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

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June 8, 2010

ST010

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Overview

Timeline

- Project Start: February 2009
- Project End: January 2014
- Percent Complete: ~20%

Budget

- Total Project Funding:
  - DOE Share: $2,051,250
  - Contractor Share: $616,250
- Funding for FY09: $350K
- Funding for FY10: $400K

Barriers (2010 Targets)

- Weight and Volume
  - 4.5 wt% and 28 g·H_2/L
- System Cost
  - TBD
- Charge and Discharge Rates
  - Charge: 1.2 kg·H_2/min (5 kg system)
  - Discharge: 0.02 (g·H_2/s)/kW

Partners

- Project Lead: Ford
- Project Partners: BASF and U. Michigan
- Center Partners: GM, UQ-TR, NREL, UTRC, PNNL, SRNL

Relevance: Project Alignment with HSECoE Goals

This project will address three of the key technical obstacles associated with development of viable hydrogen storage systems for automobile applications

Engineering Center Technical Goals	Ford-BASF-UM Project Goals
Using systems engineering concepts, design innovative system architectures with the potential to meet DOE performance and cost targets.	Task 1: Develop dynamic vehicle parameter model elements for the hydrogen storage system interfaces during realistic operating conditions.
Develop system models that lend insight into overall fuel cycle efficiency.	Task 2: Develop a manufacturing cost model for hydrogen fuel systems based on a supply chain assessment.
Compile all relevant materials data for candidate storage media and define future data requirements.	Task 3: Devise and assess optimized, system-focused strategies for packing and processing of framework-based hydrogen storage media.
Develop engineering and design models to further the understanding of on-board storage energy management requirements.	

Relevance: Project Contributions by Tech. Area

- Project outcomes contribute to multiple facets of the HSECoE research work stream [yellow]
- Core areas of project span materials data (Task 3) ⇒ systems modeling (Task 1) ⇒ performance analysis (Task 2) [red]

Hydrogen Storage Engineering Center of Excellence

D. Anton, SRNL
T. Motyka, SRNL

Materials Operating Requirements

D. Herling, PNNL

- Materials Centers of Excellence Collaboration – SRNL, LANL, NREL
- Reactivity & Compatibility – UTRC
- Adsorption Properties – NREL
- Metal Hydride Properties – SRNL
- Chemical Hydride Properties – LANL
- Media Structure - GM

Transport Phenomena

B. Hardy, SRNL

- Bulk Materials Handling – PNNL
- Mass Transport – SRNL
- Thermal Transport – SRNL

Enabling Technologies

J. Reiter, JPL

- Thermal Insulation – JPL
- Hydrogen Purity – UTRC
- Sensors – LANL
- Thermal Devices - OSU
- Pressure Vessels - PNNL

Performance Analysis

M. Thornton

- Vehicle Requirements– NREL
- Tank-to-Wheels Analysis – NREL
- Forecourt Requirements - UTRC
- Manufacturing & Cost Analysis - PNNL

Integrated Power Plant/ Storage System Modeling

D. Mosher, UTRC

- Off-Board Rechargeable - UTRC
- On-Board Rechargeable – GM
- Power Plant – Ford

Subscale Prototype Construction, Testing & Evaluation

T. Semelsberger, LANL

- Risk Assessment & Mitigation – UTRC
- System Design Concepts and Integration - LANL
- Design Optimization & Subscale Systems – LANL, SRNL, UQTR
- Fabricate Subscale Systems Components – SRNL, LANL
- Assemble & Evaluate subscale Systems – LANL, JPL, UQTR

System Architects

MH System	*CH System*	*A System*
T. Motyka/M. Veestra	T. Semelsberger/A. Sudik	J. Reiter/D. Kumar

Collaborations

(NEW!)

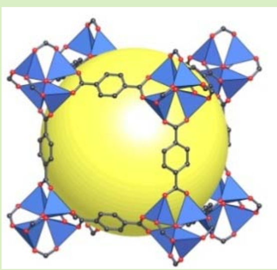
- BASF-SE (industrial subcontractor): framework materials synthesis, processing, and characterization
- University of Michigan (academic subcontractor): framework materials processing-property characterization
- GM (industrial collaborator): team member for sorbent materials operating parameters, system/vehicle-level modeling, and structured materials
- 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
- SRNL (federal lab collaborator): team lead for transport phenomena and center management

Interactions include monthly team meetings and regular data and information exchanges

Approach: Ford (+BASF+UM) Operating Requirements for Framework Materials (FMs)

