Development of Advanced Chemical Hydrogen Storage and Generation System

DOE Chemical Hydrogen Storage Center of Excellence

Millennium Cell Inc.

May 23-25, 2005

Contract ID #: DE-FC36-05GO15056
Project ID #: STP10

Timeline and Budget

Overview

Timeline

- Project start date: Fiscal Year 2005
- Project end date: Fiscal Year 2009
- Percent complete: New Start

Budget

- 5 Year (Requested) Funding:
  - DOE share: $2.4 million
  - MCEL share: $0.6 million
- Funding for FY05:
  - DOE share: $200,000
  - MCEL share: $50,000

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Barriers Addressed with Specific Partners

Overview

Tier I:

- Advancement of capacity and utility (systems development)
    - (PNNL, Rohm and Haas, Millennium Cell)
  - Engineering process and analysis
  - B. Weight and Volume
  - C. Efficiency
  - T. Heat Removal
  - Safety
- New regeneration processes taking borate to borohydride
  - Data mining on BH formation
    - (US Borax, Rohm and Haas, PNNL, LANL, Millennium Cell)
  - Engineering assessment of electrochemical reduction
    - (Rohm and Haas, Penn State, Millennium Cell)
  - Improve cost and minimize safety issues
    - (Millennium Cell)
  - R. Regeneration Processes
    - lower cost
    - energy efficiency
    - safety

Timeline of Project Tasks

Overview – Future Work

Tasks	Year 1	Year 2	Year 3	Year 4	Year 5
Task 1.0 Data mining on synthesis of B-H complexes and assessment of past IP on electrochemical methods					
Task 2.0 Provide technical evaluation for process engineering of borate reduction					
Task 3.0 System analysis and reactor module development					
Task 4.1 Preliminary design of Gen-1 prototype (P1)					
Task 4.2 Construct and conduct testing of Gen-1 prototype (P1)					
Go/No-go Decision Determine if prototype meets DOE system requirements					
Task 5.1 Design and construct scaled-up final prototype (P2)					
Task 5.2 Optimization and testing of scaled-up final prototype (P2)					
Task 6.0 Project Management					

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Improve Storage Capacity to 1.2 kWh/L (36 g H2/L) and 1.5 kWh/kg (45 g H2/kg)

Objectives

- Develop improved capability to store and generate hydrogen from concentrated sodium borohydride by focusing on reactor and system development

- Develop critical reactor technology leading to a hydrogen fuel system that will meet the system-based storage capacity of 1.2 kWh/L (36 g H_2/L) and 1.5 kWh/kg (45 g H_2/kg) .

- Utilize engineering expertise to guide Center research based on system design criteria.

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System Engineering Improvement
Approach

- Improve system storage efficiency by reducing balance of plant (BOP)
  - Improve catalyst activity
  - Understanding reactor dynamics
  - Conduct CFD modeling of reactor
  - Reduce liquid hold-up in the reactor
  - Improve overall heat integration and water management

- Improve yield of electrochemical synthesis of sodium borohydride.
  - Understanding reaction kinetics and rate limiting step(s)
  - Improve cell design to facilitate reaction rates
  - Improve reaction yield by rational selection of solvent systems.

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Milestones and Resulting Deliverables

Future Work

- **EOY 1**: Completion of System Analysis and report out computer modeling results
  - Report on thermo-processes for the synthesis of B-H from B-O
  - Report on electrochemical processes for the synthesis of B-H from B-O
  - Report on interim assessment of Tier 2 and Tier 3 results
- **EOY 2**: Completion of integrated reactor system design
  - Conceptual design package of laboratory prototype P1 with > 40 g H_2/kg and > 30 g H_2/L capacity
- **EOY 3**: Successfully built and tested laboratory prototype (P1)
  - Testing results from prototype P1 meeting the targets of > 40 g H_2/kg and > 30 g H_2/L system capacity (go/no-go)
- **EOY 4**: Design freeze of scaled-up final prototype (P2)
  - Design package of scaled up prototype P2, target capacity: > 45 g H_2/kg and > 36 g H_2/L capacity
- **EOY 5**: Successfully demonstrated the target hydrogen storage capacity in the optimized prototype (P2)
  - Testing results from prototype P2

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Engineering System Analysis

Future Work

- Model catalytic reactor using computational fluid dynamics to provide insight into improving efficiency/reducing reactor size.
- Investigate means of improving gas/liquid separation in HOD™ system.
- Determine optimum conditions for heat and water management

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Design and Testing of Prototype

Future Work

- Design laboratory-scale solid $NaBH_4$ or BH_3-amine Mix On Demand® system
- Construct and commission test system
- Utilize test bench to perform tests in order to :
  - Minimize fuel dissolution time
  - Ensure consistency of fuel concentration
  - Optimize catalytic reactor efficiency
  - Test gas/liquid separator efficiency
  - Identify diagnostic methods for identifying system failure
  - Test system safety shutdowns

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Prototype Scale-Up

Future Work

- Address issues associated with scaling up laboratory prototype to automotive system including:
    - Packaging of components
    - Exposure to extreme temperatures
    - Exposure to vibration
    - Determine method of re-fueling system

- Design and build automotive scale prototype system
    - Validation testing of scaled up system to include:
        - System efficiency vs. load profile
        - Ability to handle transients

