IV.D.1 Hydrogen Storage Engineering Center of Excellence

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- General Motors, Warren, MI
- Ford Motor Company, Dearborn, MI
- National Renewable Energy Laboratory, Golden, CO
- Los Alamos National Laboratory, Los Alamos, NM
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- Oregon State University, Corvallis, OR
- Lincoln Composites LLC, Lincoln, NE
- BASF GmbH, Ludwigshafen, Germany
- Université du Québec à Trois-Rivières, Canada

Project Start Date: February 1, 2009
Project End Date: July 31, 2014

Fiscal Year (FY) 2011 Objectives

- Develop system models that will lend insight into overall fuel cycle efficiency.
- Compile all relevant materials data for candidate storage media and define future data requirements.
- Develop engineering and design models to further the understanding of on-board storage energy management requirements.
- Develop innovative on-board system concepts for metal hydride, chemical hydride, and adsorption hydride materials-based storage technologies.
- Design components and experimental test fixtures to evaluate the innovative storage devices and subsystem design concepts, validate model predictions, and improve both component design and predictive capability.
- Design, fabricate, test, and decommission the subscale prototype components and systems of each materials-based technology (adsorbents, metal hydrides, and chemical hydrogen storage materials).

Technical Barriers

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

(A) System Weight and Volume
(B) System Cost
(C) Efficiency
(D) Durability/Operability
(E) Charging/Discharging Rates
(G) Materials of Construction
(H) Balance of Plant Components
(J) Thermal Management
(K) System Life Cycle Assessments
(L) High Pressure Conformality
(P) Lack of Understanding of Hydrogen Physisorption and Chemisorption
(S) By-Product/Spent Material Removal

Technical Targets

This project directs the modeling, design, build and demonstration of prototype hydrogen storage systems for each metal hydride, chemical hydride and hydrogen sorption material meeting as many of the DOE Technical Targets for light-duty vehicular hydrogen storage. The current status of these systems vs. the Onboard Hydrogen Storage System Technical Targets are given in Table 1.

FY 2011 Accomplishments

- Completed all requirements for moving the Center into Phase 2.
- Performed quality functional deployment analysis on Hydrogen Storage Technical Targets at both the 2010 and 2015 metrics and identified the relative trade offs incurred balancing targets with ordered list of technical targets given in Table 1.
- A unified model was completed utilizing the MATLAB®/SimuLink environment incorporating: (i) vehicle architecture and performance; (ii) fuel cell demands and requirements; and (iii) storage system demands and thermal management systems.

TABLE 1. System Status vs Technical Targets

	Technical Target	Units	2010	2015	Ultimate	Metal Hydride	Chemical Hydride	Adsorbent
Non-Quant-ified	Permeation & Leakage	scc/hr	#	#	#	s	s	s
	Toxicity		#	#	#	s	s	s
	Safety		#	#	#	s	s	s
	Gravimetric Density	$kgH_2/kgSystem$	0.045	0.055	0.075	**0.012**	**0.038**	**0.039**
Manditory	Min. Delivery Temp.	°C	-40	-40	-40	-40	-40	-40
	Max. Delivery Temp.	°C	85	85	85	85	85	85
	Min. Delivery Pressure (PEM)	bar	5	5	3	5	5	5
	Max. Delivery Pressure	bar	12	12	12	12	12	12
	Min. Operating Temperature	°C	-30	-40	-40	-30	-	-30
	Max. Operating Temperature	°C	50	60	60	50	50	50
Desirable	Min. Full Flow Rate	$[gH_2/s]/kW$	0.02	0.02	0.02	0.02	0.02	0.02
	System Cost*	$/kWh net	4	2	TBD	**49.0**	**25.6**	**18.5**
	On-Board Efficency	%	90	90	90	**78**	97	95
	Volumetric Density	$kgH_2/liter$	0.028	0.040	0.070	**0.012**	0.034	0.024
	Cycle Life	N	1000	1500	1500	1000	1000	1000
	Fuel Cost*	$/gge	3-7	2-6	2-3	7.3	-	4.89
	Loss of Useable Hydrogen	$[gH_2/hr]/kgH_2$	0.1	0.05	0.05	0.1	0.1	**0.44**
	WPP Efficency	%	60	60	60	**44.1**	**37.0**	**40.1**
	Fuel Purity	%	99.97	99.97	99.97	99.97	99.97	99.99
	Transient Response	sec.	0.75	0.75	0.75	0.75	0.49	0.75
	Start Time to Full Flow (-20°C)	sec.	15	15	15	15	1	15
	Fill Time	min.	4.2	3.3	2.5	**10.5**	**5.4**	**4.2**
	Start Time to Full Flow (20°C)	sec.	5	5	5	5	1	5

