Preliminary experimental studies into the storage capacity of cryogenic hydrogen in aerogel blanket materials

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Abstract. The abundance and diversity of hydrogen applications necessitates continued and accelerated research into advanced storage technologies. Traditionally, hydrogen has been stored as either a high-pressure, warm gas; or a low-pressure, cryogenic liquid. Methods such as cryo-supercritical and cryo-adsorbed have been explored, but are not yet mainstream. Cryo-adsorbed is attractive because higher storage densities at higher temperatures than liquid may be achieved. Recently NASA, in partnership with Eta Space, Southwest Research Institute, the University of Central Florida, and Air Liquide, have been exploring the use of inexpensive, commercially available silica aerogel blanket materials for cryo-adsorbed hydrogen storage. Unlike most adsorbents, aerogel blanket is not a powder, but a robust, composite material that can be formed into complex shapes to aid in more efficient storage system designs, and has already been proven to uptake large quantities of fluids such as nitrogen and oxygen. Recent experimental efforts into the uptake of low-pressure hydrogen gas at 77 K, and liquid hydrogen at normal boiling point (NBP) will be discussed. Although preliminary in nature, the test results are promising, showing up to a 49% increase in storage density at 77 K over the gas alone, and greater than a one-to-one volume equivalency with NBP LH_2.

1. Introduction

As the momentum behind the transition to hydrogen as a primary energy carrier continues to build across most sectors and industries, advancing storage technologies has become increasing important, especially regarding cryogenic or liquid hydrogen. Traditionally, hydrogen has been stored in one of two ways: as a high-pressure, warm gas; or a low-pressure, cryogenic liquid. Methods such as cryo-supercritical (i.e. cryo-compressed) and cryo-adsorbed have also been explored, but are not yet mainstream. High pressure, warm gas storage affords relative simplicity in that dormancy time is not a factor, and expertise into the manufacturing and implementation of such hardware, both onboard the end-use point as well as on the supply infrastructure side, is well established. As such, high pressure, warm hydrogen storage at pressures up to 700 bar has been the chosen method for most vehicle applications to-date. However, downsides to this method are relatively poor hydrogen storage density—even at 700 bar, gas density is roughly 45% lower than that of normal boiling point liquid hydrogen (LH_2)—heavy-walled, massive tanks, and increased risk of hydrogen embrittlement issues. Liquid storage provides much higher

densities at much lower storage pressures; but, because of the low boiling point (20.4 K), tank designs are more complex and typically also massive, dormancy times become an issue due to unavoidable environmental heat leakage into the liquid causing boiloff, and, in the case of dynamic end-use applications such as vehicles, liquid sloshing can pose problems. Cryo-compressed occupies a space between these two methods, storing cryogenic hydrogen as a high pressure, or super-critical fluid. This eliminates the issues related to dynamic end-uses such as sloshing, and can achieve high storage densities, even higher than liquid in some cases [1], but still suffers most of the downsides to both methods.

Cryo-adsorbed is attractive in that, depending on the adsorbent and storage conditions, higher storage densities at higher temperatures than liquid may be achieved [2]. Cryo-adsorbed relies on the physics of physisorption in very high surface area materials such as activated carbons, zeolites, metal organic frameworks (MOF), aerogels, etc. at low temperatures and/or high pressures to produce molecular or atomic packing factors on par with, or greater than that of the pure fluid at a given state condition.

Charging of a cryo-adsorbent can be done in one of two ways: "wet charging" wherein the material is directly exposed to a cryogenic liquid and allowed to saturate (i.e. equilibrate at the liquid boiling point); or "dry charging," where the adsorbent is cooled to cryogenic temperatures by a secondary means, such as a cryo-refrigerator or sacrificial cryogen coolant, while being simultaneously exposed to the adsorbate gas. Discharging is then achieved through the introduction of heat to the charged adsorbent, but regardless of charging method, the discharged fluid will always be in gaseous form.

Cryo-adsorbed-based storage systems afford high storage densities, do no not require high pressure—which affords more possibilities for conformal tank geometries and system integration—and are insensitive to dynamic applications as no liquid is present. However, these systems still suffer from the downfalls associated with managing cryogenic temperatures; and, because most adsorbents are powders, the storage media itself must be contained.