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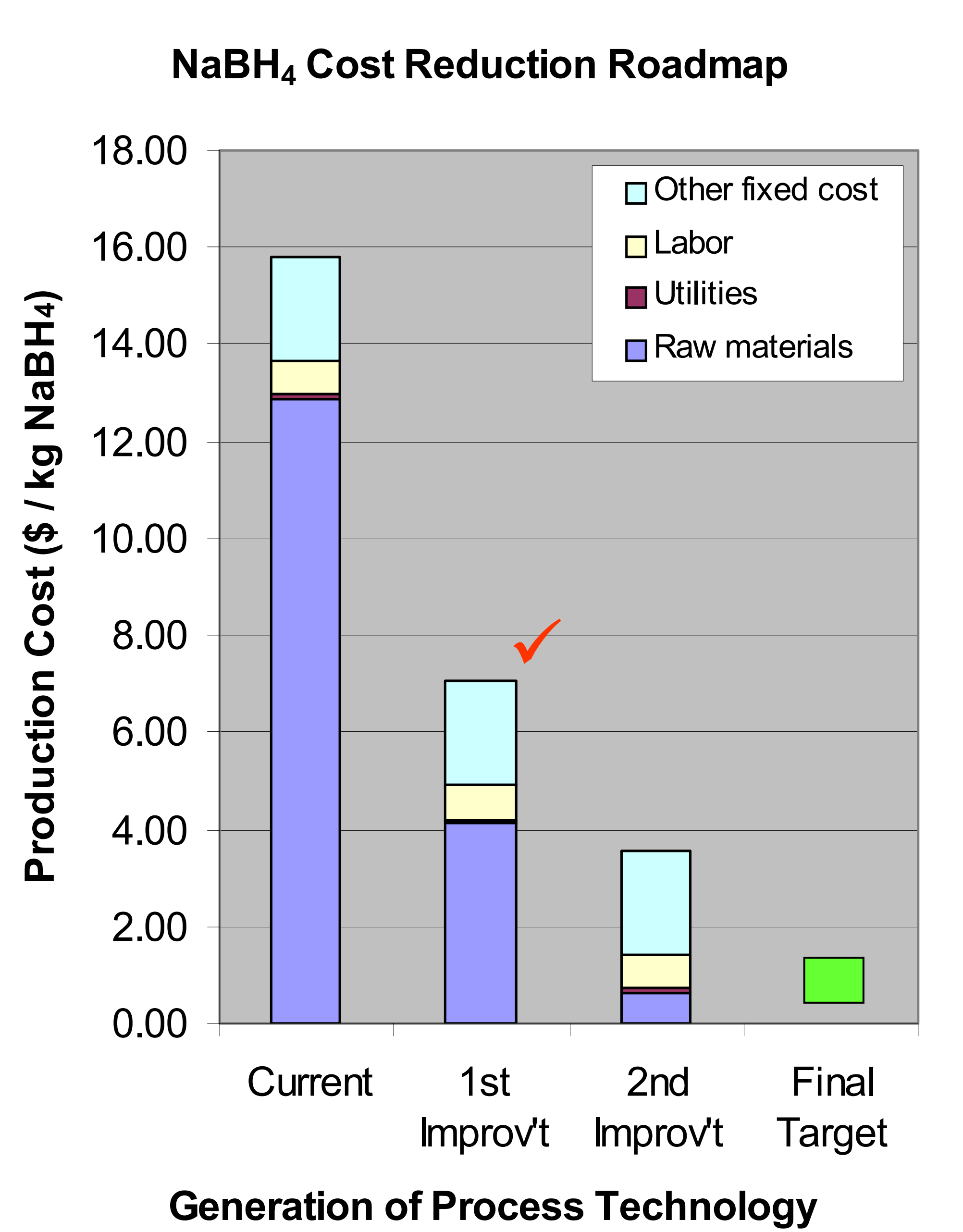
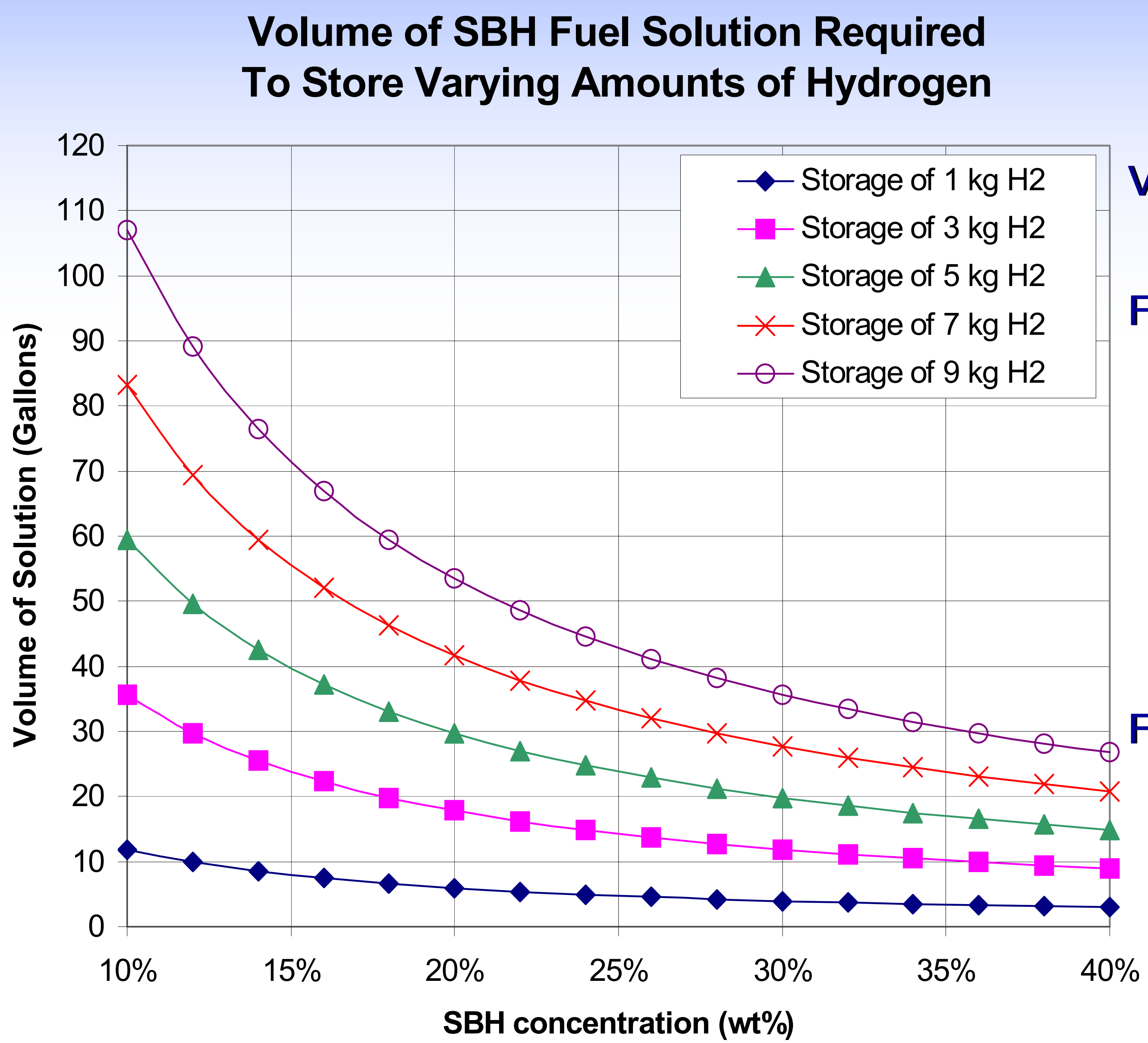
Materials Cost Reduction – 1st Improvement Accomplished In Previous MCEL Work



