Carbon Cryogel Silicon Composite Anode Materials for Lithium-Ion Batteries

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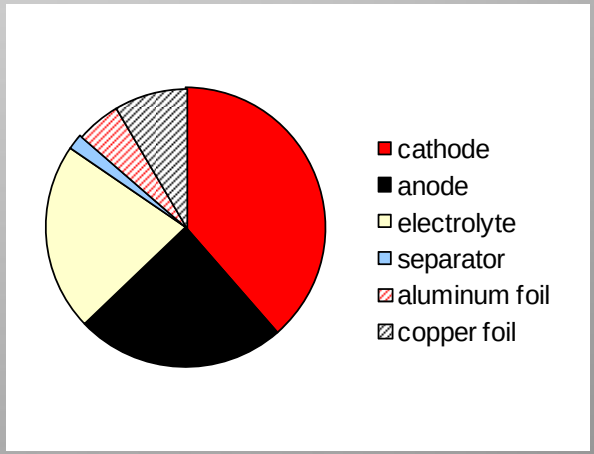
Introduction

- 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

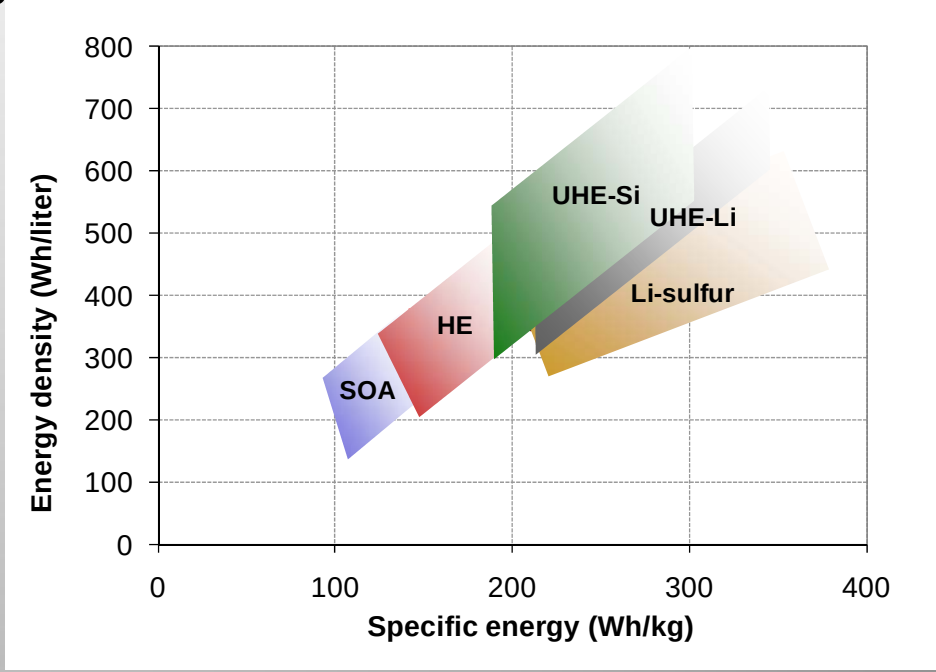


Estimates for component weight fraction in 30 Ah cell

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

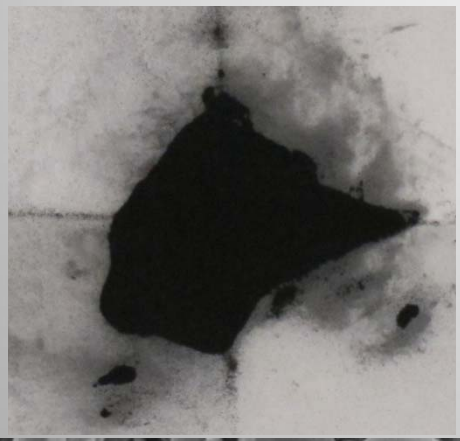


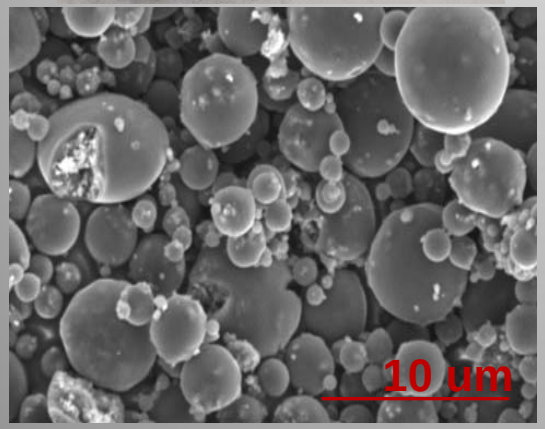
In-House Anode Synthesis

- 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

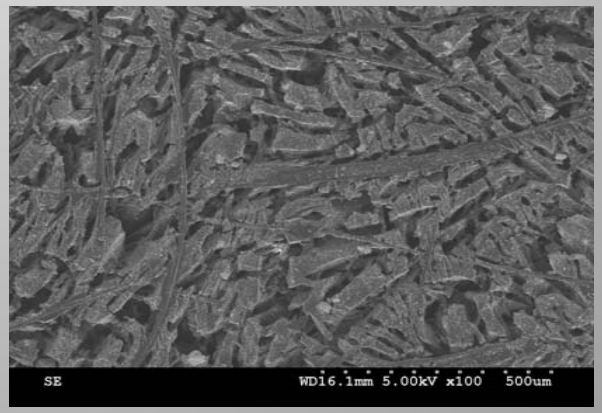
Carbon-Silicon Microbeads





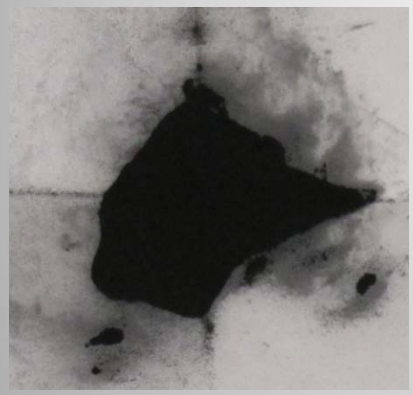
Originally investigated by Hasegawa, Mukkai, Shiratu and Tamon *Carbon* 42, 2004 pp. 2573-2579

Carbon Nanofoam with Nano-Silicon Supported on Carbon Paper

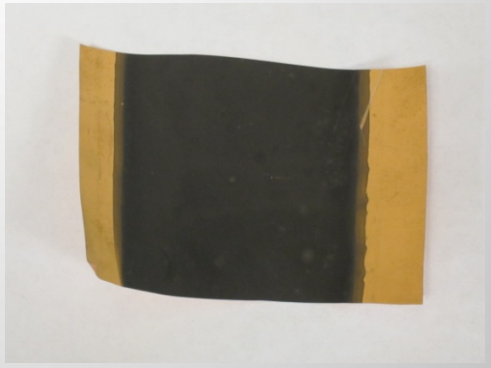


Carbon nanofoams are currently under investigation by J. Long at NRL for use in electrochemical capaciters and as electrode support materials

