



2011 Hydrogen Program

Annual Merit Review Meeting

Unitized Design for Home Refueling Appliance for Hydrogen Generation to 5,000 psi

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Project ID# PD065

This presentation does not contain any proprietary or confidential information

Overview

Phase II SBIR Program

Timeline

- **Project Start:** 08/15/2010
- **Project End:** 08/14/2012
- **Percent Complete:** 12%

Budget

- **Total Project Budget:** \$999k

Barriers

Hydrogen Generation by Water Electrolysis

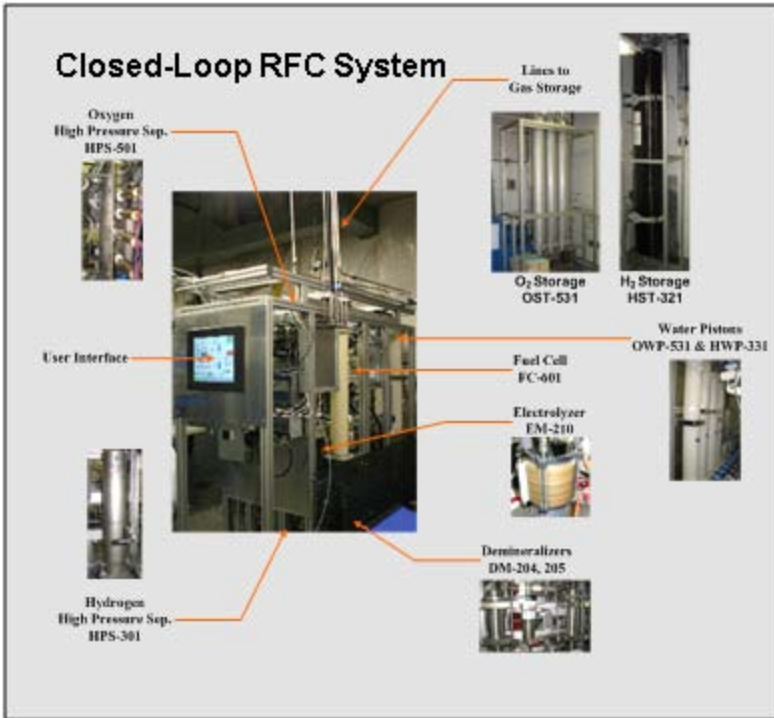
- **G. Capital Cost**
- **H. System Efficiency**

Targets

DOE TARGETS: Distributed Water Electrolysis			
Characteristics/units	2006	2012	2017 - 2020
Hydrogen Cost (\$/kg-H ₂)	4.80	3.70	2.00 – 4.00
Electrolyzer Cap. Cost (\$/kg-H ₂)	1.20	0.70	0.30
Electrolyzer Efficiency (%LHV)	62	69	74
(%HHV)	(73)	(82)	(87)

Partners

- **Prof. R. Zalosh** – Hydrogen Safety Codes
- **IAS, Inc.** – System Controls Design
- **3M Fuel Cell Components Program (Manufacturer)** – NSTF Catalyst & Membrane
- **Entegris** – Carbon Cell Separators
- **DE-FC36-08GO18065** - PEM Electrolyzer Incorporating an Advanced Low-Cost Membrane



S-10 Electrolyzer System

6 kW Electrolyzer
 ~ 40 SCFH-H₂ (~0.1 kg-H₂/hr)
 1500 ASF
 1250 psi H₂ / Ambient O₂
 Volume ~ 6 ft³

GES PEM Electrolyzer Systems

UUV Applications (V = 12.5 Ft³)

12 Cells - 0.17 ft² Cells/Stack
 6-kW Electrolyzer
 ~ 40 SCFH-H₂ (~0.1 kg-H₂/hr)
 High Current Density (1300-1500 A/ft²)
 1000 psi H₂/Ambient O₂
 No High-Pressure Water Feed Pump or Containment Vessel
 UUV Applications

EP-1 On-Site H₂ Generators

20 kW Electrolyzer
 0.35 kg H₂ / hr
 1500 ASF
 1250 psi H₂ / Ambient O₂
 Volume ~ 16 ft³

Relevance/Project Objectives

Overall Project Objectives

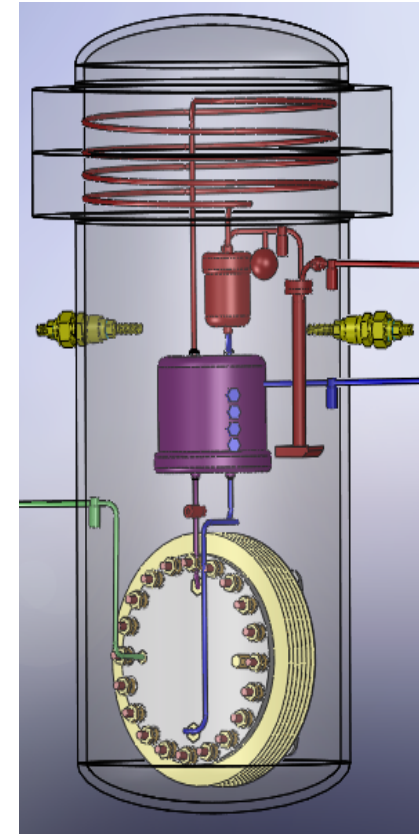
- Detail design & demonstrate subsystems for a unitized electrolyzer system for residential refueling at 5,000 psi to meet DOE targets for a home refueling appliance (HRA)
- Fabricate & demonstrate unitized 5,000 psi system (Year 2)
- Identify & team with commercialization partner(s)

Relevance

- Successfully developing a low-cost residential refueling appliance will enable early adoption of fuel cell vehicles

