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Abstract. The article presents idea of installation to energy storage in the form of hydrogen – Power to Gas (P2G). The results of laboratory tests carried out at the Silesian University of Technology in the Institute of Power Engineering and Turbomachinery (IMIUE), covering selected aspects of hydrogen generators most frequently used in these types of installations are presented. The influence of water conductivity and temperature during continuous operation of the electrolyzer at constant current value and in operation at variable current on the efficiency of the tested devices are shown. A hydrogen generator equipped with two AEM electrolyzers with a performance of 0.5 Nm³H₂/h and a generator containing four PEM electrolyzers connected in series, with a maximum performance of 1.58 Ndm³/min were tested. The efficiency characteristics of the electrolysis process, efficiency of the electrolyzers and changes in the resistance values for both types of electrolyzers were presented. Calculations to estimate effect of temperature change on the efficiency characteristic of AEM electrolyzers were also made.

Keywords: power to gas, hydrogen generator, energy storage

INTRODUCTION

Constant increasing the share of electricity produced in power plants based on renewable energy sources reduce the dependence of energy sector from fossil fuels. (Kotowicz et al., 2017). Renewable power plants (such solar or wind) are characterized by varying amounts of produced electricity, which depend mostly on current weather conditions. In addition, there are natural "peaks" and "valleys" of electricity demand in the National Power System. Increasing the potential of units based on renewable energy sources leads to the inefficient operation of the energy systems and enforced to use an additional power regulation methods. Use of units to store energy surplus during electricity overproduction and then release stored energy into the grid at the time of electricity shortage, can improve optimization process of energy systems. Current fluctuations occurring in the electricity production from renewable energy power plants are offset by existing system components, but further increasing of renewable energy sources potential will force the need to use more energy storage units to enable stable work of energy systems (Węcel, Ogulewicz, 2010, Węcel et al., 2016). At present the most commonly used units to stabilize the power grid are pumped stored hydroelectricity power plants (PSH) (Mirek, Nowak, 2015, Krupa, 2015). Intensive research and test are also carried out on the possibility of energy store in the hydrogen form (Bartela et al., 2016, Kotowicz et al., 2017, Lepszy et al., 2016, Ogulewicz et al., 2010).

POWER TO GAS INSTALLATIONS

An example of a Power to Gas installation is shown in Figure 1. Power to Gas technology makes it possible to produce high-energy potential gas (hydrogen), in water electrolysis process based on the electricity from renewable energy sources. The process of transforming electricity into chemical energy of hydrogen in such installations can be reasonable in periods, when the amount of electricity produced in energy system exceeds its demand (Gahleitner, 2013, Varone, Ferrari, 2015, Guandalini et al., 2015, Guandalini et al., 2017)

