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Analysis of Hydrogen Production in Alkaline Electrolyzers

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Abstract

Increasing the share of renewables in the energy mix at the expense of non-renewable sources, which account for a major part of base load power generation units, adversely affects the stability of power systems. In order to maintain stability, there is a need to develop electric energy storage. One solution is to store surplus energy in the form of hydrogen. At present hydrogen is mainly obtained in the processes of using non-renewable fuels. However, it may also be obtained through an electrolysis process, powered by electricity produced from renewable energy sources. This article presents the principle of operation of various types of electrolyzers and presents selected characteristics for alkaline electrolyzers.

Keywords: electrolysis, electrolyzer, hydrogen, efficiency

1. Introduction

The is growing interest in a possible hydrogen-related aspect to electricity produced from renewable energy sources. The rise of renewable energy sources has reduced the share of energy produced from fossil fuels such as coal, lignite, oil and natural gas, which are the main sources in centralized power generation units. The energy sector is therefore on the cusp of major structural changes. Generation of electricity based on renewable energy adversely affects the stable operation of power grids, because depending on the prevailing conditions (especially weather), they feed varying and unpredictable supplies of electricity into the network [1]. This problem applies particularly to energy from wind and solar farms. Increasing the share of renewable sources of energy in electricity production adversely affects the energy system and at the same time leads to non-optimal work, because the unpredictability inherent in wind and solar power supplies gives rise to a need for rapid reactions by centralized sources of energy production in the energy system [2]. Currently, variations in power are completely covered by existing elements of the power system. However, further increase in the potential (power capacity) of renewable energy sources will force energy providers to develop large amounts of energy storage to improve power system stability [3].

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2. Water electrolysis process

Electrolysis of water plays a crucial role in the production of hydrogen based on electricity from renewable energy sources. Hydrogen obtained from electrolysis is characterized by very high purity (99.9%, regardless of the type of electrolyzer), while the electrolysis process itself is easy to use and does not require a long start-up time [4].

The electrolysis process is closely linked with two laws formulated by Faraday [5]. Equation (1) presents Faraday's first law of electrolysis. According to this law, the mass of ions generated at the electrode is proportional to the total charge that flows through the electrolyte.

$$m = q \cdot k_e = I \cdot t \cdot k_e \tag{1}$$

where: m—mass of produced chemical substance, kg; q —charge flowing through the electrode, C; k_e—electrochemical equivalent, kg/C; I—current value, A; t—time, s.

Equation (2) shows Faraday's second law of electrolysis, which determines the charge q needed to separate the mass of substance m.

$$q = \frac{F \cdot m \cdot n}{M} \tag{2}$$

where: F—Faraday constant value, $F = 96485.3365$ C/mol; n—amount of ions involved in the reaction; M—molar mass of the substance, kg/mol.

Substituting equation (2) into equation (1) the relationship with the electrochemical equivalent described by equation (3) can be written.

$$k_e = \frac{M}{n \cdot F} \quad (3)$$

The above relationships based on Faraday's laws show that the mass of hydrogen produced by electrolysis of water is directly proportional to the current passing through the electrolyte and the duration of the electrochemical reaction. The number of ions involved in the reaction is $n = 2$.

Hydrogen is produced by water electrolysis due to the reaction occurring at the cathode and anode of the electrolyzers. Electricity is used in this case to break the water into two basic elements—hydrogen and oxygen [6, 7]. The oxidation process occurs at the anode and the reduction process at the cathode. Electrolyzer is constructed from a stack of connected cells responsible for the water electrolysis process. One electrolyzer does not necessarily have to consist of only one stack of cells. Electricity and heat must be supplied to maintain the electrolysis process. At low temperature the heat for the reaction is generated by the flow of current through the electrolyzer.

The reactions at the anodes and cathodes differ accoring to types of of electrolyzers, of which there are several [8]. The most popular are alkaline water electrolyzers or electrolyzers with a polymeric membrane (PEM water electrolyzers).

2.1. Alkaline water electrolyzers

This is the most common technology used in water electrolysis. The efficiency of electrolysis in such devices can reach 82% [9, 10]. Alkaline electrolyzers are characterized by high efficiency and affordable price. The purity of hydrogen obtained by electrolysis using this type of equipment is very high, ranging from 99.7% to 99.9%. In this process, water should be provided with a conductivity of less than 5 µS/cm [9]. The reaction occurring at the cathode (HER—Hydrogen Evolution Reaction) and anode (OER—Oxygen Evolution Reaction) are shown by equations (4) and (5) while the overall reaction is shown in equation (6) [9, 10].

