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 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.

References

Carbon Cryogel and Carbon Paper-Based 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
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
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](image-url)
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

## Electrode

<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>
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</table>

## 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 Nanofaom Electrodes

**Specific Capacity**

- C-Si Nanofoam-RT-A
- Carbon Nanofaom
- C-Si Nanofoam-RT-Ni Tab
- C-Si Nanofoam-RT-B
- C-Si Nanofoam-50

**Coulombic Efficiency**

- Carbon Nanofoam
- C-Si Nanofoam-RT-A
- C-Si Nanofoam-RT-Ni Tab
- C-Si Nanofoam-RT-B
- C-Si Nanofoam-50
Si-Carbon Microbeads Cell 1

Specific Capacity

Voltage and Current Vs. Test Time

Voltage (V)
Current (mA)

Test Time (h)

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
- 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
- Pre-Formation

Graph showing 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

![Current (A) and Voltage (V) Vs. Test Time (h)](chart)
Carbon-Silicon Nanofoam Electrodes

**Graph 1:**
- **dq/dv** vs. Volts Vs. Li
  - Blue: Cycle 1
  - Red: Cycle 2

**Graph 2:**
- dq/dv vs. Voltage Vs. Li
  - Blue: cycle 1
  - Red: cycle 2
  - Green: cycle 3
  - Purple: cycle 12

**Legend:**
- **Carbon-Silicon-Graphite Nanofoam**
- **Carbon-Silicon Nanofoam**
Poliyaniline Coated Carbon-Silicon Nanofoam

Carbon-Silicon-Graphite Nanofoam

Carbon-Silicon Nanofoam
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
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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

## 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/control-lers 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>
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</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>
</tr>
<tr>
<td></td>
<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></td>
<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></td>
<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>
</tr>
<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>
</tr>
</tbody>
</table>