Hydrogen Storage System Modeling: Public Access, Maintenance, and Enhancements

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DOE Hydrogen and Fuel Cells Program
2020 Annual Merit Review and Peer Evaluation Meeting
May 20, 2020

This presentation does not contain any proprietary, confidential, or otherwise restricted information.
Overview

Timeline

• Start: October 1, 2015
• End: September 30, 2021*

Budget

• Total Project Funding: $1,630,000*
  o FY16 Funding: $336,000
  o FY17 Funding: $389,000
  o FY18 Funding: $375,000
  o FY19 Funding: $275,000
  o FY20 Funding: $255,000

Barriers

A. System Weight and Volume
B. System Cost
C. Efficiency
E. Charging/Discharging Rates
I. Dispensing Technology
K. System Life-Cycle Assessment

Partners

*Project continuation and direction determined annually by DOE.
Relevance

Collaborative effort to manage, update, and enhance hydrogen storage system models developed under the Hydrogen Storage Engineering Center of Excellence (HSECoE)

• Transfer engineering development knowledge from HSECoE on to future materials research.

• Manage the HSECoE model dissemination web page.

• Manage, update, enhance, and validate the modeling framework and the specific storage system models developed by the HSECoE.

• Develop models that will accept direct materials property inputs and can be measured by materials researchers.

• **Ultimate Goal**: Provide validated modeling tools that researchers will use to evaluate the performance of their new materials in engineered systems relative to the DOE Technical Targets.
## Relevance – Addressing Barriers with Models

<table>
<thead>
<tr>
<th>Barriers</th>
<th>Model Addressing Barrier</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. System Weight and Volume</td>
<td>System Estimator</td>
</tr>
<tr>
<td>B. System Cost</td>
<td>Tank Volume/Cost Model</td>
</tr>
<tr>
<td>C. Efficiency</td>
<td>Framework Model</td>
</tr>
<tr>
<td></td>
<td>- Onboard Efficiency</td>
</tr>
<tr>
<td></td>
<td>- Fuel Economy</td>
</tr>
<tr>
<td>E. Charging/Discharging Rates</td>
<td>Framework Model</td>
</tr>
<tr>
<td></td>
<td>- Drive Cycles</td>
</tr>
<tr>
<td>I. Dispensing Technology</td>
<td>Framework Model</td>
</tr>
<tr>
<td></td>
<td>- Initial and Final System Conditions</td>
</tr>
<tr>
<td>K. System Life-Cycle Assessment</td>
<td>All Models</td>
</tr>
</tbody>
</table>
Relevance – Improving Model Utilities for Materials Researchers

Materials Research
- H₂ Capacity
- Thermodynamics
- Kinetics
- Adsorption Isotherms

Modeling Framework
- DOE Technical Targets
  - Gravimetric and Volumetric Capacity
  - Durability and Operability
  - Operating Temperature and Pressure
  - Onboard Efficiency
  - Charging/Discharging Rates
  - Start-up
  - Refueling

Stand-Alone System Design Tools
- Component and System Mass and Volume
- Isotherm Fitting Tool
- DA Parameters

Estimated Gravimetric and Volumetric Capacity

Available at www.hsecoe.org
Modeling Tools Available or In Progress

Framework Model with:
- Physical Storage UTRC/NREL
- Compressed/Cryo-Compressed H₂ SRNL/NREL
- Chemical Hydrogen (CH) PNNL/NREL
- Adsorbent (AD) SRNL/NREL
- Metal Hydride (MH) PNNL/NREL

Estimate performance of light-duty vehicles with four drive cycles for each storage system

Stand-Alone System Design Tools:
- Adsorbent (AD) SRNL New MS Excel-based tool
- Chemical Hydrogen (CH) PNNL New MS Excel-based tool
- Metal Hydride (MH) PNNL New MS Excel-based tool
- Compressed/Cryo-Compressed H₂ SRNL

Additional Tools/Models:
- MH Acceptability Envelope (MHAE) SRNL
- Tank Volume/Cost Model PNNL
- AD Isotherm Fitting Tool SRNL

Finite Element Models:
- Metal Hydride (MH) Finite Element (MHFE) SRNL
- Adsorbent (AD) – HexCell and MATI SRNL

Tank heat and mass transfer models

UTRC: United Technologies Research Center
Capabilities:

- **Stand-alone design tools** now available in Microsoft Excel for adsorbents, metal hydrides, chemical hydrogen storage, and pure hydrogen storage

- **Usable-\( \text{H}_2 \)-mass-based** and full storage-system-volume-based capabilities for each design tool