** Previous Values* # non-quantified s - satisfactory

gge - gasoline gallon equivalent; WPP - well to power plant

- Identified five drive cycles to be used in system analysis modeling.
- Systems analysis completed on metal hydride, chemical hydride and adsorbent systems resulting in:
  - Metal Hydride System
    - Completed system analysis on dual-bed $NaAlH_4$ system which was found to fully meet 10 targets, fall within 40% of six targets and below 40% of four targets (see Table 1).
    - Hydride compaction, enhanced hydride thermal conductivity and high temperature Type IV pressure vessels identified as critical technical barriers.
  - Chemical Hydride System
    - Completed system analysis on fluid ammonia borane (AB)/1-n-butyl-3-methylimidazolium chloride (BIMICl) system which was found to fully meet 13 targets, fall within 40% of four targets, below 40% of one target and two targets undefined (see Table 1).
    - Slurry identification/properties, flow through reactor control, low temperature fluid properties and reduced cost of balance-of-plant (BOP) components identified as critical technical barriers.
  - Adsorbent System
    - Completed system analysis on AX-21 system which was found to fully meet 14 targets, fall within 40% of gpit targets and below 40% of two targets (see Table 1).
    - Reduced cost of Type IV cryo-pressure vessel and BOP components; demonstration of peripheral sealing for flow through cooling, adsorbent compaction and enhanced adsorbent thermal conductivity identified as critical technical barriers.

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Introduction

The Hydrogen Storage Engineering Center of Excellence (HSECoE) brings together all of the materials and hydrogen storage technology efforts to address onboard hydrogen storage in light-duty vehicle applications. The effort began with a heavy emphasis on modeling and data gathering to determine the state of the art in hydrogen storage systems. This effort spanned the design space of vehicle requirements, power plant and BOP requirements, storage system components, and materials engineering efforts. These data and models will then be used to design components and sub-scale prototypes of hydrogen storage systems which will be evaluated and tested to determine the status of potential system against the DOE 2010 and 2015 technical targets for hydrogen storage systems for light-duty vehicles.

Approach

A team of leading North American national laboratories, universities, and industrial laboratories, each with a high degree of hydrogen storage engineering expertise cultivated through prior DOE, international, and privately sponsored programs has been assembled to study and analyze the engineering aspects of condensed phase hydrogen storage as applied to automotive applications. The technical activities of the Center are divided into three system architectures: adsorbent, chemical hydride and metal hydride matrixed with six technologies areas: Performance Analysis, Integrated Power Plant/Storage System Analysis, Materials Operating Requirements, Transport Phenomena, Enabling Technologies and Subscale Prototype Construction, Testing and Evaluation. The project is divided into three phases; Phase 1: System Requirements and Novel Concepts, Phase 2: Novel Concept Modeling Design and Evaluation and Phase 3: Subscale System Design, Testing and Evaluation.

Results

Materials

One prototypical material was selected for each storage materials type. These prototypical materials were selected due to their relatively high degree of data identified by the center and their relevance to other similar materials. These materials are not intended to be a selection of materials, but rather used to identify the current state of the art for storage system technologies.

Drive Cycles

A number of drive cycles were implemented to identify storage system performance. This is particularly relevant in the case of transient system performance, where the DOE targets have not identified the duration for which the targets need to be met. In many instances, engineering solutions have been implemented to meet the targets not directly related to the storage system media used. A summary of the drive cycles, and the targets which were determined by them are given in Table 2.

