NaSi and NaSG Powder Hydrogen Fuel Cells

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SiGNa Chemistry
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Overview

Timeline
- Start date: 08/01/2008
- End date: 01/31/2010
- Percent complete: 28%

Budget
- Total funding in FY08: $1,845,000
  - DOE share: $1,476,000
  - Contractor share: $369,000
  - Bulk of funds to be spent in FY09
- Additional funding for FY09
  - $951,500
  - To be spent in FY09/FY10

Barriers
- Hydrogen Storage Technology Capabilities
  - Specific Energy: 2kWhr/kg
  - Cost: $4/kWhr
- Enabling Technology for Near-Term High-Volume Fuel Cell Commercialization for Portable Applications

Partners
- University of Texas Austin, Center for Electromechanics
  - Reactor Mechanism Research
  - Richard Thompson and Michael Lewis
- Trulite Inc.
  - 250W Fuel Cell Demonstration System
  - Ken Pearson
Technology Overview

• Sodium Silicides rapidly liberate hydrogen from water (or water solutions) leaving a benign common industrial chemical (sodium silicate)
  – Sodium-Silica-Gel: $2\text{Na-SG} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{Na}_2\text{Si}_2\text{O}_5$
  – Sodium Silicide: $2\text{NaSi(s)} + 5\text{H}_2\text{O(l)} \rightarrow 5\text{H}_2(\text{g}) + \text{Na}_2\text{Si}_2\text{O}_5(\text{aq})$

• Significant System Benefits for Portable Power Applications (10 W to 3 kW)
  – Safety: Does not ignite or oxidize in air at standard conditions even when fully exposed to air (i.e. opened storage canister).
  – Thermal Stability: Material is stable over all practical temperature ranges (-55 to 300°C)
  – Storage: The material has been demonstrated to have a shelf-life of over two years but is capable for being stored for significantly longer
  – Pressure: The maximum developed pressure is determined by the system design not the material characteristics. The maximum pressure is expected to be under 50 psi (material capable of 1000’s)
  – Ease of Use: No catalyst required to produce hydrogen gas
  – By-products: Generates a non-toxic aqueous waste, sodium silicate.
Objectives

• Demonstrate enabling hydrogen storage technology suitable for early fuel cell market applications with high volume potential
• Demonstrate the benefits of sodium silicide technology in a push-to-start hydrogen generator system
• Develop a demonstration system capable of ~250 W for applications such as battery re-chargers, remote telecommunications, emergency responders, backup power, and personal mobility (i.e. scooter, bicycle, Segway)
• Demonstrate technology to approach DOE Hydrogen storage targets even for small systems (<1kW)
## Market Example: 11 Day Mission for Special Forces

<table>
<thead>
<tr>
<th>Technology</th>
<th>Per Unit</th>
<th>Unit Cost</th>
<th>Mission Qty</th>
<th>Mission Wt.</th>
<th>Mission Cost</th>
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</thead>
<tbody>
<tr>
<td>BA 5590</td>
<td>140 W-hrs</td>
<td>$80</td>
<td>35</td>
<td>35 kgs</td>
<td>$2,800</td>
</tr>
<tr>
<td></td>
<td>(1.0 kgs)</td>
<td></td>
<td>4,900 W-hrs</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiGNa NaSi</td>
<td>700 W-hrs</td>
<td>$84</td>
<td>7</td>
<td>11.4 kgs</td>
<td>$688</td>
</tr>
<tr>
<td></td>
<td>(1.42 kgs)</td>
<td></td>
<td>4,900 W-hrs</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Packaging: 0.2 kgs</td>
<td></td>
<td></td>
<td>Cartridges: 9.9 kgs</td>
<td>Cartridges: $588</td>
</tr>
<tr>
<td></td>
<td>• Powder: 0.4 kgs</td>
<td></td>
<td></td>
<td>Fuel Cell: 1.5 kgs</td>
<td>Fuel Cell: $3000 / 30 missions = $100</td>
</tr>
<tr>
<td></td>
<td>• Water: 0.8 kgs</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Sodium Silicide provides significant value as compared to batteries with respect to weight, cost, and logistics.**
## Technical Approach