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

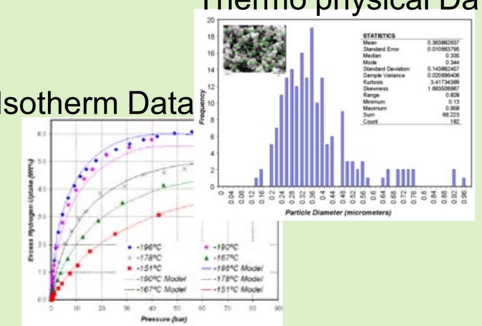
Synthesis of select FMs on kg scale



Determination of "Engineering" Properties

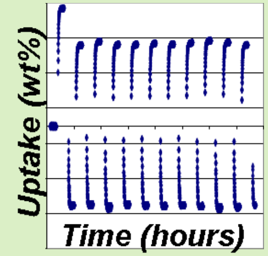
Thermo physical Data

Isotherm Data



Material Processing & Compaction

Processing-Property Relationship



feedback

Optimized FM Material Form

Go/No-Go

System Prototype

Project critically supports the system-level assessment and feasibility of FMs to meet hydrogen storage targets

Milestones: Ford (+BASF+UM) Operating Requirements for Framework Materials

Year 1 project milestones on track and aligned with HSECoE goals

	Task Number	Project Milestones	Percent Complete	Project Notes
YR 1	1	Tabulate and create database of known FM properties	100%	**Modified:** Existing FM data compiled based on literature survey
	2	Complete baseline measurements on selected MOF powders	100%	**Completed:** Select properties of four FM powders determined
	3	Selection of first "developed" FM for CoE modeling	100%	**Completed:** Coordinated with MOR team for the selection of Basolite Z100H (MOF5) as the first developed FM
	4	Deliver data set of down-selected powder FM to Transport Phenomena TA	100%	**Completed:** Completed and delivered data set for powder Basolite Z100H to MOR and TP teams
YR 2	5	Identify/Evaluate diverse processing routes and compaction schemes & measure effective materials properties for processed FM from Task 4 (and potentially other FMs)	10%	**Initiated:** Focus for Yr 2 to be on developing processing-structure-property (PSP) relationships for Basolite Z100H

Role of Project Partners:

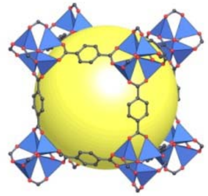
BASF-SE – Provide FMs for project and Center in Phase III; Contribute FM data (e.g. surface area/pore volume measurements, SEM images, etc); Consultant to Center regarding FM properties

University of Michigan (NEW!) – Optimization of packing density and thermal conductivity; assess impact of processing on H_2 storage properties; validation module development

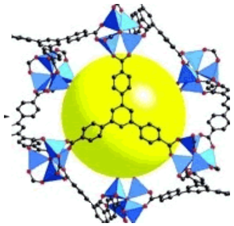
Progress: Baseline Data for Select Powder FMs

Materials For Project:

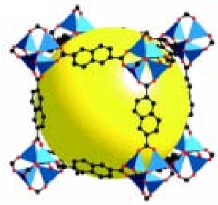
Developed Material



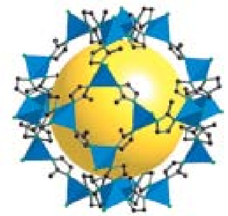
MOF-5
Basolite Z100-H



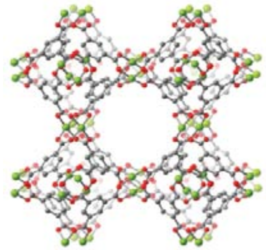
MOF-177
Basolite Z377



IRMOF-8
Basolite Z200



ZIF-8
Basolite Z1200



HKUST-1
Basolite C300

Material	Langmuir Surface Area (m^2/g)	Measured Max Excess Uptake (Wt·% H_2)	Literature Max Excess Uptake (Wt ·% H_2)	Measured Max Excess Uptake (g·H_2/L)	Measured Absolute Uptake @ 70 bar (Wt·%H_2) | (g·H_2/L)	DOE Targets (2015)
MOF-177	**5000**	**7.0**	**7.0-7.2**	**30 (SC) 13 (LP)**	**12.0 | 51 (SC) , 22 (LP)**	**Volumetric**
MOF-5	**3500**	**6.0**	**5.2-6.0**	**37 (SC) 6 (LP)**	**10.0 | 62 (SC), 10 (LP)**	**40 g·H_2/L**
IRMOF-8	**1700**	**3.3**	**3.5**	**15 (SC) 10 (LP)**	**4.3 | 19 (SC), 13 (LP)**	**Gravimetric**
ZIF-8	**1650**	**2.7**	**3.0-3.3**	**25 (SC) 6 (LP)**	**4.1 | 38 (SC), 9 (LP)**	**5.5 wt%·H_2**

'SC' and 'LP' indicate whether the volumetric capacities are based on single crystal (SC) or loose powder (LP) density, These values help by providing upper and lower bounds to volumetric uptake.

