Intermetallic Anodes

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Annual Merit Review
DOE Vehicle Technologies Program

Washington, D.C.
June 7, 2010

ES062

Overview

Timeline

- Start date: FY09
- End date: On-going
- Percent complete:

  - project on-going

Budget

- Total project funding

  - 100% DOE
- FY09: $300K
- FY10: $300K

Barriers Addressed

- Low energy
- Poor low temperature operation
- Abuse tolerance limitations

Partners

- Co-investigators:
  - L. Trahey, V. G. Pol (ANL)
- Collaborators:
  - H. H. Kung (Northwestern University)
  - N. Dietz Rago (ANL)
  - Jose M. Calderon-Moreno (Romanian Academy)

Objectives

- Design high capacity metal, semi-metal, intermetallic or composite metal oxide anodes that will provide electrochemical couples to meet the 40-mile range requirement of PHEVs
    - Exploit electrochemical deposition reactions to improve the design and performance of tin-based intermetallic electrodes
    - Explore autogenic reactions to design new or improved anode materials and architectures

Milestones (FY09-10)

- Prepare metal and intermetallic electrode architectures by electrodeposition and determine their electrochemical properties in lithium half cells and full cells – *on-going*
- Exploit autogenic processes for synthesizing and simultaneously coating Si, Sn, and metal oxides with carbon and evaluate their electrochemical properties – *on going*
- Complete study on carbon-coated SnO_2 electrodes – *project in progress*
- Establish interactions with EFRC – Center for Electrical Energy Storage - *Tailored Interfaces* (Argonne-Northwestern University-University of Illinois (Urbana-Champaign) – *interactions initiated*

Approach

- Our approach is to search for inexpensive anode materials that provide an electrochemical potential at least a few hundred mV above the potential of metallic Li.

- Our research is focused predominantly on Sn-based systems as well as composite metal oxides.

- A major thrust of our research is to design new electrode architectures by electrodeposition techniques in which a Cu foam provides an electronically connected substrate onto which electrochemically active metals can be deposited.

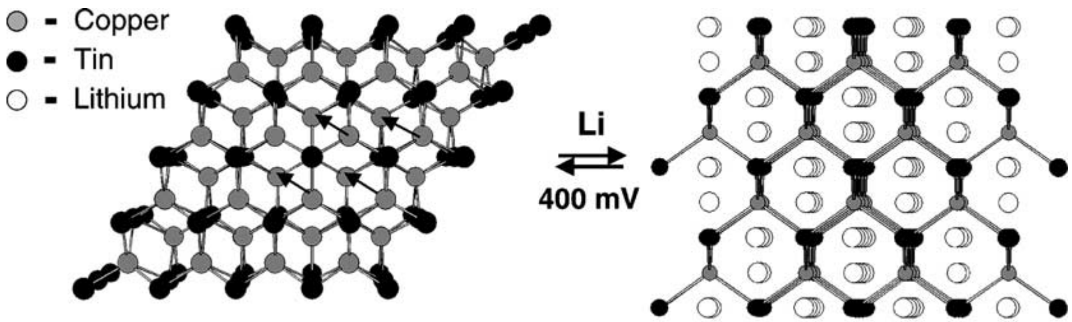
- We are exploring autogenic reactions to fabricate anode materials and architectures in a single step with an initial focus on metal oxides such as SnO_2 and SnO (with a Li alloying metal) that are either coated with carbon or embedded in a carbon matrix.

Intermetallic Anodes for Li-Ion Batteries

- Sn, Sb structures can act as hosts for Li insertion/Cu extrusion

Cu_6Sn_5

- Th. Capacity = 605 mAh/g
- Low practical capacity from ball-milled samples: 225 mAh/g)



$$10\ Li + Cu_6Sn_5 \rightarrow 5\ Li_2CuSn + Cu\ (+\ 10\ Li) \rightarrow 5\ Li_{\sim4}Sn + 6\ Cu$$

Cu_2Sb

$$3\ Li + Cu_2Sb \rightarrow Li_3Sb + 2\ Cu$$

- FCC Sb array remains intact on Li insertion
- Practical capacity = ~300 mAh/g
- Theoretical vol. capacity = 2132 mAh/mL (graphite = 818 mAh/mL)

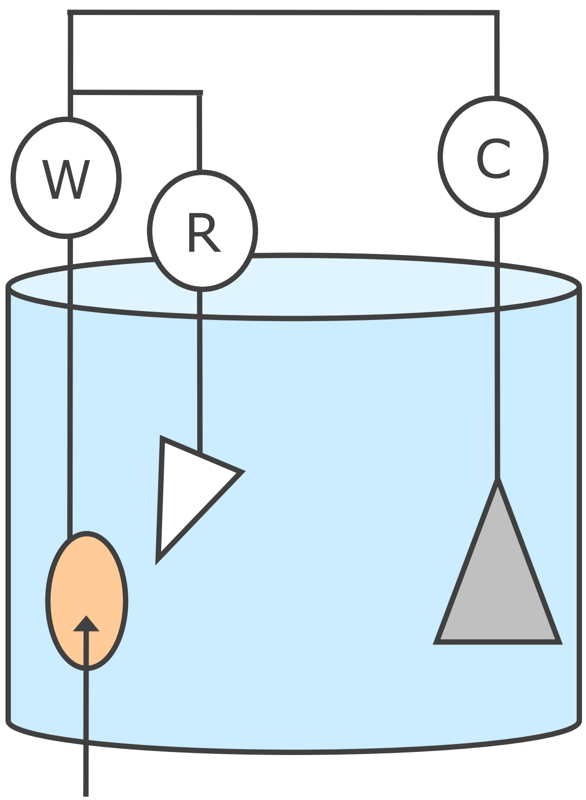
- 42% volume expansion of Sb lattice
- Complete Cu extrusion

