Manufacturable Chemical Hydride Fuel System for Hydrogen Fuel Cell Systems

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Project ID #: MFP3

Overview

Timeline

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

Barriers Addressed

- Weight and Volume
- Cost
- Manufacturing Cost

Budget

Total project: $861K

Funding breakdown:

- DOE share: $427K
- In-kind share: $434K

Partners

- Dow Chemical Company
  - Tom Gregory
- Edison Welding Institute
  - David Speth
- NextEnergy
  - Jim Saber

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

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Month-Year	Milestone
Jun-06	Complete component materials selection. Test materials for temperature range of performance, compatibility with high ph fuel solution, mechanical properties, manufacturability and cost
Nov-06	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
Mar-07	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
Aug-08	Work with film and membrane manufacturers to complete evaluation of alternate low cost and recyclable bladder and membrane materials.

Project Plan & Approach

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100% Complete

Baseline Cartridge Design

- Define subcomponent functions
- Develop process flow diagrams
- Establish robust design specifications

100% Complete

Component Materials Selection

- Recyclability
- Manufacturability
- Cost

100% Complete

Component Manufacturing Techniques

- Optimize sealing technologies

100% Complete

Cartridge Manufacturing Process

- Select robust manufacturing process
- Assess cost
- Minimize cycle time

90% Complete

Process Validation

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

90% Complete

Recyclability

- Material recyclability / life-cycle

Technology Background
Hydrogen on Demand® Reaction

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$$NaBH_4 + 4\,H_2O \rightarrow 4\,H_2 + NaB(OH)_4 + \text{heat}$$

- $NaBH_4 + 4\,H_2O$: An energy-dense chemical hydride fuel
- $\rightarrow$: Rapid H_2 production
- $4\,H_2$: High purity hydrogen
- $NaB(OH)_4$: Borate can be recycled or disposed
- heat: Reaction requires no heat input

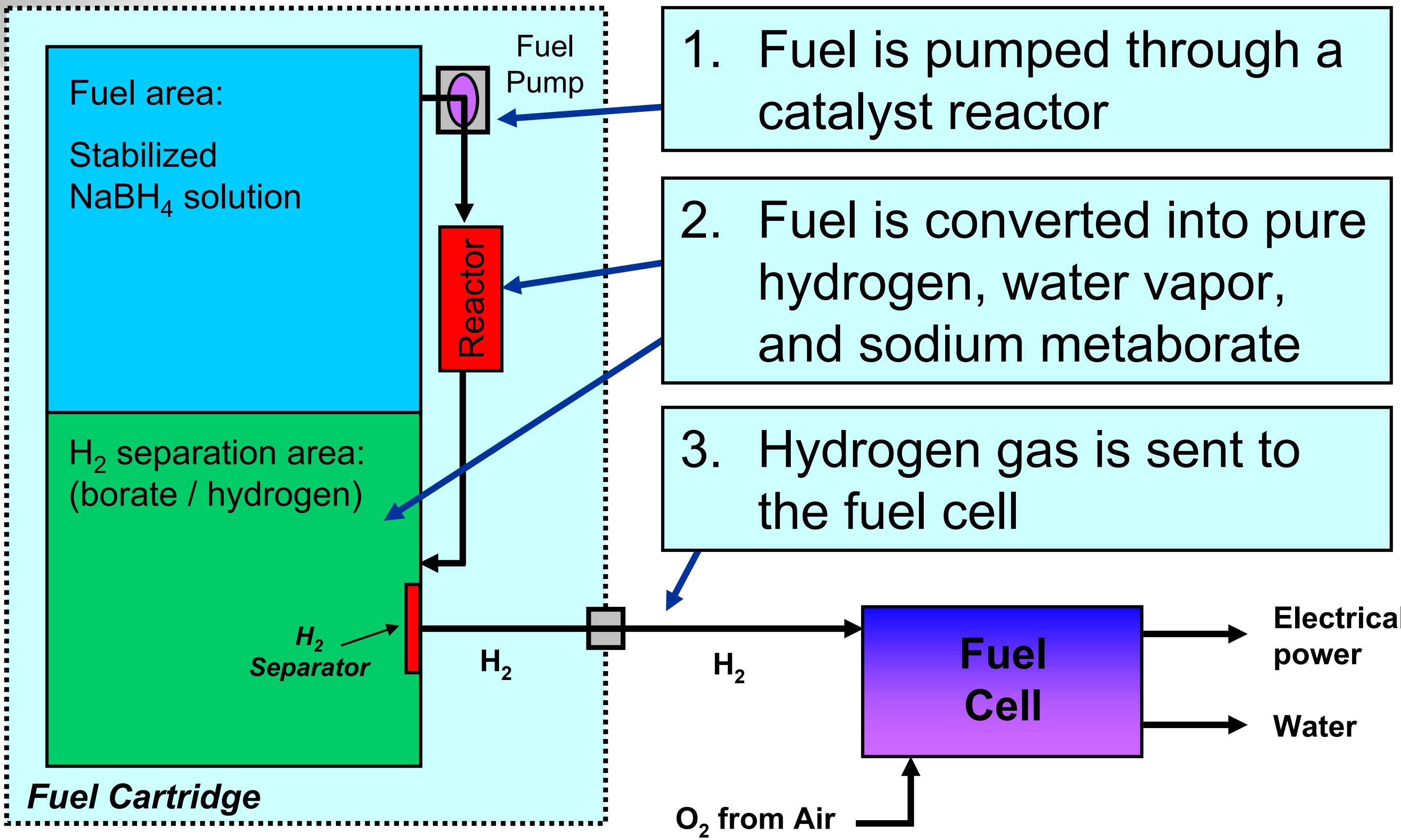
Characteristics:

