Spherical Carbon Anodes Fabricated by Autogenic Reactions

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Annual Merit Review
DOE Vehicle Technologies Program

Washington, D.C.
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ES114

Overview

Timeline

- Start date: FY11
- End date: FY12
- Percent complete:

  - This is a new project

Budget

- Total project funding

  - 100% DOE
- FY11: $300K
- FY12: $300K

Barriers Addressed

- Cost
- Abuse tolerance limitations

Partners

- Co-investigators: V. Pol (Co-PI)
- Collaborators:
  - D. Dees (ANL)
  - J. Ayala, F. Henry (Superior Graphite)
  - A. Nazri (GM)
  - S. Sanchez (University of Illinois - UC) EFRC (Center for Electrochemical Energy Storage – CEES)

Objectives

- Design spherically-shaped- and other rounded carbon anode particles for HEVs, PHEVs and EVs

  - Improve the abuse tolerance of carbon anodes without compromising their capacity or power

  - Optimize autogenic processing conditions to enhance the structural and electrochemical properties of carbon products with new architectural designs

  - Evaluate the electrochemical and thermal properties of the carbon materials in both lithium half cells and in a full lithium-ion cell configuration

Milestones (FY10-11)

- Establish collaborative interactions with Superior Graphite and General Motors to gain access to high temperature (>2000 °C) furnaces and – *collaborations established.*
- Prepare carbon samples for Superior Graphite and General Motors – *first batches completed and heated - on going*
- Evaluate the electrochemical properties of heat-treated, autogenically-prepared carbon materials in lithium half cells and full cells – *Sept. 2011*
- Evaluate the thermal properties and stability of autogenically-prepared carbon materials vs. graphite in charged lithium cells – *Sept 2011*
- Compare models of current distribution around spherically-shaped and sheet-like (graphitic) carbon particles – *Sept 2011*

Approach

- Exploit autogenic reactions to prepare spherical carbon particles (and carbon nanotubes) that can be fabricated quickly and reliably by high pressure reactions from carbon precursors.

- Collaborate with Superior Graphite and GM to make use of their high-T furnaces to increase the graphitic component within the carbon products.

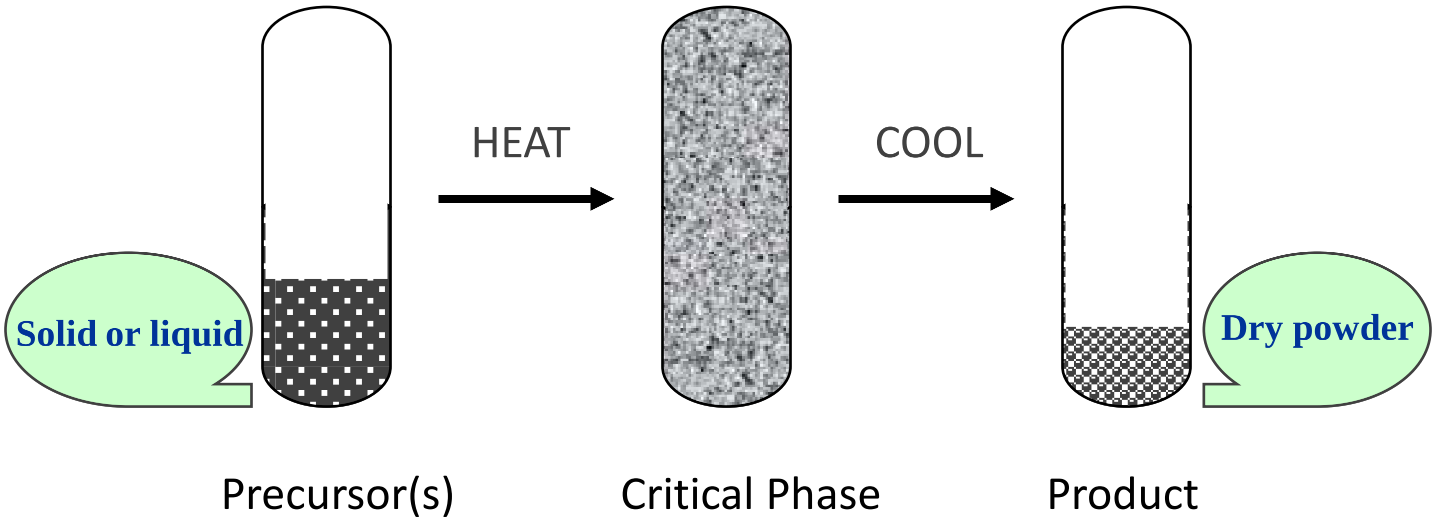
- Optimize processing conditions and evaluate the carbon products in both lithium half cells and full lithium-ion cells against Argonne's high capacity cathode materials.

- Study the chemical and thermal stability of rounded carbon particles in the electrolyte in charged lithium cells.

- Model current distribution around carbon spheres and other rounded shapes and compare with laminar (graphitic) morphologies

