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Measurement of Adsorbent Storage Capacities in the Process of Hydrogen Storage at Cryogenic Temperatures

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ABSTRACT

Storage of hydrogen is an important component of the hydrogen economy system. Its broader application is problematic due to a low-density storage in conventional pressure and cryogenic tanks, which requires using high pressures or very low temperatures. Therefore, many kinds of metal hydride and adsorption storage tanks are being tested. The technology of hydrogen adsorption on carbon materials is effective only at cryogenic temperatures, and thus, liquid nitrogen at a temperature of 77 C (-196.15 ° C) was used to lower the temperature of the storage facility.

This article discusses possible applications of cryogenic temperatures in the hydrogen adsorption on a material with a high surface area, utilizing liquid nitrogen to lower the temperature. The method of measuring the amount of adsorbed hydrogen was used to determine and quantify the amount of stored hydrogen.

Keywords: hydrogen, adsorbent, adsorption, cryogenic temperatures.

INTRODUCTION

Hydrogen storage is a key issue in application of hydrogen technologies and evaluating the economy of this element in the power industry and transport. However, the previously proposed methods of pressure and cryogenic storage did not offer the acceptable level of safety, because their implementation would require a significant amount of energy. The transition to a metal hydride and adsorption storage opened up new possibilities for safer ways of storage, whereas the challenge remains to comply with the minimum of the weight percent of hydrogen that a material can store providing optimal hydrogen efficiency value of 6.5 wt.%. A significant advantage of adsorption-based hydrogen storage is a rapid kinetics of the adsorption-desorption cycles, cyclical stability and low purchase costs of an adsorbent.

The selection of the most suitable method of storage depends on the purity of the hydrogen to be stored, the longest possible reversibility, desorption temperature and economics. Adsorption-based storage is more suitable for mobile tanks, mainly due to the lower weight of carbon materials, which, however, reduces the energy content of the stored hydrogen. It is a very energy intensive process to cool down the storage device to a temperature of 77 K. Subsequently, 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 each 199.292 kJ of heat received, one kilogram of liquid nitrogen evaporates, which represents the specific vaporization heat of nitrogen at the boiling point of 77 K and a pressure of 101.325 kPa [1,2,3,4].

Use of cryogenic temperatures and adsorption agents result in significant reduction of pressure of stored hydrogen, and thus this method is suitable for hydrogen storage. The aim of further development of storage materials is to achieve the 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 fuel cells, whose research has advanced, as well as high storage capacities.

In spite of significantly low adsorption temperature, it is possible to reduce the expenses in comparison with use of liquid hydrogen as cooling with nitrogen is more energy efficient, cheaper and available. Storage of hydrogen at a temperature of 77 K is 20% cheaper than its storage in a liquid form. The ability to store hydrogen depends on the absorbent surface area with powdered form of the adsorbent attaining larger surfaces [5,6].

The advantage of carbon materials is mainly their low density, extensive pore structure and chemical stability. Adsorption and desorption of hydrogen in carbon nano-tubes, nano-pored materials as well as activated carbon materials exhibit little or no hysteresis and have relatively fast kinetics at a given temperature.

In order to determine the amount of stored carbon, a measuring apparatus was assembled. The apparatus facilitates determination of desorption curves by measuring the volume of released hydrogen into a measuring cylinder. Thus, measuring of volume is, in respect to low hydrogen measuring mass, simpler and more accurate. Substantial progress in the ways of evaluation of an actual adsorption impact on storage capacity increase is performed by implementation of relative hydrogen storage mass percentage [7,8,9,10,11].

DESCRIPTION OF THE STORAGE APPARATUS

Activated carbon has, due to its significant porosity, lower density, which, together with the expected low storage capability represents a relatively small amount of hydrogen to be stored. The apparatus, as depicted in Figure 1, enables to measure the volume of stored hydrogen and its conversion to relative parameters (101.325 kPa and 0°C) which is favourable taking into account hydrogen density at reference parameters (0.08993 $kg.m^{-3}$).

The essential part of the apparatus is thick-walled steel pressure vessel with the volume of $10^{-5}m^3$, filled with an adsorbent and the upper part of tube is sealed with polyurethane foam.

