Carbon Cryogel Silicon Composite Anode Materials for Lithium Ion Batteries

A variety of materials are under investigation for use as anode materials in lithium-ion batteries, of which, the most promising are those containing silicon. [10] One such material is a composite formed via the dispersion of silicon in a resorcinol-formaldehyde (RF) gel followed by pyrolysis. Two silicon-carbon composite materials, carbon microspheres and nanofoams produced from nano-phase silicon impregnated RF gel precursors have been synthesized and investigated. Carbon microspheres are produced by forming the silicon-containing RF gel into microspheres whereas carbon nano-foams are produced by impregnating carbon fiber paper with the silicon containing RF gel to create a free standing electrode. [1-4,9] Both materials have demonstrated their ability to function as anodes and utilize the silicon present in the material. Stable reversible capacities above 400 mAh/g for the bulk material and above 1000 mAh/g of Si have been observed.

Carbon Cryogel Silicon Composite Anode Materials for Lithium-Ion Batteries

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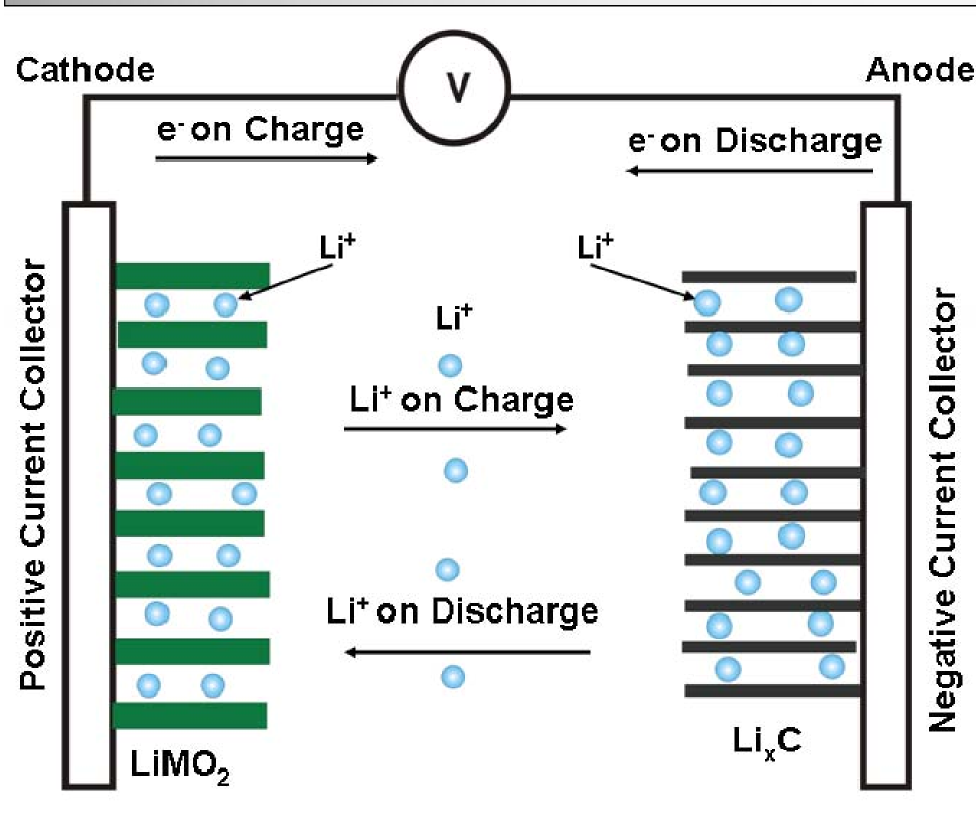
Lithium Ion Basics



Cathode

Charge

$$LiMO_2 \longrightarrow Li_{1-x}MO_2 + xLi^+ + xe^-$$

Discharge

$$Li_{1-x}MO_2 + xLi^+ + xe \longrightarrow LiMO_2$$

Anode

Charge

$$C + xLi^+ + xe^- \longrightarrow Li_xC$$

Discharge

$$Li_xC \longrightarrow C + xLi^+ + xe^-$$

Cathode

- Transition Metal Oxide
- $LiCO_2$

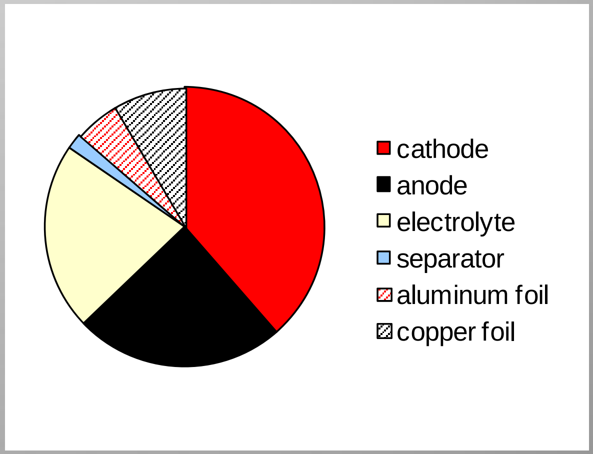
Capacity is dependent on number of Li^+ ions that can be shuttled back and forth

Anode

- Most Commonly Carbon
- Graphite
- Hard Carbon

NASA Goals

- Future missions of the National Aeronautics and Space Administration (NASA) require advanced energy storage systems
  - High specific energies (Wh/kg)
  - High energy densities (Wh/l)
- Develop advanced lithium ion cells
- Anode development is a key component
- the anode represents 24% of cell mass and additional opportunity for cell mass reduction
- Key performance parameters
  - Threshold value of 600 mAh/g
  - Goal of 1000 mAh/g

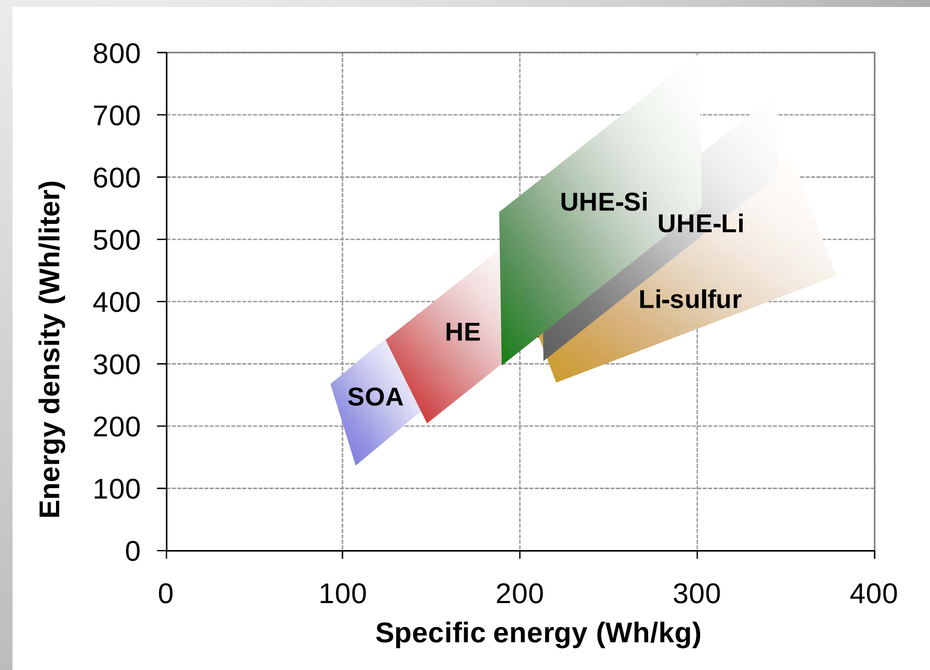


Estimates for component weight fraction in 30 Ah cell

Anode Materials

- Graphite
  - Excellent cycling characteristics
  - Theoretical capacity of 372 mAh/g (LiC_6)
- Silicon
  - Theoretical capacity of 4200 mAh/g ($Li_{15}Si_4$)
  - Expands 400% upon lithiation
  - High irreversible capacity loss
  - High fade rate
  - Poor coulombic efficiency
- Silicon carbon composites
  - Carbon matrix absorbs expansion of the silicon and maintains electrical contact
  - Carbon matrix prevents direct electrolyte contact

Estimates for cell specific energy and energy density

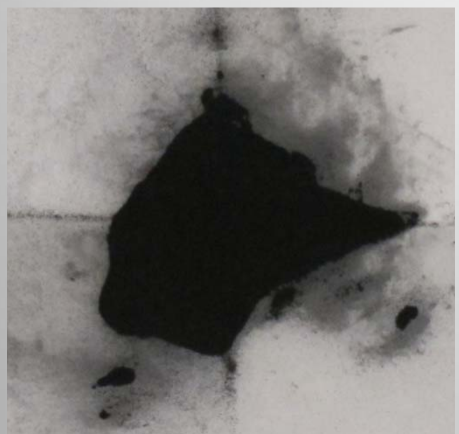


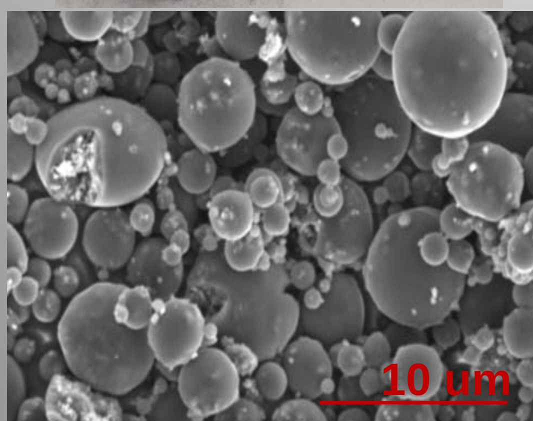
In-House Anode Synthesis

- Silicon containing carbon gel microbeads
- Carbon fiber paper supported silicon containing carbon nanofoam
- Based on resorcinol-formaldehyde gel precursors containing nano-silicon
- Porous carbon matrix will absorb the expansion of the silicon and prevent direct silicon-electrolyte contact
- Makes use of traditional cost –effective laboratory techniques

