High Capacity Composite Carbon Anodes Fabricated by Autogenic Reactions

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Annual Merit Review
DOE Vehicle Technologies Program

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Vehicle Technologies Program

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

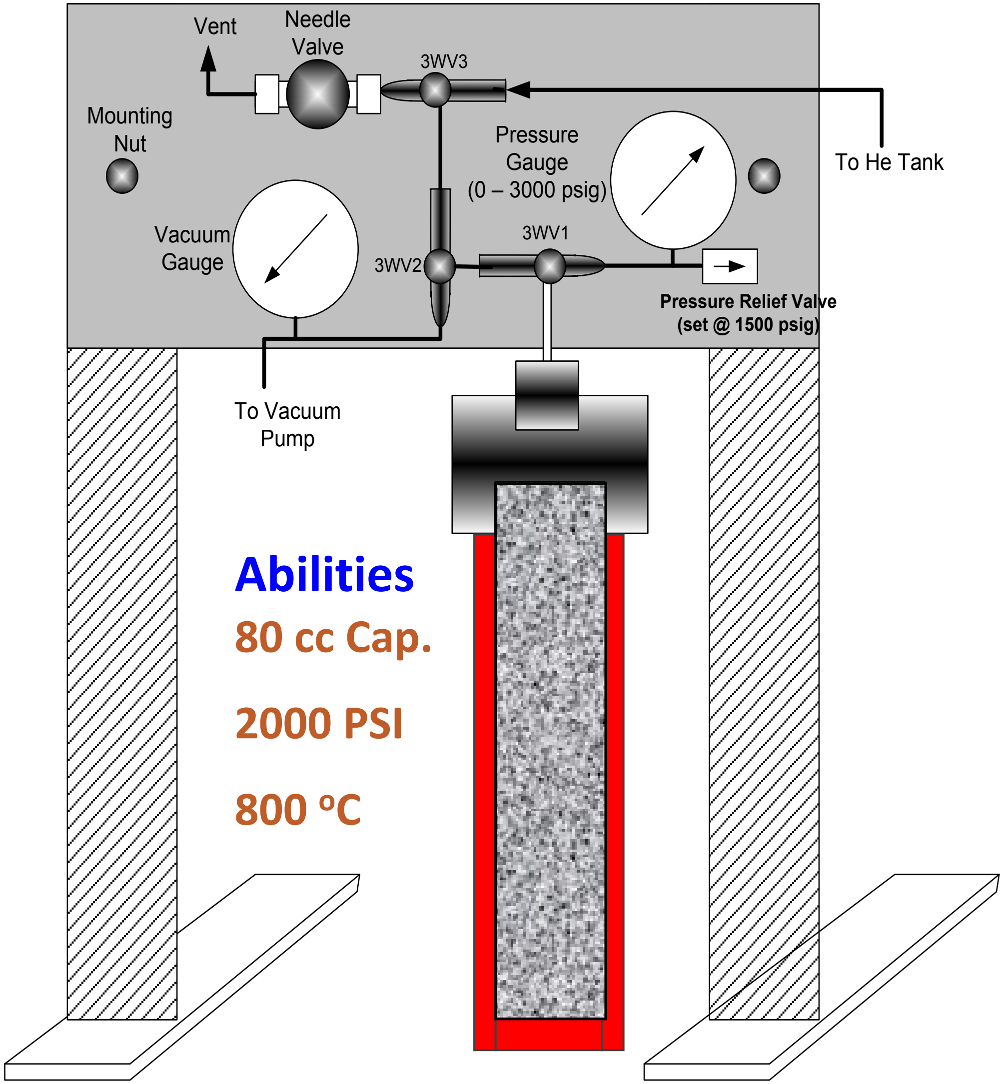
- Collaborate with industry to access high-temperature furnaces to increase the graphitic component in spherical carbon