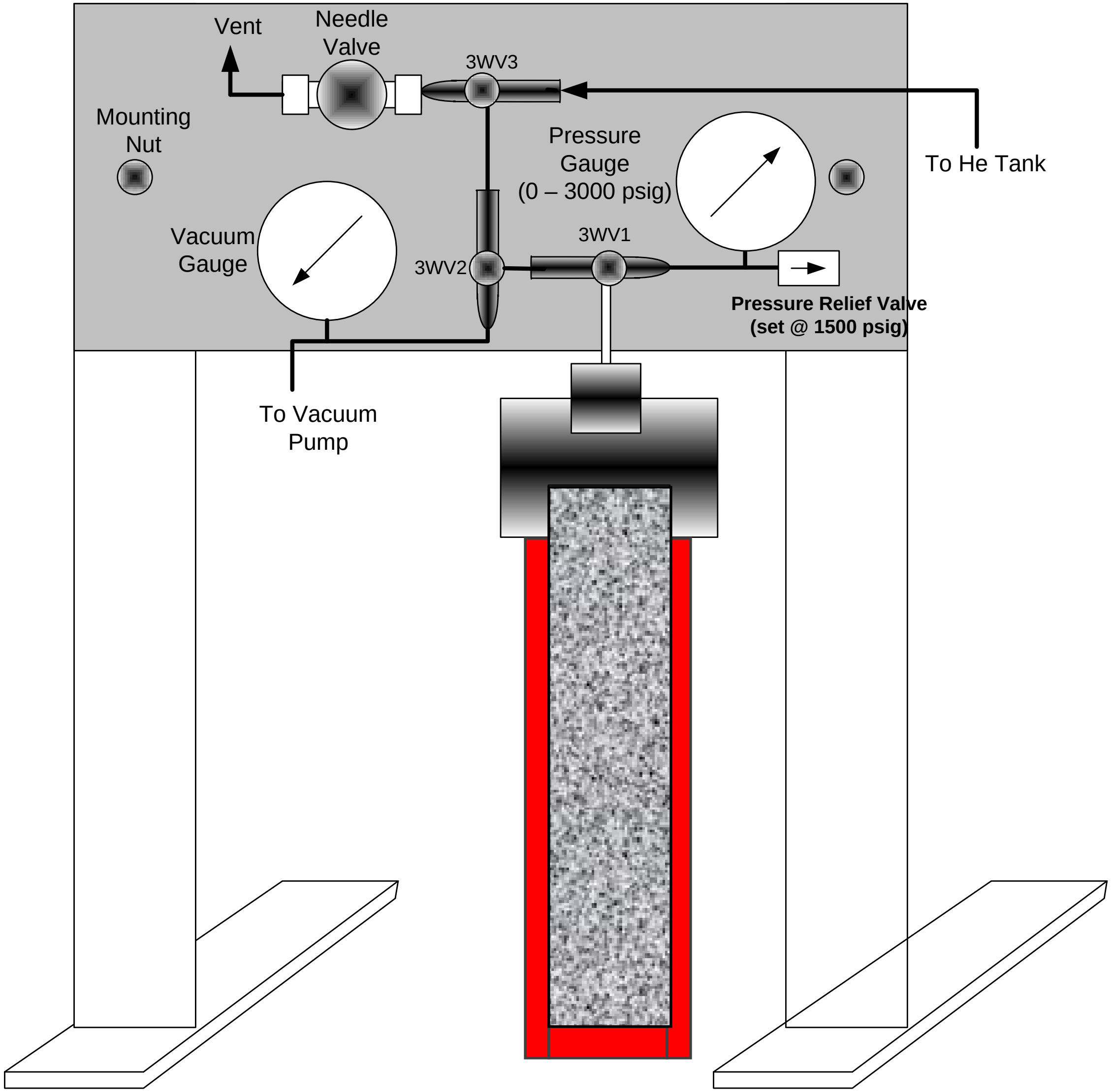
Autogenic Reactions

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



- Proven technique for producing carbon spheres, carbon nanotubes and carbon coatings, e.g. C-TiO_2
- ABR research emanates from EFRC-related studies on autogenic reactions (cathodes and anodes)

Autogenic Reactor

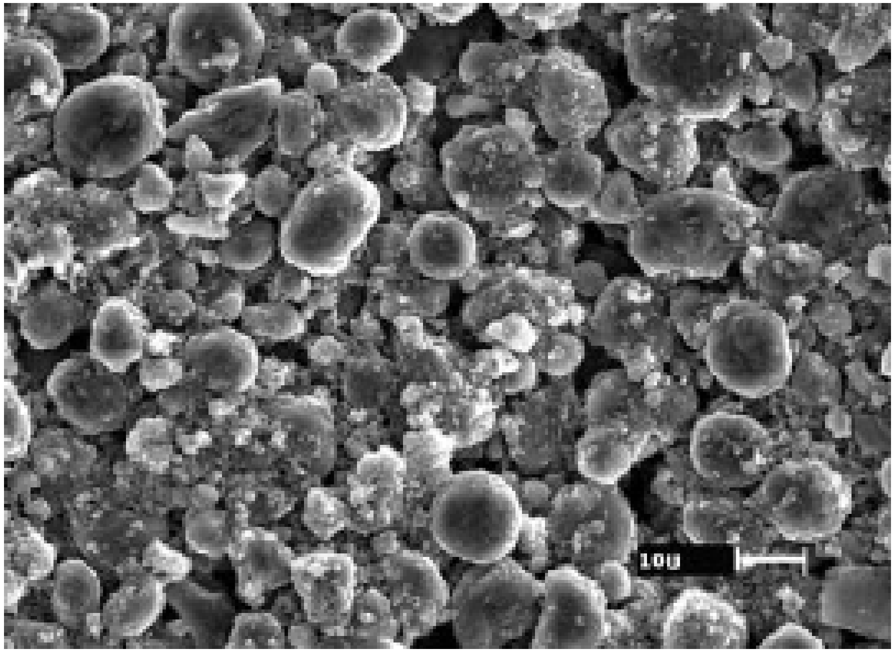


Reactor System Layout - 072610

- Single step process
- Solvent-, catalyst free
- Pure products
- Reproducible
- Economic & simple
- Scale:
  - Capacity: 80 cc
  - Max Pressure: 2000 psi
  - Max Temperature: 800 °C

