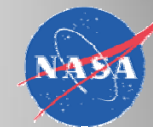


Carbon Cryogel and Carbon Paper-Based Silicon Composite Anode Materials for Lithium-Ion Batteries

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.⁶ 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.¹⁻⁵ 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.

References

1. Wang, K.; He, X.; Wang, L.; Ren, J.; Jiang, C.; Chunrong, W. *Solid State Ionics* **2007**, *178*, 115-118.
2. Hasegawa, T.; Mukai, S. R.; Shirato, Y.; Tamon, H. *Carbon* **2004**, *42*, 2573-2579.
3. Long, J. W.; Bourg, M. E.; Wallace, J. M.; Fischer, A. E.; Lytle, J. C.; Pettigrew, K. A.; Barrow, A. J.; Dysart, J. L.; Rolinson, D. R. In *215 Electrochemical Society Meeting* San Francisco CA, 2009.
4. Long, J. W., 2009, pp Personal Communication.
5. Wang, G. X.; Ahn, J. H.; Yao, J.; Bewlay, S.; Liu, H. K. *Electrochemistry Communications* **2004**, *6*, 689-692.
6. Kasavajjula, U.; Wang, C.; Appleby, J. A. *Journal of Power Sources* **2007**, *163*, 1003-1039.



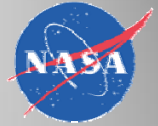
Carbon Cryogel and Carbon Paper-Based Silicon Composite Anode Materials for Lithium- Ion Batteries

James Woodworth

NASA Postdoctoral Program Fellow
Electrochemistry Branch Glenn Research
Center

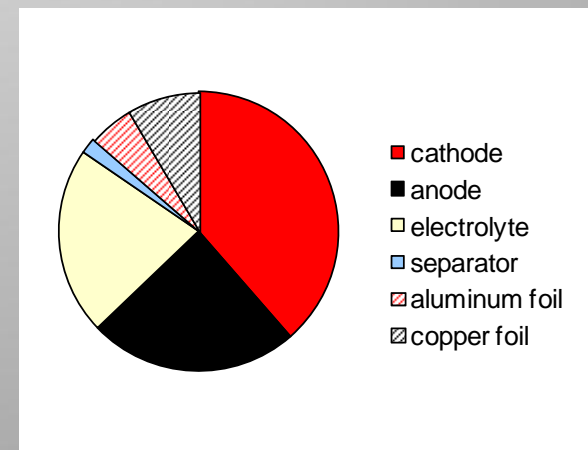
Richard Baldwin and William Bennett

Electrochemistry Branch Glenn Research
Center

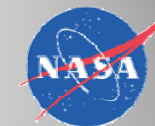


Introduction

- 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



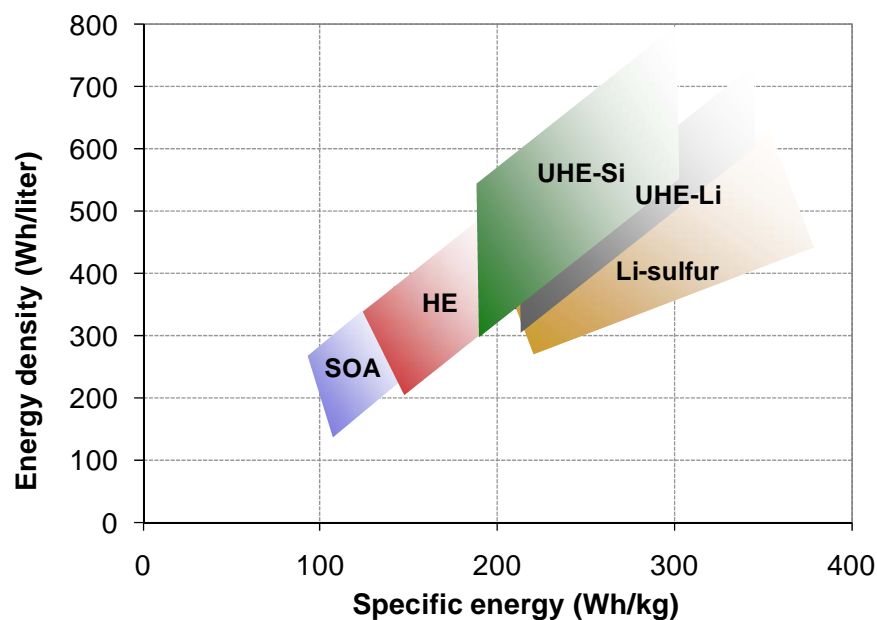
Estimates for component weight fraction in 30 Ah cell

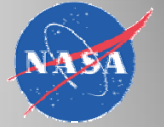


Anode Materials

- Graphite
 - Excellent cycling characteristics
 - Theoretical capacity of 372 mAh/g
- Silicon
 - Theoretical capacity of 4200 mAh/g
 - 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

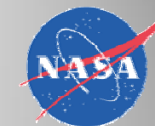
Estimates for cell specific energy and energy density





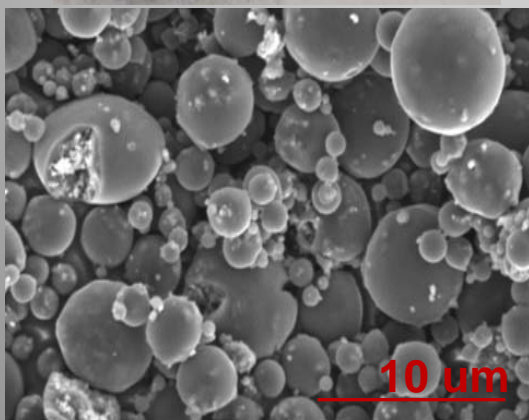
In-House Anode Synthesis

- 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



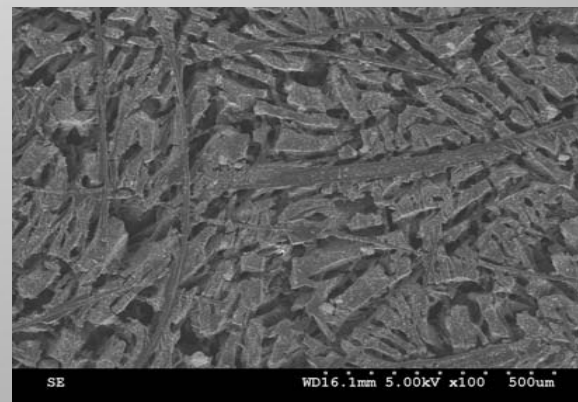
Carbon Cryogel Anode Materials

Carbon-Silicon Microbeads



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

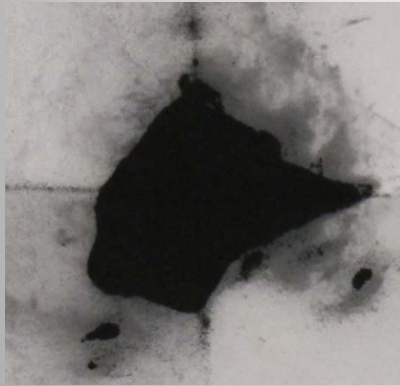
Carbon Nanofoam with Nano-Silicon Supported on Carbon Paper



