PECULIARITIES IN EXPERIMENTAL INVESTIGATION OF HYDROGEN-SORPTION CHARACTERISTICS OF CARBON NANOMATERIALS

**Pishuk V.K., Savenko A.F., Bogolepov V.A., Lototsky M.V.,
Schur D.V., Shaposhnikova T.I.**
Institute for Problems of Materials Science of NAS of Ukraine,
3 Krzhizhanovsky str, Kiev, 03142 Ukraine

Introduction

The interest of the world society in using hydrogen as universal synthetic fuel and energy carrier both for stationary and mobile applications has been intensified recently. Such an approach to solving energetic and ecological problems of our civilization is conditioned by plenum of sources of raw materials for hydrogen production, hydrogen power-consuming, technological flexibility and safe processes of energy conversion using hydrogen with respect to environment.

Hence the development of effective methods for compact hydrogen storage is the key problem of its utilization. The successful solution should be based on reliable experimental data. Therefore, before creating the experimental setup and developing the procedure for performing hydrogen-sorption investigations, authors have made thorough and fundamental analysis of methods for hydrogen storage including in metal-hydrides and carbon nanomaterials. The analysis has revealed peculiarities and defined the main technical parameters and conditions to which the modern experimental setup to measure hydrogen-sorption characteristics of carbon materials must meet.

Carbon nanomaterials as hydrogen storage

We rest our hopes upon carbon nanomaterials, fullerenes, carbon nanofibers and carbon nanotubes, and also their compositions with hydride-forming metals and alloys for their applications as hydrogen storage matrixes.

According to [1, 2], the amount of hydrogen stored by carbon nanomaterials considerably varies in the reports of different authors. In the number of cases the amount of hydrogen absorbed by carbon nanomaterials meets and significantly exceeds the requirements to this class of materials of US Energy Department [3]. The reason for the discrepancy is the absence of reliable methods for producing pure single-wall carbon nanotubes and graphite nanofibers, and also standard procedures for their characterization, for example, by the purity, the degree of “openness”, the diameter of nanotubes, the value of interlayer spacing and the amount of metal catalysts. Moreover, the preliminary treatment of carbon nanomaterials and the purity of hydrogen in use affect considerably hydrogen-sorption capacity. For this reason the results obtained in studying hydrogen sorption characterize only some particular materials and they cannot be still used to compare sorption efficiency of carbon nanomaterials of different types. The mechanism of extremely high hydrogen capacity of carbon nanomaterials is also unclear.

Nevertheless, high hydrogen capacity of new carbon nanomaterials, as we believe, is realistic. Moreover, carbon nanotubes are inert in environmental conditions, and adsorption heat of H_2 on carbon nanotubes is considerably lower than heat of formation of metal hydrides. This allows us to hope to use carbon nanomaterials in real systems for hydrogen storage.

Besides the difference in structures of materials studied by different authors and in experimental conditions (such as pressure, temperature), the sources of such a large distinction could be in the procedures of conducting measurements and further data processing.

Usually hydrogen-sorption capacity is measured volumetrically on the setups of the Siverts type. This standard method is quite precise until we operate with the samples from hydrogen-sorbing materials with certain density. In the opposite case, especially if the specific density is low, uncertainty of the value may contribute seriously the error in the determined hydrogen-sorption capacity.

Considering the close measuring system having the volume V with hydrogen at the temperature T and under the pressure P, we obtain the equation to determine hydrogen-sorption capacity

$$C_H = \frac{\Delta n}{m} + \frac{P}{ZRT}\frac{1}{\rho},$$

where m – mass of a sample, Δn – difference between the number of gas moles in the empty volume and in the volume with a sample, ρ - specific density, Z = Z(P, T) – compressibility factor for gaseous hydrogen, R – gas constant.

The above equation shows that when specific density is low, even insignificant decrease in the density of material may cause the considerable error in C_H determined (Table 1).

