Energy Effective Membrane-less Technology for High Pressure Hydrogen Electro-chemical Generation

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Water electrolysis process for hydrogen generation is widely used in various branches of industry. But it has disadvantages like important energy consumption and utilization of separate membranes, which limit the generated gases pressure.

This article describes the hydrogen and oxygen generation technology excluding the separating ion-exchange membranes and providing high gases pressure due to applying the variable valence metal chemically active electrodes as well as due to separating in time and space the electrolytic processes of water decomposition for gases liberation.

The electrolyzer based on this technology surpasses all of the known analogues by the level of technical decisions, simplicity of mounting and servicing, reliability and safety.

Introduction

Water electrolysis process for hydrogen generation is widely used in various fields of modern engineering by its ecological cleanness and simplicity of the technological scheme. Moreover, water supply is unlimited as the raw material for the electrolytic decomposition technologies.

The main disadvantages of the electrolysis process are big energy consumption and necessity to use of the separate membranes that limit the generated gases pressure. It is required to use the compressors for gas storage. Therefore, developing of hydrogen generation electrochemical technology providing minimal energy consumption is a perspective and importance way for hydrogen power engineering.

The decreased power consumption of the well-known electrolyzers is provided due to increasing the working temperature and applying the platinum and rare-earth group metals for electrodes production as well as due to applying the ion-exchange membranes that are expensive and complex for manufacturing.

All of the above mentioned reasons result in increasing cost of hydrogen generation systems and higher service requirements, as well as in decrease of systems reliability, in shortening of their resource and, the main thing, in limiting of upper pressure level of the generated gases.
Therefore, the great potential for the electrolysis power engineering may be in creation of membrane-less high pressure electrochemical hydrogen (H₂) and oxygen (O₂) generation technology that provides the specific energy consumption not more than 3.85-4.0 kW/h [1, 2].

The electrolyzer implementing such technology involves the electrolysis unit, gas-fluid flows separation system and the electronic unit intended to manage and control the electrolysis unit operation modes. The electrolysis unit is adapted to consume the “non-conditional” electrical power generated from the renewable power sources (wind, sun etc.) for producing hydrogen, an ecologically clean energy carrier, and oxygen gas.

**Experimental Part**

**Methods**

An experimental stand was developed to have the possibility for modeling the processes of H₂ and O₂ generation taking place in the electrochemical cells and to monitor these processes visually (Scheme 1). The method of experimental study of these processes is described in [3].

![Scheme 1. The experimental stand with the electrochemical cells.](image)

**Scheme 1.** The experimental stand with the electrochemical cells. PSU - power supply; ECM - electro contact manometer; LXM-8M - chromatograph; BAMM - barometer;

This stand involves the system of H₂ and O₂ electrochemical generation, main pipes, separators, container with distilled water, power supply unit, control unit and a system for measuring the flow characteristics of generated gases. The system of H₂ and O₂ electrochemical generation involves two electrochemical cells.

The proposed technology for generating high-pressure H₂ and O₂ consists of two stages that involve periodically alternating oxidizing and reducing reactions with participation of the active mass of the gas-absorbing electrode. The water-dissociation reaction isolates hydrogen and oxygen simultaneously. The process of hydrogen...
generation begins with feeding the negative potential to the passive electrode. The hydrogen gas is inputted to the high pressure pipe. The gas-absorbing active electrode operates as an anode at this stage. 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 the chemical compound). Then, this active electrode is reconditioned into initial operational state during the following stage of electrolyzer operation. This allows automatic switching of electrodes to act as anode/cathode electrodes.

The separation devices were developed with the use of the method of the gas dynamic processes modeling [4].

Results and discussion

The main data were obtained experimentally under study of the electrochemical activity of the 08X18H10T-Fe electrode pair. The voltage change during the whole cycle of H₂ and O₂ generation under electrolysis process is shown on Figure 1.

![Figure 1. Variation of the voltage during the whole cycle of H₂ and O₂ generation under electrolysis process when the 08X18H10T-Fe electrode assembly is used. Current Density: 1-J = 0.015 A/cm²; 2-J = 0.03 A/cm².](image)

The increase of voltage is accompanied by polarization taking place under electrode active mass oxidation caused by the slowing down the OH ions diffusion. For this, the diffusion rate decreases as the thickness of the reacted iron layer increases according to the following reactions:

Fe + 2OH⁻ ⇌ Fe(OH)₂ + 2e⁻, \hspace{1cm} (1)

And under big depth of the active electrode reacting mass:

Fe(OH)₂ + OH⁻ ⇌ Fe(OH)₃ + e⁻. \hspace{1cm} (2)

The gently sloping section of the first region on Figure 1 represents the voltage range of 0.28 - 0.54 V (reaction 1); the second flat region represents the voltage range from 0.54 V to 0.7 V (reaction 2). When oxidation and
reduction cycles are carried out, the amount of iron that is used under the getter reaction is determined by the depth of its reduction in the surface layers of the active electrode. The difference between the amounts of reacted substance of the porous iron electrode, when the current density is increased from 0.015 to 0.03 A/cm², is about 4%. This indicates the growth of the reacting layer of the active electrode, (Fe(OH)₂, Fe(OH)₃) depending on the increase of time of the oxidation and reduction hemicycles.

The developed electrolysis technology requires ≈ 3715 W·h/m³ of energy to generate 1 m³ of H₂ and 0.5 m³ of O₂ without taking into account compression of these gases, and the compression of gases under the electrochemical process consumes 285 W·h due to increase of the generated gases pressure in the membrane-less electrolyzer: Table 2, Scheme 2.