Cathode (-)

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad (4)$$

Anode (+)

$$2OH^- \rightarrow \frac{1}{2}O_2 + H_2O + 2e^- \quad (5)$$

$$H_2O \rightarrow H_2 + \frac{1}{2}O_2 \quad (6)$$

A typical electrolyzer of this type consists of two electrodes immersed in the electrolyte and separated by a membrane. The role of the solution is to maximize ionic conductivity. It contains mostly KOH. The operating temperature of the process ranges from 40°C to 90°C [10]. A solution of NaCl or NaOH can also be used as the electrolyte, but they are less common. A schematic diagram of the device is shown in Fig. 1.

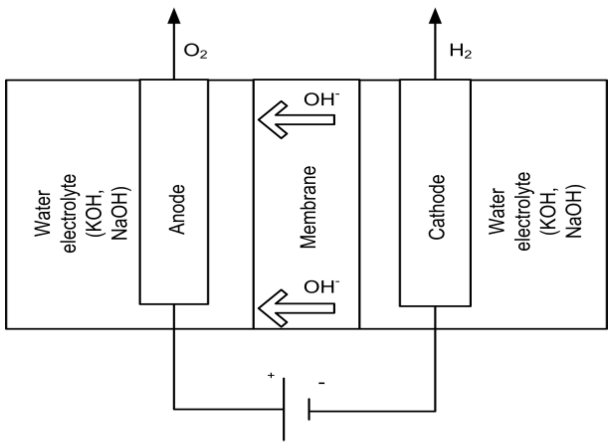

Figure 1: Schematic an of alkaline water electrolyzer

In this type of device water with electrolyte is located on both sides of the electrodes. Cathode and anode are separated by a thin polymeric membrane. This membrane is penetrated by OH- ions, which result from the reaction occurring at the cathode. Hydrogen is obtained from the cathode, and water with a small amount of oxygen from the anode. Electrolyzers of this type are characterized by long durability and lifetime.

2.2. PEM water electrolyzers

Proton exchange membrane (PEM) electrolyzers produce hydrogen of very high purity and require very pure water with low conductivity of about 1 µS/cm [9]. Water is supplied only on the anode side, where it is separated into hydrogen and oxygen ions. The membrane allows only hydrogen ions, which are then reduced at the cathode. Oxygen with moisture are obtained from the anode whereas from the cathode hydrogen is obtained with a small amount of moisture that might penetrate through the membrane. In this type of electrolyzer there is a very thin polymeric membrane separating the cathode and anode. The chemical reactions for these devices are shown by equations: (7) for the anode (8) for the cathode and (9), representing the total reaction [9–11].

Anode (+)

$$H_2O \rightarrow 2H^+ + 2e^- + \frac{1}{2}O_2 \quad (7)$$

Cathode (-)

$$2H^+ + 2e^- \rightarrow H_2 \quad (8)$$

$$H_2O \rightarrow H_2 + \frac{1}{2}O_2 \quad (9)$$

The oxidation process at the anode produces free hydrogen ions and oxygen, while at the cathode hydrogen ions are reduced. A disadvantage of these devices is progressive consumption of the membranes during work. Fig. 2 shows a schematic diagram of the PEM water electrolyzer.

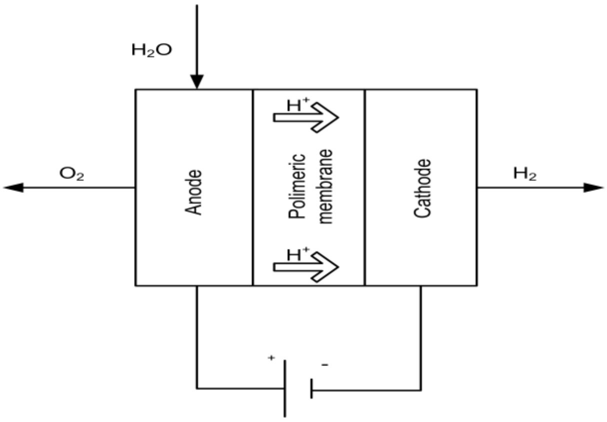

Figure 2: Schematic of PEM water electrolyzer

Table 1: Comparison of commercially available alkaline and PEM water electrolyzer technologies [12]

	Parameter	Alkaline	PEM
1	Performance,$Nm^3{}_{H2}$/h	0.25--760	0.01–240
2	Power, kW	1.8--5300	0.2--1150
3	Hydrogen purity, %	99.5--99.9998	99.9--99.9999
4	Indicative system costs, €/kW	1000–1200	1900--2300

The electrolysis process requires the cells to be supplied with a DC power source, which can result in the need to use rectifier circuits for energy from wind farms and / or energy transmitted from the national power system.