<table>
<thead>
<tr>
<th>Task 1.0</th>
<th>Task 2.0</th>
<th>Task 3.0</th>
<th>Task 4.0</th>
<th>Task 5.0</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>System Engineering</strong></td>
<td><strong>Breadboard Testing and Reaction Control Mechanism</strong></td>
<td><strong>Hardware Development</strong></td>
<td><strong>Fuel Cell System Integration</strong></td>
<td><strong>Advanced Materials Research and Manufacturing Methods</strong></td>
</tr>
</tbody>
</table>

### Key Specifications
- **Powder**
  - Current: >3100 W-Hr/kg (LHV)
  - Advanced: >4100 W-Hr/kg (LHV)
- **Packaged Canister**
  - Current: 1336 W-Hr/kg (LHV)
  - Advanced: 1676 W-Hr/kg (LHV)
- **Cartridge Capacity**
  - >500 W-Hr (net Fuel Cell)
  - < 1 kg

### Initial Results
- **Reactor Volume**
  - Demonstrated 100mL reactor
  - Fabricated 1 Liter reactor
- **Material Characteristics**
  - High Density
  - Fast Reaction Times
- **Lessons Learned**
  - Hydrogen Filtration
  - Water Distribution

### Key Specifications
- **Push-to-Start Hydrogen**
- **System:** <2kg
- Suitable for lab H₂ generation or fuel cell company evaluation

### Specs/Acquisition
- **250W with water recirculation**
- **Initiated sub-contract**

### Status
- **H₂ purity analysis (ongoing)**
- **Initiated manufacturing process dev.**
- **Initiate work for additive for low temperature operation (FY2009)**
- **Initiate Advanced Material Research (FY2009)**
System Engineering

Approaching DOE Targets Even for Small, Portable Hydrogen Storage Applications

- **Specific Energy**
  - Current Tech.: 1336 W-Hr/kg, LHV
  - Next Gen. Tech.: 1664 W-Hr/kg, LHV

- **Cost**
  - Sodium and Silicon are only production material cost
  - $4.47 / kW-Hr

Biggest Unknown: Over-Stoich Water

- Assumptions based on purchased sodium silicate / water solution
- NaSi reactivity and sodium silicate solubility will compete for water
- Temperature control and water feed system under development to perform detailed study

### Systems Analysis

#### Cost Analysis*

<table>
<thead>
<tr>
<th></th>
<th>2010</th>
<th>2011</th>
<th>2012</th>
<th>2013</th>
<th>2014</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium ($/kg)</td>
<td>$3.08</td>
<td>$3.08</td>
<td>$3.08</td>
<td>$3.08</td>
<td>$3.08</td>
</tr>
<tr>
<td>Silicon ($/kg)</td>
<td>$6.42</td>
<td>$6.42</td>
<td>$6.42</td>
<td>$6.42</td>
<td>$6.42</td>
</tr>
<tr>
<td>Sodium Silicide Production ($/kg)</td>
<td>$90.00</td>
<td>$90.00</td>
<td>$20.00</td>
<td>$20.00</td>
<td>$7.00</td>
</tr>
<tr>
<td>Sodium Silicate Use ($/kg)</td>
<td>$2.38</td>
<td>$2.38</td>
<td>$2.38</td>
<td>$2.38</td>
<td>$2.38</td>
</tr>
<tr>
<td><strong>Total ($/kg)</strong></td>
<td>$97.13</td>
<td>$97.13</td>
<td>$97.13</td>
<td>$97.13</td>
<td>$4.47</td>
</tr>
</tbody>
</table>

*Prices for Sodium & Silicon Based on Quotes From US Vendors

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[Image]
H₂ Generator Development

Schematic

Water → Pump → H₂ Sealing Check Valve → Powder → Hydrogen Separator → Pressure Transducer → H₂ Output → Relief Valve

Laboratory Unit

Controlled H₂ Generation

Beta Systems
October 2009

General Purpose H₂ Generator For Fuel Cell Partner Evaluation and Industrial Use

Progress

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Breadboard Testing Overview

- Repeated demonstration of high flows / fast reaction times in a small system
- Powder Energy Density: ~3200 W-Hr/kg (LHV of H2)
- Maximum of 48 gm Tested in a Single Fixture
- Demonstrated 3 Re-starts

