Manufacturing for the Hydrogen Economy

Manufacturing Research & Development of Onboard Hydrogen Storage Systems for Transportation Applications

Background Material for the Manufacturing R&D Workshop
to be held July 13-14, 2005
Washington, DC

July 7, 2005

Introduction

In his 2003 State of the Union Address, President Bush announced a $1.2 billion Hydrogen Fuel Initiative to accelerate the development of the hydrogen and fuel cell technologies needed to move the United States toward a future hydrogen economy. While many scientific, technical, and institutional challenges must be overcome to realize the vision of a hydrogen energy economy, moving from today's laboratory-scale fabrication technologies to high-volume commercial manufacturing has been identified as one potential roadblock to a future hydrogen economy.

The Workshop

The Federal Interagency Working Group on Manufacturing for the Hydrogen Economy was established to coordinate and leverage the current federal efforts focused on manufacturability issues such as low-cost, high-volume manufacturing systems, advanced manufacturing technologies, manufacturing infrastructure, and measurements and standards. Participants in this working group include the Department of Energy (DOE - lead organization), Department of Agriculture, Department of Commerce/National Institute of Standards (NIST), Department of Defense, Department of Transportation, Environmental Protection Agency, National Aeronautics and Space Administration, National Science Foundation, Office of Management and Budget, and White House Office of Science and Technology Policy. Over the last year, this working group has been laying the groundwork for developing a roadmap to coordinate and guide research and development (R&D) efforts on manufacturing technologies critical to commercializing hydrogen and fuel cell technologies. The *Roadmap Workshop on Manufacturing Technologies for the Hydrogen Economy* is the next step in this process.

The purpose of the Manufacturing R&D workshop is to bring together industry, university, and government representatives to discuss the key issues facing all aspects of manufacturing for hydrogen products including: (1) fuel cells that convert hydrogen into electric energy, (2) hydrogen storage systems, and (3) large-scale hydrogen production and delivery systems. The recommendations resulting from this workshop will outline the key technical problems facing the manufacture of hydrogen systems today and identify priorities for manufacturing R&D during the transition to a hydrogen economy (2005-2025), and will be incorporated into the *R&D Roadmap on Manufacturing Technologies for the Hydrogen Economy*. This roadmap will be used to guide R&D on critical manufacturing technologies and technical standards required for high-volume production, and to direct future public-private partnerships that will facilitate transfer of technology to industry through cost-shared projects.

Purpose of This Document

This document on manufacturing R&D for onboard hydrogen storage systems is one of three documents that have been prepared for the Workshop on Manufacturing R&D for the Hydrogen Economy. The other two documents cover manufacturing R&D for proton exchange membrane (PEM) fuel cell systems and for systems that produce and distribute hydrogen.

This material is intended to provide information to workshop participants for their use prior to and during the workshop. This paper was written by the DOE roadmap team and NIST in consultation with industry participants.

The paper covers the following topics that will be addressed in the workshop:

- What hydrogen system components need to be manufactured to begin the transition from petroleum to hydrogen between now and 2025?
- What is the state of manufacturing technologies for these components and systems?

In addition, the workshop will identify and prioritize topics for public-private R&D on manufacturing hydrogen storage system components.

Scope of This Document

This brief report serves only to provide an introduction to some of the issues related to manufacturing onboard storage systems and to propose a starting point in our dialogue toward developing a roadmap of manufacturing for the hydrogen economy. It does not attempt to address many of the detailed issues related to manufacturing costs, such as production rate, quality assurance, inspection, and design for manufacturing. Furthermore, it does not include some technical approaches, such as active monitoring of container integrity, which could impact manufacturing methods and costs. Finally, there are other storage technologies currently under development, particularly chemical hydrogen systems, which have not been included, even though they show great promise toward meeting technical storage requirements. These systems generally include an off board regeneration process which greatly enlarges the range of manufacturing issues beyond simply that of storage components and impacts the manufacturing needs for components related to production and distribution infrastructure.

