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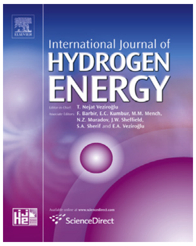

A comparative analysis of the cryo-compression and cryo-adsorption hydrogen storage methods

G. Petitpas [a,*], P. Bénard [b], L.E. Klebanoff [c], J. Xiao [b], S. Aceves [a]

[a] Lawrence Livermore National Laboratory, 7000 East Avenue, Livermore, CA 94550, USA
[b] Institut de recherche sur l'hydrogène, Université du Québec à Trois-Rivières, QC G9A 5H7, Canada
[c] Sandia National Laboratories, 7011 East Avenue, Livermore, CA 94551, USA

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ABSTRACT

While conventional low-pressure LH_2 dewars have existed for decades, advanced methods of cryogenic hydrogen storage have recently been developed. These advanced methods are cryo-compression and cryo-adsorption hydrogen storage, which operate best in the temperature range 30–100 K. We present a comparative analysis of both approaches for cryogenic hydrogen storage, examining how pressure and/or sorbent materials are used to effectively increase onboard H_2 density and dormancy. We start by reviewing some basic aspects of LH_2 properties and conventional means of storing it. From there we describe the cryo-compression and cryo-adsorption hydrogen storage methods, and then explore the relationship between them, clarifying the materials science and physics of the two approaches in trying to solve the same hydrogen storage task (~5–8 kg H_2, typical of light duty vehicles). Assuming that the balance of plant and the available volume for the storage system in the vehicle are identical for both approaches, the comparison focuses on how the respective storage capacities, vessel weight and dormancy vary as a function of temperature, pressure and type of cryo-adsorption material (especially, powder MOF-5 and MIL-101). By performing a comparative analysis, we clarify the science of each approach individually, identify the regimes where the attributes of each can be maximized, elucidate the properties of these systems during refueling, and probe the possible benefits of a combined "hybrid" system with both cryo-adsorption and cryo-compression phenomena operating at the same time. In addition the relationships found between onboard H_2 capacity, pressure vessel and/or sorbent mass and dormancy as a function of rated pressure, type of sorbent material and fueling conditions are useful as general designing guidelines in future engineering efforts using these two hydrogen storage approaches.

Introduction

Keller et al. [1] have recently provided a compelling story how hydrogen-based technologies can provide the basis for reducing our dependence on dwindling fossil fuel reserves, significantly decrease greenhouse gas (GHG) emissions, and achieve a more secure energy future. As recently reviewed by Klebanoff et al. [2], high efficiency hydrogen energy conversion devices that convert hydrogen into electrical or shaft

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* *Corresponding author*. Tel.: +1 925 423 0348.
E-mail address: petitpas1@llnl.gov (G. Petitpas).

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power are powerful drivers for hydrogen technology. These conversion devices include hydrogen internal combustion engines (ICEs), both spark ignition and turbine hydrogen engines, along with hydrogen fuel cells. Proton exchange membrane (PEM) fuel cells in particular are already finding use in the first fuel cell vehicles, and also commercial use in portable power, telecom backup power, material handling equipment and fuel cell mobile lighting [2]. Hydrogen ICEs have already been demonstrated in light-duty vehicles, with small production runs made for the BMW Hydrogen 7 vehicle [3].

Different options exist for hydrogen storage and delivery [4]. Vehicles demand compact, light vessels, and therefore fully wrapped high strength carbon fiber (type III or IV) vessels are typically used [5]. Today's hydrogen-powered ground vehicles almost exclusively use compressed gas storage, at pressures typically of 350 or 700 bar [6]. Commercial fuel cell vehicles planned for sale or lease in the next couple of years in Europe, Japan and the U.S will use Type IV 700 bar fuel systems that have been rigorously tested to automotive performance standards. For spacecraft (i.e. as a rocket propellant) or (future) aircraft applications requiring very large quantities of hydrogen, cryogenic LH_2 dewars are a better choice due to lower weight [7].

