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Development of a high-pressure microbalance for hydrogen storage materials

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Abstract

Pressure–composition isotherms (PCI's) help to determine thermodynamic properties related to hydrogen uptake of materials. PCI's are normally obtained volumetrically with a Sieverts type apparatus or gravimetrically with a microbalance. A potential problem with the gravimetric technique is that the sample is momentarily exposed to air when transferring it to the system often causing unwanted changes such as oxidation and reaction with moisture in the air. In this study, a high-pressure microbalance was built from scratch inside a glove box with inert atmosphere. The system consists of an electromagnetic microbalance, pressure resistant casing for up to 100 bar hydrogen, a flow system for hydrogen and inert gas, heating elements for temperature control, and software for controlling the system. Thermal convection effects are observed and dampened by heating on both the sample and a counterweight. The precision of the mass measurements for a 1 g sample was ±5 μg, and this range proved to be the same independent of pressure and temperature.

Keywords: Metal hydrides; Hydrogen absorbing materials; Gas–solid reactions; Thermodynamic properties; High-pressure

1. Introduction

Much effort has been put into characterizing and experimenting on materials in the search of a practical hydrogen storage system. Following studies of a broad range of conventional hydrides, the discovery of Ti-doped sodium alanate by Bogdanovic and Schwickardi [1] as a material for a reversible, relatively fast, high capacity system (around 5.6 wt.%) operating under 200 °C led to an interest for the so-called complex hydrides. A further breakthrough appeared in 2002 when Chen et al. published results [2] that showed that systems based on lithium nitride would yield high capacity reversible systems. Since then many results have broadened the field leading to groundbreaking results [3–9].

In the continuing efforts to discover new and more practical hydrogen storage systems it is worth looking at the equipment for characterization of the materials used. In particular, the enthalpy of hydriding, and the gravimetric and volumetric capacities as a function of operating temperature and pressure are of much use in order to test the practicality of the system. In order to determine these properties, it is useful to record pressure–composition isotherms (PCI's), which normally yields pressure plateaus during which either a phase change or chemical reaction occurs. The thermodynamic relationship between the hydrogen pressure and the temperature is contained in the equation:

$$\ln p = \frac{\Delta H}{RT} - \frac{\Delta S}{R} \tag{1}$$

where p is the plateau pressure, ΔH the enthalpy change, R the gas constant, T the absolute temperature, and ΔS is the entropy change. Assuming that ΔH and ΔS are constant, a plot of $\ln p$ versus $1/T$ for plateau pressures from several isotherms, a straight line with slope $\Delta H/R$ and intersection $-\Delta S/R$ will result.

Equipment used to record PCI's are generally divided between volumetric equipment based upon measuring hydrogen uptake indirectly by observing pressure changes in the system and gravimetric equipment which is based upon measuring the hydrogen uptake directly as observed as mass change in the sample.

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While gravimetric equipment has the advantage to add an online mass spectrometer during the analysis, there is a serious issue, which is that samples are contaminated during transfer to the equipment.

In this study we present a compact high-pressure microbalance made for obtaining PCI's of hydrogen storage materials gravimetrically and designed so it can fit inside a glovebox, allowing safe sample transfer. The details of the design is given below.

2. Description of the system

The high-pressure microbalance system consists mainly of three parts: (1) A microbalance in a pressure resistant casing, (2) controlled gas supply, and (3) temperature control.

2.1. Microbalance

An electromagnetic microbalance (we used an older Cahn model) was fastened inside a hollow stainless steel block, see Fig. 1. The block was sealed with a large O-ring and a plate, which was fastened with many bolts following the contour of the cavity. The block was pressure tested using oil under pressure and proved to resist pressure up to at least 250 bar.

