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Novel Sieverts' type volumetric measurements of hydrogen storage properties for very small sample quantities

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Abstract

Novel volumetric analysis instrument for studying hydrogen storage property of very small quantities (∼mg) of samples was developed and tested. Small pressure change arising from hydrogen uptake or release are precisely measured and equated to the change in the sample's hydrogen content using the gas law equation. Very small volume pressure reservoir enables these precise measurements, and all internal volumes are calibrated with high-purity helium gas. Capacity, equilibrium isotherm, and kinetic measurements can be performed in the pressure range of vacuum to 4 MPa and the temperature range from cryogenic-673 K. Test measurements were made on small carbon nanotube samples and measurement of less than ∼3 μg of hydrogen uptake was demonstrated, which corresponds to an accuracy of better than 0.15 wt% for a 2 mg sample.

Keywords: Hydrogen storage materials; Gas–solid reactions

1. Introduction

Concern over dwindling oil reserves and the environmental impact of greenhouse gas emissions has motivated an intense study of alternative fuels for mobile applications. Among the possible candidates, hydrogen is one of the most attractive because of its low mass, clean combustion and high intrinsic energy density. However, storing hydrogen with acceptable volume and mass density remains a technical challenge and has become the focus of much of today's advanced research.

Many different classes of materials have been investigated for storing hydrogen including: metal hydrides, complex chemical hydrides, inorganic and organic–inorganic hybrid materials, composites, and carbon-based materials.

Some of these materials are difficult to synthesize in bulk quantities with consistent properties. For example, the growth of single-wall carbon nanotubes (SWNT) typically yields milligrams of SWNT per batch. Unfortunately, the measurement of the hydrogen storage capacity of small-mass samples is difficult, and the wide range of hydrogen storage capacity reported for carbon nanotubes may be partially attributed to measurement errors due to the small mass of the samples. For measurement of 1 mg quantities of hydrogen storage materials with 0.1 wt% accuracy, the instrument should have both the accuracy and precision to measure changes associated with uptake or release of 1 μg of hydrogen. Ideally a measuring system should be able to achieve this accuracy while functioning in hydrogen pressures extending to 10 MPa and temperatures up to 1000 K.

Temperature-programmed desorption (TPD, also known as temperature-programmed desorption spectroscopy (TDS)), thermogravimetric analysis (TGA), and volumetric measurement are the main techniques used to study hydrogen storage capacity. In TPD, a vacuum mass-spectrometer is used to achieve very high sensitivity, allowing detection of less than 1 pg of H_2. However, quantitative measurements rely on calibration using a reference material with known hydrogen storage capacity [1]. The ratio between measured and actual gas evolution depends on evolution rate and the pumping speed of the mass-spectrometer chamber, so the accuracy of TPD hydrogen storage measurements is limited by the calibration procedure, and is typically around 0.05 wt%. Perhaps the largest disadvantage of TPD for hydrogen storage measurements, however, is the requirement of a high-vacuum environment for the mass-spectrometer, which greatly limits the hydrogen pressure ranges that can be studied.

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With such methods, in-situ measurements of hydrogen uptake are usually not possible due to the low-pressure operation, and cryogenic quenching is sometimes necessary to preserve hydrogen content upon introduction to the vacuum environment.

Thermogravimetric analysis uses a micro-balance to make sensitive mass measurements to directly deduce changes in hydrogen content. Commercial instruments are available with operation pressures up to 2 MPa and temperatures up to 1000 K. Typical resolution and drift limits of the mass measurement are 0.1 and 1.0 μg, respectively. This approach is capable of measuring a 1 mg sample with 0.1 wt% accuracy; however, the drift is just at the limit of the desired accuracy, and, at high pressures, buoyancy must be properly accounted for to avoid even larger errors (e.g. at 2 MPa, the buoyancy is a 0.3 wt% correction). Furthermore the measurement is complex and the procedure for loading samples does not lend itself to being performed in a controlled environment, making it difficult to handle air-sensitive samples [2].

