Lysenko, Olha; Ikonnikov, Valerii

Article

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Olha Lysenko,
Valerii Ikonnikov

INVESTIGATION OF ENERGY EFFICIENCY OF HYDROGEN PRODUCTION IN ALKALINE ELECTROLYSERS

The object of research is the energy efficiency of the electrolysis process in electrolyzers with alkaline electrolyte electrical parameters. The existing problem consists in obtaining the energy efficiency of the process in an electrolyzer with an alkaline electrolyte of more than 65 %.

To solve this problem, it is proposed to manufacture an electrolyzer with metal electrodes made of stainless steel and separated from each other by a gas-tight membrane (Bologna cloth) to separate hydrogen and oxygen gases. To establish the energy efficiency characteristics, an experimental installation was made, and the necessary measuring equipment was also used. In the course of the work, a research methodology was developed and the necessary calculation of the measured values was carried out. As a result, the influence of the operating voltage on the consumption of the current flowing through the electrodes of the electrolyzer and the power consumed by it was revealed, the values of which increase with the increase of the operating voltage. It was established that the energy efficiency of the process in electrolyzers with an alkaline electrolyte decreases with an increase in the operating voltage. At operating voltages of 3 V, 4 V, and 5 V, the energy efficiency is 85.7 %, 77 %, and 70 %, respectively. The proposed technique involves conducting experimental studies directly on a functioning electrolyzer.

The practical implementation of the use of a gas-tight membrane (Bologna fabric) can help reduce the cost of manufacturing an electrolyzer. Therefore, the presented research will be useful for the industrial production of hydrogen.

Keywords: *electrolysis, electrolyzer, hydrogen, environmentally friendly energy production, renewable energy sources, alkaline electrolyte.*

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1. Introduction

The modern development of hydrogen energy includes a set of technologies for the industrial production of hydrogen, its storage, transportation, supply and storage of a secondary energy carrier (hydrogen), as well as the provision of environmentally clean energy for buildings, heating and cooling. In the concept of hydrogen energy, hydrogen complements the most important secondary energy carrier – thermal energy. Energy use of hydrogen is determined by the possibility of environmentally clean energy production and long-term storage without losses.

The main elements of the pure hydrogen supply chain are production from renewable or nuclear energy sources, conversion into a transportable form, long-distance transport and regional distribution, as well as re-conversion for end-use and final consumption and distribution, followed by its use as a fuel in in cases where gas, liquid or solid fuel are used today [1, 2].

With the modern development of renewable energy, which relies on variable resources of solar and wind energy, as well as the spread of technologies of distributed generation and intelligent networks, the problem of long-term and seasonal energy storage comes to the fore. Solving this problem will ensure compensation of fluctuations, balancing of surplus and deficit of electric energy according to the needs of the energy market [3–5]. For Ukraine, an important aspect in solving the problem presented above is the wide use of hydrogen as a highly efficient energy carrier, which will provide the most promising way to solve energy problems, such as the creation of the necessary balance capacities [6]. In addition, the use of hydrogen will significantly reduce harmful emissions to the atmosphere [7].

One of the most promising ways of developing hydrogen energy is based on the use of hydrogen produced by electrolysis, for example [8–10]. Electrolysis is distinguished by the simplicity of the technological scheme, the possibility of effective use of renewable energy sources, the availability of raw materials and the relative ease of maintenance of power plants [10, 11]. However, a significant drawback of this electrochemical method of obtaining hydrogen is the high energy consumption of the water decomposition process [12]. The least energy-intensive (that is, the one with the highest energy efficiency) is the electrolysis

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method using an alkaline electrolyte. In such a device, the rate of hydrogen release and the energy efficiency of the process itself will depend on the voltage supplied to the electrolyzer and the distance between the plates, and the purity of gases (hydrogen and oxygen) will depend on the use of a gas-tight membrane. The search for optimal technological parameters is an urgent task of this work, which will provide an opportunity to establish the highest energy efficiency of the process in serial electrolyzers.

Therefore, *the aim of research* is to assess the influence of the electrical parameters of the electrolysis process in an electrolyzer with an alkaline electrolyte on its energy efficiency.

2. Materials and Methods

Different methods of hydrogen production are known, starting from traditional ones, such as, for example, conversion of hydrocarbons, and ending with biological methods, when hydrogen is released by specially selected microorganisms [13]. About 50–60 million tons of hydrogen are produced in the world by an industrial method, while almost 95 % of the hydrogen produced comes from carbon-containing raw materials, primarily fossils – natural gas and coal, as well as petroleum products. Most of the hydrogen produced is a by-product of oil refining and is used on-site in the process flow. For example, in the EU in 2006, 42 % of hydrogen was produced from petroleum products and 47 % was consumed for oil refining [2]. The second main source of hydrogen is natural gas (methane), and the area of consumption is ammonia production [2].