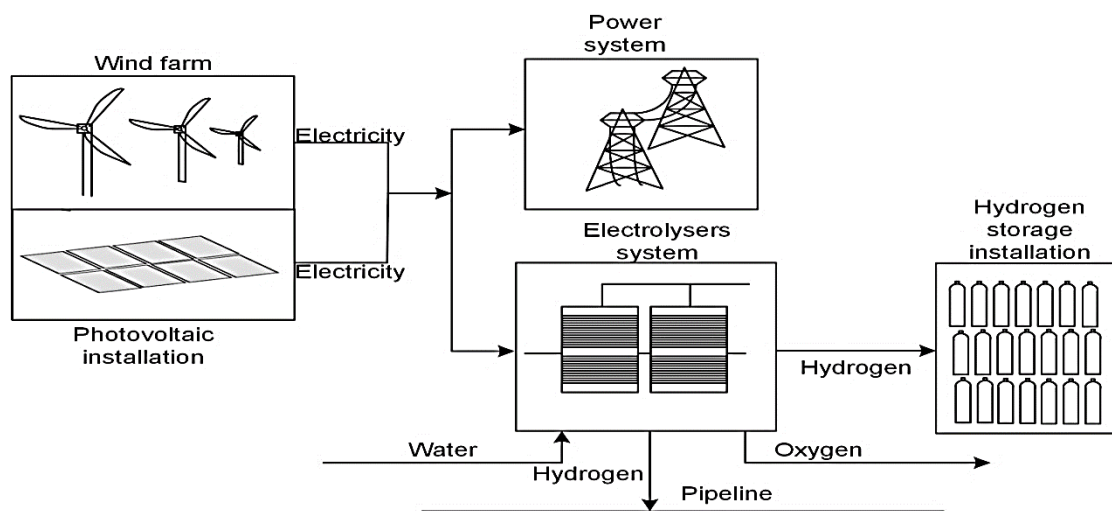


Fig. 1. Scheme of Power to Gas installation.

An important elements of any Power to Gas installation are hydrogen generators, which are responsible for water electrolysis process. In water electrolysis process hydrogen is produced by the reactions occurring on two electrodes: cathode (negative electrode) and anode (positive electrode). The hydrogen generator consists an electrolyzers and auxiliary devices, responsible for the proper operations of the generator (Kotowicz et al., 2017). The most commonly used types of electrolyzers are alkaline and PEM (*Proton Exchange Membrane*) devices. Differences in construction of these types of units are described in more detail in (Kotowicz et al., 2018, Kotowicz et al., 2017) and (Kotowicz et al., 2016).

EXPLOITATION STUDY OF HYDROGEN GENERATORS

Understanding the fundamental principles of hydrogen generators is a crucial issue for the correct design of a P2G installation, that can store energy in the hydrogen form. For this purpose, laboratory tests were made on two installations located in the Institute of Power Engineering and Turbomachinery at Silesian University of Technology. Laboratory stations allowed to study hydrogen generators equipped with two types of electrolyzers: PEM and AEM (Anion Exchange Membrane).

The first object of the study was the hydrogen generators equipped with PEM electrolyzers. For the purpose of exploitation research, configuration of four electrolyzers connected in series was examined. The measuring system made it possible to measure the value of the current supply to the electrolyzers system, the voltages on each unit and their temperature. Electrolyzers worked on a common hydrogen outlet on which gas stream and pressure were measured.

A another installation contained a generator with two AEM electrolyzers. These electrolyzers were powered independently from the supply power module. During the study, values of the supply currents and the voltages on each of the devices were measured. The stream of the generated gas and its pressure, as well as the temperature of working solution were also examined.

The purpose of the study was to determine electrolyzers and electrolysis process efficiency characteristics. The influence of water conductivity and temperature on the course of this characteristics were investigated. The analyzes were conducted in two operating modes: at constant current and at variable current values. During the test, no effect of the outlet pressure on the electrolyzers efficiency was observed.

During work, it was assumed according to Faraday's law, that the stream of hydrogen was directly proportional to the current. This relationship is described by the equation (1) (Millet, Grigoriev, 2013)

$$m = q \cdot k_e = I \cdot \tau \cdot k_e \quad (1)$$

where:

- m – mass of produced chemical substance,
- q – charge flowing through the electrode,
- k_e – electrochemical equivalent,
- I – current value,
- τ – time.

WATER CONDUCTIVITY

One of analyzed parameters was conductivity of water supplied to the electrolysis process. For each type of electrolyzers, the recommended water conductivity limit value is different. For PEM electrolyzers it is $1 \mu\text{S/cm}$, while for alkaline it is $5 \mu\text{S/cm}$ (Ursua et al., 2012). No significant effect of water conductivity on the parameters of the system was observed, such as the hydrogen flow, system efficiency or power delivered to electrolyzers. At the laboratory station water with a conductivity of $1.5 \mu\text{S/cm}$ and a conductivity about ten times greater equal about $15 \mu\text{S/cm}$ were tested. Figure 2 shows an example of a electrolysis efficiency characteristic for both conductivity as a function of PEM electrolysis system relative power.

