Hydrogen Storage Engineering
CENTER OF EXCELLENCE

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Project ID# ST004

SRNL-STI-2016-00195

Overview

Timeline

- Start: February 1, 2009
- End: December 31, 2015
- 99% Complete (as of 3/1/16)

Budget

- Total Center Funding:
  - DOE Share: $ 35,275,000
  - Cost Share: $ 3,322,000
  - FY '15 Funding: $895,000
  - FY '16 Funding: $150,000
- Prog. Mgmt. Funding
  - FY '15: $ 300,000
  - FY'16: $0

Barriers

A. System Weight and Volume
B. System Cost
C. Efficiency
D. Durability
E. Charging/Discharging Rates
G. Materials of Construction
H. Balance of Plant (BOP) Components
J. Thermal Management
K. System Life-Cycle Assessment
O. Hydrogen Boil-Off
P. Understanding Physi/Chemi-sorption
S. By-Product/Spent Material Removal

Partners

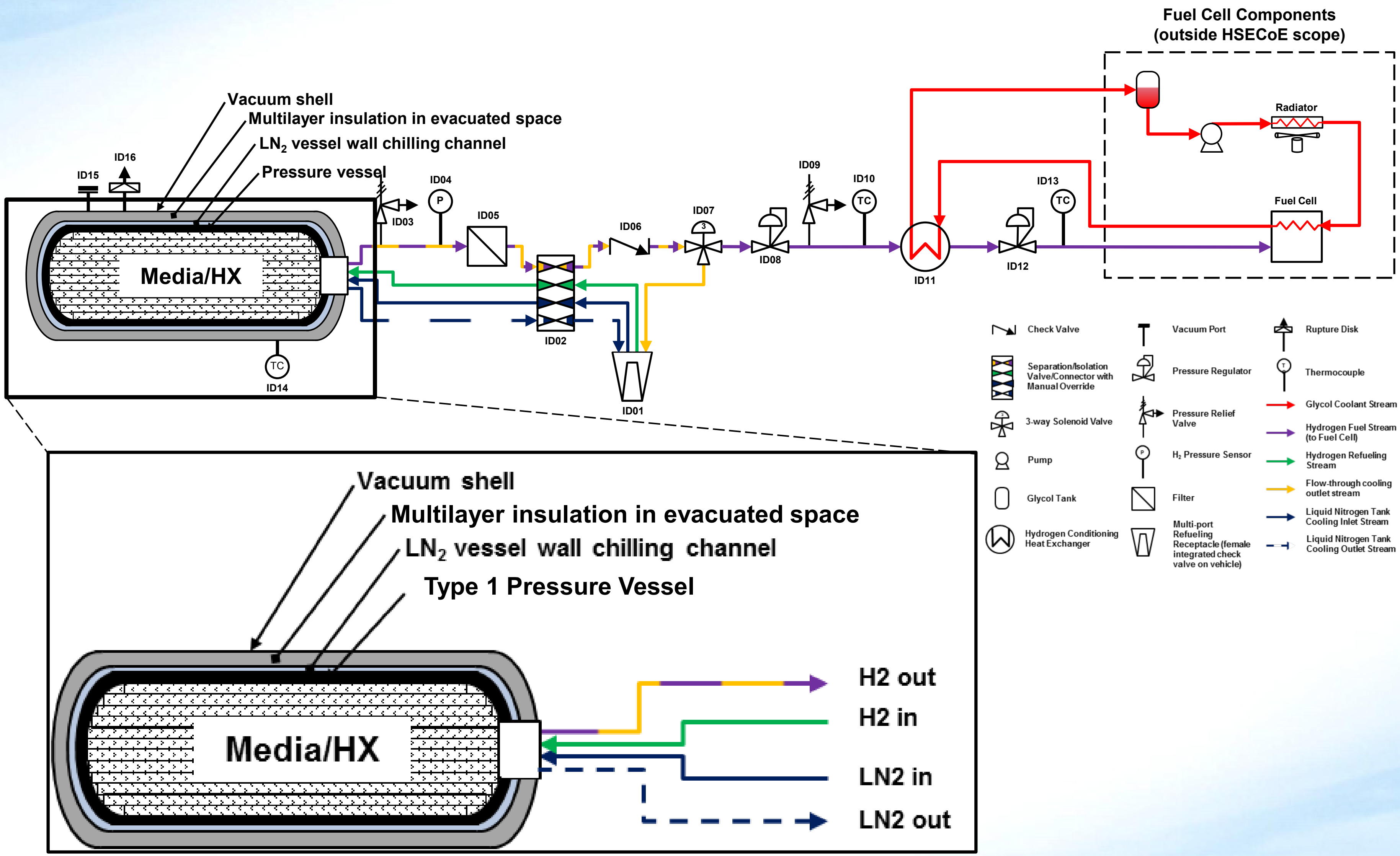
SRNL Savannah River National Laboratory
Pacific Northwest National Laboratory
Los Alamos National Laboratory
JPL Jet Propulsion Laboratory California Institute of Technology
NREL National Renewable Energy Laboratory
Michigan
OSU Oregon State University
HRI UQTR
Ford
GM
United Technologies Research Center
BASF The Chemical Company
Hexagon Lincoln

HSECoE Technical Objectives

Using systems engineering concepts, design innovative material-based hydrogen storage system architectures with the potential to meet DOE performance and cost targets.

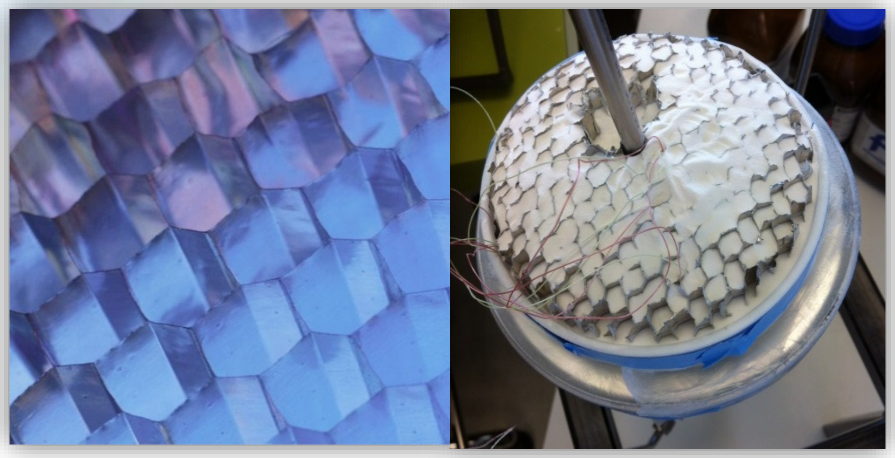
- **Develop and validate system, engineering and design models** that lend insight into overall fuel cycle efficiency.
- Compile all relevant materials data for candidate storage media and **define required materials properties to meet the technical targets**.
- **Design, build and evaluate subscale prototype systems** to assess the innovative storage devices and subsystem design concepts, validate models, and improve both component design and predictive capability.