Background and Current Status of Hydrogen Storage Development

The energy density of hydrogen stored onboard a vehicle remains a key issue in the development of hydrogen-fueled vehicles. Figure 1 is a plot of gravimetric hydrogen density (H_2 weight fraction (%)) versus volumetric hydrogen density (H_2 weight/unit volume) for a variety of materials, including pure hydrogen in liquid form and as a compressed gas. Also shown on the plot are the 2010 and 2015 FreedomCAR targets. To perform as well as or better than current vehicles, the hydrogen energy density must lie on the plot above and to the right of the target values. Furthermore, these densities must be achieved for the entire storage system and not just for the storage media. The added impact on weight and volume when systems are included is shown on the plot for current values of compressed gas and liquid hydrogen systems, a liquid borohydride system, and for a sodium alanate solid-state system.

These system values indicate the current status of hydrogen storage; that is, no current storage technology meets the FreedomCAR targets. Researchers are, however, aggressively pursuing development programs on all potentially viable storage technologies at the present time. Specifically, there are researchers investigating all of the high density materials plotted in Figure 1 with the goal of finding and developing a lightweight high density storage material. Materials are being investigated aggressively because, as shown in Figure 1, hydrogen can be packed more densely in a solid or liquid compound than in the pure hydrogen gas or liquid phases.

Engineering developments are also being pursued to achieve greater stored densities in compressed gas, cryogenic, and liquid hydrogen systems. One option is the use of cooled, compressed gas storage which can attain greater volumetric energy density than storage at ambient temperature. The viability of this approach lies in developing components which do not add too much weight and volume. Another cryogenic approach is to include a lightweight material in a lower pressure container which then adsorbs hydrogen to a higher density than would be attained in the gas phase.

The working group believes solid-state systems are too early in their development cycle to consider the issues that will arise in their manufacture. At this time, there is no one candidate material which shows significantly more promise than the others, so a specific material, or even a specific material class or family of materials, cannot be singled out for consideration. Since there are large differences between these materials in terms of fabrication, packaging, reactivity, etc., it would be difficult, at best, to attempt a generic case for solid-state storage systems.

Liquid hydrogen and compressed gas hydrogen storage systems can be considered to be commercially available; that is, such systems can be purchased from a limited number of manufacturers. Essentially all of the approximately 500 (globally) hydrogen fuel cell vehicles which have been constructed to date have used either compressed gas or liquid hydrogen for onboard storage. (There have been a few, one-of-a-kind solid state systems placed on vehicle platforms, but these have been research oriented). Next generation fuel cell vehicles planned for this year and for the next few years also will deployed utilizing one of these two storage options, with high pressure gas systems predominating. These systems, however, are only available in small quantities and no large scale production facility exists. It is these components, then, that a near term (to 2025) manufacturing initiative could focus on to foster the transition to a hydrogen economy.

Storage System Components for Manufacturing

Although a manufacturing initiative focused toward compressed gas and cryogenic systems is being advocated here, there are some components which any storage technology, including solid state storage, would have in common with the others. The most obvious, of course, is the container. Any storage approach will need a container, and this generic container shares a surprising number of attributes with current high pressure tanks. First, the container will, in general, need to be lightweight to maximize the gravimetric energy density. Second, it will need to be capable of sustaining an overpressure (at least an order of magnitude above atmospheric pressure and typically even higher) because, generally speaking, a higher pressure will be needed within the container than that required for delivering fuel to a fuel cell or ICE. In other words, a higher pressure is needed to maintain the delivery pressure within a defined range. Ambient temperature variations and rapid refueling rate requirements will also lead to higher pressure conditions for the container. For example, solid state systems generally have faster hydrogen absorption kinetics at higher overpressures.

The temperature range to which a container would be subjected is relatively narrow, independent of the storage technology, and well within the material limits of current composite materials. An endothermic solid state storage material requiring heat from a fuel cell coolant loop, for example, will need to operate below the fuel cell operating temperature (e.g., < 373 K). Cryogenic compressed gas methods or adsorbent material systems currently under study would also operate at modest temperatures, around 100 K, or even higher.

Current carbon composite tank technologies used in high pressure compressed gas systems appear to be capable of meeting the generic requirements discussed above. There are, however, significant issues related to the manufacture of such components which are discussed later.

