# HYDROGEN PRODUCTION IN A COMBINED ELECTROCHEMICAL SYSTEM: CATHODE PROCESS

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**Abstract.** Today, hydrogen is recognized as a promising fuel, which is characterized by high heat generation and combustion temperature. It is also characterized by environmental safety due to the fact that no greenhouse gases are formed during the combustion of hydrogen. There are various methods of hydrogen production: traditional methods, which include electrolysis of water and conversion of hydrocarbons, and thermochemical ones. A cheap method of hydrogen obtaining from natural gas and coke is accompanied by the carbon oxides formationю Thermochemical methods are require high temperatures (up to 1000°C). The method for hydrogen production by electrolysis of aqueous solutions of alkali metal hydroxides is the most energy-intensive. However, it is considered one of the most promising in the European Union.

To reduce energy consumption for hydrogen production, the authors suggest replacingthe positive electrode, which normally produces oxygen, with a dissolving anode with an equilibrium potential lower than that of oxygen, such as an iron electrode. In this case, with such a combined electrochemical method, the decomposition voltage in the system will be 0.44 V against 1.23 V with traditional water electrolysis. The overvoltage of iron dissolution in a chloride medium is several tens of millivolts. However, the potential difference between the anode and cathode $\Delta U$ becomes smaller than the equilibrium potential difference $\Delta E_0 = 0.44$ V.

This research aims to substantiate the choice of the composition and concentration of electrolytes: catholyte –to ensure conditions for reducing energy consumption for hydrogen release; anolyte – to prevent passivation of the iron anode, which can lead to the oxygen release. This work results in research of the cathodic process of hydrogen release in the following solutions: 1 M (= mol/L) NaCl with the addition of 1 M hydrochloric acid in the amount of 5, 10, 15, 20 mL. Platinum is used as a cathode for the electrolysis process. The anode material is an iron, St3 grade. It has been found that in the range of changes in the composition of the electrolyte from neutral (1 M NaCl) to acidic (1 M HCl), a change in the mechanism of water discharge is observed. In a neutral medium, the discharging occurs according to the Heyrovsky mechanism, and in an acidic medium - according to the Volmer mechanism. The choice of the anolyte composition and concentration is complicated by the need to provide an acidic medium containing chlorine ions to prevent passivation of the anode. The acidity of the solution must be at least 3 for the successful extraction of dissolution products of the iron anode.

**Keywords**: hydrogen, electrolysis, cathode, soluble iron anode, hydrogen energy.

## 1. Introduction

Global warming and climate change are primarily related to the formation and accumulation of greenhouse gases in the atmosphere, including carbon oxides. The primary source of carbon oxides is industry, transport, and energy. Therefore, the development of renewable energy sources (RES) becomes an integral part of the transformation of global energy. There is a change in the structure of electricity production and consumption balances due to a significant increase in carbon-free technology, which includes hydrogen energy. Hydrogen energy is a branch of energy based on the use of hydrogen as a fuel. However, at the same time, hydrogen energy includes systems of transportation, accumulation, production, and consumption of energy.

Hydrogen has been chosen as an energy carrier for several reasons.

Firstly, hydrogen is the most abundant chemical substance in the universe and forms approximately 75 % of its total mass. On Earth, hydrogen is present in chemical compounds with oxygen (water) and carbon (hydrocarbons: coal, oil, and natural gas), its mass fraction being about 1 %.

Secondly, hydrogen has a very high combustion temperature and specific heat of combustion. It is approximately 140 MJ/kg, which is several times higher than the specific heat of combustion of hydrocarbon fuels (for methane - about 50 MJ/kg). This determines its use in metallurgy, chemical industry, and energy.

Thirdly, the product of oxygen combustion is water:

$$H_2 + 1/2O_2 = H_2O$$

The absence of greenhouse gases in combustion products contributes to the reduction of carbonation in the atmosphere.

The most common methods of producing hydrogen are hydrocarbon conversion, water electrolysis, and thermochemical method. In 201975 million tons of hydrogen were used in the world. More than 3/4 of them were produced from more than 205 billion cubic meters of natural gas. This method is called steam methane conversion. It is carried out at 1000 °C, pressure 20–35 atm. [1]:

$$CH_4 + H_2O = CO + 3H_2$$
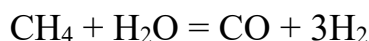
The second method is coal gasification - the oldest one in hydrogen production. Hydrogen production from coal is related to the thermal decomposition of water, and coal is used as an energy resource and a chemical reagent [2].

