"The Benefits and Challenges with On-board Liquid Hydrogen Storage Systems"

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CEC/ICMC 2023
Outline

• DOE Goals
• Medium- and Heavy-Duty Vehicle On-board Storage
• Compressed Gas versus cryo-Compressed versus LH2
• Pressure and Temperature Fatigue
• Material challenges
  ▪ Polymers
  ▪ Composites
  ▪ Metals
    ✓ Welds
• Summary
DOE-Hydrogen Fuel Cell Technologies Office is accelerating H₂ technologies for decarbonization.

Source: Ned Stetson 2021 Annual Merit Review HFTO
Motivations

• DOE Hydrogen and Fuel Cell Technology Office
  ▪ Targeting MD/HD vehicles
  ▪ Requiring onboard storage capacities of 20-100 kgs
  ▪ Constraints on weight and volume

• H₂ can be stored as gas or liquid
  ▪ High-pressure Storage
    ✓ 350 to 700 bar
    ✓ Multiple tanks to achieve on-board storage
  ▪ Cold/Cryogenic Compressed Storage
    ✓ 350 to 500 bar
    ✓ 200 K or 30-80 K
  ▪ Liquid Hydrogen Storage
    ✓ <10 bar
    ✓ -253°C (20 K)

How is hydrogen stored?

Physical-based

Material-based

Compressed Gas

Cold/Cryo Compressed

Liquid H₂

Adsorbent

Liquid organic

Interstitial hydride

Complex hydride

Chemical hydrogen

https://www.energy.gov/eere/fuelcells/hydrogen-storage

Insulated Systems CEC/ICMC 2023
Hydrogen Regions of Interest for Storage

- LH₂ Liquid Hydrogen
- CcH₂ Cryo Compressed Hydrogen
- CGH₂ Compressed Gaseous Hydrogen

- LH₁ 0.1-0.5 MPa
- 20-30 K
- Cryo Comp H₂ 50 MPa 38 K
- Cryo Comp H₂ 30 MPa 38 K
- CcH₂
- CGH₂

- Comp H₂ 70 MPa 288 K
- Comp H₂ 35 MPa 288 K

Temperature (K) vs Density (kg/m³) graph.
### DOE Goals and Targets

#### Fuel cell, on-board H₂ storage, and battery requirement for various classes of trucks

- **Light-Duty Vehicle**
  - Linde
  - Nikola One

- **Medium-Duty Vehicle**
  - Nikola Electric
  - Nikola Tree

- **Heavy-Duty Vehicles**
  - Nikola Tre (1)
  - Nikola One (1)

**Bubble Size Shows Battery Output in kW**
- Purple: Known Demonstrations
- Blue: Modeled Class 2-7
- Orange: Modeled Class 8

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#### Table 1. Technical System Targets: Class 8 Long-Haul Tractor-Trailers (updated 10/31/19)

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Units</th>
<th>Targets for Class 8 Tractor-Trailers</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Interim (2030)</td>
</tr>
<tr>
<td>Fuel Cell System Lifetime</td>
<td>hours</td>
<td>25,000</td>
</tr>
<tr>
<td>Fuel Cell System Cost</td>
<td>$/kW</td>
<td>80</td>
</tr>
<tr>
<td>Fuel Cell Efficiency (peak)</td>
<td>%</td>
<td>68</td>
</tr>
<tr>
<td>Hydrogen Fill Rate</td>
<td>kg H₂/kW</td>
<td>8</td>
</tr>
<tr>
<td>Storage System Cycle Life</td>
<td>cycles</td>
<td>5,000</td>
</tr>
<tr>
<td>Pressurized Storage System Cycle Life</td>
<td>cycles</td>
<td>11,000</td>
</tr>
<tr>
<td>Hydrogen Storage System Cost</td>
<td>$/kWh</td>
<td>9 (300)</td>
</tr>
</tbody>
</table>

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#### Volumetric and Gravimetric Capacity Targets

