IV.D.1f System Design and Media Structuring for On-Board Hydrogen Storage Technologies

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Objectives

Main objectives of this project are:

- To develop system simulation models for on-board hydrogen storage systems using metal hydride and adsorbent materials and to determine system compliance with the DOE technical targets.
- To develop storage media structures with optimized engineering properties for use in storage systems.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Fuel Cell Technologies Program Multi-Year Research, Development, and Demonstration Plan (MYPP):

(A) System Weight and Volume

(B) Efficiency

(E) Charging/Discharging Rates

(J) Thermal Management

Technical Targets

This project addresses the design of on-board hydrogen storage systems for two types of storage media - adsorbent materials and metal hydrides. In particular, the system design is to be optimized with emphasis on meeting following DOE 2010 targets.

Storage Parameter	Units	2010	2015
System gravimetric capacity	(kg H_2/kg system)	0.045	0.055
System volumetric capacity	(kg H_2/L system)	0.028	0.040
System fill time (for 5 kg H_2)	min	4.2	3.3
Minimum full flow rate	(g/s)/kW	0.02	0.02
Min-max delivery temperature	°C	-40/85	-40/85

❖   ❖   ❖   ❖   ❖

Approach

As part of the Hydrogen Storage Engineering Center of Excellence (HSECoE) team, the GM team is building system models for on-board hydrogen storage systems using metal hydrides and adsorbent materials, storage media structuring and enhancement studies, and building a cryo-adsorption vessel for validation of cryo-adsorption models.

System Modeling: Over the past year, we have concentrated our efforts on both metal hydride and adsorbent system simulation modeling. The system simulation models have been developed in a MATLAB/Simulink framework using lumped parameter representation for these systems. However, the lumped model development has been guided by estimation of necessary heat transfer parameters based on development of two-dimensional (2-D) models that include thermal transport and hydrogen absorption/adsorption kinetics. The HSECoE coordinating council decided to focus the Center efforts on sodium alanate and AX-21 as the representative metal hydride and adsorbent materials respectively. We have employed the system models for hydrogen discharge during the driving cycles and 2-D thermal transport and kinetic models for refueling the hydrogen storage system.

Storage Media Structuring and Enhancement: To enable fast refueling, it is extremely important to employ storage media with good thermal transport properties in conjunction with an optimized heat exchanger system to remove the heat generated by the exothermic process of hydrogen uptake. For metal hydrides, another challenge is the fracture of storage media during cycling. Fracturing decreases the heat

transfer and enables the increasingly smaller particles to move in the containment vessel and collect at the bottom of the tank with an adverse impact on the system performance. In addition to the potential fracturing of the hydrides, volumetric expansion during hydriding needs to be addressed. One major objective of this project is to develop, test, and optimize metal hydride composites in the form of pellets or other similar shapes to greatly enhance thermal conductivity of the storage material, and to improve cycling stability and durability of the metal hydride materials. Similarly for adsorbent materials, forming mechanically stable composite pellets out of a powderous material is very useful. Pellets or similar-shaped composites of the adsorbent material will be formed using small amounts of binders in combination with thermal enhancing materials. As with metal hydrides, the main objective is to improve thermal conductivity of the storage material and to improve cycling stability and durability of adsorbent materials.

Accomplishments

1. System Modeling of Metal Hydride Systems

We have developed system simulation models for two metal hydrides - $Ti_{1.1}CrMn$ and $NaAlH_4$.

On-board hydrogen storage systems employing high-pressure metal hydrides like TiCrMn promise advantages including high volumetric capacities and cold-start capability. We have developed a simulation model for this system in a MATLAB/Simulink platform. Transient equations for mass balance and energy balance are used and appropriate kinetic expressions are used for the absorption/desorption reactions for the Ti1.1CrMn metal hydride. During refueling, the bed is cooled by passing a coolant through tubes embedded within the bed while during driving, the bed is heated by pumping the radiator fluid through same set of tubes. The feasibility of using a high-pressure metal hydride storage system for automotive applications is explored. Drive cycle simulations for a fuel cell vehicle are performed and detailed results are presented. A paper discussing this work has been prepared and accepted for publication in the Int. J. Hydrogen Energy (2010).