- 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 H_2 produced

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

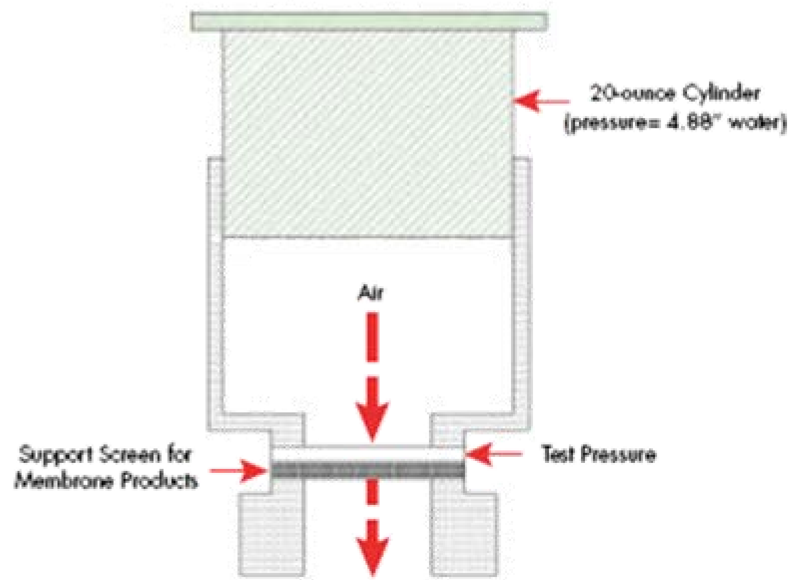


Materials Characterization
Membrane Screening Parameters

- 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

Materials Characterization
Membrane Gurley Airflow Testing

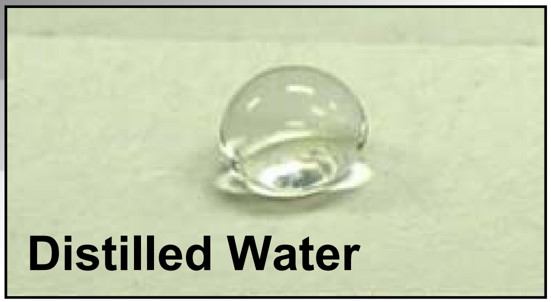
- Gurley densometers are the accepted standard for measuring the porosity of materials such as papers, wovens, plastics and membranes
- A Gurley Number is the time in seconds it takes for 100 cc of air to pass through 1 in^2 of membrane when a constant pressure of 4.88 in of water is applied

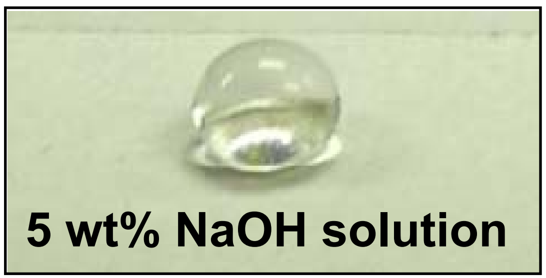


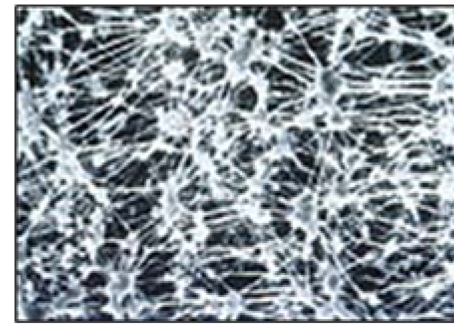
  - 31 membranes were recommended for test by Dow

