UDC 544.6.018+544.652.076.324.4:661.961 DOI: https://doi.org/10.15407/geotm2025.174.124

ANALYSIS OF ELECTROLYSER OPERATION FOR PRODUCING HYDROGEN WITH SOLUBLE IRON ANODE USING MATHEMATICAL MODEL

[1,2]Nefedov V., [1]Bichai A., [1]Polishchuk Yu.
[1]*Ukrainian State University of Science and Technologies*
[2]*M.S. Poliakov Institute of Geotechnical Mechanics of the National Academy of Sciences of Ukraine*

Abstract. The production of chemically pure hydrogen by electrochemical method has limitations due to the high cost of aqueous solutions electrolysis. To reduce the voltage on the electrolyzer, it is proposed to replace the anode process of oxygen evolution (standard potential in an acidic environment plus 1.23 V) with the dissolution of the anode from electronegative metals. Such metals can be aluminum and iron - the most common structural materials. Waste of these metals in the form of scrap or shavings is quite cheap and can be used in the form of packed electrode. The standard potential of iron is minus 0.44 V, and aluminum in an acidic medium is minus 2.30 V. When connecting an electrode (cathode) with a low overvoltage of hydrogen evolution to the anode, it becomes possible to obtain hydrogen with simultaneous generation of electricity. When using an iron anode, the voltage on the cell decreases to 0.5–0.6 V at a current density of about 0.1 A/cm^2. The calculations and preliminary experiments showed that to reduce the polarization resistances of hydrogen evolution and iron dissolution, the composition of the anolyte and catholyte should be different. To reduce the polarization and ohmic resistances during electrolysis, a 1M HCl solution was chosen as the catholyte and a 5M NaCl solution - as the anolyte. Therefore, the anode and cathode chambers of the electrolyzer should be separated. Both porous diaphragms and anion exchange membranes can be used to separate the electrode chambers. For the diaphragms, the thickness, porosity and daily tortuosity coefficients are estimated. The properties of the diaphragms are determined not only by the energy costs of electrolysis (charge transfer processes), but also by the processes of substance transfer. For a well-grounded choice of diaphragm materials and the analysis of substance transfer processes in the electrolyzer, a mathematical model is proposed. Using this model, the values of diffusion and migration flows in the reactor are estimated. Moreover, the composition of the anolyte and catholyte are optimized, ensuring the flow of electrode processes with minimal energy costs; maintaining a given composition of solutions, and the possibility of their subsequent purification from electrolysis products.

Keywords: hydrogen, electrolysis, soluble iron anode, migration, diffusion, mathematical model.

1. Introduction

Producing hydrogen for energy using environmentally friendly methods is the most important task of modern energy. The widely used processes for producing hydrogen from natural gas or coke do not meet environmental requirements, since they release a mole of carbon monoxide or dioxide per mole of hydrogen [1]. Water electrolysis meets environmental requirements, but is characterized by increased energy costs, which limits hydrogen production by this method to 4% of the total world production. High energy costs are associated with the fact that the cathode process of hydrogen release and the anode process of oxygen release occur simultaneously. To obtain gaseous products, it is necessary to break the oxygen-hydrogen chemical bond in the water molecule. The thermodynamic voltage of water decomposition, determined by the Gibbs energy of water, is 1.23 V, which is about 70% of the voltage on the best industrial electrolyzers. The remaining 30% is accounted for by overcoming polarization and ohmic resistances. To reduce energy costs while maintaining the purity of production, we propose a method of electrochemical hydrogen production with soluble anodes made of electronegative metals [2, 3, 4].

Unlike classical electrolysis, spontaneous reactions occur in this system, directed towards decreasing the energy reserve, similar to a chemical power source (CPS) with generation of electric energy:

Received: 29.05.2025 Accepted: 15.09.2025 Available online: 22.09.2025

$$E_{in}=E_f+E_{ee} \tag{1}$$

where E_{in} is the initial reserve of chemical energy of the components; E_f is the final reserve of chemical energy of the components; E_{ee} is electric energy.

Thus, instead of a reactor with a soluble iron anode, instead of an electrolyzer with a decomposition voltage of 1.23 V, we have a CPS with an electromotive force equal to the potential difference between the anode and cathode, about 0.4 V. To accelerate the process (increase the current density of hydrogen evolution), this system requires additional polarization by an electrode from an external current source. That is, this system has the features of both an CPS and electrolyzer. This allows us to reduce the cost of electricity for producing hydrogen.

All metals with a potential more electronegative than the hydrogen electrode can be used as anode materials in this method. Moreover, the more negative is the metal used as a soluble anode, the greater is the energy gain. The main requirements for anode materials are availability, widespread use, low cost, and the absence of passivation during anode polarization. To a greater extent, these requirements are met by iron and aluminum, which, as industrial waste, can be used as backfill anodes. The cathode material must have a low hydrogen realize polarization. For acidic electrolytes, such a metal is expensive platinum [5], and for alkaline electrolytes, metals, and alloys of the iron subgroup [6–11].