- **Multiple kinetics/isotherm expressions** available in the stand-alone tools and framework for each storage method

- **All models allow material-specific** property inputs measured by materials researchers to design material-specific storage systems
Accomplishments and Progress – Design Tools Flowchart

Target Mass of Usable H$_2$

H$_2$ Mass-Based System Design Path

- Calculate Mass of H$_2$
- Design Pressure Vessel & Insulation
- Operating System Specific BOP

Calculate Mass & Volume of Material & Free Space

- Design Reactor/Internal HX
- Final System Mass and Volume

Final Hydrogen Storage System Design

Design Reactor/Internal HX

- Design Pressure Vessel & Insulation
- Operating System Specific BOP

Volume-Based System Design Path

- Calculate Mass & Volume of Material & Free Space
- Operating System Specific BOP

Isotherm/Kinetic Expressions

- Design Reactor/Internal HX
- Calculate Mass & Volume of Material & Free Space

Volume-Based System Design Path

Full Storage System Volume

- Calculate Mass of H$_2$
- Design Reactor/Internal HX

Final System Mass and Volume

- Design Pressure Vessel & Insulation
- Operating System Specific BOP

Operating System Conditions ($P_i, P_f, T_i, T_f$)

- Tank/Insulation Parameters
- Isotherm/Kinetic Expressions

Final Hydrogen Storage System Design

- Calculate Mass of H$_2$
- Design Reactor/Internal HX

- Design Pressure Vessel & Insulation
- Operating System Specific BOP

- Calculate Mass & Volume of Material & Free Space
### Accomplishments and Progress – **Model Improvements**

<table>
<thead>
<tr>
<th></th>
<th>Original Model</th>
<th>Updated Model</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Adsorbent Model</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Balance of plant (BOP) for cryogenic operation only</td>
<td>BOP options for room temperature, cold, and cryogenic operations</td>
<td></td>
</tr>
<tr>
<td>Insulation thickness hard-coded to 1 inch</td>
<td>Insulation thickness is user controlled</td>
<td></td>
</tr>
<tr>
<td>LN₂ tank cooling channel always included</td>
<td>LN₂ tank cooling channels user controlled</td>
<td></td>
</tr>
<tr>
<td>D-A isotherm model used only</td>
<td>D-A and UNILAN isotherm model options</td>
<td></td>
</tr>
<tr>
<td>MOF-5 material properties hard-coded</td>
<td>User-defined adsorbent material properties (with MOF-5 default values)</td>
<td></td>
</tr>
<tr>
<td>Mass of usable H₂ is the starting point of the calculation</td>
<td>Mass of usable H₂ or maximum total storage system volume starting point</td>
<td></td>
</tr>
<tr>
<td><strong>Metal Hydride Model</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Single step irreversible reaction</td>
<td>Single step irreversible or two step reversible models selectable</td>
<td></td>
</tr>
<tr>
<td>Hard-coded reaction rate and enthalpy (30 kJ/mol)</td>
<td>Reaction parameters and material properties as inputs</td>
<td></td>
</tr>
<tr>
<td>Mass of usable H₂ is the starting point of the calculation</td>
<td>Mass of usable H₂ or maximum total storage system volume starting point</td>
<td></td>
</tr>
</tbody>
</table>
MS Excel-based tools allow universal availability without cumbersome downloads of MATLAB products

- Usable-H$_2$-mass-based and system-volume-based tools available
- Downloads available for ammonia borane and alane can be downloaded and modified for other liquid/slurry-based chemical hydrogen storage materials
Excel-Based Metal Hydride Stand-Alone Design Tools

- Separate models for mass-of-usable-H₂-constrained and system-volume-constrained design tools
- Models based on thermodynamics and heat transfer only; no kinetics or mass transfer included
Excel-Based Cryo-Adsorbent Stand-Alone Design Tools

- Separate tabs for Dubinin-Astakhov (D-A) adsorption theory isotherm and UNILAN isotherm
- Models can evaluate mass-of-usable-H₂-constrained and system-volume-constrained design tools
- Can evaluate materials at cryogenic, cold, and room-temperature conditions
Accomplishments and Progress – **Vehicle Framework GUI**

![Diagram of Vehicle Framework GUI](image)

- **Accomplishments and Progress**
- **Vehicle Framework GUI**
- **Storage Volume and Mass Outputs**
Accomplishments and Progress – **Adsorbent System Design Tool in the Framework**