    ➔ 9 had acceptable Gurley numbers for further testing

Materials Characterization
Membrane Surface Tension







Micrograph (5000) showing expanded PTFE membrane material.*

Sample	Surface Tension (dynes/cm)
SRA Reference Water (Distilled)	66.092
083101B (DI)	67.595
4MJB0618A (Liquid Borate)	86.703*
083101A (SRA mixed Fuel)	72.407**

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

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

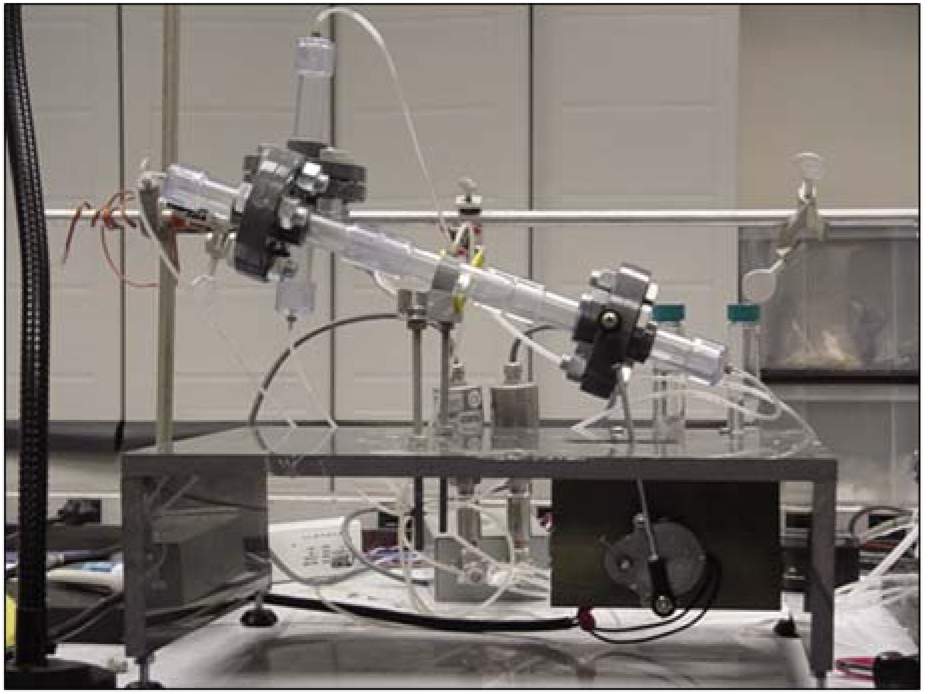
- Below "breakthrough" pressure liquids do not pass, only hydrogen gas – typically 8-10 psig differential
- Primary potential failure mode is liquid (fuel or borate) breakthrough

Materials Characterization
Membrane Liquid Intrusion Testing

- Both water and fuel were tested – different surface tension
- Liquid breakthrough water and fuel testing:
  - Membrane is placed in a fixture exposing ~3.8 cm^2 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 cm^2 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

Materials Characterization
Membrane Cost Reduction

- Before the program, membrane from Manufacturer "A" was identified as the best candidate
  - Low volume cost of > $900/m^2$
  - A typical cartridge uses ~400 cm^2
  - 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 ~$40/m^2$
  - 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