Adsorbent System Overview

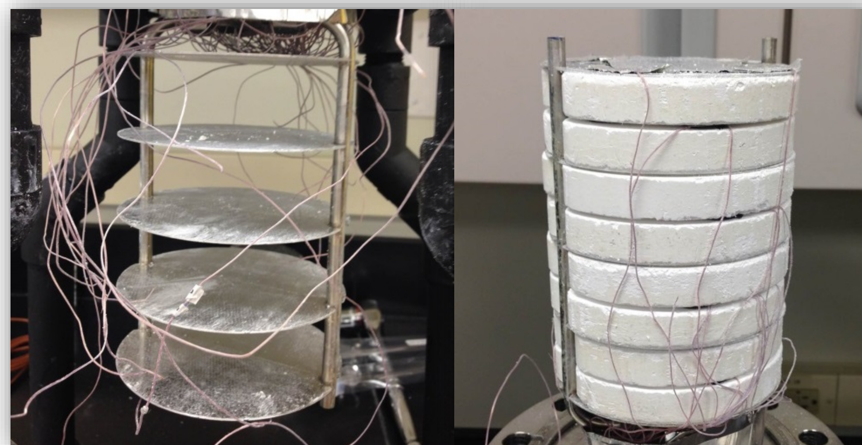


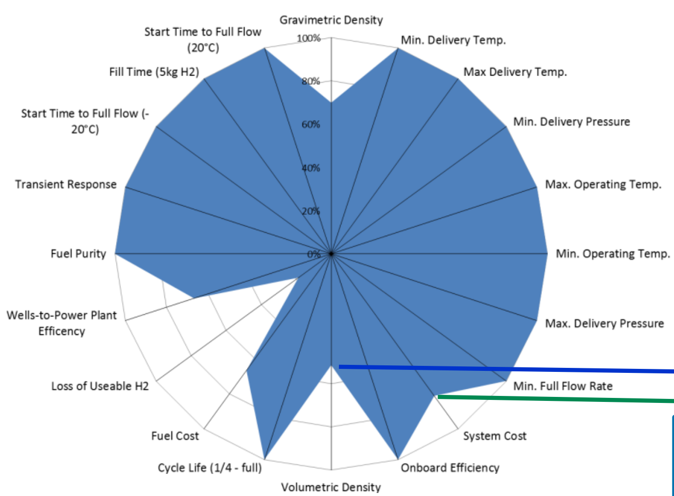
Adsorbent Heat Exchanger Types

HexCell
Flow Through Chilled H_2 Cooling



MATI
Isolated LN2 Flow Cooling

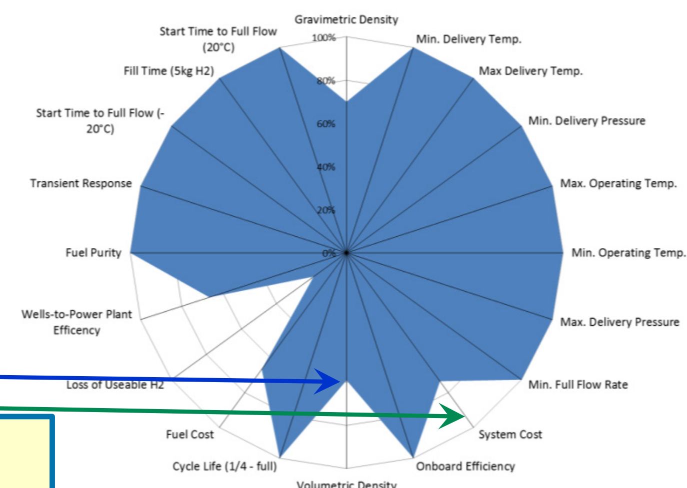




Gain Volumetric Density

in going from loose powder to compacted pucks

at expense of Cost



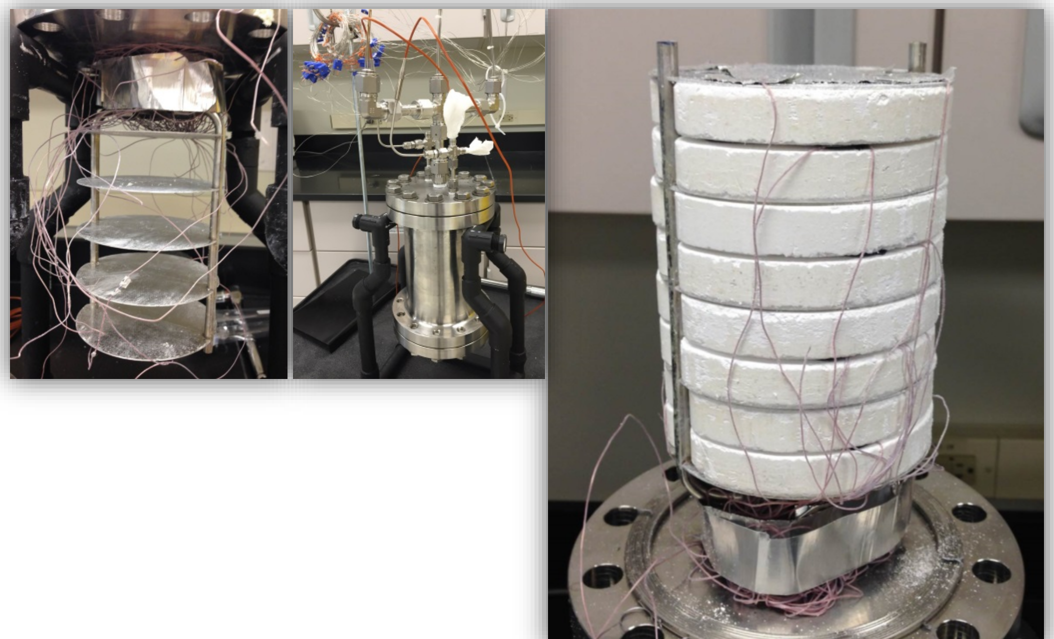
Evaluation of Novel HX Design to Prove Efficacy & Utility

Accomplishment

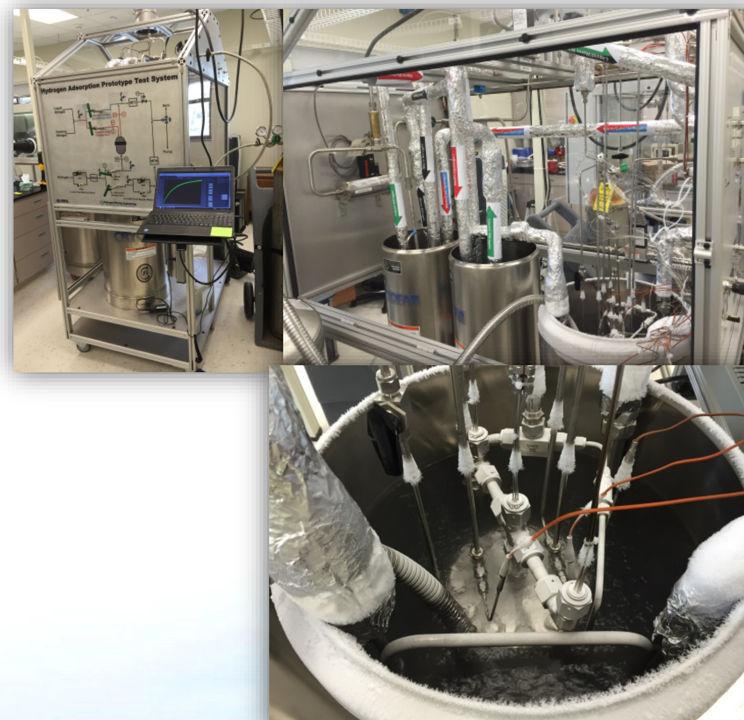
MATI Heat Exchanger & Test Systems

Demonstrate performance of subscale system evaluations and model validation of a 2L adsorbent system utilizing a MATI thermal management system having 54 g available hydrogen, internal densities of 0.10g/g(m+H_2) gravimetric, and 27 g/l volumetric.
Demonstrate a two liter hydrogen adsorption system containing a MATI internal heat exchanger provided by Oregon State University characterizing its performance against each of the sixteen performance DoE Technical Targets for On-Board Hydrogen Storage Systems.

MATI Subscale Prototype Assembled

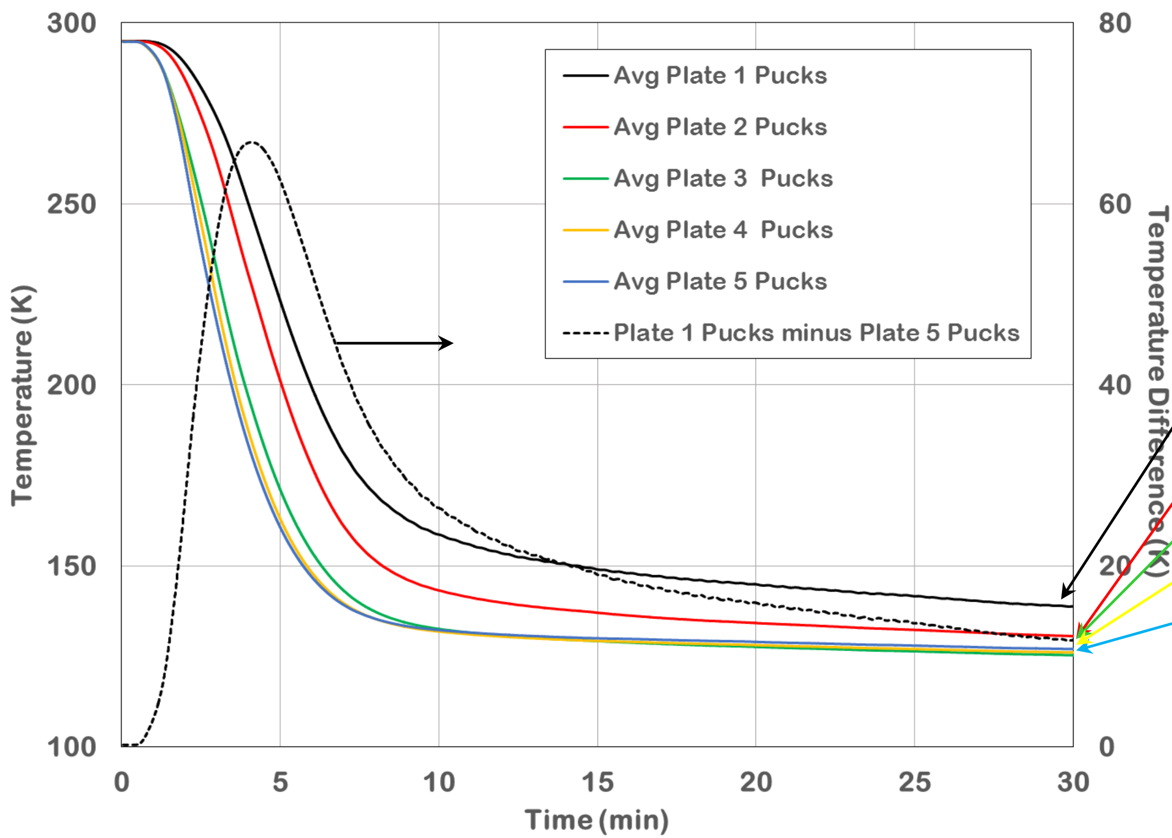


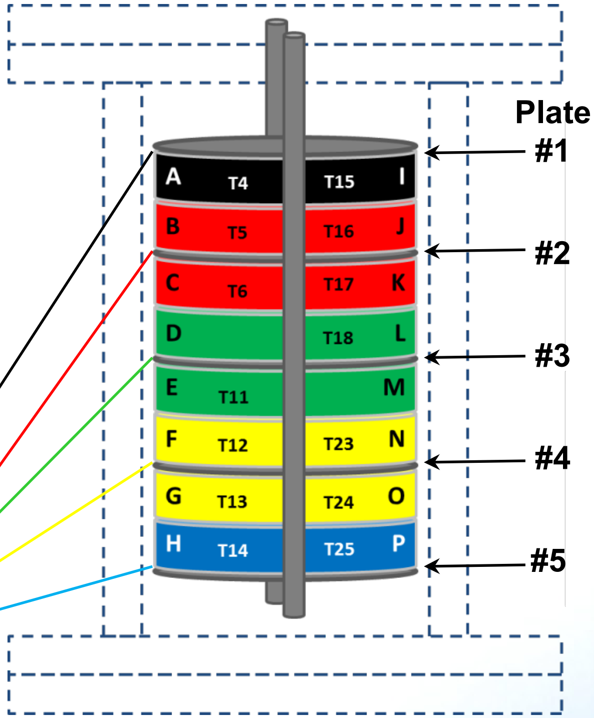
MATI Test Station



MATI Performance Tests – Puck Cooling Profiles

Entire system at ambient temperature and vacuum with LN_2 flowed through MATI

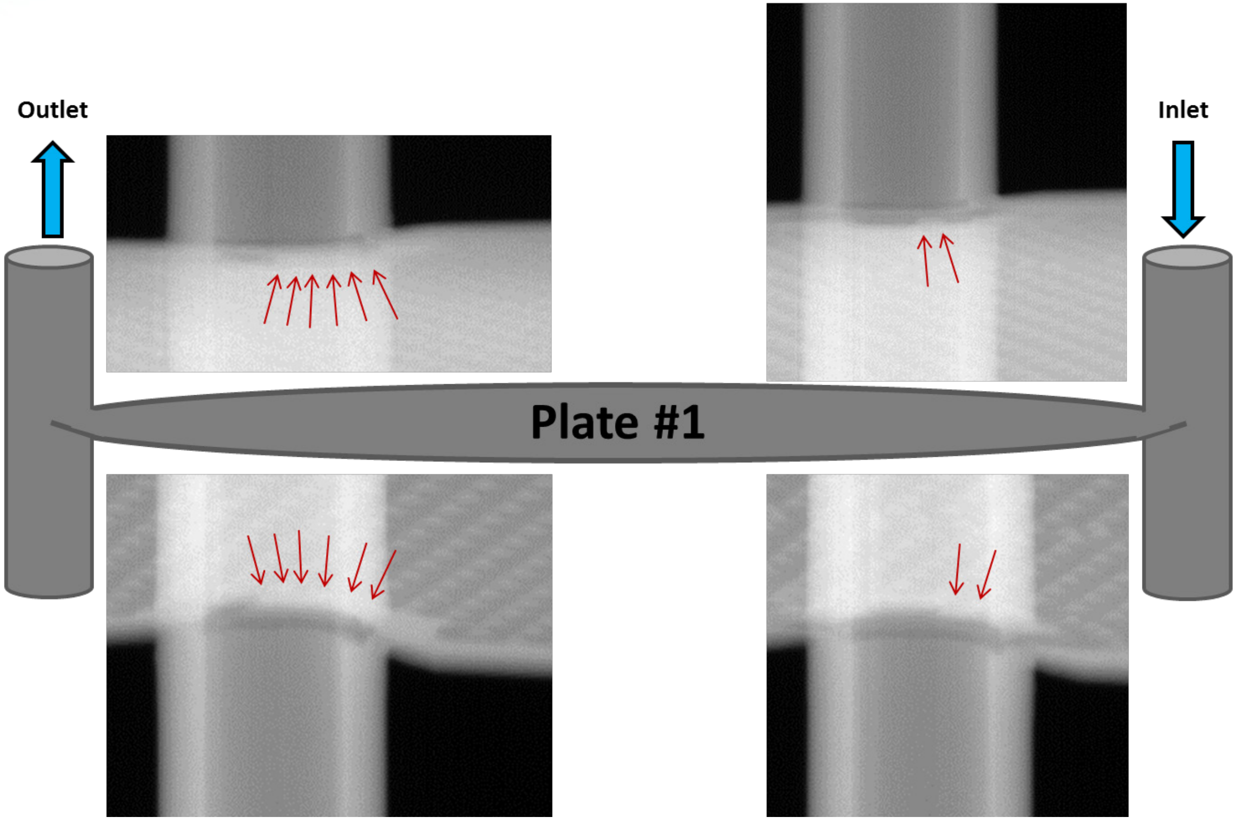




Data color coded to figure

- Significant temperature differential, up to 70 K, between pucks on top two plates, #1 & 2, and pucks on bottom 3 plates, #3-5.