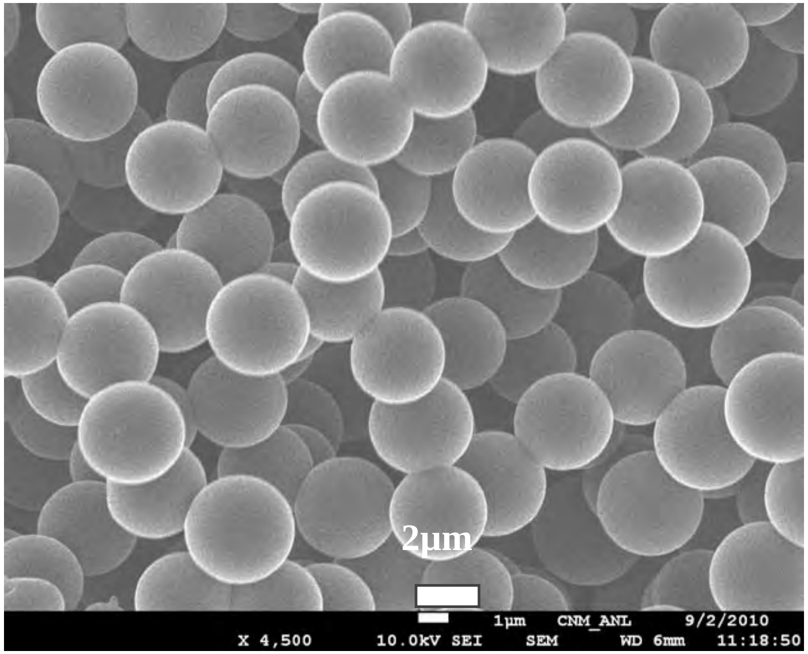
SEM Images: MCMB vs. Spherical Carbon

Mesocarbon microbeads (MCMB)



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

Argonne's carbon spheres

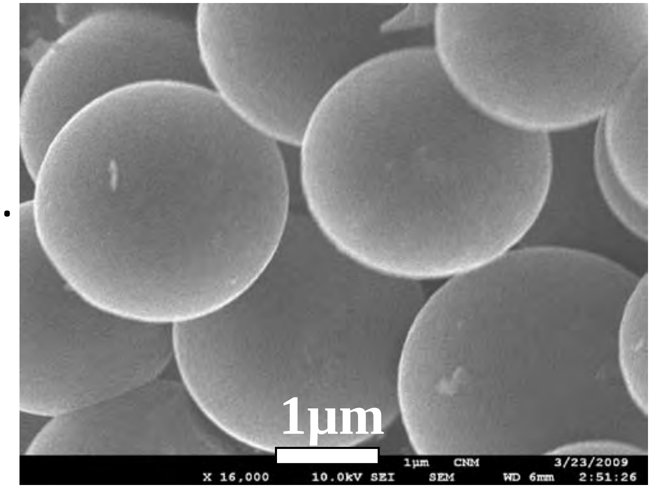


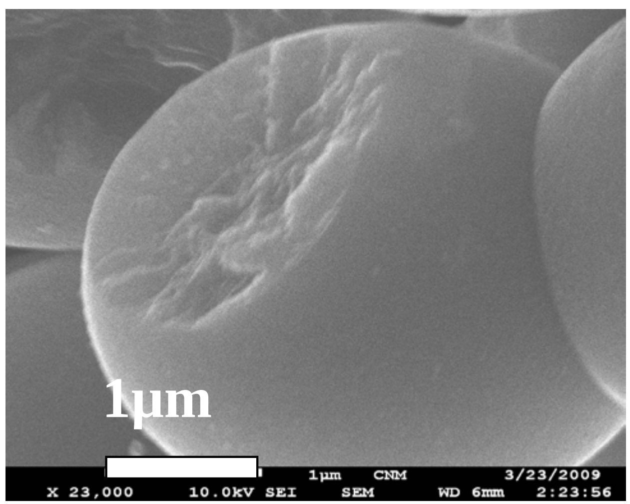
V. G. Pol, *Environmental Sci. & Tech*. 44, 4753 (2010)

Carbon Production from Plastic Waste

700 °C/1min.

490 PSI





Solid, dense

spherical carbon particles

(SCP)

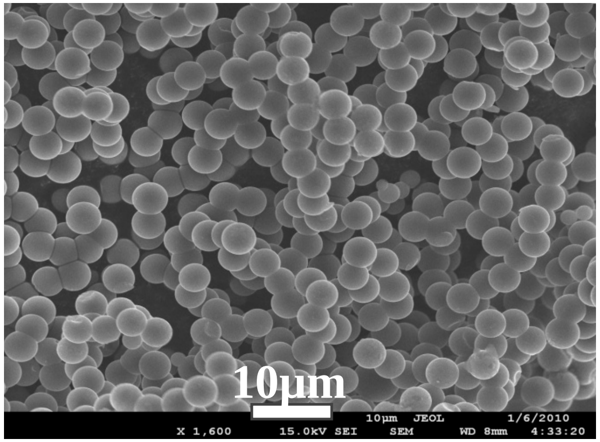
High-Temperature Treatment

Jorge Ayala and
Francois Henry

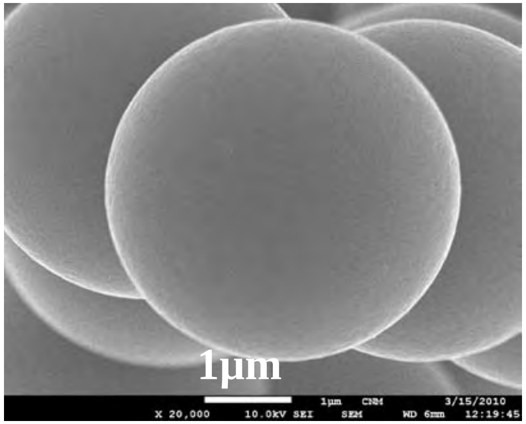
SUPERIOR GRAPHITE

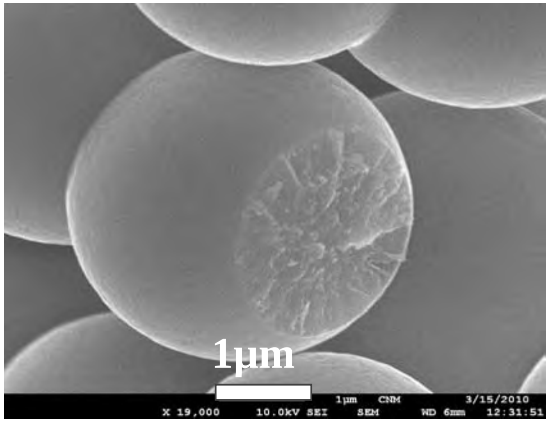
Chicago, Illinois

(2400 °C/1h/Ar)



