[1] **Victor Solovey**, D.Sc.
[2] **Leonid Kozak,** PhD
[1] **Andrii Shevchenko**
[1] **Mykola Zipunnikov**, PhD
[3] **Robert Campbell**
[3] **Fred Seamon**

[1] A. N. Podgorny Institute for Mechanical Engineering Problems, NAS of Ukraine, Kharkiv, e-mail:
solovey@ipmach.kharkov.ua
shevchenko84@ukr.net
zipunnikov_n@ukr.net
[2] Yuzhnoye State Design Office, Dnepr, Ukraine,
e-mail: kozak_dp@mail.ru
[3] CAP Holdings Company LLC, Monterrey, CA, USA, e-mail:
rcampbell@capholdings.com
fseamon@capholdingsco.com

УДК 536.2

HYDROGEN TECHNOLOGY OF ENERGY STORAGE MAKING USE OF WIND POWER POTENTIAL

Описується розробка універсальних технологій, які можуть бути застосовані для забезпечення безперервної роботи опріснювальної установки при використанні енергії вітру. Розглянуто основні принципи реалізації електрохімічного методу отримання водню та кисню високого тиску з води із використанням матеріалів електродів зі змінною валентністю. Запропоновано систему зберігання хімічної енергії у вигляді стисненого водню до високих тисків з подальшим його застосуванням в паливному елементі, яка характеризується підвищенням надійності та експлуатаційної безпеки. Надано рекомендації із застосування даного способу отримання водню (кисню) з використанням як первинного джерела відновлюваних видів енергії, що відрізняються непостійністю надходження (сонце, вітер).

Ключові слова: *водень, електролізер, газопоглинаючий електрод, електрохімічна комірка, щільність струму, вітро-воднева система зберігання енергії.*

Introduction

The use of wind as a renewable and ecologically clean source of electric power has increased substantially in regions with developed industrial electricity transmission and distribution networks. In these situations, wind power is a supplemental power source that can reduce the consumption of fossil fuels and decrease environmental contamination. In remote areas that are removed from industrial distribution networks, wind can be used as the main electrical energy source. This article describes the development of a versatile technology that can be used to provide continuous power for desalination using wind energy and energy storage [1]. The technology uses advanced electrolysis and fuel cells to efficiently store excess energy from wind generation as hydrogen for later use in fuel cells. The overall system has the ability to provide uninterrupted power for desalination or other applications needing energy storage at a reasonable cost.

Purpose and Statement of the Research Problem

The main obstacle for the use of wind power plants (WPP) is the variable inherent character of wind flow, which causes the following two basic problems:

1. The process of distributing the wind-generated energy among separate consumers and the WPP becomes very complicated when operated in combination with a local electric network. Smooth integration of the variable energy source with an existing power grid is difficult.

2. Electricity generation, storage, and conversion on a large capacity scale are needed to provide an uninterrupted steady supply of electric power to consumers. This is especially important for the application involving electricity storage for membrane-based desalination systems. These systems need to be run as long as possible without having power removed because of a failure mechanism in all existing commercial membranes known as «creep». It is the physical separation of carrier materials from end caps of the membrane caused by fluctuations in pressure due to power changes.

The first problem is solved by choosing the right electrical power equipment and by developing special-purpose algorithms to control WPP operations within local electric networks.

The second problem can be solved with maximum economic efficiency by applying innovative hydrogen storage technologies.

Successfully solving these technical problems will significantly increase number of locations where wind power sources can be employed. This is especially true for small villages located in remote continental territories, on seacoasts, and on islands where it will enable the installation of electrical power for public health systems and seawater desalination systems to provide clean drinking water.

Because of the technological features of membrane-based desalination systems, such systems require that the power supply be steady and the shutdown process controlled. Thus, it is obvious that realizing the use of such systems is not possible without large-capacity storage of the wind-generated energy.

The Results of Experimental Studies and their Discussion

A water desalination plant operating with a wind power station as its power source could encounter extraordinary situations resulting from either loss of the power supply because there is no wind or failure of a system component. In these situations, systematic shutdown of the plant would be required without the loss of the working capacity of the system.