Impact

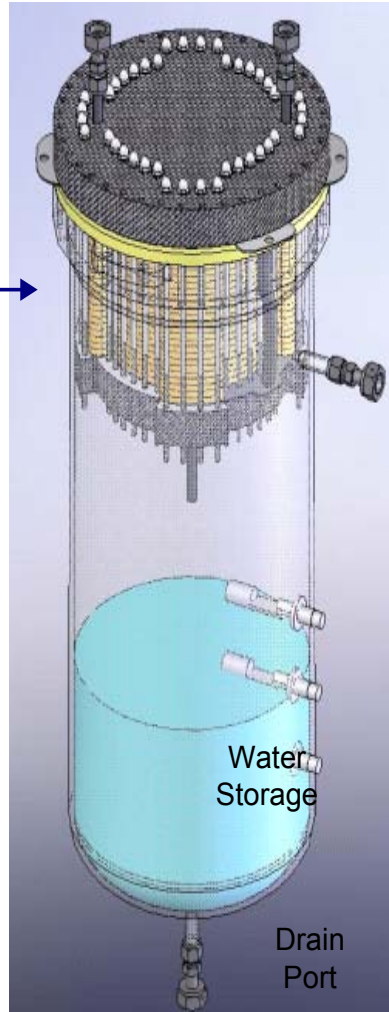
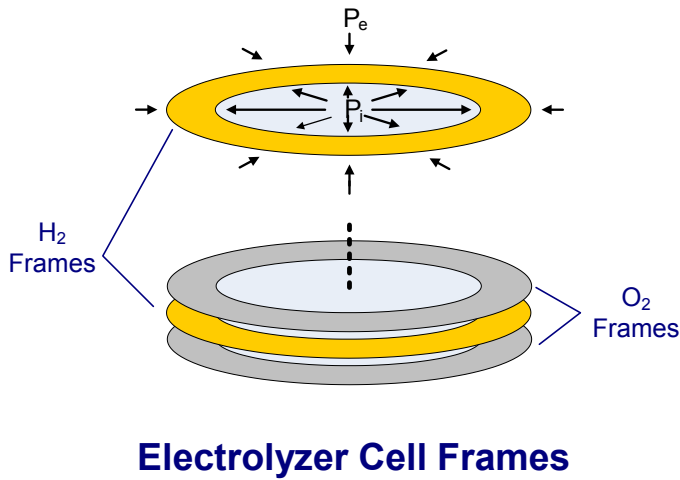
- Successfully developing a low-cost residential refueling appliance will overcome Barriers G. Capital Cost and H. System Efficiency



Innovative Approach to High Pressure Electrolyzer Operation

- Innovation Required to Overcome Significant Issues
 - Improve Efficiency
 - Good voltage performance
 - Reduce high gas cross-over rates
 - Supported MEA (long life)
 - Reduce Expense of High-Pressure Components
 - Stack
 - Phase separators
 - Valves, pumps, and piping
 - Engineer a Safe System
 - High pressure compressible gases
 - High pressure flammable hydrogen
 - High pressure high purity oxygen
- PEM Electrolysis Proven Under Balanced Pressure Conditions
 - To 3,000 psi with Gen 1 Navy stacks
 - Aerospace stacks at 400, 1,200, and 2,000 psi

Proposed Approach: Unitized Design Concept



Gas Feed to Dryer

Level Sensors

Drain Port



GES Electrolyzer Stack-Dome Assemblies

Approach: Utilize a Low-Cost Cell Design

- Take Advantage of Advances & Developments on Related Giner/DOE Projects
- Carbon Cathode
 - Multi functional part
 - One piece replaces two subassemblies
 - Eliminates 20+ component parts
 - Enables high pressure operation
 - Demonstrated to 2,000 psi (balanced and differential)
- Low Precious Metal Loadings (3M)
 - 10x reduction
 - Demonstrated performance comparable to standard anode and cathode catalysts
- Single Piece Separator (Entegris)
 - Eliminates hydrogen embrittlement
 - One subassembly reduces cell part count by 30%

Approach: High Pressure Electrolyzer Membrane

PEM Electrolyzer Efficiency

- Increase Ionomer's Conductivity (Low EW)
- Thin MEA – reduces membrane resistance
- Operate at High Temperature – reduces MEA resistance
- Reduce Ionomer's Permeability
- Enabling Technology: DSM™

Approach/Milestones

Task	Progress Notes	% Complete
Task 1: Preliminary Performance of Thermosiphon-Based Electrolyzer Stack	Completed: <ul style="list-style-type: none"> ■ Test Stand modifications complete ■ Initial tests showed importance of cathode compartment height ■ Special components designed, fabricated and ready ■ Testing underway on first cathode height 	60%
Task 2: Detailed Analysis of Hydrogen Safety Codes and Standards	Completed: <ul style="list-style-type: none"> ■ Phase I codes and standards work updated ■ Preparing to conduct HAZOP/FMEA after P&ID is finalized 	10%
Task 3: Design/Build/Test Full-Scale Home Refueling Appliance (HRA) Electrolyzer Stack	Completed: <ul style="list-style-type: none"> ■ Performed 50 cm² 2000 psig (pumped cathode feed) electrolysis tests in a pressure dome ■ Task 3 will use full-scale 160 cm² hardware tested in Task 1 ■ Preparing to down-select optimum cathode compartment height 	20%

Approach/Milestones (Cont.)

Task	Progress Notes	% Complete
Task 4: Optimize Selection of Protective Coating for Pressure Containment Dome Internals	Completed: <ul style="list-style-type: none">■ Corrosion testing of Parylene completed■ Awaiting coated coupon samples from other vendors	20%
Task 5: Design/Build/Test 5,000 psig Pressure Swing Absorber Dryer	Completed: <ul style="list-style-type: none">■ Earlier thermal swing dryer results reviewed■ Selected pressure swing sorbent materials■ Awaiting delivery of sorbents	10%
Task 6: Design PEM Electrolyzer HRA Breadboard System	Completed: <ul style="list-style-type: none">■ Began preliminary system layouts	10%
Tasks 7 - 9	Completed: <ul style="list-style-type: none">■ Not scheduled to start yet	0%

Technical Accomplishments and Progress: Membrane

System requires a high-efficiency membrane - DSM™

- **Superior Mechanical Properties**
 - No x-y dimensional changes upon wet/dry or freeze-thaw cycling
- **Much Stronger Resistance to tear propagation**
 - Superior to PTFE-based supports 10x stronger base properties
- **Improve MEA Mfg**
 - Ease of handling
 - Direct catalyst inking onto membranes
 - Low-cost, chemically-etched support
- **Improve Stack Seals**
 - Potential to bond support structures into bipolar frame to eliminate sealing issues
- **Customized MEAs**
 - Vary ionomer and thickness
 - Provide more support at edge regions and/or at ports
- **Related GES Project**
 - DE-FC36-08GO18065