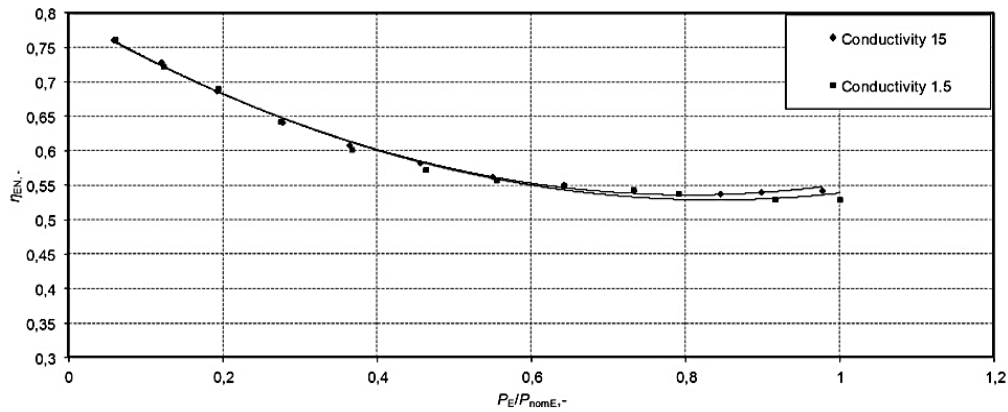


Fig. 2. Characteristic of the electrolysis efficiency for both water conductivity value as a function of PEM electrolysis unit relative power.

Electrolysis efficiency was calculated according to the equation (2) (Kotowicz et al., 2017).

$$\eta_{EN} = \frac{n \cdot V^0}{U} \quad (2)$$

where:

- η_{EN} – electrolysis efficiency,
- n – number of cell in electrolyzer,
- U – voltage value,
- V^0 – neutral thermal voltage (1.48 V).

The power delivered to the electrolyzers was defined as the sum of the supply currents and the voltages on each electrolyzer according to the relationship (3). For nominal power P_{nomE} was assumed value at the highest electrolyzer performance, so according to equation (1) for maximum supply current value.

$$P_E = \sum I_1 \cdot U_1 + I_2 \cdot U_2 + \dots + I_n \cdot U_n \quad (3)$$

where:

- P_E – power supplied to the electrolyzers,
- U – electrolyzer voltage.

Although conductivity of water does not affect on the tested systems parameters, it may have a significant effect on their durability. During long-term exploitation work, it was noted, that with time the voltage on each electrolyzers were increased. Increasing these values ultimately results in degradation of the efficiency. Figure 3 shows the characteristics of the change in

electrolysis efficiency calculated according to equation (2) after 7 years of exploitation (current results were obtained for the conductivity $1.5 \mu\text{S}/\text{cm}$).

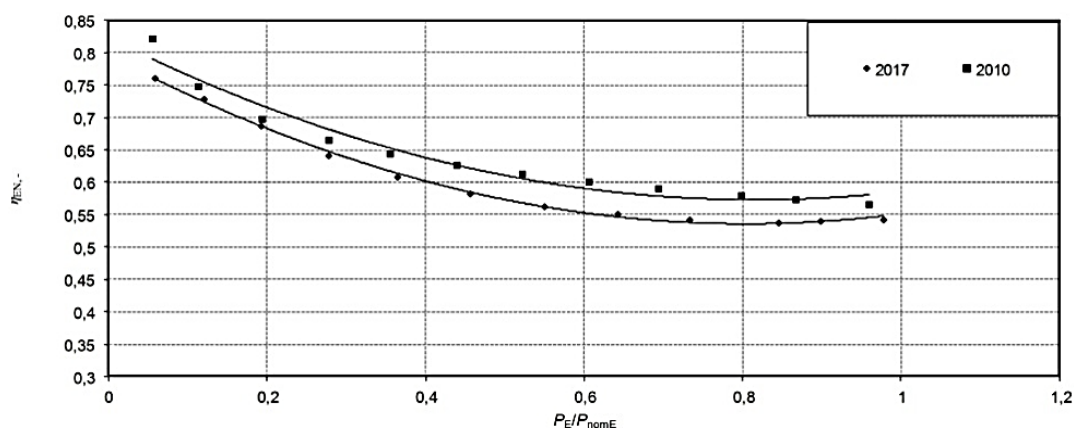


Fig. 3. Change of electrolysis efficiency as a function of PEM electrolysis unit relative power after 7 years of exploitation.

