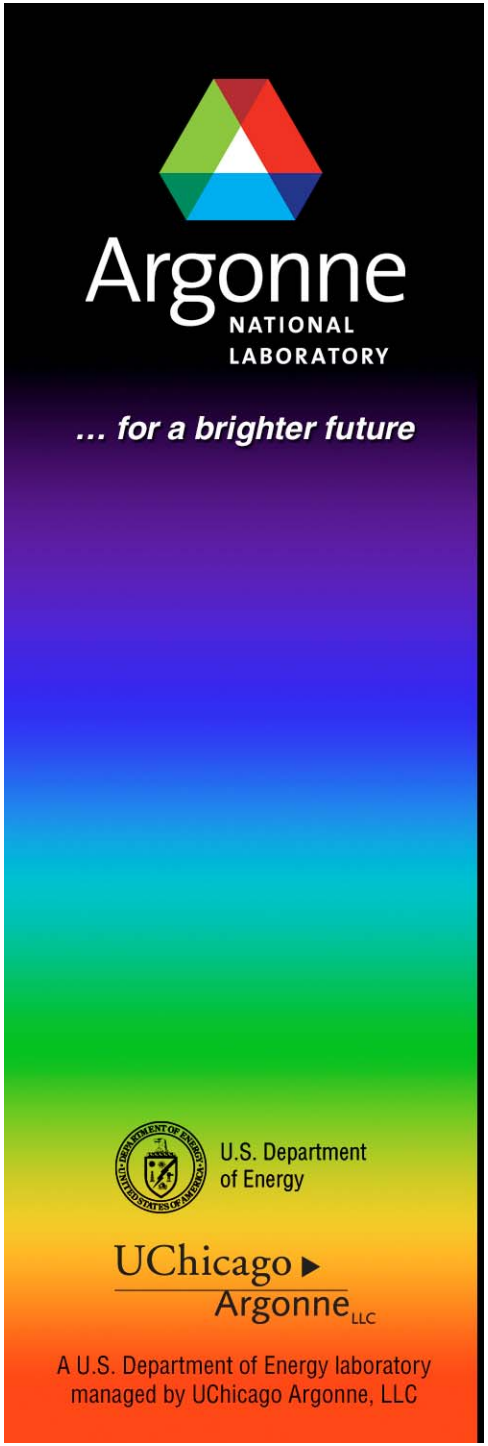

Intermetallic Anodes

presented by

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Annual Merit Review

DOE Vehicle Technologies Program

Bethesda, Maryland

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Vehicle Technologies Program

This presentation does not contain any proprietary or confidential information.

Purpose, Barriers, Approach and Collaborators

Purpose of Work

- To design and fabricate intermetallic anodes to replace graphite

Barriers

- Cost, low temperature and abuse tolerance limitations

Approach

- Search for inexpensive intermetallic electrode materials (powder laminates rather than thin films) that provide 1) an electrochemical potential several hundred mV above Li^0, e.g., Sn-based materials, and 2) a capacity of at least 400 mAh/g
- Focus on compounds in which there is a strong structural relationship between the parent and product to minimize lithium diffusion distances

Collaborators

- Co-investigators: J. Vaughey, C. Johnson
- K. Edstrom (Uppsala University, Sweden)
- Primet Precision Materials (Ithaca, NY)

Reviewers' Comments on Previous Work

- Relevance to DOE/FCVT Goal and BATT Objectives
  - *"Reviewers noted the need for high capacity anodes and found the work to be relevant"*
  - "*Goal of 300 mAh/g was too modest relative to graphite"*
    Goal increased to 400 mAh/g
    (Volumetric capacity >2000 mAh/ml for ρ>5 g/ml, *cf.* 828 mAh/ml for C_6)
- Specific Recommendations:
  - *"Research should be focused on more relevant elements, e.g., Si, Al, Mg rather than Sb"*
    Sb compounds have been very useful in providing research direction, e.g., InSb, Cu_2Sb
    Current focus is on Sn- and Mg-containing compounds
  - *"Look at amorphous materials"*
    Established collaboration with Primet Precision Materials

Topics

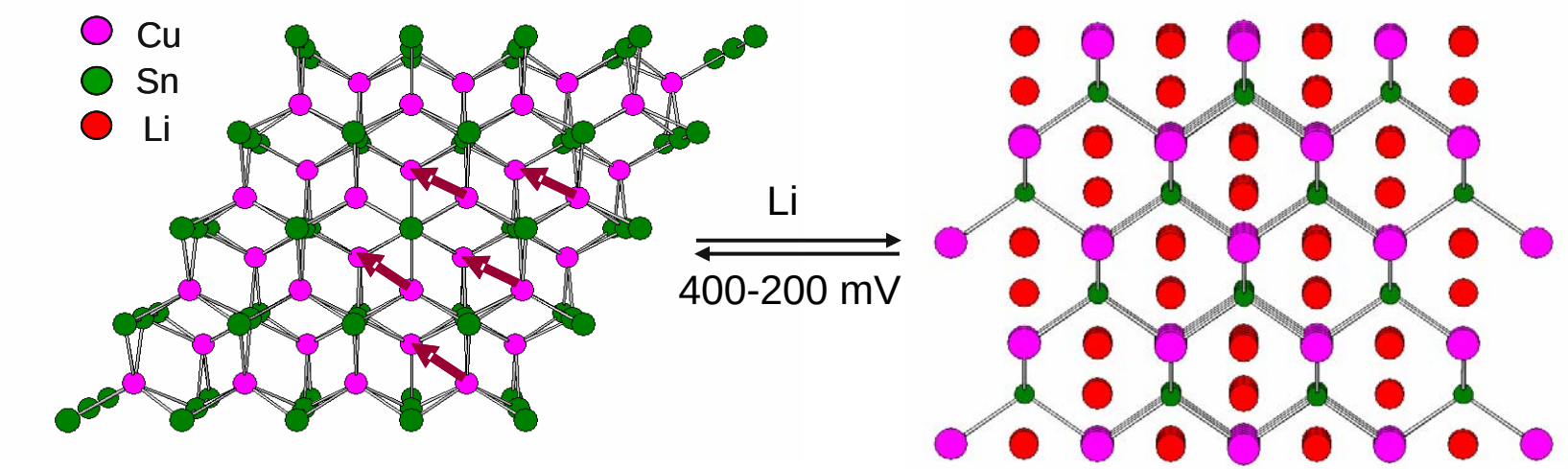
- Substituted $Cu_{6-x}M_xSn_5$ electrodes (powders rather than thin films)

- Synthesis of intermetallic compounds
  - *controlling particle size, morphology, surface area and surface reactivity*
  - *interparticle contact*
  - *Primet 'Nano-Scission™' process for fabricating nanoparticles*

- $LaSn_3$

The Cu_6Sn_5 to Li_2CuSn Transition (recap)

