

LABORATORY RESEARCH OF HYDROGEN PRODUCTION AT VSB–TECHNICAL UNIVERSITY OF OSTRAVA

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Abstract. This paper elaborates on the hydrogen technology with respect to electrical power accumulation in hydrogen via Hogen GC600 electrolyzer. Further details will include options for storage of hydrogen into containers currently available. The measurements contained in the paper illustrate laboratory research of hydrogen generation in the electrolyzer which are being taken at the Fuel Cells Laboratory, VSB–Technical University of Ostrava. The matter comprises research on impact of changes to parameters of this electrolyzer on efficiency of gaseous hydrogen production. Electric power needful for the electrolyzer supply is delivered from photovoltaic panels.

Keywords

Electrolyzer, hydrogen, metal-hydride.

1. Introduction

Electrolyzer is, in terms of efficiency, the weakest element of electrical power hydrogen accumulation cycle. For this reason we have focused our attention on research aiming at enhancing the efficiency of connected Hogen GC600 electrolyzer. During last research we have found that the total efficiency of our island hydrogen system is less than 9 %. This very low efficiency is caused by production cycle of hydrogen. Our current research consists in the effort to improve the efficiency of used hydrogen generator (electrolyzer) Hogen GC600, because this electrolyzer is the least efficient part of hydrogen storage system. Hydrogen storage methods are also important part of our research. We use pressure vessels and metal hydride containers for gaseous hydrogen storage.

2. Hydrogen Storage System

To accumulate electrical power with help of hydrogen technologies and at the same time use the advantage of zero-emission renewable energy sources (RES), hydrogen must be generated by water electrolysis. An osmotic unit in an electrolyzer processes modified water at the time of low load in electricity system or with use of electrical power from photovoltaic panels (at the Fuel Cells Laboratory, VSB–Technical University of Ostrava). Electrolyzer is the main component of hydrogen accumulation assembly as it affects the resultant technical and economic parameters of the hydrogen accumulation cycle. The performance of electrolyzer is directly proportional to surface area of electrodes, which represent the major share of the final price of this appliance. On the contrary, the amount of energy accumulated depends on the size of hydrogen storage container only. Hydrogen generation cycle contains two basic procedures:

- generation - H₂O electrolysis takes place in an electrolyzer which transforms electrical energy into chemical one the basis of synthetically produced fuel - hydrogen,
- storing, transportation of hydrogen resp.

2.1. Methods for Hydrogen Storage

Storage of hydrogen is associated with specific hindrances. Hydrogen is highly reactive element of low density. Its molecules are small allowing hydrogen to diffuse through certain materials (plastic, some metals) both in liquid and gaseous state. If causes the so called "hydrogen embrittlement" of metal structures it comes into contact with. There are several technical options to solve hydrogen storage. The most common method used deals with storage of liquid hydrogen in steel vessels under pressure of approximately 200 bar (20 MPa).

Welding vessels are used for storage of larger amounts of hydrogen. These vessels feature layered laminated walls. The internal wall layer is made from stainless steel to resist effects of pressure hydrogen. The exterior wall is made from steel suitable to withstand such pressure. In our environment, hydrogen is normally stored and distributed in pressure vessels at 200 to 350 bar. The use of pressure electrolyzers does not require any compression unit, as the gas is being compressed right inside the electrolyzer. This electrolyzer is used by the fuel cells laboratory at VSB–Technical University of Ostrava: Hogen GC600 type.

A more modern and very perspective alternate option is storage of hydrogen by means of the so called "metal hydrides", when hydrogen becomes a part of chemical structure of selected metal alloys [1].

Metal hydride storage systems make use mainly of metal alloys of nickel, magnesium, lanthanum, iron and titanium. This is the safest method for hydrogen storage, which is based on easy absorption of hydrogen into certain materials on metal basis, under higher pressure and lower temperature conditions. Therefore this is an exothermal reaction, i.e. absorption generates heat that needs to be drawn away. A reverse event-desorption, i.e. release of hydrogen from the specific material, is achieved by supplying heat within. The principle of metal hydride functioning is shown in Fig. 1.