New approach required for electrode design and current collection

K. Kepler et al,ESSL (2000); L. Fransson et al., *J. Electrochem. Soc.*, (2001)

Electrodeposition of Anode Materials

Cell Setup



Deposition of Active Material

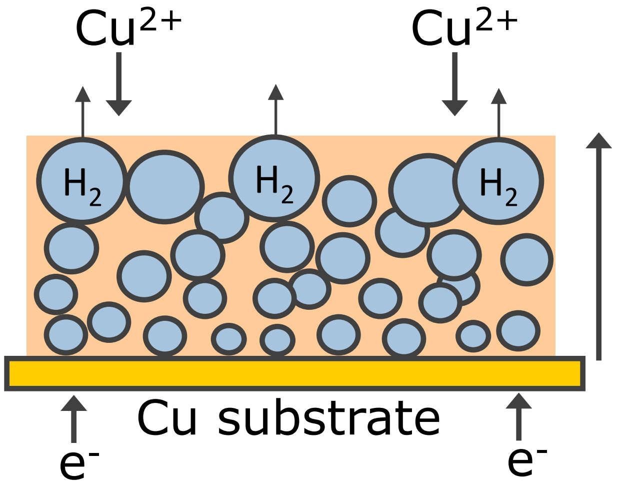
Adjustable Variables

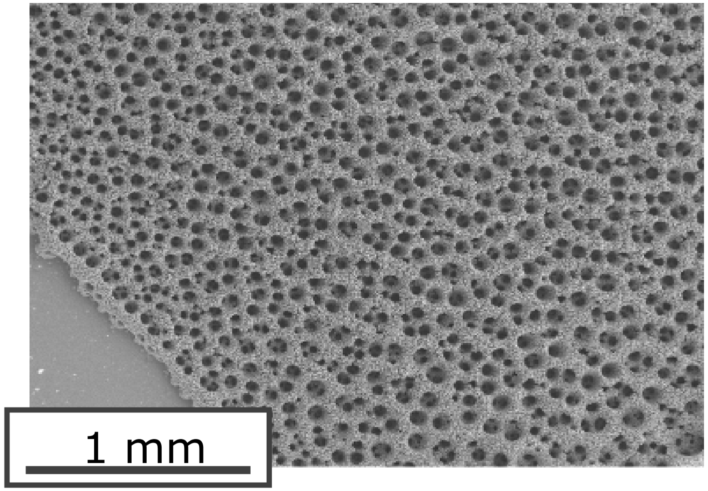
- ◇ Applied potential / current
- ◇ Duty cycle (pulse)
- ◇ Solution characteristics (pH, concentration, T, t etc)

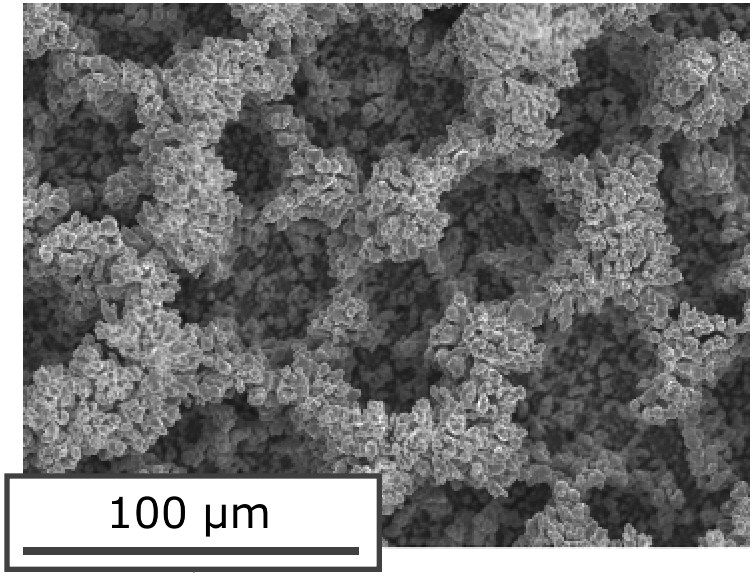
Deposited material has inherent electrical contact to current collector