Carbon-Silicon Microbeads

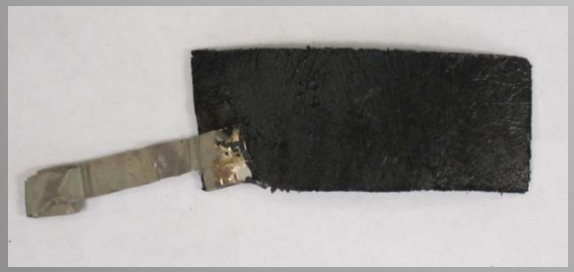


Mix microbeads with binder and cast onto copper foil current collector

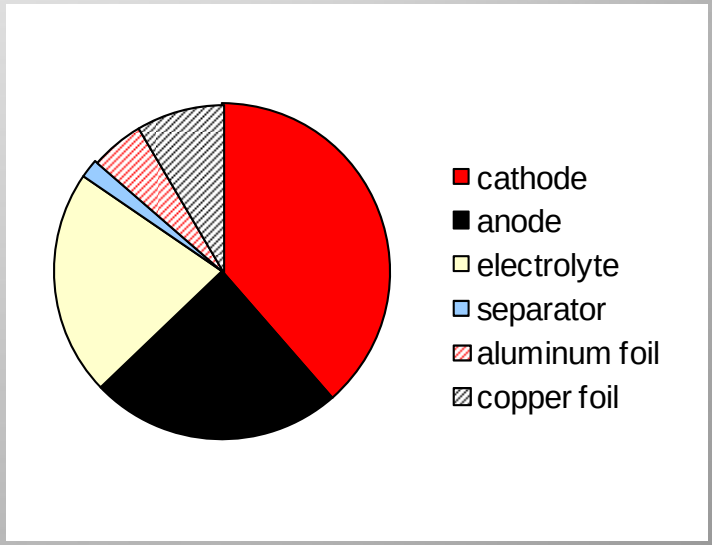


- **Advantage** : Uses conventional manufacturing techniques
- **Disadvantage** : Requires heavy copper current collector

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

Copper Foil 2g
•Not electrochemically active towards lithium

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

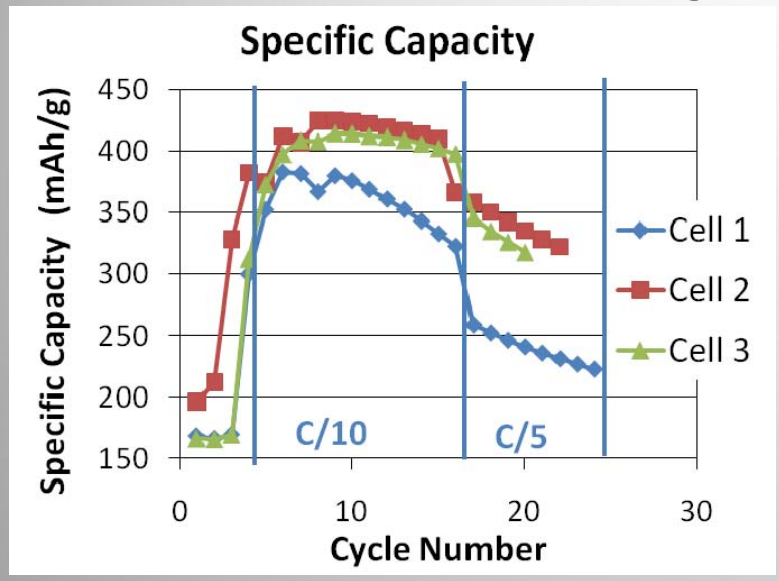
Theoretical Specific Capacities at the Active Material and Electrode Levels

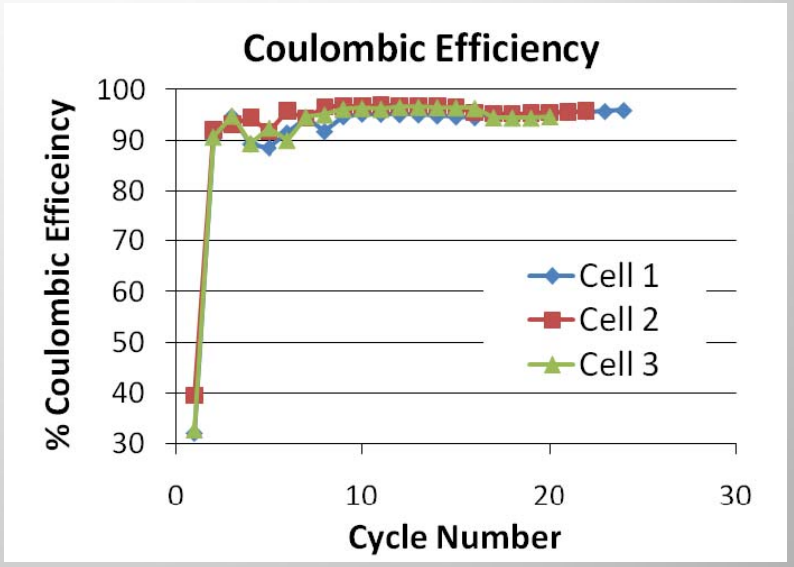
Electrode	mAh/g Active Material	mAh/g Electrode
Nanofoam	500	500
Graphite With Cu	350	170
Si With Cu	1000	312

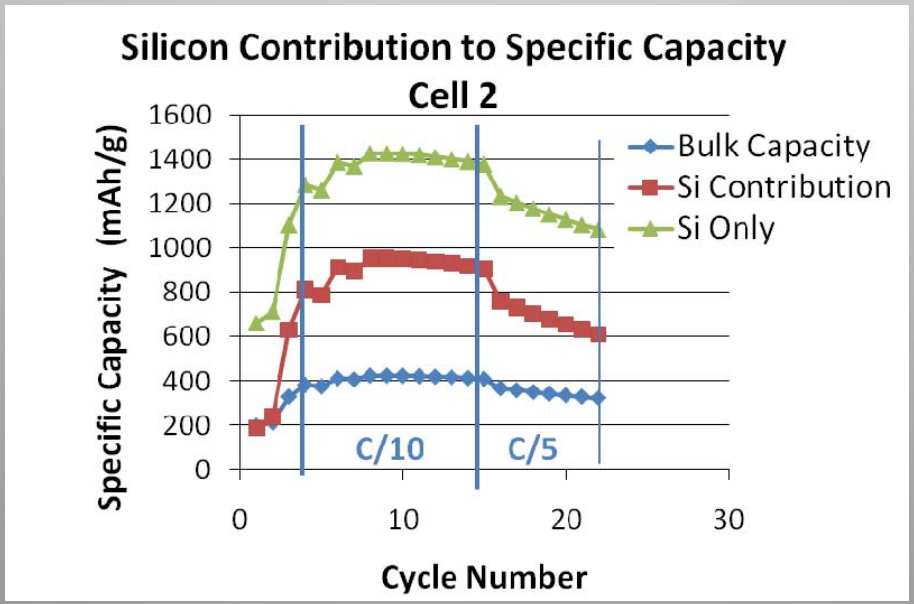
Carbon Microbead Testing

- 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

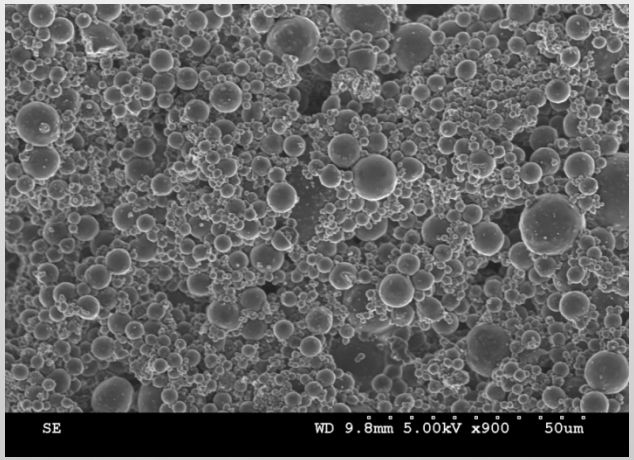
Electrochemical Cycling of Carbon Microbeads