After 7 years of exploitation, the voltages on electrolyzers were increased approximately by 1 V, that resulting in a decrease of the electrolysis efficiency by about 2 p.p. The reason of decreasing efficiency of the devices may be the aging process of the electrolyte, which during many years of operation could lose some properties, degradation of this parameters could have been accelerated by using water with too high conductivity value.

HYDROGEN GENERATOR WORK STATE

Startup process

Each hydrogen generator has specific working states. When the hydrogen generator equipped with AEM electrolyzers is turning on, the start-up phase of the device is started. Firstly, the temperature of working solution is checked by the system. If temperature is high enough, the watering process of the stack is started. The current targeted to each of electrolyzer is gradual increasing. When the maximum current is reached, hydrogen production process is beginning. Then, filling of the electrolyzers system with hydrogen is proceeding, simultaneously the pressure inside the stack is also increasing. When the specified pressure is exceeded, control system opens valve to allow hydrogen to flow out from the device.

Working at constant value of current supply

After the startup sequence, which length and mode depend largely on the type and size of the system (in case of the AEM electrolyzers system it is about 5-6 minutes), continuous operation state of the device work is followed. In the first phase of the study, a hydrogen generator was tested during operation at a constant current value. Assuming (according to equation (1)) that the generated hydrogen flow is directly proportional to the supply current value, was assumed that the value of the electrolysis process efficiency for a given current setting should be constant. However, for constant power supply settings (at the highest performance of the unit), changes in electrolyzers efficiency have been observed. This efficiency was defined according to the equation (4).

$$\eta_{EC} = \frac{HHV_{H_2} \cdot \dot{V}_{H_2}}{P_E} \quad (4)$$

where:

- η_{EC} electrolyzer efficiency,
- HHV_{H_2} hydrogen high heating value,
- \dot{V}_{H_2} hydrogen flow rate.

Analyzing the presented equations (3) and (4) for the case of parameters change, which can affecting on the value of efficiency at constant current, it was observed that the values of voltages measured on electrolyzers changed. This is due to changes in the electrolyte temperature. Resistance of electrolyzers depends on this temperature value. Relationship between currents and voltages describes the resistance value (5).

$$R_E = \frac{U}{I} \quad (5)$$

where:

R_E electrolyzer resistance.

Figure 4 shows the characteristics of the resistance change in the AEM electrolyzers as a function of temperature for a constant current supply value.

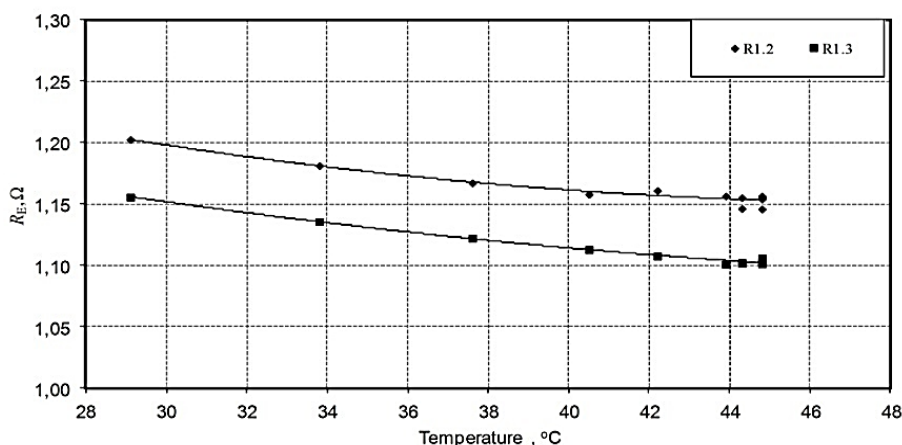


Fig. 4. AEM electrolyzer resistance value as a function of temperature.

During testing devices at constant current supply values, the resistance of electrolyzer E1.2 was change by 4% and for the electrolyzer E1.3 by 5% (in relation to maximum value). This resulted of a change voltage of 1.6 V on each of the tested devices.