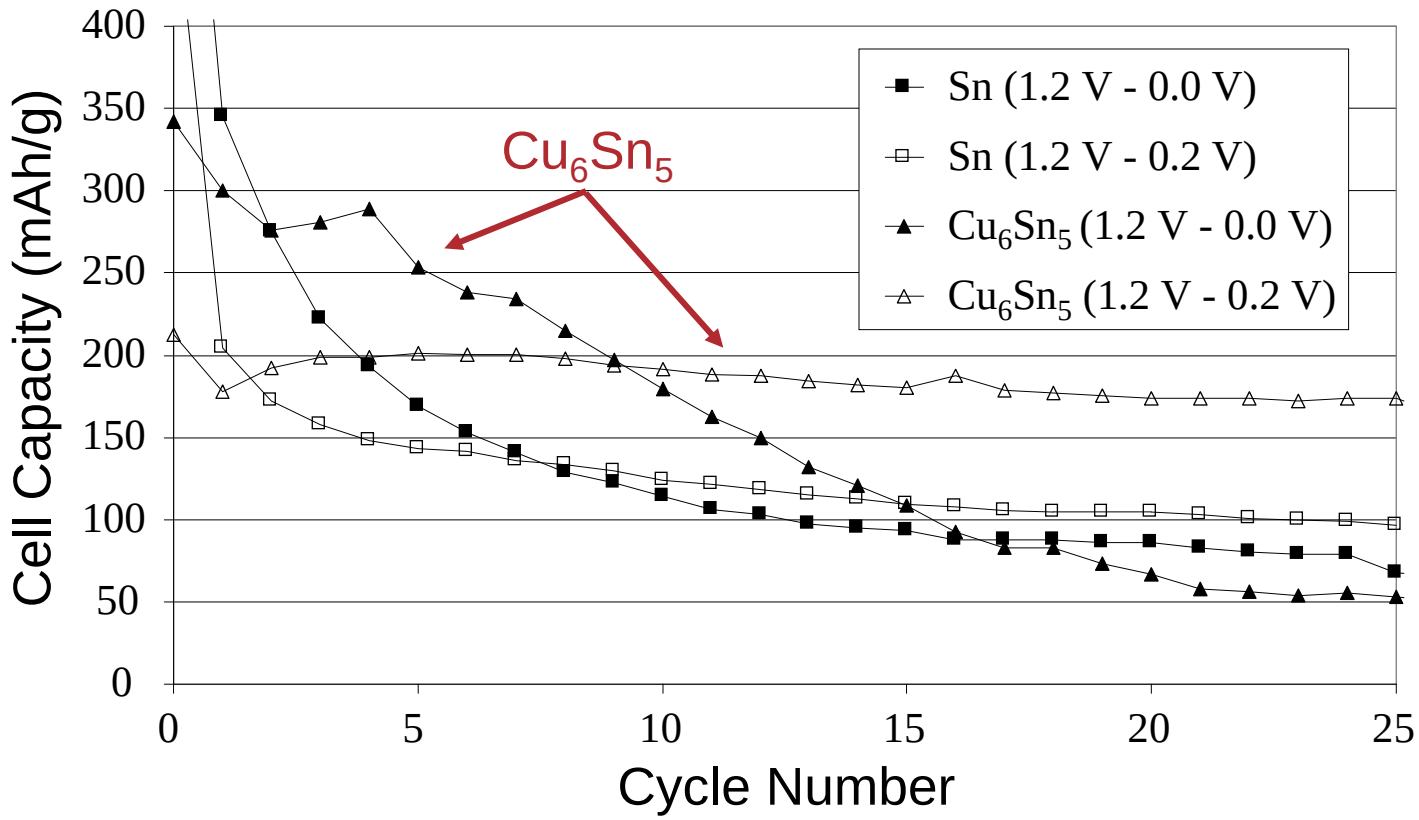
Cu_6Sn_5 (NiAs) Li_2CuSn (lithiated zincblende)



$$10\ Li + Cu_6Sn_5 \longrightarrow 5\ Li_2CuSn + Cu$$

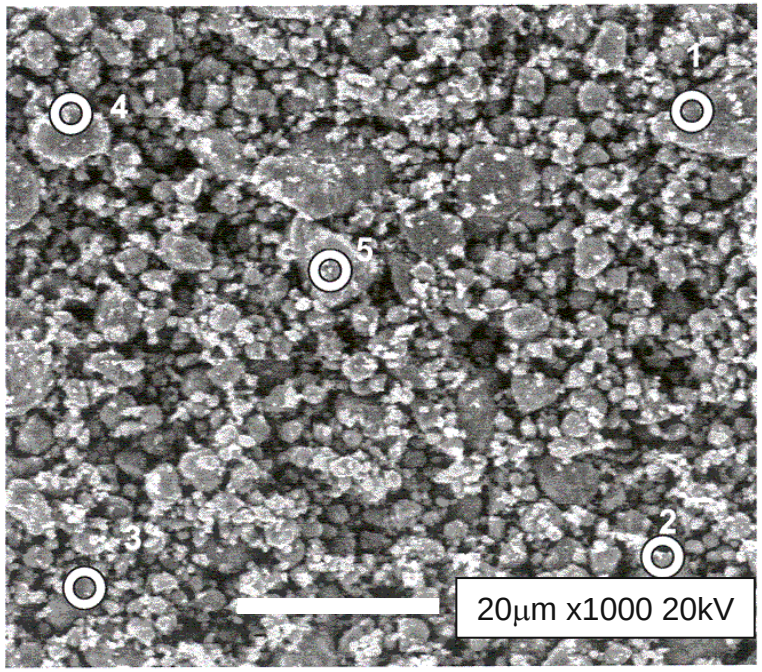
- 50% of the Sn atoms are displaced into interstitial sites
- Reversible reaction with hysteresis (Sn diffusion)
- Strong structural relationship between Cu_6Sn_5 and Li_2CuSn
- Volume Expansion = 59%; Theoretical capacity = 275 mAh/g
- Maximum capacity if reacted to $Li_{4.4}Sn$ + Cu: 605 mAh/g

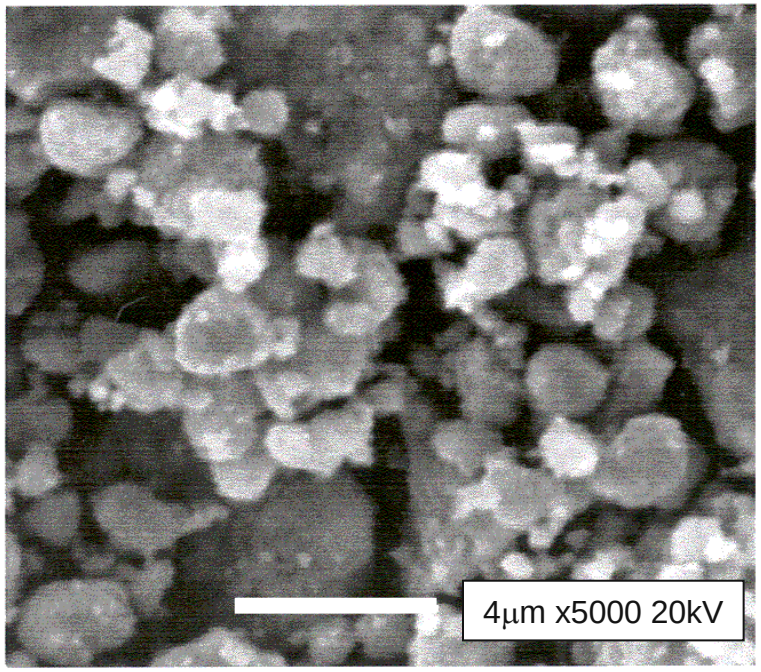
Cycling Stability: $Li/Li_xCu_6Sn_5$ vs. Li/Sn Cells Ball-milled Samples (recap)



