# The characterisation of gas storage media using the IGA system

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## Introduction

There has been a recent restoration of interest in gas storage media, which has stemmed from the drive to use hydrogen as a fuel. Hydrogen has one main benefit over other fuels. Water is the only by-product produced when using hydrogen as a fuel. Hydrogen is therefore a zero emission fuel.

Zero emission transportation is becoming more and more of a necessity due to air pollution and the limited resources of oil available. The drive to develop a "hydrogen economy" has been increased by ever tightening legislation.

The interest in hydrogen as a fuel was brought to focus in the early 1960's. At this time rechargeable metal hydrides were studied for hydrogen storage. Hydrogen has the potential to be a low pollution, multi-purpose fuel. In particular the storage of hydrogen for $H_2$ fuelled internal combustion engines was commonly discussed.

Today the emphasis is more on fuel cells but for any "hydrogen economy" to be viable a suitable means of hydrogen storage is required.

## What is required for a good hydrogen storage material?

Hydrogen gas can be stored as a compressed gas or sorbed onto a solid material (Hydrogen Storage Material). A good hydrogen storage material needs to demonstrate clear advantages over other methods.

*Safety* – Low operating pressures are desirable. Compressed gas storage methods have high operating pressures (100's of bars) whereas it is possible to have a similar capacity in a metal-hydride alloy but an operating pressure of only a few bars.

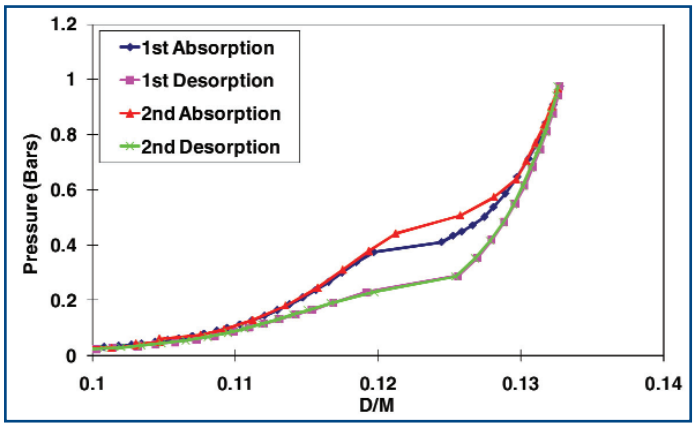



*Figure 1: Deuterium uptake on PdY alloy at 60 °C*

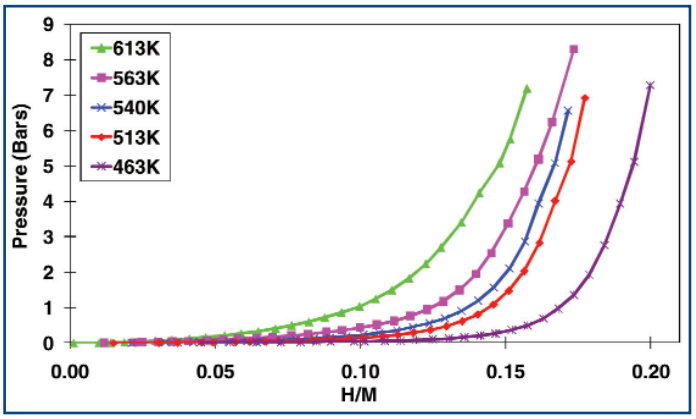
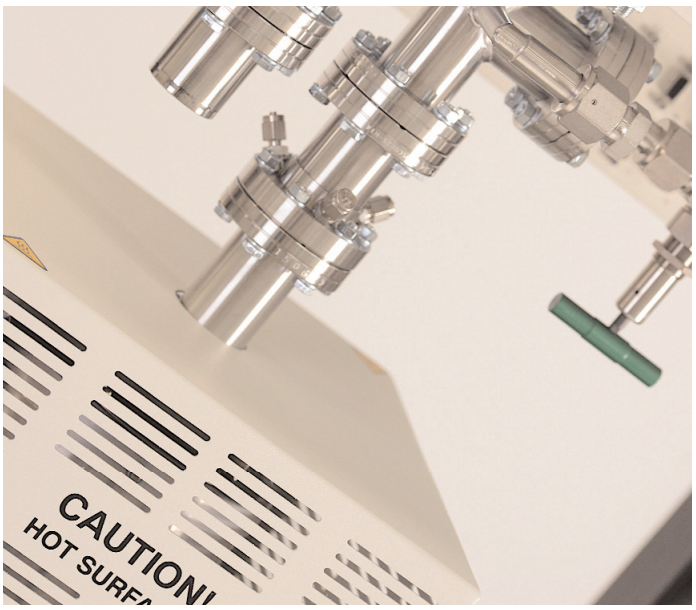