The process of hydrogen production can be written as follows:

$$C + H_2O = CO + H_2$$
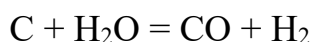
The main disadvantages of hydrogen production from natural fuels are significant capital and operating costs, which significantly increase the cost of the final product. In addition, while ideal for large-scale production, the method does not adapt well to low-capacity installations required for decentralized hydrogen production (e.g. gas stations, autonomous energy systems, etc.).

Another drawback of the method is the presence of CO and $CO_2$ impurities in the final product, which imposes additional requirements for hydrogen purification. For these reasons, the production of hydrogen from natural fuels is generally considered a transition technology, moving from today's energy market infrastructure to hydrogen energy in the future.

There is also plasma-arc decomposition. During hydrogen production by the method of plasma-arc decomposition when natural gas (mainly methane) is decomposed into hydrogen and carbon due to the effect of high-temperature plasma on it. The formation of hydrogen and carbon as a result of the methane decomposition reaction can be written as:

$$CH_4 \rightarrow C \text{ (solid)} + 2H_2 \text{ (gas)}$$

Such production uses high voltage (for decomposing natural gas/methane into carbon black and hydrogen gas) and high temperatures (more than 1400 °C). This

method satisfies the principles of green chemistry, such as atomic efficiency and reduction of by-products. However, carbon black production conflicts with the prevention of waste generation. The raw material in this process is not renewable.

It is possible to release hydrogen by the plasma method through acetylene production at the high-temperature methane decomposition. The reaction for hydrogen production by this method will look like this:

$$2CH_4 \rightarrow C_2H_2 + 3H_2 \text{ (gas)}$$
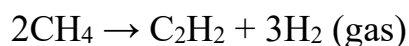
This process takes place at about 1100-1250 °C, being its main disadvantage. However, acetylene is the main product of this decomposition, being a reaction intermediate for organic synthesis. Due to its high calorific value, acetylene is used for metal welding and gas flame cutting [3].

More than 10,000 different thermochemical cycles of hydrogen production are also known [4, 5]. They use multi-stage chemical reactions that take place at different temperatures, in the range from 500 to 1000 °C, to produce hydrogen.

If the products of one reaction are the starting substances in another reaction, and only heat energy is used, this method is called a thermochemical cycle. Due to economic feasibility, in addition to heat, water, and electricity, they use reagents (X, Y, etc.), which are industrial waste: hydrogen sulfide, sulfuric anhydride, various sulfides, metal-based halides, carbon compounds, sulfur-based cycles, etc. The most competitive cycles use cheap and available reagents: oxides of iron, sulfur, carbon, and iron chlorides.

The thermochemical cycle of hydrogen production can be presented in the form of a scheme:

$$H_2O + X \rightarrow H_2 + Y$$

$$Y \rightarrow X + 0.5O_2$$
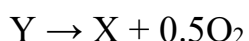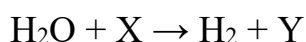
A common disadvantage is the use of high temperatures, which require the use of special heat-resistant materials, and a source of cheap heat. It is considered appropriate to use thermochemical cycles in combination with high-temperature reactors of nuclear power plants.

A method for producing hydrogen by electrolysis of aqueous solutions of alkali metal hydroxides [6], which do not discharge on the electrodes, but provide the necessary electrical conductivity, is particularly interesting to us. At the same time, the reaction takes place in the electrolyzer:

$$H_2O \pm 2F = H_2 + 1/2O_2,$$
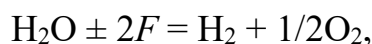
where $F$ is Faraday's number, which is equal to the amount of electricity of Avogadro's number of electrons, 96500 C (=A·s) or 26.8 A·h.

Hydrogen produced by the electrochemical method is the purest. For example, the purity of the gas at the exit from the ThyssenKrupp electrolyzer is 99.95 %. After purification, the hydrogen content in the gas is 99.999 % [7]. At the same time, at a temperature of about 90°, the water consumption is less than 1 liter per m$^3$ of hydrogen. The disadvantage of the electrochemical method is the considerable energy consumption of the process. This is because the voltage of the decomposition of a water molecule is 1.23 V when the voltage on the electrolyzer is 1.8 V. Despite this, in the European Union, the method is considered to be one of the most promising. In this regard, there is a tendency to introduce the electrolytic method of hydrogen production. In particular, conditions allowing to increase significantly the electrolyzers' efficiency and reduce their cost have been determined. After considering the advantages and disadvantages of thermo- and electrochemical methods of water decomposition, combined cycles have been proposed, their implementation being the simplest.

