U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

Advanced Composite Materials for Cold and Cryogenic Hydrogen Storage Applications in Fuel Cell Electric Vehicles

October 29, 2015

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Advanced Composite Materials for Cold and Cryogenic Hydrogen Storage Applications in Fuel Cell Electric Vehicles

Workshop Summary Report

Workshop held October 29, 2015
Omni Dallas Hotel
Dallas, TX

Sponsored by
U.S. Department of Energy (DOE) – Fuel Cell Technologies Office (FCTO)
and Pacific Northwest National Laboratory

Workshop External Presenters
Ford Motor Company
Lawrence Livermore National Laboratory
Composite Technology Development, Inc.

Workshop Website
http://www.energy.gov/eere/fuelcells/downloads/advanced-composite-materials-cold-and-cryogenic-hydrogen-storage

Contacts
John Gangloff, (202)-586-7009, john.gangloff@ee.doe.gov
David Gotthold, (509) 375-2073, david.gotthold@pnnl.gov

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Objective

The U.S. Department of Energy – Office of Energy Efficiency & Renewable Energy – Fuel Cell Technologies Office (DOE-FCTO) and Pacific Northwest National Laboratory (PNNL) hosted the "Advanced Composite Materials for Cold and Cryogenic Hydrogen Storage Applications in Fuel Cell Electric Vehicles" workshop in Dallas, Texas on Thursday, October 29, 2015. This workshop was co-located with the Composites and Advanced Materials Expo (CAMX). The objectives of this workshop were: (1) Gather input and discuss the state of knowledge on composite materials & processing for use at sub-ambient temperatures; (2) Identify research needs and recommend development pathways for use of composite materials at sub-ambient temperature in high-pressure applications. This input will be used to help guide future activities for the DOE hydrogen storage program.

Background

Compact, reliable, safe, and cost-effective storage of hydrogen is a key technology requirement for the widespread commercialization of Fuel Cell Electric Vehicles (FCEVs) and other hydrogen fuel cell applications. While some light-duty FCEVs with a driving range of about 300 miles are emerging in limited markets, affordable onboard storage still remains a roadblock to commercialization beyond limited vehicle platforms and niche markets. A key challenge is how to store sufficient quantities of hydrogen onboard without sacrificing passenger and cargo space. While the energy per mass of hydrogen is substantially greater than most other fuels, its energy by volume is much less than liquid fuels, such as gasoline. The current state of the art is to store hydrogen in Composite Overwrapped Pressure Vessels (COPVs) with polymer liners at 700 bar pressure. To make the systems more compact, longer-term research focuses on developing advanced hydrogen storage technologies that can provide greater energy density than 700 bar compressed hydrogen, at a competitive cost. Research is now being performed for high-pressure hydrogen storage at cold (e.g., ~ 200 K) and cryogenic (e.g., << 200 K) temperatures. Cold and cryogenic-compressed hydrogen storage systems allow designers to store the same quantity of hydrogen, either in smaller volumes at similar pressures, or in similar volumes at lower pressures. The intent of this workshop was to help identify the implications of using composite materials in these low-temperature, high-pressure, long cycle life applications and knowledge gaps that need to be addressed.

Agenda

8:00 The DOE H2 Storage Program, Cold and Cryogenic H2 Storage and Workshop Objectives -

Ned Stetson, DOE Fuel Cell Technologies Office

8:30 Panel Presentations and Discussions: Moderator – John Gangloff (DOE - FCTO)

- Ford Motor Company – Mike Veenstra
- Pacific Northwest National Laboratory – David Gotthold
- Lawrence Livermore National Laboratory – Gene Berry
- Composite Technology Development, Inc. – Pat Hipp

10:00 Break

10:15 Breakout Session I – Mechanics and Materials

- Identifying constituent materials (i.e. fibers, resins, additives) that are recommended for cold / cryogenic temperatures with pressure cycling
- Microstructural failure mechanisms at cold / cryogenic temperatures
- Vacuum exposure on composite materials at cold / cryogenic temperatures
- Durability and fatigue due to Coefficient of Thermal Expansion issues

11:15 Break

11:30 Breakout Session II – Processing, Characterization, and Analysis

- Composite manufacturing processes suitable for cold / cryogenic applications
- Material characterization methods for part verification and validation
- Safety codes and standards status for cold / cryogenic temperature composites
- Modeling and analysis tools for cold / cryogenic temperature composites