Storage of hydrogen in metal hydrides does not require any extremely high pressure or cryogenic temperatures as if stored in pressure vessels or liquid state. As far as desorption of hydrogen is concerned, metal hydrides are divided into high- and low-temperature ones cite1.

Storage systems involving metal hydrides are based on the principle of easy absorption of gas by certain materials under high pressure and moderate temperature conditions. These substances then release hydrogen in gaseous form, when heated up under low pressures and relatively high temperatures. It can be approximated that 1 cm³ of metal hydride contains about 1 litre of hydrogen gas, which corresponds with chemical pressure of around 1000 bar. Bonding of hydrogen belongs to exothermic reactions, so heat will be released during container filling and the contents need cooling. On the contrary, when emptying the hydrogen container, its contents must be heated up or the pressure within container needs to be released.

Hydrogen can be liquefied under certain conditions, resulting in multiple times increase of energy content per one unit of volume, yet the process requires large amount of energy and the production of LH₂ (liquid H₂) theoretically requires 1,8 kWh.kg⁻¹ of H₂. Liquid hydrogen is stored in cryogenic tanks at the temperature of -253 °C. Tank capacity depends on its design,

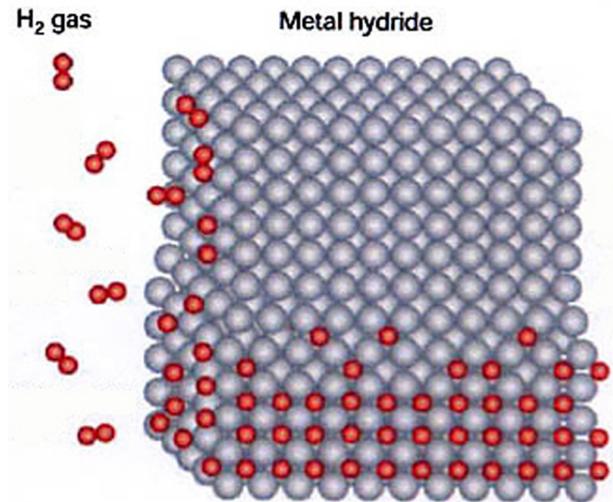


Fig. 1: Metal hydride principle.

it varies from 100 m³ up to several million of m³. Despite its low volume density, hydrogen has the greatest energy to weight ratio among all fuels. As far as gases are concerned, its density is the lowest and its boiling point ranks as second lowest among all substances known [2].

Small quantities of hydrogen can be stored in simple pressure free float containers with water closure or underground gas storage reservoirs. Capacities of underground reservoirs range up to 108 m³.

2.2. Electrolyzers

Hydrogen is acquired in a process of decomposition of demineralized water - electrolysis. If the energy used for the hydrogen production is generated with renewable energy sources, such as wind power generator or photovoltaics and burning of fossil fuels is avoided, the process of hydrogen generation is very clean and emission - free (no CO₂, SO₂, NO_x, etc. emissions). Electrolyzer is a series of cathodes and anodes immersed in water with added electrolyte (often KOH potassium hydroxide) to increase conductivity. A polymerous electrolyte with ion exchange membrane seems to be very promising. Porous electrode layers are applied on both sides of the membrane and the current is conducted with H₃O⁺ ion at the cathode and OH⁻ ion at the anode. The thickness of the membranes is 1 mm.

These electrolyzers provide for the chemical reaction listed below:

- cathode: $4\text{H}_2\text{O} + 4\text{e}^- \Rightarrow 2\text{H}_2 + \text{OH}^-$,
- anode: $4\text{OH}^- \Rightarrow \text{O}_2 + 2\text{H}_2\text{O} - 4\text{e}^-$,
- overall reaction: $2\text{H}_2\text{O} \Rightarrow 2\text{H}_2 + \text{O}_2$.

The negative electrode is usually made from nickel with platinum plating as catalyst to enable bonding of atomic hydrogen into molecules of H_2 on the electrode surface to increase hydrogen production. If the cathode lacked catalyst, the atomic hydrogen would accumulate on the electrode resulting in blocked current flow.