An external controller for the microbalance utilizes the null balance principle [10], having a light source and null detector around one end of the double-beam, which has a foil flag that cuts off the ray from the light source (a LED) before it reaches the null detector (a photodiode). A correction voltage is supplied to the servo drive of the microbalance that moves the beam, so that a constant amount of radiation is received by the null detector. This voltage is proportional to the mass of the sample, and hence the mass of the sample can be recorded.

The sample and counterweight are placed upon stiff hooks at the end of thin flexible wires. The block with microbalance was fastened on a horizontal strong beam that could be fastened on the insides of the glovebox.

Fittings in the block with the microbalance was sealed with O-rings. However, in order to seal the sample and counterweight chambers where the temperature would approach 300 °C, copper gaskets were used. For each experiment these gaskets were replaced with fresh ones.

2.2. Controlled gas supply

Fig. 2shows the gas flow system that was built for the microbalance. The system operates by using software that receives input from the pressure transducers and sets current to the magnetic solenoid valves, pressure controller and mass flow controller. In our case, we programmed the software interface so we were able to execute measurements for a series of pressures, resulting in a PCI curve, for example by first raising the pressure sequentially for absorption and then decreasing the pressure sequentially for desorption. When decreasing the pressure, the gas flow runs from the microbalance and into the pressure and mass flow controller in the same direction as when increasing the pressure. Importantly, each time the sequence is changed from absorption (pressure increase) to desorption

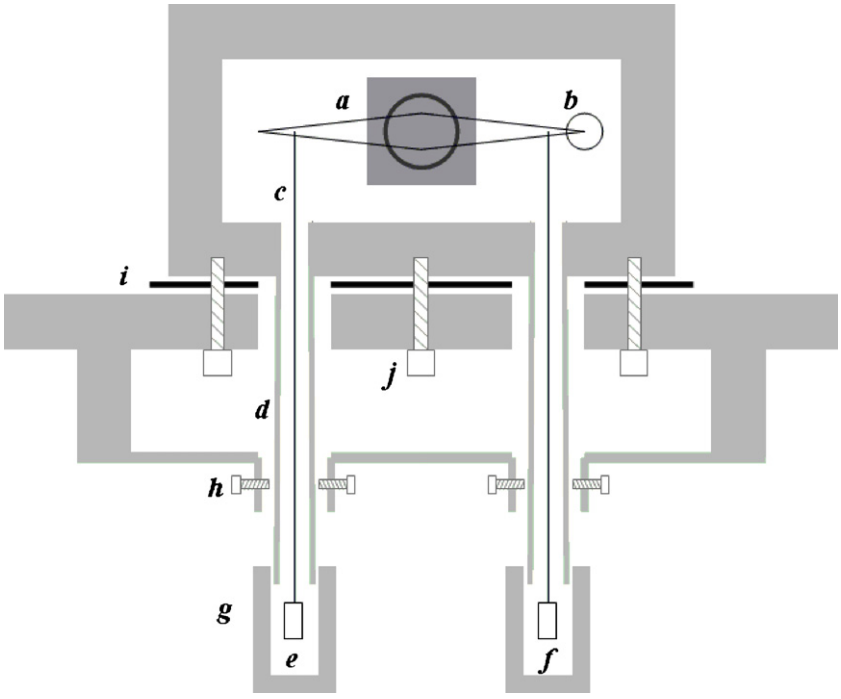

Fig. 1. Schematic diagram of the high-pressure microbalance. The material used is 316 stainless steel. (a) Electromagnetic microbalance with symmetrical double-beam; (b) LED and photodiode; (c) hang-down wire (0.1 mm Pt); (d) 10 mm tube; (e) sample hanging in Ni–Cr hook; (f) counterweight of inert material (Al or Al_2O_3); (g) round sample chamber to screw on the tube (via a fitting, not seen here); (h) screws to position the tube so the wire does not touch (four screws in a circle around each tube); (i) rubber (Viton®); (j) bolts.

