System Design and Media Structuring for On-Board hydrogen Storage Technologies

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General Motors Company

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Overview

Timeline

- Project Start: March 2009
- Phase I end: July 2011
- Phase II end: July 2013
- Project end: July 2014

Relevance/Barriers Addressed

- System weight and volume (A)
- Energy efficiency (C)
- Charging/discharging rates (E)
- Thermal management (J)

Budget

- DOE: $2,954,707
- GM Match: $738,677
- Budget spent: 20%

GM Team

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Collaborators:

United Technologies Research Center
LINCOLN COMPOSITES
A Member of Hexagon Composites Group
JPL
SRNL
SAVANNAH RIVER NATIONAL LABORATORY
NREL
National Renewable Energy Laboratory
Innovation for Our Energy Future
Ford
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Plan and Approach

Task 1: (Material identification and properties)

- Develop criteria for storage materials in the metal hydride (MH) and Adsorbent material categories and identify storage materials in the two categories

Task 2: (System simulation model for metal hydrides)

- Build storage system simulation models for sodium alanate
- Exercise simulation models for system performance
- Calculate performance metrics in relation to DOE targets
- Build detailed 2-D models to include heat transfer and reactions to guide system models

Task 3: (System simulation model for adsorbent system)

- Build storage system simulation models for activated carbon
- Exercise simulation models for system performance
- Calculate performance metrics in relation to DOE targets
- Build 2-D models to include adsorption and heat transfer to guide system models

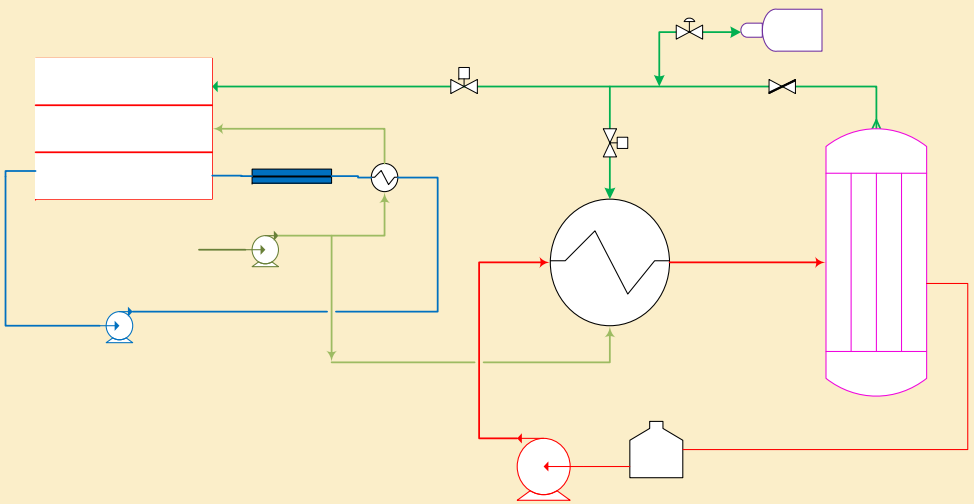
Task 4: (Pelletization of AX-21 and Sodium Alanate)

- Review of binders and additives for pelletization
- Test various binders and additives for pelletization
- Measure hydrogen uptake, thermal conductivity, and pellet strength

Task 5: (Integration with vehicle system model and fuel cell model)

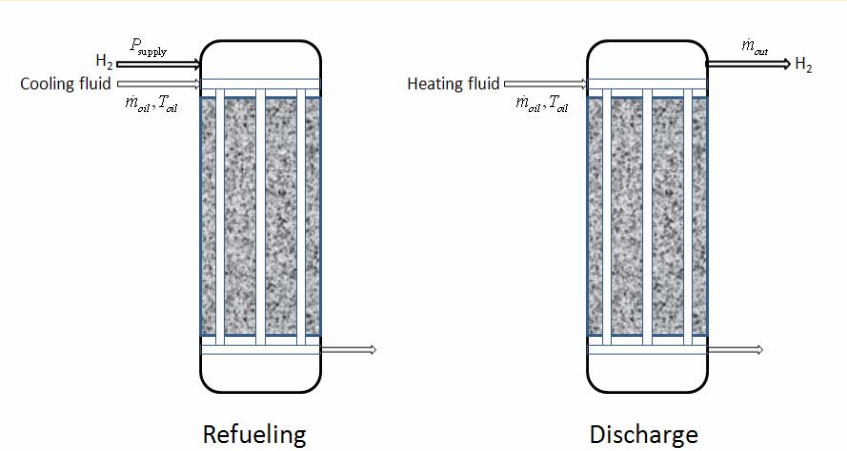
- Work with NREL, Ford and UTRC for integration of hydrogen storage models in a common framework

Schematic of Sodium Alanate storage system

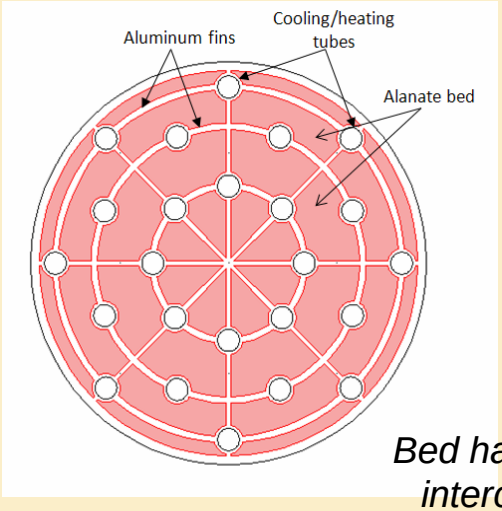


Bed Properties	values	units
Length of the bed	1	m
Inner diameter of the bed	0.417	m
Outer diameter of the tubes	0.022	m
Porosity	0.4	
Fraction of volume of the bed occupied by cooling tubes and fins	0.26	
Mass of Hydride in the bed	101	kg

Alanate bed properties	
Bulk density	1000 Kg/m³
Crystalline density	1670 Kg/m³
Specific heat	1230 J/kg-K
Enhanced thermal conductivity	8.5 W/m-K



System consists of 2 beds each of ~2.5kg usable H_2



Bed has 24 cooling tubes interconnected by fins

Coolant

Radiator

Fuel Cell

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Sodium Alanate System

System Details

- Gaseous H_2 in the free space based on bed porosity
- Overall heat transfer coefficients is based on correlation with 2-D COMSOL model
- Kinetics by Luo and Gross (2004)
- Heating fluid is set to 450K for tet phase and at 470K for hex phase decomposition
- Oil heating transients included to study cold start up capability of the system
- 50 g buffer tank is provided to handle the slow kinetics of Hex phase decomposition
- 12 kW catalytic burner for heating the oil
- 13 kg heating oil is provided within the vehicle
- Two storage beds for a full 5 kg usable H_2 system
- Efficient control system is developed to handle high transient demands

Control Strategy

Flow to fuel cell

if $P_{bed1} > P_{cut_off}$

First bed supplies the H_2 to fuel cell and burner

elseif

$P_{bed2} > P_{cut_off}$

Second bed supplies the H_2 to fuel cell and burner

else

Buffer supplies the H_2 to fuel cell and burner

Flow to buffer

if $P_{bed1} > P_{Buffer}$

First bed supplies the H_2 to buffer

elseif

$P_{bed2} > P_{Buffer}$

Second bed supplies the H_2 to buffer

else

No bed supplies to buffer

Refueling (2-D COMSOL Model)

- Obtained key information from 2-D COMSOL refueling model
  - bed design
  - overall heat transfer coefficient defined below
  - state of the bed after 10.5 min of refueling

- Initial state of the system based on 10.5 min refueling time

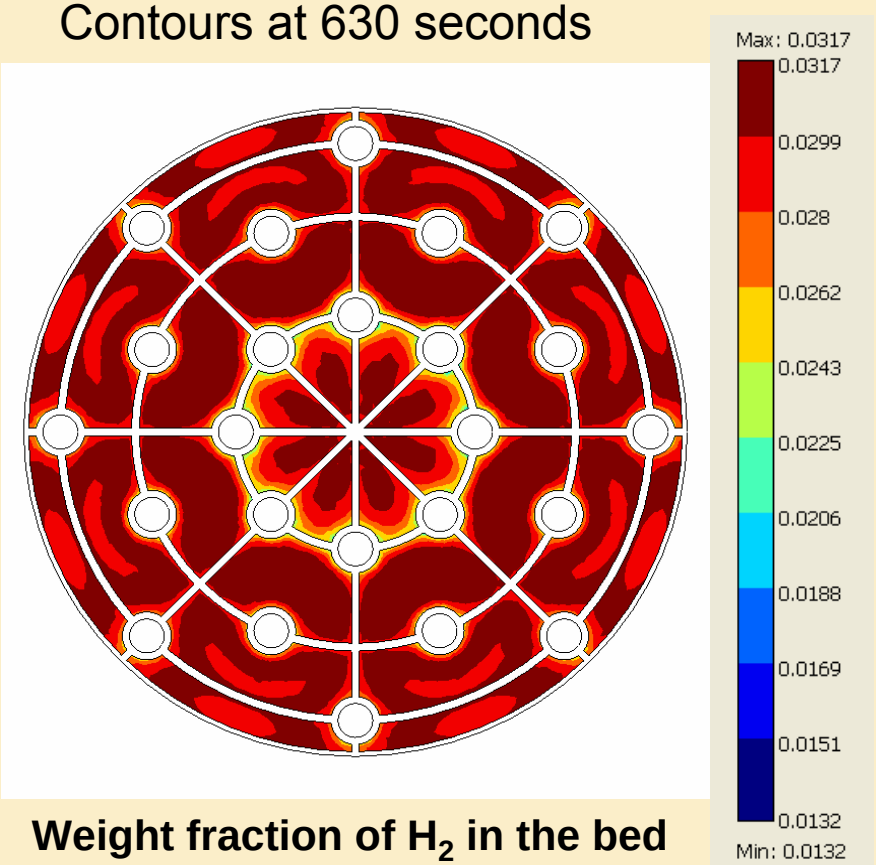
$$\frac{1}{U_{eff}} = \frac{1}{h_c \eta_f} + \frac{L_{eff}}{k_{MH}};$$