This paper considers a system with a platinum (platinized titanium) cathode (hydrogen realize potential is 0 V) and a soluble iron anode, the potential of which is minus 0.44 V, instead of plus 1.23 V for oxygen realize in an acidic ambient. To reduce polarization and ohmic resistance, it is planned to use catholyte and anolyte of different composition and concentration. To prevent mixing, the anode and cathode chambers are separated by a diaphragm or anion-exchange membrane.

2. Methods

The aim of the work is a theoretical analysis of material flows during operation of an electrolyzer with a soluble iron anode based on a mathematical model; justification of the composition, concentration and feed rate of the electrolyte depending on the density of the hydrogen evolution current, the magnitude of the diffusion and migration flows of ions between the electrode chambers for a preliminary theoretical determination of the concentration and magnitude of the volumetric flows of feed substances of the reactor model with a soluble anode.

3. Theoretical part

3.1. Initial data

It is planned to use 1M HCl as a catholyte with a minimum hydrogen emission overvoltage and a sufficiently high electrical conductivity (κ~35 S/m) [4]. The use of such an electrolyte in the anode chamber is undesirable, since the process flow diagram provides for periodic purification of the solution from iron ions ($FeCl_2$), converting them into a water-insoluble form of hydroxides [3]. When using 1M hydrochloric acid as a catholyte to form $Fe(OH)_2$ or $Fe(OH)_3$, either a significant amount of alkali or dilution with a huge amount of water to a pH greater than 3 is required.

A 5M NaCl solution with a pH of no more than 3 is planned as the anolyte. Such a solution is available and cheap. The electrical conductivity of NaCl at a concentration of 5M is 24.73 S/m, which reduces the voltage drop in the electrolyte. Iron is not passivated during anode polarization in such an electrolyte since the chloride ion is a strong depassivator, and iron ions are not hydrolyzed to form a solid phase in the electrolyzer itself.

Anion-exchange membranes or cheap and accessible porous diaphragms are planned for separating the electrode chambers. The characteristics of the diaphragms (thickness, porosity, permeability, pore tortuosity coefficient and electrical resistance) were determined experimentally and described in [11]. Some of these parameters are given in Table 1.

Table 1 – Characteristics of diaphragm materials required for calculation

Diaphragm material	Average thickness, cm	Tortuosity coefficient of pores	Porosity
Porous polypropylene strip	0.0375	2.02	0.48
Polypropylene fabric	0.013	2.25	0.25
Nylon fabric	0.021	2.68	0.32
Asbestos	0.052	1.25	0.45
Chlorine fabric	0.0285	2.99	0.56
Mipore	0.05	2.68	0.48

3.2. Material flows in an electrolyzer with an iron-soluble anode and a porous diaphragm.

The diagram of material flows in the reactor is shown in Fig. 1.

During electrolysis in this system, current and substance are transferred by diffusion and migration flows (see the diagram in Fig. 1). The hydrodynamic pressure in the anode and cathode chambers is assumed to be the same, and that there is no filtration (leakage) through the pores of the diaphragms.

As follows from the diagram, iron and sodium ions are transferred from the anode chamber to the cathode one by diffusion and migration flows, while chlorine and hydronium ions are transferred by migration flows. Chlorine ions are transferred from the cathode chamber to the anode one by migration flows, and hydronium ions by diffusion flows. As a result, the catholyte is enriched with sodium and iron ions during process.