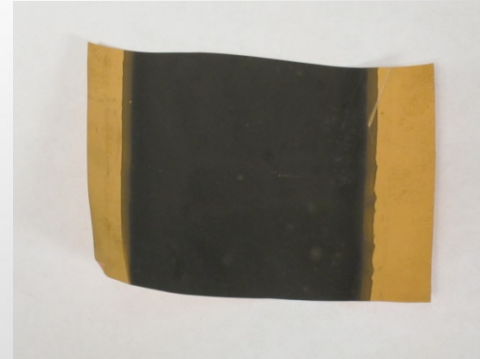
Carbon nanofoams are currently under investigation by J. Long at NRL for use in electrochemical capacitors and as electrode support materials



Carbon-Silicon Microbeads



Mix microbeads
with binder and
cast onto copper
foil current
collector

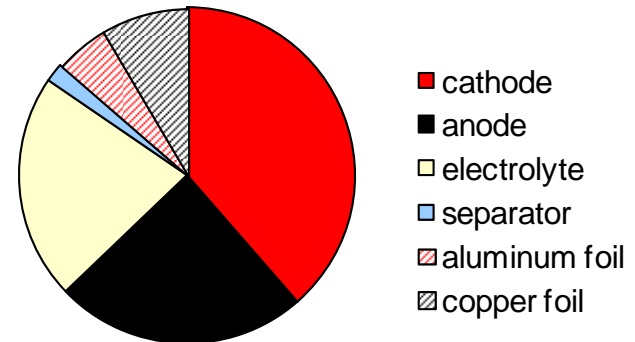


- **Advantage** : Uses conventional manufacturing techniques
- **Disadvantage** : Requires heavy copper current collector

Carbon Nanofoam with Nano-Silicon Supported on Carbon Paper

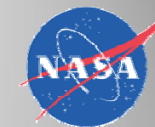


- **Advantage** : “Stand Alone” electrode that does not require the use of a current collector (Lighter)
- **Disadvantage** : Would require development of new electrode and cell manufacturing techniques



Estimates for Component Weight Fraction in 30 Ah Cell

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



Copper Vs. Carbon



Copper Foil 2g

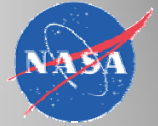
- Not electrochemically active towards lithium

Carbon Paper 0.2 g

- Electrochemically active towards Li (250 mAh/g)

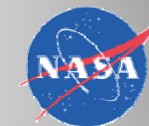
Theoretical Specific Capacities at the Active Material and Electrode Levels

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

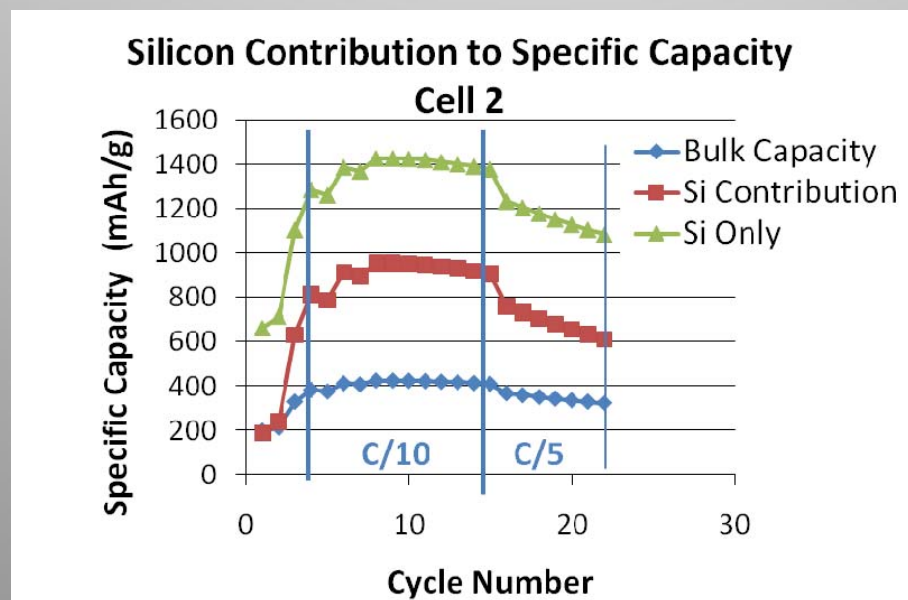
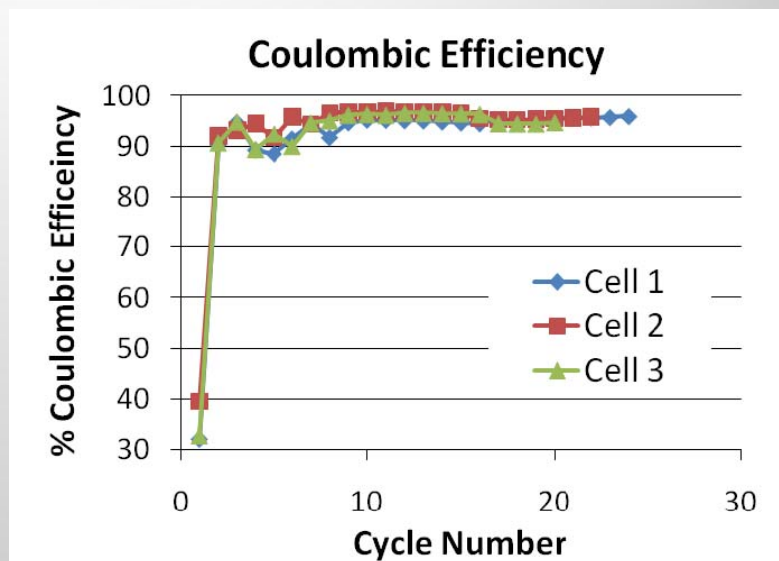
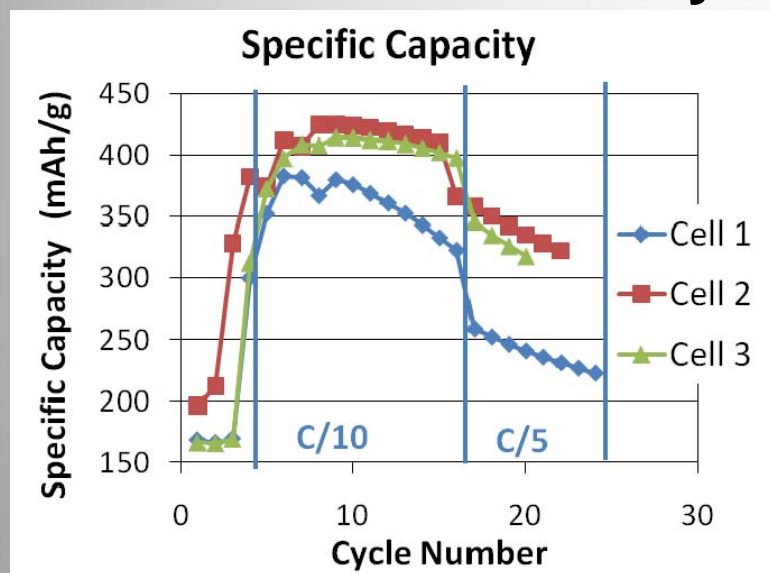


