HYDROGEN STORAGE BY GLASS MICROSPHERES AND OTHERS

Kunihiro Takahashi

Center for Supply Control and Disaster Management, Tokyo Gas Co., Ltd., Tokyo, Japan

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Summary

Based on recently published papers, this article introduces the characteristics, hydrogen storage capacity, and economic advantages of the adsorptive carbon system, zeolite, and glass microspheres as possible methods of hydrogen storage. The adsorbents for hydrogen storage now available on the market are activated carbon and zeolite. In terms of hydrogen adsorption, zeolite can adsorb 1 wt percent or so and activated carbon can adsorb 2 to 2.5 times as much as zeolite.

Improved experimental activated carbon with a greater surface area can adsorb about twice as much hydrogen as that now on the market. Graphite nanofibers as a kind of carbon-based adsorbent are still under study, but it was recently reported that it is at least one order of magnitude more adsorbent than ordinary activated carbon.

Glass microspheres are also still at the R&D stage, and about 4 wt percent is estimated as the capacity for hydrogen storage.

In terms of economy, it is predicted that modified activated carbon will be competitive with other systems, in comparison with compressed hydrogen, liquefied hydrogen, and metal hydride.

1. Introduction

The two key requirements for using hydrogen as a fuel for vehicles or airplane engines are simple storage and transportation. Various methods have been proposed to satisfy

these requirements, such as methods using compressed hydrogen or liquid hydrogen. However, the former needs both compressors and pressure vessels for compression, while the latter needs compressors and cold vessels, thus causing problems of safety, higher cost, and weight.

Methods of hydrogen storage discussed in this article include using the principle that adsorption storage by certain adsorbents having a large surface area increases as the temperature falls and hydrogen pressure rises, and another method of filling gas at a high pressure through microcavities of very fine materials.

In this report, carbon material is used as an example of an adsorbent having a large surface area. Activated carbon and graphite nanofibers are considered with reference to recently published research reports as an interesting possibility. Very fine materials such as glass microspheres of less than 1 mm in diameter and zeolite are also discussed with reference to recent reports.

This article is described mainly based on the literatures listed in the bibliography.

2. Activated Carbon

Activated carbon is a porous solid having a large surface area. When used for hydrogen storage, hydrogen is physically adsorbed into the pores.

The adsorption characteristics of the porous solid depend mainly on pore size, which may be classified into the following three sizes: micro-pores (<2nm), meso-pores (2–5nm) and macro-pores (>5nm).

The action of gas adsorption is limited only to the inside of micro-pores. And the density of the adsorbed phase into the pores is much larger than the density of the unadsorbed gaseous phase. The adsorption capability increases with the amount of micro-pore surface area available. The surface characteristics are also of importance to the adsorption process.

Because the process of hydrogen storage involves physical adsorption into the activated carbon, the storage capacity increases at a lower temperature and under a higher pressure. If pressure continues to rise gradually at a fixed temperature, the adsorption of hydrogen tends to rise with larger pressure. However, this increasing tendency slowly but gradually tapers off. In comparison with zeolite as an alternative commercial adsorbent, the adsorption of H_2 per 100g at 77K and 2MPa is only 1g or so by zeolite, but is 2 to 2.5 times greater by activated carbon.

The micro-pore surface area of commercial regular grade activated carbon is only 700 to 1800m^2g^{-1}, while that of activated carbon produced experimentally by the treatment of potassium hydroxide (KOH) is as high as 3000m^2g^{-1}.

Comparing hydrogen adsorption capacity per unit weight at 77K and 2MPa, one study reported the adsorption capacity of activated carbon treated by KOH is about twice as large as that of regular grade activated carbon. However, the bulk density tends to

decrease as the carbon surface area expands. In this instance, the bulk density of activated carbon treated by KOH is 0.3gcm^{-3}, which is considerably smaller than 0.47gcm^{-3} of commercial activated carbon having a surface area of $1100 \text{m}^2\text{g}^{-1}$.

This comparison means that the modified type of activated carbon is not so advantageous than regular grade carbon simply based on the volumetric hydrogen storage capacity with an increase of only about 25%. Because the modified type requires a complicated, expensive production process, production costs still need to be reduced greatly.

If activated carbon is used for the hydrogen storage system, the total cost is the decisive factor regarding storage conditions because lower temperature and higher pressure necessary for storage will require larger energy consumption. For reference, the following table compares the costs of alternative storage systems, including compressed hydrogen (GH_2, 20MPa), liquefied hydrogen (LH_2), metal hydride (MH_2, $FeTiH_2$) and activated carbon (AC, surface area of $2000 \text{m}^2\text{g}^{-1}$, 150K, 5MPa).

In the table, the calculations assume a storage capacity of 9600MBTU (200MW), and costs are divided largely into utility unit cost (compressor, refrigerator and vacuum pump), storage unit cost (vessel, insulating material and adsorbent) and energy cost (electric power). The result is shown in Table 1.

System	Utility unit	Storage unit	Energy consumption	Total cost ($/Mbtu)
GH_2 (19.6 MPa)	0.77	7.66	2.50	10.93
LH_2	1.21	2.23	14.50	17.94
MH_2 ($FeTiH_2$)	0.57	7.40	5.10	13.07
AC (150 K, 5.3 MPa)	1.98	2.46	2.52	6.96

Table 1. Total cost of storage system.

From Table 1, the use of activated carbon appears to be as competitive as other alternatives in terms of cost, though it may require cooling by liquid nitrogen or refrigeration, in addition to pressurization up to 5MPa.

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Biographical Sketch

Kunihiro Takahashi was born 28 January 1942 in Japan; he graduated from Chemical System Engineering Department, Faculty of Engineering, the University of Tokyo; completed master course with major in engineering, the University of Tokyo; joined Tokyo Gas Co., Ltd.; presently general manager of the Center for Supply Control and Disaster Management, Tokyo Gas Co., Ltd. Previous positions: appointed as a member of General Research Laboratory of Tokyo Gas Co., Ltd. (1967–1977); appointed as general manager of Technical Development Department, general manager of Engineering Department, and general manager of System Energy Department of The Japan Gas Association (1994–1997); appointed as a member of Sub-task-1-committee of WE-NET committee of New Energy and Industrial Technology Development Organization (1994–1997); has held present position since June 1997; studied research themes: research on production processes and catalysts for hydrogen-rich gas and methane-rich gas.