12:30 Adjourn

Workshop Introduction, Panel Presentations, and Discussions

The opening session consisted of an introduction presentation by Dr. Ned Stetson of DOE-FCTO and four overview presentations to frame the discussions. The introduction presentation discussed the FCTO Hydrogen Storage Program mission and current program activities. Specifically, the introduction presentation highlighted physical-based hydrogen storage approaches that employ the extensive use of composite materials at ambient temperature conditions. Focus was shifted to cryogenically compressed hydrogen storage as a long-term research pathway providing more potential to achieve DOE hydrogen storage targets compared with conventional storage systems operating at ambient temperature conditions. Publically available content from BMW was included to showcase their current work on cryogenic compressed hydrogen storage. The technical challenges for the development of suitable composite materials for cryogenic compressed hydrogen storage were noted. This setup the premise for the workshop to explore the current state-of-the-art for composite materials in cryogenic environments and how best to address the technical challenges that exist for the technology.

Photographs from the workshop introduction with Dr. Ned Stetson (DOE-FCTO) (left) and audience (right).

Mike Veenstra, Ford Motor Company, next presented an OEM perspective on the requirements for onboard hydrogen storage. All design tradeoffs are framed in respect to customer expectations, including: driving range, refuel time, cargo space, cost, and safety. Technical considerations, such as the actual storage technology, durability, or vehicle weight are only relevant in how they affect the other customer expectations. For low temperature storage, insulation becomes a key technical challenge, with maximum 5-7 W heat leakage needed to achieve a reasonable dormancy and a target lifetime to match that of the FCEV, about 15 years.

David Gotthold, Pacific Northwest National Laboratory, presented work on the development of a storage tank system that uses the improved storage density of cold (200 K) gas. The lower temperature enables storage of an equivalent volumetric density compared to a 700 bar ambient temperature tank while using a lower pressure (500 bar) design with a corresponding lower cost. The moderately low temperature provides flexibility in operation, and with lower insulation requirements for equivalent dormancy.

Gene Berry, Lawrence Livermore National Laboratory, presented work on cryogenic compressed hydrogen, which has potential for the highest volumetric density for hydrogen gas by using both low-temperature (40-80K) and high-pressure (700 bar). The insulation used is multi-layer vacuum insulation where the composite tank, as the internal wall, is in direct contact with the vacuum space. To maintain the vacuum stability and avoid having to frequently regenerate the vacuum, low-volatility resins and materials need to be used in the composite layers of the pressure vessel.

Patrick Hipp, Composite Technology Development, Inc., presented an aerospace view of composites testing. Several key points were raised. First, low temperature material testing is still an evolving area, with ASTM E1450 being the only official standard for cryogenic testing, and only for metals at 4 K. Current polymer and composite testing methods use standard ASTM test standards modified for low temperature. CTD has developed a wide range of low temperature tests and the appropriate equipment for testing down to 4 K. Low temperature cyclic testing is particularly difficult, with long cycle times and expensive liquid coolants.

During the Q&A session of the panel discussion, a few questions were raised:

1. What happens when a cold hydrogen tank warms up and hydrogen boils off?

   The panelists discussed how excess hydrogen can be used for power generation to charge batteries, run the AC, or other temporarily useful loads. A point was raised that the tank can be cooled by controlling the vent speed and volume, which may provide additional operating time.

2. Is there an ideal aspect ratio for the gas cylinder?

   The panel noted how the ideal tank would be easily adapted to the vehicle design constraints. An example brought forth was how Toyota uses multiple tanks for better fit within their Mirai design and operating conditions outweigh cost. In addition, it was noted how the torpedo shape is best for safety and cost and it fits well in many vehicle configurations (i.e. along the drive shaft hump in conventional cars). Also, an additional point was made where cold and cryogenic temperature compressed systems are usually single tank designs to reduce insulation complexity; whereas, ambient temperature compressed systems are commonly multi-tank designs. This constrains the design space for cold and cryogenic temperature compressed systems.

3. What is the best approach for accelerated testing for cold temperatures?

   The panel noted that LLNL is working with BMW to test tanks at two thermal cycles/day. It was also noted that serious questions remain about the effect of thermal transients on the tank performance.

After the Q&A session was concluded, the workshop participants were broken up into two separate groups of ~10 attendees each to discuss the topics of the following breakout sessions.

Breakout Session I – Mechanics and Materials

Breakout Session I generally focused on materials and materials testing. The specific discussion topics of this breakout session were the following: (1) Identifying constituent materials (i.e. fibers, resins, additives) that are recommended for cold / cryogenic temperatures with pressure cycling; (2) Microstructural failure mechanisms at cold / cryogenic temperatures; (3) Vacuum exposure on composite materials at cold / cryogenic temperatures; (4) Durability and fatigue due to Coefficient of Thermal Expansion issues.