Recently, NASA has been exploring the cryo-adsorbing capabilities of inexpensive, commercially available silica aerogel blanket materials [3]; and developed the patent-pending Cryogenic Flux Capacitor (CFC) technology [4] that employs the material for use in storage systems. Unlike most adsorbents, aerogel blanket is not a powder, but a robust, composite material that can be formed into a variety of shapes to aid in more efficient storage system designs, and has already been proven to uptake large quantities of fluids such as nitrogen and oxygen through wet charging [5]. Beginning in 2022, NASA, in partnership with Eta Space, Southwest Research Institute (SwRI), the University of Central Florida (UCF), and Air Liquide, have been extending the use of aerogel blanket, and the CFC technology [6,7], into hydrogen storage.

In 2022, a series of wet charging experiments were carried out at Eta Space facility in Rockledge, Florida to determine the hydrogen uptake at normal boiling point in two different aerogel blanket types from Aspen Aerogels: Cryogel® and Spaceloft Subsea®. And at the University of Central Florida, a small dry charging test rig was designed and fabricated that utilized liquid nitrogen (LN$_2$) as a coolant to test hydrogen gas uptake at 77 K. Cryogel® was dry charge tested using the small test rig at 1 bar absolute pressure, at two different aerogel blanket packing densities. The details of each test setup and program will be presented and discussed, as well the wet and dry charging test results.

2. Aerogel Blanket Material

Development on aerogel blanket materials for advanced cryogenic insulation began in 1993 through a NASA Small Business Innovation Research (SBIR) program between Aspen Systems, Inc. (now Aspen Aerogels) and NASA Kennedy Space Center (NASA-KSC) [8]. It is now a commercially scaled product, and is utilized in a variety of industries and applications; most notably, the product has found extensive use in the liquified natural gas (LNG) industry [9].

As opposed to brittle monolithic silica aerogels—sometimes referred to as "frozen smoke" due to its virtually transparent appearance—aerogel blanket is a composite material, with a non-woven fiber-matrix batting that is completely encapsulated by the silica aerogel. This combination gives the blanket overall robustness and flexibility, while retaining the insulative properties of the aerogel. Figure 1 shows

an example of a piece of monolithic aerogel used during the NASA Stardust mission under examination, and 10-mm thick Cryogel® product from Aspen Aerogels.
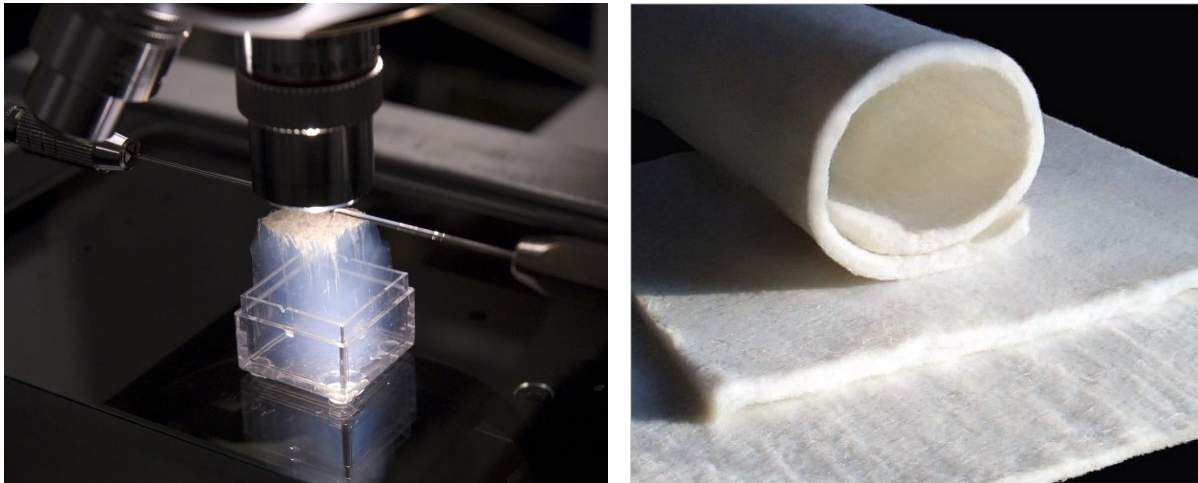

Figure 1. Examination of a Monolithic Silica Aerogel Sample Obtained from the NASA Stardust Mission (left); 10-mm Thick Aerogel Blanket (Cryogel®) Product from Aspen Aerogels (right)