Carbon Cryogel Anode Materials

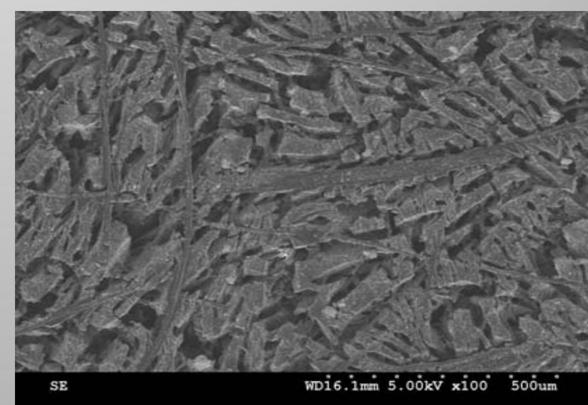
Carbon-Silicon Microbeads





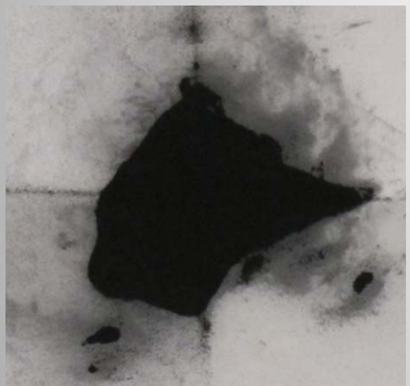
Originally investigated by Hasegawa, Mukkai, Shiratu and Tamon *Carbon* 42, 2004 pp. 2573-2579

Carbon Nanofoam with Nano-Silicon Supported on Carbon Paper

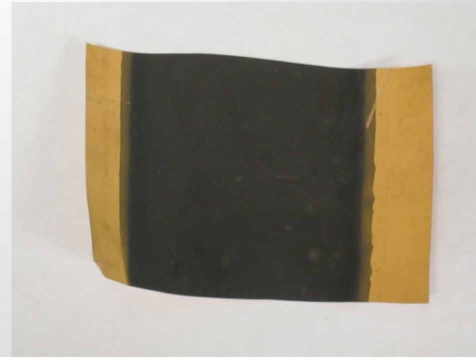


Carbon nanofoams are currently under investigation by J. Long at NRL for use in electrochemical capaciters and as electrode support materials

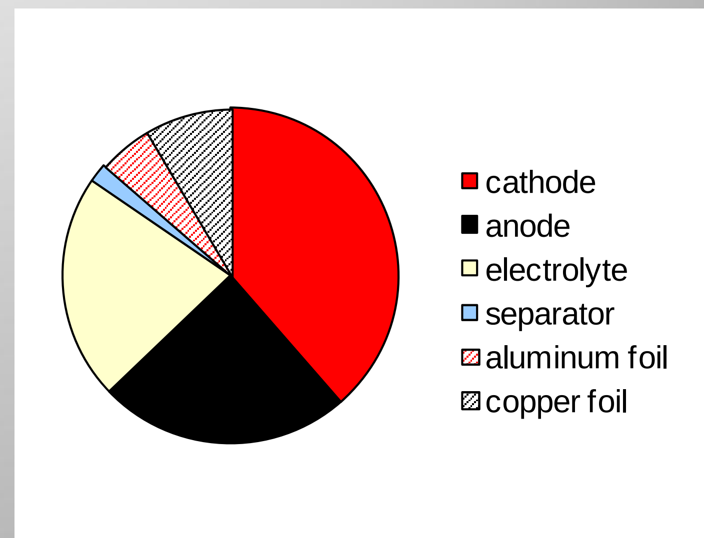
Carbon-Silicon Microbeads



Mix microbeads with binder and cast onto copper foil current collector



- **Advantage** : Uses conventional manufacturing techniques
- **Disadvantage** : Requires heavy copper current collector



Carbon Nanofoam with Nano-Silicon Supported on Carbon Paper

- **Advantage** : “Stand Alone” electrode that does not require the use of a current collector (Lighter)
- **Disadvantage** : Would require development of new electrode and cell manufacturing techniques

Estimates for Component Weight Fraction in 30 Ah Cell

Anode copper current collector represents a significant weight fraction (8%)

Copper Vs. Carbon

Theoretical Specific Capacities at the Active Material and Electrode Levels

Electrode	mAh/g Active Material	mAh/g Electrode
Nanofoam	500	500
Graphite With Cu	350	170
Si With Cu	1000	312

Copper Foil 2g
- Not electrochemically active towards lithium

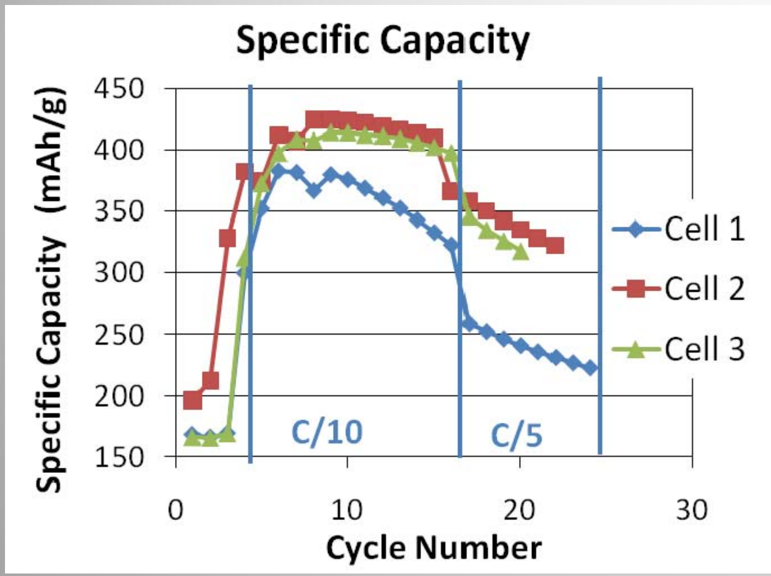
Carbon Paper 0.2 g
- Electrochemically active towards Li (250 mAh/g)

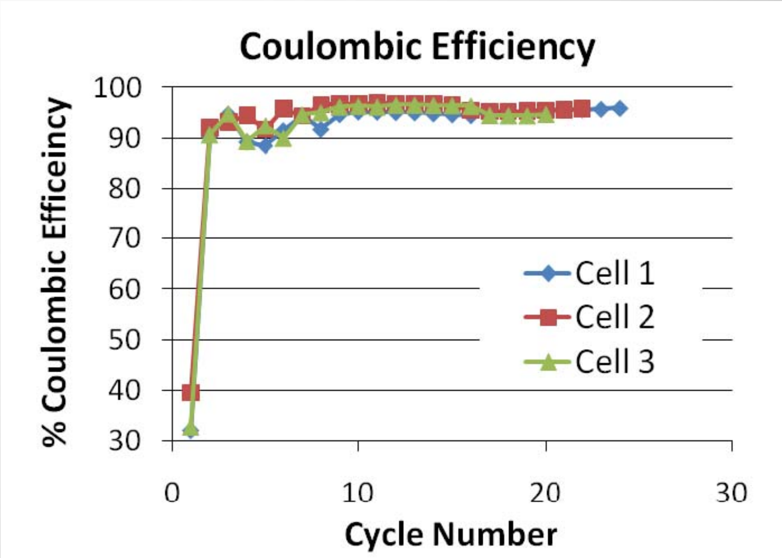
Carbon Microbead Testing

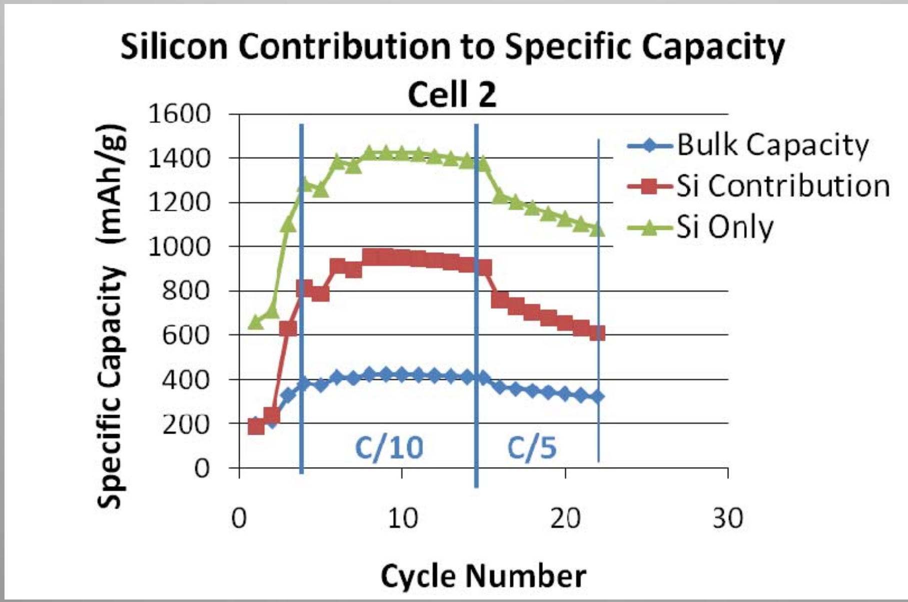
- Carbon microbeads were slurried with NaCMC
- 0.005” film cast onto copper foil
- Anodes placed in coin cells using lithium as the counter electrode
- Electrolyte: 1M $LiPF_6$ 1:1:1 ethylene carbonate, diethyl carbonate and dimethyl carbonate
- Cells formed at C/10 and cycled from 10mV to 1.5 V