Key technologies for obtaining hydrogen from hydrocarbons, coal and biomass include:

– conversion (in particular steam conversion of methane);
– partial oxidation and autothermal conversion;
– gasification;
– biological methods (fermentation, photolysis). Thermochemical methods are based on the intermediate production of synthesis gas, which is a mixture of carbon monoxide and hydrogen in proportions up to 1:3 [13].

When obtaining hydrogen from raw materials, it is possible to obtain intermediate products, such as synthetic liquid fuels, biogas, etc. using such methods as pyrolysis, torrefaction, hydrolysis, esterification, anaerobic fermentation, alcoholic fermentation, etc. These intermediate products can also be processed into hydrogen [13]. The most widespread method of obtaining hydrogen is the electrolytic decomposition of water (electrolysis). The main types of electrolysis differ in the type of charge carriers, such as hydroxide ions in alkaline electrolysis of water and protons in acid electrolysis. High-performance alkaline electrolysis systems are currently produced by many foreign companies, such as CETH2/Areva H2Gen, Hydrotechnik, Hydrogenics, ITM Power, McPhy Energy, NEL, Next Hydrogen, PERIC, Siemens [14]. During production, each electrolyzer is equipped with auxiliary systems of water preparation, cooling and purification up to 99.999 %, the service life is 6–11 years. But this method of hydrogen decomposition has a rather low efficiency, which directly affects the energy efficiency of the process. For serial alkaline electrolyzers, the efficiency in terms of the lower heat of combustion of hydrogen at the beginning of operation is in the range of 52–62 % [14]. Research and development aimed at reducing anodic and cathodic overvoltages is underway. Currently, much attention is paid to the implementation of porous separating diaphragms (membranes) in order to reduce ohmic losses. Bolognese fabric was chosen as the material of the porous diaphragm.

3. Results and Discussion

To carry out experimental research on the process of obtaining hydrogen and oxygen, an experimental laboratory device was made (Fig. 1).

The laboratory device for studying the electrolysis process (Fig. 1) consists of a laboratory autotransformer 1, necessary for voltage regulation, a transformer 2 with a rectifying diode bridge 3, necessary for reducing the voltage and its rectification, a voltmeter-ammeter DSN-VC288 (China) 4 and 5, an electrolyzer 6, two chambers with a volume of 10 ml for the accumulation of hydrogen 7 and a volume of 10 ml for the accumulation of oxygen 8. During experimental studies, an electrolyzer was made with metal electrodes made of stainless steel and separated from each other by a gas-tight membrane (Bologna fabric) for the separation of hydrogen and oxygen gases. By using bologna fabric as a gas-tight membrane, it was possible to minimize the distance between the plates (0.8 mm). The time of hydrogen accumulation was measured with a stopwatch (not shown in the diagram).

The energy efficiency indicator of the electrolysis process was determined as:

$$\eta = \left(1 - \frac{W_{\Sigma 2}}{W_{\Sigma 1}}\right) \cdot 100, \quad (1)$$

where $W_{\Sigma 2}$ – consumption of electrical energy for hydrogen production, J/m^3; $W_{\Sigma 1}$ – the lower calorific value that can be obtained by burning hydrogen. According to [15], the lower calorific value of hydrogen is 120 mJ/m^3.

The research methodology was developed, which consisted of the following. Electrolyzer 6 was filled with electrolyte (sodium bicarbonate dissolved in purified medical distilled water in a ratio of 15/100 g/ml). After that, the set DC voltage was applied to the electrodes, which during one study was kept constant and did not change. The values of DC voltages at which the studies were conducted were as follows: U_1=3 V; U_2=4 V; U_3=5 V. Voltage values are set taking into account previous studies and methods presented in [16]. At each voltage at the electrodes of electrolyzer 6, the current, hydrogen accumulation time, and the volume of hydrogen obtained were measured.

The power spent on hydrogen production was calculated according to the formula within the given time:

$$P_i = I_i \cdot U_i, \quad (2)$$

where I_i – the current flowing through the electrodes of the electrolyzer, A; U_i – the operating voltage of the process, V.