Volumetric analysis is the most versatile and direct approach for hydrogen storage capacity measurement. Hydrogen uptake or release from the sample material is deduced by measuring pressure changes in a known, reference volume held at a fixed temperature, remote from the sample. Hydrogen storage over a wide range of sample temperatures and pressures can be measured by employing a wide range of pressure transducers and appropriate gas handling materials. However, small samples (∼1 mg) present difficulty due to the small pressure changes in the typical reference volumes. Here we present measurements made on a novel apparatus developed by Hy-Energy LLC and tested at Stanford University for the hydrogen storage properties of very small samples. Using small reference and sample volumes, a controlled environment, and an appropriately designed instrument, we achieved measurement capable of detecting the uptake or evolution of less than 3 μg of hydrogen. This corresponds to the equivalent of 0.3 wt% accuracy for 1 mg sample.

2. Experimental method

2.1. Standard setup for volumetric measurements

The heart of a volumetric hydrogen storage capacity apparatus (also known as a Sieverts' apparatus) is a gas manifold with a series of tubes and valves connecting the sample chamber to one or more gas reservoirs of known volume, and pressure transducers for measuring reservoir pressure (Fig. 1). A typical measurement consists of a series of steps: (1) pre-treat sample as needed (e.g. see the procedure used below on carbon nanotubes) and bring the sample to desired temperature. (2) Close the valve between the sample and reservoir and introduce gas into the reservoir to bring it to the pressure of interest, (3) open the valve between the sample and reservoir and observe reservoir pressure change. The amount of gas uptake (or release) by the sample is deduced from the resulting reservoir pressure drop (or rise), after accounting for the previously-measured dead volume in the sample chamber. For full capacity and kinetics measurements, the reservoir will ideally hold significantly more gas than the uptake or release in the sample so that the pressure will not vary significantly during uptake or release. By monitoring the change in reservoir pressure versus time, the kinetics of hydrogen uptake or release can be measured. By repeating the measurement at different pressures at a fixed temperature, the pressure–composition isotherm can be obtained.

The apparatus with standard sample holder described here is a commercially-available volumetric apparatus (PCTPro-2000 from Hy-Energy LLC). It includes a temperature-controlled gas system, computer-controlled valves, and two pressure transducers covering a pressure range from 100 Pa to 20 MPa. The standard instrument has calibrated reservoirs that allow dosing from mililiters to liters of gas. High-pressure hydrogen and helium (used for purging the system and for measuring the sample holder dead-space volume) are supplied from regulated tanks and a scroll pump can be used to pump the system and sample holder to a base pressure of ∼0.3 Pa. For standard sample sizes (1–10 g) a temperature-controlled, 316 stainless steel sample holder (chamber) is used with a maximum operating pressure of 20 MPa and a standard temperature up to 673 K.

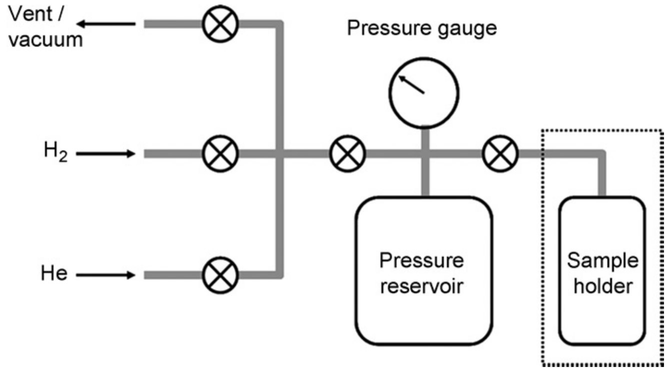

Fig. 1. Schematic diagram of the volumetric analysis apparatus.

It is instructive to estimate the smallest mass of hydrogen measurable with the typical standard Sieverts' system. Using the ideal gas law and assuming a measurable pressure difference corresponding to the pressure transducer accuracy at 1 MPa (i.e. 1 MPa × 1.0% = 0.01 bar), and using a typical reservoir volume (10 ml), we find that the smallest measurable hydrogen mass is approximately 90 μg at room temperature. It is likely that uncertainty in dead-space and valve volumes and other sources of error such as temperature fluctuations will make the smallest measurable mass larger than this value, but even this value allows us to place limits on the sample mass needed for acceptable accuracy. For example, with a 10 mg sample this smallest measurable mass corresponds to an uncertainty of approximately 0.8 wt%, which is an appreciable fraction of the typical total mass storage ratio of around 5%. Obviously measuring hydrogen storage in a 1 mg sample would not be possible with the typical equipment.