National Aeronautics and Space Administration

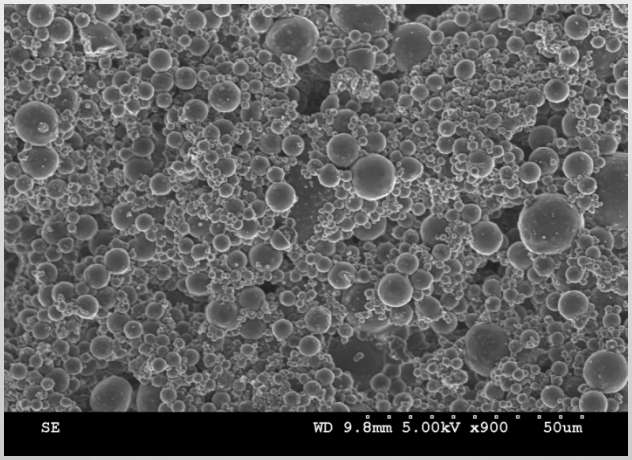
Electrochemical Cycling of Carbon Microbeads



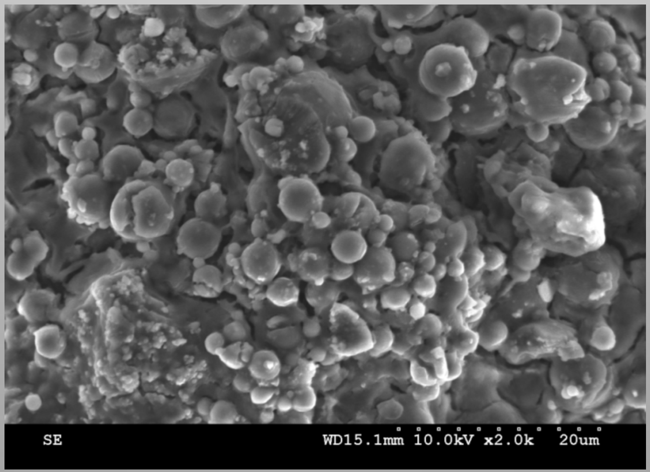




Carbon-Silicon Microbead Electrodes



As Cast Nano- Silicon Carbon Gel Microbead Electrode

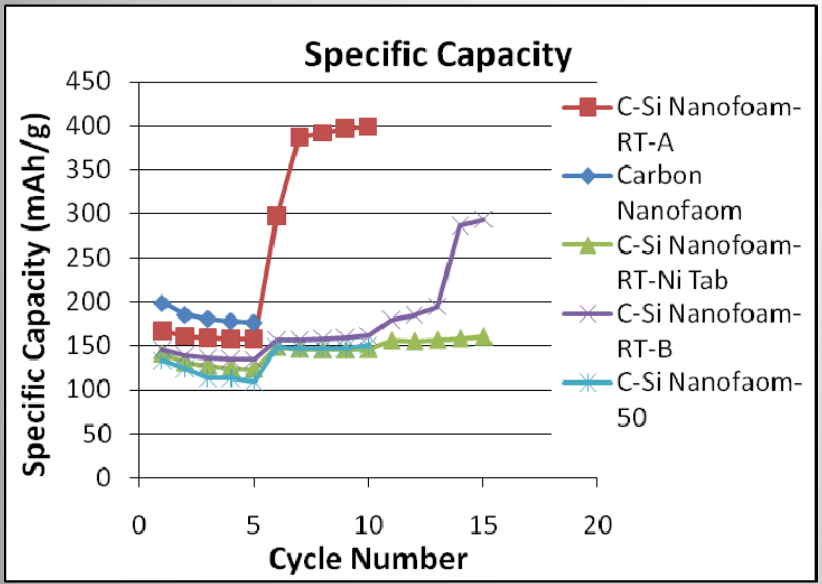


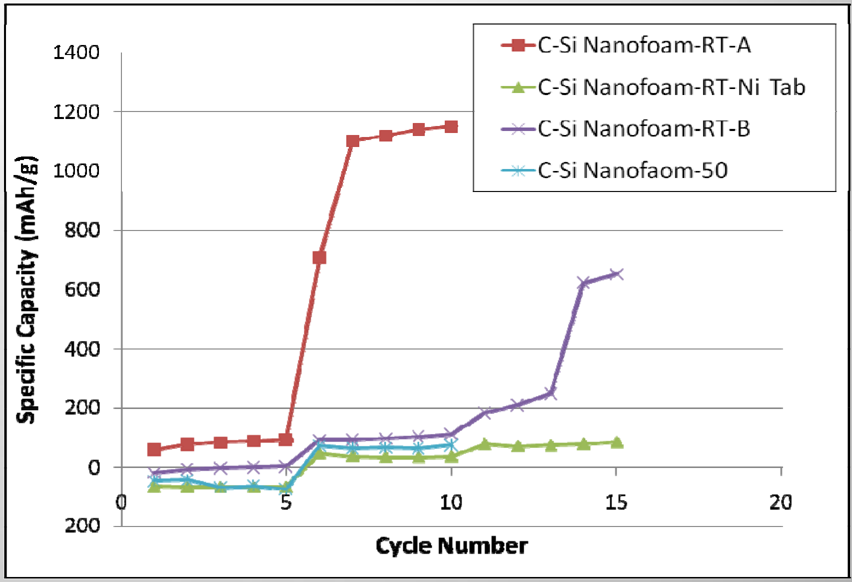
Cast Nano- Silicon Carbon Gel Microbead Electrode After Cycling

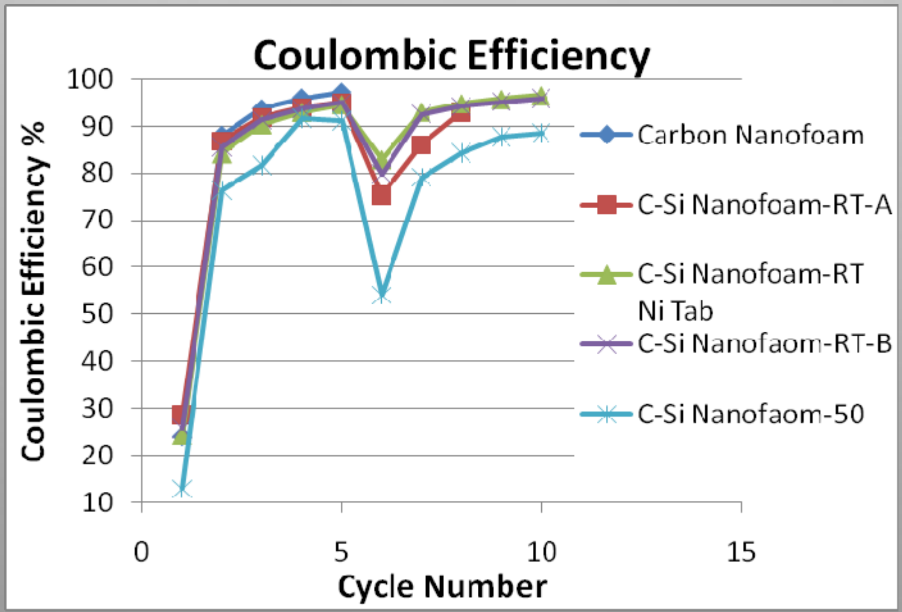
Carbon Nanofoam Half Cells

- Pouch cells
- Nanofoam material placed on copper foil current collectors
- Nickel tab spot-welded instead of the copper foil
- Lithium counter electrode
- First formation at approximately C/5
- Second formation at C/20

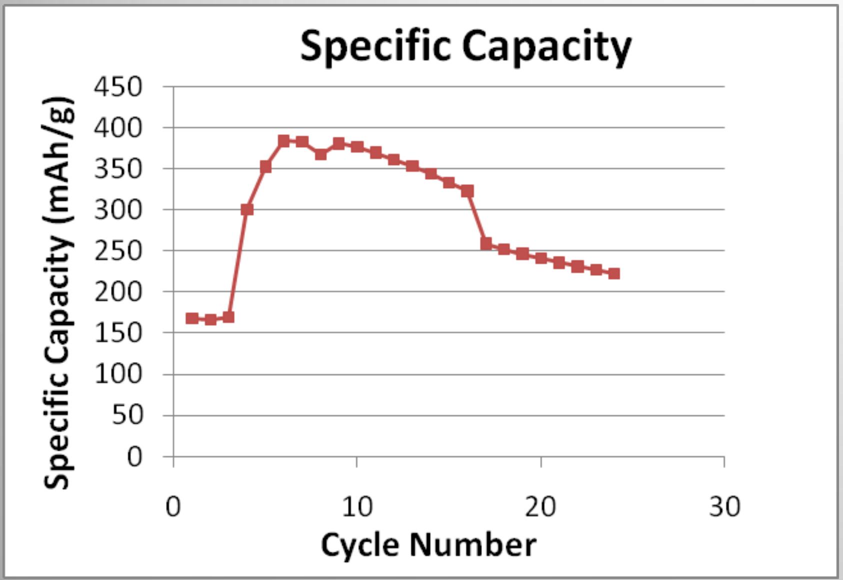
Electrochemical Cycling of Carbon Nanofoam Electrodes

