ELSEVIER

Journal of Alloys and Compounds 330–332 (2002) 666–669

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

# Hydrogen adsorption in carbonaceous materials–How to determine the storage capacity accurately

Tetsu Kiyobayashi[a,]*, Hiroyuki T. Takeshita[a], Hideaki Tanaka[a], Nobuhiko Takeichi[a],
Andreas Züttel[b], Louis Schlapbach[b], Nobuhiro Kuriyama[a]

[a]*Chemical Metallurgy Section, Department of Energy and the Environment, Osaka National Research Institute, AIST, MITI, Midorigaoka 1-8-31, Ikeda, Osaka 563-8577, Japan*

[b]*Forschungsgruppe Festkörperphysik, Physik Department, Universität Fribourg, Pérolles, CH-1700 Fribourg, Switzerland*

## Abstract

A volumetric apparatus for gas phase hydrogen/helium adsorption and desorption measurement aimed at carbon materials was constructed. The performance of the apparatus was assessed using activated carbons and vapor grown carbon nanofibers, and was proved to be applicable for these materials of low apparent densities with sufficient accuracy. Materials used in this study did not show a significant storage capacity of hydrogen. The obtained result, however, will provide reference data for future study to develop the carbon material for hydrogen storage. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Hydrogen adsorption; Carbonaceous materials; Storage capacity

## 1. Introduction

Hydrogen has been considered as an ideal energy medium for replacing fossil fuel to mitigate the global environmental issues. A challenge we have to contend with is how to transport the hydrogen safely and efficiently. Recent claims that some new carbon materials can store a large amount of hydrogen [1–3] have thus aroused worldwide excitement and revived the research on the hydrogen storage by carbon sorption [4–9]. There are several ways to store hydrogen into carbon materials, such as high pressure gas phase storage, electrochemical storage [10–14] and mechanical grinding [15]. A significant discrepancy still remains, however, among recent reports as to the capacity of storage, especially that determined by the gas phase method [16–21]. One of the causes of discrepancy is due to the fairly low bulk density of carbon material than that of metal hydride, for it limits the amount of material in the measurement cell and leads to the big uncertainties in the experiments. A pertinent experimental procedure to evaluate the storage capacity for low density material is thus urgent necessity.

In our laboratory, a precise volumetric adsorption/desorption apparatus (Sieverts' apparatus) is under construction aimed at carbon material. In this article we describe the assessment of our volumetric apparatus with using some commonplace carbon materials.

## 2. Experimental

### 2.1. Material used

Carbon materials used in the present study are: (1) activated carbon Norit Darco G-60 (Aldrich); (2) high surface area activated carbon Maxsorb MSC-30 (Kansai Netsu Kagaku) whose surface area is 3000 $m^2 \cdot g^{-1}$; (3) Pt particle loaded activated carbon; and (4) vapor grown carbon nanofibers. The Pt loaded sample (3) was prepared by using the Norit Darco (1) on which the Pt particles were loaded by the cation-exchange method with tetraammineplatinum(II) dichloride solution $[Pt(NH_3)_4]Cl_2(aq)$. The material was dried and reduced under the hydrogen gas flow at 270°C. The vapor grown carbon nanofiber (4) was prepared by the decomposition of ethylene:hydrogen = 1:1 gas flow over Fe:Cu = 1:1 catalyst at 600°C. Admittedly, the characterization of the samples

---

*Corresponding author.

0925-8388/02/$ – see front matter
PII: S0925-8388(01)01436-0

and the optimization of the preparation procedure are far from sufficient for claiming that these materials are for hydrogen storage. We consider these materials as references for assessing the apparatus and for the future investigation.

For the adsorption and desorption measurement, about 500 mg of sample was filled into the sample cell and evacuated at 220°C for 2 h prior to the adsorption and desorption measurement. The real density of all the sample $r_{\mathrm{real}}$, which is necessary to calculate the volume occupied by the sample $v_{\mathrm{smp}}$ (see Section 2.4), was taken to be $r_{\mathrm{real}}$ $(\mathrm{g \cdot cm^{-3}}) = 1.9$ for all samples.