For this reason, it would be necessary to include energy storage into the technological scheme of the power-generating complex; sufficient energy must be stored to enable the desalinating plant to continue operation during periods when the wind power source is not available.

This paper describes a new energy storage system that can be installed as an additional element in the WPP system. This element involves hydrogen energy storage amounting to 12 MW·h that could supply uninterrupted energy during non-standard periods of operation and emergency shutdown of the system.

This hydrogen technology has been developed at the Institute of Mechanical Engineering Problems (IPMach) of the National Academy of Science of Ukraine. The technology developed at IPMach enables the generation and storage of high-pressure hydrogen without using a compressor. The stored hydrogen then can be converted to electrical energy using commercial fuel cells. The main element of this hydrogen accumulation system is an electrolyzer that, in essence, is a generator combined with a hydrogen-storage system as a component part of the system, thus providing energy storage and subsequent use when needed.

Approaches also have been developed for optimizing various operational modes that are typical of the actual conditions involving WPPs.

The method used for water electrolysis in our system differs from other hydrogen-generation methods several ways: the simplicity of its technological scheme, the availability of the raw material, and the simplicity of the process for generating hydrogen. The main disadvantage of this method, water electrolysis for hydrogen generation, is that the amount of energy required is very high. To address this disadvantage, one of the project tasks has been the development of an electrolyzer for generating hydrogen that requires low power input [2].

Power requirements typical electrolyzers are low because they use 1) platinum group metals as the electrode material and 2) ion-exchange membranes that are expensive and technically difficult to produce [3]. This results in increased equipment cost, increased maintenance requirements, decreased reliability, and the use of resources. These disadvantages can be overcome with the proposed innovative hydrogen-generation technology. The bases of this technology are the electro-catalytic conversion process and the use of variable-valency metals as electrode materials. Such metals interact chemically with oxygen generated under the process of water dissociation.

This new technology for generating high-pressure hydrogen [4–6] consists of two stages that involve periodically alternating oxidizing and reducing reactions with participation of the active mass of the gas-absorbing electrode. The principal scheme of the technology with an electrochemical cell and gas-absorbing electrode is shown in Fig. 1.

The process of hydrogen generation begins with applying negative potential to the passive electrode. The gas-absorbing active electrode operates as an anode at this stage. The water-dissociation reaction produces hydrogen and oxygen simultaneously. The hydrogen is isolated at the passive electrode in the gaseous state, and the oxygen is chemically combined at the active electrode (i.e., it is accumulated as an oxide). This active electrode is reconditioned to its initial operational state during the following stage of electrolyzer operation. This operational sequence is provided by automatic switching of electrodes to act as anode/cathode electrodes.