η_f is fin efficiency

L_{eff} is characteristic bed length

η_f, L_{eff} are evaluated from 2D COMSOL model

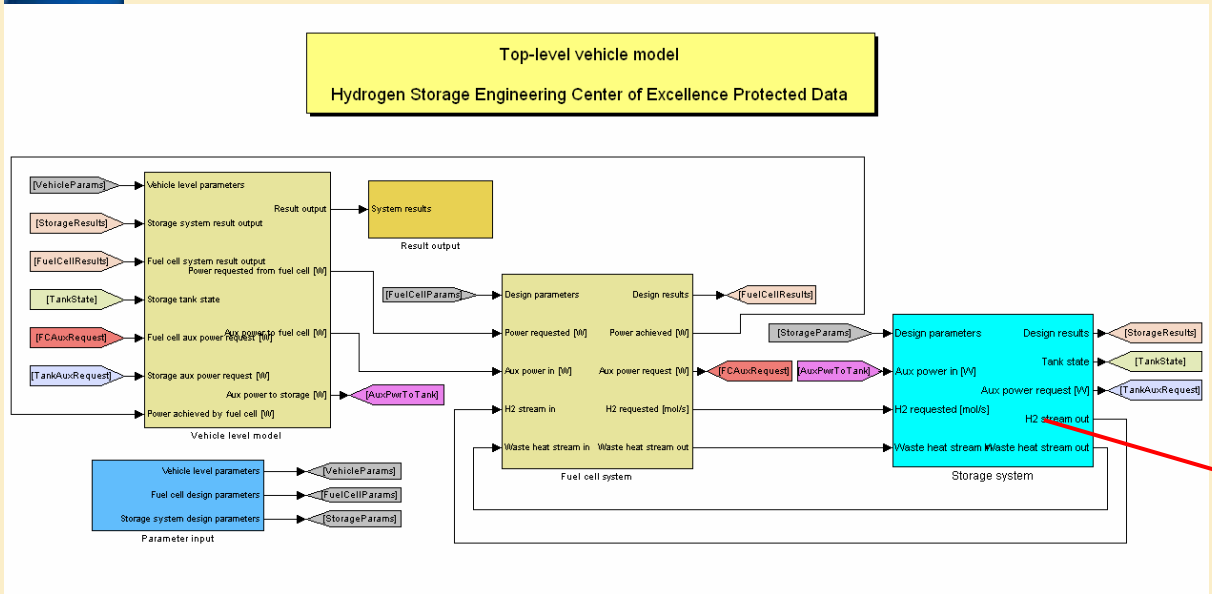
Contours at 630 seconds



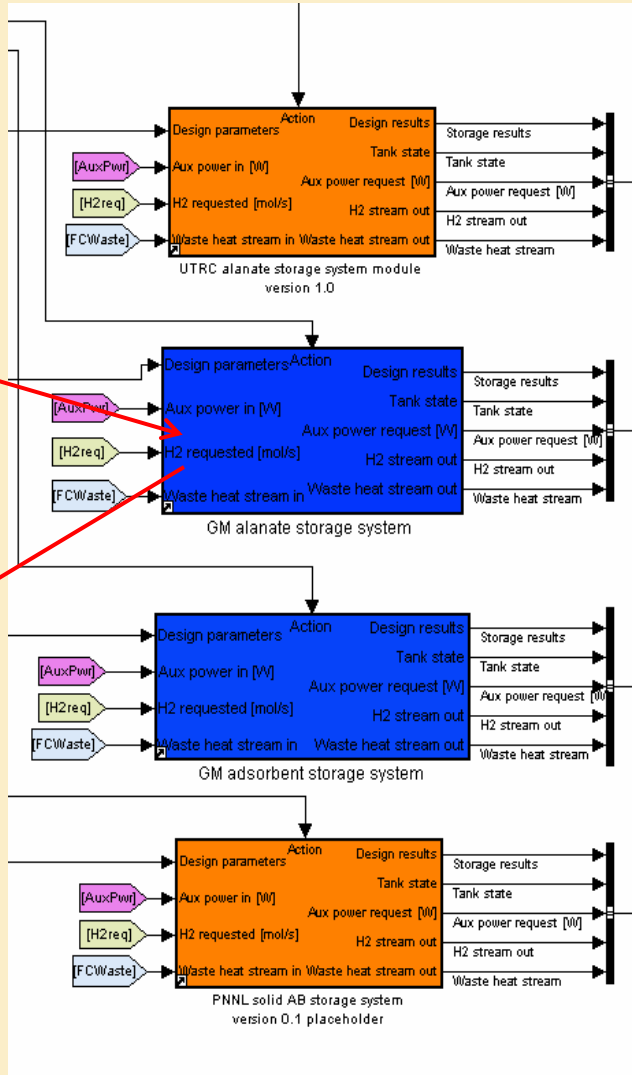
Weight fraction of H_2 in the bed

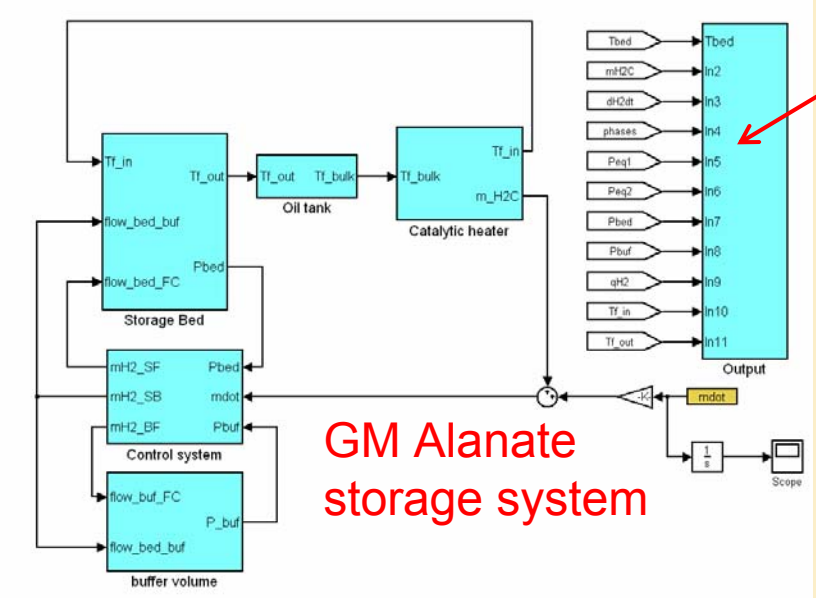
Average weight fraction in the bed is 0.305