MATI Performance Tests - X-ray of Brazed Joints



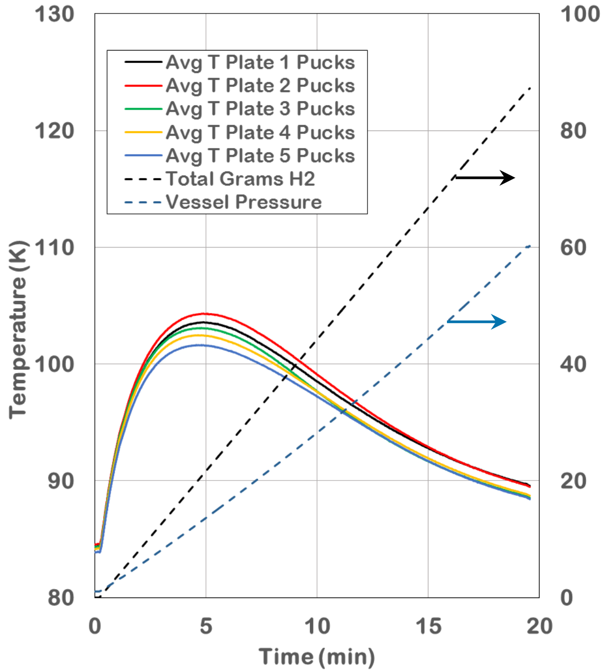
- NDE analysis indicates significant blockage of outlet passage resulting in reduced LN2 flow and degraded cooling efficiency.

HSECoE

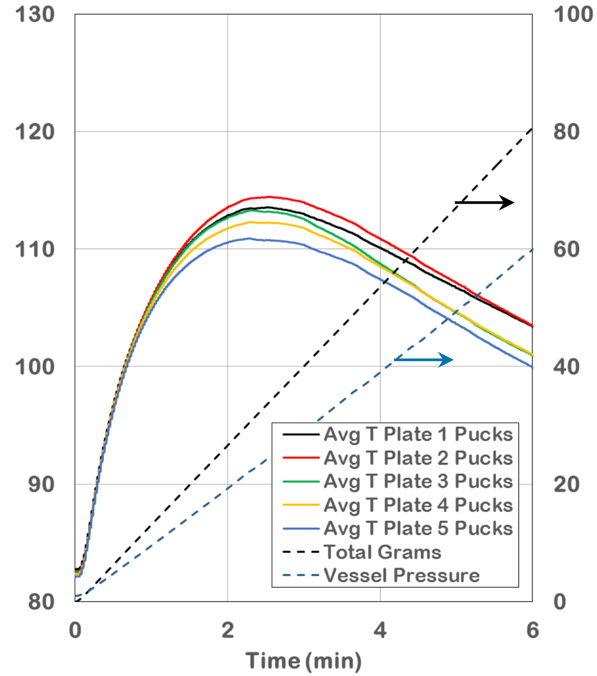
MATI Charging – Varied H_2 Flow

constant LN_2 flow at 150 SLPM

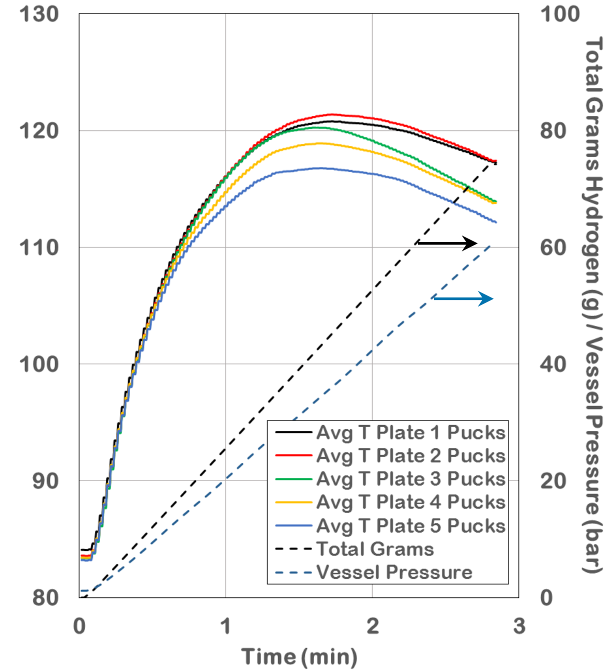
50 SLPM H_2



150 SLPM H_2



300 SLPM H_2

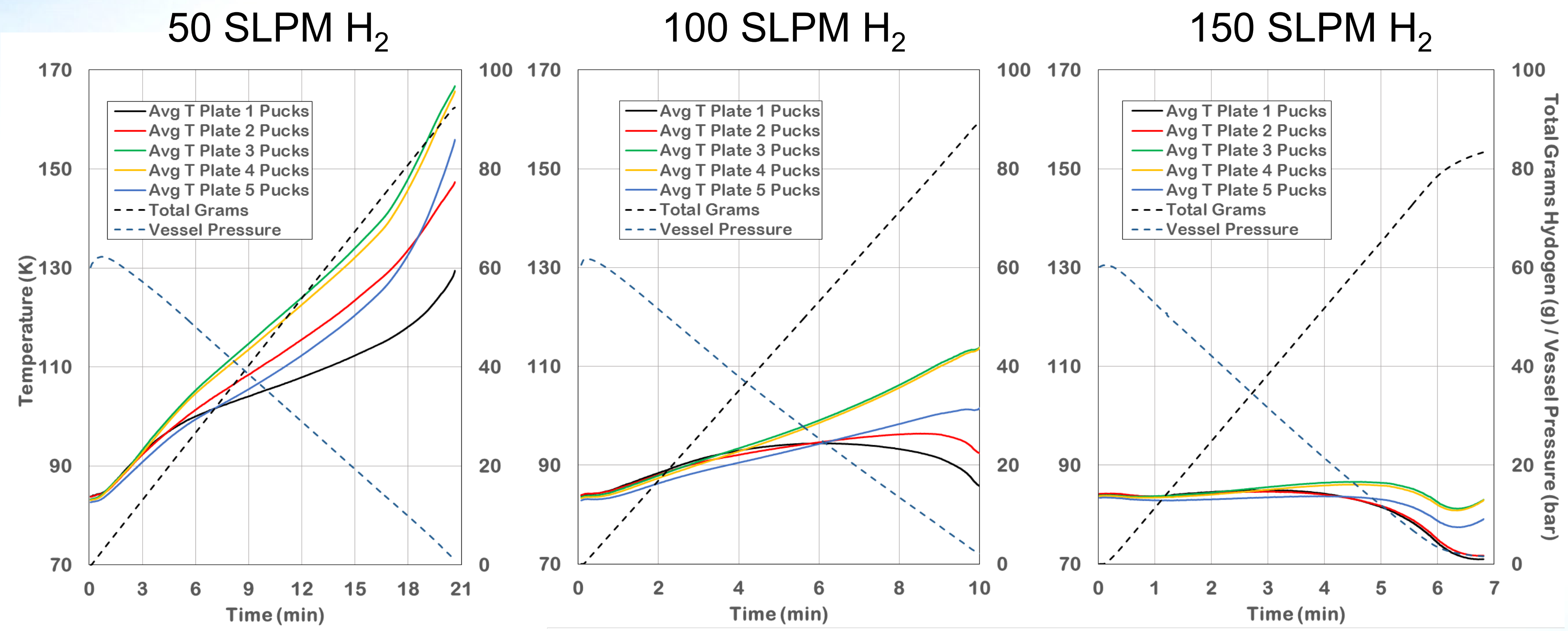


- 20% increase in average bed temperature at 300 SLPM vs 50 SLPM H_2 flow due to faster adsorption.
- 13% decrease in total grams of hydrogen into system at 300 SLPM compared to 50 SLPM H_2 flow due to warmer adsorbent.
- Thermal models for the MATI system were not completed due to personnel changes at OSU, thus comparison of models and experiments could not be made.

HSECoE

MATI Discharging – Varied H_2 flow

constant GN_2 flow at 150 SLPM



- Slower outgoing hydrogen flow allows for greater heating of the adsorbent.
- Max. average bed temperature decreases (160, 112 and 85 K respectively) with increasing H_2 flow rate.
- Total mass of H_2 through the mass flow meter decreased (92, 91 and 84 grams) with increasing H_2 flow rate due to chilled system.

