Ford/BASF-SE/UM Activities in Support of the Hydrogen Storage Engineering Center of Excellence

Andrea Sudik (PI), Mike Veenstra, and Jun Yang

Ulrich Müller and Stefan Maurer

Justin Purewal, Dong'an Liu, Don Siegel, and Jun Ni

Overview

Timeline

- Project Start: February 2009
- Project End: January 2014
- Percent Complete: ~40%

Budget

- Total Project Funding:
  - DOE Share: $2,051,250
  - Contractor Share: $616,250
- Funding for FY10: $400K
- Funding for FY11: $300K

Barriers

- All DOE System Targets*

  *http://www1.eere.energy.gov/hydrogenandfuelcells/storage/pdfs/targets_onboard_hydro_storage.pdf

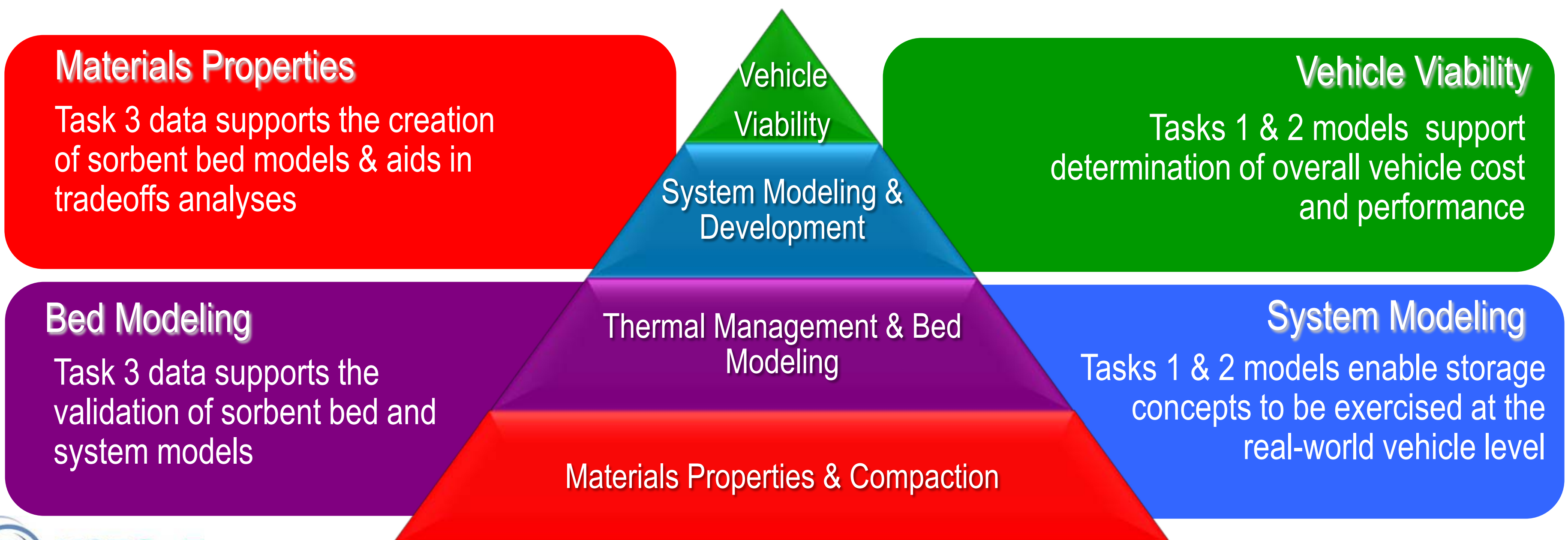
Partners

- Project Lead: Ford
- Subcontractors: BASF and U. Michigan
- Center Partners:

Relevance: Technical

Three Technical Tasks Contribute to Overall HSECoE Mission

Task 1: Develop dynamic vehicle parameter model that interfaces with diverse storage system concepts	Ford
Task 2: Development of robust cost projections for storage system concepts	Ford
Task 3: Devise and develop system-focused strategies for processing and packing framework-based sorbent hydrogen storage media	Ford, BASF, Michigan

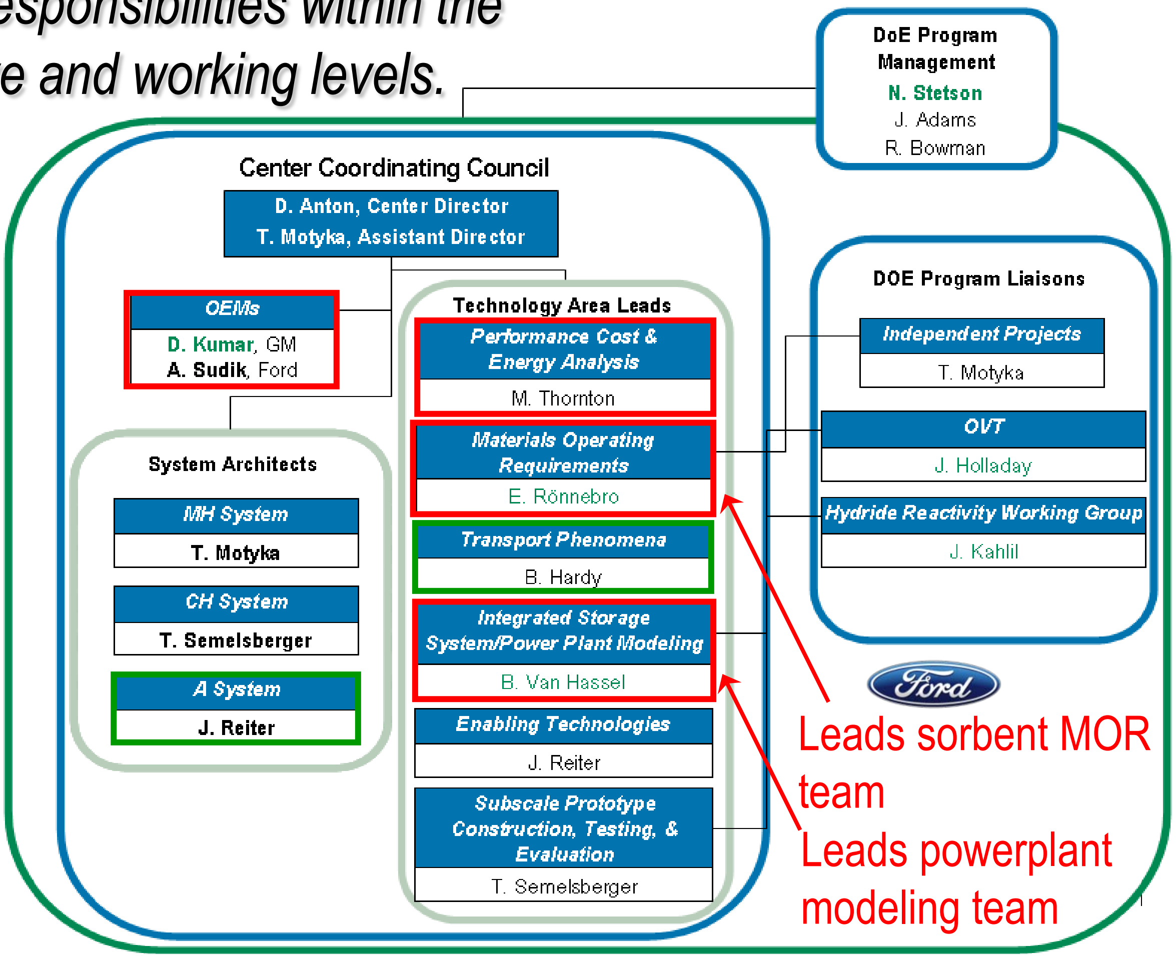


Relevance: Organizational

Project has many roles and responsibilities within the HSECoE at both the executive and working levels.

Key organizational functions:

- As technical contributors, disseminate data & models across the HSECoE
- As team leads, foster inter-partner communication & streamline & align research
- Act as liaisons between the HSECoE and the C&S and Storage Tech. Teams
- Provide an automotive perspective & context



- Core contribution areas of project outcomes [red]
- Ancillary contribution areas of project outcomes [green]

Approach to the Development of Framework Materials (FMs): Research pathway

Project Goal: Devise optimized, system-focused strategies for packing and processing of framework-based hydrogen storage media via determination of processing-structure-properties (PSP) relationships.

