## Overview

### Timeline
- Project start date: Jan 2006
- Project end date: Aug 2008
- Percent complete: 95%

### Weight and Volume

### Cost

### Messaging

<table>
<thead>
<tr>
<th>Partners</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dow Chemical Company</td>
</tr>
<tr>
<td>Edison Welding Institute</td>
</tr>
<tr>
<td>NextEnergy</td>
</tr>
</tbody>
</table>

### Barriers Addressed
- Weight and Volume
- Cost
- Manufacturing Cost

### Budget
- Total project: $861K
- Funding breakdown:
  - DOE share: $427K
  - In-kind share: $434K
Project Objectives

- Develop manufacturing concepts to reduce the process and product costs of chemical hydride hydrogen generation & storage technology
- Develop a modified design to demonstrate high volume manufacturability of fuel cartridges based on Millennium Cell’s patented Hydrogen on Demand® technology
- Utilize strengths of NCMS partners to achieve highly reliable fuel cartridge/tank performance
  - Dow: Material selection
  - EWI: Sealing techniques
  - NextEnergy: System testing
- Assess recyclability for all fuel system components, consistent with performance and manufacturability
## Milestones

<table>
<thead>
<tr>
<th>Month-Year</th>
<th>Milestone</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jun-06</td>
<td>Complete component materials selection. Test materials for temperature range of performance, compatibility with high ph fuel solution, mechanical properties, manufacturability and cost</td>
</tr>
<tr>
<td>Nov-06</td>
<td>Finalize bladder assembly process and cartridge manufacturing → select optimal sealing technology for sealing fitments, membranes and bladders. Identify and finalize cartridge manufacturing process and obtain tooling</td>
</tr>
<tr>
<td>Mar-07</td>
<td>Complete pilot product/process validation. Set up pilot line for bladder manufacture at MCEL. Set up quality control tooling to screen bladder sets at different steps during manufacturing process. Send at least 25 bladder sets for testing at NextEnergy</td>
</tr>
<tr>
<td>Aug-08</td>
<td>Work with film and membrane manufacturers to complete evaluation of alternate low cost and recyclable bladder and membrane materials.</td>
</tr>
</tbody>
</table>
### Project Plan & Approach

#### Baseline Cartridge Design
- Define subcomponent functions
- Develop process flow diagrams
- Establish robust design specifications

#### Component Materials Selection
- Recyclability
- Manufacturability
- Cost

#### Component Manufacturing Techniques
- Optimize sealing technologies

#### Cartridge Manufacturing Process
- Select robust manufacturing process
- Assess cost
- Minimize cycle time

#### Process Validation
- Set up pilot line
- Define DFM design
- Manufacture/Test prototypes

#### Recyclability
- Material recyclability / life-cycle

<table>
<thead>
<tr>
<th>Component</th>
<th>Status</th>
<th>Completion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Baseline Cartridge Design</td>
<td>100% Complete</td>
<td>100% Complete</td>
</tr>
<tr>
<td>Component Materials Selection</td>
<td>100% Complete</td>
<td>100% Complete</td>
</tr>
<tr>
<td>Component Manufacturing Techniques</td>
<td>90% Complete</td>
<td>90% Complete</td>
</tr>
<tr>
<td>Cartridge Manufacturing Process</td>
<td>100% Complete</td>
<td>100% Complete</td>
</tr>
<tr>
<td>Process Validation</td>
<td>90% Complete</td>
<td>90% Complete</td>
</tr>
<tr>
<td>Recyclability</td>
<td>100% Complete</td>
<td>100% Complete</td>
</tr>
</tbody>
</table>
Technology Background

Hydrogen on Demand® Reaction

Characteristics:

- Gaseous hydrogen is produced only when needed
  - Amount of hydrogen produced is proportional to pump speed
- Fuel is non-flammable; at ambient pressure and temperature
- Relatively low reaction temperature (~80°C)
- Moderately exothermic reaction, ~67 kJ/mol H₂ produced

\[ \text{NaBH}_4 + 4 \text{H}_2\text{O} \rightarrow 4 \text{H}_2 + \text{NaB(OH)}_4 + \text{heat} \]

- An energy-dense chemical hydride fuel
- Rapid H₂ production
- High purity hydrogen
- Borate can be recycled or disposed
- Reaction requires no heat input
Technology Background

Cartridge Functionality

1. Fuel is pumped through a catalyst reactor
2. Fuel is converted into pure hydrogen, water vapor, and sodium metaborate
3. Hydrogen gas is sent to the fuel cell

Fuel Cartridge

- Fuel area:
  - Stabilized NaBH₄ solution
- H₂ separation area: (borate / hydrogen)

Fuel Pump

Reactor

Fuel Cell

Fuel

O₂ from Air

Electrical power

Water

Project # MFP3
Criteria evaluated in the materials selection process for hydrogen separation membranes:

- Gurley Numbers
- Maximum membrane holdback fluid pressure for a 30 minute duration
- Time to breakthrough for a membrane under constant fluid pressure
- Membrane clogging
- Cost
- Recyclability
Gurley densometers are the accepted standard for measuring the porosity of materials such as papers, wovens, plastics and membranes.

