated electrochemical deposition and stripping.
- Analogous to porous Ni current collector in high-temperature Na/$NiCl_2$ cells.

A Search for New Materials: $LaSn_3$ Electrodes (Recap)

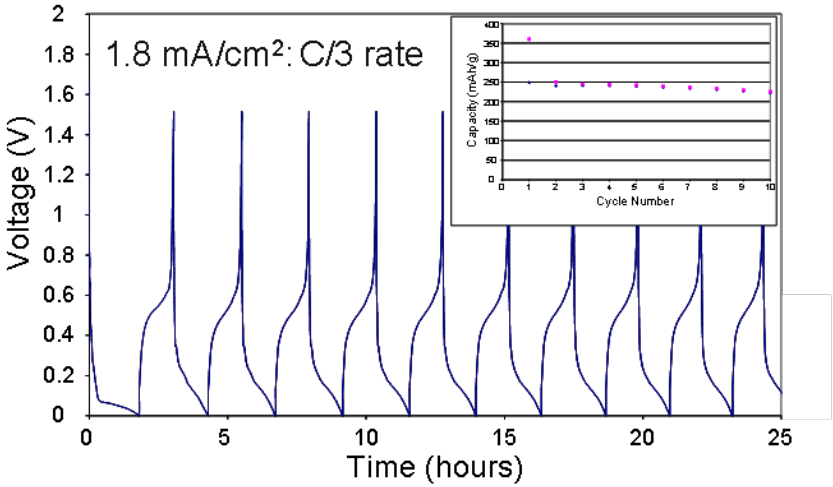


- Sn-rich, defect perovskite-type structure
- Theoretical capacity: 650 mAh/g or 4920 mAh/ml (ρ_{LaSn3} = 7.57 g/ml)
- 12 interstitial (octahedral, tetrahedral and edge-shared) sites
  - 1 Li + $LaSn_3$ → $LiLaSn_3$ (54 mAh/g)
  - 12 Li + $LaSn_3$ → $Li_{12}LaSn_3$ (hypothetical reaction – 650 mAh/g)
  - 12.75 Li + $LaSn_3$ → La + 3 $Li_{4.25}Sn$ (690 mAh/g)

Cycling Profile of a Li/$LaSn_3$ Cell (Recap)

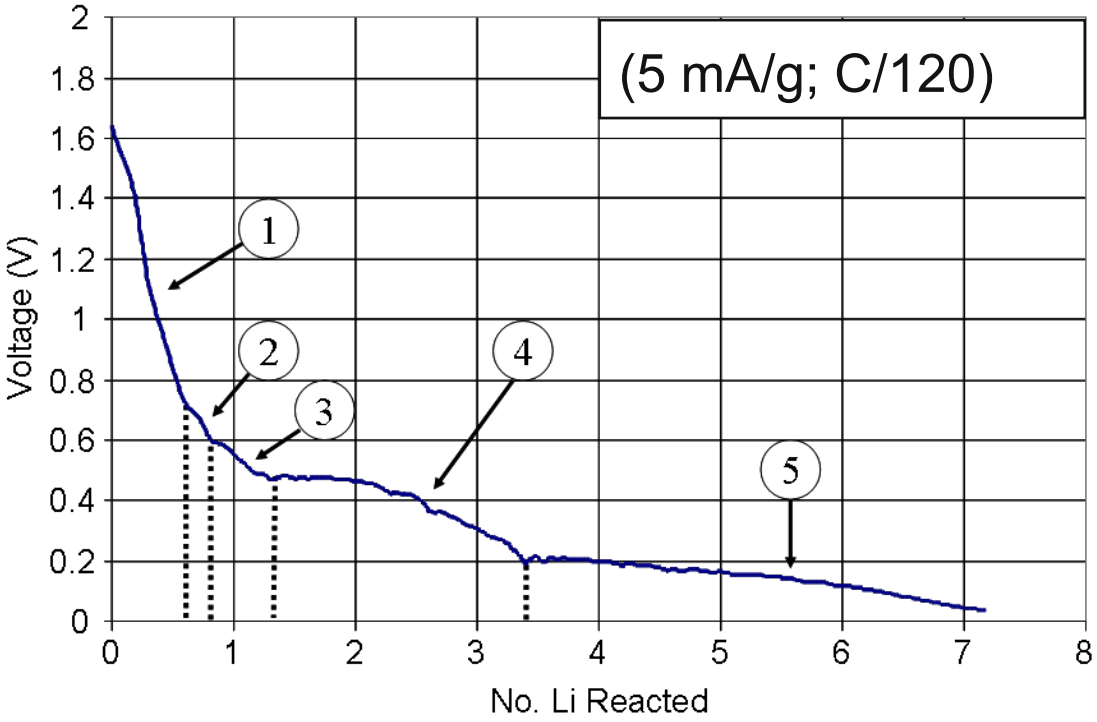


XRD patterns of ball-milled $LaSn_3$ samples consistently show ~10 % free Sn



- Initial capacity ~360 mAh/g
- Reversible 250-225 mAh/g (~4.5 Li)
- 35-38% of theoretical value (650 mAh/g)
- 1st cycle irreversible capacity loss, ~30%
- Insertion or displacement reaction?
- Maximum practical capacity?

