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

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Overview

Timeline

- Project Start: February 2009
- Project End: June 2014
- Percent Complete: 55%

Budget

- Total Project Funding:
  - DOE Share: $2,140K
  - Contractor Share: $643K
- Funding for FY11: $240K
- Funding for FY12: $400K

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 the Overall HSECoE Mission

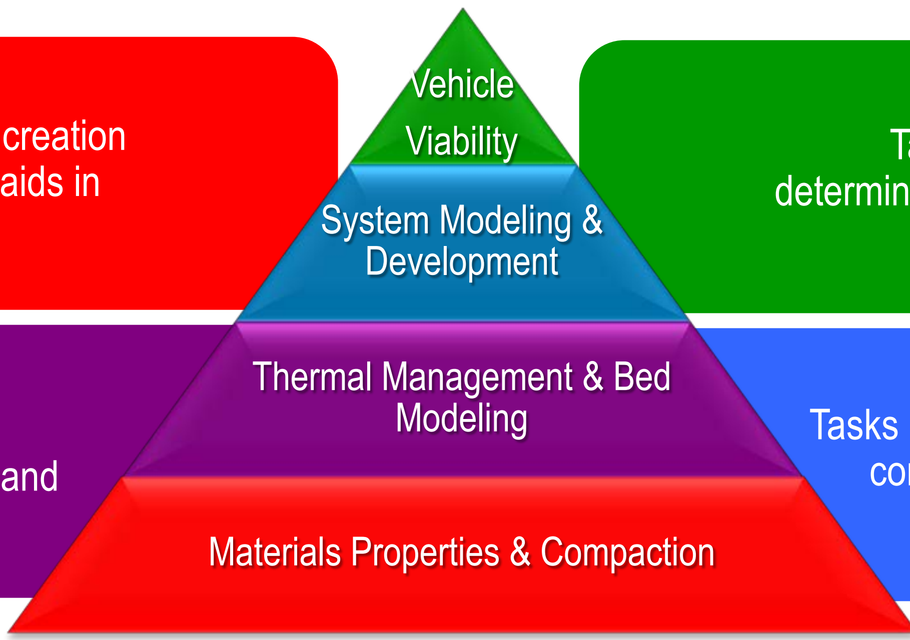
Task 1: Develop dynamic vehicle parameter model that interfaces with diverse storage system concepts
Task 2: Development of robust cost projections for storage system concepts
Task 3: Devise and develop system-focused strategies for processing and packing framework-based sorbent hydrogen storage media

Materials Properties

Task 3 data supports the creation of sorbent bed models & aids in tradeoffs analyses

Vehicle Viability

Tasks 1 & 2 models support determination of overall vehicle cost and performance



Bed Modeling

Task 3 data supports the validation of sorbent bed and system models

System Modeling

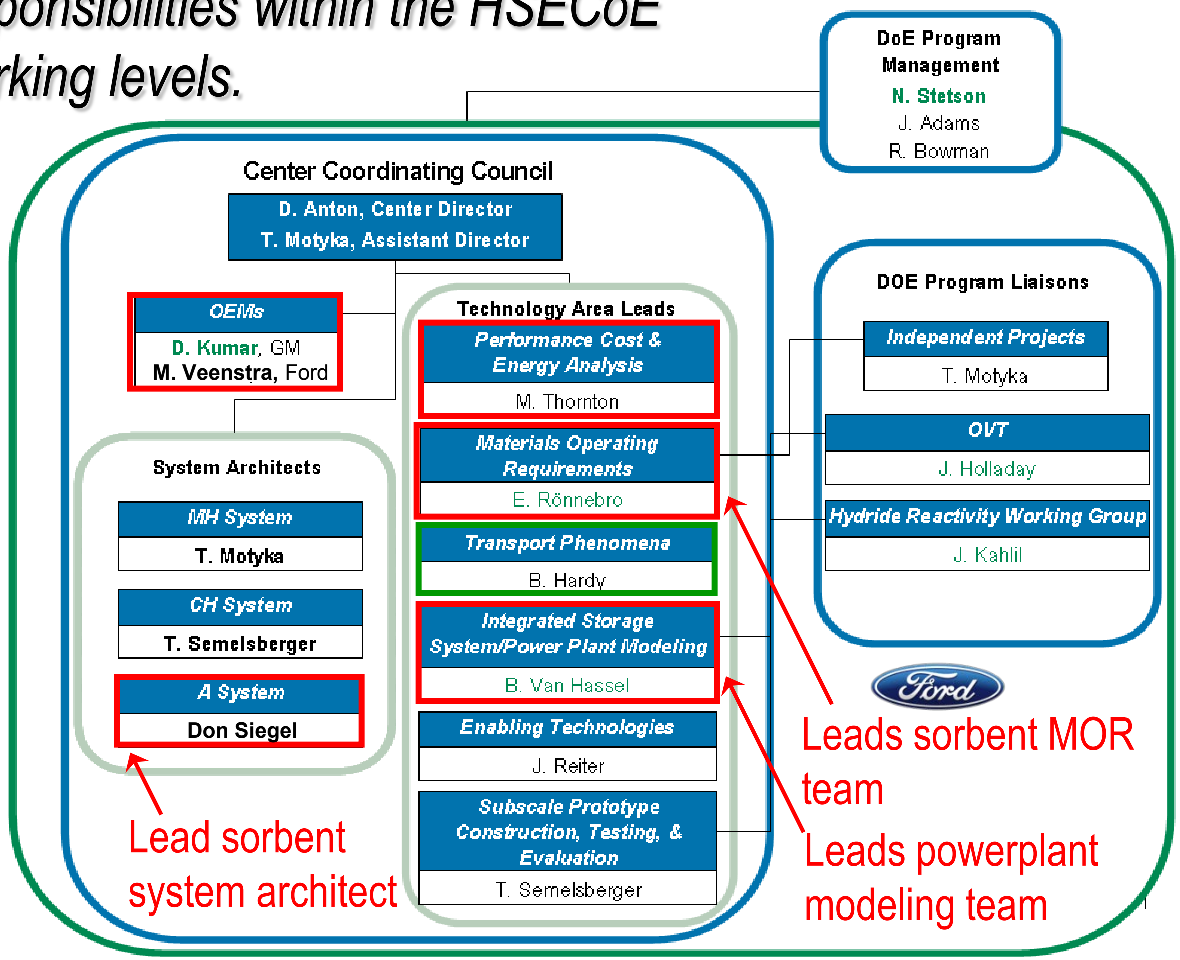
Tasks 1 & 2 models enable storage concepts to be exercised at the real-world vehicle level

Relevance: Organizational

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

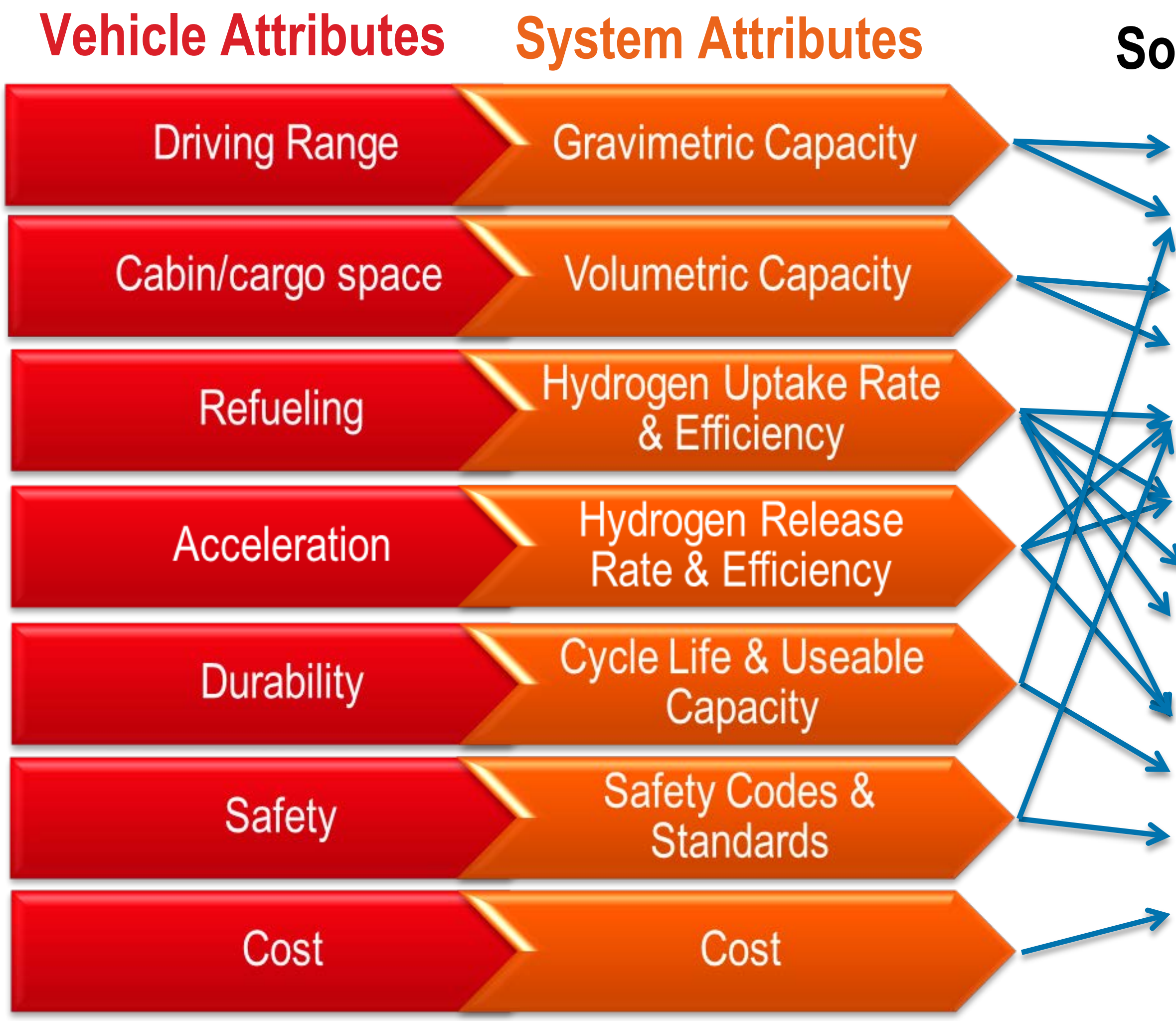
Key organizational functions:

- 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: Identify Material Performance Gaps



Sorbent Materials Properties

- Surface Area ✓
- Isotherm Parameters
- Bulk Density ✓
- Pore Volume ✓
- Reaction (binding) energy
- Kinetics
- Permeability
- Particle Size
- Thermal Conductivity
- Crush Strength
- Hazard Class
- Cost (process, raw materials)

✓ = Data typically available in literature for sorbents

Approach: Develop Processing-Structure-Property Relationships

Sorbent Materials Objective: Devise optimized, system-focused strategies for packing and processing of sorbent hydrogen storage media via determination of processing-structure-properties relationships.

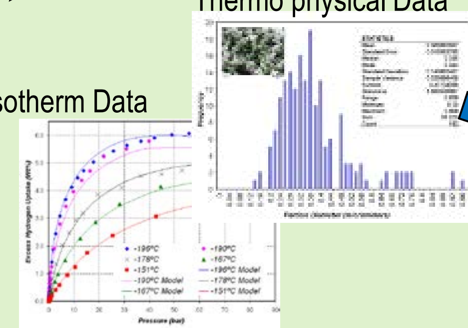
Synthesis of sorbents on kg scale

MOF-5

Determination of “Engineering” Properties

Thermo physical Data

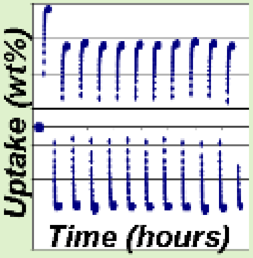
Isotherm Data



Material Processing, Optimization & Compaction

feedback

Processing-Property Relationship



Optimized FM Material Form

Go/No-Go

System Prototype

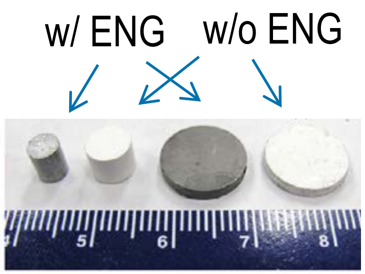
Sorbent MOR critically supports the system-level assessment and feasibility of sorbent materials to meet (DOE) commercialization targets

Approach: Focus on the Critical Technical Challenges for the MOF-5 system

- Modeling data (SRNL, GM) for projected powder MOF-5 system reveals two primary material property gaps:

1. Volumetric Capacity

Strategy: Material densification from 0.13 g/cc (tapped density) to 0.3 to 0.5 g/cc.
[Note: Single crystal density is 0.6 g/cc]



2. Thermal Conductivity

Strategy: Addition of thermal conductivity aid, expanded natural graphite (ENG), up to 10 wt.% loading.

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

Progress: MOF-5 Material Characterization

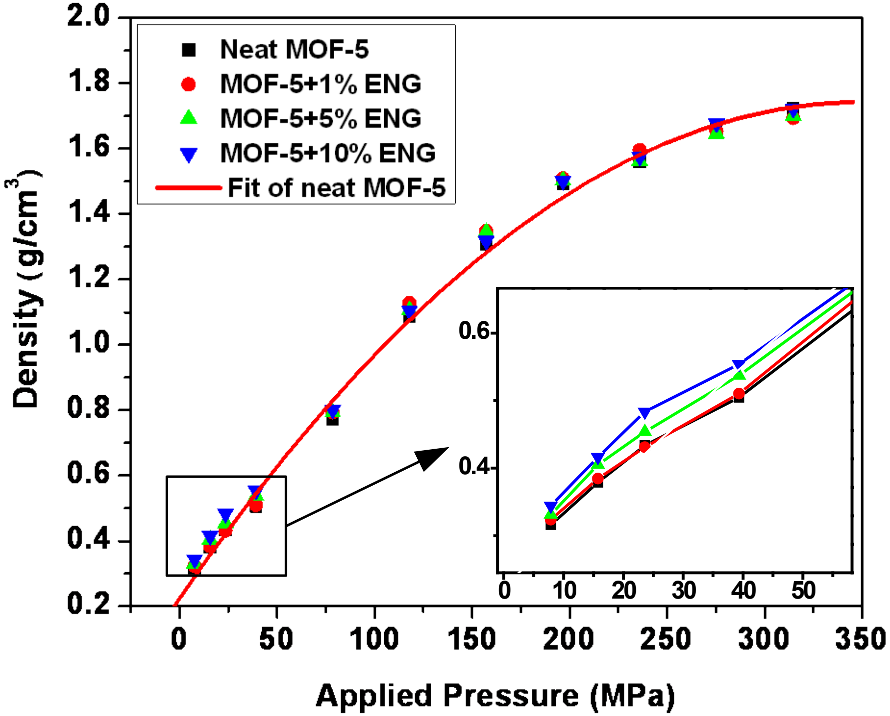
- Diverse engineering property data for MOF-5 complete (see below)
- Similar engineering property data for activated carbon is limited due to current densification challenges (i.e. compaction process conditions & binder quantities)

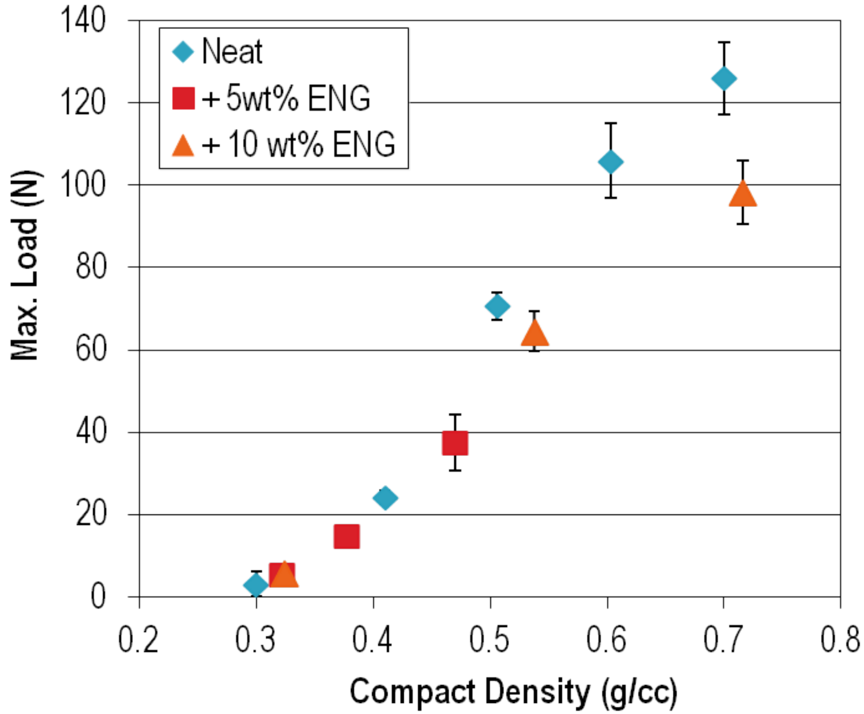
Focus Q1 CY2012 **Focus CY2011**

Material	*Bulk Density*	*TC Enhancer*	*D-A Parameters*	*Permeability*	*Thermal Conductivity*	*Heat Capacity*	*Effective Kinetics*	*Thermal Contact Resistance*	*BET Surface Area*	*Total or Micropore Volume*	*Mechanical Strength*	*Framework Density*
MOF-5	Powder	None	Complete	N/A	N/A	Complete	Not Started	Not Started	Complete	Complete	N/A	Complete
MOF-5	Medium	None	Complete	In Progress	Complete	Complete	Not Started	Not Started	Complete	Complete	Complete	In Progress
MOF-5	Medium	Medium	Complete	Not Started	Complete	Complete	Not Started	Not Started	Complete	Complete	Complete	Not Started
MOF-5	Medium	High	Complete	Not Started	Complete	Complete	Not Started	Not Started	Complete	Complete	Complete	Not Started
MOF-5	High	None	Complete	In Progress	Complete	Complete	Not Started	Not Started	Complete	Complete	Complete	In Progress
MOF-5	High	Medium	Complete	Not Started	Complete	Complete	Not Started	Not Started	Complete	Complete	Complete	Not Started
MOF-5	High	High	Complete	Not Started	Complete	Complete	Not Started	Not Started	Complete	Complete	Complete	Not Started

Notes:
- Bulk Density: High = 0.5 g/cc, Medium = 0.3 g/cc
- TC Enhancer: High = 10 wt% ENG, Medium = 5 wt% ENG
- D-A Parameters: Based on at least 3 isotherms including 77, 200, and 298 K
- Thermal Conductivity: 25 to 65ºC data [Ford] and select data to -270ºC [GM]
- Permeability: Initially limited to room-temperature and He gas.