The comments above do not necessarily apply to liquid hydrogen storage systems. These generally operate at or near ambient pressure (a few bar) and the liquid needs to be maintained at about 4 K in order to be in equilibrium at this pressure. The design and construction of liquid hydrogen systems are quite different from the carbon fiber composite tanks used in ambient-temperature high-pressure systems. A schematic example of a liquid hydrogen system is shown in Figure 2. The inner container, containing liquid hydrogen with a relatively low overpressure, typically can be fabricated with compatible metal alloys. Furthermore, thermal insulation barriers, which must be very effective to extend latency of the stored liquid, form a substantial portion of the tank structure. All of these factors indicate that the manufacturing process will be quite different than for carbon composite vessels and that there will be very different manufacturing issues to consider and overcome.

There are additional components that a generic storage system would need which are also used today in high pressure systems and in liquid hydrogen systems. These “balance of plant” components include pressure regulators, control valves, PRD’s (pressure relief devices), mounting fittings, tubing, and refueling components. Figure 3 identifies some of these components in a compressed gas storage system. They are also identified for the liquid hydrogen system in Figure 2. All of these parts are generally fabricated using metal alloys and are needed to satisfy operational and safety considerations. The manufacturing of “balance of plant” components must focus on cost, low weight and volume, reliability, and ability to withstand long term hydrogen exposure. Fatigue issues due to storage system cycling, particularly in high pressure systems, and thermal cycling issues (ambient and operational) may also be important in specific applications and could impact manufacturing requirements in terms of material selection, manufacturing design, manufacturing defects, etc.

In summary, hydrogen storage systems will, potentially, operate under more hostile conditions than present-day gasoline tanks used in conventional vehicles. Hydrogen will be contained either at high pressure, at cryogenic temperatures, or in a material which will likely be quite reactive to air or water exposure. Hence, manufacturing processes will need to address product reliability, consistency, and safety over the lifetime of the system. Furthermore, manufactured systems will need to have the ability to be qualified and easily inspected under a variety of conditions.

Carbon Fiber Composite Cylinders

High pressure compressed gas containers are generally made of filament wound carbon fiber construction and are cylindrical in shape. A partial cross-sectional view (Quantum Technologies) is shown in Figure 4. The cylinders consist of an internal liner, made with either a lightweight metal such as an aluminum alloy, or, as shown in Figure 4, a high density polymer. The liner forms a permeation barrier for the gas and also acts as the form for winding the fiber. The fiber wrap is then impregnated with a filler material (e.g., an epoxy) and a protective outer coating. Metallic bosses are used on the hemispherical ends to connect to a regulator, valves, PRD, etc. This type of construction has been quite successful in producing robust, lightweight, high strength tanks and can form the basis for a generic container that could be used in solid-based, liquid-based, cryogenic adsorption, or pressurized gas storage systems.

Current carbon composite systems, however, are prohibitively expensive. The manufacturing processes for these containers are time consuming, very expensive, and require multiple inspection steps. Scaling up production quantities while significantly bringing down unit costs will be particularly challenging.

Adapting this high pressure container to one of the other storage modes will also require significant changes to the manufacturing processes. With a solid-state system, for example, one must also fill the internal volume with the storage media at some stage of the fabrication. Also, some form of metal foam, plates, or fins must be an integral part of the storage media structure to enhance thermal management. Hence, the current method of fabricating the inner liner and subsequent fiber wrapping would need to be altered to allow manufacturers to insert material and subsequently seal the container.

Additionally, any storage method that must operate below ambient temperatures (e.g., adsorptive carbon systems) would need to include low cost, low volume, and lightweight thermal insulation into the manufacturing process. One final consideration for adapting high pressure composite cylinders to other, lower pressure storage options, would be to explore the potential for fabricating these containers in non-cylindrical geometries, such as, for example, approximately rectangular shapes, to allow the storage system to better conform with existing volumes onboard vehicles.

As stated earlier, a major issue with current construction methods is unit cost. Currently, the costs of these containers, in small quantities, are orders of magnitude too high for widespread use as vehicular fuel tanks. One would expect economies of scale to bring the unit price down, but the primary price driver is material cost, specifically the carbon fiber. Carbon fiber cost accounts for 40%-80% of the container cost (K. Newell, Quantum Technologies, Inc.). We should mention at this time that the carbon fiber cost may be mitigated to some extent for solid-state or other alternative storage modes because these options generally operate at much lower pressures (e.g., < 70 bar) rather than the 350 – 700 bar pressure range typically used for compressed gas storage.

