Argonne NATIONAL LABORATORY

High Capacity Composite Carbon Anodes

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Annual Merit Review
DOE Vehicle Technologies Program

Arlington, VA
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ES114

Vehicle Technologies Program

U.S. DEPARTMENT OF ENERGY

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)

Objective

- 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

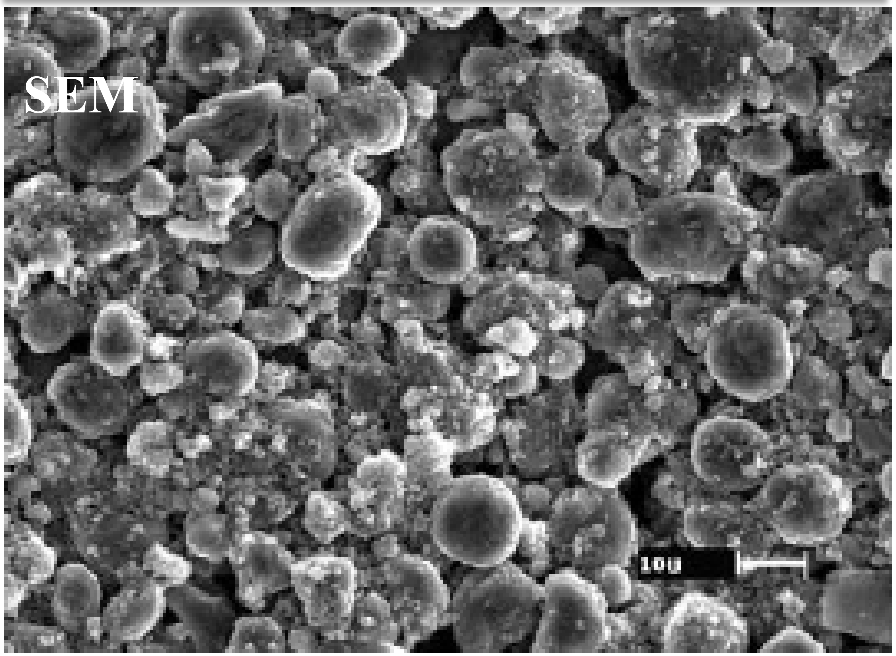
Approach

- 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?

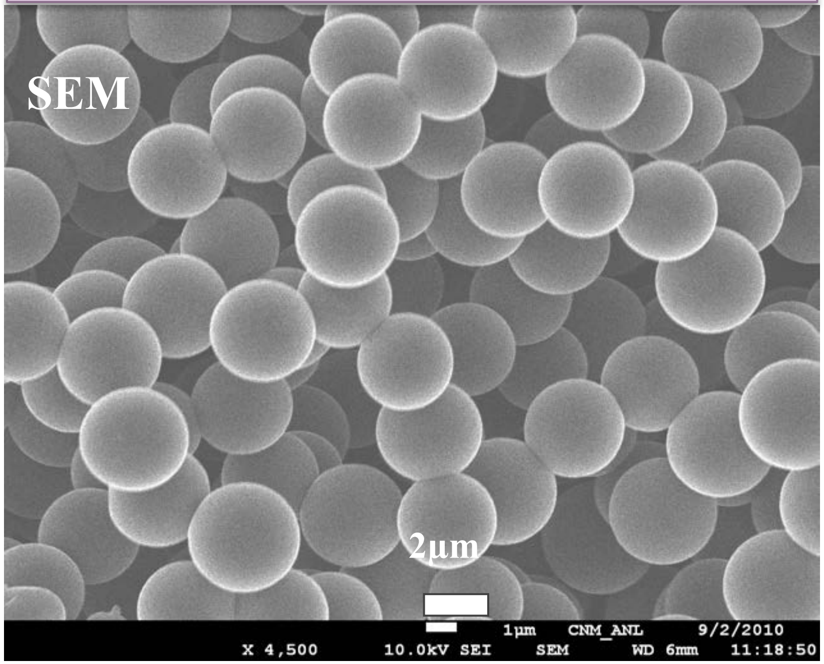
- SCPs provide sloping voltage profile similar to hard carbon – safer than graphite
- SCPs offer the possibility of *smoothing the current distribution* at the carbon electrode surface during charge, thereby reducing the risk of lithium dendrites

Mesocarbon microbeads (MCMB)



Liu H.K. *Electrochem. Solid State Lett*. 7, A250, 2004

Argonne's carbon spheres (SCPs)



Pol V.G. *Environmental Sci. & Tech.* 2010, 44, 4753

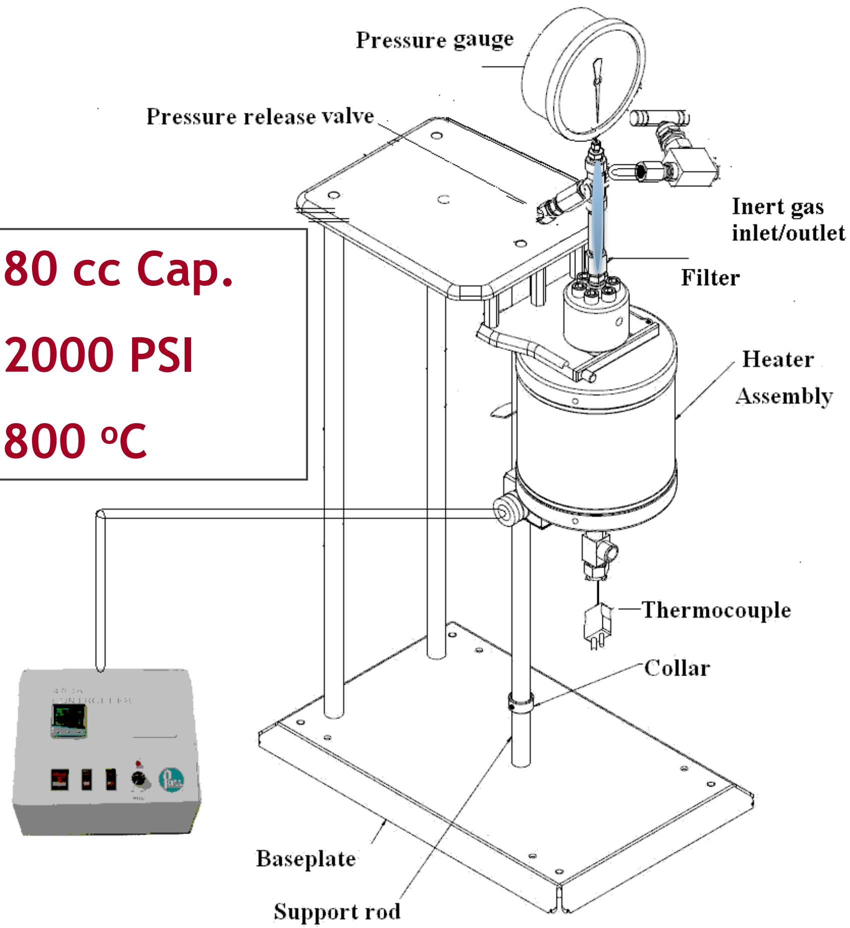
Autogenic Synthesis of Spherical Carbon Particles

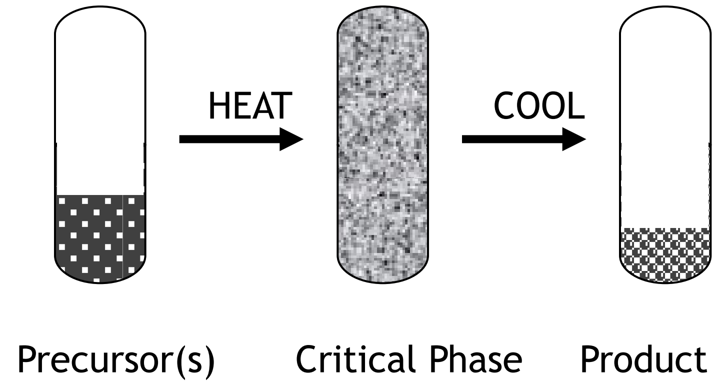
Autogenic Reactions: Self-generating reactions that occur within an enclosed vessel, typically at high pressure and temperature

80 cc Cap.