Figure 5 shows the change in the resistance value of the two tested AEM electrolyzers as a function of time, while system work at a constant current supply value.

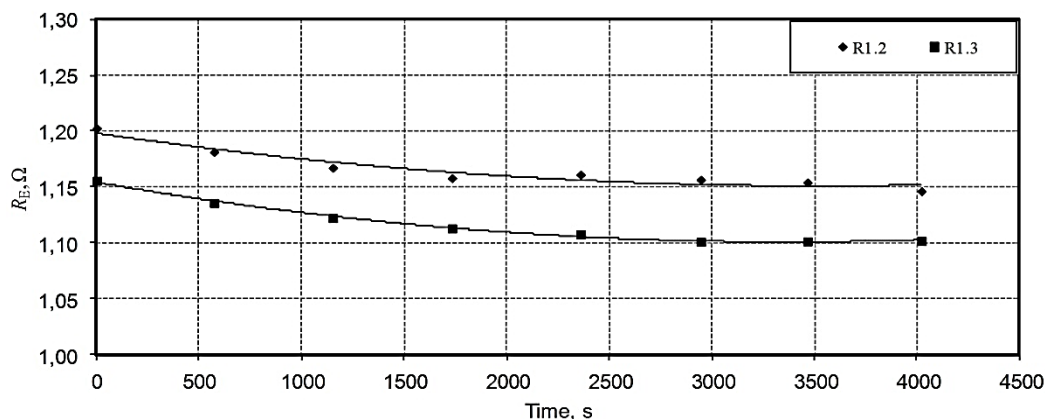


Fig. 5. Change in the resistance value of the two tested AEM electrolyzers as a function of time.

According to data presented in Figure 5, the resistance stabilizing process in AEM electrolyzers takes about 45 minutes. The value of the supply currents was 29 A for E1.2 and 30 A for E1.3. The hydrogen stream was about 7.35 Ndm³/min.

Changing the resistance affects to the efficiency value. This is due to the dependence (6), which was derived from equation (4) and (5).

$$P_E = \sum I_1 \cdot U_1 + I_2 \cdot U_2 + \dots + I_n \cdot U_n = \sum I_1^2 \cdot R_1 + I_2^2 \cdot R_2 + \dots + I_n^2 \cdot R_n \quad (5)$$

In case of calculation the electrolyzers efficiency temperature plays a crucial role. Stabilization of the temperature in the electrolysis system is not immediate and consequently also, the change of electrolyte resistance during the work of the device can be noticed.

Using the eq. (4) and (6) and also data presented in Figure 5, the change in the efficiency value during the temperature stabilization process was determined. This characteristic is shown in Figure 6.

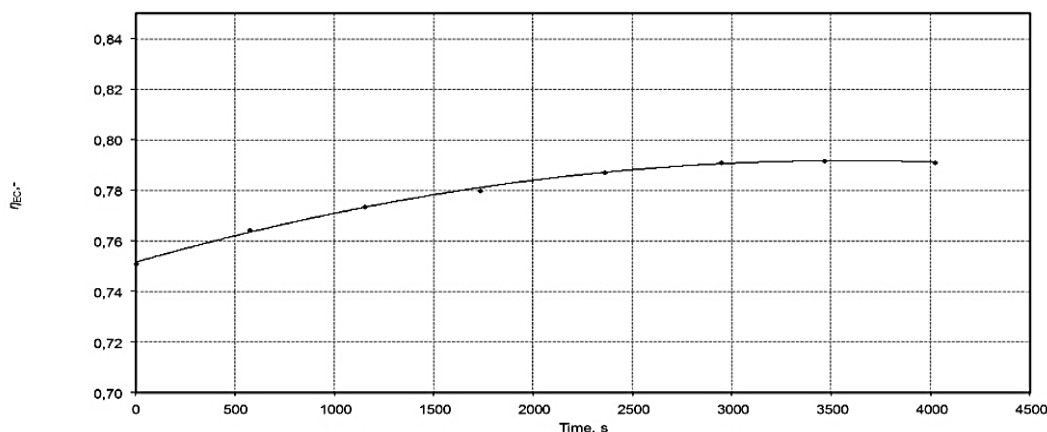


Fig. 6. Changing the electrolyzers efficiency in the function of time during the temperature stabilization process.