Baseline measurements on powder FMs initially focused on:

- Calculation of surface area
- Determination of excess and absolute hydrogen capacity---gravimetric and volumetric---at 77 K and 100 bar
- Determination of single crystal (Lit.), loose powder, and He skeleton (framework) density (Ford & BASF data)

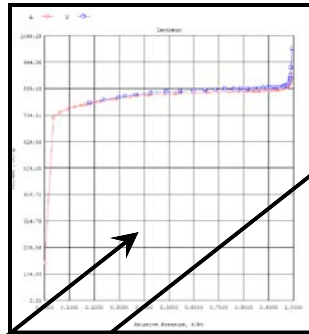
FM property data served as a means for validation with data from the literature and other CoE partners and also aided in the selection of Basolite Z100H (MOF-5) and other FMs as adsorbents for modeling analysis

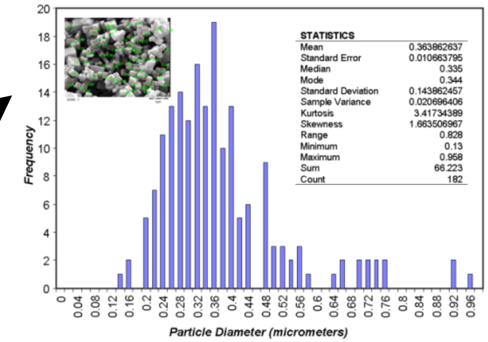
Progress: Data Set Creation for Basolite Z100H (MOF-5)

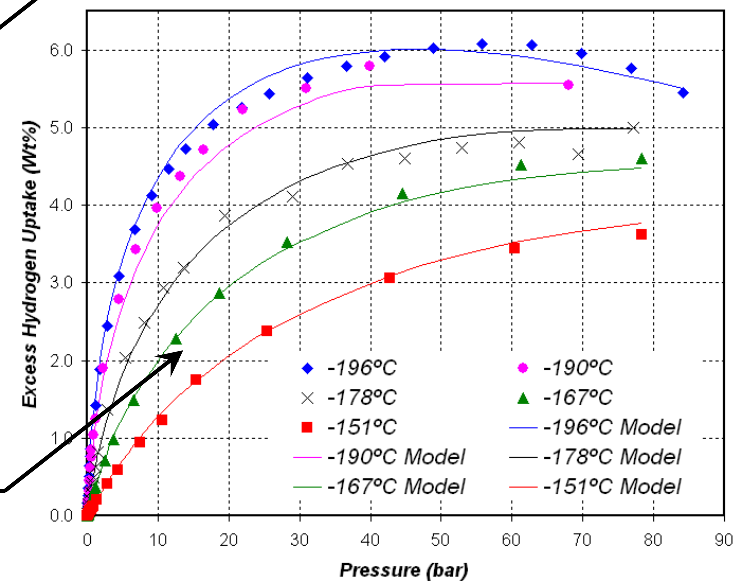
Data set for MOF-5 completed and delivered to MOR and TP teams.
Similar data sets for other powdered FMs can be generated.

Thermal Properties	
Thermal Conductivity ($Wm^{-1}K^{-1}$)	0.3
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})	0.14
Material Density (gcm^{-3})	2.03
Specific Surface Area (m^2g^{-1})	3500 (2570) Lang. (BET)
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







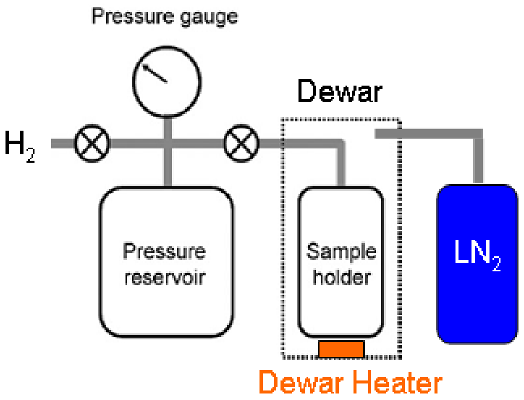
$$n_{ex} = n_{\max} \exp\left(-\left(\frac{RT}{\alpha+\beta T}\right)^2 \ln^2\left(\frac{P_o}{P}\right)\right) - \rho_g V_a$$

HSECoE

Progress: Toward Robust Cryogenic H_2 Storage Measurements

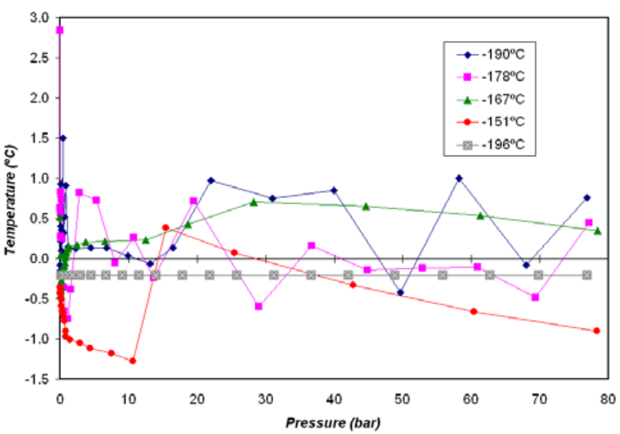
Background: Volumetric hydrogen storage measurements rely on simultaneous and accurate knowledge of temperature, volume, and pressure to determine hydrogen concentration. Data collection at cryogenic temperatures is highly sensitive to fluctuations in temperature, corresponding to fluctuations in hydrogen concentration.