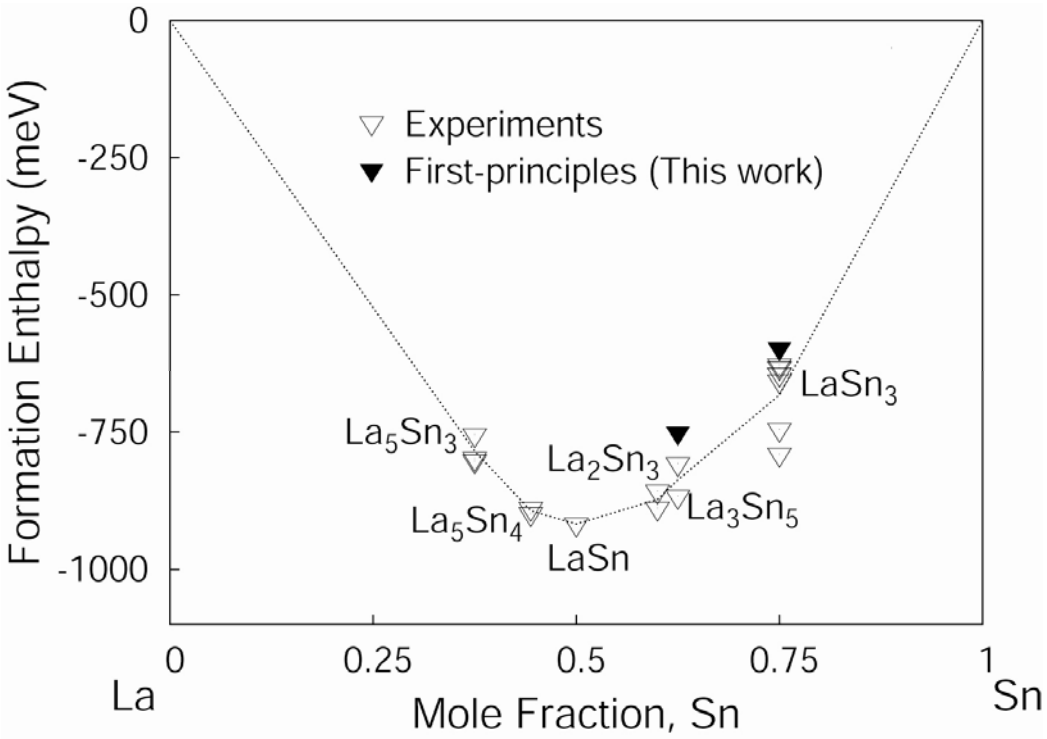
Li/$LaSn_3$ Cell: Slow Electrochemical Titration



1. Electrolyte reactions (SEI formation)
2. Sn → Li_2Sn_5
3. Sn → LiSn
4. $LaSn_3$ + Sn
5. $LaSn_3$ + Sn

- $LaSn_3$ + Sn capacity at C/120 (~320 mAh/g), corresponding to regions 2 to 5 in plot is equivalent to that delivered during the initial reaction at C/3: ⇒ La_3Sn_5 formation?
- Li cycles with Sn in an 'inert' La_3Sn_5 matrix?

Formation Enthalpies of La-Sn Compounds



- Experiment suggests that LaSn is the most thermodynamically stable.
- Only $LaSn_3$, La_3Sn_5, La_5Sn_4 and La_5Sn_3 have been prepared as single crystals, not La_2Sn_3 and LaSn (ICSD database).
- Theoretical values for $LaSn_3$ and La_3Sn_5 consistent with experiment.