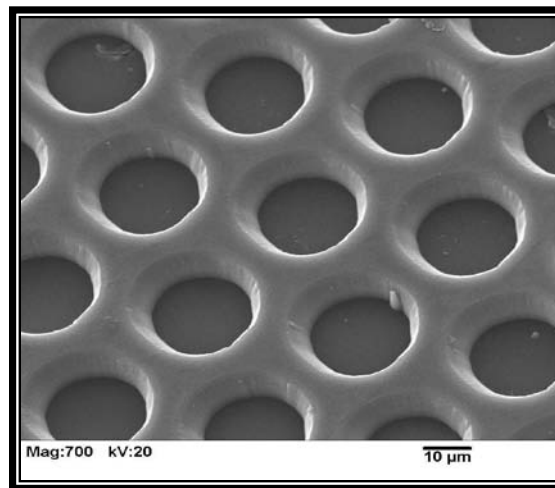
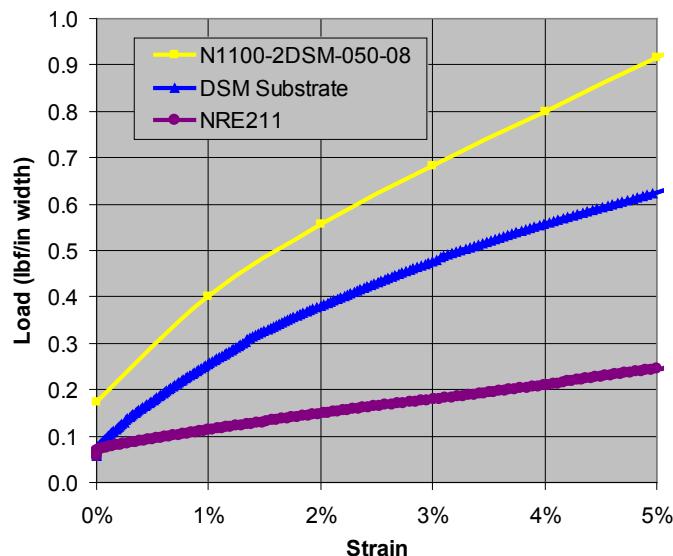


Figure 1. Scanning Electron Microscope (SEM) micrograph of the polymer membrane support structure with definable straight hole pattern

Figure 2. Dynamic Mechanical Analysis (DMA) shows the increased tensile strength of the DSM™ versus its components (wet at 80°C)



Demonstration of DSM™ in Cathode Feed

■ Cathode Feed

- System configuration advantages
- Limits Max. current density

■ Performance of the Advanced DSM™ is superior to that of Nafion® 117 and 115

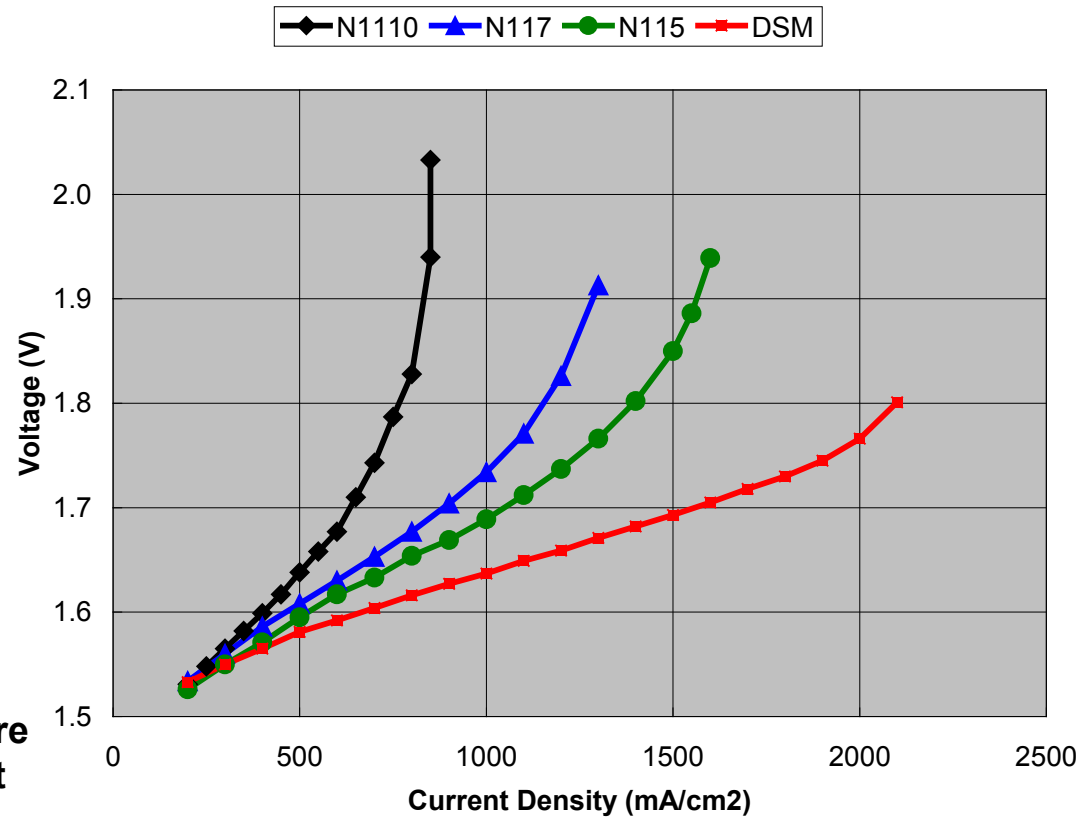
■ Current Density Limits

- N1110 = 600 mA/cm²
- N117 = 900 mA/cm²
- N115 = 1200 mA/cm²
- DSM = 2000 mA/cm²

