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MASS SPECTROMETRIC STUDIES OF HYDROGEN GENERATION UNDER ELECTROLYSIS PROCESS WITH THE USING TUBE CATALITYC ELECTRODES

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The work presents some experimental results obtained in the new module construction of an electrolyzer with tube electrodes: mass spectra of the mixtures of gases, generated during electrolysis, volt-ampere characteristics, etc. It has been shown that at electrolytes (H_2O + 1 wt.% $NaHCO_3$, H_2O + 1 wt.% Na_2CO_3) temperature of ~ 50 °C and a pressure in the electrolyzer chamber of ~ 2 atm, the generated gas is 92 vol.% consists of hydrogen. Estimations show from two to four times (in dependence on electrolyte composition) higher effectiveness of converting electrical energy into the amount of electrolysis gas for new electrolysis setup construction compared to the previous version.

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INTRODUCTION

The main obstacle to the widespread use of electrolysis hydrogen is its high cost, due to high electricity consumption during production, and the need to purify such hydrogen from impurities (mainly, water and oxygen). The latter one can reduce using non-separated mixture of gases obtained during electrolysis, i.e., to use it directly as a fuel. Note that in this case gas mixture can be an explosive (explosion limits for mixtures of hydrogen with oxygen are 4.1…96 vol.% and with air 4…75 vol.% [1]). Therefore, it is very important to know composition of gas mixture produced during electrolysis process.

Early, in the work [2], it has been shown that at an electrolyte temperature of 50 °C and a pressure in the electrolyzer chamber of 4at the observed composition of the generated gas was 94 vol.% consists of hydrogen, 3 vol.% H_2O and 1.5 vol.% each of CO and oxygen. Such composition is not explosive in air and it can be used as a fuel. To measure the composition of the generated gas, a mass-spectrometric method used.

In above-mentioned work the electrolysis setup represented very simple construction, which included two Ni tube-electrodes (distance between electrodes was about 22 mm) placed in the stainless steel chamber filled with the electrolyte (H_2O + 1 wt.% $NaHCO_3$). It had been shown that the Ni membrane cathodes after several hours of work did not manifested any signs of erosion, or other damages. As for the anodes, even with electrolysis of clean water (14 ppm), noticeable erosion and surface damage observed [3].

In this work new module construction of electrolyzer with Pd tube catalytic electrodes had been tested and mass-spectrometric investigation of generated gas had been carried out.

1. EXPERIMENTAL AND RESULTS

A schematic diagram of the installation shown in Fig. 1 consists of the chamber 1 (E-2), made of thick-walled stainless steel 12Cr18Ni10Ti, four electrolysis modules 2 (it is seen in the picture only three ones), placed on the flange 6 through fluoroplastic seal-insulator 5.

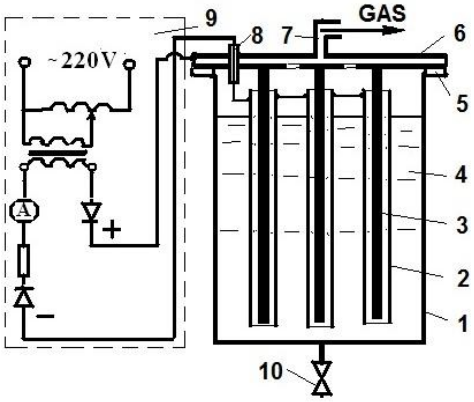
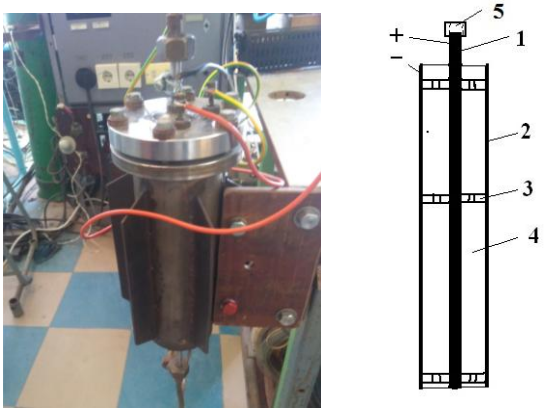