Analyzing the current state of the problem of producing high-purity hydrogen with reduced energy consumption, the aim of this research can be formulated as follows:

- to substantiate the composition of the electrolyte in the cathode space (catholyte) and its concentration;

- to ensure the condition of reducing the energy consumption for the release of hydrogen in a new combined system open for mass transfer;

- to determine the parameters of the cathodic process of hydrogen release depending on the type of electrolyte.

## 2. Methods

The research on the process of hydrogen release in an acidic medium was carried out by studying the polarization curves in the potentiostatic mode at a temperature of 20 ºC.

The research was carried out in 1 M NaCl (100 mL) with the addition of 1 M hydrochloric acid in the amount of 5, 10, 15, 20 mL; 1 M HCl and Na$_2$SO$_4$ solution with a concentration of 1 mol/L. For each electrolyte, the pH of the solution was determined using a pH meter.

The following electrodes were used: cathode - platinum, size 9 x 9 mm$^2$; soluble anode - St3 grade iron, size 5 x 5 mm$^2$; the reference electrode is a saturated chlorine-silver Ag/AgCl electrode.

The current load on the electrolyzer was carried out from the B5-49 current source, the potentials of the electrodes were measured relative to the chlorine-silver reference electrode using the B7-16A voltmeter.

## 3. Theoretical part

In traditional electrolysis, oxygen is released in an acidic medium according to the reaction:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$
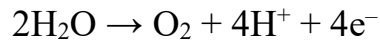
The equilibrium potential of the reaction $E_0$ is equal to 1.229 V. To reduce the energy consumption for hydrogen production by the electrochemical method, we propose replacing the anode, on which oxygen is released, with a soluble anode. A mandatory condition for the material is the value of the equilibrium potential below the oxygen release potential. Such a material can be iron, for example, metal scrap sent for processing. The iron anode dissolves at room temperature according to the reaction:

$$Fe^0 - 2e = Fe^{2+} \; (E_0 = 0.44 \text{ V})$$
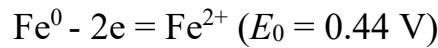
At the platinum cathode, the reaction of hydrogen evolution takes place:

$$2H^+ + 2e = H_2 \; (E_0 = 0 \text{ V})$$
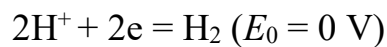
In this case, the decomposition voltage in this system is 0.44 compared to 1.23 in traditional water electrolysis. The overvoltage of iron dissolution in a chloride medium is several millivolts and the cathode potential shifts to the negative side when the current density increases. As a result, the anode and cathode potential difference $\Delta U$ becomes smaller than the equilibrium potential difference $\Delta E_0 = 0.44$ V.

The principle technological scheme (Fig. 1) can be described as follows: the hydrogen-saturated catholyte enters the separator, where the liquid and gas phases are separated.
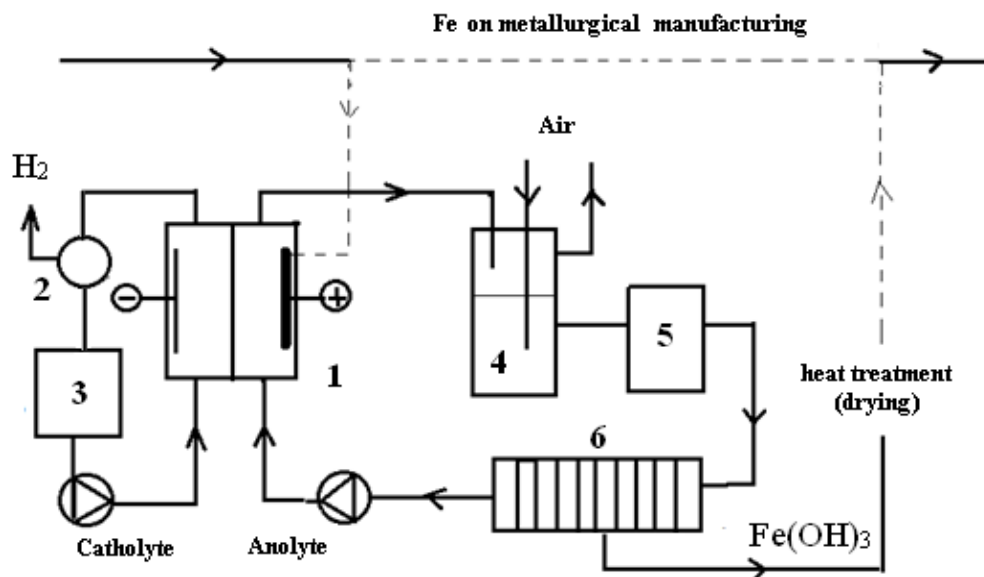