→ *No binders?*

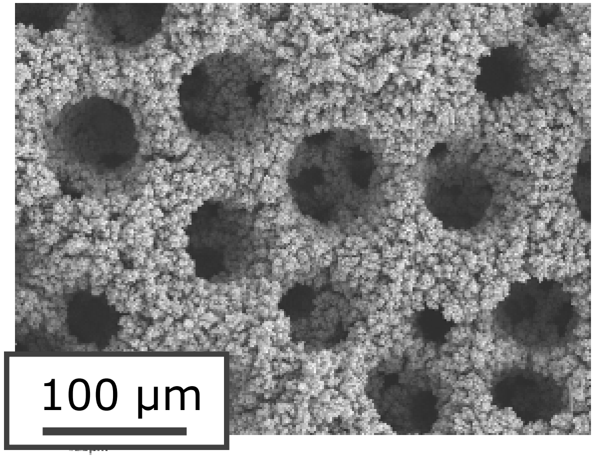
Copper Foam Current Collectors







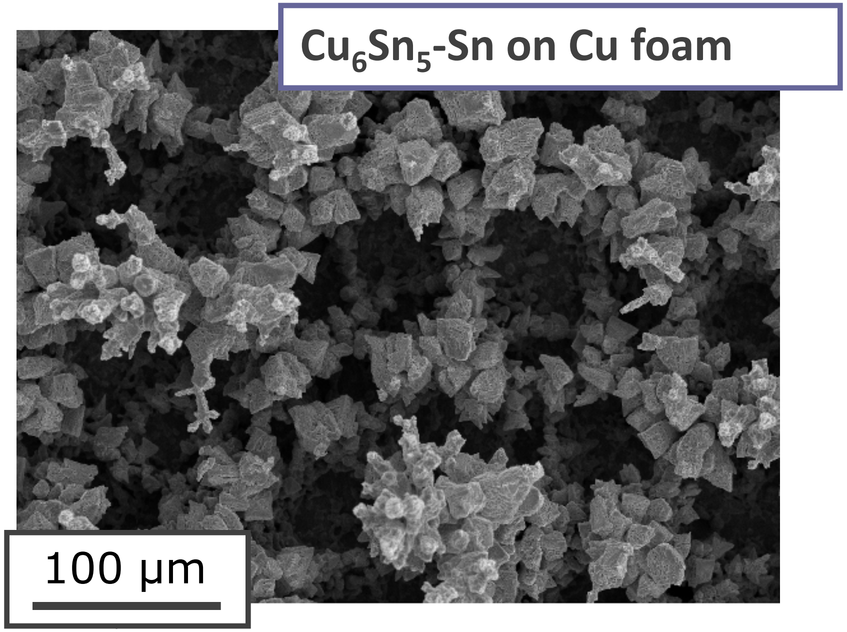
500 °C, Ar

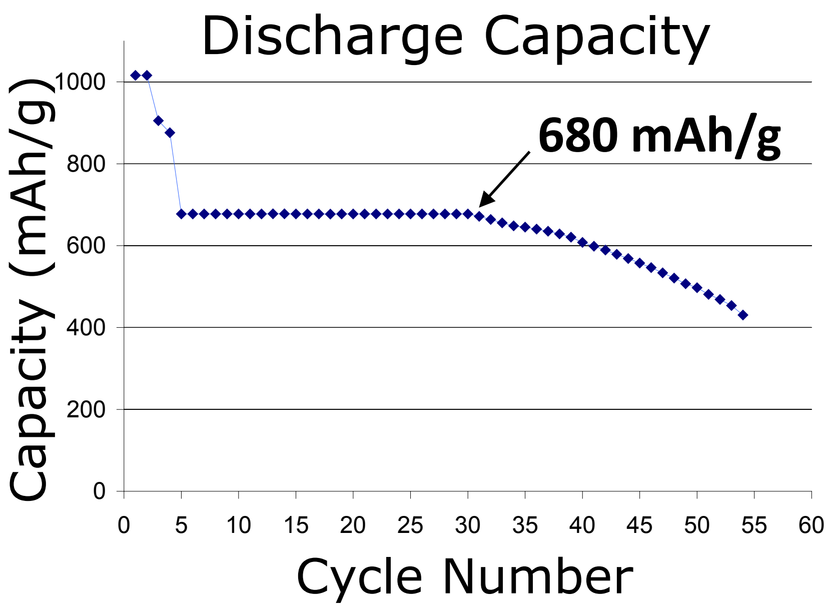


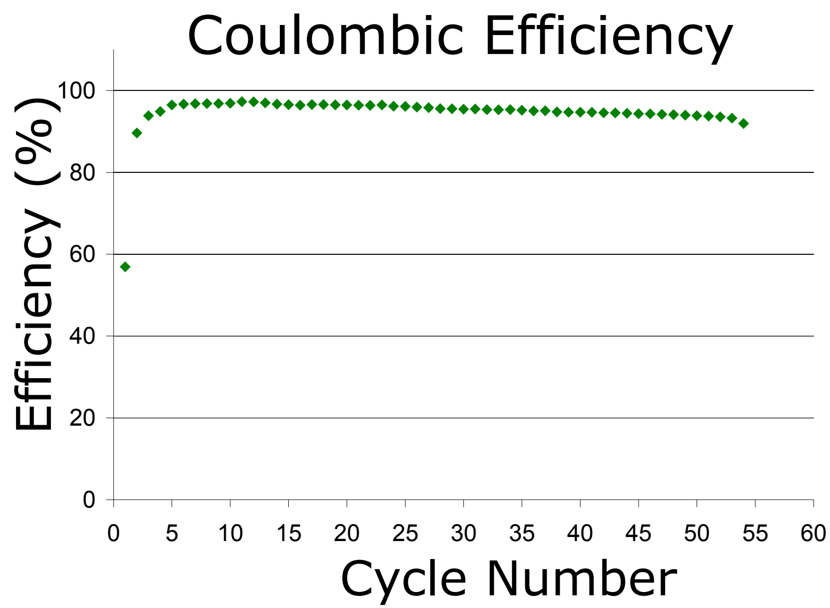
H. –C. Shin et al., *Adv. Mater.* **2003**, *15*, 1610

Cu_6Sn_5-Sn Anodes (Recap)

- As-deposited Cu-foam is brittle.
- Annealing at 500 °C strengthens Cu-foam to Cu foil contact, providing a sufficiently robust substrate for electrodeposition of Cu and Sn.
- Morphology maintained after Cu_6Sn_5/Sn electrodeposited at -600 mV vs. SCE.
- Reversible 680 mAh/g for 30 cycles