- Significantly improved cycling stability is achieved by restricting the discharge to the topotactic reaction of lithium with Cu_6Sn_5

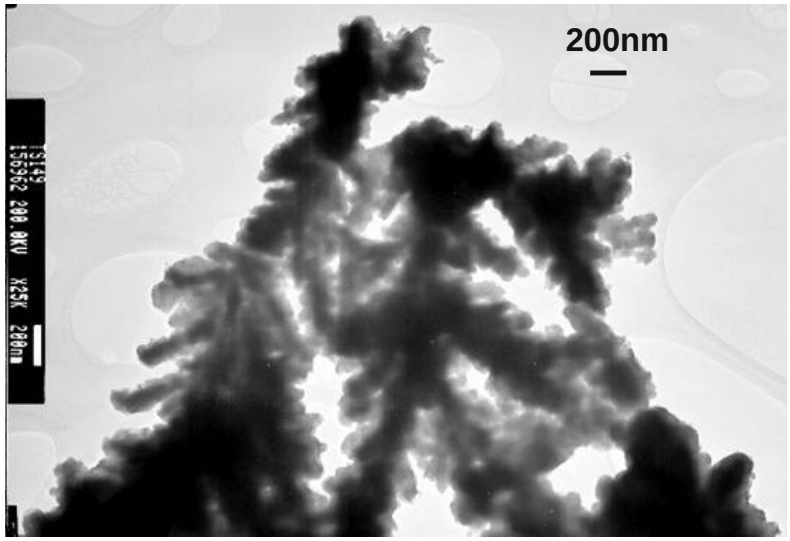
Synthesis and Morphology of Intermetallic Compounds: 1. Ball-milled Copper-Tin Sample



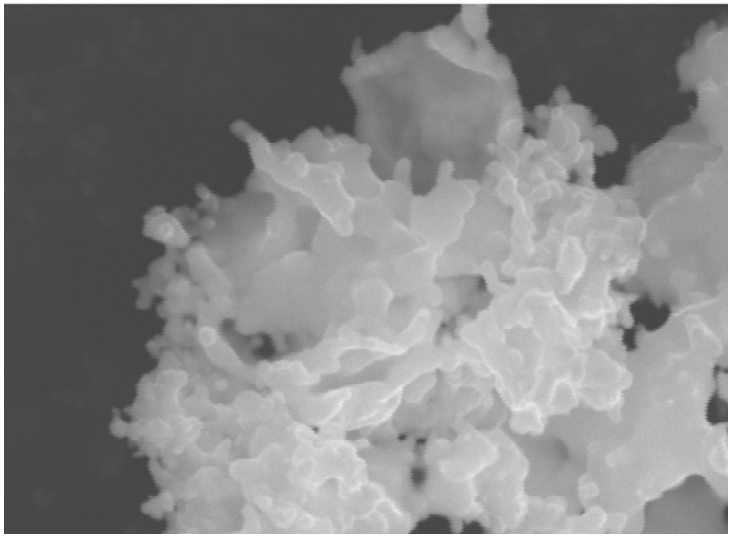


- Irregularly shaped particles – wide particle size distribution
- Samples sieved to remove >30 μm particles
- Insufficient control of sizing process

2. Cu_6Sn_5 Prepared from Solution

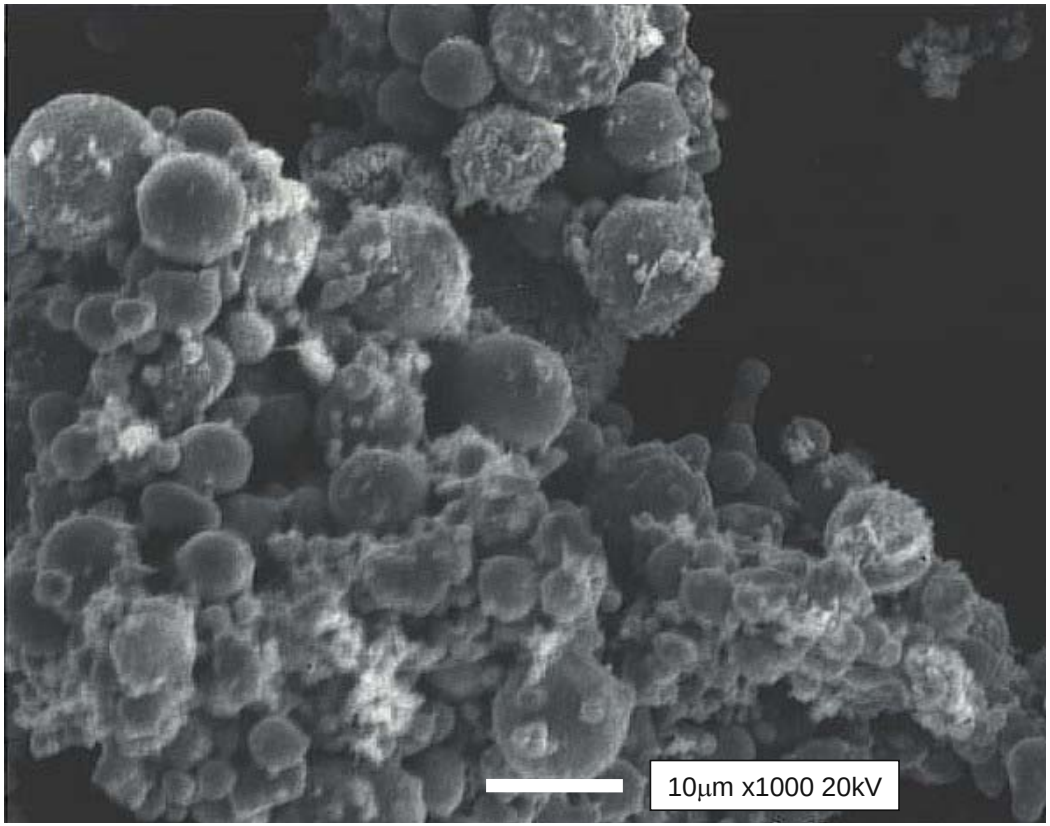


- Zn reductant
- Metal salt/alcohol solution
- Nano-dendritic morphology
- Poor electrochemical performance
- Surface oxidation?