During temperature stabilization, electrolyzers efficiency changed from 75.1% to 79.2%.

It can be calculated (eq. (3)), that voltage increase by 1 V on each of the tested AEM electrolyzer (at currents for maximum device performance) causes an increase in power required to supply electrolyzers by about 3% (59 W). This change results in a degradation of the electrolyzers efficiency by approximately 2.4 p.p., from 79.2% to 76.8%.

In the serial configuration of four PEM electrolyzers, the value of the current supply, at the maximum system performance (1.58 Ndm³/min), was approximately 12 A. By adopting an analog calculation algorithm for this system configuration, power needed to supply this installation was calculated (for average voltage value UAV=13.64 V) by 656 W (eq. (3)). In this case, increase the voltage by 1 V on each of these devices, for maximum system performance, can results an increase in power supply value by 48 W (7.3% of nominal value), to 704 W. This is equivalent with reducing the electrolyzers efficiency by 3.5 p.p., from 51.3% to about 48.8%.

Hydrogen generator work at variable supply current values

Temperature through the electrolyte resistance has a significant impact on the efficiency, during exploitation of the hydrogen generator. Under real operating conditions, in cooperation with renewable energy source installations, characterized by a variable value of generated electricity in time, the values of currents supply to the electrolyzers can change. Reduction of the supply currents, causes decreasing the solution temperature, what results in a slight increase of the voltage. Rise of the working solution temperature can be achieve by increasing of current value, what in consequence decrease the voltage value. The described changes occur until the steady state is reached.

Figure 7 shows the dependence of PEM electrolyzers resistance and Figure 8 shows analogue characteristics for AEM devices.

During exploitation work with changing value of supply current, change of the electrolyzers resistance value can be observed. Resistance values change from 1 to 3.5 Ω for PEM electrolyzers (Fig. 7) and from 1 to 2.5 Ω for AEM devices (Fig.8).

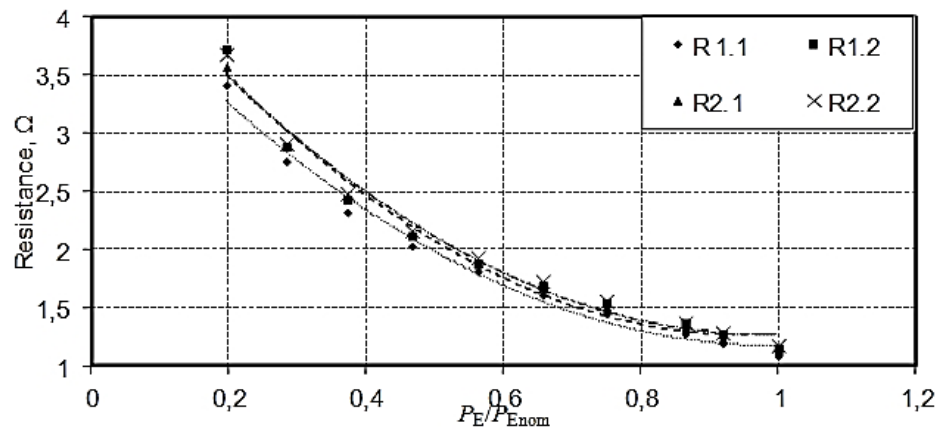


Fig. 7. PEM electrolyzers resistance as a function of the system relative power (temperature $\sim 25.5^\circ\text{C}$).