Liquid hydrogen is often considered too costly and energy intensive for widespread applicability, including higher CO_2 emissions. However, recent modeling [4] indicates that liquefaction energy is a good investment that greatly simplifies hydrogen delivery and dispensing, resulting in a total dispensing cost comparable to other higher-temperature approaches (pipeline and/or trailer). The overall cost reductions for transporting LH_2 might make it the physical state of choice for a hydrogen energy infrastructure especially for large scale commercial fueling stations, as illustrated in a recent California Air Resources Board (CARB) report [8] that predicts future deployment of H_2 fueling stations for different sources of H_2 (liquid delivery, gaseous delivery, or on-site steam methane reforming). CARB anticipates that, regardless of the rate of H_2 vehicle introduction, most fueling stations will be supplied with LH_2 by 2020–2025. Future deployment of a LH_2 delivery infrastructure would, in turn, favor cryogenic hydrogen storage.

The two cryogenic hydrogen storage approaches examined in this paper improve the volumetric density and dormancy of hydrogen storage beyond that available from conventional low-pressure LH_2 dewars, while taking advantage of the thermal insulation techniques developed over the years in conventional LH_2 dewar technology. The first approach, initiated at the Lawrence Livermore National Laboratory (LLNL), is called cryo-compressed storage [9], and seeks to incorporate a high-pressure capability into the cryogenic dewar design, thereby increasing the volumetric storage capacity achieved by high-pressure storage while extending storage times before significant fuel venting occurs. The second approach to storing hydrogen is called cryo-adsorption. Recent advances in the materials science and engineering of hydrogen cryo-adsorption materials have been reviewed by Ahn and Purewal [10] and by Johnson and Bénard [11]. Cryo-adsorption is based on the weak binding of H_2 molecules to solids with large surface areas (i.e., usually much greater than 1000 m^2/g) and highly porous structures. Most attention has been focused on activated carbons and metal organic framework (MOF) compounds, although nanocarbons, zeolites, microporous polymers, and other materials have also been investigated over the past two decades [10] [11]. Since adsorption bonding arises from relatively weak van der Waals attractions of the H_2 molecules to the sorbent surfaces, the binding energies are usually about 2–10 kJ/mol H_2 (in the physisorption range), allowing hydrogen to bind reversibly as a diatomic molecule. However, because the binding of hydrogen is so weak, small increases in temperature lead to desorption, which impedes significantly storage capacities at room temperature. As a result, the sorbent materials need to be cooled to cryogenic temperatures (e.g. <100 K) for significant hydrogen storage capacities to be realized. Since these materials generally have very rapid kinetics for adsorption as well as other potentially attractive properties for hydrogen storage, several systems have been proposed and their thermal performance parameters analyzed for vehicular applications [12].

Recently, Ahluwalia and co-workers conducted extensive modeling of many types of hydrogen storage systems for light duty vehicles [13–18], including well to wheel analyses [4]. Engineered embodiments of both the cryo-compressed and cryo-adsorption methods showed a substantial improvement in the gravimetric and volumetric storage densities of hydrogen when attempting to store 5.6 kg of hydrogen [18], meeting and exceeding the 2017 U.S. Department of Energy (DOE) targets [19]. Cryogenic storage also offers safety advantages: in addition to the cryogenic temperature that minimizes the burst energy in case of an accidental release, the design of cryogenic vessels (pressure vessel encapsulated in a vacuum jacket) provides an extra layer of protection and confinement if the innermost vessel fails [20].

We present here a comparative analysis of the cryo-compressed and cryo-adsorption hydrogen storage approaches in order to clarify the underlying science of these approaches and to identify specific regimes of temperature and pressure where the two methods are optimal. We review first some basic aspects of the transition between the gaseous and liquid states of hydrogen to better understand the regimes of operation near 20 K, together with a brief review of conventional (low pressure) storage of LH_2 in dewars. The cryo-compressed and cryo-adsorption hydrogen storage methods are reviewed individually, and then explored together, clarifying the materials science and physics of the two approaches in trying to solve the same hydrogen storage task.

Storage of liquid hydrogen in low-pressure dewars and the liquid–gas phase transition

Bowman and Klebanoff recently reviewed the historic methods of storing hydrogen, including low-pressure storage of LH_2 in dewars [7]. Storing hydrogen as a liquid increases both the gravimetric and volumetric storage efficiencies beyond that available from compressed gaseous hydrogen. The volumetric density of liquid hydrogen at its 20 K boiling point is 71 g per liter, which is nearly twice that of 700 bar compressed gas at room temperature [7]. Still, LH_2 is itself a