Progress: Mechanical Strength Data for MOF-5

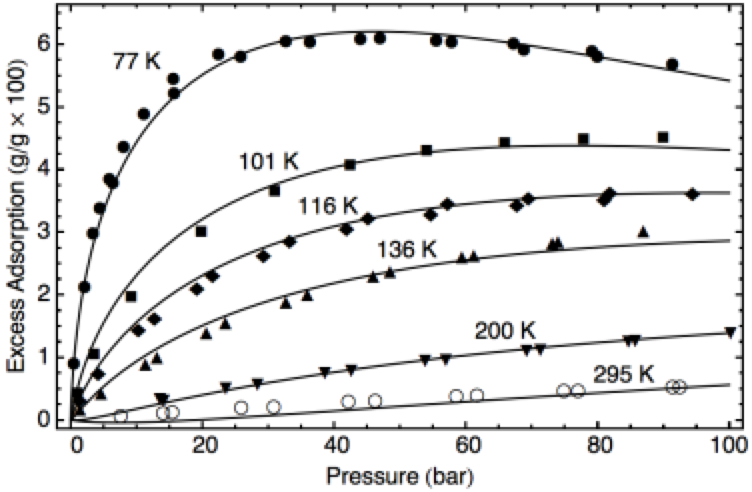




- **Applied pressure verses density curves for all MOF-5/ENG composites have been generated.**
- **Mechanical strength of compacts with and without ENG have been quantified and, in general, are not statistically different.**

Progress: Excess Gravimetric Hydrogen Uptake for MOF-5 Compacts

Neat MOF-5 @ ~0.3 g/cc

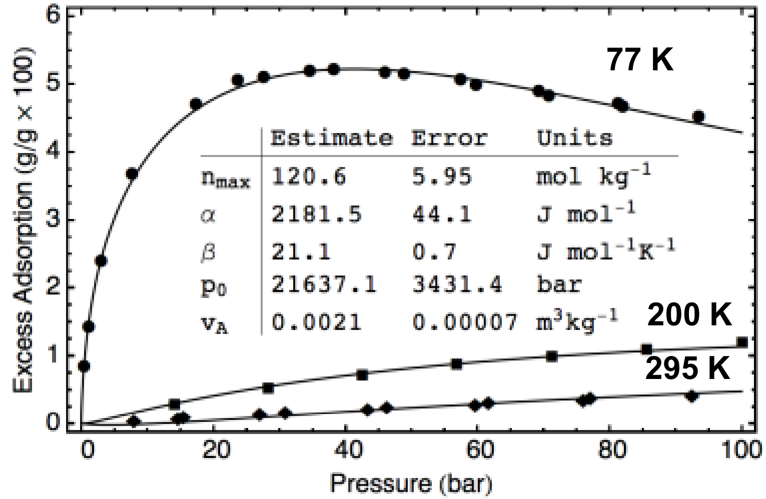


	Estimate	Error	Units
n_{max}	139.6	7.0	mol kg^{-1}
α	2123.0	55.9	J mol^{-1}
β	19.6	0.6	J mol^{-1}K^{-1}
p_0	16049.5	2108.8	bar
v_A	0.0023	0.00013	m^{3}kg^{-1}

Values for the D-A parameters [n_{max}, α, β, P_0, and V_a] obtained by nonlinear regression on all measured isotherms simultaneously.

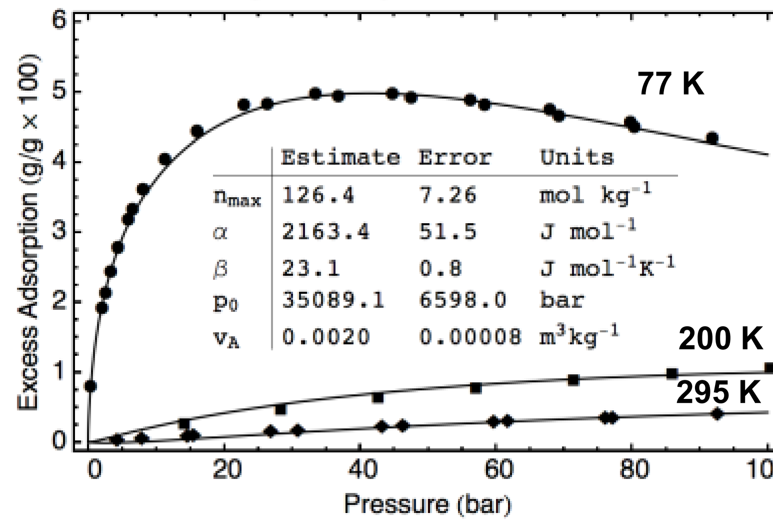
$$n_{ex} = n_{\max} \exp\left(-\left(\frac{RT}{\alpha + \beta T}\right)^2 \ln^2\left(\frac{P_o}{P}\right)\right) - \rho_g V_a$$

MOF-5 @ ~0.3 g/cc + 5 wt% ENG



	Estimate	Error	Units
n_{max}	120.6	5.95	mol kg^{-1}
α	2181.5	44.1	J mol^{-1}
β	21.1	0.7	J mol^{-1}K^{-1}
p_0	21637.1	3431.4	bar
v_A	0.0021	0.00007	m^{3}kg^{-1}

MOF-5 @ ~0.3 g/cc + 10 wt% ENG



	Estimate	Error	Units
n_{max}	126.4	7.26	mol kg^{-1}
α	2163.4	51.5	J mol^{-1}
β	23.1	0.8	J mol^{-1}K^{-1}
p_0	35089.1	6598.0	bar
v_A	0.0020	0.00008	m^{3}kg^{-1}

Progress: Summary of MOF-5 Isotherm Data Collected

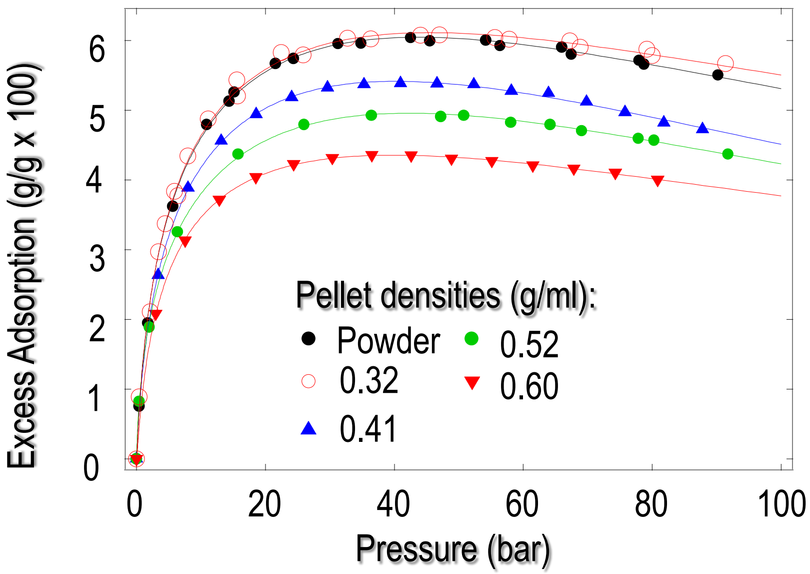
- **Approximately 30 unique isotherms collected for MOF-5 with varying density and ENG content.**

	Powder (0.13 g/cc)	0.3 g/cc	0.5 g/cc
0 wt.% ENG	77, 101, 120, 143, 200, 295 K	77, 101, 116, 136, 200, 295 K	77, 103, 143, 295 K
5 wt.% ENG	N/A	77, 200, 295 K	77, 106, 123, 143 K
10 wt.% ENG	N/A	77, 200, 295 K	77, 200, 295 K

Note: Parameters based on adsorption data from 0 to 80 bar.

- Data delivered to and used by SRNL & GM modelers to assess system-level performance metrics.

Progress: Excess Gravimetric Adsorption Data for MOF-5 at 77 K

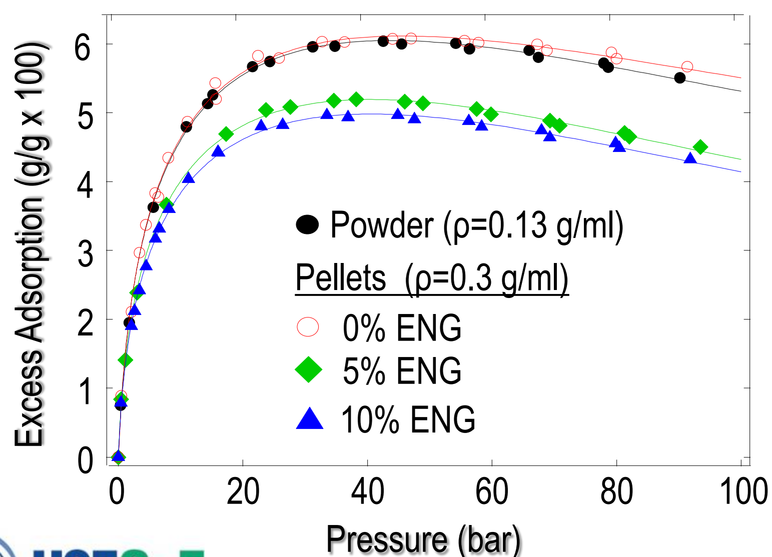


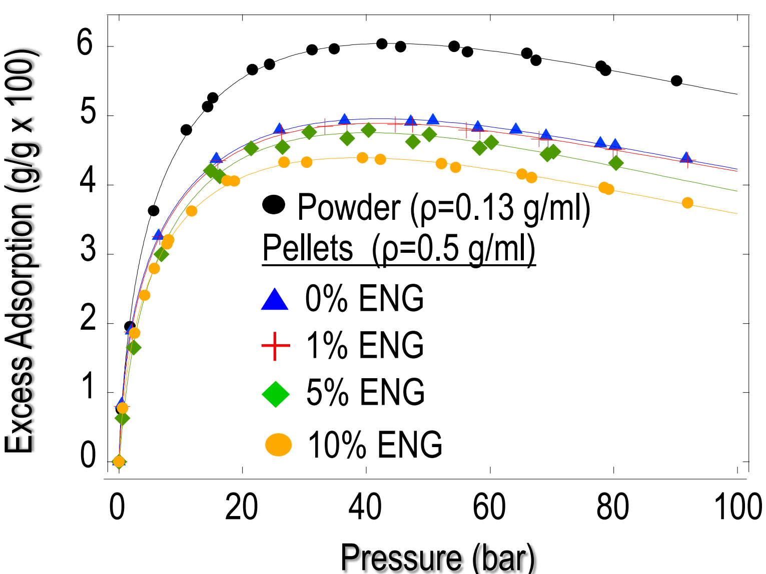
Impact of Densification:

- No impact in grav. capacity up to 0.3 g/cc (>2× volumetric improvement)
- ~20% decrease in grav. capacity at 0.5 g/cc (4× volumetric improvement)

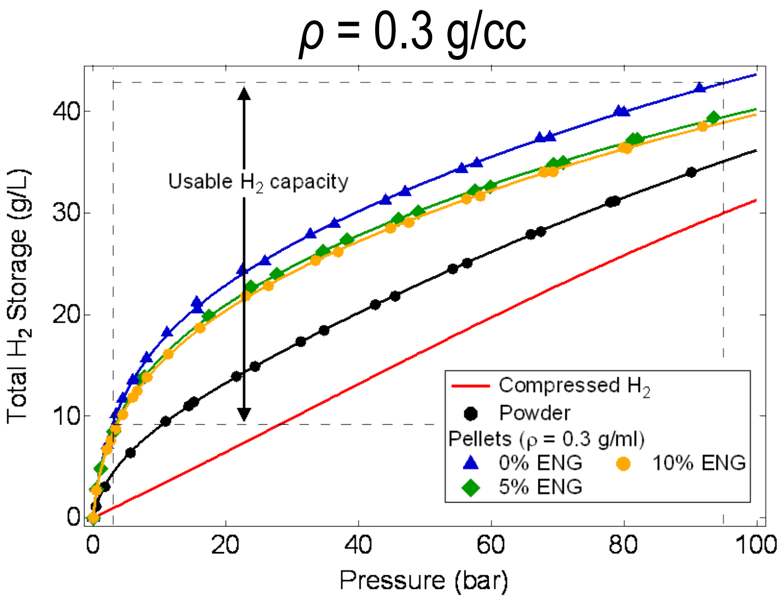
Impact of ENG:

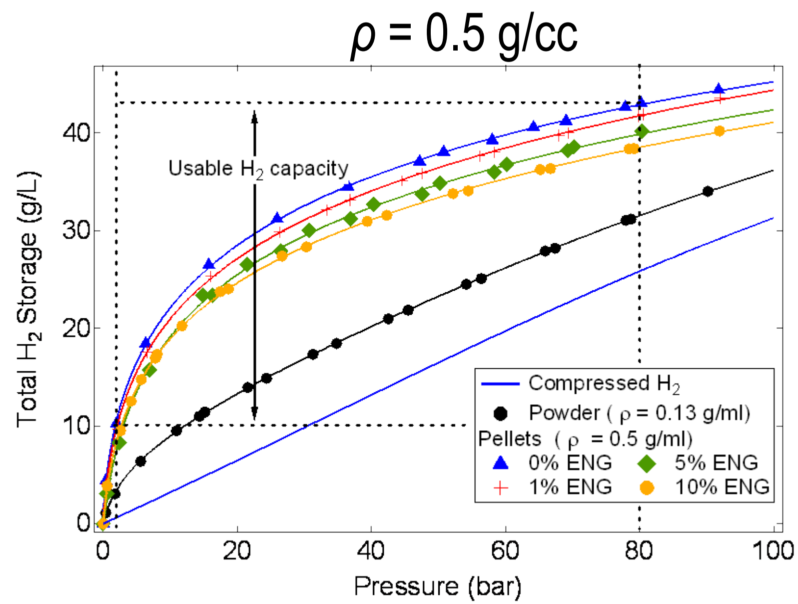
- 15% or 20% loss in grav. capacity for 5 or 10 wt.% ENG at 0.3 g/cc.
- 20% or 30% loss in grav. capacity for 5 or 10 wt.% ENG at 0.5 g/cc.





Progress: 77 K Total Volumetric Adsorption Data for MOF-5 (Materials-Basis)

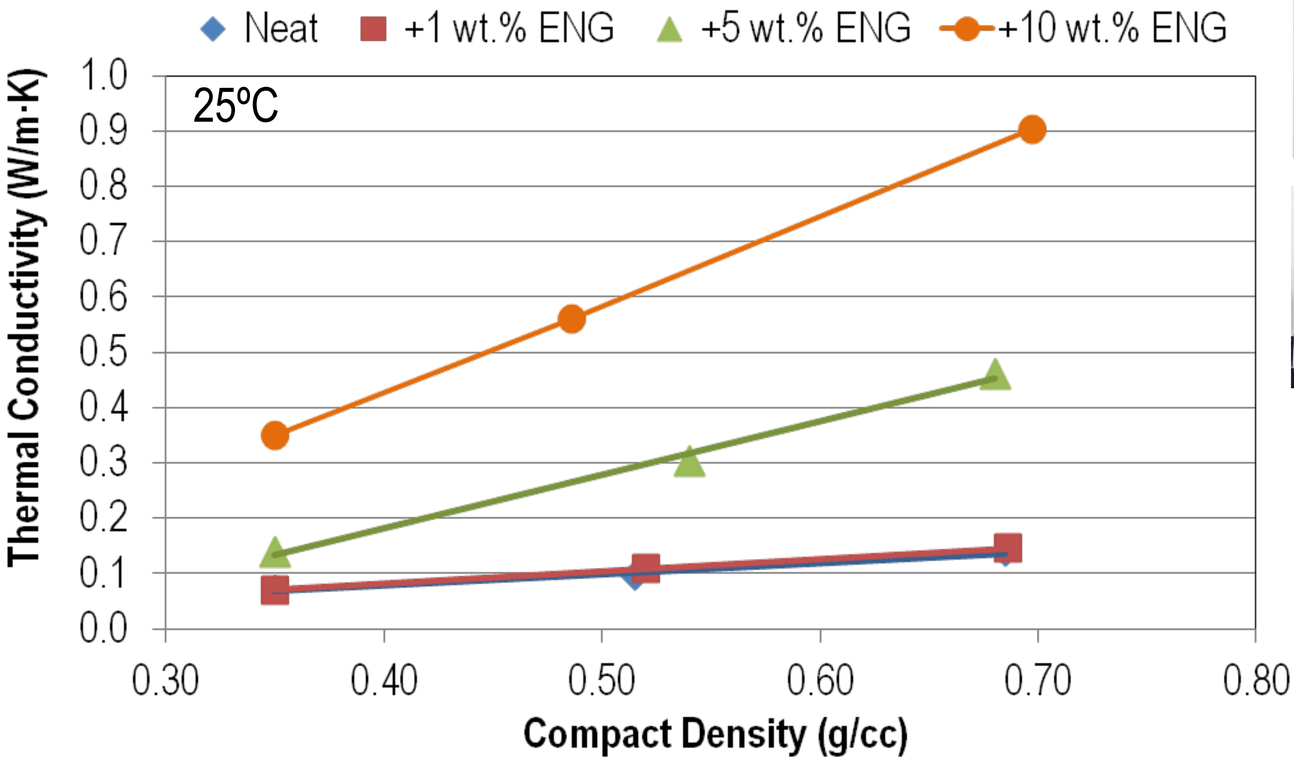


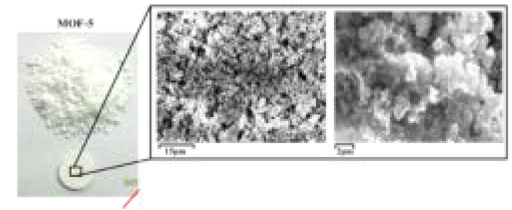


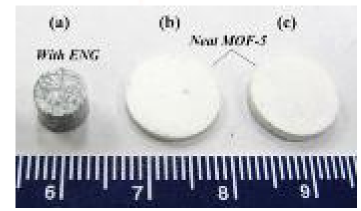
- **Note: All curves currently assume skeletal densities of 2 g/cc.**
- **Total volumetric materials capacity up to 100 bar for MOF-5 containing 5-10 wt% ENG is ~38 or 40 g/L for 0.3 or 0.5 g/cc compact densities (assuming 100% pellet packing).**
- **Over 30% improvement in volumetric capacity compared to compressed hydrogen (at same T-P conditions).**