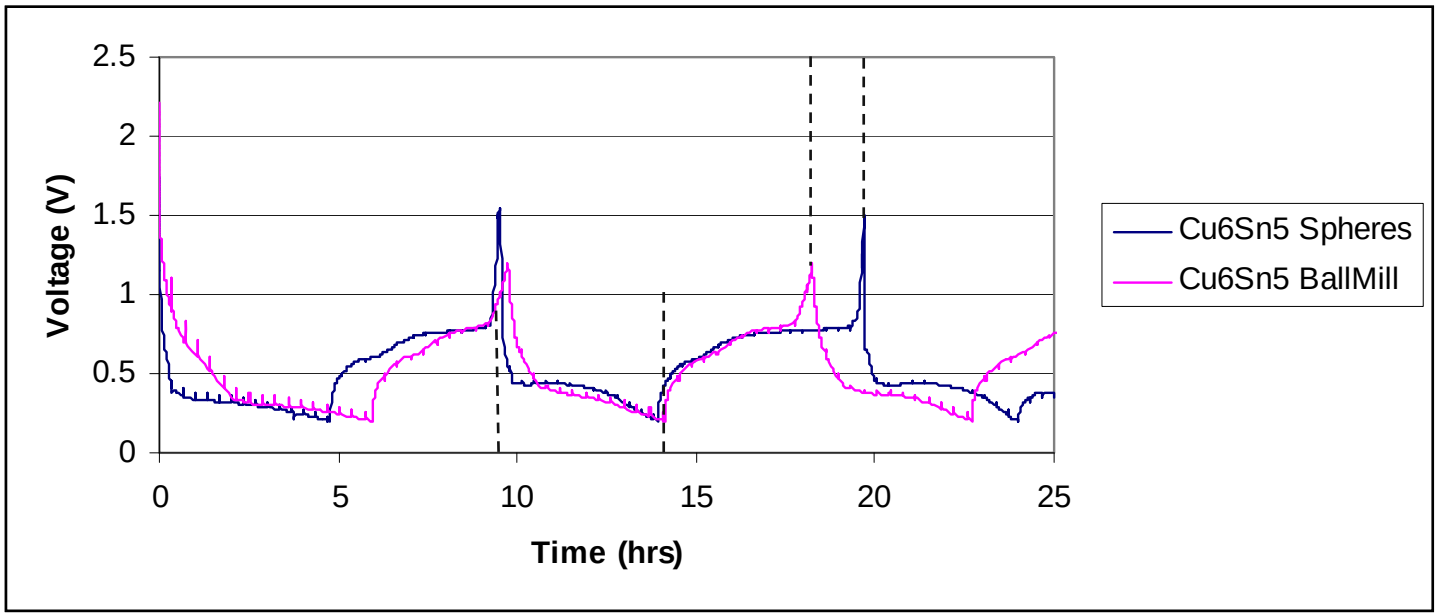
- KBH_4 reductant
- Tetraethyleneglycol solvent
- Annealed at 130 °C
- Morphology similar to melts
- Performance similar to ball-milled samples

3. Commercial Sample of Cu_6Sn_5



- Undisclosed process – metal spray technique?
- Average particle size ~5μm
- Clean surfaces – minimum oxidation?

Electrochemistry of Commercial Cu_6Sn_5



- Commercial (spherical) Cu_6Sn_5 provides similar capacity to ball-milled sample between 0.45 and 0.20 V (Sn-based capacity)
- Cycling efficiency of commercial sample inferior to ball-milled sample.
- Commercial sample provides significantly lower first-cycle capacity loss (8% vs. 27%), consistent with cleaner surface

Substituted $Cu_{6-x}M_xSn_5$ Electrodes

- Evaluate the electrochemical performance of substituted $Cu_{6-x}M_xSn_5$ electrodes (M = Zn, Co, Ni, Fe)

- The 18-electron rule can be used as a rough guide to predict whether stable Li_2MSn compounds can be synthesized or not, *e.g.*,

  Li_2ZnSn (18e) – known compound

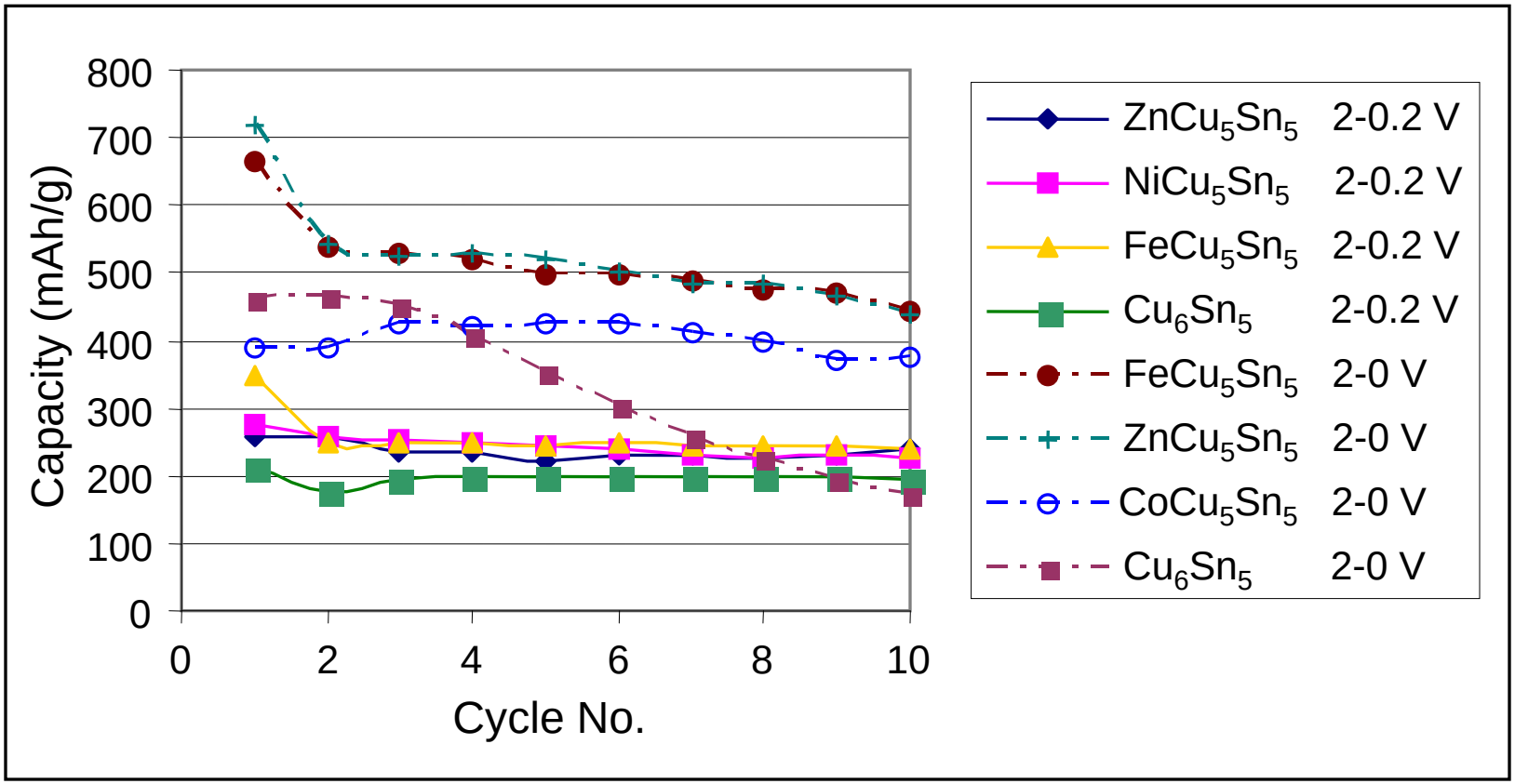
  Li_2CuSn (17e) – known compound

  Li_2CoSn (15e) – unknown compound

  $Li_2Cu_{0.8}Co_{0.2}Sn$ (16.6e) derived from $CoCu_5Sn_5$ – possible?