Fig. 1. Scheme of the experimental electrolysis setup: 1 – electrolysis chamber (E-2); 2 – cathode; 3 – anode; 4 – electrolyte; 5 – fluoroplastic seal-insulator; 6 – flange; 7 – pipe branch; 8 – current lead; 9 – power supply; 10 – valve



a *b*

Fig. 2. General view of the E-2 chamber (a); electrolysis module (b): 1 – anode; 2 – cathode; 3 – fluoroplastic insulator; 4 – electrolyte; 5 – flange fitting

The general view of the electrolyzer chamber E-2 and the scheme of the one from four modules is given in the Fig. 2. Anodes 1 in the form of Pd tubes, with a diameter of 3 mm, a thickness of 1 mm and a length of 150 mm, mechanically fixed to flange 6 through flange

fitting 5 with good electrical contact. The cathodes (see 2 in the Fig. 2) made of Pd tubes with a diameter of 10 mm, a thickness of 0.2 mm and a length of 150 mm, mechanically fixed to anodes 1 through fluoroplastic insulators 3 (see Fig. 2). The distance between electrodes is about 3 mm. A constant voltage between the anode and cathode was switched on a positive to flange 6, and negative, through – current lead 8 (see Fig. 1), to cathodes.

The power supply (see 9 in Fig. 1) is a rectifier on two V200 diodes connected through current transformer to the autotransformer. As an electrolyte, a 1 wt.% sodium bicarbonate (soda) solution in ordinary filtered water was used (mineralization measured using the TDS Meter 3 device was 157 ppm). Also, it was tested the electrolyte, which produced by long time boiling (~ 100 °C, 2 h) of soda solution in water. The electrolysis chamber (E-2) is connected through a valve (not shown in the diagram) to the inlet system of the high-vacuum installation GAS [2, 4, 5] (Fig. 3), which allows, using mass spectrometer, to determine the composition of the mixture of gases formed during the electrolysis process.

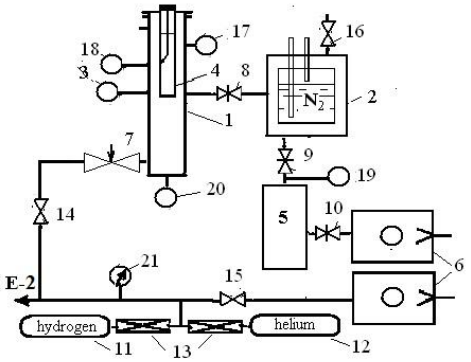


Fig. 3. Scheme of the GAS experimental setup [2, 4, 5]: 1 – vacuum chamber; 2 – cryogenic pump; 3 – mass spectrometer MX-7304; 4 – sample; 5 – diffusion pump M-500; 6 – fore-vacuum pumps 3NVR-1D; 7– fine adjustment valve; 8, 9, 10 – high-vacuum valves; 11 – hydrogen balloon; 12 – helium balloon; 13 – gas reducers; 14, 15, 16 – high pressure valves; 17 – ionization gauge PMI-10; 18, 19 – thermocouple gauges PMT-2; 20 – ionization gauge PMI-2; 21 – pressure gauge

Hydrogen produced by electrolysis in the E-2 chamber as follows. First, the internal volume of the chamber 1 and the connecting pipes pumped out to a pressure of about 10^{-3} Torr. Then the electrolysis process is started in chamber 1 (see Fig. 1) by switch on a constant voltage between the anode and cathode.

In Fig. 4 the current-voltage characteristics of the electrolysis process are shown. For comparison, in Fig. 5 the current-voltage characteristic of the electrolysis process in the electrolysis chamber E-1 [2] is presented.

After gas pressure increasing in the GAS inlet system (see manometer 21 in Fig. 3) up to atmosphere pressure, the GAS inlet system pumped once more through valve 15. Such procedure (gas "washing") repeated thrice. In this time, the temperature of the electrolyte monotonically increases, reaching 50 °C after half hour of operation of the electrolyzer.