A Gurley Number is the time in seconds it takes for 100 cc of air to pass through 1 in\(^2\) of membrane when a constant pressure of 4.88 in of water is applied.

- 31 membranes were recommended for test by Dow.
  - 9 had acceptable Gurley numbers for further testing.
### Materials Characterization

**Membrane Surface Tension**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface Tension (dynes/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SRA Reference Water (Distilled)</td>
<td><strong>66.092</strong></td>
</tr>
<tr>
<td>083101B (DI)</td>
<td><strong>67.595</strong></td>
</tr>
<tr>
<td>4MJB0618A (Liquid Borate)</td>
<td><strong>86.703</strong></td>
</tr>
<tr>
<td>083101A (SRA mixed Fuel)</td>
<td><strong>72.407</strong></td>
</tr>
</tbody>
</table>

*Surface tension calculated using the determined density of 1.41g/mL.

**Surface tension calculated using the determined density of 1.06 g/mL.

- Below “breakthrough” pressure liquids do not pass, only hydrogen gas – typically 8-10 psig differential
- Primary potential failure mode is liquid (fuel or borate) breakthrough
Both water and fuel were tested – different surface tension

Liquid breakthrough water and fuel testing:
- Membrane is placed in a fixture exposing ~3.8 cm² of membrane
- Water or fuel pressure is applied to the membrane
- Starting at 5 psi pressure is increased in 5 psi increments every 0.5 hrs until the membranes leak. The result is the highest pressure held for 0.5 hrs.
- Only 4 of the 9 membranes held back pressures greater than 15 psig
- Same test were performed at elevated temperatures of 60°C and 80 °C on the final candidate. Pressure was held to 20 psig and 10 psig respectively.

Long-term fuel solution holdback:
- Membrane is placed in a fixture exposing ~3.8 cm² of membrane
- Fuel is applied at 6 psig and maintained to the membrane. The membrane is checked every hour until it leaks max. of 72 hours
- Three membranes were tested and all passed
Materials Characterization
Membrane Test Fixture

- Fixture used to test borate infiltration of the membrane
- The fixture tilted back and forth to periodically expose membrane to borate
- Gas flow through membrane was held at a constant rate
- Pressure drop measured to determine membrane blockage
- Final candidate membrane lasted 93 hrs without signs of impediment or degradation
Before the program, membrane from Manufacturer “A” was identified as the best candidate

- Low volume cost of > $900/m²
- A typical cartridge uses ~400 cm²
- Cost of membrane per cartridge is ~$40
- A more cost effective membrane was required

Materials characterization work in this program showed that membrane from Manufacturer “B” has sufficient performance

- Low volume cost ~$40/m²
- Membrane was tested and obtained similar results
- Required minor changes to the backer material to aid in sealing for later tasks
Final Materials Selection

- The membrane backer and sealing technologies were the main influences on the selection of the film and fitment materials, along with operating requirements.

- Membrane
  - Manufacturer “B” Micro-porous Membrane with PP/PE backing

- Film
  - Manufacturer “C” Polypropylene Film

- Fitment Material
  - Polypropylene

- Cartridge Material
  - Delrin
Adhesive Technology Screening

- Original systems utilized adhesives for bonding membranes to films
- At left: the adhesive bond between the bladder and the membrane materials has failed
- This is a common failure mode:
  - Highlights the need to improve bond between these two components
- Goal → membrane material delaminates before the adhesive bond fails
Peel Testing

Multiple adhesives / materials combinations were tested

Interfacial peel failure surface for UV-curable adhesive shown here
- The adhesive is failing in a cohesive mode
- Teflon surface (left) and urethane surface (right)

* Approximately 1/2"-wide strips.

**Screening Peel Tests (excerpt)**

<table>
<thead>
<tr>
<th>Adhesive</th>
<th>Combination</th>
<th>Peel Values (g)*</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>3105 (UV)</td>
<td>Urethane-PTFE</td>
<td>140 62 37 80</td>
<td>Cohesive failure of adhesive</td>
</tr>
<tr>
<td></td>
<td>Urethane-PE</td>
<td>685 418 410 504</td>
<td>Pulling PE off the PTFE</td>
</tr>
<tr>
<td>3379 (HM)</td>
<td>Urethane-PTFE</td>
<td>210 243 209 221</td>
<td>Adhesive failure at PTFE</td>
</tr>
<tr>
<td></td>
<td>Urethane-PE</td>
<td>856 1300 818 991</td>
<td>Pulling PE off the PTFE</td>
</tr>
</tbody>
</table>

Bonded sample constructed by EWI
Polyethylene membrane side bonded to a urethane film

The adhesive is pulling the laminate (right – bonded to urethane) off the PTFE (left)

Failure mode shows that the membrane to bladder bond is improved
Conclusion… adhesives possibly OK, however:

- Repeatability questionable
- Not necessarily conducive to high-volume manufacturing

Move to heat sealing → more manufacturing friendly

- Higher repeatability / robustness → reliability
- Ultimately enables roll-to-roll processes
Heat Sealing