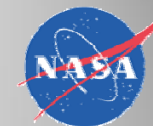
Carbon Microbead Testing

- 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

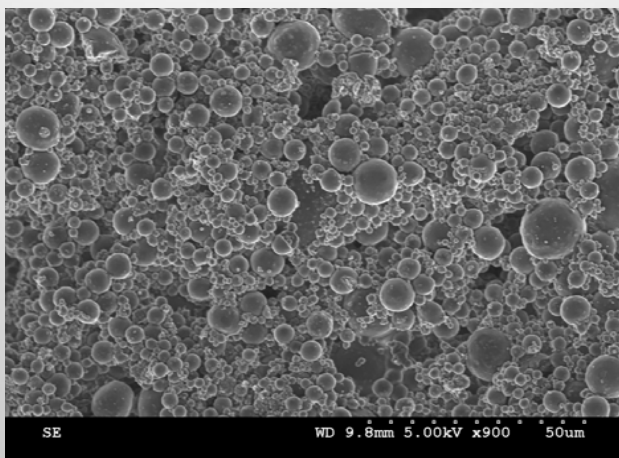


Electrochemical Cycling of Carbon Microbeads

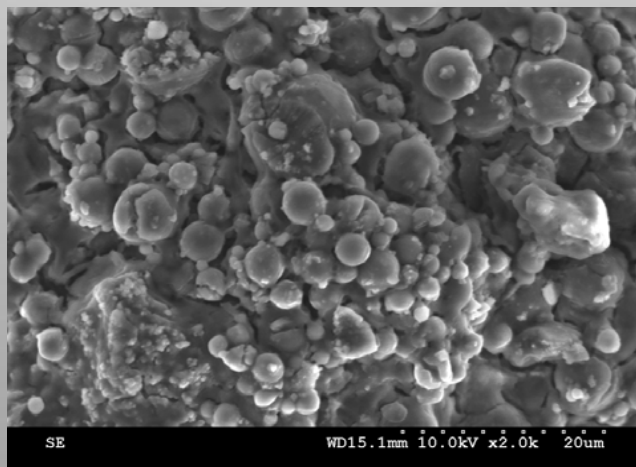




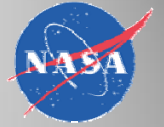
Carbon-Silicon Microbead Electrodes



As Cast Nano- Silicon Carbon Gel Microbead Electrode

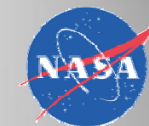


Cast Nano- Silicon Carbon Gel Microbead Electrode After Cycling

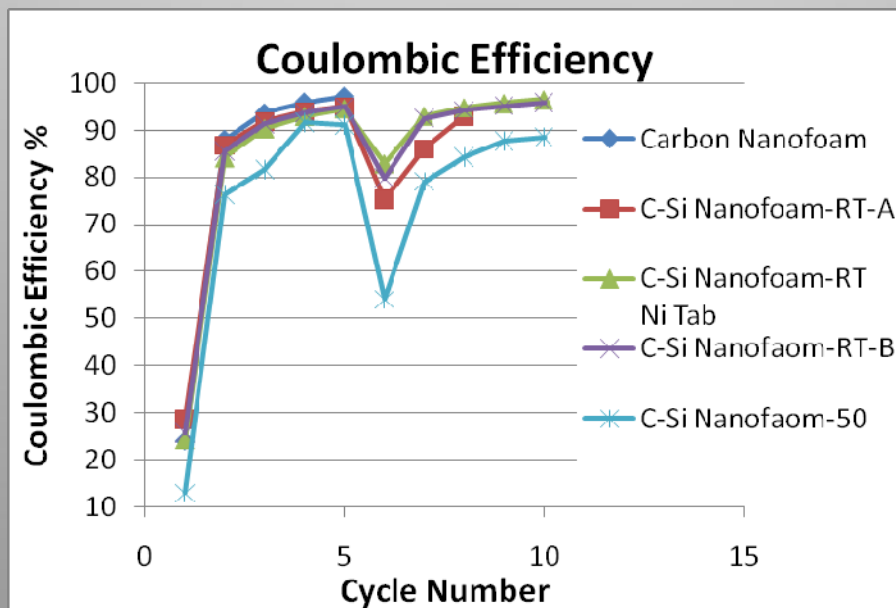
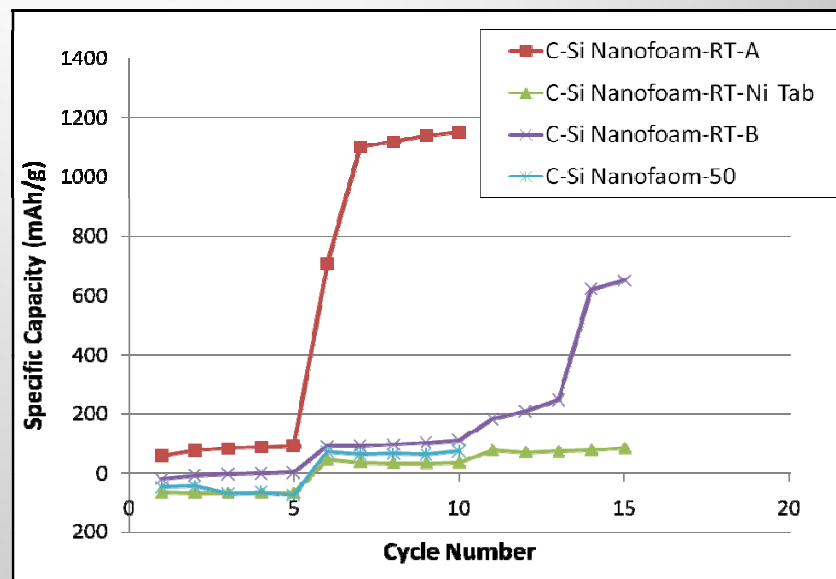
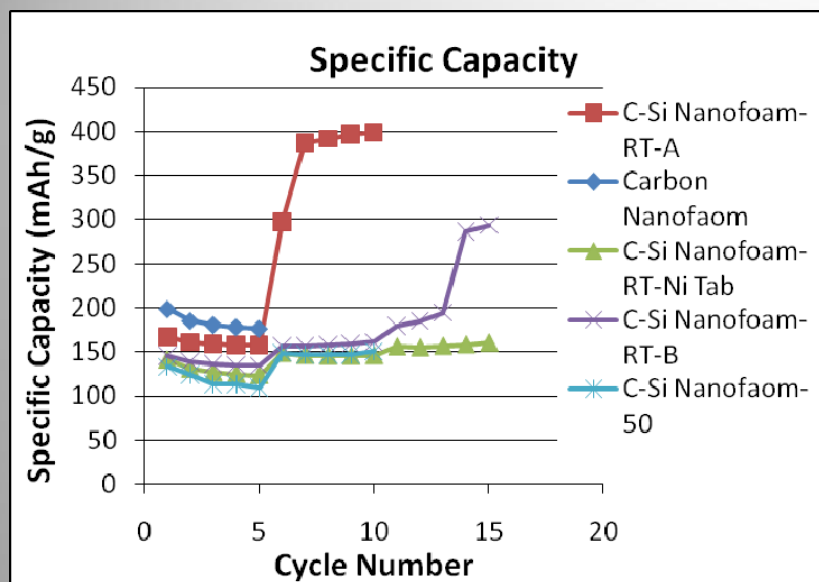