Goal: Understand and reduce temperature variation toward robust hydrogen capacity measurements and improved fit between experimental and model data.

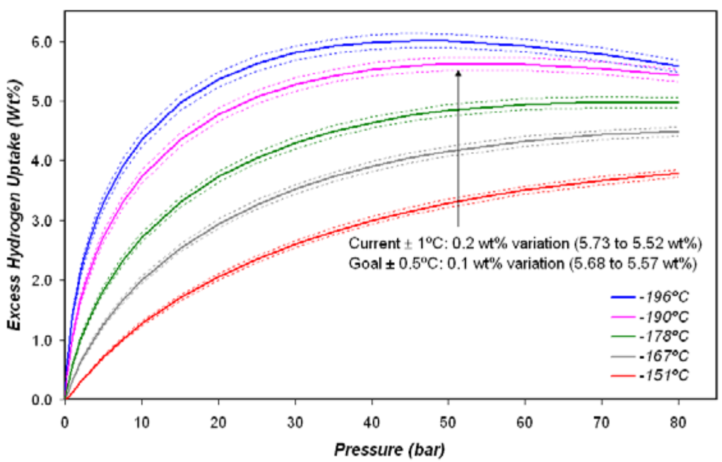


Characterizing and Improving Temperature Control Capability

1) Evaluated current temperature control [process capability is ± 1ºC]



2) Assessed sensitivity of temperature variation on uptake [e.g. at -190ºC and 50 bar ± 1ºC ⇒ ± 0.1 wt%]



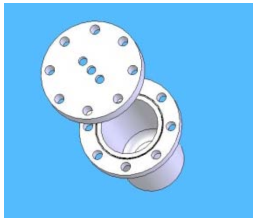
3) Utilized Cause-and-Effect Matrix to identify top 3 key process input variables (KPIVs)

4) General full factorial design of experiments (DOE) formulated consisting of 3 factors: dewar heater, control method, and operator.

HSECoE

Proposed Future Work: Materials Operating Requirements for Framework Materials (FMs)

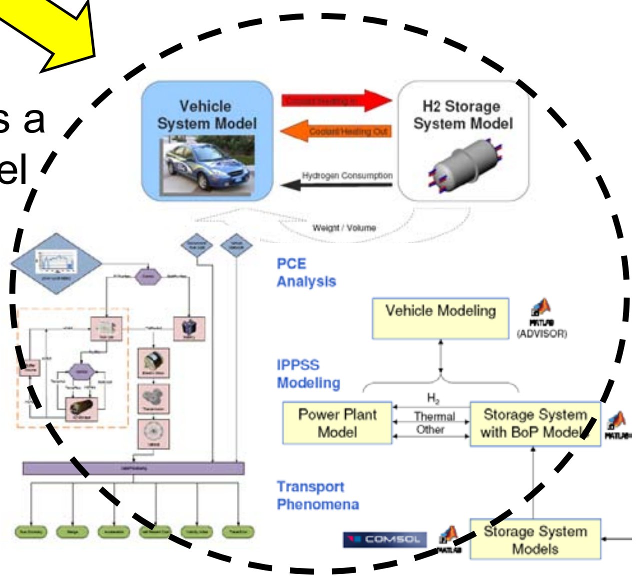
- Pursue detailed densification studies of Basolite Z100H (and other FMs as appropriate) which includes investigation of the impact of the following processing parameters on the resulting hydrogen storage properties:
  - binder
  - compaction temperature, time and pressure
  - pellet and particle size size and shape
  - additives (e.g. thermal conductivity aids)
- Identify initial processing-structure-property relationships for down-selection and optimization of a subset of processed Basolite Z100H packing schemes based on above study
  - project go/no-go decision for moving to Phase 2 based on the theoretical potential for these “generation 1” packing concepts to meet system level performance requirements (see appendix)
- Continue development of lab-scale testing module for rudimentary testing of processed FMs [vessel construction complete; next step is design and assembly of test-bench and data acquisition system]



Approach: Universal Framework & Fuel Cell Power Plant Modeling

Project Goal: Develop center-wide universal modeling framework which includes *dynamic* parameter model elements and system interfaces applicable to diverse realistic operating conditions [Red indicates Ford project focus (i.e. fuel cell modeling and interface characterization)]

Existing model serves as a basis for HSECoE model derivations

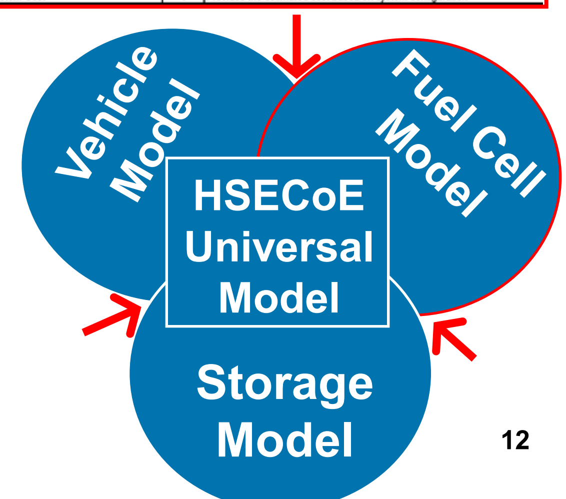


Team develops common aspects and integrates new functionality of universal model (e.g. capability to study dynamics & boundary conditions)