### 2.2. Volumetric apparatus

A schematic diagram of the volumetric apparatus is shown in Fig. 1. Principle of the measurement follows the historical Sieverts' method [22] as well as several modernized procedures [24–26]. The volumes of the pressure reservoir $V_{\mathrm{res}}$ and the sample cell $V_{\mathrm{cell}}$ are 7.98 and 2–5 $\mathrm{cm^3}$, respectively. The measurement is automated by using a personal commuter with an IEEE-488 interface for pressure and temperature measurements, and with a relay board for pneumatic valve operation. Several features of our apparatus to improve the accuracy and precision are: (1) The pressure transducer and indicator, Druck Ltd. DPI145 (PT in Fig. 1) were calibrated by the manufacturer within 0.015% of reading in the pressure range of $0.1 < p$ $(\mathrm{MPa}) < 10$, and a traceability certificate to relevant International Standards is provided. (2) The principal part of the apparatus (pressure transducer, pressure reservoir and sample cell — referred as 'system' hereafter) is contained in an air thermostat (TS). Its temperature, measured at the transducer with a thermocouple (TC), is held at 35±0.2°C. To make the pressure measurement more perfect, the temperature is kept recorded and is taken into account to correct the pressure. (3) In order to avoid the local heat-up during the measurement, we use pneumatic diaphragm valves (PV1-4) instead of solenoidal valves. (4) Yang has suggested that a trace amount of water contained in a hydrogen cylinder affected significantly the adsorption measurement for alkali metal doped carbon [18]. Although no alkali metal doped materials were used in the present work, we used a high purity hydrogen (99.9995%) and a liquid nitrogen trap (LN1), just in case. To avoid the contamination from the rotary pump (RP), another liquid nitrogen trap (LN2) was also used. (5) To minimize the leakage, the pressure reservoir and the sample cell are connected with using a metal gasket face seal. Gaskets with 0.5 μm-filter are used at the sample cell and the pressure transducer to avoid the entrainment of carbon particles.

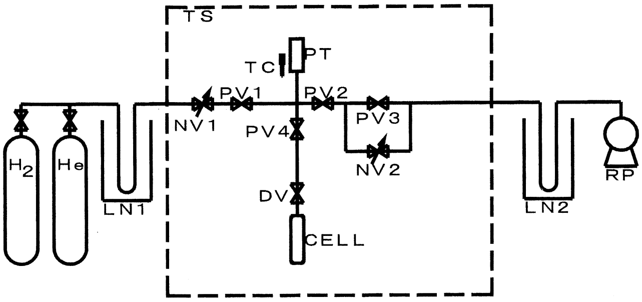

Fig. 1. Schematic diagram of the volumetric apparatus. TS, air thermostat; PT, pressure transducer; TC, thermocouple; PV1–4, pneumatic valves; NV1–2, needle valves; DV, diaphragm valve; CELL, sample cell; LN1–2, liquid nitrogen traps; RP, rotary pump.

### 2.3. Leak test and calculation of the cell volume

No real high pressure tubing can avert the leakage. It is necessary to assess the leak rate properly for the precise measurement. The system with an empty sample cell was charged with hydrogen to a certain initial pressure $p_0$ and left still. The pressure of the system was monitored for 10–20 h. Thus obtained pressure profiles were fitted to an exponential decay function, $p(t)/p_0 = \exp(-kt)$ where $k$ is the leak rate. We found the leak rate $k$ was always less than $10^{-8}$ $\mathrm{s^{-1}}$ when the sample cell was connected firmly. This leak rate was negligible for short time measurement (less than 1 h for each step of equilibration). For long-time measurement, such as a 20-h exposure to high pressure gas, we can know whether or not the material is adsorbing gas by observing the decay rate and comparing it to the leak rate determined above.

The volume of the empty sample cell $V_{\mathrm{cell}}$ is determined as follows. The same procedure is followed in case of the adsorption measurement of the sample in order to cancel out the systematic error. (1) Evacuate the system to obtain the zero-offset of the pressure transducer. (2) Close the valve PV4 and the pressure reservoir is charged with either hydrogen or helium to an initial pressure $p_{\mathrm{i}}$. (3) Open the valve PV4 and equilibrated. The final pressure of the system $p_{\mathrm{f}}$ is obtained. The cell volume $V_{\mathrm{cell}}$ is calculated by solving the equation $n(p_{\mathrm{i}}, V_{\mathrm{res}}, T) = n(p_{\mathrm{f}}, V_{\mathrm{res}} + V_{\mathrm{cell}}, T)$ where $n(p, V, T)$ is the molar number of the gas given by a mechanical equation of state. In the present study we used the 32-term modified Bennedict–Webb–Rubin equation of state for which the up-to-date parameters and program source code for the PC are provided by the National Institute of Standards and Technology (NIST), USA [27].