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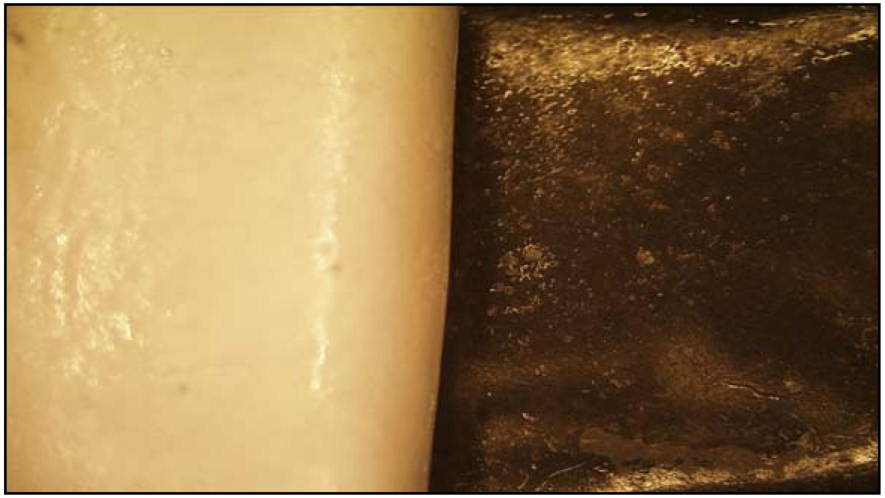
- Original systems utilized adhesives for bonding membranes to films
- At left: the adhesive bond between the bladder and the membrane materials has failed
- This is a common failure mode:
  - Highlights the need to improve bond between these two components
- Goal → membrane material delaminates before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

Adhesives / Materials
Peel Testing

Screening Peel Tests (excerpt)						
Adhesive	Combination	Peel Values (g)*				Comments
		S1	S2	S3	**AVE**	
3105 (UV)	Urethane-PTFE	140	62	37	**80**	Cohesive failure of adhesive
	Urethane-PE	685	418	410	**504**	Pulling PE off the PTFE
3379 (HM)	Urethane-PTFE	210	243	209	**221**	Adhesive failure at PTFE
	Urethane-PE	856	1300	818	**991**	Pulling PE off the PTFE

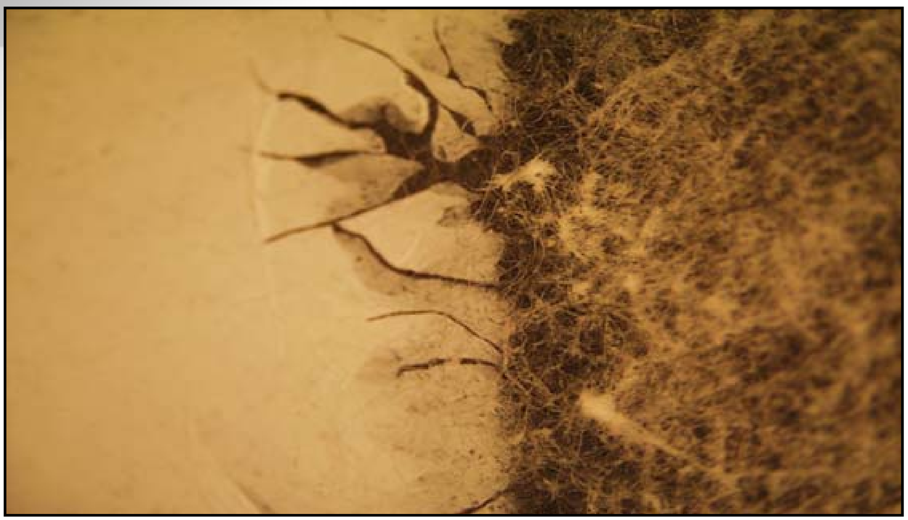
* Approximately 1/2"-wide strips.



Bonded sample constructed by EWI

- 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)