HSECoE

Accomplishment

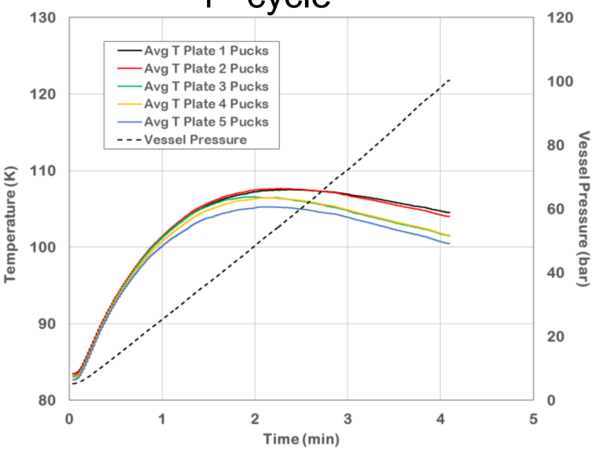
MATI 60 & 100 bar H_2 Cycling

- Performed with vessel start conditions of 5 bar and ~80 K
- Cycles performed to 60 and 100 bar max. pressure
    - Depending on gas supply, 10 consecutive cycles for 60 bar and 4 consecutive cycles for 100 bar
- Adsorption conditions: 300[1] SLPM H_2, LN_2 150 SLPM (gas equivalent)
    - Adsorptions halted once pressure reached (60 or 100 bar) regardless of vessel temperature, system switched over to perform desorption
- Desorption conditions: 130[2] SLPM H_2, GN_2 150 SLPM
    - Desorption halted once pressure reached (5 bar) regardless of vessel temperature, system switched over to perform adsorption

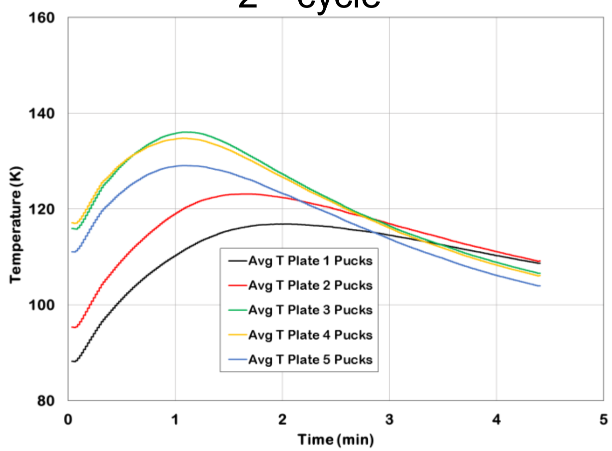
[1]-adsorption rate to meet scaled Technical Target of 3 min. fill time
[2]-desorption rate to meet scaled US-06 max. flow rate

100 bar Cycling, Adsorption Curves

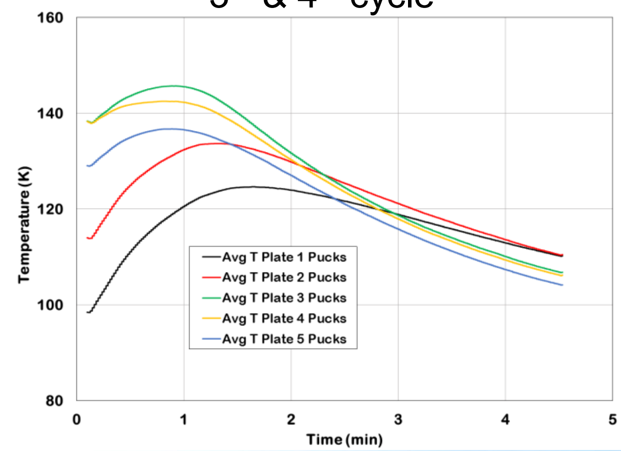
1st cycle



2nd cycle



3rd & 4th cycle

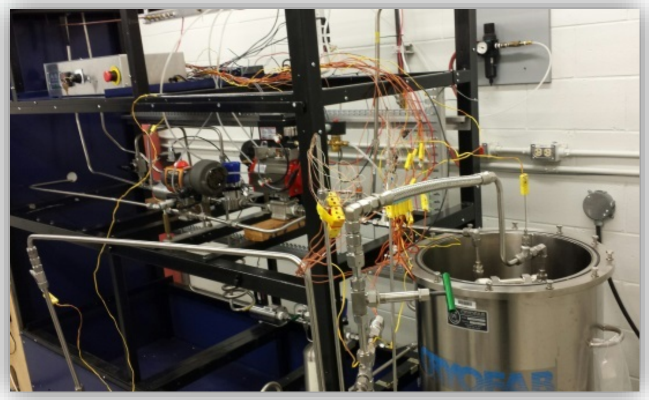


- Twenty cycles performed at 60 bar and eight cycles performed at 100 bar
- No degradation in capacity observed.

HSECoE

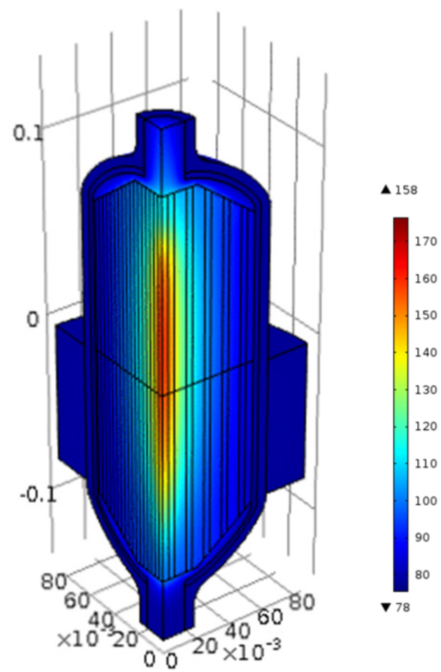
HexCell Heat Exchanger & Test System

Demonstrate performance of subscale system evaluations and model validation of a 2L adsorbent system utilizing a HexCell heat exchanger having 46g available hydrogen, internal densities of 0.13g/g gravimetric, and 23.4g/L volumetric.

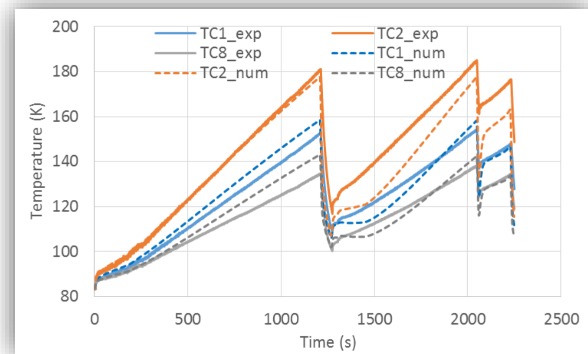


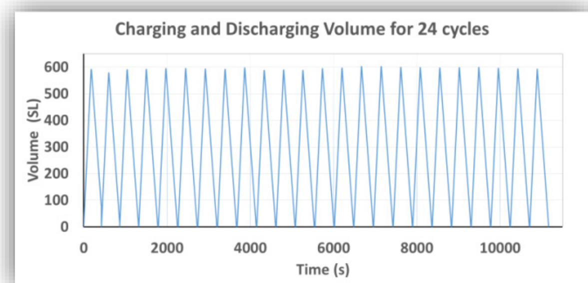
2L HexCell Test System

2L HexCell System Assembly



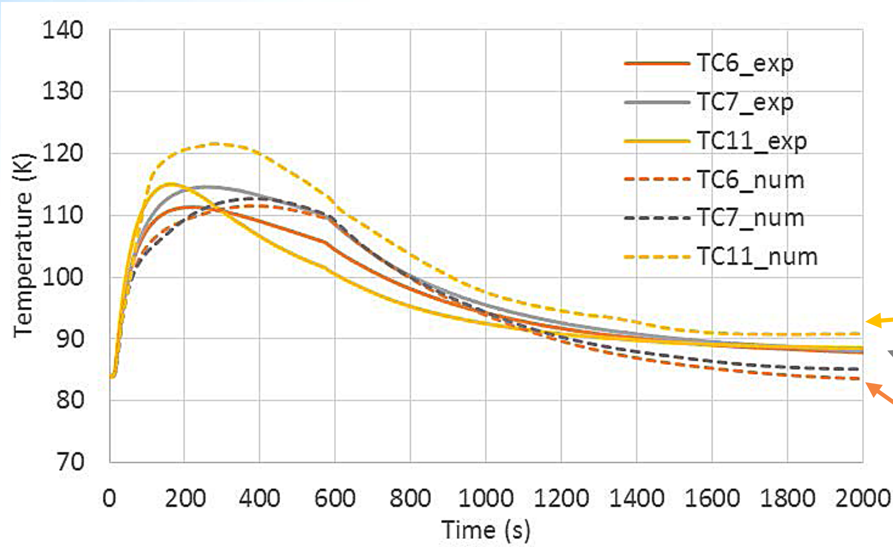
2L HexCell Thermal Models Complete & Validated

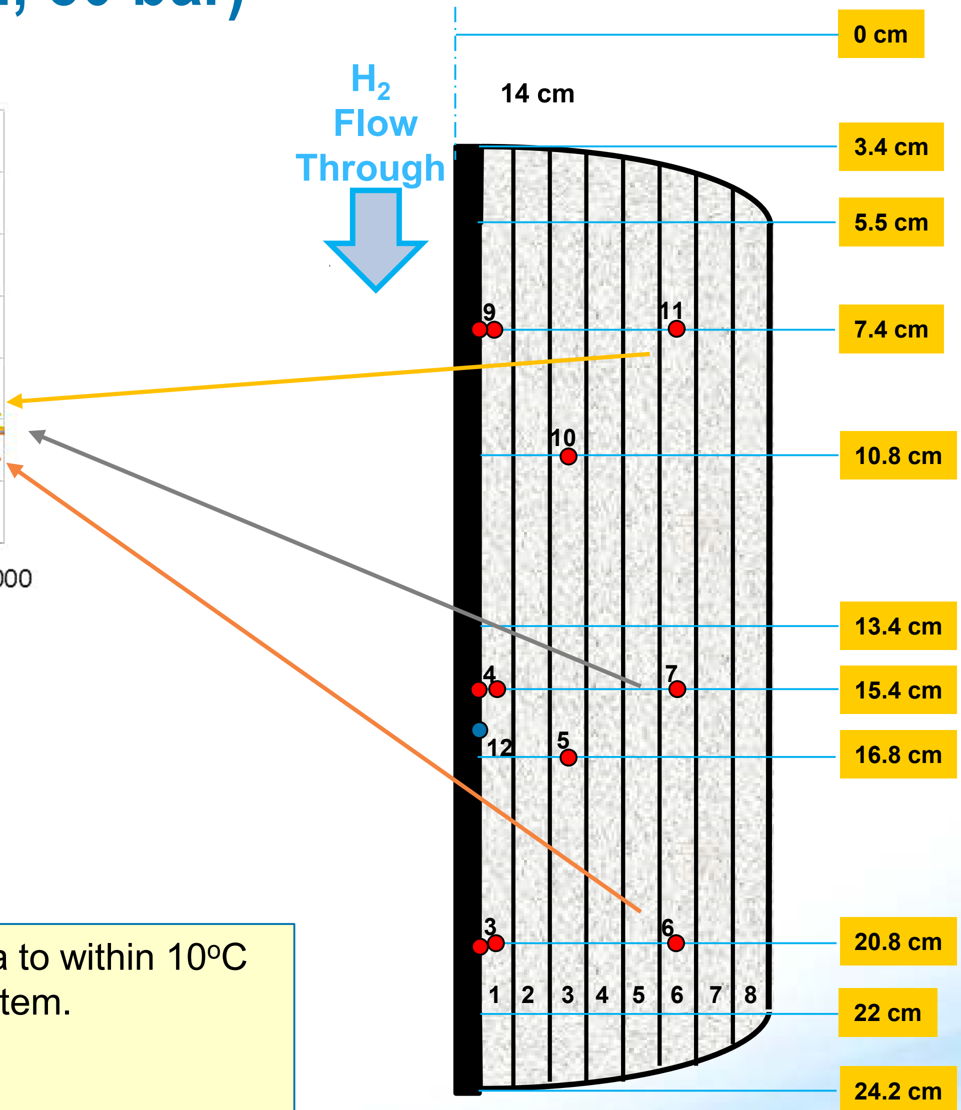




2L HexCell Test Results

HexCell Charging (100 SLPM, 80 bar)