Progress: Thermal Conductivity Data for MOF-5 Compacts

Thermal Conductivity Data of MOF-5 and MOF-5/ENG Composites



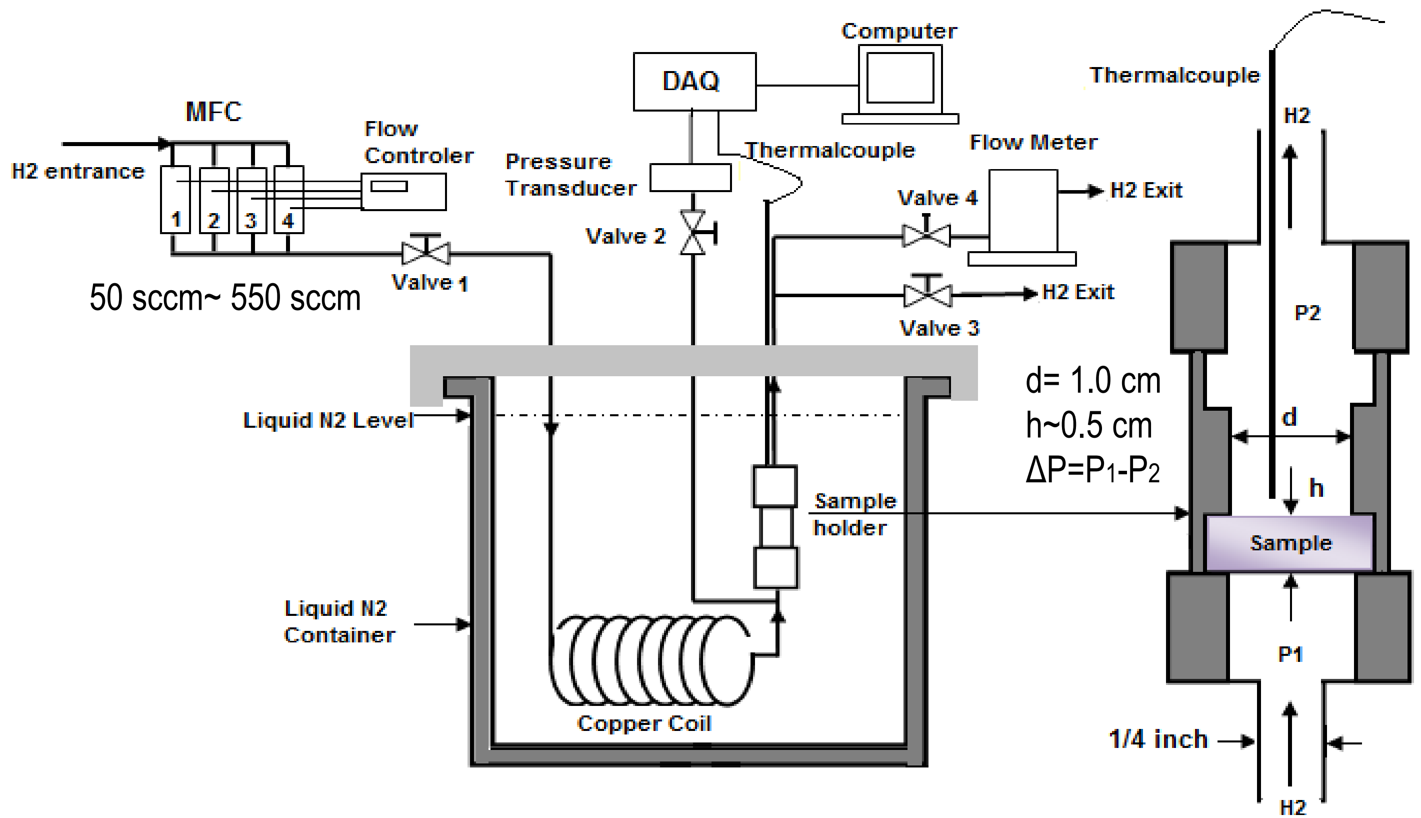




- 1 wt.% ENG does not provide an appreciable increase in thermal conductivity.
- Thermal conductivity more sensitive to density changes with larger ENG content.
- 6× improvement in thermal conductivity possible for 10 wt.% ENG at 0.5 g/cc.

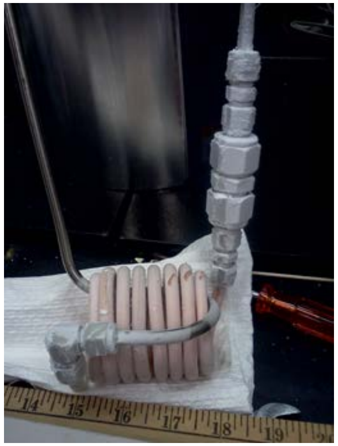
Progress: Gas Permeability Set-Up

Hydrogen permeability test-stand built to assess pressure drop across MOF-5 with/without ENG compacts as a function of hydrogen gas flow.



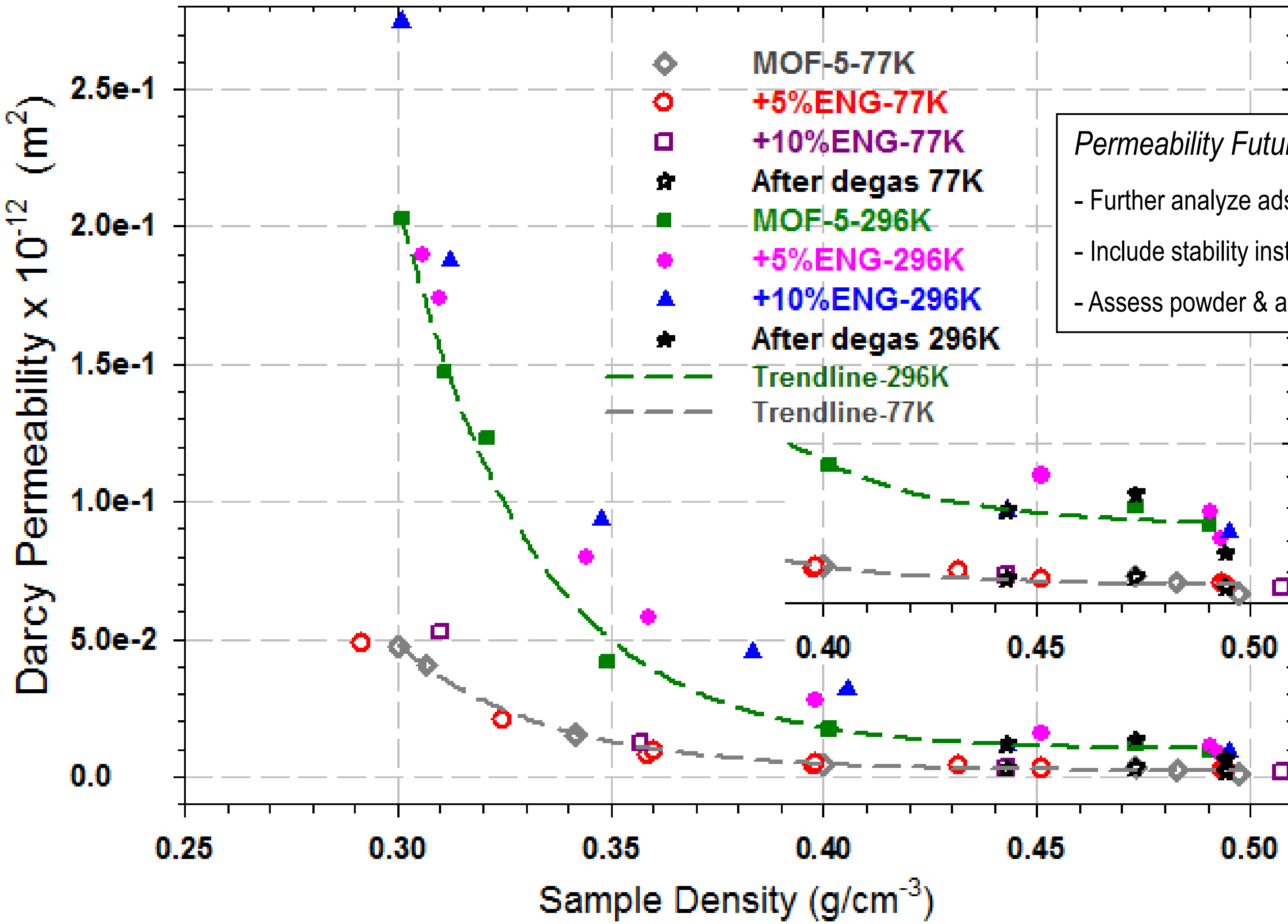
a. Setup diagram

b. Sample Holder



Progress: Initial Hydrogen Permeability Results for MOF-5 at 77 K and RT

Preliminary Data based on Current Permeability Set-up



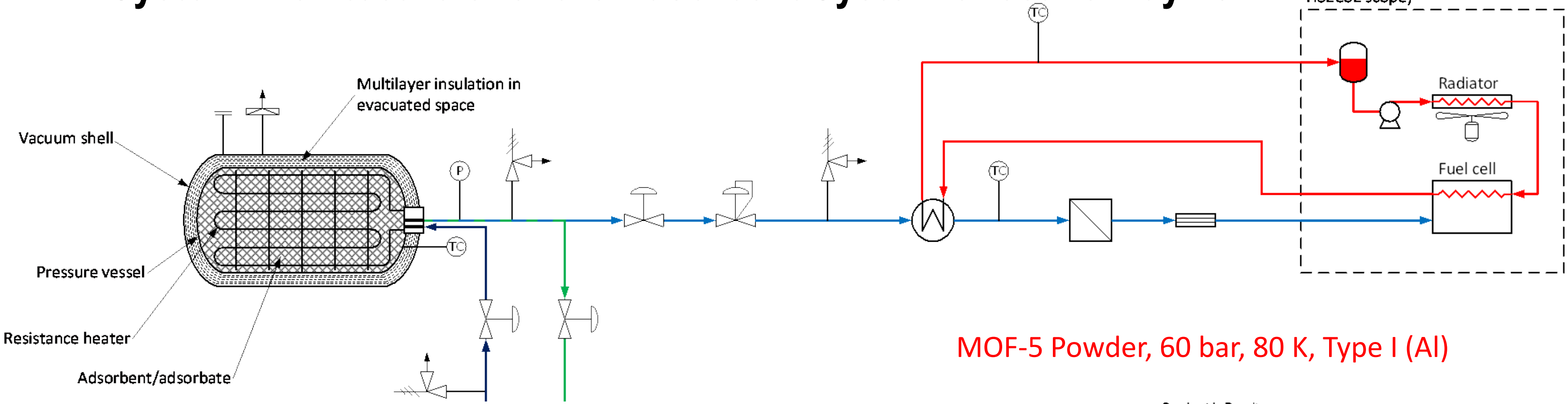
Permeability Future Work

- Further analyze adsorption effects
- Include stability instrumentation
- Assess powder & aspect ratio data