■ High Pressure Operation

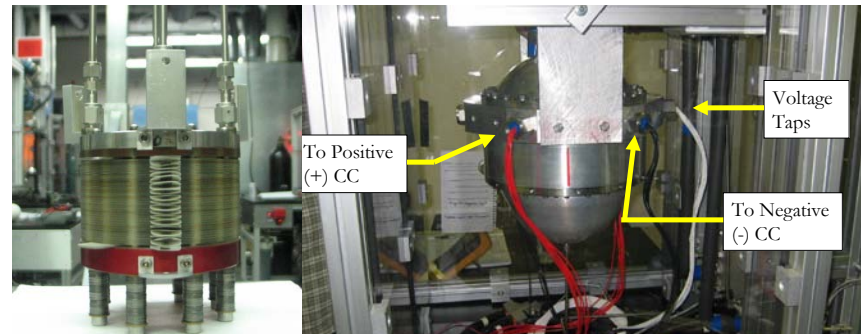
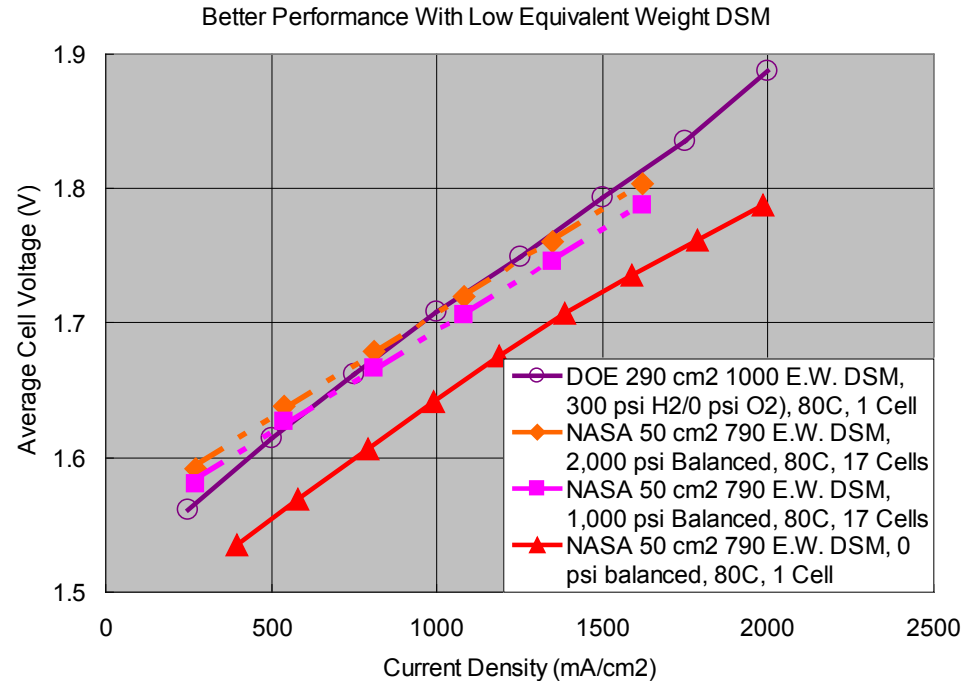
- Similar performance benefits measured at balanced pressure
- Anticipate higher Max. current with differential pressure operation

Membrane Comparison In Cathode Feed, 80oC, Low Pressure Operation



Demonstration of DSM™ in Pressure Dome

- **Successful Pumped Cathode Feed Operation of 50 cm² 17-Cell Stack in 2000 psig Pressure Dome**
- **2 DSM™ Structures Shown**
 - 1 is “Standard” 1100 Equivalent Weight (E.W.) ionomer (for differential pressure operation)
 - 1 is low-resistance 790 E.W. ionomer (for better electrical efficiency with no differential pressure operation)
- **Results in Graph Show Lower Voltage At 1,000 mA/cm² With Low E.W. Ionomer at 1,000 psi Operation Than At Ambient Pressure**
 - Equal performance at 1,000 mA/cm² and 2,000 psig operation
 - Over 500 mV better performance at 1,000 mA/cm² and 0 psig operation



Preliminary Performance: System Pressure Drop

- Top Figure Illustrates High Pressure Drop in Cathode of Conventional Electrolyzer

- 3 Features of HRA Low-Pressure Drop Operation

- Efficient electrolyzer operation, to minimize heat generation
- External cooling of stack, to minimize catholyte heating
- Larger, low pressure-drop cathode compartment design, compared to anode compartment