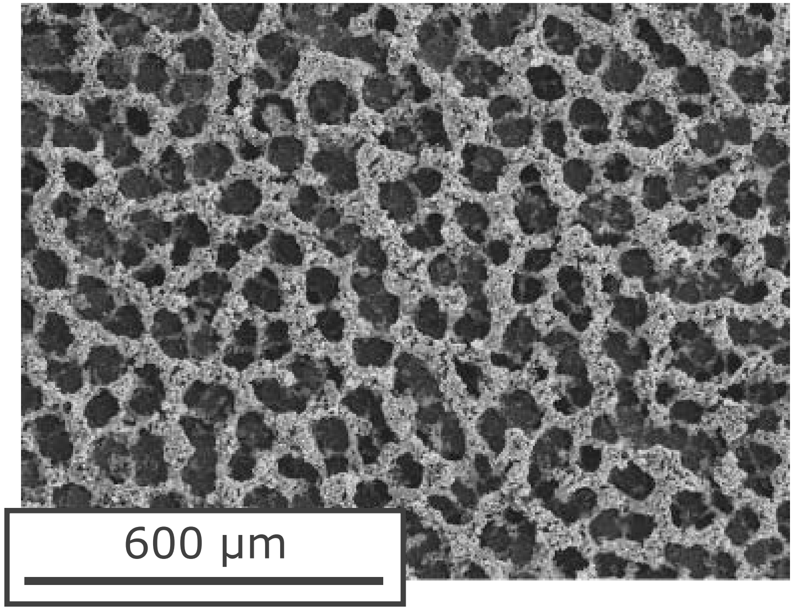


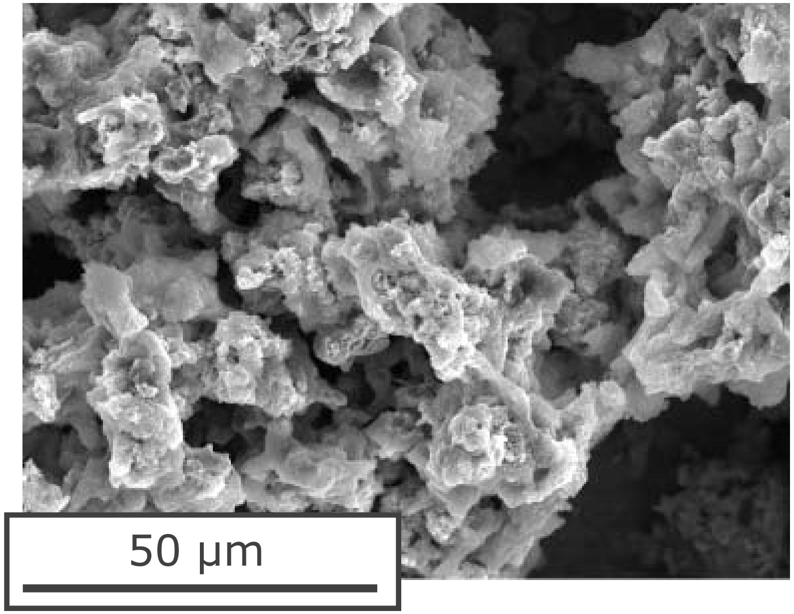


L. Trahey et al, *J. Electrochem. Soc.*, **2009**, *156*, A385.

Failure Analysis

Cu_6Sn_5-Sn electrode after 55 cycles

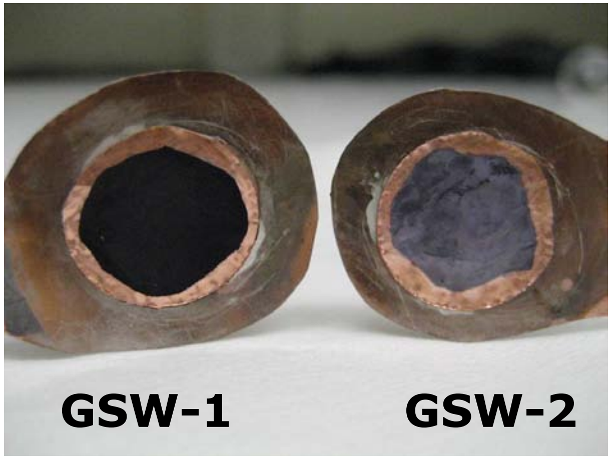




- Cu foam architecture still intact
- Particles rounded, indicative of repetitive deposition and stripping of Cu?
- Cu solubility?
- XRD analysis showed only crystalline Cu
- Sn products (detected by SEM) amorphous

Trahey et al., *J. Electrochem. Soc.*, 2009, *156*, A385.

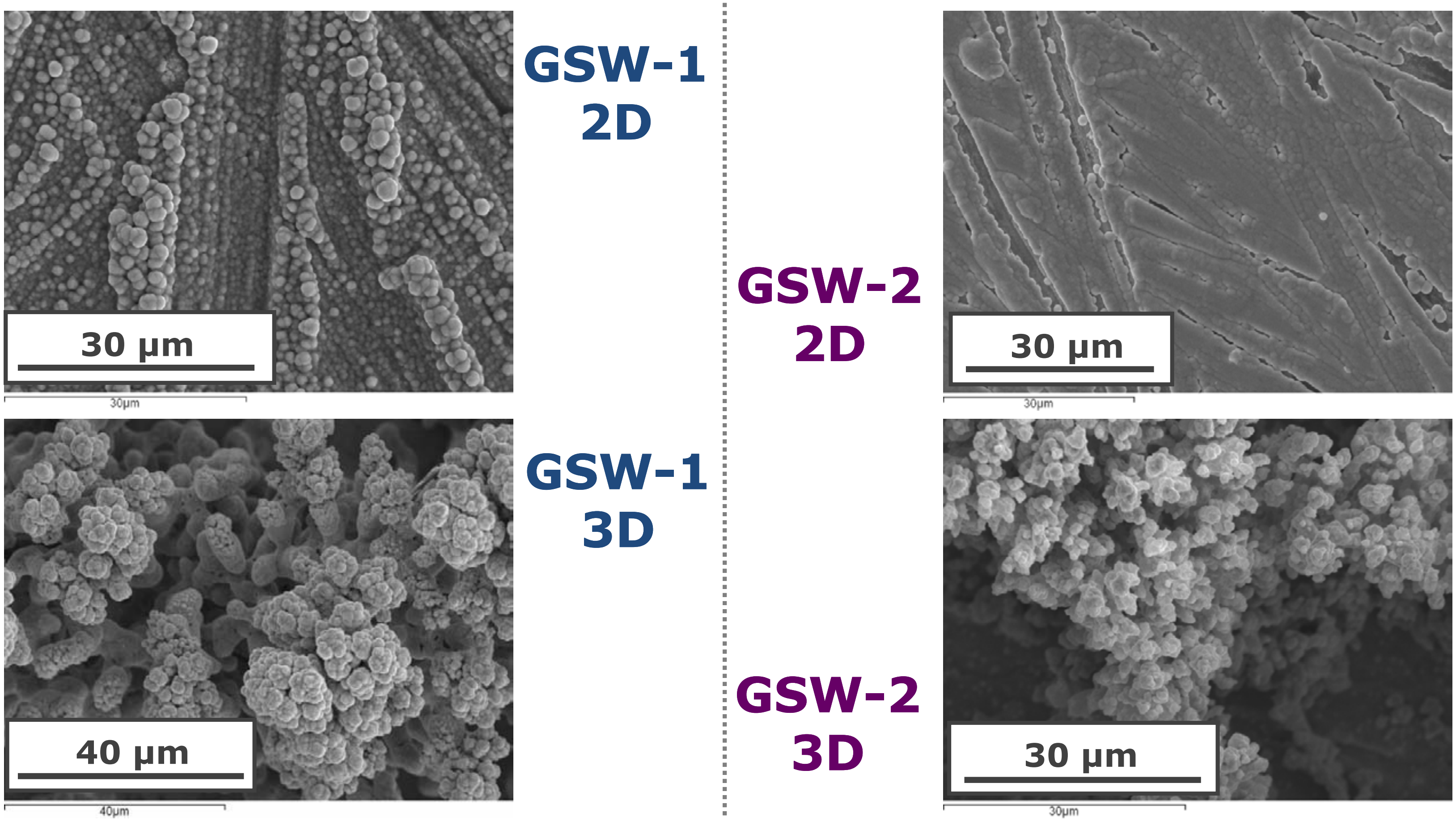
2-D vs. 3-D Electrodeposited Electrodes



- Cu_2Sb investigated as a model system to evaluate 2-D vs. 3-D electrodes prepared by electrodeposition.

