High Capacity Composite Carbon Anodes

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Annual Merit Review
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Overview

Timeline
- Start date: FY11
- End date: FY14
- Percent complete: On-going project

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

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 (EFRC-CEES)
The objective of this project is 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.
Milestones (FY12)

- Consolidate industrial collaborations for this project

- Prepare carbon samples for industrial partner for heat-treatment; prepare carbon-composite samples from Argonne’s carbon materials and from industrial products

- Evaluate and optimize the electrochemical properties of carbon-composite samples in lithium half cells and full cells

- Determine the chemical, physical and thermal properties of Argonne’s carbon-composite anodes with commercial carbon-composite materials
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 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
Why Spherical Carbon Particles (SCPs) as an Anode?

- SCPs provide sloping voltage profile similar to hard carbon – safer than graphite
- SCPs offer the possibility of *smoothing the current distribution* at the carbon electrode surface during charge, thereby reducing the risk of lithium dendrites

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**Mesocarbon microbeads (MCMB)**


**Argonne’s carbon spheres (SCPs)**

Pol V.G. *Environmental Sci. & Tech.* 2010, 44, 4753
**Autogenic Synthesis of Spherical Carbon Particles**

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

- **Advantages**
  - Single step, efficient process
  - Solvent-, catalyst free
  - Produces pure products
  - Proceeds at moderate temp.

**Diagram Details**

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

**Diagram Elements**

- Pressure gauge
- Pressure release valve
- Inert gas inlet/outlet
- Filter
- Heater Assembly
- Thermocouple
- Collar
- Baseplate
- Support rod

**Process Flow**

- **HEAT** → **COOL**

  - Precursor(s)
  - Critical Phase
  - Product
‘Upcycling’ of Carbon Waste

- Solid, dense, micron sized spherical carbon particles with smooth surfaces
- Can also be prepared from C₉H₁₂, Naphthalene, hexane, ethanol etc.

Industrial implications
Electrochemistry of Li/SCP Cells

- First cycle capacity loss ~60%, steady cycling for hundreds of cycles
- As-prepared SCPs (700°C) collapse during lithiation and delithiation

SCP:acetylene black: PVDF ratio = 85:8:7
1.2M LiPF$_6$ in EC:DMC

~1C rate
Morphology of SCPs is preserved after heat treatment (still solid and dense)
Graphitic order is improved in SCP-HT24 particles

Jorge Ayala and Francois Henry
Electrochemistry of Li/SCP-2400 °C Cells

- 25% first cycle capacity loss, sloping potential profile, steady cycling
- >99% coulombic efficiency, heat-treated SCPs remain intact during cycling
High Temperature Treatment of SCPs
(2800 °C/1h/Ar)

- Morphology of SCPs is maintained at 2800 °C
- Dense, solid particles with smooth surfaces
- Sintering of particles is observed
Electrochemistry of Li/SCP-2800°C Cells

- 15% first cycle capacity loss, several break in cycles required
- >99% coulombic efficiency, steady cycling
No significant changes in the spherical shape of SCP-2400 °C particles (200 cycles)

Local strain induced and graphitic character decreases within the SCPs during electrochemical cycling
A Comparison: SCP vs. MCMB

Raman Spectra

- ID/IG
  - MCMB: 0.12
  - SCP: 0.35

Electrochemical performance

- Initial several break in cycles were required for both types of carbon
- SCPs behave like a hard carbon unlike the graphitic character of MCMBs
Li-Ion Full Cell: SCP/High Capacity LMR-NMC
(LMR-NMC = 0.5Li$_2$MnO$_3$•0.5LiNi$_{0.44}$Mn$_{0.31}$Co$_{0.25}$O$_2$)

- First-cycle capacity loss = 28% (cell balancing is required)
- Specific capacity of cathode: ~160 mAh/g

Courtesy: Donghan Kim, ANL
SCP electrodes generate less heat than natural graphite (NG) on reaction with the electrolyte between 100-200 °C.
Heated SCPs are significantly more crystalline than the as-prepared spheres, as reflected by an increase in the (002) XRD peak intensity.

A decrease in the ID/IG ratio (Raman data) confirms the increase in the graphitic character of the carbon spheres.
Increasing the capacity of SCP by SnO$_2$ deposition

Sonication
SCP-2400 °C + Sn precursor in organic solvent $\rightarrow$ SnO$_2$@SCP nanoparticles

- SCPs are thinly and uniformly coated (elemental mapping) by Sn precursor
- Heat treatment (500 °C/Ar) turns Sn precursor into <10 nm SnO$_2$ crystallites
Capacity vs Cycle No. Plot: Li/SnO$_2$-SCP(2400 °C) Cell

- SnO$_2$-coated SCP electrodes deliver significantly higher capacity than pure SCPs (340 mAh/g at a C/2.7 rate vs. ~250 mAh/g for SCP-2400 °C)
- Very stable cycling
- Implications for further improvement (Sn coatings) and industry carbons.
Metallic Sn nanoparticles were successfully decorated on the surface of industrial graphite particles. The presence and uniform distribution of Sn was confirmed by XRD, EDS and elemental X-ray dot mapping.
Electrochemical data of industry graphite and C₆/Sn

- Industry graphite intercalates lithium below 0.2 V, while the Sn component provides additional capacity by alloying with Sn at ∼0.4 V vs. Li⁰.
- Work is in progress to stabilize the cycling capacity of graphite/Sn composite electrodes (cf. SCP/Sn) – e.g., manipulating sonication process to improve binding of Sn to graphite.

- At moderate rate (∼C/3), the graphite/Sn composite electrode initially provides higher capacity than bare graphite (∼10 cycles)
Future Work - FY2012/FY2013

- Optimize autogenic reaction parameters to improve electrochemical capacity of spherical carbon particles and other rounded shapes.

- Fabricate smaller carbon spheres (<1 µm).

- Further increase the electrochemical capacity of the carbon spheres by combining the spheres with a lithium-alloying component (Si, Sn and Sb), e.g., by sonication.

- Extend processing studies to fabricate high-capacity carbon-composite anode materials using commercially available carbon products.

- Extend electrochemical studies to include full cell evaluations.
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. Li⁰. 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% (SCP-HT/1h).
- Higher heat treatment (2800 °C) does not significantly increase the capacity of the carbon spheres.
- The electrochemical capacity of the carbon spheres can be significantly increased by decorating the surface with ~10 wt.% Sn nanoparticles.
- Very stable cycling capacity is achieved.
- Efforts to increase the anode capacity of industrial carbon/Sn composites well above the theoretical value for graphite using the same surface coating techniques are underway.

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