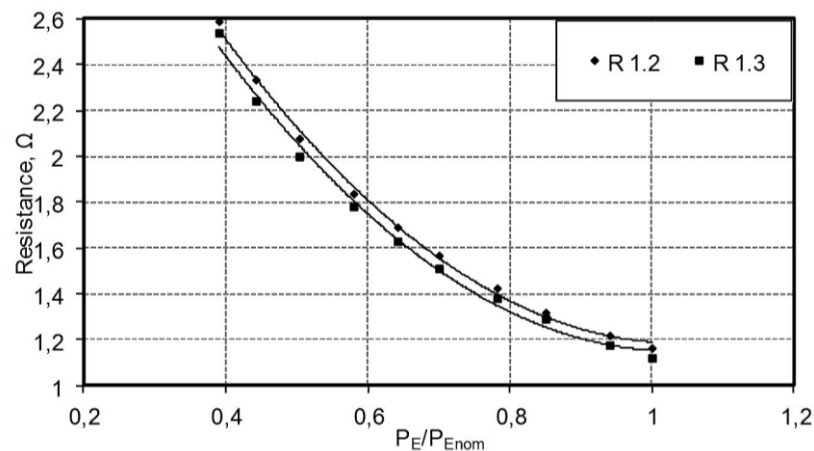


Fig. 8. AEM electrolyzers resistance as a function of the system relative power (temperature $\sim 42^\circ\text{C}$).

In order to calculate the influence of temperature to supply power value and on the efficiency of the tested devices, the data presented in Figure 4 was used. For knowing values of the supply currents (29 A and 30 A), function $R(t)$ was transformed using equation (5) to function $U(t)$. Then, the correction factor (k_{Ut}) was calculated, which shows the influence of temperature change to voltage values on the electrolyzers. These functions are shown in Figure 9.

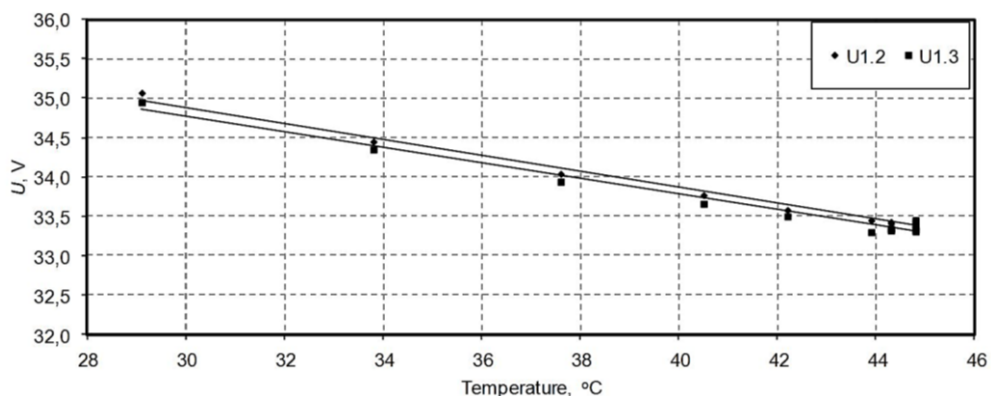


Fig. 9. Change of voltages on AEM electrolyzers for constant supply current as a function of temperature.

Calculated (k_{Ut}) factor is about $0.105 \text{ V}/^\circ\text{C}$ for electrolyzer E1.2 and $0.098 \text{ V}/^\circ\text{C}$ for electrolyzer E1.3. In further calculations it was assumed, that the (k_{Ut}) factor have the same value for the different current supply value. Then the influence of temperature on the efficiency of the tested devices was determined for three assumed temperature values: 50°C , 30°C and 20°C . Firstly,

the voltages on the electrolyzers for each assumed temperature were calculated by use equation (7).

$$U_t = U + k_{U_t} \cdot (t_r - t) = U + k_{U_t} \cdot \Delta t \quad (5)$$

where:

U_t voltage value for assumed temperature value,

k_{U_t} correction factor,

t_r real temperature value,

t assumed temperatures (e.g. 50°C, 30°C, 20°C)

Power required to power electrolyzers system was determined according to equation 3, taking into account the voltages (U_t) calculated for each temperatures. Hydrogen flow stream were measured on the outlet from hydrogen generator. For tested range of supply currents, hydrogen flow 7.35 Ndm³/min was maximum value and the lowest value was 2.9 Ndm³/min. Then the efficiency of the electrolyzers were calculated (eq. 4) for various temperature from 20°C to 50°C (typical temperature range for tested device). These characteristics are shown in Figure 10.