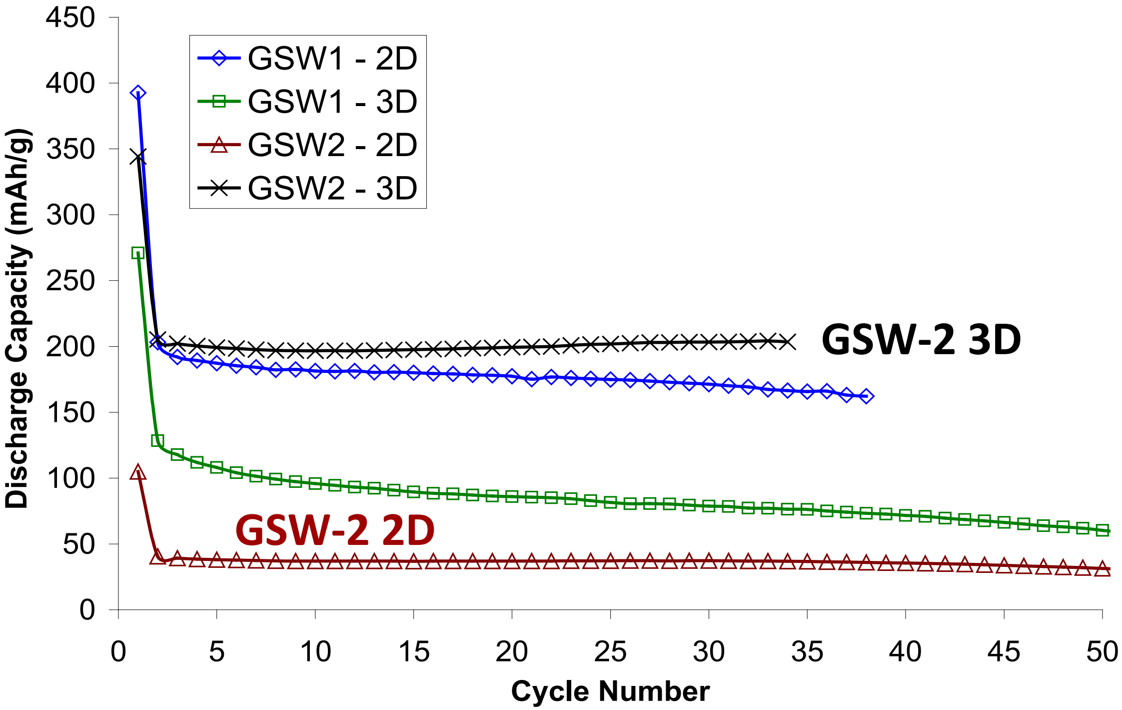
Deposition parameters (2 Cu : 1 Sb solution) Note: Both Cu and Sb deposit at -0.24 V vs. SCE	Theoretical mass of deposit	Denoted in the following slides
Long pulse: -10 mA (30 s) / 0 mA (10 s); 20x	2.2 mg	**GSW-1**
Short pulse: -10 mA (1 s) / -1 mA (10 s); 300x	2.2 mg	**GSW-2**

Electrodeposited Cu_2Sb Morphologies



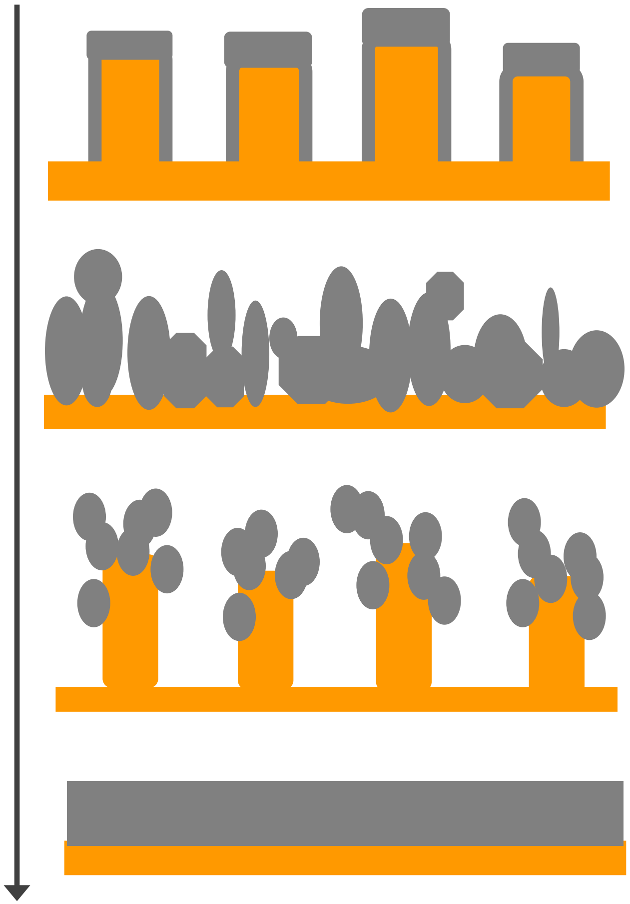
- Short (1-sec) pulse protocol (GSW-2) provides smoother 2D films and smaller Cu_2Sb particles on 3D Cu-foam.