- **1st Improvement:**
  - High efficiency Na production to reduce raw material cost
  - Feasibility demonstrated by MCEL/APCI, confirmed by RH
- **2nd Improvement:**
  - Combined production of Na metal and H_3BO_3 to further reduce raw material cost
  - Laboratory feasibility shown
- **Final Target:**
  - Direct conversion of B-O to B-H
  - One-pot BH_4 synthesis achieved
  - Larger scale production to gain scale advantage and reduce fixed cost

Volumetric Storage Capacity of Materials Under Study can meet Targets



Volumetric storage efficiency of 30 wt% fuel = ~63 g H_2/L

For comparison:

Liquid H_2 = ~71 g H_2/L

5000 psi compressed = ~23 g H_2/L

10000 psi compressed = ~39 g H_2/L

For a practical system, Balance of Plant (both volumetrically and gravimetrically) is key

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Scope of Work under the Center Will Focus on System Development

- Overall Goal:
  - Continue to explore synthetic chemistry of B-O to B-H
  - Demonstrate improved system storage efficiency toward DOE targets
- How do we propose to do it?
  - **Increase** Activity of catalyst and throughput of reactor (decrease processor volume/weight)
  - **Decrease** Ballast and BOP volume/weight
  - **Decrease** System volume/weight
  - **Increase** Volumetric and gravimetric storage efficiency
- Roadmap for improvements.
  - System Modeling → 5 kW system → 50 kW system
  - Final target: **Prototype 2 (P2): > 45 g H_2/kg and > 36 g H_2/L**

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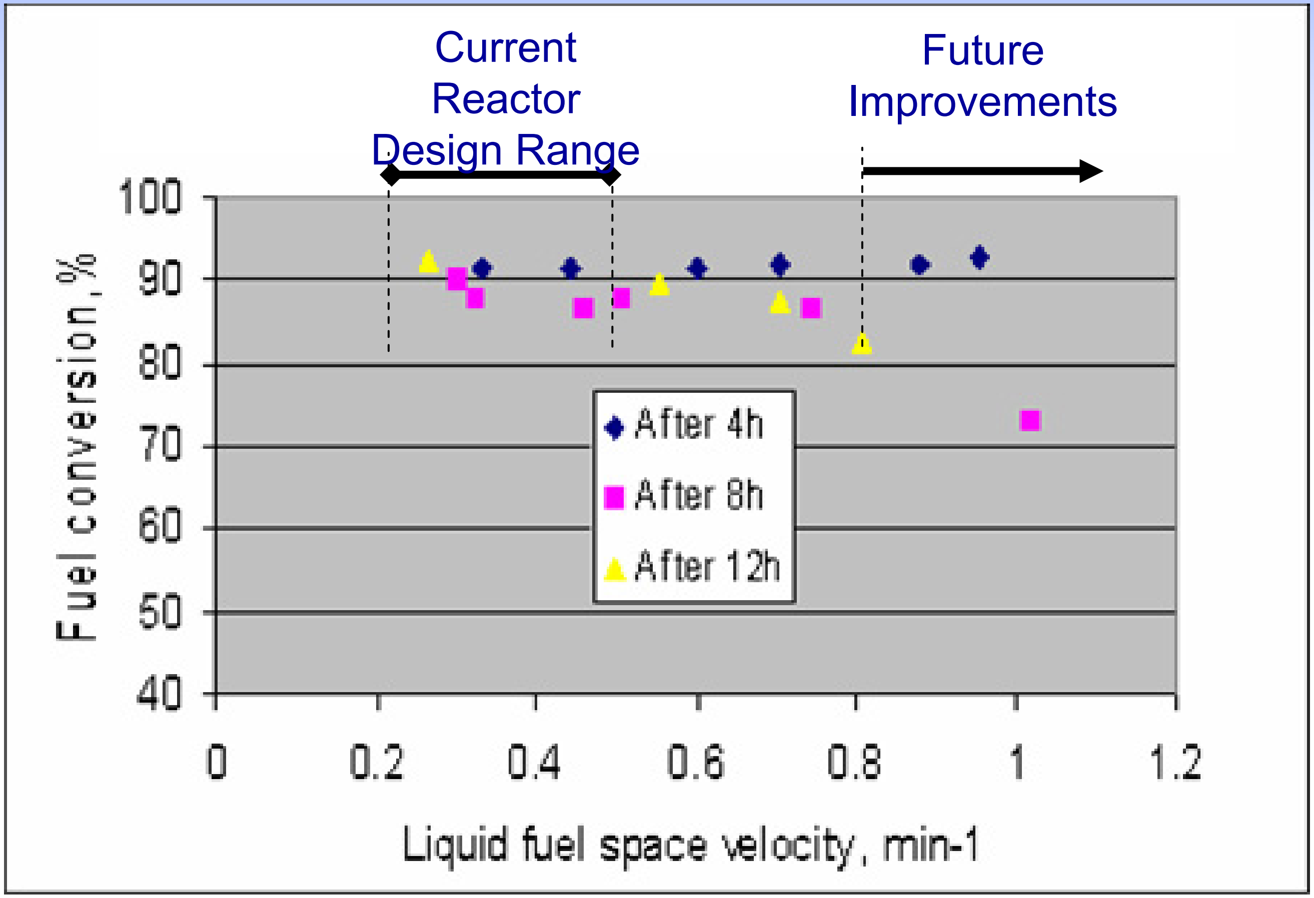
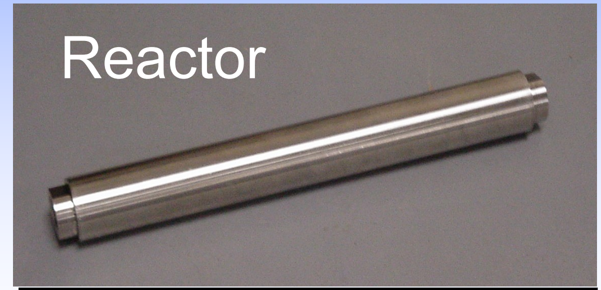
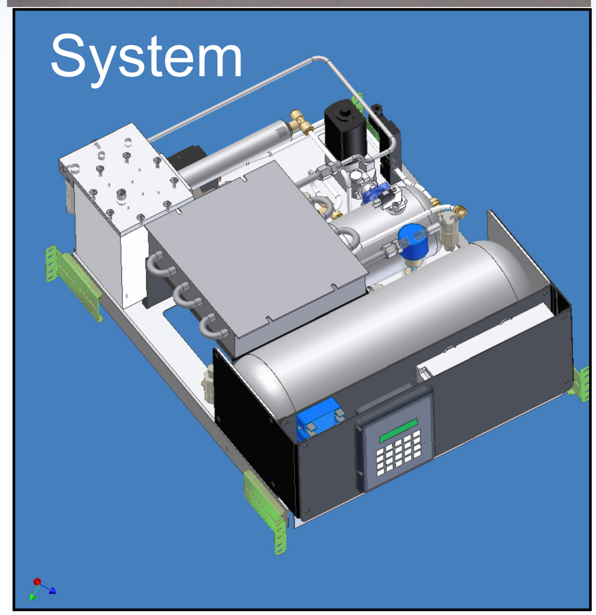
Improved Catalyst Technology and Reactor Engineering have Resulted in Increases in Fuel Velocity and Reactor Durability