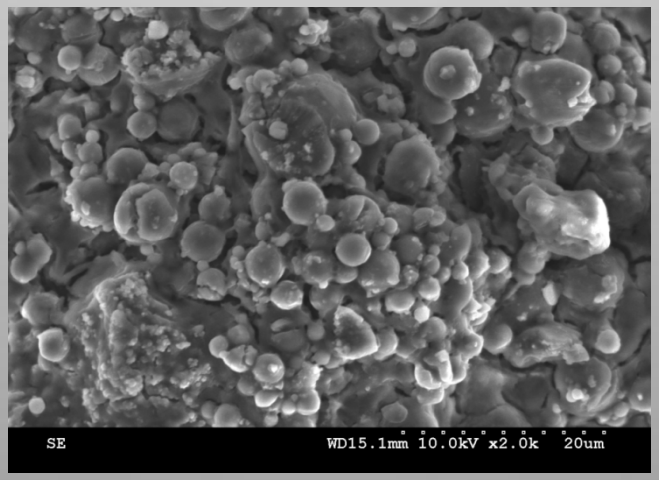




Carbon-Silicon Microbead Electrodes



As Cast Nano- Silicon Carbon Gel Microbead Electrode

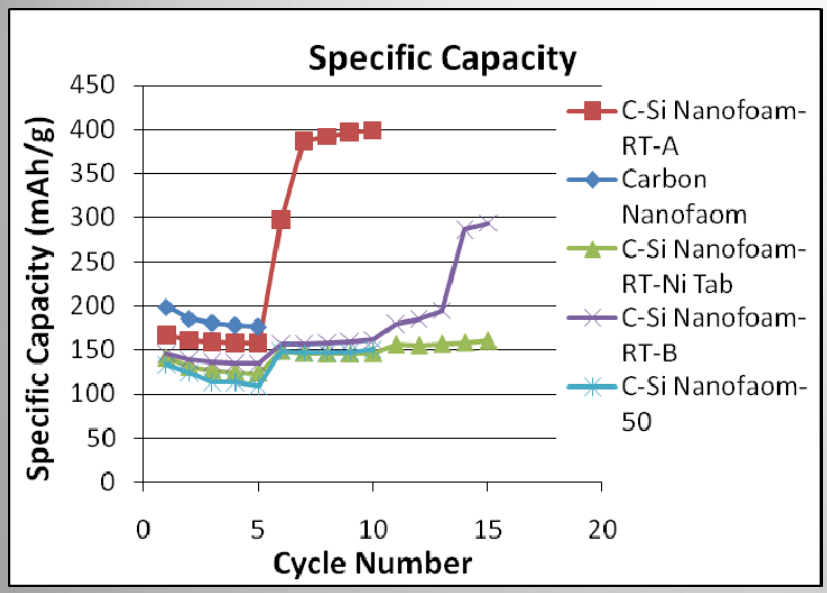


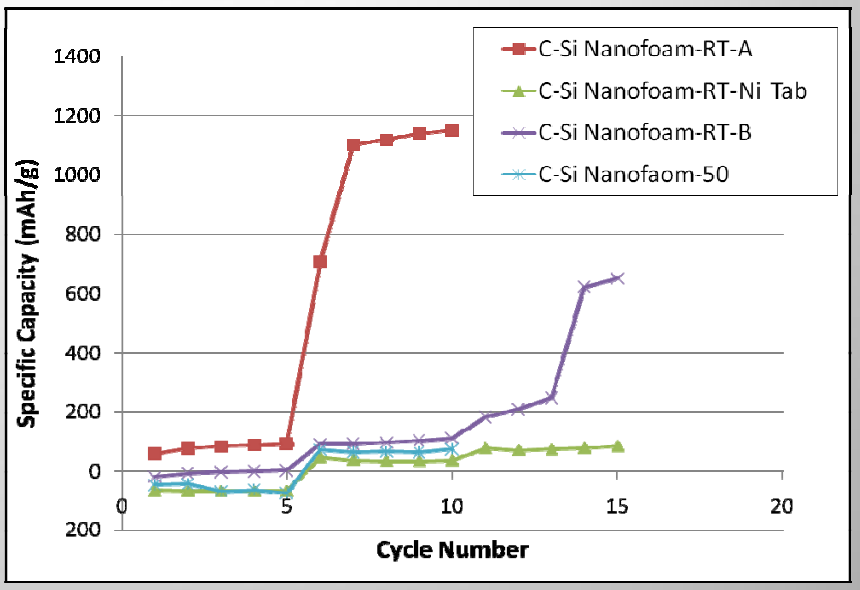
Cast Nano- Silicon Carbon Gel Microbead Electrode After Cycling