Integration in the Framework



Framework developed by UTRC-FORD-GM

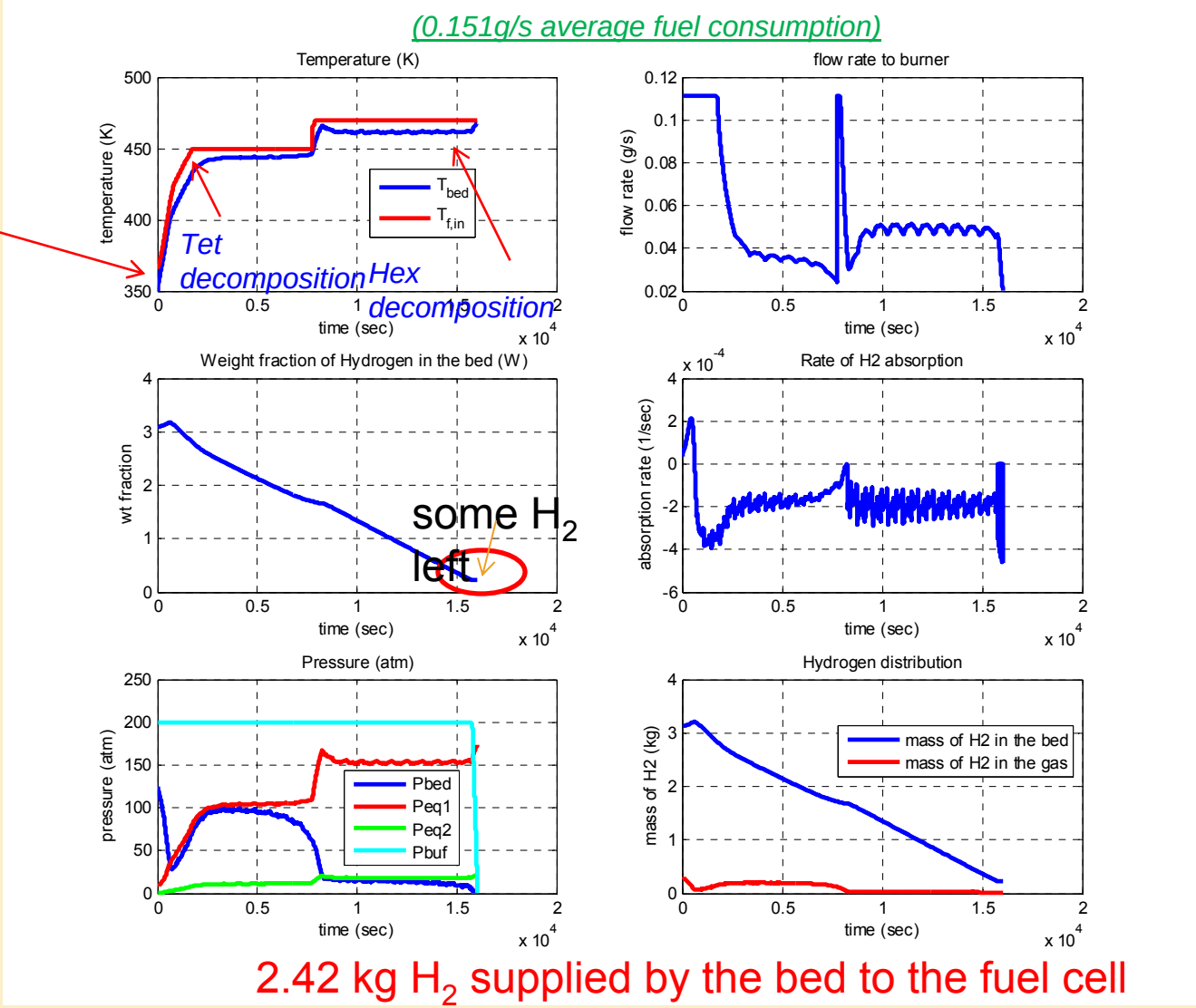




GM Alanate storage system

Drive Cycle Simulation (HWY)

Bed initially at 350 K



2.42 kg H_2 supplied by the bed to the fuel cell

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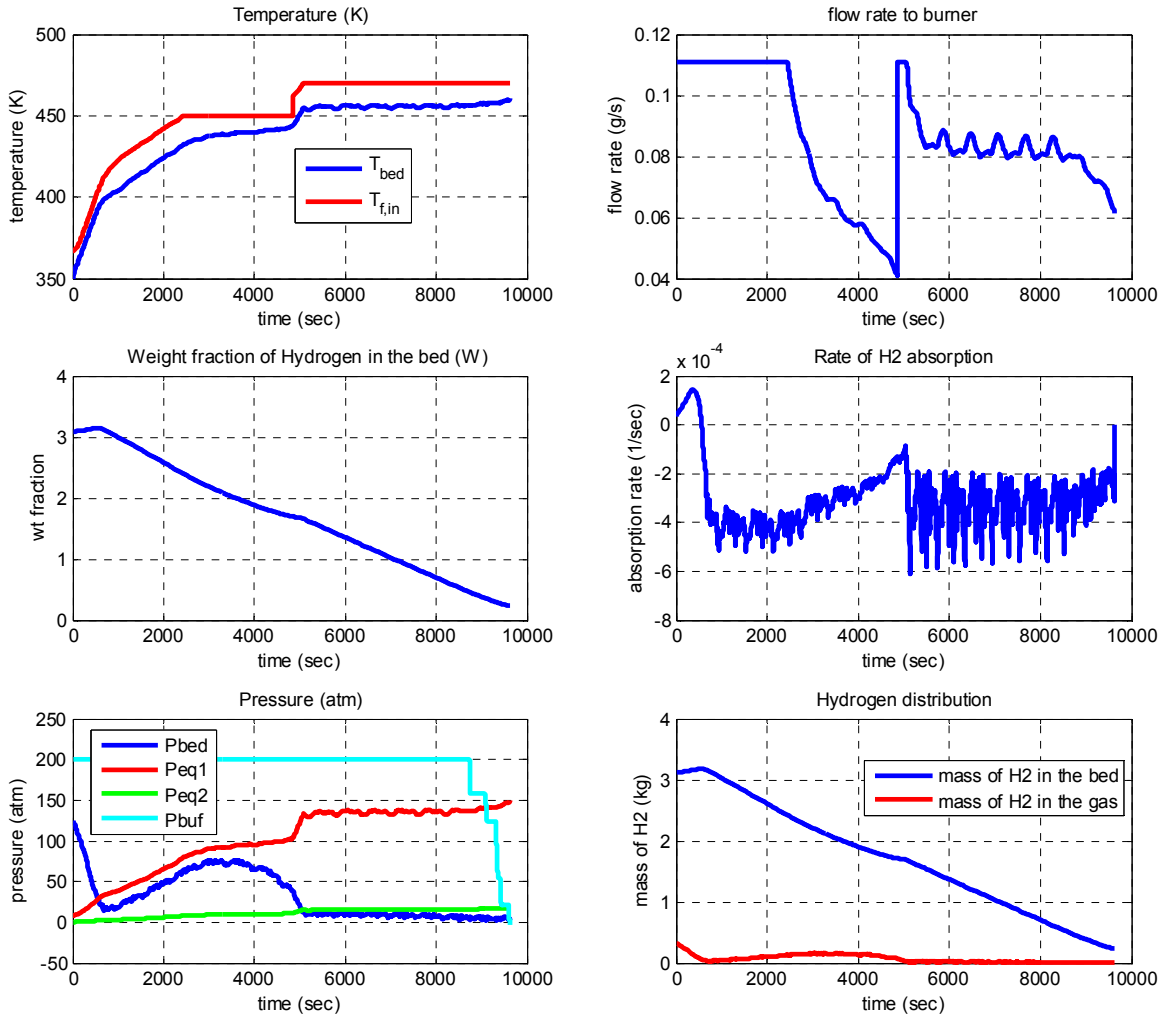
Drive Cycle Simulation (US06)

(0.252g/s average fuel consumption)



2.43 kg H_2 supplied by the bed to the fuel cell

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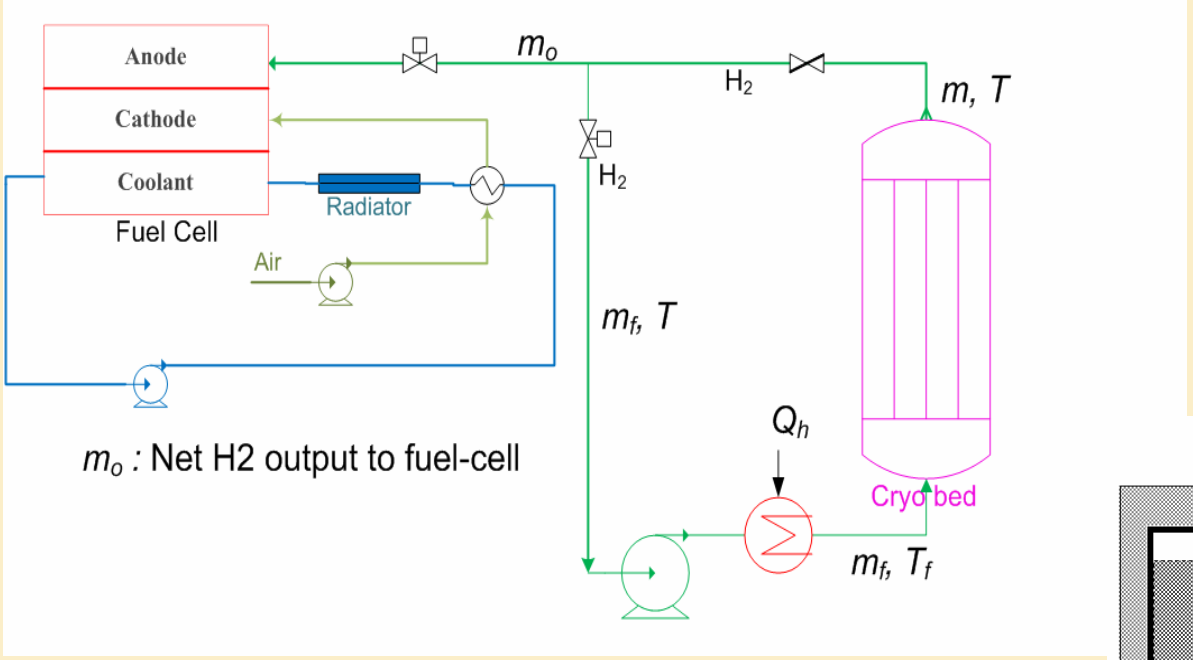
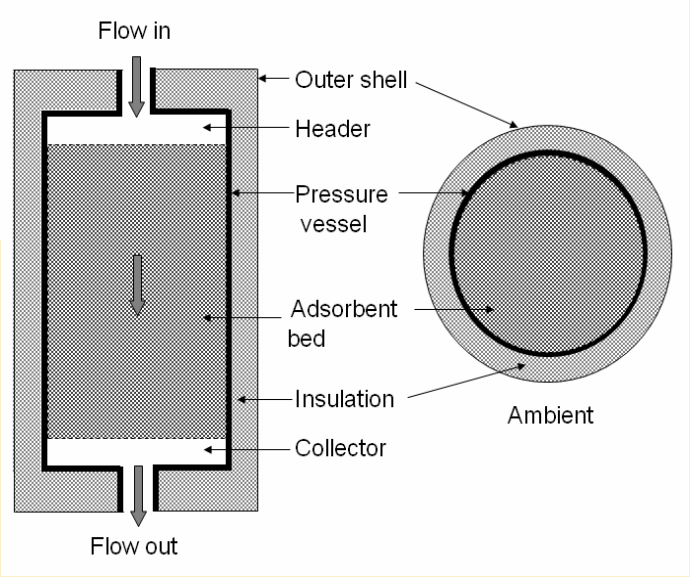
Cryoadsorption System