- Interest in Co-Sn compounds – Sony Nexelion Cell

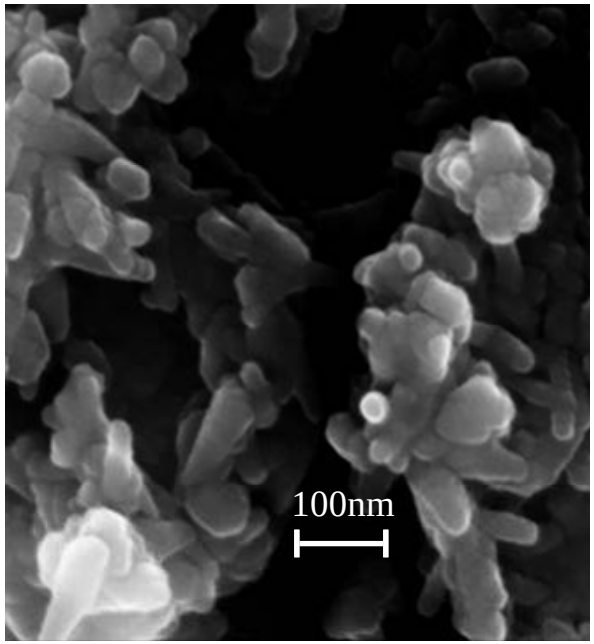
Cycling Stability of Ball-milled $Cu_{6-x}M_xSn_5$ Electrodes



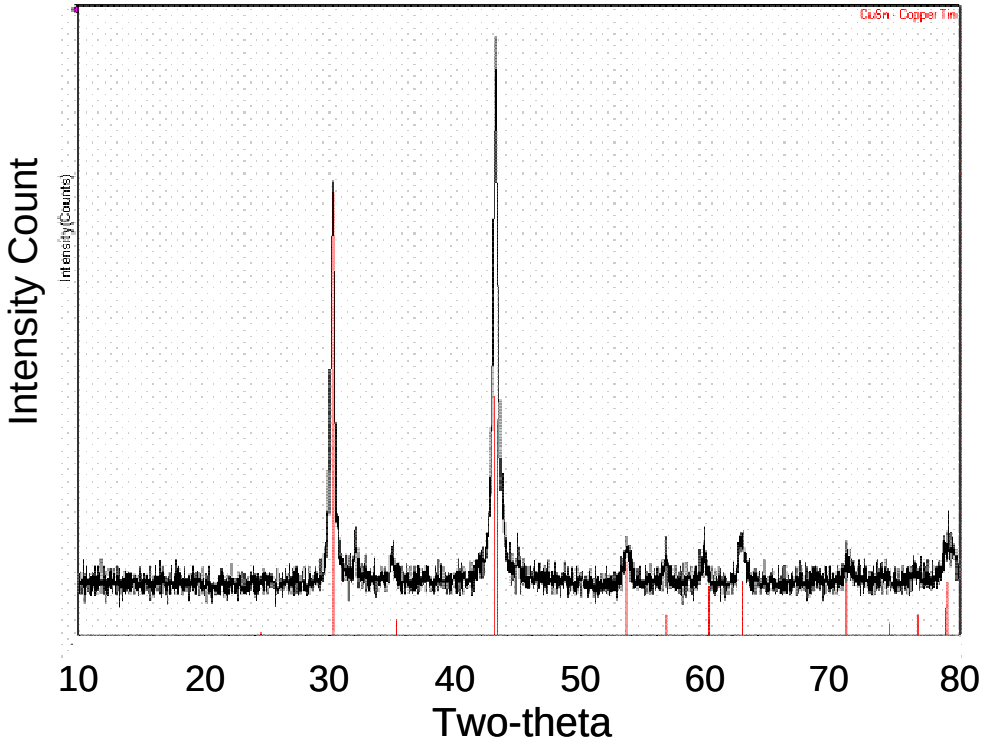
- $CoCu_5Sn_5$ shows highest capacity (400 mAh/g) and best stability (2-0 V)
- $CoCu_5Sn_5$ therefore selected as composition for further study