Carbon Fiber Manufacturing

As mentioned in the previous section, the cost of carbon fiber used in filament wound composite tanks (350 – 700 bar operating pressures) accounts for 40%– 80% of the total cost of a container. This relatively large range of fiber cost contribution can be accounted for to some extent by understanding the relationship between the unit fiber cost and the strength of the fiber. The following table shows the strong dependence of fiber cost on tensile strength.

Table 1. Graphite Fiber Cost and Tensile Strength

(K. Newell, Quantum Technologies, Inc.)

Carbon fiber type	Tensile Strength	Approximate fiber cost
Low cost	711 ksi	$20/kg
Mid performance	790 ksi	$58/kg
High performance	900 ksi	$170/kg

Although less high strength fiber would be needed to fabricate a tank with a given operating pressure, the cost increases much faster than the amount of fiber. For example, about twice the amount of low cost fiber might be needed compared to a high performance fiber for a specific tank design, but the total cost of fiber then would still be lower by a factor of 4. The trade-off, of course, is that the resulting lower cost tank would be somewhat larger and heavier. It would appear, then, that lowering the manufacturing costs of high strength carbon fibers would make a substantial impact on the cost of most hydrogen storage system technologies.

Lowering the cost of high strength fibers would require developments in manufacturing processes as well as in reduced precursor costs. At the present time, high strength fibers are produced using a PAN polymer precursor. PAN contains about 45% carbon, so that the cost of the fiber will be at least twice the cost of the precursor (D. Edie, Center for Advanced Fibers and Films, Clemson University).

Cross Cutting Issues

(prepared by NIST)

As outlined in the previous section, manufacturing for the hydrogen economy covers a large spectrum of manufacturing technologies, from continuous chemical processes to discrete mechanical fabrication processes. As such, there are diverse issues and challenges associated with each of these manufacturing technologies. However, there are significant mutual influences among these technologies to affect the overall feasibility of the hydrogen economy. For example, while some continuous chemical process technologies rely on advances in discrete mechanical fabrication for cost reductions (e.g. fuel injectors used in gasifiers, feed systems) other discrete manufacturing technologies benefit from advances in continuous processes (e.g. gas purity, water management). Thus, the working group is able to identify a small set of challenges that are applicable to most of the manufacturing technologies. This section provides a preliminary summary of these cross cutting issues.

Metrology and Standards

Metrology provides quantitative information about a manufacturing process and its output. Thus it is key to understanding and improving any manufacturing technology. The ability to reliably measure various process parameters and other critical manufacturing process outputs enables cost effective manufacturing. Specific metrology needs of manufacturing for the hydrogen economy include the areas of dimension and form of components, micro structures and surfaces, particle size and distribution, thin and thick film coatings, pressure, temperature, vacuum, gas flow, water transport, resistance, conductivity, and electrical power.

Related issues include the need for standard measurement methods and protocols for these properties. Such standards ensure quality in the supply chain, lower costs, enhance international trade, and improve the quality of the end products.

Modeling and Simulation

Modeling and simulation can significantly advance the development and optimization of manufacturing processes, and thus are key elements in the development of a viable manufacturing for hydrogen economy.

Knowledge Bases

To support modeling efforts, there is a need for information and knowledge about new materials and sealants, including their processibility, formability, machinability, and compatibility with other materials and gases. There is also a need for new process technologies, fundamental correlations between manufacturing parameters, and performance parameters. Creating pre-competitive, easily accessible, user-friendly knowledge bases for the use of the hydrogen industry will foster further innovation in this area.

Design for Manufacturing and Assembly

In order to cost effectively move from existing small-batch production to high-volume production, design-for-manufacturing (DFM) methodologies have to be used at the earliest stages of product development. DFM principles that should be considered include component selection for reduced parts counts designs that can be produced consistently at both low and high volumes, and realistic tolerance analysis and specifications.