HSECoE Modeling Framework Interface Matrix - draft version 1.3

From:	To:	Interface Title	Interface Category*	Description
Between Vehicle Model and Fuel Cell Model				
VM	FCM	Power Requested	I	Provides the power requirement based on the drive cycle profile
FCM	VM	Power Achieved	E	Provides the power available based on H2 flow rate and pressure
FCM	VM	Fuel Cell System Weight	I	Provides the estimated weight based on net peak power
FCM	VM	Fuel Cell System Cost	I	Provides the estimated cost based on net peak power
FCM	VM	Hydrogen Storage Delivery Pressure Range	I	Provides overall hydrogen storage performance for HSECoE targets
FCM	VM	Hydrogen Storage Delivery Flow Rate Range	I	Provides overall hydrogen storage performance for HSECoE targets
FCM	VM	Hydrogen Storage Delivery Temperature Range	I	Provides overall hydrogen storage performance for HSECoE targets
Between Fuel Cell Model and Hydrogen Storage Model				
FCM	HSM	Fuel Cell Flow Request	I	Provides the required H2 flow based on the power requested
HSM	FCM	H2 Flow Rate	M	Provides the H2 flow available
HSM	FCM	H2 Pressure	M	Provides the H2 pressure available
HSM	FCM	H2 Temperature	M	Provides the H2 temperature
FCM	HSM	Waste Heat Stream - HSM Input Temp	M	Provides waste heat temperature available from fuel cell
HSM	FCM	Waste Heat Stream - HSM Output Temp	[illegible]	[illegible]
FCM	HSM	Waste Heat Stream - HSM Input Flow	M	Provides waste heat flow rate available from fuel cell
HSM	FCM	Waste Heat Stream - HSM Output Flow	M	Provides resulting fluid flow rate from storage system
FCM	HSM	Waste Heat Stream - HSM Input Pressure	M	Provides waste heat pressure available from fuel cell
HSM	FCM	Waste Heat Stream - HSM Output Pressure	M	Provides resulting fluid pressure from storage system
FCM	HSM	Waste Heat Stream - Heat Transfer Parameters	I	Provides density, viscosity, thermal conductivity, and specific heat.
Between Vehicle Model and Hydrogen Storage Model				
HSM	VM	Hydrogen Storage System Aux. Load Request	I	Provides the electrical auxilary power consumption requested
VM	HSM	Hydrogen Storage System Aux. Load	E	Provides the electrical auxilary power
HSM	VM	Hydrogen Storage System Weight	I	Provides the estimated weight based on system configuration
HSM	VM	Hydrogen Storage System External Volume	I	Provides the estimated package volume based on system configuration
HSM	VM	Hydrogen Storage System Cost	I	Provides the estimated cost based on system configuration