The positive electrode is mostly made from copper and nickel. Its surface is covered with oxides of manganese, ruthenium or tungsten. These metals enable bonding of atomic oxygen to form molecules of O_2 . Separation of these two parts during unobstructed flow of ions inside electrolyzer is ensured by means of a diaphragm, based on asbestos and resistant to temperatures $80^\circ C$ to prevent mutual blending of oxygen and hydrogen. Figure 2 shows electrolyzer principle [3].

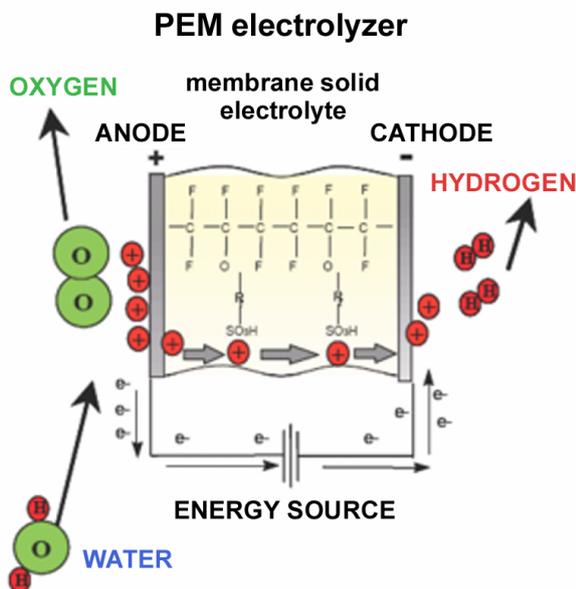


Fig. 2: Simplified diagram of electrolyzer.

Potential compensation of electric power savings can be represented by heat supplied into the reaction. It is convenient mainly for the reason that the cost of heat is lower compared to electric power and rising temperature contributes towards efficiency of electrolysis. The minimum voltage for reaction is $1,228\text{ V}$ at $25^\circ C$ (298 K), yet the heat is insufficient, therefore it has to be supplied from ambient environment to prevent zero yield from production. Voltage increase to $1,47\text{ V}$ at the same temperature of $25^\circ C$ (298 K) results in increase of temperature in reaction, so there is no need for additional heat supply. If the voltage level rose even more, the excess heat would dissipate into the ambient environment.

3. Efficiency of H_2 Production

The task of laboratory measurements was to analyse the changes of efficiency of Hogen GC600 electrolyzer with different pressures on the electrolyzer panel. The pressure can be adjusted within the span $3\text{--}13,8\text{ bar}$. This electrolyzer is shown in Fig. 3 and its parameters are shown in Tab. 1. Hydrogen flow within the span $0\text{--}600\text{ cm}^3/\text{min}$ is also dependent on the set pressure. The level of the flow is displayed on the flowmeter connected between the electrolyzer and the hydrogen-storing cylinders. At the same time the date on the flow are stored in a computer with expert software. The data can be further analysed for needed overview and graphs.



Fig. 3: Hogen GC600 electrolyzer.

The voltage for Hogen GC600 electrolyzer use for hydrogen production was supplied from solar polycrystalline panels type Schott Poly 165 with the total installed output of 1980 Wp with optional extension to 2970 Wp . The circuit was further provided with lead batteries determining the voltage level on direct bus as well as alternating load (200 W lighting units). The diagram in Fig. 4 shows mutual linkage of individual system parts, including location of measuring points. Electric values measured are processed using the NI USB-6218 measuring card. All the energy from solar panels was intended for hydrogen production using the electrolyzer, so there was no load connected to the alternate current bus. The intensity of solar radiation M_e (W/m^2) was sufficient both to supply the electrolyzer as well as to recharge batteries to 56 V as required.

3.1. Measuring Data

The needed measurements are in Tab. 2, Tab. 3, Tab. 4, Tab. 5 and Tab. 6 informing on values in given 30 minute periods and also average values of adjusted criteria [6].

3.2. Measurement Evaluation

Graphics and table images illustrate generation cycle of hydrogen in Hogen GC600. The starting value of pressure is 7 bar (so-called "cold" condition) and the

Tab. 1: Product specification Hogen GC600 [4].