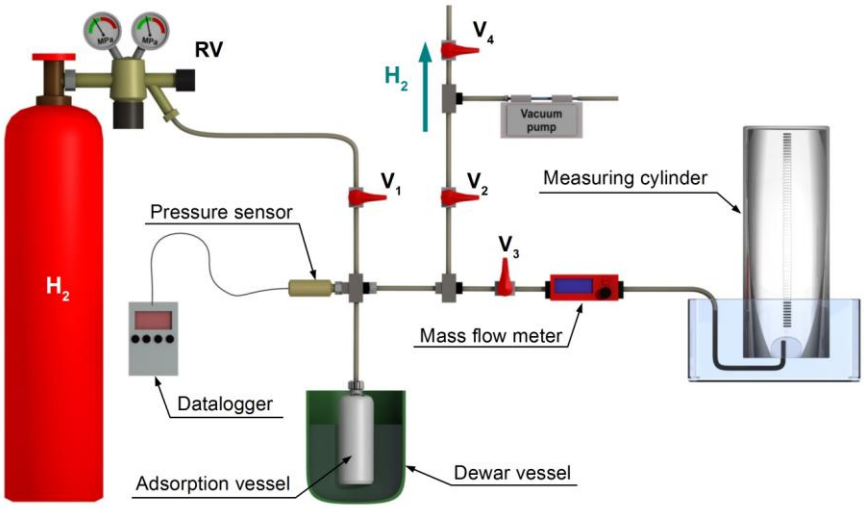

Figure1. *Scheme of the laboratory apparatus designated to determine hydrogen adsorption at cryogenic temperatures by volume measuring.*

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 immerged 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 a possibility to lower the temperature in the pressure vessel with activated carbon to 77 K.

The apparatus consists of a pressure vessel filled with hydrogen under the pressure of 20 MPa and the purity of 3.0 (99.9%) where given purity is sufficient for adsorption as activated carbon is not prone to degrade its storage capacity at certain additions in gas (mainly O_2) as it is the case with various types

of metal-hydrides. To lower and regulate the pressure of hydrogen in the pressure vessel of max 2 MPa, reduction valve FC 2000 5-H-200 conforming to norm EN ISO 2503 was used. 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. A cylinder with the volume of $2 \cdot 10^{-3}$ m^3 is placed at the end of the mass flow meter and controls the volume of released hydrogen. Measuring in graduated cylinder requires knowing the state values in order to calculate the reference conditions. This is why the apparatus has a barometer, which reads the atmospheric pressure.

Safe elimination of air from piping system is realized before each replacement of pressure vessel, or if there is air in the system. Process of making of hydrogen atmosphere is realized in following steps:

1. Suction of the air to absolute pressure of 1.8 kPa using air pump,
2. and subsequent hydrogen filling to the value of 2 MPa,
3. release of gas mixture through exhaust valve V_2 and V_4.

This procedure is repeated at least two times in order to achieve a mixture with the lowest portion of initial air. The advantage of air pump is finishing vacuum drying of the sample. After the hydrogen atmosphere is created at the atmospheric pressure, the pressure vessel is submerged in small Dewar vessel with liquid hydrogen that is transferred there from the storage Dewar vessel. Due to the heat transfer, temperature of the vessel decreases to the temperature of liquid hydrogen 77 K and as the pressure increases, the hydrogen adsorbs to activated carbon.

The valve V 1 closes once the maximum pressure of 2 MPa and stabilized adsorption is achieved. After the valve V_3 is open, the mass volume meter with measuring cylinder is attached in order to measure the volume of released hydrogen.

Subsequently, the pressure in storage vessel decreases as the feeding valve V_3 slowly opens, and evaporated hydrogen is collected in the measuring cylinder. In order to plot curves, measurements of collected hydrogen at 10 different pressure levels are taken. By means of conversion, relation between stored amount of hydrogen and relative mass storage percentage of a given type of adsorption material is obtained.

PREPARATION OF ADSORBENTS

Selected adsorbents used in the measurement of storage capacities were prepared at the Department of Power Engineering at the Faculty of Mechanical Engineering at the TU Košice.

Preparation of Activated Carbon in a Pyrolysis Kiln

Activated carbon (AC) was made by means of chemical activation with potassium hydroxide (KOH) and annealing of AC at various temperatures in the pyrolysis kiln.

Annealing of AC SIL 15 Extra

Activated carbon SIL 15 Extra was milled in a grinding mill and subsequently annealed at 350°C and 700°C.

Chemical Activation of Carbon using KOH

Chemical activation of carbon was done using the activating agent KOH. For the purpose, used black, grinned coal was a source of carbon.

Preparation of Activated Carbon In A Plasma Reactor

The waste is decomposing in the plasma reactor with the power of 10kVA in inert nitrogen atmosphere and at temperature of 1550°C. The by-product of this decomposition is a fine graphite dust – soot used to store the hydrogen.