- Improved Reactor Engineering has already resulted in
  - 3x throughput increase
  - 2x durability increase

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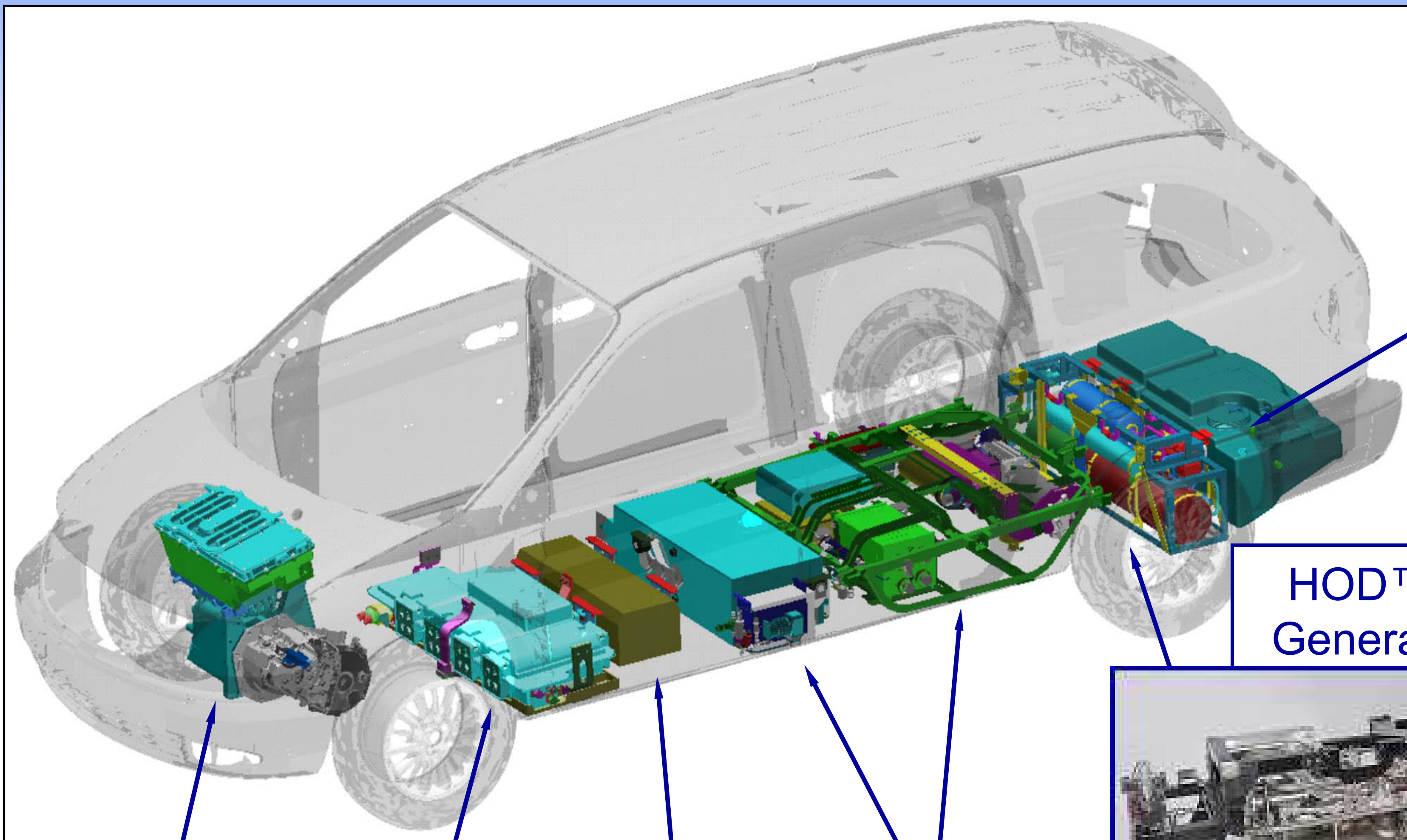
MCEL's HOD™ Systems have been Demonstrated at Multiple Power Levels