Maximum Hydrogen Flow Rate	0-600 cm ³ /min
Delivery Pressure	3-13,8 bar (45-200 psig), ± 5 % Full Scale Output, 0,5 ppm Water Vapor
Hydrogen purity	100 %
DI Water Tank Capacity	1,9 l (approx 0,5 gallon), Full Level to Shutoff Level
Water Consumption (approximate)	0,6 cm ³ /min at Full Rated Output, Equivalent to 0,9 l per 24 h of Operation
Power	100-240 VAC, 47/63 Hz
Outdoor temperature	10 °C/35 °C (min./max.)

Tab. 2: Adjusted value 7 bar.

Time (s)	Consumption (Wh)	H ² volume (l)	*EEQ (Wh)	Efficiency (%)
0	0	0	0	0
300	48	1,75	5,62	11,7
600	94	4,58	14,7	15,64
900	132	8,68	27,87	21,11
1200	169	12,28	39,42	23,33
1500	198	15,45	49,6	25,05
1800	233	18,7	60,03	25,76

Tab. 3: Adjusted value 8 bar.

Time (s)	Consumption (Wh)	H ² volume (l)	*EEQ (Wh)	Efficiency (%)
0	0	0	0	0
300	46	3,09	9,92	21,56
600	88	7,02	22,54	25,61
900	121	10,96	35,18	29,08
1200	159	14,54	46,68	29,36
1500	203	18,66	59,9	29,51
1800	232	21,55	69,18	29,82

Tab. 4: Adjusted value 9 bar.

Time (s)	Consumption (Wh)	H ² volume (l)	*EEQ (Wh)	Efficiency (%)
0	0	0	0	0
300	45	3,71	11,91	26,47
600	74	6,47	20,77	28,07
900	104	9,7	31,14	29,94
1200	137	12,95	41,57	30,65
1500	175	16,04	51,49	29,42
1800	200	19,08	61,25	30,63

Tab. 5: Adjusted value 10 bar.

Time (s)	Consumption (Wh)	H ² volume (l)	*EEQ (Wh)	Efficiency (%)
0	0	0	0	0
300	35	3,95	12,68	36,23
600	64	6,78	21,77	34,01
900	84	9,66	31,01	36,92
1200	113	12,08	38,78	34,32
1500	143	15,78	50,66	35,43
1800	176	18,8	60,35	34,29

Tab. 6: Adjusted value 13,79 bar.

Time (s)	Consumption (Wh)	H ² volume (l)	*EEQ (Wh)	Efficiency (%)
0	0	0	0	0
300	36	3,57	11,46	31,84
600	70	7,18	23,05	32,93
900	96	10,25	32,91	34,28
1200	131	13,88	44,56	34,01
1500	165	16,92	54,32	32,92
1800	190	19,9	63,88	33,62

Tab. 7: Final values.

	Consumption (Wh)	H ² volume (l)	*EEQ (Wh)	Efficiency (%)
7 bar	233	18,7	60,03	25,76
8 bar	232	21,55	69,18	29,82
9 bar	200	19,08	61,25	30,63
10 bar	176	18,8	60,35	34,29
13,79 bar	190	19,9	63,88	33,62

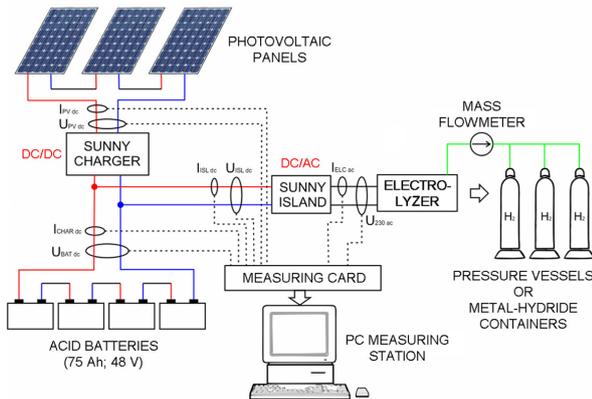


Fig. 4: Block diagram of a solar hydrogen storage system. [5].

maximum value is 13,79 bar. Other adjusted values are taking into account a warmed up electrolyzer with pre-heated water which means higher efficiency of the process.