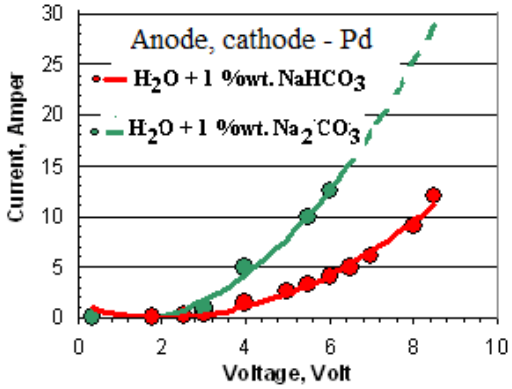


Fig. 4. Current-voltage characteristic under electrolysis process in the chamber E-2: red points – 1 wt.% solution of soda ($NaHCO_3$) in water, green points are for solution of soda ash in water

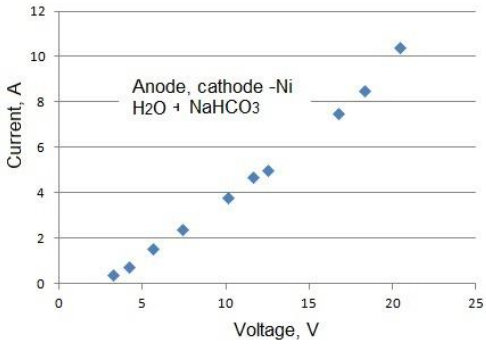


Fig. 5. Current-voltage characteristic under electrolysis process in the chamber E-1 [2] of 1 wt.% soda ($NaHCO_3$) solution in water

At the same time, the current changed in the region 11…12 A and the voltage between the electrodes decreased from 8.5 to -7.5 V. Gas pressure in electrolysis chamber reached two atmospheres (~ 0.2 l = 200 cm^3 of gas at the normal conditions). It was enough to carry out measurements of mass spectra.

To determine the composition of the gas mixture formed during electrolysis, vacuum chamber 1 of the GAS installation (Fig. 3) pumped out through valves 8, 9, 10 to a pressure of $(1…2)\cdot10^{-7}$ Torr. Then, the gas, generated during the electrolysis process, through valves 14, 7 (see Fig. 3) was released into vacuum chamber 1 of the GAS device to a pressure of $(0.1…0.4)\cdot10^{-4}$ Torr.

The mass spectra measured with MX-7304 mass spectrometer and recorded, using the WAD-AIK-BUS analog module and a computer. The Fig. 6,a,b shows the spectra before and during the puffing of gas, generated during electrolysis, into the vacuum chamber E-2. In this case, the pressure in the electrolyzer chamber was about 2 atm, and the electrolyte temperature was ≈ 50 °C. For comparison, the spectra measured during electrolysis process in E-1 electrolysis chamber (see Fig. 6,c) [2] and, when pure hydrogen (99.99% by vol.) was puffed from a balloon to GAS installation (see Fig. 6,d), presented, too.