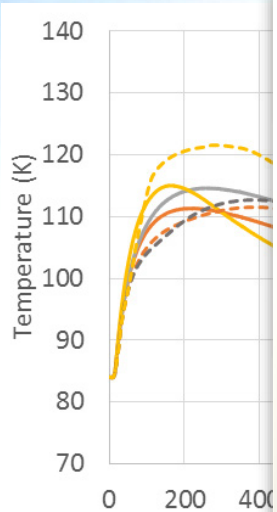


- Initial conditions: 85K, 1.7 bar
- Approximate full charging time 30 minutes
  - Vessel Inlet hydrogen = 280 g
  - Vessel Outlet hydrogen = 242 g
  - Mass of MOF5 = 270 g at 217 kg/m^3

- Modeling agrees with experimental data to within 10^{o}C
- Flow-through is an effective cooling system.
- Achieved weight capacity of ~ 4.1 %
- Achieved volumetric capacity of ~19 g/l
- 14% H_2 Adsorbed

HSECoE

HexCell Charging (100 SLPM, 80 bar)



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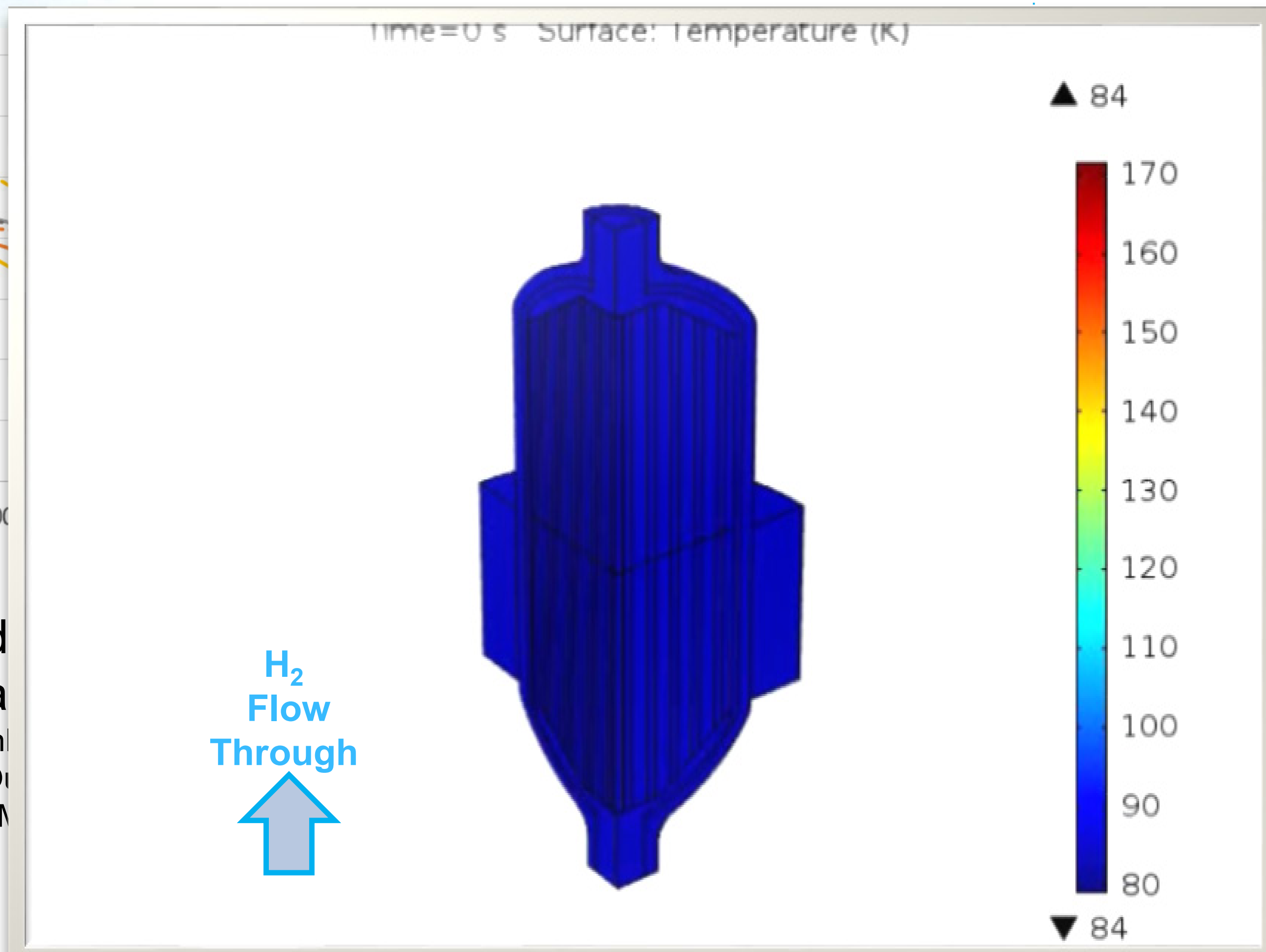
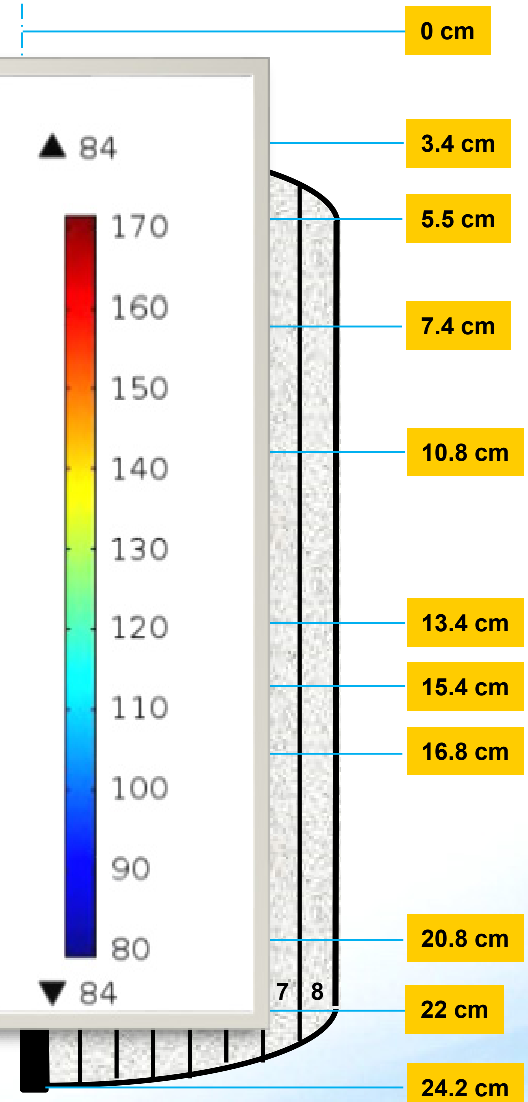


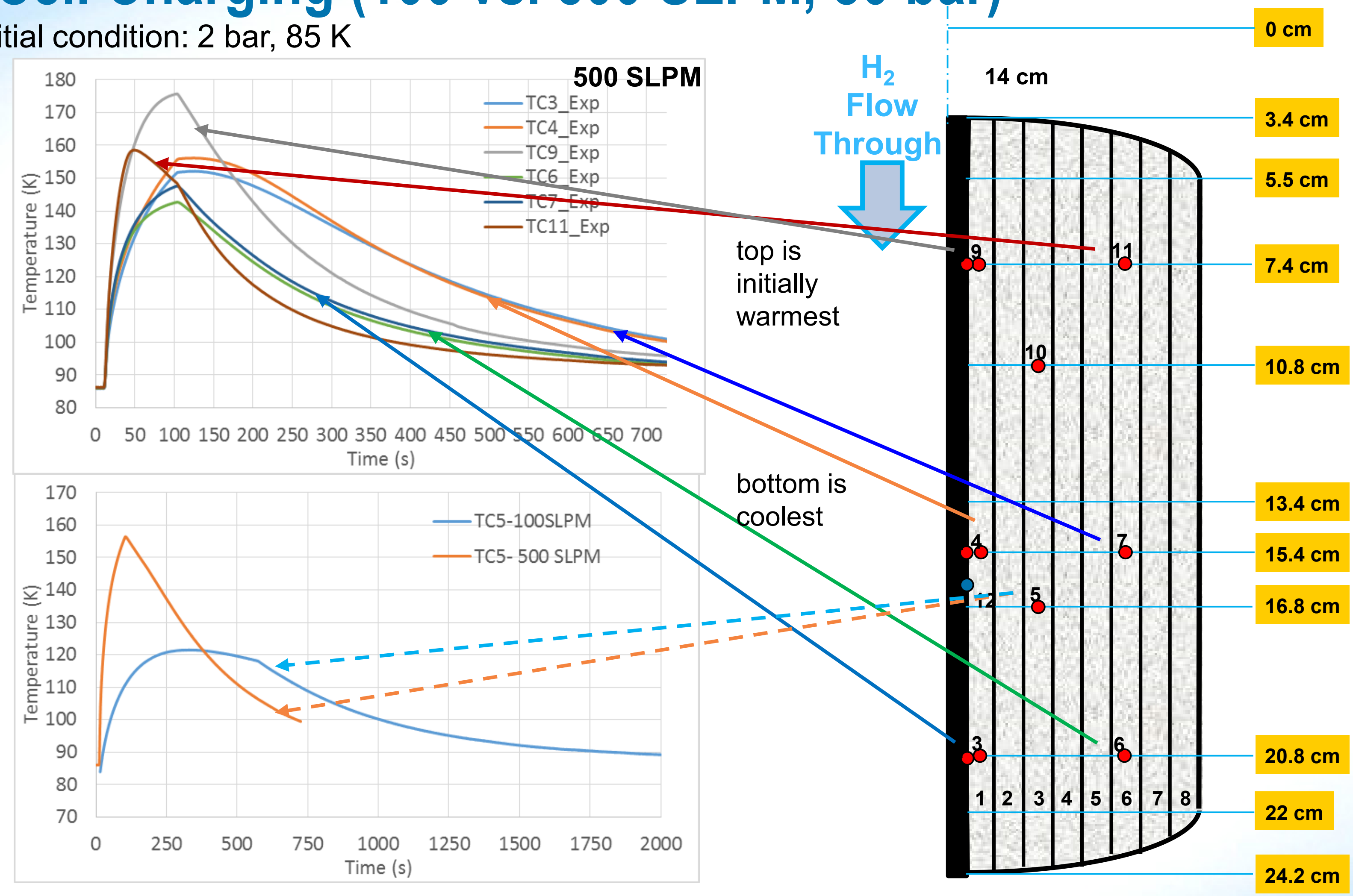


- Initial start 150 K inlet H2 warms tank and MOF before steady state cooling dominates.