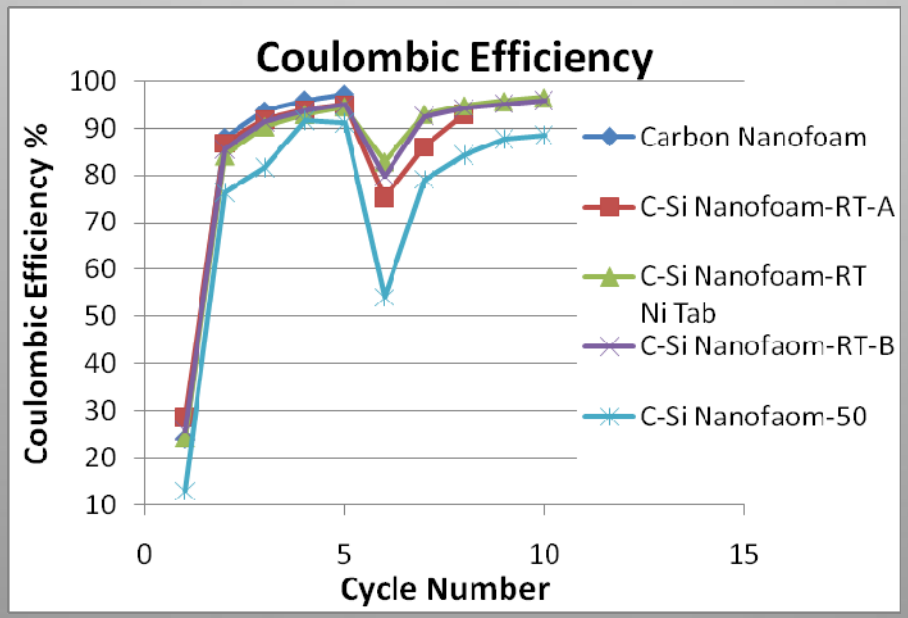
Carbon Nanofoam Half Cells

- 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

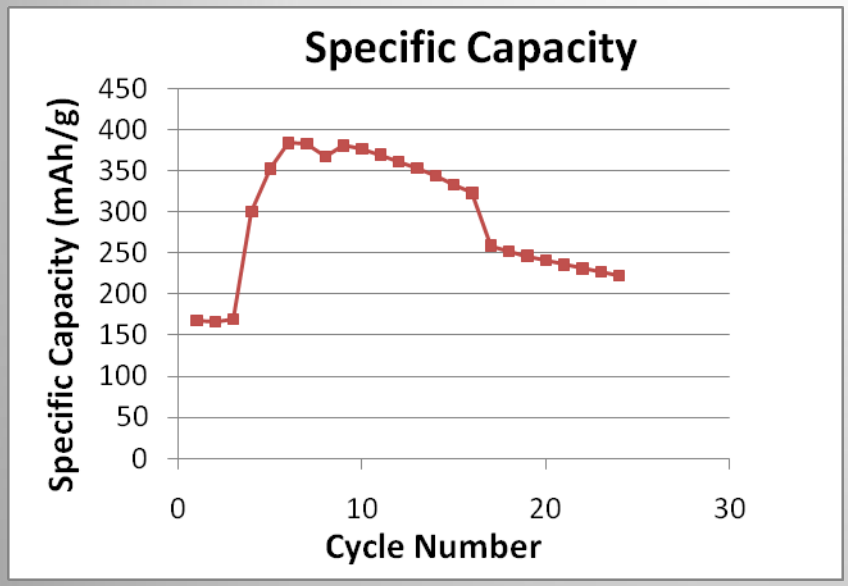
Electrochemical Cycling of Carbon Nanofoam Electrodes