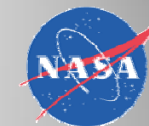
Carbon Nanofoam Half Cells

- 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

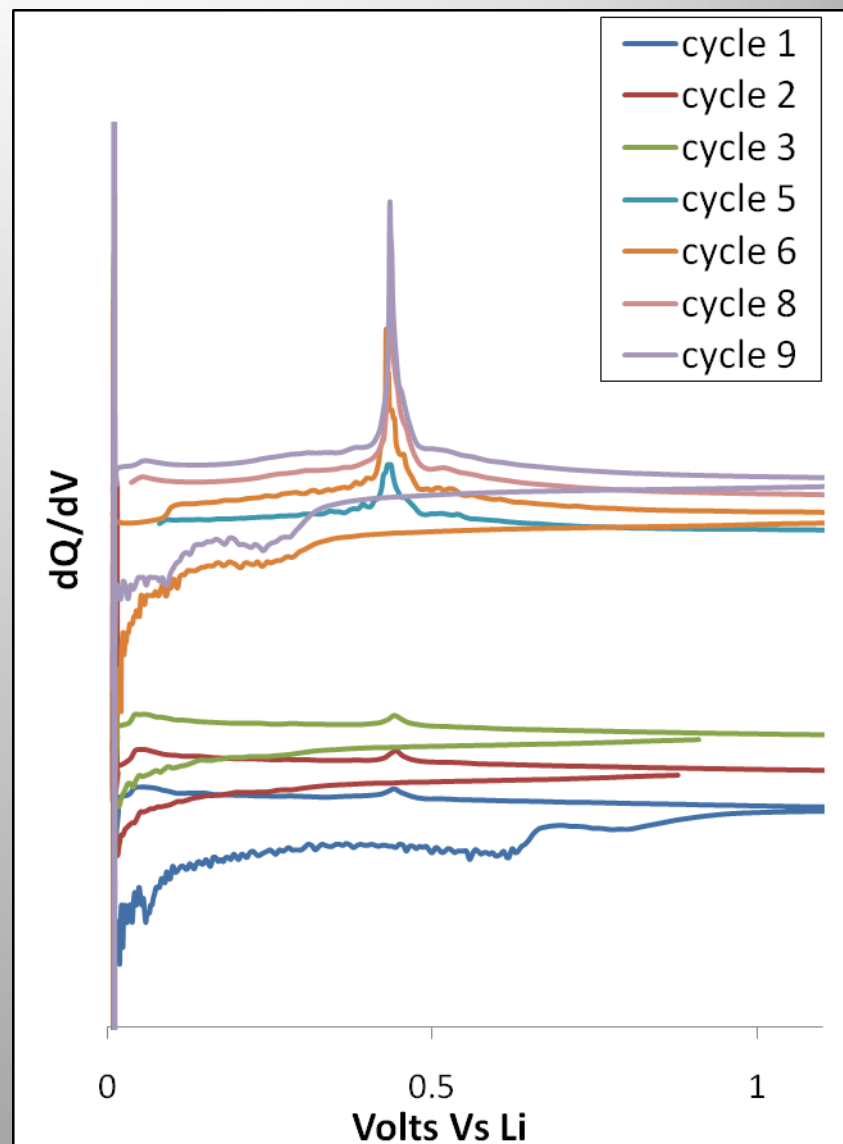
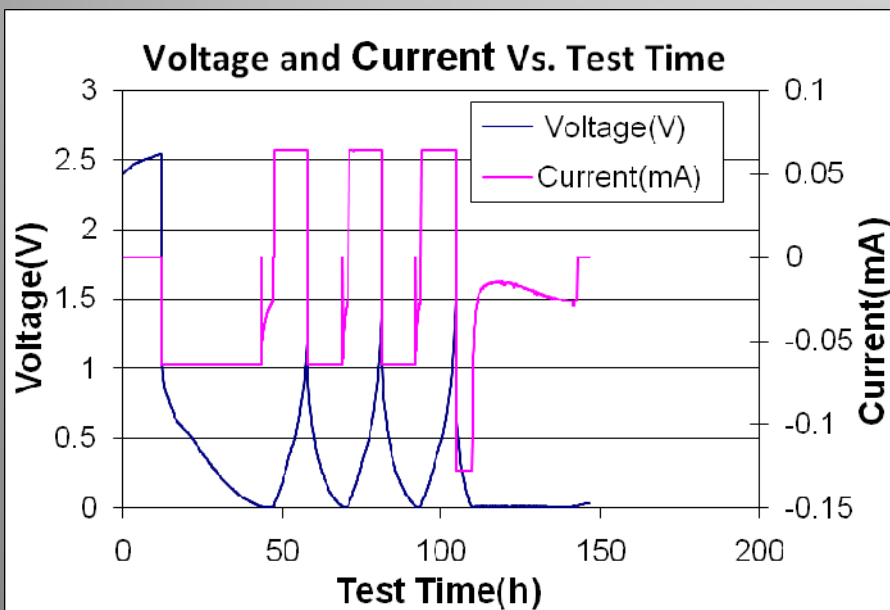
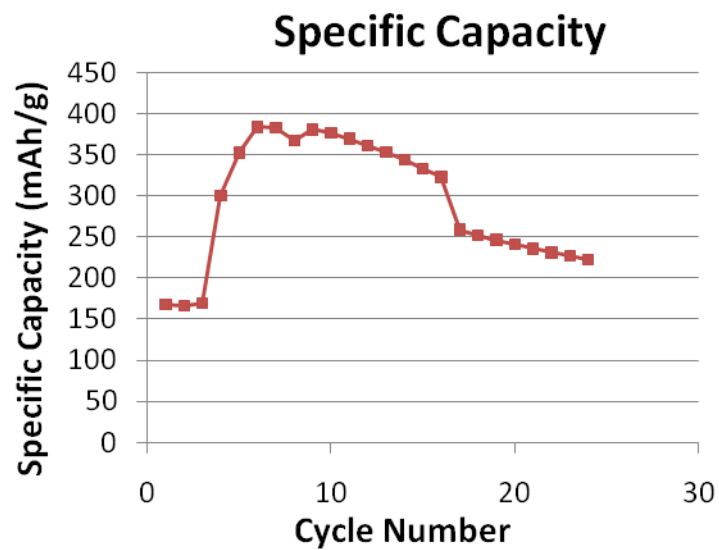


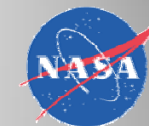
Electrochemical Cycling of Carbon Nanofoam Electrodes



