

Assessing the Performance of Potential Hydrogen Storage Materials

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1. Introduction

The potential use of hydrogen as an energy carrier in a future sustainable energy system has recently been attracting a significant amount of attention, with many of the major car manufacturers currently developing hydrogen fuel cell cars. The first to be released was the Honda FCX Clarity, which has been available to lease in limited numbers in California in the United States (US) since mid-2008, but hydrogen-fuelled concept cars and demonstration vehicles have been produced by many of the major players in the automotive industry including BMW, Chrysler, General Motors, Hyundai, Mazda, Mercedes-Benz, Nissan, Renault and Toyota. However, one of the major technical problems with the use of hydrogen fuel cell technology is the efficient storage of hydrogen. Current prototype and demonstration vehicles store hydrogen as a compressed gas, typically at pressures of 35 or 70 MPa, a method that has advantages over liquid storage because, unlike the latter, it does not require low temperatures and does not suffer from so-called boil-off losses. However, compressed hydrogen gas storage has a limited volumetric storage capacity, which can lead to driving range limitations, while the required compression imposes a significant energy penalty on the overall process. Another approach, which can potentially provide a high volumetric storage density at a relatively low pressure, is solid state hydrogen storage, and this is therefore seen as a promising alternative to conventional pressurised and liquid hydrogen storage technology [1-3].

In 2003, the US Department of Energy (DOE) set a series of challenging system targets for onboard hydrogen storage. The original 2010 figures included a gravimetric system storage capacity of 6.0 wt.% and a volumetric system storage capacity of 0.045 kg H₂ L⁻¹, while the 2015 targets included a gravimetric capacity of 9.0 wt.% and a volumetric capacity of 0.082 kg H₂ L⁻¹. These figures were subsequently revised and the current 2017 gravimetric and volumetric targets, at the time of writing, stand at 5.5 wt.% and 0.040 kg H₂ L⁻¹, respectively. However, these requirements have not yet been satisfied by any known material and so the search for a suitable candidate storage medium continues.

The existing materials that can be used to store hydrogen can generally be classified as either metal hydrides or microporous media [3]. Metal hydrides store hydrogen by chemically absorbing atomic hydrogen (H) into their crystallographic structure, whereas microporous materials adsorb molecular hydrogen (H₂) on the internal surfaces of their pores. Recent research into microporous media for hydrogen storage has tended to focus on microporous carbons, zeolites, metal-organic frameworks and microporous organic polymers. Research into the use of hydrides for hydrogen storage, meanwhile, which has actively been pursued since the 1970s, has focussed traditionally on metallic interstitial hydrides, including intermetallic compounds such as LaNi₅ and TiFe, and their substitutional derivatives, and

vanadium-based solid solution alloys [4]. More recently, however, researchers in this area have been concentrating on complex hydrides, such as NaAlH_4 , LiBH_4 and the Li-N-H system, because of the higher gravimetric hydrogen storage capacities exhibited by these compounds.

One significant advantage of using metal hydrides for solid state hydrogen storage is the impressive volumetric storage densities that can be achieved with this class of material. Such densities can generally exceed that of liquid hydrogen. However, the challenge of reaching a sufficient gravimetric storage density can be appreciated by considering the wt.% capacity of one of the prototypical intermetallic hydrides, LaNi_5H_x (where x expresses the atomic hydrogen content per formula unit). Even though this material can achieve a hydrogen-to-metal ratio greater than unity at moderate temperatures and pressures, its reversible gravimetric storage capacity is only around 1.25 wt.%, due to the low atomic mass of hydrogen and the relatively high atomic masses of La and Ni. It is also important to note that the DOE targets, and the important parameters for practical applications, apply to an entire storage system, not just the material itself. Reversible capacities on a materials basis therefore have to be considerably higher than the DOE targets, in terms of both volumetric and gravimetric density, in order to satisfy the overall storage system requirements.

When assessing the performance of potential hydrogen storage materials, a meaningful comparison of the capabilities of different candidates is not particularly straightforward due to the considerable interplay between the different storage properties of each type of material. The task is additionally hindered by the differing definitions of hydrogen storage capacities commonly used in each case and the significantly different hydrogen adsorption or absorption behaviour of each class of material as a function of temperature and hydrogen pressure. The simple comparison of the gravimetric capacities of different materials, for example, is not sufficient to determine, conclusively, whether one is superior to another. Furthermore, hydrogen sorption measurements can be susceptible to significant amounts of experimental error, which can add further uncertainties to the process of comparing different potential candidates. In this article, we will therefore address some of the issues surrounding the experimental characterisation of potential hydrogen storage materials and the assessment of their performance. We begin, in the next section, by introducing the different types of materials that are currently being considered for hydrogen storage applications before discussing, in Sect. 3, the important properties for practical hydrogen storage, with a focus on mobile (transportation) applications. The experimental laboratory or analytical methods used for their characterisation will then be introduced. In Sect. 5, we then discuss some of the factors that can affect the experimental determination of the hydrogen storage properties of materials, before concluding with a brief discussion of the issues addressed and future research directions in this area.

2. Potential Hydrogen Storage Materials

2.1. Microporous Materials

Microporous materials adsorb molecular hydrogen. The term *adsorption*, as opposed to *absorption*, has traditionally been reserved for surface processes, which in the case of hydrogen can include the non-dissociative physical adsorption (*physisorption*) of H₂ and the chemical adsorption (*chemisorption*) of atomic hydrogen (H). Adsorptive hydrogen storage tends to involve physisorption, and it relies on the large internal surface areas and pore volumes of microporous materials. Another crucial factor is pore size, which according to the International Union of Pure and Applied Chemistry (IUPAC) classification scheme [5] is less than 2 nm for micropores. Pores of this dimension tend to adsorb significant amounts of hydrogen, under certain conditions of temperature and pressure, due to the overlap of the adsorption potentials of the opposing pore walls.