Hot Tool Welding

- Simple process, commonly used in the food packaging industry
  - Heated tool in the shape of the weld opposed by a ram → forces the tool onto the films
  - The tool is held in position in contact with the film for a controlled time period

- Some limitations:
  - Each weld geometry requires a distinct and separate shaped die
  - Several heated tools may be necessary for the production of a single unit.
  - A contact process → e.g., too much pressure applied can create a thin spot at the weld edge, compromising the strength and seal integrity of the weld

- Original film was expensive → need new materials
  - Polyolefins are among the least expensive materials, readily available in film form
  - Polypropylene (PP, m.p. 165 ºC) can provide the necessary performance
  - Required a change in the membrane backing material since PE is not weldable to PP
  - Two suppliers of a membrane with a polypropylene nonwoven backing were sourced
Heat Sealing Variables

- Temperature
  - Need proper temperature to melt materials

- Time
  - Need proper contact time to allow layers to melt together

- Pressure
  - Need correct pressure to allow the two materials to melt together

General failure modes of heat seals:

- (1) First layer of material will melt too much → thinning / holes in first layer
  → Causes: Too high of a temperature, too much time, or too much pressure

- (2) First layer of material will not melt through to the second layer
  → Causes: Too low of a temperature, not enough time, or not enough pressure
Fitment Design Improvements (Dow)

Original fitment design:
- Excessive flash
- Poor sealing surfaces

Final Dow fitment design:
- Improved mold design
- Added sealing ridge
Heat Sealing Line
Set up at EWI → Transferred to MCEL
Quality Control Testing

Equipment was developed to test each step of the assembly process.
Final Heat-Sealed Bladder Assemblies

- Polypropylene fitments and film
- Micro-porous PTFE membrane
- Heat sealing manufacturing processes
Fuel Canister → Machined PVC body, brass hydrogen valve / interface, ring board FC electrical interface

Fuel Bladder Assembly → Polyurethane film, rapid-prototyped (SLA) fitments, original hydrophobic membrane, glued components
Final Bladder and Cartridge Assemblies

- Fuel Canister → Injection molded Delrin body, brass valve FC gas interface, ring board FC electrical interface
  - Valve can also potentially be made from PP plastic
- Fuel Bladder Assembly → PP film, PP fitments, PTFE hydrophobic membrane, all heat sealed components
- Pilot run of fuel canisters and bladder assemblies completed
29 bladder assemblies were delivered to NextEnergy

Tested operating at ~1000 sccm H₂ flow and ~20 psig pressure

System was turned off for periodic cooling cycles to simulate usage

Bladder ass’y showing no signs of liquid leaks → positive result

~50% failure rate in initial 16 runs → system issue → faulty check valve

100% pass rate on final 13 bladder assemblies after valve replaced
  - Issue not manufacturing related
Significant Manufacturing Process Improvements

- Fabrication scrap rate of the various sub-assemblies reduced from ~75% to less than 5%
- Bladder assembly process steps reduced by 25%
- Reduced fabrication process times by more than a factor of 10
- Projected manufacturing processing costs reduced by a factor of 8-10
Cartridge Life Cycle Summary

MCEL
Bladder Assembly, Reactors

Fuel Cell Partner
Fuel Cartridges Assembled

Customer
Use and Return of Fuel Cartridges

NaBH₄
Users

Cartridge Recycling Center

Reactors Shells
Recycled Parts

Unused Fuel
Borate (solid & liquids)

Borate Users

Local Landfill

Discarded Components, Borate (solid)

Unused Fuel
Borate (solid & liquids)

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Reactors Shells
Recycled Parts

Unused Fuel
Borate (solid & liquids)

Borate Users

Local Landfill

Discarded Components, Borate (solid)
Original bladder assembly design
- Used six (6) different polymer materials
- None are recyclable

Resulting bladder assembly design
- Reduced to 2 materials (polypropylene, PTFE)
- All cartridge subcomponents except PTFE membrane and hydrogen valve body are now are directly recyclable
  - Potential to move to recyclable valve and membrane
  - Existing PP membranes are not sufficient

Identified other components within cartridge for potential re-use
- e.g., Catalyst reactor bodies, outlet valve assembly
Future Work

- Conduct large-scale evaluation of cartridge and component manufacturing
  - Assess failure rates, process yield and scrap
- Refine cartridge and component design
  - Minimize assembly steps
  - Reduce scrap
  - Reduce manufactured cost
- Eliminate PTFE membrane and brass hydrogen valve body
  - Use PP membrane and valve body
- Scale up component design and manufacturing processes to address higher power level operation
Summary

- **Relevance:** High-volume manufacturability of hydrogen generation cartridge components

- **Approach:** Develop cartridge manufacturing technology, execute pilot production of cartridges, assess recyclability

- **Technical Accomplishments and Progress:** Pilot run completed, heat sealing successful for fuel bladder assemblies and hydrogen separation membranes

- **Collaborators:** Dow Chemical, EWI, NextEnergy

- **Future Work:** Move to fully recyclable materials, scale up to higher power level

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