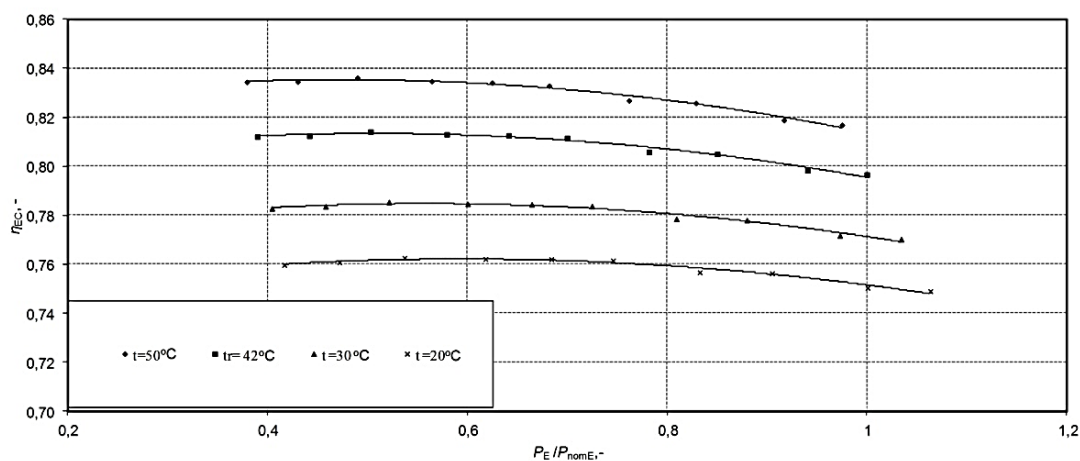


Fig. 10. The efficiency of the AEM electrolyzers for different temperatures as a function of the power referenced to the nominal power of the system.

From data presented in Figure 10 results, that increase of the electrolysis process temperature by 30°C, results of increase the efficiency for about 7 p.p. The nominal power value, was assumed the power from tests conducted for an electrolyte temperature equal 42°C and maximum device performance. The real efficiency characteristics of the examined AEM electrolyzers were shown in Fig. 10 as $t_r = 42^\circ\text{C}$ and determined based on the values of currents and voltages measured on the installation and implemented in to eq. (4). In calculations, it was assumed in according to eq. (1) that the hydrogen stream depends only on the value of the supply current. Exceeding value 1 for the P_E/P_{nomE} power ratio, results from the fact, that using equation (4) to determine the efficiency for different electrolyte temperature, only values of the power delivered to the device is change (denominator of equation 4). The value of the numerator remains unchanged.

CONCLUSION

- In case when potential of renewable energy sources in the energy systems is growing, the development of energy storage technologies is important.
- One of dynamically developing methods of energy storage is its storage in the hydrogen form. The electrolysis of water is a crucial process in the hydrogen generation based on renewable energy sources. Investigating fundamental principles of operations and characteristics of hydrogen generators is a key for correct design of P2G systems.
- Each type of electrolyzer have a limit value of water conductivity, which can be used in the electrolysis process. Using a water with too high conductivity does not affect on measured

parameters of tested systems. However, it may adversely affect to the materials used to build electrolyzer, shortening device lifetime. This can also affect to the efficiency degradation process, by increasing the voltages values on electrolyzers.

- Based on analyzes, it was found that after 7 years of operation, electrolysis efficiency of PEM electrolyzers decreased by 2 percent points. For degradation of efficiency is responsible aging of the electrolyte process, which has lost some properties in long time of work. The aging process of the device could have been accelerated by using water with too high conductivity value.
- A very important parameter for the electrolyzers systems is their temperature. Temperature affects to the resistance of the electrolyzers, so also on the power taken to supply the tested devices. These changes leads to changes in the efficiency of tested equipment.
- The analysis shows, that increasing the temperature of the electrolysis process by 30°C (from 20°C to 50°C) results in increase the efficiency of electrolyzers for about 7 p.p, when installation working with changing current values.

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