Adhesives / Materials
Peel Testing



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

Migration from Adhesives to Heat Sealing

UV-Cured Adhesive Test Disc

Heat sealed Test Disc

- 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

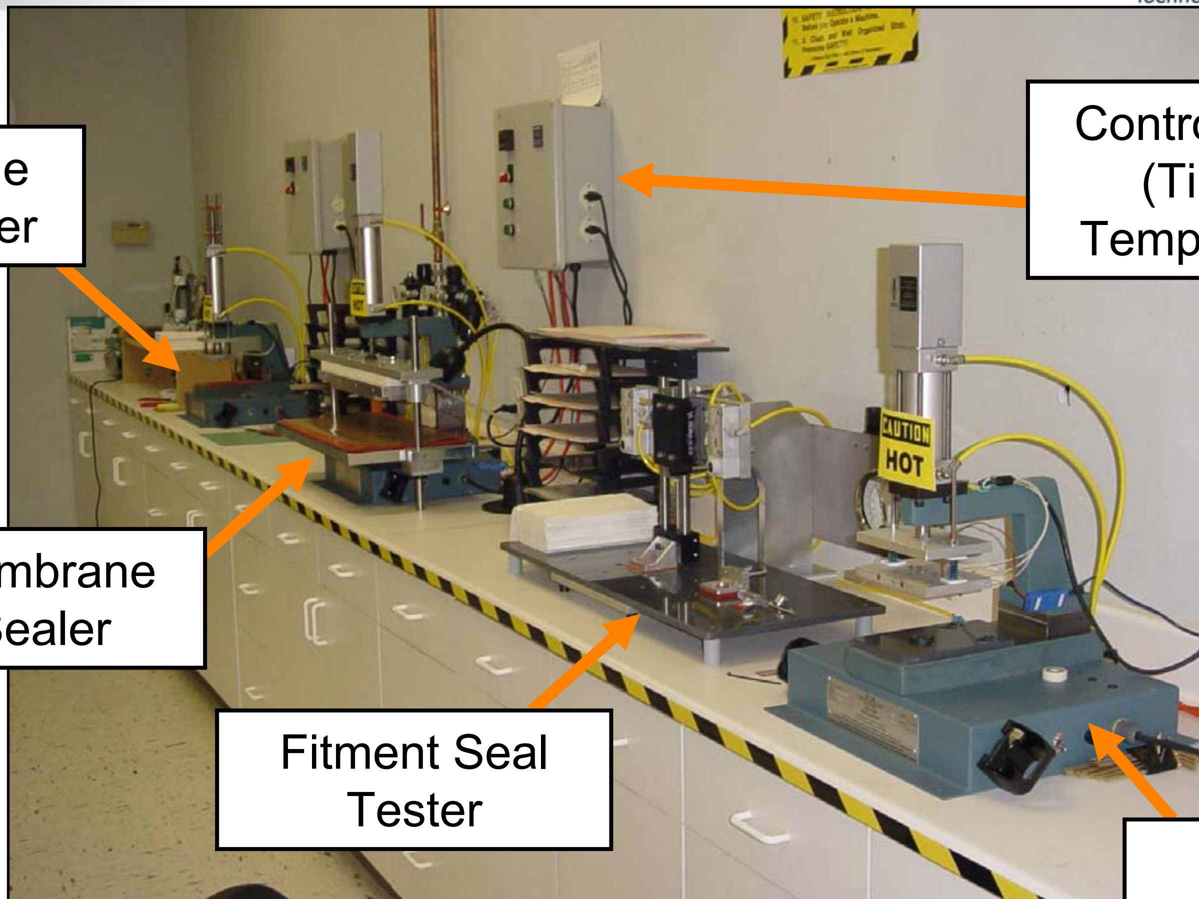
Fitment Design Improvements (Dow)

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



Membrane Seal Tester

Control Boxes (Time & Temperature)

Membrane Sealer

Fitment Seal Tester

Fitment Sealer

Quality Control Testing

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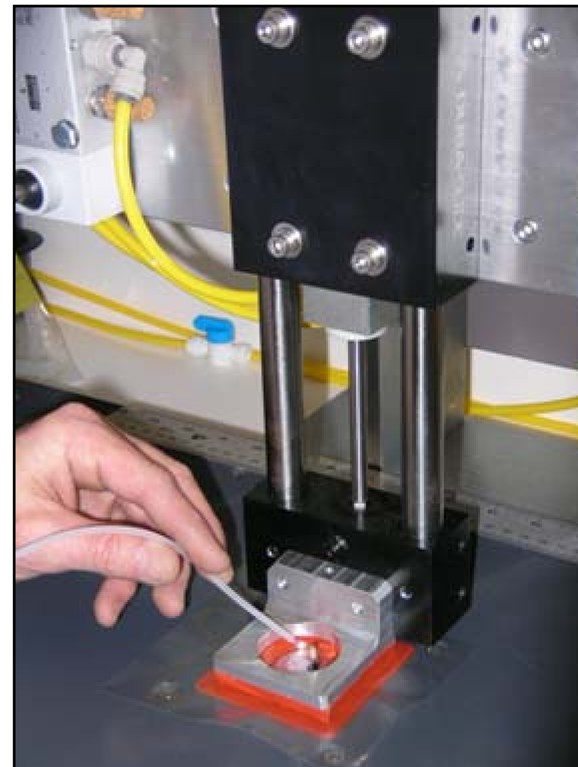
Equipment was developed to test each step of the assembly process

