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. 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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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

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

Charge

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

Discharge

\[ \text{C} + x\text{Li}^+ + xe^- \rightarrow \text{Li}_x\text{C} \]

Charge

\[ \text{Li}_x\text{C} \rightarrow \text{C} + x\text{Li}^+ + xe^- \]

Discharge
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 \((\text{LiC}_6)\)

- **Silicon**
  - Theoretical capacity of 4200 mAh/g \((\text{Li}_{15}\text{Si}_4)\)
  - 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](chart.png)
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)

<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>

Theoretical Specific Capacities at the Active Material and Electrode Levels
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**: 0 to 30
- **Specific Capacity (mAh/g)**: 150 to 450
- **Cells**: Cell 1, Cell 2, Cell 3
  - Cell 1: Blue line
  - Cell 2: Red line
  - Cell 3: Green line
  - Labels: C/10, C/5

**Coulombic Efficiency**
- **Cycle Number**: 0 to 30
- **% Coulombic Efficiency**: 30 to 100
- **Cells**: Cell 1, Cell 2, Cell 3
  - Cell 1: Blue line
  - Cell 2: Red line
  - Cell 3: Green line

**Silicon Contribution to Specific Capacity**
- **Cell**: Cell 2
- **Specific Capacity (mAh/g)**: 0 to 1600
- **Cycle Number**: 0 to 30
- **Labels**: C/10, C/5
  - Bulk Capacity: Blue line
  - Si Contribution: Red line
  - Si Only: Green line
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**

![Graph showing specific capacity versus cycle number for different samples.](image)

**Coulombic Efficiency**

![Graph showing coulombic efficiency versus cycle number for different samples.](image)
Si-Carbon Microbeads Cell 1

**Specific Capacity**

Cycle Number

**Voltage and Current Vs. Test Time**

Voltage (V)

Current (mA)

Test Time (h)

**dQ/dV**

Volts Vs Li

- cycle 1
- cycle 2
- cycle 3
- cycle 5
- cycle 6
- cycle 8
- cycle 9
Formation of Lithium Ion Diffusion Pathways

Pre-Formation
Full Intercalation of Li+ Ions Into Carbon Matrix and 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

Volts Vs Li
0 0.5 1

dQ/dV

cycle 1
cycle 2
cycle 3
cycle 5
cycle 6
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>
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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**
  - Composition: Si+graphite, Si, Si+PAN, Si+graphite+PAN

- **Silicon Contribution to Specific Capacity**
  - Composition: Si+graphite, Si, Si+PAN, Si+graphite+PAN

- **Coulombic Efficiency**
  - Composition: Si+graphite, Si, Si+PAN, Si+graphite+PAN
Carbon-Silicon Nanofoam Electrodes

Carbon-Silicon-Graphite Nanofoam

Volts Vs. Li

Voltage Vs. Li

Cycle 1
Cycle 2
Cycle 1
Cycle 2
Cycle 1
Cycle 2
Cycle 3
Cycle 12
Poylaniline 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
  - Carbon Nanofibers
- Investigate different binders or coatings
- Investigate different gel formulations
- Remove oxygen from matrix
Acknowledgements

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

![Graph showing specific capacity over cycle number for different materials: Si+Graphite-1, Si-29%, Si+PAN, Si+grGraphite+PAN, Si+Graphite-2, Si-34%, Si+Nanotubes.](image-url)
Updated Results for Carbon-Silicon Nanofoam Electrodes Continued

Silicon Contribution to Specific Capacity

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

Specific Capacity (mAh/g)

Cycle Number

0  5  10  15  20  25
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+Graphite

**Conductive Additive Contribution to Specific Capacity**

- Si+Graphite+PAN
- Si+Graphite-1
- Si+Graphite-2
- Si+Graphite
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

## Key Performance Parameters for Battery Technology Development

<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>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Safe, reliable operation</strong></td>
<td>No fire or flame</td>
<td>Instrumentation/controllers 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><strong>Battery-level</strong> 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 at C/10 &amp; 30°C (HE) 170 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><strong>Lander:</strong> 150 – 210 Wh/kg 10 cycles</td>
<td><strong>Rover:</strong> 160-200 Wh/kg 2000 cycles</td>
<td><strong>EVA:</strong> 270Wh/kg 100 cycles</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Cell-level</strong> specific energy [Wh/kg]</td>
<td>130 Wh/kg at C/10 &amp; 30°C 118 Wh/kg at C/10 &amp; 0°C</td>
<td>199 at C/10 &amp; 23°C (HE) 213 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>180 Wh/kg at C/10 &amp; 0°C “High-Energy” 260 Wh/kg at C/10 &amp; 0°C “Ultra-High Energy”</td>
<td></td>
</tr>
<tr>
<td><strong>Lander:</strong> 311 Wh/l 10 cycles</td>
<td><strong>Rover:</strong> TBD</td>
<td><strong>EVA:</strong> 400 Wh/l</td>
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<tr>
<td><strong>Cathode-level</strong> specific capacity [mAh/g]</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>280 mAh/g at C/10 &amp; 0°C</td>
<td></td>
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<tr>
<td><strong>Anode-level</strong> specific capacity [mAh/g]</td>
<td>280 mAh/g (MCMB)</td>
<td>330 @ 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>
<td>1000 mAh/g at C/10 0°C “Ultra-High Energy”</td>
<td></td>
</tr>
<tr>
<td><strong>Energy density</strong></td>
<td><strong>Battery-level</strong> energy density</td>
<td>250 Wh/l</td>
<td>n/a</td>
<td>270 Wh/l “High-Energy” 360 Wh/l “Ultra-High”</td>
<td>320 Wh/l “High-Energy” 420 Wh/l “Ultra-High”</td>
</tr>
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<td><strong>Lander:</strong> 311 Wh/l 10 cycles</td>
<td><strong>Rover:</strong> TBD</td>
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<td></td>
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<tr>
<td><strong>Cell-level</strong> energy density</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>
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</tr>
<tr>
<td><strong>Operating environment</strong></td>
<td><strong>Operating Temperature</strong></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>
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<tr>
<td><strong>0°C to 30°C, Vacuum</strong></td>
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</tbody>
</table>

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**Notes:**
- “High-Energy” = HE
- “Ultra-High Energy” = UHE
- “High-Energy” = HE
- **“Ultra-High Energy” = UHE
- ***Additional information regarding safety and thermal abuse protection.