- Results in Lower Figure Show Predicted Lower Pressure Drop

- Natural convection supplies circulating water
- Low resultant pressure drop

Figure 1. Pressure Drop In Conventional (Pumped) Cathode-Fed Electrolyzer

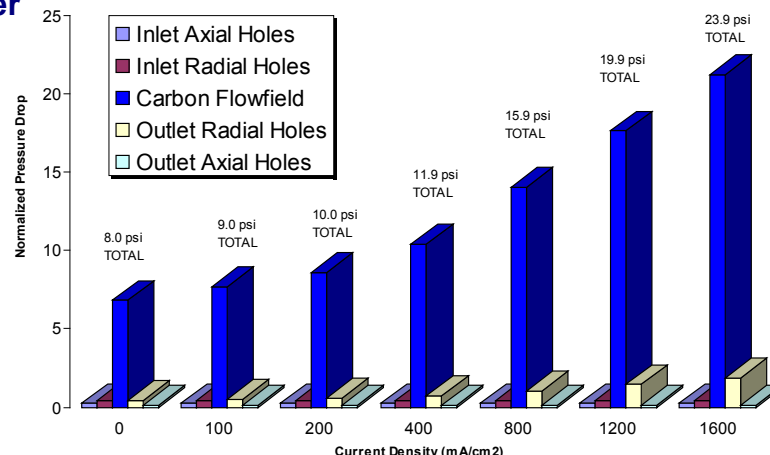
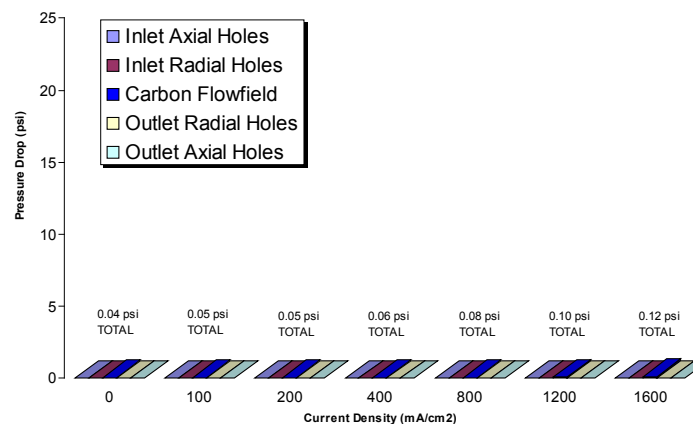
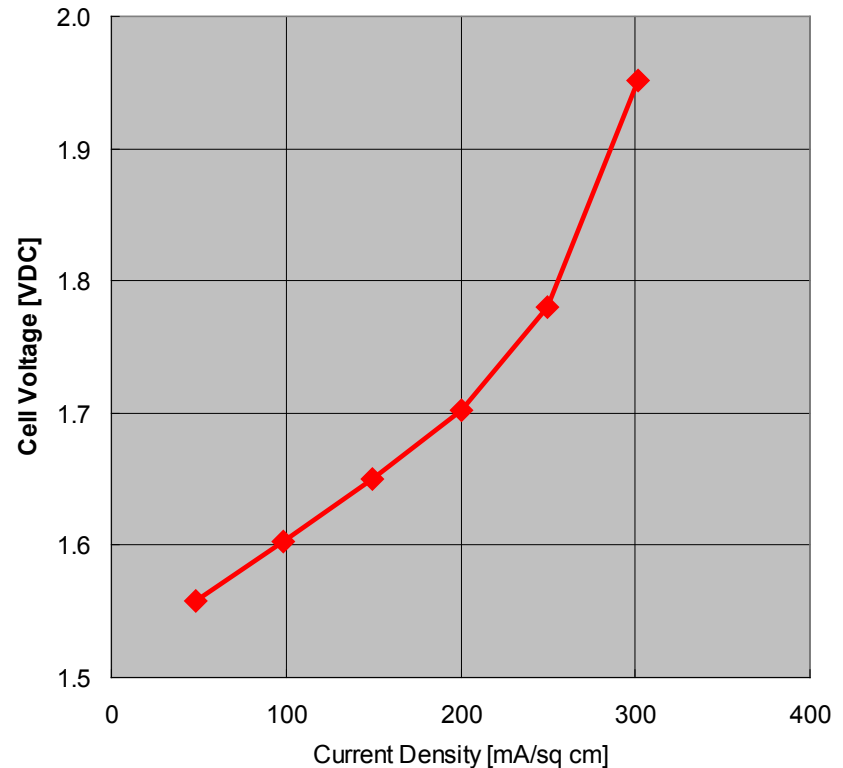


Figure 2. Predicted Pressure Drop In Natural Convection Cathode-Fed Electrolyzer



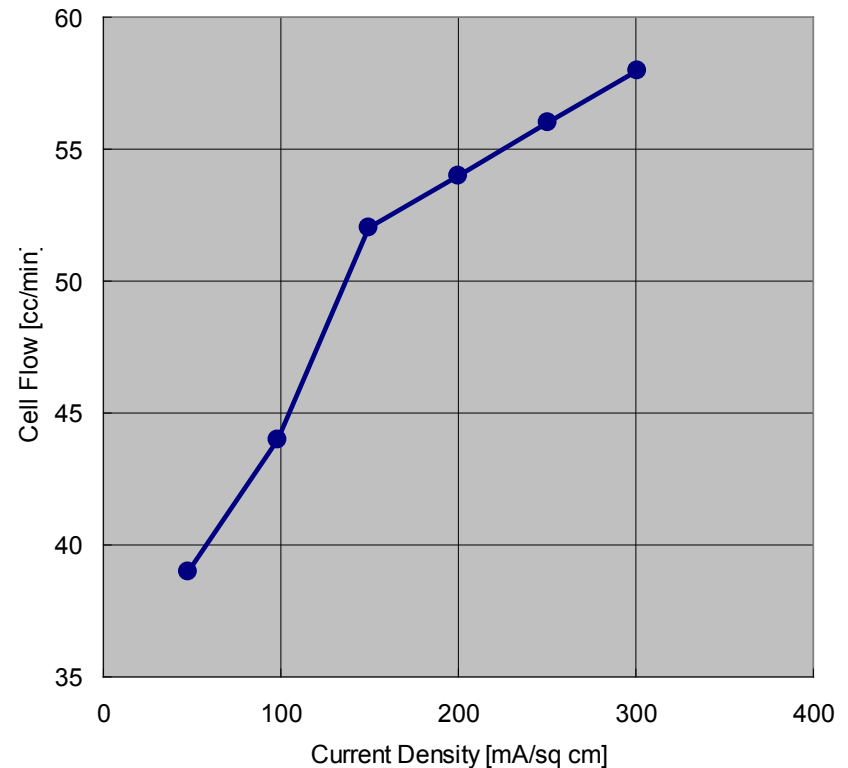
Thermosiphon HRA Single-Cell Tests

- Single-Cell Testing at 160 cm² Underway
 - GES-Treated Nafion® 115 Membrane, Standard Catalyst, Room Temperature Operation
- Maximum Current Density \approx 300 mA/cm²
 - Investigating Low Maximum Current Density
- Cathode Compartment Height Being Varied
 - 90 mil thick
 - 120 mil thick
- Increased Height Will
 - Decrease Pressure Drop
 - Permit Operation at Higher Current Densities