1 – reactor; 2 – separator for separating hydrogen from catholyte, 3 – sediment tank;
4 – saturator; 5 – coagulator; 6 – filter press

Figure 1 – Schematic diagram of an electrochemical method of hydrogen production open by mass transfer

The anolyte from the electrolyzer is sent to the saturator, where it is oxidized by air oxygen to the trivalent state and, at pH > 3, it is hydrolyzed, turning into the water-insoluble form $Fe(OH)_3$:

$$Fe^{2+} + 0.5O_2 + 2H_2O \rightarrow Fe(OH)_3 + H^+$$

The iron hydroxide enters the sediment tank, where the solid phase particles are aggregated (coagulated), filtered on filter presses, and subjected to heat treatment to remove moisture. The resulting sediment can contain about 66% of pure iron and can be processed at a metallurgical enterprise. The solution containing dissolved oxygen is returned to the anode space of the electrolyzer. To prevent dissolved oxygen from reaching the cathode, it is necessary to separate the cathode and anode space with a diaphragm or membrane.

## 4. Experimental part

The scheme of the experimental setup is presented in Fig. 2. It shows $l$ – the distance between the cathode and anode, $l_x$ – the distance between the working electrode (anode) and the reference electrode ($x = l_x / l$). The scheme allows measurements either at a small distance l between the electrodes or at a significant distance between the electrodes (shown by an arrow in Fig. 2).
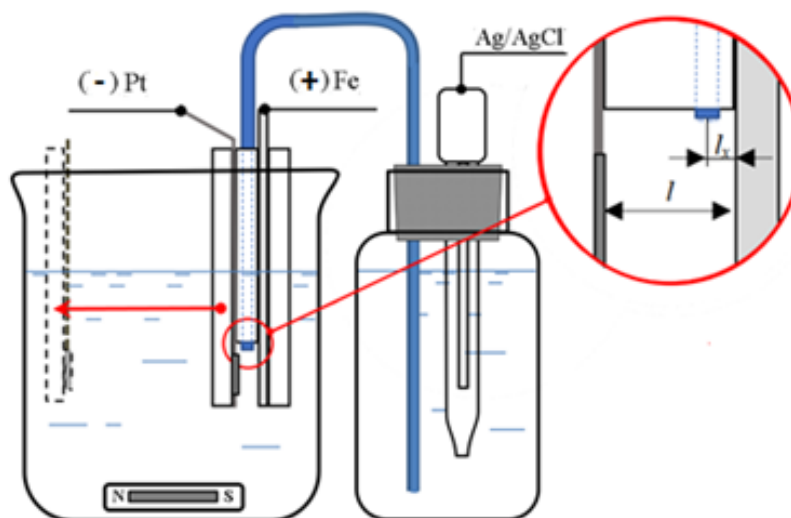


Figure 2 – Scheme of the experimental setup for hydrogen release process studying

## 5. Results and discussion

For stable operation of the combined hydrogen release system, the electrolyte must meet the following requirements:

1. Minimum possible overvoltage of hydrogen release at the cathode.

2. Lack of passivation of the iron anode.

3. Solid phase of iron hydroxides should not form in the anode space of the electrolyzer.

4. Maximum possible electrical conductivity.

5. Low corrosion activity to the material of the equipment.

6. Availability and low cost.

The 1st requirement is met by acidic solutions, in which the overvoltage of hydrogen evolution on platinum is minimal. At the same time, the use of sulfuric or nitric acids is undesirable, since they have an oxidizing effect that contributes to the passivation of the anode and the release of oxygen on it.

The 2nd requirement is met by solutions, for example, containing fluorine or chlorine ions.