Systems

In order to determine the current state-of-the-art system performance, preliminary system architectures were designed and used in the unified modeling system run under MATLAB®-SimuLink and developed by the HSECoE. This SimuLink model included the hydrogen storage system, fuel cell system and vehicle system models.

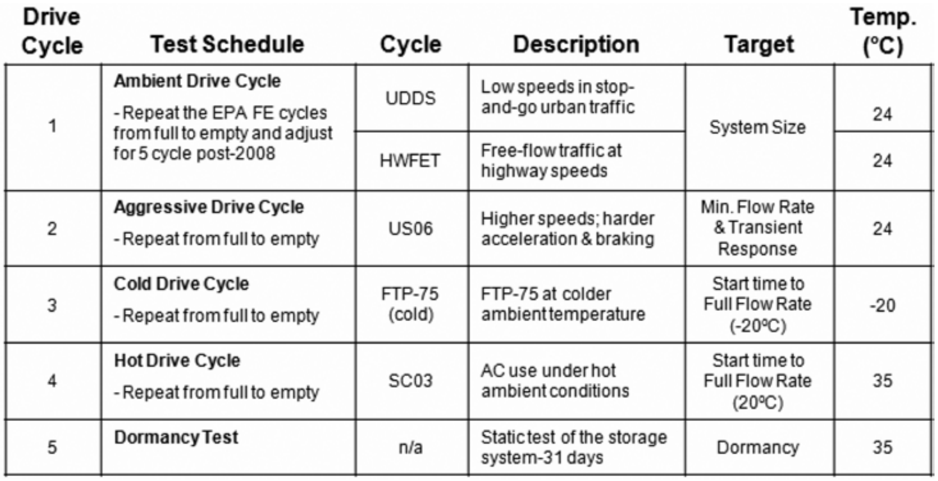
Metal Hydride Systems

The baseline material used in this effort was sodium aluminum hydride ($NaAlH_4$), ball milled with 3 mole per cent $TiCl_3$ as a catalyst. The system used in this effort is given in Figure 1a and is composed of dual Type III $NaAlH_4$ tanks operational at 150 bar with an accompanying catalytic burner to supply the required enthalpy of dehydrogenation. A 150 bar buffer tank is included to facilitate cold-start and transient operations. The heat exchange system is a radial tube/fin design depicted in Figure 1a. The summary of these attributes is given in the spider diagram of Figure 1b where full realization of the target is denoted by filling in to the outer diameter.