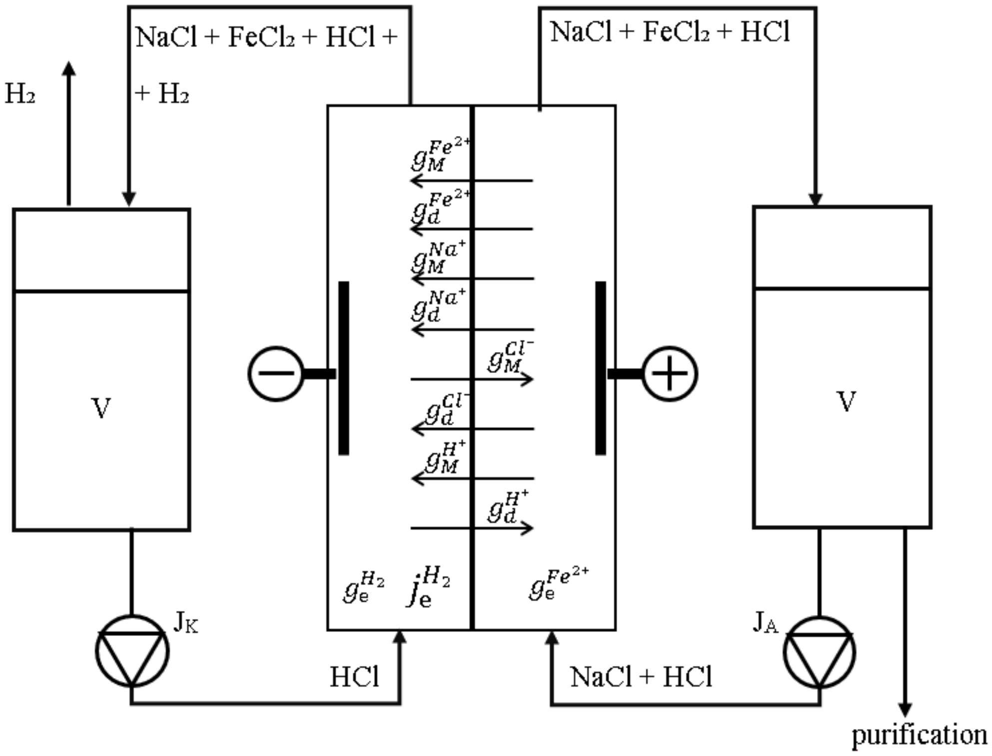
Initial condition: the material balance of the electrolyzer is made in moles per hour. The system units mol/m^3, mol/A s, m^3/s are ultimately converted to mol/l, mol/A h, l/h.

Electrode process:

Anode: $$Fe^{0} \rightarrow Fe^{2+} + 2F \quad (2)$$

Cathode: $$2H_2O^{+} + 2F \rightarrow H_2 + H_2O \quad (3)$$

where F = 96500 C/mol or 26.8 A·hour/mol is the Faraday number.



gM is the mass migration flow (mol/hour); *gd* is the mass diffusion flow (mol/hour);
j is the volume flow (m3/hour), g_e, j_e is electrochemical reaction substance flow,
V is the solution volume in the tanks

Figure 1 – Diagram of a reactor with an iron soluble anode and a porous diaphragm

In the anolyte of the given composition, iron passivation does not occur and oxygen is not released at the anode.

3.2.1 Electrochemical reaction flows:

Anode dissolution: $g_{Fe^{2+}} = k_{Fe^{2+}} I$

$k_{Fe^{2+}} = \dfrac{M_{Fe}}{2F}$ – electrochemical equivalent of iron, mol/ A·hour.

Hydrogen evolution at the cathode: $g_{H_2} = k_{H_2} I$ is mass flow; $k_{H_2} = \dfrac{M_{H_2}}{2F}$ is electrochemical equivalent of hydrogen; $j_{H_2} = k_{H_2} I$ is volume flow of hydrogen, *I* is the current, A.

Since the concentrations of substances in the anode and cathode chambers differ, diffusion flows arise aimed at equalizing the concentrations.

3.2.2. Diffusion flows

The diffusion flow through the diaphragm is calculated using the formula:

$$g_d = \frac{D\Delta C S \Pi}{\delta\beta}, \tag{4}$$

where D is ion diffusion coefficient, m^2/s; ΔC is a difference in substance concentrations in the anode and cathode chambers, mol/m^3; S is the diaphragm geometric surface, m^2; Π is the diaphragm porosity (dimensionless value); β is the diaphragm pore tortuosity coefficient (dimensionless value); δ is the diaphragm thickness, m.

During the first (single) anolyte flow through the electrochemical reactor, the concentration of iron ions is determined by the electrolyte flow rate and the electrochemical reaction rate:

$$C_{Fe^{2+}} = \frac{g_{Fe^{2+}}}{j_A}. \tag{5}$$

There are no iron ions in the cathode chamber. The flow of iron ions is directed from the anode chamber to the cathode one:

$$g_{Fe^{2+}} = \frac{D C_{Fe^{2+}} S \Pi}{\delta\beta}. \tag{6}$$

Chloride ions are present in both the anode and cathode chambers. This leads to the following formula:

$$g_d = \frac{D\left(C^A_{Cl^-} - C^K_{Cl^-}\right) S \Pi}{\delta\beta}. \tag{7}$$

When calculating the hydronium ion flow, we consider that to prevent hydrolysis of the divalent iron ions formed by the anode reaction, the pH in the anode chamber should be maintained at 3 (0.001 M)

$$g_d = \frac{D\left(C^A_{H^+} - C^K_{H^+}\right) S \Pi}{\delta\beta}. \tag{8}$$

3.1.6 Migration flows

Transfer of electricity in the reactor is carried out by ions of different signs, sizes and charges, i.e., by migration flows. Anions in the electric field move from the anode chamber to the cathode chamber, and cations - on the contrary.