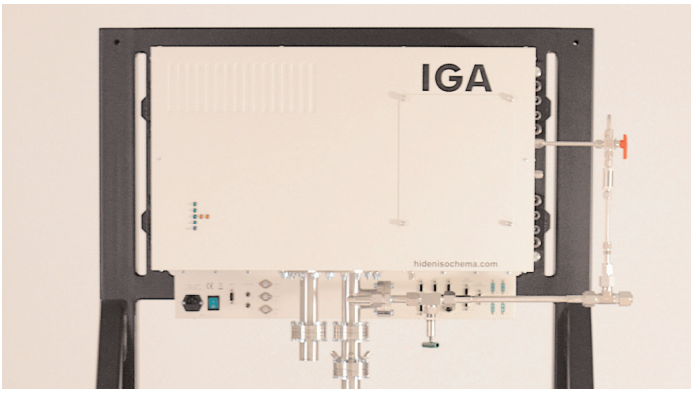

*Figure 2: Hydrogen absorption in PdY alloy.*

*Capacity* – A good gas storage material has to hold a large quantity of hydrogen.
*Compactness* – The storage needs to be compact and light for use on vehicles.

*Cycle life* – The materials need to be reusable and therefore require the ability to adsorb and desorb the same amount of hydrogen repeatedly without deterioration.

*Cost* – The cost of the material needs to be economically viable.






## What type of materials are being studied for use as hydrogen stores?

The most studied materials are metal alloys, the best known of which is $LaNi_5$. Research still continues to find less expensive materials with greater capacities at near-ambient conditions. At present there is also a great deal of interest high surface area carbon materials and synthetic metal oxide frameworks.

## The application of the IGA system for the characterisation of gas storage media

The Intelligent Gravimetric Analyser (IGA) was initially developed for the accurate determination of hydrogen and deuterium absorption (desorption) characteristics in various storage alloys and intermetallics. Accurate, high-resolution measurement and reproducibility, afforded by the IGA system, are essential qualities when performing such studies.

The intelligent nature of the IGA method is a pre-requisite to performing such experiments where equilibration time scales can increase by orders of magnitude during a hydride phase transition. Measurement of the desorption branch enables the full hysteresis envelope to be determined.

The nature of the IGA method is to hold the pressure constant (after step change in system pressure) during the weight equilibration phase. This guarantees that the true absorption/desorption branch is measured as the boundary conditions, and hence the driving chemical potential, are held constant.

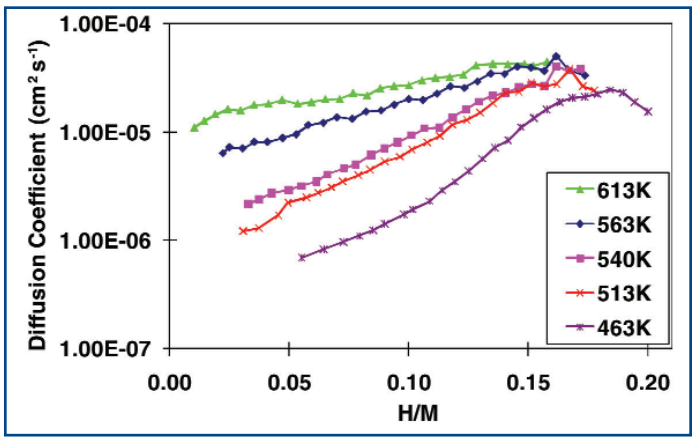


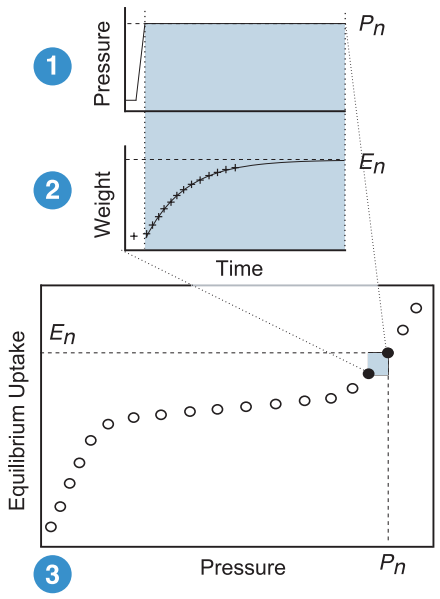

*Figure 3: Chemical diffusion coefficient of H in PdY alloy.*

This is not the case in a volumetric measurement where the pressure is allowed to relax: if the pressure relaxes the final equilibration value is not the true absorption/desorption branch but some pseudo-value within the hysteresis loop. Hence the volumetric isotherm will be dependent on the pressure step size.

The real-time analysis of the individual mass relaxation in response to a step change in system pressure gives valuable insight into the dynamics of the absorption/desorption process and an added extra dimension to the P-C-T data.

BET surface area measurements are easily performed in-situ by immersing the sample reactor in liquid nitrogen. Nitrogen or Argon can be used as the working gas and automatic analysis in software allows for quick calculation of the surface area. Such surface area determination can be carried out without removing the sample from the vacuum system and can thus be performed periodically during the course of a series of hydrogen absorption/desorption isotherms.