HSECoE

HexCell Charging (100 vs. 500 SLPM, 80 bar)

- Initial condition: 2 bar, 85 K



- Higher flow through rate results in higher maximum temperature due to greater availability of fresh gaseous hydrogen.
- Doubling flow through rate decreased charge time >30%.

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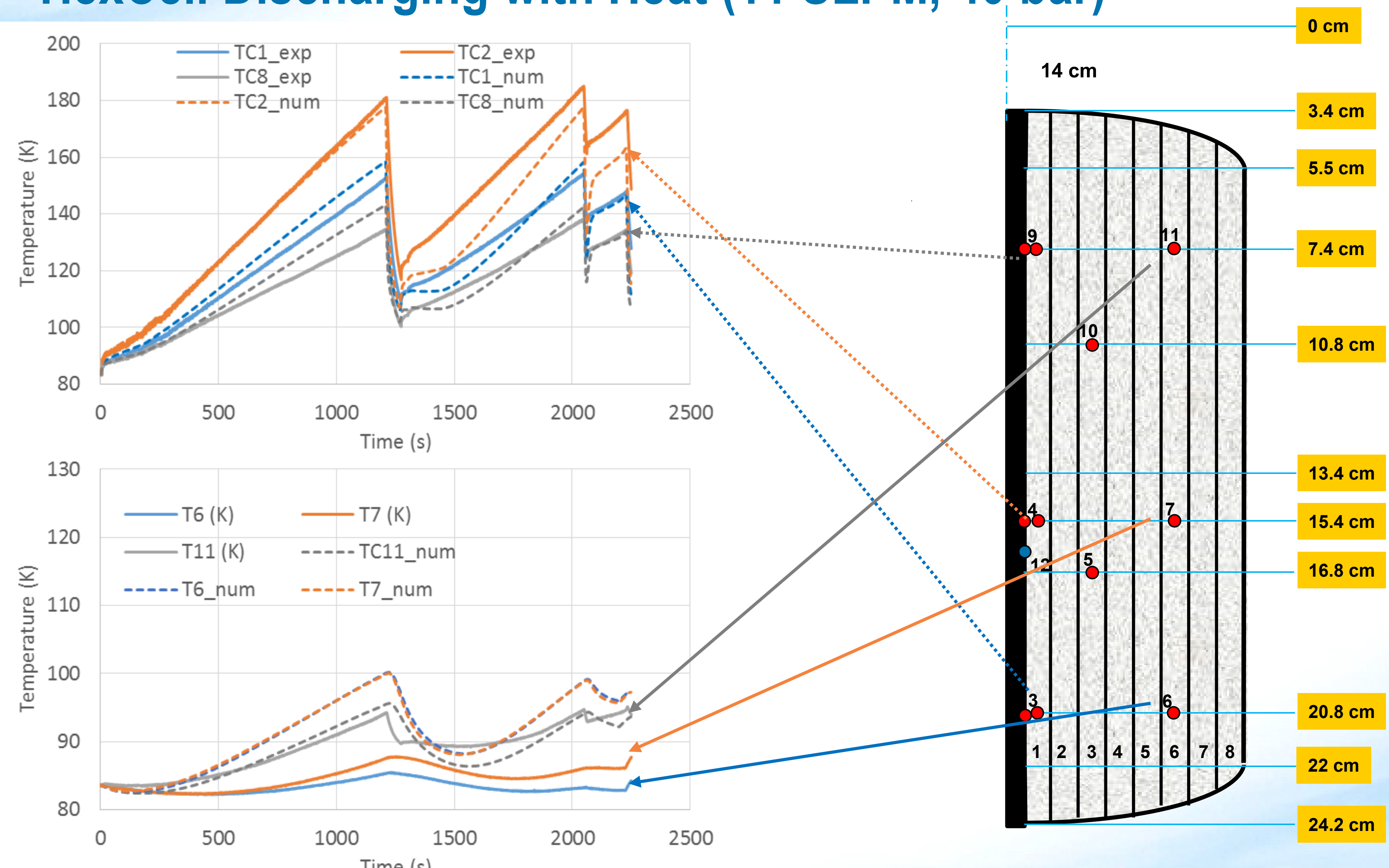
Accomplishment

HexCell Discharging with Heat (11 SLPM, 40 bar)

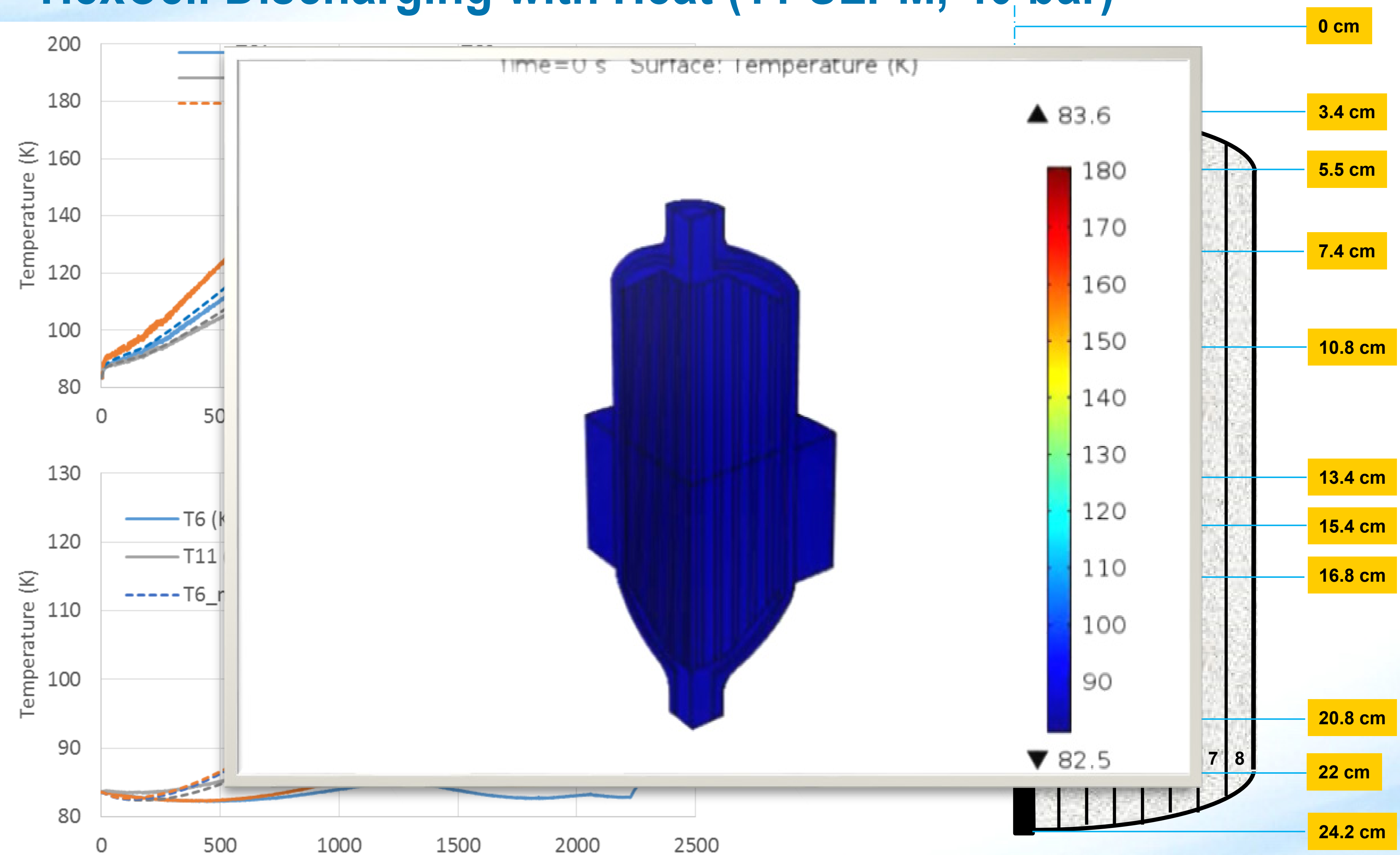


- Models agree with experimental results within 15 K.
- Error results from non-uniform heating rod thermal distribution.

HSECoE

Accomplishment

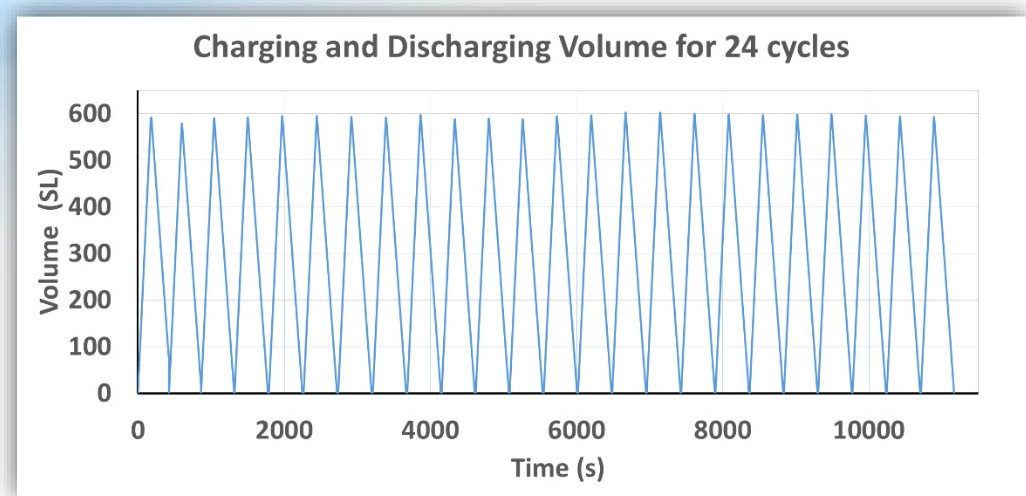
HexCell Discharging with Heat (11 SLPM, 40 bar)



- Manual heater output control results in potential local overheating and requires periodic cycling to meet hydrogen demand.