2000 PSI

800 ^{o}C





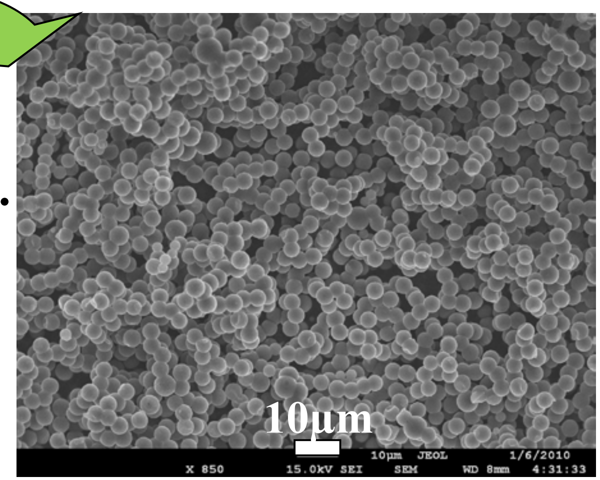
Advantages

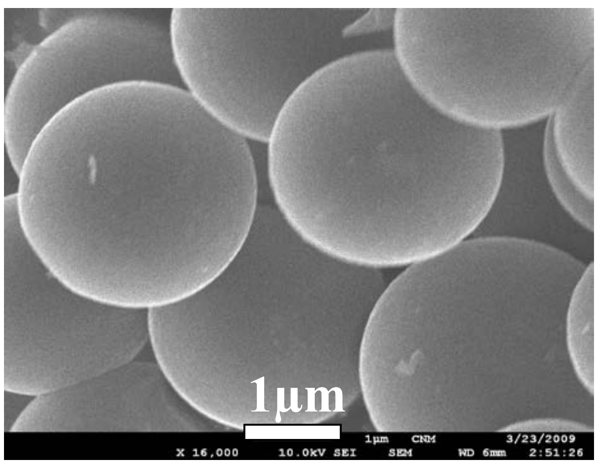
- Single step, efficient process
- Solvent-, catalyst free
- Produces pure products
- Proceeds at moderate temp.

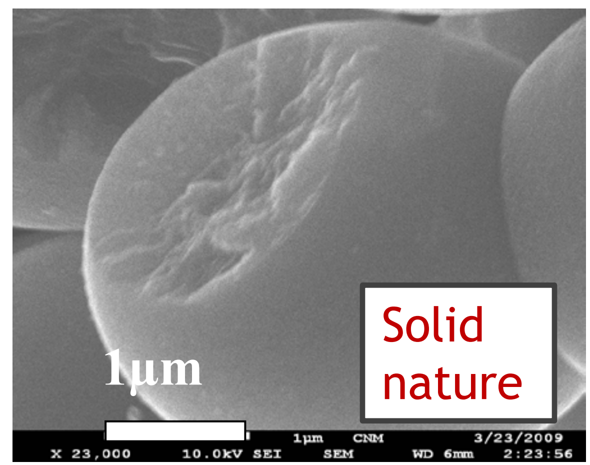
‘Upcycling’ of Carbon Waste

700 ^{0}C/1min.

490 PSI



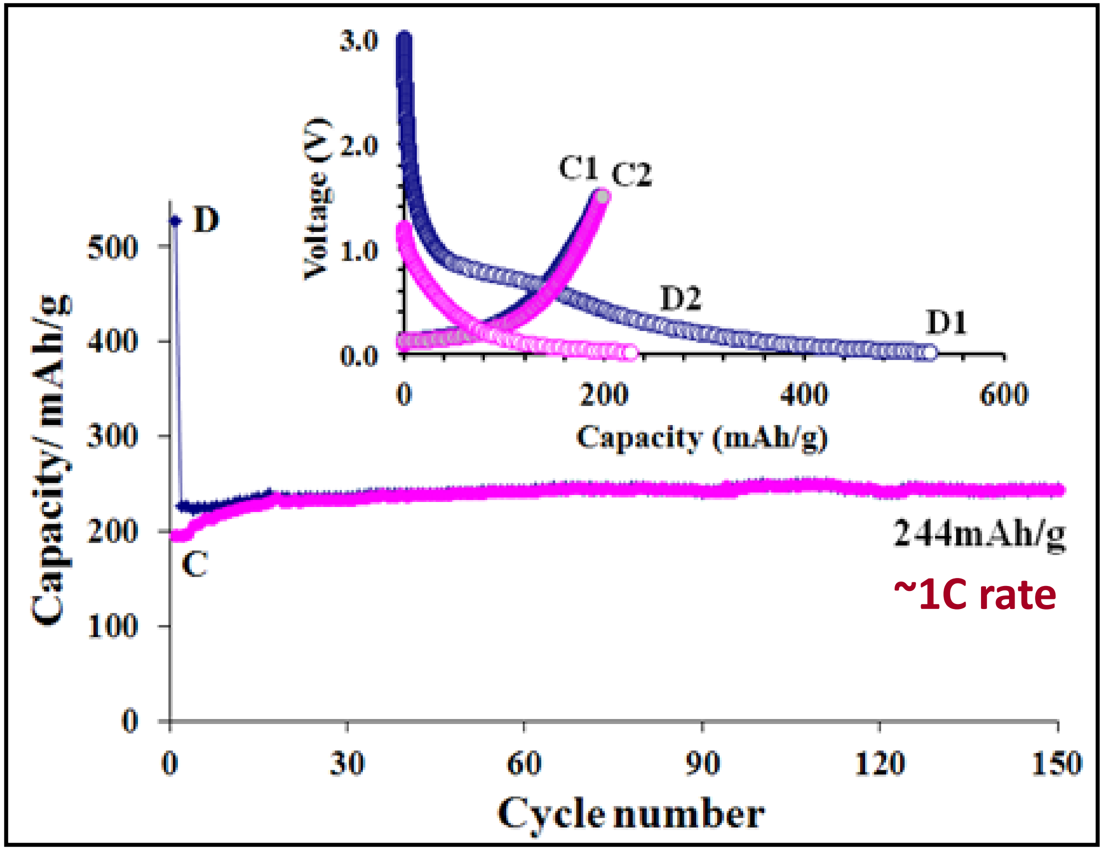




- Solid, dense, micron sized spherical carbon particles with smooth surfaces
- Can also be prepared from C_9H_{12}, Naphthalene, hexane, ethanol etc.

Industrial implications

Electrochemistry of Li/SCP Cells



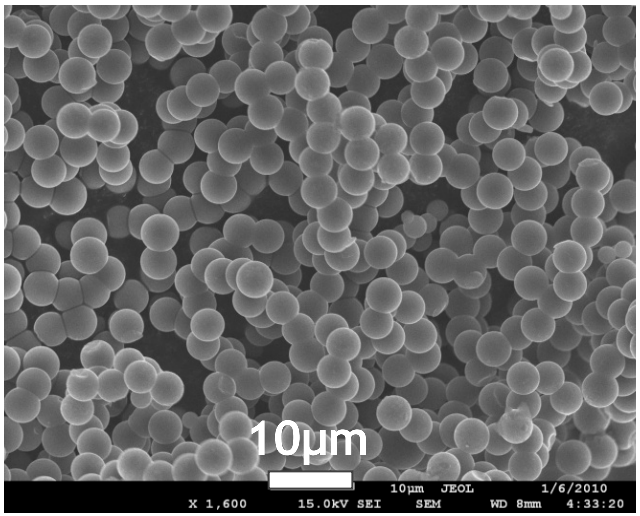
SCP:acetylene black: PVDF ratio = 85:8:7

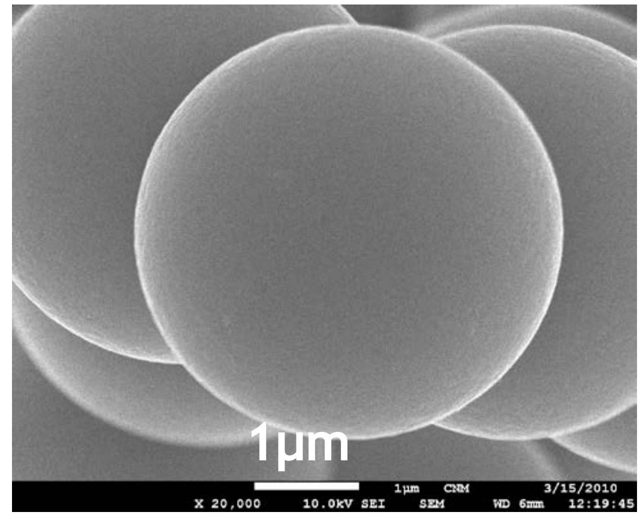
1.2M $LiPF_6$ in EC:DMC

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

High Temperature Treatment of SCPs

(2400 ^{o}C/1h/Ar)