3. Comparison of selected types of electrolyzers

Table 1 shows a comparison of commercially available alkaline and PEM water electrolyzer technologies [12].

The data presented in Table 1 show that alkaline electrolyzers enjoy greater efficiency and power (for single unit) as well as lower capital cost than PEM electrolyzers. However, the hydrogen produced using PEM electrolyzers is characterized by a slightly higher purity than is the case with alkaline electrolyzers. The power of units producing hydrogen can be improved by combining individual electrolyzers.

The alkaline water electrolysis process is well-known technology. Alkaline electrolyzers are characterized by long term durability and high power of the units, but also small current density and a low range of partial load. While PEM water electrolyzers are more compact and dynamic, they also have high current density, effective load of partial work and can produce very high purity hydrogen. However, they are characterized by lower durability and higher price than alkaline water electrolyzers [10, 12, 13].

4. Object of the study

The object of the research and analysis was a hydrogen generator with performance of 500 Nl H_2/h, maximum pressure 35 bar and water consumption of 0.4 l/h. The tested generator consists of three integrated modules: Power supply module, electrolysis module and dryer module. The structure of the entire hydrogen generator is presented in Fig. 3.

4.1. Power supply module

This module includes two power supplies responsible for the supply of electrolyzers (P1.2 and P1.3) while a third is responsible for the power supply control systems and security included in all generator modules. This module is also equipped in a main board controller system responsible for the start-up process and all operations of the hydrogen generator and internal measurement system. This measurement system is responsible for measured current and voltage values, stack and outlet hydrogen pressure and also temperature of the KOH solution. A schematic diagram of the power supply module is presented in Fig. 4.

4.2. Electrolysis module

The electrolysis module is composed of two independently powered alkaline electrolyzers with anion exchange membrane (AEM) working at the common hydrogen outlet, an electrolyte tank, a cooler, an electrolyte circulation pump and a pump responsible for refilling water. KOH water solution (electrolyte) is delivered to the electrolyzers. Fig. 5 shows a schematic diagram of this module.

4.3. Dryer module

Adding an extra dryer module in the hydrogen generator can raise the purity of hydrogen to 99.999%. This very high purity means the hydrogen can be stored in special absorbing tanks, used to power fuel cells or used in chemical processes with ultra high purity requirements. The use of an additional drying module is optional. Improving the purity of hydrogen results in increased dimensions and energy consumption of the system. The drying module consists of two alternating operating dryers that ensure the desired purity of hydrogen for the
device. The module also includes valves and fans. Fig. 6 shows a schematic diagram of the dryer module.

After the generator is turned on the stack hydration phase lasts 30 to 60 seconds, depending on the software installed in the device. Then, the generator control system checks the temperature of the solution. If it exceeds 20°C, the electrolyzer is given voltage to start the production of hydrogen, which is gradually increased to the nominal device capacity. Then installations of the electrolyzer fill with hydrogen. After the pressure inside the electrolysis module exceeds 33 bar the outlet valve is opened to allow the hydrogen to flow to the dryer module. Then the dryer module installation is filled withgas. After the dryer module fills up and the pressure reaches a steady state in the whole hydrogen generator, the