Sensing and Process Control

Sensors and process control technologies are key enablers for increasing the reliability and quality of manufacturing processes while reducing cost. Low cost sensing and sensor fusion technologies with reliable sensor networks are therefore needed for in-process sensing of processes and in-operation sensing of product performance.

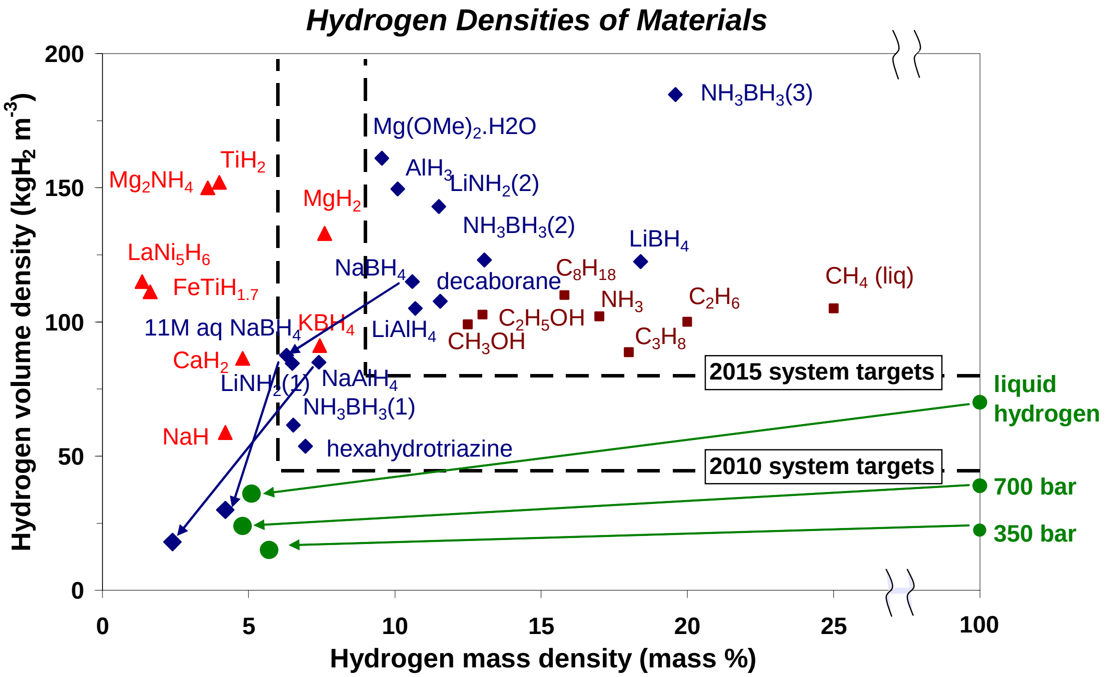

Figure 1. Plot of Hydrogen Mass Density vs. Hydrogen Volume Density for Some Hydrogen Storage Materials. The plot also includes the weight and volume parameters for compressed hydrogen gas at 350 bar and at 700 bar and for liquid hydrogen at 1 bar. System values are included for compressed gas and liquid hydrogen systems and for a sodium borohydride liquid system and a sodium alanate solid state system.