The system simulation model for $NaAlH_4$ is more complicated and employs additional elements. Because of the high enthalpy of hydrogen absorption and desorption, this system requires burning part of the stored hydrogen to heat up the bed for hydrogen desorption. Thus a catalytic heater that burns hydrogen and heats a warming fluid is a necessary part of the $NaAlH_4$ system. In addition, a buffer volume storing gaseous hydrogen is needed for periods when the bed is unable to meet the fuel cell demand. This occurs when the bed is cold or contains only hex-phase (Na_3AlH_6) which has slow hydrogen desorption kinetics. Figure 1
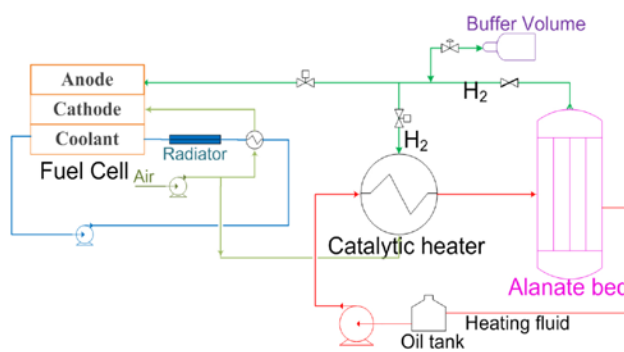

FIGURE 1. A Schematic of the Sodium Alanate-Based Hydrogen Storage System

shows a schematic of the sodium alanate-based hydrogen storage system. System simulation results for the US06 drive cycle are shown in Figure 3.

2. System Modeling of Adsorbent System

A system model for a cryo-adsorber tank employing the activated carbon AX-21 has also been developed. We have selected the lumped parameter model developed earlier at General Motors to develop system simulation models for the processes in the cryo-adsorber tank. A system simulation schematic for the discharge cycle of a cryo-adsorption system is shown in Figure 2. Hydrogen is discharged from the cryo-adsorber tank using pressure and temperature control. It is necessary to both raise the tank temperature and reduce pressure to desorb and use most of the hydrogen stored in the tank. Temperature of the system is increased by supplying heat either through an electric heater or through a heated sidestream of hydrogen. System simulations for the US06 drive cycle for the case of a constant heat input are shown in Figure 4.

A preliminary evaluation of the system performance for both sodium alanate and AX-21 systems in relation to the DOE performance targets is shown in Table 1.

3. Storage Media Structuring and Enhancement

Sodium alanate pellets were prepared using a die and pressures up to 50,000 psi. Use of a binder is not necessary for formation of the alanate pellets. We have studied the hydrogen uptake, thermal conductivity as well as kinetics of sodium alanate pellets of various sizes. Some of the results on hydrogen uptake by the pellets and loose powder are shown in Figures 5. We are also working with AX-21 activated carbon as the adsorbent material for media structuring studies. Results were presented at the 2010 DOE AMR Meeting in Washington, D.C.
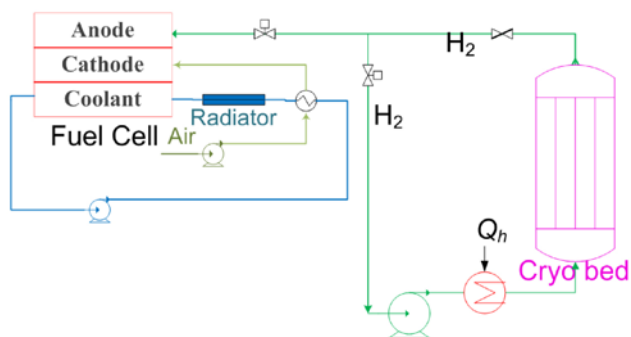
FIGURE 2. A Schematic of the AX-21-Based Cryo-Adsorbent Hydrogen Storage System
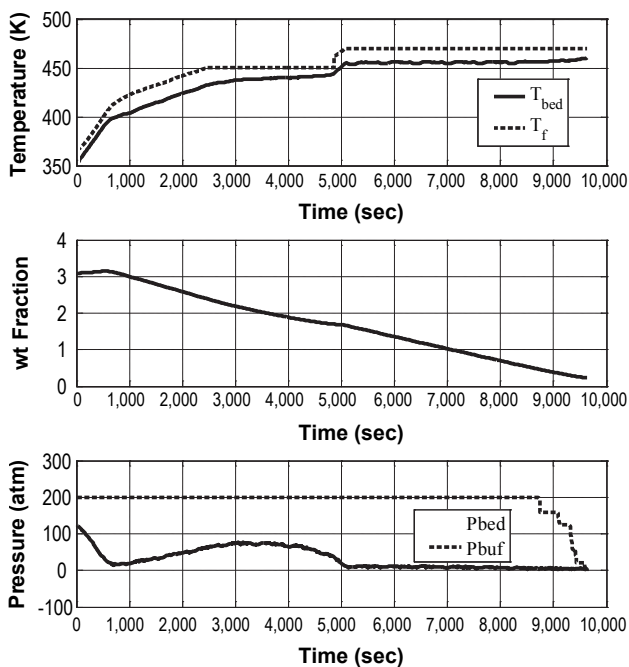