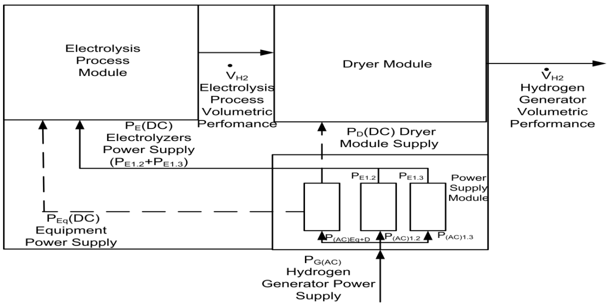

Figure 3: Structure of hydrogen generator system

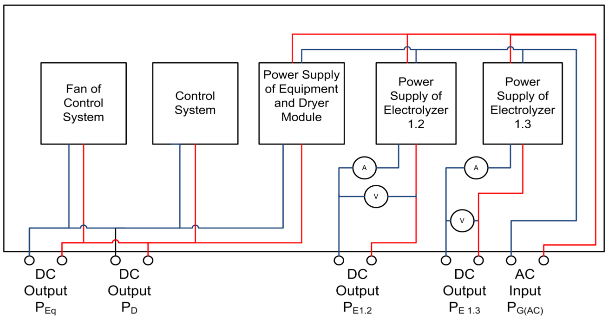

Figure 4: Schematic of power supply module

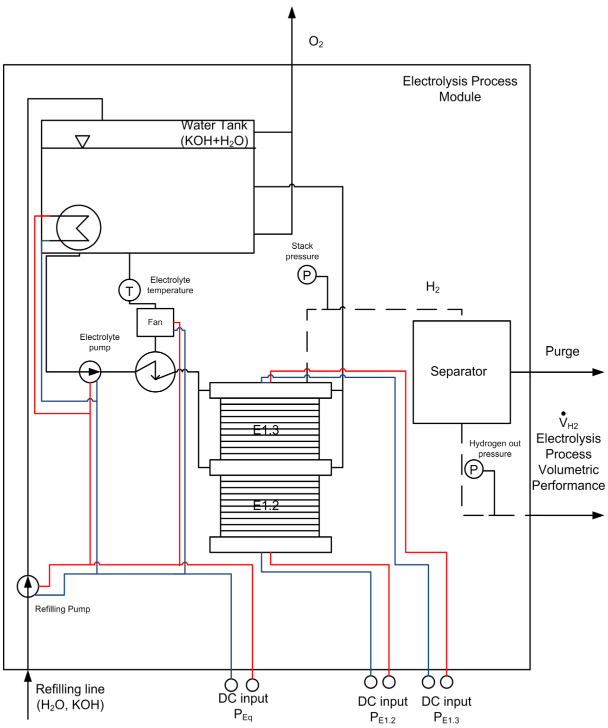

Figure 5: Schematic of electrolysis process module

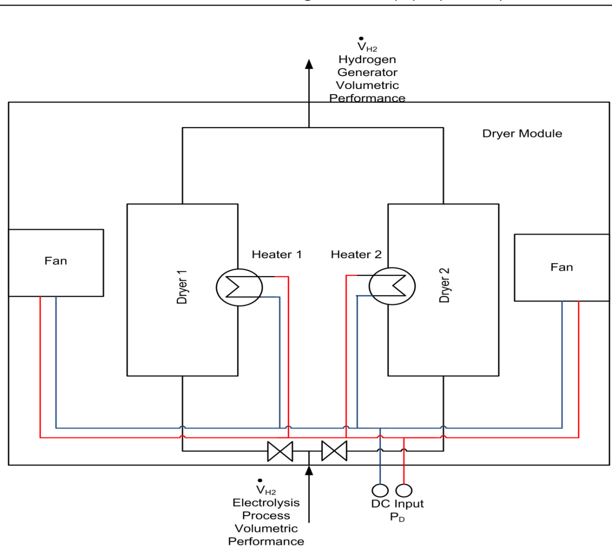

Figure 6: Schematic of dryer module

Table 2: Summary the operating modes of generator

	Process	Power (AC), W	Time, s
1.	Refilling (only for low water level)	101	--
2.	Stand by	34	–
3.	Heating (solution temperature < 20°C)	100	--
4.	Stack Hydration	123	30–60
5.	Ramp up	123–2520	120
6.	Hydrogen production	2520–2730 (Filling Installation)	180
		2400–2800 (Stable Work)	--

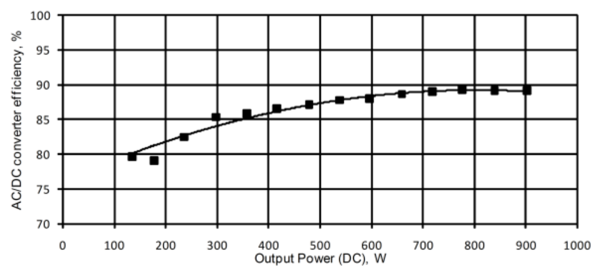

Figure 7: Efficiency of tested AC/DC converter according to the output DC power for stabilized voltage value

main control unit opens the outlet valve at the end of the hydrogen generator. The entire start-up process of the hydrogen generator from cold state takes about 5–6 minutes.