STORAGE CAPACITY OF ADSORBENTS

Due to problematic calculation of the volume of the storage device together with a distribution piping, an indirect method to estimate the volume was selected, namely, using compressed hydrogen and subsequent calculation of the volume (Figure 2).

The principle of such volume calculation lies in pressurizing the vessel with hydrogen to the level of a running pressure and its consequent release to a measuring cylinder.

By means of volume conversion to relative conditions it is possible to obtain the weight of stored hydrogen in relation to absolute hydrogen pressure. The state equation for apparatus under pressure reads as follows:

$$p_m \cdot V_m = z_m \cdot m \cdot r \cdot T_{H_2} \tag{1}$$

Where: p_m – is absolute pressure (Pa); V_m – is a volume of storage vessel (m^3), m – mass of hydrogen storage (kg), z_m – is a compressibility factor at the pressure pm (-), r – is a specific gas constant of hydrogen ($J \cdot kg^{-1} \cdot K^{-1}$) and T_{H2} is a gas temperature (K). The state equation for gas in a measuring cylinder disregards the compressibility factor due to low pressure ($p_c \sim p_{atm}$) and it reads as follows:

$$p_c \cdot (V_m + V_c) = m \cdot r \cdot T_{H_2-c} \tag{2}$$

Where: p_C the pressure in a measuring cylinder (Pa), V_C - a measured amount of hydrogen in the measuring cylinder (m^3), $T_{H2\text{-}C}$ - a temperature of hydrogen in the measuring cylinder (K). The equation (2) is mathematically correct only if the temperature of a whole system remains constant.

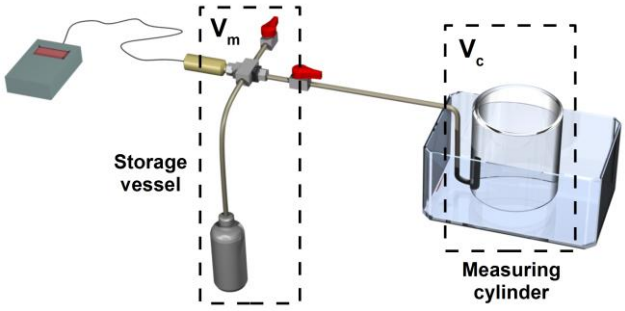

Figure2. *Description of the measuring apparatus*

The measurements take place at the ambient temperature without the use of liquid nitrogen, and thus the condition is met. Since the mass of hydrogen in the system is constant with the valves V1 and V2 closed, both state equations (1) and (2) enable determination of the volume of the storage device as follows:

$$V_m = \frac{p_c \cdot V_c}{T_{H_2-c} \cdot \left(\frac{p_m}{z_m \cdot T_{H_2}} - \frac{p_c}{T_{H_2-c}} \right)} \quad (m^3) \tag{3}$$

Pressure in the measuring vessel is calculated based on the equation:

$$p_c = p_{atm} - h \cdot \rho_{H_2O} \cdot g \qquad (Pa) \tag{4}$$

Where: h is the height of water in a measuring cylinder (m); ρ_{H2O} - is water density (kg · m^{-3}), G - gravitational acceleration (m · s^{-2}). The average value of the pipe volume is $4.7 \cdot 10^{-5}$ m^3.

Figure 3 depicts overpressure – mass of stored hydrogen diagram. Red colour represents average value of three measurements and will serve as a reference curve for measures with adsorbents.

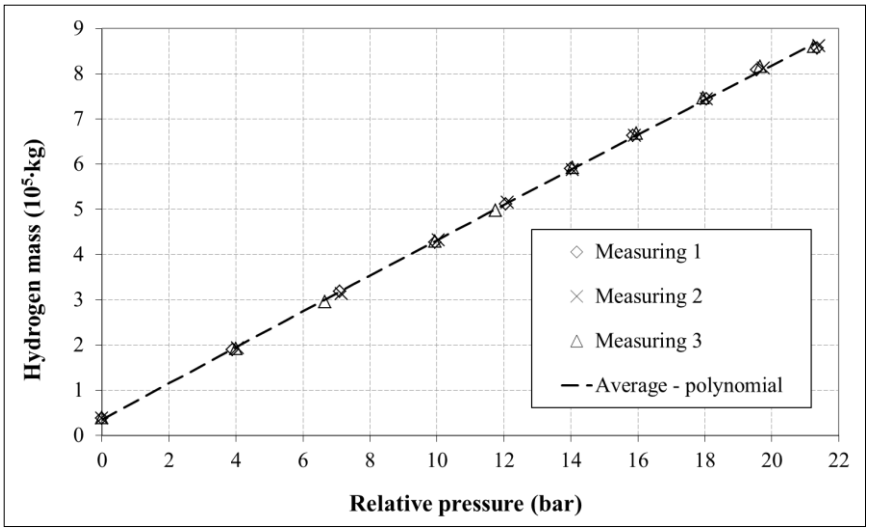

Figure3. *Overpressure – mass of stored hydrogen diagram at the temperature of 293 K without use of adsorbent*