Several issues with outgassing and vacuum stability were noted:

1. The outgassing of composite materials is still uncertain (i.e. not enough data). For example, some epoxies and urethanes are demonstrated to have reasonable vacuum compatibility and vinyl esters, with their high styrene contents, are generally poor for outgassing. However, most testing is done for space applications, which have different performance thresholds than passenger vehicles Current outgassing data is typically measured either at ambient temperatures (~300 K) or at space relevant temperatures (<100 K), so the quality of outgassing data is questionable for cold and cryogenic compressed gas storage.

2. Current space-focused testing is typically for either very low cycle life (single launch cycle plus 2-3 tests) or for short overall operational life (build to launch < 1-2 years). Automotive applications are typically >10-15 years with many cycles (thousands).

3. In space applications, vacuum is free and outgassing is more of an issue for other impacted systems (optics, etc.).

Issues related to tank system lifetime as well as monitoring and remediation of these issues were also discussed:

1. In-situ inspection is not well understood and there are no/few low-cost tools that can easily be integrated for long-term monitoring. This is more of an issue with the vacuum insulated tanks, where direct inspection of the composite tanks requires dismantling of the outer vacuum chamber.

2. Accelerated outgassing of the matrix materials with vacuum may have unexpected effects on lifetime (i.e. degradation of composite ultimate strength, interlaminar shear strength, and stiffness).

3. Vehicle level fatigue and vibration is a much more serious issue, with respect to cycle life, compared to aerospace applications (i.e. years vs. minutes). This is particularly an issue due to the difficulty and infrequent nature of automotive inspections (relates to point 1). Long-term fatigue and aging effects are unknown. Microcracking hurts fatigue life. Resin toughening helps. Tension-driven loads are okay if you have some microcracking.

4. Real-time repair through self-healing matrix materials was raised as a way to achieve multi-decade lifetimes (i.e. helps mitigate micro-cracking networks). Also, the idea of tank patching was raised, but it was unclear if this would work at cryogenic temperatures.

5. Composite ply thickness is related to residual stress buildup. Thin plies (i.e. <2.5 mm) help resist microcracking at cryogenic temperatures. Thin plies also make energy release easier. This application has thick composite walls. A design goal is to match resin / fiber coefficient of thermal expansions (CTE) or have resin tougheners. Higher modulus fibers can lead to microcracking.

Breakout Session II – Processing, Characterization, and Analysis

Breakout Session II was intended to be more focused on processing and characterization. However, it became clear in Breakout Session I that the processing and materials attributes of composites are extremely difficult to separate. The specific discussion topics of this breakout session were the following: (1) Composite manufacturing processes suitable for cold / cryogenic applications; (2) Material characterization methods for part verification and validation; (3) Safety codes and standards status for cold / cryogenic temperature composites; (4) Modeling and analysis tools for cold / cryogenic temperature composites.

Several issues with filament winding processes were noted:

1. Optimization of fiber layups remains an area of interest. Toyota has recently demonstrated improvements to their layup designs, but there was some discussion about whether their initial layups were fully optimized. Several individuals raised the issue of multi-fiber optimization, especially as new, low-cost fibers that are not aerospace focused, become more widely available. Also the idea of dry nanoscale fiber (i.e. carbon nanotube based) was mentioned.

2. Interlaminar shear stress is currently not well represented in standard models.

3. There was significant discussion about wet-winding vs. prepreg winding for tank layup. Wet- winding is a proven high-volume manufacturing process, and by careful adjustment of resin take-up and winding rates, the void volume can be minimized. However it has its own processing issues (i.e. wet-winding slippage, irregular fiber tow thicknesses, low fiber volume fraction). In contrast, prepreg winding enables higher shear and more complex windings without slippage, but the likelihood of voids is higher. Also the process of dry-winding with later resin infusion was discussed.

In addition, there were several discussion points on modeling and analysis. It was noted how tank manufacturers tend to do their own modeling for their own specific tank designs. This implies that there is a lack of agreement on design principles for composites in cryogenic temperature environments. The breakout groups identified the need to determine the main groups that do extreme temperature modeling of composite materials, either at low or high temperatures. It was discussed how aerospace OEMs typically do their own extreme temperature modeling of composite materials, relying strongly on empirical relationships to correlate modeling assumptions with experimental observations.

It was noted how difficult it is to get material properties at cryogenic temperatures. A posed question was if one can adapt room temperature modeling tools at the cryogenic regime? Would the room temperature assumptions still be valid for low temperature modeling / how far off would they be? Can one trust ambient temperature relationships at cryogenic temperatures?