A Coriolis flow meter was installed in the hydrogen generator's measuring system to measure the flow of hydrogen produced. Table 2 gives a summary of the operating modes of the generator (values are given for the nominal operating point of the device).

5. Reaserch results

5.1. Analysis of supply electrolyzers system

The electrolyzers subject to analysis are powered by the AC mains through an AC/DC converter. In view of need to use the converter in the power supply module, there is some loss of electricity. The energy conversion efficiency in these devices depends on the power, and ranges from 70% for a low load to 90% for the nominal device power. So, any power transformation reduces the efficiency of the system [6]. For large AC/DC converters, efficiency can reach 95% for nominal device power.

The first stage of the study was to determine the characteristics of power supplies responsible for the supply of individual electrolyzers. Nominal power of this power supply is 1500 W and nominal voltage is 48 V. The efficiency of the tested AC/DC converter was determined as the ratio of output DC power ($P_{E1.2}$) to input AC power ($P_{(AC)1.2}$) and calculated by equation (10).

$$\eta_{AC/DC} = \frac{P_{E1.2}}{P_{(AC)1.2}} \tag{10}$$

where: $\eta_{AC/DC}$—AC/DC converter efficiency; $P_{E1.2}$—output DC power, W; $P_{(AC)1.2}$—input (AC) power, W.

Fig. 7 shows the efficiency of the tested AC/DC converter according to the output power measured for stabilized voltage value of 30 V, calculated by equation (10).

The efficiency of the tested power supply ranged from about 80% for small values of the load (about 10% of rated power) to about 90%. The efficiency obtained for voltages greater than 30 V was only slightly higher. The voltage of operating electrolyzers is load-dependent and in the range 30-34 V. Fig. 8 shows the efficiency of the AC/DC converter for different values of output voltage for a constant value of output current of 30 A (nominal current value), calculated by equation (10).

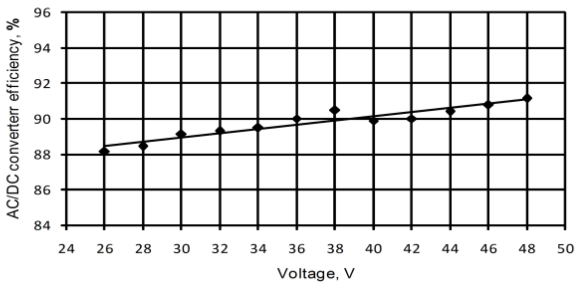

Figure 8: Efficiency of AC/DC converter for different values of voltages at a constant current value

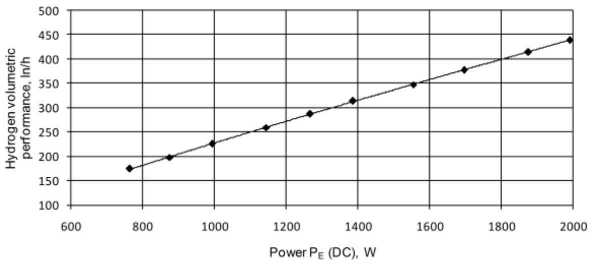

Figure 9: Volumetric performance of electrolysis process according to power delivered to electrolyzers

The highest efficiency (91%) was obtained for the highest voltage (48 V), which is equivalent to the nominal parameters of power supply.

5.2. Analysis of electrolyzers

In the next stage of the research the characteristics of performance, efficiency and electrical consumption of tested hydrogen generator and electrolyzers were determined. Volumetric performance of the electrolysis process was determined by changing current value supply electrolysers. Fig. 9 shows the volumetric performance of the electrolysis process ($\dot{V}_{H2}$) as a function of power delivered to electrolyzers.

The characteristics in Fig. 9 shows that the maximum volumetric performance of a hydrogen generator for nominal parameters obtained from the measurements is 440 dm$^3{}_n$/h. According to the Faraday laws presented earlier, performance of electrolysis process is linearly dependent on the value of the supply current.