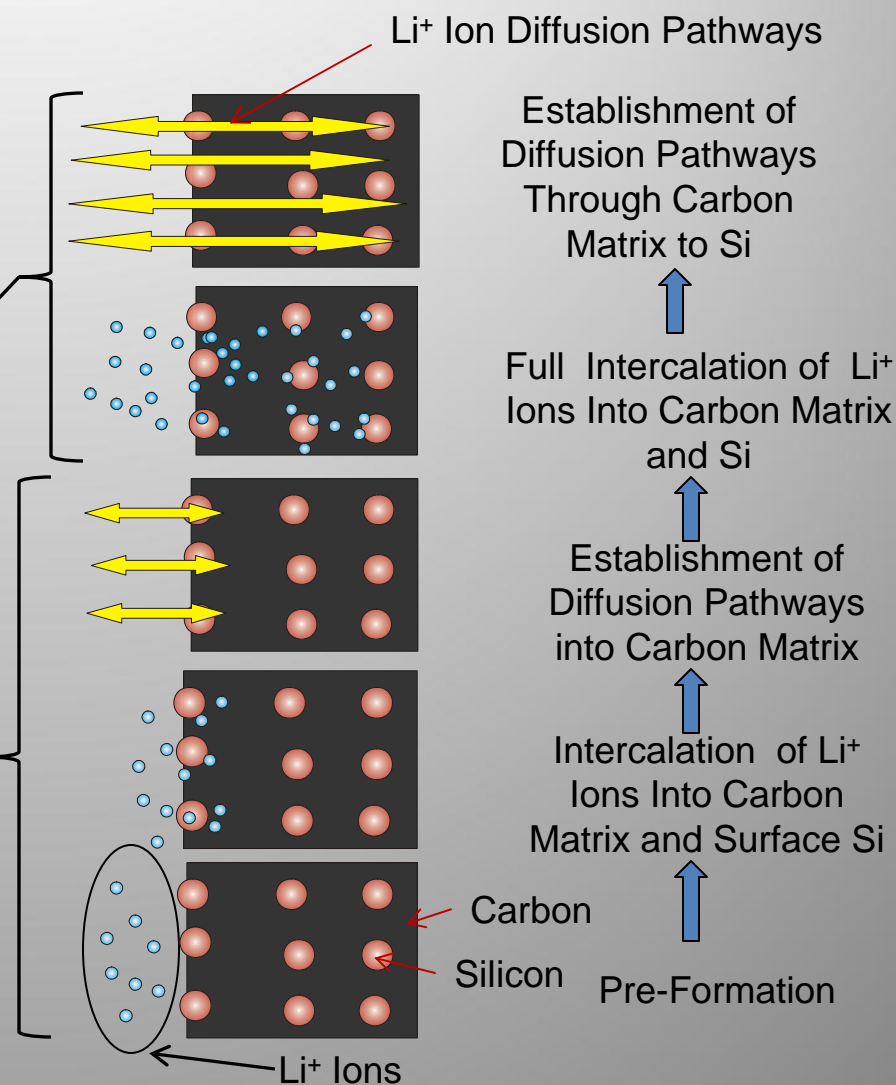
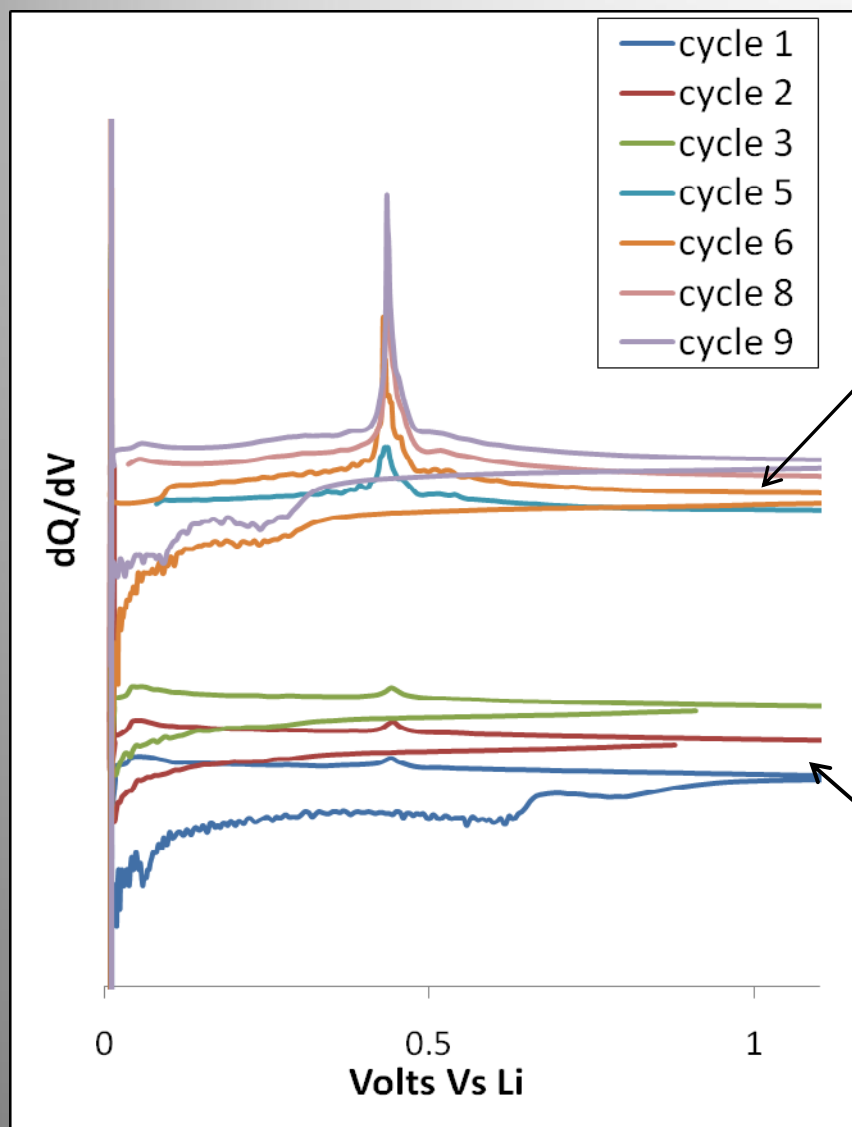


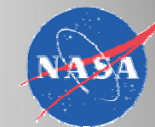
Si-Carbon Microbeads Cell 1





Formation of Lithium Ion Diffusion Pathways



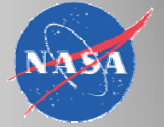


Initial Results

- **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

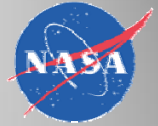
Theoretical Specific Capacities at the Active
Material and Electrode Levels