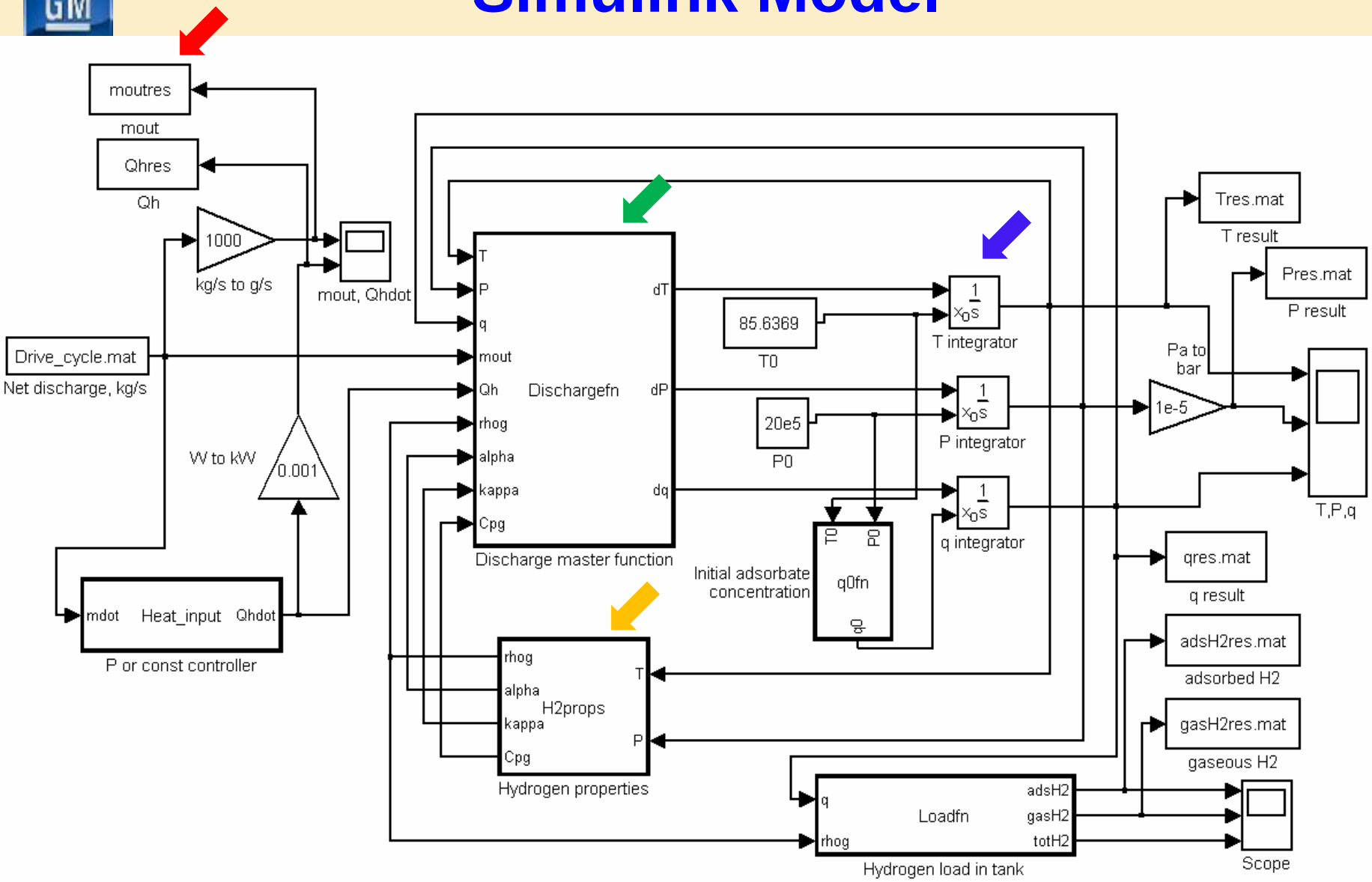


Schematic of the cryoadsorption system

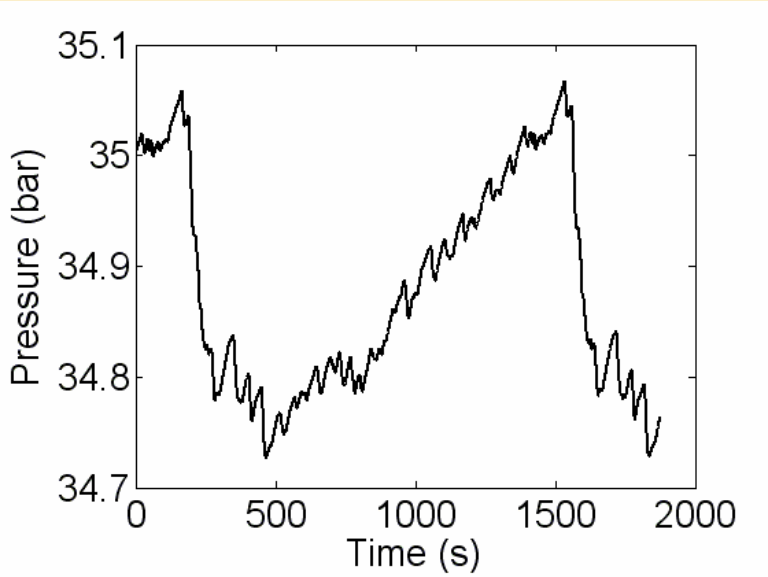
Cryoadsorption System

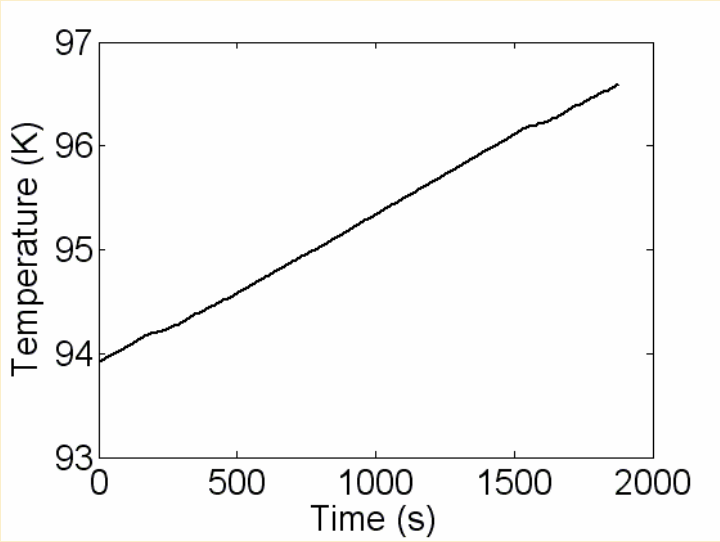
- System model based on mass balance, energy balance, and adsorption equilibrium
- Heat needs to be added during discharge to avoid very low tank temperatures and discharge most of the hydrogen.
- Various heat addition rate schemes investigated
  - Varying heat input proportional to the hydrogen demand by the fuel cell
  - Constant heat input proportional to the average hydrogen demand over the drive cycle
- Heat could be added into the tank by heating a part of the recirculating gas or by an electric heater.
  - Since the gas is in intimate contact with the bed, first mode of heating could be efficient
  - The electric heater, though less efficient, might be beneficial in terms of gravimetric / volumetric capacities of the system, since there are no auxiliary components