System Volume Input and Mass Output

- **Load System**
  - Inputs
    - Name: Cryoadsorbent system based on MOF-5. Cooling during refuel is done either with a microchannel heat exchanger (MATI) or with flow-through of cold gas.
  - System Vol: 267,678
  - Adsorbent: 2
  - Temp_op: 3
  - Add_Cool: 0
  - Emax: 0.5640
  - Emin: 1.050
  - nmax: 67.75
  - Vv: 0.00140392
  - rho_ads: 130
  - k: 0.3
  - Cp: 730
  - Ads_Cost: 11.8
  - Thenn: 0
  - Hemoly: 0
  - Vessel: 1
  - TType: 4

- **Run System Design**
  - H2stored: 5,718 kg_H2
  - H1usable: 5,684 kg_H2
  - System_mass: 151,5204 kg

- **Save Results to Excel**
  - System_Vol: 267,678 L

- **Create Model File**

- **System Diagram**

- **Exit**

- **Design Documentation**
- **General Documentation**

- **Storage Sizing Tools**
  - By Usable H2
  - Adsorbent D-A
  - Adsorbent Unilan
  - Cryo Compressed
  - Cryo Compressed
Accomplishments and Progress – Models Provide Input to Spider Charts

NaAlH$_4$ Estimates

Information provided by design tool

- Gravimetric Density
- Min. Delivery Temp.
- Max Delivery Temp.
- Min. Delivery Pressure
- Max. Operating Temp.
- Min. Operating Temp.
- Max. Delivery Pressure
- Min. Full Flow Rate
- System Cost
- Onboard Efficiency
- Volumetric Density

- Start Time to Full Flow (20°C)
- Fill Time (5kg H2)
- Start Time to Full Flow (-20°C)
- Transient Response
- Fuel Purity
- Wells-to-Power Plant Efficiency
- Boil-off loss
- Fuel Cost
- Cycle Life (1/4 - full)
Accomplishments and Progress – **Models Provide Input to Spider Charts**

**NaAlH₄ Estimates**

Information provided by Framework Model using available drive cycles

- **Cold FTP**
  - Start Time to Full Flow (20°C)
  - Transient Response

- **US06**
  - Fuel Purity
  - Wells-to-Power Plant Efficiency
  - Boil-off loss
  - Fuel Cost
  - Cycle Life (1/4 - full)

- **UDDS**
  - System Cost
  - Onboard Efficiency

- **Hot SC03**
  - Min. Delivery Temp.
  - Max Delivery Temp.
  - Min. Delivery Pressure
  - Max. Operating Temp.
  - Min. Operating Temp.
  - Max. Delivery Pressure
  - Min. Full Flow Rate

- **TBD**
Accomplishments and Progress – Exercise Models

Thermal Conductivity vs. Bed Density on Tank Mass

Impact of Metal Hydrides on System Mass

Approach to Achieving DOE Gravimetric Technical Target

Relationship between Usable H₂ and System Volume
Learning: **Nanoscale materials have higher system gravimetric and volumetric capacity** in spite of lower hydrogen storage capacity

- *Improved δH and δS result in significantly reduced operating temperature, reducing tank mass and hydrogen burned*

- *Improved thermal conductivity improves heat transfer during refueling and reduces the number of coolant tubes required*
Accomplishments and Progress – Metal Hydride Materials Evaluation

Framework Model Compares Nanoscaled vs. Bulk Materials

Kinetic Differences between Bulk and Nano

Fit Data with First Order Reaction

\[ r = -\left(161,154e^{\frac{-79677}{RT}}\right)C_{\text{Li}_3\text{N}} \]

Nano-Li$_3$N Results from Framework Model

Learning: Nanoscaled Li$_3$N has fast enough kinetics and low enough temperatures to allow all drive cycles to be met; bulk Li$_3$N does not

- *Bulk Li$_3$N reaction does not initiate for any of the drive cycles*

Usable $H_2 = 5.8$ kg
Onboard Eff = 76.5%
Pressure $>$5 bar over 6.9 h
HRL is evaluating NaAlH₄ milled with 0.03TiCl₃ mixed 50:50 wt % with diglyme. This mixture has faster kinetics and reaches complete conversion sooner than the control without diglyme.