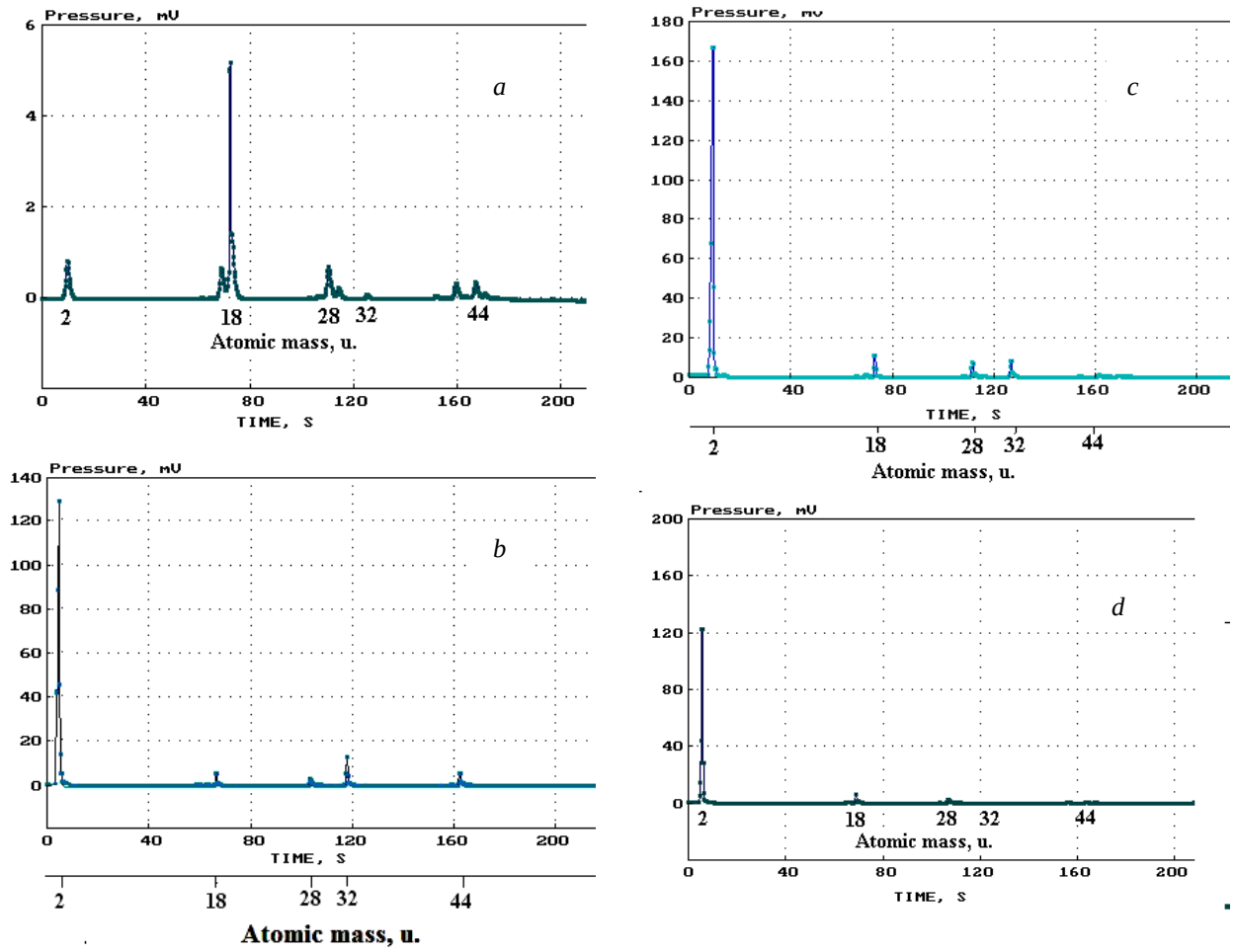


Fig. 6. Mass spectra of gases in the GAS chamber: a – before gas inlet; b – during inlet of gas from the electrolyzer E-2; c – during inlet of gas from electrolyzer E-1[2]; d – hydrogen puffing from hydrogen balloon

2. DISCUSSION

Measurements of the spectral composition of the generated gas carried out at the temperatures about ~ 50 °C. It caused by the fact that, when the electrolyte temperature reaches 60 °C, the transformation of Na bicarbonate into soda ash begins:

$$2NaHCO_3=Na_2CO_3+CO_2+H_2O.$$

After long time boiling at 100 °C the new electrolyte is produced with soda ash instead of soda. It is seen in Fig. 4 that this fact strongly influences on the current value. The analysis of the data shown in Figs. 4, 5 allows to say that the new electrolyzer construction provides higher currents at much lower input power (~ 55…82 W instead of ~ 200 W at 10 A current). According the first law of Faraday: $m=k\cdot I\cdot t$ [6], where m – mass of generated gas; k – electrochemical equivalent; I – current; t – time, the mass of generated gas is proportional to current value. Therefore, at the same power input the quantity of generated gas in the new module electrolyzer, from two to four times higher (in dependence on electrolyte composition), than in the previous construction [2]. There could be some reasons for this: new module construction, decreasing of distance between electrodes, using another material for electrodes (Pd instead of Ni), different composition of an electrolyte, etc. Additional researches are needed to find out the true reasons. Here note only, that long timework in the electrolyte did not lead to any signs of erosion, or other damages both for Pd cathodes and for anodes, in difference from Ni anodes behavior [3].

Processing of the instrumental spectra curves shown in Fig. 6,b allows saying, that in our case, the gas generated during electrolysis consists of ~ 92 vol.% of hydrogen, 4 vol.% oxygen, 1.5 vol.% each of H_2O and CO_2, and 1 vol.% of CO. It was taken into account, that the sensitivity of the mass spectrometer for hydrogen is approximately two times lower than for air. The spectrum of the generated gas differs from the spectra of hydrogen produced in the previous electrolyzer [2]: 1.5 vol.% of water vapors was observed instead of ≈ 3 vol.%, and 4 vol.% oxygen, instead of only 1.5% in [2]. These results are very different from the literature data on water electrolysis: reaction equation $2H_2O=2H_2+O_2$ (66% H_2+34% O_2). We are inclined to explain this by the fact of strong differences in the constructions of devices for hydrogen generation by electrolysis and compositions of electrolytes. Using different electrodes materials may make a big difference. To clarify the physicochemical reasons for this, additional researches are necessary, in particular, to study electrode material behavior.