Not only is silica aerogel blanket a superior thermal insulator in an ambient pressure environment, with an effective thermal conductivity of 12.3 mW/m-K for Cryogel® in nitrogen [10], but owing to its high specific surface area (~1000 m^2/g) it is also an excellent adsorbent material, and will readily uptake large quantities of fluids at cryogenic temperatures. Prior wet charging tests using liquid nitrogen, argon, oxygen, and air at their normal boiling points (NBP) revealed uptake ratios (mass of adsorbed fluid vs. dry blanket mass) as high as 7.4:1, with an average of 6.4:1; and a 1:1 average volume ratio (volume of liquid at NBP vs. dry blanket volume) across all the cryogens tested [5]. This strong adsorption attribute of aerogel blanket, along with its relative insensitivity to the choice of fluid, commercial availability, robustness, and ability to be shaped into complex and/or conformal geometries, makes the product well-suited for a wide variety of fluid storage applications. Hydrogen storage in particular is a thriving space, with large investments being made globally over the entire ecosystem, and one where innovation can have an immediate and substantial impact.

3. Liquid Hydrogen Testing
As with the prior liquid cryogen examinations, testing aerogel blanket in LH$_2$ was a crucial step in characterizing the wet charging performance of the material, and the ability to map that to potential storage applications. However, unlike prior testing on inert fluids and oxygen, LH$_2$ presented several additional complexities and hurdles. The most notable is not safety-related as most would probably expect—although safety is also a primary concern—but that the current LH$_2$ supply chain in the United States is not equipped to provide small, "lab-scale" quantities (e.g. <250-L) of LH$_2$. Instead, the supply chain is set up to provide tanker loads at a time, at volumes of roughly 56,000-L. This is a major impediment, both logistically and economically, to lab-scale LH$_2$ testing at the moment, and typically demands on-site production at reasonable quantities; or, put another way, it requires in-house liquefiers. Such capabilities are still scarce; however, Eta Space in Rockledge, Florida has recently commissioned a 150-L Integrated Refrigeration and Storage (IRAS) hydrogen liquefier powered by a Gifford-McMahon cryocooler, which was utilized to produce and supply NBP LH$_2$ to the aerogel blanket wet charging test setup.

3.1 LH$_2$ Wet Charging Test Setup
The wet charging setup consisted of three primary components: A roll-around, open-top, double-nested test dewar, with an inner LH$_2$ dewar volume of 10-L, surrounded by 50-L LN$_2$ shield dewar; a hand-