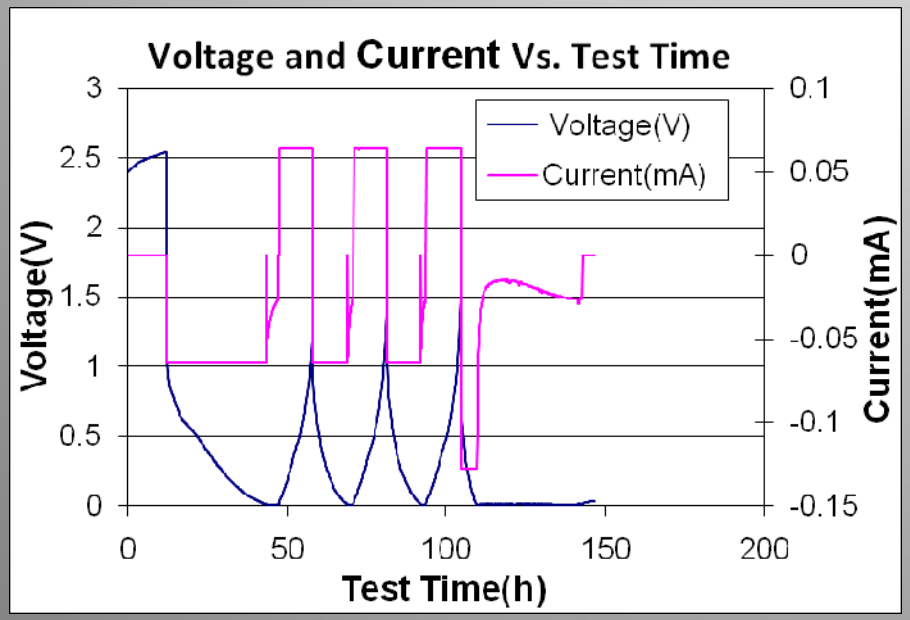


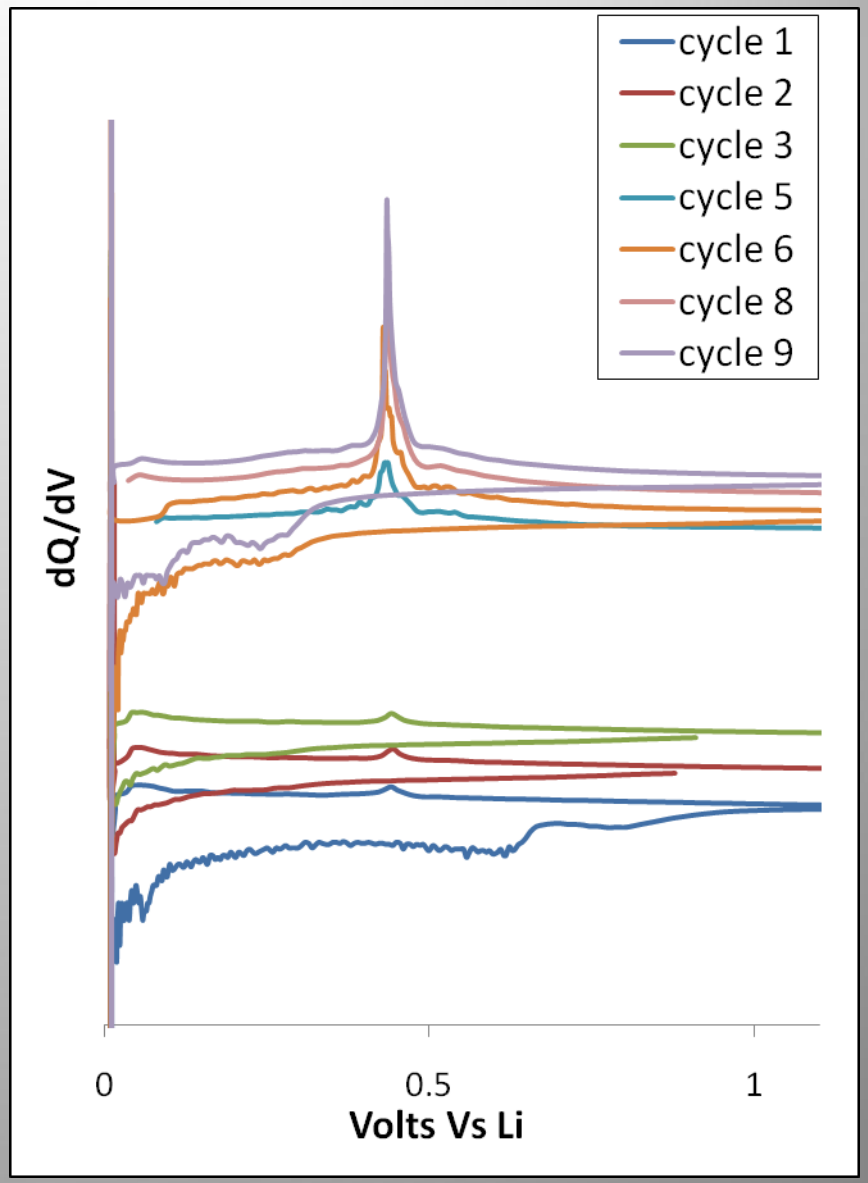




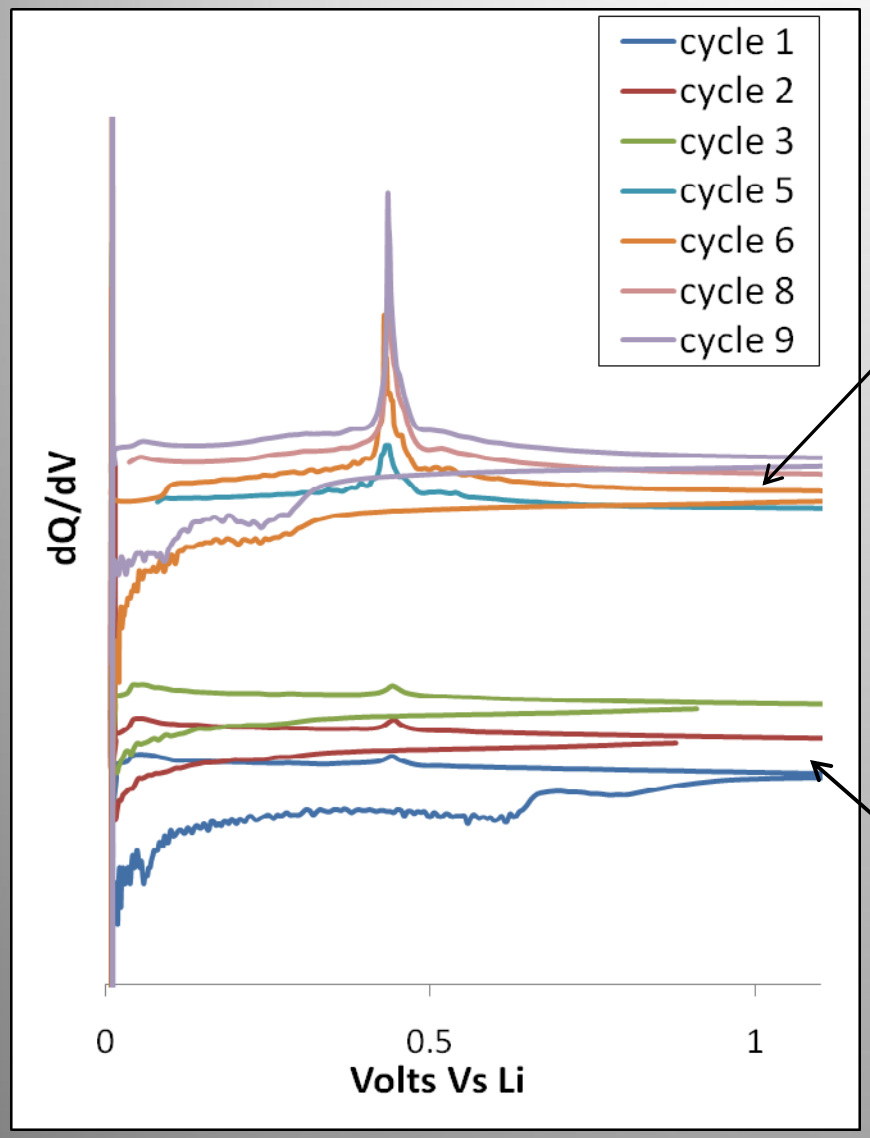
Si-Carbon Microbeads Cell 1

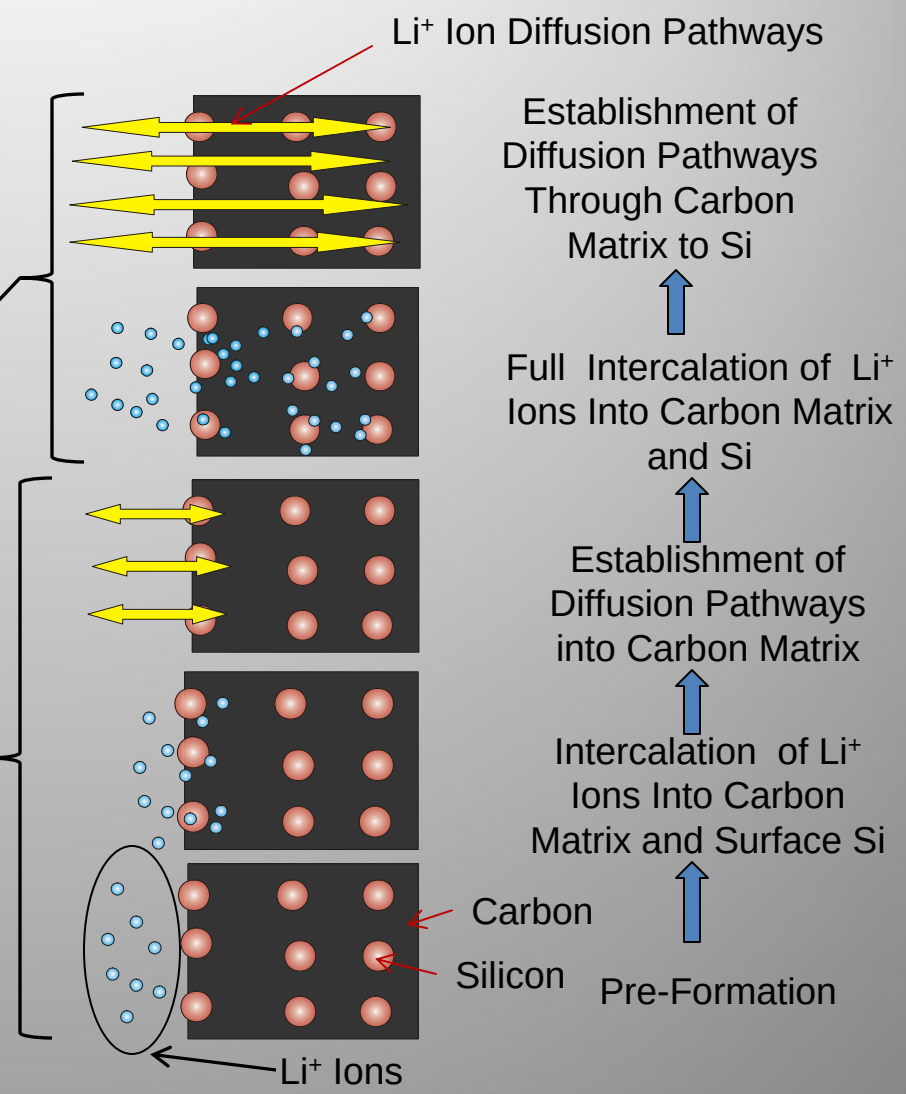






Formation of Lithium Ion Diffusion Pathways





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

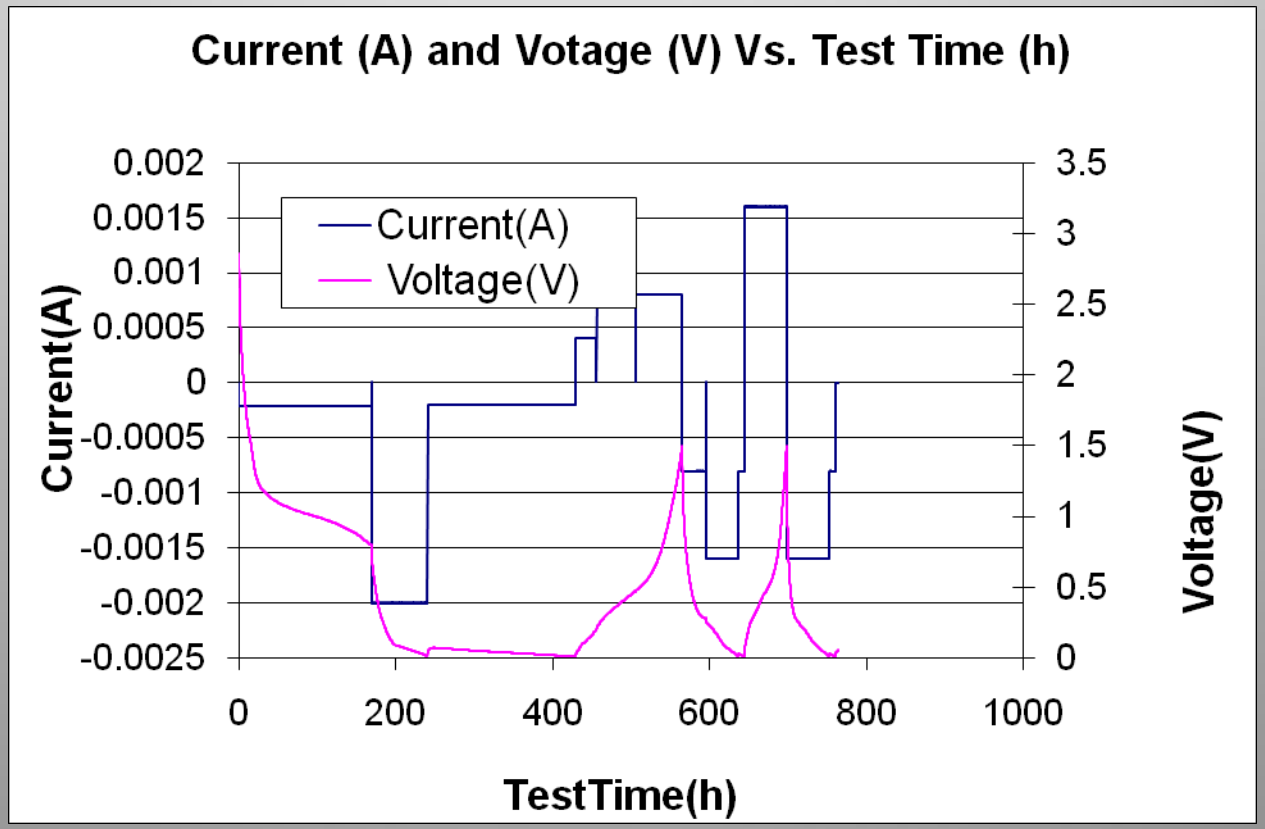
Electrode	mAh/g Active Material	mAh/g Electrode
Nanofoam	500	500
Graphite With Cu	350	170
Si With Cu	1000	312

New Experiments