- 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

Reactor System Layout - 072610

Advantages

Single step

Reproducible

Solvent-, catalyst free

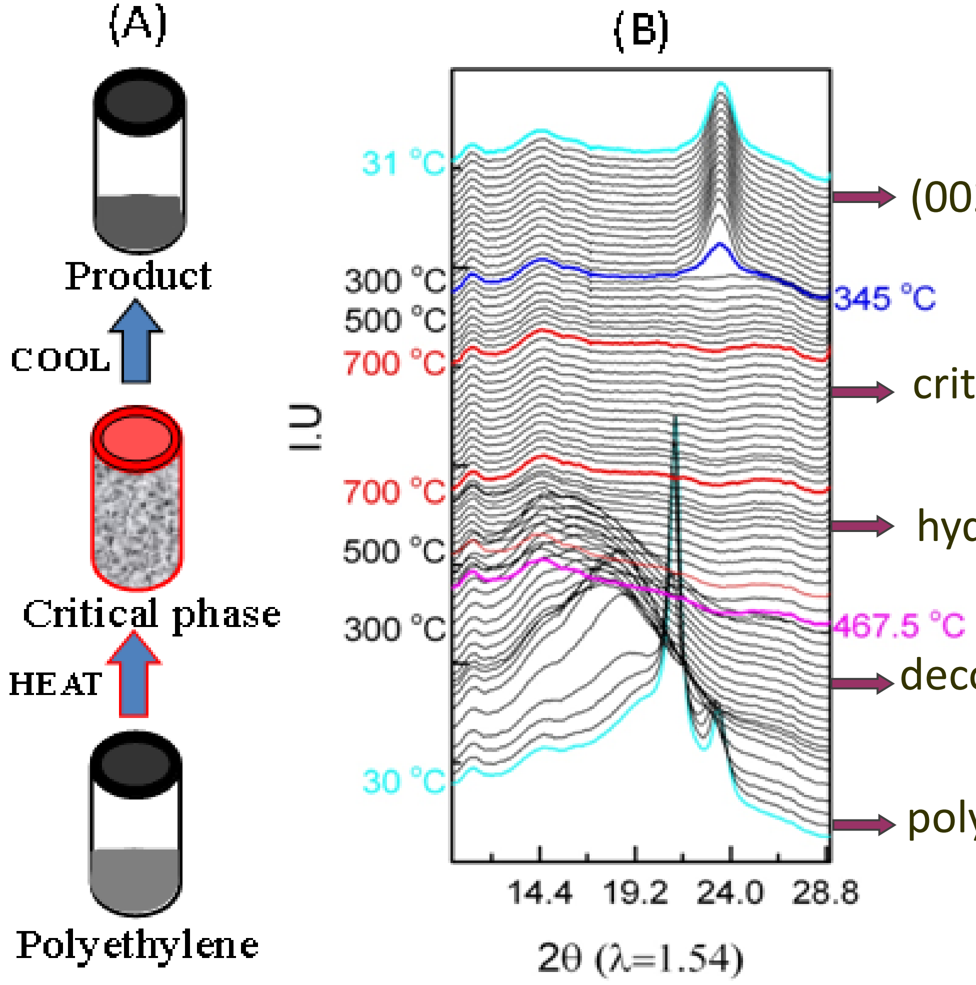
Produces pure products

Proceeds at moderate temp

Efficient & environmentally friendly

Distinct Synthetic Approach

In-situ X-ray scattering (16BM-D) to probe CSs synthesis



(002) diffraction peak of hard carbon

critical phase, x-ray amorphous

hydrocarbon products remain molten

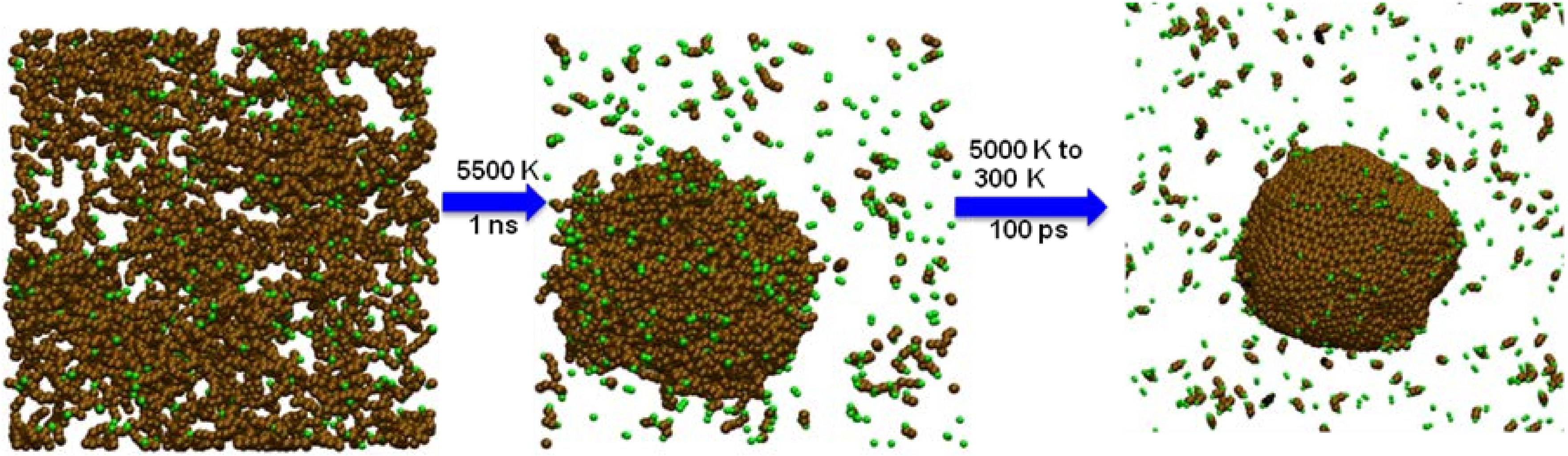
decomposition of the polyethylene, 105 ^{o}C

polyethylene

- The amorphous carbon moieties nucleates at ~ 350 ^{o}C, during cooling

Courtesy: Chi-Kai Lin, ANL

Understanding spherical shape of CSs: Molecular dynamic simulations-I



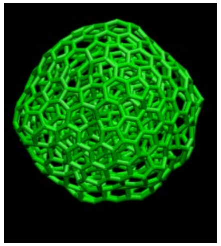
Initial C-H configuration; carbon sphere formation at 5500 K; cooling to 300 K

- 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.

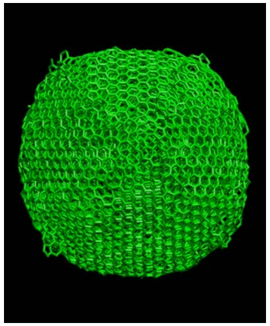
Courtesy: S. A. Deshmukh, S. Sankaranarayanan, ANL

Understanding spherical shape of CSs: **Molecular dynamic simulations-II**

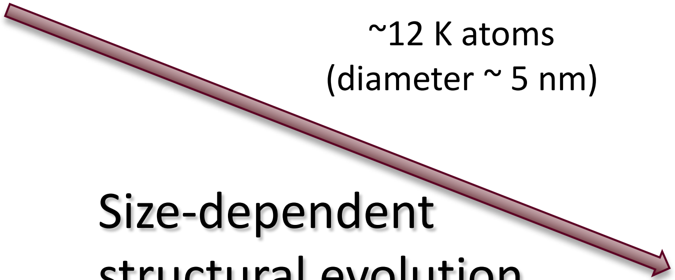
- What is the structure and role of interfaces (inner and outer surfaces) in facilitating lithium intercalation and de-intercalation?
- Up to 30 nm (million atoms) at temperatures from 300-3000 K



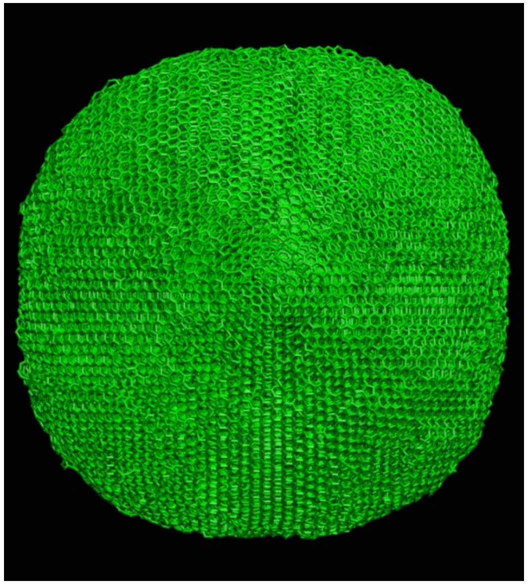
~730 atoms
(d ~ 2 nm)



~12 K atoms
(diameter ~ 5 nm)



Size-dependent
structural evolution



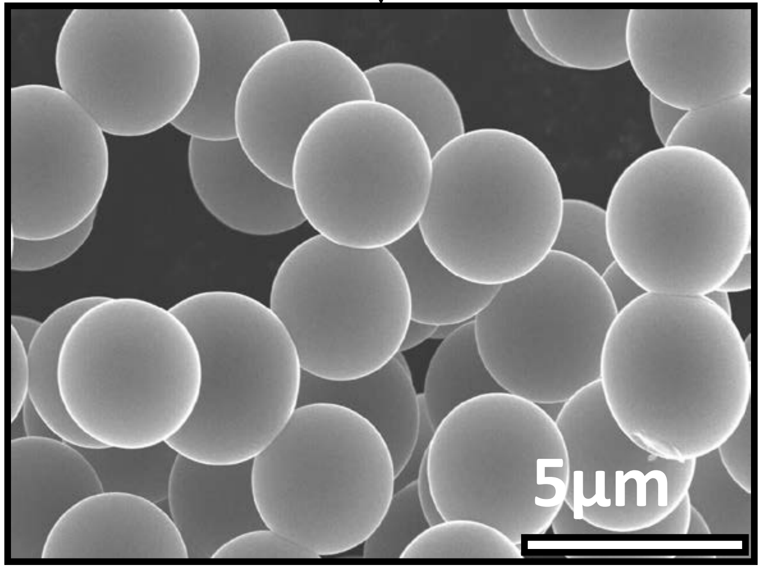
~92 thousand atoms
(diameter ~ 10 nm)