Several types of microporous material have been investigated for hydrogen storage. Synthetic zeolites, which are crystalline aluminosilicates, tend not to exhibit the gravimetric capacities required for mobile applications and appear unlikely to be able to satisfy the demands of a practical mobile store. Microporous carbons, on the other hand, have shown considerable potential, particularly due to more recent advances in their synthesis through templating techniques. Two recent examples are zeolite-templated carbons and carbide-derived carbons, both of which possess more clearly defined pore size distributions than traditional activated carbons and carbon molecular sieves; zeolite-templated carbons, in particular, have been reported to exhibit particularly high gravimetric hydrogen storage capacities, which can exceed 8 wt.% [6].

Metal-Organic Frameworks (MOFs) form a relatively new class of porous material, and have attracted a great deal of attention for adsorptive hydrogen storage since the first report of their use for this purpose in 2003 [7]. The intense interest in these inorganic-organic hybrid solids [8] has resulted in a vast array of new compounds being reported in the literature, and the hydrogen storage properties of hundreds of MOFs have been investigated over the last few years [9]. New MOFs exhibiting particularly high hydrogen storage capacities include MOF-210 [10] and NU-100 [11]. These two compounds have reported gravimetric hydrogen adsorption capacities of 176 mg g⁻¹ and 164 mg g⁻¹, respectively.

Microporous organic polymers, meanwhile, include amorphous materials, such as Hyper-Crosslinked Polymers (HCPs) and Polymers of Intrinsic Microporosity (PIMs), and the crystalline organic analogues of MOFs, known as Covalent Organic Frameworks (COFs). The latter have been reported to possess gravimetric hydrogen storage capacities exceeding 18 wt.%, although these theoretical figures are for materials with large pore volumes, which unfortunately exhibit relatively poor volumetric capacities as a result.

Compared to the DOE targets, it can be seen that some of these adsorptive gravimetric capacities are very impressive. The main drawback of adsorptive hydrogen storage, however, is the low temperature required in order for substantial adsorption to occur, and much of the recent research, particularly on MOFs, has focussed on approaches to increasing the temperature at which significant amounts of hydrogen is adsorbed. The long term viability of

porous hydrogen storage materials is therefore likely to depend, to a certain extent, on the amount of progress made in this specific area.

2.2. Hydrides

Conventional metal hydrides, which have been studied for many years and include host materials such as Pd, LaNi₅ and TiFe, generally exhibit gravimetric storage capacities that are too low for mobile applications. However, a number of specific compositions, or substitutional derivatives, satisfy many of the practical requirements very well, in terms of their cyclic stability, absorption and desorption kinetics, and operating temperatures and pressures. For example, in the 1980s, a fleet of Daimler cars and vans operated using the non-stoichiometric compound Ti_{0.98}Zr_{0.02}Cr_{0.05}V_{0.43}Fe_{0.09}Mn_{1.5} for hydrogen storage purposes, even though this material has a gravimetric storage capacity of only 1.8 wt.%. Since the late 1990s, however, hydrogen storage material research has increasingly focussed on the so-called *complex hydrides*. These materials bind hydrogen in complexes as part of their structure, which upon desorption then decompose into two or more products, one of which is gaseous molecular hydrogen. This is in contrast to the conventional metal hydrides mentioned above in which hydrogen occupies interstitial sites in the host metallic lattice, which stays relatively intact throughout the reversible hydrogen absorption and desorption process.

The main types of complex hydride are Ti-doped NaAlH₄, LiBH₄ and the Li-N-H system, although there are many variants and derivatives that are currently the subject of a significant worldwide research effort [12]. Of these, LiBH₄ has the highest storage capacity, as it contains 18.5 wt.% of hydrogen, but the decomposition temperature is too high for practical purposes. Many mixed compositions and modified (destabilised) composites are, however, currently under investigation. The high temperatures required for hydrogen absorption and desorption, and the slow kinetics of both processes, remain a problem for the majority of these materials, perhaps with the exception of Ti-doped NaAlH₄, although this material does not exhibit a particularly high reversible gravimetric hydrogen storage capacity. It is nonetheless worth noting that the seminal discovery in the mid-1990s, by Bogdanović and Schwickardi [13], of the remarkable effect that Ti-based dopants have on the reversibility of the hydrogen sorption process in NaAlH₄ was one of the main drivers behind the extensive research effort into hydrogen storage by complex hydrides that continues today. MgH₂, meanwhile, is another hydride with a high hydrogen storage capacity (7.6 wt.%) that has been attracting a significant amount of attention for a number of years. However, although doping and nanostructuring, primarily through the use of mechanical milling, improves its storage performance, the high operating temperatures and slow kinetics still unfortunately hinder its practical use.

3. Important Hydrogen Storage Properties

As we have seen, the US DOE has defined a number of ambitious hydrogen storage targets. These cover most of the key properties required for effective hydrogen storage performance.

Perhaps obviously, one of the most important is the hydrogen storage capacity, which can be defined in gravimetric or volumetric terms. The current 2017 targets for these two properties, at the time of writing, are 5.5 wt.% (1.8 kWh kg⁻¹) and 0.04 kg L⁻¹ (1.3 kWh L⁻¹), respectively. Others, however, include a refuelling time of less than 3.3 min (1.5 kg min⁻¹ for a 5 kg store), a minimum lifetime of 1500 hydrogenation/dehydrogenation cycles, a delivery pressure in the range 5-12 bar (0.5-1.2 MPa) and a net storage system cost of less than \$2 kWh⁻¹. As noted above, it is important to recognise that these are system, rather than materials, targets and so the gravimetric capacity, for example, of the material must be significantly higher than 5.5 wt.% in order for these criteria to be fully satisfied. In this section, we will discuss how these practical technical requirements relate to the hydrogen sorption properties of the materials, as determined using the laboratory characterisation methods that we will describe in more detail later.

