Measurement of the operational characteristics of hydrogen storage in a metal-hydride tank

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***Abstract*— The presented article describes measuring of the operational characteristics of hydrogen storage in intermetallic alloy La0.85Ce0.15Ni5, which stores energy produced by a photovoltaic system. The paper proposes a method of determining a wide range of PCI curves with a single absorption cycle.**

Keywords— hydrogen electrolyzer, metal hydride, absorption, storage capacity

I. INTRODUCTION

From an environmental point of view, hydrogen is the most suitable fuel, and its conversion to electrical energy in fuel cells can be performed with high efficiency reaching values of up to 60% [1].

The application of hydrogen in the power industry is closely related to the possibility of its accumulation maximizing the energy content. Owing to its low molecular weight, density of the gas at standard conditions reaches is also relatively low [2,3,4,5]. By means of pressurizing of hydrogen and its storage in pressure vessels, it is possible to achieve the energy density of 6.2 $GJ.m^{-3}$ (at 750 bars and 20°C). Such types of containers, however, require the use of composite materials. These include mainly metal storage tanks reinforced by carbon materials. When storing hydrogen in a liquid form, the energy density is 10 $GJ \cdot m^{-3}$, however, the actual liquefaction is an energy intensive process. Therefore, especially in case of stationary applications, it is preferable to employ metal hydride (MH) materials that allow absorption of hydrogen into the intermetallic lattice. This method of hydrogen storage is safer as compared with the conventional techniques. Intermetallic alloys, as well as similar alloys with the addition of cerium, rank among the most widely available MH materials. The operational pressure of $LaNi_5$ lies within the interval 1 - 10 bars and the temperature ranges from 20 to 60°C, which are the values compatible with the selected types of high pressure electrolysers and fuel cells [6,7,8]. Measuring the hydrogen storage capacities for each type of alloy widens the knowledge concerning a specific amount of stored gas; however, determining the characteristics at actual operating conditions presents a new view of thermal fields, energy flows and other related parameters of the equipment used.

II. ARRANG MENT DIAGRAM OF THE EXPERIMENTAL MEASUREMENT APPARATUS

Measuring was carried out in a laboratory equipped by a complex range of connected energy devices which enable production of hydrogen by means of water electrolysis utilizing electricity produced by solar power sources. Energy transformation is performed by 12 photovoltaic panels Sanyo HIT 250 with the rated power of 250 W. Continuous current then flows into a PV inverter SunnyBoy connected to the island grid whose voltage is maintained by the Battery OFF-Grid Inverter type 2224. Two Hoppecke batteries with a total capacity of 3.24 kWh are used to compensate for the electricity supply outages caused by instability of solar radiation.

The island grid deliver electricity to all the devices required for hydrogen production and to secure autonomous operation. A device representing primary load is a high-pressure alkaline electrolyser Nitidor H_2. The production rate of the electrolyser is 0.5 $m^3 \cdot h^{-1}$ of hydrogen and its outlet pressure peaks at 20 bars. The electrolyser achieves the efficiency of 58.5% with the maximum input power of 3 kVA. The essential component of the device is a bipolar electrolyser with a KOH electrolyte. The electrolysis yields hydrogen with the purity of 99%. Then the gas passes through a drying unit, undergoes a catalytic combustion of residual oxygen and is transported into another drying unit where the adsorption of water vapour occurs. Hydrogen produced in this process has the purity of 99.85%.

The hydrogen produced is then divided into a majority part fed into an MH storage tank, and a smaller part flowing into the analyser (the ratio is controlled by a proportioning valve). The analyser is equipped with a built-in sensor to measure the oxygen content. If the oxygen level exceeds the limit values a total system shutdown is initiated.

The majority part of hydrogen runs through a mass flow meter Bronkhorst F-111B-10K-AGD-33-V into a metal-hydrid storage tank filled with 56 kg of $La_{0.85}Ce_{0.15}Ni_5$ alloy, which acts as hydrogen-absorbing material. The pressure is measured by a pressure transmitter DMP-331. The storage tank can hold up to 9 m^3 of hydrogen, which, at very low hydrogen density, represents the weight of 0.80892 kg H_2. The weight storage capacity of metal-hydride at a nominal hydrogen storage volume is 1.43%. The tank has an integrated heat exchanger, which allows for the supply and removal of heat by means of a water cooling system. It comprises of 7 internal tubes, 50 mm in diameter and wall thickness of 2 mm filled with metal hydride and placed inside the storage vessel with the diameter of 168 mm and 2 mm thick walls with the possibility of liquid cooling during absorption (heating during desorption).