The mass migration flow is calculated using the formula:

$$g_M = kIt \text{ ,} \tag{9}$$

where $t = \dfrac{z_i C_i \lambda_i}{\sum (z_+ C_+ \lambda_+ + z\_ C\_ \lambda\_)}$ is the transfer number of the given ion type; z_i is the charge of the given ion; z_+ is the charge of cations; z_- is the charge of anions; C_i is the concentration of the given ion, M; C_+ is the concentration of cations, M; C_- is the concentration of anions, M; λ_i is the mobility of the given ion, Ohm^{-1} m^2 mol^{-1}; λ_+ – cation mobility; λ_- – anion mobility.

The values of the diffusion coefficients and ion mobility are given in Table 2. The thickness, porosity, and tortuosity coefficient of the pores of various diaphragm materials were determined experimentally using the methods described in [12] and are given in Table 2.

Table 2 – Ion mobility and diffusion coefficients at 25°C

Ion	Ion mobility λ, Ohm^{-1} m^2 mol^{-1}	Ion diffusion coefficients at 25°C D, m^2 s^{-1}
Fe^{2+}	53.5×10^{-4}	0.6×10^{-9}
Cl^-	76.3×10^{-4}	2.04×10^{-9}
H^+	349.8×10^{-4}	9.34×10^{-9}
Na^+	50.3×10^{-4}	1.34×10^{-9}
OH^-	199.2×10^{-4}	5.28×10^{-9}

Iron ion flow:

$$g_M^{Fe^{2+}} = k_{Fe^{2+}} I t_{Fe^{2+}} \tag{10}$$

$$t_{Fe^{2+}} = \frac{2 C_{Fe^{2+}} \lambda_{Fe^{2+}}}{2 C_{Fe^{2+}} \lambda_{Fe^{2+}} + C_{Na^+} \lambda_{Na^+} + C_{Cl^-} \lambda_{Cl^-} + C_{H^+} \lambda_{H^+}} \tag{11}$$

Chlorine ion flow:

$$g_M^{Cl^-} = k_{Cl^-} I t_{Cl^-} \tag{12}$$

$$t_{Cl^-} = \frac{C_{Cl^-} \lambda_{Cl^-}}{2 C_{Fe^{2+}} \lambda_{Fe^{2+}} + C_{Na^+} \lambda_{Na^+} + C_{Cl^-} \lambda_{Cl^-} + C_{H^+} \lambda_{H^+}} \tag{13}$$

Sodium ion flow:

$$g_M^{Na^+} = k_{Na^+} I t_{Na^+} \tag{14}$$

$$t_{Na^+} = \frac{C_{Na^+}\lambda_{Na^+}}{2C_{Fe^{2+}}\lambda_{Fe^{2+}} + C_{Na^+}\lambda_{Na^+} + C_{Cl^-}\lambda_{Cl^-} + C_{H^+}\lambda_{H^+}} \tag{15}$$

Hydronium ion flow:

$$g_M^{H^+} = k_{H^+} I t_{H^+} \tag{16}$$

$$t_{H^+} = \frac{C_{H^+}\lambda_{H^+}}{2C_{Fe^{2+}}\lambda_{Fe^{2+}} + C_{Na^+}\lambda_{Na^+} + C_{Cl^-}\lambda_{Cl^-} + C_{H^+}\lambda_{H^+}} \tag{17}$$

3.3. Material balances

Material balances are compiled on the basis of certain flows of electrochemical reactions, diffusion and migration flows in order to determine the concentrations of substances at the outlet of the reactor.

3.3.1. Anode chamber material balance:

$$\begin{gathered} j_a C_{NaCl}^{in} + j_a C_{HCl}^{in} - g_e^{Fe} + g_e^{Fe^{2+}} - g_M^{Fe^{2+}} - g_d^{Fe^{2+}} - g_M^{Na^+} - g_d^{Na^+} + g \\ - g_d^{Cl^-} - g_M^{H^+} + g_d^{H^+} - j_a C_{NaCl}^{out} - j_a C_{HCl}^{out} - j_a C_{FeCl_2}^{out} - 2F = 0 \end{gathered} \tag{18}$$

Ferrum ion concentration in the outflow:

$$g_e^{Fe^{2+}} - g_M^{Fe^{2+}} - g_d^{Fe^{2+}} - j_a C_{Fe^{2+}}^{out} = 0 \tag{19}$$

$$C_{Fe^{2+}}^{out} = \frac{g_e^{Fe^{2+}} - g_M^{Fe^{2+}} - g_d^{Fe^{2+}}}{j_a} \tag{20}$$

Sodium ion concentration in the outflow:

$$j_a C_{Na^+}^{in} - g_M^{Na^+} - g_d^{Na^+} - j_a C_{Na^+}^{out} = \tag{21}$$

$$C^{out}_{Na^+} = \frac{j_a C^{in}_{Na^+} - g^{Na^+}_M - g^{Na^+}_d}{j_a} \tag{22}$$

