System Level Analysis of Hydrogen Storage Options

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Project ID: ST19
Overview

Timeline
- Project start date: Oct 2004
- Project end date: Sep 2009
- Percent complete: 33%

Budget
- FY05: $250 K
- FY06: $350 K

Barriers
- Addresses H₂ Storage Technical Barriers:
  - A: Cost
  - B: Weight and Volume
  - C: Efficiency
  - E: Refueling Time
  - M: Hydrogen Capacity and Reversibility
  - Q: Thermal Management
  - R: Regeneration Processes
  - T: Heat Removal

Interactions
- FreedomCAR and Fuel Partnership
- Storage Systems Analysis Working Group, MH COE, CH COE
- TIAX, LLNL, SNL, MCEL, APCI, H2A, University of Quebec
Objectives

- Perform independent systems analysis for DOE
  - Provide input for go/no-go decisions
- Model and analyze various developmental hydrogen storage systems
- Analyze hybrid systems that combine features of more than one concept
- Develop models that can be used to “reverse-engineer” particular technologies
  - Provide guidance to meet targets
- Identify interface issues and opportunities, and data needs for technology development
Approach

- Develop thermodynamic and kinetic models of processes in complex metal, carbon, and chemical hydrogen storage systems
- Calibrate, validate and evaluate models
- Work closely with the DOE Contractors, Centers of Excellence, Storage Tech Team, and Storage Systems Analysis Working Group
- Assess improvements needed in materials properties and system configurations to achieve $\text{H}_2$ storage targets
Technical Accomplishments

Metal Hydrides (Milestone: March 2006)
- Developed an Excel-based tool to help scientists evaluate how well their material, when used in a full-scale device, can meet DOE’s storage targets

Carbon Storage (Milestone: December 2005)
- Determined under what conditions activated carbons at low T & high P can meet DOE’s 2007 storage targets

Cryo-Compressed Hydrogen (Milestone: June 2006)
- Determined combinations of P & T to achieve 4.5 wt% gravimetric and 36 kg/m³ volumetric capacity

Chemical Hydrogen (Milestone: September 2006)
- Evaluated regeneration energy consumption and fuel cycle efficiencies of candidate materials and processes
**MHtool: Metal-Hydride Hydrogen Storage System Analysis Tool**

To develop and make available to DOE contractors and Centers of Excellence a tool for use by the material developers to

- Evaluate the performance of the material, when used in a full-scale device, vis-à-vis DOE’s H₂ storage targets;

- Identify the specific deficiencies in material properties and their impact on performance of the storage system;

- Assess how much improvement is needed in the deficient material properties to meet the storage targets.
Modular Approach

Written on Microsoft Excel platform, modules run sequentially
- MCM characterizes storage material for composition and capacity
- SCM calculates the reversible storage capacity of medium, maximum DOD and SOC
- HTM determines the size of heat transfer system
- SM determines gravimetric and volumetric capacity of the system
- DM calculates the dynamic sorption behavior of the MH considering chemical kinetics and heat transfer

MHtool: Metal-Hydride Hydrogen Storage System Analysis Tool
Example: Reversible Storage Capacity of Alanate Medium

Operating Conditions: 4% TiCl$_3$, 1.6 g/s min full flow rate of H$_2$, 100 bar supply P, 115$^\circ$C discharge, 165$^\circ$C charge

Effect of minimum delivery P on maximum DOD
- NaAlH$_4$ dehydrogenation: 65% at 8 bar, 70% at 4 bar, 71% at 3 bar
- Na$_3$AlH$_6$ dehydrogenation: 0 at P<1.8 bar, 39% at 0.1 bar

Effect of refueling rate on maximum SOC
- 98% at 0.5 kg/min, 77% at 1.5 kg/min, 67% at 2 kg/min

Effect of discharge kinetics on maximum DOD
- 65% at 1X, 79% at 2X, 90% at 5X, 95% at 10X kinetics

Reference kinetics: Sandrock, Gross & Thomas, J Alloys Compounds, 2002
High-Pressure, Low-Temperature Storage of Hydrogen on Activated Carbon

- Determine the volumetric and gravimetric capacity of AC storage systems at low temperatures (77-150 K) and high pressures (P > 100 bar).
  - Compare amounts of H₂ adsorbed on AC and in void space.
  - Evaluate the heating and cooling requirements for the AC tank and how they may be accomplished.
  - Characterize dormancy and boil-off losses.
  - Estimate energy consumed in storing hydrogen.

