High Capacity Composite Carbon Anodes Fabricated by Autogenic Reactions

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**Annual Merit Review**

**DOE Vehicle Technologies Program**

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Overview

Timeline
- Start date: FY11
- End date: FY12
- Percent complete: 50%

Budget
- Total project funding: 100% DOE
- FY11: $300K
- FY12: $300K
- FY13: Discontinued

Barriers Addressed
- Cost
- Abuse tolerance limitations

Partners
- Co-investigators: M. Thackeray (Co-PI)
- Collaborators:
  - M. Ewen, Z. Mao (ConocoPhillips)
  - J. Ayala, F. Henry (Superior Graphite)
  - L. Curtiss, K. C. Lau (ANL, EFRC-CEES)
  - S. A. Deshmukh and S. Sankaranarayanan (ANL, EFRC-CEES)
Objective

- To evaluate spherically-shaped carbon anode materials, particularly when combined with lithium-alloying elements (e.g., Sn, Sb) to produce high-capacity carbon-metal composite anodes for HEVs, PHEVs and EVs, and to compare their electrochemical behavior with commercial carbon materials in collaboration with industry.
Milestone completed (FY12)

- Consolidated industrial collaborations for this project
- Prepared carbon samples and supplied samples to industrial partner for heat-treatment; prepared carbon-composite samples from Argonne’s carbon materials and from industrial products
- Evaluated the electrochemical properties of carbon-composite samples in lithium half cells
- Determined the chemical, physical and thermal properties of Argonne’s carbon-composite anodes and compared them to commercial carbon-composite materials

Note: This is an overall summary report of the project (FY11-FY13), which includes recent results from collaborative EFRC-supported research on these carbon materials, notably theoretical calculations and in-situ monitoring of decomposition and cooling reactions during synthesis, that were not part of the ABR project.
Approach

- Exploit autogenic reactions to prepare spherical carbon quickly, cost effectively and reliably
- Collaborate with industry to access high-temperature furnaces to increase the graphitic component in spherical carbon
- Increase the capacity of the carbon spheres (CSs) by combining them with lithium alloying elements to form carbon-composite anode materials
- Study and compare the electrochemical, chemical, physical and thermal properties of Argonne’s carbon-composite products with commercially available carbon materials
- Optimize processing conditions and evaluate the electrochemical properties of pristine and carbon-composite materials
Argonne’s autogenic reaction approach

**Abilities**
- 80 cc Cap.
- 2000 PSI
- 800 °C

**Advantages**
- Single step
- Reproducible
- Solvent- and catalyst free
- Produces pure products
- Proceeds at moderate temp
- Efficient & environmentally friendly

**Distinct Synthetic Approach**
In-situ X-ray scattering (16BM-D) to probe CSs synthesis

- The amorphous carbon moieties nucleates at ~ 350 °C, during cooling

**Courtesy: Chi-Kai Lin, ANL**
Polyethylene decomposes via a series of decomposition reactions, forming shorter chain hydrocarbon fragments.

- Leading to complete decomposition into carbon and releasing free hydrogen.
- Polymerization of dissociated carbon to form ‘amorphous hard carbon sphere’.
- Free hydrogen can combine to form hydrogen gas molecules.
- The ‘rumpled’ and ‘domed’ structures are evident even in small carbon nanoparticles.

*Courtesy: S. A. Deshmukh, S. Sankaranarayanan, ANL*
What is the structure and role of interfaces (inner and outer surfaces) in facilitating lithium intercalation and de-intercalation?

- Up to 30 nm (million atoms) at temperatures from 300-3000 K

Size-dependent structural evolution

- Topological ring defects (missing atoms)
- ‘Graphene-like’ edges
- Defects provide flexible multi-dimensional diffusion paths for Li ions

Courtesy: K. C. Lau and Larry Curtiss, ANL
Solid, dense, micron sized CSs with smooth surfaces can also be prepared from C_9H_{12}, naphthalene, hexane etc.

First cycle capacity loss ~60%, steady cycling for hundreds of cycles

As-prepared CSs (700°C) collapse during lithiation and delithiation
Morphology and electrochemistry of Li/CSs-2400°C cells

- Morphology of CSs is preserved after heat treatment to 2400 °C (still solid and dense)
- 25% first cycle capacity loss, sloping potential profile, stable capacity on cycling
- >99% coulombic efficiency, heat-treated CSs remains intact during cycling

Courtesy: CSs were heat treated to 2400 °C by Jorge Ayala and Francois Henry from Superior Graphite
Morphology and electrochemistry of Li/CSs-2800 °C cells

- Morphology of CSs is maintained at 2800 °C with some sintering of particles
- 15% first cycle capacity loss, several break-in cycles required
- >99% coulombic efficiency, stable capacity on cycling

Courtesy: CSs were heat treated to 2800 °C by Mark Ewen and Zhenhua Mao from ConocoPhillips
Increasing the capacity of CSs by SnO$_2$/Sb deposition

Sonication
SCP + Sn + Sb precursors in organic solvent $\rightarrow$ SnO$_2$/Sb@CSs nanoparticles

