Materials and systems for hydrogen storage in the connected state

Tarasov B. P., Dr., Head of Laboratory
Institute of Problems of Chemical Physics of the Russian Academy of Science, Chernogolovka, Russia
E-mail: btarasov@icp.ac.ru

Search of the new materials capable reversibly in a wide interval of temperatures and pressures to absorb the molecular hydrogen is one of the major problems of hydrogen chemistry, hydrogen energy and technology. Such materials are perspective for the organization of technically and economically effective method of storage and transportation of hydrogen, in preparative chemistry, for maintenance with a feed of low-temperature fuel cells, in systems of isolation and purification of hydrogen, in thermo sorption compressors and thermal pumps.

As a result of long-term researches in Laboratory of hydrogen storage materials the intermetallic compounds, alloys and composites are developed, which absorb reversibly and selectively significant amounts of hydrogen, are propose the compositions for hydrogen storage with regulation of pressure of hydride dissociation and the techniques of obtaining high-pure hydrogen by selective sorption of it from various gas mixtures.

In the field of research of carbon nanomaterials in Laboratory the techniques of synthesis of fullerenes, one-wall, two-wall and multiwall carbon nanotubes and different types of carbon nanofibres are developed. Techniques of fullerite hydrogenation are proposed and chemical transformations in fullerene − metallic phase − hydrogen system are investigated. It is shown, that the quantity of hydrogen adsorbed by nanotubes and nanofibres at pressure of 100 atm and temperature of 25°C does not exceed of 1 wt. %, and at temperature of -196°C – 3.5 wt. %, and depends on their diameter. Techniques of plating of metallic clusters on carbon nanostructures are developed. It is shown, that such materials are effective catalysts of hydrogenation of organic compounds and the oxidation-reduction processes occurring in fuel cells.

At research of polymetallic composites it is shown, that hydrogenation speed of eutectic alloys of magnesium with nickel and REM increases with reduction of the magnesium sizes, and at the first stage the REM hydride is formed only. Hydrogenation process of the eutectic alloys of magnesium subjected to equal channel angular pressing is investigated and is shown, that such preliminary treatment of alloys essentially improves their hydrogen-accumulating characteristics. Techniques of hydrogen-accumulating polymetallic composites formation are developed. It is shown, that pseudo-alloys "Mg-REM-Ni" obtained of high-dispersed powders of hydrides are better hydrogenated, than cast alloys, and small additives of easily forming hydride intermetallic compounds essentially improve dynamics of hydrogenation of magnesium alloys. The special attention is given to questions of activation by mechano-chemical treatment and modification of metal hydrides, in particular of magnesium and aluminium hydrides, by additives of hydrides and amides of metals. It is established, that under identical conditions of composite preparation the decomposition temperature of phase AlH_3 decreases depending on composition of additives in a number: VH_x − MgH_2 − LiH − $LiAlH_4$ − TiH_2.

The formation techniques of metal-hydride − carbon composites on the basis of hydrides MgH_2 and AlH_3 and various carbon materials are developed. It is shown, that mechanical activation of MgH_2 mixtures with carbon materials leads to decrease in dehydrogenation temperature and to increase of repeated hydrogenation speed. The opportunity of system MgH_2—C use for creation of hydrogen accumulators of repeated action is revealed. Laws of mechanical activation influence on kinetic

parameters of thermal decomposition of AlH_3 and composites on its basis are certain. That can be used for regulation of temperature and speed of hydrogen isolation from generators on the AlH_3 basis.

The interaction of magnesium hydride with water, water solutions of inorganic and organic acids and solutions of acid salts is in detail investigated. It is shown, that the treatment in a spherical mill increases the MgH_2 activity in interaction reaction with water and acid salts. The carbon introduction at mechanical MgH_2 treatment prevents an agglomeration of MgH_2 particles, promotes additional increase in a surface and interferes with formation of continuous layer of $Mg(OH)_2$ at hydrolysis that can be used at creation of chemical generators of hydrogen.