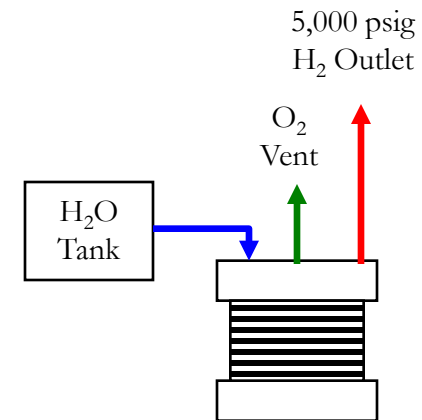
Thermosiphon HRA Single-Cell Tests

- Single-Cell Testing at 160 cm² Underway
 - No Circulation Pump – Thermosiphon Only
 - 90 mil Cathode Height
- Water Circulation Measured by Capturing Cathode Effluent Water (“Bucket Test”)
- Relative Water Circulation Rate Decreases above 150 mA/cm²
- Could Explain Low Limit to Current Density
- Increased Height Will
 - Decrease Pressure Drop
 - Permit Operation at Higher Current Densities



Static-Feed WaMM Membrane Development for HRA

- NASA is Funding GES to Develop a Water Management Membrane (WaMM) Technology
 - WaMM originally for unitized regenerative fuel cell
- Advantages
 - No electrolyzer circulation pump – static water feed
 - Dry H₂ outlet – no separator required
 - Can use lower-quality water
- This Program Will Further Its Development As Risk Mitigation for Thermosiphon-Fed Electrolyzer
- Currently Fabricating 50 cm² Hardware to Test at 2,000 psig in Pressure Dome
- Testing Later in 2011



Static Water Feed Electrolyzer

Progress: Preliminary System Design

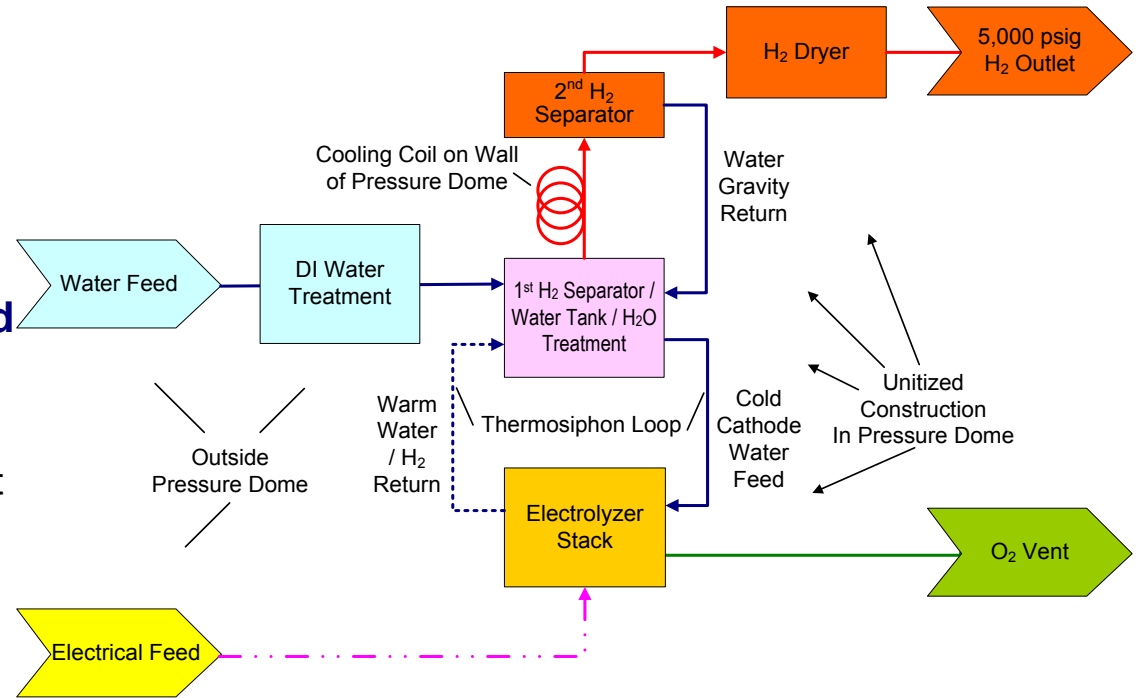
□ Preliminary P&ID, PFD Completed

- Equipment and Flow Paths Determined
- Instrumentation Selected
- Flow Rates and Conditions Calculated

□ System Layout Started

□ Component Studies Planned

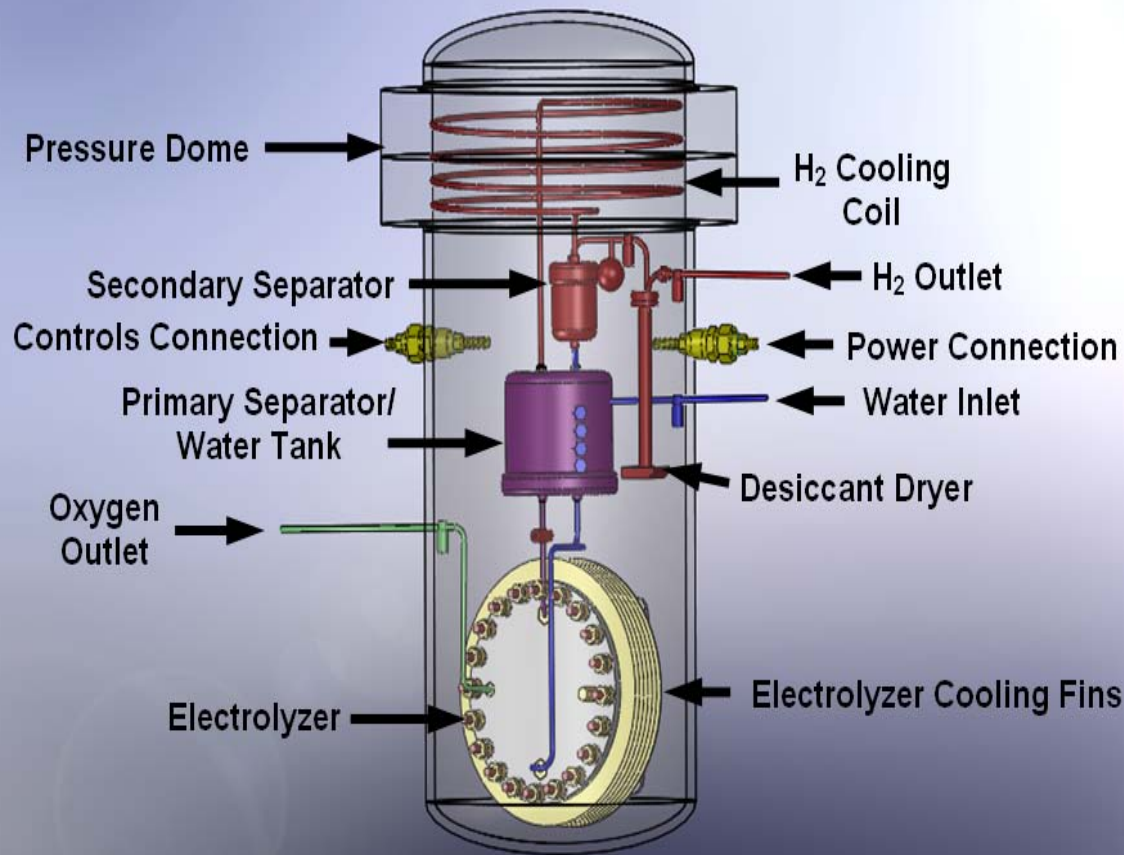
- Electrolyzer Stack
- Passive Stack Cooling
- Prelim. Pressure Containment Dome
- Passive Hydrogen Cooling
- Regenerative Dryer
- Cathode Circulation Thermosiphon (Natural Circulation)