Determination of regression curves of individual measurements, as well as the assessment of a final equation of average curve of three measurements was done in Qti Plot program. This software was developed for analyzing and data processing. A regression curve of a second-degree polynom was chosen for data processing. The final shape of the regression curve measured without use of adsorbent at the ambient temperature is expressed as follows:

$$m_{H_2}^{average} = 3.5071 \cdot 10^{-6} + 4.0206 \cdot 10^{-6} \cdot p_p - 5.218545 \cdot 10^{-9} \cdot p_p^2 \quad (5)$$

Where: is the mass of stored hydrogen (kg) - and p_p is overpressure in the storage vessel (bar).

Determining the Mass of Stored Hydrogen

Conventional procedure to measure the amount of gas stored on absorbents is direct measuring of a sample mass at increased pressure and temperature decrease to 77 K. A disadvantage of such procedure is low hydrogen density, which is, under standard conditions, only about 0.08993 g for a 1 dm^3 of gas.

Volume measuring is thus rendered less complicated, more financially efficient mainly because of lower expenses related to research equipment. Thus, it is more convenient to measure the mass indirectly, by measuring the volume and then recalculating the storage mass percentage at different hydrogen pressures.

The volume of released hydrogen into the measuring cylinder represents the decrease of its volume from storage vessel, which, under normal conditions, is:

$$V_i^{ST} = V_{nn} - V_i + V_m \ (m^3) \quad (6)$$

where: the amount of hydrogen in the storage equipment under standard conditions (m^3) V_{nn} - maximum measured volume at zero overpressure - under normal conditions (m^3), V_i - normal volume of the measuring cylinder (m^3), V_m - volume of the piping system with pressure vessel - under standard conditions (m^3), ($V_m = 4.7 \cdot 10^{-5}$ m^3).

The equation (5) operates standard volumes – hydrogen volume under pressure of 101.325 Pa and temperature of 0 °C. Conversion to V_i and V_{nn} is consequently done based on the relation stemming from the state equation:

$$V_{i,nn} = \frac{\left(p_{atm} - h \cdot \rho_{H_2O} \cdot g\right) \cdot V_{no} \cdot 273.15}{101325 \cdot T_{H_2-c}} \quad (7)$$

Where: V_{no} – is an instant volume measured from the measuring vessel (m^3).
The mass of stored hydrogen is calculated from the state equation of ideal gas, since under atmospheric pressure the compressibility factor equals approximately 1 (z_m = 1.00026).

$$m_i = \frac{p_{nc} \cdot V_i^{ST}}{r \cdot T_{nc}} = \frac{101325 \cdot V_i^{UZ}}{4124{,}49 \cdot 273{,}15} = 0{,}08993 \cdot V_i^{UZ} \quad (8)$$

Where: p_{nc} – is a standard pressure (101.325 Pa) and T_{nc} – is a standard temperature (273 K).

Storage percentage of hydrogen mass (Ψ) is based on a ratio of mass of stored hydrogen (m_i) and mass of weighted adsorbent agent:

$$\psi = \frac{m_i}{m_{AC}} \cdot 100\ \% \quad (\%) \quad (9)$$

Where: m_{AC} – is the mass of the adsorbent agent (kg).

To compare the efficiency of adsorption properties, the following diagrams show relative storage percentage of hydrogen mass Ψ_r, which represents relative increase of adsorption attributes in comparison with use of an empty storage vessel under the same physical conditions.

$$\psi_r = \frac{m_i - m_{H2}^{average}}{m_{AC}} \cdot 100\ \% \quad (10)$$

In case the porous material exhibit low adsorption ability, increased pressure and the absence of the adsorbent's proper volume, the value of Ψ_r could decrease or even reach negative values (this would render the adsorbent unsuitable for hydrogen storage).

Hydrogen Storage on Adsorbents at the Temperature 77 K

Pressure vessel containing the sample was submerged to 2/3 of its height into liquid nitrogen and was sealed with a lid (to prevent nitrogen evaporation). After 10 minutes that are required to balance the temperature of the vessel at 77 K, the experiment was carried out the same way as in case without cooling agent.

The ability to store hydrogen on the absorbent material was also compared with the amount of hydrogen stored in an empty container cooled down to 77 K.