- **2025 Target**
  - LH₂: 350 bar
  - cCH₄: 700 bar

- **2020 Target**
  - LH₂: 350 bar
  - cCH₄: 700 bar

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#### Cost Estimation on 500,000 units/yr

- **Ultimate Target**
  - LH₂: $5
  - cCH₄: $10

- **2025 Target**
  - LH₂: $15
  - cCH₄: $20

- **2020 Target**
  - LH₂: $10
  - cCH₄: $15

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https://www.hydrogen.energy.gov/pdfs/review19/st100_james_2019_o.pdf
Liquid hydrogen’s high density provides fewer truck transports compared to compressed hydrogen

**Compressed Hydrogen**

- 275 bar, composite
- 1,152 kg H₂ capacity/tanker

**LH2**

- 160-190 bar, steel
- 300 kg H₂ capacity/tanker

1. Adapted from Petitpas et al. DOE FCTO AMR June 6th 2017.
2. https://www.catecgases.com/
• Increased interlaminar shear strength performance
• Matrix and composite failure indicator models developed with 20K data
• Observed hydrogen effects on metals and welds at 20K
Resins for Cryogenic Service

- Low temperature and toughened resin systems provide for cryogenic composite systems for lightweighting
- Low coefficients of thermal expansion (CTE) provide reduced composite stress during thermal cycling
- Still meets processing property requirements

**Challenges**

- Critical gap in understanding lower glass transition temperature impacts ambient to higher temperature composite performance
- Outgassing into vacuum space
  - Epoxy materials have specific outgassing signatures which are easily identified and quantitated. This technique is useful to optimize pre-seal bake out and to identify thermal stress by-products
  - Moisture and CO2 are generally the main compounds outgassed from epoxy materials mainly because of under curing or over curing problems
  - GC/MS analysis will detect organic constituent differences between properly and improperly cured or mixed samples, typically silicones
Resin Mechanical Testing

- ASTM D638
  - Square cross-section
  - Defect sensitivity at corners

- ASTM E8
  - Circular cross-section
  - Reduced specimen size
  - ~40% increase in strength at -130°C

- Cryo results
  - Increase in modulus at lower temperatures
  - Defect sensitive reduces strength
Composites for Cryogenic Service

- Composites provide excellent weight reduction and strength
  - Common fibers are carbon and glass fibers
- Technologies proven in aerospace and space applications
- Tailored system designs with resin, fiber, and storage vessel performance

Challenges

- Thermal cycling of composites
  - Coefficient of thermal expansion differences between resin and fiber
  - Matrix microcracking coalesces into macro cracks
  - High strain at the fiber/resin interface produces interfacial debonding
- Combined pressure cycling for fatigue endurance with thermal effects
Composite overwrap

- Matrix thermal embrittlement
  - Defect sensitive
- Fiber-matrix thermal expansion mismatch
  - Fiber-matrix bond
- Non-isotropic layup
  - Hoop windings at 85-89°
  - Helical windings at 10-15°
- Matrix cracking
  - Thermal-induced
  - Pressure-induced
  - Fatigue-induced
Materials Modeling to Storage Vessel Approach

**Temperature-dependent composite**

- Layup: Al liner/90°/+10°/-10°
- Fiber volume fraction: 0.6
- Dome simulated with distributed load

**Temperature-dependent liner**

- NASA report Nr. TM X-53436, 1966

**Tank**

- Layup: Al liner/90°/+10°/-10°
- Fiber volume fraction: 0.6
- Dome simulated with distributed load
Modeling: Loading scenarios

Tank

- Layup: Al liner/90°/+10°/-10°
- Fiber volume fraction: 0.6
- Dome simulated with distributed load

Pressure Vessel Liner Issues

Metallic material H2 compatibility

• Welding liner materials
  ▪ Weld quality
  ▪ Weldability of materials
  ▪ Fatigue endurance limits of welds
  ▪ Cryogenic performance

• Coefficient of thermal expansion mismatch with metallic liner and composite
  ▪ Compressive cyclic fatigue
  ▪ Added mass to compensate for fatigue endurance limits