In Fig. 2, we show thus calculated cell volume at $T$ $(°\mathrm{C}) = 35$ as well as that calculated by the ideal gas approximation. As clearly shown in the figure, you cannot treat helium as an ideal gas, let alone hydrogen, at this pressure range, otherwise a huge error ensues. Ideally, the empty cell volume should be independent from the pressure so long as the expansion by pressure is ignored. The calculated empty cell volume even with using the equation of state is still slightly dependent on the pressure and on the gas. This 'apparent' dependency on the pressure, which must arise from miscellaneous causes, leads to a sys-

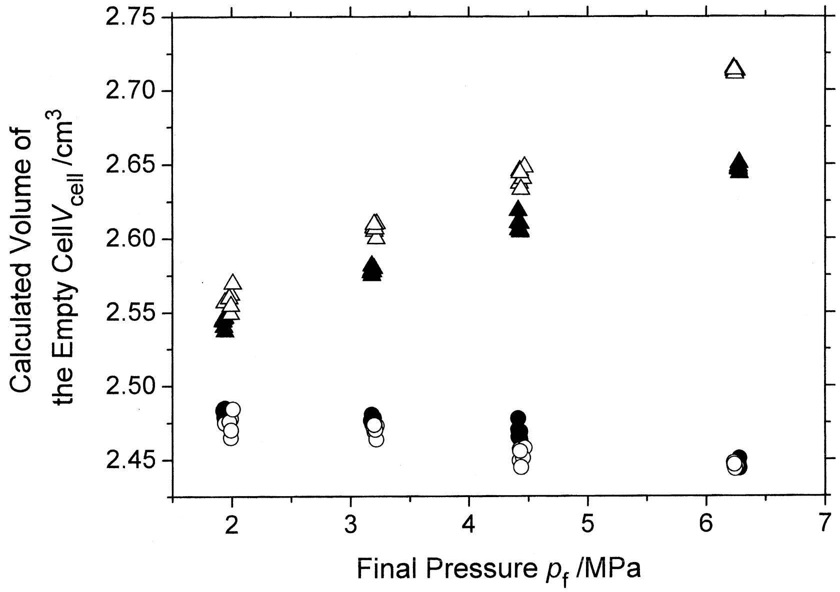

Fig. 2. Calculated 'apparent' volume of the empty cell. Open and filled symbols are of hydrogen and of helium, respectively. Triangles and circles are calculated by the ideal gas approximation and by an equation of state of the gas, respectively.

tematic error and thus was taken into account when the amount of adsorption is calculated.

### *2.4. Adsorption–desorption measurement*

As mentioned above. the procedure to determine the amount of adsorption of a gas on the sorbent is the same as in the case of cell volume determination. In order to make sure that the accumulation of the error was not occurring, we did not apply the step-by-step method for adsorption measurement, i.e. instead of changing the pressure step-by-step and summing up the amount of adsorption at each step [23–26], we evacuated whole the system every time for each point of pressure. The amount of adsorbed gas is calculated with using the volume of the void space of the cell which is given by $V_{cell} - v_{smp}$, where $V_{cell}$ is the apparent volume of the empty cell (see the previous section) and $v_{smp}$ is the volume occupied by the sample. For desorption measurement we applied the step-by-step method. Unlike the adsorption measurement, this is the only way for desorption to be carried out with this apparatus. As is shown later, however, the desorption isotherm coincides well with that of adsorption so long as the materials used in this article are concerned: the accumulation of the error is negligible.