Beginning with the storage capacity targets, the *gravimetric storage capacity* defines the amount of hydrogen stored by weight and the *volumetric storage capacity*, the amount stored by volume. Although in this context the terms gravimetric and volumetric are somewhat self-explanatory, the precise definition of these two quantities can be problematic. In the case of hydrides, the hydrogen contained within the compound is usually included in the denominator when calculating the gravimetric capacity or content, $C_{wt.\%}$, of a material. It is therefore given by,

$$C_{wt.\%} = \left(\frac{\left(\frac{H}{M}\right)M_H}{M_{Host} + \left(\frac{H}{M}\right)M_H} \times 100 \right) \% \quad (1)$$

where H/M is the atomic hydrogen-to-metal ratio, M_H is the molar mass of hydrogen, and M_{Host} is the molar mass of the host element or compound [4]. In this case, the hydrogen-to-metal ratio is defined by the amount of hydrogen that has physically entered the geometric volume of the metallic lattice. When experimentally characterising the uptake of molecular hydrogen adsorption by microporous materials, however, we do not determine the same parameter, but instead determine what is known as the *excess adsorption*, which is the amount of additional hydrogen contained within the entire dead volume (or void space) of the apparatus, or more practically speaking in the storage container, compared to the amount that would be present in the absence of adsorption in the same volume. This leads to an ambiguity regarding our knowledge of the total quantity of hydrogen that is physically adsorbed by the material, and prevents the performance of a calculation analogous to Eq. (1). Gravimetric uptakes in the case of adsorption, whether the experimentally-measured excess values or a total (absolute) adsorbed quantity calculated on the basis of an appropriate assumption, are normally reported as a percentage of the “empty” or dry sample mass, so that the gravimetric capacity, $C_{wt.\%}$, is given by,

$$C_{wt.\%} = \left(\frac{n_a M_H}{n_{Host} M_{Host}} \times 100 \right) \% \quad (2)$$

where n_a is the number of moles of adsorbed hydrogen and n_{Host} is the number of moles of adsorbent. This convention originates from the measurement of gas adsorption for other purposes, such as the characterisation of the surface area and porosity of materials [14], although it is also logical in the sense that the adsorbed hydrogen does not become part of a new (hydride) compound but instead just resides on the (internal) surface of the material or within its pores. However, for storage purposes, it is important that the calculation of the “weight percentage” includes all of the matter within the store. The same ambiguity exists with regard to the volumetric capacity because the volume in which the adsorption occurs (the adsorbed phase volume or the adsorption space) is unknown. As a result, the pore volume of the material is often used for the calculation, i.e. the assumption is made that the adsorbed hydrogen occupies the fixed internal pore volume of the material. One potential problem with this assumption is that the measured pore volume of a material depends strongly on the method used for its determination. A further complication, with regard to the volumetric storage capacity, which applies to both hydrides and porous materials, is that the usual methods for calculation consider only the volume of the material itself, whereas the volumetric performance of a material in a practical storage unit will be strongly dependent on the packing (bulk) density of the material bed [4,14].

In addition to practical considerations relating to the definition of either the gravimetric or volumetric storage density of the material discussed above, another important factor in the real performance of a storage material is the difference between the reversible storage capacity and the maximum or total capacity of a material; it is the former that is of greater technological significance but it is often the latter that is reported in the literature. The relationship between the overall capacity of a material and its reversible counterpart is dependent primarily on its uptake and desorption behaviour as a function of pressure, as well as temperature. This can vary greatly between different material types. Conventional metal hydrides tend to show, at a particular temperature, a small amount of uptake at low pressures, when the hydrogen is present in a dilute solid solution (α) phase. Once a certain threshold pressure is reached, a hydride (β) phase begins to form and the material absorbs a large amount of hydrogen through a mixed ($\alpha + \beta$) phase region before the majority of the sample has been transformed into the hydride. Once the transformation is complete, the increase in uptake is again relatively low as a function of pressure. This behaviour is shown in Fig. 1, using the prototypical hydride-forming compound LaNi_5 . The reversible storage capacity is then defined, approximately, by the uptake of the material through the mixed ($\alpha + \beta$) phase plateau region, because it is this part of the isotherm that is practically exploited for the purpose of reversible hydrogen storage.

The uptake behaviour of porous materials, however, is markedly different. Hydrogen adsorption isotherms for microporous materials are typically of Type I in the IUPAC classification scheme, which is concave to the pressure axis and saturates at a finite limit, as demonstrated by the isotherms for Na-X zeolite shown in Fig. 2. In this case, a relatively large amount of uptake occurs at low pressures, and there is no above-ambient pressure plateau (on which large amounts of uptake would occur for a relatively small change in pressure). In a storage unit operating at a fixed temperature, with an above-ambient delivery pressure, this means that much of the storage capacity at low pressures will not be utilised. In

practice, it is likely that a temperature increase would be used to desorb further hydrogen from the storage bed, but the important point is that in this case the reversible capacity will be strongly dependent on the maximum (storage) and minimum (delivery) pressure, and will be significantly lower than the maximum storage capacity [15].