(SCP-HT)



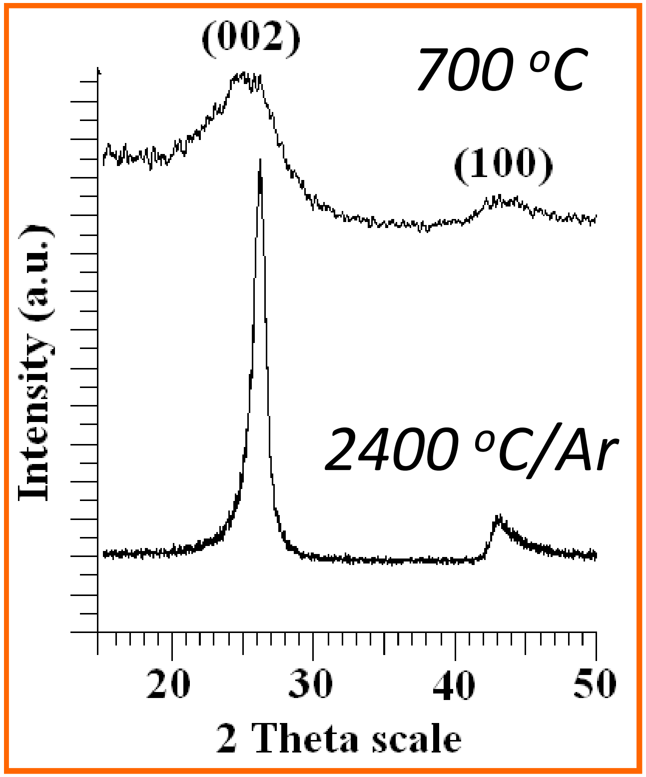


Spherical morphology preserved on heat treatment to 2400 °C

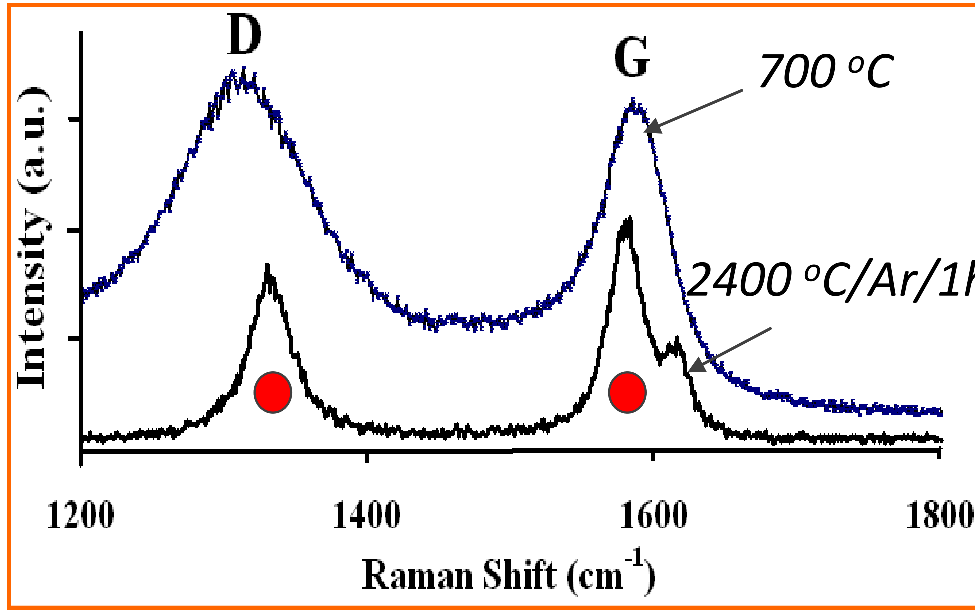
Pol V. G. and Thackeray M. M. *Energy & Environ. Sci.*, 2010, *in press*

Structural Evolution on Heat Treatment

XRD



Raman spectroscopy



- Heating the hard carbon spheres to 2400 °C increases turbostratic order and graphitic character

Physical Properties

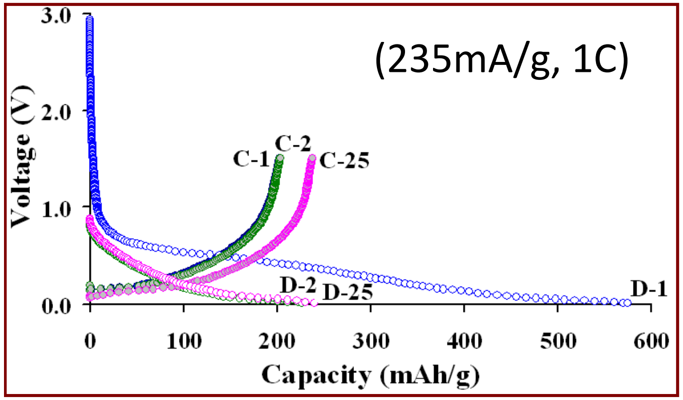
Spherical Carbon	Density	BET	Pore Volume
SCP (700 ^oC)	2.2 g/cc	4.4 m^2/g	0.0078cc/g
SCP-HT (2400 ^oC)	2.1 g/cc	1.1 m^2/g	0.0043cc/g