1 darcy=0.9869233x10^{-12} m^2

Progress: System Architect Role (D. Siegel) for the Adsorbent System

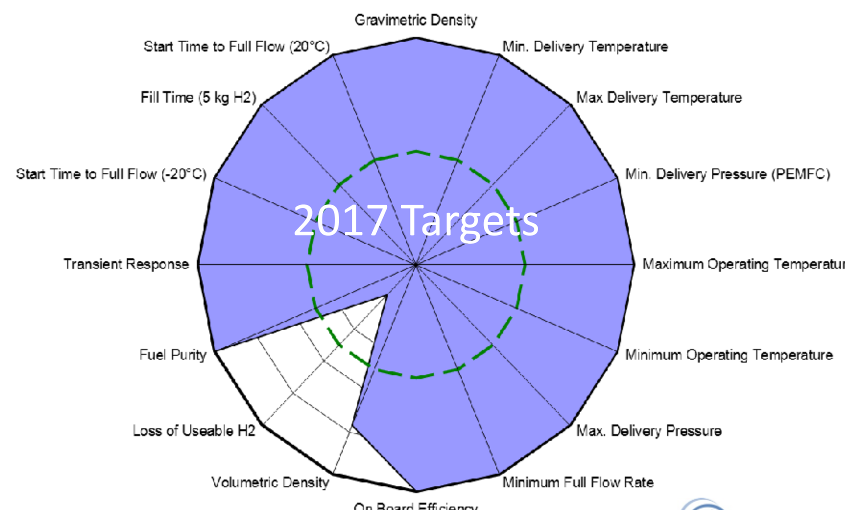
System Architect role for the Adsorbent System effective May 2011



- Coordinated design status with Adsorbent Team
- Identified and prioritized the research gaps
- Developed SMART milestones and GANTT chart
- Completed materials downselection process
- Conducted multiple meetings with Adsorbent Team

→ 4 face-to-face, monthly telecons, and numerous others

MOF-5 Powder, 60 bar, 80 K, Type I (Al)



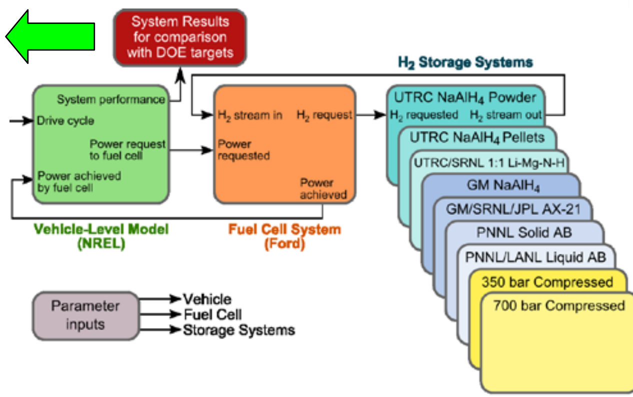
Progress: Dynamic parameter model framework

- Assessed the various storage systems in a consistent and dynamic approach
- Developed required interfaces for hydrogen storage systems to fuel cell (i.e. waste heat)
- Verified the integrated system model results for a complete evaluation against the targets

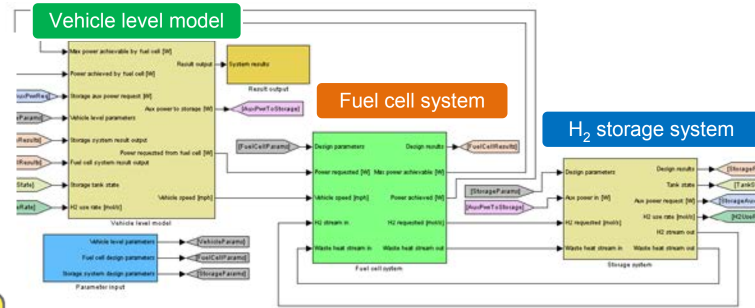
Hydrogen Storage System Targets

Prioritized Target	Units	2010	2015	Ultimate
Permeation & Leakage	scc/hr			
Toxicity				
Safety				
Gravimetric Density	kg H_2/kg System	0.045	0.055	0.075
Min. Delivery Temp.	°C	-40	-40	-40
Max. Delivery Temp.	°C	85	85	85
Min. Delivery Pressure (PEMFC)	bar	5	5	3
Max. Delivery Pressure	bar	12	12	12
Min. Operating Temperature	°C	-30	-40	-40
Max. Operating Temperature	°C	50	60	60
Min. Full Flow Rate	[g H_2/s]/kW	0.02	0.02	0.02
System Cost*	$/kWh net	4	2	TBD
On-Board Efficency	%	0.9	90	90
Volumetric Density	kg H_2/liter	0.028	0.040	0.070
Cycle Life	N	1000	1500	1500
Fuel Cost*	$/gge	3-7	2-6	2-3
Loss of Useable Hydrogen	[g H_2/hr]/kg H_2	0.1	0.05	0.05
WPP Efficency	%	60	60	60
Fuel Purity	%	99.97	99.97	99.97
Transient Response	sec.	0.75	0.75	0.75
Start Time to Full Flow (-20°C)	sec.	15	15	15
Fill Time	min.	4.2	3.3	2.5
Start Time to Full Flow (20°C)	sec.	5	5	5

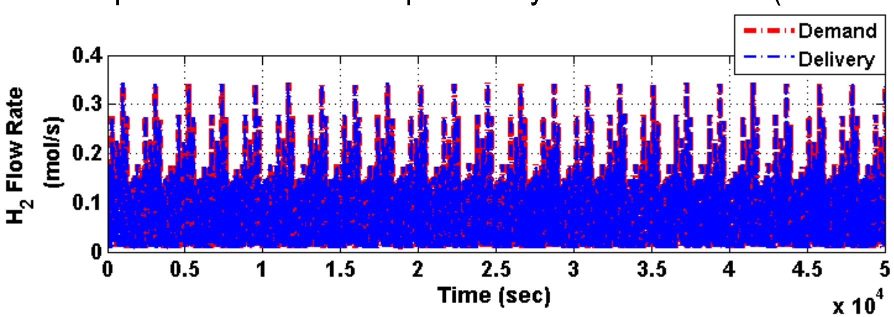
Illustration of integrated HSECoE model

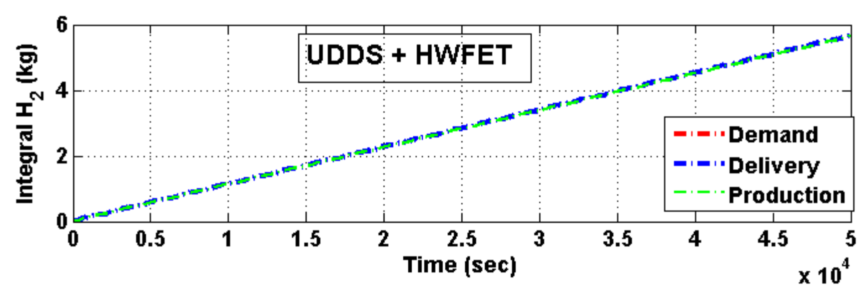


High-Level Simulink HSECoE model blocks



Example of PNNL/LANL Liquid AB System Simulation (Case 1 from the HSECoE Test Matrix)





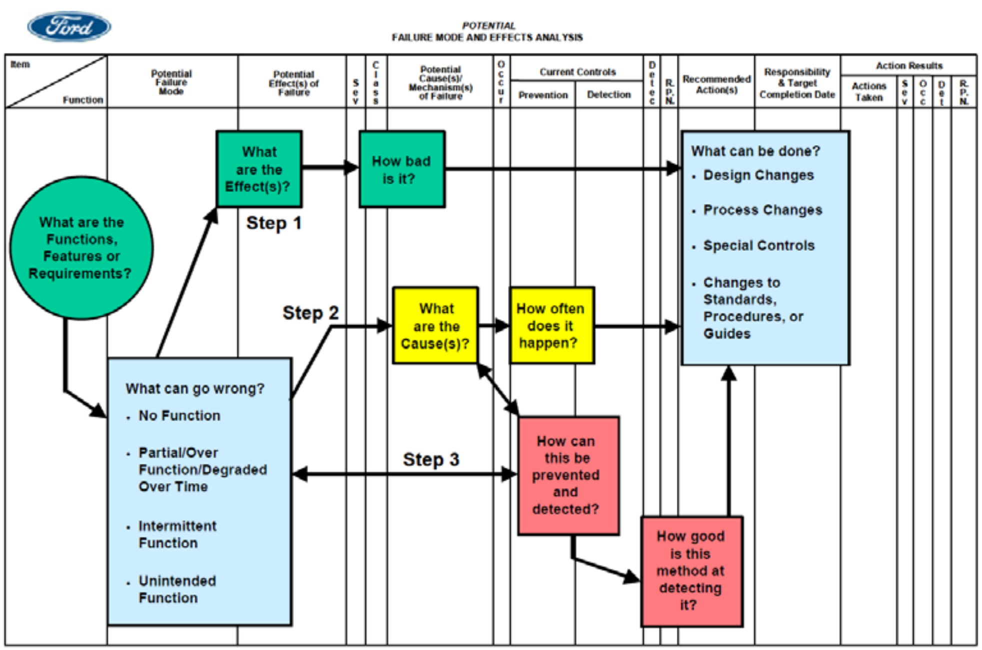
Progress: Conducted System Design FMEAs

FMEA = Failure Mode and Effects Analysis (industry tool per SAE J1739)