Primet $CoCu_5Sn_5$ Particles

SEM image

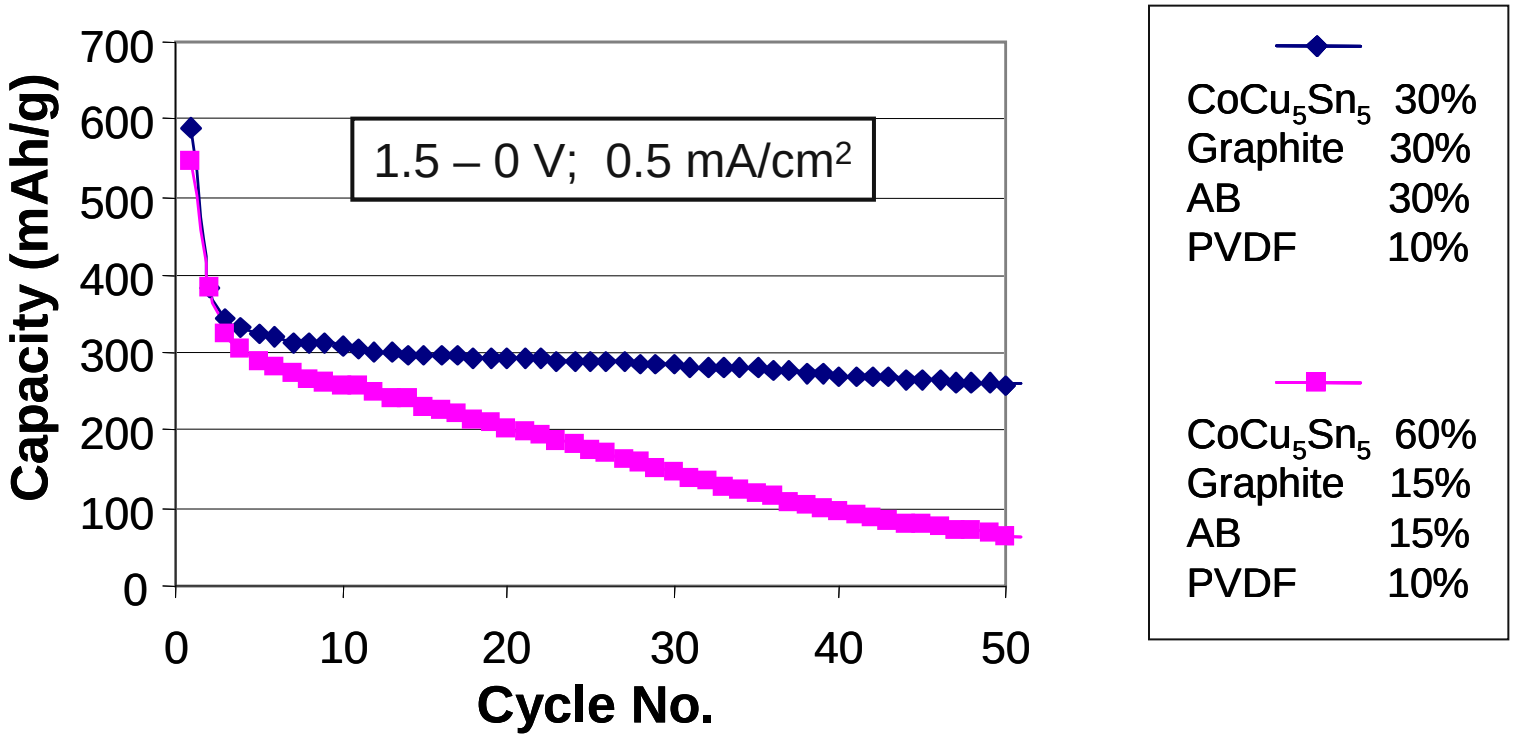


X-ray diffraction pattern



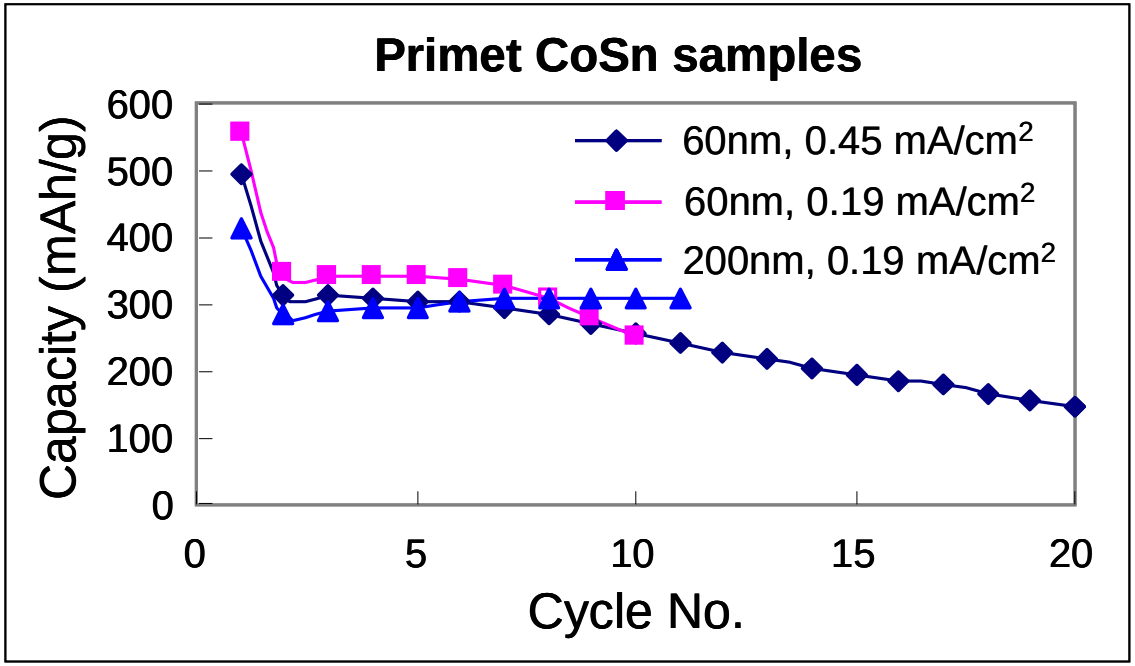
- No damage incurred to $CoCu_5Sn_5$ by Primet's *'Nano-Scission™'* process
- X-ray diffraction pattern shows peak broadening, consistent with particle size reduction
- Reasonably uniform particle size distribution, average ~60nm

Relative Cycling Stability of Primet $CoCu_5Sn_5$ (60 nm) - Graphite Composite Electrode



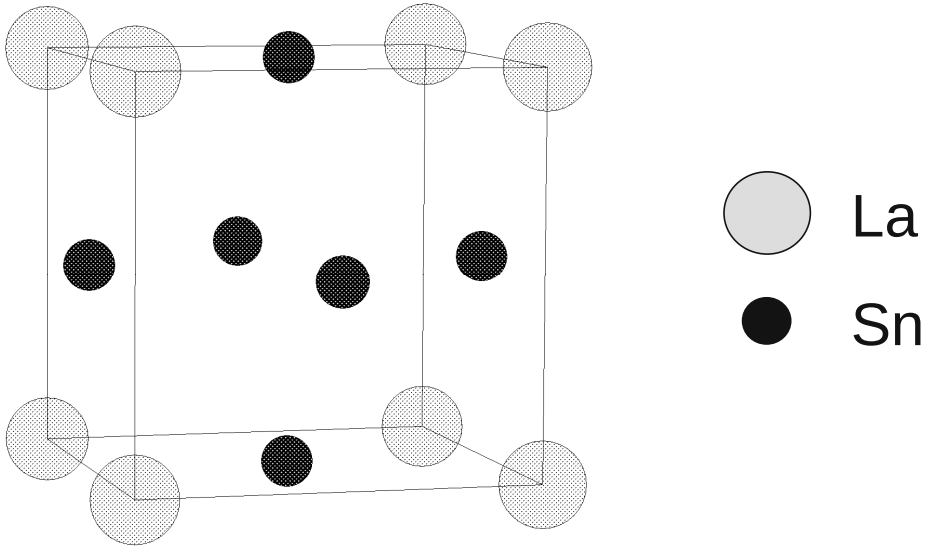
- Addition of surplus graphite and carbon to the electrode significantly improves cycling stability through improved electronic connectivity, *cf.* Si electrodes, but capitalizes on capacity of graphite component
- Does not resolve safety problem

