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MEASUREMENT OF STORAGE CAPACITY OF ADSORBENTS IN A HYDROGEN STORAGE PROCESS AT CRYOGENIC TEMPERATURES

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ABSTRACT
Hydrogen storage is a very important component of the hydrogen economy. A low storage density in conventional pressure and cryogenic vessels, for which it is necessary to use high pressures or very low temperatures, is the issue of the broader application of this element. Therefore, the various types of metal hydride and adsorption storage vessels are extensively tested. Hydrogen adsorption technology on to carbon materials is effective only at cryogenic temperatures and therefore liquid nitrogen with a temperature of 77 K (-196.15 °C) was used to reduce the temperature of the storage device. This article discusses the possibilities of using cryogenic temperatures for hydrogen adsorption on to materials with a large surface area while using liquid nitrogen to reduce temperature. A volume method for measuring the amount of adsorbed hydrogen was used to determine and quantify the amount of hydrogen stored.

KEYWORDS: hydrogen, adsorbent, adsorption, cryogenic temperatures, storage capacity.

INTRODUCTION
Hydrogen storage is a key issue in the implementation of hydrogen technologies and the assessment of the economy of using this element in power engineering and transport. However, the proposed processes of pressure and cryogenic storage did not offer the required safety because a considerable amount of energy is required for their implementation. The transition to the metal hydride and adsorption storage created new opportunities for safer disposal, while the problem is to maintain the minimum hydrogen storage weight percentage set for optimal utilization at 6.5 wt. %. A significant advantage of the adsorption hydrogen storage is high kinetics of the adsorption-desorption cycles, the cyclic stability and low acquisition cost of the adsorbent.

Choosing the right type of storage depends on the purity of the hydrogen stored, on the ability of the longest reversibility, the desorption temperature and the economic point of view. Adsorption storage is more suitable for mobile tanks, mainly due to the lower weight of carbon materials, which also reduces the energy content of the stored hydrogen. The cooling of the storage device to 77 K itself is energetically demanding. Subsequently, it is necessary to fill the liquid nitrogen to cover the losses of nitrogen due to the evaporation caused by the thermal flow from the environment. Depending on the quality of the thermal insulation, 1 kg of liquid nitrogen evaporates for every 199.292 kJ of heat input, which represents the specific vaporizing heat of the nitrogen at a boiling point of 77 K and a pressure of 101,325 Pa.

The use of cryogenic temperatures and the adsorption substances results in a significant reduction of the pressure of hydrogen stored, and hence the method is suitable for the storage. The goal of further development of the storage materials is to achieve the greatest storage ability of hydrogen at the lowest possible weight of the whole device, especially for mobile applications. This effort is required for the possibility of using hydrogen in fuel cells, whose research has advanced considerably, and it is necessary to achieve higher storage capacity for higher output powers.

Despite the relatively low adsorption temperature, it is possible to reduce costs compared to the use of liquid hydrogen since cooling with nitrogen is cheaper, more energy-efficient and more affordable. The storage of hydrogen gas at a temperature of 77 K is about 20% cheaper than the store in liquid form. The ability to store hydrogen depends on the surface size of the adsorbents, while larger surfaces are obtained with the adsorbents in powder form.

The advantage of carbon materials is mainly their low density, large porous structure and chemical stability. Adsorption and desorption of hydrogen in carbon nanotubes, nanoporous materials and activated carbon exhibit show little or no hysteresis and have relatively rapid kinetics at a temperature.

In order to determine the amount of stored hydrogen, a measuring apparatus was constructed, which allows you to determine the desorption curves by measuring the volume of hydrogen discharged into the measuring cylinder.

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Volume measurement is simpler and more accurate due to the low density of hydrogen. The change and significant progress in the possibilities of evaluating the real impact of adsorption to increase the storage capacity of the vessels is accomplished by introducing a relative weight storage percentage of hydrogen.