In this case, the pressure of the generated H₂ and O₂ influences heterogeneous reactions. The changes of the Gibbs free energy are determined taking into account the effect of the isolated gases pressure [5]:

\[ \Delta G = \Delta G_0 + RT \ln \left( \frac{P_2}{P_1} \right), \]

where \( \Delta G_0 \) is the Gibbs energy in the standard state, kJ/kg; \( R \) - is the gas constant, J/(kg K); \( T \) - is the temperature, K; \( P_2, P_1 \) - the final and initial pressure in the electrolyzer, atm.

The difference between the values of the standard Gibbs energy (\( \Delta G \)) and Gibbs energy taking into account the pressure change (\( \Delta G_p \)) is ≈ 3%, which proves that the pressure increase in the indicated range influences on the electrolysis process insignificantly.

The energy consumption by a membrane compressor (efficiency 60%) to compress 1 m³ of H₂ and 0.5 m³ of O₂ is 475 W·h. In this case, the total energy consumption for generation and
compression of these gases amounts, taking into account the compressor equipment consumption, is ≈ 4.2 kW h/ m$^3$ (Scheme 3).

Scheme 3. The technological scheme of H$_2$ and O$_2$ production with additional compressors.

The pressure change in the electrolyzer of 20 L/h capacity, when current density is 0.015 A/cm$^2$, is presented on Figure 2.

![Figure 2. The diagram of pressure increase under H$_2$ and O$_2$ generation by the electrolyzer of 20 liters/hour capacity when current density is 0.015 A/cm$^2$.](image)

As to the level of technical decisions, simplicity of mounting and servicing, reliability and safety, the electrolyzer implementing the described technology surpasses all of the known analogues (Table 3).

<p>| Table 3. The comparative characteristics of the proposed electrolyzer and the industrial analogues. |</p>
<table>
<thead>
<tr>
<th>Electrolyzer title, manufacturer, country</th>
<th>Productivity of H$_2$, m$^3$/h</th>
<th>Productivity of O$_2$, m$^3$/h</th>
<th>Power consumption, kW/h</th>
<th>Working pressure, atm</th>
<th>Weight, kg</th>
<th>Consumed energy resources</th>
<th>Hydrogen purity, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>EHP-1.0-150, IMEP, Ukraine</td>
<td>1</td>
<td>0.5</td>
<td>3.9-4.1</td>
<td>1-200</td>
<td>1200</td>
<td>Electrical power, KOH</td>
<td>99.998</td>
</tr>
<tr>
<td>EU-2/3.2, “Electrolysis Technologies” Ltd., Russia</td>
<td>2</td>
<td>1</td>
<td>4.7</td>
<td>32</td>
<td>1300</td>
<td>Electrical power, KOH</td>
<td>99.8</td>
</tr>
<tr>
<td>BLUE LINE, “McPhy Energy”, France</td>
<td>1</td>
<td>0.5</td>
<td>6.2</td>
<td>4-8</td>
<td>-</td>
<td>Electrical power, water, nitrogen</td>
<td>99.998</td>
</tr>
<tr>
<td>HOGEN S40, Proton Onsite, USA</td>
<td>1.05</td>
<td>0.525</td>
<td>8.3</td>
<td>13.8</td>
<td>215</td>
<td>Electrical power, KOH</td>
<td>99.995</td>
</tr>
<tr>
<td>HySTAT™-A-10000Q-40-25, Hydrogenics Europe NV, Belgium</td>
<td>10</td>
<td>5</td>
<td>4.9</td>
<td>25</td>
<td>2550</td>
<td>Electrical power, KOH</td>
<td>99.9</td>
</tr>
</tbody>
</table>

Conclusions:

1. Separating in time and space the electrolytic processes of water decomposition for gas liberation (H$_2$ and O$_2$) provides high pressure (up to 200 atm and more) and excludes the use of separating membranes in the electrolyzer construction, what results in increase of its reliability and operation safety.

2. Due to increase of voltage in the electrolysis cell, the OH ions diffusion velocity is decreased as the thickness of the (Fe(OH)$_2$, Fe(OH)$_3$) reacted active electrode layer is increased. The difference between the amounts of reacted substance of the porous iron electrode, when the current density is increased from 0.015 to 0.03 A/cm$^2$, is about 4 %. This indicates the
growth of the reacting layer of the active electrode, \((\text{Fe(OH)}_2, \text{Fe(OH)}_3)\), what depends on increase of time of oxidation and reduction hemicycles.

3. The difference between the values of the standard Gibbs energy \((\Delta G)\) and Gibbs energy taking into account the pressure change \((\Delta G_p)\) is \(\approx 3\%\), what proves that pressure increase in the indicated range (up to 200 atm) affects the electrolysis process insignificantly.

4. Under use of the developed electrolysis technology it is required \(\approx 3715\) W·h/m\(^3\) of energy to generate 1 m\(^3\) of hydrogen \((\text{H}_2)\) and 0.5 m\(^3\) of oxygen \((\text{O}_2)\), without taking into account compression of these gases. The compression of gases under electrochemical process consumes 285 W·h due to increase of the pressure of generated gases in such membrane-less electrolyzer.

5. The described here membrane-less gases generation technology does not require to use mechanical compressors for putting gases into a buffer storage system because in such technology gases are directly generated under high pressure. In the same time, the reliability and safety of electrolyzer operations are increased.

References