Cu_2Sb: GSW-1 vs. GSW-2



cross-section schematics

Highest Capacity

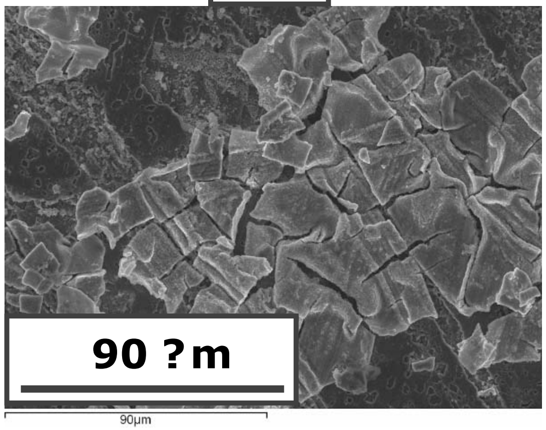


Lowest Capacity

- Deposition parameters and morphology strongly influence capacity and cycling stability
- Smooth film (GSW-2 2D) has worst performance
- 3-D electrode (short pulse, GSW-2 3D) provides best capacity and cycling stability

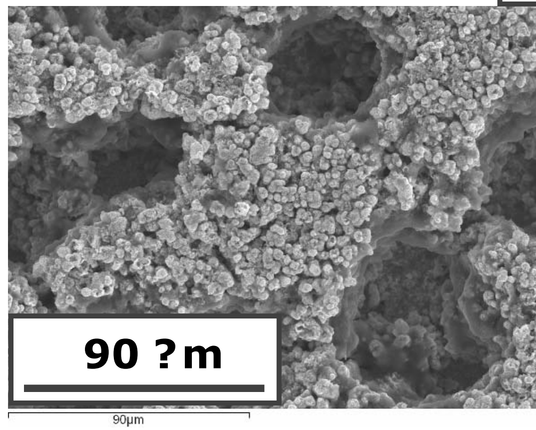
Cu_2Sb: GSW-2 after Cycling

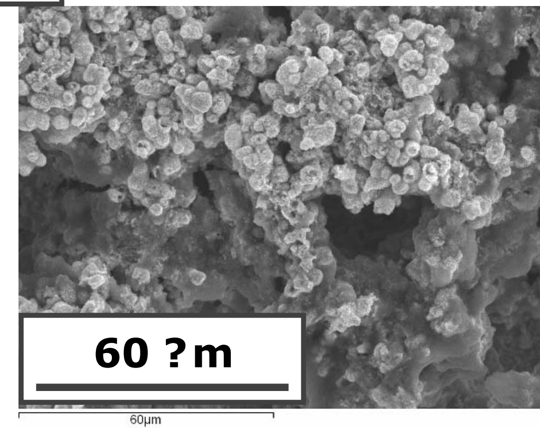
2D



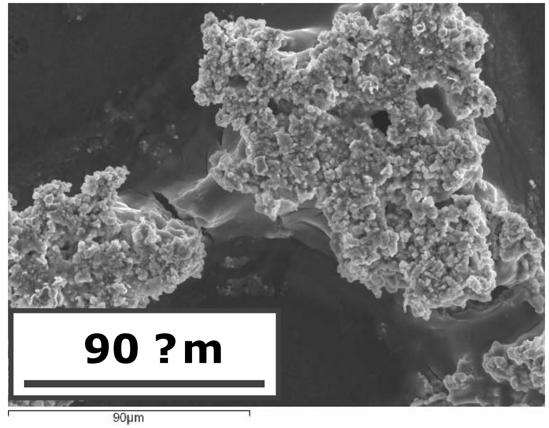
- Cracking of 2D films from volume expansion

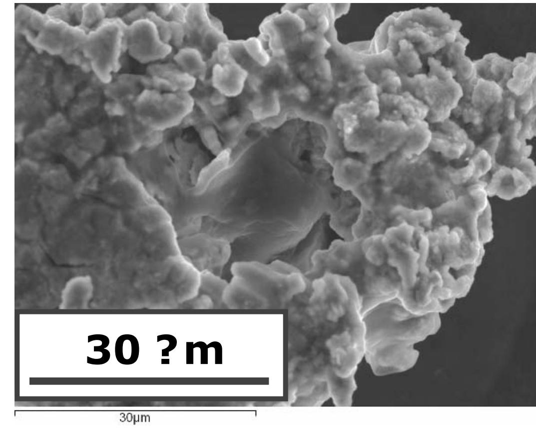
3D





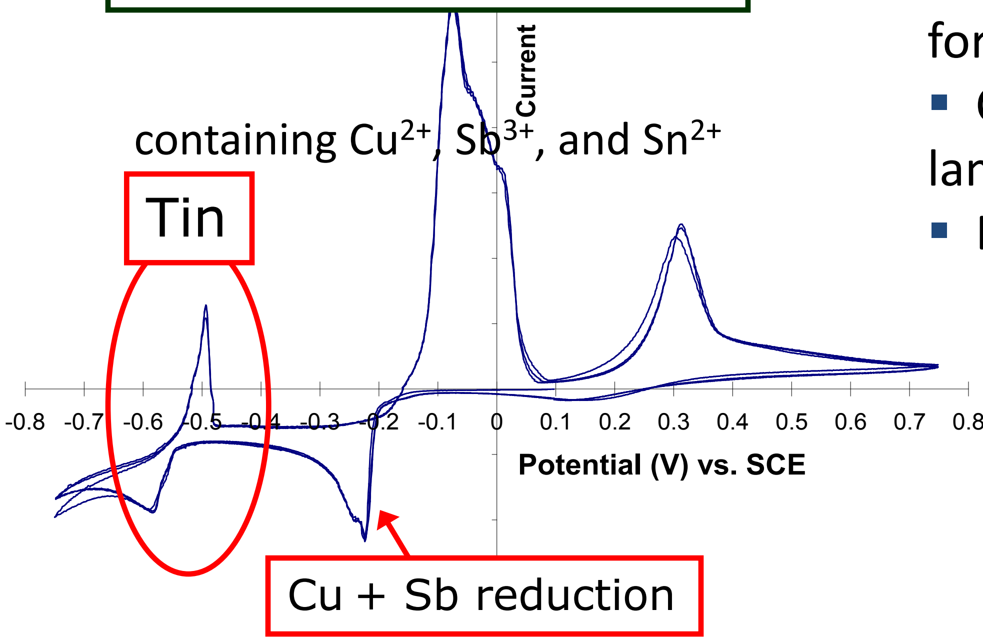
- No visible cracking on high-surface area Cu electrode
- Found on separator: Dislodged anode material