Membrane and Seal Tester



Fitment Seal Tester

Final Heat-Sealed Bladder Assemblies

- Polypropylene fitments and film
- Micro-porous PTFE membrane
- Heat sealing manufacturing processes

Original Bladder and Cartridge Assemblies

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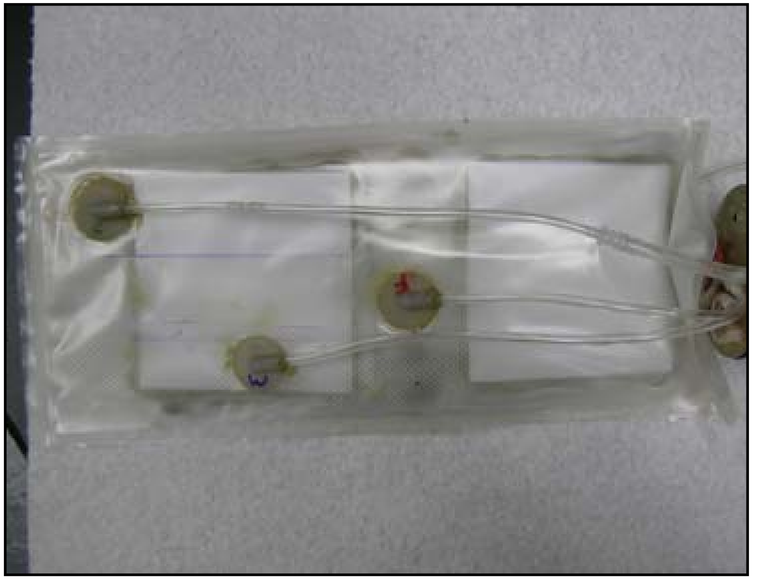

- Fuel Canister → Machined PVC body, brass hydrogen valve / interface, ring board FC electrical interface
- Fuel Bladder Assembly → Polyurethane film, rapid-prototyped (SLA) fitments, original hydrophobic membrane, glued components

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

Cartridge / Bladder Testing

At NextEnergy Facility

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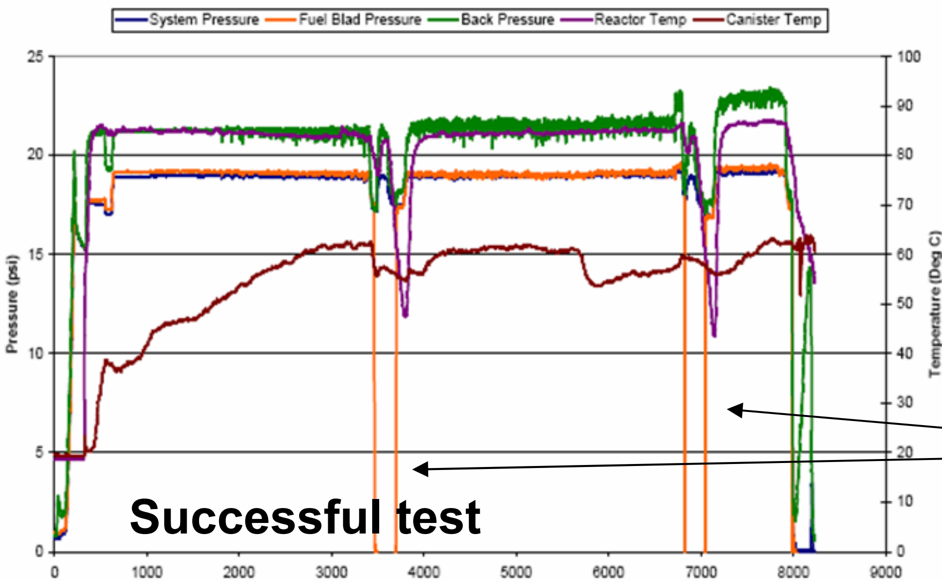