- True density is equivalent to graphite
- Tap density is <1 g/cc

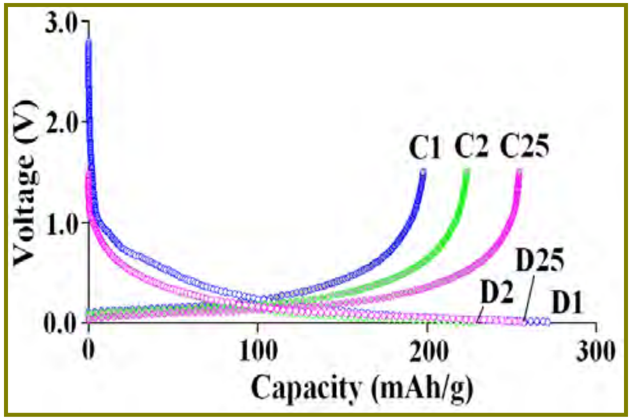
Data courtesy of: D. Dambournet, A. Abouimrane

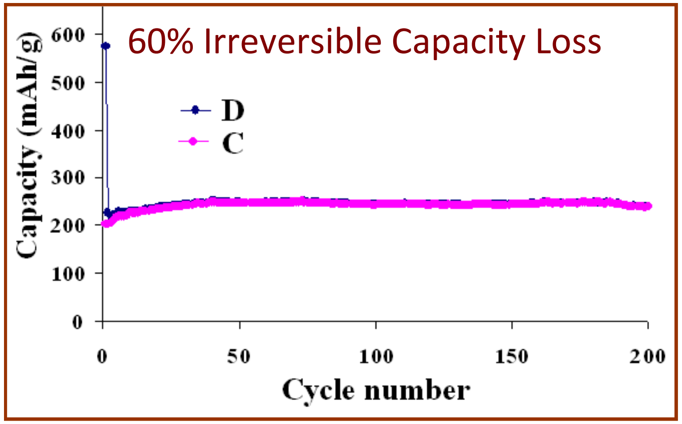
Electrochemistry of Carbon Spheres (~1C)

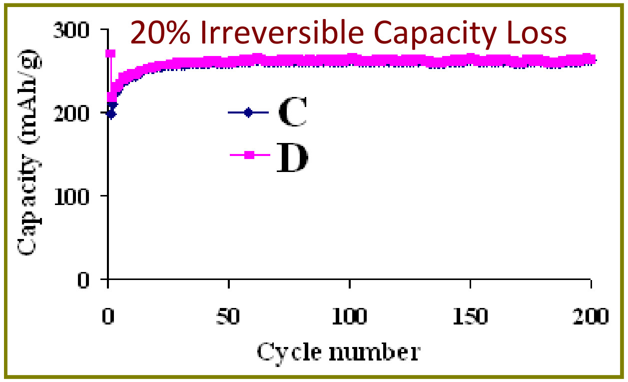
Li/SCP cells



Li/SCP-HT cells



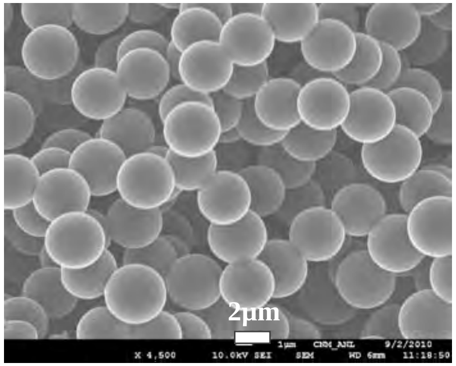


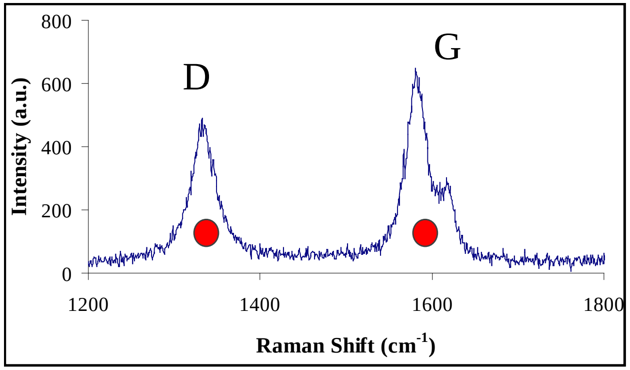


- Heating the spheres to 2400 °C significantly reduces the 1st cycle irreversible capacity loss

V. G. Pol and M. M. Thackeray M. M. *Energy & Environ. Sci.*, 2010, *in press*

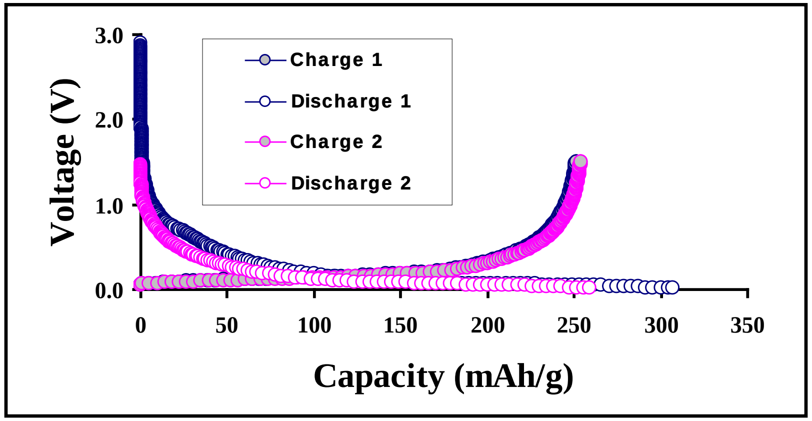
Heat Treatment at 2400 ℃ for 8 h

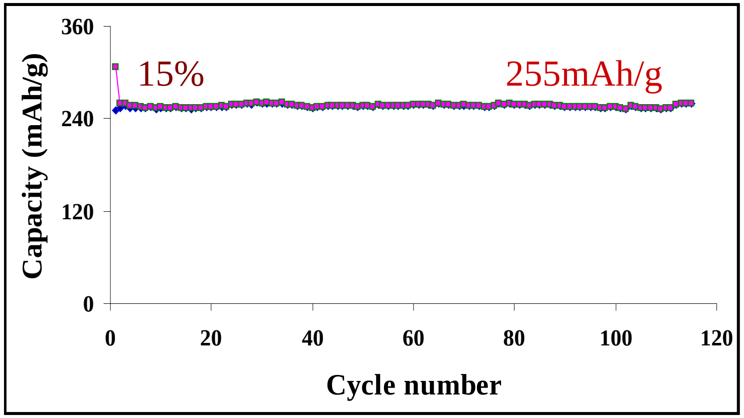




- Morphology and structure unaffected by longer heat treatment time (1–8 h)