Acidic solutions have the maximum possible electrical conductivity. In addition, to prevent the hydrolysis of ferrous ions formed during the anode dissolution, the pH of the medium should be about 3. However, the use of acidic solutions contradicts the 5th requirement, which complicates the process leading to an increase in the cost of the equipment.

Sodium chloride sufficiently meets the 6th requirement.

Based on the listed requirements and features, solutions of 1 M NaCl (100 mL) with the addition of 1 M hydrochloric acid in the amount of 5, 10, 15, 20 mL, as well as a 1 M HCl solution have been analyzed. The acidity of the working electrolytes ranges from 3 to 1. The polarization curves (dependence of current density $i$ on electrode potential $E$) of hydrogen release on the platinum cathode are presented in Fig. 3.
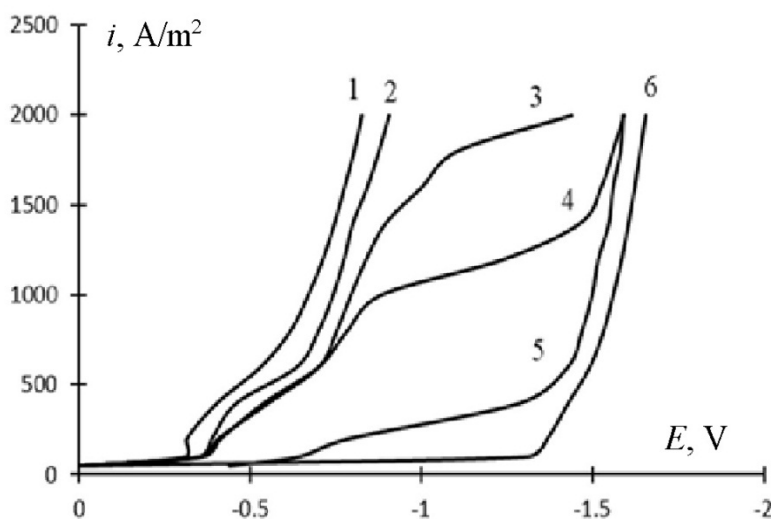


1 – 1 M HCl; 2 – 1 M NaCl + 20 mL 1 M HCl; 3 – 1 M NaCl + 15 mL 1 M HCl;
4 – 1 M NaCl + 10 mL 1 M HCl; 5 – 1 M NaCl + 5 mL 1 M HCl; 6 – 1 M NaCl

Figure 3 – Polarization curves of hydrogen release on the platinum cathode in solutions

The different position of the polarization curves in Fig. 3 demonstrates that the hydrogen release overvoltage on platinum is highly dependent on the composition and concentration of the electrolyte. In a pure 1 M hydrochloric acid solution, the polarization at a current density of 1000 A/m$^2$ is about 400 mV (curve 1), and in a 1 M NaCl solution, the polarization is about 1000 mV (curve 6).

The difference in the course of the curves and the magnitude of the overvoltage is associated with different mechanisms of the first stage of hydrogen release in a neutral environment, by the Heirovsky mechanism, and in an acidic environment, by the Vollmer mechanism [8, p. 588]:

$$H_3O^+ + e \rightarrow H_{ads} + H_2O \text{ (Heyrovsky)}$$

$$H_2O + e \rightarrow H_{ads} + OH^- \text{ (Vollmer)}$$
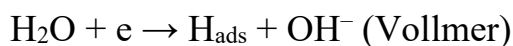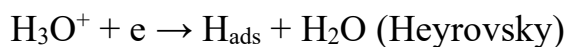
where $H_{ads}$ is an atom adsorbed on the electrode surface.

It is obvious that the hydration energy of the $H^+$ cation is less than the energy of the $H^+$–$OH^-$ bond in the water molecule. Therefore, the energy consumption for the elementary act of discharging a hydrogen ion in an acidic medium is lower than in a neutral (or alkaline) medium.  In this case, the process of hydrogen release proceeds at a higher speed and with a lower electrode polarization.

Theoretically, the dependence of overvoltage on the composition and pH of the electrolyte was substantiated by A.M. Frumkin in the theory of delayed discharge [9].