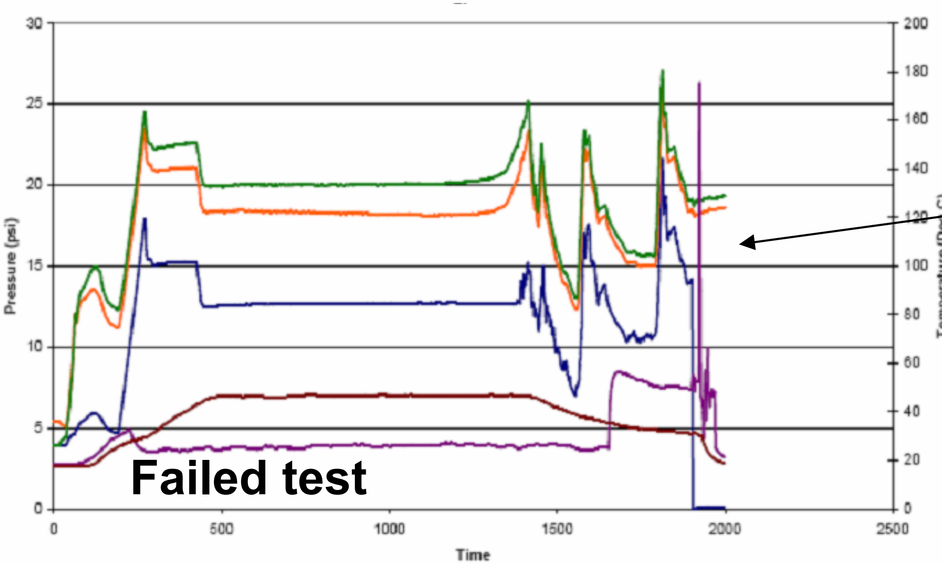

- **29 bladder assemblies were delivered to NextEnergy**
- Tested operating at ~1000 sccm H_2 flow and ~20 psig pressure
- System was turned off for periodic cooling cycles to simulate usage
- Bladder ass'y showing no signs of liquid leaks → positive result
- ~50% failure rate in initial 16 runs → system issue → faulty check valve
- **100% pass rate on final 13 bladder assemblies after valve replaced**
  - Issue not manufacturing related

