

Accuracy in hydrogen sorption measurements

D.P. Broom*, P. Moretto

Institute for Energy, DG Joint Research Centre, European Commission, P.O. Box 2, 1755 ZG Petten, The Netherlands

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Abstract

The accuracy of gas phase sorption measurements performed on potential hydrogen storage materials has been the subject of much controversy in recent years, particularly in the case of adsorption by carbon nanostructures. As the technological interest in the solid state storage of hydrogen increases, it has become increasingly necessary to investigate the methods used to determine the sorption properties, and hence the storage capacities, of new and existing materials. In this paper, we briefly review the different techniques available and recent literature on the topic, discuss the possible sources of errors and present some comparative measurements on some AB₅ hydrogen-absorbing intermetallics. Equilibrium pressure-composition isotherm data measured on two LaNi_{5-x}Al_x samples using commercial gravimetric and volumetric instrumentation were found to be in good agreement with each other.

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1. Introduction

If hydrogen is to become a viable energy carrier in the future there is a clear need for a lightweight, safe and affordable hydrogen storage method. This has led in recent years to the well-documented search for potential hydrogen storage materials. A number of recent review articles give good overviews of this work and the large quantity of published research in the field [1–3]. One area, however, that has not been covered in any great detail in the literature is that of the repeatability and reproducibility of measurements made on materials' hydrogen storage characteristics, and hence the accuracy of these measurements. The importance of this issue is perhaps best illustrated by the recent controversy over the storage properties of carbon nanotubes. In this case, problems appear to have been caused by insufficient microstructural materials characterisation of the samples and a lack of care taken in the experimental work used to determine their storage capacity [4].

Some recent work has focused on the topic of accuracy in storage capacity measurement but this has tended to concentrate either on hydrogen sorption in carbon nanostructures [5] or the description of a single experimental set-up [6–8] rather than an objective comparison of different techniques. A thorough examination of the different characterisation techniques available and the sources of error would be valuable and could help prevent further questions over the genuine storage capacities of new materials. Further investigation into both the repeatability and reproducibility of measurements would help separate out the combined effects of poor experimental procedures, systematic errors caused by limitations in the measurement principles themselves and the fundamental uncertainties in the sorption properties of the material. In this paper we briefly review the different techniques available and recent literature on the topic, discuss the possible sources of errors and present some comparative measurements on some AB₅ hydrogen-absorbing intermetallics.

2. Characterisation techniques

In general, the bulk gas phase hydrogen sorption properties of materials can be measured either volumetrically or gravimetrically. Volumetric techniques measure the amount of hydrogen ab/adsorbed by a sample by monitoring the drop in hydrogen

* Corresponding author. Current address: Hiden Isochema Ltd., 231 Europa Boulevard, Warrington, Cheshire WA5 7TN, UK. Tel.: +44 1925 244678; fax: +44 1925 244664.

E-mail addresses: dbroom@hidenisochema.com, darrenbroom@inbox.com (D.P. Broom).

pressure in a fixed volume in direct contact with the sample [9]. Conversely, during the desorption process, the quantity of hydrogen released is determined by the increase in the hydrogen pressure. Gravimetric techniques on the other hand measure the amount of hydrogen ab/adsorbed by monitoring changes in the mass of the sample [10]. In addition, there are also temperature-programmed techniques, known as temperature-programmed desorption (TPD) or thermal desorption spectroscopy (TDS), which can be performed either gravimetrically or volumetrically. The principle is that the sample is heated in a controlled manner and the quantity of released hydrogen is then measured. TPD and its variants can also be performed using apparatus equipped with a mass spectrometer, in which the mass spectrometer signal is used to determine the amount of hydrogen released in a flowing system [11]. Temperature-programmed techniques do not, strictly speaking, measure equilibrium properties of hydrogen-sorbing materials but can be used to determine the storage capacity of a material loaded at a particular temperature and pressure, along with characteristic desorption temperatures.

3. Previous work

There is a vast quantity of published literature available on hydrogen-sorbing materials and their properties. Over the last 30 years or so, however, probably the largest amount of work, in terms of the determination of the bulk hydrogen sorption properties of materials, has been carried out on the intermetallic hydrides. This is primarily due to their use as nickel–metal hydride (Ni–MH) battery electrode materials [12–14]. As a consequence, a number of Japanese Industrial Standards [15–19] exist that relate to the determination of the properties of these materials. Another mature field is the determination of the gas adsorption properties of porous materials and recently, following the intense interest in the use of carbon nanotubes as a hydrogen storage medium, other microporous materials have been attracting attention [20–22]. There are IUPAC guidelines [23] that include a check list to help in the measurement of adsorption isotherms, many points of which are applicable to the case of hydrogen sorption. The gravimetric and volumetric techniques are described and outgassing procedures are also covered. The issues outlined are discussed in more detail by Rouquérol et al. [24]. Although the book does not cover hydrogen adsorption specifically, much of the practical advice and information is applicable.