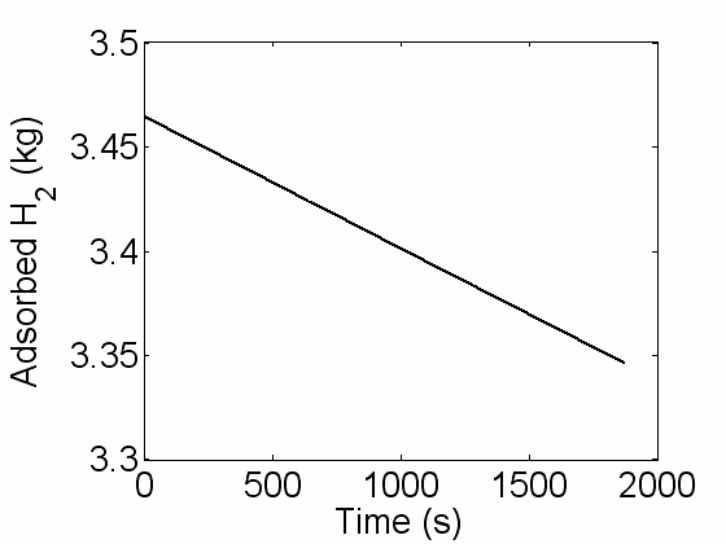
Simulink Model

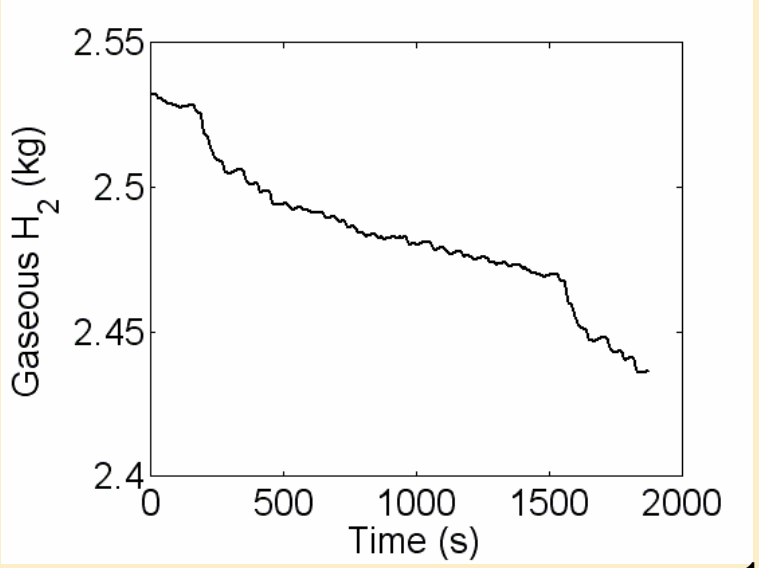


AX-21: FTP-75, 0.36 kW Constant Heating Rate









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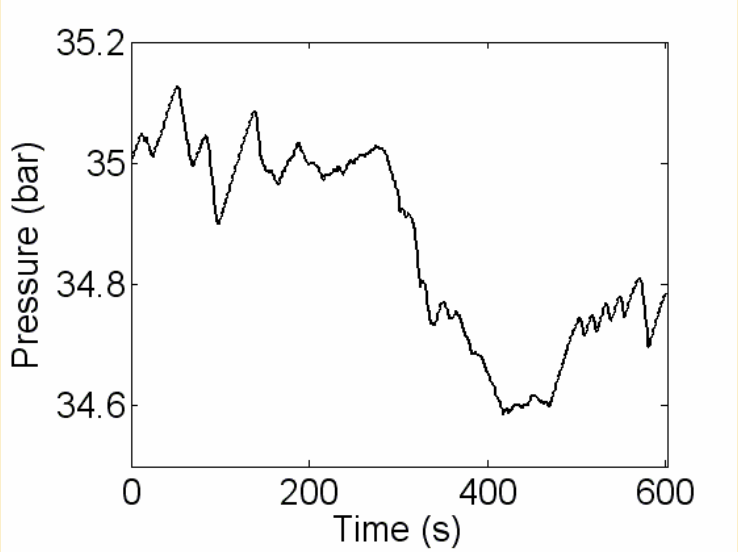
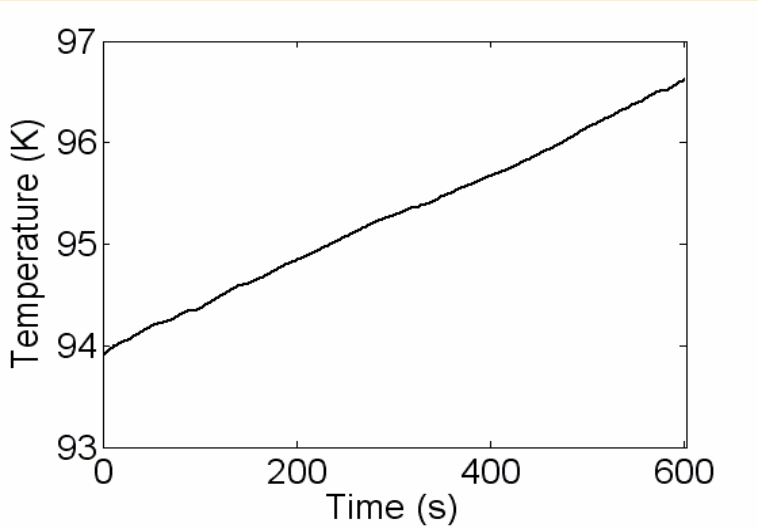
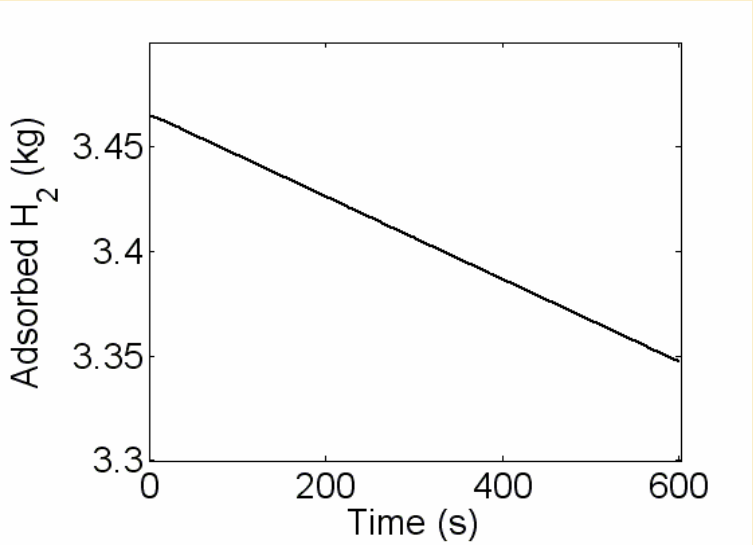
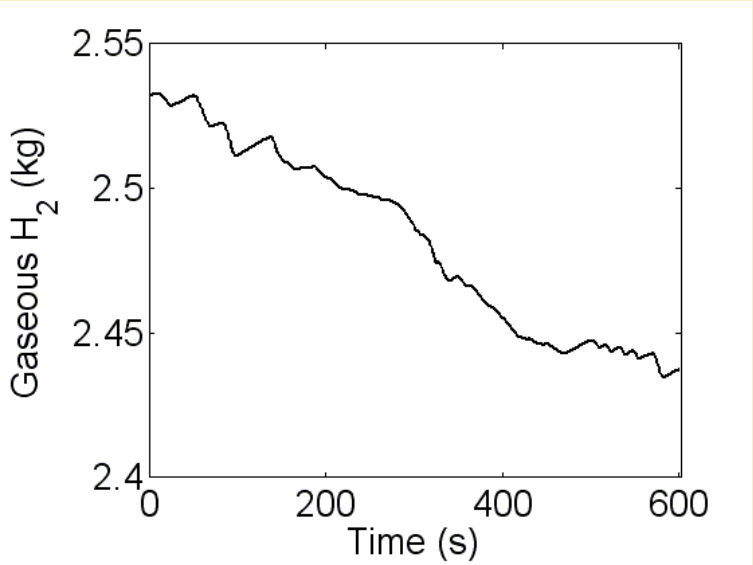
AX-21: US-06, 1.13 kW Constant Heating Rate