- 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

Morphology and electrochemistry of Li/CSs Cells

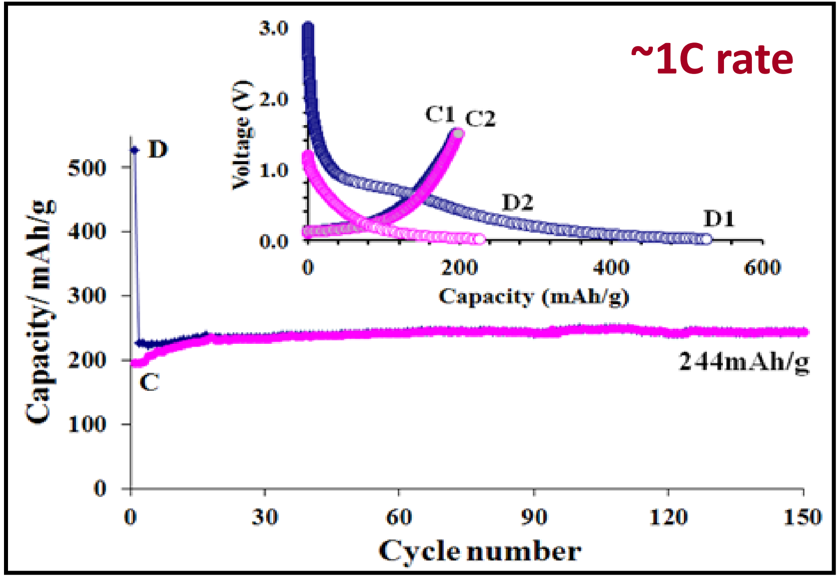
700 ^{0}C/1min. ↓ 490 PSI



Electrode composition

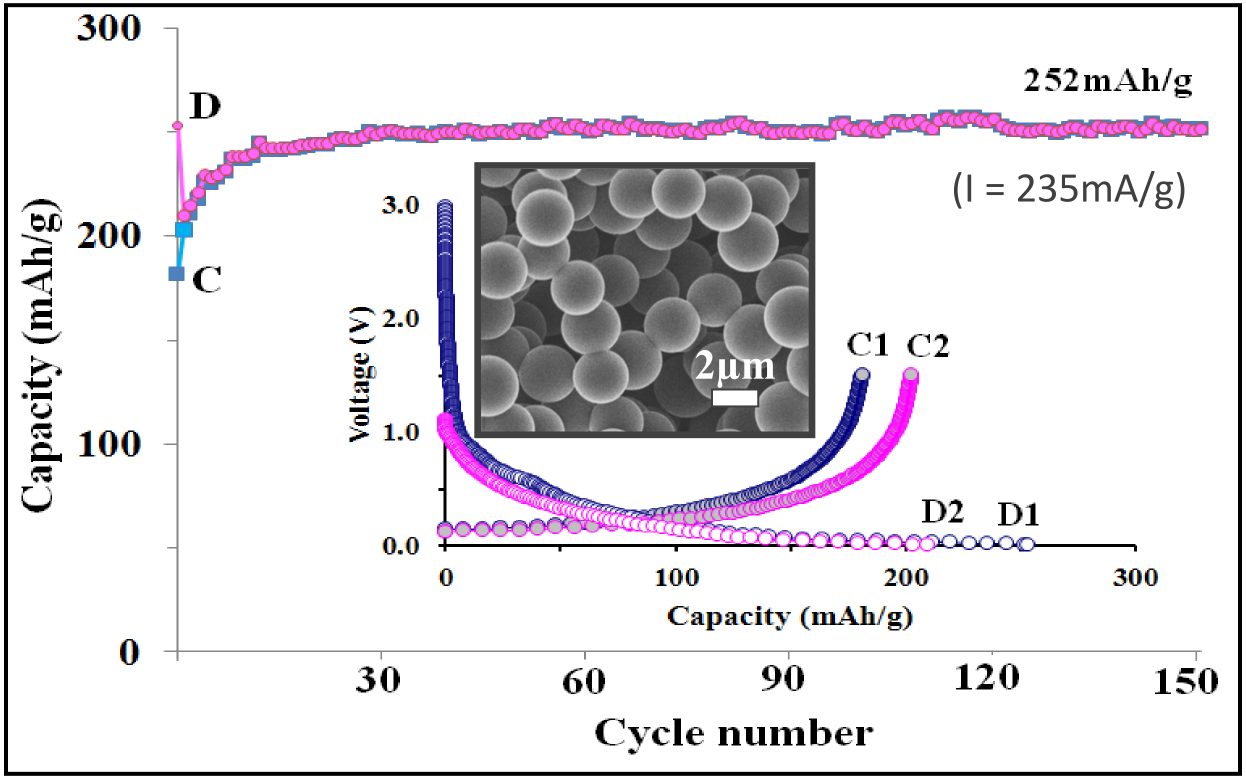
CSs:acetylene black:PVDF ratio = 85:8:7

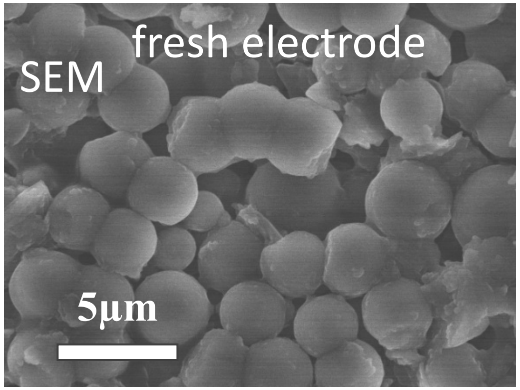
1.2M $LiPF_6$ in EC:DMC

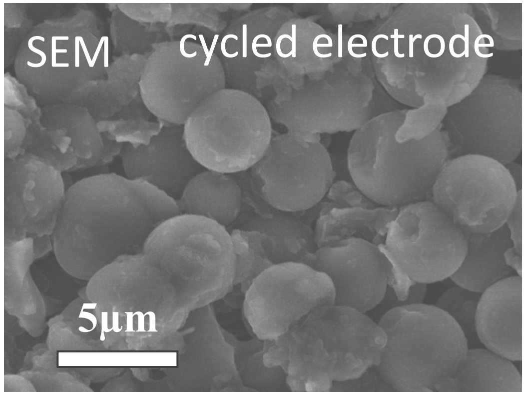


- Solid, dense, micron sized CSs with smooth surfaces can also be prepared from C_9H_{12}, naphthalene, hexane etc.
- First cycle capacity loss ~60%, steady cycling for hundreds of cycles
- As-prepared CSs (700^{o}C) collapse during lithiation and delithiation