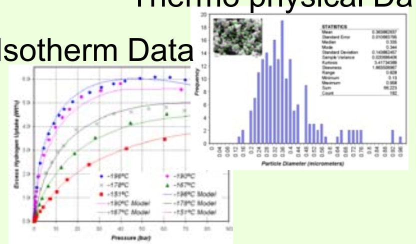
Synthesis of MOFs on kg scale (tunable crystallite sizes)

Basolite Z100H™

Determination of “Engineering” Properties

Thermo physical Data

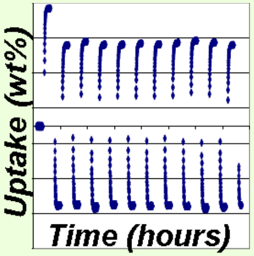
Isotherm Data



Material Processing & Compaction

Optimization

Processing-Property Relationship

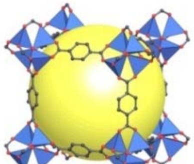


Optimized FM Material Form

Go/No-Go

System Prototype

MOF materials data critically supports the system-level assessment of FMs to meet commercialization targets

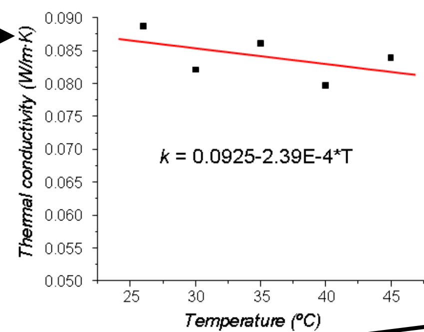


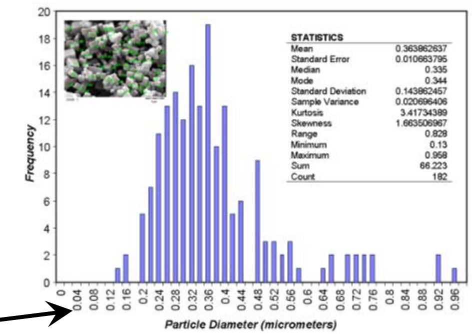
HSECoE selection of MOF-5 (Basolite™ Z100H) is based on materials availability, literature prevalence, & performance (properties among best-in-class)

Progress (Review): Complete engineering property data set for powder MOF-5 determined

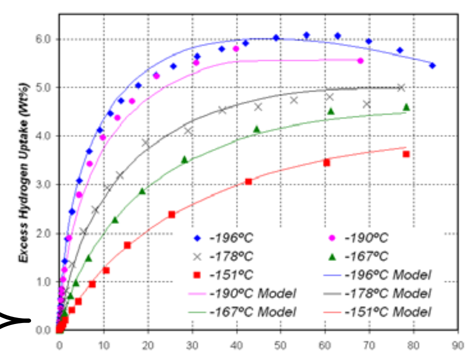
2009/2010: Data set for powder MOF-5 was completed and delivered to sorbent bed (SRNL) & system modeling (GM SRNL) teams.

Thermal Properties	
Thermal Conductivity ($Wm^{-1}K^{-1}$)	0.088
Bulk Thermal Conductivity ($Jmol^{-1}K^{-1}$)	
Wall Thermal Contact Resistance (wt%)	
Heat Capacity ($kJkg^{-1}K^{-1}$)	0.78
Bulk Properties	
✓ Bulk Density (gcm^{-3})	0.13
Skeletal Density (gcm^{-3})	2.03
✓ Specific Surface Area (m^2g^{-1}) Lang. (BET)	3500 (2570)
✓ Micropore Volume (cm^3g^{-1})	1.64
Particle Diameter (μm)	0.36
Total Porosity (%)	92.5
Inter-Particle Porosity (%)	24.6
Intra-Particle Porostiy (%)	67.9
Diffusivity (cm^2s^{-1})	2.4×10^{-5} (77K)
Bed Permeability	





Modified D.-A. Isotherm Parameters	
α ($Jmol^{-1}$)	2490
β ($Jmol^{-1}K^{-1}$)	10.5
n_{max} (wt%)	16.61
P_o (MPa)	296
V_a (mlg^{-1})	1.75



$$n_{ex} = n_{\max} \exp\left(-\left(\frac{RT}{\alpha + \beta T}\right)^2 \ln^2\left(\frac{P_o}{P}\right)\right) - \rho_g V_a$$

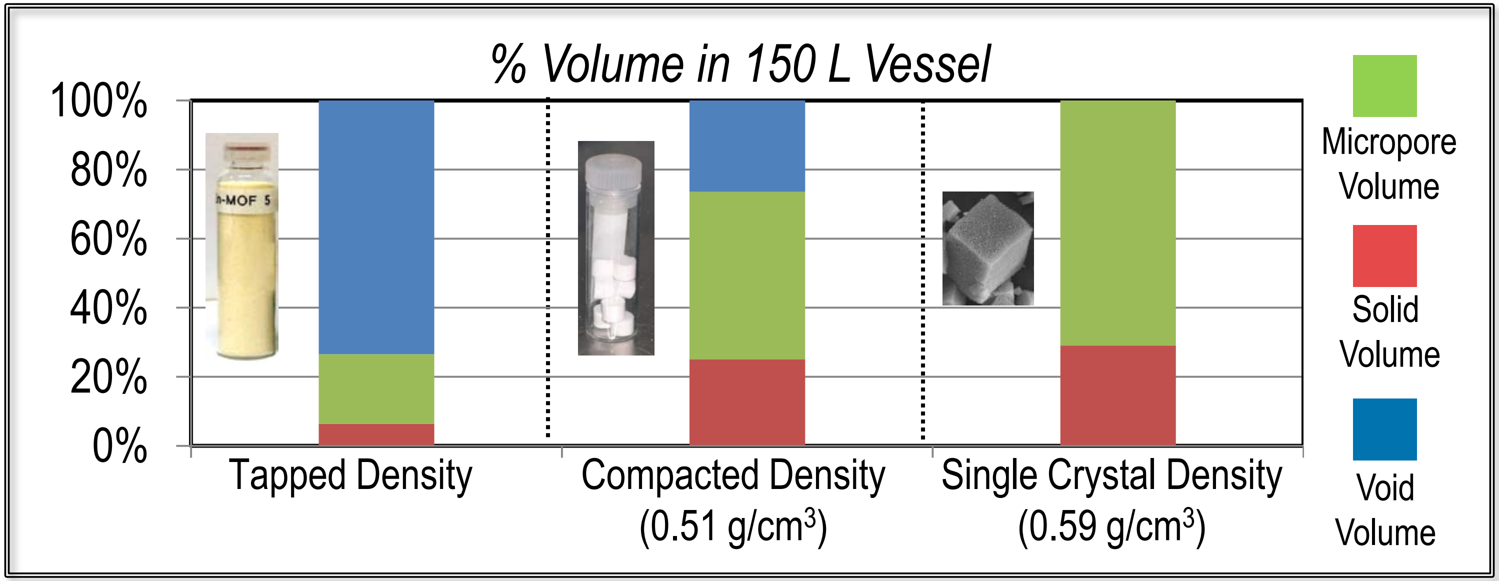
✓ = Data typically available in literature for MOFs

Key gaps for MOF-5 (powder) based on modeling results:

- Volumetric capacity (bulk density)
- Thermal conductivity

Progress: Motivation for compaction

Compacting MOF-5 offers the opportunity to maximize high-density hydrogen sites (i.e. micropore volume) as compared to powder (i.e. for improved volumetric capacity).



Guiding Question:

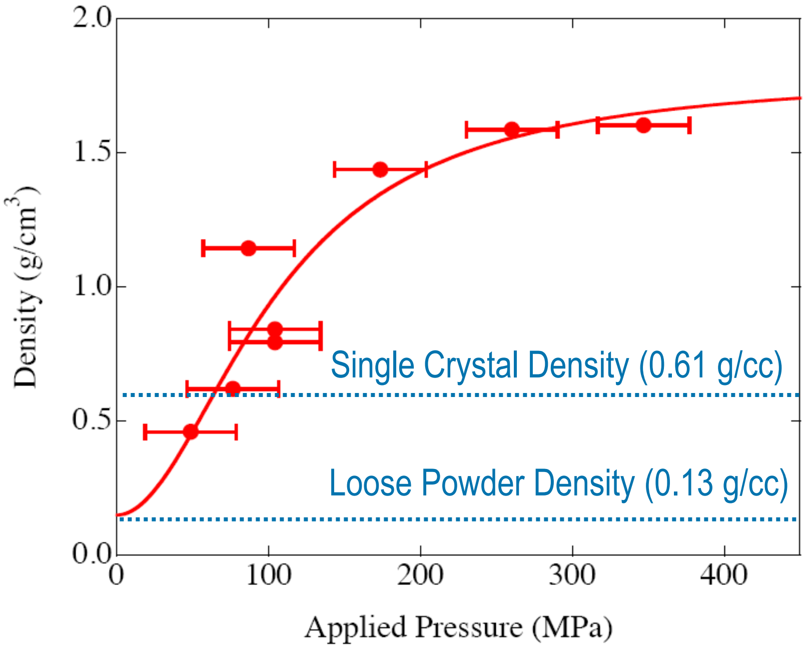
- How (and to what extent) does materials compaction impact other engineering or system properties, for example, surface area, operation conditions (temperature/pressure swings), thermal conductivity, gas permeability, mechanical strength, etc.?