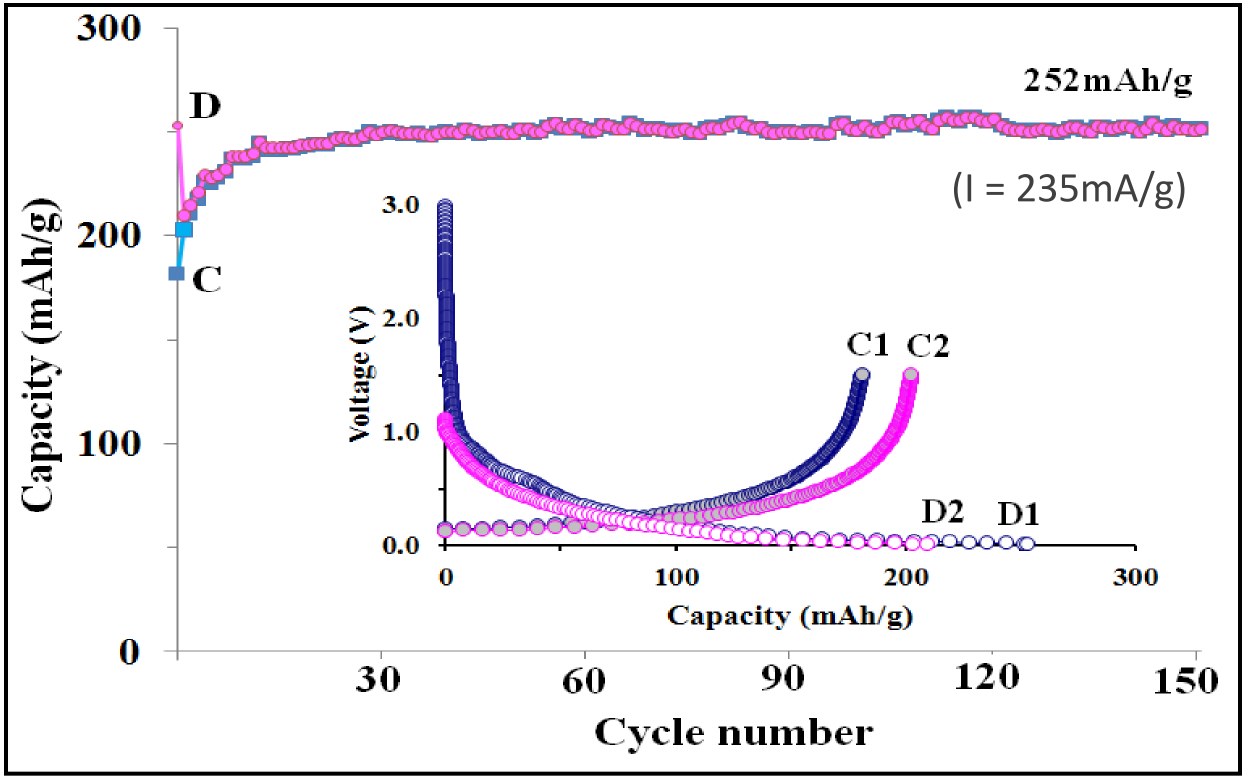


- Morphology of SCPs is preserved after heat treatment (still solid and dense)
- Graphitic order is improved in SCP-HT24 particles

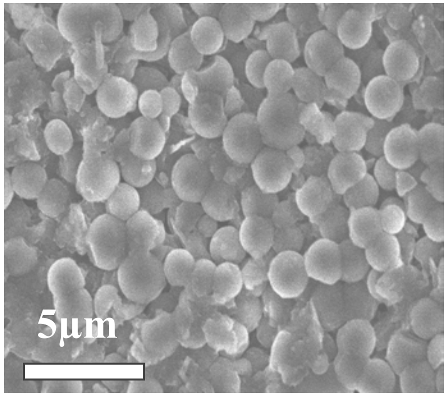
Jorge Ayala and
Francois Henry

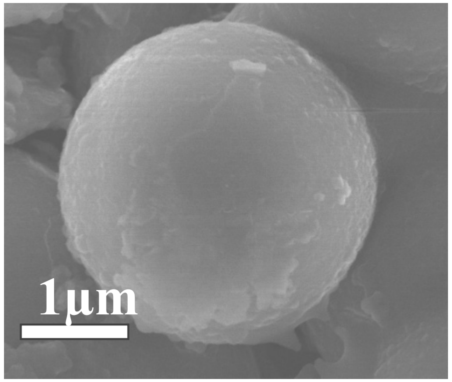
SUPERIOR GRAPHITE

Electrochemistry of Li/SCP-2400 °C Cells



SEM
cycled electrode

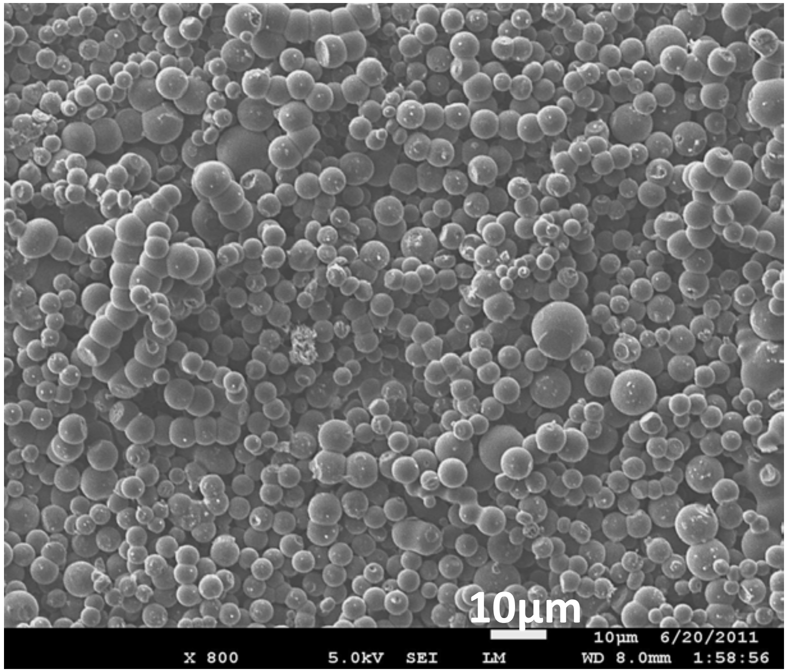


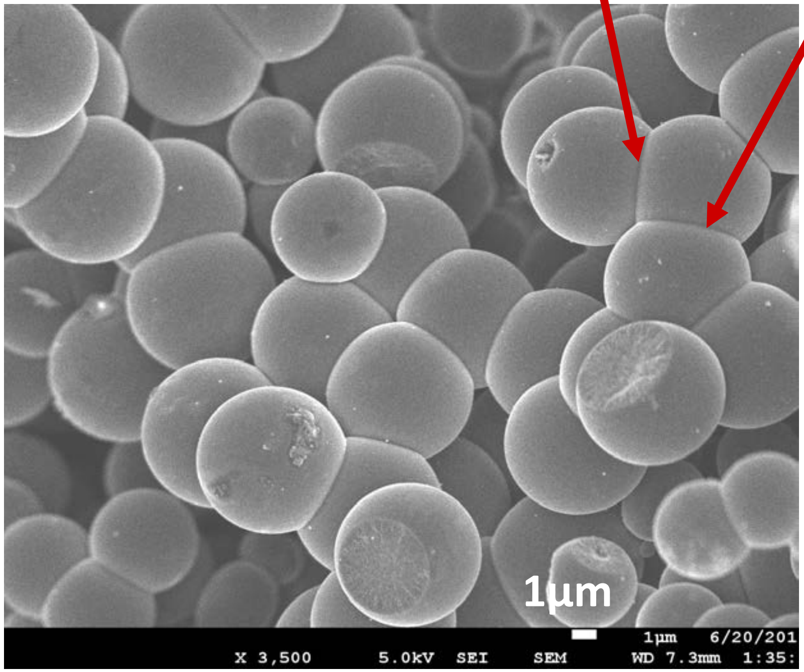


- 25% first cycle capacity loss, sloping potential profile, steady cycling
- >99% coulombic efficiency , heat-treated SCPs remain intact during cycling

High Temperature Treatment of SCPs
(2800 ^{o}C/1h/Ar)