- Determine the attributes of advanced AC/sorbents that can help meet 2007 targets of 4.5 wt% H₂ and 36 kg H₂/m³ (1.2 kWh/L).
**AC H₂ Storage System**

Thermally insulated, filament wound carbon fiber/epoxy PV
- Super AC powder medium
- Metal foam support
- In-tank HX and manifolds
- Al liner

- Carbon fiber
- Multi-layer vacuum insulation
- Al shell
- Miscellaneous
Recoverable $H_2$ Storage Density of AX-21 Medium at 100 K with Temperature Swing

- With 50-K $\Delta T$, the breakeven pressure is 380 bar.
- At 75% volumetric efficiency, 36 kg/m$^3$ target is reached at 280 bar.
- At breakeven point, AX-21 stores 16.5% of recoverable $H_2$ at 100 K.

Storage Capacity of AC System at 100 K

- At 100 K, the storage capacity of AC system is >4.5 wt% for P >150 bar and approaches 36 kg/m³ at P = 380 bar.
  - Calculated volumetric capacity of AC medium is 60-62% at 150-380 bar.

- Need to increase sorption capacity of AX-21 by 61-82% and bulk density by ~100% to satisfy 2007 targets at 100 K and 100 bar.
Storage Capacity of Cryo-cH2 System at 100 K

Assumption: No on-board heat transfer system needed because the tank is charged with H₂ subcooled below 100 K.

- May simultaneously meet the 2007 targets of 4.5 wt% and 36 kg/m³ at P > 355 bar.
- May meet the 2010 target of 6 wt% but not the 45 kg/m³ target.
- 8.9 wt% peak gravimetric capacity at 300 bar.
Weight and Volume Distribution
Cryo-cH2 System: 100 K, 355 bar (Preliminary)

8.9 wt% gravimetric capacity
• CF accounts for 30% of the total weight

36 kg/m^3 volumetric capacity
• Gas medium accounts for 70% of the total volume
FCHtool: Fuel Cycle Efficiency of Different Hydrogen Storage Options

Defined efficiencies on the basis of primary energy consumed in producing, distributing and storing hydrogen

- Distinction between primary energy feedstocks (petroleum, coal, etc) and process fuels (gasoline, hydrogen, electricity, etc.)

Simple Microsoft Excel based tool with embedded Macros in Visual Basic Application language

- Arbitrary process steps to simulate any fuel cycle (H₂ pathway)
- GREET derived reference database for process fuel production, electricity generation, hydrogen production, hydrogen distribution, hydrogen storage, regeneration steps
- Outputs for primary energy consumption, efficiencies, and emissions of regulated pollutants and GHGs
- Consistency with H2A spreadsheet
Case Study

Considered centralized production of H₂ by SMR+PSA, 73% efficiency

Compressed H₂ at 350 or 700 bar
- 20 bar to 180 bar at production site, 5-stage compressor*
- 180 bar to 425 or 850 bar at refueling station, 2 or 3-stage compressor*
- Delivery by tube trailers for 1% & pipeline for 10% market share*

Liquid H₂ storage option
- Liquefaction plant at production site, >200,000 kg/d capacity*
- Delivery truck capacity: 400 kg (1% market), 4000 kg (10% market)*

MgH₂ slurry
- Included only electricity consumed by LTF-SOM process at 1150°C
- BU 2005 data: 3-V cell voltage (~1-V dissociation potential with H₂), 100% current eff., 6.7 kWh/kg Mg (SafeH₂ quoted 10 kWh/kg)

SBH system
- Included only electricity consumed by H-assisted NaOH electrolysis
- MCEL data: 1.2-V cell voltage (~1.07-V theoretical with H₂), 100% current eff., 1.6 kWh/kg Na (MCEL quoted 1.8 kWh/kg)

*Assumptions consistent with H2A
Primary Energy Consumed in Production, Storage and Distribution Steps (Preliminary)

- **cH₂** option: Energy consumed in storage & delivery steps relatively small
- **LH₂**: Liquefaction requires 40% of energy consumed in production
- **SBH**: Energy consumed in storage & production steps about equal
- **MgH₂**: Regeneration requires >2.2 times energy consumed in production

![Diagram showing energy consumption in various steps for different hydrogen options.](image)

- **Production**
  - SMR: H₂ at 20 bar
- **Distribution**
  - Pipeline transmission
  - Trucking
- **Storage**
  - Compression
  - Liquefaction
  - CH regeneration
Preliminary Fuel Cycle Efficiencies

WTT efficiencies

- 58.1% for cH₂ at 350 bar and 54.5% at 700 bar
- 43.9% for LH₂ option
- 31.3% for SBH and 19.2% for MgH₂ options
Future Work

Continue to work with DOE contractors and COE to model and analyze various developmental hydrogen storage systems.