Progress: A series of MOF-5 compacts have been prepared

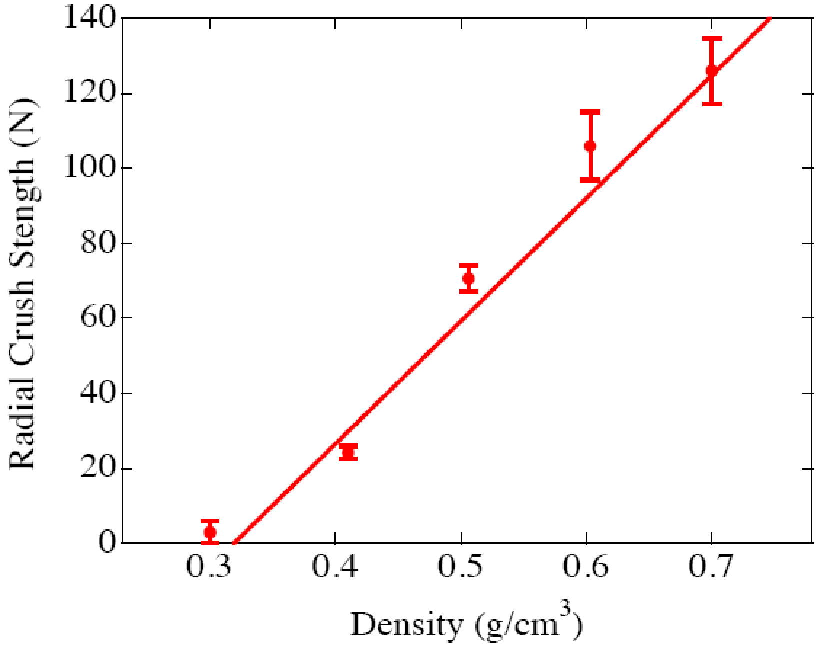
Sample Origin	Density (g/cm^3)	Reference Densities
BASF	0.48	Loose Powder
Ford-UM	0.31	0.13 g/cm^3
Ford-UM	0.51	Single Crystal
Ford-UM	0.70	0.61 g/cm^3
Ford-UM	0.79	

A set of variable-density neat MOF-5 compacts (*diameters = 4.5, 6.35, or 12.7 mm*) have been prepared with the potential to realize >4x volumetric capacities verses powders

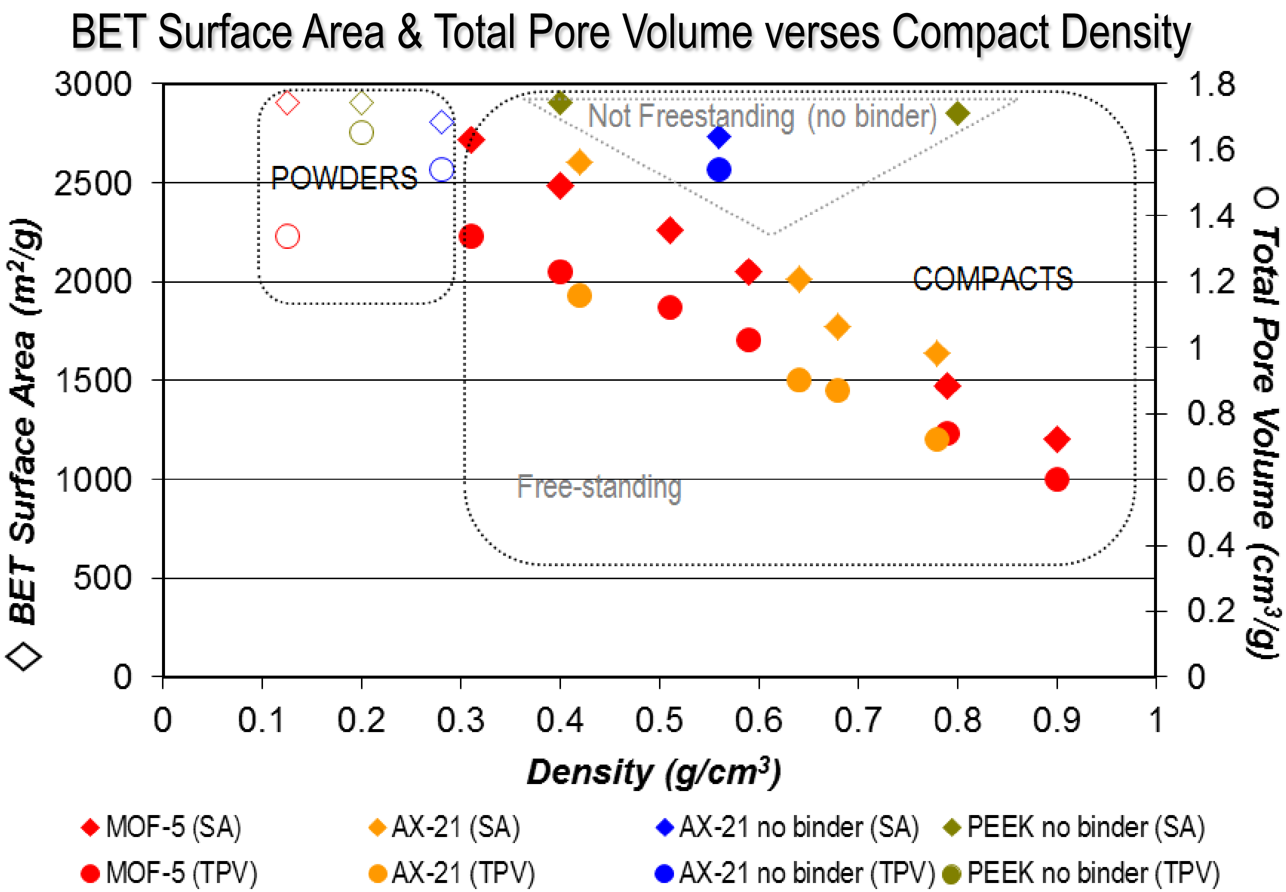
Density vs. Applied Pressure



Crush Strength vs. Density



Progress: Comparative physical property data for MOF-5 compacts



Ref. HSECoE Data:

AX-21 (binder)

AX-21 (no binder)

PEEK (no binder)

For free-standing compacts of MOF-5 & AX-21, BET surface area & total pore volume scale linearly with bulk density. Unlike AX-21 and PEEK, MOF-5 does not require addition of a binder to generate a free-standing pellet.

Progress: Excess gravimetric and volumetric hydrogen uptake data for MOF-5 compacts at 77 K

RESULTS SUMMARY:

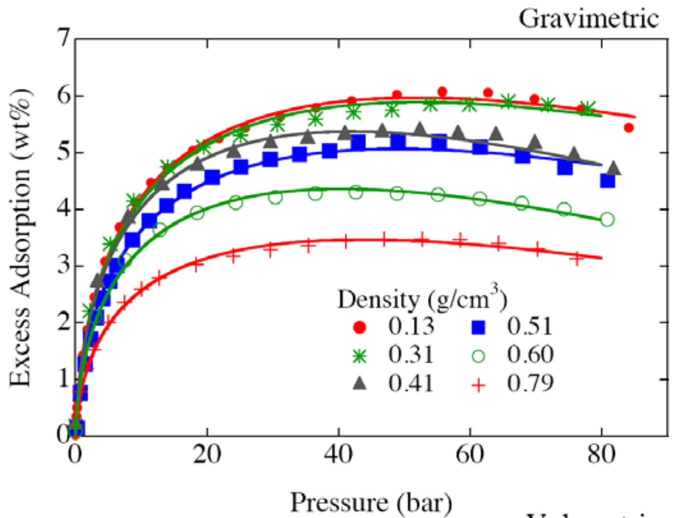
Excess Volumetric Capacity:

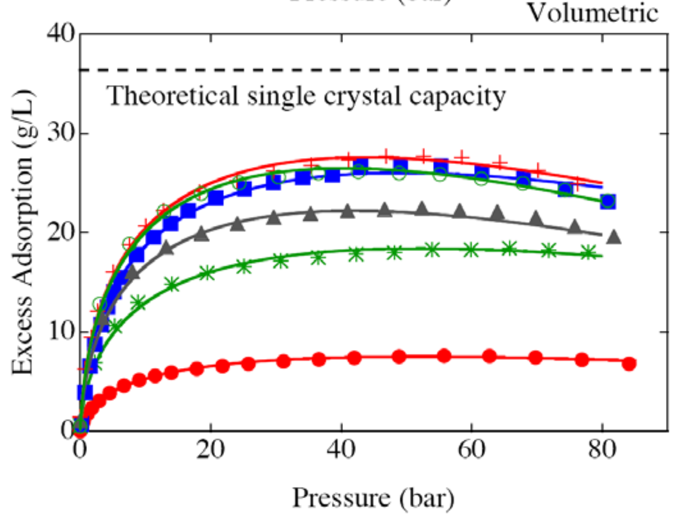
- 4x densification from 0.13 to 0.51 g/cm^3 results in a 4x improvement in excess volumetric capacity (7 g/L for tapped powder to 28 g/L for compact).