Electrochemistry (~1C rate)

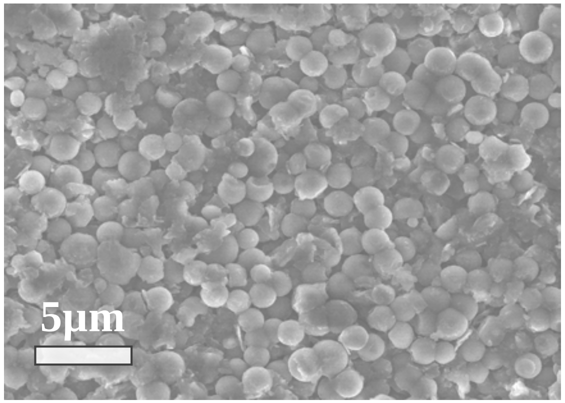


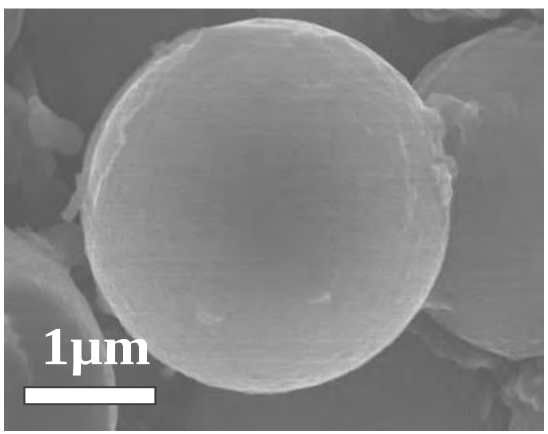


- Longer heating time reduces first-cycle irreversible capacity loss (~15%) – comparable to MCMB anodes

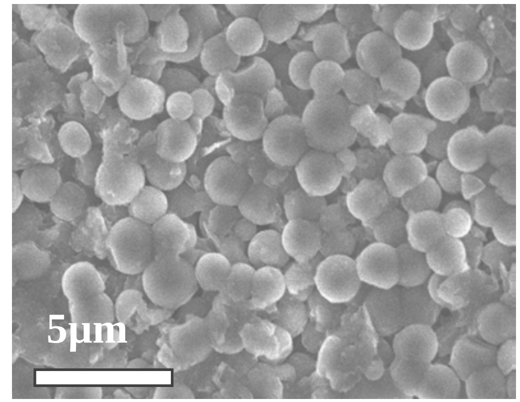
Morphological Studies – Cycled Electrodes