DESCRIPTION OF THE MEASURING DEVICE

Active carbon, due to its significant porosity, is characterized by low density, which together with low expected storage capacity represents a relatively small amount of stored hydrogen. The device constructed according to Fig.1 allows the measurement of the volume of stored hydrogen and its conversion to the relative parameters (101,325 Pa and 0°C), which is advantageous with respect to the hydrogen density at reference conditions (0.08993 kg $\cdot m^{-3}$).

The basic part of the device is a thick-walled steel pressure vessel with a volume of 10^{-5} m^3, which is filled with adsorbent and is sealed with foam polyurethane in the upper part of the neck. [2].

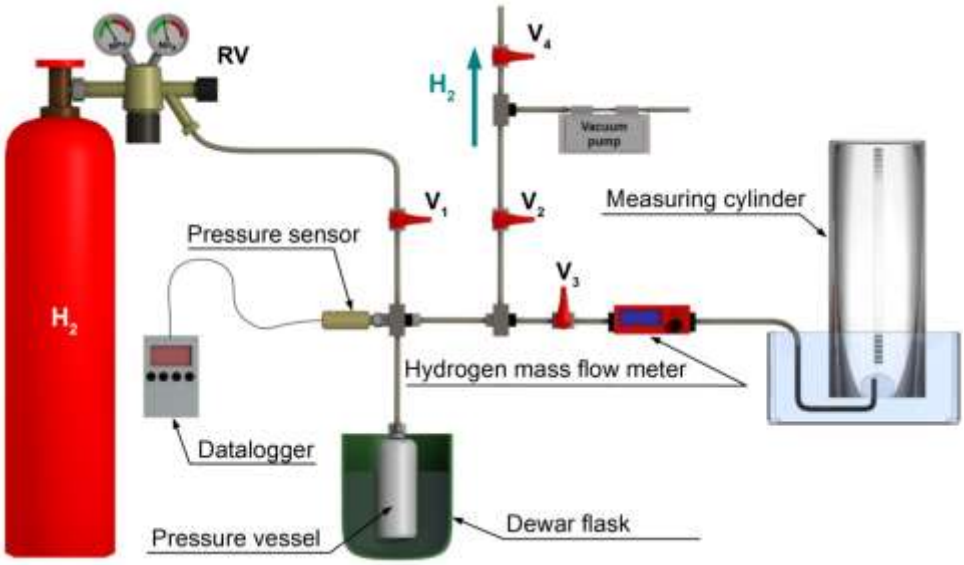

Figure. 1 Scheme of a laboratory device for measuring hydrogen adsorption at cryogenic temperatures by using volume measurement

This allows a continuous flow of hydrogen without blowing off the fine particles of the filling. Teflon, which resists cryogenic temperatures up to -200 °C, was used as an insulating material on thread. The vessel is submerged in liquid nitrogen, which is located in a Dewar vessel with a volume of 10^{-3} m^3. The laboratory equipment is used for measuring adsorption up to a hydrogen pressure of 2 MPa with the possibility of reducing the temperature in a pressure vessel with activated carbon at 77 K.

The device consists of a pressure vessel with hydrogen with a pressure of 20 MPa and purity of 3.0 (99.9 %), while the purity used is sufficient for use in the event of adsorption due to the fact that the active carbon is not prone to degradation of the storage capacity in case of various contaminants in the gas (especially O2), as it is the case with some types of metal hydrides. To reduce and control hydrogen pressure from the pressure vessel up to max. 2 MPa, a FC 2000 5-H-200 reduction valve is used, which complies with standard EN ISO 2503. The gas distribution itself is performed with the MS 63 brass pipe.