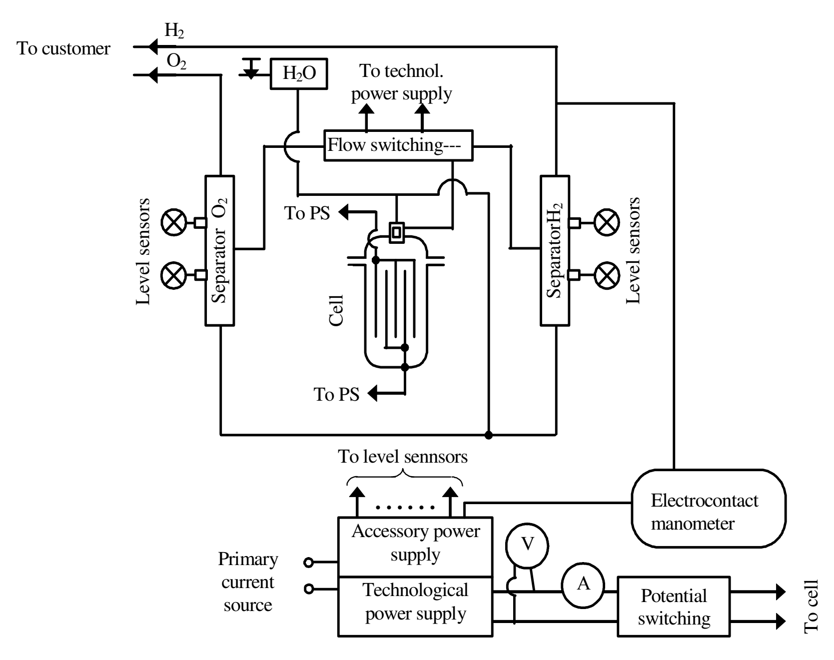

Fig. 1. Schematic of an installation with an electrochemical cell using a gas absorbing electrode

Supplying the electrolysis cell with electric power is synchronized with an electromagnetic switch that controls the gas flow. As a result, hydrogen is isolated under high pressure and only fills a hydrogen pipeline. In the same manner, oxygen is fed to a separate pipeline. Primary cleaning of the electrolyte streams occurs in a gas-liquid separator that separates the flow into separate gas and liquid streams.

The water-dissociation reaction is initiated by increasing the voltage at the electrodes during the gas-generation process (Fig. 2). Automatic control of the gas-generation process is based on the process's voltage-current characteristics, which were determined experimentally.

When the voltage value equals the design value, a polarity inversion occurs that simultaneously switches on the electromagnetic valve to redirect the gas flow into the appropriate pipeline. After redirection, the passive electrode becomes the anode, and the active electrode becomes the cathode. Accordingly, isolation of the gaseous oxygen takes place at a passive electrode (anode), while at the cathode, the active mass of the gas-absorbing electrode is reactivated by hydrogen.

Upon reaching the design value of voltage, which is used as a parameter for controlling the duration of the oxygen-isolation process, polarity inversion at electrodes occurs and recycling takes place.

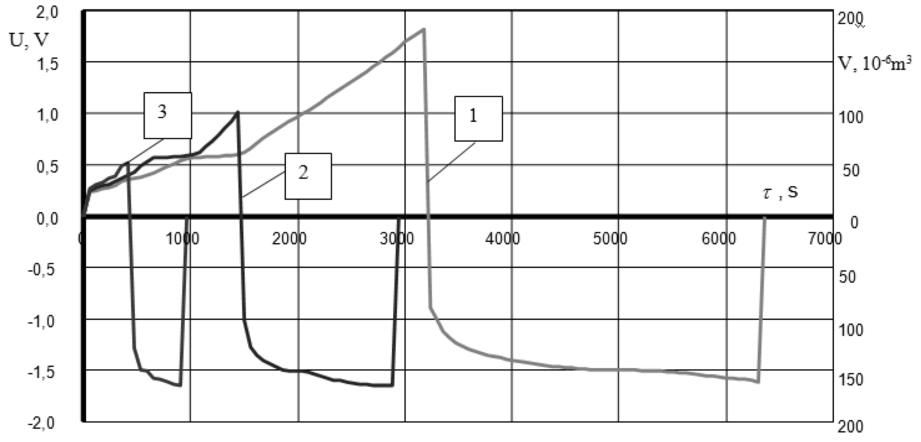

Fig. 2. The cyclograms of the high pressure electrolyzer operation when voltage is limited from 1.8 to 0.3 V and current is J = 0.02 A/см^2:
1 – U = 1.8 V; 2 – U = 1.0 V; 3 – U = 0.5 V

By using a variable-valency material that chemically bonds oxygen (e.g., spongy iron) as a gas-absorbing electrode, the working process in area (A – B) of Fig. 2 corresponds to the following reaction:

$$Fe + 2OH^- <=> Fe(OH)_2 + 2e^-. \qquad (1)$$

The larger mass of the active electrode reacts with oxygen, which results in more intensive workup of the electrode mass:

$$Fe(OH)_2 + OH^- <=> Fe(OH)_3 + e^-. \quad (2)$$

Area (B – C) of Fig. 2 corresponds to the conversion of Fe(II) to Fe(III) during the hydrogen isolation cycle, and the oxygen isolation cycle corresponds to electrochemical reduction of iron hydroxides.