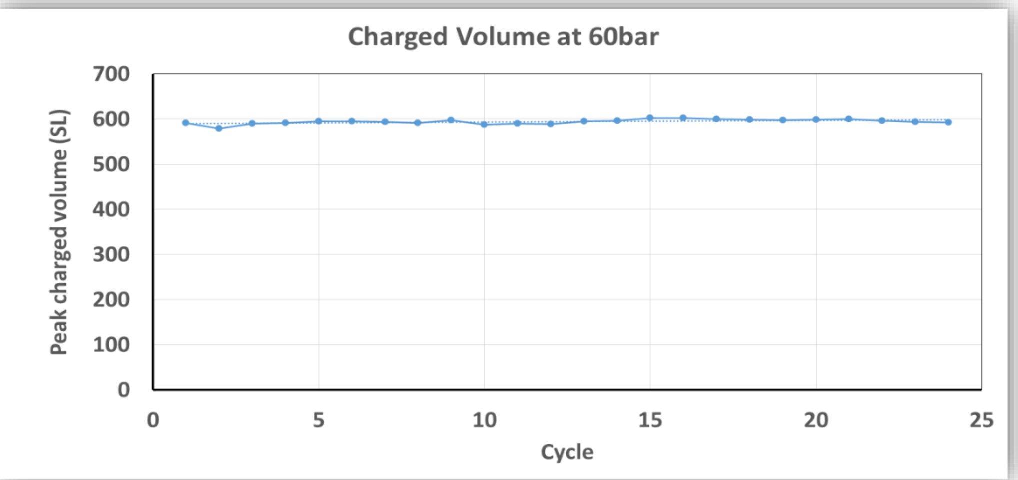
HSECoE

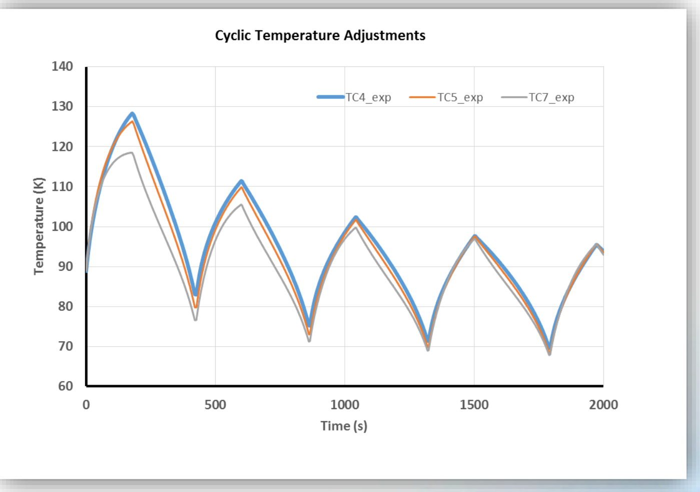
HexCell Cycling Tests



Conditions:

- Pressure swing 5 – 60 bar
- Quasi isothermal (submerged in LN2)
- Flow-through charging at 200 SLPM H_2
- Discharging H_2 at 130 SLPM.





- Temperature swing stabilized after four cycles
- Cycling results in no system capacity degradation observed after 24 cycles.

HSECoE

Comparison of HexCell, MATI and Type 4 Systems

	What we did: **2 liter Materials & HX Only** *(measured)*	**What we could do:** **5.6 Kg H_2 Full Scale Type I Tank w/BoP** *(projected)*
HexCell	90K,80bar ⇨ 85K,1.7bar	80K,100bar ⇨ 160K,5bar
Gravimetric Density	0.112 g/g	0.032 g/g
Volumetric Density	23.6 g/l	18.9 g/l
MATI	84.5K,100bar ⇨ 83.7K,1.1bar	80K,100bar ⇨ 160K,5bar
Gravimetric Density	0.092 g/g	0.031 g/g
Volumetric Density	37.2 g/l	21.0 g/l
Physical Storage, Type 4 Tank		293K,700bar ⇨ 293K,5bar
Gravimetric Density		0.026 g/g
Volumetric Density		20.1 g/l

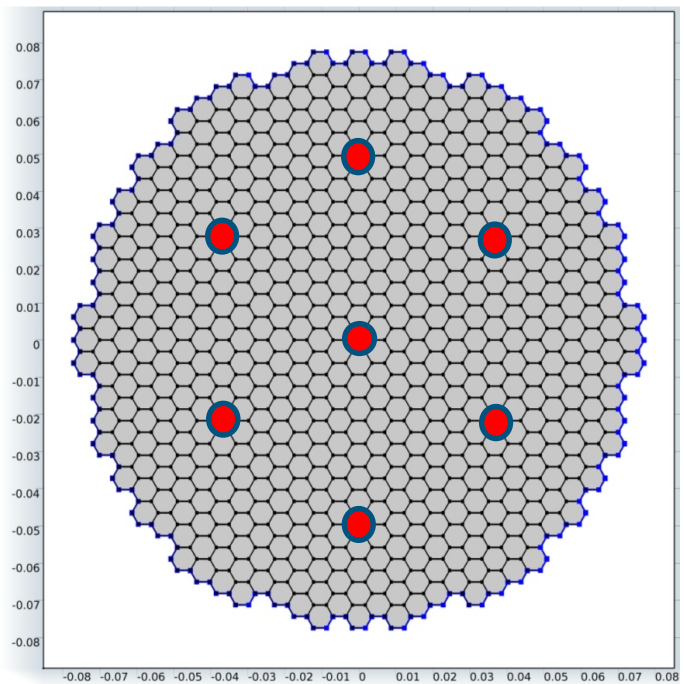
equilibrium conditions

- **Compacted MOF-5/MATI/Type I tank surpasses compressed gas at 700 bar/Type 4 tank in gravimetric and volumetric capacity!**

HSECoE

Full Scale Type 1 HexCell System Design Concept

- Internal LN2 cooling channel
- MLVI Insulation



System Capacity:
5.6 kg useable H_2 under US06 Drive Cycle

Operating Conditions:
80K-160K
100bar-5bar

System Components:
Type 1 Al Tank (1.8m x 0.46m dia.)
7 x 100W heaters
HexCell HX - 9mm hex/76μm foil
60-100 layer MLVI – 25.4mm
Internal LN2 tank cooling channel

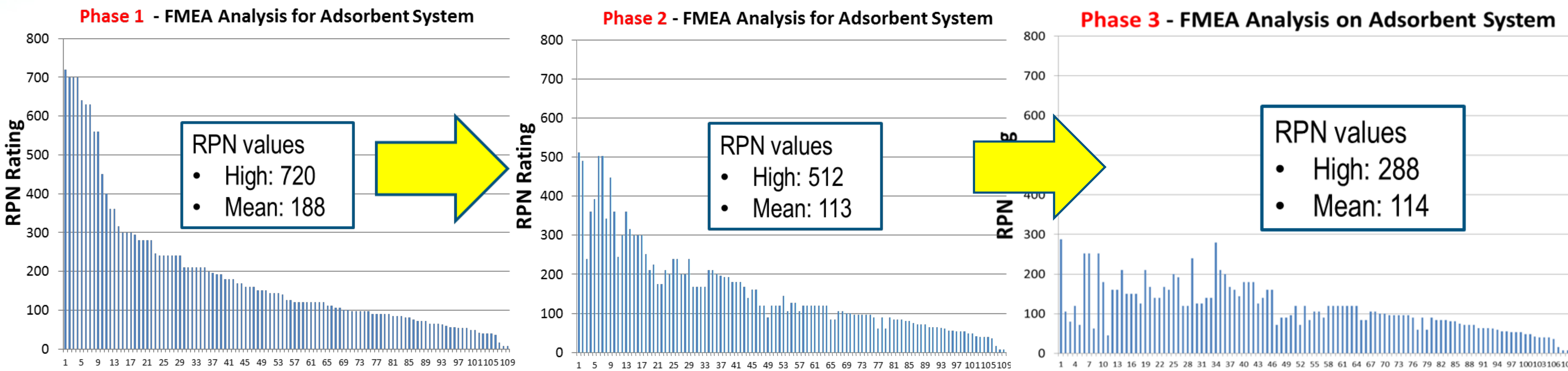
Full Scale System:

Tank	107.0kg	109.0l
HX	9.8kg	3.6l
MOF	35.1kg	166.4l
BoP	16.7kg	16.5l
Total	174.5kg	295.8l

- Model completed and being used to simulate drive cycle response.

Adsorbent System FMEA

Complete the failure mode and effects analysis (FMEA) associated with real-world operating conditions for a MOF-5-based system, for both HexCell and MATI concepts based on the Phase 3 test results. Report on the ability to reduce the risk priority numbers (RPN) from the phase 2 peak/mean and identify key failure modes.



Key Failure Modes

- Material uptake/discharge rates insufficient due to hydrogen impurities
- Material uptake/discharge rate insufficient due non-uniform thermal conductivity
- Impact damage to system
- Pressure relief valve does not open upon accidental over pressurization
- Loss of useable hydrogen rate insufficient due to performance/damage of thermal isolation system

- **MATI**
  - Material uptake/discharge rate insufficient due non-uniform flow in micro-channel plates
- **HexCell**
  - Material uptake rate insufficient due to inhomogeneous adsorbent packing density

Remaining Adsorbent Engineering Issues

- **Build and test fully functional prototype adsorption system, including tank cooling channel concept, to assess real life charging characteristics.**
- **Develop charging control algorithms to minimize charging time and H_2 flow through.**
- **Develop discharge control algorithm to meet drive cycle hydrogen demands.**
- **Denser MOF compacts would yield higher volumetric capacities.**
- **The effectiveness of enhanced thermal conductivity methods such as MATI pins need to be demonstrated.**
- **Manufacturing methods of MOF/HX systems in a sealed Type I pressure vessel needs to be demonstrated.**
- **Optimized refueling stations needs to be designed to meet recirculation demands imposed by either MATI or HexCell systems.**

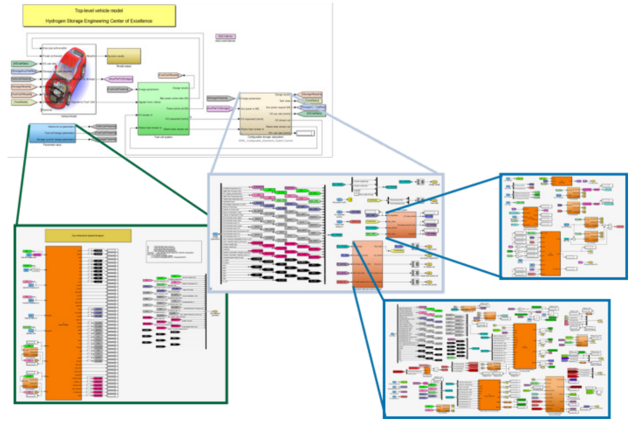
Continuing Efforts

Model Updates *(NREL, PNNL, SRNL)*

Develop a stand-alone isotherm data fitting routine to convert raw excess adsorption H_2 data into its D-A parameters.

Update the adsorbent hydrogen storage equations for additional theoretical formulations (such as UNILAN and/or 2-state Langmuir).

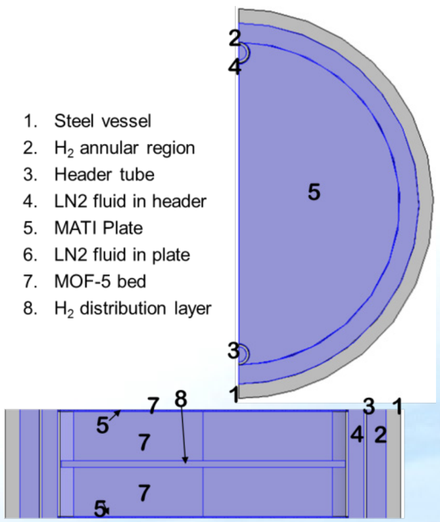
Update the built-in material properties database to include new adsorbents (such as AC, HKUST-1, etc.).