- Primary propulsion (~50 kW)
  - "Chrysler Natrium" minivan
- Electric vehicle range extension (~5 kW)
  - Duffy Electric Boat
  - Peugeot "H_2O" Vehicle
- Battery chargers, standby power (1.5 kW)
  - Telecom-Rack Mount System (RM-1500)
- Battery replacement, Portable Power (<100 W)
  - Protonex/MCEL P1 30W Military Portable Power Source
  - M2 Fuel Cell Powered Notebook PC

HOD™ System has Already been Demonstrated in an Automobile Application - *Chrysler Town & Country Natrium®*



HOD™ Hydrogen Generation System

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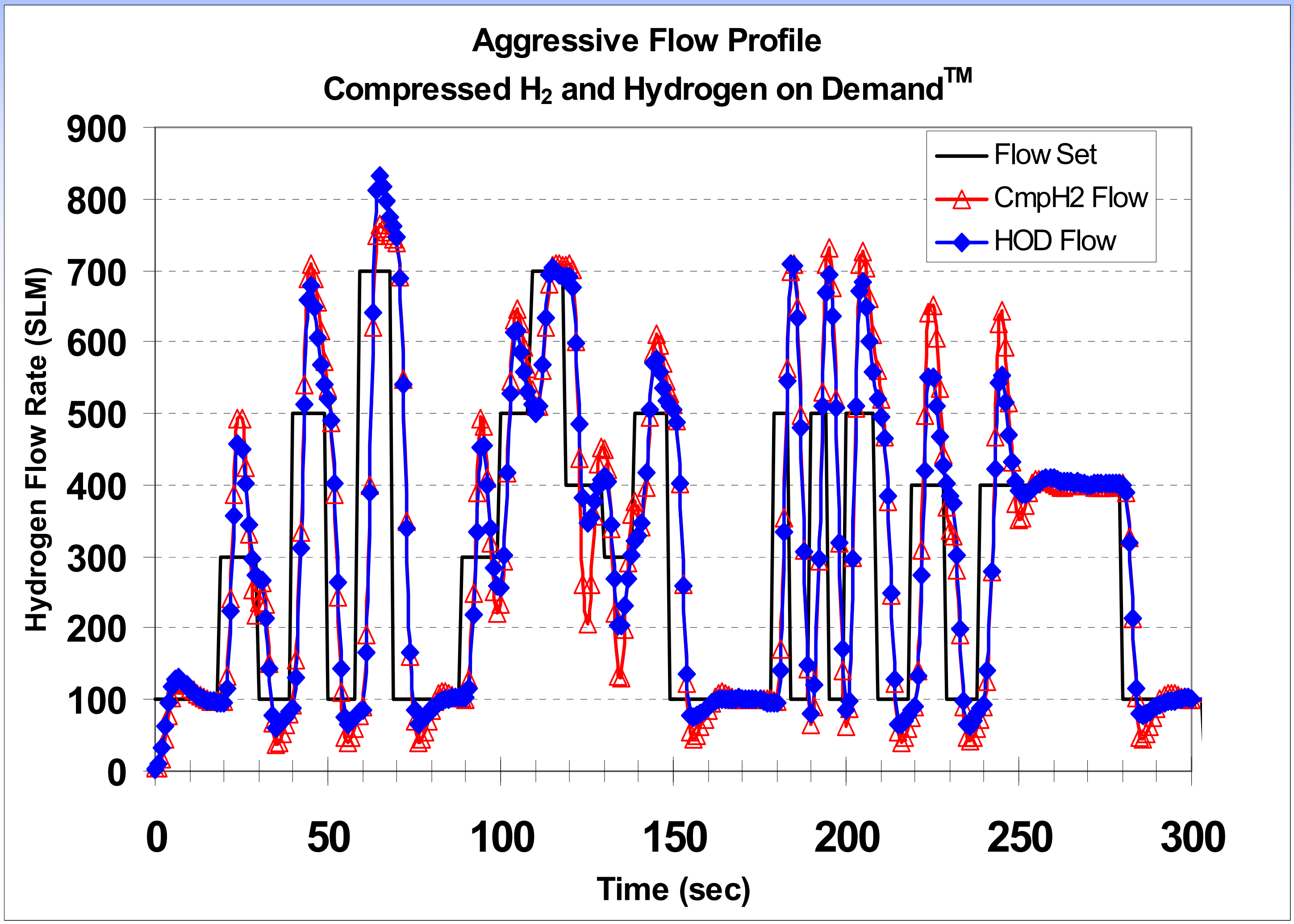
Proven Methods and Instrumentation for High Power Testing: Fuel Cell Emulator



- Data taken on MCEL H_2 Internal Combustion Engine Taxi
- Flow profile through fuel cell emulator
- Compressed H_2 baseline and Hydrogen on Demand™ running shown
- Ability to "load follow", even with aggressive transients

Taken from: Mohring, *et al*, SAE World Congress 2002, Paper No. 2002-01-0098.