2.2. Small-sized sample attachment

The approach to achieving the accuracy and precision required for measuring small (∼1 mg) samples is simple in concept—use small reservoir and sample volumes. In practice this is made difficult by the requirement of precise inlet and outlet control of these small volumes and the use of standard valves and fittings.

To achieve the desired small reservoir volume the standard sample holder (dotted region in Fig. 1) was replaced by a custom attachment with a much smaller dosing volume (MicroDoser, Hy-Energy LLC). Using the pressure transducer's 0.3% accuracy of reading, smallest accurately measurable mass change for this system is estimated at 3 μg of hydrogen. This would indicate that a change of 0.3 wt% could be measured for a 1 mg sample. With a heater attached to the sample holder, the sample can be heated to around 673 K. Low temperature measurements are possible by placing the sample tube in a cryogenic liquid bath.

3. System performance

To evaluate the performance of this system we have measured the hydrogen uptake capacity in two small samples (both 2 mg): a SWNT grown using plasma-enhanced chemical vapor deposition (PECVD) [3] and a multi-walled carbon nanotube (MWNT) grown using hot-wire (HW) CVD [4]. The measurement procedure followed for these samples is typical of that for

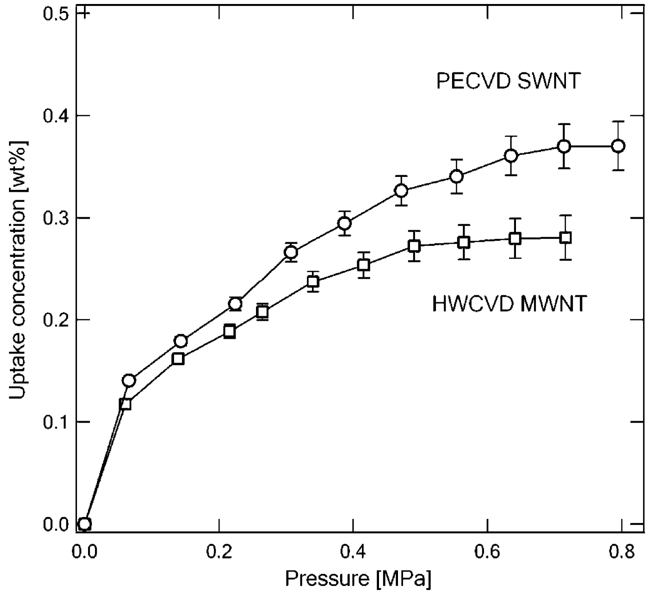

Fig. 2. Room temperature PCT isotherms from 2 mg PE CVD SWNT and HW CVD MWNT.

many types of hydrogen storage materials. The sample is loaded into the sample and the system is evacuated by a vacuum pump and purged by helium a few times to ensure there is no residual air or other contaminants in the manifold. The system is checked for leaks by applying helium gas at pressures ranging from 0.3 to 0.5 MPa. The sample is then outgassed at elevated temperatures and purged with helium if necessary (523 K for 6 h, for our measurements). The sample holder is then removed and weighed to determine the mass of the sample by subtracting the known mass of the empty sample holder. A final, short outgassing can be preformed upon reattachment of the sample holder to the manifold. Additional activation processes at high temperatures may be required, depending on the type of material being tested. Uptake isotherm is typically obtained in an additive way in which small increment of pressure is repeatedly applied to the sample instead of applying a large pressure at a single pressurizing step. By doing the procedures, the dynamic temperature change due to the abrupt expansion of hydrogen gas into the sample chamber at high pressure regimes can be avoided [5]. Measurements and operational procedures are controlled and recorded using the supplied computer software.