The consumption of electrical energy for the hydrogen production by a laboratory electrolyzer was calculated according to the formula:

$$W_i = P_i \cdot (t_{i+1} - t_i), \quad (3)$$

where W_i – the consumption of electrical energy for hydrogen production during time $(t_{i+1}–t_i)$, J; $(t_{i+1}–t_i)$ – the time during which a certain amount of energy was spent to obtain the corresponding volume of hydrogen, p.

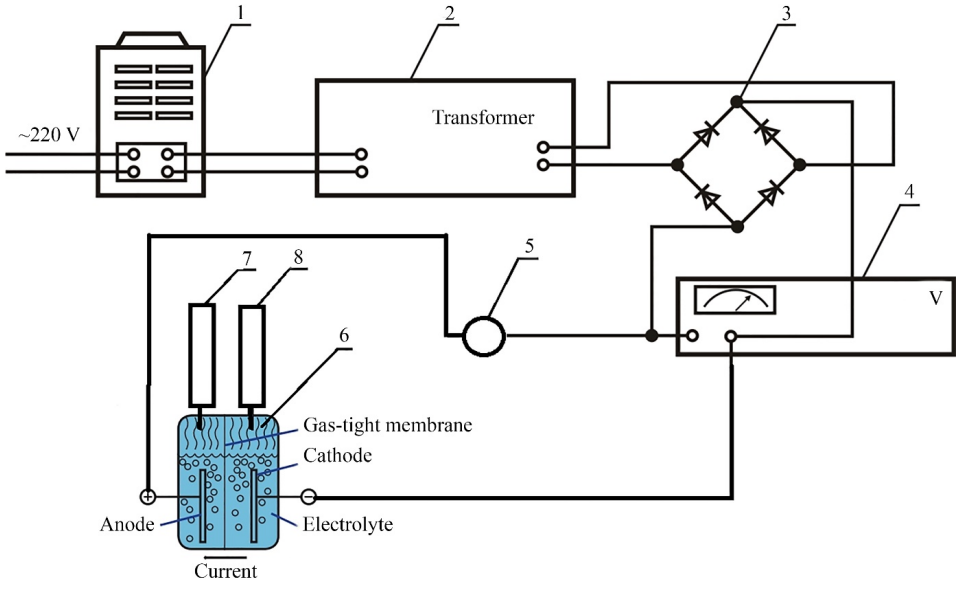

Fig. 1. Diagram of a laboratory device for electrolysis research:
1 – laboratory autotransformer; 2 – transformer; 3 – rectifier diode bridge; 4, 5 – voltmeter-ammeter DSN-VC288; 6 – electrolyzer; 7 – chambers with a volume of 10 cm^3 for the accumulation of oxygen; 8 – chamber with a volume of 10 cm^3 for storing hydrogen

In the studies, the time interval Δt during which parameter values were fixed taking into account previous studies [16] was set at the level of Δt=10 s. Thus, the value (t_{i+1}–t_i) was determined by the difference between the time during which the current trial t_{i+1} was performed and the time during which the previous trial t_i (or Δt) was performed.

The total consumption of electric energy for the production of hydrogen was calculated according to the formula:

$$W_{\Sigma 2} = \sum W_i. \quad (4)$$

The energy efficiency of the process was calculated according to formula (1) taking into account the amount of hydrogen obtained during research. That is, if the lower calorific value for 1 m^3 of hydrogen is $W_{\Sigma 1}$=120 mJ/m^3, and the maximum 8 ml was obtained during the research, then for this amount of hydrogen, the $W_{\Sigma 1}$ indicator will be 0.96 kJ.

The conducted studies determined the dependence of the current flowing through the electrodes I, A (Fig. 2) and the power spent on the production of hydrogen P, W (Fig. 3) on the hydrogen accumulation time t, s at different values of the operating voltage U, B. The extreme right points of all dependencies indicate that the full volume of the hydrogen chamber was obtained during this time, namely V=8 ml.

The analysis of dependencies (Fig. 2, 3) established that the time of hydrogen accumulation in the chamber with a volume of V=8 ml decreases with an increase in the operating voltage of the hydrogen production process. Thus, at an operating voltage of U=3 V, the time during which the chamber is filled with a volume of V=8 ml is t=810 s; at U=4 V, t=330 s; at U=5 V, t=220 s.

