Technical note

Photoelectrical plant for hydrogen and oxygen productions by water electrolysis under pressure

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Abstract

Basic diagram of the plant with buffered storage battery and the volt–ampere characteristics of the photoelectric plant at intensity of solar radiation 900, 710, 660, 300 and 225 W/m² are given. It was determined that at using buffered storage battery current variation in the electrolyzer circuit does not exceed of 2–6 A. The voltage is changed between 12.8–14.0 V. Availability of buffered storage battery is ensured power supply in conditions of changing solar radiation intensity. Also basic diagram of the electrolysis plant with small-size regulator of pressure difference is given. It is shown that the regulator provides production of hydrogen and oxygen with high purity (hydrogen—99.98%; oxygen—99.85%) and safely works in wide interval of changing solar radiation intensity. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Using a photoelectrical station (PES) is of great importance in the field of solar–hydrogen energetic [1,2] especially as a power source for realizing water electrolysis. Imperfection of the station consists in changing its output parameters dependence on weather condition. Therefore, in the photoelectrical plant (PEP) that is described below, we used a photoelectrical station jointly with a buffered storage battery (BSB). This battery smoothes current change in the electrolyzer chain.
At the carrying out of water electrolysis under pressure the reduced voltage in the cell and the technological scheme of the electrolysis plant is simplified. A small-size pressure regulator of indirect operation is the basic element of the electrolysis plant. This regulator is intended for maintenance of pressure balance in the electrolyzer hollows.

2. Results and discussion

The photoelectrical plant diagram is presented in Fig. 1.

PES consists of 20 separate silicon solar batteries, which are connected in parallel between themselves. These batteries have power ~100 W ($U=14$ V; $J=7$ A) at a solar radiation intensity equal to 900 W/m².

The electrolyzer consists of six filter-press type cells and works under a pressure of 10 atm.

PEP operates in the following way. Electric current produced by PES1 and BSB2, flowing through the electrolyte (25% concentrated KOH solution in distilled water) decomposes the water molecules into positive ions H⁺ and negative hydroxyl ions OH⁻. As a result of discharge of these ions in appropriate electrodes into the cathode space of electrolyzer 3 hydrogen is extracted and oxygen is extracted into the anode space. Produced gases pass through washers 4 and 5, dryers 6 and 7 and pressure regulator 8 to reach receivers 9 and 10 respectively.

The pressure difference regulator 8 is used to maintain the pressure of hydrogen and oxygen into the electrolyzer hollows at the same level. This regulator consists of a three-pin U-shaped differential manometer 11, and electromagnetic valves 13 and 14, which are installed in the hydrogen and oxygen lines. The U-shaped differential manometer 11 is provided by three electrodes. Two electrodes are of the needle
type. One electrode was created as an expanded lath. This is to allow decreased ripple amplitude at the initiation difference between the pressures of hydrogen and oxygen. The height of the manometer is equal to 1000 mm. The total height of the electrolyte in its volume is equal to 1200 mm. Interposing relay 12 consists of a two-stage transistor amplifier.

Increasing the pressure of one of the gases, for example hydrogen, causes the electrolyte level in the differential manometer 11 on the side of oxygen to rise by means of an upper electrode which completes the feed circuit of the interposing relay coil 12; the latter engages the electromagnetic valve 13. This valve discards excess hydrogen into the air. Thus, the pressures of hydrogen and oxygen are equalized.

Hydrogen production with purity up to 99.98% is achieved due to high accuracy of maintenance pressure balance (maximum value of pressure difference gases in the moment of engaging one of the electromagnetic valves is equal to 6–10 mm of water).

The interposing relay 12 operates at low currents (~15 µA). It ensures an explosion-proof operating regime of the U-shaped differential manometer in contrast to the electrolysis plants which use something similar to the pressure difference regulator [3]. The control unit 15 serves both for the plant startup and protection from maximum pressure.

Fig. 2 shows the volt–ampere characteristics families of PES at various solar radiation intensities (curves I–V) and for an electrolyzer with different numbers of cells which are connected in series (curves 1–7). The points corresponding to maximum power delivered to PES at fixed solar radiation intensities are marked by ×. As is obvious, the intersection points of curve 6 with volt–ampere characteristics of PES are nearer to the points of maximum power than the intersection points of curves 1–5 and 7. Hence, the optimum amount of cells for electrolyzer (n=6) for specified PES has been determined.