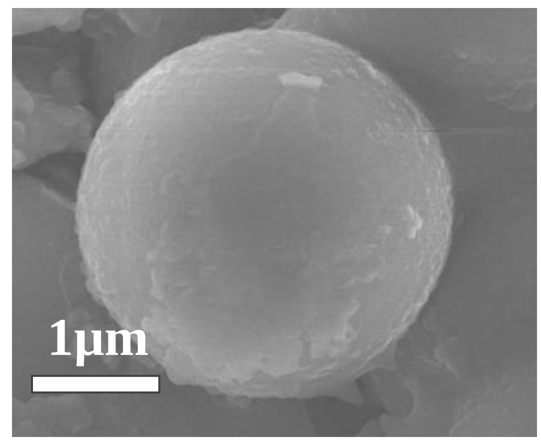
Fresh electrodes





Li/SCP-HT electrodes

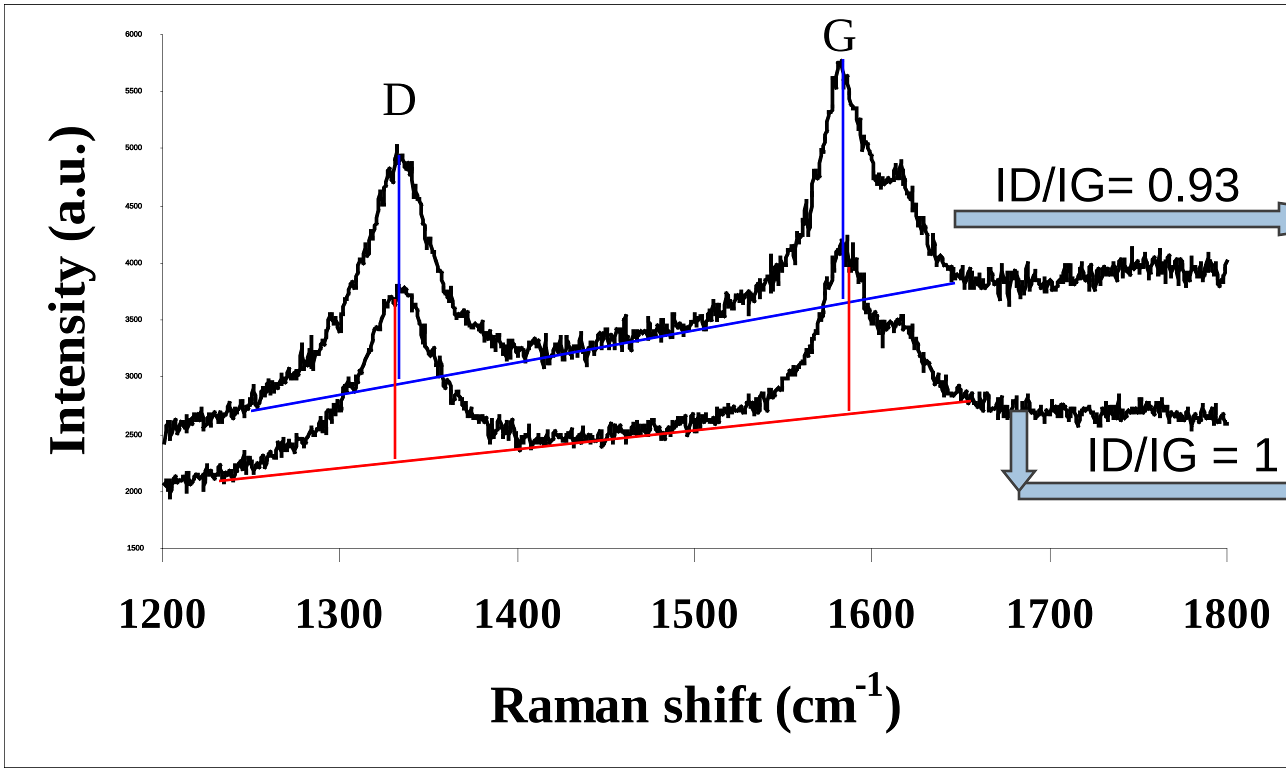




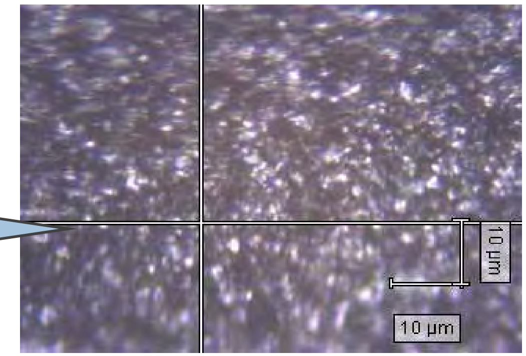
- No observable changes in the spherical shape of SCP-HT/1h electrode particles after 200 cycles

Structural studies of Li/SCP-HT cells (200 cycles)

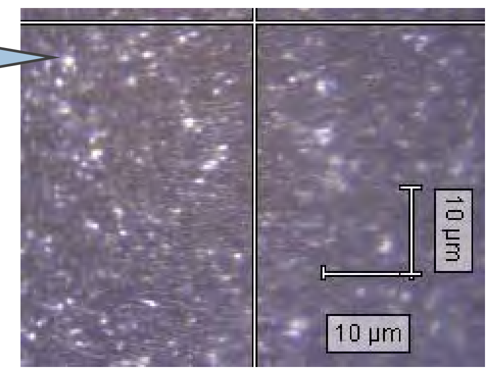
Raman data



Fresh electrodes



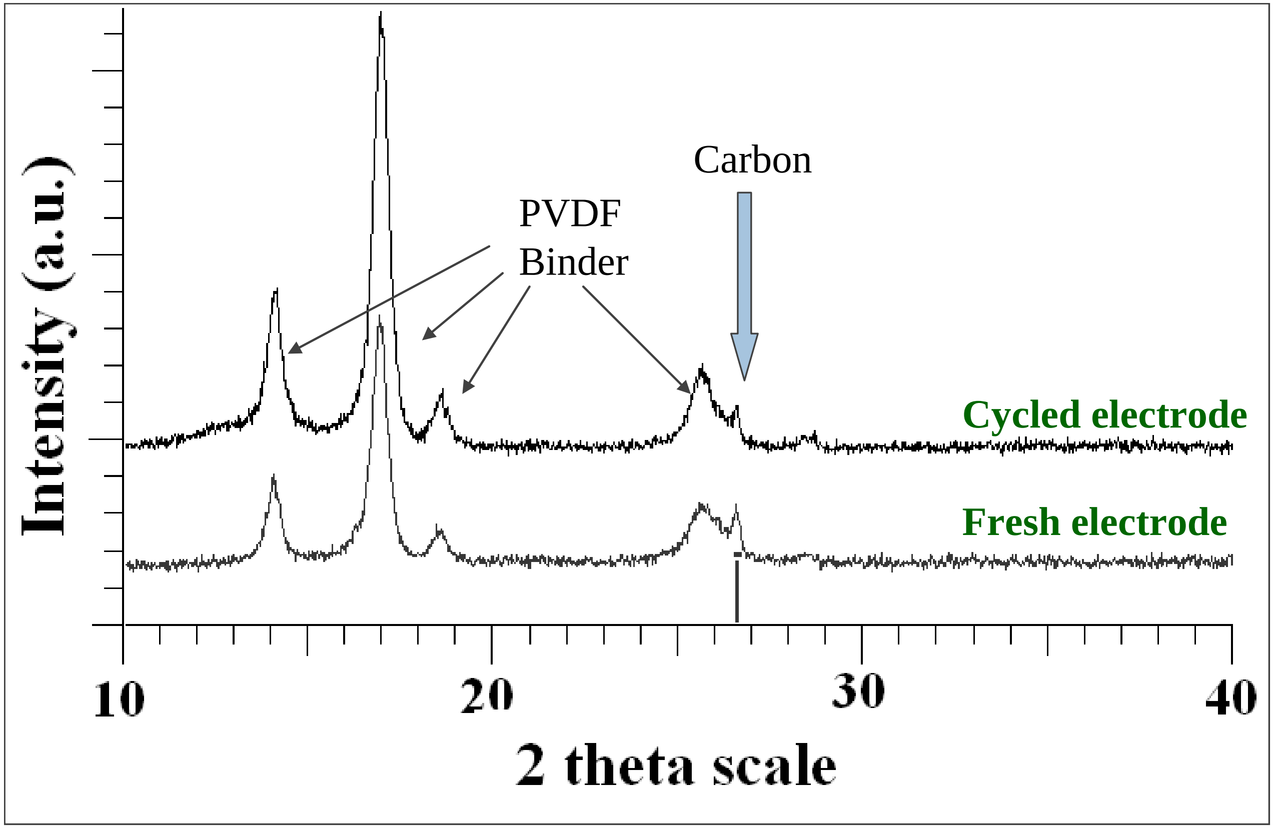
After 200 cycles



- Cycling at a C rate may induce local stresses, increasing the ID/IG ratio
- A small change of anode surface reactivity with the electrolyte may be expected