Excess Gravimetric Capacity:

- 4x densification from 0.13 to 0.51 g/cm^3 results in only a 10% decrease in excess gravimetric capacity (5.9 wt% for loose powder to 5.2 wt% for compact)

Sample exchange (AX-21 & MOF-5) and validation experiments between UQTR & Ford-UM-BASF underway





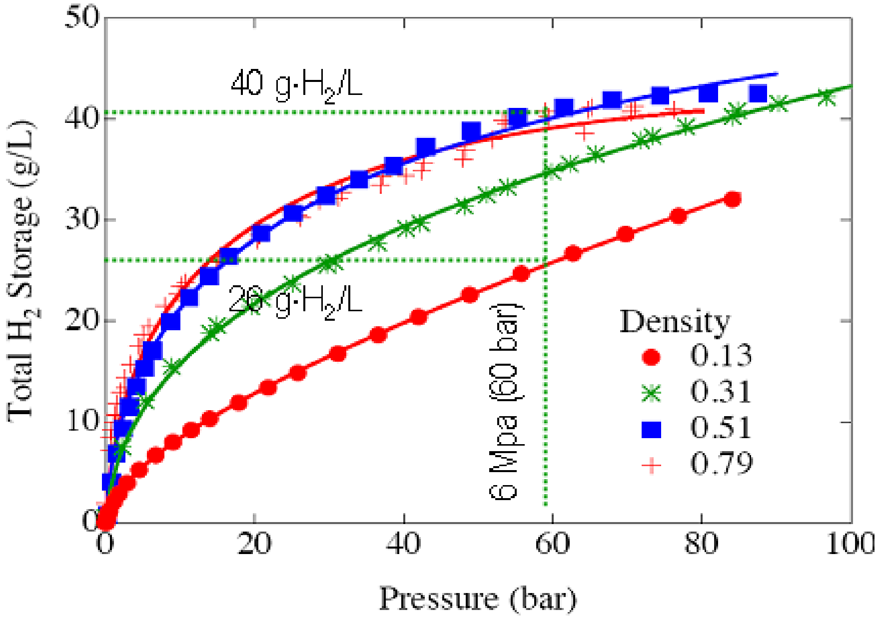
J. Purewal, *et al Int. J. Hydrogen Energy,* **2011, *Accepted.***

Progress: Total volumetric hydrogen uptake and data summary for compacted MOF-5 (ρ = 0.51 g/cc)

	COMPACTED MOF-5 (0.51 g/cc)
Thermal Properties	
Thermal Conductivity ($Wm^{-1}K^{-1}$)	0.088 (neat)
Bulk Thermal Conductivity ($Jmol^{-1}K^{-1}$)	
Wall Thermal Contact Resistance (wt%)	
Heat Capacity ($kJkg^{-1}K^{-1}$)	0.76
Bulk Properties	
Bulk Density (gcm^{-3})	0.51
Skeletal Density (gcm^{-3})	
Specific Surface Area Lang. (BET) (m^2g^{-1})	2995 (2260)
Micropore Volume (cm^3g^{-1})	0.872
Particle Diameter (µm)	0.36
Total Porosity (%)	
Inter-Particle Porosity (%)	
Intra-Particle Porostiy (%)	
Diffusivity (cm^2s^{-1})	
Bed Permeability	

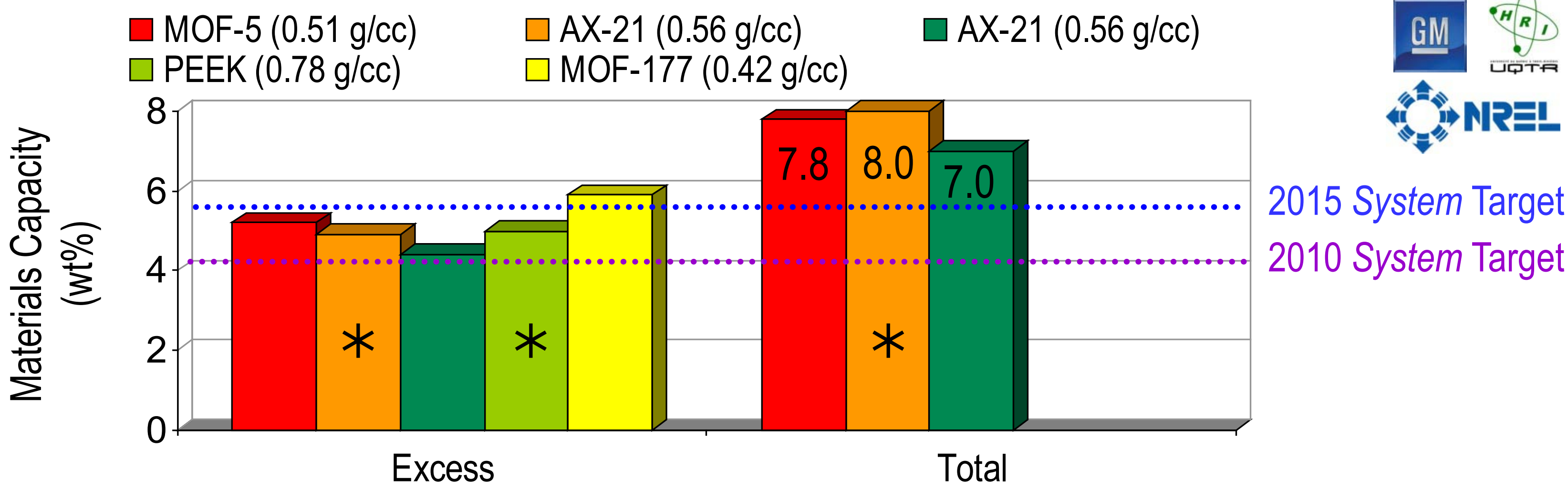
Modified D.-A. Isotherm Parameters	
α ($Jmol^{-1}$)	2430
β ($Jmol^{-1}K^{-1}$)	11.6
n_{max} (wt%)	14.98
P_o (MPa)	357
V_a (mlg^{-1})	1.57

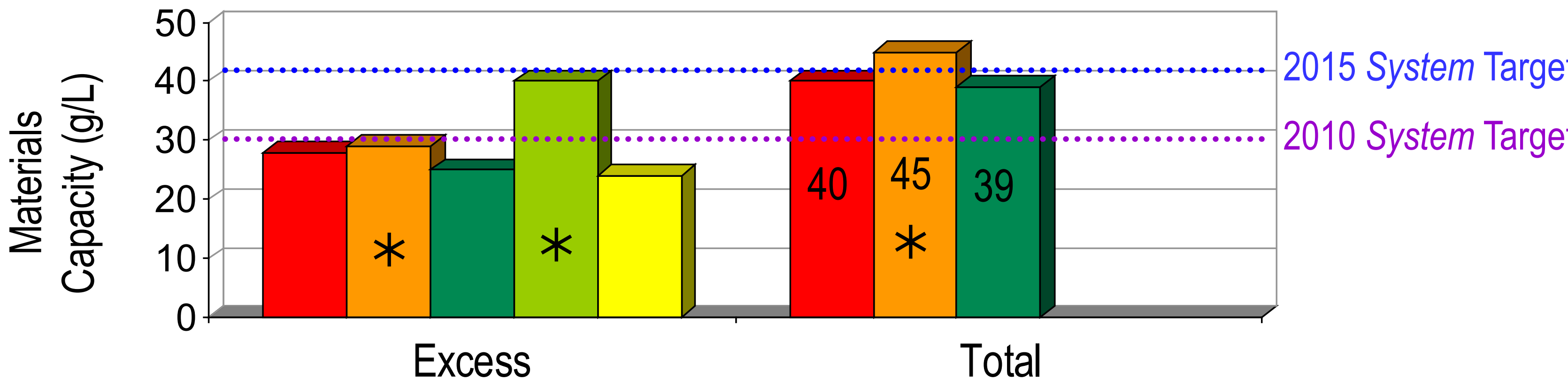
Total Hydrogen Uptake for MOF-5 at 77 K



- Total *materials-based* volumetric capacity for 0.51 g/cm^3 MOF-5 compact at 60 bar & 77 K is 40 g/L.
- A 1.5 x improvement in total volumetric capacity practically achieved for MOF-5 compact as compared to powder (0.13 g/cm^3).