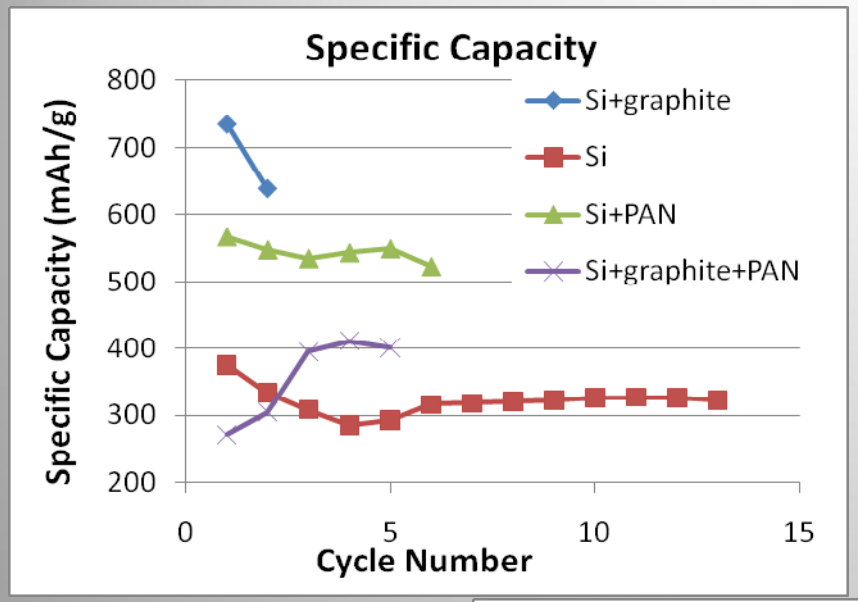
- Improve the performance of the Si-carbon nanofoams by addition of conductive additives or binders
  - Addition of graphite to resorcinol formaldehyde gel
  - Coat with polyaniline doped with $LiPF_6$
- New formation procedure

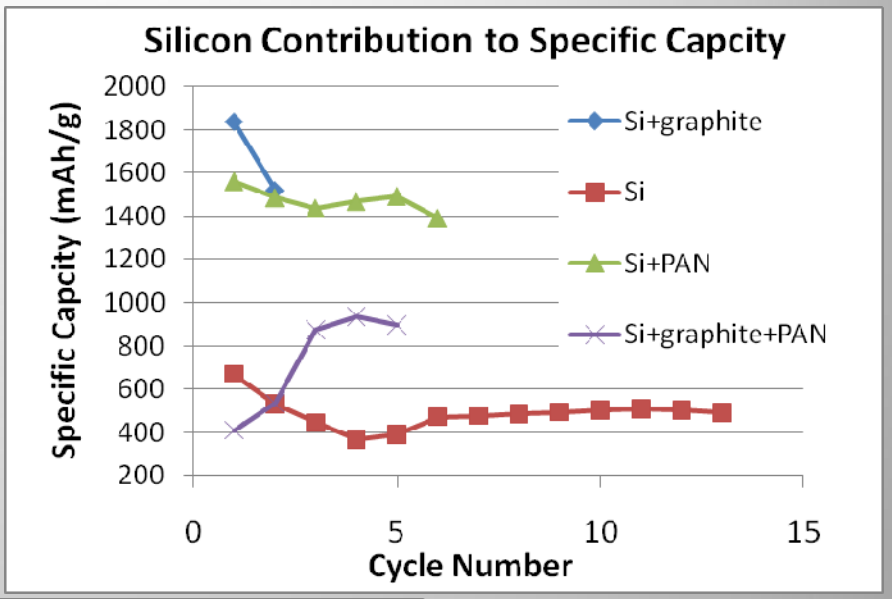
New Formation Procedure

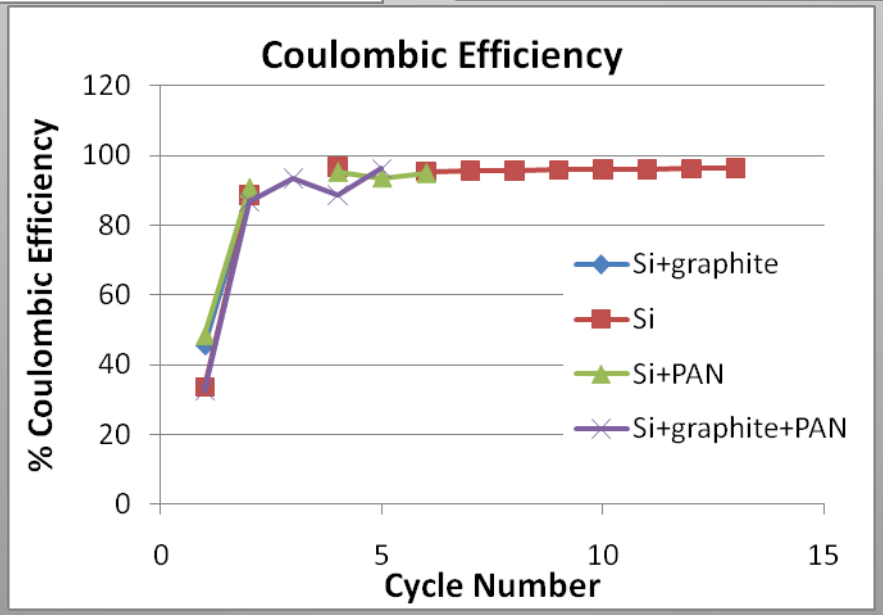
- Very slow initial formation to 10 mV
- Replace taper charge with very low constant current to 10mV