Knowing the volumetric performance of the electrolysis process, voltages and currents, it is possible to determine the efficiency of the electrolysis process defined by the equation (11).

$$\eta_E = \frac{\dot{V}_{H2} \cdot HHV_{H2}}{P_{E(DC)}} \tag{11}$$

where: η_E—electrolysis process efficiency; $\dot{V}_{H2}$—hydrogen volumetric performance, m$^3{}_n$/h; HHV_{H2}—hydrogen high heating value, J/ m$^3{}_n$, $P_{E(DC)}$—power delivered to electrolyzers, W.

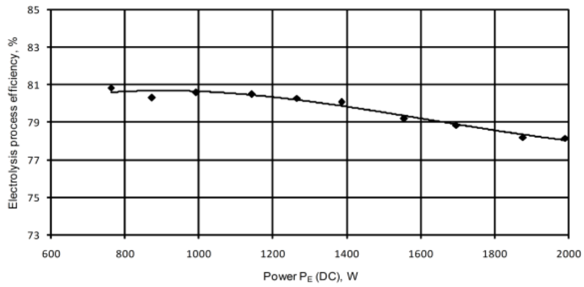

Figure 10: Efficiency of the electrolysis process as a function of the power delivered to electrolyzers

The power delivered to electrolyzers was expressed as the sum of products of currents and voltages measured at each of them. This value was calculated by equation (12).

$$P_{E(DC)} = P_{E1.2} + \mathrm{P}_{\mathrm{E1.3}} = I_{1.2} \cdot U_{1.2} + I_{1.3} \cdot U_{1.3} \tag{12}$$

where: $P_{E1.2}$—power to supply electrolyzer 1.2 W; $P_{E1.3}$—power to supply electrolyzer 1.3 W; $I_{1.2}$—current intensity measured on electrolyzer 1.2 A, $U_{1.2}$ —voltage measured on electrolyzer 1.2 V; $I_{1.3}$—current intensity measured on electrolyzer 1.3 A; $U_{1.3}$—voltage measured on electrolyzer 1.3 V.

The characteristic of efficiency of the electrolysis process calculated by eq. (11) as a function of the power delivered to electrolyzers (eq. 12) are shown in Fig. 10.

Electrolysis process efficiency decreases with increasing power. For rated power, the efficiency of electrolysis is 78%, but for about 30% of rated power the efficiency rises to 81%.

The next step of the research was to determine hydrogen generator efficiency. Hydrogen generator efficiency was calculated according to equation (13).

$$\eta_G = \frac{\dot{V}_{H2} \cdot HHV_{H2}}{\mathrm{P}_{\mathrm{G(AC)}}} \tag{13}$$

where: η_G —hydrogen generator efficiency; $\dot{V}_{H2}$—hydrogen volumetric performance, m$^3{}_n$/h; HHV_{H2}—hydrogen high heating value, J/ m$^3{}_n$; $P_{G(AC)}$—power delivered to hydrogen generator, W.

Hydrogen generator input power $P_{G(Ac)}$ was calculated according to equation (14).

$$P_{G(AC)} = P_{E(DC)} + (P_{Eq} + P_D) + \Delta P_{\eta(\mathrm{AC/DC})} \tag{14}$$

where: $P_{G(AC)}$—power delivered to hydrogen generator, W; $P_{E(DC)}$—power delivered to electrolyzers, W; (P_{Eq}+P_D)—power to supply another equipment in hydrogen generator, W; $\Delta P_{\eta(AC/DC)}$—AC/DC converter power losses, W.

Value of $P_{E(DC)}$ was regulated by current depending on demand for hydrogen. (P_{Eq}+ P_d) value was determined at constant level for stable generator work and was 400 W. Value

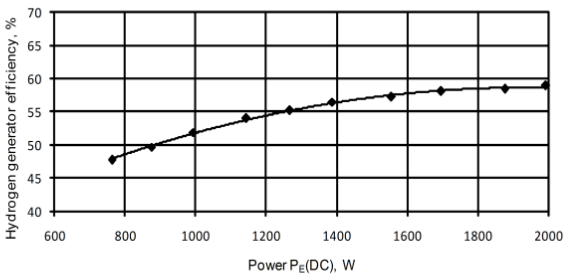

Figure 11: Hydrogen generator efficiency as a function of electrolysis process power supply (DC)

$\Delta P_{\eta(AC/DC)}$ was calculated using the value of AC/DC converter efficiency (eq. 10) and power delivered to electrolyzers (eq. 12) and defined by equation (15).

$$\Delta P_{\eta(AC/DC)} = P_{E(DC)} \cdot \left(\frac{1}{\eta_{AC/DC}} - 1\right) \tag{15}$$

The characteristics of hydrogen generator efficiency at measured points as a function of the electrolysis process power supply (DC) are shown in Fig. 11.