Comparative Summary: Materials-based uptakes for compacted sorbents at 77 K & 60 bar

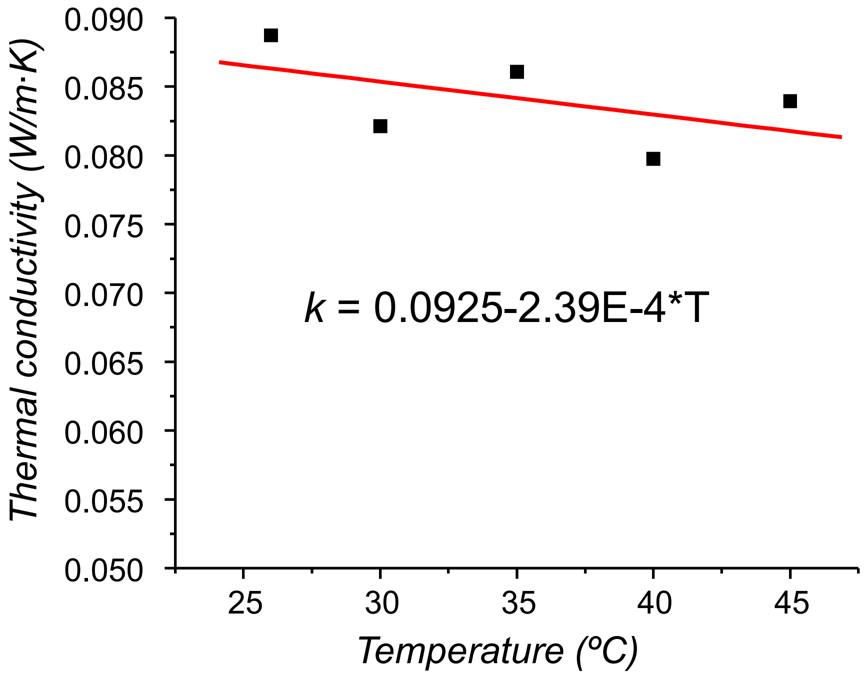




* = Data based on pellet in press vessel (i.e. freestanding compacts not yet obtained)

MOF-177 data from R. Zacharia et al, *J. Mater. Chem.* 2010, 20, 2145.

Progress: Thermal conductivity for *neat* MOF-5 characterized



$$k = \alpha \times \rho \times c_p$$

- Sample mass = 0.1109 g
- Sample volume = 0.2838 cm^3
- Sample density=0.39 g/cm^3

⇒ ***k* (25ºC) = 0.088 W/m·K**

Ref: *k* (25ºC) = 0.3 W/m·K SX MOF-5

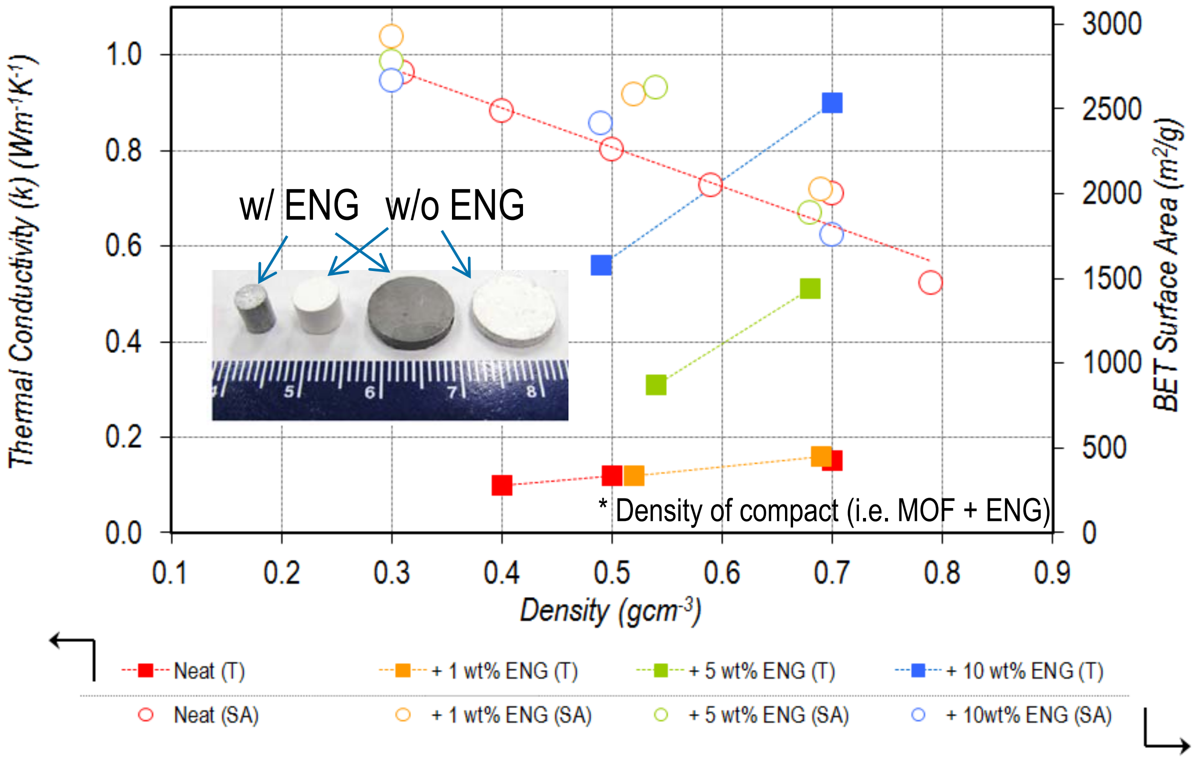
Huang *et al. Int. J. Heat & Mass Trans.* 2007, 50, 405

Conclusions:

- Thermal conductivity of MOF-5 pellet (~0.4 g/cc) is 1/3 that of the single crystal.
- Single crystal data does not show variation in *k* at T>-200ºC.
- No significant difference in thermal conductivities for varying density pellets (i.e. 0.3 to 0.8 g/cc).
- Need to improve *k* up to an order of magnitude for more desirable system heat transfer.

Progress on Properties for Compacted Sorbents: Thermal conductivity for *Enhanced* MOF-5

Thermal conductivity at 25ºC for MOF-5 as a function of density and amount of expanded natural graphite (ENG) [*Preliminary Data]*



- Addition of ENG is effective for improving thermal conductivity of MOF-5 5x for 0.5 g/cm^3 compacts from 0.1 W/m·K (neat) to 0.56 W/m·K (10 wt% ENG)
- Addition of ENG does not appear to affect BET surface area (i.e. can improve thermal conductivity without degrading surface area)

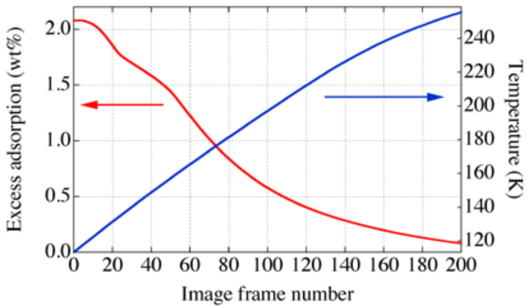
Progress: Neutron imaging for model validation

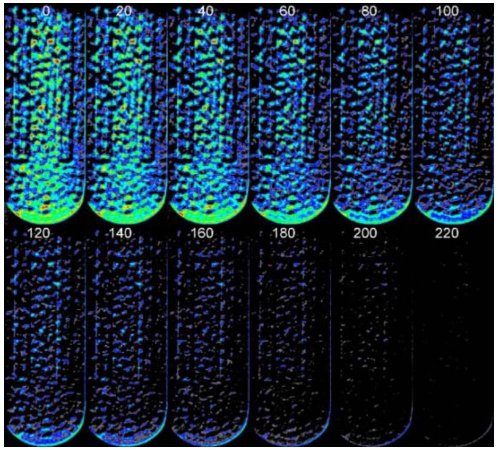
First *in situ* characterization (via neutron imaging) of hydrogen dynamics in a cryogenic storage vessel. Experiments on MOF-5 pellets (22.2 g, ρ = 0.5 g/cc).