In the case of intermetallic hydrides, in an article specifically on the accuracy of gas phase sorption measurements, Wang and Suda [25] outline the most important considerations in determining the isothermal absorption kinetics of these materials. They give an excellent example of the poor reproducibility of results from bulk hydrogen storage material characterisation, although equilibrium property measurements are less likely to vary as much. It is also specific to AB₅ hydrides (or, at least, intermetallic hydrides) rather than hydrogen storage compounds as a whole. More recently, there has been some work on adsorption measurement accuracy prompted by the interest in carbon nanostructures. Kiyoyabashi et al. [6] published work on the accurate measurement of carbonaceous materials, describing volumet-

ric apparatus designed for activated carbons and nano-fibres. Zhang et al. [7] also recently published work on the accurate determination of hydrogen uptake in carbonaceous materials. Like Kiyobayashi et al. [6] they describe their volumetric apparatus, but do not compare the results from their measurements with those from other instruments. In fact, they comment on the significant difference in the uptake rates from their samples compared with similar studies. However, they concentrate on the importance of the careful processing of experimental data and make an important point about the use of equations of state (EOS) other than the ideal gas law when performing calculations with hydrogen at higher pressures (>1 MPa). The use of alternative EOS was also examined by Zhou and Zhou [26].

Becher et al. [4] review previous work on hydrogen adsorption on carbon nanotubes and comment on the sources of error in these type of measurements. In another paper Hirscher et al. [27] discuss the accuracy of sorption measurements but concentrate on TPD measurements. A comparative study was published by Ansón et al. [5], in which they performed measurements using three different techniques: two gas phase and one electrochemical. They comment in their introduction on the difficulty of finding agreement between adsorption data using different techniques, although this is specifically in reference to carbon nanostructures. Blackman et al. [8] and Checchetto et al. [9] both presented volumetric systems. The former a “differential” system for carbon materials and the latter a system for the measurement of kinetics and equilibrium properties in hydrides.

4. Sources of error

This section will be limited to the consideration of errors in the volumetric and gravimetric techniques. Temperature monitoring and control are clearly important in all temperature and pressure ranges in both techniques. In general, the further the sample temperature is from ambient, or the operating temperature of the system, the greater the likelihood of problems with temperature gradients. Therefore, adsorption measurements performed at liquid N₂ temperatures and high temperature measurements performed on hydrides may be affected the most. However, a poorly thermostatted system will obviously cause problems regardless of the sample temperature. In principle, it is easier for the sample temperature to be measured directly in the volumetric technique because a temperature sensor can be in contact with the sample during measurement. In gravimetric measurements the sensor can only be in the vicinity of the sample. The temperature control and measurement issue also includes the problem of ‘cold spots’, leading to a false measure of sorption, and the opposite effect of ‘hot spots’. The problem of thermal effects as a result of the heat of reaction, either exo- or endo-thermic, is another related issue, although of more significance in the case of hydrides. Direct temperature measurement in the volumetric technique allows this temperature variation to be monitored more closely but it is an issue in equilibrium uptake measurements in general. In the same way as it is essential to ensure that the hydrogen sorption has reached the required ‘equilibrium’ at each isotherm point, it is also necessary for the sample to either still be at thermal equilibrium, or

to have returned to the required temperature if there is a large heat of reaction. This is obviously dependent on the nature of the sample and its size.

Gas purity is important, including both the original supplier's purity and the filtration applied *in-situ*. Filtration is particularly important if the gas bottle is not connected directly to an instrument, as gas delivery lines can introduce significant levels of contamination. In adsorption measurement, impurities can preferentially adsorb, greatly affecting results, and in absorption measurements impurities can poison the surface of materials, preventing the dissociation of molecular hydrogen, or decompose more sensitive samples. The system volume to sample mass, or sample size, ratio is an important consideration in volumetric instruments, which affects both system design and sample size choice. There are a number of interrelated factors, which depend very much on what is required of the instrument. The system volume must be low enough for the required quantity of sorbed hydrogen to result in initial and final hydrogen pressures significantly far apart for the resolution of the chosen pressure measuring device. This may require either variable reference volumes or the careful choice of sample size, based on knowledge of the sorption properties of the material, or both. However, it may be necessary to ensure that the initial pressure is not too high, in the case of materials that may undergo a phase transition during hydrogenation, in order to reduce material-related problems like the so-called 'large-aliquot effect' [28]. However, in the case of adsorption, it is considered necessary to minimize the dead volume, bearing in mind that in this case the dead volume includes any accessible pore volume, as well as (interparticle) void space.