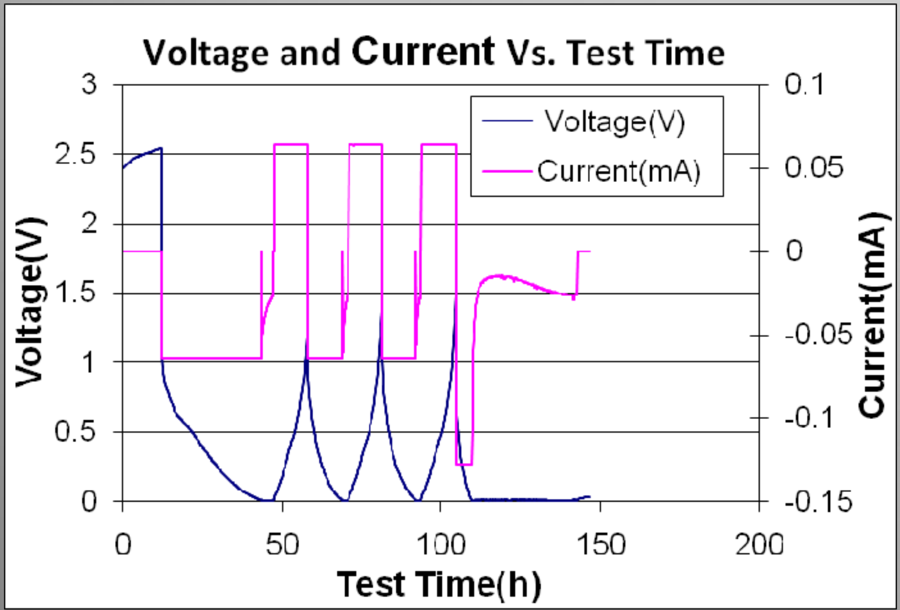


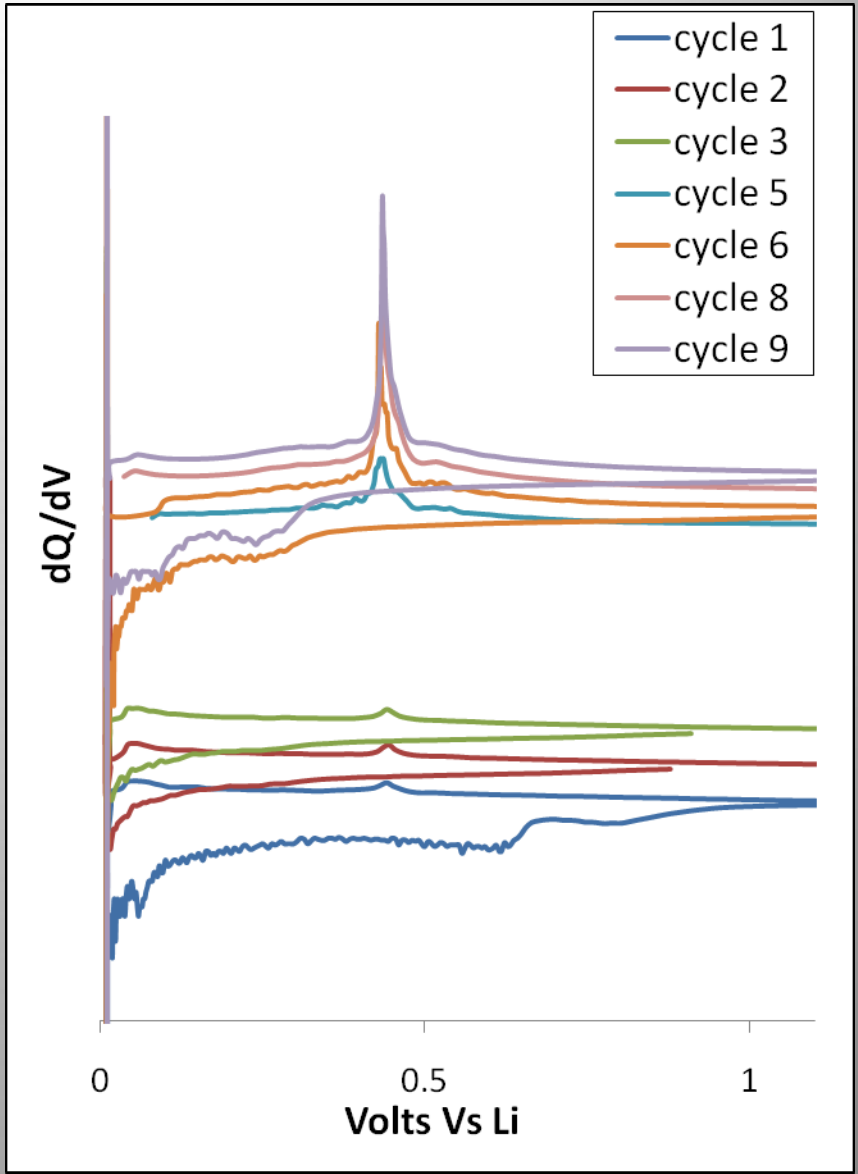




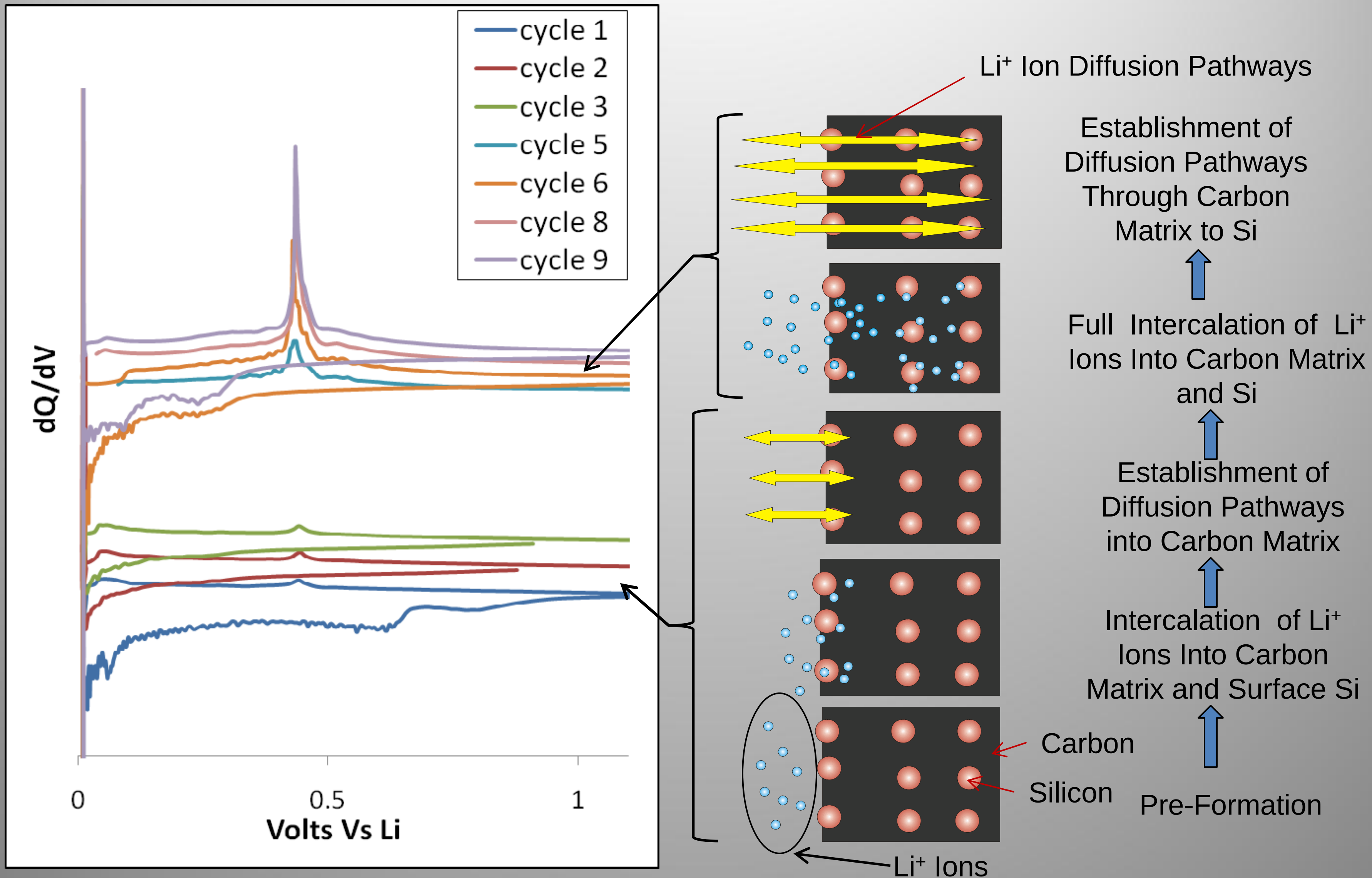
Si-Carbon Microbeads Cell 1







Formation of Lithium Ion Diffusion Pathways



Initial Results

- **Microbeads**
  - 425 mAh/g
  - Short of threshold value of 600 mAh/g and goal of 1000 mAh/g
- **Nanofoam**
  - Initial results showed 400 mAh/g at the electrode level
  - "Stand Alone" anode 100% active material
  - Determined to have a higher potential to meet or exceed goals
  - Decided to focus on development of the carbon nanofoam anodes