Chlorine ion concentration in the outflow:

$$j_a C^{in}_{Cl^-} + g^{Cl^-}_M - g^{Cl^-}_d - j_a C^{out}_{Cl^-} = 0 \tag{23}$$

$$C^{out}_{Cl^-} = \frac{j_a C^{in}_{Cl^-} + g^{Cl^-}_M - g^{Cl^-}_d}{j_a} \tag{24}$$

Hydronium ion concentration in the outflow:

$$j_a C^{in}_{H^+} + g^{H^+}_d - g^{H^+}_M - j_a C^{out}_{H^+} = \tag{25}$$

$$C^{out}_{H^+} = \frac{j_a C^{in}_{H^+} + g^{H^+}_d - g^{H^+}_M}{j_a} \tag{26}$$

3.3.2. Cathode chamber material balance

$$\begin{gathered} j_K C^{in}_{HCl} - 2 g^{H^+}_e + g^{H_2}_e + g^{Fe^{2+}}_M + g^{Fe^{2+}}_d + g^{Na^+}_M + g^{Na^+}_d - g^{Cl^-}_M + \\ + g^{Cl^-}_d + g^{H^+}_M - g^{H^+}_d - j_K C^{out}_{NaCl} - j_K C^{out}_{HCl} - j_K C^{out}_{FeCl_2} + 2F = 0 \end{gathered} \tag{27}$$

Ferrum ion concentration in the outflow:

$$g^{Fe^{2+}}_M + g^{Fe^{2+}}_d - j_K C^{out}_{Fe^{2+}} = 0 \tag{28}$$

$$C^{out}_{Fe^{2+}} = \frac{g^{Fe^{2+}}_M + g^{Fe^{2+}}_d}{j_K} \tag{29}$$

Sodium ion concentration in the outflow:

$$g^{Na^+}_M + g^{Na^+}_d - j_K C^{out}_{Na_+} = 0 \tag{30}$$

$$C^{out}_{Na_+} = \frac{g_M^{Na^+} + g_d^{Na^+}}{j_K} \tag{31}$$

Chlorine ion concentration in the outflow:

$$j_K C^{in}_{Cl^-} - g_M^{Cl^-} + g_d^{Cl^-} - j_K C^{out}_{Cl^-} = 0 \tag{32}$$

$$C^{out}_{Cl^-} = \frac{j_K C^{in}_{Cl^-} - g_M^{Cl^-} + g_d^{Cl^-}}{j_K} \tag{33}$$

Hydronium ion concentration in the outflow:

$$j_K C^{in}_{H^+} - g_e^{H^+} + g_M^{H^+} - g_d^{H^+} + j_K C^{out}_{H^+} = 0 \tag{34}$$

$$C^{out}_{H^+} = \frac{j_K C^{in}_{H^+} - g_e^{H^+} + g_M^{H^+} - g_d^{H^+}}{j_K} \tag{35}$$

The electrolyte volume exchange ratio of the reactor shows how many times a complete change of electrolyte occurs per unit of time:

$$K_0 = \frac{j}{V_P} \tag{36}$$

where V_P is the internal volume of the reactor (anode or cathode chamber of the reactor).

Change in solution concentration in reserve tanks after *n* passes:

$$C_i^P = \frac{njC_i}{V} \tag{37}$$

4. Results and discussion

4.1. Determination of limiting current densities that ensure the maintenance of the pH_3 value in the anode chamber.

Iron ions accumulating in the solution are oxidized by atmospheric oxygen in the saturator to Fe^{3+} when leaving the reactor, undergo hydrolysis, and are separated from the solution on filter presses.

For stable operation of the reactor, it is necessary that the medium pH at the reactor outlet should not exceed 3. At high pH values, hydrolysis of divalent iron is possible directly in the reactor, with the formation of a solid phase in the electrolyzer channels.

Hydroxonium ions, which determine the pH value, are transferred to the anode chamber with the input electrolyte, by diffusion flows g_d from the cathode chamber (9), and from the anode chamber to the cathode chamber - by migration flows g_m (16).

Fig. 2 shows the ratio of migration and diffusion flows of hydronium ions through various diaphragm materials at constant speed and concentration of the feed solution.

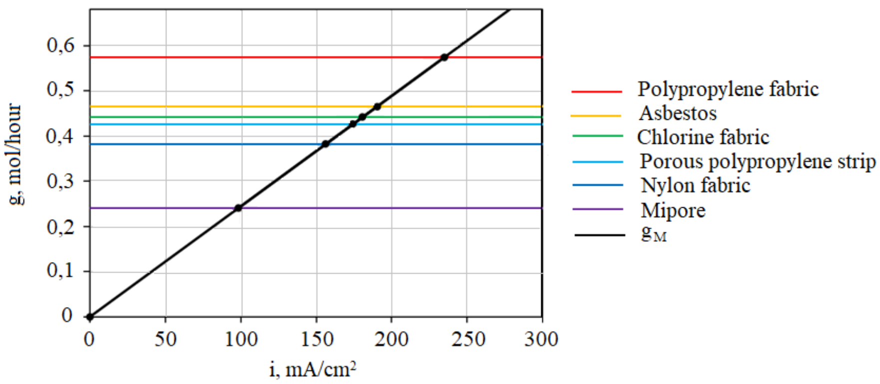


Figure 2 – The ratio of migration and diffusion flows of hydronium ions through various diaphragm materials. The NaCl concentration is 5 M in the anode chamber