The storage tank is made of stainless steel. The total length of the tank including the tubes without the inlet valve is 1612 mm. The tubes are welded at both ends and all components together form a compact unit. The intake and outlet of cooling water is realized in a radial conduction. The tank is insulated against convection and radiation to eliminate heat gains and losses within heat exchange with the environment.

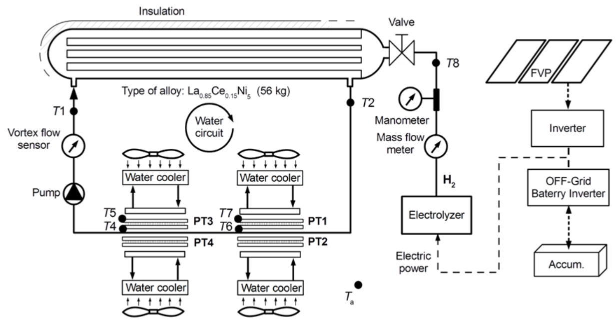

Fig. 1 *Simplified connection diagram of the devices*

The process of hydrogen absorption into the alloy generates heat, which is removed by a heatsink. Without cooling the gas pressure inside the storage tank would build up considerably, and, even with a small amount of hydrogen stored, it would exceed the permissible limit of 15 bars. On the contrary, the process of hydrogen desorption requires supply of constant specific heat to prevent a pressure drop, which could slow down the kinetics of hydrogen release. Simplified connection diagram of the devices is shown in Fig. 1.

A. Procedure of measuring of the operating parameters during hydrogen production and storage

Measuring during hydrogen production and storage is performed in several independent stages. Measuring of the surface temperature of an MH storage tank, ambient temperature and the temperature of entering and escaping cooling water are done by a cooler fitted with sensors SMT160-30. The cooler enables to measure the flow rate of cooling deionized water, which removes the heat produced during hydrogen absorption. The electric quantities are measured by DIRIS A10. Another component is an electrolyser equipped with a hydrogen mass flowmeter and the sensors monitoring the temperature of hydrogen and oxygen produced.

The objective of such measuring is to determine the operating parameters during hydrogen production by means of water electrolysis and to model PCI curves in the course of a single absorption cycle for multiple temperature levels. This goal can be attained by performing a gradual hydrogen absorption into metal-hydride.

During the process of measuring, hydrogen was absorbed at the volume rate ΔV of approximately 1 m^3. Thus, considering a total capacity of the storage tank was 9 m^3, nine absorption readings were taken. The container was completely empty before the initiation of the absorption process and using an air pump hydrogen was pressurized to the value of 3.8 kPa. Hydrogen production rate was set to 67% of a maximum rate of 0.5 $m^3.hr^{-1}$. 0.906 m^3 of hydrogen was stored within the first storage stage. Once the absorption was complete, the hydrogen inlet closed and the MH tank was cooled down to the temperature of 15°C. Circulation of cooling water was maintained for 20 minutes to attain temperature field stabilization. Subsequently, the tank was heated up by the cooler switched to the heating mode, and the temperature was increased by 2°C intervals. Each temperature increment of 2°C was followed by a 5-minute stabilization period of the MH material temperature field. The pressure of hydrogen inside the container was read after each stabilization. The final storage tank temperature at the time of measurement was 33°C.

Reduction of the MH storage tank temperature down to 25°C allowed further absorption of 1m^3 of hydrogen. The alternation of the absorption process and temperature regulation inside a storage tank is required to achieve maximum storage capacity. Fig. 2 shows a time course of hydrogen production and the power output of the electrolyser during filling up between 6.193 to 7.224 m^3 of absorbed hydrogen.

