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. 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. 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

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

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![Energy density vs Specific energy](chart.png)

*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

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

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

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

- **Cycle Number**
- **Specific Capacity (mAh/g)**
  - Cell 1
  - Cell 2
  - Cell 3
  - C/10
  - C/5

**Coulombic Efficiency**

- **Cycle Number**
- **% Coulombic Efficiency**
  - Cell 1
  - Cell 2
  - Cell 3

**Silicon Contribution to Specific Capacity**

- **Cell 2**
- **Specific Capacity (mAh/g)**
  - Bulk Capacity
  - Si Contribution
  - Si Only
  - C/10
  - C/5
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 Nanofaom Electrodes

![Graphs showing specific capacity and coulombic efficiency over cycle number for different carbon nanofaom electrodes.](image-url)
Si-Carbon Microbeads Cell 1

Specific Capacity

- Cycle Number vs. Specific Capacity (mAh/g)

Voltage and Current Vs. Test Time

- Voltage (V) and Current (mA) vs. Test Time (h)

dQ/dV

- Volts Vs Li vs. Volts (V)
Formation of Lithium Ion Diffusion Pathways

- Pre-Formation
- Full Intercalation of Li+ Ions Into Carbon Matrix and Surface Si
- Establishment of Diffusion Pathways Through Carbon Matrix to Si
- Establishment of Diffusion Pathways into Carbon Matrix
- Intercalation of Li+ Ions Into Carbon Matrix and Surface Si
- Carbon
- Silicon
- Li+ Ions
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

<table>
<thead>
<tr>
<th>Cycle Number</th>
<th>Si+graphite</th>
<th>Si</th>
<th>Si+PAN</th>
<th>Si+graphite+PAN</th>
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<tbody>
<tr>
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<td>700</td>
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<tr>
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</tr>
<tr>
<td>15</td>
<td>500</td>
<td>400</td>
<td>300</td>
<td>200</td>
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Silicon Contribution to Specific Capacity

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<th>Cycle Number</th>
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<th>Si</th>
<th>Si+PAN</th>
<th>Si+graphite+PAN</th>
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<td>1600</td>
<td>1400</td>
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<tr>
<td>5</td>
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<td>1600</td>
<td>1400</td>
<td>1200</td>
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<tr>
<td>15</td>
<td>1400</td>
<td>1200</td>
<td>1000</td>
<td>800</td>
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Coulombic Efficiency

<table>
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<tr>
<th>Cycle Number</th>
<th>Si+graphite</th>
<th>Si</th>
<th>Si+PAN</th>
<th>Si+graphite+PAN</th>
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</thead>
<tbody>
<tr>
<td>0</td>
<td>120</td>
<td>100</td>
<td>80</td>
<td>60</td>
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<tr>
<td>5</td>
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<td>10</td>
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<tr>
<td>15</td>
<td>60</td>
<td>40</td>
<td>20</td>
<td>0</td>
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</tbody>
</table>
Carbon-Silicon Nanofoam Electrodes

Volts Vs. Li

Carbon-Silicon-Graphite Nanofoam

Voltage Vs. Li

Carbon-Silicon Nanofoam
Poylaniline Coated Carbon-Silicon Nanofoam

Carbon-Silicon-Graphite Nanofoam

Volts Vs. Li

Carbon-Silicon Nanofoam

Volts Vs. Li
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
Acknowledgements

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  – 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

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