Measurement 56 (2014) 219–230

Contents lists available at ScienceDirect

Measurement

journal homepage: www.elsevier.com/locate/measurement

Evaluation of hydrogen storage capacities on individual adsorbents

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ARTICLE INFO

Article history:
Received 20 May 2014
Received in revised form 23 June 2014
Accepted 10 July 2014
Available online 18 July 2014

Keywords:
Hydrogen
Hydrogen storage
Adsorbents
Capacities

ABSTRACT

Storage of hydrogen is an important component of the hydrogen economy system. Hydrogen must be stored at the production site, as well as at the point of its application. Often, significant part of hydrogen is used directly in the manufacturing process and thus eliminates the necessity of its supply. However, the development of automotive industry and the use of hydrogen for energy production require its storage in order to ensure continuous operation. The need of hydrogen supply itself increases with a use of alternative energy sources. These sources do not allow a constant supply of energy and, as a result, hydrogen serves as an intermediary: an energy carrier. The drawback of its broader application is a low-density storage in conventional pressure and cryogenic tanks, where it is necessary to use high pressures, respectively very low temperatures. Therefore, various types of metal-hydride and adsorption storage tanks are widely tested. Technology of hydrogen adsorption on carbon materials is effective only at cryogenic temperatures and so liquid nitrogen with temperature of 77 K (−196.15 °C) was used for the purpose of lowering the temperature of the storage device. This article discusses the possibilities of use of cryogenic temperatures in the adsorption of hydrogen on materials with broad surface area whereby liquid nitrogen is used to lower the temperature. The method of measuring the amount of adsorbed hydrogen was used to determine and quantify the amount of stored hydrogen.

1. Introduction

Storage of hydrogen is a key issue for building hydrogen technologies and economics of use of this element in the energy and transport [1–4]. Previously designed procedures of pressure and cryogenic storage, however, did not offer the required safety and their implementation would require significant amounts of energy. The transition to metal-hydride and adsorption storage has opened up new possibilities for safer storage, while faced with the problem of compliance with minimum hydrogen storage mass percentage set for optimal use of the value of 6.5 wt.%. A major advantage of hydrogen adsorption storage is high kinetics of adsorption–desorption cycles, cyclic stability and low cost of adsorbent.

Various methods of hydrogen storage show considerable variations in the required parameters. The research of different catalysts and technological processes of manufacturing of tanks compensate this situation. The main objective is to improve conditions of absorption and desorption. It is important to achieve the desired kinetic

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http://dx.doi.org/10.1016/j.measurement.2014.07.002
0263-2241/

processes in order to secure sudden unstable intakes so to prevent an immediate need for a large amount of hydrogen while reducing functionality of the whole system. Choosing a suitable type of storage depends on the purity of stored hydrogen, the ability of the longest possible reversibility as well as on the desorption temperature and economics [5,6].

Adsorption storage is more suitable for mobile tanks, mainly due to the lower weight of carbon materials, which, on the other hand, also reduces the energy content of the stored hydrogen. It is very energy consuming to cool down the storage device to a temperature of 77 K [7–9]. Consequently, it is necessary to replenish the liquid nitrogen to cover losses of nitrogen evaporation caused by the heat flow from the environment. Depending on the quality of the thermal insulation, for every 199.292 kJ of heat received one kilogram (1 kg) of liquid nitrogen evaporates, which represents the specific vaporization heat of hydrogen at the boiling point of 77 K and a pressure of 101.325 kPa. Use of cryogenic temperatures and adsorption agents lead to a large reduction of pressure of stored hydrogen and therefore this method is suitable for its storage.

Objective of further development of storage materials is to achieve maximum of storage capability of hydrogen at the lowest possible weight of the entire equipment, especially for mobile applications. This effort is required for the possibility of using hydrogen in advanced fuel cell research where enhanced performance requires high storage capacities.