- Improves the quality, reliability, and safety of the evaluated product
- Identifies and evaluates the potential failure of a product and its effects
- Documents the risk and helps prioritize the key actions to reduce failures

Key steps for developing the FMEA (after functions defined):

1. Determine the effects and associated severity rating (OEM)
2. Brainstorm potential causes of failure and associated occurrence rating (FMEA team)
3. Evaluate the current detection controls and associated detection rating (FMEA team)



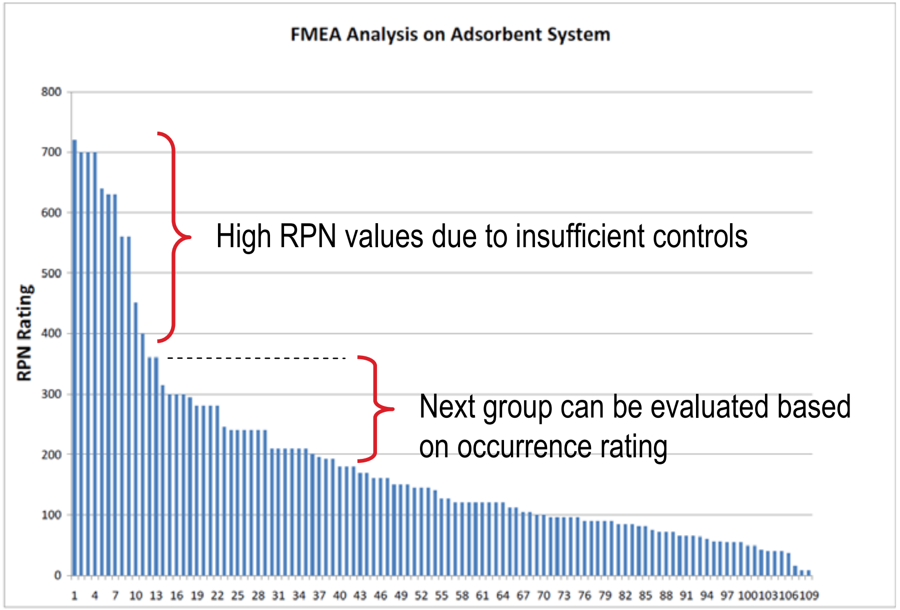
Progress: Completed System Design FMEAs

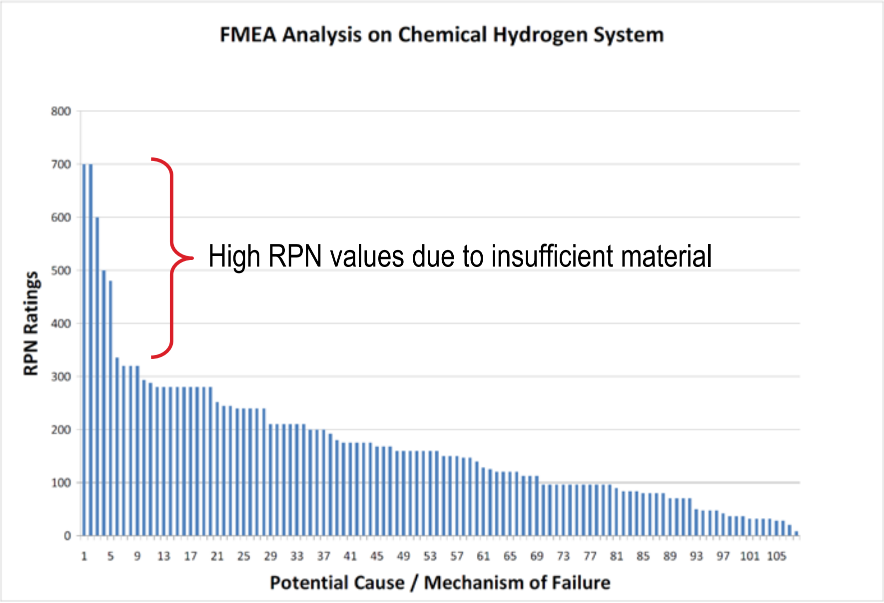
Adsorbent (MOF-5) System Results

- Identified group of potential causes that need further control testing such as insufficient release due to non-homogenous materials or impurities and in-service activation compatibility with the vessel
- Acknowledged the need for to develop the WPP and manufacturing assumptions

Chemical Hydrogen (AB) System Results

- Recognized high RPN grouping due to insufficient weight percentage and regeneration material (out of scope)
- Discovered reoccurring potential cause relates to flocculation and clogging
- Modified system design to include prevention items of on-board issues

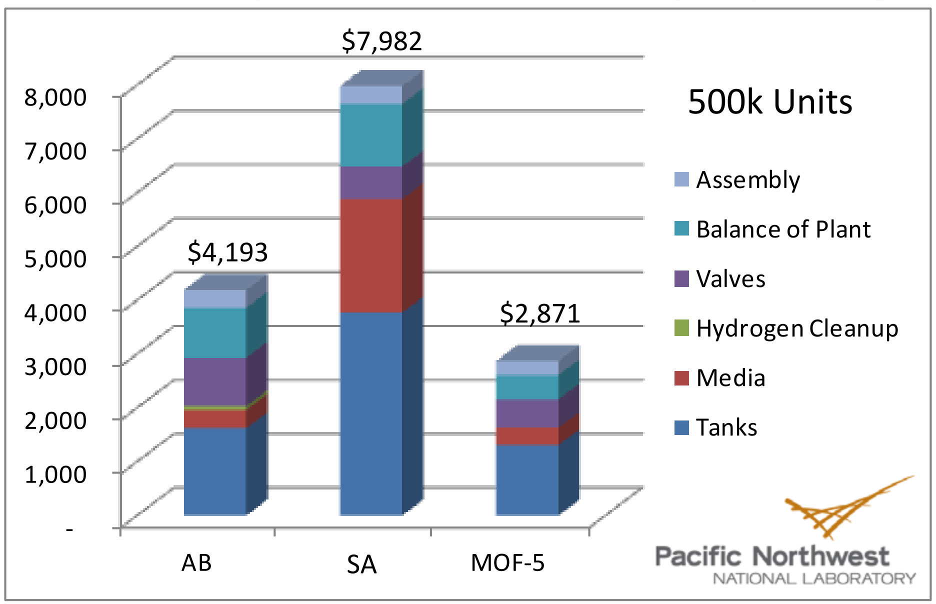




Progress: Analyzed initial system cost projections

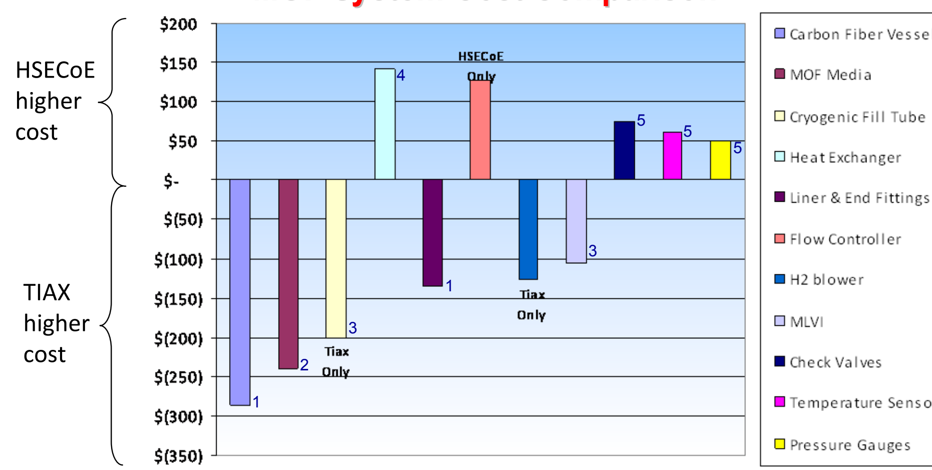
- Supported PNNL in developing the bill of materials for the various storage systems
- Assessed industry available parts with appropriate capabilities for system conditions
- Reviewed quotes from distributors and manufactures for different quantity levels
- Evaluated progress ratio models based on production level and volume
- Compared costs with direct material models and other benchmarks

HSECoE System Comparison ($/System)



$23/kWh **$43/kWh** **$15/kWh**

MOF System Cost Comparison



Comments / Observations

1. Further analysis is required to evaluate pressure vessel cost (fiber and liner)
2. MOF media difference is expected (MOF-177 with Tiax vs MOF-5 with HSECoE
3. The insulation criteria for the fill tube and MLVI needs confirmation
4. Heat exchanger details needs to be expanded into individual items
5. The main difference is related to the number of parts assumed in the system