Significant Manufacturing Process Improvements

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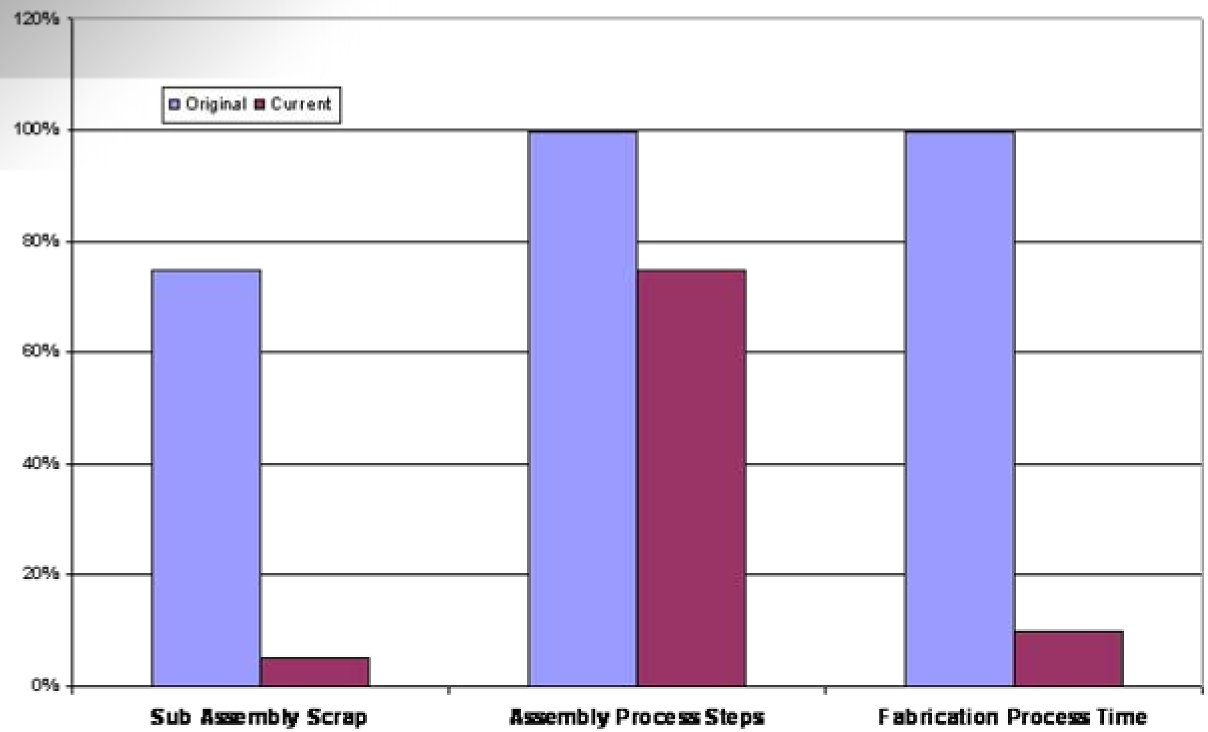
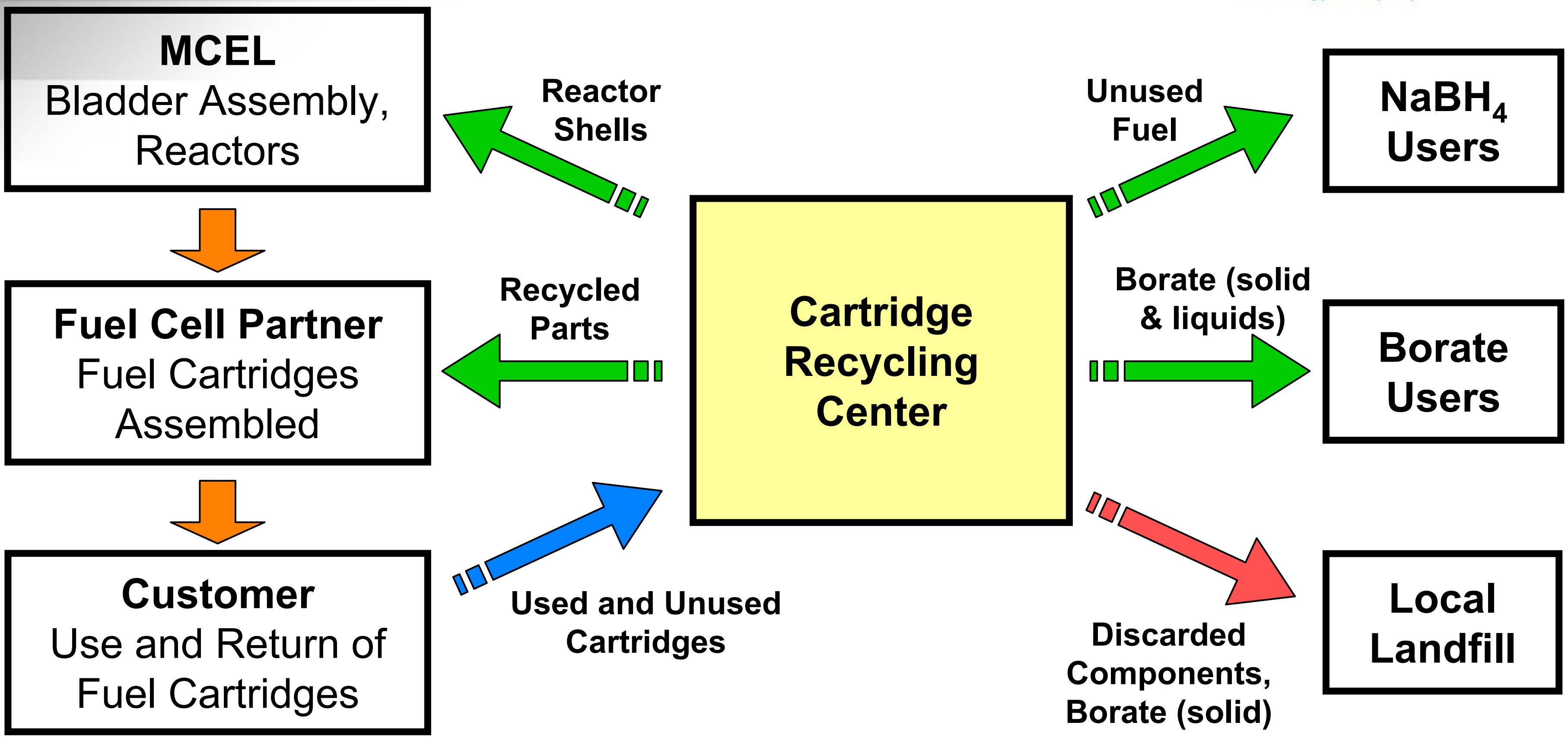


- Fabrication scrap rate of the various sub-assemblies reduced from ~75% to less than 5%
- Bladder assembly process steps reduced by 25%
- Reduced fabrication process times by more than a factor of 10
- Projected manufacturing processing costs reduced by a factor of 8-10

Cartridge Life Cycle Summary



Program Results: Improvements to Cartridge Recyclability

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- 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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