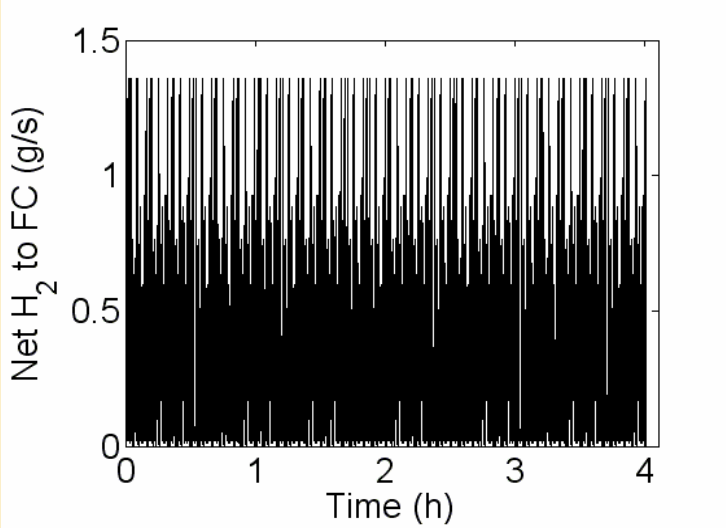


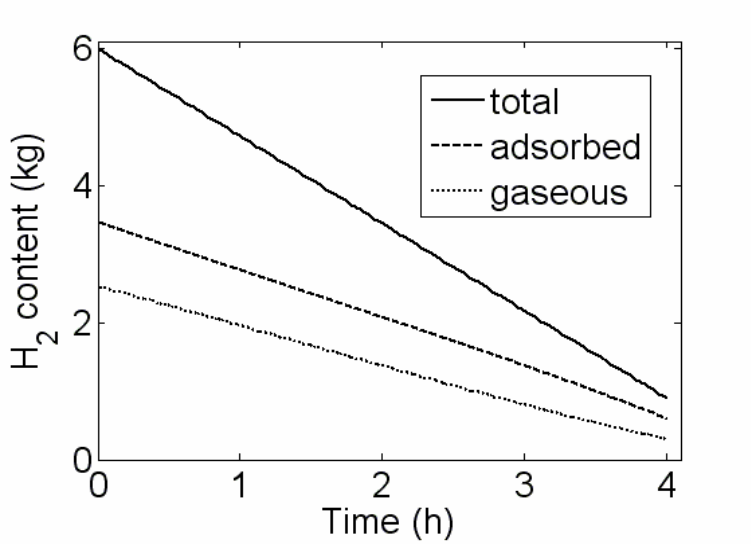


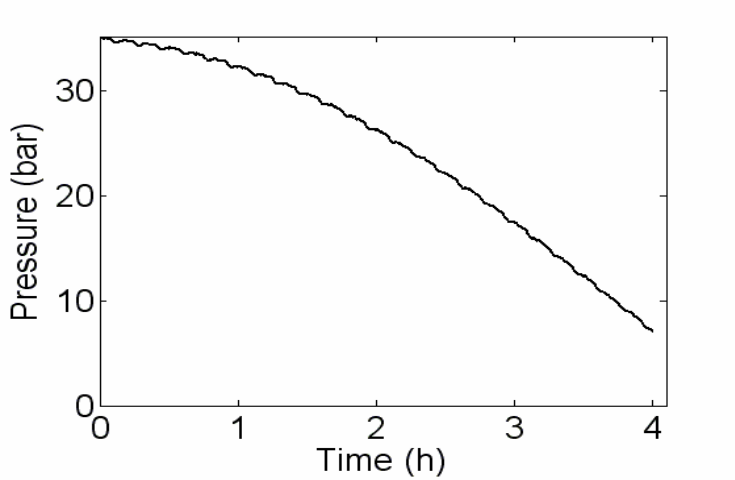


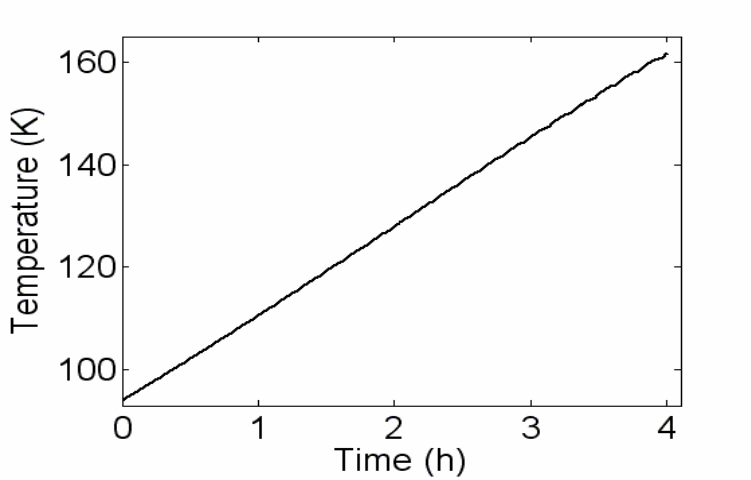


AX-21 bed: Repeated US-06 cycles









Preliminary Gravimetric and Volumetric Densities for sodium alanate system

Number of beds		2
Deliverable hydrogen	kg	4.85
Total length of the bed	mm	1292.0
Diameter of the bed (inner)	mm	416.0
Diameter of the bed (outer)	mm	436.9
Shell material		Composite carbon
Weight of 2 vessels including liner	kg	61.4
Total Weight of alanate	kg	202.00
Weight of tubes and fins	kg	143.10
Accessories (manifolds, end plates etc.)	kg	20
Pump/HEX/burner	kg	8.00
Other BOP components	kg	7
Oil mass	kg	13.00
Buffer	kg	5.05
Buffer volume	liters	11.30
Total volume of the beds		387.5
Total system volume	liters	407.8
Total system mass	kg	459.50
Gravimetric density		0.0105
Volumetric density		0.0119

Vessel thickness and materials estimates by Lincoln Composites

Preliminary Gravimetric and Volumetric Densities for Activated Carbon system

System Temp & Pressure	77 K, 35 bars
Final pressure	4 bar
Adsorbent volume (L)	265.5
Total usable H2	5 kg
Adsorbent mass (kg)	75.3
Total inner volume (L)	307.4
Cylinder L (cm)	104
2 Hemispheres D (cm)	53
INNER VESSEL & OUTER VESSEL Material	Aluminum 6061
Inner vessel Mass	47.5
Outer vessel mass (kg)	12.4
Insulation mass (kg) – MLVSI (1" thick)	12
BOP components (kg)	15
Total mass (kg)	162.2
Gravimetric capacity	**0.0308**
Outer Volume(L)	398.3
Volumetric density (kg/L)	**0.0126**

			$NaAlH_4$	Comments	AX-21	Comments	2010	2015	ultimate
Gravimetric	Gravimetric Density	*(Kg H_2/Kg system)*	**0.0105**	composite vessel, aluminum HEX	**0.0308**	Inner and outer vessels aluminum	**0.045**	**0.055**	**0.075**
Volumetric	Volumetric Density	*(Kg H_2/liter)*	**0.0119**	HEX significant vol and wt fraction	**0.0126**	MLVI btwn vessels	**0.028**	**0.040**	**0.070**
Cost	System Cost	*($/KWh net)*					**4**	**2**	**TBD**
	Fuel Cost	*($/gge)*					**133**	**67**	**TBD**
Durability/ Operability	Minimum Operating Temperature	*(°C)*	**-30**	with buffer and void-space H2, seems OK	**-30**	not an issue	**-30**	**-40**	**-40**
	Maximum Operating Temperature	*(°C)*	**50**	can be done	**50**	if enough insulation	**50**	**60**	**60**
	Min. Delivery Temperature	*(°C)*	**-40**	Not a problem	**-40**	not an issue	**-40**	**-40**	**-40**
	Max Delivery Temperature	*(°C)*	**85**	H2 cooled in the tank to FC delivery	**85**	not an issue	**85**	**85**	**85**
	Cycle Life (1/4 - full)	*(N)*	**NA**		**NA**		**1000**	**1500**	**1500**
	Cycle Life (90% confidence)	*(% mean)*	**NA**		**NA**		**90**	**99**	**99**
	Min. Delivery Pressure (PEMFC)	*(bar)*	**4**	Not a problem	**4**	Not a problem	**4**	**3**	**3**
	Min. Delivery Pressure (ICE)	*(bar)*	**?**	Could be an issue	**?**	Could be an issue	**35**	**35**	**35**
	Max. Delivery Pressure FC/ICE	*(bar)*	**12**	OK	**12**	OK-FC, issue for ICE	**12/100**	**12/100**	**12/100**
	On Board Efficiency	*(%)*	**75%**	41 kJ/mole, 90% eff burner, heat media	**95%**	6 kJ/mole + mCpΔT	**90%**	**90%**	**90%**
	Wells to Power Plan Efficiency	*(%)*	**NA**		**NA**		**90%**	**90%**	**60%**
Charge/ Discharge Rates	Fill Time (5Kg H_2)	*(min.)*	**10.5 min**		**4.2 min**	Cold H2	**4.2**	**3.3**	**2.5**
	Minimum Full Flow Rate	*([g/s]/KW)*	**0.02**	H2(g) in buffer and void-space	**0.02**	H2 in gas-phase	**0.02**	**0.02**	**0.02**
	Start Time to Full Flow (20°C)	*(sec,)*	**5**	H2(g) in buffer and void-space	**< 5**	H2 in gas-phase	**5**	**5**	**5**
	Start Time to Full Flow (-20°C)	*(sec,)*	**15**	H2(g) in buffer and void-space	**< 15**	H2 in gas-phase	**15**	**15**	**15**
	Transient Response	*(sec,)*	**0.75**	H2(g) available, mech/elect issue	**0.75**	H2(g) available, mech/elect issue	**0.75**	**0.75**	**0.75**
Fuel Purity	Fuel Purity	*(%)*					**99.99%**	**99.99%**	**99.99%**