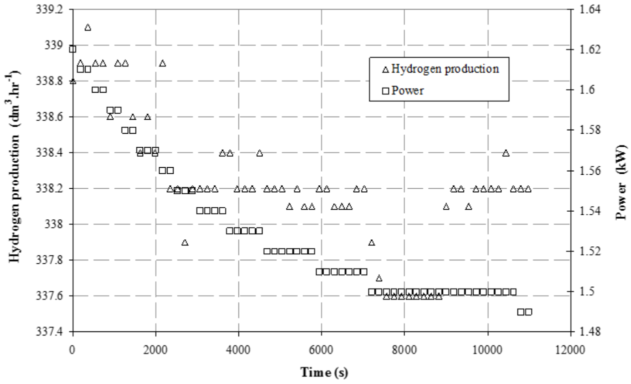

Fig. 2 *Time course of hydrogen production and input power of the electrolyser*

During measuring, the input power of the electrolyser decreased by 7.4%, whereas hydrogen production changed by only 0.44%. The decrease in performance stems from gradual heating of the electrolyte until its maximum temperature of 67°C. As the temperature grows, the input power of an electrolyser decreases.

Produced hydrogen is then transported to the MH storage tank, which is cooled by a cooler employing Peltier elements. The temperature of the storage tank did not exceed 25°C despite a gradual rise of the ambient temperature (Fig.3).

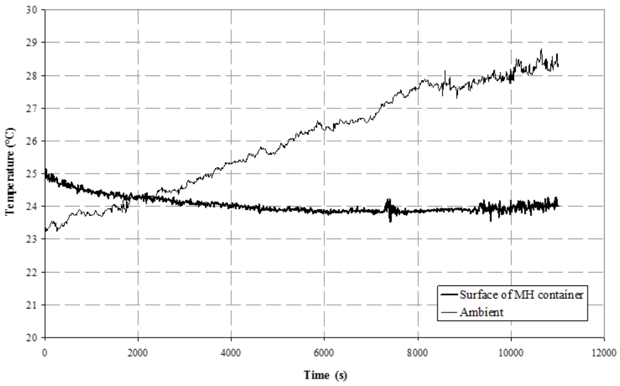

Fig. 3 *Course of the surface temperature of the MH container and the ambient temperature*

The output cooling power of the cooler during hydrogen absorption had a digressive tendency (Fig. 4), resulting from the ambient temperature rise exaggerated by a temperature difference between the warm and cold side of a Peltier element. In order to promote efficiency and performance of the PT cells, it is crucial to maintain the temperature difference between the heat transfer surfaces as low as possible, which may be difficult to achieve at higher ambient temperatures. Gradual decline of the cooling power causes the convex course of the storage tank surface temperature and starts to rise slightly after 8000 seconds.

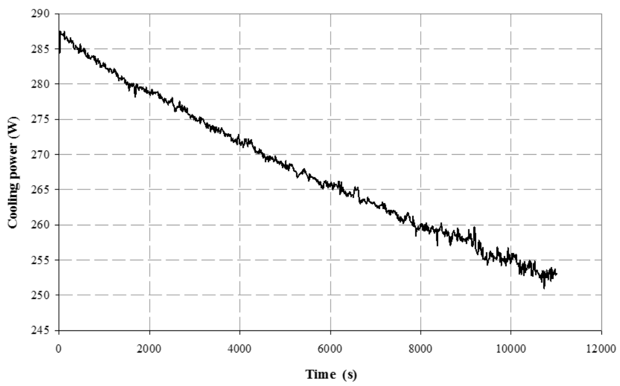

Fig. 4 *Course of cooling power during hydrogen absorption in the MH storage tank*

Increase of the temperature of MH material in the initial phase of hydrogen absorption cannot be eliminated unless a temperature gradient between the cooling water and the absorbent is formed. At this stage, a steep pressure increase later stabilises (Fig. 5). In the final phase of measuring, hydrogen pressure reaches adequate levels as the temperature of the storage tank rises.

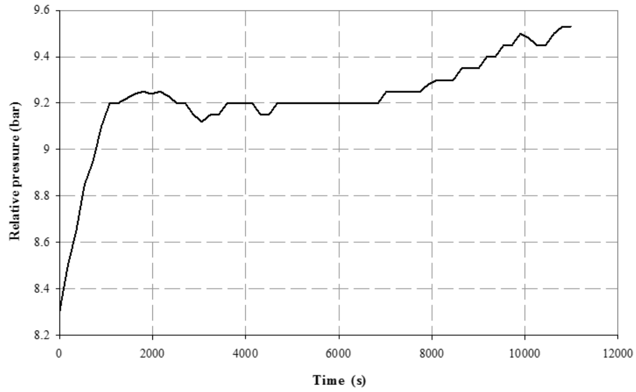

Fig. 5 *Course of the relative hydrogen pressure in the storage tank during measuring*

After hydrogen absorption is compete, it is necessary to cool the storage tank to the temperature of the lowest isotherm which is 15°C. Once the storage tank is cooled, the value of pressure in the tank at the temperature of 15°C is read and the temperature is then gradually raised in the increments of 2°C. It is crucial to ensure that the temperature increments are the same for each volume of stored hydrogen. Time required for temperature field stabilization was set to 600 seconds, which was also verified by means of numerical methods [3]. Repeated temperature regulation of the storage tank for different volumes of stored hydrogen yielded data for modelling the absolute pressure - temperature curves (Fig. 6).

