Developing High Capacity, Long Life anodes

Ali Abouimrane, (P.I)
Bo Liu, and Khalil Amine
Argonne National Laboratory
DOE merit review
May 14, 2012

Project ID ES020
Overview

**Timeline**
- Start - October 1\(^{st}\), 2009.
- Finish – September 2014
- 70% complete

**Budget**
- Total project funding: 1200K
  - FY12: 300K
  - FY11: 300K
  - FY10: 300K
  - FY09: 300K

**Barriers**
- Safety of the battery.
- Power density of the battery.
- Cycle & calendar life span of the battery.

**Partners**
- Z. Fang (University of Utah).
- FMC, Northwestern University.
Objectives

- Develop new advanced high energy anode materials with long life and improved safety for PHEV and EV applications.
- Develop a low cost synthesis methods to prepare high energy anodes
- Full structural and electrochemical characterizations of the prepared anode materials.
- Demonstrate the high capacity and cycle life of these anodes in half and full cell systems.
Approaches

- **MO-Sn\textsubscript{x}Co\textsubscript{y}C\textsubscript{z}** (MO=SiO, SiO\textsubscript{2}, SnO\textsubscript{2}, MoO\textsubscript{3}, GeO\textsubscript{2}) anode materials were selected for investigation as high energy anode based on the following criteria:
  - Sn\textsubscript{x}Co\textsubscript{y}C\textsubscript{z} alloys are known to provide a capacity of 400-500mAh/g for hundreds of cycles.
  - MO anodes are known to provide more than 1000 mAh/g with poor cycleability.
  - The formation of Sn\textsubscript{x}Co\textsubscript{y}C\textsubscript{z} and MO composite could lead to the increase in the capacity, reduce the amount of cobalt in the material and improve the cycleability since Sn\textsubscript{x}Co\textsubscript{y}C\textsubscript{z} can play a role of buffer against the MO volume expansion.
  - This anode system is more safer than the graphite and possess low potential in the range of 0.3-0.75V (expect high voltage cells when combined with high cathodes)
  - This anode system could offer high practical capacity and high 1\textsuperscript{st} cycle charge discharge efficiency
  - This anode system offers high packing density (up to 3 g/cc), much higher than graphite (1.1g/cc) (expect high volumetric density)
Milestones FY 11:
High capacity and long life anodes

- Prepare composite anode by mechanical alloying using metal (Co, Sn) carbon and oxides (MO). *(Completed)*

- Perform comparative studies between MO-Sn$_x$Co$_y$C$_z$ (MO=SiO, SiO$_2$, SnO$_2$, MoO$_3$, GeO$_2$) based on their electrochemical properties and cost. *(Completed)*

- Investigate structural rearrangement of these anode composite during the intercalation and de-intercalation of lithium. *(Completed)*

- Select promising candidates for further electrochemical characterization in full cell tests. *(On going)*

- Improve the 1$^{st}$ cycle charge discharge efficiency of promising anode. *(On going)*
Recent accomplishments and progress

- Prepared successfully (50 wt% SiO – 50 wt% Sn_{30}Co_{30}C_{40} ) composite using ultra-high energy ball milling equipment UHEM.

- Improved performance of (50 wt% SiO– 50 wt% Sn_{30}Co_{30}C_{40}) composite prepared by UHEM by 30% vs. traditional ball mills.

- Demonstrated high capacity and long cycle life of (50 wt% SiO – 50 wt% Sn_{30}Co_{30}C_{40} ) composite prepared by UHEM.

- Determined the structure of the (50 wt% SiO – 50 wt% Sn_{30}Co_{30}C_{40} ) composite prepared by UHEM using PDF.