Metal Hydrides
- PCT deconvolution module
- Module to derive kinetic constants from experimental data

Carbon Storage
- Extend work to carbon and other sorbents

Cryo-Compressed Hydrogen
- Independent analysis in support of DOE’s go no-go decision

Chemical Hydrogen
- Evaluate regeneration energy consumption and fuel cycle efficiencies of candidate materials and processes
- Develop CHtool to help scientist evaluate how well their material can perform in a full scale on-board system to satisfy DOE’s storage targets (kinetics, energetics, thermodynamics)
Summary and Additional Results

Metal Hydrides
- MHtool (Version 1.0) is being beta-tested prior to its release this FY.

Carbon Storage
- Commercially available AX-21 vs. cryo-cH2 at 100-150 K.
- >9.5 kWh/kg-H₂ energy consumed in N₂ liquefaction system*
- 10-90 days dormancy, boil-off rate < 2 g/h*
- To satisfy 2007 targets at 100 K and 100 bar, need to increase sorption capacity of AX-21 by 61-82% and bulk density by ~100%.

Cryo-Compressed Hydrogen
- At 100 K, cryo-cH₂ may meet 2007 targets at P>350 bar.
- Preliminary estimate of energy to fuel with cryo-cH₂: 5.6 kWh/kg H₂*.

Chemical Hydrogen
- Life cycle analysis needed to compare energy consumed in regenerating chemical hydrides.
- FCHtool (Version 2.0) is being beta-tested prior to its release this FY.

*Report being written to document the results
BACKUP MATERIAL
Response to Reviewers’ Comments

Maintain high degree of fidelity to DOE program goals
- Program plan closely aligned with DOE milestones and decision points.
- Monthly teleconference with DOE program manager
- Reviewed by Tech Team on semi-annual basis

Closer coordination with every project
- Formed Storage Systems Analysis Working Group
- Made presentations to teams from MH-COE and CH-COE
- Working closely with LLNL on cryogenic storage

Specific recommendations and additions or deletions to work scope
- Need to give more resources
- Need to give this project a higher priority
- Need to protect them from external pressures
- Need to develop parallel pathways for various storage alternatives
Publications and Presentations


Refueling of MH Tank

Refueling of MH medium depleted to maximum DOD, 115°C initial T
- Coolant flow rate varied to attempt to keep MH at 150-155°C
- Medium cannot be maintained at T at which charge rate is maximum
- Refueling time determined by intrinsic kinetics and heat transfer
Cryo-\(cH_2\) vs. AX-21 System

- Gravimetric capacity higher with cryo-\(cH_2\) storage
- Below 265-bar breakeven \(P\), volumetric capacity higher with AX-21
- Cryo-\(cH_2\) simultaneously meets the 2007 gravimetric and volumetric capacity targets at lower pressure than AX-21
Storage System Parameters

Super AC powder medium
• AX-21: 2800 m²/g, 300 kg/m³, 0.1 W/m.K

Metal foam support
• 2-wt% Al 2024, 2.4 W/m.K

In-tank HX and manifolds
• Al 2024 construction
• 9.5-mm OD, 1.2-mm thick tubes
• 0.9-mm thick tube sheets

2-mm thick Al alloy liner

T700S carbon fiber
• 68%CF+32%resin, 1600 kg/m³
• 2550 MPa tensile strength
• Fiber translation: 70% at 700 bar, 85% at 350 bar
• 2.25 SF

MLVSI
• Aluminized mylar sheets with Dacron spacer, 70 layers/in.
• 59.3 kg/m³
• 10⁻⁵ torr
• 5.2x10⁻⁴ W/m.K
• 1 W heat transfer

3-mm thick Al alloy shell

System
• L/D = 2, 3:1 oblate ellipsoid head
• Miscellaneous: pipes, insulation supports, etc., 20 kg, 10 L
• LN2 cooling
• H₂ refueled at +100 bar, tank T
• 5.6 kg recoverable H₂ capacity
• 0.5-2 kg/min H₂ refueling rate