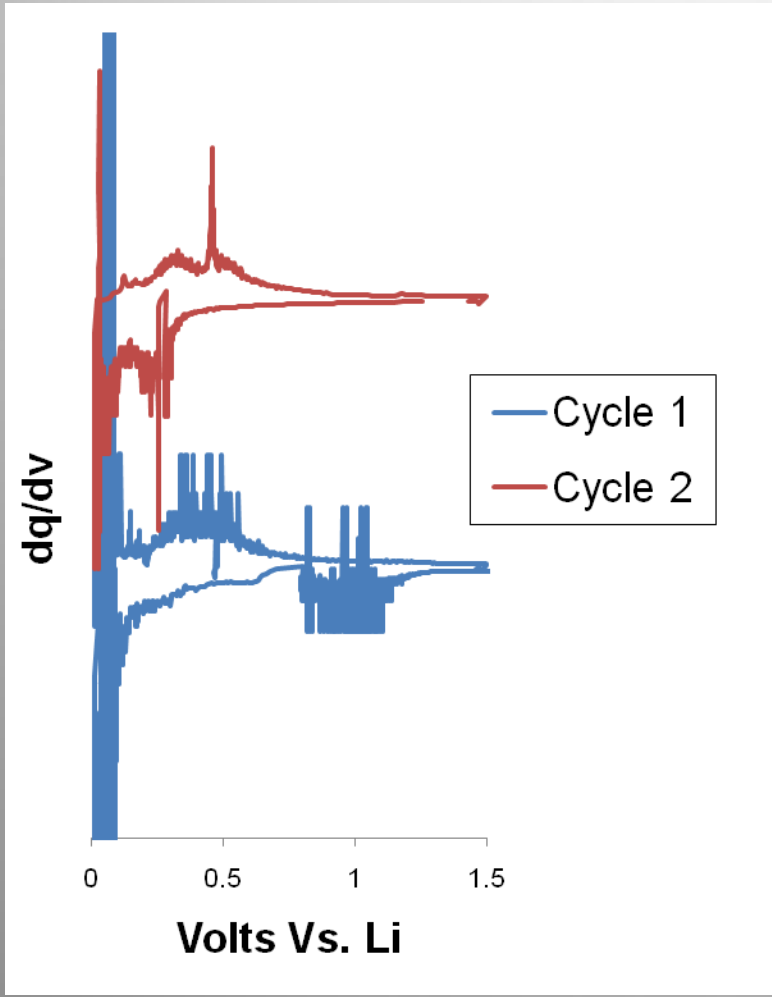
Silicon-Carbon Nanofoams



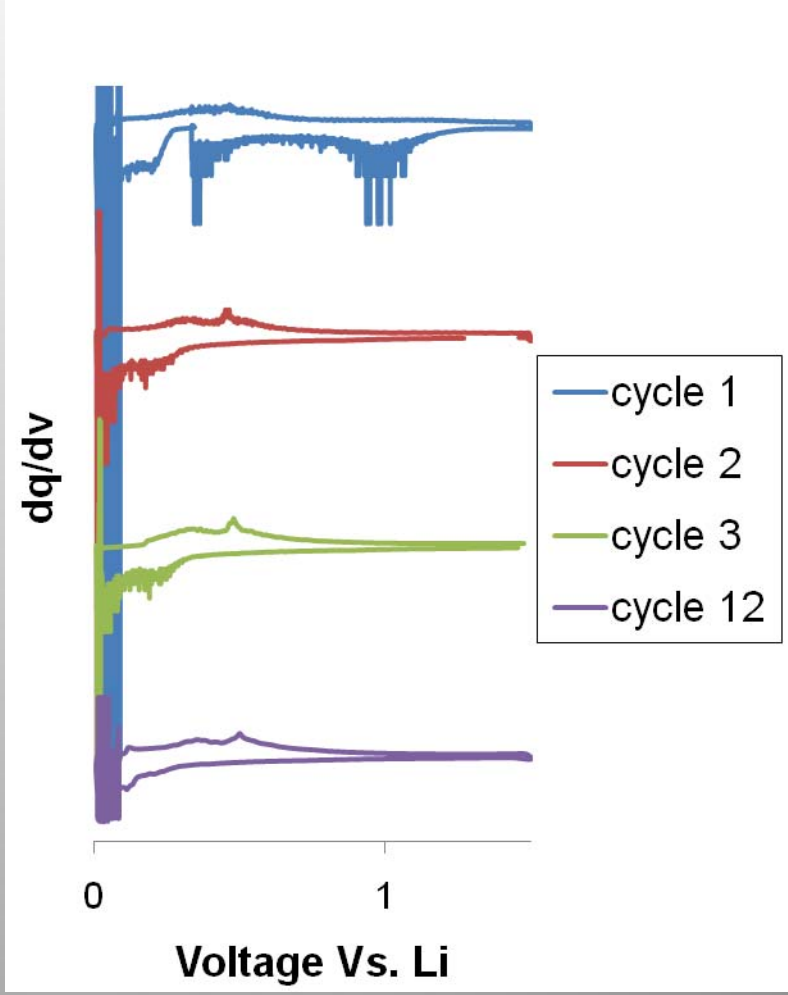




Carbon-Silicon Nanofoam Electrodes

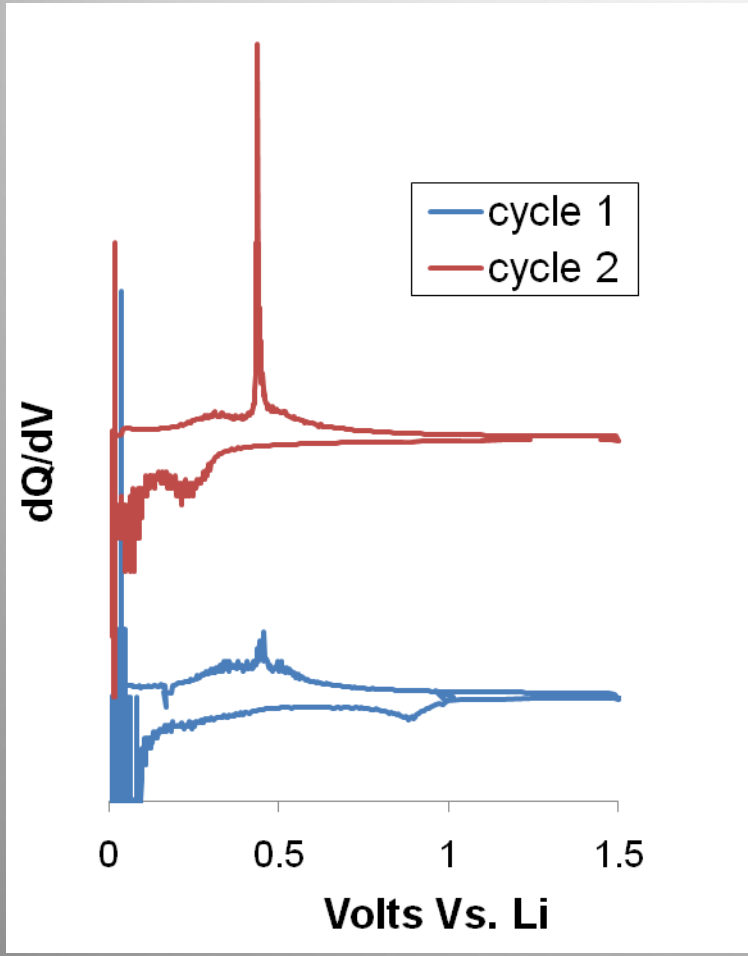


Carbon-Silicon-Graphite Nanofoam

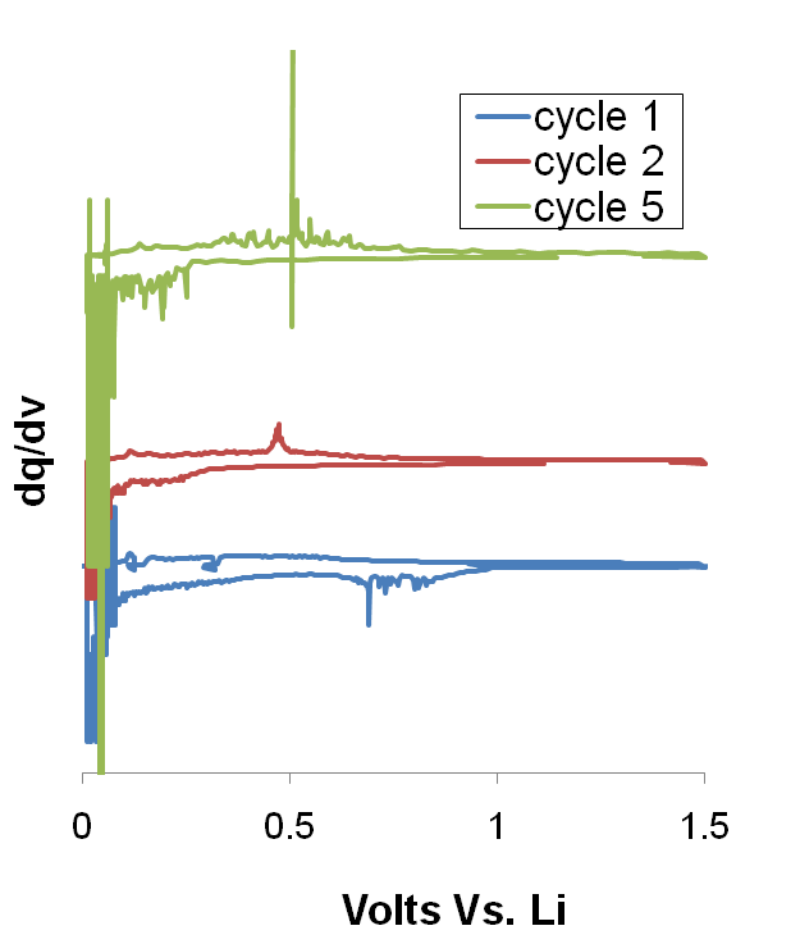


Carbon-Silicon Nanofoam

Polyaniline Coated Carbon-Silicon Nanofoam