In a neutral medium or an acidic medium in the presence of an excess of a foreign electrolyte (HCl + KCl), the overvoltage value increases as the current density increases and the acid concentration decreases:

$$\eta = const + \frac{RT}{\alpha F} \ln i - \frac{1 - \alpha}{\alpha} \frac{RT}{F} \ln[H^+ ]$$

where: $\eta$ – value of overvoltage; $R$ – universal gas constant, J/mol; $T$ – temperature on the Kelvin scale, K; $\alpha \sim 0.5$ – transfer coefficient; $i$ – current density, A/cm$^2$; $[H^+]$ – hydrogen concentration, mol/L.

Based on the shape of the obtained polarization curves 3-5 in Fig. 3, it can be concluded that the magnitude of polarization is much greater than could be expected from the proposed equation. This fact may be related to the fact that sodium ions, which are present in the solution in a large excess, form a dense liquid part of the electric double layer, which prevents the delivery of hydrogen ions to the electrode surface.

According to the data obtained, it is possible to conclude that the catholyte composition of 1 M NaCl + 20 mL of HCl is appropriate for use in the cathode chamber as the one that best meets the above requirements.

## 6. Conclusions

1. The release of hydrogen on a platinum electrode in a neutral medium (1 M NaCl) is carried out at a significant polarization, which reaches 1 V.

2. When the working solution is acidified with hydrochloric acid, the polarization decreases and reaches 0.5 V at a current density of 1500 A/m$^2$.

3. In the range of changes in the composition of the electrolyte from neutral (1 M NaCl) to acidic (1 M HCl), a change in the water discharge mechanism is observed.

In a neutral medium, the discharge occurs according to the Heyrovsky mechanism, and in an acidic medium - according to the Vollmer mechanism.

4. It is advisable to use 1 M NaCl + 20 mL of HCl as a catholyte.

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## ОТРИМАННЯ ВОДНЮ В КОМБІНОВАНІЙ ЕЛЕКТРОХІМІЧНІЙ СИСТЕМІ. 1. КАТОДНИЙ ПРОЦЕС
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**Анотація.** Насьогодні водень є визнаним у світі перспективним паливом, яке відрізняється високою теплогенерацією та температурою згоряння. Також він характеризується екологічною безпекою завдяки тому, що при згорянні водню не утворюються теплічні гази.

Відомі різні способи виробництва водню: традиційні, до яких відносять конверсію вуглеводнів, електроліз води і термохімічні методи. Дешевий спосіб отримання водню з природного газу та коксу супроводжується утворенням оксидів вуглецю, а термохімічні методи потребують високих температур (до 1000ºС). Спосіб отримання водню електролізом водних розчинів гідроксидів лужних металів розглядається в Європейському Союзі як один з найперспективніших. алеце найбільш енергоємний спосіб.

Щоб зменшити споживання енергії для виробництва водню, автори пропонують замінити позитивний електрод, який зазвичай виробляє кисень, на анод, що розчиняє, з рівноважним потенціалом, нижчим за кисневий, наприклад, залізний електрод.. Таким чином, при такому комбінованому електрохімічному способі напруга розкладання в системі дорівнюватиме 0,44 В проти 1,23 В при традиційному електролізі води. Перенапруга розчинення заліза в хлоридному середовищі становить кілька десятків мілівольт, а різниця потенціалів анода і катода $\Delta U$ стає меншою за різницю рівноважних потенціалів $\Delta E_0 = 0,44$ В.

Метою даного дослідження є обґрунтування вибору складу та концентрації електролітів: католіту – для забезпечення умов зменшення енерговитрат на виділення водню; аноліту – для запобігання пасивації залізного аноду, яка може призвести до виділення кисню.

В даній роботі представлені результати дослідження катодного процесу виділення водню у розчинах: 1 M NaCl з додаванням соляної кислоти концентрації 1 M у кількості 5, 10, 15, 20 мл. У якості катоду для проведення процесу електролізу використовували платину. Матеріал аноду – залізо, марка Ст3. Було встановлено, що в діапазоні зміни складу електроліту від нейтрального (1 M NaCl) до кислого (1 M HCl) спостерігається зміна механізму розряду води: в нейтральному середовищі розряд протікає за механізмом Гейровського, в кислому – за механізмом Фольмера.

Вибір складу та концентрації аноліту ускладнюється необхідністю забезпечення кислого середовища, в якому містяться іони хлору, для запобігання пасивації  аноду. Для вилучення продуктів розчинення залізного аноду кислотність розчину pH має бути не менше 3.

**Ключові слова**: водень, електроліз, катод, розчинний залізний анод, воднева енергетика