Pressure sensing is performed with a PS100-50BAR sensor {max. 5MPa) connected to the PS-9302 datalogger with the ability to collect data on the computer. The initial venting of the system with vacuum drying of the sample is performed by a diaphragm vacuum pump with a minimum pressure of 1.8 kPa. The GCA-C9EA-FA20 mass flow meter is used for sensing the flowed amount of hydrogen. A measuring cylinder with a total volume of 2.10^{-3} m^3, which controls the volume of released hydrogen, is located at its output. Measuring the volume in the measuring cylinder requires known values of state variables for conversion to the reference conditions. Part of the measurement is therefore also the barometer for the detection of atmospheric pressure.

Safe removal of air from the piping system shall be implemented prior to any exchange of the pressure vessel or when the piping system is aerated. The progress of hydrogen atmosphere formation is performed in the following steps:

1. The air suction through the vacuum pump on to the absolute pressure of 1.8 kPa;
2. the beginning of the filling by hydrogen at a pressure of 2 MPa;
3. the discharge of a mixture of gases through the V_2 and V_4 discharge valves.

This procedure is repeated at least 2 times to obtain the mixture with the smallest possible proportion of the primary air. Vacuum drying of the sample is an advantage of using a vacuum pump. After forming a hydrogen atmosphere at atmospheric pressure, the pressure vessel is immersed into a small Dewar vessel with liquid nitrogen, into which the nitrogen was poured from the storage Dewar flask. By a heat transfer, the vessel cools to the liquid nitrogen temperature, which is 77 K. Upon pressure increase, hydrogen is adsorbed on to the active carbon.

A V_1 valve will close after reaching a maximum pressure of 2 MPa and after the stabilization of adsorption. After opening valve V_3, a mass flow meter with measuring cylinder for measuring the volume of leaked hydrogen is connected.

Subsequently, the pressure in the storage device will be gradually reduced by the gradual opening of the V_3 fine dosing valve and by recording the leaked hydrogen into the measuring cylinder. The leaked volumes will be measured at 10 different pressures to compile the curves. By recalculation, the dependencies of the stored amount of hydrogen and the relative weight storage percent of the given type of the adsorption material are obtained.

PREPARATION OF ADSORBENTS

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

Preparation of active carbon in the pyrolysis furnace

Chemical activation with potassium hydroxide (KOH) and annealing AC at various temperatures in the pyrolysis furnace was chosen for the production of active carbon (AC).

Annealing of SIL 15 Extra active carbon

SIL 15 Extra active charcoal was annealing after grinding in the cluster mill at a temperature of 350 °C and 700 °C.

Chemical activation of carbon using KOH

Chemical carbon activation was performed by using KOH activating agent while ground black charcoal was used as the carbon source.

Preparation of the active carbon in the plasma reactor

In a 10 kVA plasma reactor, in an inert nitrogen atmosphere, the waste is decomposed at a temperature of up to 1,550 °C, while a fine graphite carbon black emerged as a byproduct – carbon blacks used in laboratory hydrogen storage tests.

STORAGE CAPACITY OF ADSORBENTS

Due to the problematic calculation of the volume of the storage device together with the distribution pipeline, an indirect method of volume determination was chosen, with the aid of compressed hydrogen, followed by a volume calculation (Fig. 2).

The principle of volume determination consists in pressurizing the device with hydrogen for the operating pressure with the subsequent discharge of hydrogen into the graduated cylinder.
By calculating the volume in reference conditions, it is possible to obtain the weight of stored hydrogen in relation to the absolute hydrogen pressure. The equation for the device under pressure is:

$$p_{\mathrm{m}} \cdot V_{\mathrm{m}} = z_{\mathrm{m}} \cdot m \cdot r \cdot T_{\mathrm{H_2}} \qquad (1)$$

where: p_{m} is the absolute pressure (Pa), V_{m} – the volume of the storage device (m^3), z_{m} – the compressibility factor at pressure p_{m} (-), r – the specific gas constant of hydrogen ($J \cdot kg^{-1} \cdot K^{-1}$), T_{H2} – gas temperature (K). The state equation for gas in the graduated cylinder neglects the compressibility factor due to the low pressure ($p_{\mathrm{c}} \sim p_{\mathrm{atm}}$) and has the form:

$$p_{\mathrm{c}} \cdot \left(V_m + V_{\mathrm{c}}\right) = m \cdot r \cdot T_{\mathrm{H_2-c}} \qquad (2)$$

where: p_{c} is the pressure in the graduated cylinder (Pa), V_{c} – the measured volume of hydrogen in the graduated cylinder (m^3), $T_{\mathrm{H2\text{-}c}}$ – the hydrogen temperature in the graduated cylinder (K). The equation (2) is mathematically correct only if the temperature of the whole system is constant.

