Improvement of the Membrane - less Electrolysis Technology for Hydrogen and Oxygen Generation

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Keywords: *iron hydroxide, electrode potential, electrolyzer.*

To provide the most efficient electrolysis process of hydrogen and oxygen generation and the electrode twain design there were studied the following:

- The process of high pressure hydrogen and oxygen cyclic generation in the membrane less electrolysis systems.
- The permissible ranges of voltage variation on the electrodes were determined depending on the electrochemical reactions taking place on the active electrode.
- There was studied the process of hydrolysis and oxidation of the active electrode hypoferrite at the corresponding half-cycles of hydrogen and oxygen release.
- There was studied the effect of variation of the distance between the active and passive electrodes onto the electrolysis process efficiency.

Introduction

Water electrolysis hydrogen generation method differs from other methods by the technological scheme simplicity, availability and cheapness of the raw materials. But the main disadvantage of this method is its high energy expending. So, an urgent task is the development of hydrogen generation electrochemical technologies providing minimal energy consumption [1-5]. The comparative analysis of the technologies shows that the alkaline electrolysis of water is the main method of the electrolytic hydrogen large-scale production. In this regard, the problem of developing the energy-saving alkaline electrolysis technology is becoming particularly relevant for improving the hydrogen technologies [6-9].

Under exploitation of the membrane electrolyzers, the following problems were found that negatively affect their reliable performance.

The fluctuation of the pressure difference in the electrolyzer inter-electrode space and the dehydration of the upper part of the membrane, placed there, due to separation of the phases of the gas-liquid mixture cause chipping of this membrane's part and, as a result, the electrolyzer destruction.

Some firms, for example, Engineers Corp. Ltd, equip the electrolyzer with additional current distribution electric systems for increasing the current density uniformity and, correspondently, for providing the homogeneous gas distribution in the inter-electrode space [10].

To prevent the gas-liquid mixture phase decomposition in the inter-electrode space, the high velocity movement of the gas-liquid mixture is provided by means of forced circulation of the electrolyte in the electrolyzer.

Such measures result in decreasing the risk of electrolyzer destruction and in increasing its reliability, but do not solve the problems fundamentally. The most effective approach for solving all problems is a technical solution that eliminates the use of the separation membranes.

The up-to-date hydrogen technology realized, in particular, at the electrochemical units created at the Institute of Mechanical Engineering Problems of National Academy of Science of Ukraine, gives the possibility for hydrogen generating and its accumulating under high pressure without additional compressors. Such membrane-less high pressure technology uses the electrodes made from the non-deficient metals of variable valence and provides decreasing the specific energy consumption by 15-17 % compared with the others known electrolysis technologies [11, 12].

Purposes and research tasking

The aim of the study is the increase the energy efficiency of the hydrogen and oxygen generation process in the electrolyzer. For this it is necessary to determine the rational range of voltage variation at the electrolysis cell depending on the electrochemical reactions, taking place on the active electrode, as well as the optimal distance between the passive and active electrodes. By the other words, this aim is

achieved when selecting of the inter-electrode distance and determining of the operating characteristics of the electrolysis process of hydrogen (oxygen) release in the range of optimal threshold values of voltages.

Experimental part

Methods

The comprehensive studies of the electrolysis processes of water decomposition in the alkaline electrolyte were carried out on the experimental two-cell test bench giving the possibility for simulating the processes taking place in the main elements of the electrolysis system. This system involves: an electrochemical cell, the connecting pipes, separators, and corresponding valves and fittings made of the materials that give the opportunity for visual monitoring of the hydrogen generation processes.

The technique described in [11-12] was used when conducting experimental studies.

Results and discussion

As an example, figures 1, 2 show the data obtained experimentally under study of the electrochemical activity of the electrode twains Ni and porous Fe at $I = 150 \text{ A/m}^2$ current density. 25% KOH solution is used as electrolyte.

The low overvoltage of hydrogen release (0.21 V) and oxygen (0.06 V) on the passive nickel electrode makes it possible to obtain these gases cyclically practically from the moment of the power is supplied to the electrolysis system.

Figure 1. The voltage diagram for the whole cycle of hydrogen and oxygen release under electrolysis process with the use of Ni-Fe (porous) electrode twain as a result of its electrochemical activity at $I = 150 \text{ A/m}^2$ current density.