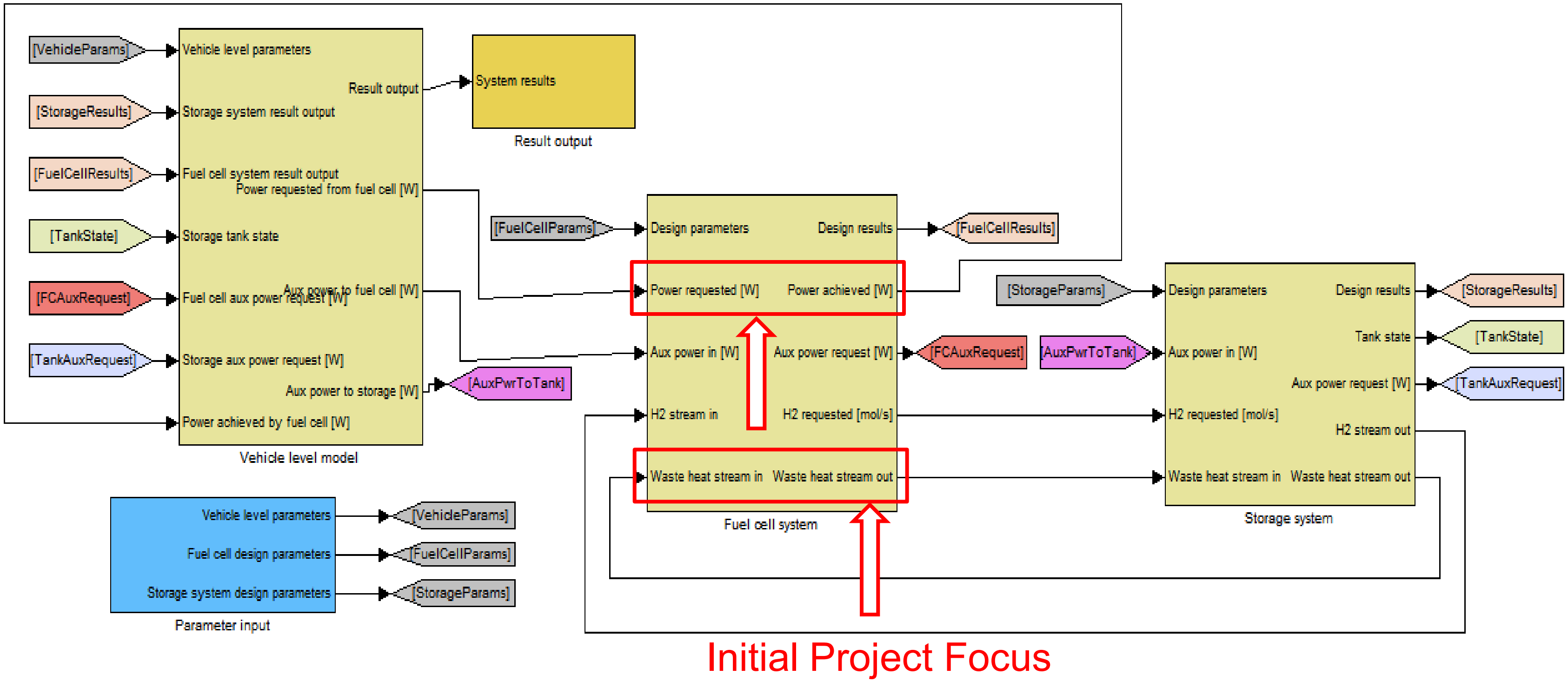
↑ = Interface Matrix



HSECoE

Progress: Development of HSECoE Modeling Framework

- Developed high-level input and output parameters between vehicle, fuel cell, and storage systems models
  - Aided in characterization of interfaces
  - Facilitated drill-down of parameter models (e.g. waste heat availability)



Each parameter set may require development of a detailed parameter model:
Ford project currently addressing fuel cell power & waste heat parameter models

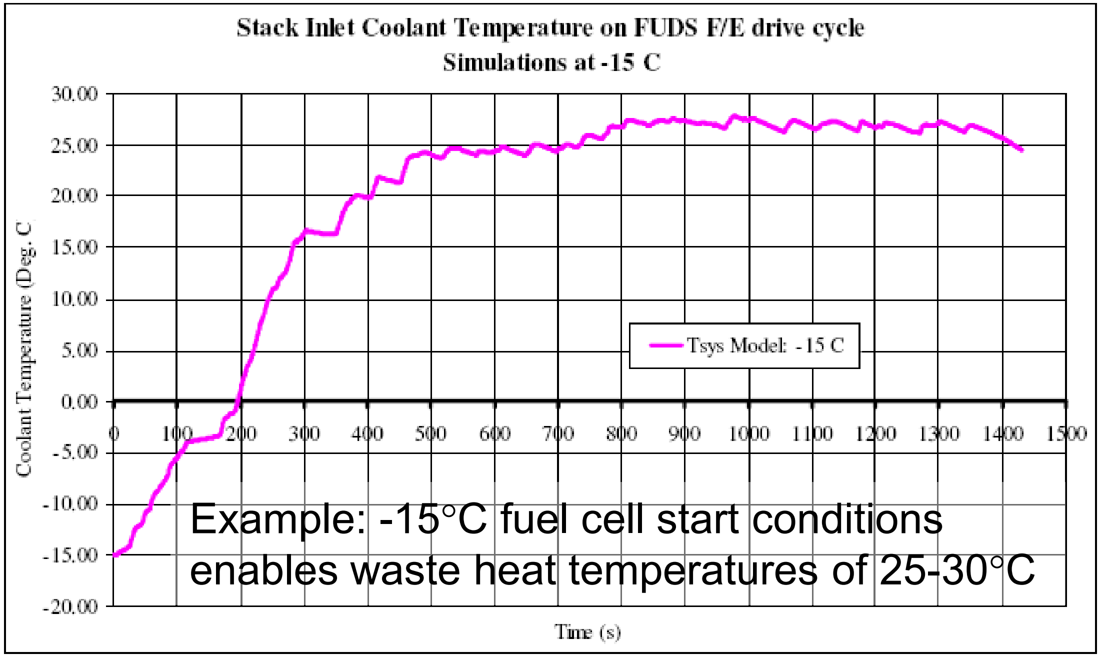
Progress: Assessing Dynamic Fuel Cell Waste Heat Profiles

Determination of dynamic waste heat profiles under a variety of real-world driving scenarios provides critical materials selection and thermal management information

Example Information:

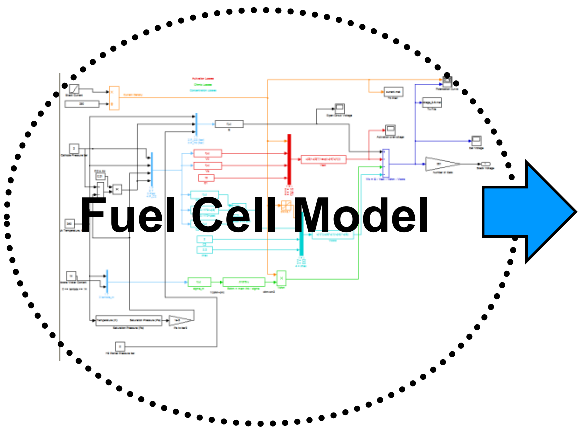
80º C fuel cell waste heat availability and & 4 bar minimum pressure requirements translate to materials enthalpies **ΔH = 17 – 47 kJ/mol H_2**

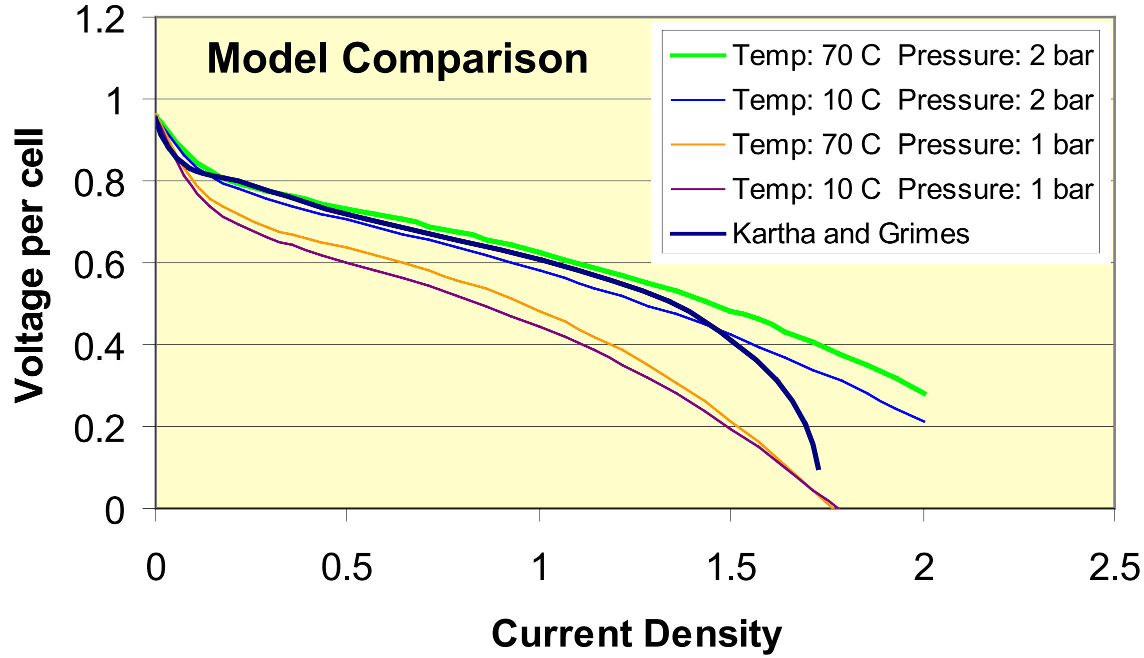
25º C fuel cell waste heat availability and & 4 bar minimum pressure requirements translate to materials enthalpies **ΔH = 17 – 39 kJ/mol H_2**



Progress: Fuel Cell Power Plant Modeling

- **Starting Point:** Existing HSSIM model utilized static fuel cell polarization and power curves (source: Kartha & Grimes, 1994) and thus was incapable of probing fuel cell boundary conditions (e.g. cold starts etc.)