Despite significantly low adsorption temperature it is possible to reduce expenses when comparing with use of liquid hydrogen. Cooling with nitrogen is cheaper, more energy efficient and accessible. Storage of hydrogen at a temperature of 77 K is about 20% cheaper than its storage in liquid form [10]. The ability to store hydrogen depends on the size of the absorbent surface, while in powdered form of the adsorbent larger surfaces are attainable. Advantage of the carbonaceous materials is mainly due to their low density, large pore structure and chemical stability.

Adsorption and desorption of hydrogen in the carbon nano-tubes, nano-pored materials as well as in activated carbon materials have little or no hysteresis and have relatively fast kinetics at a temperature of 77 K [11–13].

One of the options to activate carbon, which means to obtain carbon with the maximum micro-porous surface, is it chemical activation. The chemical activation agent could be potassium hydroxide. Coarse powdered carbon grinds together with hydroxide in ball mill. Compound ratio of carbon and hydroxide is from 1:1 to 1:5. The mixture commences warming up in the kiln with speed of 5 K/min until the activation temperature (approx. 1000 K) while using inert argon or nitrate atmosphere. Activation finishes after two hours. The final product is rinsed in distilled water in order to get rid of residual hydroxide. Subsequently, the product is dried at the temperature of 423 K for a period of three hours.

Research of activated carbon has been also directed on the modification of surface of activated carbon fibres using fluorine and nickel. The influence of the fluorine is less significant comparing to one of nickel. The second has not significantly changed the surface dimension of microspores, however the mass amount of hydrogen has changed significantly due to catalytic effects of nickel. Nickel doping was carried out by impregnation of activated carbon fibres using nickel nitrate ($NiNO_3$). The final product after drying was activated carbon called Ni–A15. Compare to activated carbon R-A15 that the Ni–A15 was made of, the new product shows 0.4 wt.% higher hydrogen storage capacity.

In order to determine the amount of stored carbon a measuring apparatus was assembled. It enables to determine desorption curves by measuring the volume of released hydrogen to measuring cylinder. The volume measuring is, in respect to low hydrogen measuring mass, more simple and accurate. Development and significant progress in possibilities of evaluation of an actual adsorption impact on storage capacity increase is done by implementation of relative hydrogen storage mass percentage.

2. Description of the storage apparatus

Because of its significant porosity, the activated carbon is defined by low density that together with expected low storage capability represents relatively small amount of stored hydrogen. Apparatus assembled according to Fig. 1 enables measuring the volume of stored hydrogen and its conversion to relative parameters (101.325 kPa and 0 °C) that is favourable if we take into consideration hydrogen density to relative parameters (0.08993 kg m^{-3}). The central part of the apparatus is thick-walled steel pressure vessel with volume of 10^{-5} m^3. The vessel is filled with adsorbent and the upper part of tube is sealed with foam polyurethane (Fig. 2).

This enables continuous hydrogen flow without exhausting of fine particles. Teflon was used as an insulation material, since it resists the cryogenic temperatures of up to −200 °C. The vessel is submerged in liquid hydrogen that is located in Dewar vessel with volume of 10^{-3} m^3.

The laboratory apparatus measures hydrogen adsorption up to 2 MPa with possibility to lower the temperature in a pressure vessel with activated carbon to −196 °C (77 K). Apparatus consists of a pressure vessel filled with hydrogen under the pressure of 20 MPa and purity of 3.0 (99.9%). Given purity is sufficient for adsorption, because activated carbon is not prone to degrade its storage capacity at certain additions in gas (mainly O_2) as it is at various types of metalhydrides. To lower and regulate the pressure of hydrogen in pressure vessel of max. 2 MPa we use reduction valve FC 2000 5-H-200 conforming to norm EN ISO 2503. The gas distribution is conducted by brass piping MS 63.

Pressure is read with pressure sensor PS100 – 50 BAR (max. 5 MPa) with connection to data logger PS-9302 with option to collect data on the computer. Membrane flux with minimum pressure of 1.8 kPa does the initial system venting with vacuum sample drying. Mass flow meter GCA-C9EA-FA20 does the reading of the hydrogen flow. Graduated cylinder with volume of $2 \cdot 10^{-3}$ m^3 is placed at the end of the mass flow meter. The cylinder controls