Cycling Stability Relative to Particle Size
Primet CoSn - 60 nm and 200 nm



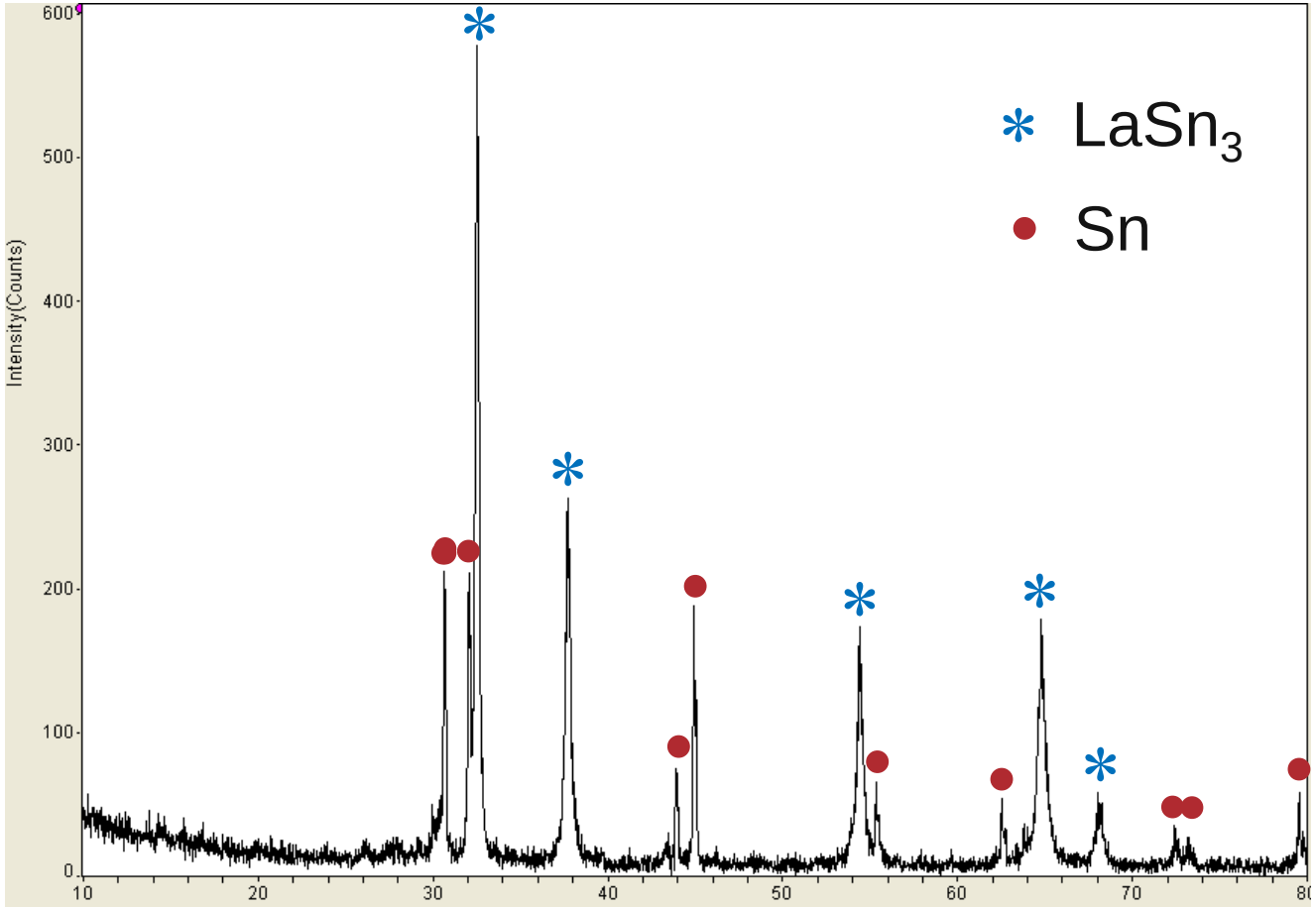
- Approximate composition of Sony's 'Nexelion' anode used for investigation
- Studies show that larger (200 nm) particles are more effective than 60 nm particles for Argonne's electrode design
- Need better electronic connectivity between particles

The $LaSn_3$ Structure



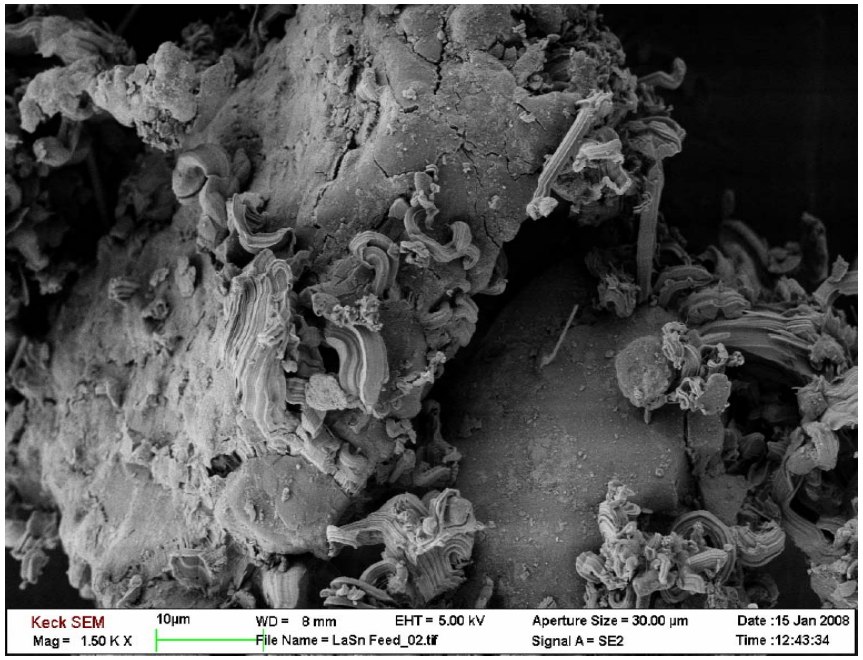
- Defect perovskite-type structure
- 12 interstitial (octahedral, tetrahedral and edge-shared) sites
  - 12 Li + $LaSn_3$ → $Li_{12}LaSn_3$ (hypothetical reaction)
  - 12 Li + $LaSn_3$ → La + 3 Li_4Sn (650 mAh/g)
- Theoretical capacity: 650 mAh/g or 4920 mAh/ml (ρ_{LaSn3} = 7.57 g/ml)