Particle sintering



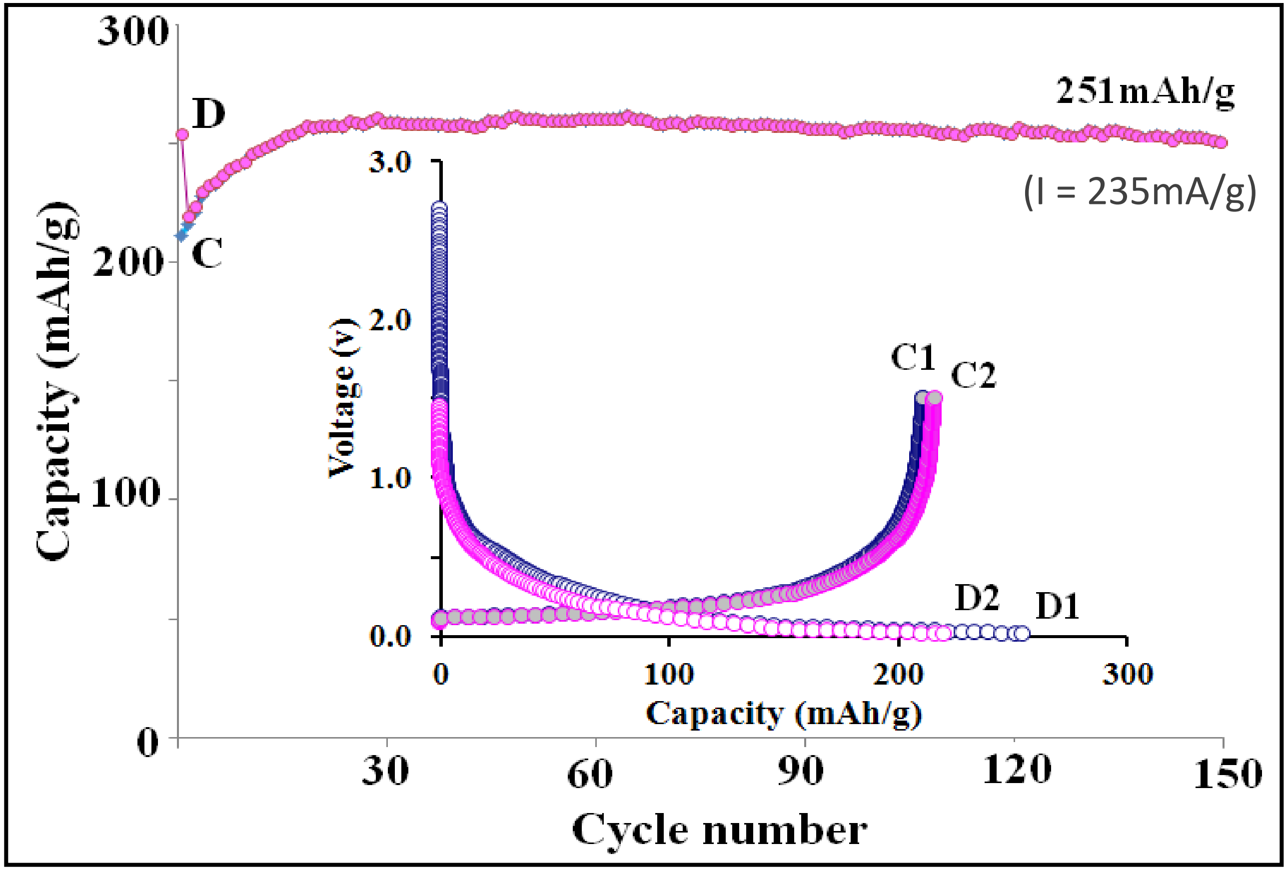


- Morphology of SCPs is maintained at 2800 ^{o}C
- Dense, solid particles with smooth surfaces
- Sintering of particles is observed

Mark Ewen and
Zhenhua Mao

ConocoPhillips

Electrochemistry of Li/SCP-2800°C Cells



- 15% first cycle capacity loss, several break in cycles required
- >99% coulombic efficiency, steady cycling

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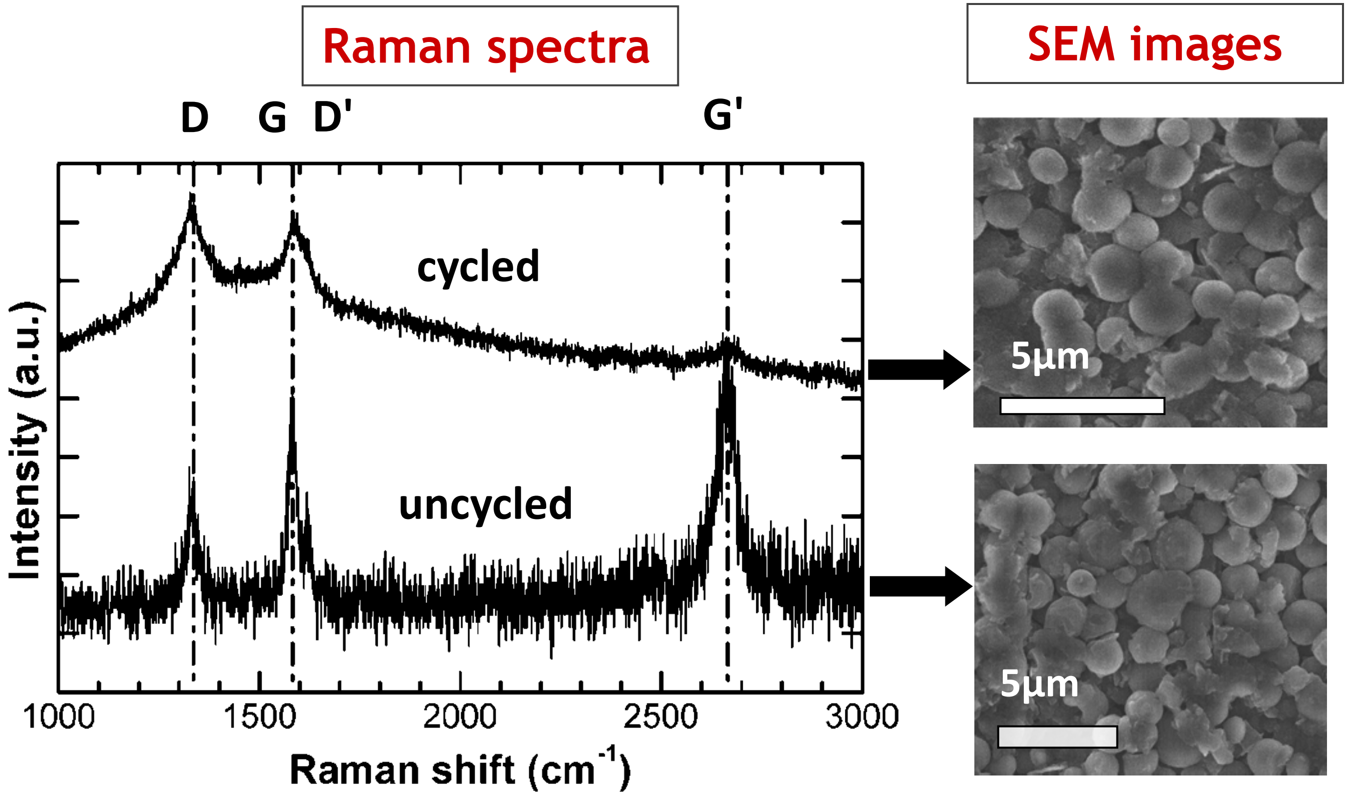
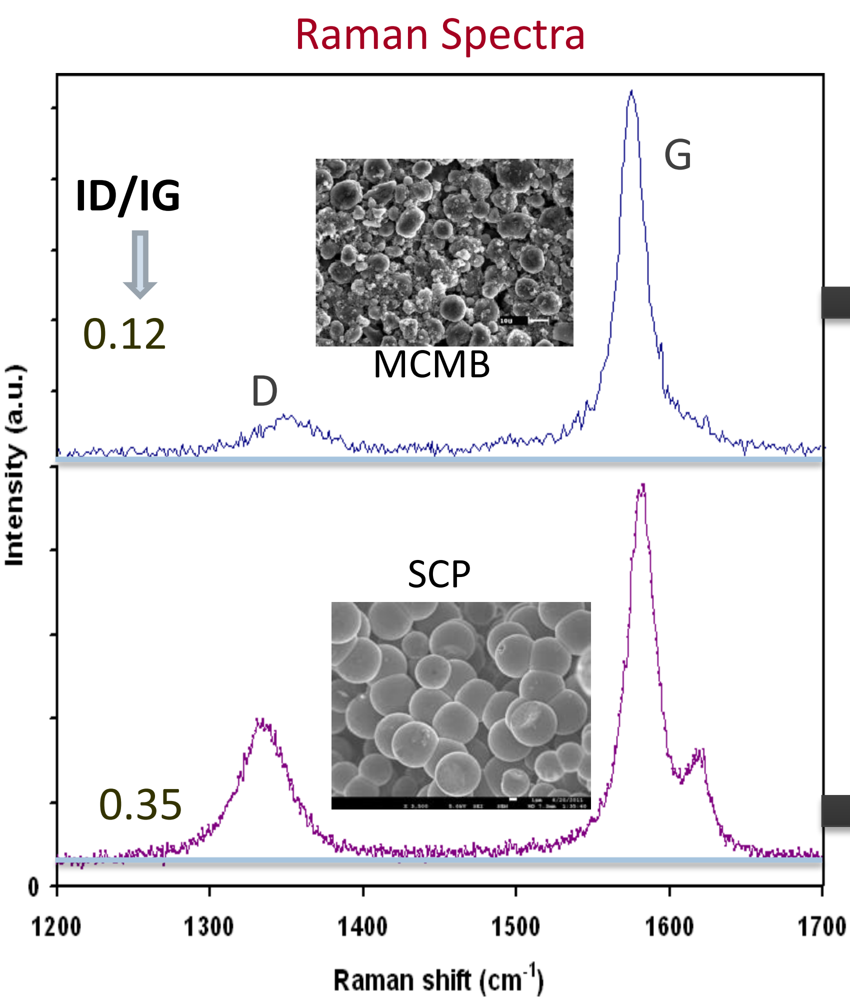
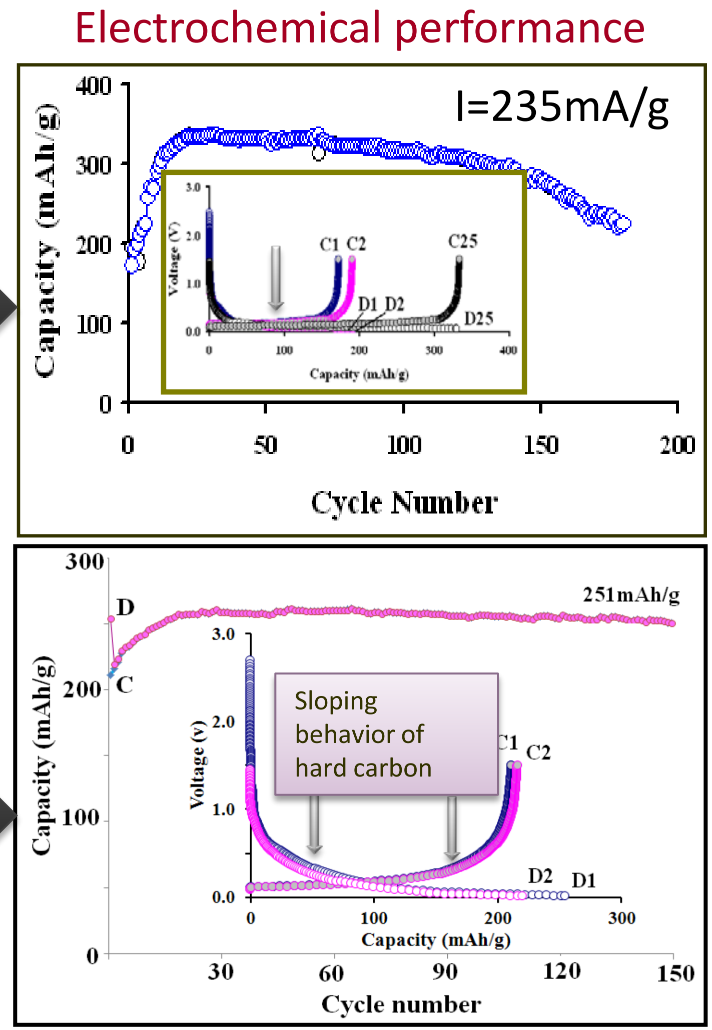
Structural and Morphological Studies – Cycled Electrodes