Theoretical Specific Capacities at the Active Material and Electrode Levels

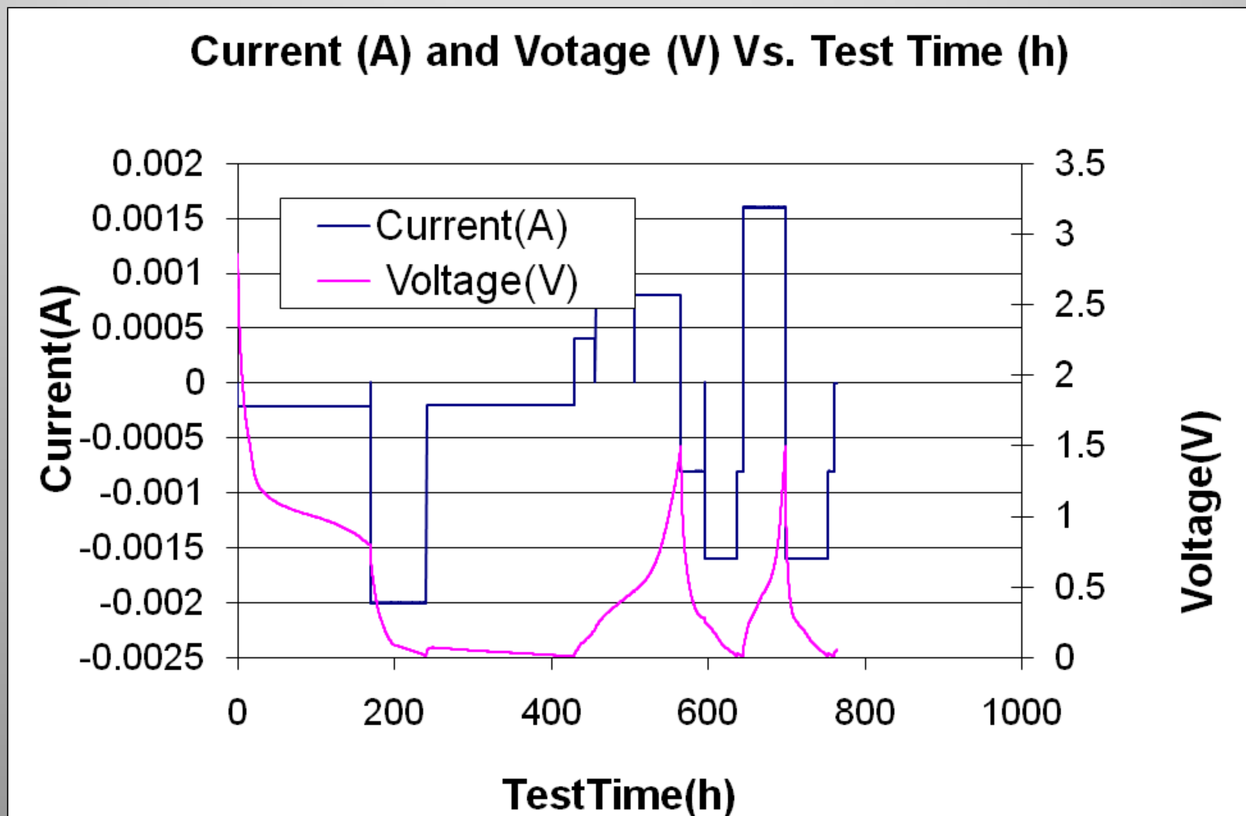
Electrode	mAh/g Active Material	mAh/g Electrode
Nanofoam	500	500
Graphite With Cu	350	170
Si With Cu	1000	312

New Experiments

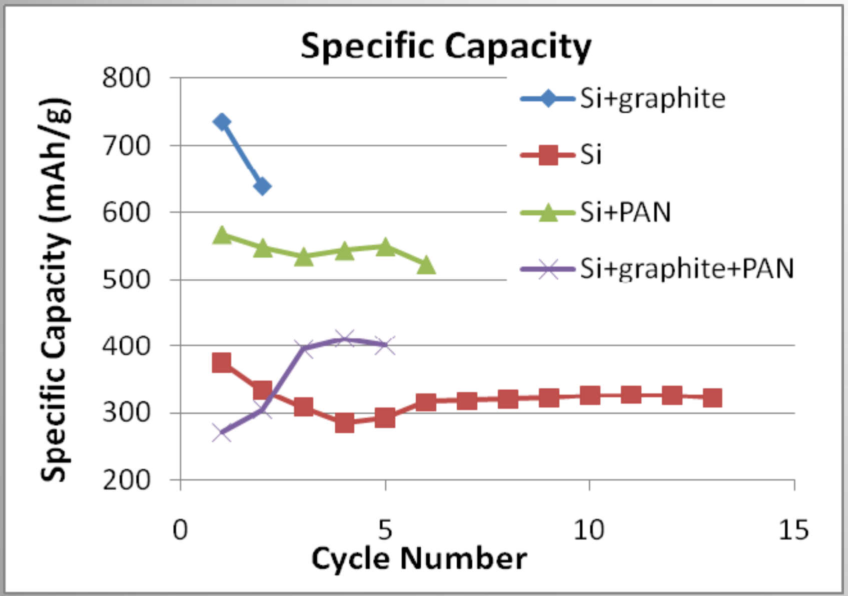
- Improve the performance of the Si-carbon nanofoams by addition of conductive additives or binders
  - Addition of graphite to resorcinol formaldehyde gel
  - Coat with polyaniline doped with $LiPF_6$
- New formation procedure

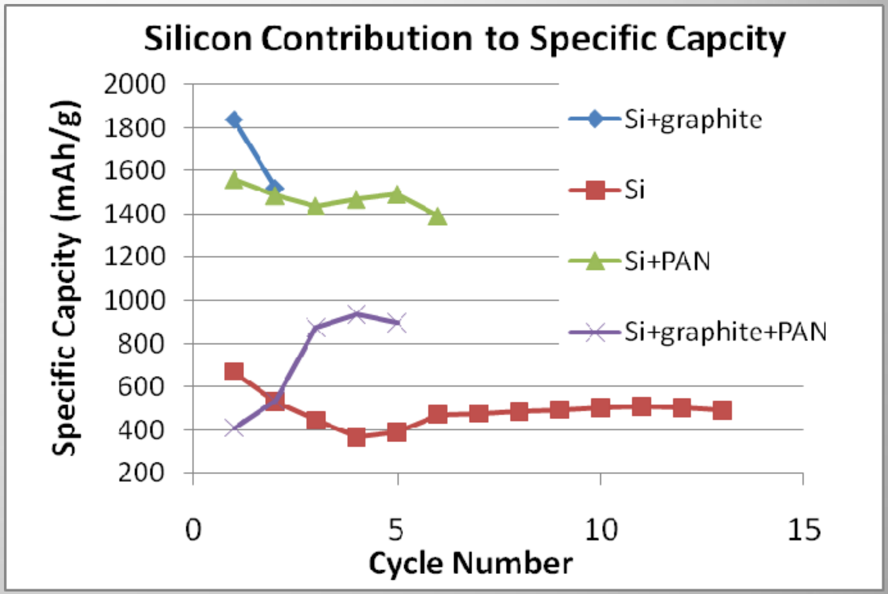
New Formation Procedure

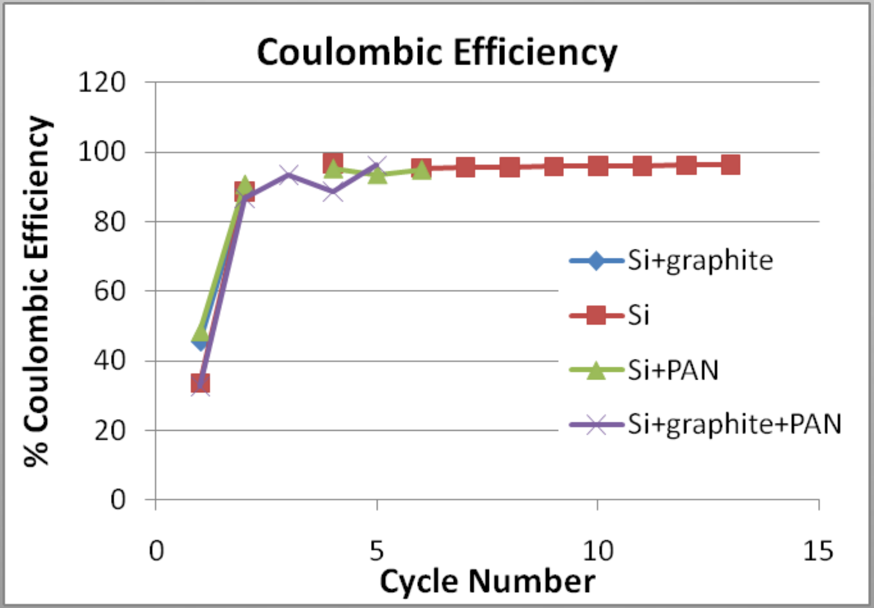
- Very slow initial formation to 10 mV
- Replace taper charge with very low constant current to 10mV