<table>
<thead>
<tr>
<th></th>
<th>Control</th>
<th>Best 2ₚrd</th>
<th>Best 2ₚrd with higher k</th>
</tr>
</thead>
<tbody>
<tr>
<td>Useable Hydrogen Capacity (wt%)</td>
<td>0.04</td>
<td>0.048</td>
<td>0.048</td>
</tr>
<tr>
<td>Inert Fraction</td>
<td>0</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Bed Thermal Conductivity (W/mK)</td>
<td>1</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>System mass (kg)</td>
<td>678</td>
<td>680</td>
<td>622</td>
</tr>
<tr>
<td>System volume (m³)</td>
<td>0.315</td>
<td>0.317</td>
<td>0.290</td>
</tr>
<tr>
<td>Mass H₂ Burned (kg)</td>
<td>1.63</td>
<td>1.66</td>
<td>1.66</td>
</tr>
<tr>
<td>Tank Outer Diameter (m)</td>
<td>0.475</td>
<td>0.476</td>
<td>0.461</td>
</tr>
<tr>
<td>Tank Length (m)</td>
<td>1.83</td>
<td>1.83</td>
<td>1.77</td>
</tr>
<tr>
<td>Total Hydride Mass (kg)</td>
<td>181</td>
<td>181</td>
<td>181</td>
</tr>
<tr>
<td>Tank Mass (kg)</td>
<td>408</td>
<td>409</td>
<td>372</td>
</tr>
</tbody>
</table>

2ₚrd: Assuming 20% diglyme and the higher usable H₂ capacity result in nearly the same tank size as Control 1st. An assumed doubling of thermal conductivity reduces system mass and volume by 8.5%.
Accomplishments and Progress – Metal Hydride Materials Evaluation

Framework Compares Two Forms of NaAlH₄, Maximum T = 160°C

Usable H₂ = 4.675 kg
Onboard Efficiency = 74%
Distance Traveled = 244 miles

SA+diglyme continues, although at very low pressure

Usable H₂ = 3.77 kg
Onboard Efficiency = 74%
Distance Traveled = 192 miles

Control stops after 1st reaction completes, second reaction not started

Enhanced material decreases the maximum possible operating temperature with the drive cycles by 5°–10°C
Activity almost every week; 85% of sessions were by new visitors

- U.S. had most sessions, followed by China
- Starting on Home or Models page
- 1st interaction is mostly on Models page followed by Technology Areas; 2nd interaction is mostly on Models page
Accomplishments and Progress – Model Website Analytics: Locations (April 1, 2019–March 30, 2020)

Activity by city shows global interest in countries and regions including China, Australia, Japan, EU, and others.
## Accomplishments and Progress – Model Downloads (through March 30, 2020)

<table>
<thead>
<tr>
<th>MODEL</th>
<th>Total</th>
<th>Totals AMR2019</th>
<th>Additional through 2020Q2</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂ Storage Tank Mass and Cost Model</td>
<td>268</td>
<td>241</td>
<td>27</td>
</tr>
<tr>
<td>MHAE Model</td>
<td>75</td>
<td>66</td>
<td>9</td>
</tr>
<tr>
<td>MHFE Model</td>
<td>121</td>
<td>107</td>
<td>14</td>
</tr>
<tr>
<td>Vehicle Simulator Framework Model</td>
<td>192</td>
<td>165</td>
<td>27</td>
</tr>
<tr>
<td>CH System Design Stand-Alone</td>
<td>44</td>
<td>31</td>
<td>13</td>
</tr>
<tr>
<td>Adsorbent System Design Stand-Alone</td>
<td>56</td>
<td>30</td>
<td>26</td>
</tr>
<tr>
<td>MH System Design by Usable H₂</td>
<td>5</td>
<td>-</td>
<td>5</td>
</tr>
<tr>
<td>MH System Design by System Volume</td>
<td>4</td>
<td>-</td>
<td>4</td>
</tr>
</tbody>
</table>

Most downloads are for *Tank Mass and Cost Model* and *Vehicle Simulator Model*
<table>
<thead>
<tr>
<th>Organization</th>
<th>Relationship</th>
<th>Type</th>
<th>Responsibility</th>
</tr>
</thead>
<tbody>
<tr>
<td>NREL</td>
<td>Team Member</td>
<td>National Lab</td>
<td>Update website and framework</td>
</tr>
<tr>
<td>SRNL</td>
<td>Team Member</td>
<td>National Lab</td>
<td>Adsorbent and compressed gas modeling</td>
</tr>
<tr>
<td>PNNL</td>
<td>Team Member</td>
<td>National Lab</td>
<td>Chemical hydrogen and metal hydride modeling</td>
</tr>
<tr>
<td>Ford</td>
<td>Consultant</td>
<td>Industry</td>
<td>Beta testing, fuel cell model, adsorption data</td>
</tr>
<tr>
<td>University of Michigan</td>
<td>Material Developer</td>
<td>Academia</td>
<td>Adsorption data</td>
</tr>
<tr>
<td>University of California Berkeley</td>
<td>Material Developer</td>
<td>Academia</td>
<td>Adsorption data</td>
</tr>
<tr>
<td>HyMARC Seedling—Liox</td>
<td>Material Developer</td>
<td>National Lab/Collaboration</td>
<td>Metal hydride data</td>
</tr>
<tr>
<td>HyMARC—Sandia</td>
<td>Material Research</td>
<td>National Lab/Collaboration</td>
<td>Metal hydride data</td>
</tr>
</tbody>
</table>
## Proposed Future Work – FY20 Milestones and Next Steps