Chemical Hydride Systems

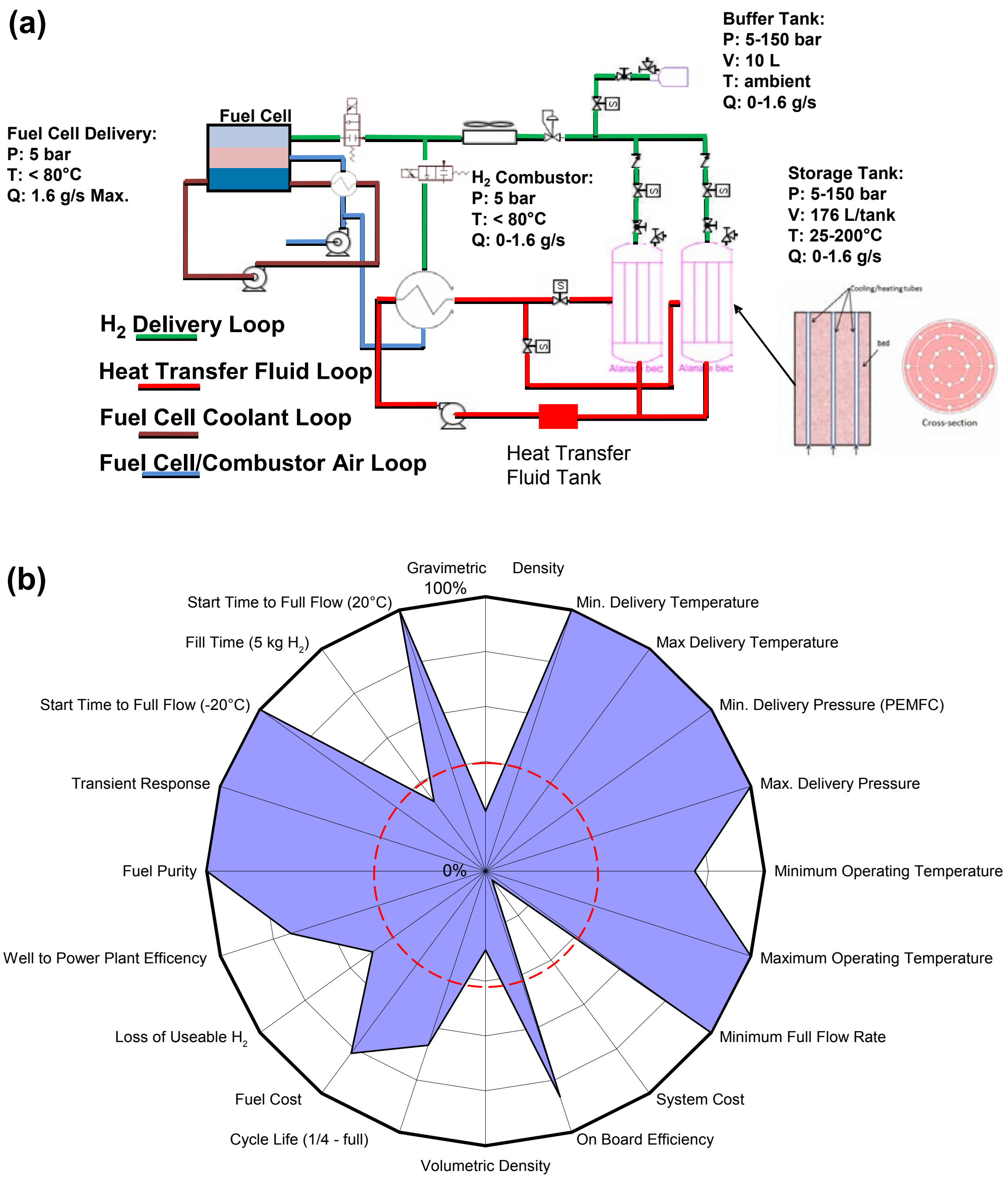
The baseline material used in this effort was liquid AB composed of pure NH_3BH_3, dissolved in the ionic liquid BIMICl to a mass fraction of 50% AB. The chemical hydride system used in this effort is given in Figure 2a and is composed of bladder tank feeding a flow through reactor and a gas liquid separator which serves to separate the gaseous species from the spent fuel and as a high pressure

TABLE 2. Drive Cycles Utilized in System Target Status



Drive Cycle	Test Schedule	Cycle	Description	Target	Temp. (°C)
1	**Ambient Drive Cycle** - Repeat the EPA FE cycles from full to empty and adjust for 5 cycle post-2008	UDDS	Low speeds in stop-and-go urban traffic	System Size	24
		HWFET	Free-flow traffic at highway speeds		24
2	**Aggressive Drive Cycle** - Repeat from full to empty	US06	Higher speeds; harder acceleration & braking	Min. Flow Rate & Transient Response	24
3	**Cold Drive Cycle** - Repeat from full to empty	FTP-75 (cold)	FTP-75 at colder ambient temperature	Start time to Full Flow Rate (-20°C)	-20
4	**Hot Drive Cycle** - Repeat from full to empty	SC03	AC use under hot ambient conditions	Start time to Full Flow Rate (20°C)	35
5	**Dormancy Test**	n/a	Static test of the storage system-31 days	Dormancy	35

UDDS - Urban Dynamometer Driving Schedule; HWFET - Highway Federal Emissions Test; FTP75 - Federal Test Procedure; SC03 - supplementary cycle number 3; n/a - not applicable



PEMFC - proton exchange membrane fuel cell

FIGURE 1. Metal Hydride System (a) configuration and (b) spider chart depicting metal hydride system performance characteristics against the 2015 technical targets.

ballast tank to feed hydrogen to the fuel cell in start-up and transient conditions. A pump is included to maintain both fresh and spent fuel flow with a portion of the spent fuel recirculate to absorb excess heat generated at the reactor. The summary of these attributes is given in the spider diagram of Figure 2b where full realization of the target is denoted by filling in to the outer diameter.