MATI System Modeling *(SRNL)*

Complete a fluid-flow model to examine flow distribution within the MATI channels and the feasibility of the "unit cell" assumption.

Complete and validate a prototype-scale COMSOL model of MATI system and upload to WEB site.



Materials Based Hydrogen Storage Systems Summary

	Mass* (kg)	Volume* (liters)	Cost* ($)	Gravimetric Density (gH_2/g system+gH_2)	Volumetric Density (gH_2/liter system)	Cost ($/kWh)
Metal Hydride System						
$NaAlH_4$/Ti	457	489	8008	1.2%	11.5	43.0
Chemical System						
AB	122	136	3011	4.6%	41.0	16.5
AlH_3	164	151	4133	3.4%	37.0	22.2
Adsorbent System						
HexCell/MOF-5	174	296	2720	3.2%	18.9	14.6
MATI/MOF-5	178	267	2897	3.1%	21.0	15.5
Compressed Gas						
Type 4 Tank/700 bar	212	278.6	2740[#]	2.6%	20.1	14.8[#]
2020 DOE Target				5.5%	40.0	10.0

* 5.6kg usable hydrogen

[#] DOE Record #15013

- AB chemical system surpasses DOE 2020 volumetric target
- AlH_3 chemical system surpasses 700 bar Type 4 tank gravimetric and volumetric capacities
- MATI/MOF-5 adsorbent system surpasses 700 bar Type 4 tank volumetric capacity
- HexCell/MOF-5 adsorbent system surpasses 700 bar Type 4 tank cost metric

HSECoE

Technical Back-Up Slides

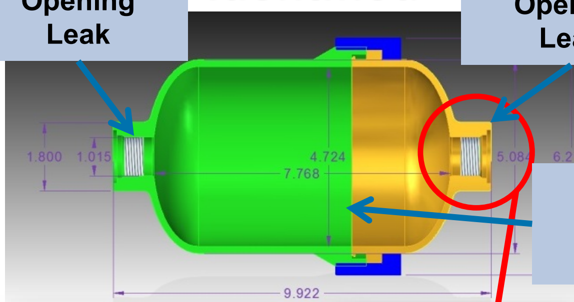
Risk Management: Pressure Vessel Cryogenic Leaks

- Teflon seals observed to leak at LN2 temps.
- This issue could affect schedule and cost (as of 3/31 3-4 months behind schedule)
- *Tank Seal Tiger Team* formed with weekly telecoms scheduled
- Numerous approaches attempted to solve both waist and large plug leaks
- Waist seal solved with composite Teflon/steel washer allowing testing of HexCell system.
- Large opening seal not solved due to lack of mating surfaces – New stainless steel flange tanks designed, manufactured, tested and delivered allowing MATI system testing.

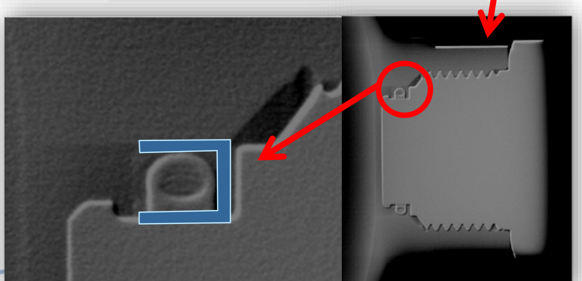
Problem Identified

Small Opening Leak

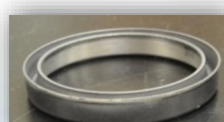
Large Opening Leak



Main Body Leak



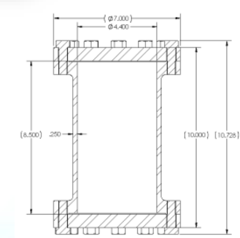
Potential Solutions Investigated



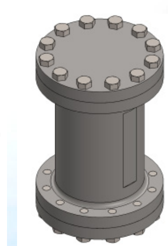
Final Solutions Implemented

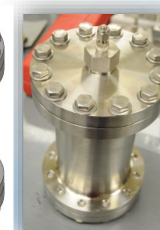
SO: Crush Seal
WB: Teflon coated steel washer/w external clamp

HexCell HX



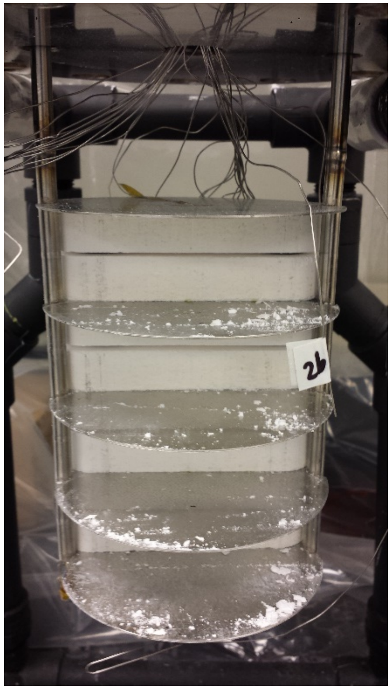
MATI HX

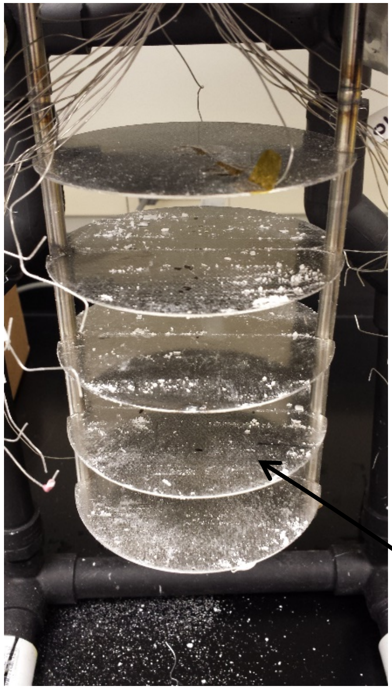




2L Flange Tank

MATI Prototype Decommissioning






- Pucks were in good condition after testing
- Any noticeable chips due to handling (pucks fit very tightly into MATI)
- Any significant amounts of loose powder due to assembly/disassembly
- Only trace amounts found in bottom of vessel after MATI and pucks removed

Summary of Metal Hydride Requirements

- Low enthalpy materials (i.e. ΔH < 27 kJ/mol-H_2), can operate with just the waste heat of the fuel cell for discharge, while high enthalpy materials require extra H_2 (~10%) for combustion and additional BoP.
- A material H_2 absorption kinetics needs to be 3-8X greater than catalyzed $NaAlH_4$, at charging pressures <100 bar.
- Materials with both high gravimetric capacity and low enthalpy of formation need to be developed.

$$\left(\frac{dC}{dt}\right) = A\exp\left(-\frac{E_a}{RT}\right)\left(\frac{P_e - P}{P_e}\right)(C)^{\chi}$$

Parameter	Units	Range*
Gravimetric Capacity, ΔH<27 kJ/mol	g_{H2}/g_{media}	11%
Gravimetric Capacity, ΔH<40kJ/mol	g_{H2}/g_{media}	17%
Equilibrium Pressure, P_e	bar	$5<P_e<100$
Exponential, χ		1
Activation Energy, E_a	kJ/mol	3.05
Pre Exponential, A		6.2×10^8
Bulk Density	$g_{media}/volume_{media}$	70% Crystal Density
Thermal Conductivity, κ	W/m K	>10

J.M. Pasini, C. Corgnale, B.A. van Hassel, T. Motyka, S. Kumar, K. L. Simmons, *Metal hydride material requirements for automotive hydrogen storage systems*, Intl. J. Hydrogen Energy 2013; 38:9755-9765.

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Summary of Chemical Hydrogen Requirements

- Slurry or liquids are optimal for mass transport and must be stable both before and after reaction
- Efficient chemical hydrogen regeneration needs to be developed to address fuel cost and WTPP efficiency gap.
- Hydrogen gas stream clean up has been demonstrated with the loss of gravimetric density
- Chemical hydrogen which can discard spent fuel environmentally (one-way) optimal business solution.

$$\left(\frac{dC}{dt}\right) = A \exp\left(-\frac{E_a}{RT}\right) (C)^n$$

T.A. Semelsberger & K.P. Brooks, ***Chemical hydrogen storage material property guidelines for automotive applications***, Journal of Power Sources 279 (2015) 593-609.

Parameter	Units	Range*
Gravimetric Capacity (liquids)	g_{H2} / $g_{material}$	~ 0.078 (*0.085*)†
Gravimetric Capacity (solutions)	g_{H2} / $g_{material}$	~ 0.098 (*0.106*)†
Gravimetric Capacity (slurries)	g_{H2} / $g_{material}$	~ 0.112 (*0.121*)†
Endothermic Heat of Reaction	kJ / mol H_2	≤ +17 (*15*)†
Exothermic Heat of Reaction	kJ / mol H_2	≤ -27
Kinetics: Activation Energy, E_a	kJ / mol	117-150
Kinetics: Pre-exponential Factor, A		$4 \times 10^9 – 1 \times 10^{16}$
Maximum Reactor Outlet Temperature	°C	250
Media H_2 Density	kg H_2 / L	≥ 0.07
Regeneration Efficiency	%	≥ 66.6%
Viscosity	cP	≤ 1500

† (if hydrogen gas clean-up needed)
* To meet 2020 targets

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Summary of Adsorbent Requirements

- Volumetric density improved with microchannel MATI HX design via MOF compaction demonstrated.
- Charge time target requires external tank and H_2 cooling.
- Low enthalpy adsorbents ($\Delta H<15$ KJ/mol) require low temperatures, MLVI, and eventual loss of hydrogen in dormancy.
- Method of fabricating higher density powder compact need to be developed without loss of adsorption sites to address volumetric density.

$$n_a = \frac{n_{max}RT}{(E_{max} - E_{min})} ln\left(\frac{e^{-\Delta S_0/R} + \frac{P}{P_0}e^{E_{max}/RT}}{e^{-\Delta S_0/R} + \frac{P}{P_0}e^{E_{min}/RT}}\right)$$

$$n_{Total} = n_a + c(V_v - V_p)$$

Parameter	Units	Range*
Maximum Excess Capacity, n_{max}	mol_{H2}/kg_{media}	~ 200
Minimum Binding Energy, E_{min}	KJ/mol	~ 4.49
Maximum Binding Energy, E_{max}	KJ/mol	~E_{min}
Entropy, ΔS_o	J/mol K	≤ -65
Reference Pressure, P_0	bar	1
Absolute Pressure, P	bar	5<P<100
Bulk Density, ρ_{bulk}	Kg/m^3	181
Bed Void Volume, V_v-V_p	m^3/kg_{media}	0.00391
Temperature, T	K	77<T<160

Personal Communication B.J. Hardy
*** to meet 2020 DOE targets using MOF-5 as nominal starting material**