The sample pretreatment, sample history and the outgassing of the sample are important interconnected issues that can affect not just the accuracy of a sorption measurement but also its validity. Without clear knowledge of the history of the sample, together with adequately detailed microstructural information, the validity of a measurement is questionable. The problems associated with this issue can vary greatly from material to material. Microporous adsorbents must be outgassed thoroughly. Gravimetric instruments allow this process to be monitored by observing the change in mass with time. Careful attention must be paid to the achievable vacuum on the sample, which often cannot be measured using a vacuum gauge. UHV components and large bore tubing will allow a higher vacuum to be achieved in an equivalent system, than fine bore or capillary tubing [29], for example. If a sufficiently high vacuum cannot be achieved, it may be necessary to flush through with an inert gas, depending on the material. It may also be possible to analyse the desorbing species using a mass spectrometer, in order to ensure the outgassing has been performed properly. In terms of reversible hydrides, knowledge of the sample history, including the source, the activation procedure, any periods of storage and exposure to air, is crucial, particularly if data from two samples are to be compared.

The measurement of pressure is obviously another key point in both techniques. In volumetric measurements it is used to calculate the sorbed quantity and therefore must be determined to sufficient accuracy; however, the accurate determination of

the pressure is also crucial for gravimetric techniques. An issue associated more with high pressure measurements is the accurate representation of the compressibility of hydrogen. Our own calculations [30] indicate that, although some of the alternative EOS describe the experimentally determined behaviour of hydrogen well over part of the range of pressures and temperatures relevant for storage, assuming one of these is suitable over the entire range can introduce significant errors. At low pressures, another source of error is thermal transpiration, whereby a thermal gradient along a tube of a diameter close to, or below, the mean free path of the gas molecule will result in a pressure gradient along the length of that tube. In practical terms, this can occur when measuring the pressure of a system, or the pressure of a sample cell, that is at a different temperature than the pressure measuring device. Wallbank and McQuillan [31] applied thermal transpiration corrections to Ti/H data at low pressures, showing that the effects can be significant, and the issue is also covered by Rouquérol et al. [24] in the context of adsorption measurements.

Two commonly quoted error sources are leaks and buoyancy effects in the volumetric and gravimetric techniques, respectively. The prevention of significant leakage is obviously important but this can be helped by careful selection of the system components and valves, and the use of filtration to prevent internal contamination from the sample. Thorough leak testing obviously needs to be carried out and potential errors can be identified by the determination of isotherms using relatively well understood materials. In the same way, the buoyancy corrections have to be applied carefully but should not cause significant errors at lower pressures. As the pressure increases, however, the corrections become larger and so, combined with the effects of thermal disturbances of the microbalance, may cause problems at particularly high pressures and temperatures.

5. Some comparative data

5.1. Experimental details

The $\text{LaNi}_{5-x}\text{Al}_x$ materials were purchased from LabTech Int. Co. Ltd., Bulgaria, through Hexion B. V., The Netherlands. The compounds were produced using La of 99.5% purity, Ni of 99% purity and Al of 99.99% purity. They were prepared by high frequency vacuum melting of the elemental metals and were not annealed after preparation. Microstructural characterisation using scanning electron microscopy (SEM) and X-ray powder diffraction (XRD) showed the presence of a secondary phase. The XRD data confirmed the crystallographic structure of the secondary phase to be that of γ' AlNi_3 and the chemical composition determined by electron probe microanalysis (EPMA) confirmed this. Analysis of the SEM images for each sample using Zeiss KS400 image analysis software estimated the proportion of secondary phase for the $x=0.1$ and 0.5 samples to be 1.4% and 7.2% by volume, respectively, and the composition of the primary phase determined by EPMA was $\text{LaNi}_{4.74}\text{Al}_{0.07}$ and $\text{LaNi}_{4.37}\text{Al}_{0.37}$.

The raw materials were initially crushed using a steel anvil, to produce a coarse powder. The samples were then activated in an