Cathode Feed Process Flow Diagram

Progress: Phase I System Design

(Unitized Packaging Layout)



- Operates in Thermosiphon Cathode Feed Mode
- Low-Pressure Stack Hardware
 - Thin end plates
 - Machine bolts not specialty metal parts
 - Thermoplastic frames
- Utilize Pressure Inside Pressure Containment Dome
 - Minimizes stack compression needs
 - Benefits contact resistance
 - Allows use of unreinforced plastic frames
 - Enhances safety
 - Use unreinforced, low-cost components and piping

Progress: Inert Coating for Pressure Dome Internal Components

- To Provide Protective Coatings Over Low-Cost HRA Components (i.e. Carbon Steel Pressure Dome)
- Parylene Coated Samples from Speedline
 - Poly-para-Xylylene coating film formed by the chemical vapor deposition (CVD) process
 - Claimed to be pinhole-free
- Corrosion Test
 - Place SS coupon with 1 mil thick Parylene coating in 3 N H₂SO₄ and polarize sample to +1.3 V anodic vs. DHE
- Corrosion Test Results Showed Corrosion and Activity after 380 hours of exposure

Additional Inert Coating Work

- Thin Parylene Coating (1 mil) Not Adequate
- Thicker (25 – 40 mil) Coatings Used for Ultra-Pure Chemical Industry (i.e. Semiconductor)
 - PFA and E-CTFE offer low permeabilities
 - Flame spraying PEEK does not require an oven to cure coatings
- Thicker Coatings being Procured

Progress: Hydrogen Dryer

- **Earlier Giner Dryers Used Type 4A Molecular Sieves as Sorbent**
 - Require excessive (>400°F) regeneration temperatures
 - Results in long cycle times and excessive hydrogen purge loss during regeneration
- **Alternate Sorbents Being Down-Selected**
 - Lower regeneration temperatures/shorter cycle times
 - Type 3A Molecular Sieves, aluminosilicates
- **Currently Preparing For Pressure-Swing Adsorption (PSA) Tests**
 - Heat-free regeneration
 - Aluminosilicates are primary candidate sorbents (on order)
 - Hardware being procured/assembled
- **Lab Tests Will Use Helium as a Surrogate Gas**
 - Testing will cover 290 – 5000 psig gas pressure (full range of allowed vehicle tank pressure)
 - Brassboard prototype will dry product hydrogen

Progress: Residential H₂ Refueling Appliance Applicable Codes & Standards

- Prof. Zalosh – H₂ safety expert
- Reviewed National & International Codes & Standards
- Giner Invited to Contribute Comments to ISO/DIS 22734-2 Draft
- One Significant Concern
 - NFPA 52-2100, Chapter 9 (no indoor refueling)
 - International fire code – no impediment to indoor refueling
 - NFPA will be approached to resolve discrepancy

Design Progress: Codes Pertinent to Residential Hydrogen Refueling Systems

Component Examples



IEC 60335 Parts 1, 2, 3, 5
Household and Similar Electrical Appliances
IEC 60079-10-1: Explosive Atmospheres, Classification of Areas



ISO 4126-1, -2: Safety Devices for Protection Against Excessive Pressure: Valves & Rupture Disks



CSA America HGV 4.7-2009: Automatic Valves for Use In Gaseous Hydrogen Fueling Stations



SAE J2600: Compressed Hydrogen Fueling Receptacles

Electrolyzer System



ISO/DIS 22734-2: Hydrogen Generators Using Water Electrolysis Process; Part 2: Residential Systems



Eventual UL and CSA Versions of **ISO/DIS 22734-2**

Residential Installation



NFPA 52-2010, Chapter 9: GH₂ Compression, Gas Processing, Storage, and Dispensing Systems



International Fire Code Section 2209: Hydrogen Motor Fuel Dispensing and Generation Facilities

Vehicle Refueling



CSA America HGV 4.1-2009: Hydrogen Dispensing Systems



International Fire Code Section 2209: Hydrogen Motor Fuel Dispensing and Generation Facilities