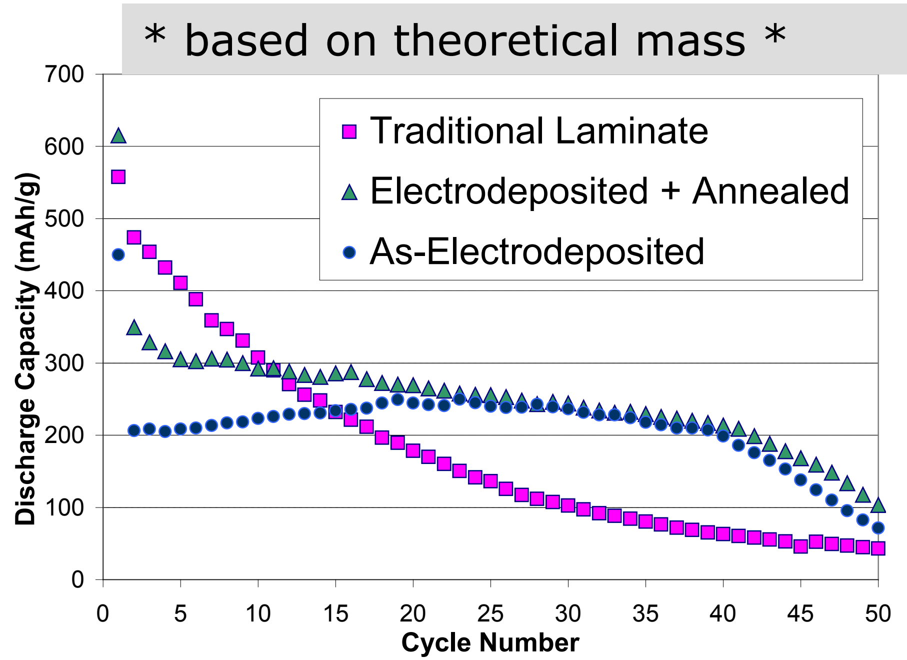
Multi-Component Intermetallic Anodes

CV of deposition solution containing Cu^{2+}, Sb^{3+}, and Sn^{2+}



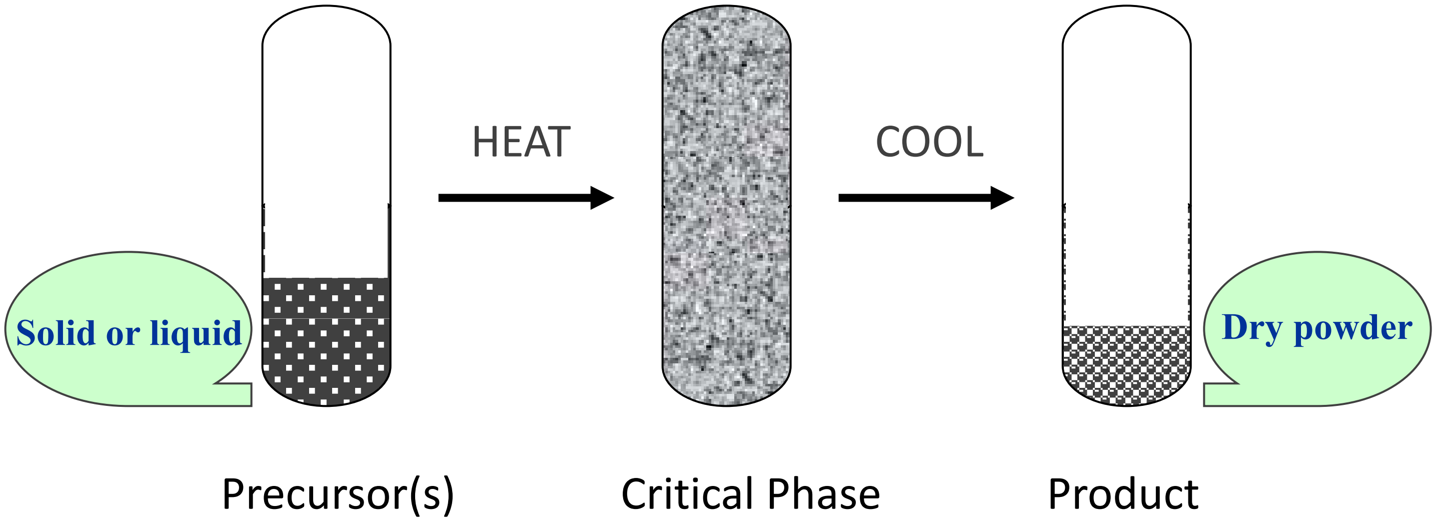
- Cu, Sn and Sb components deposited to form composite intermetallic electrodes
- Composites outperform traditional laminated Cu_6Sn_5, Cu_2Sb, SnSb electrodes
- Effects of annealing investigated

Step 1: Cu_6Sn_5 film deposition
Step 2: Cu_2Sb film deposition
Step 3: Repeat 1 & 2
Step 4: anneal (150 °C) or not
Step 5: cycle



Autogenic Reactions

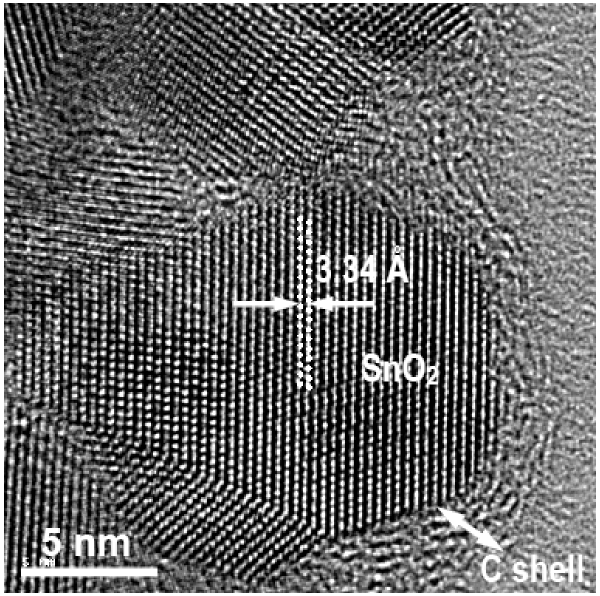
Autogenic Reactions: Self-generating reactions that occur within an enclosed vessel, typically at high pressure and temperature