Morphology and electrochemistry of Li/CSs-2400°C cells



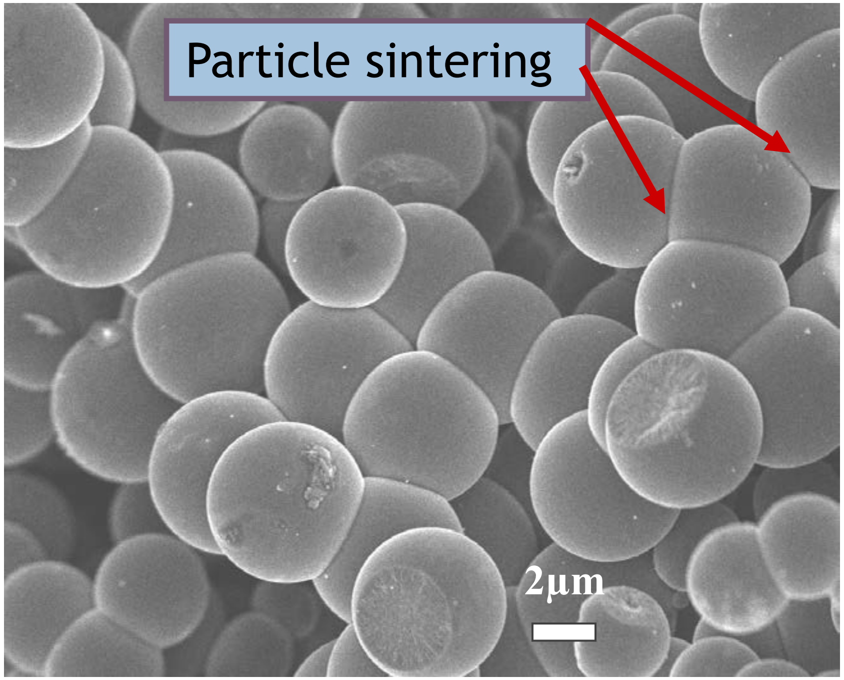


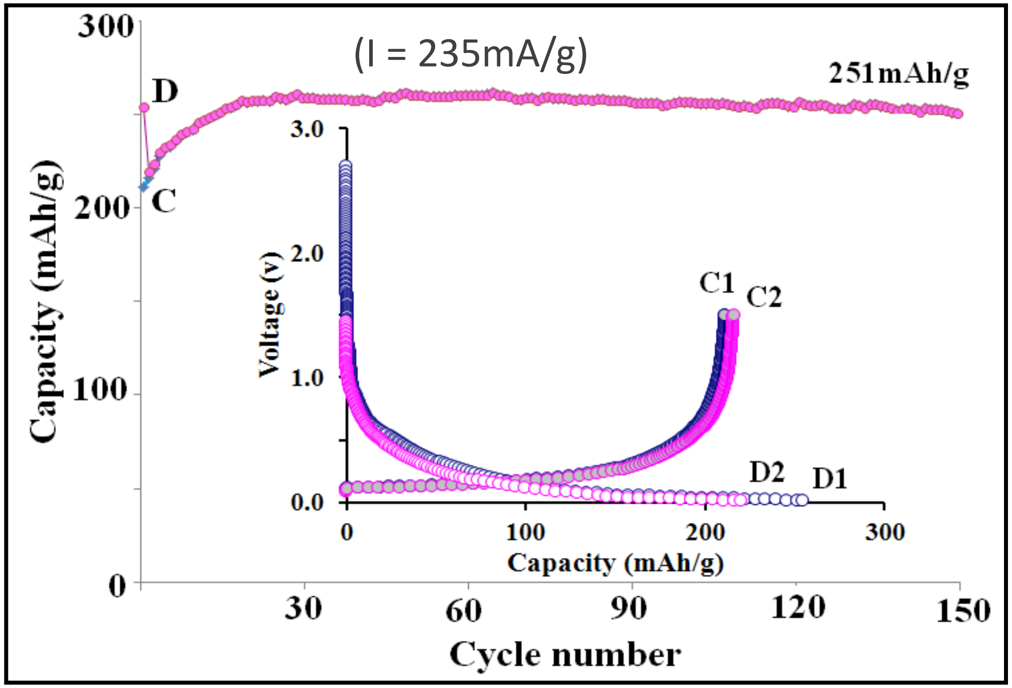


- Morphology of CSs is preserved after heat treatment to 2400 ° C (still solid and dense)
- 25% first cycle capacity loss, sloping potential profile, stable capacity on cycling
- >99% coulombic efficiency , heat-treated CSs remains intact during cycling

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

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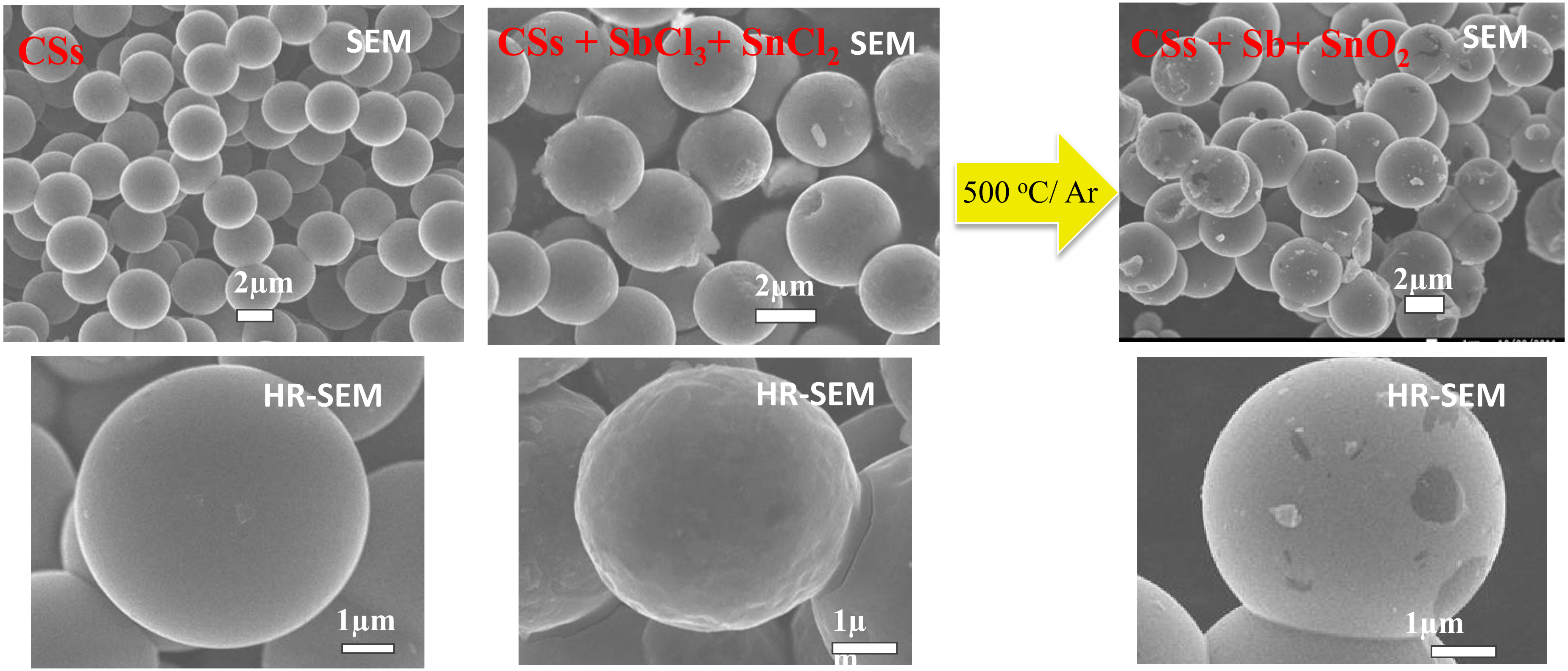
Increasing the capacity of CSs by SnO_2/Sb deposition