operated lift mechanism with a horizontal platform above the dewar; and the 150-L IRAS LH_2 tank that supplied liquid to the test dewar via a vacuum-insulated flexhose. The test specimen was comprised of a stack-up of 120-mm diameter aerogel blanket discs, totaling roughly 100-mm tall, located at the end of a 12.5-mm diameter, 0.66-m long G-10 fiberglass epoxy tube. This test assembly was suspended from a loadcell attached to the horizontal lift platform, and hung down into the test dewar. Two aerogel specimens were tested, Cryogel® and Spaceloft Subsea®, with total masses of 165.7 g and 166.5 g respectively, and total volumes of approximately 1136-cm^3. Figure 2 shows the overall setup, and Spaceloft Subsea® test article.
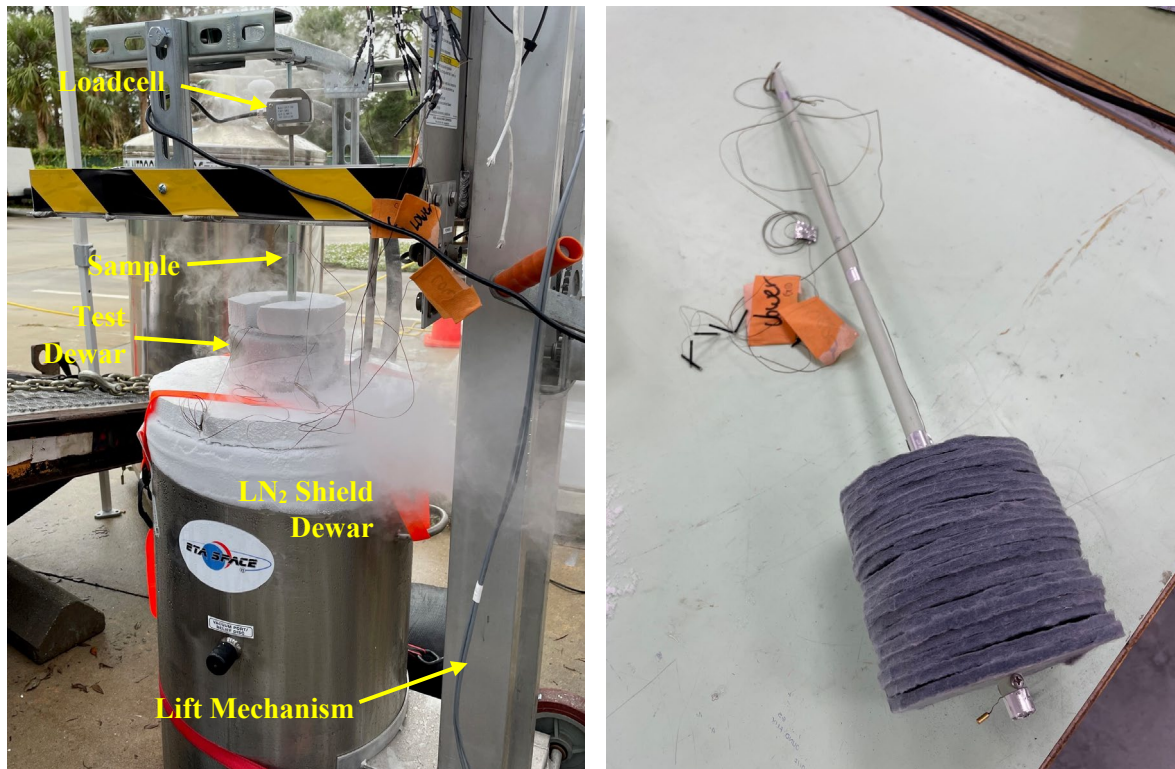

Figure 2. LH_2 Wet Charging Test Setup (left); Spaceloft Subsea® Test Article (right)

Silicon diode temperature sensors were located on the G-10 tube, above and below the sample, to determine when the aerogel blanket was completely submerged in liquid, and on the inside of the test dewar for fill level determination. All data was captured via a custom LabView program.

Procedurally, the test dewar was filled with LH_2 (with the LN_2 shield already full), the loadcell was zeroed, and then the sample lowered into the liquid by hand using the lift mechanism until the diodes confirmed complete submersion. After allowing the sample to thermalize for a short period, the sample was raised back out of the liquid, with the loadcell capturing the change in mass between wet and dry (i.e. the uptake mass). For safety purposes, all testing was conducted outdoors at Eta Spaces' facility, following all internal safety processes and reviews, and using trained personnel. This process was initially carried out using LN_2 instead of LH_2 on the Cryogel sample to validate the test setup and procedure, and for comparison to prior test data.

3.2 LH_2 Uptake Data & Discussion
The procedure described in section 3.1 above was repeated numerous times on each sample, four for Cryogel® and five for Spaceloft® Subsea, in LH_2 to establish an average hydrogen uptake. However, further testing is required to establish greater statistical confidence in the results. The combined preliminary results of both test series are presented in figure 3 and table 1.
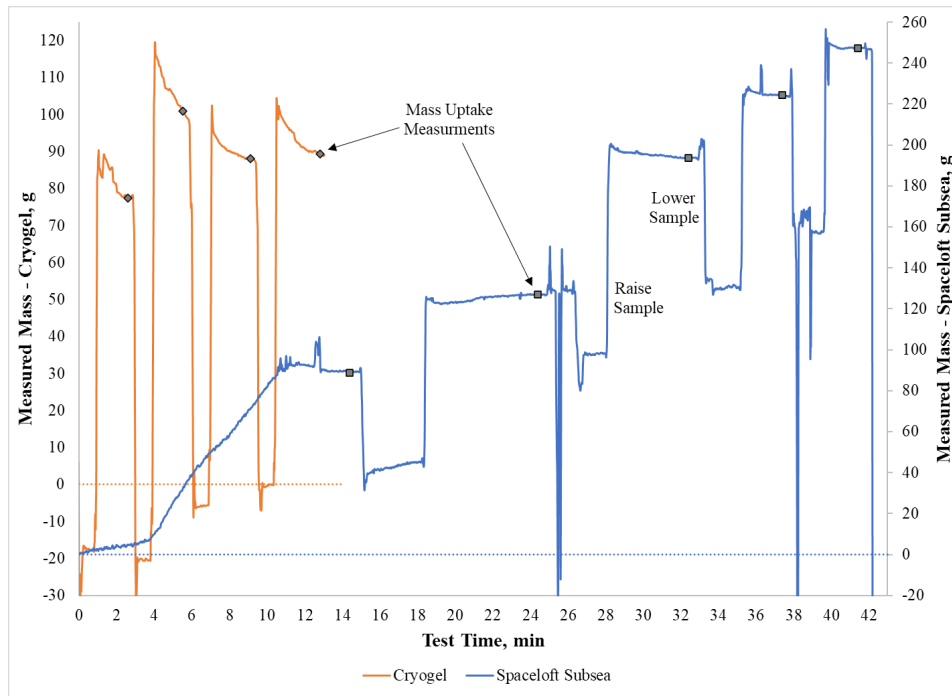
Figure 2. LH$_2$ Wet Charging Test Setup (left); Spaceloft Subsea® Test Article (right)