However, at low illuminance the current of PES sharply decreases, which leads

![Fig. 2. The volt–ampere characteristics families of photoelectrical station, where curves I–V correspond to solar radiation intensities 900, 710, 660, 300 and 225 W/m² respectively; curves 1–7 correspond to the number of cells n=1–7 pieces respectively.](image-url)
to decreasing electrolysis current density and at solar radiation intensities lower than 300 W/m² the electrolyzer operates in the nonlinear section of the volt–ampere characteristic (bc section of curve 6). As the plant operates PES a similar change of electrolysis current density is repeated every day, especially in cloudy weather. Therefore, normal conditions of the electrolyzer operation are disturbed [4]. The normal operation of PEP automatic nodes is also disturbed with variation of the solar radiation intensity.

The mentioned imperfection of PEP is removed by use of a buffered storage battery in the electrolyzer feed circuit. A storage battery with voltage 14 V was selected subject to the contra-electromotive force of the electrolyzer (∼10 V) and voltage value of electromotive force in the ab section of curve 6 (12.8–14.4 V). This battery was assembled from even elements of the standard storage battery.

Fig. 3 shows the curves of current change in the electrolyzer during a working day for fair weather in the summer season without (···) and with (———) use of a buffered storage battery. In the morning (up to 8:30 a.m.) and in the evening (after 6:00 p.m.) the solar radiation intensity is equal to 0–300 W/m². Therefore, the electrolyzer power supply is provided from the storage battery with initial discharge rate ∼5 A.

From 8:30 a.m. to 6:00 p.m. the electrolyzer power supply is realized from PES, simultaneously with battery charging (the total quantity of energy at battery charging is equal to the crosshatched region).

In the case using a buffered storage battery, the current fluctuation in the electrolyzer chain does not overstep the limits of 2–6 A, the voltage is varied from 12.8 to 14.0 V (see Fig. 2). This battery provides normal operation of PEP automatic nodes.

![Fig. 3. The curves of current change in the electrolyzer during working day for fair weather (· · · without using buffered storage battery and ——— with use of buffered storage battery).](image-url)
Thus, undisturbed operation of the electrolyzer and automatic nodes is ensured in the wide interval at changing solar radiation intensity with insertion in the PEP feed circuit of a buffered storage battery.

The regulator of pressure difference between hydrogen and oxygen is one of the main elements of the electrolyzer that is operating under pressure.

Usually, in the electrolysis plants [1,2] float-type governors of direct action are used. In spite of good reliability of operation, these governors have low precision of regulation. Therefore, high purity of the produced gases is not achieved.

The small-size indirect action regulators of pressure difference between hydrogen and oxygen are used in some laboratory-scale plants [3,4]. These regulators allow to obtain a high purity of the gases. However, the regulators have the following vital imperfections:

1. Operating U-shaped differential manometer is accompanied by spark formation that at decreasing level of electrolyte in the electrolyzer hollows (in the dissociation process) is explosive.
2. As the differential manometer is a contact pressure manometer, then it operates as an autonomous electrolysis cell, and therefore, in due course, the level of electrolyte is decreased and control accuracy is diminished.

Besides, the regulator that is used in a laboratory-scale electrolysis plant [4] is supplied by an electric current loom stable power source that is an electricity supply network. Consequently, the regulator is seldom used in the autonomous solar electrolysis plants.

In other plants [3] the pressure difference regulator is supplied by an electric current from a single photoelectric battery, and the electrolyzer consists of a few cells which are connected in series. It prevents operating irregularity of the regulator and possible short circuits in the electrolyzer feed circuit. However, stability of the electricity supply for the pressure difference regulator is not provided at changing solar radiation intensity.

The load volt–ampere characteristics of a solar battery, which supplies the pressure difference regulator by electric current, have been obtained for determination of the process operating irregularity of the regulator at changing solar radiation intensity. The volt–ampere characteristics were obtained at various intensities of solar radiation (Fig. 4, curves 1–3). The right lines 1', 2', and 3' present current change in the windings of single electromagnetic valves with various numbers of coils and resistors ($R_1=ctg\alpha_1< R_2=ctg\alpha_2< R_3=ctg\alpha_3$), from voltage variation.

As is obvious, the current passing through windings of electromagnetic valves linearly decreases (along right lines 1’, 2’, and 3’ respectively) with decreasing solar radiation intensity. At intensities less than 600 W/m² the current becomes less than the value of the actuating current ($J<J_{act3}<J_{act2}<J_{act1}$). Therefore, the work of electromagnetic valves stops in the section $oa; ob; oc$. It leads to work stoppage for the regulator of pressure difference.