Future Work: Technical gaps & near-term plans

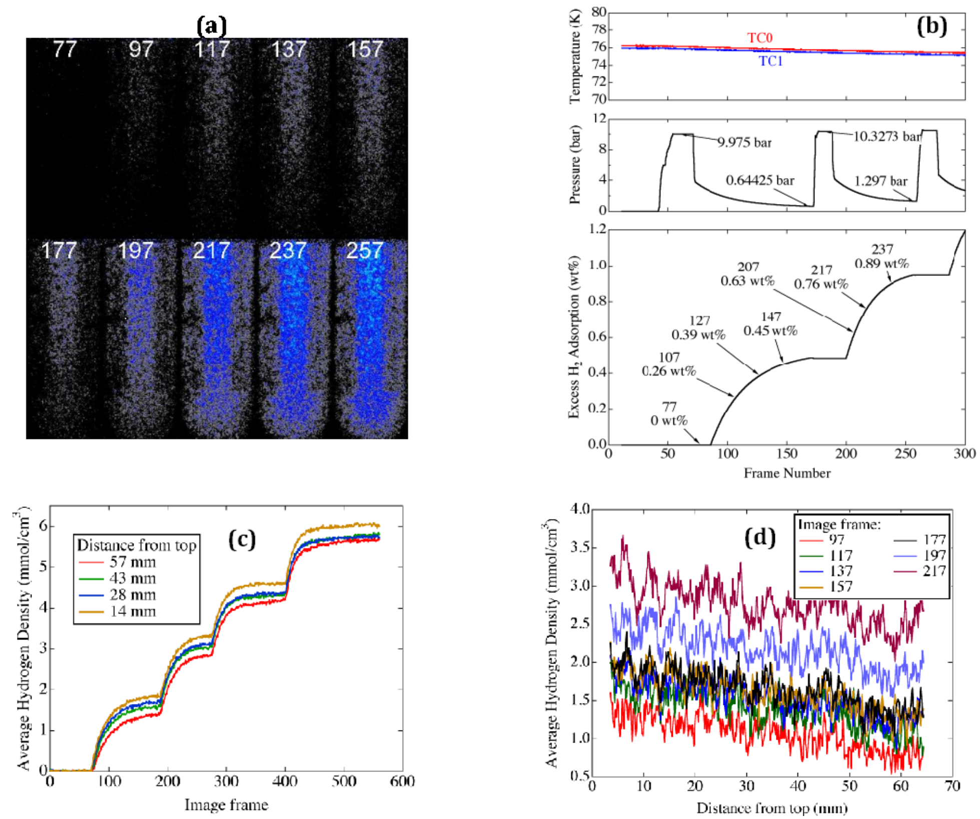
- **Gas Permeability:**
  - Finalize the assessment of H_2 permeability for MOF-5 compacts as functions of density, ENG loading, and L:D.
- **Adsorption Measurements:**
  - Complete any high-pressure and/or low-temperature measurements to support modeling efforts
- **Thermal Conductivity:**
  - Continue to assess impact of thermal conductivity aids on material properties and system attributes
- **Compact Durability:**
  - Investigate mechanical stability of compacts with respect to P-T cycling and/or mechanical vibration and subsequent effects on the respective material properties.
- **System Design and FMEA Action Items**
  - Develop system assembly and MOF-5 integration concepts.
  - Study degradation effects of MOF-5 upon exposure to air/moisture.
  - Evaluate uptake robustness by analyzing pellet variations and impurities.
  - Select material and operating conditions for Phase III design and sub-scale testing.
- **Vehicle and On-board Storage Parameter Modeling:**
  - Complete model validation and framework refinement based on component bench tests
  - Provide the necessary system model results for the Phase III prototype direction and design
- **Storage System and Manufacturing Cost Projections**
  - Development of component material assumptions and predictive usage model
  - Establish the activity-based manufacturing cost model for the key storage system components

Future Work: Next Generation Neutron Imaging

Continuation of *in situ* neutron imaging of MOF-5 media for model validation in Phase 2.

Specific objectives:

1. Quantify H_2 permeation in densified MOF-5 “pucks”.
2. Measure steady-state spatial H_2 distribution as a function of fill and temperature.
3. Characterize transient behavior associated with recharge and discharge as a function of rate and degree of fill.
4. Correlate steady state and transient H_2 concentrations with temperature gradients.



Proposal Submitted to NIST Center for Neutron Research

Summary

Task 1: Vehicle parameter modeling.

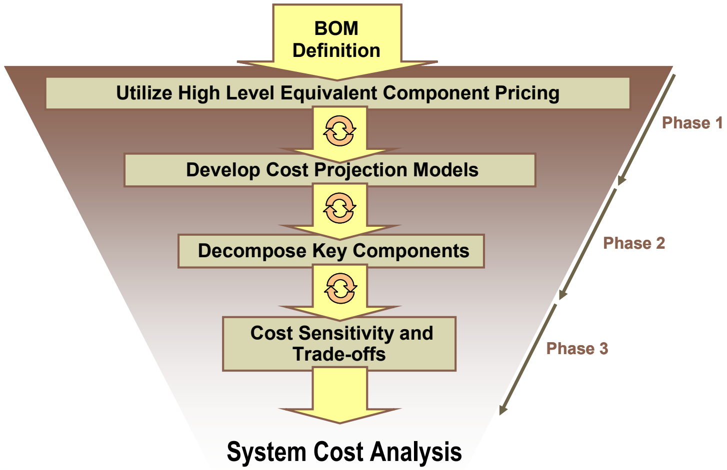
- Benchmarked the system modeling results in comparison to other hydrogen storage analysis.
- Enhanced the modeling framework and assumptions to confirm the initial vehicle level results.

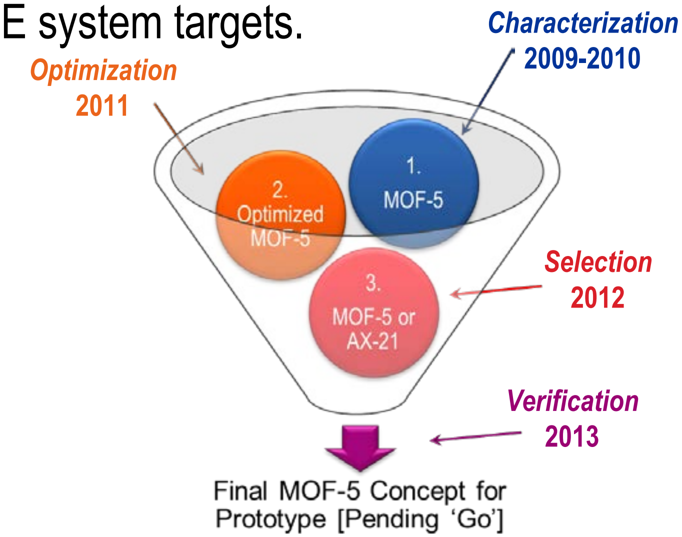
Task 2: Manufacturing cost modeling.

- Supported the development of the preliminary storage system cost projections for the HSECoE.
- Analyzed and progressed the storage system balance of plant through technical design reviews.

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

- Conducted MOF-5 material parameter characterization and optimization for the system models
- In the system architect role, collaborated with partners to identify the system attributes, material requirements, and gaps in the pursuit of the DOE system targets.





Collaborations: HSECoE Partners

- 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

Technical Back-up Slides

General FMEA Overview and Approach

The FMEA is based on the required system functions from the technical targets.

Table 2 Technical Targets: Onboard Hydrogen Storage Systems

Storage Parameter	Units	2010	2017	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]:	\$/kWh net (\$/kg H_2)	TBD (TBD)	TBD (TBD)	TBD (TBD)
• Fuel cost [c]	\$/gge at pump	3-7	2-4	2-4
Durability/Operability:				
• Operating ambient temperature [d]	ºC	-30/50 (sun)	-40/60 (sun)	-40/60 (sun)
• Min/max delivery temperature	ºC	-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)	5 FC/35 ICE	5 FC/35 ICE	3 FC/35 ICE
• Max delivery pressure from storage system [f]	bar (abs)	12 FC/100 ICE	12 FC/100 ICE	12 FC/100 ICE
• Onboard Efficiency	%	90	90	90
• "Well" to Powerplant Efficiency	%	60	60	60
Charging / Discharging Rates:				
• System fill time (5 kg)	min (kg H_2/min)	4.2 (1.2)	3.3 (1.5)	2.5 (2.0)
• 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

Cost of Ownership
(Provide a competitive system)

Accept Fuel
(Fill storage system)

Deliver Fuel
(Supply H_2 from storage system)

Store Fuel
(Manage H_2 in the system)

General FMEA Overview and Approach

Severity x Occurrence x Detection = RPN

Effect	Ranking
Hazardous without warning	10
Hazardous with warning	9
Very High	8
High	7
Moderate	6
Low	5
Very Low	4
Minor	3
Very Minor	2
None	1

Probability of Failure	Ranking
Very High: Persistent Failures	10
	9
High: Frequent Failures	8
	7
Moderate: Occasional Failures	6
	5
	4
Low: Relatively Few Failures	3
	2
Remote: Failure is Unlikely	1

Likelihood of Detection	Ranking
Absolute Uncertainty	10
Very Remote	9
Remote	8
Very Low	7
Low	6
Moderate	5
Moderately High	4
High	3
Very High	2
Almost Certain	1

Risk

Priority

Number