- Adsorption and desorption experiments performed with Sievert's-type instrument and cryostat with P and T data logged
- Goal is to characterize transient dynamics associated with recharge and discharge as a function of rate and degree of fill.
- Data from this (and future imaging) experiments will be used for model validation

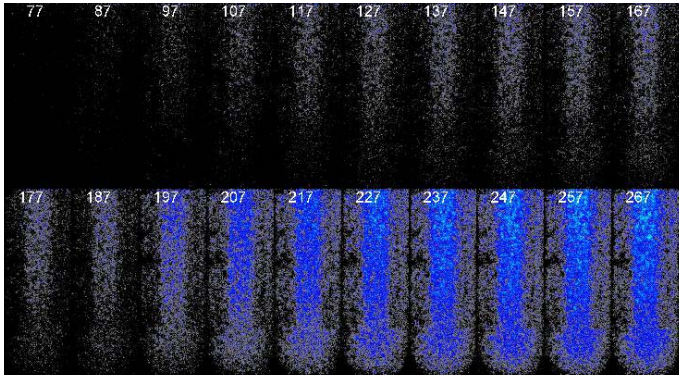
Data acquired at NIST Center for Neutron Research

Thermally programmed H_2 desorption (p_{int} = ~*3 bar*)





Isothermal H_2 adsorption (70 K, p = ~*10 bar*)



HSECoE

Future Work: Technical gaps & near-term plans

H_2 Capacity

- Validate model parameters at higher pressure (i.e. up to 200 bar).
- Improve volumetric capacity and thermal conductivity while maintaining other desirable properties (grav. capacity, gas permeability, etc.).
- Optimization: Collaboratively with modeling, determine best ratio between excess & free gas.

Thermal Conductivity

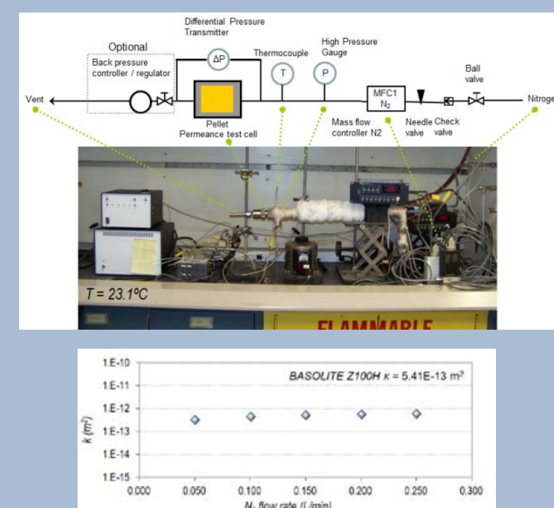
- Continue to assess impact of conductivity aids on other properties (grav. capacity, etc.)
- Identify correlation between densification conditions, microstructure, and conductivity
- Optimization: Collaboratively with modeling, determine required value to yield desired system performance.

H_2 Transport in Compacts

- Establish relationship between density and gas transport
- Optimization: Collaboratively with modeling, determine required value to optimize compact dimensions and shape

Model Validation

- Continue to support the experimental validation of sorbent bed and system models

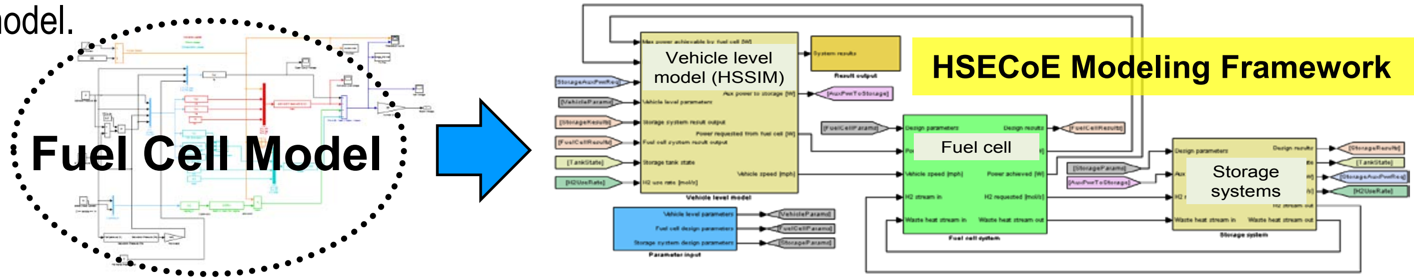


Preliminary gas permeability for MOF-5

Progress: Summary of Tasks 1 and 2

Progress

- Evaluated and constructed baseline fuel cell model to support the interaction with the vehicle and hydrogen storage system model.



- Completed classification of the 2010 and 2015 DOE hydrogen storage targets for optimization and tradeoff analysis amongst the storage system concepts.
- Developed a common set of drive-cycles for vehicle simulation performance evaluations.
- Supported the manufacturing and cost analysis technology team in the evaluation of the initial cost assessments for the hydrogen storage systems.
- Assisted in the approach of using the component library to decompose the key system elements to evaluate the cost drivers and establishing cost sensitivity items for future trade-offs.

Future Work

- Additional development of the waste heat interface and polarization effects at lower ambient temperature will be integrated in the fuel cell model to allow for usage by the hydrogen storage system models.
- The universal modeling framework will continue to be refined for the purpose of simulating the various storage systems and developing the required system/material attributes needed to satisfy the targets.
- Further analysis and benchmarking of the component library with other analysis models will be progressed for decomposing the storage system assessments into the key cost drivers.

Progress: Classification of DOE H_2 Storage Targets

Led OEM 'assignment' [GM CHRYSLER Ford] for classifying DOE H_2 Storage Targets in order to provide guidance for system design trade-offs

Motivation for prioritization of hydrogen storage technical targets

- All targets must still be met simultaneously
- Benefits to HSECoE
  - Guides HSECoE Milestone criteria. Ex. 4 of 2010 targets to be met at 100% level and remainder at $\geq$40% level
- Benefits beyond HSECoE
  - Identifies 'performance must-have' vs. 'design choice' target levels
  - Guides design trade-offs to optimize overall system/vehicle performance to meet customer expectations

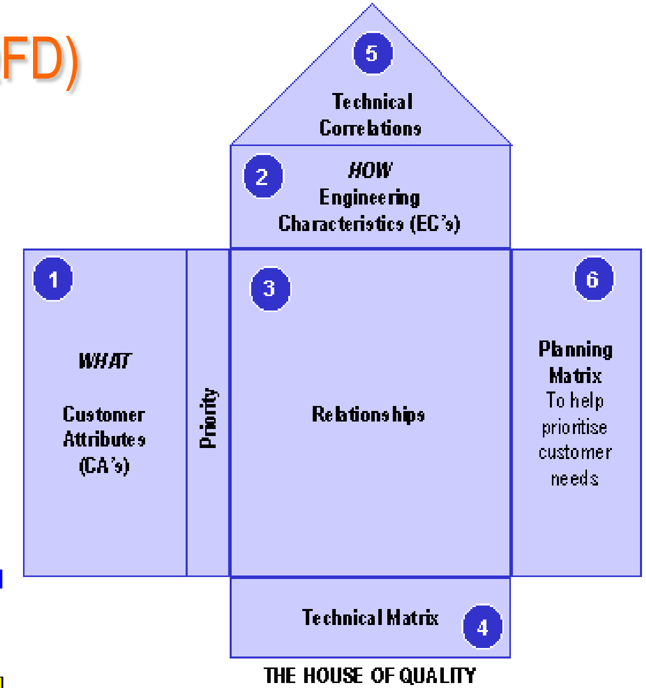
Table 2 Technical Targets: Onboard Hydrogen Storage Systems[f]