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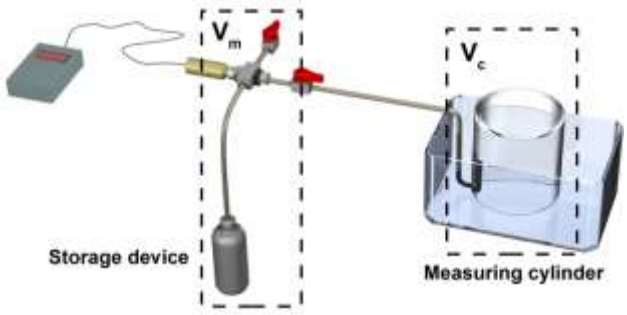

Figure. 2 Model of the measuring device

The measurement is performed at ambient temperature without the use of liquid nitrogen, and therefore this condition is fulfilled. Since the weight of hydrogen in the entire system does not change and is constant when valves V_1 and V_2 are closed, it is possible to express the volume of the storage device V_m from equations (1) and (2) in both state equations:

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

The gas pressure in the graduated cylinder is calculated according to the relationship:

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

where: h is the height of the water column in the graduated cylinder (m), ρ_{H2O} – the density of water (kg·m^{-3}), g – gravitational acceleration (m·s^{-2}). The average value of the volume of the pipe is $4.7 \cdot 10^{-5}$ m^3.
Fig. 3 shows a diagram of the dependence of the stored hydrogen weight from overpressure, while the mean value of the three measurements will also be used as a comparison curve for the measurements with adsorbents.

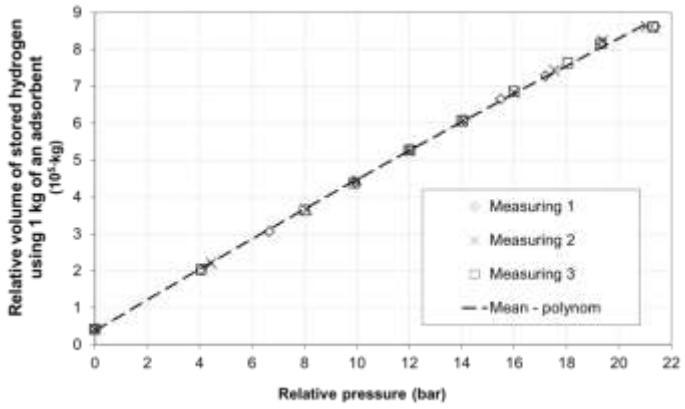

Figure. 3 Weight dependence of stored hydrogen from overpressure at 293 K without using an adsorbent

The determination of the regression curves of individual measurements as well as the determination of the resulting equation of the mean curve with three measurements was performed in the QtiPlot program. This software is designed for analysis and data processing. A regression curve of the second-level polynomial type was selected for processing. The resulting shape of the mean regression curve measured without using an adsorbent agent at ambient temperature is expressed by:

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

where: $m_{H_2}^{average}$ is the mass of stored hydrogen (kg), p_p – the overpressure in the storage device (bar).

DETERMINATION OF THE WEIGHT OF THE STORED HYDROGEN

A normal procedure for measuring the amount of stored gas on adsorbents is to directly measure the weight of the sample at elevated pressure and cooling to 77 K. The disadvantage of this process is low hydrogen density, which under normal conditions is only 0.08993 g per 1 dm^3 of gas.