- No significant changes in the spherical shape of SCP-2400 ^{o}C particles (200 cycles)
- Local strain induced and graphitic character decreases within the SCPs during electrochemical cycling

A Comparison: SCP vs. MCMB

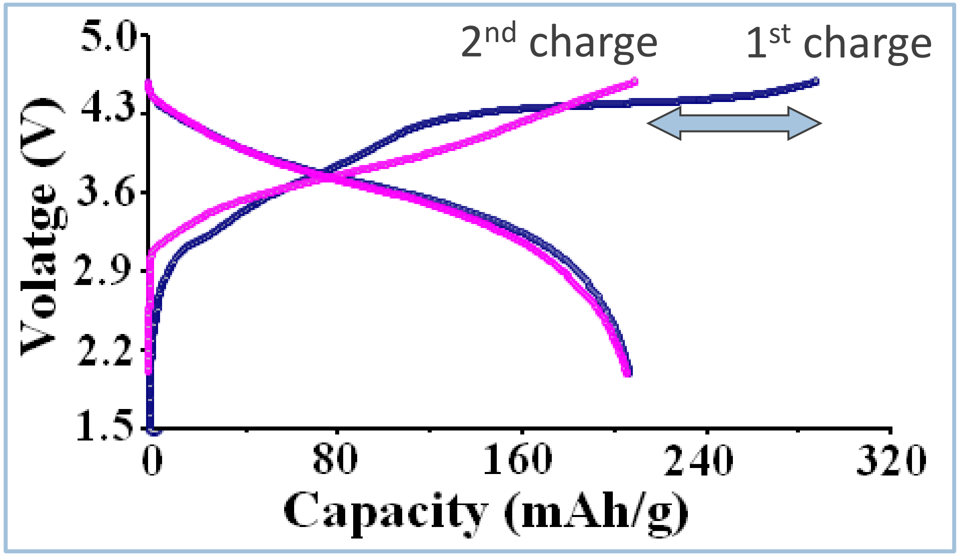


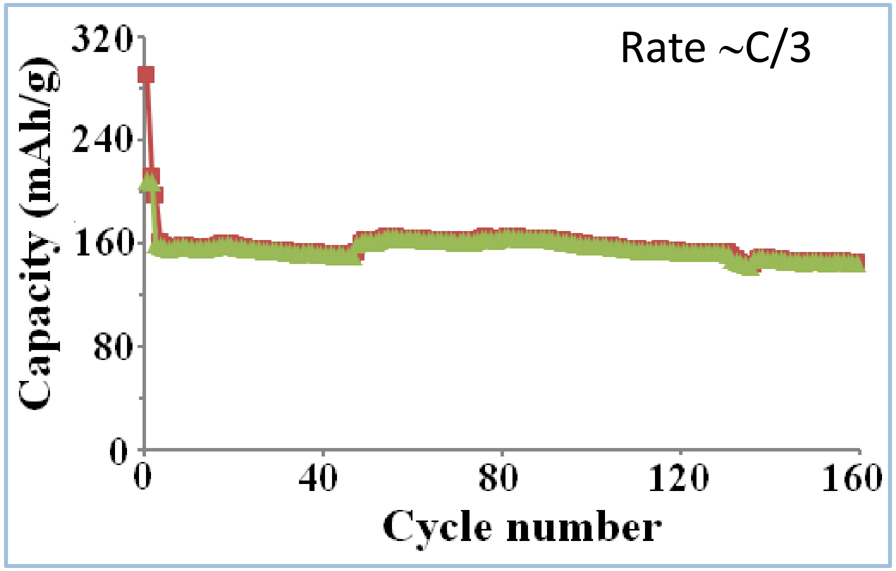


- Initial several break in cycles were required for both types of carbon
- SCPs behave like a hard carbon unlike the graphitic character of MCMBs

Li-Ion Full Cell: SCP/High Capacity LMR-NMC

(LMR-NMC = $0.5Li_2MnO_3 \bullet 0.5LiNi_{0.44}Mn_{0.31}Co_{0.25}O_2$)