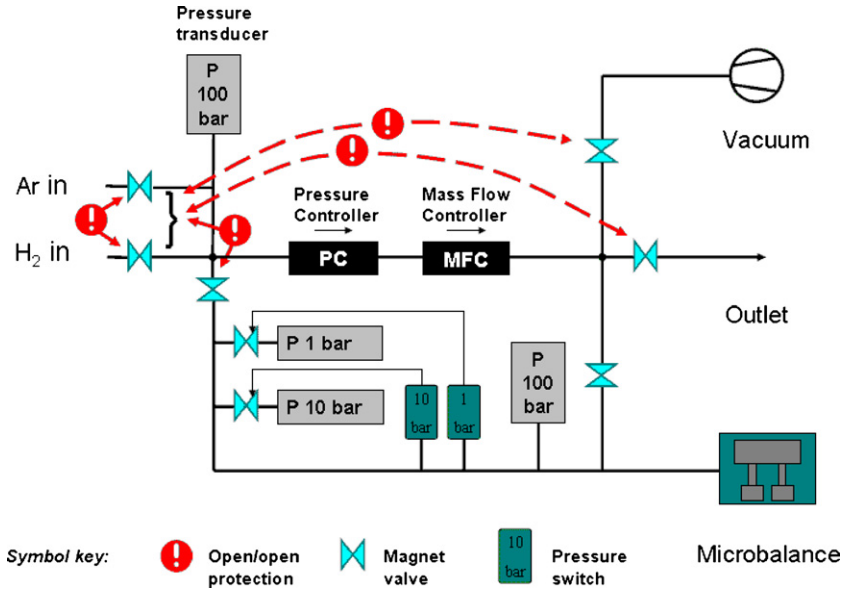

Fig. 2. Gas supply for the high-pressure microbalance. The pressure controller sets the pressure so that the differential pressure over the mass flow controller is no more than 5 bar. The open/open protections (controlled via software) ensure against damaging the low pressure transducers and various unwanted flow lines. The pressure switches protect the pressure transducers from higher pressure than they are meant for.

(pressure decrease), the gas reservoir between the pressure controller and valve to the hydrogen tank must be reduced in pressure to closely match the pressure in the microbalance cavity, so that there will not be a violent change in pressure when the valve between the microbalance and the pressure controller is opened, potentially knocking the sample off the hook.

In order to achieve a maximum range of resolution in the pressure reading, transducers for various ranges were used. Mechanical pressure switches were added to protect the lower range transducers against too high-pressure. Also, at the 1 bar transducer (Pirani in combination with piezo resistive) and at the vacuum outlet, overpressure valves were placed as an extra precaution to protect the equipment against accidental high-pressure.

The gas inlet to the microbalance was set in fittings that combine the tubes for the hangdown wires and sample/counterweight chambers (not seen in Fig. 1). In this way the hot gas in the chambers will not pass around the microbalance, which may not be able to sustain high temperatures.

2.3. Temperature control

Heating elements were placed around the sample and counterweight chambers. Sheets of flexible graphite (Papyex®) were used to provide a close connection between the heating elements and the chambers. Thermocouples were pressed down into the flexible graphite sheets. Furthermore, a thermocouple was placed inside the block with the microbalance, and thermocouples were welded through drilled holes in the fittings for the sample and counterweight chambers, so that the temperature could be read as close to the sample and counterweight as possible.

3. Testing of the system

The system was tested for stability with regard to variations in the readings of the mass as a function of time, pressure and temperature.

Fig. 3 shows the result for a stability test of the microbalance over several hours. As it is seen, there is some noise covering ca. 10 μg. However, this degree of noise did not increase significantly at neither temperatures up to 300 °C or pressures up to 40 bar.

The precision of ±5 μg for successive readings means that the precision in wt.% hydrogen uptake for a 1 g sample will be ±0.0005 wt.%.