As can be seen from the figure, the maximum current density, at which the pH value of 3 is maintained in the output flow, depends on the type of diaphragms and ranges from 99 mA/cm^2 for Mipore, 190 mA/cm^2 for asbestos, and 235 mA/cm^2 for polypropylene fabric.

The magnitude of the migration flow of H^+ ions from the anode chamber to the cathode one depends on the amount (concentration) of Na^+, Fe^{2+}, H^+ cations on one side and Cl^- anions on the other side. It is assumed that different sodium chloride contents are supplied to the anode chamber in the feed solution at a constant HCl concentration of 0.001 M. Calculations have shown that at a flow rate of up to 10 l/hour for the anode and cathode chambers, the change in iron concentration can be neglected.

The higher is the concentration of sodium chloride in the feed anolyte, the lower is the migration flow of hydronium ions from the anode chamber to the cathode one, and the higher can be the current density in the electrolyte (at the anode) (Fig. 3).

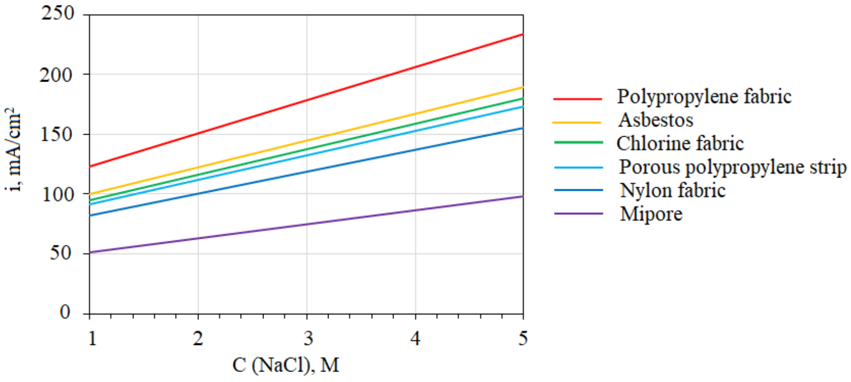


Figure 3 – Dependence of the current density in the anolyte while maintaining pH 3 on the current density for different diaphragm materials

Figure 4 shows the calculated relationships between the concentrations of the feed solution circulating through the anode chamber and the current densities at which pH 3 is maintained in the effluent anolyte for different diaphragm materials.