### Breadboard Result Summary

<table>
<thead>
<tr>
<th>Date</th>
<th>Serial</th>
<th>Test #</th>
<th>Powder Type</th>
<th>Mass (g)</th>
<th>H2 (std L)</th>
<th>Grams H2</th>
<th>Correct mL H2O</th>
<th>Watt-Hrs/Kg Powder</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/29/2009</td>
<td>BB4Ni</td>
<td>23</td>
<td>NaSi</td>
<td>26</td>
<td>28.6</td>
<td>2.4</td>
<td>82.9</td>
<td>1586.0</td>
</tr>
<tr>
<td>1/30/2009</td>
<td>BB4Ni</td>
<td>24</td>
<td>NaSi</td>
<td>21.4</td>
<td>23.8</td>
<td>2.0</td>
<td>77.2</td>
<td>1603.2</td>
</tr>
<tr>
<td>2/2/2009</td>
<td>BB4Ni</td>
<td>27</td>
<td>NaSi</td>
<td>17.9</td>
<td>19.5</td>
<td>1.6</td>
<td>59.6</td>
<td>1568.8</td>
</tr>
</tbody>
</table>

Net: assumes 50% fuel cell conversion efficiency

**Progress**
**Issue:** Sodium Silicate Waste Product Can Slow Restarting

**Solution:** Multiple Water Injection Ports Distributed Through Powder

**Initial Results**
- Significant decrease in system restart time
- 3 Re-starts Demonstrated on 48 gm of powder
  - Start #2: > 24 hrs off time
  - Start #3: > 168 hours off time
- Approximately 1/3 consumed per use = 25 W-Hrs (net fuel cell)

(H₂ flow starts at 10 PSI due to back-pressure regulator)

**After 7-Day Restart**
- System Pressure (PSI)
- Water Flow (x10 mL/min)
- H₂ Flow (slpm)

- Restart after 7 Days at Room Temp

- H₂ flow starts at 10 PSI due to back-pressure regulator

**Spiraled water feed network tube**

**Water feed tube spraying inside Canister**

**Close-up of laser drilled holes in water feed tube**

- 0.0051” Hole

**Water Input**
Filtration Cleaning

- Significant foaming observed in test reactor with cross-sectional area of ~1.5 in²
- Almost zero foaming observed in test reactor with cross-sectional area of ~6 in²
- Using small / low volume reactor: a cleaning nozzle is required
- All spray water runs-off to reaction sites and utilized
- Initial testing was done with crude holes spraying on the filter in isolated areas
- Current laser drilled precision holes with controlled spray patterns are under evaluation

Membrane Resistance With and Without Filter Cleaning Spray

Delta Pressure/Flow (PSI/SLPM)

Time (Minutes)

No Filter Cleaning

Filter Cleaning Nozzles Used

Only Two Nozzles Used

Fine Water Spray From Micro-Nozzle
Cartridge Design

Design Characteristics

- Up to 500 gm Per Cartridge (Limit Set by DOT Shipping Regulations)
- Stores all waste product
- Net Fuel Cell Energy
  - >800 W-Hr / Cartridge
- Low Pressure
  - Nominal: 30 psi
  - Max. Continuous Design: 100 psi
  - Expected Burst: >300 psi
- Dimensions: 3.5" Dia X 9" Length
- Weight
  - 0.28 kg in 2009
  - 0.20 kg in 2010
- Thin Walled Canister Designed for Heat Removal
  - 60 W / slpm|H₂