Figure 4 shows comparison of relative volume of stored hydrogen for individual examined materials at the temperature of 77 K. For the purpose of this article, the relative volume is described as volume representing a difference between storage capacities when compared with volume of hydrogen stored with no adsorbent agent.

Activated carbon SIL15 Extra seems to be the most suitable material for hydrogen storage. When annealing at the temperature of 350 °C, slight decrease of the adsorption pressure was observed which correlates with the maximum storing volume.

Optimum pressure for hydrogen storage on activated carbon is 0.8–1.2 MPa at 77 K, which facilitates achieving a maximum storage capacity comparing to an empty pressure vessel.

Higher pressures result in decreasing of storage capacity because adsorption material takes up certain volume in the container at the expense of hydrogen that could be stored there. One kilogram of carbon SIL 15 Extra is able to store approximately 0.063 Nm^3 of hydrogen at the temperature of 77 K and the pressure of 11 bars, which represents 804 kJ of stored energy compared to a vessel with no adsorbent.

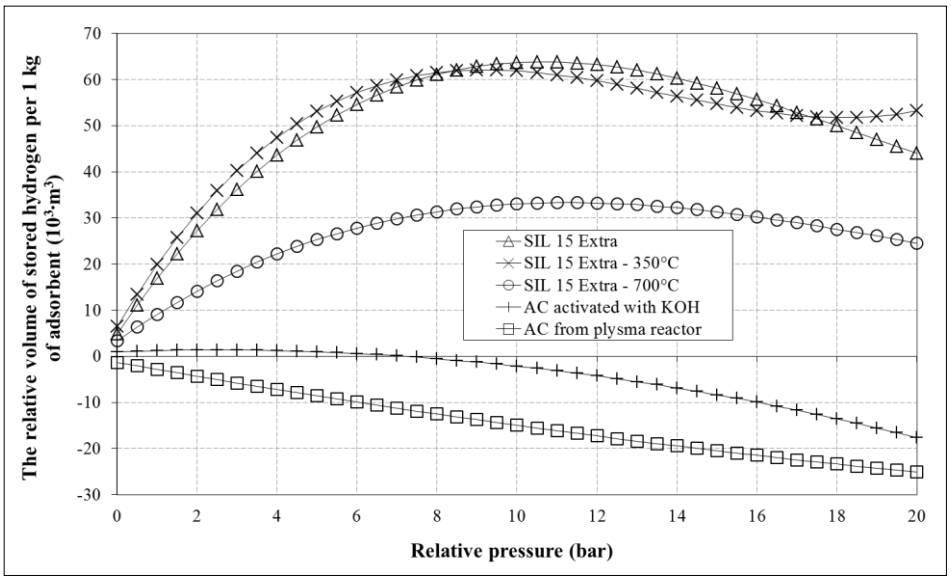

Figure4. *Relative volume of stored hydrogen under standard conditions (101,325 Pa, 273.15 K) per 1 kg of adsorbent at the temperature of 77 K*

CONCLUSION

Activated carbon, as well as other materials with porous surface, allows increasing the amount of stored hydrogen compared to the amount stored in an empty container at the temperature of 77 K. The assumption is fulfilled only in case activated surface of material, and only up to critical pressure, with the individual volume of adsorbent having a significant influence. By increasing pressure above the level of critical pressure, the amount of stored hydrogen decreases when compared to the amount stored in a vessel with no adsorbent agent. Influence of adsorbent volume itself is noticeable also when desorption curves decrease at the pressure values higher than 12 bars.

The experiments reveal that one kilogram of activated carbon SIL 15 Extra is able to store by 804 kJ more compared to an empty vessel cooled to the temperature of 77 K. This type of carbon in its original form, or annealed at 350°C exhibits the most suitable attributes required to store hydrogen.

In case adsorbent agents are used, the amount of stored energy increases, which thus increase the applicability of this technology in practice.

The influence of annealing on adsorption attributes of carbon SIL 15 Extra does not deliver the expected results that assumed increased storage ability.

The research also produced an important finding that, despite relatively high percentage values of hydrogen storage mass per unit of adsorbent mass, the percentage of stored hydrogen is 10 times lower in comparison with an empty vessel cooled down to the constant temperature of 77 K.

Conventional storage mass percentage measured gravimetrically in hydrogen atmosphere at the temperature of 77 K reach 5–6 mass % of stored hydrogen, although the volume of carbon atoms themselves is not taken into consideration. The procedure described in this paper demonstrated that if we take into account the volume of the adsorbent itself, we can take a different view as for the efficiency of given technology in comparison with an empty pressure vessel.

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