A discussion on material choice and processing at low cost was brought forth. The automotive industry strives for low cost at high production volumes. Does material choice drive manufacturing process or manufacturing process drive materials choice? There was discussion on which philosophy is better for the cryogenic composite tank? It was noted that wet winding is currently the manufacturing technique of choice because it is cheaper than prepreg processing; however, if prepreg were cheaper, would tank makers be willing to change processes to reap the benefits of prepreg processing? Prepreg winding has similar machinery to wet winding. The limiting factor is cycle time (i.e. wet-winding time vs. curing time with prepregs).

A discussion on testing and inspection followed the materials and processing discussion. Failure mechanisms of composite materials across temperatures is not well understood. Knowledge of these failure mechanisms is necessary before testing standards can be developed. One question posed was if failure modes that happen at ambient temperatures happen at cold/cryogenic temperatures? Would testing at cryogenic temperatures be good enough to validate the composite for ambient temperatures? Also, there is the requirement for tank proof testing at 150% of design strength (i.e. factor of 1.8-2.5). The thermal history matters for polymers. Would there need to be different tests for different COPV types (i.e. military planes vs. cars). Also, the point was raised whether the duty cycle matters for cryogenic COPVs? Also, knowledge of cryogenic composites during crashes or impact events is not well understood, but is of strong interest to automotive OEMs for vehicle certification.

A point was raised for the need to have a clear distinction between “cold gas” and “cryogenic gas”. One idea posed to the breakout group was if one tank design could handle cold, cryogenic, and ambient gases in order to support cold/cryogenic and ambient refueling and use.

Inspection via acoustics was deemed popular for composite materials in cryogenic environments. A discussion on *in situ* versus destructive testing tomography was posed. It was noted how it is difficult to do tomography with carbon fiber. Ultrasonics could be good enough for the design space. Robotic fiber placement head can detect tape placement defects in real time. Evaluation after testing during operation was discussed using ultrasonic or infrared based methods.

Path Forward

The main outcome of the workshop is clear evidence that further research and development of cold and cryogenic composites for onboard vehicular hydrogen storage is needed. The stakeholders represented at the workshop showed a lot of interest in DOE's future research activities within this technical research area. In addition, it was clear that innovations made in this area for automotive applications can have cross-cutting benefits in other aerospace applications where composite materials are exposed to cryogenic environments.

The workshop also highlighted the need for additional standard testing specifications and procedures for low temperature material testing, since current standards are limited in both varieties of materials and temperature ranges. In addition, thermal expansion mismatch, fatigue, and impact performance are not currently measured.

Finally, it is clear that vacuum applications require low vapor pressure materials. In space – low vapor pressure is needed to prevent damage to other components in the system, but low vapor pressure is necessary to maintain thermal insulation properties for low temperature onboard storage applications. Vacuum compatible materials are readily available, but they are expensive for onboard applications. Also, outgassing of atmosphere (voids) is less of an issue in space, but is likely an issue in a vacuum jacketed onboard storage system.

Presentation Citations

Stetson, N., "Cold/Cryogenic Composites for Hydrogen Storage Applications in FCEVs", *Department of Energy Fuel Cell Technologies Office*, Advanced Composite Materials for Cold and Cryogenic Hydrogen Storage Applications in Fuel Cell Electric Vehicles, October 29, 2015.

Veenstra, M., "Hydrogen Storage System Challenges", *Ford Motor Company*, Advanced Composite Materials for Cold and Cryogenic Hydrogen Storage Applications in Fuel Cell Electric Vehicles, October 29, 2015.

Gotthold, D., "Type IV COPV Cold Gas Operation Challenges", *Pacific Northwest National Laboratory*, Advanced Composite Materials for Cold and Cryogenic Hydrogen Storage Applications in Fuel Cell Electric Vehicles, October 29, 2015.

Aceves, S., Berry, G., Petitpas, G., Switzer, V., "Cryogenic Pressure Vessels for H2 Vehicles Rapidly Refueled by LH2 pump to 700 bar", *Lawrence Livermore National Laboratory*, Advanced Composite Materials for Cold and Cryogenic Hydrogen Storage Applications in Fuel Cell Electric Vehicles, October 29, 2015.

Hipp, P., Fabian, P., "Testing at Cryogenic Temperatures Engineering, Materials, and Testing Support", *Composite Technology Development, Inc.*, Advanced Composite Materials for Cold and Cryogenic Hydrogen Storage Applications in Fuel Cell Electric Vehicles, October 29, 2015.

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