- Product highly dependent on precursor and reaction conditions

SnO_2-C Electrodes - Preparation

$$Sn(OC_2H_5)_2 \xrightarrow[100\ psi]{600\ ^oC} Sn_{(s)} + C_{(s)} + \text{gaseous products}\uparrow$$

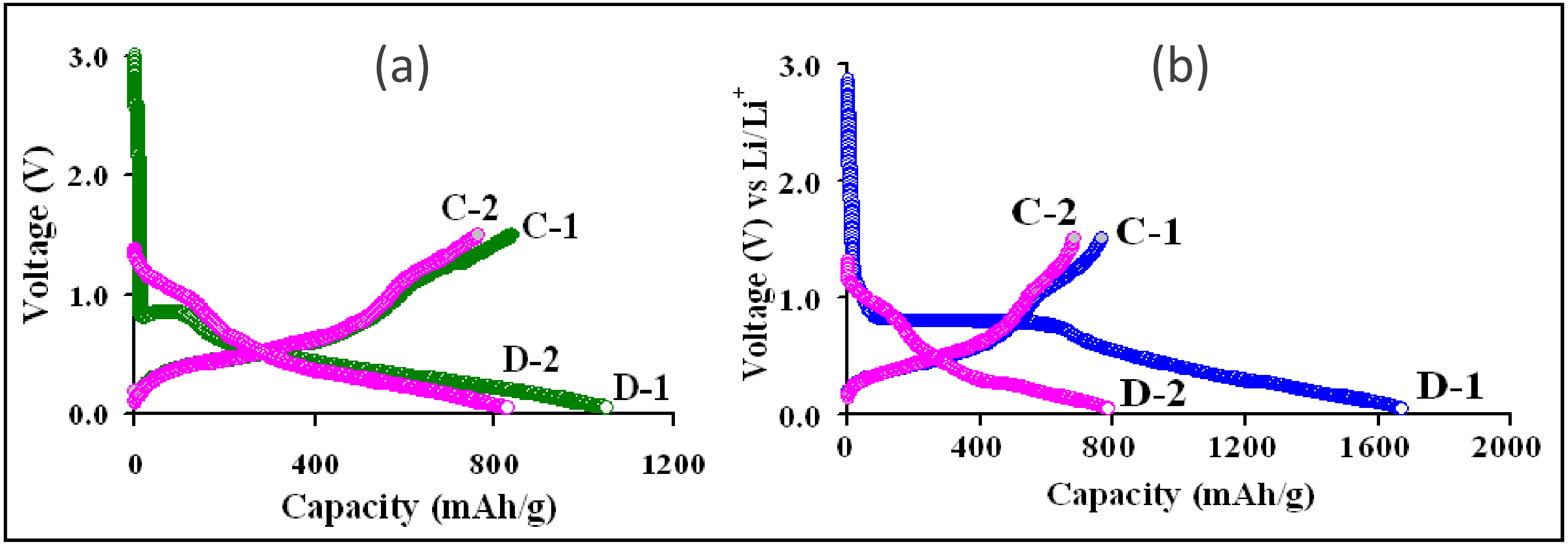


- HRTEM image of a SnO_2 nanoparticle encapsulated by a carbon nanolayer

- The autogenic technique is extremely versatile and can be used to prepare a wide variety of C-protected nanoparticulate materials

- The approach has implications for preparing new electrode materials and architectures (both anodes and cathodes).

SnO_2-C Electrodes - Electrochemistry



- Electrochemical profiles of the initial two cycles of lithium half cells with (a) a carbon-coated SnO_2 electrode, and (b) a SnO_2 electrode after burning off the carbon coating.
- First-cycle irreversible capacity loss is reduced by the carbon coating
- Electrodes provide 800 mAh/g. O_2 content in parent SnO_x electrode can be controlled – optimization of composition, carbon content and cycling stability in progress.

Future Work - FY2010/FY2011

- Exploit autogenic reactions to design new anode materials and architectures – *Expand the current, promising project on SnO_2/Sn*.
- Evaluate electrodeposition reactions for fabricating Sn films on 3-D porous metal foam substrates - *On-going (incomplete) project*.
- R&D motivated by the need to find alternative anode materials to graphite that will provide sufficiently high gravimetric and volumetric capacities to meet the battery requirements for 40-mile range PHEVs (>500 mAh/g, >1500 mAh/ml).
- Two proposals outlining new approaches have been submitted to the BATT Program in response to their Call for Proposal 0212100 *"Synthesis and Characterization of Novel Anode Materials and Structures for Use in Lithium Batteries"*.

Summary

- A comparison of the electrochemical performance of 2-D vs. 3-D electrodes prepared by electrodeposition was made:
  - Cu_2Sb used as a model system
  - Deposition parameters and the resulting electrode morphology are key influences on capacity and cycling stability.
  - Short (1-sec) pulse protocol provides smoother 2D films and smaller Cu_2Sb particles on 3D Cu-foam than long pulse protocol
  - 3-D electrodes (short pulse) provide best capacity and cycling stability
- Electrodeposited 3-D composite Cu-Sn-Sb electrodes outperform traditional laminated electrodes

  $\Rightarrow$ *motivation to continue studies of electrodeposited Sn electrodes*
- Autogenic reactions are extremely versatile and can be used to prepare C-protected nanoparticulate materials with enhanced electrochemical properties. The approach has implications for preparing new electrode materials and architectures (both anodes and cathodes) – *future work*

Acknowledgment

Support for this work from DOE-EERE, Office of Vehicle Technologies is gratefully acknowledged

- Tien Duong, David Howell