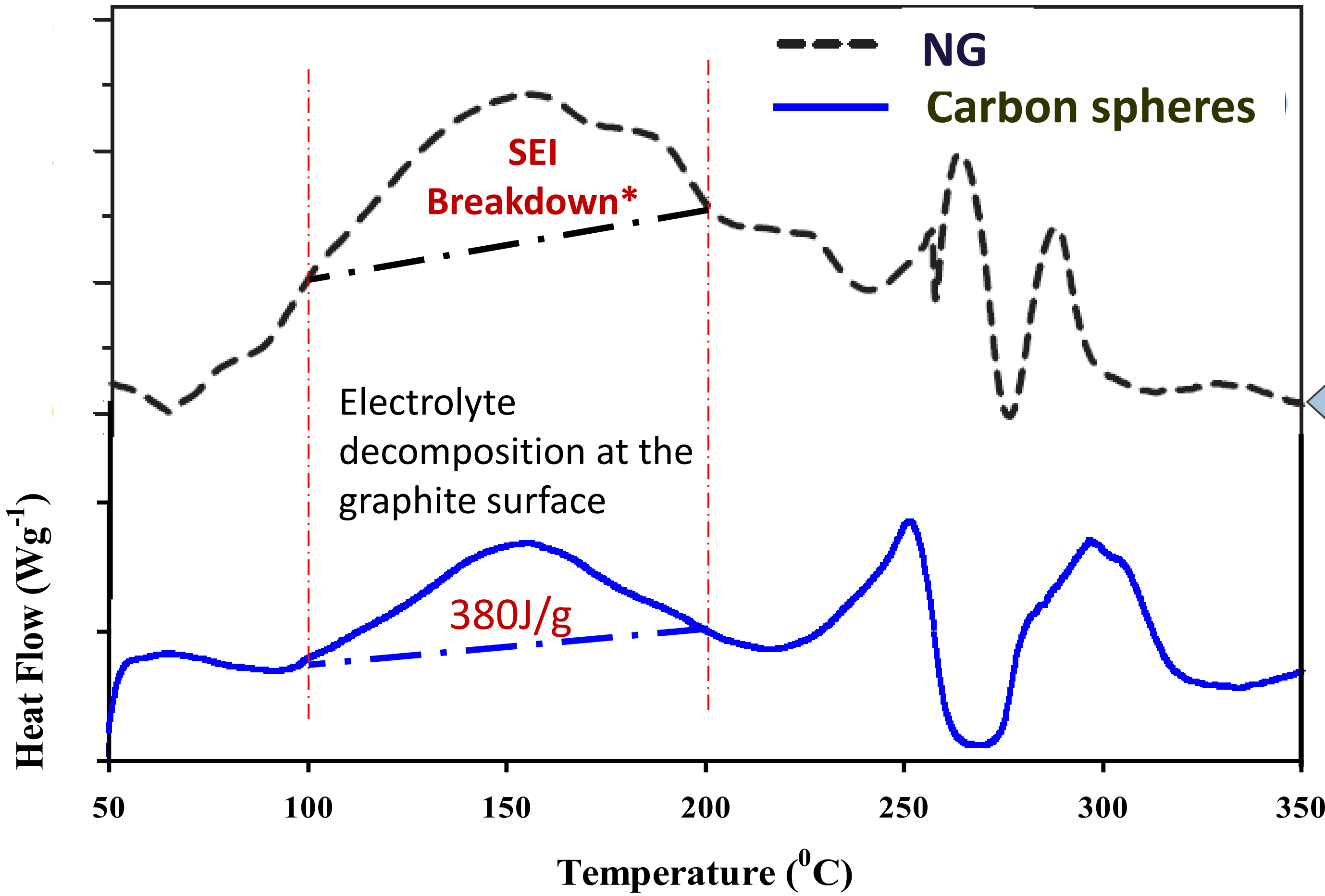




- First-cycle capacity loss = 28% (cell balancing is required)
- Specific capacity of cathode: ~160 mAh/g

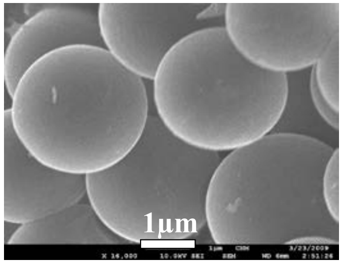
Courtesy: Donghan Kim, ANL

Heat generation during SEI breakdown – DSC data



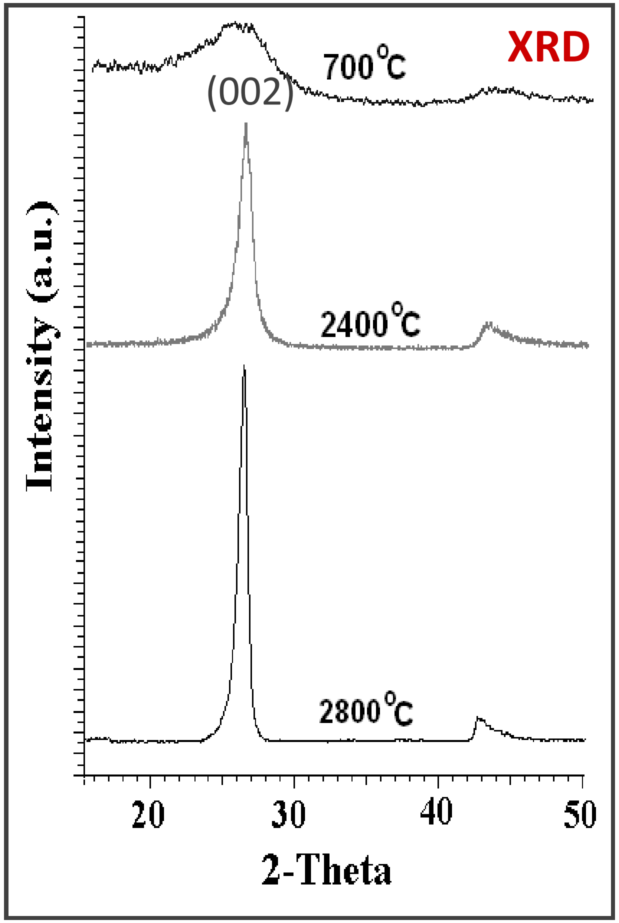
*1960 J/g reported for flaky graphite
(ANL Report-03/16 2003)

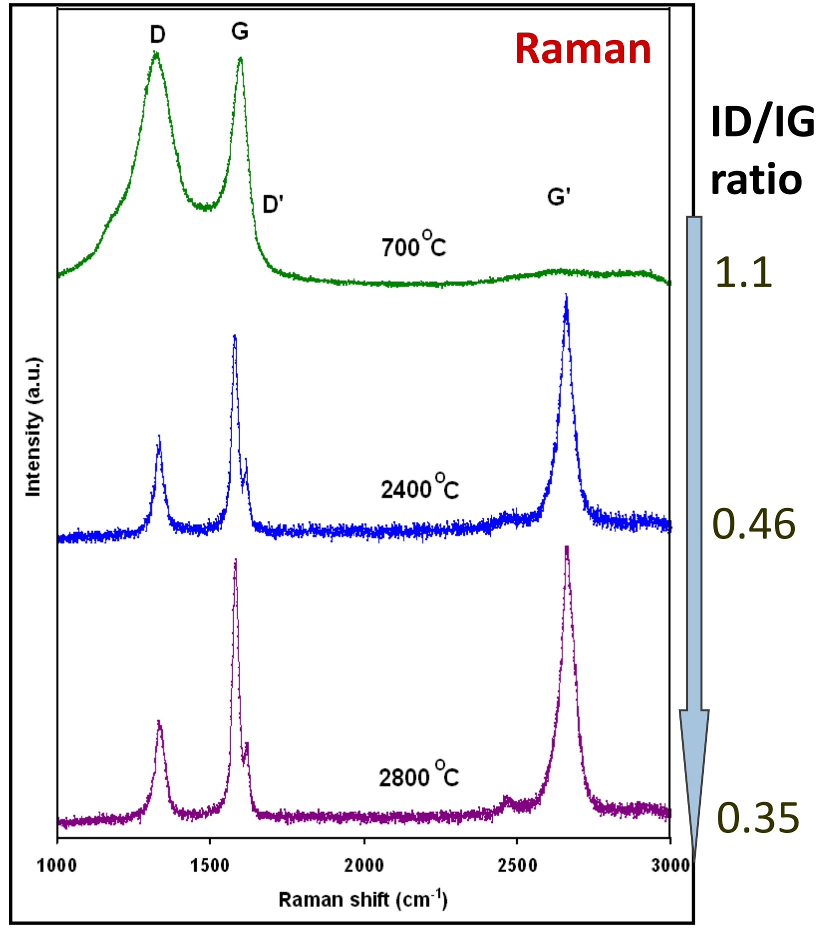
Lee, et al. Adv. Mater. 22, 2172 (2010)



- SCP electrodes generate less heat than natural graphite (NG) on reaction with the electrolyte between 100-200 °C.