FIGURE 3. Simulation Results for the US06 Drive Cycle for the Alanate-Based Storage System

FIGURE 4. Simulation Results for the US06 Drive Cycle for the Cryo-Adsorbent Storage System

Future Directions

- Explore the sensitivity of system performance for the cryo-adsorbent system to various storage pressures.
- Compare the impact of cold-hydrogen and liquid hydrogen refueling on cryo-adsorbent system performance.
- Conduct simulation studies for both the refueling and discharge cycles a new metal hydride system.
- Optimize binders for pelletizing activated carbon and metal hydride materials with respect to engineering properties of interest for hydrogen storage.
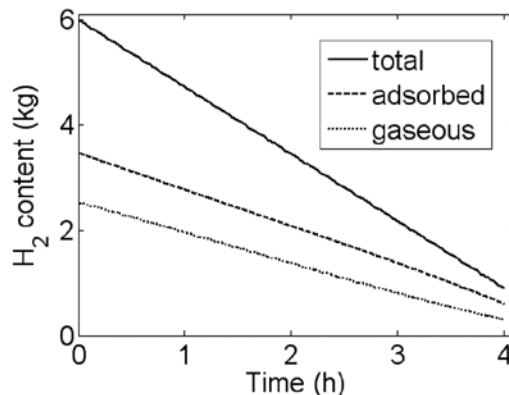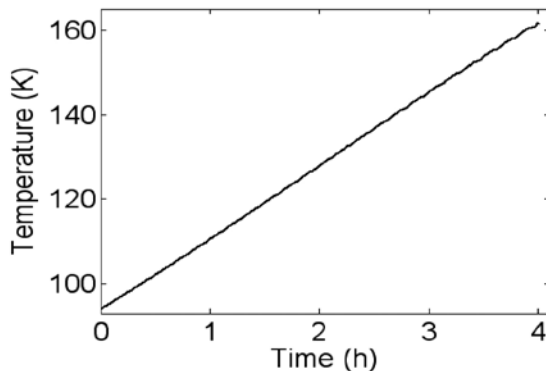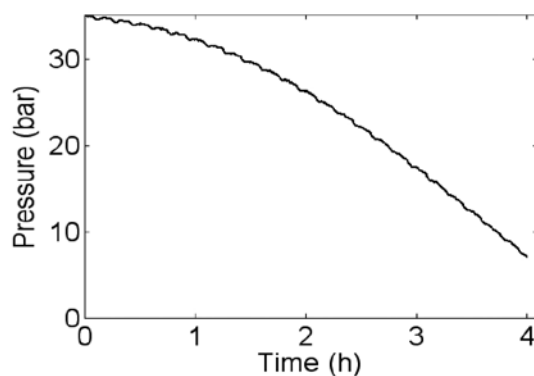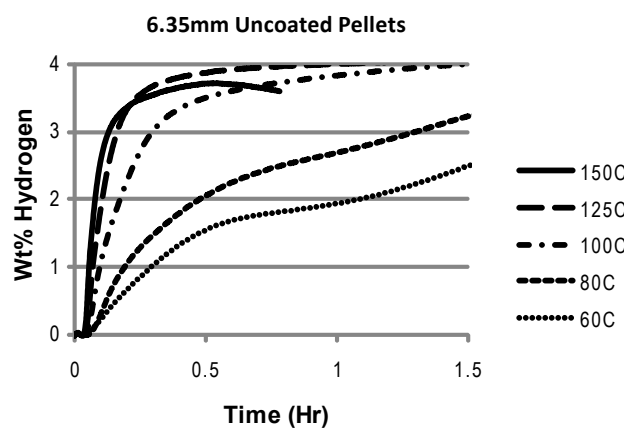
FY 2010 Publications/Presentations