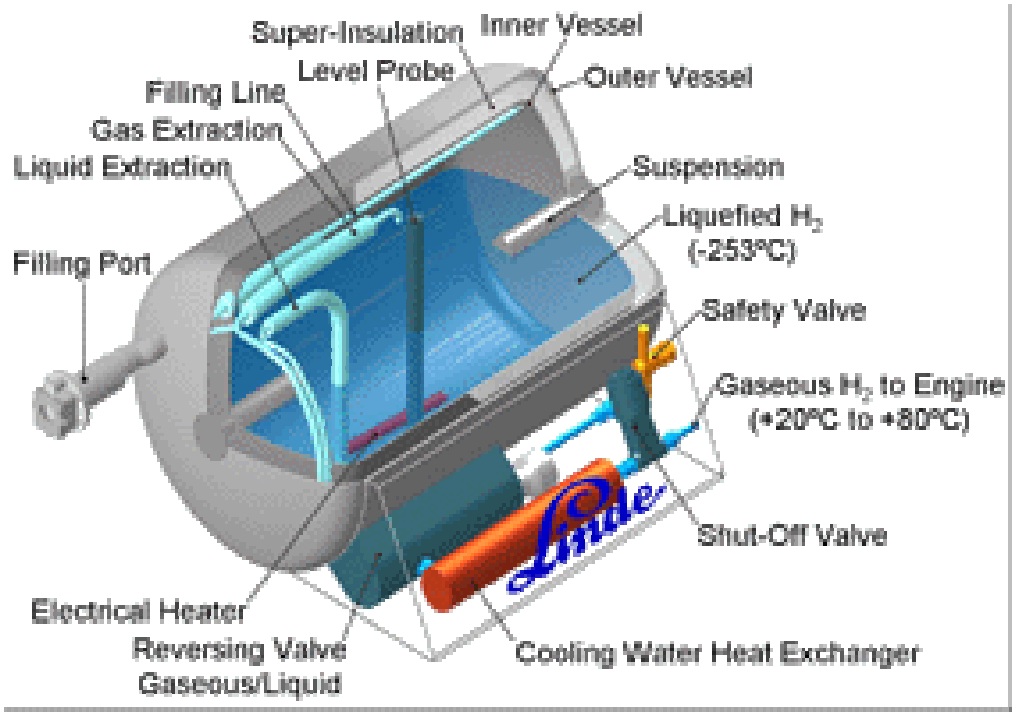

Figure 2. A Schematic Representation of a Liquid Hydrogen Storage System.
(Linde)