Structural evolution of carbon spheres



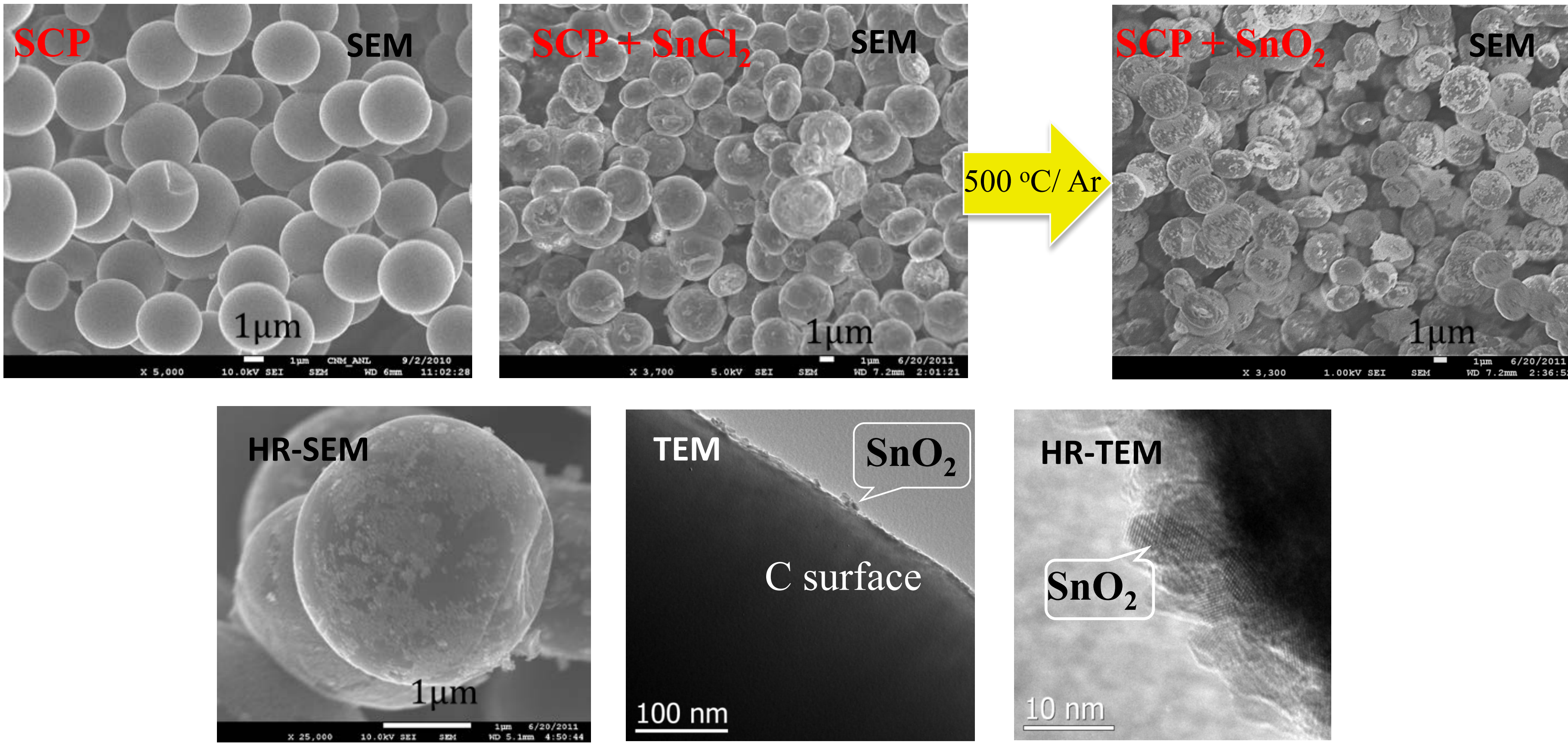


- Heated SCPs are significantly more crystalline than the as-prepared spheres, as reflected by an increase in the (002) XRD peak intensity
- A decrease in the ID/IG ratio (Raman data) confirms the increase in the graphitic character of the carbon spheres

Increasing the capacity of SCP by SnO_2 deposition

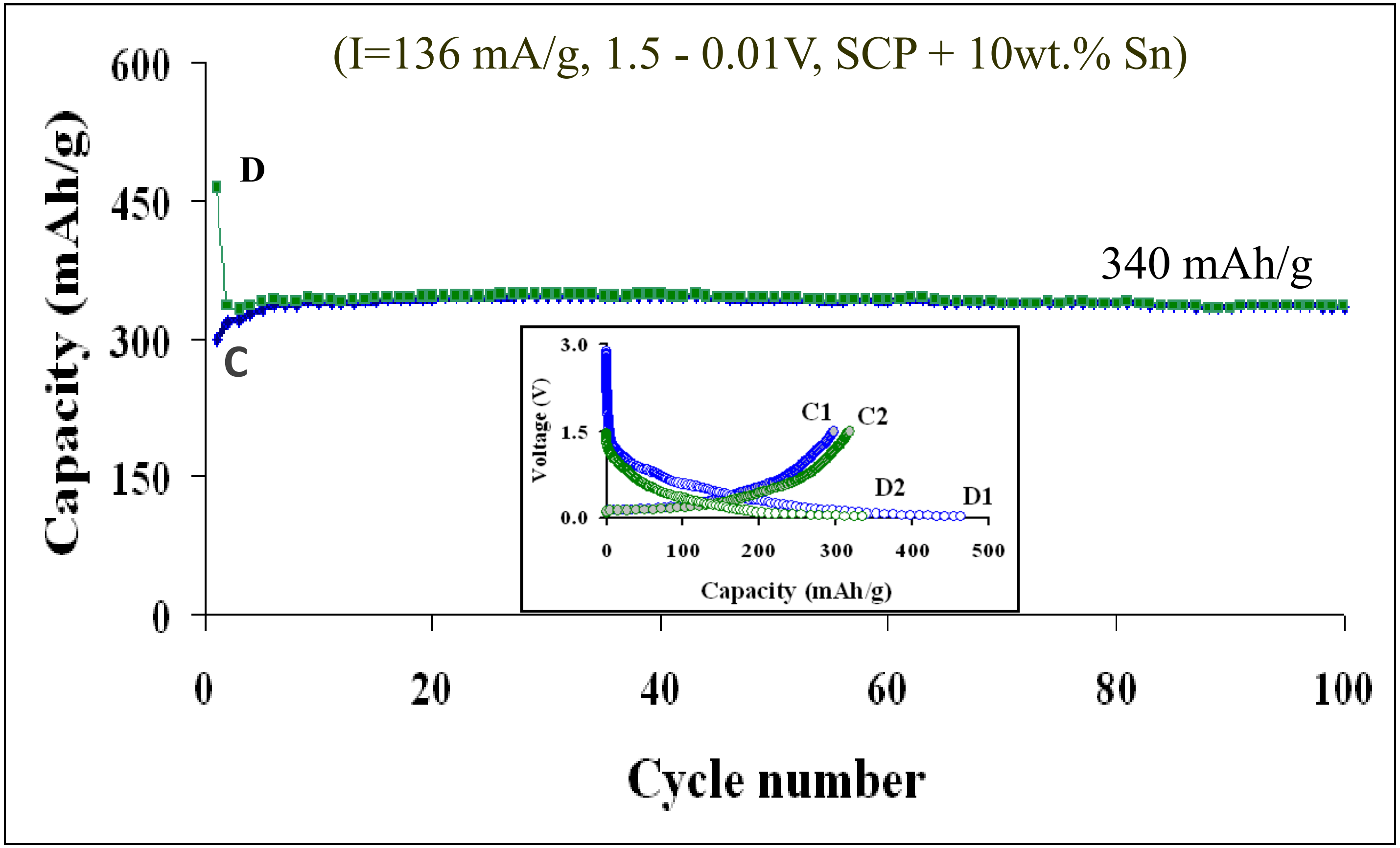
Sonication

SCP-2400 °C + Sn precursor in organic solvent)))))) → 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