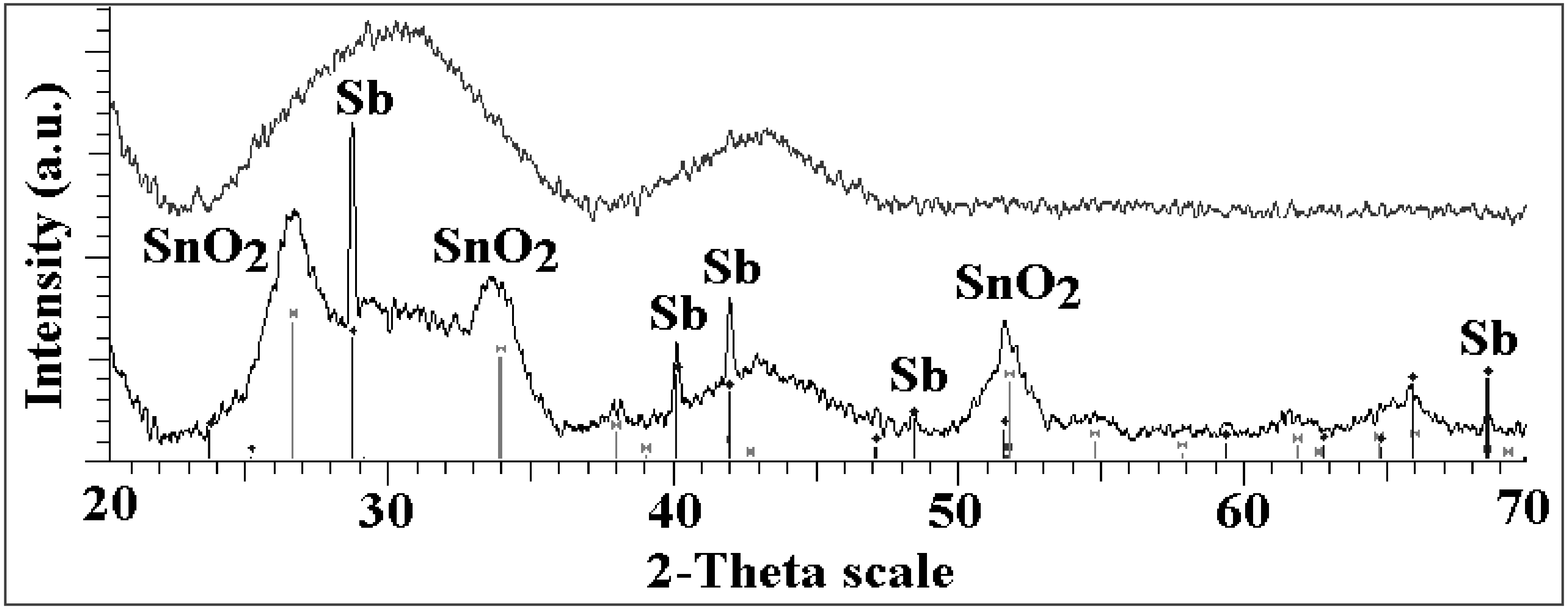
Sonication

SCP + Sn + Sb precursors in organic solvent)))))) → SnO_2/Sb@CSs nanoparticles



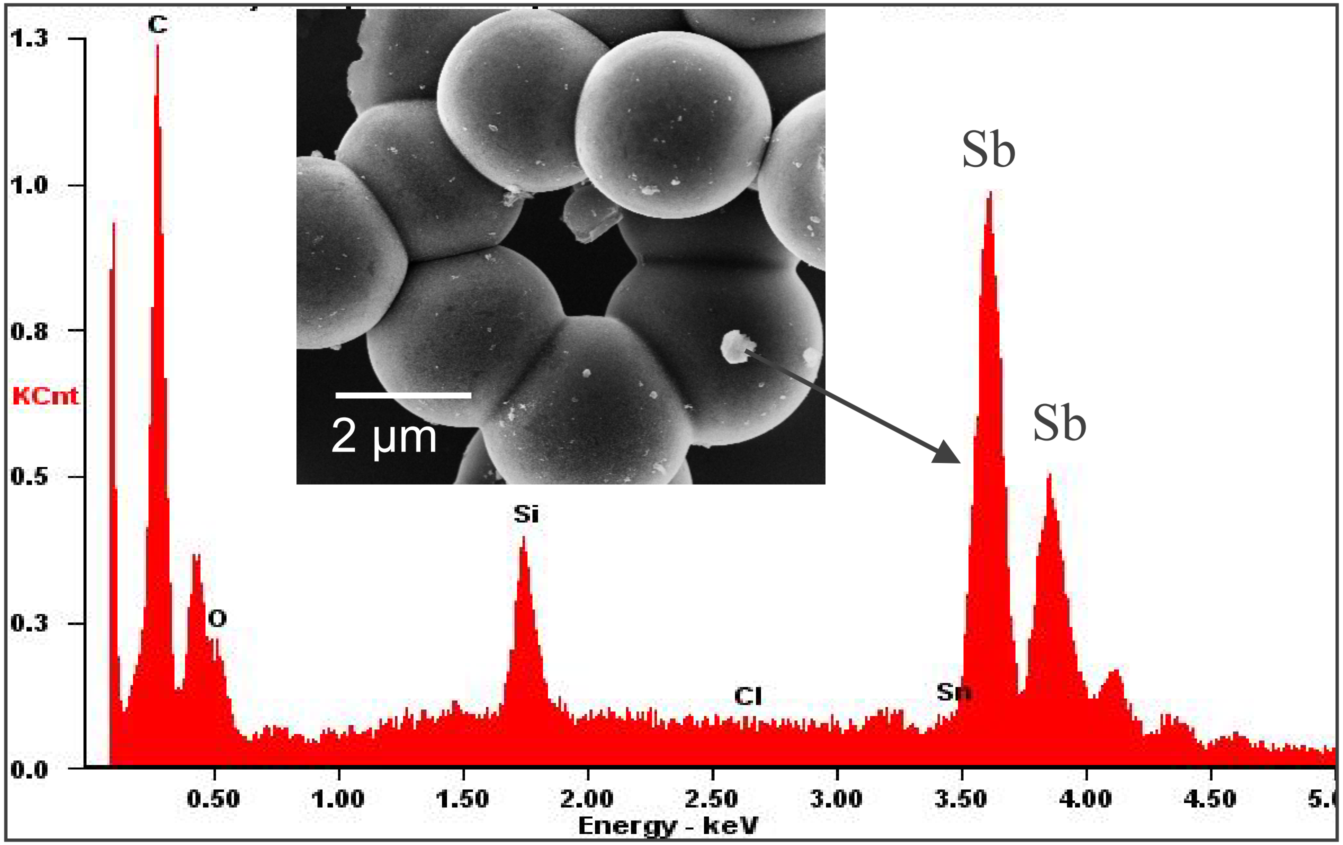
- CSs particles are thinly and uniformly coated by Sn/Sb precursors
- Heat treatment (at 500 °C/Ar) facilitated Sn product adherence on the CSs surface