<table>
<thead>
<tr>
<th>Canister Part Description</th>
<th>Pre-Production Weight (kg)</th>
<th>Estimated Production WL (kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Can</td>
<td>0.11657</td>
<td>0.09999</td>
</tr>
<tr>
<td>Cap/Cap Capture Ring</td>
<td>0.02082</td>
<td>0.01770</td>
</tr>
<tr>
<td>Cap</td>
<td>0.10718</td>
<td>0.06431</td>
</tr>
<tr>
<td>O-Ring (cap to can ID seal)</td>
<td>0.00091</td>
<td>0.00091</td>
</tr>
<tr>
<td>Dip Tube (reaction chamber pressure relief)</td>
<td>0.00272</td>
<td>0.00204</td>
</tr>
<tr>
<td>O-Ring (pressure relief valve seal)</td>
<td>0.00091</td>
<td>0.00091</td>
</tr>
<tr>
<td>Pressure Relief Valve</td>
<td>0.00925</td>
<td>0.00925</td>
</tr>
<tr>
<td>Retaining Ring, internal self locking (relief valve)</td>
<td>0.00091</td>
<td>0.00091</td>
</tr>
<tr>
<td>Filter Capture Ring</td>
<td>0.00580</td>
<td>0.00000</td>
</tr>
<tr>
<td>O-Ring (H₂ output filter ID)</td>
<td>0.00091</td>
<td>0.00000</td>
</tr>
<tr>
<td>O-Ring (H₂ output filter OD)</td>
<td>0.00091</td>
<td>0.00000</td>
</tr>
<tr>
<td>Filter (H₂ output)</td>
<td>0.00136</td>
<td>0.00136</td>
</tr>
<tr>
<td>Screen (H₂ output)</td>
<td>0.00741</td>
<td>0.00000</td>
</tr>
<tr>
<td>RFID Transponder</td>
<td>0.00045</td>
<td>0.00045</td>
</tr>
<tr>
<td>Fitting (center fluid feed)</td>
<td>0.00045</td>
<td>0.00045</td>
</tr>
<tr>
<td>Tube (center fluid feed)</td>
<td>0.00272</td>
<td>0.00272</td>
</tr>
<tr>
<td>Tube (H₂ filter sprayer)</td>
<td>0.00091</td>
<td>0.00091</td>
</tr>
<tr>
<td>O-Ring (H₂/H₂O) /O ports</td>
<td>0.00091</td>
<td>0.00091</td>
</tr>
<tr>
<td>Check Valve (H₂/H₂O /O ports)</td>
<td>0.00454</td>
<td>0.00454</td>
</tr>
<tr>
<td>Total Weight (kg)</td>
<td></td>
<td>0.28</td>
</tr>
</tbody>
</table>

Weight Balance

Heat Output at Different Hydrogen Flow Rates

WWW.SIGNACHEM.COM
Specifications

- Dimensions: 9” X 9” X 10” (height)
- Approx. System Weight: <2 kg
- H2 Flow Rate (Continuous): 3 slpm
- H2 Flow Rate (Peak): 8 slpm (0.25 seconds every 2 minutes)
- Watt-Hrs/Cartridge: >1500 W-Hr (LHV)
- Regulated Output Pressure: 25 psi
- Initial Target Operating Temp: -5 to 40°C
- Start-up Time: 1 min
- Restarts: >5 / cartridge (expect >10 to 20)

Seeking Development Partners for Beta System Evaluation: October 2009
Collaborations

• Subcontract to Trulite Inc.
  – Development of a 250W Fuel Cell System with Water Recirculation
  – Status: Subcontract has been awarded. Early stages of development.
  – Principal Investigator: Ken Pearson

• Subcontract to the University of Texas Austin, Center for Electromechanics
  – Alternative reaction mechanism development and control
  – Status: Subcontract has been awarded. Early stages of development.
  – Principal Investigators: Richard Thompson and Michael Lewis
Proposed Future Work

• FY2009
  – Complete hydrogen purity verification
  – Complete development of prototype system
  – Demonstrate technology in an end customer application (late FY2009 – Early FY2010)
  – Research and develop high volume manufacturing methods for sodium silicide
  – Conduct additional experiments with additives to improve low temperature operability (below freezing)
  – Initiate research on ultra-high density sodium silicides

• FY2010
  – Deliver ~10 systems for Hydrogen Generator beta testing (early FY2010)
  – Improve hydrogen generation system performance and robustness
  – Work with development partners for end system integration
  – Demonstrate high volume manufacturing process for sodium silicide
  – Continued research on ultra-high density silicides
Summary

- Sodium silicides enable real-time hydrogen generation for portable applications that require low weight and cost

- Sodium silicides have unique technical attributes that enable simple systems with significant benefits over competitive hydrogen storage technologies
  - Fast starting
  - Low temperature
  - Low pressure
  - Long term storage
  - High temperature stability

- Continued research on ultra-high density sodium silicides will enable packaged fuel to approach doe targets of 2 kW-Hr/kg and $4/kW-Hr for mobile power solutions