Intermetallic Anodes

presented by

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This presentation does not contain any proprietary or confidential information.
Overview

**Timeline**
- Start date: FY08
- End date: On-going
- Percent complete:
  - LaSn₃ 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 Li⁰, notably Sn-based materials, and a capacity of at least 400 mAh/g.
  - use high surface area copper foam current collectors and electrodeposited Cu₆Sn₅ 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., LaSn₃ that has a high Sn content.
Cu₆Sn₅ (Recap)

Cu₆Sn₅ to Li₂CuSn transition

Electrochemistry: Cu₆Sn₅ vs. Sn

21.25 Li + Cu₆Sn₅ → 5 Li₂⁺ₓCu₁₋ₓSn + (1+5x) Cu → 6 Cu + 5 Li₄.25Sn

- Strong structural relationship between Cu₆Sn₅, Li₂CuSn and “Li₃Sn” (x=1) exists.
- Li insertion/Cu displacement reaction: Th. Cap. ≈600 mAh/g; Pr. Cap. ≈200 mAh/g
- Mimics Na/NiCl₂ reaction (100% efficient): 2 Na + NiCl₂ → 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
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$_6$Sn$_5$.

Cu$_6$Sn$_5$ and Sn deposited at -600 mV vs. SCE reference electrode (pulsed).

<500 mV produces Cu$_4$Sn; >-600 mV produces dendritic structures.
XRD patterns and SEM images

- XRD pattern of as-deposited product shows predominantly Sn, trace Cu₆Sn₅.
- XRD pattern of annealed product reveals Cu₆Sn₅ and Sn.
- EDS analysis shows average composition of product as being ~90 at.% Sn and ~10 at% Cu.
Electrodeposited $\text{Cu}_6\text{Sn}_5$/Sn on Cu Foam Electrodes

1. As-deposited Cu foam
2. Annealed Cu foam (500 °C)
3. $\text{Cu}_6\text{Sn}_5$/Sn on Cu foam

- 1. As-deposited Cu-foil is brittle and powdery.
- 2. Annealing at 500 °C strengthens Cu-foil to Cu foil contact, providing a sufficiently robust substrate for electrodeposition of Cu and Sn. Overall porosity maintained.
- 3. Morphology maintained after $\text{Cu}_6\text{Sn}_5$/Sn pulsed electrodeposition at -600mV vs. SCE. Sn concentration varies from ~20% within the porous electrode to ~90% at outermost surfaces.
Significant improvement in reversible capacity achieved (650 mAh/g vs. 200 mAh/g for ball-milled Cu₆Sn₅ 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 Cu₆Sn₅/Sn electrode?
SEM Image of Cycled Cu₆Sn₅/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/NiCl₂ 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 ($\rho_{\text{LaSn}_3} = 7.57$ g/ml)
- 12 interstitial (octahedral, tetrahedral and edge-shared) sites
  - $1 \text{ Li} + \text{LaSn}_3 \rightarrow \text{LiLaSn}_3$ (54 mAh/g)
  - $12 \text{ Li} + \text{LaSn}_3 \rightarrow \text{Li}_{12}\text{LaSn}_3$ (hypothetical reaction – 650 mAh/g)
  - $12.75 \text{ Li} + \text{LaSn}_3 \rightarrow \text{La} + 3 \text{Li}_{4.25}\text{Sn}$ (690 mAh/g)
Cycling Profile of a Li/LaSn₃ Cell (Recap)

- 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?

XRD patterns of ball-milled LaSn₃ samples consistently show ~10% free Sn
Li/LaSn₃ Cell: Slow Electrochemical Titration

1. Electrolyte reactions (SEI formation)
2. Sn → Li₂Sn₅
3. Sn → LiSn
4. LaSn₃ + Sn
5. LaSn₃ + Sn

- LaSn₃ + 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: ⇒ La₃Sn₅ formation?
- Li cycles with Sn in an ‘inert’ La₃Sn₅ matrix?
Formation Enthalpies of La-Sn Compounds

- Experiment suggests that LaSn is the most thermodynamically stable.
- Only LaSn₃, La₃Sn₅, La₅Sn₄ and La₅Sn₃ have been prepared as single crystals, not La₂Sn₃ and LaSn (ICSD database).
- Theoretical values for LaSn₃ and La₃Sn₅ consistent with experiment.
## Formation Enthalpies and LaSn\textsubscript{3} Capacities for Competing Reactions

<table>
<thead>
<tr>
<th>Reaction type</th>
<th>Reactions</th>
<th>Theor. Cap. (mAh/g)</th>
<th>$\Delta H$ (meV/Li)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Insertion</td>
<td>Li + LaSn\textsubscript{3} $\rightarrow$ LiLaSn\textsubscript{3}</td>
<td>54</td>
<td>864</td>
</tr>
<tr>
<td></td>
<td>12 Li + LaSn\textsubscript{3} $\rightarrow$ Li\textsubscript{12}LaSn\textsubscript{3}</td>
<td>650</td>
<td>3232</td>
</tr>
<tr>
<td>Displacement</td>
<td>66 Li + 5 LaSn\textsubscript{3} $\rightarrow$ 5 La + 3 Li\textsubscript{22}Sn\textsubscript{5}</td>
<td>715</td>
<td>-252</td>
</tr>
<tr>
<td></td>
<td>51 Li + 4 LaSn\textsubscript{3} $\rightarrow$ 4 La + 3 Li\textsubscript{17}Sn\textsubscript{4}</td>
<td>690</td>
<td>-275</td>
</tr>
<tr>
<td></td>
<td>88 Li + 15 LaSn\textsubscript{3} $\rightarrow$ 5 La\textsubscript{3}Sn\textsubscript{5} + 4 Li\textsubscript{22}Sn\textsubscript{5}</td>
<td>318</td>
<td>-368</td>
</tr>
<tr>
<td></td>
<td>17 Li + 3 LaSn\textsubscript{3} $\rightarrow$ La\textsubscript{3}Sn\textsubscript{5} + Li\textsubscript{17}Sn\textsubscript{4}</td>
<td>307</td>
<td>-395</td>
</tr>
</tbody>
</table>

- Theory predicts that La\textsubscript{3}Sn\textsubscript{5} formation is more favorable than La.
- Theory confirms recent experiment that Li\textsubscript{17}Sn\textsubscript{4} (Li\textsubscript{4.25}Sn) reflects the maximum uptake of Li by Sn, not previously reported Li\textsubscript{22}Sn\textsubscript{5} (Li\textsubscript{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.

Promising start – to be continued in FY2010.
Future Work - FY2009/FY2010

- Continue studies of electrodeposited Cu$_6$Sn$_5$ 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

- LaSn₃ project complete.
- High capacities (>600 mAh/g) achieved from composite Cu₆Sn₅/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.
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- David Howell