Storage Parameter	Units	2010	2015	Ultimate
System Gravimetric Capacity: Usable, specific-energy from H_2 (net useful energy/max system mass)[a]	kWh/kg (kg H_2/kg system)	1.5 (0.045)	1.8 (0.055)	2.5 (0.075)
System Volumetric Capacity: Usable energy density from H_2 (net useful energy/max system volume)	kWh/L (kg H_2/L system)	0.9 (0.028)	1.3 (0.040)	2.3 (0.070)
Storage system cost[b] (& fuel cost)[c]	\$/kWh net (\$/kg H_2) \$/gge at pump	TBD (TBD) 3-7	TBD (TBD) 2-6	TBD (TBD) 2-3
Durability/Operability				
• Operating ambient temperature[d]	°C	-30/50 (sun)	-40/60 (sun)	-40/60 (sun)
• Min/max delivery temperature	°C	-40/85	-40/85	-40/85
• Operational cycle life (1/4 tank to full)[e]	Cycles	1000	1500	1500
• Min delivery pressure from storage system; FC= fuel cell, ICE= internal combustion engine	bar (abs)	5FC/35 ICE	5FC/35 ICE	3FC/35 ICE
• Max delivery pressure from storage system[f]	bar (abs)	12	12	12
• Onboard Efficiency	%	90%	90%	90%
• "Well" to Powerplant Efficiency	%	60%	60%	60%
Charging/discharging Rates				
• System fill time (for 5-kg H_2)	min (Kg H_2/min)	4.2 min (1.2 kg/min)	3.3 min (1.5 kg/min)	2.5 min (2.0 kg/min)
• Minimum full flow rate	(g/s)/kW	0.02	0.02	0.02
• Start time to full flow (20°C)[g]	s	5	5	5
• Start time to full flow (-20°C)[g]	s	15	15	15
• Transient response 10%-90% and 90% -0%[h]	s	0.75	0.75	0.75
Fuel Purity (H_2 from storage)[i]	% H_2	SAE J2719 and ISO/PDTS 14687-2 (99.97% dry basis)		
Environmental Health & Safety				
• Permeation & leakage[j]	Scc/h	Meets or exceeds applicable standards		
• Toxicity	-			
• Safety	-			
• Loss of useable H_2[k]	(g/h)/kg H_2 stored	0.1	0.05	0.05

Target Classification: Approach

General Approach: Quality Function Deployment (QFD)

1. List Customer Attributes (What's)
   - Establish Customer Priorities
2. List Technical Requirements (How's)
3. Develop Relationship (What's & How's)

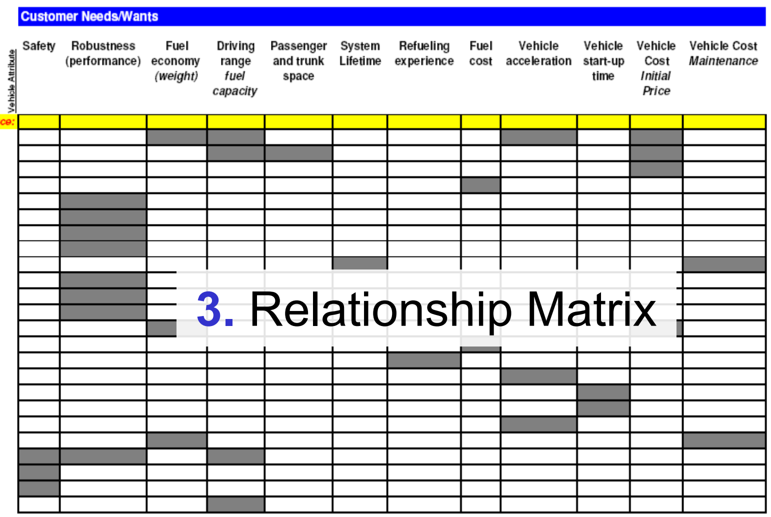


2. Technical Targets

HSECoE System Target Priority

Parameter	Units	Target 2010
Gravimetric Density	($Kg\ H_2/Kg$ system)	0.045
Volumetric Density	($Kg\ H_2$/liter)	0.028
System Cost	($/KWh net)	TBD
Fuel Cost	($/gge)	TBD
Minimum Operating Temperature	(°C)	-30
Maximum Operating Temperature	(°C)	50
Min. Delivery Temperature	(°C)	-40
Max Delivery Temperature	(°C)	85
Cycle Life (1/4 - full)	(N)	1000
Min. Delivery Pressure (PEMFC)	(bar)	5
Min. Delivery Pressure (ICE)	(bar)	35
Max. Delivery Pressure	(bar)	12
On Board Efficiency	(%)	90%
Wells to Power Plant Efficency	(%)	60%
Fill Time (5Kg H_2)	(min.)	4.2
Minimum Full Flow Rate	([g/s]/KW)	0.02
Start Time to Full Flow (20°C)	(sec.)	5
Start Time to Full Flow (-20°C)	(sec.)	15
Transient Response	(sec.)	0.75
Fuel Purity	(%)	99.97%
Permiation & Leakage*		1
Toxicity*		1
Safety*		1
Loss of Useable H_2	([g/hr]/$Kg\ H_2$)	0.1

1. Customer Attributes



Qualitative mapping of customer attributes and technical targets

Target Classification: Ranking scheme

Method for establishing customer priority

- Using AHP along with Kano Model, Sales Data, and Survey Data
- Ask: How important is the vehicle attribute to the customer's purchasing decision?

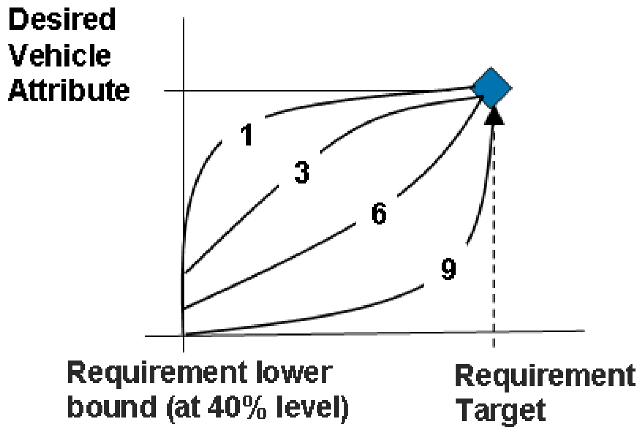
- The Analytic Hierarchy Process (AHP) is a decision-making method for prioritizing multiple criteria / objectives.
- The decision makers are guided through a series of pair-wise comparison judgments to express the relative strength or impact of one element verses another

Verbal judgment	Numerical Judgment
• Extremely important	9
• Very Strongly important	7
• Strongly important	5
• Moderately important	3
• Equally to moderately more important	2
• Equally important	1

	QUALITY	COST	SERVICE	DELIVERY
QUALITY	1	2/1	4/1	3/1
COST	1/2	1	3/1	3/1
SERVICE	1/4	1/3	1	2/1
DELIVERY	1/3	1/3	1/2	1

Method for rating cause-effect relationship

- Using Minitab weight / sensitivity analysis approach
- Ask: How much would a change in the requirement target effect the vehicle attribute?