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



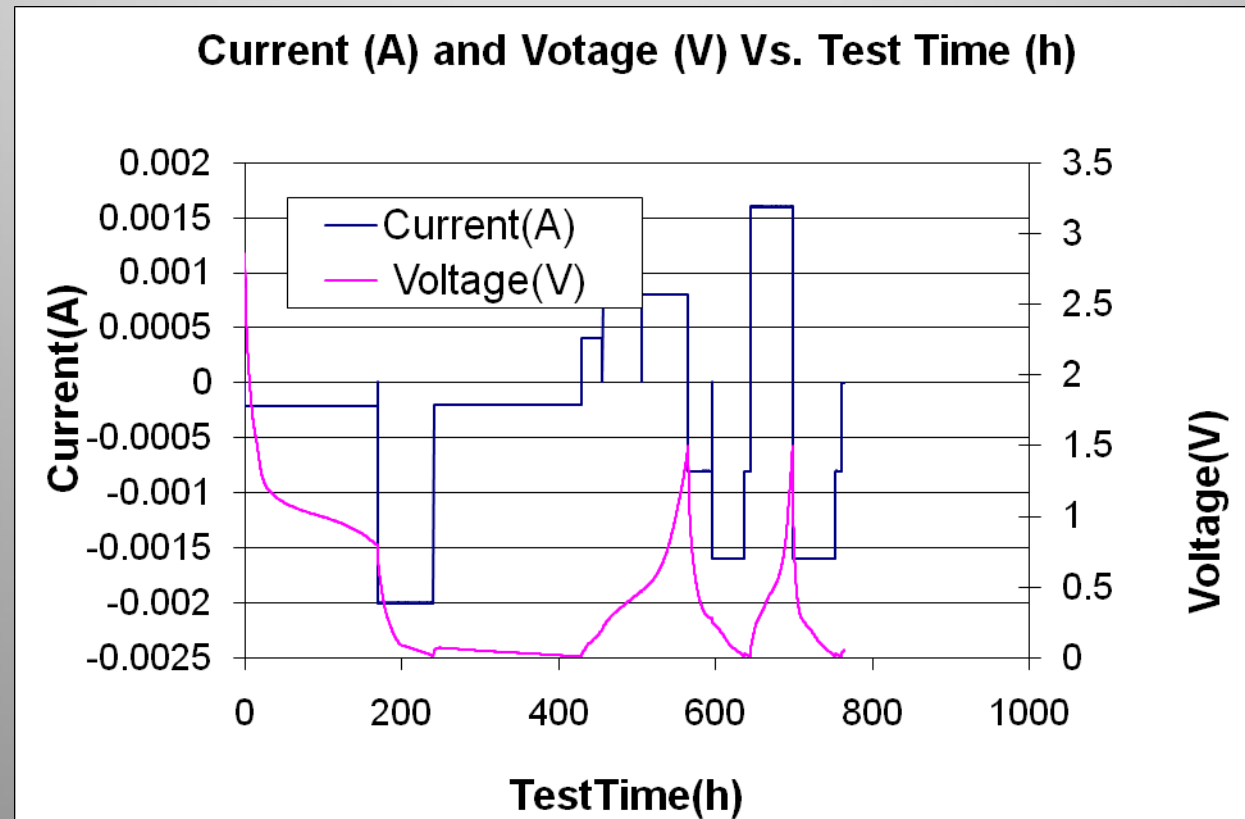
New Experiments

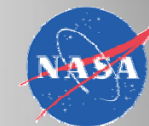
- Improve the performance of the Si-carbon nanofoams by addition of conductive additives or binders
 - Addition of graphite to resorcinol formaldehyde gel
 - Coat with polyaniline doped with LiPF_6
- New formation procedure



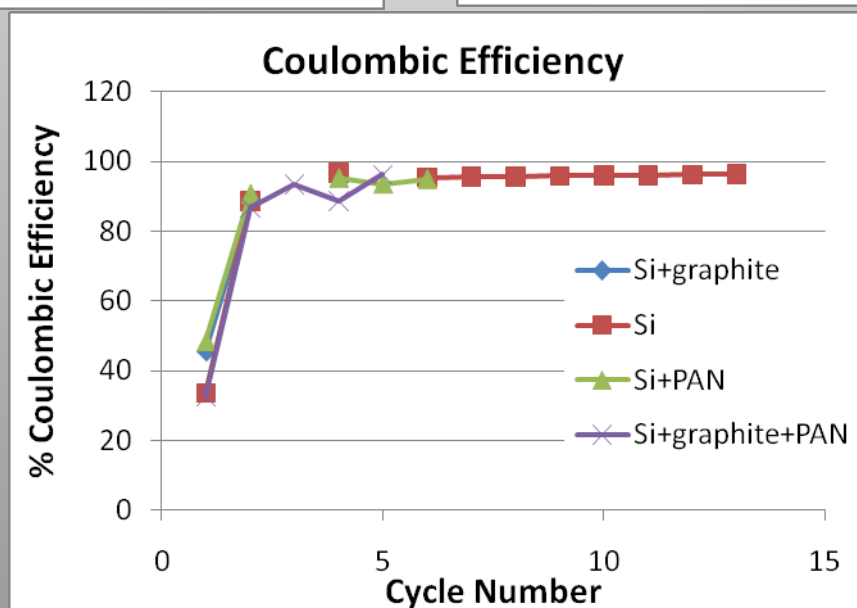
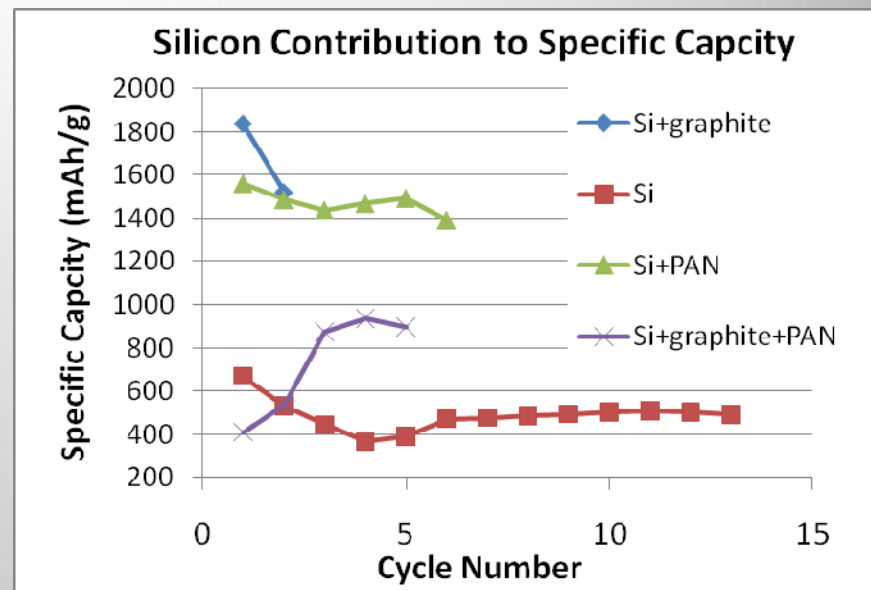
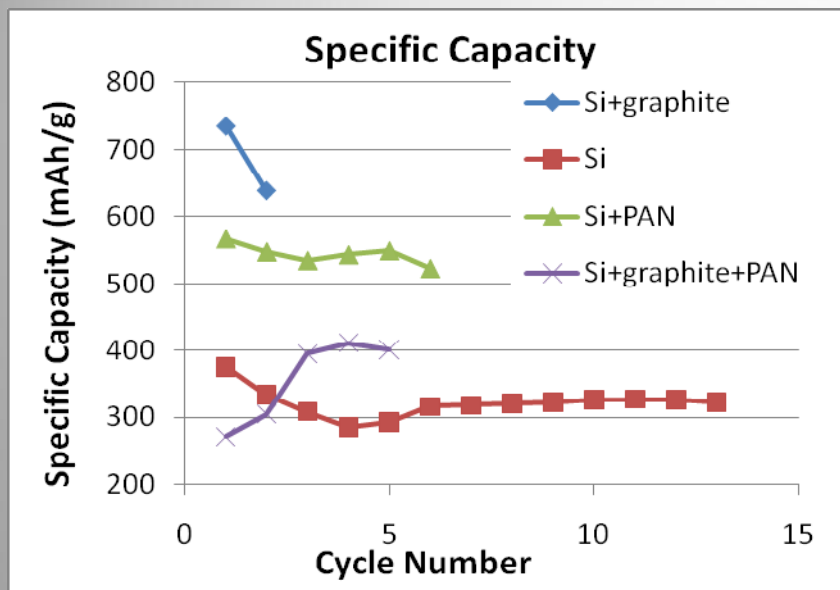
New Formation Procedure

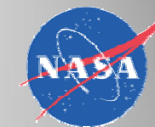
- Very slow initial formation to 10 mV
- Replace taper charge with very low constant current to 10mV