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

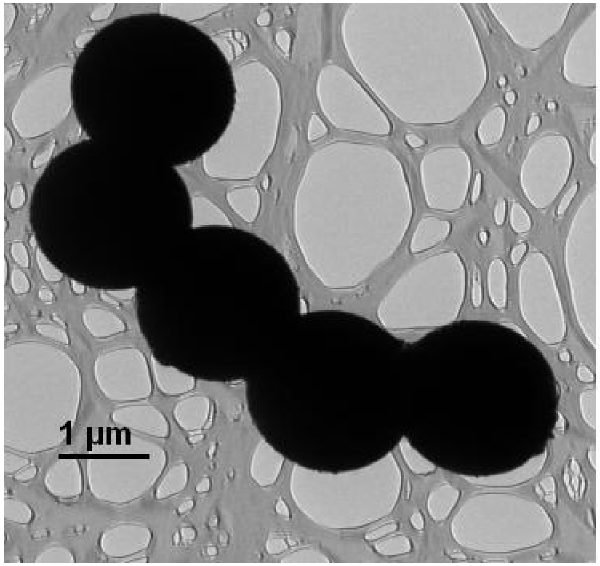
Selected area energy dispersive X-ray analysis of heat-treated CSs-Sb/SnO_2 particles

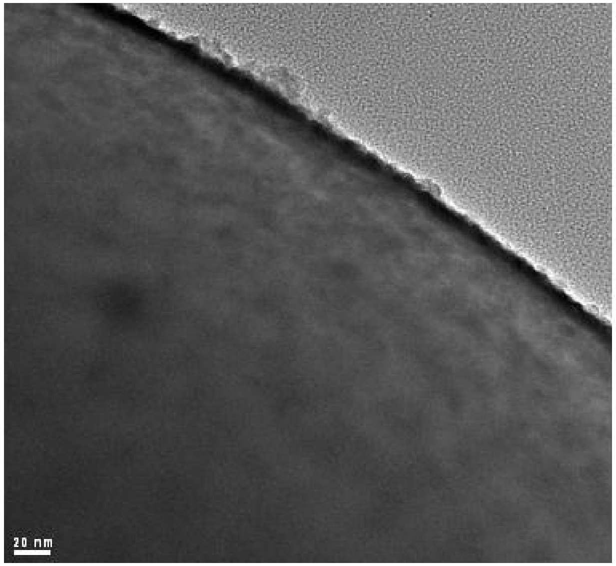


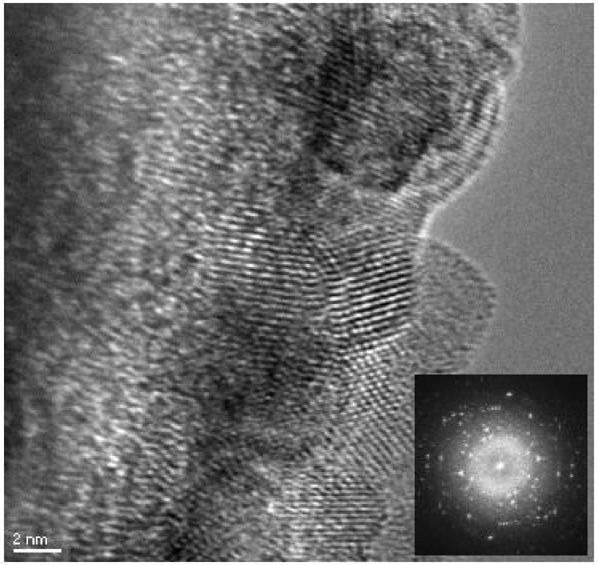
- SEM indicates that SnO_2 nanoparticles are uniformly deposited on CSs surfaces
- Deposited Sb particles are clusters of ~400nm size, yielding sharp X-ray diffraction peaks
- The Si peak originated from the sample holder Si wafer

Courtesy: Dean Miller and Jianguo Wen, ANL

Transmission electron micrographs of heated CSs-Sb/SnO_2 composite



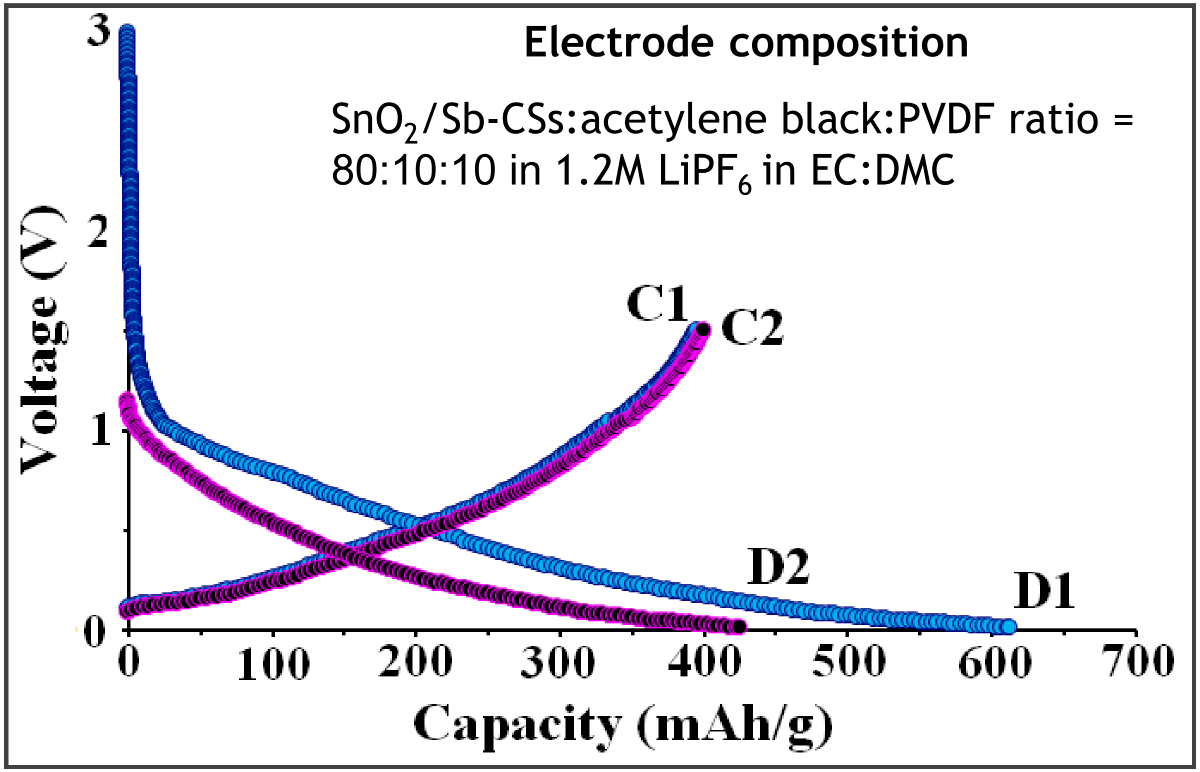




- Transmission electron micrographs shows <10nm SnO_2 nanoparticles, uniformly deposited on the CSs surfaces
- Deposited nanoparticles shown in HR-TEM are indexed to tetragonal SnO_2 (CIF-154960) using inserted FFT pattern

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)