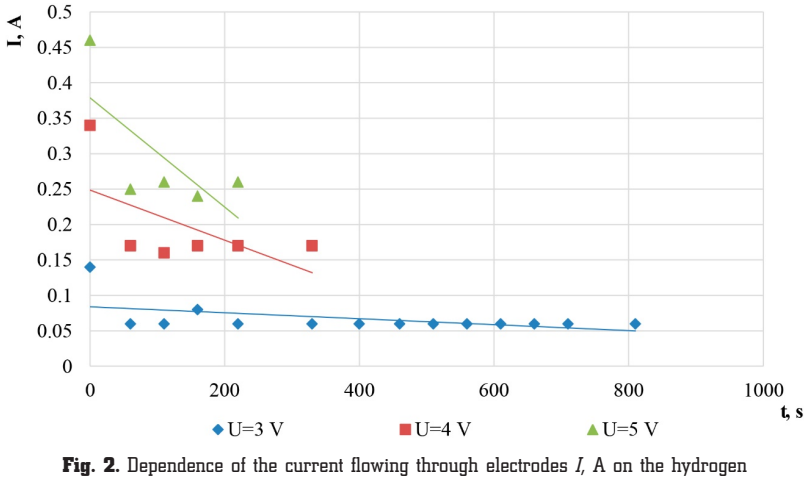

Fig. 2. Dependence of the current flowing through electrodes I, A on the hydrogen accumulation time t, s

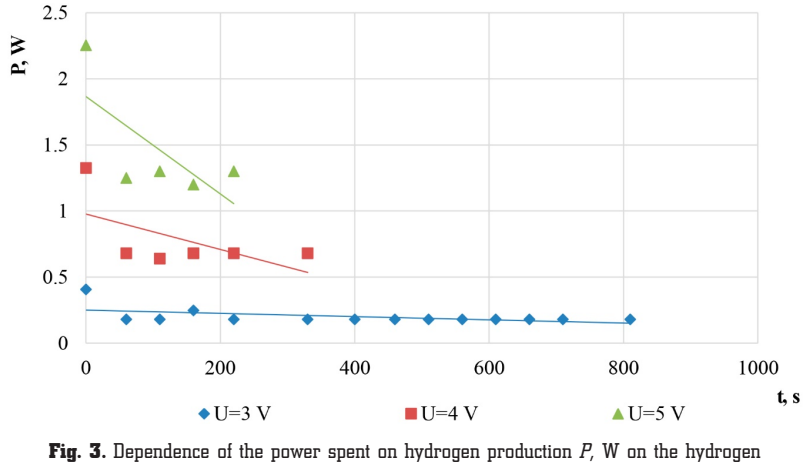

Fig. 3. Dependence of the power spent on hydrogen production P, W on the hydrogen accumulation time t, s

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In addition, it was found that in the process of hydrogen accumulation, the consumption of the current flowing through the electrodes of the electrolyzer and, accordingly, the power consumed by it decreases at any operating voltage. This is explained by a decrease in the area of water contact with the electrodes of the electrolyzer during the electrolysis process.

With an increase in the operating voltage of the process, there is an increase in the consumption of the current flowing through the electrodes of the electrolyzer (Fig. 2) and, accordingly, taking into account the formula (2), the power consumption (Fig. 3). This state of affairs, taking into account formulas (1)–(4), makes it possible to conclude that the efficiency of the installation decreases with an increase in the operating voltage. Thus, it was established that at an operating voltage of $U=3$ V, the total consumption of electrical energy for the production of hydrogen is $W_{\Sigma 2}=137.1$ J; at $U=4$ V, $W_{\Sigma 2}=219.2$ J; at $U=5$ V, $W_{\Sigma 2}=286.5$ J. Then, the energy efficiency for the corresponding voltage will be $\eta=85.7$ %, $\eta=77$ % and $\eta=70$ %.

The regression equations of the obtained dependencies (Fig. 2, 3) have the form:

– at $U=3$ V with restrictions $10\leq t\leq 810$:

$$I=-0.0017t+0.9;\ P=-0.0026t+1.35; \quad (5)$$

– at $U=4$ V with restrictions $10\leq t\leq 330$:

$$I=-0.0016t+1.323;\ P=-0.0026t+2.248; \quad (6)$$

– at $U=5$ V with limits $10\leq t\leq 220$:

$$I=-0.0018t+1.507;\ P=-0.0037t+3.015. \quad (7)$$

In addition, the obtained results make it possible to estimate the influence of the operating voltage on the current consumption. The drawback of the study is that the loss of energy for heating the electrolyte was not taken into account. Therefore, it is likely that when used in practice, the obtained results may differ from the theoretical ones. This requires further adaptation for specific conditions.

A limitation of the research is the assumption that the supplied voltage is a stabilized constant 3 V, 4 V or 5 V and the studies are performed at room temperature.

The development of this research is possible in changing the density of the electrolyte.

