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. 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 nanofoams are produced by impregnating carbon fiber paper with the silicon containing RF gel to create a free standing electrode. 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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Electrochemistry Branch Glenn Research Center

Richard Baldwin and William Bennett
Electrochemistry Branch Glenn Research Center
Lithium Ion Basics

Cathode
- Transition Metal Oxide
- LiCO₂

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

Anode
- Most Commonly Carbon
- Graphite
- Hard Carbon

Cathode
Charge
\[ \text{LiMO}_2 \rightarrow \text{Li}_{1-x}\text{MO}_2 + x\text{Li}^+ + xe^- \]
Discharge
\[ \text{Li}_{1-x}\text{MO}_2 + x\text{Li}^+ + xe \rightarrow \text{LiMO}_2 \]

Anode
Charge
\[ \text{C} + x\text{Li}^+ + xe^- \rightarrow \text{Li}_x\text{C} \]
Discharge
\[ \text{Li}_x\text{C} \rightarrow \text{C} + x\text{Li}^+ + xe^- \]
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
Anode Materials

- **Graphite**
  - Excellent cycling characteristics
  - Theoretical capacity of 372 mAh/g (LiC<sub>6</sub>)

- **Silicon**
  - Theoretical capacity of 4200 mAh/g (Li<sub>15</sub>Si<sub>4</sub>)
  - 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

<table>
<thead>
<tr>
<th>Energy density (Wh/liter)</th>
<th>Specific energy (Wh/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li-sulfur</td>
<td>UHE-Li</td>
</tr>
<tr>
<td>UHE-Si</td>
<td>HE</td>
</tr>
<tr>
<td>SOA</td>
<td></td>
</tr>
</tbody>
</table>
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

Carbon Nanofoam with Nano-Silicon Supported on Carbon Paper

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

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

Theoretical Specific Capacities at the Active Material and Electrode Levels

<table>
<thead>
<tr>
<th>Electrode</th>
<th>mAh/g Active Material</th>
<th>mAh/g Electrode</th>
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<tbody>
<tr>
<td>Nanofoam</td>
<td>500</td>
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<td>350</td>
<td>170</td>
</tr>
<tr>
<td>Si With Cu</td>
<td>1000</td>
<td>312</td>
</tr>
</tbody>
</table>

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
Electrochemical Cycling of Carbon Microbeads

Specific Capacity

Coulombic Efficiency

Silicon Contribution to Specific Capacity
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

Specific Capacity

Coulombic Efficiency

Cycle Number

Specific Capacity (mAh/g)

Coulombic Efficiency %

0 5 10 15 20

0 50 100

0 200 400 600 800 1000 1200 1400
Si-Carbon Microbeads Cell 1

Specific Capacity

Voltage and Current Vs. Test Time

Volts Vs Li
Formation of Lithium Ion Diffusion Pathways

Pre-Formation

Establishment of Diffusion Pathways Through Carbon Matrix to Si

Full Intercalation of Li⁺ Ions Into Carbon Matrix and Si

Establishment of Diffusion Pathways into Carbon Matrix

Intercalation of Li⁺ Ions Into Carbon Matrix and Surface Si

Carbon

Silicon

Li⁺ Ions

Li⁺ Ion Diffusion Pathways

Volts Vs Li

dQ/dV

cycle 1
cycle 2
cycle 3
cycle 4
cycle 5
cycle 6
cycle 7

cycle 8

cycle 9
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

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</tr>
</tbody>
</table>
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 10 mV
Silicon-Carbon Nanofoams

Specific Capacity

Silicon Contribution to Specific Capacity

Coulombic Efficiency
Carbon-Silicon Nanofoam Electrodes

![Graphs of dq/dv vs. Volts Vs. Li and dq/dv vs. Voltage Vs. Li for Carbon-Silicon-Graphite Nanofoam and Carbon-Silicon Nanofoam with cycle 1, cycle 2, cycle 3, and cycle 12.]
Popolyaniline Coated Carbon-Silicon Nanofoam

Carbon-Silicon-Graphite Nanofoam

Carbon-Silicon Nanofoam

Volts Vs. Li

dq/dv
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
  – Carbon Nanofibers
• Investigate different binders or coatings
• Investigate different gel formulations
• Remove oxygen from matrix
Acknowledgements

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  – Dave Yendriga (Sierra Lobo)
  – Marjorie Moats (SGT)
  – Michelle Manzo (Electrochemistry Branch Chief NASA GRC)
Supplementary Slides
Updated Results for Carbon-Silicon Nanofoam Electrodes

![Graph showing Specific Capacity vs Cycle Number for different materials]
Updated Results for Carbon-Silicon Nanofoam Electrodes Continued

![Graph showing Silicon Contribution to Specific Capacity](image-url)
Contribution of Non-silicon Components to the Specific Capacities Carbon-Silicon Nanofoam Electrodes

Carbon Contribution to Specific Capacity

- Si+Graphite+PAN
- Si+PAN
- Si+Graphite-1
- Si+Graphite-2
- Si-29%
- Si-34%
- Si+Nanotubes

Conductive Additive Contribution to Specific Capacity

- Si+Graphite+PAN
- Si+Graphite-1
- Si+Graphite-2
- Si+Nanotubes
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° C 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

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<tr>
<th>Customer Need</th>
<th>Performance Parameter</th>
<th>State-of-the-Art</th>
<th>Current Value</th>
<th>Threshold Value</th>
<th>Goal</th>
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<td>Safe, reliable</td>
<td>No fire or flame</td>
<td>Instrumentation/</td>
<td>Preliminary results indicate a small reduction in performance using safer</td>
<td>Tolerant to electrical and thermal abuse such as over-temperature, over-charge,</td>
<td>Tolerant to electrical and thermal abuse such as over-temperature, over-charge, reversal, and short circuits with no fire or thermal runaway***</td>
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<td>to prevent</td>
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<td>Specific energy</td>
<td>Battery-level specific energy</td>
<td>90 Wh/kg at C/10</td>
<td>160 at C/10 &amp; 30°C (HE)</td>
<td>135 Wh/kg at C/10 &amp; 0°C “High-Energy”**</td>
<td>150 Wh/kg at C/10 &amp; 0°C “High-Energy”</td>
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<td>83 Wh/kg at C/10 &amp; 0°C (MER rovers)</td>
<td>170 at C/10 &amp; 30°C (UHE)</td>
<td>150 Wh/kg at C/10 &amp; 0°C “Ultra-High Energy”**</td>
<td>220 Wh/kg at C/10 &amp; 0°C “Ultra-High Energy”</td>
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<td>80 Wh/kg at C/10</td>
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<td>165 Wh/kg at C/10 &amp; 0°C “High-Energy”</td>
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<td>118 Wh/kg at C/10 &amp; 0°C (predicted)</td>
<td>213 at C/10 &amp; 23°C (UHE)</td>
<td>180 Wh/kg at C/10 &amp; 0°C “Ultra-High Energy”</td>
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<td>EVA: 270Wh/kg</td>
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<td>100 Wh/kg at C/10</td>
<td>252 mAh/g at C/10 &amp; 25°C</td>
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<td>[Wh/kg]</td>
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<td>Cathode-level specific capacity</td>
<td>280 mAh/g (MCMB)</td>
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<td>[mAh/g]</td>
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<td>Anode-level specific capacity</td>
<td>280 mAh/g (MCMB)</td>
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<td>[mAh/g]</td>
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<td>Battery-level energy density</td>
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<td>0°C to +30°C</td>
<td>0°C to 30°C</td>
<td>0°C to 30°C</td>
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