Another important parameter is electrical consumption. This parameter shows how much energy is needed to produce a certain product stream. The next step of research was to determine electrical consumption for the hydrogen generator and electrolysis process. Electrical consumption was determined as a ratio of power delivered to generator or electrolysis process to volumetric hydrogen performance. Electrical consumption was calculated according to equation (16).

$$E_C = \frac{P_i}{\dot{V}_{H2}} \tag{16}$$

where: E_C—electrical consumption of hydrogen generator or electrolysis process, kWh/m$^3{}_n$; P_i—power delivered to hydrogen generator or electrolysis process (for generator P_i is equal $P_{G(AC)}$ from eq.(14) and for electrolysis process P_i is equal to $P_{E(DC)}$ from eq.(12), W; $\dot{V}_{H2}$—hydrogen volumetric performance, m$^3{}_n$/h.

Fig. 12 shows the characteristics of electrical energy consumption in the electrolysis process and amount of electrical energy consumption by the entire generator for different hydrogen performance.

It is possible to describe the correlation between efficiency and electrical energy consumption. This correlation is presented by equation (17).

$$\eta = \frac{1}{E_c} \cdot HHV_{H2} \tag{17}$$

where: η—electrolysis process/hydrogen generator efficiency; E_C—electrical consumption of hydrogen generator/electrolysis process, kWh/m$^3{}_n$, HHV_{H2}—hydrogen high heating value, kWh/m$^3{}_n$.

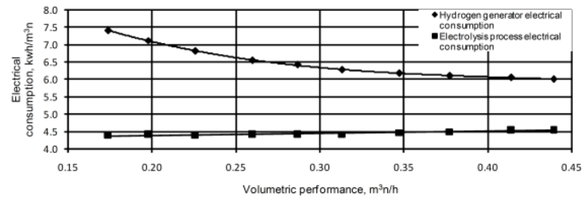

Figure 12: Electrical energy consumption in the electrolysis process and by the entire hydrogen generator for different hydrogen volumetric performance

6. Summary/Conclusions

Hydrogen has many qualities that may qualify it as the fuel of the future. However, it should be emphasized that this paper concerns hydrogen obtained in processes using renewable energy sources. It is worth noting that hydrogen is currently obtained mainly from the gasification of coal or refining of natural gas, which is associated with the use of energy from non-renewable fossil fuels. The Energy Returned on Energy Invested (ERONEI) coefficient for hydrogen is about 0.8 which is far below the value of 1 [14]. Hydrogen production is only justified when this process is supplied by energy from renewable energy sources.

Increasingly, hydrogen is being produced by water electrolysis involving electrolyzers powered directly from renewable sources of energy. Technological progress has made it possible to create a device in which the efficiency of the electrolysis process is often above 80%, and the purity of hydrogen obtained is close to 100%. Electrolyzers used in alkaline hydrogen generators are a perfect example of this.

The hydrogen generator subject to analysis is equipped with two alkaline AEM electrolyzers and the KOH solution satisfies the role of the working solution. The article presents the characteristics of the electrolyzers studied and of the entire hydrogen generator. The maximum performance of the device was about 440 dm$^3{}_n$/h and the highest efficiency of the electrolysis process is about 81%. The highest efficiency of the electrolysis process was received for the lowest hydrogen volumetric performance. The temperature of the KOH solution during measurement was about 40°C. After turning from a cold state, hydrogen appears at the outlet of the generator (with the currently installed system control algorithm) after about 6 minutes.

Hydrogen generators cooperating with renewable energy sources and fuel cells are attracting more research interest, as they can provide an interesting solution for storing large amounts of energy [15–17]. The use of renewable energy sources to power electrolysis could resolve the problem with the stochastically varying amounts of energy these installations to the power system. Surpluses of energy resulting from the operation of renewable energy sources would be used to produce hydrogen through water electrolysis, which would then be stored. The stored hydrogen could then be readily converted to electricity during shortages in the energy system. This would lead to greater stability in power systems and would equalize the loads of transmission networks.

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