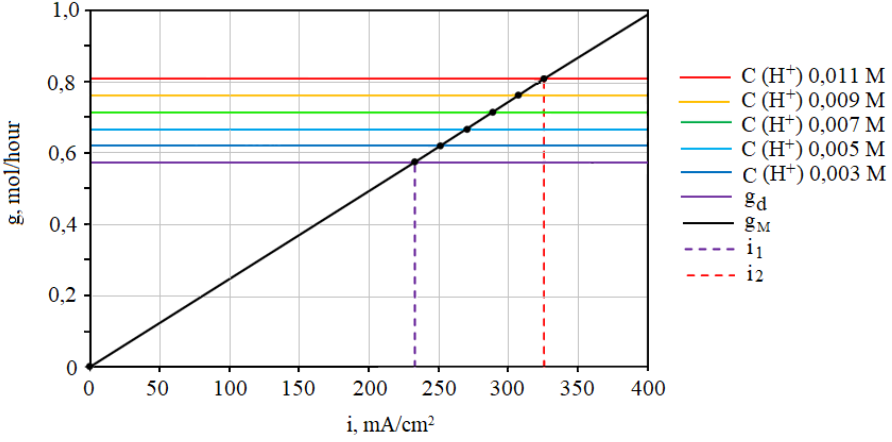


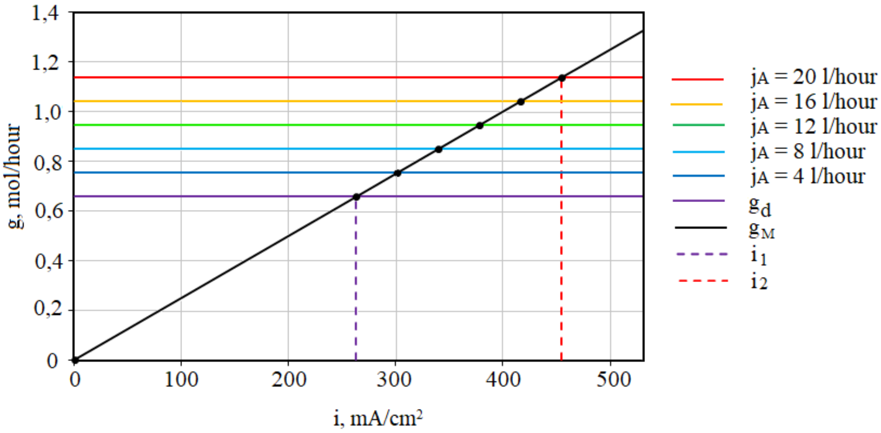
Figure 4 – Dependence of the flows on current density at different concentrations of HCl in the anolyte and NaCl concentration of 5 M in the catholyte using polypropylene fabric at an electrolyte flow rate of 24 l/hour for each of the chambers separated by the diaphragm

It also follows from the figure that the maximum current density achievable when using the HCl feed solution with a concentration of 0.001 M and NaCl feed solution with a concentration of 5 M is 235 mA/cm^2 for this model. If it is necessary to intensify the process of iron dissolution and hydrogen evolution, an additional supply of hydronium ions with the feed solution is required by the equilibrium equation (47):

It is evident from the figure that an additional introduction of 0.0011 M hydrochloric acid into the feed anolyte allows increasing the current density from 230 to 330 mA/cm^2.

4.2. The influence of flow rate on the concentration of components in the anode chamber.

The change in the ion concentration in the anode chamber was calculated using formulas (18)–(26) and is shown in Fig. 5. As it can be seen, increasing the flow rate through the anode chamber from 4 l/hour to 20 l/hour allows increasing the current density to 450 mA/cm^2 while maintaining the given pH value in the output flow.



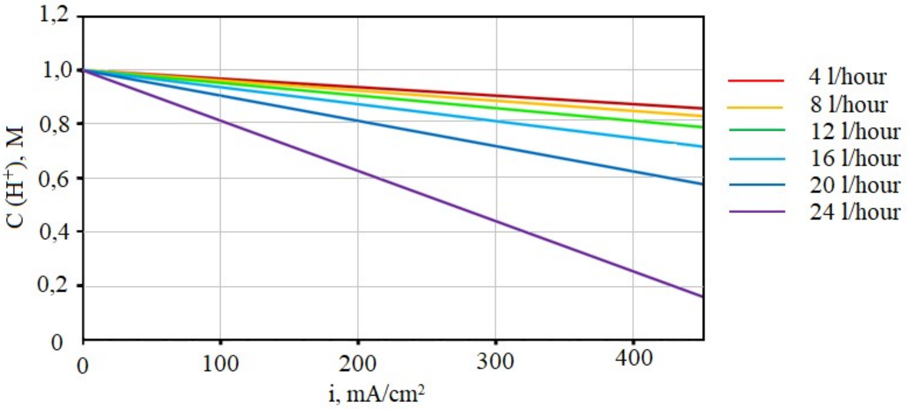
Figures 5 – The ratio of migration and diffusion flows of hydronium ions through polypropylene fabric for different electrolyte flow rates. The concentration of NaCl is 5 M, and the concentration of HCl is 0.025 M for the anode chamber

4.3. Analysis of changes in the composition and concentration of acidic catholyte when separating electrode chambers with an anion-exchange membrane.

When separating electrode chambers with porous diaphragms, intensive diffusion and migration transfer of sodium, iron, and chlorine ions from the anode chamber to the cathode chamber occurs, see Fig. 1. Accumulation of sodium and iron ions in the catholyte leads to a decrease in the electrical conductivity of the solution and an increase in the overvoltage of hydrogen evolution. At the same time, the wide range of ion sizes and charges involved in matter and current transfer makes this task quite complex, which will inevitably lead to a cost increase and, as a result, an increase in the cost of hydrogen produced.

It is much easier to organize work using an anion-exchange membrane for separating electrode chambers, through which the transfer of matter and electricity is carried out only by chlorine anions moving from the cathode chamber to the anode one (see the diagram in Fig. 1). Due to the discharge of hydronium ions and the transfer of chlorine ions from the cathode chamber to the anode one, the acid concentration decreases by two moles during the passage of two Faradays of electricity. Fig. 6 shows the change in the hydronium ion concentration at the cathode compartment outlet depending on the catholyte flow rate.

Our work has shown that reducing the hydronium ions concentration in the catholyte to 0.2 M significantly increases the hydrogen evolution overvoltage that leads to an increase in energy consumption, which is unacceptable. Therefore, the flow rate cannot be reduced below 24 l/hour. Moreover, it is advisable to use a pump with a higher capacity.