The refuelling and discharge times of a hydrogen store depend primarily on the kinetics of the sorption (uptake) and desorption (release) processes. In a practical storage unit these processes will be dominated by the heat and mass transfer characteristics of the storage bed, although the intrinsic kinetics of the hydrogenation and dehydrogenation processes can still play a significant role. Hydrogen adsorption and desorption by microporous materials are typically rapid processes because the rate of molecular hydrogen diffusion through porous media is very high. For hydrides, hydrogen dissociation on the surface, surface penetration, atomic hydrogen diffusion and the hydride formation process can be considerably more sluggish. For some materials, such as MgH_2 , the hydrogen diffusion and hydride formation processes can be rate-limiting and the nanostructuring of the material through, for example, mechanical milling can greatly increase the charging and discharging rates because of the reduced diffusion or hydride phase formation lengths or depths required for materials with a small grain or particle size. However, the strongly exothermic and endothermic nature of the hydrogen absorption and desorption processes, respectively, can also greatly hinder the refuelling and discharge rates of a practical store. These factors must therefore be taken into account during the assessment of the performance of a particular material. In most cases, the underlying reasons for differences in sorption or desorption rates are not fully understood and an assessment should be made on representative samples of an appropriate size, in order to account for the mass and heat transport limitations of larger storage beds. The engineering of practical hydrogen storage units, using heat exchangers, for example, can however alter the performance of such hydrogen stores, and so this is an important aspect of solid state hydrogen storage technology.

The durability of a material, in terms of repeated hydrogen charging and discharging, depends on its *cyclic stability* or *long term cycling stability*. This is the resistance, or otherwise, of a material to repeated hydrogenation and dehydrogenation. In the case of microporous materials, this should be relatively high, providing the material is chemically and thermally stable under the relevant hydrogen pressure and temperature conditions, which is generally the case for the microporous examples mentioned earlier in this article. For hydrides, it is a more complex issue because the host materials can be subject to both intrinsic and extrinsic degradation. The former is dependent on the chemical, microstructural and thermodynamic properties of the material in the presence of pure hydrogen; the latter on gaseous impurities that may be present in the hydrogen supply and their interaction with the material in question, which will also depend on the chemistry of the host or its surface composition.

The main mechanism responsible for the *intrinsic degradation* of hydrides is *disproportionation*, in which a hydride-forming compound separates into more thermodynamically stable decomposition products in the presence of hydrogen; however, in the case of interstitial hydrides, it appears that dislocation and defect formation upon hydrogen absorption and desorption also plays a significant role. *Extrinsic degradation*, on

the other hand, occurs as a result of the impurities present in the hydrogen gas. For interstitial hydrides, Sandrock and Goodell [16] proposed four separate mechanisms: poisoning, retardation, reaction and innocuous. Each of these has a different effect on the hydrogen absorption and desorption properties of the material. *Poisoning* results in a rapid loss of hydrogen storage capacity without a decrease in the kinetics of the unaffected portion of the sample, *retardation* reduces the kinetics of hydrogen absorption but does not reduce the storage capacity, *reaction* reduces the capacity due to bulk corrosion of the alloy, and the fourth mechanism, *innocuous*, decreases the sorption kinetics due to inert gas blanketing. Under this categorisation, therefore, the effects of extrinsic degradation on the cyclic stability of an interstitial hydride are dominated by the mechanisms of poisoning and reaction.

The susceptibility of a particular material to any of the above intrinsic and extrinsic degradation mechanisms is strongly dependent on the physical and chemical properties of the material, although the precise reasons for this are not yet fully understood. In the case of some interstitial hydrides, the resistance of a material can be increased by partial substitution of the host compound: for example, pure LaNi₅ shows reasonable cyclic stability, in that the hydrogenation process is reversible, but its capacity begins to reduce over the course of a few tens of cycles; however, a remarkable improvement in the cyclic stability can be achieved by partially substituting the Ni with either Al or Sn. The resistance of a material to intrinsic or extrinsic degradation can be empirically assessed by repeated cycling of the material in pure or impure hydrogen, respectively: by monitoring the reversible capacity of the material, as a function of cycles, the stability of the material can be determined.

The thermodynamics of the hydrogen-solid interaction is a further consideration in the characterisation of materials for hydrogen storage applications, although this is not explicitly included in the US DOE criteria. For adsorptive hydrogen storage, the most important characterisation parameter is the *isosteric enthalpy of hydrogen adsorption*, and for storage in metal hydrides it is the *enthalpy of hydride formation and decomposition*. These two parameters define, approximately, the temperature at which materials will operate at useful pressures. Generally speaking, both hydrogen adsorption and absorption (and the associated desorption processes) follow the van 't Hoff relation,

$$\ln P = \frac{\Delta H}{RT} - \frac{\Delta S}{R} \quad (3)$$

where P is the pressure, ΔH is the enthalpy change, R is the universal gas constant (8.314 kJ mol⁻¹ K⁻¹), T is the temperature, and ΔS is the entropy change. In the case of hydrides, the characterisation parameter often quoted is either the enthalpy of hydride formation or the enthalpy of hydride decomposition determined from the mid-plateau pressure [4]. A so-called *van 't Hoff plot* is typically constructed from the mid-plateau pressures of isotherms measured at a number of temperatures. Fig. 3 shows van 't Hoff plots for various hydrides, with the optimum region for storage applications, in terms of operating temperature and pressure, clearly indicated. For microporous materials, the isosteric enthalpy of adsorption is determined from the pressure dependence, as a function of temperature, of constant uptake points on the respective isotherms. The isosteric enthalpy of adsorption can therefore be

plotted as a function of uptake for any given material, although it should be noted that the method used to analyse the data can have a significant effect on the calculated values [15]. For adsorptive hydrogen storage, at ambient temperature with a delivery pressure of 1.5 bar, Bhatia and Myers [17] estimated that the optimum adsorption enthalpy change is approximately $15 \text{ kJ mol}^{-1} \text{ H}_2$, although a higher figure of approximately $20 \text{ kJ mol}^{-1} \text{ H}_2$ is often quoted [9]. For both metal hydrides and microporous materials, the enthalpy change is therefore a crucial characterisation parameter in the assessment of the performance of a material for hydrogen storage purposes.