Research results have shown that, to provide the low power input needed for hydrogen generation, it is best to use the process corresponding to the gently sloping area of area (A – B) of Fig. 2 with the formation of $Fe(OH)_2$ (Reaction (1)). Furthermore, the $Fe(OH)_2$ (under intensive workup, area (B – C)) is transformed in to $Fe(OH)_3$ (Reaction (2)). The presence of $Fe(OH)_3$ in the active mass of the gas-absorbing electrode results in additional consumption of electric power. Therefore, to decrease the power required for the hydrogen-generation process, the electrochemical cell operational mode needs to be optimized.

The proposed method of decreasing the specific power requirements needed during hydrogen generation involves choosing the voltage value for electrode polarity switching. Based on the research results, we constructed an electrode assembly that did not have a membrane between the cathode-anode pair (chromium-nickel steel 08X18H10T-Fe, Fig. 3). This configuration achieved pressures of 15.0 MPa, and its power consumption was less than 3.9 to 4.0 kW·h/m^3 of hydrogen generated.

Application of the new electrolysis technology, as compared to the technologies used in traditional electrolyzers, provides the following advantages:

1. Decreases the power requirements for the production of the target products up to 10 to 15% (specific power consumption is from 3.8 to 4.1 kW·h/m^3 of hydrogen generated and of 0.5 m^3 of oxygen generated);
2. Provides high-pressure gas generation limited only by the pressure ratings of the materials of construction;
3. Eliminates dividing membranes in the electrodes, thus improving system reliability and operational safety;
4. Eliminates the use of rare-earth and platinum-group metals in the hydrogen and oxygen high-pressure electrochemical generator, thus decreasing the cost of the primary equipment and, thereby, lowering capital costs;
5. Eliminates the need to compress the generated hydrogen for transfer to the energy-accumulation and storage-buffer system.

The most important characteristics of the electrolysis system are the amounts of generated gases and their pressures because those two characteristics determine the system design, size, and cost.

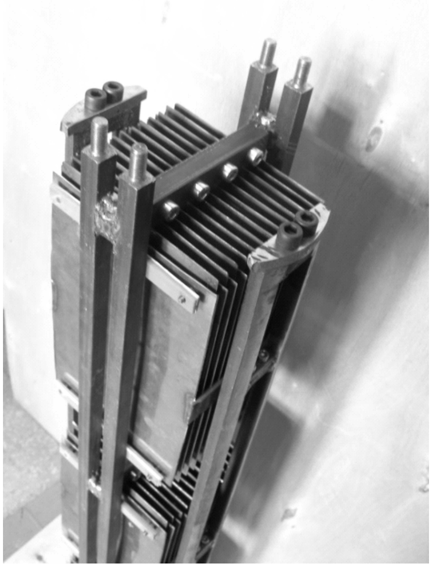

Fig. 3. Electrode assembly without a membrane for the high-pressure electrolyzer

Analysis of the engineering design of the electrolysis technique indicates that increasing the working pressure requirement to more than 150 to 200 atm significantly increases the capital and operating expenses for the hydrogen-generation system.

Figure 4 shows reference data for the costs to manufacture and operate the electrolyzers with respect to the working-pressure levels.

There is a dramatic increase in equipment cost when the electrolyzer operation pressure is ≥ 200 atm because of the need for higher strength construction materials and more complex technical decisions that, in turn, require more expensive components (e.g., shutoff and regulating apparatuses, current leads, circulating and supply pumps, etc.).

After evaluating the total expenditures for creation and operation of the electrolysis hardware, we have concluded that it is feasible to provide hydrogen pressures from 100 to 200 atm. Such pressures are achievable using the by IPMach-developed electrolyzers described in this paper. To provide higher hydrogen pressure, it is necessary to use the combination of variants in a technical scheme of «electrolyzer-compressor-consumer».