Table 1. Performance Metrics for the Tested Sample

Material	Test — LN$_2$			Test — LH$_2$		
	MR	VR	LVE	MR	VR	LVE
Cryogel	4.5	0.82	930	0.537	1.21	1256
Spaceloft Subsea	---	---	---	0.541	1.22	1272

Mass Uptake Ratio (MR) = mass of fluid / mass of material = mass uptake / mass of material
Volume Uptake Ratio (VR) = volume of fluid / volume of material = LVE / volume of material
Liquid Volume Equivalent (LVE) [cm^3] = mass uptake / liquid density at NBP [g/cm^3]

Comparing the tests in figure 2, two marked differences are seen: 1. The measured mass uptake for the Spaceloft Subsea® sample consistently increased over time, whereas the Cryogel® tests did not; and 2. The shape of the curves when the samples were raised out of the liquid are noticeably different (a notable point, the shape of the Cryogel® curve for the LN$_2$ testing was very similar to the LH$_2$ testing). The former is attributed to the accumulation of ice on the G-10 sample rod during testing, which was mitigated to a large extent for Cryogel® testing by adding a polystyrene foam cap to the LH$_2$ test tank (this cap can be seen in figure 2). This ice accumulation was fairly consistent between cycles, and averaged out to be around 5.1 g/cycle. Ice accumulation was subtracted out of the mass uptake calculations for the Spaceloft Subsea® sample, resulting in an average hydrogen uptake of 90.1 g/cycle, with a standard deviation of 4.64. The average hydrogen uptake for Cryogel® was 89 g/cycle, with a standard deviation of 8.32.

Comparing performance metrics in table 1 for LN$_2$ to those previously reported [5], the LH$_2$ wet charging test setup and method of calculating the mass uptake resulted in a 13.5% lower MR, and 18% lower VR. This is primarily attributed to the variability in the two different test/analysis methods, which ultimately affects the reported mass uptake value: if the mass uptake values were taken earlier upon a

raise out of the liquid in the current wet charging test setup, then the values would be much closer to those previously reported.

The LH$_2$ performance metrics for Cryogel® and Spaceloft Subsea® are very similar; a trend witnessed during prior testing with other cryogens as well. The mass uptake ratio is much smaller than for the much denser cryogens, as expected, however, the volume uptake ratio is markedly higher at 1.2, suggesting that the LH$_2$ saturated aerogel blankets tested store more hydrogen than an equivalent volume of liquid hydrogen. Much more testing is required to shore-up these results, but the preliminary data is certainly positive, pointing to aerogel blankets' propensity, and potential usefulness in storing significant quantities of hydrogen at/near the normal boiling point.

4. Gaseous Hydrogen Testing at 77 K

Due to the various challenges associated with working with LH$_2$ at 20 K, it could be advantageous to store hydrogen at warmer temperatures if relatively high densities could still be achieved. Much work has been done in the past on developing gaseous hydrogen (GH$_2$) adsorbent materials [11,12]; however, none to-date have explored aerogel blanket. To this end, a small dry-charging setup was devised by a team from UCF, NASA-KSC, SwRI, and Air Liquide, and built, and tested at UCF utilizing LN$_2$ to estimate the GH$_2$ uptake in Cryogel® at 77 K.