4. Characterisation Methods

In order to thoroughly assess the performance of a potential hydrogen storage material it is clearly necessary to determine each of the properties described above. The uptake of gaseous hydrogen by materials can be measured using a number of different methods, which can be separated generally into the volumetric, gravimetric and temperature-programmed techniques.

Volumetric techniques use the real gas law,

$$PV = nZRT \quad (4)$$

where P is the pressure, V is the volume, n is the number of moles, Z is the compressibility factor, R is the universal gas constant and T is the temperature, in order to determine the amount of gas absorbed or adsorbed in a system of a given volume. The most common implementation of this approach is the *manometric method*, which is also known in metal hydride research as *Sieverts' Method*. In this case, the measurement is performed in a system of fixed volume. Hydrogen is dosed from a calibrated volume to a sample cell and the final pressure used to determine the amount of uptake. If the calibrated volume is given by V_1 and the so-called *dead volume* of the sample cell, which is the space not occupied by the sample, by V_2 , then the uptake of the material, Δn , when starting from vacuum, is given by,

$$\Delta n = \frac{P_i V_1}{Z_{i,T} RT} - \frac{P_f (V_1 + V_2)}{Z_{f,T} RT} \quad (5)$$

where P_i and P_f are the initial and final pressures, respectively, and $Z_{i,T}$ and $Z_{f,T}$ are the compressibility factors for hydrogen at a temperature, T , and pressures, P_i and P_f , respectively. The process of measuring a full isotherm is then iterative. The use of the dead volume of the sample cell constitutes a correction for the volume of the sample itself. This is commonly known as the *dead volume correction*, and is a crucial consideration in accurate manometric sorption measurement, particularly for porous adsorbents in which the dead volume includes the accessible pore volume of the sample, as well as the interparticle void space.

The gravimetric technique, on the other hand, uses the measurement of the change in the weight of the sample to determine the amount of hydrogen absorbed or adsorbed. This is typically performed using a temperature-controlled microbalance housed in a pressure and

vacuum-compatible chamber. Beginning at vacuum, a hydrogen pressure is applied to the microbalance chamber and the weight change of the sample is monitored. Once an appropriate level of equilibrium has been achieved, the amount of hydrogen absorbed or adsorbed by the sample, m_{sorb} , is then given by,

$$m_{sorb} = m_{exp} - m_{solid} + \rho_g \left(\frac{m_{solid}}{\rho_{solid}} \right) \quad (6)$$

where m_{exp} is the experimentally-determined mass, m_{solid} is the mass of the sample under vacuum, and ρ_g and ρ_{solid} are the densities of the hydrogen gas and the material, respectively. The final term on the right hand side of Eq. (6) is known as the *buoyancy effect correction*, which is the equivalent of the dead volume corrections that are necessary for the manometric technique, as mentioned above. By increasing the applied hydrogen pressure and monitoring the sample weight after each pressure change, a full isotherm can be determined.

In contrast to the isotherm determination methods described above, temperature-programmed techniques use a temperature ramp or increase to desorb hydrogen from a sample. The desorbed hydrogen can be detected in one of a number of ways. One of the most sensitive is quadrupole mass spectrometry, which also allows the detection of other desorbed or evolved species. In the case of a linear applied thermal ramp, the result of such a measurement is a thermal desorption spectrum, which will show peaks at the desorption temperatures that are characteristic of the studied material. Integration of the desorption data, according to the following expression, will then give the total desorbed quantity, n_{tot} ,

$$n_{tot} = \int_{t_0}^{t_f} n(t) dt \quad (7)$$

where $n(t)$ is the desorption rate as a function of time, t , and t_0 and t_f are the start and end times of the measurement, respectively.

5. Important Experimental Considerations

The measurement of hydrogen uptake using the techniques described above can be significantly affected by a number of experimental errors. The susceptibility of hydrogen sorption measurement to such error was most notably illustrated by the controversy regarding the hydrogen storage properties of carbon nanotubes and other carbon nanostructures, which began over a decade ago. A wide variety of storage capacities were reported at the time, with the most impressive apparently being due mostly to the erroneous measurement of hydrogen uptake [18]. Potential errors should therefore be considered carefully when characterising materials for hydrogen storage applications and, in this section, we shall therefore discuss some of the most important error sources. The following discussion is based on previous work by the author [3,18-20].

5.1. Sample Degassing and Activation

Before a sorption measurement, a sample must first be degassed or activated. Microporous materials require only degassing to remove pre-adsorbed contaminants or remnants from the synthesis process, although in the case of materials prepared by wet chemistry methods, samples need to be activated in the sense that any solvent used in the synthesis must be removed from the pore network. Hydrides, on the other hand, often have to undergo an activation procedure, which in the case of intermetallic hydrides can involve the cycling of the material in hydrogen for a number of cycles. During this process, the hydrogen absorption and desorption properties can change significantly and so it is important that the material is fully activated before characterisation. Differences in both the sample degassing and activation conditions between different samples could therefore lead to a variation in their determined hydrogen storage properties, and so insufficient degassing and activation, in this case, will lead to an erroneous measurement.