• Need material data for pressure vessel designs for applicable temperatures:
  ▪ Yield strength
  ▪ Ultimate strength
  ▪ Fatigue strength
  ▪ Ductility limits
  ▪ Creep
  ▪ Thermal expansion coefficients
Modeling: Full tank FEA

• Illuminates issues associated with dome section and boss
  - Liner buckling during autofrettage
  - Gap formation during cooling

After cooling down (80 K)

Gap developed due to CTE mismatch

Liner buckling at boss during autofrettage

Aluminum liner (80K) w/ empty pressure of 0.5 MPa

Steel liner (80K) w/ empty pressure of 0.5 MPa

CTE mismatch

Liner buckling during autofrettage

Gap formation during cooling
Metals for cryogenic service

- Austenitic stainless steels are baseline for LH2 service: 304L and 316L
  - Stable austenitic stainless steels may offer improved performance: Nitronic 40 (XM-11) and Nitronic 50 (XM-19)
- Aluminum alloys are not degraded at cryogenic temperature
  - Weldable alloy for space shuttle LH2 tanks: AA2219

**Challenges**

- Welds are suspect in applications that require welded-construction with high fatigue stresses, such as cryo-compressed containers
- Aluminum alloys tend to display inferior fatigue properties compared to steels
- Appropriate test methodology for cryogenic hydrogen is not known
  - For example, time scales for hydrogen uptake and transport at low temperature may determine the manifestation of hydrogen effects
  - Testing artifact at low temperature or representative of long term behavior?
Approach to understanding materials behavior in cryogenic hydrogen environments

- Establish baseline behavior of low-cost candidate materials in cryogenic hydrogen environments (temperature: 30 to 300K) relative to accepted performance metrics for ambient service and baseline materials
  - Use H-precharging to overcome kinetics of hydrogen uptake†
  - Evaluate high-performance welds and base materials of austenitic stainless steel: 304L
  - Evaluate high-performance welds and base materials of austenitic stainless steel: Nitronic 50 (XM-19)

†must consider effect of H-supersaturation on strength properties and kinetics of hydrogen transport at low temperature
Storage Vessel Metal Liners

- **Materials**
  - 304, 316, Nitronic 50 steels
  - Aluminum 2219

- **Welded zones**
  - Traditional welding
  - Friction stir welding

- **Test temperatures**
  - 113 K (-160°C) - LNG
  - 77 K (-196°C) - LN$_2$
  - 20 K (-253°C) - LH$_2$

- **Temperature effects**
  - $\sigma_y$ increase

- **Hydrogen embrittlement**
  - $\varepsilon_f$ decrease

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Welded dome-ends

Akin et al, "Design, Analysis and Manufacture of Composite Overwrapped Xenon Propellant Tank" 2017

Friction Stir Welding - ASME Columbia Basin
Testing conditions

<table>
<thead>
<tr>
<th>Cooling Method</th>
<th>Temperature</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Environmental chamber</td>
<td>LN$_2$-cooled</td>
<td>25, 298</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-40, 233</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-80, 193</td>
</tr>
<tr>
<td>Cryostat</td>
<td>LN$_2$-cooled</td>
<td>-160, 113</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-196, 77</td>
</tr>
<tr>
<td></td>
<td>LHe-cooled</td>
<td>-253, 20</td>
</tr>
</tbody>
</table>

Hydrogen pre-charged
- H$_2$ gas at 138 MPa, 573 K, 10 days
- 140 wt ppm (saturated)

Composition of metals used in this study

<table>
<thead>
<tr>
<th>Designation</th>
<th>Fe</th>
<th>Cr</th>
<th>Ni</th>
<th>Mn</th>
<th>Mo</th>
<th>Si</th>
<th>C</th>
<th>N</th>
<th>S</th>
<th>P</th>
<th>Cu</th>
<th>Co</th>
<th>Sn</th>
<th>V</th>
<th>Cb</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>304L Bal</td>
<td>18.17</td>
<td>8.50</td>
<td>1.38</td>
<td>0.320</td>
<td>0.21</td>
<td>0.017</td>
<td>0.077</td>
<td>0.024</td>
<td>0.034</td>
<td>0.38</td>
<td>0.26</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>N50 (XM-19) Bal</td>
<td>21.36</td>
<td>11.90</td>
<td>4.98</td>
<td>2.12</td>
<td>0.034</td>
<td>0.34</td>
<td>0.002</td>
<td>0.022</td>
<td>0.40</td>
<td>&lt;0.05</td>
<td>0.003</td>
<td>0.15</td>
<td>0.15</td>
<td>0.005</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- Machine rate: 0.039 in/min
- Nominal strain rate: 2.3e-3 s$^{-1}$
304L Baseline