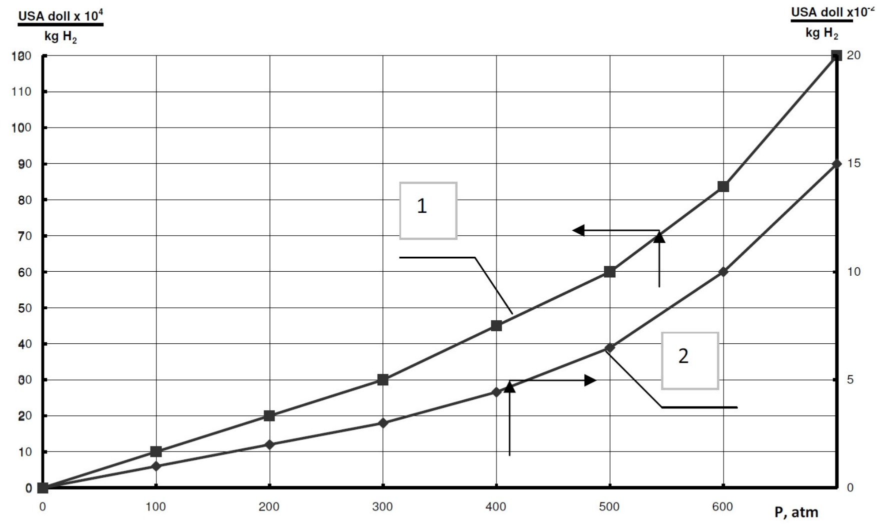

Fig. 4. Total costs per kg of hydrogen for the hydrogen-generation system vs. the hydrogen pressure level:
1 – the capital expenditures are related to the electrolyzer productivity in terms of 1 kg of hydrogen per hour. With respect to calculating the total capital expenditures, the index of the left scale of the diagram is multiplied by the plant hydrogen productivity index; 2 – The specific operation expenditures (without expenditures for electrolysis). With respect to calculating the operation expenditures, the index of the right scale of the diagram is multiplied by the plant hydrogen productivity index. When calculating the total operation expenditures it needs to add the cost of electricity to provide the electrolysis process. This process takes 44 kW·h per 1 kg of hydrogen

It also is possible to successfully use metal hydride thermal sorption installations instead of mechanical compressors at pressures near 500 atm. These installations use heat at a relatively low temperature (up to 300 °C) to compress hydrogen. As a result, the compressing technology realized by these installations is more reliable, safer, and more economical [7].

Based on the above analysis, when creating an energy buffer system for a desalination complex using wind-generated power, it would be reasonable to limit pressure to 200 atm. To transfer the hydrogen power into the autonomous power source intended for feeding the desalination plant in accordance with the given schedule, it is necessary to include a hydrogen storage system.

The gas-cylinder system needed to store 12 MW·h energy is provided by the accumulation and storage of 4.0×10^3 Nm^3 hydrogen (with a hydrogen thermal value of 10.8 MJ/m^3). If the construction of the hydrogen storage system is modular and its base element is assumed to be a gas cylinder manufactured according to the «12247-80» standard ($V = 1.0$ m^3 and $p = 200$ atm.), then 28 gas cylinders would be needed to accumulate the required energy.

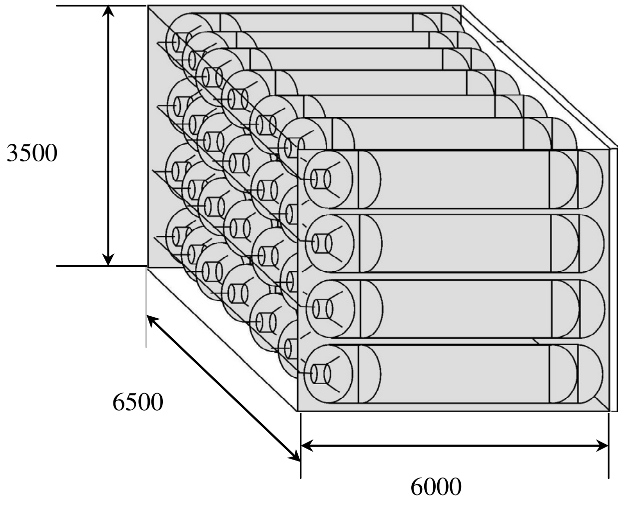

Fig. 5. Schematic arrangement of a gas-cylinder hydrogen storage system capable of supplying 12.0 MW·h of power

Construction of the hydrogen storage system in series-parallel connected modules is envisioned as four rows of seven modules each. This arrangement for the hydrogen storage system with a 4.0×10^3 Nm^3 hydrogen capacity is shown in Fig. 5.