1. S. Kumar(2010): System design and media structuring studies for on-board hydrogen storage technologies, presented at the 2010 DOE Hydrogen Program Annual Merit Review Meeting, Washington, D.C.

2. M. Raju, J.P. Ortmann, and S. Kumar (2010) System simulation model for high-pressure metal hydride hydrogen storage systems, accepted for publication in Int. J. Hydrogen Energy.

3. V.S. Kumar and S. Kumar(2010): Generalized model development for a cryo-adsorber and 1-D results for the isobaric refueling period, Int. J. Hydrogen Energy, 35, pp. 3598-3609.

6.35mm Uncoated Pellets

Loose Powder

FIGURE 5. Hydrogen Uptake by Sodium Alanate Pellets and Loose Powder

4. M. Sulic, M. Cai, and S. Kumar (2010): Sodium alanate as a practical automotive on-board solid-state hydrogen storage medium, presented at the Int. Symposium on Metal-Hydride systems, Moscow, July 2010.
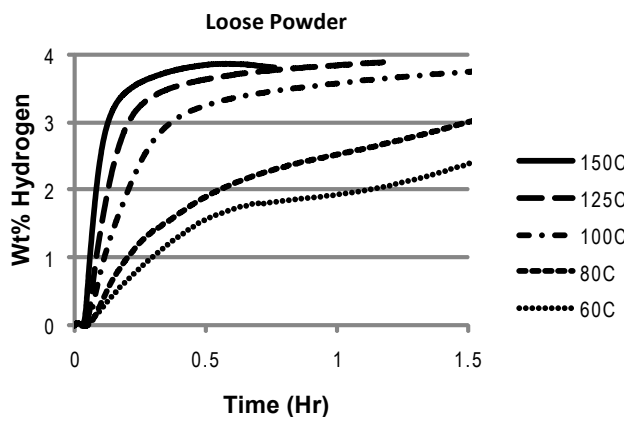
TABLE 1. Preliminary System Performance for the Sodium Alanate and AX-21 Systems in Relation to the DOE Targets

			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 between 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 H$_2$, 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	H$_2$ cooled in the tank to FC delivery	85	not an issue	85	85	85
	Cycle Life (1/4 - full)	(N)	NA		NA		1,000	1,500	1,500
	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%
	Well to Power Plant Efficiency	(%)	NA		NA		90%	90%	60%
Charge/ Discharge Rates	Fill Time (5 Kg H$_2$)	(min.)	10.5 min		4.2 min	Cold H$_2$	4.2	3.3	2.5
	Minimum Full Flow Rate	([g/s]/KW)	0.02	H$_2$(g) in buffer and void-space	0.02	H$_2$ in gas-phase	0.02	0.02	0.02
	Start Time to Full Flow (20°C)	(sec,)	5	H$_2$(g) in buffer and void-space	< 5	H$_2$ in gas-phase	5	5	5
	Start Time to Full Flow (-20°C)	(sec,)	15	H$_2$(g) in buffer and void-space	< 15	H$_2$ in gas-phase	15	15	15
	Transient Response	(sec,)	0.75	H$_2$(g) available, mech/elect issue	0.75	H$_2$(g) available, mech/elect issue	0.75	0.75	0.75
Fuel Purity	Fuel Purity	(%)					99.99%	99.99%	99.99%

HEX = heat exchanger; MLVI = multi-layer vacuum insulation; gge = gasoline gallon equivalent; FC = fuel cell; ICE = internal combustion engine; TBD = to be determined; NA = not applicable