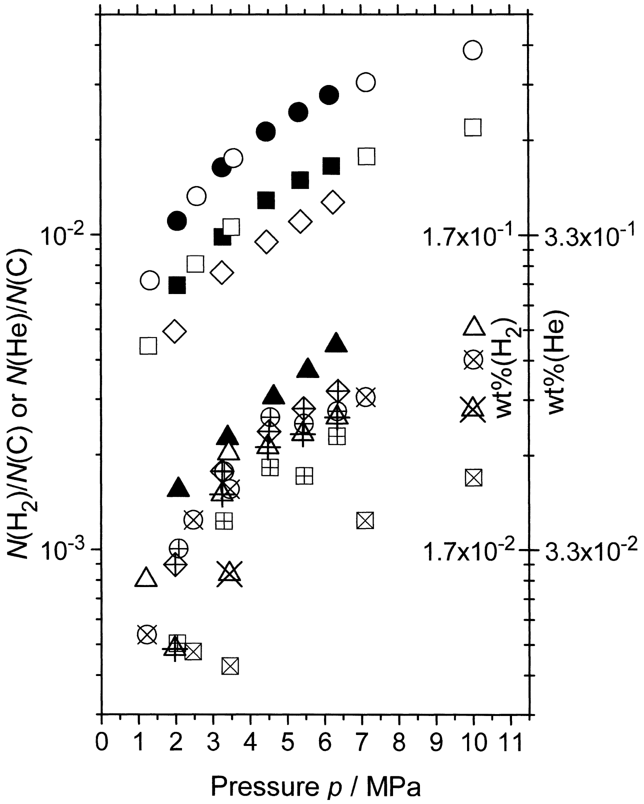

Fig. 3. Result of adsorption and desorption measurement at 35°C. Molar ratio $N(H_2)/N(C)$ and weight percentages wt.%($H_2$) and wt.%(He). Squares, circles, diamonds and triangles are respectively represent Norit Darco, Maxsorb, Pt loaded activated carbon and carbon nanofibers. Filled and open symbols are respectively, adsorption and desorption of hydrogen and symbols with + and × are respectively, adsorption and desorption of helium.

## 3. Result and discussion

The result of the adsorption–desorption measurement carried out at 35°C is shown in Fig. 3. Though we do not claim that all the findings are quite new (see, for example, Refs. [4–9]), you can see some interesting features. (1)

The amount adsorbed and desorbed is significantly larger for hydrogen than for helium. (Notice the logarithmic ordinate.) This means that there are some sites on the carbon material where the hydrogen molecules can be pressed together but not the helium. (2) Comparing the result of Maxsorb and Norit, you can see the difference in the surface area is clearly reflected by the amount of adsorption–desorption of either gas. (3) The coincidence between adsorption and desorption capacities indicates these processes are reversible for these materials. (4) The vapor grown carbon nanofibers in the present study neither adsorbs nor desorbs hydrogen as much as activated carbons do. Enhancement of capacity by Pt particles is not observed in this study. (5) The scatter of data below the molar ratio of $10^{-3}$ indicates the precision of this apparatus lies around this level. Since about 500 mg of sample was used in the present study, this means that our apparatus can detect about $10^{-5}$ mol of adsorption and desorption.

As Gupta et al. suggested, some material may adsorb or start to adsorb hydrogen when the reaction takes a long time [21]. We exposed the vapor grown carbon nanofibers under 10 MPa of hydrogen at 35°C for 24 h and observed the decay rate of the pressure to see if it happened. However, the observed decay rate $k$ was less than $10^{-8}$ $s^{-1}$ (the normal leak rate of the apparatus, see Section 2.3) and therefore showed no adsorption.

We conclude that the volumetric apparatus and the procedures described in the present article provides an accurate adsorption and desorption measurements on carbon materials. Exploration into the synthesis and characterization of a variety of carbon materials which can be applied for the hydrogen storage is now under progress and will be described elsewhere.