We propose an electrolysis installation that could produce 220.0 m^3/h of hydrogen to fill the above-described storage system with hydrogen. The technological scheme of a «block-multi-module» electrolyzer was developed for this system. The advantages of the multi-module electrolyzer as compared to a singular-module electrolyzer are:

1. Comparatively low mass of the electrolysis cell (module) and, hence, simplicity of the mounting-assembly operation for inspections and preventive maintenance

2. Ability to switch off separate electrolyzer cells during an emergency. This also improves system serviceability.

A thorough investigation of the electrode assemblies intended for the electrolysis cell body in conjunction with the gas cylinders proposed for the buffer hydrogen storage system was completed. The results showed that the module can provide hydrogen productivity of 6 m^3/h. Therefore, 40 modules would be needed to construct an electrolyzer that could produce 220.0 m^3/h of hydrogen. The system provides the possibility for an overvoltage of up to 10% of the consumed power from the wind power station, which means that the electrolyzer could continue to operate for a short period of time (up to 30 minutes) using power from a WPP that exceeds by 10% the nominal power value certified by the electrolyzer operation schedule.

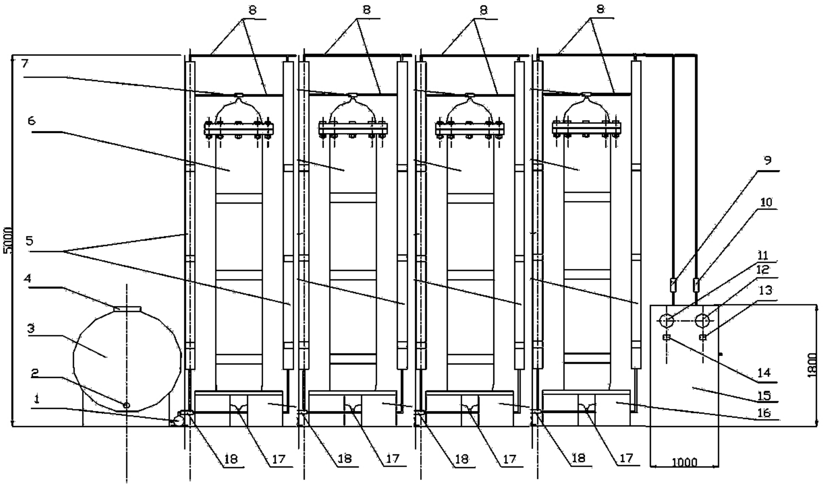

Fig. 6. Principal scheme of the high-pressure electrolyzer:
1 – plunger pump for distilled water supply; 2 – distilled water draining valve; 3 – distilled water vessel; 4 – filling throat; 5 – separators; 6 – electrolysis cell; 7 – gas flow switching; 8 – gas flow lines; 9 – hydrogen feed check valve; 10 – oxygen feed check valve; 11 – hydrogen manometer; 12 – oxygen manometer; 13 – voltmeter; 14 – ammeter; 15 – feeding and control unit; 16 – fundament; 17 – electrolyte drain valve; 18 – distilled water backflow prevention valve

When the electrolyzer is arranged as a multi-cell unit, its footprint would be 100 m^3. The scheme for a module with four electrolysis cells (total of 10 for the desired application) is shown in Fig. 6.

For the power-technological complex described in this paper to be safe and reliable, operation of the WPP generators and the high-pressure electrolyzer as a consumer of the electric power generated by the WPPs must be synchronized. Original algorithms of the automatic control system developed at the «Yuzhnoye» State Design Office, Dnipropetrovsk, Ukraine, will help with this synchronization. These algorithms are based on current data about the electrolyzer structural and operational features.