5.2. Hydrogen Purity

Hydrogen sorption measurement can be affected significantly by the presence of impurities in the gas phase hydrogen. This is particularly true for gravimetric measurement in which the mass signal for impurities such as water and hydrocarbons will be much greater than the hydrogen signal; however, the gravimetric technique generally allows for easier diagnosis of gaseous impurity problems, due to its ability to directly determine changes in the sample weight as a function of both time and hydrogen pressure. The measurement of hydrogen uptake by microporous materials is also more susceptible to impurity contamination because the micropores will tend to preferentially adsorb impurities before hydrogen (unless the impurities are excluded from the micropores due to their size). The adsorbed impurities may block pores or occupy adsorption sites that would otherwise accommodate hydrogen. The measurement of highly reversible hydrogen adsorption isotherms, such as those shown in Fig. 2 for Na-X zeolite, would tend to suggest that the purity of the gas is sufficiently high because gaseous contamination often leads to hysteresis. For hydrides, the potential problems with gas purity are dependent on the material, but contamination could potentially lead to any of the processes responsible for extrinsic degradation, as discussed in Sect. 3.

5.3. Sample Density and Volume

Knowledge of the volume of the sample is required for the dead volume corrections in the manometric method, while the density is required in order to correct for buoyancy effects in the gravimetric case. These two quantities are, of course, interchangeable if we know the mass of the sample. Density is a straightforward concept but it can actually be quite difficult to deal with for real materials. There are many different definitions of density [14] but practically, for hydrogen sorption measurement, we require the *skeletal density* of the material, which is the density calculated from the volume of the sample, excluding all accessible pore volume.

The dead volume and buoyancy effect corrections both increase with decreasing sample density, as well as increasing pressure and gas density. They are therefore most significant for microporous materials, which tend to, firstly, have very low densities and, secondly, be characterised at low temperatures at which the gas phase hydrogen density is greater for any given pressure. The skeletal density of a microporous material is typically determined using helium, the method commonly implemented by commercial pycnometers, under the assumption that helium does not adsorb at the temperature at which the density determination is performed. For hydrogen adsorption measurement purposes, this approach also assumes that the helium can 'see' the same volume as the hydrogen. Any discrepancy between the real skeletal density of the material and its apparent helium density could potentially contribute to measurement error, particularly at higher pressures, and so it is important that the likelihood of such a discrepancy is carefully assessed. This problem is particularly acute for manometric measurement, in which any error introduced by such a discrepancy will accumulate through the isotherm (see Sect. 5.5).

5.4. Equilibration Times

During isotherm determination the hydrogen sorption process must reach an appropriate level of equilibrium at each isotherm point, both in terms of sorption and the achievement of thermal equilibrium (if there is an accompanying temperature excursion). The equilibration times required are strongly dependent on the material. For microporous materials, the adsorption and desorption processes tend to be very rapid, but for hydrides they will generally be slower and, in some cases, very sluggish. It is therefore crucial that sufficient time is allowed for equilibrium to be achieved, otherwise significant errors could be introduced into the measured isotherm. Practically speaking, the use of insufficient equilibration times will lead to the measurement of isotherms under non-equilibrium conditions.

5.5. Accumulative Errors

In the manometric method, the errors present in each sorption dosing step accumulate through the isotherm measurement. Each step has, according to Eq. (5), contributions from at least two pressure measurements, two compressibility factors, a temperature measurement and two volume calibrations. Eq. (5) is, however, a somewhat simplified expression, and therefore in a real sorption measurement system there are likely to be more actual contributions than this. It is therefore beneficial to minimise the number of points measured per isotherm, in order to avoid accumulating error unnecessarily; although, of course, enough points must be measured to provide sufficiently detailed information regarding the form of the uptake as a function of pressure. It is also clear that minimising the error in the volume calibration, the temperature measurement and the pressure measurement will minimise the error contributed by each dosing step to the overall measured uptake.

5.6. Real Gas Behaviour

Both the buoyancy effect and dead volume corrections require the real gas behaviour of hydrogen at elevated pressures to be described accurately. This typically involves the use of an Equation of State (EOS) but tabulated compressibility factor values can also be applied. The state-of-the-art EOS for hydrogen, at the time of writing, was developed by Leachman et al [21] and is implemented in the current version of the US National Institute of Standards and Technology (NIST) REFPROP thermophysical properties database [22]. It is clearly critical to use a sufficiently accurate EOS but it is also worth noting that an error in the pressure or temperature measurement could lead to an error in the value of Z calculated for the assumed hydrogen pressure or temperature. Therefore, the use of a highly accurate EOS does not necessarily guarantee that the real gas behaviour of hydrogen is described accurately for hydrogen sorption measurement purposes. This is an additional reason for paying particular attention to the accuracy of the pressure and temperature measurement, as mentioned above, especially in the case of the manometric method.

6. Discussion and Future Research

Careful consideration of the above experimental sources of error is important when assessing the performance of potential hydrogen storage materials. The ability of a sorption measurement system to provide a clean enough system for sample degassing and activation purposes, and to deliver hydrogen of sufficient purity are crucial factors in the development of instrumentation for the measurement of hydrogen uptake. The ability of a system to control and measure temperature and pressure to a high accuracy are also important in this respect, together with the ability of the system to operate without leakage. Consideration of the sample density and volume, the equilibration times and possible accumulative errors, meanwhile, are issues that affect the development of experimental methodology, while the effective and accurate representation of the real gas behaviour of hydrogen is important in the calculation of the hydrogen uptake from raw data, and is therefore an issue relating to data reduction.