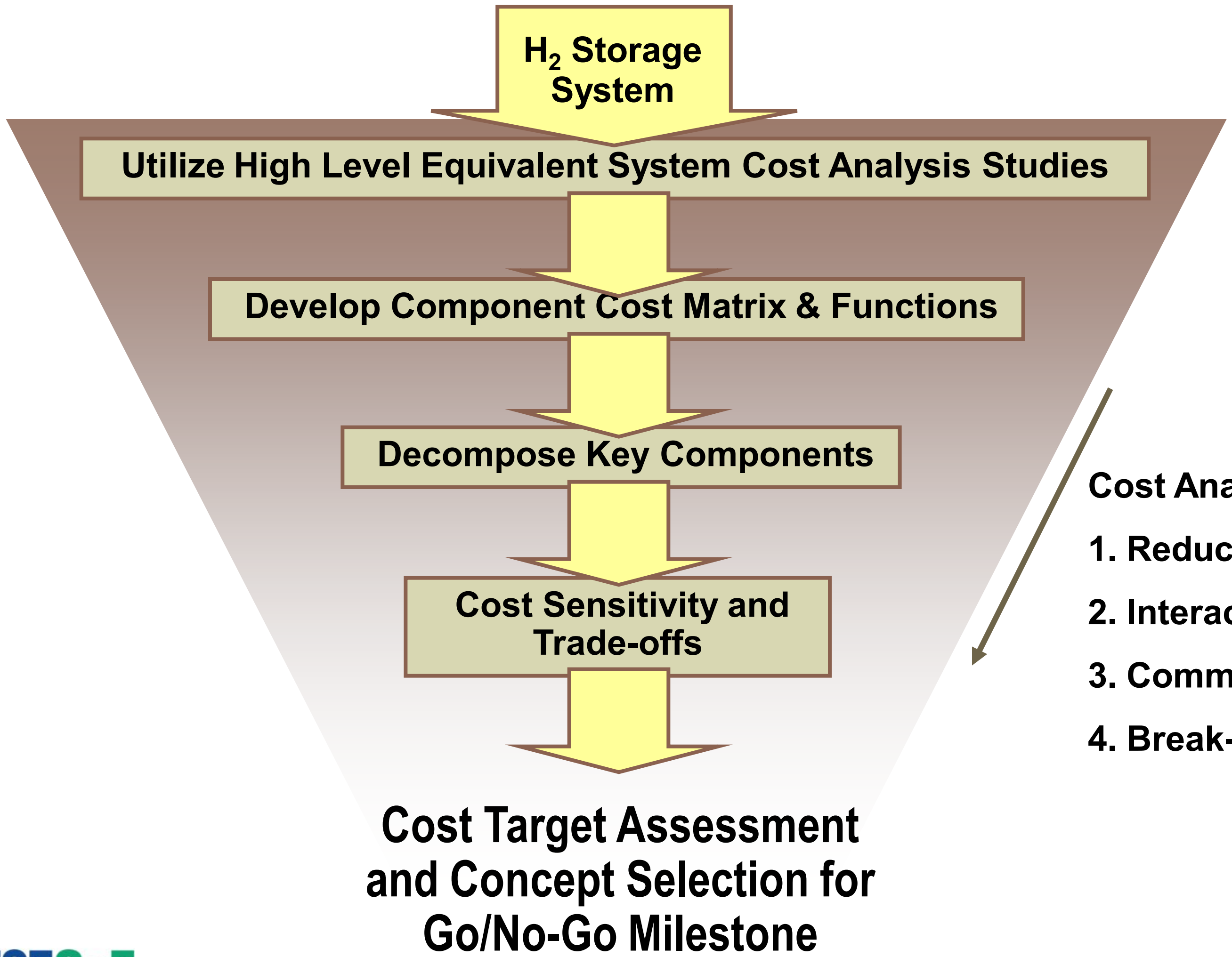
- **New Progress:** Adapted control-oriented modeling/analysis framework for fuel cell systems (source: Pukrushpan, Peng, & Stefanopoulou, 2004) for investigation of impact of diverse fuel cell temperature–pressure scenarios on resulting storage requirements [Note: goal of power plant modeling effort only to characterize---NOT to optimize or propose new designs for fuel cell systems]

Proposed Future Work: Universal Modeling Framework and Fuel Cell Power Plant Modeling

- Complete the integration of the fuel cell stack waste heat model and enhance the fuel cell polarization model at sub-zero temperatures with validation of empirical data.
- Determine the appropriate integration of static parameters (i.e. cost, weight, volume) within the dynamic performance modeling framework.
- Support the development of the vehicle and storage system modeling, including the implementation of the waste heat interaction, refinement of the weighting coefficients for the viability index, and confirming the vehicle characteristics parameters for current and projected future levels.
- Provide the necessary scope, operating profiles, boundary conditions, and model results to support the Phase 1 Go/No-Go deliverables.

Approach: Manufacturing Cost Analysis

- The cost analysis approach is a cascade of increased fidelity to develop the fundamental cost transfer functions for the entire center (led by PNNL)



Cost Analysis Development

1. **Reduce uncertainty**
2. **Interactive with system model**
3. **Common cost assumptions**
4. **Break-down cost drivers**

HSECoE

Proposed Future Work: Manufacturing Cost Analysis

- Support the completion of the hydrogen storage system component cost matrix for the System Architects to use as a common reference.
- Evaluate the key components in order to establish their cost functions in relation to the performance model variables.
- Decompose the key components into their direct and indirect cost elements for the purpose of assessing cost drivers and opportunities.
- Provide hydrogen storage system cost estimate support for evaluating the targets at the Phase 1 Go/No-Go milestone.

Summary

- The Ford (BASF, University of Michigan) project scope contributes to three areas critical to developing commercially-viable hydrogen storage systems --- *system modeling, cost modeling, and materials engineering*. Recent highlights for each technical area include:
  1. Aided in the development of a center-wide universal modeling framework which is capable of high-level input and output parameters between vehicle, fuel cell, and storage systems models
  2. Developed rudimentary fuel cell waste heat and power models which account for realistic interactions between the H_2 storage system and the vehicle power plant and are capable of analyzing boundary scenarios
  3. Refined critical assumptions for system component costing matrix, the first step toward developing robust cost projections for various hydrogen storage system configurations
  4. Assessed and delivered complete data set to center's modeling team for Basolite Z100H (MOF5); performed property screening for diverse FMs; initiated study aimed at reducing variation in critical hydrogen storage measurements.