Figure 7 shows an electrolysis installation with its control system and a 500 kW WPP tower with a 4.9-m base diameter.

Fig. 7. Electrolysis installation composed of a wind-hydrogen energy storage system

Based on the information discussed above, a buffer system involving an electrolyzer and hydrogen power storage fits organically into the technological scheme of a WPP. Such a buffer system solves the problem of providing power to a customer (in this case to a seawater desalination plant) during periods when there is no wind. This is achieved by a system connecting a windmill-electrolyzer system to store the needed electrical energy as hydrogen and then an electrolyzer-fuel cell system to provide power back to the electrical grid or consumer using appropriate mechanisms for transferring the electrical energy from the fuel cell to the desired application.

Conclusions

We have presented in this paper a new technology that electrochemically generates hydrogen and oxygen. This new technology uses variable-valency metals as electrodes. The technology has a number of advantages when compared with traditional electrolysis technologies. One significant advantage is high-pressure gas generation that does not require the use of mechanical compressors to supply the gases to the buffer storage system. Another advantage is the use of an iron sponge as an active electrode, which decreases the power needed to generate 1 m^3 of hydrogen (0.5 m^3 of oxygen) by up to 3.85 kW·h. By using an ingenious switching approach, the technology also provides cyclic hydrogen and oxygen generation that eliminates the need for ion-exchange membranes to separate the gases.

The systems described in this paper provide high-pressure gas generation along with improved reliability and operational safety. The hydrogen-generation system allows the chemical reaction rate to be controlled by controlling the current intensity and, hence, the consumed power can be controlled. This is especially important when the primary energy source for the electrolysis installation is wind power, which is not constant and is affected by climatic factors.

Our efforts to further improve the proposed hydrogen-generation method are focused on continued research into new electrode materials, with an initial focus is on gas-absorbing electrodes. Application of such electrodes could potentially decrease irreversible losses that occur during the electrochemical reaction of water dissociation. This would lead to improved operational effectiveness of wind-powered desalination complexes that use the buffer hydrogen-storage system instead of compressors.

References

1. *Autonomous* wind-hydrogen stations / V. V. Solovey, V. A. Glazkov, V. K. Pishuk, M. V. Lototsky // Hydrogen Materials Sci. and Chemistry of Carbon Nanomaterials, 2007. – 861-865 p.
2. *Yakimenko, L. M.* Water Electrolysis / L. M. Yakimenko. – M.: Chemistry, 1970. – 267 p.
3. *Yakimenko, L. M.* The Electrode Materials for Applied Electrochemistry / L. M. Yakimenko. – M.: Chemistry, 1977. – 264 p.
4. *Pat.* 90421 МПК51, C25B 1/02; C25B 1/04; C25B 1/12. Ukraine. The Electrolysis Device for Generation High-pressure Hydrogen and Oxygen / V. V. Solovey, O. Ivanovsky, A. Shevchenko, O. Zhirov, O. Makarov. – Made public on April 26, 2010, Bulletin № 8.
5. *Pat.* 98705 МПК51, C25B 1/02; C25B 9/04. Ukraine. Mode of Operation of the Electrolysis Device for Generation High-pressure Hydrogen and Oxygen / V. V. Solovey, A. Shevchenko, O. Zhirov, O. Makarov. – Made public on June 11, 2012, Bulletin № 11.
6. *Pat.* 103681 МПК C25B 1/12, C25B 1/03. Ukraine. The Device for Generation High-pressure Hydrogen / V. V. Solovey, A. Shevchenko, A. Kotenko, O. Makarov. – Made public on November 11, 2013, Bulletin № 21.
7. *The Scientific* Bases for Creation of the Gas-Turbine Plants Using Thermal-Chemical Compression of an Actuating Medium / Y. M. Matsevity, V. V. Solovey, V. N. Goloschapov, A. V. Rusanov. – Kiev: The Scientific Ideas, 2011. – 252 p.

Надійшла до редакції 18.12.16