SAE TIR J2601
Compressed Hydrogen Fueling Protocol

Additional Codes/Standards

■ Residential Installation and Vehicle Refueling

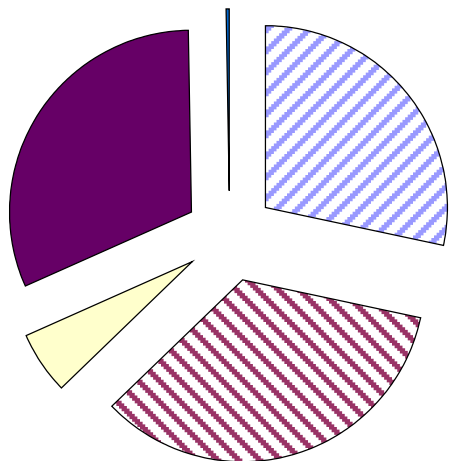
- NFPA 55, Standard for Storage, Use and Handling of Compressed Gases and Cryogenic Fluids in Portable and Stationary Containers, Cylinders and Tanks
- International Fire Code Section 3005, Use and Handling of Compressed Gases
- International Fire Code Section 3503, General Requirements, Flammable Gases
- CGA G-5.4, Standard for Hydrogen Piping Systems at Consumer Locations (Compressed Gas Association)
- CGA G-5.5, Hydrogen Vent Systems (Compressed Gas Association)
- SAE J2600, Compressed Hydrogen Surface Vehicle Refueling Connection Devices
- ISO 17268:2006, Gaseous Hydrogen Land Vehicle Refueling Connection Devices

■ Additional Codes Need Consideration

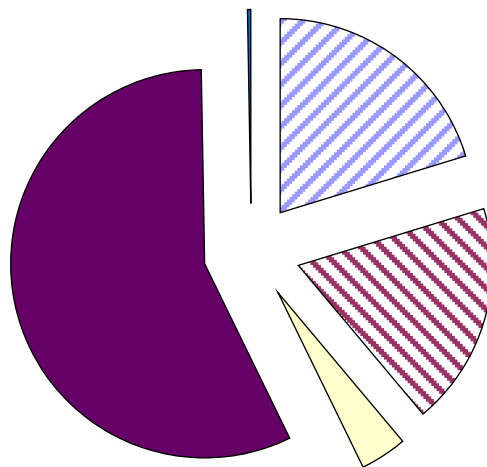
- Proposed ASTM Analysis Methods for Hydrogen Purity, etc.

Design Progress: Projected H₂ Cost

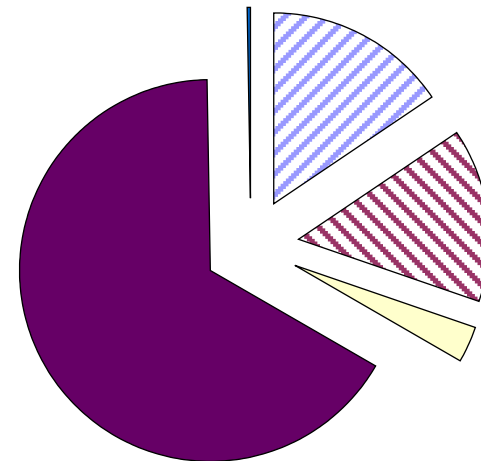
H2A Model Analysis (Forecourt Model rev 2.1.1)



1,000 Units



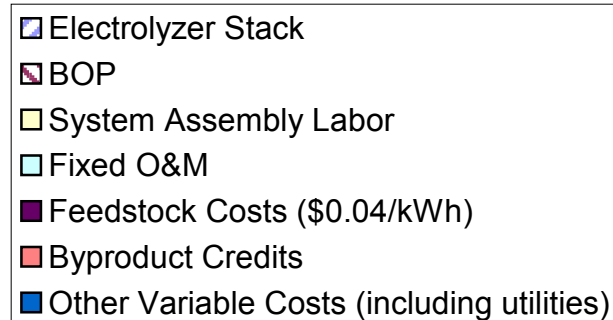
100,000 Units



1,000,000 Units

- Design capacity: 1 kg H₂/day
- Operating Capacity Factor: 64%
- Single stack/unit

- H₂ generated at 5000 psig – no H₂ compressor needed
- Renewable electricity at \$0.039/kWhr (nights & weekends)
- \$2.99/kg-H₂ at volume of 1 Million/yr



Collaborations

- Professor Robert Zalosh
 - Vendor
 - University
 - Review of applicable codes and standards
 - Assist with HAZOP/FMEA safety analysis
- IAS, Inc.
 - Vendor
 - For-profit company
 - Will develop low-cost controller prototypes
 - Will assist with control system development and projecting production costs
- GES, LLC (DOE Cost-Shared Grant DE-FC36-08GO18065)
 - Same Company
 - For-profit company
 - Within DOE H₂ program
 - Multiple overlapping components and subsystems [also Parker, 3-M (NSTF Catalyst & Membrane) and Entegris (Carbon Cell Separators)]
- GES, LLC (Government and Private Electrolyzer Development Programs)
 - Same Company
 - For-profit company
 - Outside DOE H₂ program
 - Several NASA programs, one DARPA Prime Contractor, electrolyzers for several private companies

Proposed Future Work (This Year and Next)

- Detailed HAZOP/FMEA Analysis of Hydrogen Refueling Appliance
- Test Full-Scale Home Refueling Appliance (HRA) Electrolyzer Stack
- Optimize Selection of Protective Coating for Pressure Containment Dome Internals
- Build/Test 5,000 psig Pressure Swing Absorber Dryer
- Complete Design, Fabrication & Demonstration of Unitized HRA System
- Preliminary Design and Economic Analysis of Commercial HRA System
- Identify & Team With Commercialization Partner(s)

Summary

- **Innovative System Design**
 - No compressors, pumps, or fans required; only one pressure vessel
 - Reduces costs (capital, operating & maintenance)
 - Improves reliability, safety, efficiency
- **Innovative High-Strength Low-Permeability Supported Membrane Required**
 - Advanced DSM™
 - High efficiency
- **Testing Progress**
 - Thermosiphon feed electrolyzer testing underway (testing at full-scale 160 cm² unit size)
 - 2,000 psig pumped cathode feed electrolyzer tests in pressure containment dome complete
 - Hardware being fabricated for WaMM static feed electrolyzer tests at 2,000 psig in pressure dome (risk mitigation and cost comparison)
 - Protective coating coupon tests ongoing
 - Pressure swing dryer components/sorbent being procured
- **Codes & Regulations & HAZOP/FMEA Analysis Ongoing**
- **“Unitized” Breadboard HRA System Design Begun**
- **Hydrogen Costs Meet DOE Target of \$2 - \$4/kg**
 - Will require significant sales volumes