Adsorbent Systems

The baseline material used in this effort was a super activated carbon commercially available and designated as AX-21. The adsorbent system used for this effort is given in Figure 3a. It is composed of a 200 bar high pressure Type III pressure vessel enclosed in a multilayer vacuum insulated jacket with a 5 W heat leak at 80 K. Charging is achieved

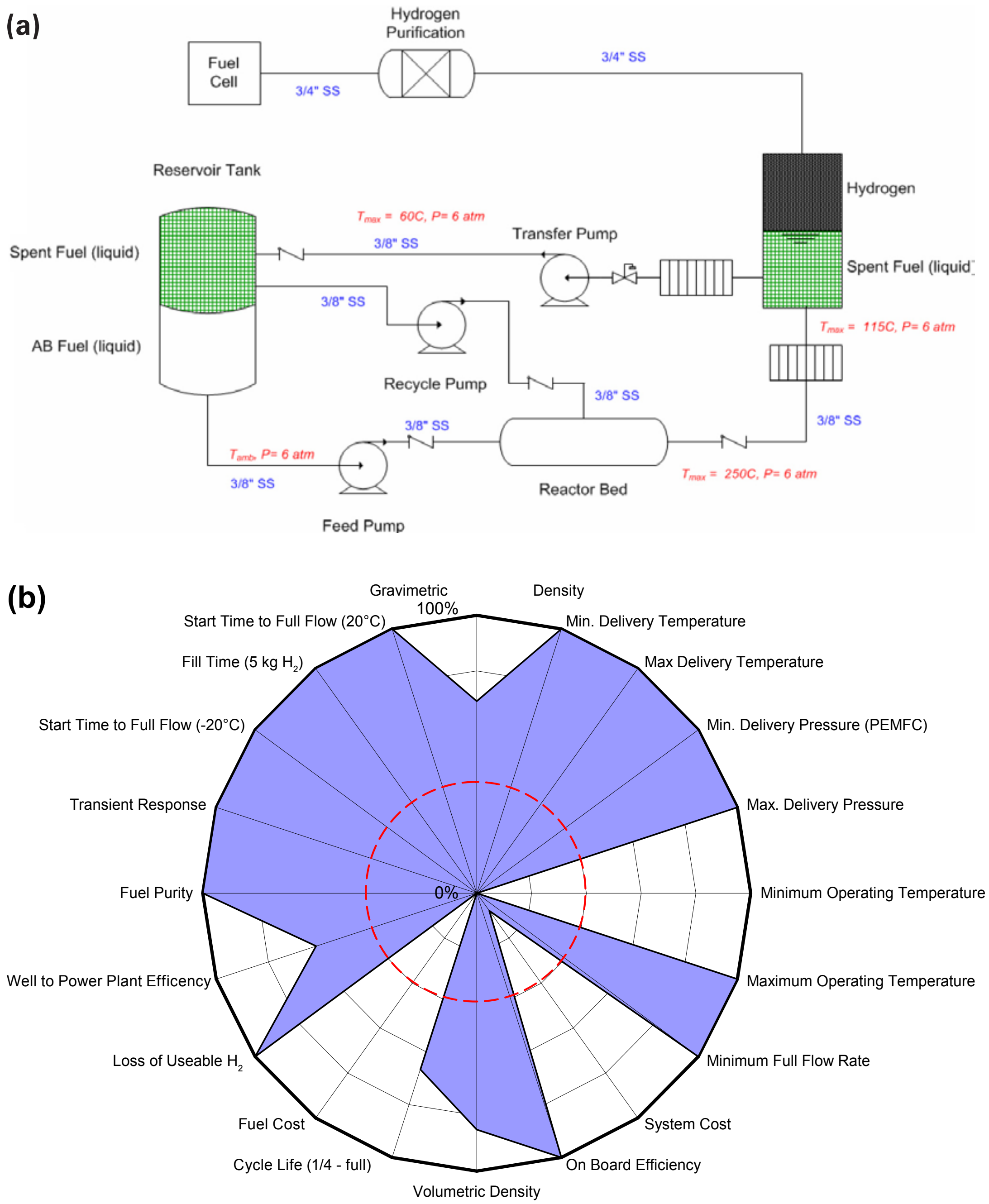


FIGURE 2. Chemical Hydride System (a) configuration and (b) spider chart depicting metal hydride system performance characteristics against the 2015 technical targets.