Advanced Materials Corporation (Pittsburgh, USA) Gas Reaction Controller (GRC), a commercial volumetric instrument that operates with a furnace in the temperature range 293–773 K and up to 200 bar. The instrument operates with a rotary pump. The samples were outgassed overnight at a furnace temperature of 473 K. The activation was then performed using 10 hydrogenation cycles up to a pressure of 20 bar for both samples, and a temperature of 313 K for the $x=0.5$ sample and 333 K for the $x=0.1$ sample. The masses were 2.61209 g for the $x=0.1$ sample and 2.50698 g for the $x=0.5$ sample. For the $x=0.1$ sample, after activation, a series of isotherms were measured in the GRC at temperatures of 313, 333, 353, 373 and 393 K. For the $x=0.5$ sample, after activation, a single isotherm was measured at 313 K, up to a pressure of 20 bar, in the GRC. In both cases, a portion of each sample was then transferred to a Hidden Isochema (Warrington, England) Intelligent Gravimetric Analyser (IGA) [10], allowing brief exposure to air. The sample masses were 173.2 and 180.7 mg. They were first outgassed overnight under high vacuum conditions (10^{-5} mbar) at a furnace temperature of 473 K and then exposed to a hydrogen pressure of 20 bar to allow rehydrogenation. Absorption and desorption isotherms were then determined at a furnace temperature of 317 K giving the average sample temperatures indicated in Fig. 1. A further measurement was made on the $\text{LaNi}_{4.5}\text{Al}_{0.5}$ sample for further comparison at a higher temperature (~ 393 K), although this was performed after the activated sample had been stored under air for a significant period.

5.2. Results

Fig. 1 shows the absorption isotherms for the $\text{LaNi}_{4.9}\text{Al}_{0.1}$ and $\text{LaNi}_{4.5}\text{Al}_{0.5}$ samples. It can be seen that each pair of 313 K isotherms show generally good agreement with each other. There is some discrepancy in hydrogen content at either end of the plateau region, which could be due to small leaks in the volumetric system or the effect of accumulative errors in the volumetric

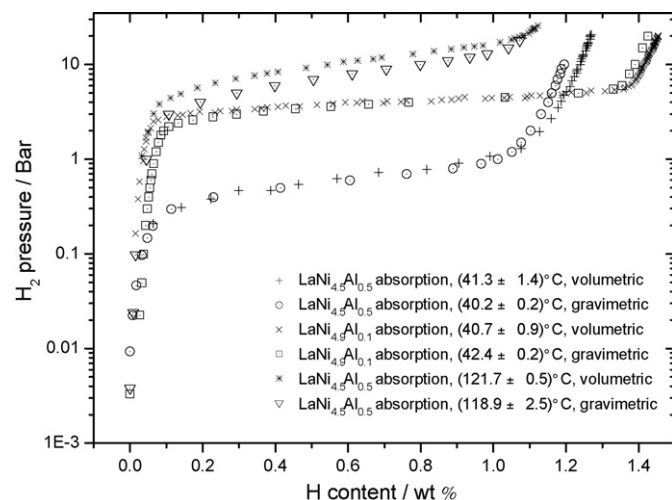


Fig. 1. Absorption isotherms for $\text{LaNi}_{4.9}\text{Al}_{0.1}$ and $\text{LaNi}_{4.5}\text{Al}_{0.5}$. The temperatures shown in the legend were determined from the average sample temperature through each isotherm measurement, with the indicated error determined from the spread in values.

technique. It could also be due to a material-related issue such as the ‘large-aliquot effect’, as there are some differences in the step sizes between the sets of measurements. However, the step sizes are essentially the same through the plateau region of the 313 K isotherm for $\text{LaNi}_{4.5}\text{Al}_{0.5}$ (average pressure step of 0.099 bar for the volumetric data versus an average pressure step of 0.100 bar for the gravimetric data) but significantly different (average pressure step of 0.063 bar for the volumetric data versus an average pressure step of 0.292 bar for the gravimetric data) for the $\text{LaNi}_{4.9}\text{Al}_{0.1}$ sample, yet there appears to be a fairly consistent difference between the overall uptake measured by each instrument in each case. Furthermore, the large-aliquot effect [28] tends to affect the measured absorption equilibrium plateau pressure rather than the plateau width, and so is unlikely to play a significant role in the differences seen here. The higher temperature measurements show greater overall discrepancy, which is most likely due to the difference in the real temperatures of the samples, despite the similarity in the measured sample temperatures. Using a value of $-38.09 \text{ kJ mol}^{-1}$ for the heat of reaction of the $\text{LaNi}_{4.5}\text{Al}_{0.5}$ sample, determined from the desorption plateau pressures measured volumetrically at six temperatures, the difference in the higher temperature plateau pressures in Fig. 1 corresponds to a temperature difference of approximately 10 K, which is a significantly greater difference than indicated in the legend. This suggests that the sample in the gravimetric instrument could be at a lower temperature than is indicated by the measured sample temperature.

6. Conclusion

The different gas phase techniques available for hydrogen storage material characterisation and related literature on their accuracy have been briefly reviewed, and potential error sources have been discussed. Some comparative volumetric and gravimetric measurements on two $\text{LaNi}_{5-x}\text{Al}_x$ samples have been presented. The measurements performed at 313 K were in good agreement with each other, in terms of the plateau pressures. An additional set of measurements performed at 393 K show greater disagreement, with a difference in the plateau pressures that corresponds to an approximate sample temperature difference of 10 K.

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