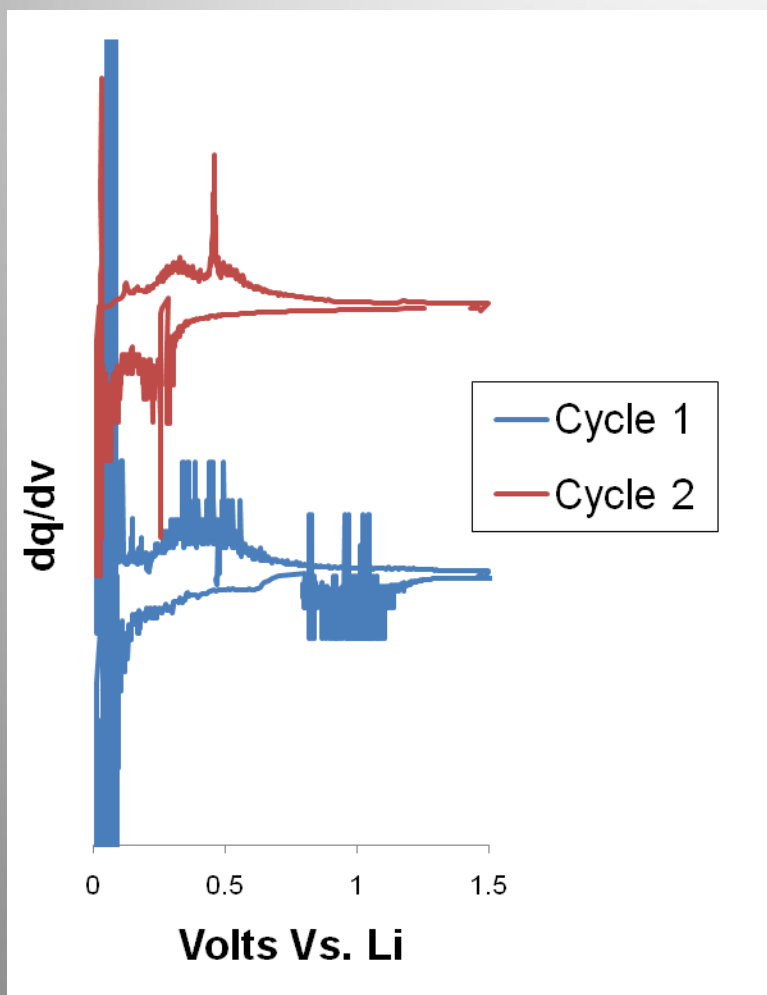


Silicon-Carbon Nanofoams

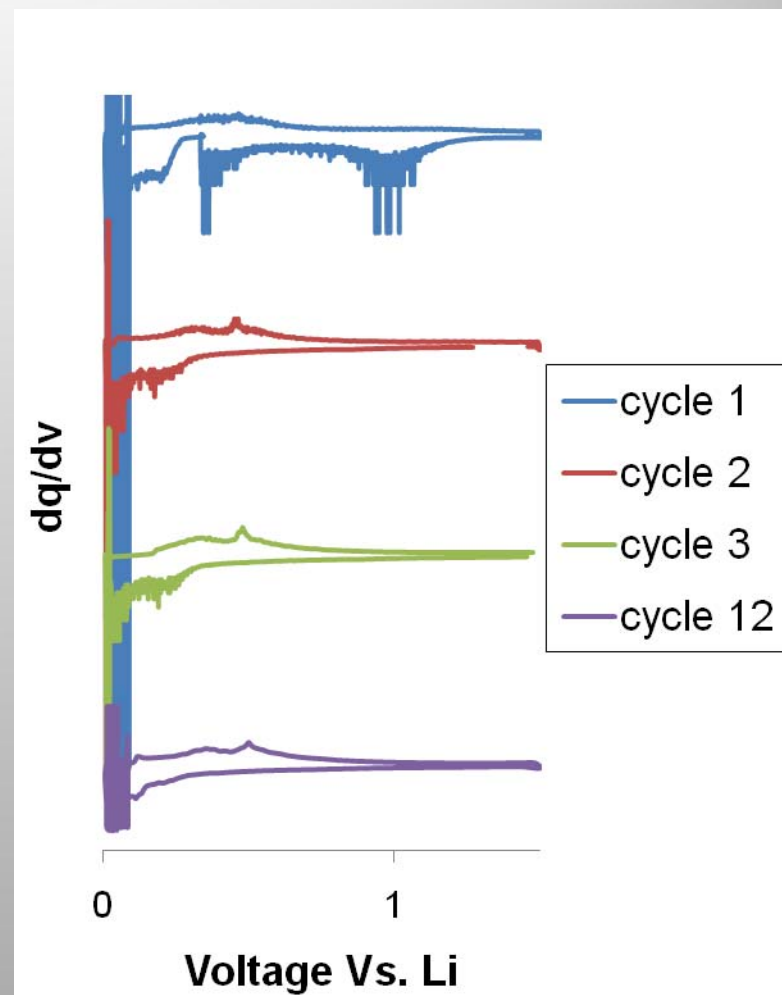




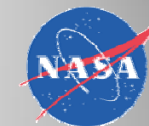
Carbon-Silicon Nanofoam Electrodes



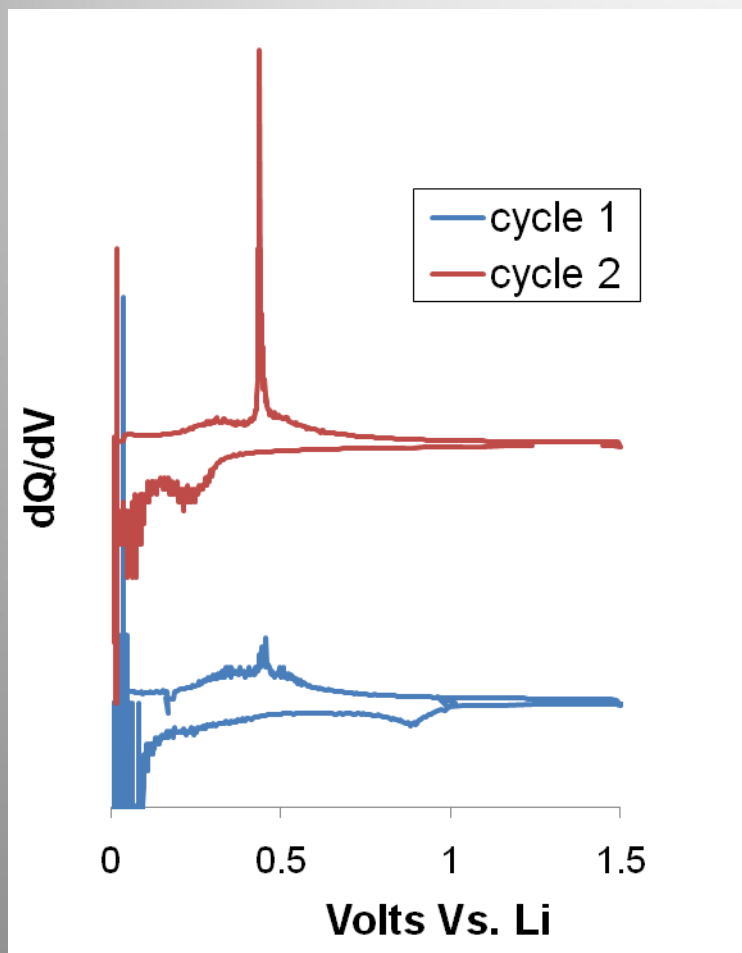
Carbon-Silicon-Graphite Nanofoam



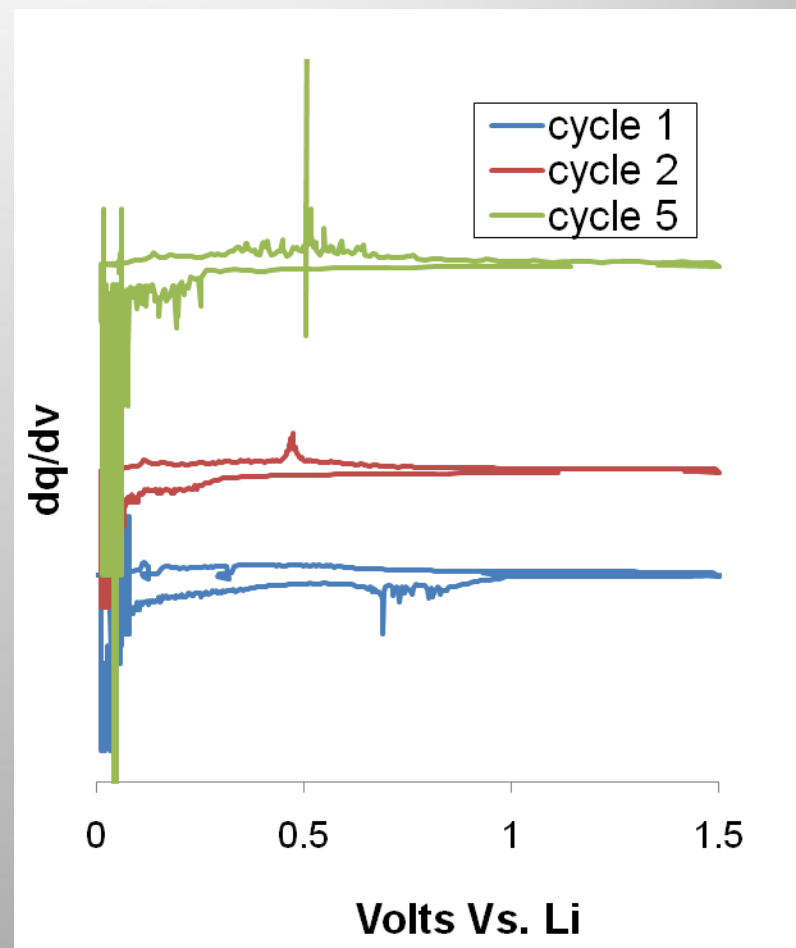
Carbon-Silicon Nanofoam



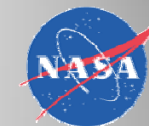
Polyaniline Coated Carbon-Silicon Nanofoam



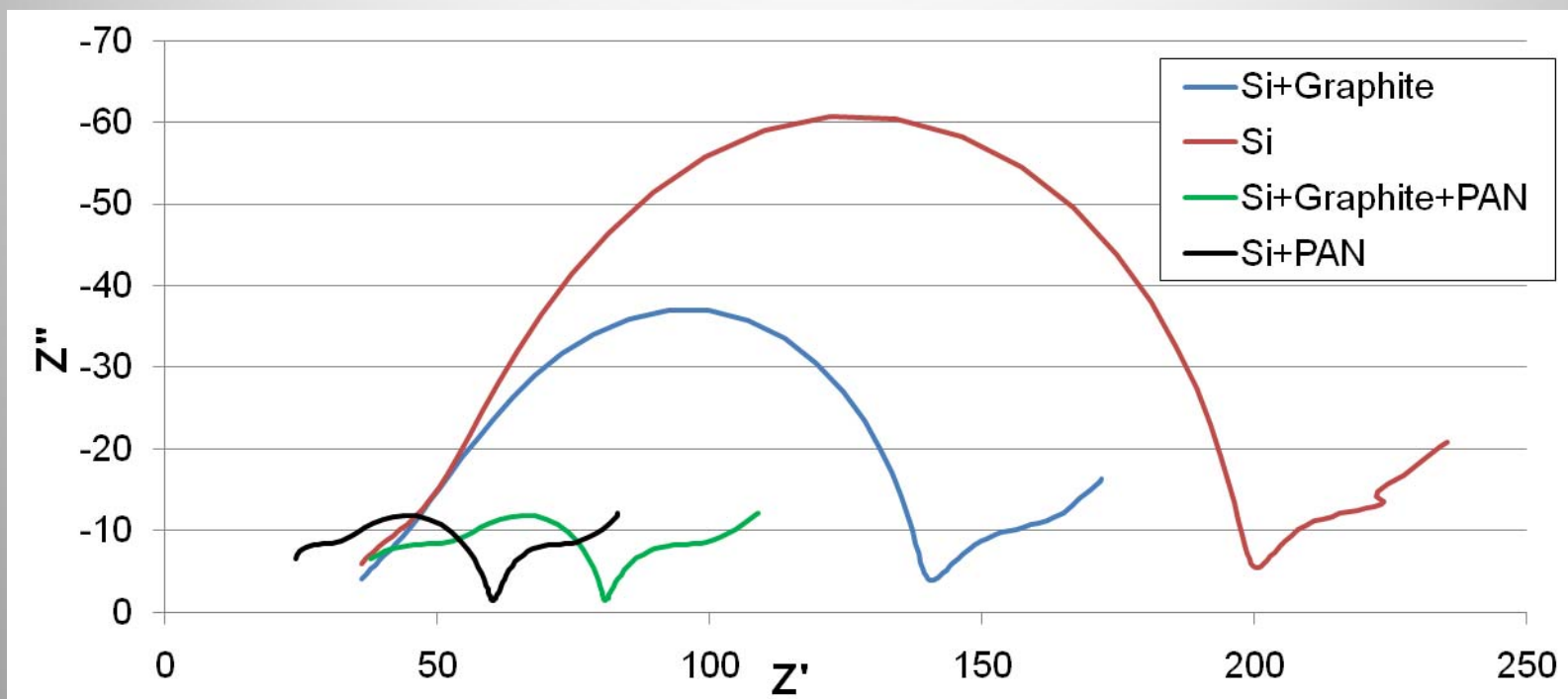
Carbon-Silicon-Graphite Nanofoam



Carbon-Silicon Nanofoam



Nyquist Plot For Si-Carbon Nanofoam Anodes

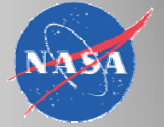


- The nanofoam containing graphite has a lower impedance than the nanofoam which does not contain graphite
- Samples coated with polyaniline/ LiPF_6 show drastically lower impedances than those without the coating
- The presence of graphite in combination with the polyaniline coating resulted in a higher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



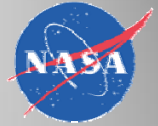
Conclusions

- 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



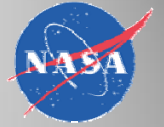
Future Work

- Investigate the use of various conductive additives
 - Graphites
 - Carbon Nanotubes
- Investigate different binders or coatings
- Investigate different gel formulations

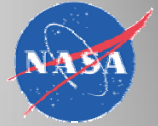