Structural studies of Li/SCP-HT cells (200 cycles)

XRD data

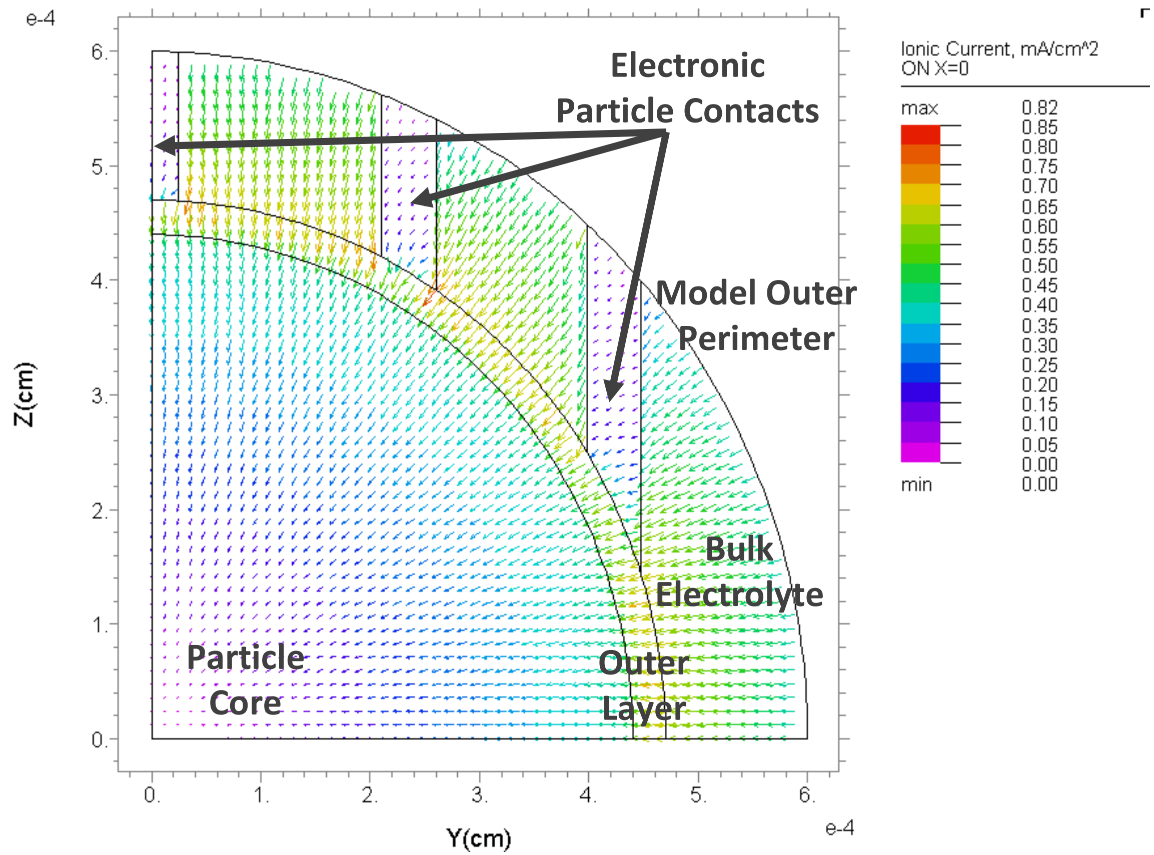


- A slight decrease in the relative intensity of the (002) graphitic peak on cycling is consistent with the increase in the ID/IG ratio of the Raman data

Electrochemical Modeling of Current Distribution in Spherical and Graphitic Carbon Electrodes (initiated)

- Use Dees' 3D Electrochemical Model Developed for Spherical Secondary Particles:
  - Electrochemical model with simplified SEI relation applied to particle scale
  - Secondary particle assumed to be made of primary particles with independent core and outer layer characteristics
  - Particle porosity allows access of electrolyte and ionic current to reach into the particle core

Ionic Current Distribution in Secondary Particle



Future Work - FY2011/FY2012

- Continue to exploit autogenic reactions and optimize reaction parameters to fabricate rounded carbon particles to improve the safety characteristics of carbon electrodes.
  - e.g., evaluate carbon prolate spheroids vs. carbon spheres
- Increase heat-treatment temperature to 2800-3000 °C to increase graphitic order within the spheres (with General Motors)
- Conduct thermal analysis of lithiated carbon sphere electrodes (preliminary results obtained)
- Extend electrochemical studies to full cells
- Continue electrochemical modeling to compare current distribution in spherical and graphitic carbon electrodes (just started)

Summary

- A dry autoclaving approach has been developed for the facile fabrication of spherical carbon particles, which maintain their morphology after high temperature treatment and electrochemical cycling in lithium cells.
- Spherical carbon behaves electrochemically like a hard carbon, delivering approximately 250 mAh/g when cycled between 1.5 V and 5mV 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/8h).
- Higher heat treatment protocols are being planned to increase the graphitic order in carbon spheres even further (in collaboration with General Motors).
- Carbon spheres offer the possibility of smoothing the current distribution at the carbon electrode surface during charge, thereby reducing the risk of lithium dendrite formation, leading to the fabrication of safer battery electrodes.

Acknowledgments

Support for this work from Peter Faguy and David Howell of DOE-EERE, Office of Vehicle Technologies, is gratefully acknowledged. Superior Graphite is thanked for heating various carbon samples to 2400 °C.