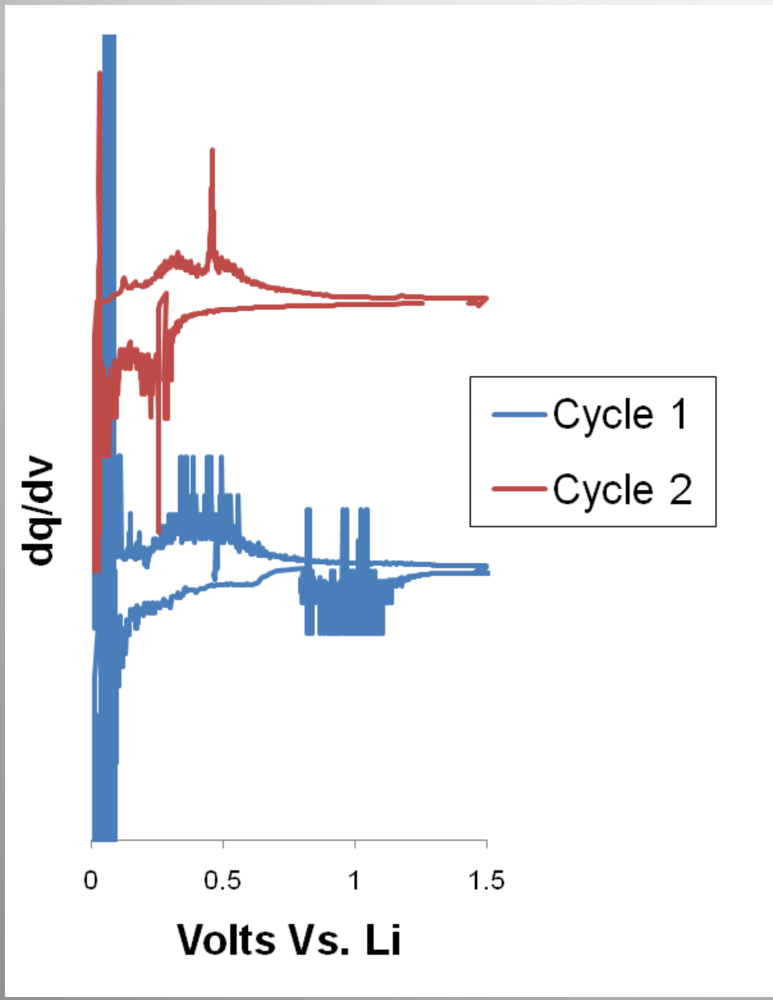
Silicon-Carbon Nanofoams



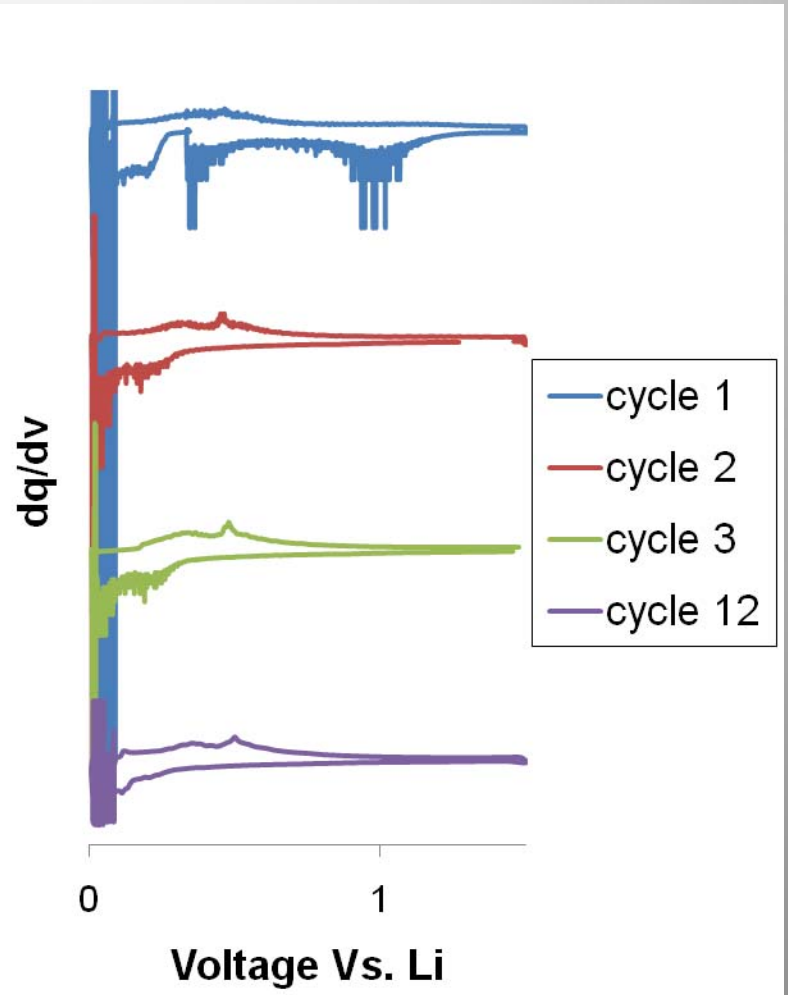




Carbon-Silicon Nanofoam Electrodes

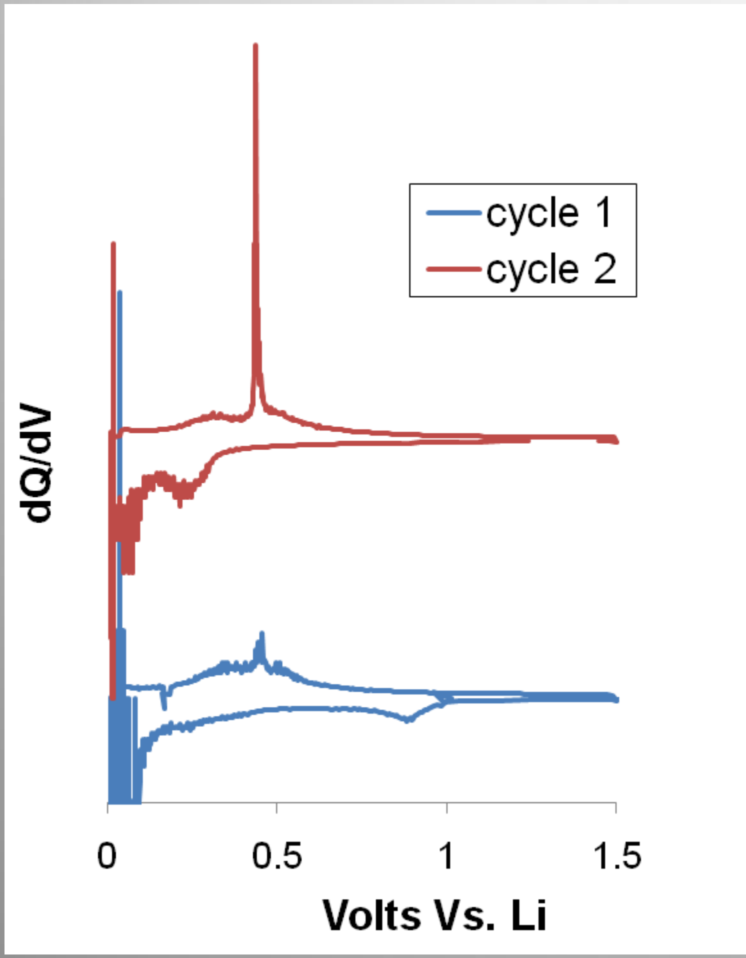


Carbon-Silicon-Graphite Nanofoam

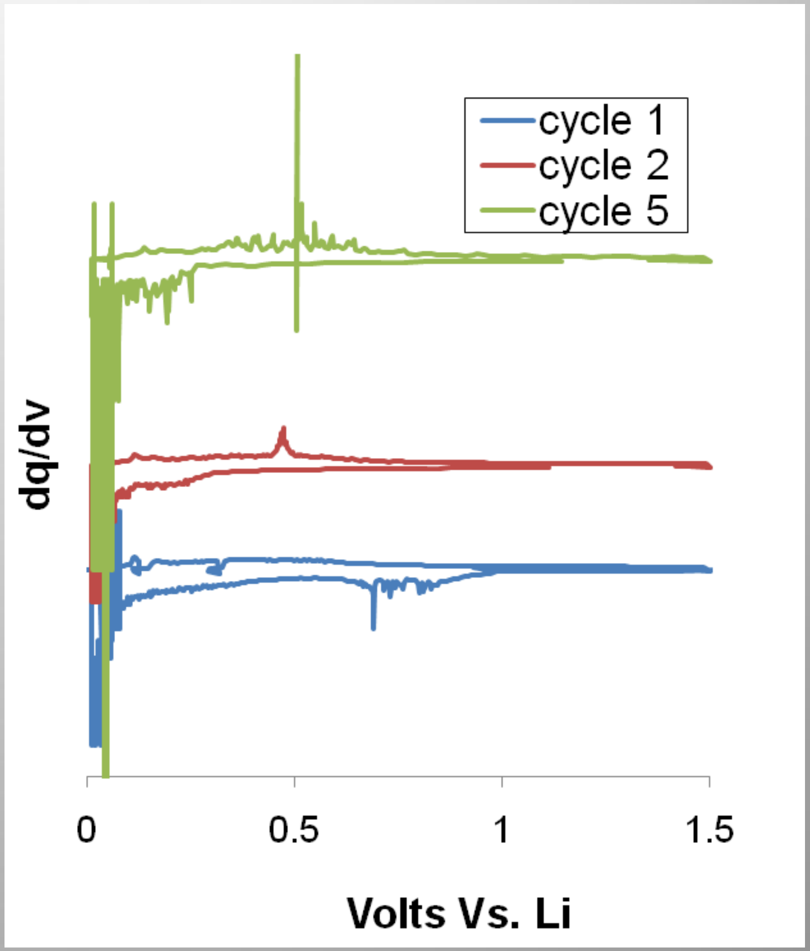


Carbon-Silicon Nanofoam

Polyaniline Coated Carbon-Silicon Nanofoam

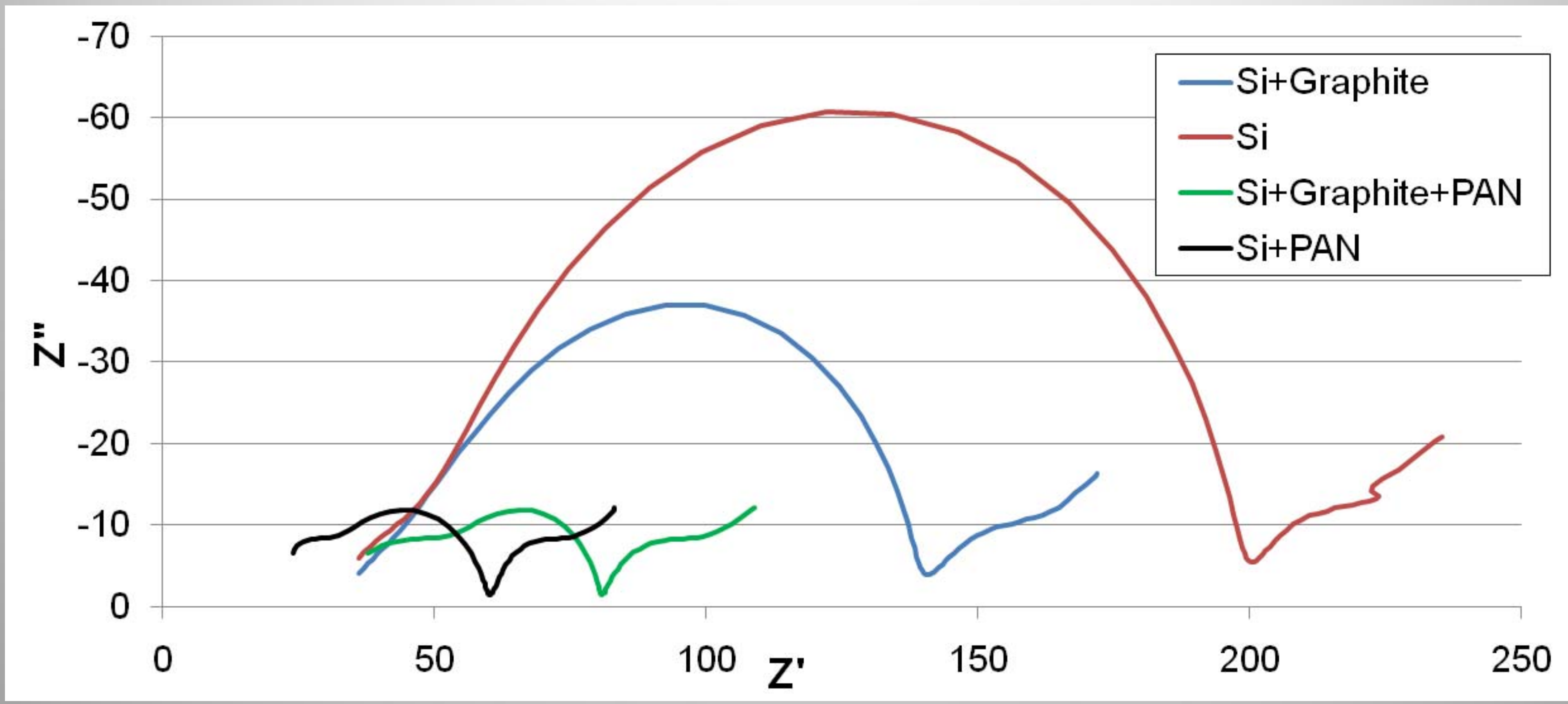


Carbon-Silicon-Graphite Nanofoam



Carbon-Silicon Nanofoam

Nyquist Plot For Si-Carbon Nanofoam Anodes



- The nanofaom containing graphite has a lower impedance than the nanofoam which does not contain graphite
- Samples coated with polyaniline/$LiPF_6$ show drastically lower impedances than those without the coating
- The presence of graphite in combination with the polyaniline coating resulted in a higher impedance than that of a coated sample not containing graphite

Conclusions

- A "Stand Alone" anode has been synthesized with specific capacities that meet and/or exceed the ETDP threshold value of 600 mAh/g and would likely compare favorably, with regard to specific capacity, at the electrode level to conventional coated anode materials