The hydrogen-accumulating and hydrogen-generating materials developed in Laboratory (tab. 1) are used as working substances at creation of compact hydrogen accumulators of repeated action and chemical hydrogen generators of cartridge type with various operating characteristics.

Table 1. Developed materials for hydrogen storage in the connected state

Reversible hydrides and composites	Hydrogen sorbents	Irreversible hydrides and composites	Metals and hydrides reacting with water
La (Mm) Ni5, Mg2Ni, Mg-Mm-Ni, MgH_2, MgH_2–$LiNH_2$, MgH_2–C	carbon nanotubes, carbon nanofibres, metal-carbon nanocomposites	AlH_3, AlH_3–hydride, AlH_3–Carbon, $LiAlH_4$	Mg, MgH_2, Mg-Al, Mg-Al-Li

For maintenance with a feed of low-temperature hydrogen-air fuel cell the series of metal-hydride accumulators of hydrogen working at a room temperature are specially produced (Fig.1). Besides such hydrogen accumulators are highly effective as a hydrogen source for synthesis of new hydrides, for regulation and creation of a hydrogen high pressure, for preparation of high-pure disperse powders of metals and alloys.

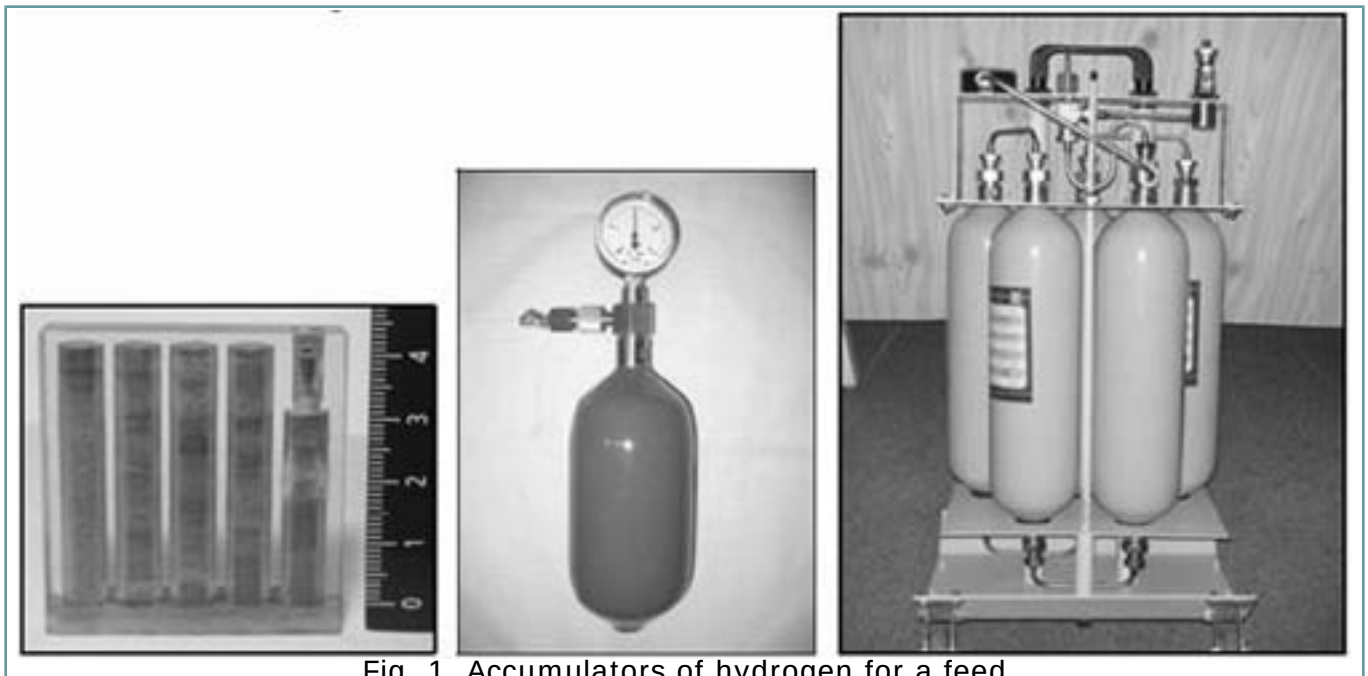

Fig. 1. Accumulators of hydrogen for a feed of fuel cellswith power of 2, 100 and 2000 W

For creation of the metal-hydride hydrogen accumulator on the basis of magnesium alloys the original construction of the container is developed. It represents the tubular case inside of which the heat exchanger on the basis of ribbed pipe for an intensification of heat transfer, limiting dynamics of absorption/desorption of hydrogen by hydride-forming powder is located.