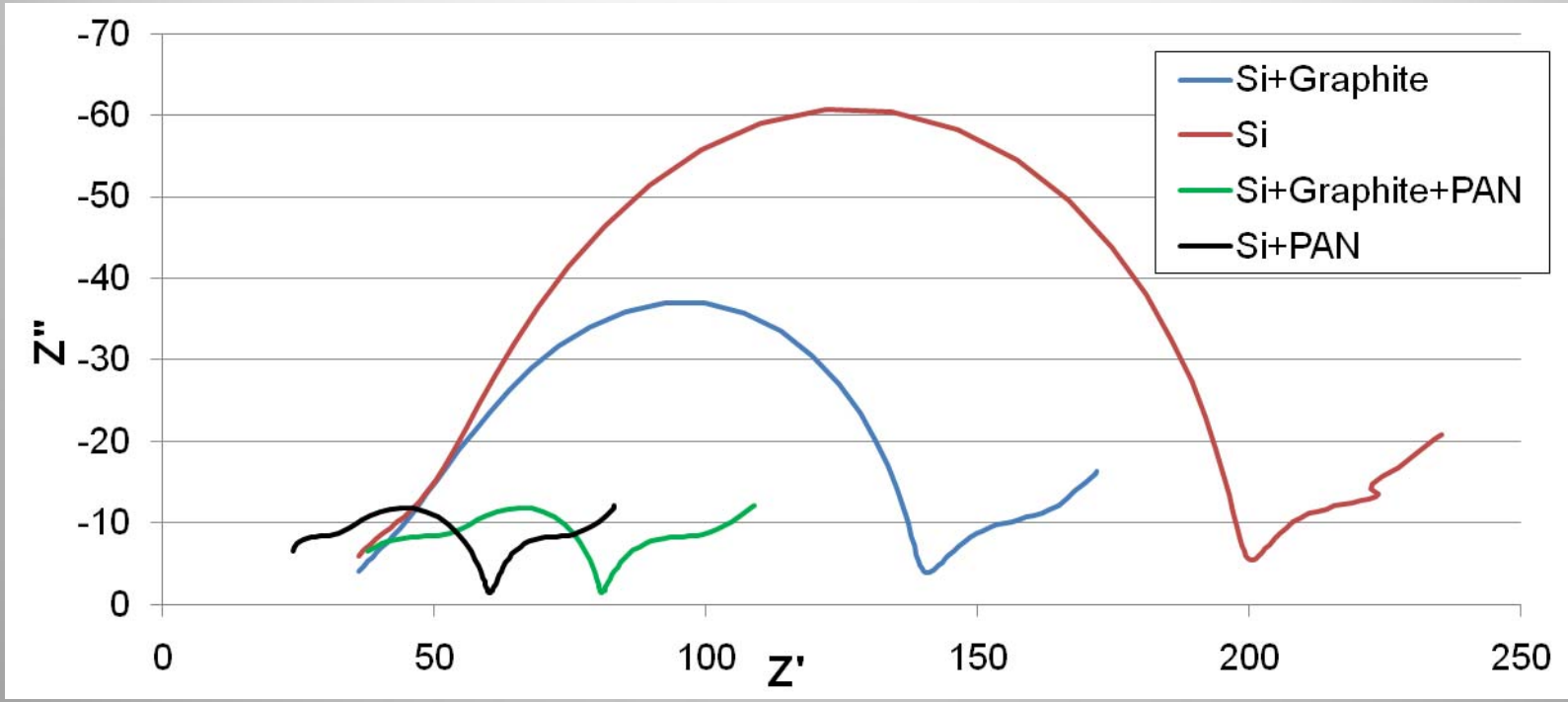


Carbon-Silicon-Graphite Nanofoam



Carbon-Silicon Nanofoam

Nyquist Plot For Si-Carbon Nanofoam Anodes



- The 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
- Investigate different binders or coatings
- Investigate different gel formulations

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