Table 7 shows comparison of final values of all pressures as measured over the period of 30 minutes. Efficiency indicator was the most important one. The highest efficiency of hydrogen production cycle was achieved at the pressure of 10 bar. This is the hydrogen output pressure on electrolyzer.

Efficiency is closely connected with another critical parameter - electrical power consumption during the generation cycle. As Fig. 5 shows, consumption decreases with rising pressure manually adjusted on the electrolyzer unit. Consequently (see Fig. 6), hydrogen generated during electrolysis is compared with equivalent energy quantum (EEQ).

4. Conclusion

Measurement comprised setting of operation pressure levels of hydrogen on electrolyzer, specifically within the range between 7 and 13,79 bar. The duration of hydrogen production period per set pressure level was 30 minutes.

The measurement process experienced several drop-outs of the electrolyzer off the operating mode, when the cause for such failures was mainly due to low level of input de-mineralised water. Remedy of failure by oper-

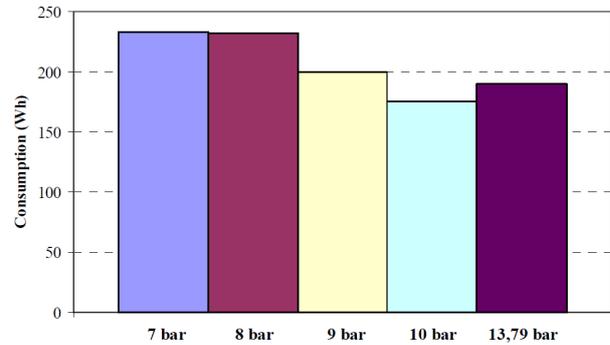


Fig. 5: Comparison of consumption for various adjusted pressures.

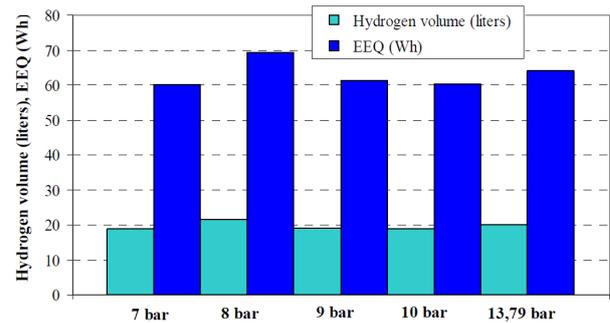


Fig. 6: Comparison of hydrogen volume produced.

ator always required repetition of the electrolyzer pressurising cycle. That was projected in increased consumption of electric power, which resulted in decreased efficiency of hydrogen production in electrolyzer. As far as research is concerned, such drop-outs can be deemed remote observations which were not considered during data evaluation. The effect of so called "blow-offs" in electrolyzer leading to minor escape of hydrogen gas into ambient atmosphere, detected by the relevant apparatus. However, the resultant concentration of hydrogen in air never reached even the 10 % threshold of explosiveness that matches settings of safety sensors inside laboratory.

The final stage was associated with comparison analysis of data obtained by measurement for all hydrogen pressure levels set on the electrolyzer output. Those values were 7, 8, 9, 10 and 13,79 bar respectively. The data obtained from measurement was used to evaluate the efficiency of hydrogen production. The weak-

est efficiency (25,76 %) was achieved with pressure of 7 bar. The production cycle for pressure of 7 bar shows the worst values in all aspects. Except for the highest pressure (13,79 bar), the efficiency of hydrogen production increased with rising pressure, while the electric power was decreasing. As far as efficiency (34,29 %) is concerned, the best results were rendered with hydrogen pressure level of 10 bar. That did not confirm the assumption that the highest efficiency of hydrogen production was achieved at the highest pressure level (33,62 %).

Another parameter definitely affecting efficiency of hydrogen production is the temperature of reaction demineralised water at input to the Hogen GC600 electrolyzer. Further research will be aimed in this respect.

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