Table 1. The value of $\frac{P}{ZRT}\frac{1}{\rho}$, cm^3 H_2/g STP, and its deviation caused by density change by 10%.

ρ, g/cm^3	P=20 bar; T=300 K		P=20 bar; T=77 K	
	value	deviation	value	deviation
8.0	2.2	0.2	9.1	1.0
2.5	7.1	0.8	29.0	3.2
1.3	13.7	1.5	55.7	6.2
0.5	35.5	3.9	144.9	16.1
0.3	59.2	6.6	241.5	26.8

Hence the error in the hydrogen-sorption capacity determined may be too large especially at low temperatures.

Therefore, a special attention should be paid to the calibration accuracy of volumes (especially when the change of the volume is caused by the sample introduced into the system of volumes) in the course of volumetric measurements of hydrogen sorption in carbon nanomaterials.

Experimental setup to measure hydrogen-sorption characteristics

The setup that was manufactured on the base of performed evaluative calculations and analysis of literature is designed for investigation of hydrogen-sorption characteristics, mainly carbon materials and composites on their base with low specific density, by the volumetric method at 0.01-16 MPa H_2 and the temperatures beginning from the boiling point of liquid nitrogen to heating up to 500°C (Fig.1).

Fig.1. General view of the setup to investigate hydrogen-sorption properties.

Constructively, this design is a gas system of high pressure. It consists of distribution pipelines, the main manifold and the manifold of low pressure, two buffer capacities for branching fault of gas, the reactor with the heating system.

The metal-hydride unit for hydrogen storage and compression for 200 l of gas has been manufactured and is used to produce hydrogen of high purity. The unit provides the controlled letting-to-gas at a pressure up to 16 MPa.

The volume of the empty reactor and the volume of connecting systems of capillary pipelines have been carefully determined by letting-to-hydrogen from the calibrated system-defined volume. The mean square deviation corresponding the error in the volume determined is less than ±0.01 cm^3. The volume of the empty reactor with the capillary pipeline is 9.5 cm^3. Control over pressure is performed using diaphragm pickups of high (to 16 MPa) and low (to 1.6 MPa) pressure in order to bring operating pressure to the upper level of the measurement range. The accuracy of measurements is 0.15%. The selected pressure transducers allow the easy integration into the control system. The temperature regime in the reactor is provided for the furnace in which the heating regime is set and controlled by the precision program controller RIF-101. The control over temperature of the sample inside the reactor and the heating element in the furnace is realized using thermocouples accurate to ±1°C. Low-temperature measurements are carried out by immersing the reactor in the Dewar vessel with liquid nitrogen (T=77 K). The vacuum system has been assembled on the base of the universal vacuum station VUP-5. The meterages are processed by the Agilent interface unit. The program of investigations is given by PC. Scanning and data processing are performed automatically.

Conclusions

The setup designed at Institute for Problems of Materials Science of NAS of Ukraine for investigations of hydrogen-sorption properties completely meets the modern requirements for the experimental equipment of this class. The setup makes it possible to investigate hydrogen-sorption characteristics of different materials including nanocarbon structures with low specific density by the volumetric method at 0.01-16 MPa H_2 and in the temperature range of –180°C – 500°C. The setup provides the sufficient degree of accuracy.

References

1. Tarasov BP, Gol’dshleger NF, Moravskiy AP, Uspekhi Khimii, 70; Vol. 2: 149 (2001) *(in Russian)*.
2. Trefilov VI, Schur DV, Tarasov BP, Schul’ga YuM, Chernogorenko AV, Pishuk VK, Zaginaichenko SYu. Fullerenes – Background of Materials of the Future. – K.: ADEF-Ukraine. – 2001. – 148 p *(in Russian)*.
3. A Multiyear Plan for the Hydrogen R&D Program. Rationale, Structure, and Technology Roadmaps, Office of Power Delivery, Office of Power Technologies, Energy Efficiency and Renewable Energy, U.S. Department of Energy, August 1999.

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