- "Stand Alone" carbon-silicon nanofoam anodes have the greater potential to address NASA goals
- "Stand Alone" carbon-silicon nanofoam anodes have the potential to significantly increase the specific energies (Wh/kg) for lithium-ion cells
- Addition of graphite to the silicon containing carbon nanofoam dramatically increases capacity
- Use of the conductive binder polyaniline doped with $LiPF_6$ dramatically increases capacity
- Very slow formation cycle is required to fully lithiate silicon

Future Work

- Investigate the use of various conductive additives
  - Graphites
  - Carbon Nanotubes
  - Carbon Nanofibers
- Investigate different binders or coatings
- Investigate different gel formulations
- Remove oxygen from matrix

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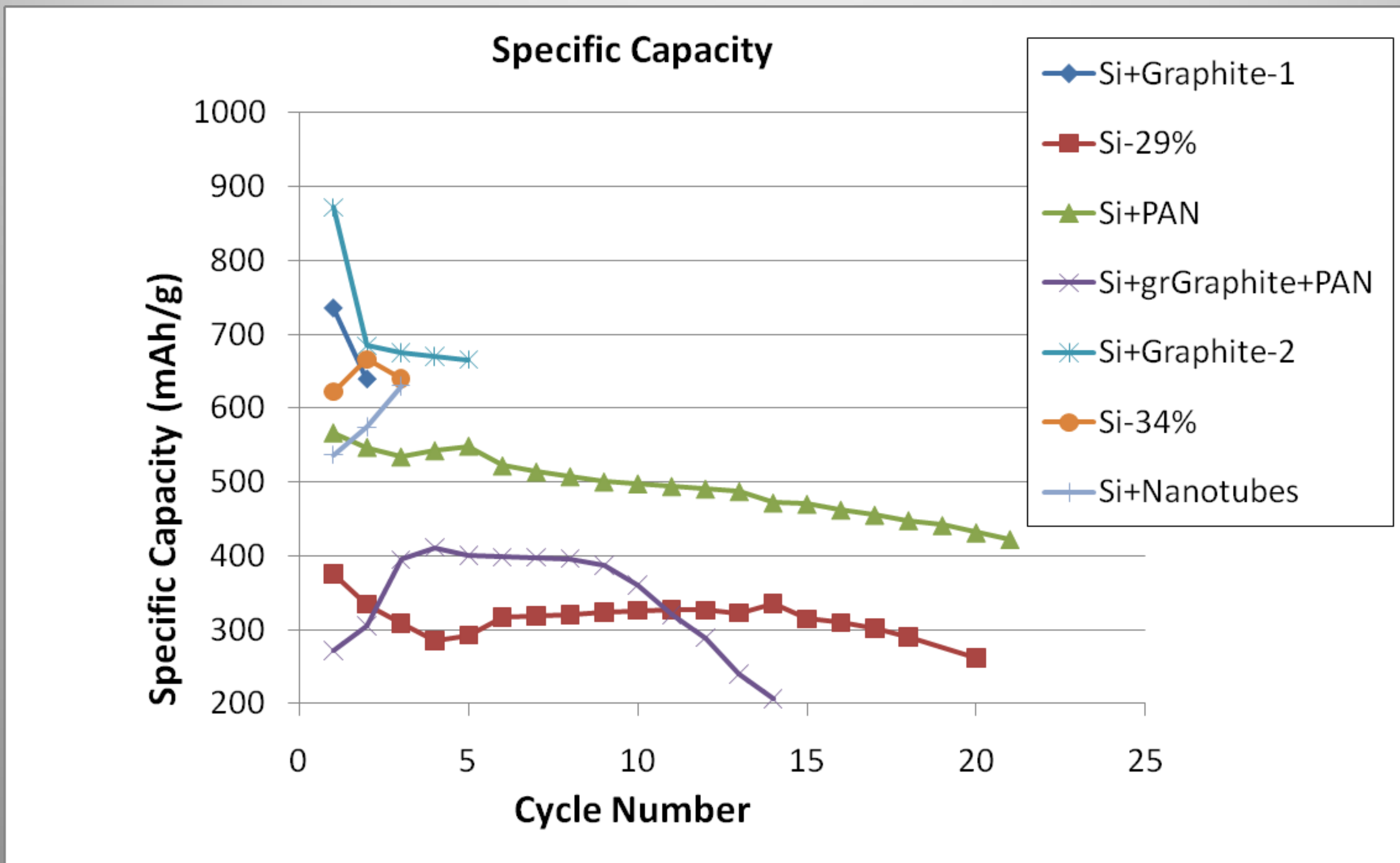
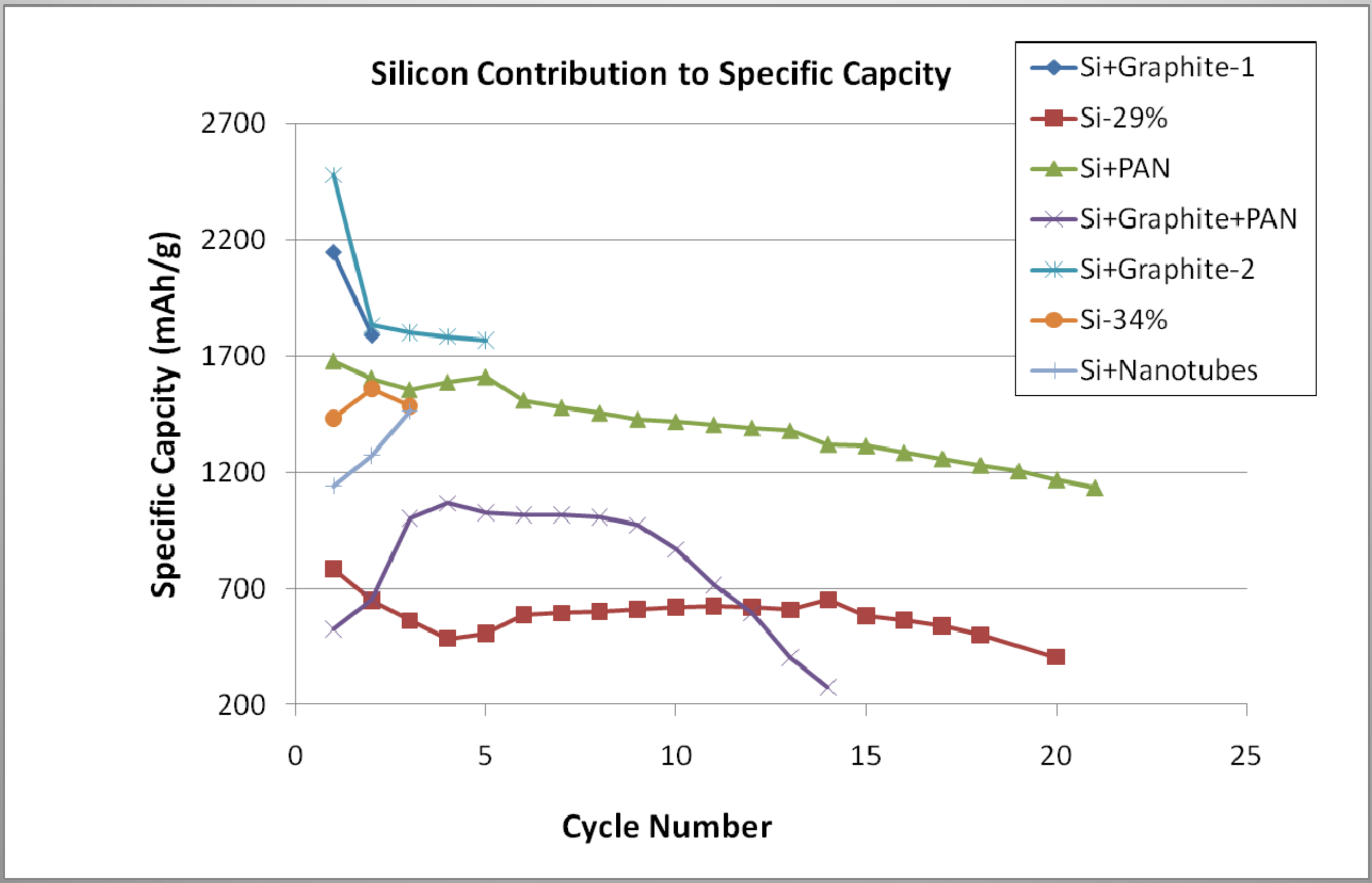
  - Marjorie Moats (SGT)
  - Michelle Manzo (Electrochemistry Branch Chief NASA GRC)