<table>
<thead>
<tr>
<th>Deliverable</th>
<th>Due</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>FY20-Q1</strong></td>
<td>Provide update related to HyMARC collaboration and application of models and post new Framework Model version, including Excel version for all Stand-Alone Models.</td>
</tr>
<tr>
<td><strong>FY20-Q2</strong></td>
<td>Provide update on web portal activity—website hits and time on site, website use locations, and model downloads.</td>
</tr>
<tr>
<td><strong>FY20-Q3</strong></td>
<td><strong>SMART Milestone:</strong> Update framework storage, fuel cell, and vehicle models to accommodate medium-duty (vocational, class 4–6) and heavy-duty (line-haul, class 8) vehicle platforms in addition to the existing midsize passenger car option. This will also include the modification of the Framework Model test cases to include up to three additional cases based on representative medium- and heavy-duty drive cycles (e.g., heavy-duty UDDS, HHDDT, HTUF-4, NY Comp. or CBD).</td>
</tr>
<tr>
<td><strong>FY20-Q4</strong></td>
<td>Submit at least two of the following three journal articles: (1) New framework paper—demonstrate models by exercising them using available HyMARC material data, (2) paper related to the sensitivity analysis and develop hierarchy of parameters to adjust to assist material developers, and (3) paper on the tank mass and volume estimator (i.e., Tankinator).</td>
</tr>
</tbody>
</table>

Any proposed future work is subject to change based on funding levels.
Technology Transfer Activities – Updated HSECoE Model Website

HSECoE website: [http://hsecoe.org/](http://hsecoe.org/)

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**Modeling and Engineering Analysis**

For the development of hydrogen storage systems, it is critical to have a comprehensive understanding of the various aspects involved. This includes the materials, the design, and the performance. The HSECoE model website provides a comprehensive analysis of the various technologies and approaches used in the field of hydrogen storage.

**Our Approach**

- **On-Board Storage System**
  - The focus is on developing efficient and reliable storage solutions for hydrogen. This involves understanding the materials used, the design of the storage devices, and the management of the system.

**Models**

- **Hydrogen Vehicle Simulation Framework**
  - The framework is designed to simulate the performance of different hydrogen storage systems. It considers various factors such as the design of the system, the materials used, and the operational conditions.

**HYDROGEN AND FUEL CELL RESEARCH**

Projects focus on materials, concepts, testing, and system analysis.
| Summary |
|-----------------|--------------------------------------------------|
| **Relevance**   | • Provide materials-based hydrogen storage researchers with models and materials requirements to assess their material’s performance in an automotive application. |
| **Approach**    | • Improve stand-alone model and framework utility by bridging the gap between the information generated by the materials researcher and the DOE Technical Targets. |
| **Technical Accomplishments and Progress** | • Stand-alone tools have been developed in Microsoft Excel as a replacement for MATLAB and placed on the modeling website. These models allow easier use by the hydrogen storage community.  
• Stand-alone tools and framework have been used to evaluate materials for HyMARC and help better understand the benefits (or not) of new materials. |
| **Collaborations** | • Project team includes NREL, SRNL, and PNNL.  
• Consultants from industry participate in team meetings and provide input.  
• Material developers from HyMARC and academia provide new material properties. |
| **Proposed Future Research** | • Expand the use of models by demonstrating their utility with other storage materials and vehicle class options. |
Remaining Challenges and Barriers

- Increase the use of the models by material developers
  - Expand the researcher base that uses the models
  - Simplify the model use for nonmodelers
- Increase the use of the models by systems engineers
  - Potential expansion of the model capabilities to other vehicle classes and system platforms
- Demonstrate the models’ utility to other researchers
  - Applying the models to their applications
- Find available data to validate the models
- Reverse engineering—using the models to better inform materials developers of what properties are most important
Publications and Presentations


• This project was not reviewed last year