When using an active electrode made from the porous iron that chemically binds oxygen, the working process in the range of 0.25 - 0.5 V (Fig. 1) corresponds to the reaction

With prolonged operation of the electrode active mass, a deeper oxidation of iron (Fe) occurs.

The range of voltage 0.5 – 1 V on this cyclorama during a half-cycle of H_2 release (Fig. 1) corresponds to transformation of the two-valence iron Fe (II) to the three-valence iron (III) and a half-cycle of oxygen release O_2 corresponds to the electrochemical reduction of Fe.

During a half-cycle of hydrogen release, the iron protoxide hydrate is formed as a result of hydrolysis of the hypo-ferrite (HFeO_2^-)

$\text{Fe}(\text{OH})_2$ retains a porous structure and has got a developed surface of the contact with electrolyte. Polarization, taking place during oxidation of the electrode active mass, is caused

by slowing down of the OH^- ions diffusion. The diffusion rate decreases with increasing the thickness of the reacted iron layer.

The half-cycle of O_2 release is characterized by reducing the hypo-ferrite ions on the active electrode that results in preventing the porous iron electrode corrosion process.

When the cycles of oxidation and reduction are carried out, the amount of iron involved into the electrolysis reaction is determined by the depth of the reduction process penetration into the active electrode volume. The area of the gas absorption active surface, which is available for the electrolyte, depends on the electrode dispersity and the structure. The deeper the chemical reaction penetrates into the electrode, the greater must be the activation energy and the lower the rate of the electrochemical reaction, which determines the rate of the electrolysis process and is the reason for overvoltage appearance. When the cycles of oxidation and reduction are carried out, the amount of iron involved into the electrolysis reaction is determined by the depth of the reduction process penetration into the active electrode volume. The area of the gas absorption active surface, which is available for the electrolyte, depends on the electrode dispersion and structure. The deeper the chemical reaction penetrates into the electrode, the greater must be the activation energy and the lower the rate of the electrochemical reaction, which determines the rate of the electrolysis process and is the

reason for overvoltage appearance.

Thus, to provide low energy consumption for hydrogen and oxygen generation, it is advisable to use a process corresponding to the cyclogram flat region of 0.25 - 0.5 V when $\text{Fe}(\text{OH})_2$ is forming. In the voltage range more than 0.5 V, the iron hydroxide $\text{Fe}(\text{OH})_2$ is transformed into $\text{Fe}(\text{OH})_3$. Its presence in the active mass of the gas absorption electrode causes additional power consumption. Therefore, to reduce the energy consumption for hydrogen and oxygen generation process, it is necessary to optimize the operating modes of the electrochemical cell by selecting the voltage change limits during the electrochemical reaction process.

Figure 2 shows the diagram of the voltage change on the time of the full cycle of hydrogen and oxygen generation when the distance between the active (Fe) and passive (Ni) electrodes were changing.

Figure 2. The diagram of the voltage change on the time of a full cycle of hydrogen and oxygen release during electrolysis when an electrode assembly of Ni - porous Fe is used and a variable the distance between the active and passive electrodes is variable: 1) 2 mm; 2) 3-4 mm; 3) 6 mm. The current density is $I = 150 \text{ A/m}^2$.

The analysis of the obtained results shows that the optimum distance between electrodes is in the range of 3-4 mm. In this case, the initial voltage of hydrogen release is 0.27 V and oxygen (-0.9 V), which is caused by the uniform distribution of hydrogen and oxygen ions between the electrodes – table. 1, fig. 3.

Figure 3. Dependence of the change of the initial voltage on the distance between the active and passive electrodes (2-6 mm) during electrolysis when the Ni – Fe (spongy) electrode twain is used. The current density is $I = 150 \text{ A/m}^2$.

Reducing the distance between the active and passive electrodes up to 2 mm promotes for the ionic depletion and for increasing of the polarization effect in the inter electrodes space. It results in increasing the initial voltage needed for hydrogen release up to 0.4 V and (-1.4 V) for oxygen release – Table 1. The resistance of current moving in the electrolyte increases significantly at the presence of extraneous inclusions - dielectrics (gas bubbles), which results in narrowing of the electrolyte cross section and in elongating the path of current moving because of it becomes tortuous. Gas-filling-up of the

electrolyte is increasing with increasing the current density, electrode height, electrolyte viscosity and with decreasing the distance between the electrodes. These factors cause a decrease of the electrolyte volume of in the cell.

Table 1. The results of the electrochemical activity of Ni-Fe (porous) electrode twain.