via flow-through cooling with an initial bed temperature 80 K. Desorption is achieved utilizing an in-tank electrical resistance heater. An external heat exchanger is utilized to heat the released hydrogen to ambient temperatures. The summary of these attributes is given in the spider diagram of Figure 3b where full realization of the target is denoted by filling in to the outer diameter.

Conclusions and Future Directions

The critical technical barriers identified to date and potential solutions being evaluated are given below for each of the storage system types.

- Metal Hydride System
  - Hydride compaction via mechanical constraint.

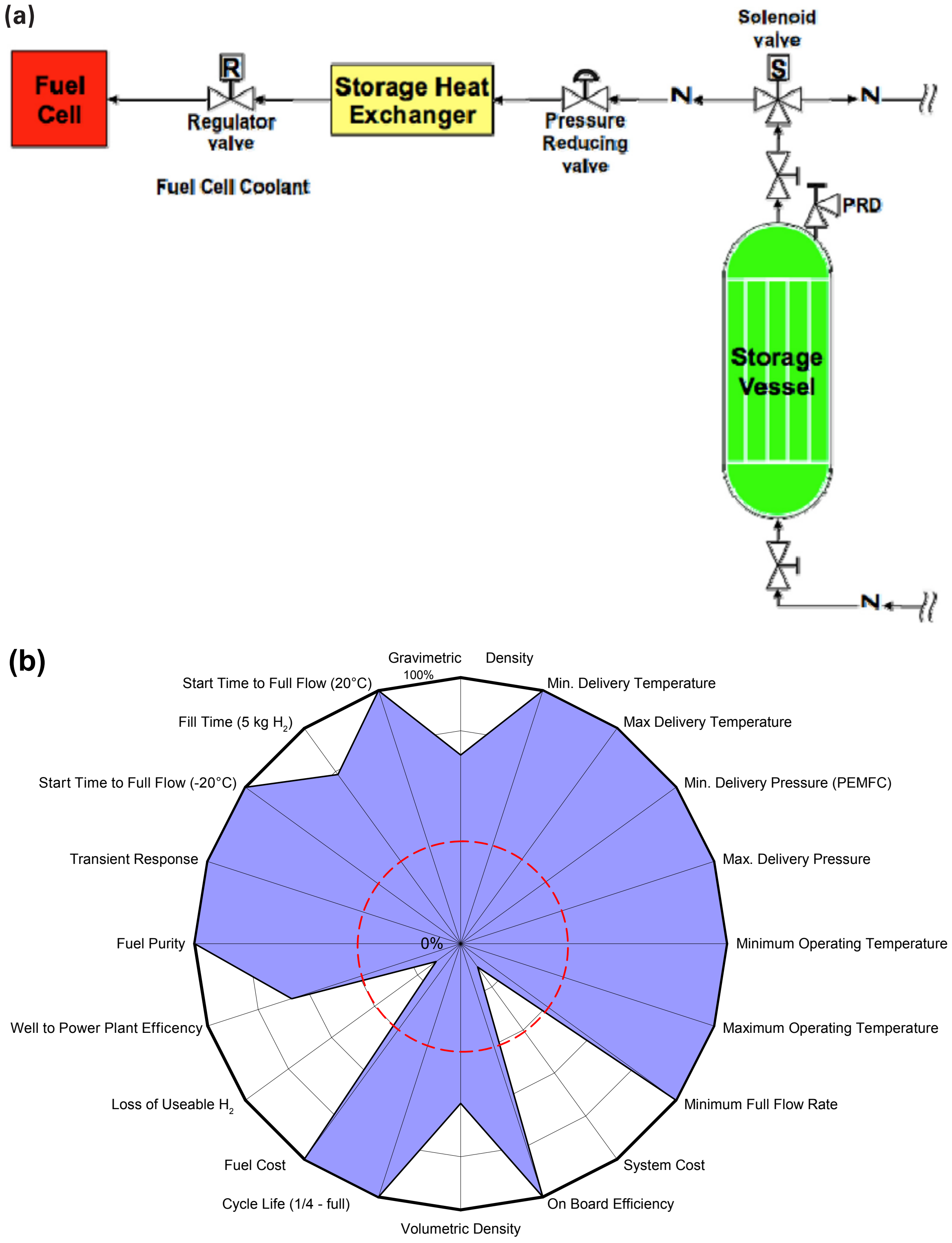


FIGURE 3. Adsorbent System (a) configuration and (b) spider chart depicting metal hydride system performance characteristics against the 2015 technical targets.

- Enhanced hydride thermal conductivity via additions of expanded natural graphite.
- High temperature Type IV pressure vessel development.

- Chemical Hydride System
  - Slurry/solvent identification/properties with nonreactive organic liquids/ionic, liquids.
  - Flow through reactor thermal control via spent fuel feedback.
  - Low temperature fluid properties.
- Adsorbent System
  - Type IV cryo-pressure vessel development.
  - Peripheral sealing for flow through cooling.
  - Adsorbent compaction via low temperature binderless techniques.
  - Enhanced adsorbent thermal conductivity via expanded natural graphite additions.

FY 2011 Publications

1. Systems Modeling, Simulation and Material Operating Requirements for Chemical Hydride Based Hydrogen Storage, Devarakonda, M., Brooks, K.P., Rassat, S., and Rönnebro, E., International Journal of Hydrogen Energy (Submitted).

2. Dynamic Modeling and Simulation Based Analysis of an Ammonia Borane (AB) Reactor System for Hydrogen Storage, Devarakonda, M., Holladay, J., Brooks, K.P., Rassat, S., and Herling, D., ECS Transactions, 33(1), pp. 1959-1972, 2010.