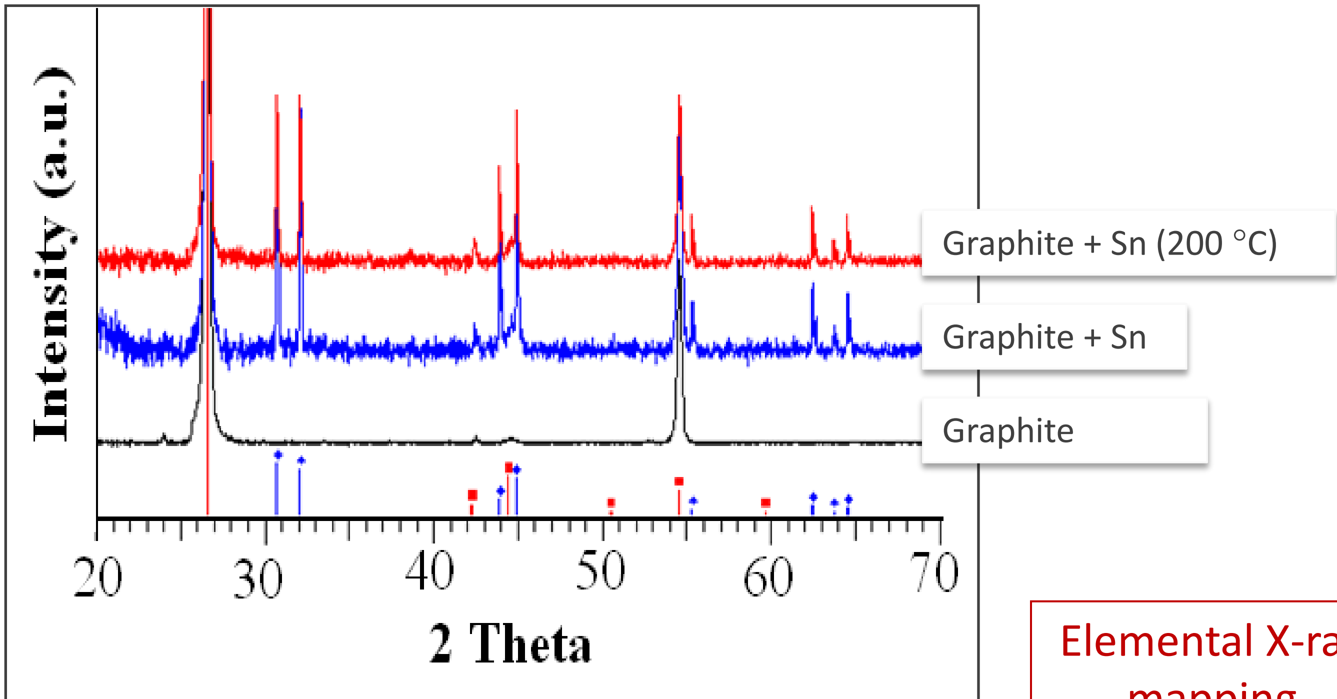


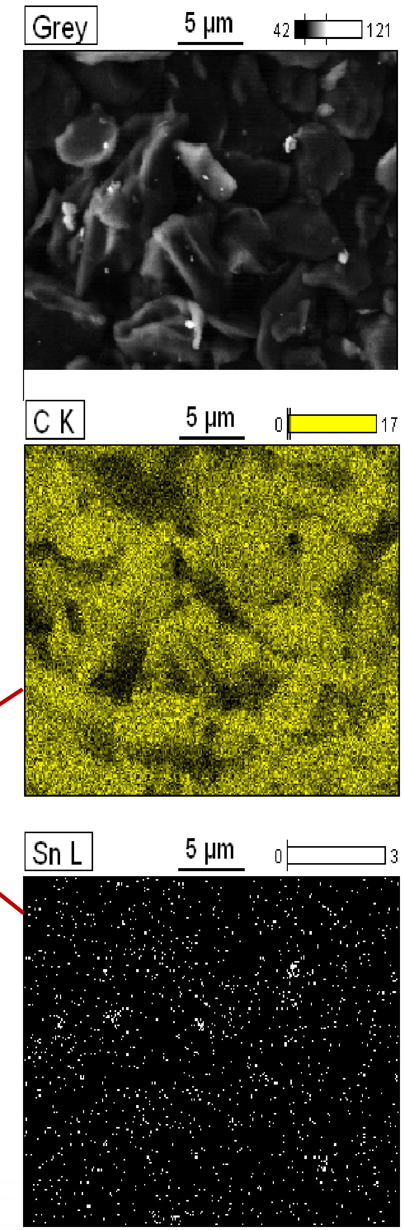
- SnO_2-coated SCP electrodes deliver significantly higher capacity than pure SCPs (340 mAh/g at a C/2.7 rate vs. ~250 mAh/g for SCP-2400 °C)
- Very stable cycling
- Implications for further improvement (Sn coatings) and industry carbons.

Industry Graphite/Sn Composite Anodes

Source: ConocoPhillips

XRD patterns: C_6 + tetragonal Sn

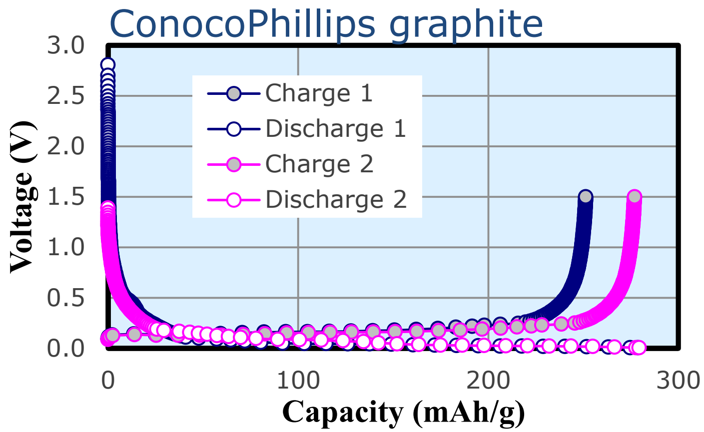


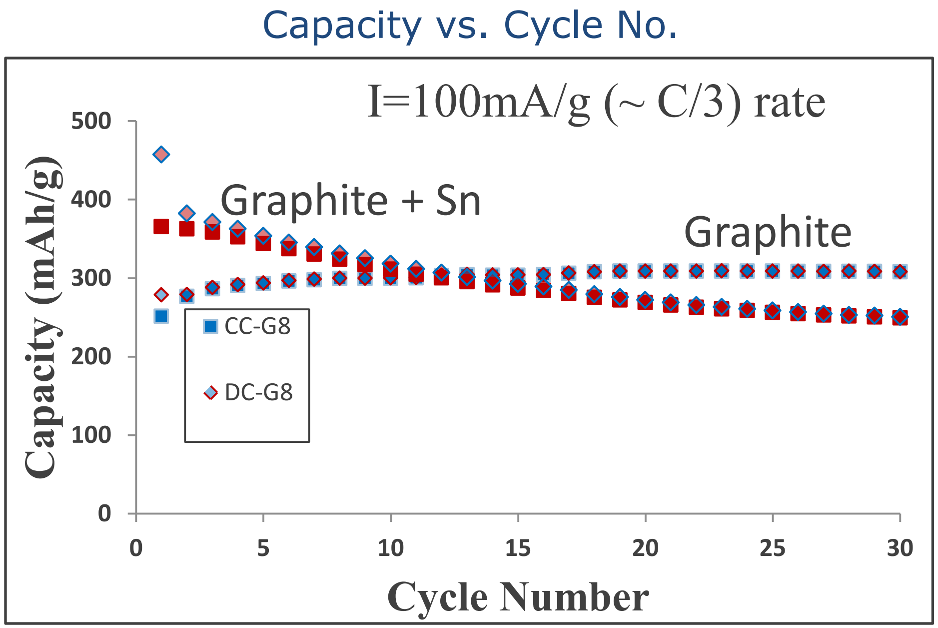


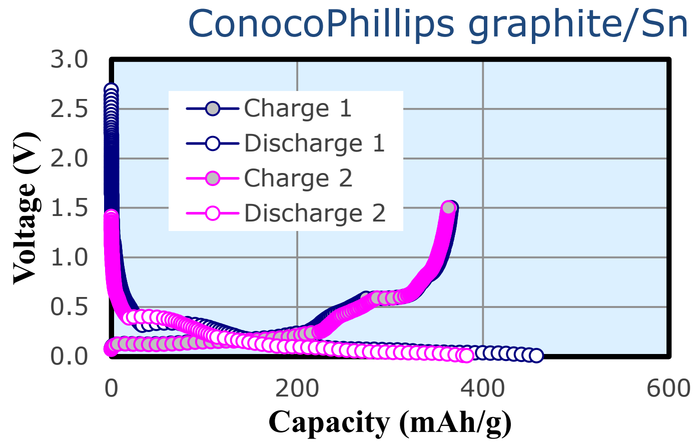
Elemental X-ray mapping

- 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 C_6/Sn







- At moderate rate (~C/3), the graphite/Sn composite electrode initially provides higher capacity than bare graphite (~10 cycles)

- Industry graphite intercalates lithium below 0.2 V, while the Sn component provides additional capacity by alloying with Sn at ~0.4 V vs. Li^0.
- 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

Future Work - FY2012/FY2013

- Optimize autogenic reaction parameters to improve electrochemical capacity of spherical carbon particles and other rounded shapes
- Fabricate smaller carbon spheres (<1μm)
- 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. Li^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% (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.

Acknowledgements

Support for this work from Peter Faguy and David Howell of DOE-EERE, Office of Vehicle Technologies, is gratefully acknowledged. Superior Graphite and ConocoPhillips are thanked for the high-temperature treatment of the carbon spheres and for providing graphite samples.