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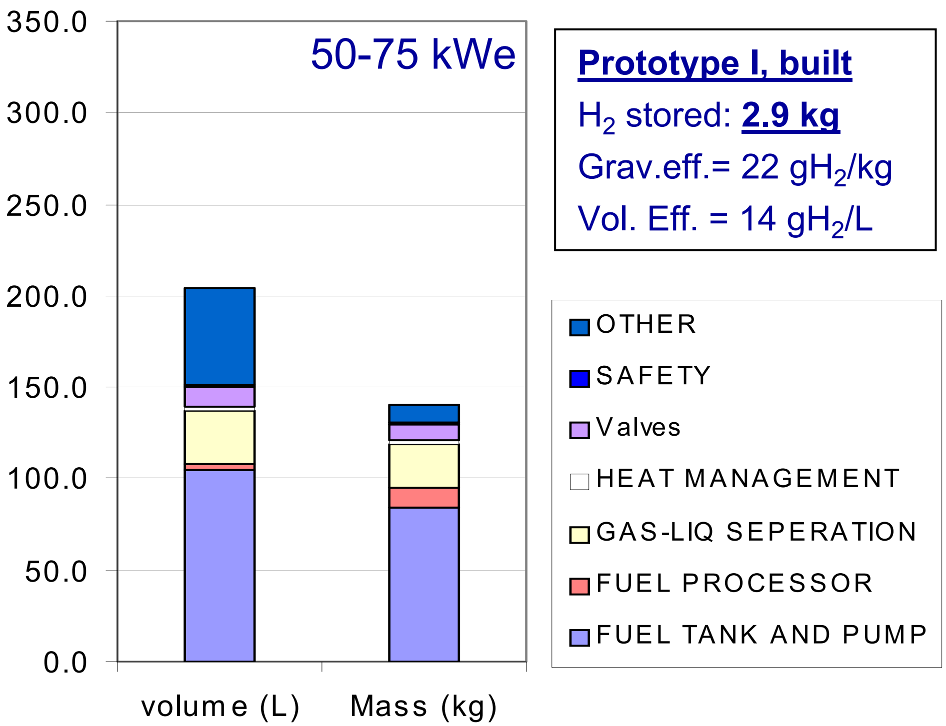
System Development will Result in Higher Hydrogen Storage Density

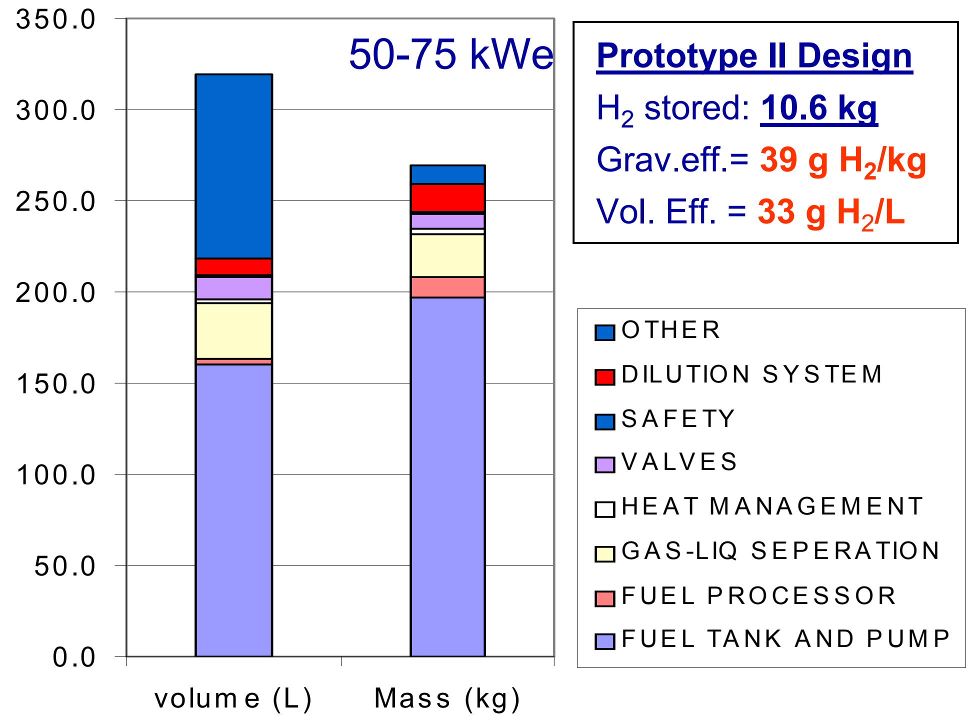
- "Material-only" hydrogen density: 10.6 wt%
- Stoichiometric hydrogen density in hydrolysis:
  - $NaBH_4 + 2\ H_2O \rightarrow NaBO_2 + 4H_2$ 10.8%
  - $NaBH_4 + 4\ H_2O \rightarrow NaBO_2\ 2H_2O + 4\ H_2$ 7.3%

Control of reaction conditions to achieve high storage density

- System storage efficiency of Hydrogen on Demand®, example prototypes



Prototype I, built
H_2 stored: **2.9 kg**
Grav.eff.= 22 gH_2/kg
Vol. Eff. = 14 gH_2/L



Prototype II Design
H_2 stored: **10.6 kg**
Grav.eff.= **39 g H_2/kg**
Vol. Eff. = **33 g H_2/L**