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Media Structuring Studies

Hydrogen storage media are generally characterized by low density and low thermal conductivity leading to low gravimetric and volumetric energy densities

Motivation : To engineer compaction of the storage media for

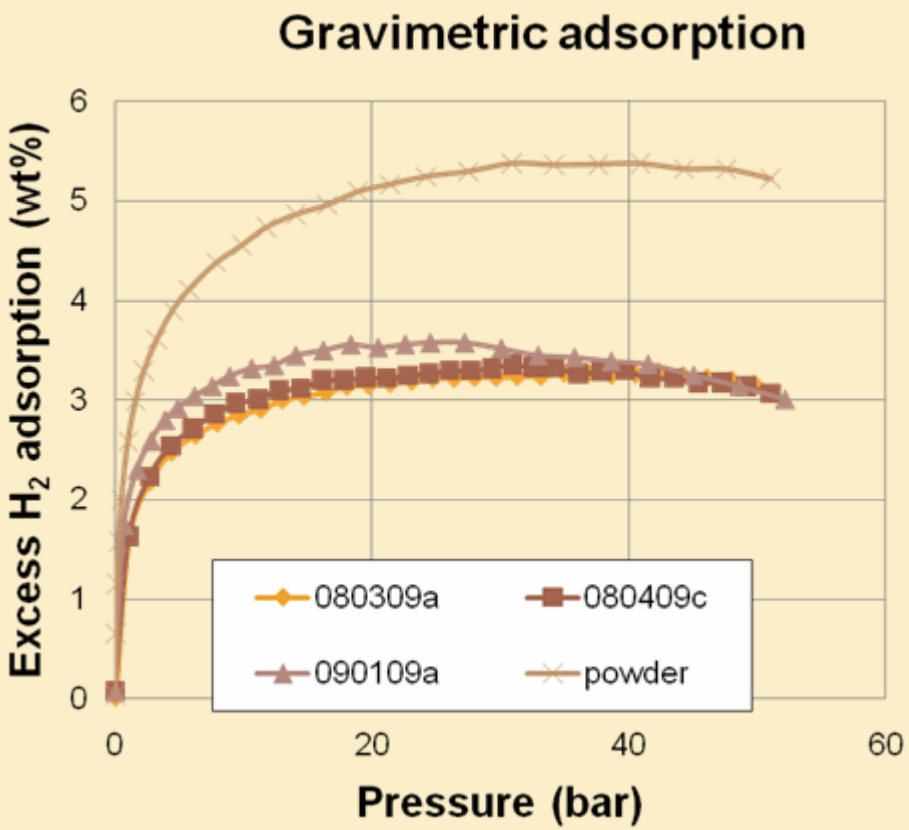
- increased density
- increased thermal conductivity, and
- easier handling, while
- maintaining hydrogen absorption/adsorption capacity, and
- kinetics

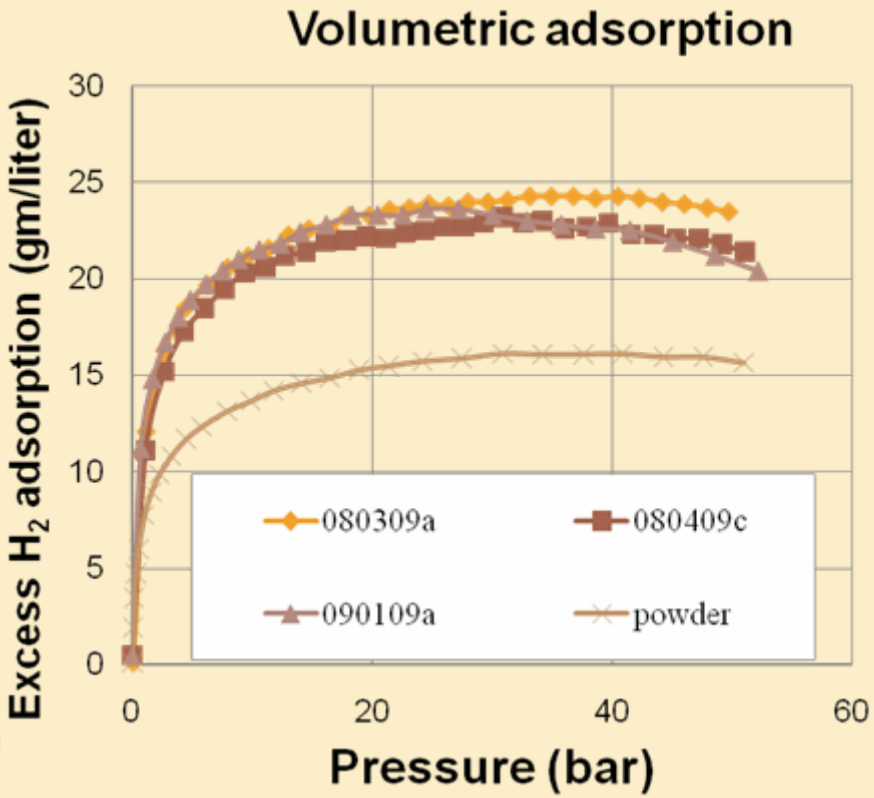
AX-21 Pelletization Data – Surface area and density

Adsorbent surface area is a good indicator of its hydrogen adsorption capacity

Sample ID	Binder	T (°C)	P (MPa)	ρ (g/cm^3)	S_{BET} (m^2/g)	V_{micro} (m^3/g)	ρ*S (10^6 m^{-1})
AX-21	-	-	-	0.3	3070	1.39	921
072809a	PVDF-HSV900- 5 wt%	200	197	0.59	2078	0.92	1230.2
080309a	PVDF-HSV900 - 5 wt%	200	280	0.74	1744	0.80	1290.6
092809a	PVDF-HSV900 - 5 wt%	200	375	0.84	1645	0.71	1381.8
080409c	PVDF-301F - 5 wt%	200	280	0.68	1880	0.87	1278.4
081109a	PVDF-301F - 5 wt%	200	375	0.77	1622	0.72	1248.9
090109a	PVA solution - 5 wt%	230	280	0.64	2012	0.90	1291.7

AX-21 Pellets
Gravimetric and Volumetric Capacity at 77 K





Pellets have a lower gravimetric but higher volumetric adsorption capacity than the original graphite AX-21 powder.