Supplementary Slides

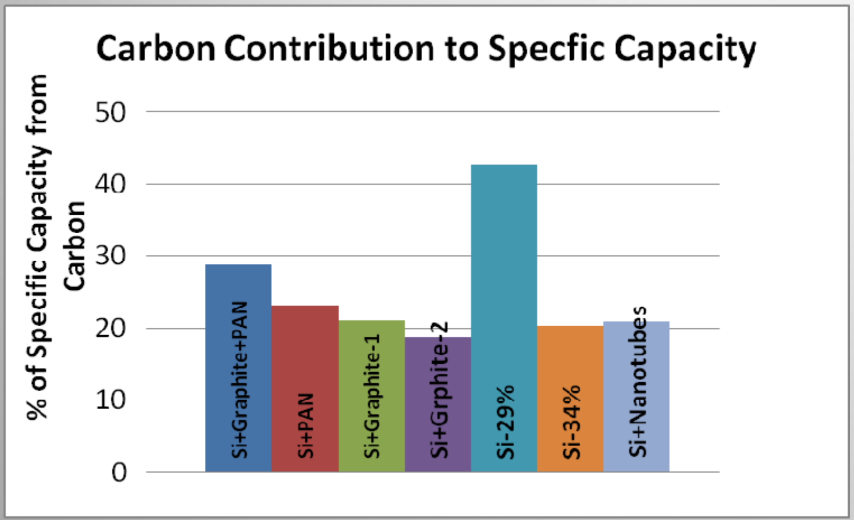
Updated Results for Carbon-Silicon Nanofoam Electrodes

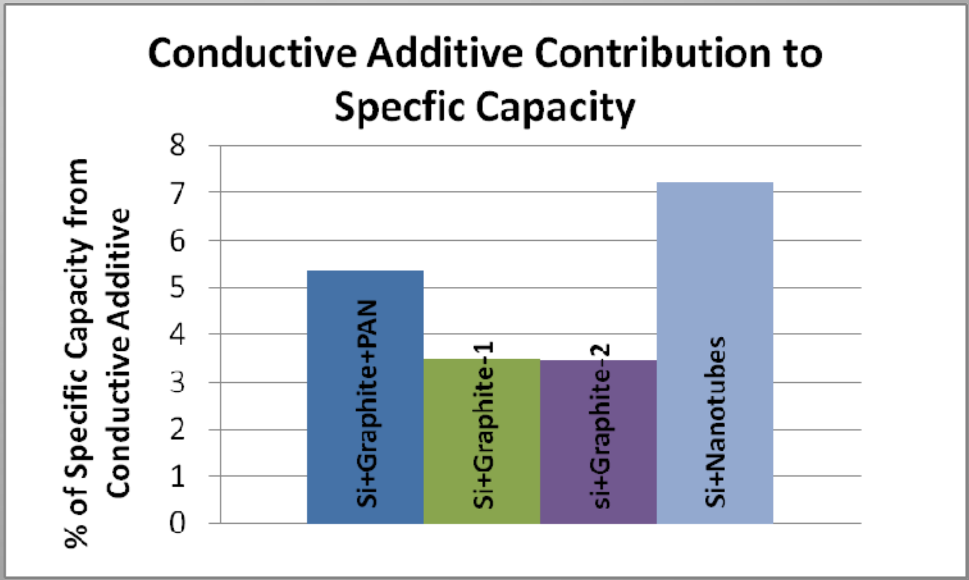


Updated Results for Carbon-Silicon Nanofoam Electrodes Continued



Contribution of Non-silicon Components to the Specific Capacities Carbon-Silicon Nanofoam Electrodes





Synthetic Conditions

- **Carbon-Silicon Microspheres**
- Resorcinol-Formaldehyde containing 50 nm silicon is dispersed in a solution of cyclohexane and Span 80 surfactant
- Sonicated
- Stirred for two days a room temperature
- Recovered and rinsed
- Freeze dried in t-butanol
- Pyrolyzed at 1000º in argon

- **Carbon-Silicon Nanofoam**
- Carbon fiber paper impregnated with resorcinol-formaldehyde gel containing 50 nm silicon particles
- Sealed in plastic bags and placed between glass plates
- Cured at room temperature for2 days
- Freeze dried in t-butanol
- Pyrolyzed at 1000º C in argon

Hasegawa, T.; Mukai, S. R.; Shirato, Y.; Tamon, H. *Carbon* **2004**, *42*, 2573-2579.
Yamamoto, Sugimoto, Suzuki, Mukai, Tamon *Carbon* **2002**, *40*, 1345-1351.

National Aeronautics and Space Administration

Key Performance Parameters for Battery Technology Development

Customer Need	Performance Parameter	State-of-the-Art	Current Value	Threshold Value	Goal
Safe, reliable operation	No fire or flame	Instrumentation/controllers used to prevent unsafe conditions. There is no non-flammable electrolyte in SOA	Preliminary results indicate a small reduction in performance using safer electrolytes and cathode coatings	Tolerant to electrical and thermal abuse such as over-temperature, over- charge, reversal, and short circuits with no fire or thermal runaway***	Tolerant to electrical and thermal abuse such as over-temperature, over-charge, reversal, and short circuits with no fire or thermal runaway***
Specific energy Lander: 150 – 210 Wh/kg 10 cycles Rover: 160-200 Wh/kg 2000 cycles EVA: 270Wh/kg 100 cycles	**Battery-level** specific energy* [Wh/kg]	90 Wh/kg at C/10 & 30°C 83 Wh/kg at C/10 & 0°C (MER rovers)	160 at C/10 & 30°C (HE) 170 at C/10 & 30°C (UHE) 80 Wh/kg at C/10 & 0°C (predicted)	**135** Wh/kg at C/10 & 0°C "High-Energy"** **150** Wh/kg at C/10 & 0°C "Ultra-High Energy"**	**150** Wh/kg at C/10 & 0°C "High-Energy" **220** Wh/kg at C/10 & 0°C "Ultra-High Energy"
	Cell-level specific energy [Wh/kg]	130 Wh/kg at C/10 & 30°C 118 Wh/kg at C/10 & 0°C	199 at C/10 & 23°C (HE) 213 at C/10 & 23°C (UHE) 100 Wh/kg at C/10 & 0°C (predicted)	**165** Wh/kg at C/10 & 0°C "High-Energy" **180** Wh/kg at C/10 & 0°C "Ultra-High Energy"	**180** Wh/kg at C/10 & 0°C "High-Energy" **260** Wh/kg at C/10 & 0°C "Ultra-High Energy"
	Cathode-level specific capacity [mAh/g]	180 mAh/g	252 mAh/g at C/10 & 25°C 190 mAh/g at C/10 & 0°C	**260** mAh/g at C/10 & 0°C	**280** mAh/g at C/10 & 0°C
	Anode-level specific capacity [mAh/g]	280 mAh/g (MCMB)	330 @ C/10 & 0°C (HE) 1200 mAh/g @ C/10 & 0°C for 10 cycles (UHE)	**600** mAh/g at C/10 & 0°C "Ultra-High Energy"	**1000** mAh/g at C/10 0°C "Ultra-High Energy"
Energy density Lander: 311 Wh/l Rover: TBD EVA: 400 Wh/l	**Battery-level** energy density	250 Wh/l	n/a	**270** Wh/l "High-Energy" **360** Wh/l "Ultra-High"	**320** Wh/l "High-Energy" **420** Wh/l "Ultra-High"
	Cell-level energy density	320 Wh/l	n/a	**385** Wh/l "High-Energy" **460** Wh/l "Ultra-High"	**390** Wh/l "High-Energy" **530** Wh/l "Ultra-High"
Operating environment 0°C to 30°C, Vacuum	Operating Temperature	-20°C to +40°C	0°C to +30°C	**0°C** to **30°C**	**0°C** to **30°C**