The volume measurement in the manner described below is less technically and financially demanding, mainly due to lower experimental device costs. Therefore, it is more suitable to measure the weight of the stored gas indirectly – by measuring the volume and then converting the mass storage percentage of this gas at different pressures of hydrogen.

The volume of released hydrogen in the graduated cylinder represents a loss of volume from the storage device, and therefore the volume at normal conditions in the storage device is:

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

where: V_i^{ST} is the volume of hydrogen in the storage device under normal conditions (m^3), V_{nn} – the maximum measured volume at zero overpressure – recalculated to normal conditions (m^3), V_i – volume in the graduated cylinder measured in normal conditions (m^3) – volume of the pipeline system with a pressure vessel calculated for normal conditions (m^3) ($V_m = 4.7 \cdot 10^{-5}$ m^3).

In equation (5), the volumes used are converted to normal conditions, i.e. the volume of hydrogen at a pressure of 101.325 Pa and a temperature of 0° C. The conversion for V_i and V_{nn} is performed according to the relation from the state equation:

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

where: V_{no} is an immediate volume reading from the graduated cylinder (m^3).

The weight of stored hydrogen is calculated from the state equation of ideal gas since at atmospheric pressure, the compressibility factor is approximately 1 (z_m = 1.00026).

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

where: p_{nc} is the normal pressure (101.325 Pa), T_{nc} is the normal temperature (273 K).

The weight storage percentage of hydrogen (Ψ) is determined on the basis of the ratio of the weight of the stored hydrogen (m_i) and the weight of the adsorbent agent:

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

where: the m_{AC} is the weight of the adsorption agent (kg).

To compare the usability of the adsorption properties, the relative weight storage percent of Ψ_r will be demonstrated in the following graphs, which represents a relative increase in adsorption properties compared to the use of an empty storage vessel in the same physical conditions.

$$\psi_{\mathrm{r}} = \frac{m_i - m_{\mathrm{H2}}^{\mathrm{average}}}{m_{\mathrm{AC}}} \cdot 100\ \% \tag{10}$$

In the event when the porous material exhibits a low adsorption capacity, it may occur during a pressure increase, as a result of the absence of the adsorbent's own volume, that Ψ_r decreases or negative values are acquired (in this case, the adsorbent is unsuitable for hydrogen storage).

STORAGE OF HYDROGEN IN ADSORBENTS AT 77 K

The pressure vessel with the sample was immersed in 2/3 of its height in liquid nitrogen and closed with a lid (to minimize nitrogen evaporation). After the 10 minutes required to equalize the temperature of the vessel with 77 K, the measurements continued as with the measurements without using the cooling medium.

The ability to store hydrogen for the adsorbent materials was also compared with the capability of hydrogen storage in an empty vessel cooled at a temperature of 77 K.

Fig. 3 shows a comparison of the relative volume of the stored hydrogen for each of the tested materials at a temperature of 77 K. For the purposes of this article, the relative volume is described as a volume with increased storage capacity compared to the volume of hydrogen stored in the vessel without the adsorbent.

The most promising material for storage of hydrogen is SIL 15 Extra activated carbon. After annealing at a temperature of 350 °C, there was a slight reduction in the adsorption pressure, which corresponds to the maximum storage volume.

The optimal pressure for the storage of activated carbon at a temperature of 77 K is 0.8 up to 1.2 MPa when the maximum storage amount is reached when compared to an empty pressure vessel.

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At higher pressures, the storage capacity is decreasing because the adsorbent material occupies a volume in the vessel which could be filled with hydrogen if there is no adsorbent. 1 kg of SIL 15 Extra carbon is able to store approx. 0.063 Nm3 of hydrogen at a temperature of 77 K and 11 bar, representing 804 kJ of stored energy against the vessel without the use of an adsorbent.