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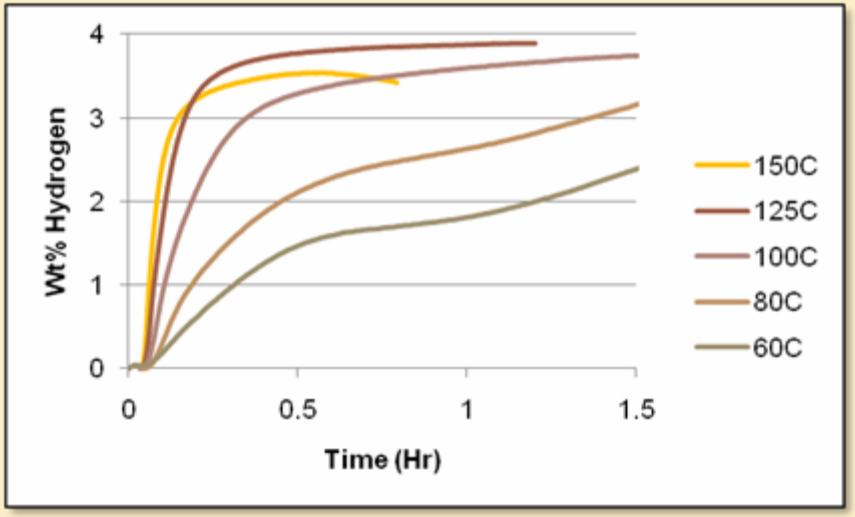
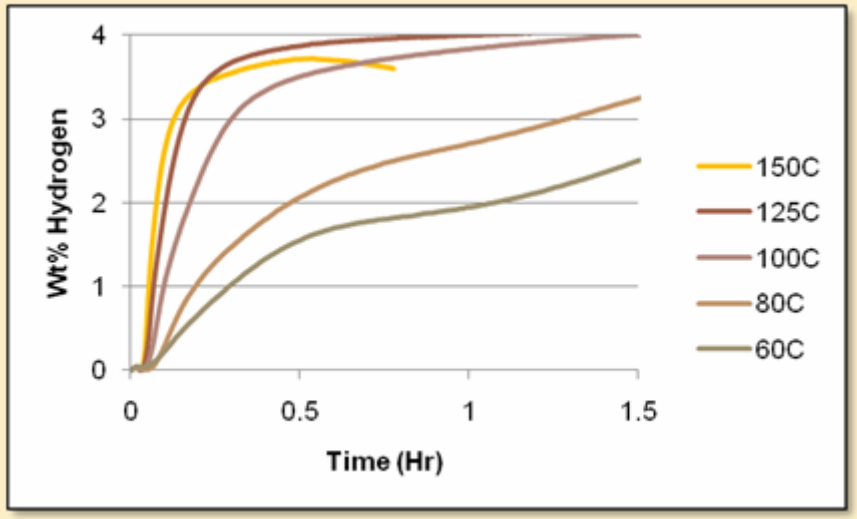
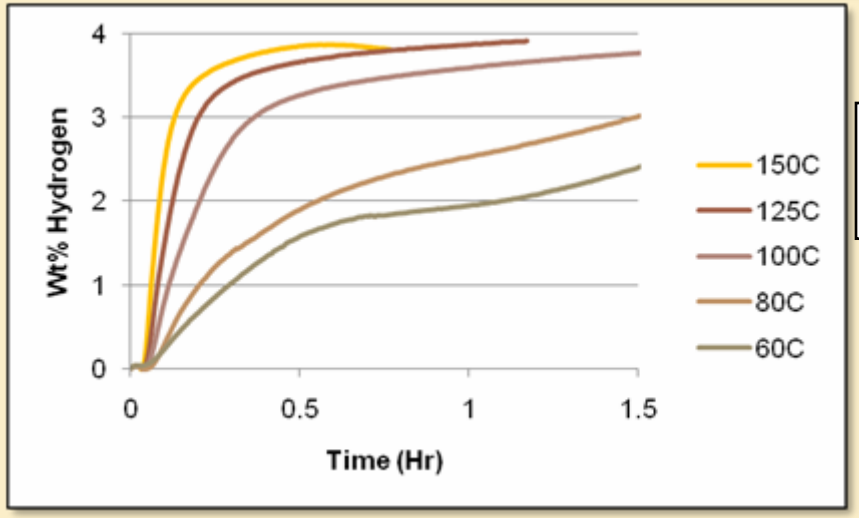
Sodium alanate: Hydrogen Uptake – Various Temps

6.35mm EPDM Coated Pellets



6.35mm Uncoated Pellets





Loose Powder

Sodium alanate pellets
Thermal conductivity (W/m°K)

Thermal Conductivity measurements (All Pellets: 9.525 mm die)		Die Pressure (psi)	Uncoated Pellets	One coat	Three coats
Alanate with excess aluminum		50,000	9.6	9.43	9.44
+ 5 mol% expanded graphite	High-energy mixing	50,000	5.74	5.93	6.74
+ 5 mol% graphite flakes	High-energy mixing	50,000	5.95	7.10	7.28
+ 5 mol% expanded graphite	Low-energy mixing	50,000	8.56	-	-
+ 5 mol% graphite flakes	Low-energy mixing	50,000	8.86	-	-
+ 5 mol% expanded graphite	Low-energy mixing	10,000	2.98	-	-
+ 5 mol% graphite flakes	Low-energy mixing	10,000	3.26	-	-

Summary

1. Systems designed and Simulink models built for sodium alanate and AX-21 systems
2. Both system models integrated within the Simulink framework and system simulations performed for various operating conditions and drive cycles
3. For the adsorbent system,
   - H_2 in the adsorbed phase responds to the steady demand while the gas- phase H_2 responds to demand fluctuations.
   - A constant heating rate addressing the heat of desorption for the average FC demand is sufficient during the discharge cycle.
   - An electrical heater may offer advantages because of its simplicity

AX-21 Pellets

- Gravimetric hydrogen uptake decreases, but the volumetric capacity increases in comparison with powder
- Modifications needed in the pelletization process

Sodium alanate Pellets

- Coatings diminish pellet damage
- H_2 uptake capacity not affected by the coating
- Thermal conductivity depends on the pressing pressure but the coating does not hinder thermal conductivity

Collaborations

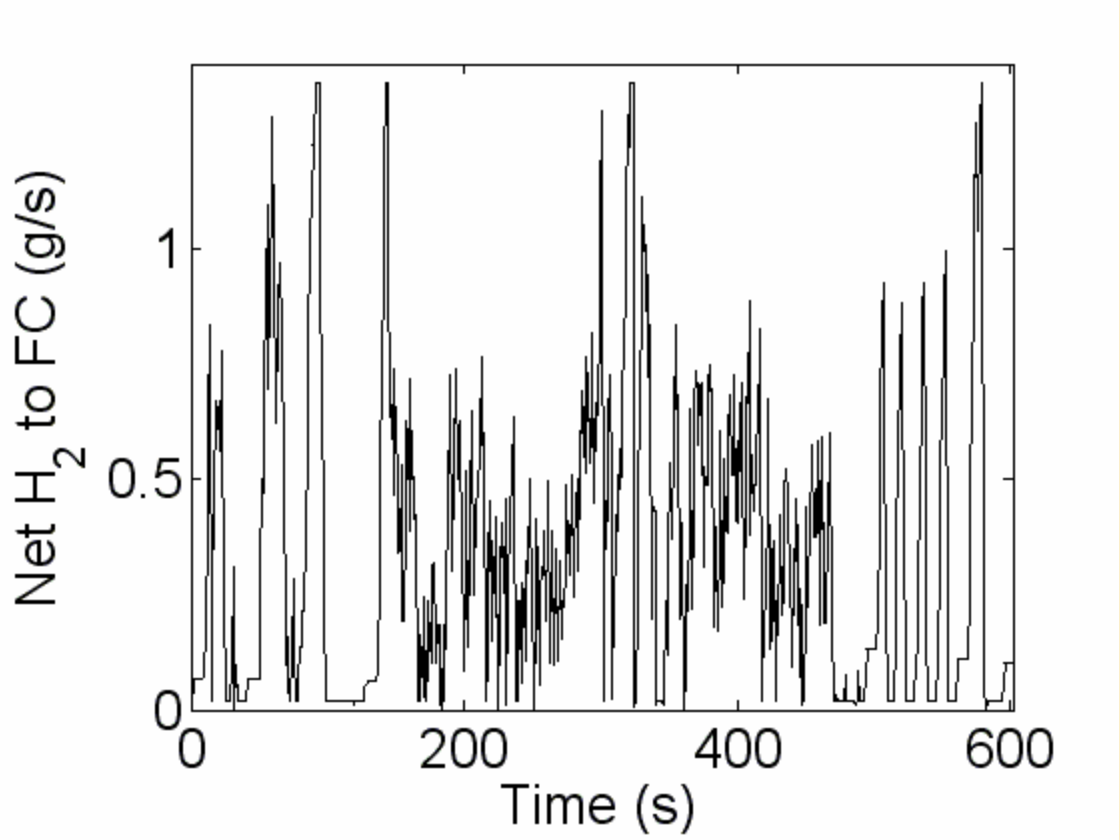
- UTRC, NREL, Ford – system modeling and development of integrated framework
- SRNL – Detailed COMSOL models including heat and mass-transfer, reaction kinetics, and flows in systems
- UTRC, Ford, UQTR – Media compaction studies
- JPL, UQTR, SRNL – System architecture for prototype systems
- OSU – micro-channel heat exchangers and catalytic burner

Proposed Future Work

1. Evaluate metal hydride and adsorbent systems for additional drive cycles and operating conditions
2. Test system performance at extreme temperatures and sensitivity studies for various parameters
3. Adapt and improve system model for next metal hydride candidate
4. Cryoadsorbent system models and performance metrics for higher pressures
5. Refueling strategies for cryoadsorbent systems
6. Examine kinetics, mechanical stability and thermal conductivity dependence on pellet diameter and binder/coating material
7. Improve pelletization techniques to make pellets faster with no or minimal adverse impact on hydrogen uptake capacity and kinetics

Supplementary Slides

US-06 Cycle: Hydrogen Demand



The US-06 cycle is a shorter but more aggressive cycle than FTP-75

It consumes 212.54 g of H_2 in 601 s, for an average demand of 0.354 g/s.

- AX-21: For ΔH of 3.2×10^6 J/kg, and 0.354×10^{-3} kg/s average discharge rate, the heating rate = 3.2x0.354 kW = 1.13 kW

Sodium Alanate Pelletization

- Presses easily into pellet, no addition of binder required to maintain pellet integrity. However, binder coating slows oxidation in air.
- EPDM dissolved in solvent. Pellets dipped into solutions and allowed to dry between coatings
- Average binder wt < 1% for each coating of 70:4 EPDM
- EPDM = Ethylene Propylene Diene Monomer (M-class) rubber
  - Ethylene content ≈ 45 – 75% , Diene content ≈ 2.5 – 12wt% (provides resistance to tackiness), EPDM mixtures – 70:4, 50:4, 50:8 & 60:4.