The system was also tested for thermal convection effects. It is natural that there will be an effect of thermal convection as gas close to the sides of the sample and counterweight chambers heats up and moves upwards, then cools and moves down

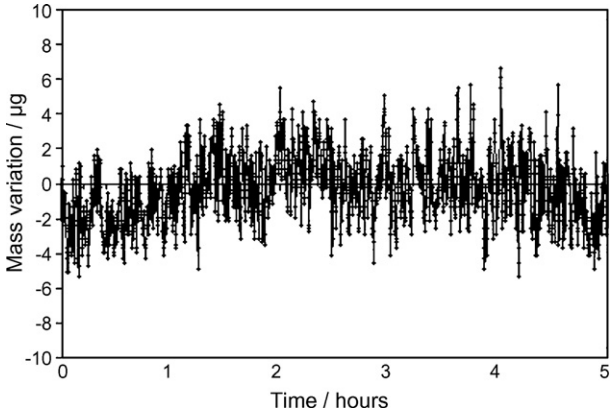

Fig. 3. Stability test of the microbalance. A 1 g aluminum sample and 800 mg aluminum counterweight in 10 bar hydrogen and 25 °C was used.

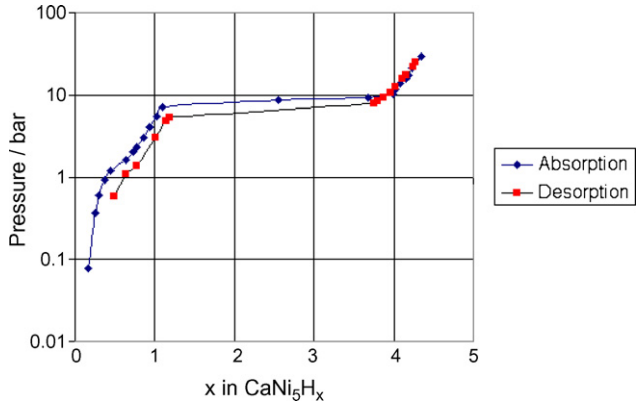

Fig. 4. PCI of $CaNi_5$ at 100 °C.

through the center of the tubes. The convection flow will exert force on the sample and counterweight effectively increasing the mass reading when the sample is larger than the counterweight (which will normally be the case). For this system, it was shown that while the mass reading increased 500 μg when heating the sample chamber to 200 °C and keeping the counterweight chamber at room temperature, the mass reading increased only 100 μg when heating both the sample and counterweight chambers to 200 °C. This shows that the thermal convection effect can be eliminated to some degree by heating on both chambers.

The temperature in the block with the microbalance was measured as a function of the temperature of the sample and counterweight chambers as they were heated up. The temperature only increased 3 °C close to the microbalance as a result of increasing the temperature in the chambers from room temperature to 300 °C. Hence, there will not be any risk of damaging the microbalance material while heating the sample to high temperatures.

No evidence of hydrogen embrittlement was observed even after lengthy exposure to hydrogen at high-pressures and temperatures. This is in agreement with a model by Shih and Johnson and experimental Nelson curves [11], which have shown that for plain carbon steel a safe area of operation at 300 °C for 100 h was up to at least 350 bar hydrogen pressure. At 100 bar for 100 h it was safe up to 350 °C. Embrittlement primarily stems from the formation of methane in the material, so plain carbon steel provides a worse scenario than austenitic stainless steel with a maximum carbon content of 0.15% compared to a maximum carbon content of 2.1% for plain carbon steel.

4. Using the system to obtain a PCI

In order to test the high-pressure microbalance for real use, a PCI for a $CaNi_5$ alloy, purchased from Ergenics, was obtained. A 750 mg sample was activated at 30 bar and 100 °C. Fig. 4 shows the result of an absorption and desorption cycle.

5. Conclusion

The design of a high-pressure microbalance for operation in a glovebox was presented. The precision of the system was ±5 μg corresponding to ±0.0005 wt.% for a 1 g sample. The system was able operate at temperatures up to 300 °C and pressures up to 100 bar hydrogen.

Acknowledgement

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