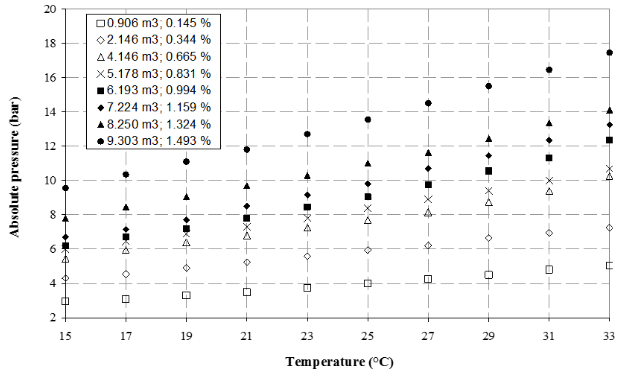

Fig. 6 *Course of the absolute hydrogen pressure and the temperature of the MH storage tank for different volumes of stored hydrogen*

The key for Fig. 6 gives the volume of stored hydrogen as well as weight percentage of hydrogen stored. Increase of the volume of stored hydrogen also causes climbing of the pressure – temperature gradient, which can be applied in the design of a hydrogen compressor exploiting the same alloy. If the measuring data are evaluated for the individual isothermic curves, pressure - percentage by weight relation can be obtained (Fig. 7).

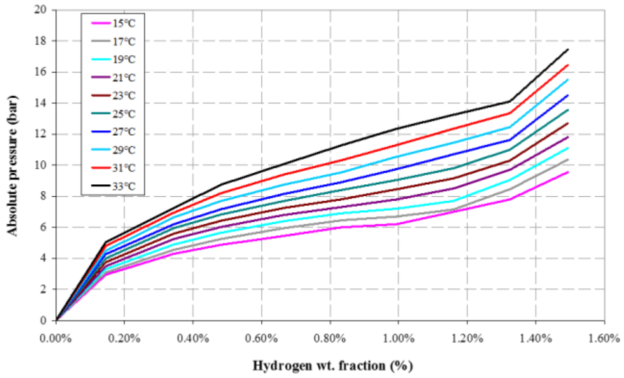

Fig. 7 *PCI curves of the temperature range 15-33°C*

The curves depict a noticeable increase in pressure in the initial stages of the hydrogen storage process until the onset of absorption. The pressure rises moderately during hydrogen absorption up to the point of alloy saturation is reached and further hydrogen storage requires more intensive pressurization. Smoother PCI curves during absorption can be obtained by using smaller volumetric quantities between individual temperature increments. If attaining a wider temperature range of PC isothermal curves is needed measurements of the pressure inside a storage tank should take place at predefined temperatures.

III. Conclusion

Hydrogen storage is a key issue and a major challenge for its wider application in practice. A viable option appears to be hydrogen accumulation in MH materials, which is suitable mainly for stationary applications. A complex apparatus comprising of various energy and electrical devices was used for the purpose of a hydrogen-based accumulation of electricity from a solar power source. The data of the operating conditions allow to get a detailed view of the changes of relevant variables during the process of absorption. Gradual alternation of the absorption process and temperature regulation of the MH storage tank enabled us to model the absolute pressure - material temperature curves for different volumes of stored hydrogen. PCI curves of the alloy $La_{0.85}Ce_{0.15}Ni_5$ within the temperature range 15-33°C were subsequently obtained by means of transformation. The advantage of the proposed method of measuring PCI curves is a possibility to run only one hydrogen absorption cycle. The results may be used to design a heat powered compressor for the purpose of hydrogen compression exploiting MH materials.

Acknowledgment

This paper was written with the financial support of the granting agency APPV within the project solution No. APVV-15-0202, of the granting agency VEGA within the project solution No. 1/0752/16 and of the granting agency KEGA within the project solution No. 005TUKE-4/2016.

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