## References

[1] A. Chambers, C. Park, R.T.K. Baker, N.M. Rodriguez, J. Chem. Phys. B102 (1998) 4253.
[2] A.C. Dillon, K.M. Jones, T.A. Bekkedahl, C.H. Kiang, D.S. Bethune, M.J. Heben, Nature 386 (1997) 377.
[3] P. Chen, X. Wu, J. Lin, K.L. Tan, Science 285 (1999) 91.
[4] C. Carpetis, W. Peschka, Int. J. Hydrogen Energy 5 (1980) 539.
[5] J.S. Noh, R.K. Agarwal, J.A. Schwarz, Int. J. Hydrogen Energy 12 (1987) 693.
[6] K.A.G. Amankwah, J.S. Noh, J.A. Schwarz, Int. J. Hydrogen Energy 14 (1989) 437.
[7] R. Chahine, T.K. Bose, Int. J. Hydrogen Energy 19 (1994) 161.
[8] S. Hynek, W. Fuller, J. Bentley, Int. J. Hydrogen Energy 22 (1997) 601.
[9] M.A. Wōjtowicz, B.L. Markowitz, W.W. Smith, M.A. Serio, Int. J. Soc. Materials Eng. Resorces 7 (1999) 253.
[10] Ch. Nützenadel, A. Züttel, D. Chartouni, L. Schlapbach, Electrochem. Solid-State Lett. 2 (1999) 30.
[11] Ch. Nützenadel, A. Züttel, Ch. Emmenegger, P. Sudan, L. Schlapbach, in: D. Tománek, R.J. Enbody (Eds.), Science and Application of Nanotubes, Kluwer Academic/Plenum, New York, 2000, p. 205.
[12] Ch. Nützenadel, A. Züttel, L. Schlapbach, Electrochemical storage of hydrogen in carbon single wall nanotubes, Electronic properties of novel materials, in: H. Kuzmany, J. Fink, M. Mehring, S. Roth (Eds.), Science and Technology of Molecular Nanostructures, American Institute of Physics, Melville, New York, 1999, pp. 426.
[13] A. Züttel, Ch. Nützenadel, Ph. Mauron, Ch. Emmenegger, P. Sudan, L. Schlapbach, A. Weidenkaff, T. Kiyobayashi, S. Orimo, Proc. EuroCarbon 9, Berlin, 2000.
[14] S.M. Lee, K.S. Park, Y.C. Choi, Y.S. Park, J.M. Bok, D.J. Bae, K.S. Nahm, Y.G. Choi, S.C. Yu, N. Kim, T. Frauenheim, Y.H. Lee, Synth. Metals 113 (2000) 209.
[15] S. Orimo, G. Majer, T. Fukunaga, A. Züttel, L. Schlapbach, H. Fujii, Appl. Phys. Lett. 75 (1999) 3093.
[16] C. Liu, Y.Y. Fan, M. Liu, H.T. Cong, H.M. Cheng, M.S. Dresselhaus, Science 286 (1999) 1127.
[17] H.M. Cheng, C. Liu, Y.Y. Fan, F. Li, G. Su, H.T. Cong, L.L. He, M. Liu, Z. Metallkd. 91 (2000) 306.
[18] R.T. Yang, Carbon 38 (2000) 623.
[19] C.C. Ahn, Y. Ye, B.V. Ratnakumar, C. Witham, R.C. Bowman Jr., B. Fultz, App. Phys. Lett. 73 (1998) 3378.
[20] Y. Ye, C.C. Ahn, C. Witham, B. Fultz, J. Liu, A.G. Rinzler, D. Colbert, K.A. Smith, R.E. Smalley, Appl. Phys. Lett. 74 (1999) 2307.
[21] B.K. Gupta, O.N. Srivastava, Int. J. Hydrogen Energy 25 (2000) 825.
[22] A. Sieverts, Z. Phys. Chem. 60 (1907) 129.
[23] K. Nomura, S. Ono, K. Kōgaku, Chem. Eng., Soc. Chem. Eng. Jpn. 49 (1985) 630, (in Japanese).
[24] K. Oguro, A. Kato, H. Suzuki, H. Miyamura, E. Ishii, Bull. Gov. Res. Inst. Osaka 38 (1987) 28, (in Japanese).
[25] K. Nomura, E. Akiba, Y. Ishido, H. Hayakawa, S. Ono, J. Nat. Chem. Lab. Indust. 85 (1990) 89, (in Japanese).
[26] Japanese Industrial Standards Committee, Method of determining the PCT relations of hydrogen-absorbing alloys JIS H 7201 (1991) (in Japanese).
[27] National Institute of Standards and Technology, NIST Standard Reference Database No. 12, Thermophysical Properties of Pure Fluids, Version 3.0, Standard Reference Data Program.