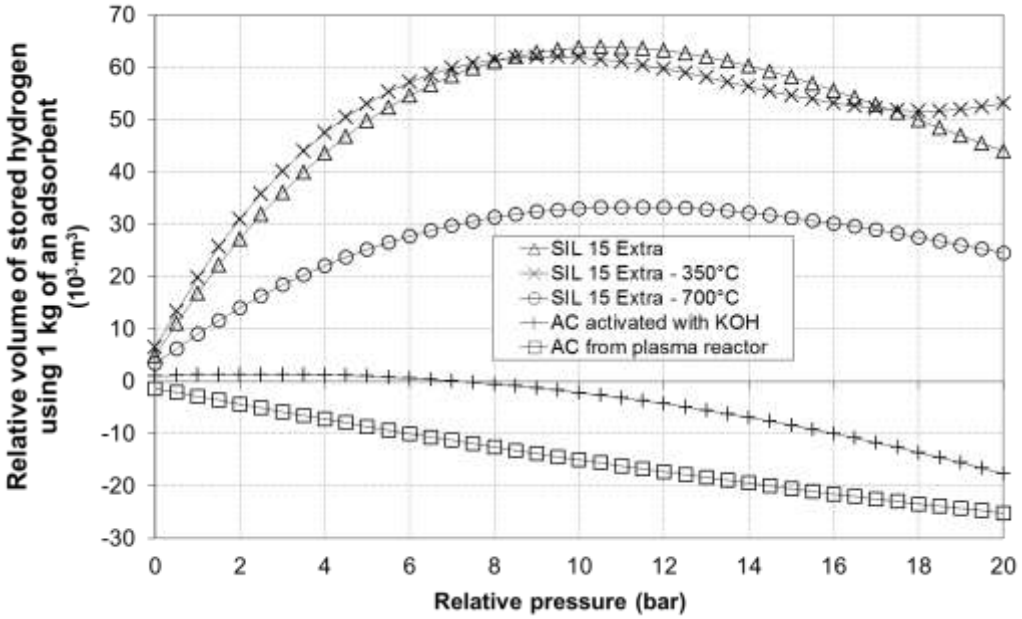

Figure. 3 The relative volume of stored hydrogen converted to normal conditions (101,325 Pa, 273.15K) using 1 kg of an adsorbent at a 77 K adsorption temperature

CONCLUSION

Activated carbon as well as high porous surface materials allow the amount of stored hydrogen to increase through gas adsorption against an amount that can be stored in an empty vessel at a temperature of 77 K. This assumption is fulfilled if an active surface is used and only up to a critical pressure, where the adsorbent's own volume plays an important role. Increasing pressure above the mentioned critical pressure causes the reduction of the amount of stored hydrogen when compared to the container without an adsorbent. The impact of the adsorbent substance's own volume can also be observed when the desorption curve decreases at pressures higher than 12 bar.

The measurements show that 1 kg of SIL 15 Extra active carbon is able to store 804 kJ more energy than in an empty 77 K vessel. This type of carbon in its original form, or annealed at 350 °C, demonstrates the most favorable properties required for the storage of hydrogen.

When using adsorbents, the amount of stored energy increases and thus also increases the usability of this hydrogen storage technology in practice.

The impact of annealing on the adsorption properties of SIL 15 Extra carbon does not correspond with the expected result, where an increase in storage capacity was expected.

An important knowledge that has resulted from the research is that despite the high weight percentages of the stored hydrogen per weight unit of the adsorbent, the percentage of stored hydrogen compared to an empty pressure vessel cooled to the same temperature of 77 K is 10-times less.

Normally, achieved mass storage percentages measured by gravimetry in a hydrogen atmosphere at a temperature of 77 K reach between 5 and 6 wt. % of the hydrogen stored, but not with their own volume of carbon atoms. In the method described in this work, it has been shown that when we consider the adsorbent volume, it shows a realistic view of the usability of the technology in comparison with the empty pressure vessel.

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