3. Systems Modeling of Ammonia Borane Bead Reactor for OnBoard Regenerable Hydrogen Storage in PEM Fuel Cell Applications, Brooks, K.P., Devarakonda, M., Rassat, S., King, D.A., and Herling, D., Proceedings of ASME 2010 Eighth Fuel Cell Science, Engineering and Technology Conference, Volume 1, ISBN: 978-0-7918-4404-5 pp. 729-734, 2010.

4. Increased volumetric hydrogen uptake of MOF-5 by powder densification, J. Purewal, D. Liu, J. Yang, A. Sudik, D.J. Siegel, S. Maurer, U. Mueller, Int. J. Hydrogen Energy, 2011, Accepted.

5. Engineering Improvement of NaAlH4 System, B.A. van Hassel, D. Mosher, J.M. Pasini, M. Gorbounov, J. Holowczak, X. Tang, R. Brown, B. Laube and L. Pryor, Int. J. Hydrogen Energy. (in press)

6. System modeling methodology and analyses for materials-based hydrogen storage, José Miguel Pasini, Bart A. van Hassel and Daniel A. Mosher, Int. J. Hydrogen Energy. (in press)

7. Sensitivity study of alanate hydride storage system, M. Bhouri, J. Goyette, B.J. Hardy, D.L. Anton., International Journal of Hydrogen Energy 36 (2011) 621-633.

8. Evaluation of Acceptability Envelope for Materials-Based H2 Storage Systems, C. Corgnale, B. Hardy, D. Tamburello, S. Garrison and D. Anton, Int. J. Hydrogen Energy. (in press)

9. Automatic Optimization of Metal Hydride Storage Tanks and Novel Designs, S. Garrison, M. Gorbounov, D. Tamburello, B. Hardy, C. Corgnale, D. Mosher and D. Anton, Int. J. Hydrogen Energy. (in press)

10. System Simulation Models for High-Pressure Metal Hydride Hydrogen Storage Systems, Raju M., Ortmann JP, Kumar S., Int J Hydrogen Energy 2010; 35: 8742- 54.

11. System Simulation Modeling and Heat Transfer in Sodium Alanate based Hydrogen Storage Systems, Raju M. and Kumar S., Int J Hydrogen Energy 2011; 1578-1591.