4.1 GH$_2$ Dry Charging Test Setup

The dry-charging test setup consisted of a 1.51-L cylindrical pressure vessel, 101.6-mm diameter by 228.8-mm long, that was completed filled with 95.3-mm diameter, 10-mm thick Cryogel® discs. Each disk featured a 9.53-mm hole in the middle to accommodate an axial GH$_2$ feed tube. The top flange of the vessel featured two feedthroughs: one for temperature and pressure instrumentation and a pressure relief valve, and the other for hydrogen feed and vacuum pumping. Inside the vessel, 11 type-T thermocouples (TC) were employed: nine measuring the radial and axial temperature distribution inside the aerogel disks, and two measuring the interior wall temperature and the incoming gas temperature at the flange level. Three thermocouples were positioned radially within the top, middle, and bottom layers, while the middle layer included a wall temperature thermocouple. During testing, the entire test article was submerged in LN$_2$ inside a glass dewar flask to create an isothermal, 77 K boundary. Figure 3 shows the test article and components, and chill down
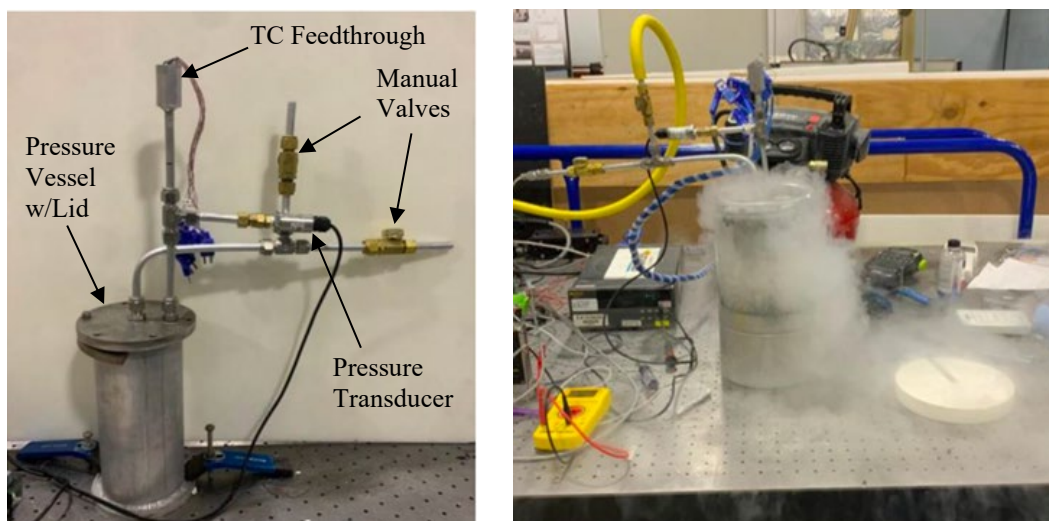

Figure 3. Dry-Charging Test Article and Components (left); Test Article During Cooldown (right)

Procedurally, the test article was evacuated and purged with hydrogen three times to eliminate any air in the vessel and plumbing. Another evacuation was then performed, and the article precooled with liquid nitrogen until the bulk temperature of the aerogel reached 110 K. GH$_2$ was then introduced from

a gas bottle through a mass flow controller until a stable pressure of 1 bar absolute and temperature of 77 K were obtained. Mass flow data was analyzed post-test to estimate the total hydrogen uptake.

To establish a benchmark for comparison, a series of experiments were conducted on an empty pressure vessel initially, followed by testing at two different aerogel packings—one using 20 discs and the other using 23 discs, which translated to total aerogel masses of 86.2-g and 99.1-g respectively, and an increase in active aerogel surface area inside the vessel of roughly 15%.

4.2 GH₂ Uptake Data & Discussion

The results of the benchmark testing showed that the empty vessel contained 4.71 liters and 0.43 grams of H_2 at 1 bar absolute and 77 K, resulting in a density of 0.284 kg/m^3, which was 2.57% lower than the predicted density using GH_2 properties at temperature and pressure of the experiment. Considering the uncertainties of the instruments used, the measurement was deemed accurate, and aerogel blanket testing commenced. Multiple hydrogen tests were conducted on the Cryogel® sample, and the overall results are summarized in table 2, with the experimental density defined as the mass of stored hydrogen divided by the empty vessel volume (i.e. 1.51 liters).