CONCLUSION

The experimental setup designed, produced, and tested, to study the processes during electrolysis in the module electrolyzer with Pd tube electrodes.

The spectra of the generated gas and current-voltage characteristics of the electrolysis process had been measured.

It has been shown that at electrolytes (H_2O + 1wt.% $NaHCO_3$, and solution of soda ash in water) temperature of ≈ 50 °C and a pressure in the electrolyzer chamber of 2 atm, the generated gas is 92 vol.% consists of hydrogen, and 4 vol.% of oxygen, 1.5 vol.% each of H_2O and CO_2, and 1 vol.% of CO. This mixture is not explosive in the mixture with air and it can be used as a fuel. When oxygen or air to add, the mixture becomes explosive.

Estimations showed from two to four times (in dependence on electrolyte composition) higher effectiveness of converting electrical energy into the amount of electrolysis gas for new electrolysis setup construction compared to the previous version [2].

REFERENCES

1. V. Schroder, B. Emonts, Holger Janban, H.-P. Schulze. Explosion limits of hydrogen/oxygen mixtures at initial pressure up to 200 bar // *Chemical Engineering and Technology*. 2004, v. 27(80), p. 847-851; DOI 10.1002/ceat.200403174

2. Gennadiy Glazunov, Aleksey Konotopskiy, Dmitriy Elisieiev, Igor Garkusha, Sergey Maznichenko. Hydrogen generation under electrolysis process using Ni diffusion catalytic membranes as electrodes // *International Journal on Applied Physics and Engineering.* 2023, v. 2, p. 194-198;
DOI: 10.37394/232030.2023.2.17

3. G.P. Glazunov, A.S. Bodnar, A.L. Konotopskiy, D.M. Vinogradov, S.M. Maznichenko, and I.E. Garkusha. Erosion behavior of nickel diffusion membranes in conditions of water electrolysis // *Problems of Atomic Science and Technology. Series "Plasma Physics" (28).* 2022, N 6(142), p. 111-113

4. G.P. Glazunov, D.I. Baron, V.E. Moiseenko, M.N. Bondarenko, A.L. Konotopskiy, A.V. Lozin, A.I. Lyssoivan, T. Wauters, and I.E. Garkusha. Characterization of wall conditions in Uragan-2M stellarator using stainless steel thermal desorption probe // *Fusion Engineering and Design. 2*018, v. 137, p. 196-201.

5. G.P. Glazunov, A.A. Andreev, D.I. Baron, V.M. Shulaev, V.A. Stolbovoy, V.Ya. Chernyshenko. The influence of the method of applying vacuum-arc TiN coatings on their outgassing in a vacuum at high temperatures // *Physical engineering of the surface.* 2009, v. 7, N 4, p. 341-346.

6. Ehl Rosemary Gene, Ihde Aaron. Faraday's Electrochemical Laws and the Determination of Equivalent Weights // *Journal of Chemical Education*. 1954, v. 31, p. 226-232; DOI:10.1021/ed031p226

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МАС-СПЕКТРОМЕТРИЧНІ ДОСЛІДЖЕННЯ ГЕНЕРАЦІЇ ВОДНЮ У ПРОЦЕСІ ЕЛЕКТРОЛІЗУ З ВИКОРИСТАННЯМ ТРУБЧАСТИХ КАТАЛІТИЧНИХ ЕЛЕКТРОДІВ

Г.П. Глазунов, О.Л. Конотопський, І.Є. Гаркуша, Д.А. Єлісєєв

Представлено деякі експериментальні результати, які отримані у новій модульній конструкції електролізера: мас-спектри сумішей газів, що утворюються протягом електролізу, вольт-амперні характеристики тощо. Показано, що при температурі електролітів (H_2O + 1 ваг.% $NaHCO_3$, H_2O + 1 ваг.%. Na_2CO_3) ~ 50 °C і тиску в електролізері ~ 2 атм утворюється газ, якій на 92 об.% складається з водню. Оцінки показують від 2 до 4 разів (у залежності від складу електроліту) більшу ефективність перетворення електричної енергії у кількість електролізного газу для нової електролізної установки у порівнянні з попередньою версією.