X-ray Diffraction Pattern of $LaSn_3$ Feed

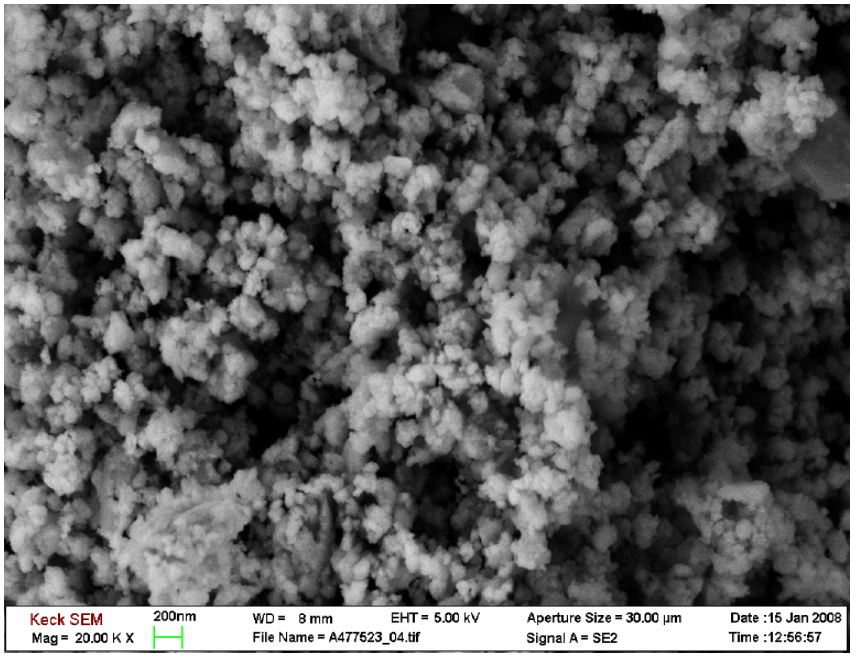


- Sample contains some unreacted Sn

$LaSn_3$ Particles Before and After Primet Process



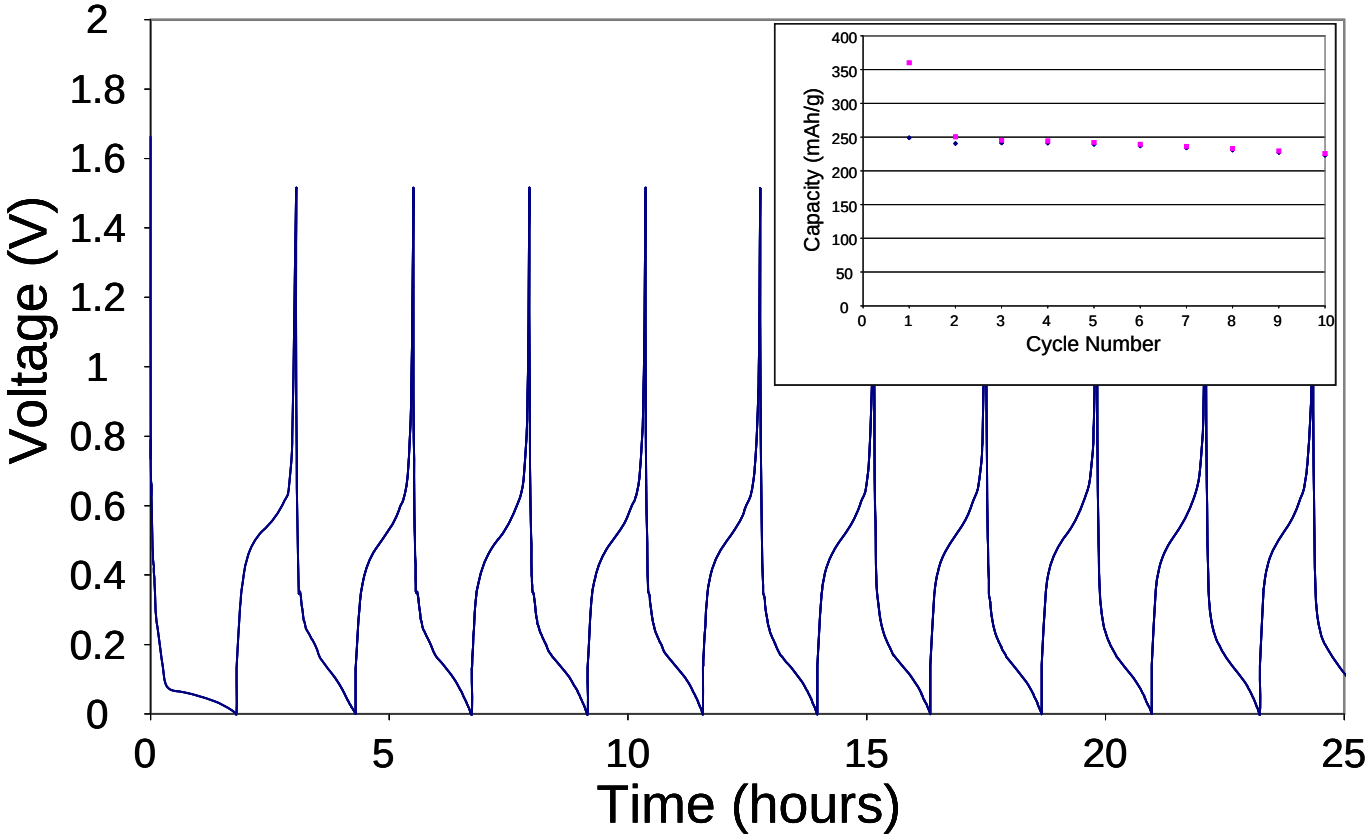
Ball-milled $LaSn_3$ precursor



<200 nm primary particles

- Unreacted Sn whiskers (m.p. = 232 °C) visible throughout $LaSn_3$ sample
- Primet process homogenizes the sample and reduces the particle size to <200 nm

Cycling Profile of a Li/$LaSn_3$ Cell



- 225-250 mAh/g (1703-1893 mAh/ml) obtained between 1.5 and 0 V
- 35-38% of theoretical value (650 mAh/g)
- 1st cycle irreversible capacity loss ~30% (surface oxidation?)

Publications

- 2007 Publications

1. M. Sterndahl, H. Bryngelsson, T. Gustafsson, J. T. Vaughey, M. M. Thackeray and K. Edstrom, *Surface Chemistry of Intermetallic AlSb Anodes for Li-ion Batteries*, Electrochim. Acta, **52**, 4947 (2007).

2. M. Morcrette, D. Larcher, J. M. Tarascon, H. Bryngelsson, K. Edström, J. T. Vaughey and M.M. Thackeray, *Influence of Electrode Microstructure on the Reactivity of Cu_2Sb with Lithium*, Electrochim. Acta. **52**, 5339 (2007).

3. J. T. Vaughey, A. M. Geyer, N. Fackler, C. S. Johnson, K. Edstrom, H. Bryngelsson, R. Benedek and M. M. Thackeray, *Studies of Layered Lithium Metal Oxide Anodes in Lithium Cells*, J. Power Sources, **174**, 1052 (2007).

4. J. T. Vaughey, J. Owejan and M. M. Thackeray, *Substituted $M_xCu_{6-x}Sn_5$ Compounds (M=Fe, Co, Ni, Zn) for Lithium Batteries*, Electrochem. and Solid State Lett. **10**, A220-A224 (2007).

Patents and Technology Transfer

- Patents from BATT Program

  1. M. M. Thackeray, K. D. Kepler and J. T. Vaughey, *Anodes for Rechargeable Lithium Batteries*, US Patent No. 6,528,208 (4 March, 2003).

  2. M. M. Thackeray, J. T. Vaughey, C. S. Johnson, L. M. L. Fransson, K. Edstrom and G. Henriksen, *Intermetallic Negative Electrodes for Non-Aqueous Lithium Cells and Batteries*, US Patent No. 6,730,429 (4 May, 2004).

  3. J. T. Vaughey, L. M. L. Fransson and M. M. Thackeray, *Negative Electrodes for Lithium Cells and Batteries*, US Patent No. 6,885,460 (15 February, 2005).

- Option to license agreement negotiated: Patents 1, 2 and 3.

- No technology transfer agreements

Future Plans

- Continue to work with Primet Precision Materials to exploit nano-particulate intermetallic anode materials
  - Improve quality of surface, minimize oxidation during processing
  - Engineer and design effective current-collecting and binding media to increase capacity and cycle life
- Study SEI films and formation (XPS) on substituted $Cu_{6-x}M_xSn_5$ materials (in progress with K. Edstrom Uppsala University)
- Pursue alternative materials, e.g., $LaSn_3$ and substituted derivatives
- Initiate theoretical modeling studies of intermetallic structures and lithiated products to screen most promising materials

Acknowledgments

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  - Tien Duong, David Howell