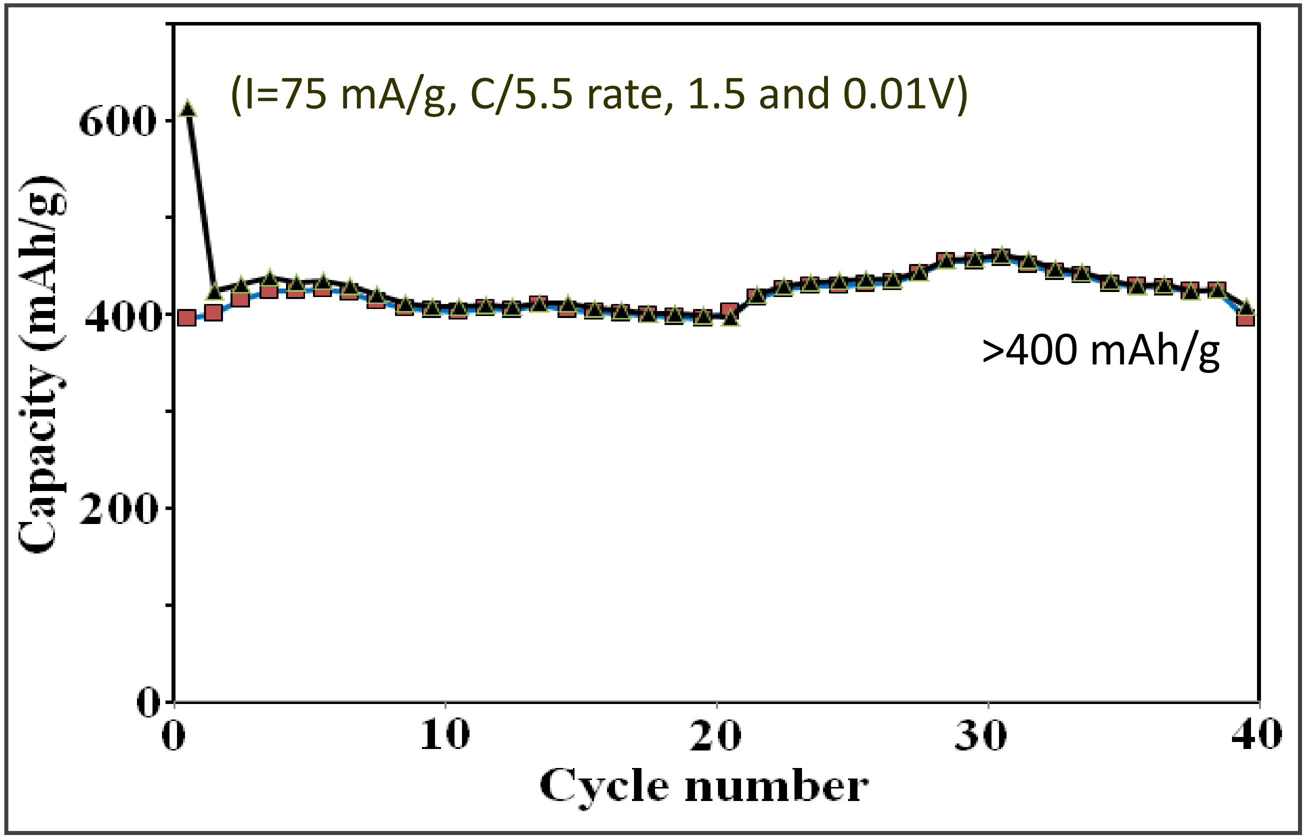


Electrode composition

SnO_2/Sb-CSs:acetylene black:PVDF ratio = 80:10:10 in 1.2M $LiPF_6$ in EC:DMC

- 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

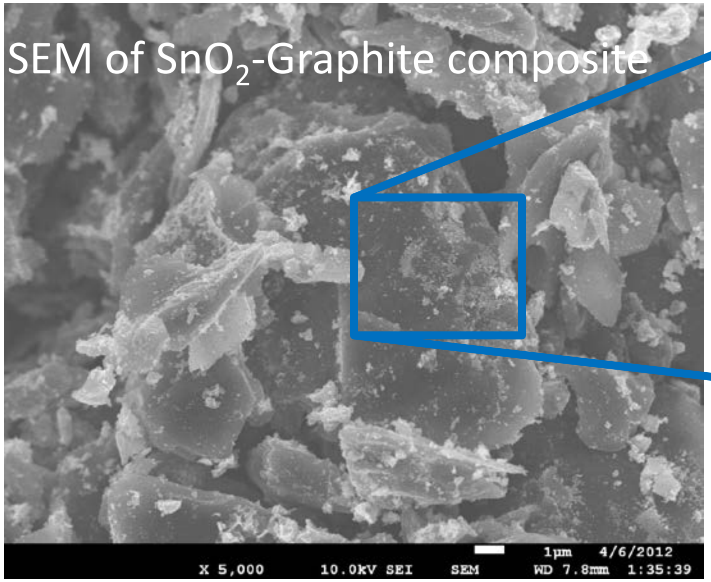
- **Sonochemical reaction**

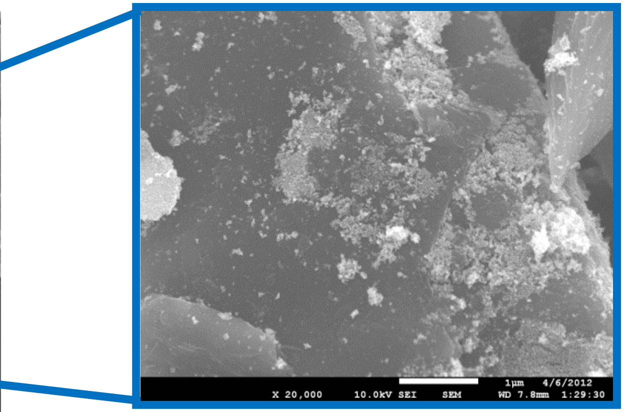
G8 graphite (heat-treated 600°C/6 hr under He/H_2) + Ethanol + $SnCl_2$ precursor

↓ **Sonication**

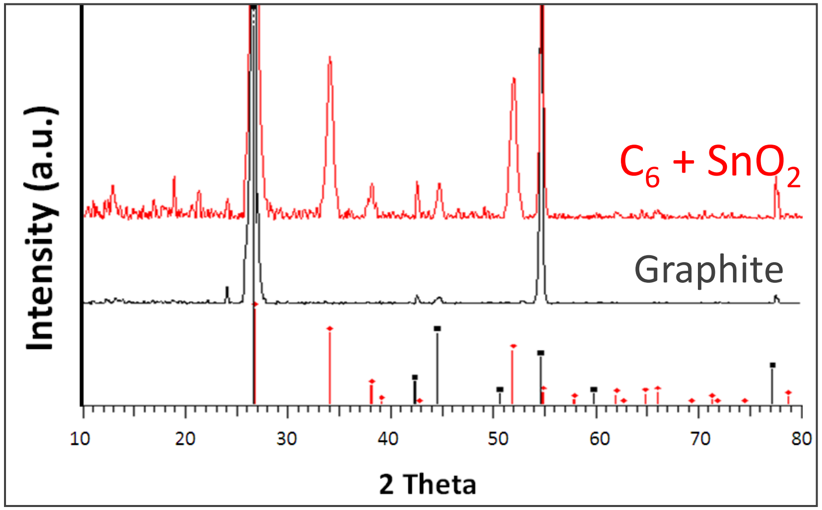
As-prepared composite, further heated to 500°C/2 hr/Ar

