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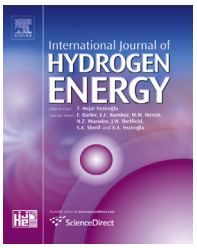

Experimental set-up for investigations of hydrogen-sorption characteristics of carbon nanomaterials

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ABSTRACT

The set-up for investigations of hydrogen capacity of materials has been created. It completely meets the modern requirements for the experimental equipment of this class. The set-up design makes it possible to investigate hydrogen-sorption characteristics of different materials with low specific density, including nanocarbon structures and composites on their basis, by the volumetric method in the pressure range between 0.01 and 16 MPa H_2 and at temperatures from 77 K to 1273 K. It is equipped with a metal-hydride unit for hydrogen storage/compression. The design and service conditions of this device are discussed.

Introduction

As we noted in our work [1] and many authors of others papers [2–15], currently increasing deficit of hydrocarbon fuels caused by depletion of their natural resources is responsible for instability in the advancement of the world economics. In addition, ecological problems related to the harmful effluents from burning hydrocarbon fuels gain momentum and become a global problem. Therefore, the interest in using hydrogen as universal synthetic fuel and energy carrier both for stationary and mobile applications has been intensified worldwide. Such

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an approach for solving problems of our civilization is conditioned by plenum sources of raw materials for hydrogen production, high energy capacity of hydrogen, technological flexibility and safe processes of energy conversion using hydrogen with respect to environment. Hydrogen storage is clearly one of the key issues in developing hydrogen economy.

Hydrogen is the lightest of known substances and therefore certain difficulties appear in solving problems of its storage in small containers. At the same time, the value of specific energy capacity of hydrogen per unit weight is much higher compared to the other natural or synthetic fuels and in its utilization environmental pollution is minimum. The chief drawback of hydrogen is too low specific energy capacity per unit volume because in the normal conditions hydrogen is in a gaseous state and has very low boiling and critical points. At the room temperature and atmospheric pressure one gram of gaseous hydrogen occupies 11 L and an electric car with fuel cells should store about 33,000 *l* of gaseous hydrogen that provide 100 km run [2]. Hence, the development of effective methods for compact hydrogen storage is a key problem of its use.

A successful solution of this problem should be based on the reliable experimental data. Therefore, before creating an experimental set-up and developing a procedure for performing hydrogen-sorption studies, authors have made thorough and fundamental analysis of methods for hydrogen storage including in metals, chemical or complex hydrides and carbon nanostructures. Carbon materials such as activated carbons, carbon nanotubes and carbon nanofibers have been the subject of intensive research. Investigation on hydrogen storage in carbon materials has been dominated by announcements of high storage capacities in carbon nanostructures. The analysis has revealed peculiarities and defined the main technical parameters and conditions which the modern-day experimental set-up for measurements of hydrogen-sorption characteristics of carbon materials must fully meet.

Hydrogen storage in carbon nanomaterials

After the discovery of fullerenes, the scientific community has been taking an active interest in peculiarities of the fullerene formation and structure, physical and chemical properties. The fourth allotropic modification of carbon (fullerene) is unique molecule having a spatial structure with icosahedral symmetry and showing distinctive properties in interaction with other substances. Under certain conditions fullerenes can accept and donate hydrogen atoms to form hydrofullerenes.

Peculiarity of the fullerene molecule formation also reveals itself in a fullerite crystal structure. Cubic crystal lattices of fullerites and hydrofullerites behave like those of different metals and alloys. Fullerene molecules are distributed in the lattice sites while atoms of elements are distributed in the octa- and tetrahedral interstitial sites forming the interstitial solid solutions. Fullerene molecules substitute each other in the sites of lattice and form the substitution solid solutions. Forming exo- and endocompounds, fullerene molecules that are in the lattice sites can change considerably the properties of crystal, whereas its crystalline structure remains unchanged.

Researchers all over the world have concentrated attention to the unusual hydrogen-sorption behavior of fullerenes [3–25]. Theoretically, the prospects for application of the new materials as a hydrogen storage are sufficiently optimistic. In the case when one hydrogen atom is added to each carbon atom (what is quite possible), there appears a possibility to prepare a sorbing matrix based on these materials. The matrix allows the accumulation of 7.7 wt.% of hydrogen.

This index meets and exceeds the requirements for this class of materials (DOE, Energy Departments, USA [25,26] and requirements of other international organizations).

Therefore a search for the method of conducting the reversible and complete reaction

$$C_x + \frac{x}{2}H_2 \leftrightarrow C_xH_x, \quad \text{where } x = 60,\ 70,\ 72,\ 84, \tag{1}$$

with consideration for peculiarities in the structure and properties of the materials would allow their use as sorbents to accumulate and store hydrogen in many fields of engineering and technology. As it is known, the absence of this class of materials retards a wide application of hydrogen as a universal fuel and an energy carrier.

Other carbon nanomaterials, such as single-wall carbon nanotubes (SWNT), graphite nanofibers (GNF) and their modifications doped with metals are reasonably promising for hydrogen accumulation. The generalized results on hydrogen-sorption capacity of SWNTs and GNFs (Table 1) point to that fact [27–29]. For clearness and analysis, the data on hydrogen store in metal-hydrides (MH) are given in the [30–36].

In a number of cases the amounts of hydrogen absorbed by carbon nanomaterials far exceed the values required for the mobile systems of hydrogen storage although different researchers report considerably different results on the amounts of hydrogen accumulated by these materials. The reason for this discrepancy is the absence of reliable methods of production of pure SWNTs and GNFs as well as universally accepted procedures for their characterization, as an example, by purity, a degree of "opening", diameters of nanotubes, interlayer spacing and amounts of metallic catalysts. In addition, hydrogen-sorption capacity is greatly affected by the preliminary treatment of carbon nanomaterials and the purity of hydrogen in use. For this reason, the data on hydrogen sorption describe only some particular materials and cannot be still employed to compare sorption efficiency of carbon nanomaterials of different types. The mechanism of this

Table 1 – The values of $(P/Z\,RT)\,(1/\rho)$, $cm^3\ H_2/g$ STP and the deviations caused by the change in the density of 10% [37].

ρ, g/cm³	P = 2 MPa; T = 300 K		P = 20 MPa; 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

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