The development of an accepted set of measurement guidelines for hydrogen sorption measurement would clearly help improve the comparability of reported data [3,20,23,24]. However, clarification and standardisation of the definitions of the various measurement parameters would also be of great benefit. Achieving good agreement between the uptake determined for different adsorbents is a challenge in itself [23,24], although there has been some success in this respect for certain materials [25]. However, the definition of a framework in which hydrides and microporous materials can be compared on a like-for-like basis presents a further challenge. A related area is the investigation of the relationship between basic materials properties and the performance of real storage units. Further information on this aspect of solid state hydrogen storage technology is likely to emerge from current collaborative projects such as the US DOE-funded Hydrogen Storage Engineering

Center of Excellence (HSECoE),¹ which runs until mid-2014,² together with other related activities.^{3,4}

The advancement of our understanding of the behaviour of hydrogen in porous media is perhaps of a more fundamental nature, but progress in this area could also contribute significantly to the practical characterisation of hydrogen adsorption by microporous adsorbents. This is primarily due to our current lack of understanding of the nature, including both the volume and density, of the adsorbed phase in such materials. Research areas of relevance to this aspect of hydrogen storage material characterisation include the use of complementary techniques, such as NMR spectroscopy and neutron scattering or transmission [26,27], and the application of computer simulation [28] to the study of hydrogen adsorption in microporous media. Any significant progress made in any of the above areas would clearly aid the reliable assessment of the performance of potential hydrogen storage materials, and also help reduce any future uncertainty regarding the reported hydrogen sorption properties of new candidate materials.

7. Conclusion

In this article, the solid state storage of hydrogen has been introduced, together with the materials that can be used for this purpose. We have seen that potential hydrogen storage materials can be separated generally into microporous materials and metal hydrides. The important performance characterisation properties for hydrogen storage applications include the storage capacity, the cycling stability, the charge and discharge kinetics and resistance of the material to impurities in the hydrogen fuel. These parameters can be determined using one of a number of experimental laboratory methods, including the volumetric (manometric), gravimetric and temperature-programmed techniques, which were described in more detail in Sect. 4. The measurements made using these methods can be subject to a number of experimental errors, which we have also discussed. The experimental considerations and sources of error that we have covered include sample degassing and activation, hydrogen purity, our knowledge of the sample density and volume, the chosen sorption and thermal equilibration times, the accumulative errors inherent in the manometric method, and the description of the real gas behaviour of hydrogen at elevated pressures. These sources of error, and their minimisation, should therefore be considered carefully during the hydrogen storage material performance characterisation process. We have also briefly discussed areas for future research that could lead to better comparability of hydrogen sorption data and the more reliable comparison of the new candidates that are likely to emerge as the search for new solid state hydrogen storage materials continues.

¹ <http://hsecoe.srs.gov/>, accessed 5th February 2012.

² http://www.hydrogen.energy.gov/pdfs/progress11/iv_d_1_anton_2011.pdf, accessed 5th February 2012.

³ http://www.hydrogen.energy.gov/pdfs/progress11/iv_e_6_miller_2011.pdf, accessed 5th February 2012.

⁴ http://www.hydrogen.energy.gov/pdfs/progress11/iv_e_7_gross_2011.pdf, accessed 5th February 2012.

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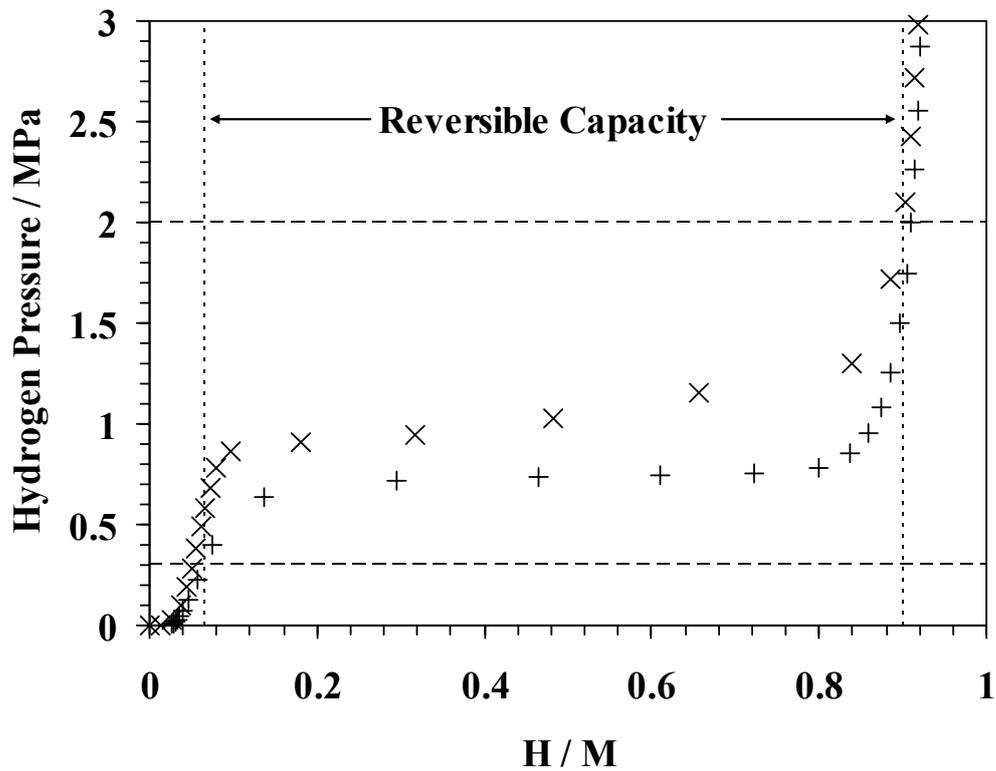


Figure 1. A hydrogen absorption and desorption isotherm for the prototypical hydride-forming compound LaNi_5 at 60°C (333 K), indicating the reversible capacity, in terms of the hydrogen-to-metal ratio, determined by assuming a charging pressure of 2 MPa and a delivery pressure of 0.3 MPa [3].