4. Conclusions

It has been established that with an increase in the operating voltage, the time of hydrogen accumulation of a certain volume decreases. Thus, at $U=3$ V, the time during which the hydrogen chamber with a volume of $V=8$ ml is filled is $t=810$ s; at $U=4$ V, $t=330$ s; at $U=5.0$ V, $t=220$ s.

The influence of the operating voltage on the consumption of the current flowing through the electrodes of the electrolyzer and the power consumed by it was revealed, the values of which increase with an increase in the operating voltage. Accordingly, the efficiency ratio (efficiency) in the studied electrolyzer decreases with an increase in the operating voltage. At the operating voltage $U=3$ V, the energy efficiency is $\eta=85.7$ %; at $U=4.0$ V, $\eta=77$ % and at $U=5.0$ V, $\eta=70$ %.

Conflict of interest

The authors declare that they have no conflict of interest in relation to this research, whether financial, personal, authorship or otherwise, that could affect the research and its results presented in this paper.

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The study was performed without financial support.

Data availability

The manuscript has associated data in a data repository

Use of artificial intelligence

The authors confirm that they did not use artificial intelligence technologies when creating the current work.

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Olha Lysenko, *Doctor of Technical Sciences, Professor, Department of Electric Power Engineering and Electrical Technologies, Dmytro Motornyi Tavria State Agrotechnological University, Zaporizhzhia, Ukraine, ORCID: https://orcid.org/0000-0001-7085-7796*

✉ ***Valerii Ikonnikov,*** *Postgraduate Student, Department of Electrical Technologies and Thermal Processes, Dmytro Motornyi Tavria State Agrotechnological University, Zaporizhzhia, Ukraine, ORCID: https://orcid.org/0000-0001-6381-1925, e-mail: valeriyik1977@gmail.com*

✉ *Corresponding author*

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**Nataliia Dorogan,
Lev Chernyak,
Victoria Pakhomova,
Oleg Shnyruk**

PRODUCTION OF WHITE CEMENT BY LOW-TEMPERATURE FIRING

The object of research was silicate systems based on $CaO–SiO_2–Al_2O_3$ oxides for the production of white cement under the condition of reducing the maximum firing temperature and energy intensity of the products. A complex of raw materials of different genesis was chosen for the study – chalk, pyloquartz, aluminum hydroxide. The criteria for the selection of raw materials were increased reactivity during firing and minimization of the content of colored oxides. During the research, methods of physico-chemical analysis of silicates and standardized testing of properties were comprehensively applied. Determination of the rational compositions of the raw material mixture was carried out using the created computer program «RomanCem». Based on the analysis of the calculation results, a significant value of the quantitative ratio of aluminum-silica-containing components Ca/Cp was determined. It was established that in the interval of the quantitative ratio Ca/Cp from 0.4 to 0.6, the silica modulus of the binder changes in an inversely proportional dependence within n=3.8–2.5 at a low content of colored iron oxides at the level of C=0.14–0.17 %. The compositions of the raw material mixture based on chalk with the use of an aluminum-silica-containing complex of aluminum hydroxide-powder quartz were determined, which allow, at the maximum firing temperature of 1100–1200 °C, to obtain a mineral binder that exceeds natural or Roman cement in terms of strength (21–27 MPa versus 10–15 MPa) and whiteness (80–85 % versus 55–60 %). Peculiarities of phase transformations in the material during low-temperature firing as a factor of structure and properties are noted. The development and practical use of white cement, obtained by reducing the maximum firing temperature and, accordingly, specific fuel consumption, reveals additional reserves for the production of mineral binders, contributes to the comprehensive solution of issues of resource conservation and production technology of silicate building materials.

Keywords: *white cement, raw material mixture, low-temperature firing, phase composition, silica-containing component, colored oxides.*

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1. Introduction

The production of the most common mineral binder, Portland cement, is characterized by significant energy costs during high-temperature firing (1400–1500 °C) of clinker and its grinding with additives to a highly dispersed state [1–3].

To a large extent, this applies to the technology of white cement production, where special requirements regarding the chemical composition of raw materials with the minimization of the content of colored oxides are added to the high energy intensity specified for Portland cement [4, 5].

Modern resource conservation requirements increase the relevance of the production of hydraulic mineral binders of low-temperature firing (≤1200 °C) such as natural cement [6–8] or Roman cement [9–11], which can become a substitute for more energy-intensive and expensive Portland cement in a number of construction works (Fig. 1).

The production of white hydraulic mineral binder under low-temperature firing conditions requires the development of new compositions of raw material mixtures, the chemical composition of which corresponds to the system of $CaO–SiO_2–Al_2O_3$ oxides [12]. At the same time, a high