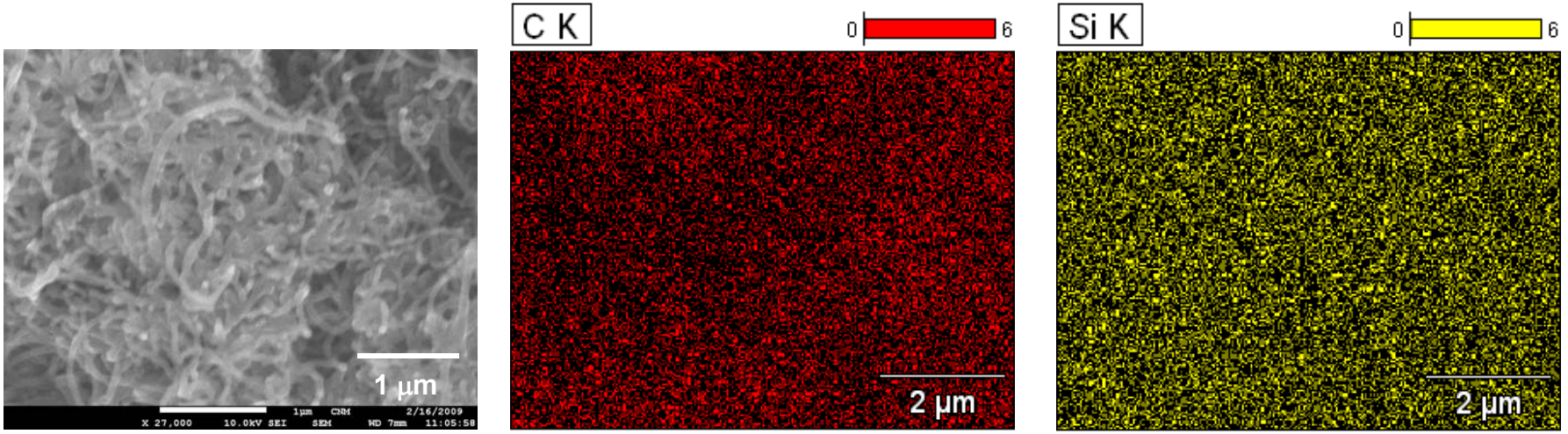
Formation Enthalpies and $LaSn_3$ Capacities for Competing Reactions

Reaction type	Reactions		Theor. Cap. (mAh/g)	ΔH (meV/Li)
Insertion	$Li + LaSn_3 \rightarrow LiLaSn_3$	(1)	54	864
	$12\ Li + LaSn_3 \rightarrow Li_{12}LaSn_3$	(2)	650	3232
Displacement	$66\ Li + 5\ LaSn_3 \rightarrow 5\ La + 3\ Li_{22}Sn_5$	(3)	715	-252
	$51\ Li + 4\ LaSn_3 \rightarrow 4\ La + 3\ Li_{17}Sn_4$	(4)	690	-275
	$88\ Li + 15\ LaSn_3 \rightarrow 5\ La_3Sn_5 + 4\ Li_{22}Sn_5$	(5)	318	-368
	$17\ Li + 3\ LaSn_3 \rightarrow La_3Sn_5 + Li_{17}Sn_4$	(6)	307	-395

- Theory predicts that La_3Sn_5 formation is more favorable than La.
- Theory confirms recent experiment that $Li_{17}Sn_4$ ($Li_{4.25}Sn$) reflects the maximum uptake of Li by Sn, not previously reported $Li_{22}Sn_5$ ($Li_{4.40}Sn$).

Nano-particulate Si-C Electrodes (New)

- Novel processing technique is currently being evaluated to prepare nano-particulate single-phase- and composite anode and cathode materials.
- Initial studies have focused on nano-particulate Si-C materials.
- Use C nanotubes as interconnected electronically conducting substrate



SEM and elemental mapping of Si deposited on C nanotubes

- Promising start – to be continued in FY2010.

Future Work - FY2009/FY2010

- Continue studies of electrodeposited Cu_6Sn_5 on metal foam substrates. Promising results from initial studies bode well for improvement – both in electrode design and performance.
- Extend studies to other Sn-based intermetallic systems.
- Continue studies of nanoparticulate Si-C composite electrodes via novel proprietary processing technique.
- R&D motivated by need to find an alternative anode to graphite having a sufficiently high gravimetric and volumetric capacity to meet the battery requirements for 40-mile range PHEVs. (>500 mAh/g, >1500 mAh/ml)

Summary

- $LaSn_3$ project complete.
- High capacities (>600 mAh/g) achieved from composite Cu_6Sn_5/Sn electrodes electrodeposited on high surface area copper foam substrates.
- Excellent cycling stability during early operation (30 cycles) – needs improvement for long-term cycling – future work.
- The approach opens the door for investigation of other electrodeposited intermetallic systems – future work.
- New (proprietary) synthesis technique shows promise for fabricating nano-composite Si-C electrodes – future work.

Acknowledgment

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- David Howell