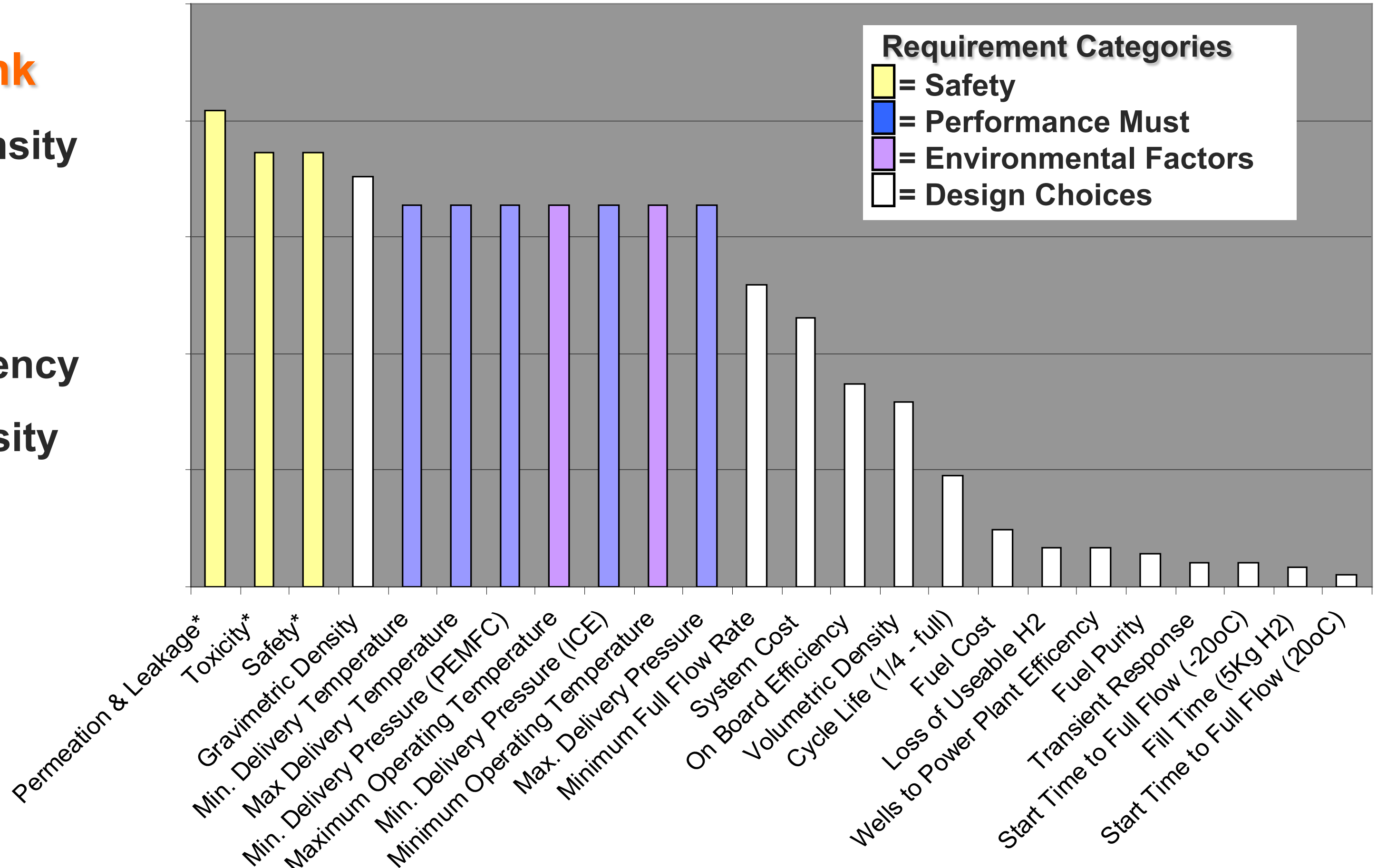


Relationship Ratings		
	9 =	High Effect on Customer/Vehicle Attribute
	6 =	Medium-High Effect on Customer/Vehicle Attribute
	3 =	Medium-Low Effect on Customer/Vehicle Attribute
	1 =	Low Effect on Customer/Vehicle Attribute

Target Classification: Hydrogen Storage System 2010 Results

2010 Target Rank

1. Gravimetric Density
2. Min. Full Flow
3. System Cost
4. On-board Efficiency
5. Volumetric Density
6. Cycle Life



<u>Disclaimer for the approach</u>

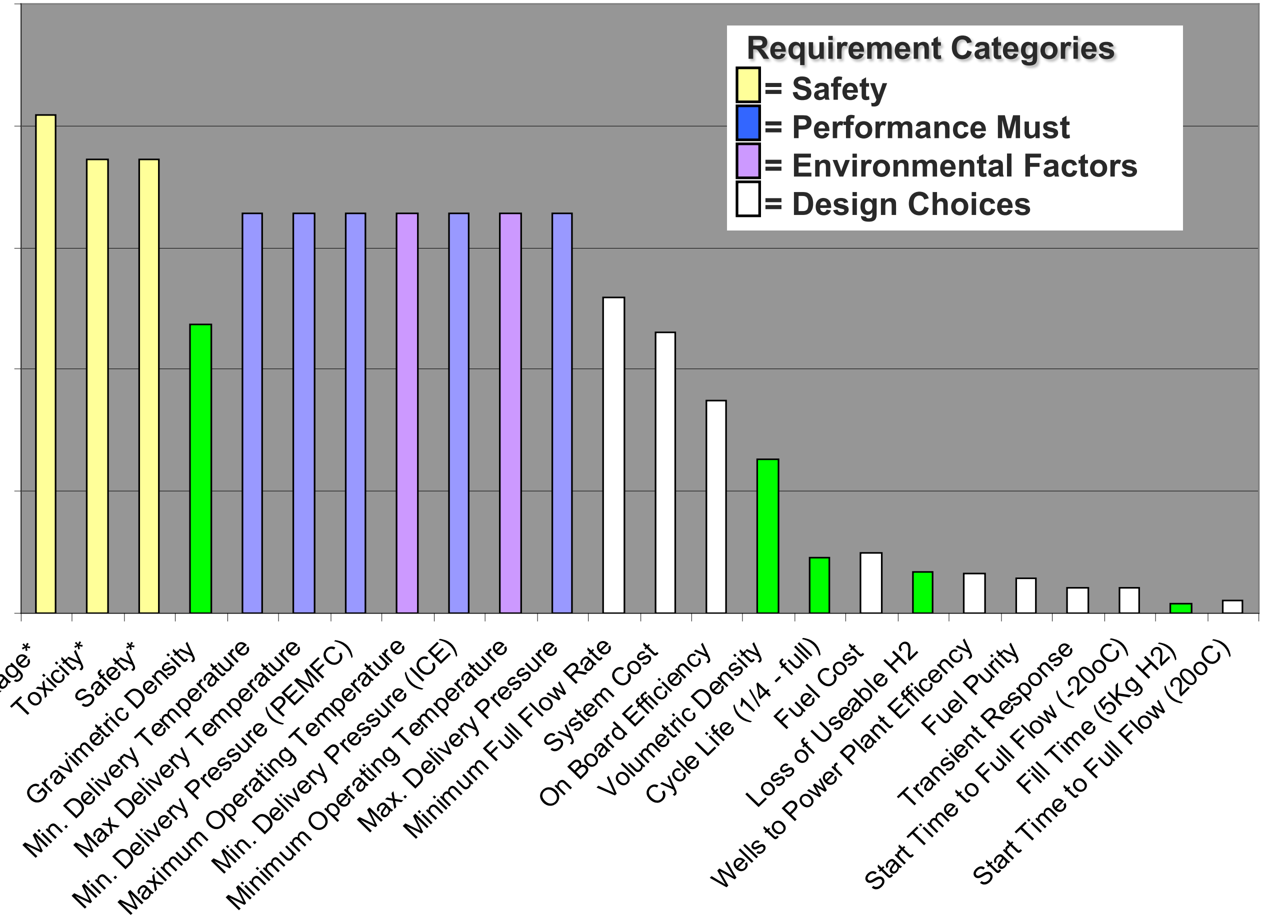
1. All targets are important and must be achieved.
2. Input from OEM individuals (not company perspectives) within HSECoE along with FreedomCAR
3. Assessment is only valid based on a **<u>40% lower limit of the 2010 target values</u>** when assessing the rank
4. Guidance provided for HSECoE system architects to determine research and development focus

Target Classification: Hydrogen Storage System 2015 Results

2015 Target Priority

1. Min. Full Flow
2. Gravimetric Density
3. System Cost
4. On-board Efficiency
5. Volumetric Density

NOTE: Green bars indicate the change in the rankings between the 2010 and 2015 target classification



Disclaimer for the approach

1. All targets are important and must be achieved.
2. Input from OEM individuals (not company perspectives) within HSECoE along with FreedomCAR
3. Assessment is only valid based on a **50% lower limit of the 2015 target values** when assessing the rank
4. Guidance provided for HSECoE system architects to determine research and development focus

Summary

Task 1: Vehicle parameter modeling.

- Determined MATLAB/Simulink as the common platform for HSECoE simulation models.
- Led the development of a common set of drive-cycles for vehicle performance evaluations.
- Led the classification of the 2010 and 2015 DOE hydrogen storage targets for optimization and tradeoff analysis amongst the storage system concepts.

Task 2: Manufacturing cost modeling.

- Established initial phase of cost analysis through the development of a component cost matrix.
- Supported the manufacturing and cost analysis technology team in the evaluation of the initial cost assessments for the hydrogen storage systems.

Task 3: Assessment of framework-based hydrogen storage media.

- Developed processing-property relationships for *neat, compacted* MOF-5 including impact of compact density on surface area, pore volume, hydrogen uptake, and thermal conductivity
- Collected, compiled, and communicated all requisite materials engineering data for *compacted* MOF-5 including isotherm parameters, thermal properties, and bulk properties.
- Initiated studies involving addition of thermal conductivity aids to MOF-5 compacts
- Designed, fabricated, and conducted neutron imaging studies on MOF-filled hydrogen storage module to be used for model validation.

APPENDIX

Collaborations

- BASF-SE (industrial subcontractor): framework materials synthesis, processing, and characterization
- University of Michigan (academic subcontractor): framework materials processing-property characterization
- GM (industrial collaborator): team member for sorbent materials operating parameters, sorbent system modeling, system/vehicle-level modeling
- Universite du Quebec a Trois-Rivieres (university collaborator): team member for sorbent materials
- NREL (federal lab collaborator): team leader for vehicle level modeling and liaison to sorbent materials CoE
- UTRC (industrial collaborator): team member for structured materials and on-board system modeling
- PNNL (federal lab collaborator): team lead for cost modeling and materials operating requirements
- JPL (federal lab collaborator): sorbent system architect lead
- SRNL (federal lab collaborator): team lead for sorbent (bed) transport phenomena models and center management

Interactions include monthly team meetings (sorbent system, material operating req., system modeling), regular data and information exchanges, and four HSECoE face-to-face meetings