ADVANCED COMPOSITE HYDROGEN STORAGE MATERIALS ON THE BASIS OF NANOSCALE CARBON AND METAL HYDRIDES

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Introduction

The present status of hydrogen energy and technology in the world is characterised by the stable growth rates mainly conditioned by the environment factor. The corresponding activities are mainly financed from state and international public budgets. The Hydrogen Program of the USA Department of Energy (DOE) [1], the Program of International Energy Agency (IEA) [2] and a number of others are the typical examples. Apart from state and non-government public organisations, a number of commercial companies, mainly from the motor-car industry [3] invests the hydrogen energy R&D activities. The main priorities in these investments are hydrogen fuel cells, as well as improvement of existent and creation of new hydrogen storage methods.

Hydrogen storage and transportation is the main problem which restricts its usage, especially in the fields connected to the small- and medium-scale autonomous applications, such as transport or stand-alone energy systems. None of the existing methods of hydrogen storage do not completely satisfy the demands of these applications.

Solid-state hydrogen storage: problems

On the basis of the detailed analysis of the state of the art in hydrogen storage [4], it is possible to conclude that the most promising solutions are in the usage of physical-chemical methods based on the reversible hydrogen interaction with a hydrogen storage material. In this connection, the problem of development of the new H storage materials, whose characteristics (first of all, weight and volumetric hydrogen storage capacities) should satisfy to the contradictory requirements of hydrogen end-consumers to the storage systems, becomes the one of special importance.

The promising method of the solid-state hydrogen storage is based on its reversible absorption – desorption with hydride forming metals and intermetallic compounds. The metal hydride (MH) units can be used not only for very compact hydrogen storage, but also for its extraction from gas mixtures and purification, for the machineless thermo-sorption compression of hydrogen, heat management, as well as for controlled hydrogen supply into fuel cells [5,6]. At the same time, the known up-to-date hydride forming materials have a number of disadvantages. The most commonly used AB_5 and AB_2 intermetallic compounds have too low H sorption capacity (not more than 1.5–2 wt.%). The more weight-efficient (up to 7 wt.% H) magnesium-based MH do require too high temperatures (more than 300 ^oC) to provide required hydrogen output [7,8]. The MH systems on the basis of catalysed alanates [9] have too slow H_2 sorption – desorption kinetics, as well as the low safety caused by the increased chemical activity of the alanates to oxygen and water vapours. Another problem of the MH hydrogen storage units is in their poor dynamic performances caused by low effective heat conductivity of the powdered MH beds. The problem of degradation of hydrogen sorption properties due to the sintering of the MH is actual as well.

The other approach to the creation of the solid-state H storage units is in the usage of recently discovered carbon nanostructures (fullerenes and nanotubes) as hydrogen absorbents [10,11]. In particular, carbon nanotubes and nanofibres were reported to reversibly absorb very significant amounts of hydrogen, around 10 wt.%. However, the available data about hydrogen-sorption capacity of these materials are still yet rather contradictory and have to be specified. First of all, the reliable technique of characterisation of these materials should be developed to clear their application potential as to hydrogen storage. It is also necessary to find the way of controlling the H sorption properties of carbon nanomaterials, in order to fit into the numerous specifications of different consumers.

Proposed solution

We have submitted a Project Proposal #3461 entitled "Advanced composite hydrogen storage materials on the basis of nanoscale carbon and metal hydrides" to the Science and Technology Center in Ukraine (STCU). The main idea of the project is in the creation of the composite materials containing both hydride forming alloys and carbon nanostructures. As it was shown, the addition of hydride-forming intermetallides improves hydrogen-sorption properties both for fullerites [12] and for nanotubes [13]. On the other hand, as it has been recently noted, carbon (graphite) addition to MH alloys significantly improves their heat-conductive performances [14], and, also facilitates the hydriding / dehydriding kinetics, especially in the course of the first hydrogenation [15].

It is known that nanoscale hydride-forming alloys have much better H sorption properties than their micro-scale analogs [16]. However, these materials are thermodynamically unstable, and after several sorption – desorption cycles the H sorption properties return to their starting values characterising the starting materials. It is possible that in the composites containing nanoscale carbon this undesirable effect will be much less pronounced due to surface modification of the metal nanoparticles. In particular, sintering, surface oxidation and other processes worsening H sorption characteristics of the MH will be deferred.

The question about mechanism of improving hydrogen-sorption properties of the nanoscale carbon (as well as about certainty of the available data about high, more than 4 wt.% H, hydrogen-sorption capacity of the corresponding materials) is much less clear. However, as it was fairly noted in some critical works on the subject [17], the single way of such an improvement is in the increase of the affinity of the carbon matrix to hydrogen, i.e. transfer from the mechanism of physical sorption of the H_2 molecules to *chemisorption* mechanism. On our opinion, the presence of the nanoparticles of hydride-forming metals (or their carbides forming interstitial compounds with hydrogen [18]) in the nanoscale carbon is one of the ways to realize such an approach.

The activities under the Project include the detailed studies of structure and hydrogen-sorption properties of micro- and nanoscale powders of hydrogen-sorption alloys of Mg, Ti and V; carbon nanostructures (nanotubes, nanofibres, nanographite) with improved hydrogen-sorption properties; and, finally, the composites made of these materials. For the metal-carbon composites with the highest hydrogen sorption efficiency, the preparation technology will be developed and experimental series (up to 1 kg) will be produced. The obtained material will have H sorption capacity up to 8 wt.% and will be used in the demonstration hydrogen storage unit (storage capacity 100 litres STP) to be developed, created and tested on the final stage of the Project.

The results of the Project are expected to have a notable application potential in hydrogen energy and technology both in and outside Ukraine. The most significant output includes new composite materials "nanoscale carbon - hydride-forming alloy" with a high weight hydrogen sorption capacity fitting into the DOE criteria for mobile hydrogen storage systems. The new composite materials "hydride-forming alloy - nanoscale carbon" with a moderate weight storage capacity, but having a high volumetric hydrogen density (more than 0.1 g/cm^3) and good dynamic performances as to hydrogen sorption / desorption are expected to be the second practically significant output. Both kinds of the developed materials can be used in stationary hydrogen storage systems and other applications like thermo-sorption hydrogen compressors, heat pumps, etc.

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