- Initiated a full cell study using LiNi_{0.5}Mn_{0.5}O_{4} and 50 wt% SiO–50 wt% Sn_{30}Co_{30}C_{40} composite prepared by UHEM.
Densities of 50 wt% MO – 50 wt% Sn$_{30}$Co$_{30}$C$_{40}$ (MO= MoO$_3$, SnO$_2$, GeO$_2$, SiO$_2$, SiO)

<table>
<thead>
<tr>
<th>Material</th>
<th>Tap density g/cc</th>
<th>True density g/cc</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 wt% MO – 50 wt% Sn$<em>{30}$Co$</em>{30}$C$_{40}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MO = MoO$_3$</td>
<td>2.74</td>
<td>6.05</td>
</tr>
<tr>
<td>MO = SnO$_2$</td>
<td>3.02</td>
<td>7.13</td>
</tr>
<tr>
<td>MO = GeO$_2$</td>
<td>2.62</td>
<td>5.06</td>
</tr>
<tr>
<td>MO = SiO$_2$</td>
<td>1.43</td>
<td>3.58</td>
</tr>
<tr>
<td>MO = SiO</td>
<td>1.89</td>
<td>3.78</td>
</tr>
</tbody>
</table>

- Materials based on tin, molybdenum and germanium have the highest tap density.
- Materials based silicon and tin are the cheapest.
Voltage profile, capacity and cycleability of 50 wt% MO – 50 wt% Sn_{30}Co_{30}C_{40} (MO=MoO_{3}, GeO_{2}, SnO_{2}, SiO_{2}, SiO) and Sn_{30}Co_{30}C_{40}

- SiO-Sn_{30}Co_{30}C_{40} is the most promising in term of price, capacity, cycleability and voltage.
- SnCoC capacity varies with precursors (Co and Sn metals or CoSn_{2} alloy, electrode loading)
Scheme for ultra-high energy ball milling machine (UHEM)

- Custom-made planetary mill machine (rotation in 2 directions) that creates a very high centrifugal field, confining the particles firmly in the interstices of the ball mass was used. (~250 gr of the material can be prepared in 1 shot).

- Traditional ball mills, adopt stirred mills or vibration mills. Only few grams of material can be made.

SiO-SnCoC composite was prepared using both techniques for comparison study.
SEM Mapping

(a) SEM images and EDX elemental mapping of
(b) Si,
(c) O,
(d) Co,
(e) C,
(f) Sn

- Si (b) and Sn (f) exhibit similar distribution, especially in the yellow-circled areas.
- Sn and Si may formed a new alloy after high energy ball milling (UHEM).
Voltage profile of 50 wt% SiO–50 wt% Sn₃₀Co₃₀C₄₀

Charge-discharge curves of cells with UHEM anode cycled at rates of (a) 300 mA g⁻¹ (~C/3) and (b) 900 mA g⁻¹ (~1C)

- A Voltage ~ 0.3V higher than the graphite was observed.
- 1ˢᵗ cycle charge discharge efficiency ~65%.
**dQ/dV plot of 50 wt% SiO–50 wt% Sn\textsubscript{30}Co\textsubscript{30}C\textsubscript{40}**

- For SiO-SnCoC, an SEI layer appeared to form at 0.6 V to 0.3 during the first cycle discharge.
- During the charge, the 0.29 V peak correspond to delithiation of Li\textsubscript{x}Si alloy of SiO.
- The peak at 0.57 V might be related to the delithiation of Si-Sn alloy.
Cycle performance of 50 wt% SiO–50 wt% Sn<sub>30</sub>Co<sub>30</sub>C<sub>40</sub>

- Anode made by UHEM delivers a specific capacity of 900 mA h g<sup>-1</sup> at the rate of 300 mA g<sup>-1</sup>, much higher than that (~600 mA h g<sup>-1</sup>) of the anode made by SPEX at the same current.

- Anode made by UHEM exhibits excellent rate capability, over 700 mA h g<sup>-1</sup> at high rate 1C (900 mA g<sup>-1</sup>).

- Anode made by UHEM shows good stability and excellent cycle life (no capacity fade after 100 cycles).
Question: why 300 mAh/g difference between SPEX and UHEM milling samples?