Table 2. GH₂ Dry-Charging Test Results for Cryogel® at 1 bar and 77 K

Aerogel Packing	Total Volume of H₂ Input (Std. Liters)	Experimental H₂ Density (kg/m³)	Theoretical H₂ Density at Experimental Temp. & Press. (kg/m³)	H₂ Stored (grams)
0% (Empty Pressure Vessel)	4.71	0.284	0.291	0.43
100% (20 layers, no packing)	7.15	0.424	0.311	0.64
115% (23 layers, mild packing)	7.72	0.458	0.307	0.69

The 100% packing results from table 2 reveal that the maximum hydrogen density increase achievable under the test conditions due to the presence of the aerogel blanket was 36% compared to the theoretical GH_2 density at the temperature and pressure of the experiment. Further packing an extra three layers of aerogel into the vessel, resulting in a 15% increase in surface area, increased the stored hydrogen density inside the pressure vessel by 12.9% compared to the experiment with 20 aerogel disks. And the overall stored hydrogen density of the 115% aerogel packing was found to be 49% higher compared to theoretical value. Increasing the surface area inside of the vessel by adding additional layers of aerogel and compressing them resulted in maximum increase in storage hydrogen density of 61% compared to the empty vessel. Further testing with even higher aerogel packing densities is needed to determine the if an optimum exists, and if there are diminishing returns.

5. Future Work

Both efforts reported here, wet-charging with LH_2 and dry-charging with GH_2 at 77 K, represent small-scale, relatively inexpensive lab testing, with custom-designed, one-off hardware development, and where trial-and-error were very much at play. Development of the methodology, and gaining understanding—especially for the LH_2 testing—were of almost equal importance to the acquired data. Therefore, the most important work going forward is to simply perform more tests, and refine the methodology, to build greater confidence in the results presented here.

The second priority is to address the impact, if any, of ortho-para (O-P) hydrogen concentration and/or conversion on the uptake performance of the material. Some studies suggest that the adsorption physics is preferential to orthohydrogen [13], and that the silica aerogel itself may act as an O-P catalyst [14]—both of which are expected to impact the uptake performance in some way. Although acknowledged early on during both test campaigns as a factor that could possibly have a meaningful

impact, neither effort had the resources to properly explore the topic. For LH_2 testing, liquid was created straight from high pressure gas bottles (i.e. normal hydrogen, approx.75% ortho and 25% para) over the course of roughly a week, without any O-P catalyst, and sat in zero boil-off mode inside the stainless-steel IRAS tank for a few days prior to testing. It is unclear if this amount of time was sufficient to fully convert normal hydrogen to >99% parahydrogen at 20 K, therefore, the O-P composition of the test liquid was unknown. Similarly, for the dry-charging testing, normal hydrogen was drawn from a compressed gas bottle, fed to the test article, and allowed to stabilize near 77 K, where the equilibrium O-P concentration is roughly 50/50. However, it was unknown what the actual O-P concentration was.

6. Conclusion

To explore the hydrogen storage capability of silica aerogel blanket materials at cryogenic temperatures, NASA, in partnership with Eta Space, Southwest Research Institute, the University of Central Florida, and Air Liquide, undertook two different experimental test campaigns—one addressing the performance when the material is exposed to liquid hydrogen at the normal boiling point, referred to as "wet-charging," and the other when exposed to gaseous hydrogen at 1 bar pressure and liquid nitrogen temperatures, referred as "dry-charging." Much more testing is believed to be required to fully characterize the hydrogen storage potential; however these preliminary efforts were promising. Results of liquid hydrogen wet-charging testing showed uptake performances in-line with prior testing using different cryogens, with volume ratios, defined as the volume of equivalent stored liquid at the normal boiling divided by the aerogel blanket volume, slightly greater than unity, implying aerogel blanket may be able to store more hydrogen by volume than liquid hydrogen at normal boiling point. And dry-charging of gaseous hydrogen at LN_2 temperatures and relativity low pressure yielded an increase in stored density of 61% over that of the gas alone at the same conditions.

7. References

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