The extensive *IGASwin* software package can be pre-programmed to perform a suite of isothermal measurements at several temperatures and a built in event sequencer can be used to perform cyclic pressure and temperature operations during sample activation. Semi-




*The IGA Method*

1. The gas pressure or composition in the balance chamber is ramped to the setpoint, $P_n$, and then held constant through active control of the inlet gas flow
2. The weight change is analyzed in real time to determine kinetic parameters and simultaneously predict the equilibrium point, $E_n$
3. Equilibrium points are then collected, corrected for buoyancy, and plotted as an isotherm

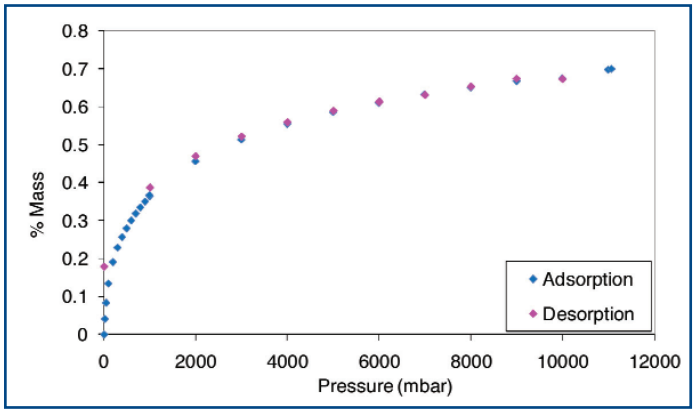



*Figure 4: Hydrogen uptake by carbon nanotubes at 77 K*

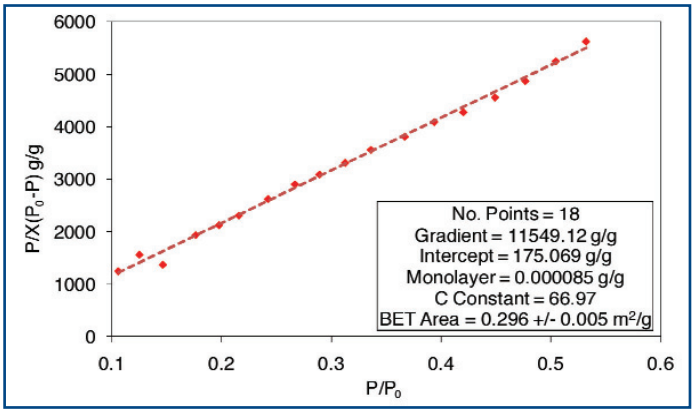



*Figure 5: BET surface area measurement for $LaNi_5$.*

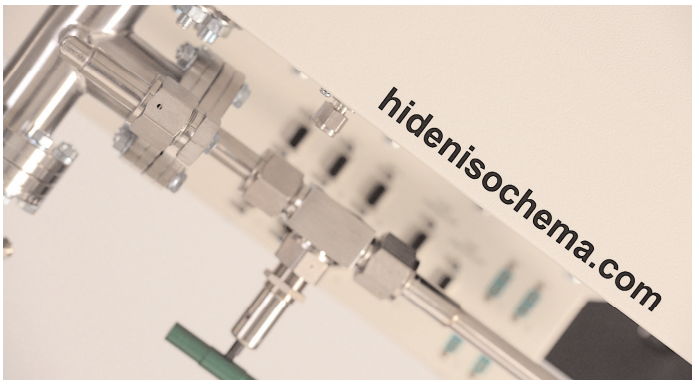
automatic features allow for pressure ramp and pressure cycle operations to be performed.

In summary the IGA can measure capacity, kinetics, P-C-T maps, operating pressures and can determine lifetimes using cycling studies.

## Examples of hydrogen storage studies with the IGA

Hydrogen absorption/desorption cycling studies can be performed using the IGA to assess the useful lifetime of storage materials. Cycles can be set-up in the user friendly software and run automatically. Fig. 1, shows deuterium adsorption and desorption isotherms during two cycles measured on a PdY alloy, notice the change in the second adsorption branch.

The capacity of hydrogen in materials as a function of pressure and temperature (P-C-T maps) can be measured using the IGA by measuring the absorption isotherms of materials. Fig. 2 shows hydrogen absorption isotherms measured on a PdY


alloy at 5 different temperatures. In addition to measuring capacity the IGA also provides kinetic information in the form of chemical diffusion coefficients, Fig. 3. The kinetic parameters provide important information when considering a material for hydrogen storage applications, the speed of hydriding and dehydriding.

Fig. 4 is an example of an hydrogen absorption/desorption isotherm measured using the IGA to characterise carbon nanotubes. This measurement was performed at liquid nitrogen temperatures in order to enhance the hydrogen capacity. Reports have been made of capacities of 50% in the literature but these were determined using the volumetric method. They have not yet been verified using the more accurate gravimetric method. The debate at present is centred on proving that the adsorption measured is truly hydrogen and not impurities in the hydrogen such as water. The interesting feature in figure 4 is the reversibility of the isotherm. Any impurity sorption at 77 K would be irreversible. The high degree of reversibility indicates that the sorption measured is primarily hydrogen.

An example of a BET analysis on the storage material $LaNi_5$ after activation and cycling is shown in Fig. 5. BET analysis can be performed before and after activation and cycling *in-situ*, avoiding the need to remove the sample from the apparatus and thus avoiding exposure to air.