Surface of the active electrode, cm^2	Current, A	Current density, A/cm^2	Distance between the electrodes, m		Voltage at the beginning of gas release, V		Change of the standard Gibbs energy, $-\Delta G$, J/kg		Electric energy consumption, kWh/m^3
			H_2	O_2	H_2	O_2	H_2	O_2	
28,35	0,44	150	2,0	0,4	-1,4		$3,86 \cdot 10^7$	$8,443 \cdot 10^6$	3,9
			3,0 – 4,0	0,27	-0,9		$2,605 \cdot 10^7$	$5,428 \cdot 10^6$	3,77
			6,0	0,35	-1,2		$3,377 \cdot 10^7$	$7,237 \cdot 10^6$	3,85

An increase of the distance between the active and passive electrodes up to 6 mm results increasing the initial voltage of hydrogen release up to 0.35 V and oxygen (-1.2 V) – Table 1, which is associated with an increase of the electrolyte volume resistance due to an elongation of the current path in the inter electrode space.

Figure 4 represents the volt-ampere characteristics of existing and promising industrial electrolyzers.

Figure 4. Volt-ampere characteristics of existing and promising industrial electrolyzers: 1 - Modern industrial alkaline electrolyzers: ΦB , COY (Russia), Weuder Model, De Nora (Italy), Norsk (Norway), Stuart Imet (Belgium), Teledyne (USA), Loncza, Demag (Germany); 2 - Prospective alkaline electrolyzers (363 - 413 K, 0.1-2 MPa): Hamilton Sundstrand (USA), Proton Energy Systems Inc (USA), H-tec (Germany), RRC "Kurchatov Institute" (Russia); 3 - Electrolyzers with polymer electrolyte (423 K, 0.1 MPa): Matsushita Electric Works Ltd, Fuji Electric Co Ltd (Japan), Norwegian University of Science and Technology (Norway), David Systems and Technology (Spain); 4 - High-temperature electrolyzers (1373 K, 0.1 MPa): General Electric Co (USA), Brown Boveri (Switzerland); 5 – High pressure electrolyser with getter electrode (353 - 423 K, 20 MPa): IPMASH (Ukraine).

Changes of the Gibbs free energy, calculated taking into account the electrode potential (ϕ) in the initial period of gas liberation, are given in Table 1

$$\Delta G = -zF\phi,$$

where z is the number of electrons participating in the process; F is the Faraday constant; ϕ is the electrode potential at the initial period of H_2 (O_2) gassing.

The negative values of the Gibbs energy change indicate a high probability of the beginning of the gases (H_2 and O_2) release process. Increasing or decreasing the distance between the electrodes, more or less than 3–4 mm, leads to an increase of the gassing initial potential and, consequently, to an increase of the time from the moment when the voltage is applied to the cell to the moment of gassing process beginning. It results in the corresponding increase in energy consumption per 1 m^3 of hydrogen produced.

Conclusions

1. To provide minimum energy consumption for hydrogen and oxygen generation, it is advisable to use the hydrogen release process corresponding to the cyclogram flat region at a voltage level of 0.25 – 0.5 V when $Fe(OH)_2$ is forming (Fig. 1). In the voltage range more than 0.5 V, the iron hydroxide $Fe(OH)_2$ transforms into $Fe(OH)_3$. Its presence in the active mass of the gas absorption electrode causes additional power consumption.

2 The Gibbs free energy change (ΔG) was calculated taking into account the electrode potential at the initial period of gas release during the corresponding half-cycles depending on the distance between the electrodes in the range from 2 to 6 mm. The negative values of this change indicates a high probability H_2 (O_2) release reactions.

3. Reducing the distance between the active and passive electrodes less than 2 mm

causes the ionic depletion of the inter-electrode space and increasing the polarization effect there that becomes the reason for increasing the initial voltage needed for hydrogen release up to 0.4 V and (–1.4 V) for oxygen release.

4. An increase of the distance between the active and passive electrodes up to 6mm results in increasing the initial voltage of hydrogen release up to 0.35 V and oxygen (–1.2 V), which is associated with an increase of the electrolyte volume resistance due to an elongation of the current path in the inter electrode space.

5. It has been established that minimum value of the specific energy consumption under the process of hydrogen generation is provided due to uniform distribution of the hydrogen ions in the inter electrode space when the distance between electrodes is in the range of 3–4 mm and the initial voltage of hydrogen release is 0.27 V and oxygen (–0.9 V).

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