Sonochemically deposited SnO_2 nanoparticles on the surface of activated graphite


SEM of SnO_2-Graphite composite

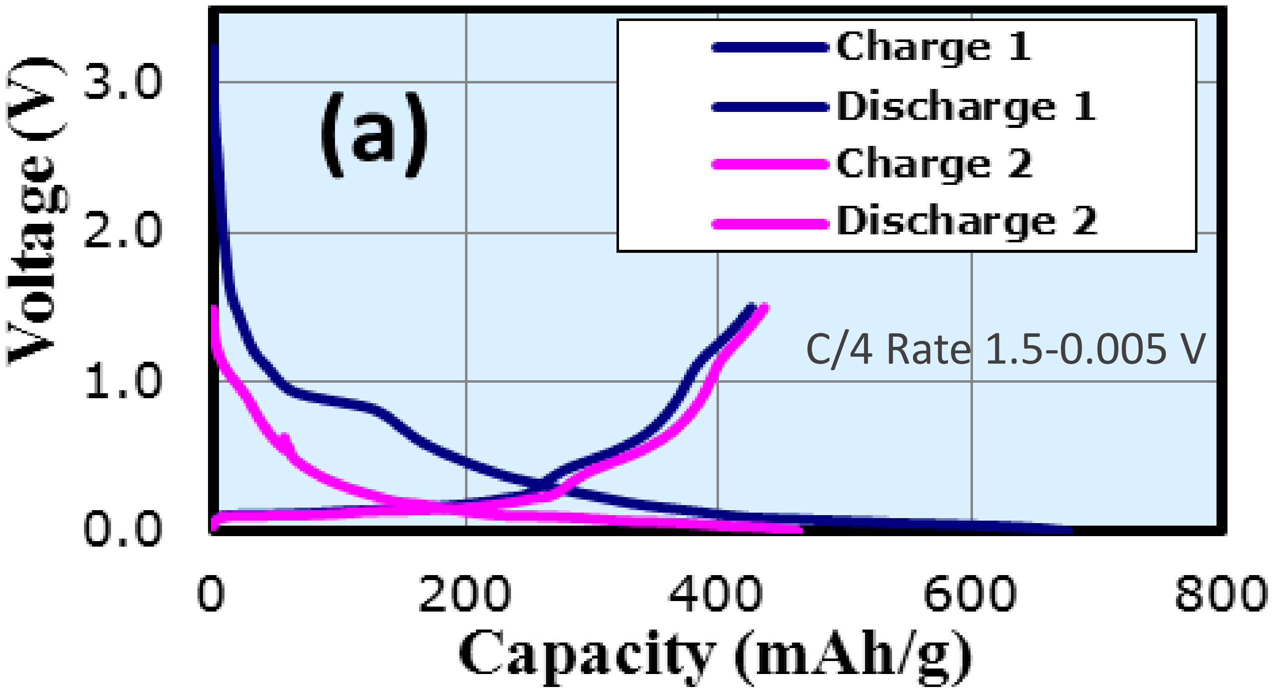


XRD patterns



- 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

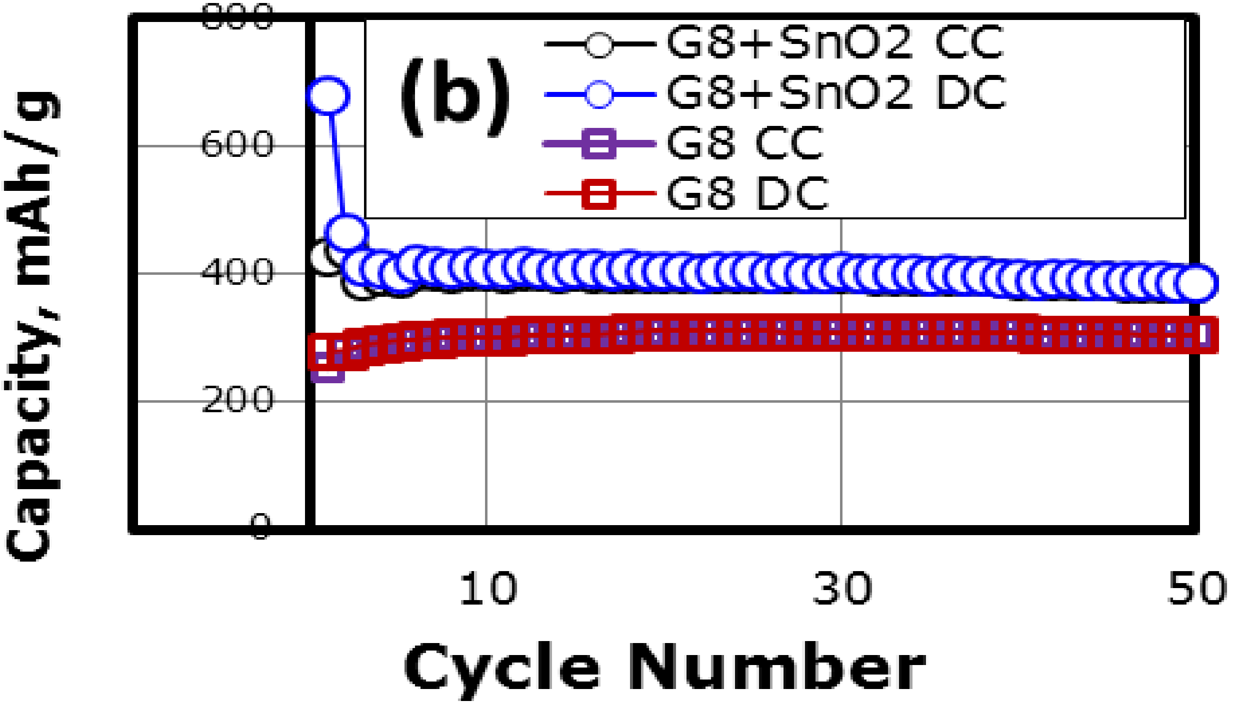


- The first-cycle discharge and charge capacities of a surface activated G8 graphite sonochemically coated with SnO_2 composite electrode are 665 mAh/g and 427mAh/g, respectively. (The first cycle irreversible capacity loss is ~36%)

- The discharge (0.8V) and charge (0.7V) plateaus indicate the presence of lithium alloying and de-alloying with the SnO_2 nanoparticles.

The capacity vs cycle number plot of a Li/industrial graphite-SnO_2 cell

25 wt % of SnO_2 nanoparticles



- A stable reversible capacity of 400 mAh/g was obtained at the C/4 rate for 50 cycles, when 25 wt % SnO_2 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^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_2/Sb nanoparticles.
- Using a similar surface coating technique, the capacity of surface activated industrial carbon/SnO_2 composite anodes were increased to a level well above the theoretical value for graphite (400 mAh/g).

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.