Pressure–concentration isotherms (PCT) of the two samples at room temperature are shown in Fig. 2. Significant uptake in the low pressure regime is observed for both types of samples, which is attributed to the combination of storage on the large outer surface and within the nanotube bundles. It is noted that the measurement accuracy is ~1 μg of hydrogen in the pressure regime, and the error bar is mainly associated with small mass of the samples.

Measurements (shown in Fig. 3) were also performed on an activated carbon sample, using masses of 6, 39 and 251 mg. The hydrogen uptake isotherm using the MicroDoser and 30 mg sample is shown in Fig. 3(a) with curve fit (dotted line). For calibration purposes, a stainless steel rod with the same volume as the 39 mg sample was prepared and tested under the same conditions. The negligible uptake measured (open circles in Fig. 3(a)) indicates that the metal rod does not absorb hydrogen and, more importantly, the dead-volume calibration using helium gas is accurate. The uptake measurement using the standard sample holder setup with a 251 mg sample is also plotted for comparison in Fig. 3(b). All show good agreement even though the measurements have more relative scatter due to insufficient sample quantity with respect to the size of the standard setup. The isotherm of 6 mg activated carbon shows the largest deviation from the other two, corresponding to an uncertainty of ~0.06 wt% at 3 MPa of hydrogen pressure and room temperature.

In summary, novel volumetric sorption measurements were made on very small samples using a specially designed instrument to achieve μg sensitivity in measuring hydrogen storage capacity of important hydrogen storage materials.

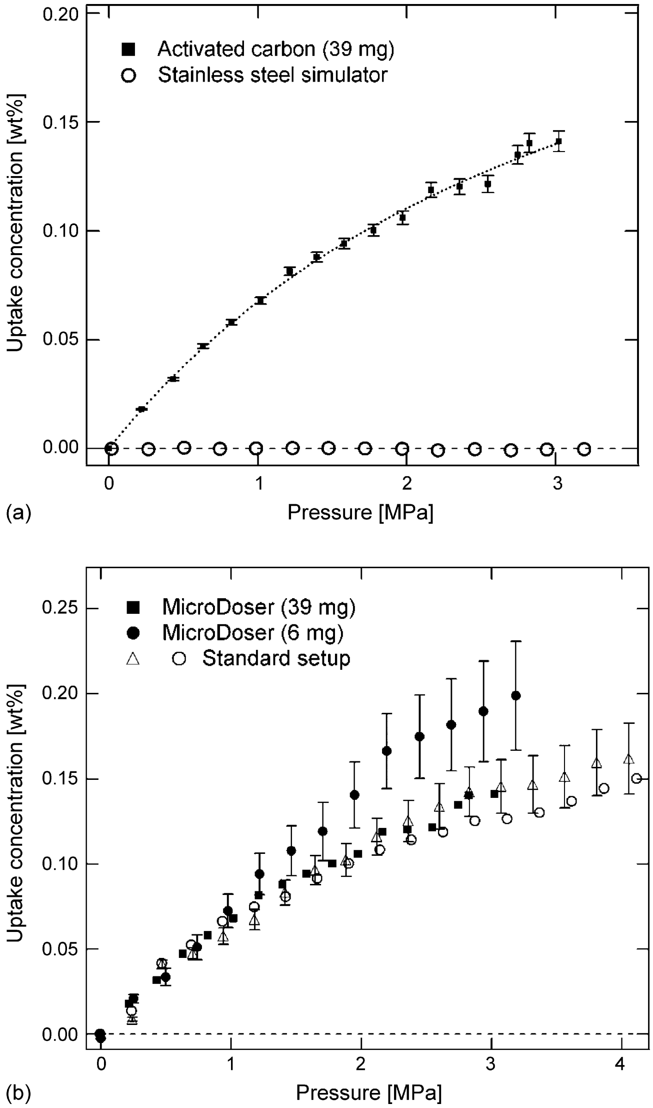

Fig. 3. (a) Hydrogen uptake PCT isotherm of 39 mg of activated carbon sample and a stainless steel blank with the same gas displacement volume, and (b) comparison of measurements using the MicroDoser (39 and 6 mg) with those obtained using the standard sample holder setup with a 251 mg activated carbon sample (open triangles and circles).

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