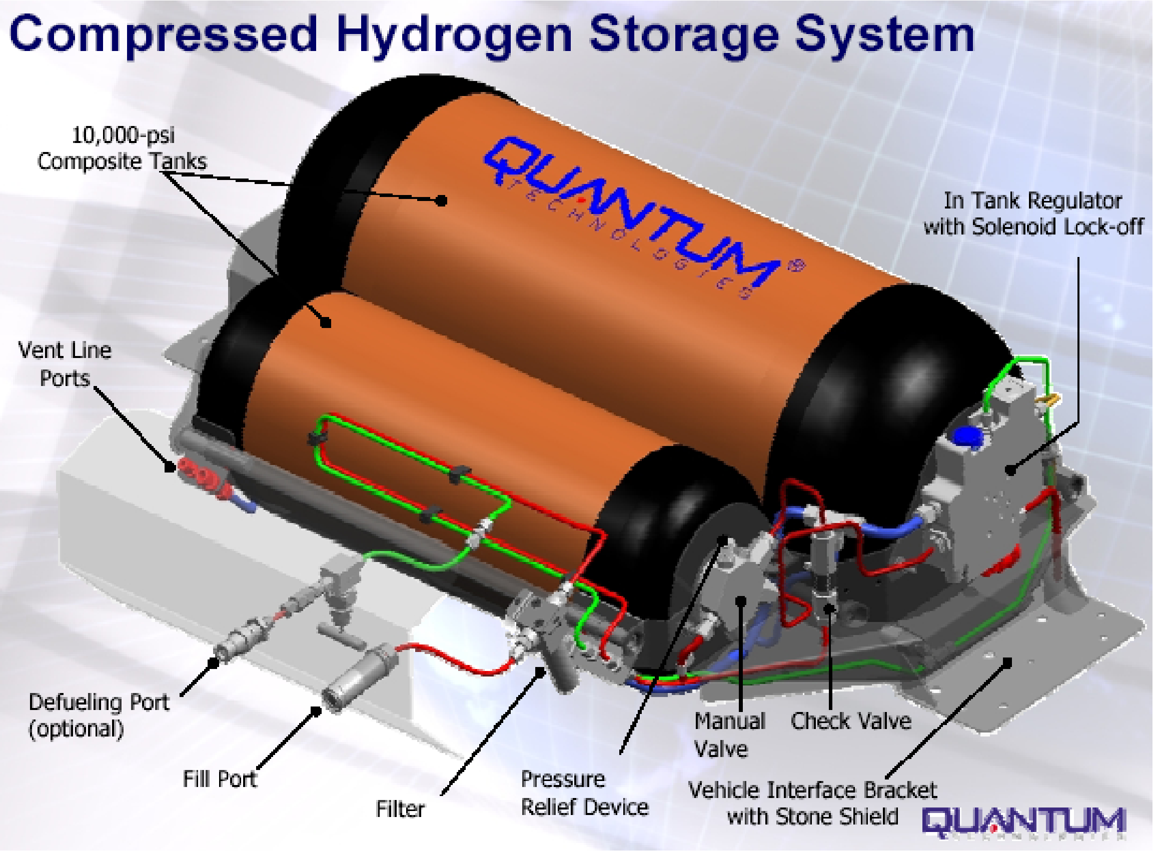

Figure 3. Schematic Representation of a Compressed Gas Hydrogen Storage System Identifying the Balance of Plant Components Needed. (K. Newell, Quantum Technologies, Inc.)

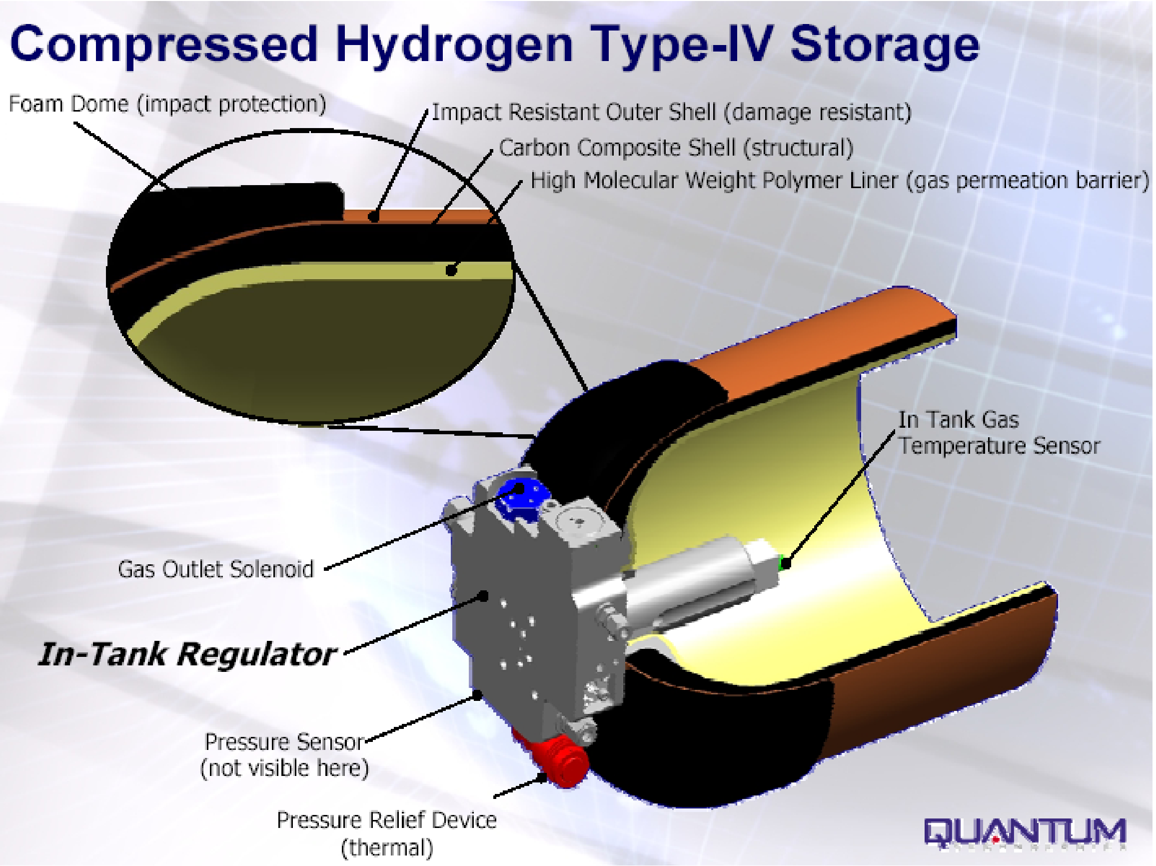

Figure 4. Schematic Representation of a Filament Wound Composite High Pressure Tank. (K. Newell, Quantum Technologies, Inc.)