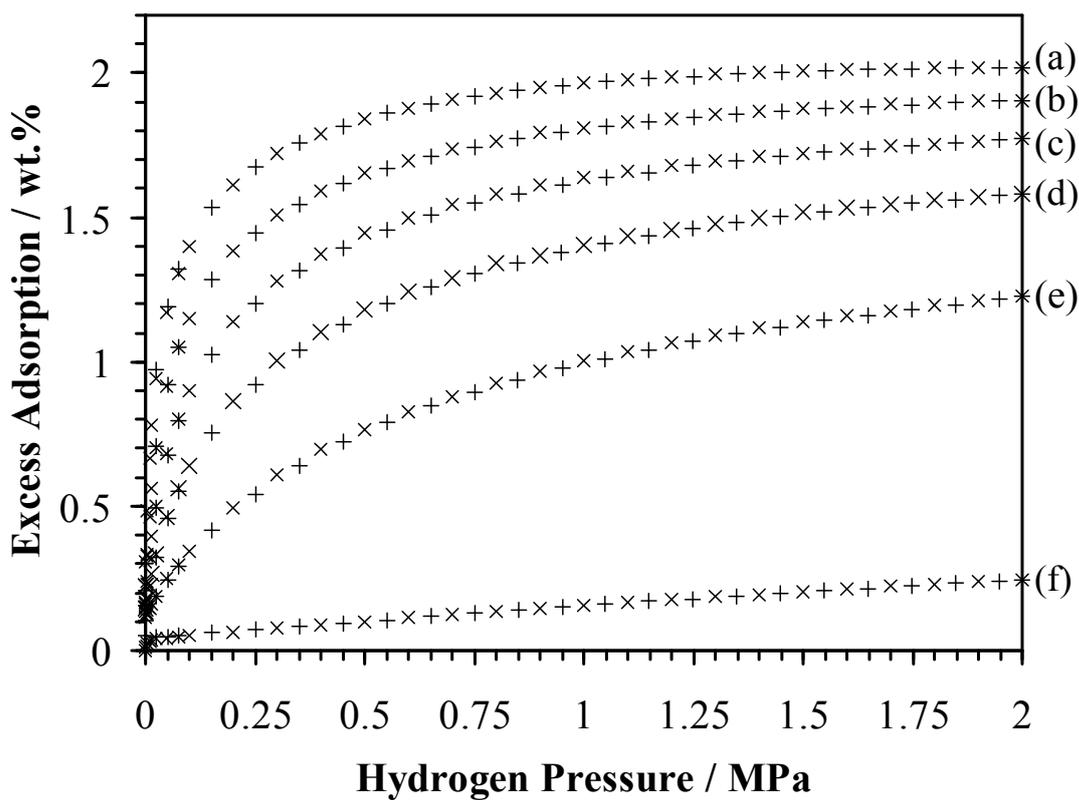


Figure 2. Hydrogen adsorption (+) and desorption (×) isotherms for Na-X zeolite measured at a number of sub-ambient temperatures [3]: (a) 87 K, (b) 97 K, (c) 107 K, (d) 117 K, (e) 137 K and (f) 237 K.

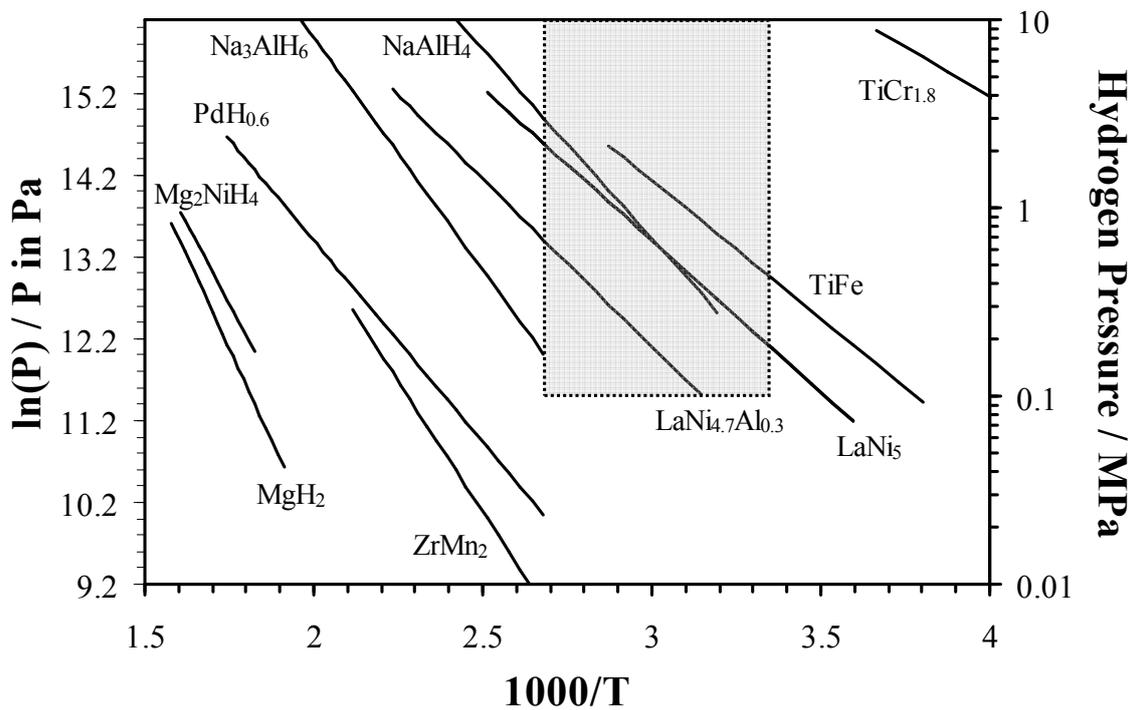


Figure 3. Van 't Hoff plots for a number of hydrides, with the main region of interest for storage applications indicated by the shaded box, which marks the approximate temperature range of ambient to 100°C (373 K) and the pressure range from ambient to 100 bar (10 MPa). Reprinted from [3] with permission from Springer