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.\textsuperscript{10} 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.\textsuperscript{1-4,9} 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

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

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

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

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**

[Graph showing energy density vs. specific energy for different materials]

- UHE-Si
- UHE-Li
- Li-sulfur
- HE
- SOA

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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

- **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

<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>
<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>
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Theoretical Specific Capacities at the Active Material and Electrode Levels

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

Cell 2
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

Graphs showing the specific capacity and coulombic efficiency of various carbon nanofoam electrodes over different cycle numbers.
Formation of Lithium Ion Diffusion Pathways

- Pre-Formation
  - Li⁺ Ions

- Establishment of Diffusion Pathways into Carbon Matrix
  - Carbon
  - Silicon

- Intercalation of Li⁺ Ions into Carbon Matrix and Surface Si

- Full Intercalation of Li⁺ Ions into Carbon Matrix and Si

- Establishment of Diffusion Pathways Through Carbon Matrix to Si

Graph with dQ/dV vs Volts Vs Li for cycles 1 to 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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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**

- Si+graphite
- Si
- Si+PAN
- Si+graphite+PAN

**Silicon Contribution to Specific Capacity**

- Si+graphite
- Si
- Si+PAN
- Si+graphite+PAN

**Coulombic Efficiency**

- Si+graphite
- Si
- Si+PAN
- Si+graphite+PAN
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
  – 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
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) vs Cycle Number
Contribution of Non-silicon Components to the Specific Capacities Carbon-Silicon Nanofoam Electrodes
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>Safe, reliable operation</td>
<td>No fire or flame</td>
<td>Instrumentation/controlled devices 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>Specific energy</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 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>
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<tr>
<td>Lander: 150 – 210 Wh/kg 10 cycles</td>
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<tr>
<td>Rover: 160-200 Wh/kg 2000 cycles</td>
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<td>EVA: 270Wh/kg 100 cycles</td>
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<tr>
<td>Cell-level 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>
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<tr>
<td>Cathode-level 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>
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<tr>
<td>Anode-level 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>
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<tr>
<td>Lander: 311 Wh/l</td>
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<td>Rover: TBD</td>
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<td>EVA: 400 Wh/l</td>
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<tr>
<td>Operating environment</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>
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