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- This research was supported by an appointment to the NASA Postdoctoral Program at NASA Glenn Research Center administered by Oak Ridge Associated Universities through a contract with NASA.
- NASA Exploration Technology Development Program Energy Storage Project
- NASA Glenn Research Center Electrochemistry Branch with special thanks to:
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 - Concha Reid (NASA GRC)
 - Tom Miller (NASA GRC)
 - Dave Yendriga (Sierra Lobo)
 - Marjorie Moats (SGT)
 - Michelle Manzo (Electrochemistry Branch Chief NASA GRC)



Supplementary Slides



Synthetic Conditions

- **Carbon-Silicon Microspheres**

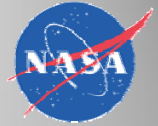
- Resorcinol-Formaldehyde containing 50 nm silicon is dispersed in a solution of cyclohexane and Span 80 surfactant
- Sonicated
- Stirred for two days at room temperature
- Recovered and rinsed
- Freeze dried in t-butanol
- Pyrolyzed at 1000° in argon

- **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 for 2 days
- Freeze dried in t-butanol
- Pyrolyzed at 1000° 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.



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 <u>Lander:</u> 150 – 210 Wh/kg 10 cycles <u>Rover:</u> 160-200 Wh/kg 2000 cycles <u>EVA:</u> 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