- Annealed
  - $1050^\circ C$ 30 min
  - Water quenched

- Apparent influence on serration amplitude at low strain

Strain rate effects on 304L Baseline at 20 K

Smaller amplitude at high strain rate (red)
Hydrogen effects on 304L

- Charged to 140 wt ppm
- Reduced $\alpha'$-martensite formation in H-charged 304L
  - Apparent in strain-hardening rate
  - Measured by magnetic methods

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Baseline (0H)</th>
<th>Hydrogen-pre-charged (140H)</th>
</tr>
</thead>
<tbody>
<tr>
<td>113 K (-160°C)</td>
<td>53.1 ± 1.7</td>
<td>42.6 ± 0.8</td>
</tr>
<tr>
<td></td>
<td>54.7 ± 0.8</td>
<td>43.8 ± 1.6</td>
</tr>
<tr>
<td>77 K (-196°C)</td>
<td>54.1 ± 1.0</td>
<td>45.3 ± 1.2</td>
</tr>
<tr>
<td></td>
<td>54.4 ± 1.2</td>
<td>45.5 ± 0.7</td>
</tr>
<tr>
<td>20 K (-253°C)</td>
<td>51.2 ± 1.1</td>
<td>45.2 ± 1.1</td>
</tr>
<tr>
<td></td>
<td>53.9 ± 2.0</td>
<td>45.5 ± 2.4</td>
</tr>
</tbody>
</table>

Mass% $\alpha'$-martensite present at fracture surface evaluated by magnetic measurements.
Hydrogen effects on 304L

- Specimens charged to 140 wt ppm
- Secondary cracking observed in fracture surfaces of H-charged specimens
Hydrogen effects on 304L

- Fracture facets observed at 113 K are common observations at high temperature (e.g. 223 K)
Hydrogen effects on 304L Welds

- Non-charged welded specimens indicate weld ductility down to 20K
- Hydrogen pre-charged welded specimens show hydrogen impacting ductility
- Loss of martensite formation in the hydrogen-charged welded specimens influences the loss in weld ductility
Nitronic 50 (XM-19) Baseline

- Annealed
  - 1065°C  30 min
  - Water quenched
- Increase in yield and ultimate stress with a decrease in temperature
- Reduced ductility below -80°C
Nitronic 50 (XM-19) Hydrogen Pre-charged

- Annealed
  - 1065°C  30 min
  - Water quenched
Summary

- DOE – DOE goals are to increase on-board hydrogen storage capacity and to reduce the cost for storage. Cryogenic storage is one method to help meet those goals, but the cost in cryogenic systems, and materials of construction for storage systems to continue for reliability

- Resins – resins are a critical component for lightweight composite systems, but need to be carefully considered for outgassing, fracture toughness, and CTE

- Composites – composites provide reduced weight and high performance, but have a high cost, designs need to consider CTE liner limits, and composite microcracking from both thermal and stress cycling

- Modeling – high quality modeling can provide optimum design performance based on the filling profiles and construction design, but there is limited data below 77K for material performance for the models

- Metals – metal selection for liners should be considered carefully and tested. Assumptions of stainless steel are not affected by hydrogen are often incorrect. Materials should be carefully selected and tested with proper hydrogen exposure for fracture and fatigue to mitigate premature lifetime performance

- Welds – welds can be challenging for cryogenic service. The addition of hydrogen into the weld affected zone will impact the performance at cryogenic conditions and should be design appropriately for their limitations
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