1- Particle size:

<table>
<thead>
<tr>
<th>OAC</th>
<th>BET surface area (m²/g)</th>
<th>Particle size distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>UHEM</td>
<td>7.521</td>
<td>50% particle size &lt; ~2.5µm</td>
</tr>
<tr>
<td>SPEX</td>
<td>4.733</td>
<td>50% particle size &lt; ~13 µm</td>
</tr>
</tbody>
</table>

- Nanomaterials can decrease the (SEI) resistance and lead to higher specific capacities at high charge/discharge rates.

2- Materials structure:

sample made by UHEM shows high amount of CoSn₂ (CoSn₂ delivers more capacity than CoSn)*.

(*) J.J. Zhang et al., JES, 153 (A) A1466-A1471 (2006)
3-Short-range order structure: Pair distribution function

The $G(r)$ gives the probability of finding an atom at a given distance $r$ from another atom and can be considered as a bond length distribution.

XRD patterns only contain information about the long-range average structure.

PDF analysis has been successfully used to investigate short-range order in lithium-ion battery electrode materials.
PDF study of 50 wt% SiO–50 wt% Sn$_{30}$Co$_{30}$C$_{40}$

- 2.35 Å peak of SPEX-milled anode is present and weak.
- 2.35 Å peak of UHEM anode disappears.
- 3.42 Å peak of UHEM anode is strong.
- 3.42 Å peak didn’t exist in (SiO, Sn, Si or Sn$_{30}$Co$_{30}$C$_{40}$,).

- 3.42 Å peak is attributed to the Si-Sn bond of Si-Sn amorphous alloy.
- The intensity of the Si-Si peak at 2.35 Å decreased with the emergence of the 3.42 Å peak. So large amount of Si-Sn alloy is formed in UHEM, SiO/Sn and Si/Sn.
- For example Si$_{0.66}$Sn$_{0.34}$ prepared by sputtering method showed approximate 3000 mAh/g capacity (*)

(*) L. Y. Beaulieu et al., *JES*, **150** (2) A149-A156 (2003).
5V/SiO–50 wt% Sn_{30}Co_{30}C_{40} Full cell

- The anode was first lithiated using lithium metal anode as we have 30% 1\textsuperscript{st} cycle irreversibility. (rate is 45 mA/g)

- 4.3 V cell with LiNi_{0.5}Mn_{0.5}O_{4}.

- ~ 110 mAh/g in Full cell (capacity based on the cathode, cathode limited).

- Preliminary result shows good cycleability and good charge-discharge efficiency.
Summary

- MO-Sn$_x$Co$_y$C$_z$ (MO = SiO, SiO$_2$, SnO$_2$, MoO$_2$, GeO$_2$) systems were prepared by mechanical alloying using SPEX ball milling.

- MO-Sn$_x$Co$_y$C$_z$ system where (MO = SiO, SiO$_2$, SnO$_2$) are the most competitive system in term of cost.

- 50wt% SiO - 50wt% Sn$_{30}$Co$_{30}$C$_{40}$ system shows promising properties in terms of cost, tap density, capacity, cycleability and 1$^{st}$ cycle charge discharge efficiency.

- Improved electrochemical performance can be achieved by ultra high energy ball milling to obtain nanoparticles and new phase alloys.

- PDF study demonstrated the formation of Si-Sn amorphous alloy, which is the main reason of the improvement of electrochemical performance.
Future Works

⇒ Investigate of MO-$\text{Sn}_x\text{Co}_y\text{C}_z$ (MO = SiO) system in full cell configuration.
⇒ Explore alternative to Co such as Fe in the composite
⇒ Surface characterization of lithiated anode materials by XPS
⇒ Investigate the pulse-discharge and charge performance of designed cell based on MO-$\text{Sn}_x\text{Co}_y\text{C}_z$ (MO = SiO, SiO$_2$, SnO$_2$, MoO$_3$, GeO$_2$) system anode through hybrid pulse power characterization (HPPC test).
⇒ Understand the causes of the first cycle charge discharge irreversibility and try to reduce it.
Collaborations

• FMC corporation

• PJ. Chupas, and Y. Ren Advanced Photon Sources, Argonne

• Z. Fang University of Utah.