- CSs particles are thinly and uniformly coated by Sn/Sb precursors
- Heat treatment (at 500 °C/Ar) facilitated Sn product adherence on the CSs surface
Structural analysis of CSs (700 °C-top) and heated SnO$_2$/Sb coated CSs (Bottom)

- The powder X-ray diffraction pattern of sonochemically as-prepared SnO$_2$/Sb coated CSs shows the amorphous nature of the coated materials.
- After heating the as-prepared product to 500 °C/3h/Ar, crystalline body-centered tetragonal SnO$_2$ (broad peaks) and hexagonal Sb (sharp peaks) are identified.
- Energy dispersive X-ray analysis technique was further implemented to understand antimony’s sharp X-ray peaks.
Selected area energy dispersive X-ray analysis of heat-treated CSs-Sb/SnO$_2$ particles

- SEM indicates that SnO$_2$ nanoparticles are uniformly deposited on CSs surfaces
- Deposited Sb particles are clusters of ~400nm size, yielding sharp X-ray diffraction peaks
- The Si peak originated from the sample holder Si wafer

Courtesy: Dean Miller and Jianguo Wen, ANL
Transmission electron micrographs of heated CSs-Sb/SnO$_2$ composite

- Transmission electron micrographs shows <10nm SnO$_2$ nanoparticles, uniformly deposited on the CSs surfaces.
- Deposited nanoparticles shown in HR-TEM are indexed to tetragonal SnO$_2$ (CIF-154960) using inserted FFT pattern.
The first two discharge-charge voltage profiles of a Li vs SnO$_2$/Sb-CSs cell

(i=75 mA/g, C/5.5 rate, 1.5 and 0.01V)

- First cycle capacity loss is ~ 35%, which is significantly lower than the 60% obtained using a pure CSs electrode
- All components of the electrode, SnO$_2$/Sb and CSs are electrochemically active
The capacity vs cycle number plot of a Li vs SnO$_2$/Sb-CSs cell

- Deposition of 12 ± 2 wt % SnO$_2$/Sb nanoparticles on the surface of CSs delivered specific capacity to ~400 mAh/g at the ~C/5.5 rate
- Coulombic efficiency of the Li vs SnO$_2$/Sb-CSs cell is >98 %
Increasing the capacity of industrial carbon by sonochemical deposition of SnO$_2$ nanoparticles

- **Issue**
  Industrial graphite (ConocoPhillips G8) particles already have additional smooth surface carbon coating, which does not permit the deposition of SnO$_2$ nanoparticles sonochemically; eventually forming individual SnO$_2$ aggregates in the composite. As a result, a rapid decrease in capacity is observed during cycling.

- **Plan**
  To do surface activation of industrial graphite by pre-heat treatment in a reducing atmosphere for sonochemical deposition of SnO$_2$ nanoparticles

- **Sonochemical reaction**
  
  G8 graphite (heat-treated 600°C/6 hr under He/H$_2$) + Ethanol + SnCl$_2$ precursor

  \[
  \text{Sonication} \quad \downarrow \\
  \text{As-prepared composite, further heated to 500°C/2 hr/Ar}
  \]
Sonochemically deposited SnO$_2$ nanoparticles on the surface of activated graphite

- After pre-heat treatment to graphite in a reducing atmosphere, the graphite surface was activated and the sonochemical coating of SnO$_2$ nanoparticles is improved.
- X-ray diffraction pattern confirmed the presence of tetragonal SnO$_2$, as well as graphite.
The first two discharge-charge voltage profiles of a Li/industrial graphite-SnO$_2$ nanoparticle cell

- The first-cycle discharge and charge capacities of a surface activated G8 graphite sonochemically coated with SnO$_2$ composite electrode are 665 mAh/g and 427 mAh/g, respectively. (The first cycle irreversible capacity loss is ~36%)

- The discharge (0.8V) and charge (0.7V) plateaus indicate the presence of lithium alloying and de-alloying with the SnO$_2$ nanoparticles.
A stable reversible capacity of 400 mAh/g was obtained at the C/4 rate for 50 cycles, when 25 wt % SnO₂ nanoparticles were sonochemically deposited.

Comparatively, the capacity delivered by the surface activated G8 graphite alone is lower (306 mAh/g).
Summary

- Spherical carbon particles were prepared by autogenic reactions, maintaining their morphology after high temperature treatment with improved graphitic character.
- Spherical carbon behaves electrochemically like a hard carbon, delivering approximately 250 mAh/g when cycled between 1.5 V and 5 mV vs. Li\textsuperscript{0}. High temperature treatment at 2400 °C, under inert conditions, increases the graphitic character of the carbon spheres and significantly reduces the first cycle capacity loss from 60% (700 °C preparation) to 15% (CSs-HT/1h).
- The electrochemical capacity of the carbon spheres can be significantly increased (to 400 mAh/g) by decorating the surface with ~12 wt % SnO\textsubscript{2}/Sb nanoparticles.
- Using a similar surface coating technique, the capacity of surface activated industrial carbon/SnO\textsubscript{2} composite anodes were increased to a level well above the theoretical value for graphite (400 mAh/g).

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