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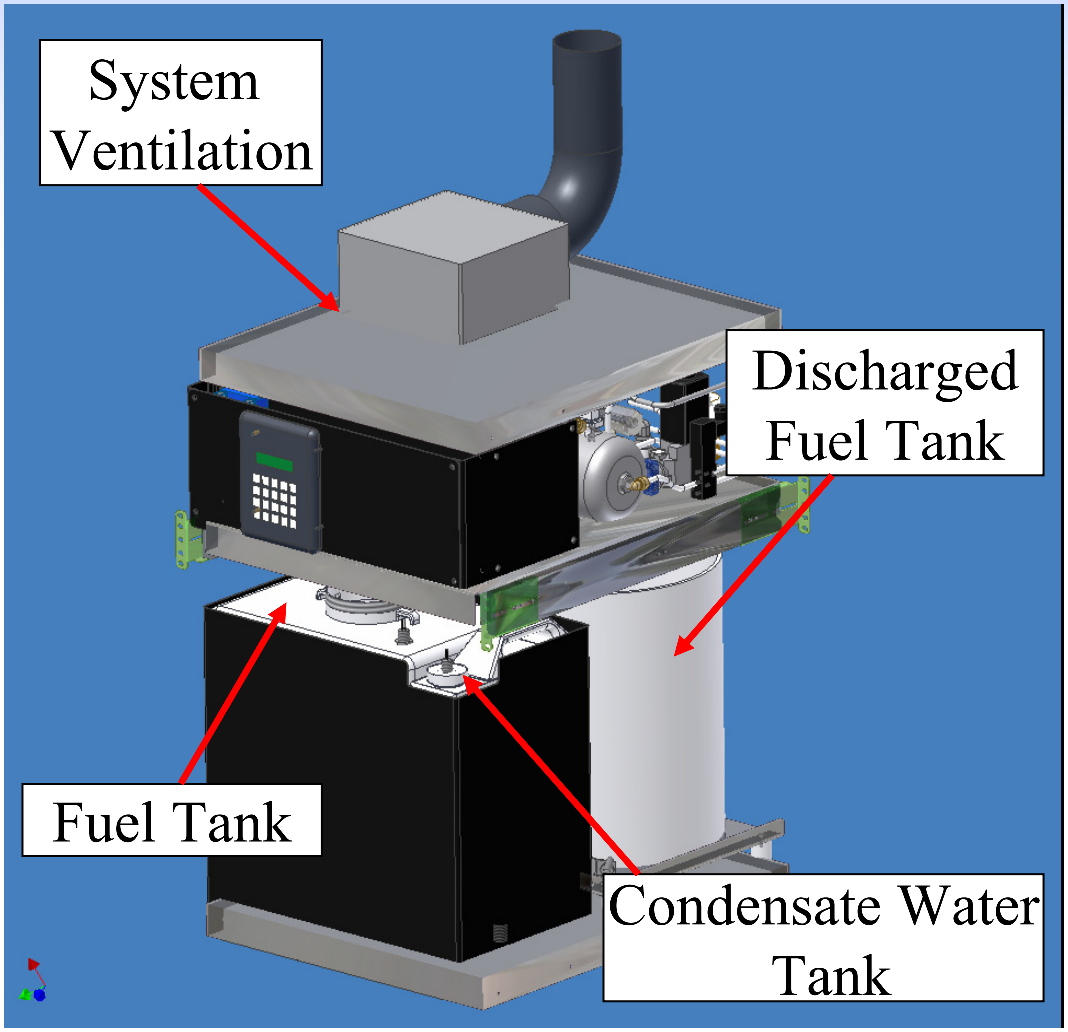
1.5 kW RM-1500 HOD™ System has been Demonstrated for Standby Power Application



- 10,000 SL of Stored Hydrogen
- BOP dimensions: 17" wide x 6.5" high x 21" deep (1.34 SCF)
- Fuel Drawer: 17" wide x 7.5" high x 21" deep (1.55 SCF)
- Dry Weight: 50 lbs.

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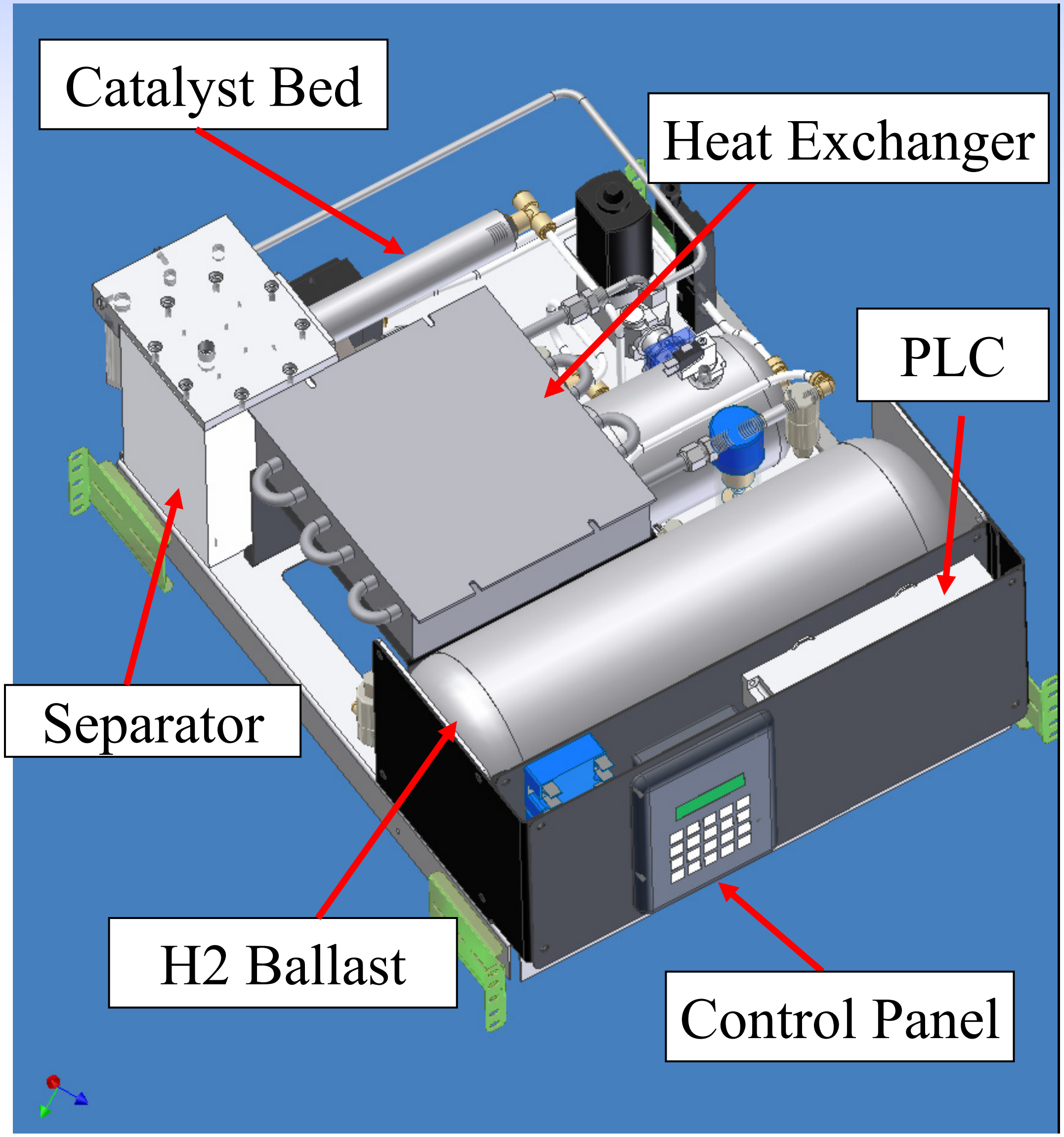
System Development Has Resulted in a Much Improved BOP for the 1.5 kW System