Using an electromagnetic valve with low actuating current (tuning in small value
of solar radiation intensity), also does not give good results, as in this case at large solar radiation intensities (~600–900 W/m²) normal operation of the regulator is not achieved. Thus, the current passing through the winding of the electromagnetic valve becomes approximately \((2–3)J_{ac_1}\) and it leads to premature failure of the regulator.

Thus, as each of the selected electromagnetic valves can satisfactorily operate only at small intervals of changing solar radiation intensity, then by means of parameters selection for the electromagnetic valve it is not possible to provide normal operation of the pressure difference regulator in a wide range of changing solar radiation intensities.

Let us examine the schema (see Fig. 5) of a solar electrolysis plant with a small-size indirect action pressure difference regulator of hydrogen and oxygen. This plant was designed and constructed by the authors. The plant is free from the above-mentioned imperfections.

The plant consists of the following main nodes: photoelectrical station 1; electrolyzer 2 with buffer balloons 3 and 4; regulator of pressure difference 5; accumulating reservoirs of hydrogen 22 and oxygen 23.

The operation principle of the solar electrolysis plant is the same as for the plant described earlier, but with one difference, that in the regulator of pressure difference, instead of electromagnetic valves which discharged excess hydrogen and oxygen into the air, sealed sylpons 14 and 15, regulating valves 6 and 7 were used, which through screw gear 11 are moved by servomotor 12 that is operated by way of relay block 13 from a low-capacity U-shaped manometer with magnetically operated contacts.

The pressure difference regulator maintains the pressure balance of hydrogen and oxygen in the system up to regulating valves for this plant. The pneumatic governors of direct action 26 and 27 are used for adjustment of pressure difference of produced gases in the storage reservoirs.
Fig. 5. The scheme of solar electrolysis plant with small-size regulator of pressure difference of hydrogen and oxygen of indirect action, where 1—photoelectrical station; 2—electrolyzer; 3 and 4—buffer balloons; 5—regulator of pressure difference; 6 and 7—regulating valves; 8 and 9—magnetically operated contacts; 10—valve level; 11—screw gear; 12—servomotor; 13—relay block; 14, 15—sealed sylpons; 16, 17—permanent magnets; 18, 19—floats; 20, 21—communicating vessels; 22—hydrogen reservoir, 23—oxygen reservoirs; 24, 25—maximum pressure valves; 26, 27—direct-action pneumatic governors; 28—switch; 29—storage battery.

Experimentally it was established that the purity of produced gases during water electrolysis in many respects depends on the total system pressure and accuracy of maintenance of pressure balance for gases in the anode and cathode spaces of the electrolyzer. Fig. 6 illustrates the curves which reflect dependence of purity of pro-

Fig. 6. The curves, which reflect dependence of purity of produced hydrogen on pressure balance in the anode and cathode spaces of the electrolyzer, where curves 1, 2 and 3 correspond to the electrolyzer operation under pressure 0.1, 0.3 and 0.6 MPa respectively.
duced hydrogen on accuracy of maintenance of pressure balance in the anode and cathode spaces of the electrolyzer.

Degree of purity for hydrogen and oxygen has been determined by gas chromatography analysis at a maintenance of pressure difference equal to 100, 200, 300, 400 and 500 Pa for the cases of electrolyzer operation under atmospheric pressure and under pressures of 0.3 and 0.6 MPa.

The obtained curves show that purity of hydrogen is higher than below values of pressure difference of gases other conditions being equal. It is explained by a decrease of pressure difference that occurs in the electrolyzer of a diffusive mutual permeation of anolyte and catholyte through diaphragms between electrode zones.

The installation of magnetically operated contacts 8 and 9 in the corresponding position allows to ensure that the electrolyzer operates with the lowest pressure difference (6–10 mm of water), due to a hydrogen purity equal to 99.98%, and oxygen 99.85%.

The high accuracy and stability of regulator operation is ensured by means of a low-capacity U-shaped differential manometer with magnetically operated contacts, relay control unit and actuating mechanism of regulating valves. Use of a buffered accumulator battery 29 jointly with a photoelectric station 1 ensures a guaranteed power supply of reversing control unit and servomotor in the conditions of a stochastic nature of changing solar radiation intensity. Here, the change of load voltage is within 12.8–14.0 V, as a result of which the current in the circuit of the relay block and in the windings of the servomotor is changed within relatively small limits (no more than 8–10%). This explains why, in contrast to the electrolyzer, the automatic nodes have no counter-electromotive force.

Long testing of the plant showed that the change of current within the above-mentioned limits does not influence the life duration of the automatic nodes of the pressure difference regulator.

References