The further efforts of Laboratory are directed on use of the light composite metal-polymeric balloons and search of the new hydrogen-accumulating materials absorbing hydrogen at an ambient temperature and pressure up to 350 atm and isolating it at pressure not less 2 atm at temperature -30°C. Such hybrid system can come nearer to modern requirements to mobile systems of hydrogen storage. Also the big interest for Laboratory search of new hydrogen sorbents with the high specific surfaces represents, which adsorb a significant amount of hydrogen at temperature of liquid nitrogen. Such cryoadsorptive systems will be quite perspective for hydrogen storage. Significant interest composites on the basis of amides and hydrides of the light metals represent also, which contain more 5 wt. % of hydrogen. In sphere of Laboratory interests nanostructured alloys and composites on the magnesium basis remain. Such materials are able reversibly to absorb significant amounts of hydrogen and to eliminate the lacks connected with bad kinetics of hydrogenation, sensitivity to impurities, and propensity to sintering. The investigation of "organic hydrides" (reversibly hydrogenating organic compounds and polymers) and composites "metal-hydride − unsaturated compound" and "metal-hydride − unsaturated polymer" is interestingly also. The application of such materials can reduce technical complexities of hydrogen isolation at low temperatures. It is important to continue works on creation of composites on the basis of the aluminium hydride, containing hydrogen bulk and allocating it at heating up to 180°C. Probably, by modification and making of nanostate it will be possible to overcome the main problem − the difficulty of direct synthesis of aluminium hydride.

Also works on creation of chemical generators of hydrogen on the basis of interaction reaction of metals and hydrides with water will be continued. On potential ability to hydrogen formation at interaction with water and on its quantity on gram of compound, and also in view of density and availability, the most perspective materials are $NaBH_4$, Al, Mg and their hydrides.

The list of the literature

1. Tarasov B. P., Lototskii M. V. Hydrogen energetic: past, present, prospects. // Rossiiskii Khim. Zh. 2006. V. L. No. 6. P. 5 (in Russian).
2. Tarasov B. P., Shilkin S. P. About an opportunity of isolation and accumulation of hydrogen of high purity by means of hydride-forming intermetallic compounds. // Zh. Prikladnoi Khim. 1995. V. 68. No. 1. P. 21 (in Russian).
3. Tarasov B. P. Mechanism of hydrogenation of fullerite−metal compositions. // Zh. Obshch. Khim. 1998. V. 68. No. 8. P. 1245 (in Russian).
4. Tarasov B. P., Goldshleger N. F., Moravskii A. P. Hydrogen-containing compounds of carbon nanostructures: synthesis and properties. // Uspekhi Khimii. 2001. V. 70. No. 2. P. 149 (in Russian).
5. Tarasov B. P., Maehlen J. P., Lototsky M. V., Muradyan V. E., Yartys V. A. Hydrogen sorption properties of arc generated single-wall carbon nanotubes // J. Alloys Comp. 2003. V. 356−357. P. 510.
6. Lukashev R. V., Klyamkin S. N., Tarasov B. P. Obtaining and properties of hydrogen-accumulating composites in MgH_2−C system. // Neorg. Mater. 2006. V. 42. No. 7. P. 803 (in Russian.
7. Tarasov B. P., Lototskii M. V., Yartys' V. A. Problem of hydrogen storage and prospective uses of hydrides for hydrogen accumulation. // Rossiiskii Khim. Zh. 2006. V. L. No. 6. P. 34 (in Russian).