- Hydrogen Output: 0-20 slpm, 99.99% Purity
- Delivery Pressure: 20-30 psig
- Hydrogen Temp < 10 deg. Celsius above ambient temperature
- Load Following Hydrogen Supply
- Modular PLC controls generator
- Startup Time < 60 seconds

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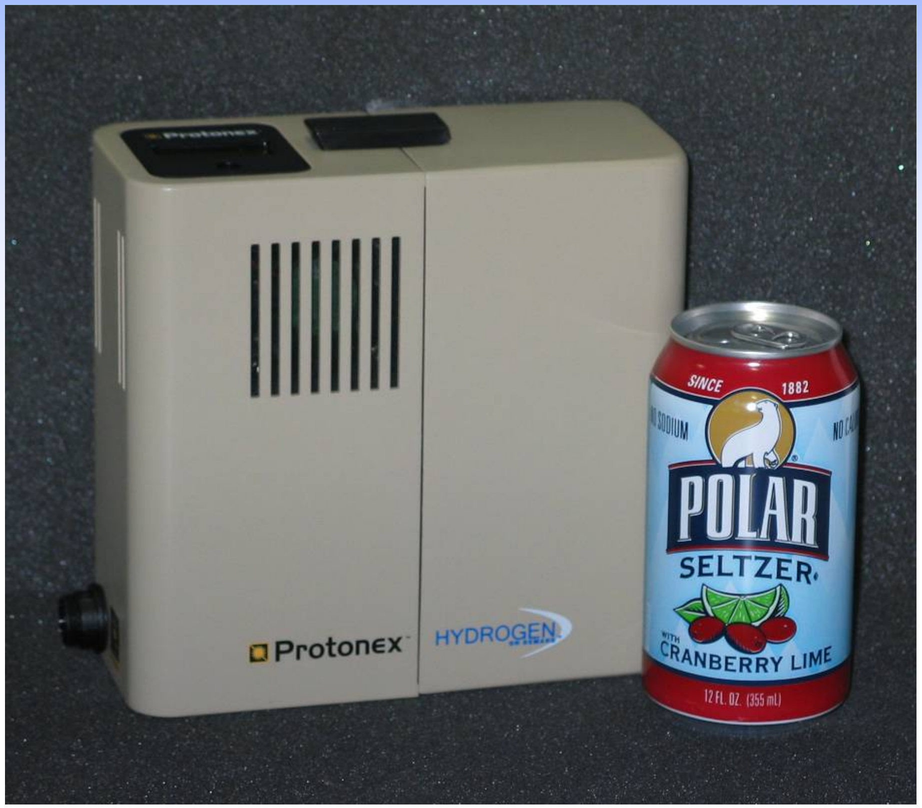
Demonstrated Protonex/MCEL P1 30 W Military Portable Power Source



Demonstrated Jan 2005:
~700 Wh (H_2 LHV)/L and > 600 Wh (H_2 LHV)/kg for a complete power system

- 30 W Net Power, >15 Hour Runtime per cartridge
- 930 Wh (H_2 LHV) net single cartridge only ➔ 1.2 L, 1.25 kg

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Summary of Milestones and Deliverables

Year	Main Tasks	Milestones	Deliverables
1	• Data mining on the synthesis of BH • Provide technical evaluation for Tier 2 and 3 results with system criteria. • Assessment of past IP relating to electrochemical methods of BO→BH. • System analysis and Reactor Module Development.	• Completion of system analysis and report out computer modeling results	• Report on thermo- and electrochemical processes • Interim assessment of Tier 2 and Tier 3 results • Reactor modeling results
2	• Design laboratory prototype based on modeling and process intensification studies	• Completion of integrated reactor system design	• Conceptual design package of laboratory prototype P1
3	• Construct and test initial laboratory prototype system.	• Successfully built and tested laboratory prototype (P1)	• Testing results from prototype P1
4	• Design and construct scaled-up hydrogen generation system	• Design freeze of scaled-up final prototype (P2).	• Design package of scaled up prototype P2
5	• Perform validation testing of final prototype system	• Have demonstrated the target hydrogen storage capacity in the optimized P2	• Testing results from prototype P2

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Hydrogen Safety

- The most significant hydrogen hazard associated with this project is:
  - Unexpected reactant or hydrogen release due to leakage or reactor rupture due to overpressure
    - as a result of hydrogen input
    - as a result of reactant or fuel clogging
    - as a result of uncontrolled reaction

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YW7

Hydrogen Safety

- Our approaches to deal with this hazards are:
  - Regular and routine equipment inspection
  - Safety reviews prior to any new experiments
  - Reactor engineering to allow for controlled failure of reactor
    - Use only commercially-obtained pressure vessels in good condition, with documented manufacturer's pressure rating and temperature limits, and suitable overpressure-relief valves
    - Control system will automatically shut down the feed of reactants
    - Apparatus for admitting hydrogen to any vessel will be designed so that the hydrogen flow can be interrupted by a valve, which makes any fire self-extinguishing without risk of flashback to make an explosive mixture
  - Pressure of hydrogen admitted to vessels will be limited to 80% of the rated pressure at the temperature of use
  - Air/oxygen will be purged from any vessel before hydrogen is added
  - Conduct experiments in vented hoods and behind proper shielding

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Slide 24

YW7 pls add more that you can think of in terms of safety related to HOD.
Ying Wu, 4/9/2005