Figures 6 – Dependence of the concentration at the outlet of the cathode chamber on the current density for different flow rates of the catholyte

5. Conclusions

1. A theoretical analysis of material transfer in a reactor for hydrogen production with a soluble iron anode was carried out.
2. The possibility of using inexpensive diaphragm materials made of asbestos or polypropylene fabric is shown.
3. The maximum acid concentrations in the anolyte was calculated, ensuring the absence of hydrolysis of divalent iron in the anode chamber of the electrolyzer, but allowing the separation of iron from the electrolyte after its oxidation with atmospheric oxygen with subsequent hydrolysis.
4. The influence of the electrolyte flow rate in the anode and cathode chambers on the change in ion concentration is investigated.
5. Separating the anode and cathode chambers with an anion-exchange membrane simplifies operating the reactor. The calculations are provided for adjusting the composition of the electrolytes.

Conflict of interest

Authors state no conflict of interest.

REFERENCES

1. Kozin, L.F. and Volkov, S.V. (2002), *Vodorodnaya ehnergetika i ehkologiya* [Hydrogen energy and ecology], Naukova Dumka, Kyiv, Ukraine.
2. Nefedov, V.G., Matveev, V.V., Sykhyy, K.M., Bulat, A.F., Bluss B.O. and Mukhachev, A.P., M.S. Poliakov Institute of Geotechnical Mechanics of the National Academy of Sciences of Ukraine (2023), Sposib kompleksnogo oderzhannya vodnyu ta generatsii elektroenergii [Method for Integrated Hydrogen Production and Electricity Generation], State register of Patens of Ukraine, Kyiv, UA, Pat. No. 152585.
3. Nefedov, V.G., Matveev, V.V., Sykhyy, K.M., Bulat, A.F., Bluss B.O. and Mukhachev, A.P., M.S. Poliakov Institute of Geotechnical Mechanics of the National Academy of Sciences of Ukraine (2023), Sposib otrimannya vodnyu u vIdkritIy za masoperenosom elektrohImIchnIy sistemI zI znizhenimi energovitratami [Method for hydrogen producing in an open mass transfer electrochemical system with reduced energy consumption], State register of Patens of Ukraine, Kyiv, UA, Pat. No.154218.
4. Nefedov V., Matveev V., Sukhyy K., Polishchuk Yu., Bulat A., Bluss B. and Mukhachev, A. (2023), “Electrochemical production of hydrogen in reactors with reduced energy costs”, *IOP Conf. Ser.: Earth Environ. Sci.,* vol. 1156, 012034. https://doi.org/10.1088/1755-1315/1156/1/012034
5. Karchiyappan, T. (2019), “A review on hydrogen energyproduction from electrochemical system: benefits and challenges”, *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, vol. 41, no. 7, pp. 902–909. https://doi.org/10.1080/15567036.2018.1520368

6. Suryanto, B.H.R., Wang, Y., Hocking, R.K., Adamson, W. and Zhao, C. (2019), “Overall electrochemical splitting of water at the heterogeneous interface of nickel and iron oxide”, *Nature Communications*, vol. 10, no. 44, 5599. https://doi.org/10.1038/s41467-019-13415-8

7. Ren, F., Xu, J. and Feng, L. (2024), “An effective bimetallic oxide catalyst of RuO$_2$-Co$_3$O$_4$ for alkaline overall water splitting” *NanoResearch,* vol.17, pp. 3785–3793. https://doi.org/10.1007/s12274-023-6316-4

8. Subbaraman, R., Tripkovic, D., Chang, K.C. Strmcnik, D., Paulikas, A. P., Hirunsit, P., Chan, M., Greeley, J., Stamenkovic, V. and Markovic, N. M. (2012), “Trends in activity for the water electrolyser reactions on 3*d* M(Ni,Co,Fe,Mn) hydr(oxy)oxidecatalysts”, *Nature Materials,* vol. 11, pp. 550–557. https://doi.org/10.1038/nmat3313

9. Sakhnenko, M.D., Ved, M.V., Shtefan, V.V. and Volobyev, M.M. (2011), *Teoretichni osnovi himii ridkisnih I rozsiyanih elementiv* [Theoretical foundations of the chemistry of rare and scattered elements], HTU HPI, Kharkiv, Ukraine.

10. Yermolenko, I.Y., Ved, M.V. and Sakhnenko, M.D. (2014), Elektrohimichniy retsikling psevdosplaviv volframu [Electrochemical recycling of tungsten pseudoalloys], HTU HPI, Kharkiv, Ukraine.

11. Ved, M.V. and Sakhnenko, M.D. (2010), Katalitichni ta zahisni pokrittya splavami i skladnimi oksidami: elektrohimichniy sIntez, prognozuvannya, vlastivostey [Catalytic and protective coatings with alloys and complex oxides: electrochemical synthesis, prediction, properties], HTU HPI, Kharkiv, Ukraine.

12. Nefedov, V., Matveev, V., Polishchuk, Yu., Sukhyi, M. and Tulskyi, H. (2024), “Transfer processes in porous diaphragms and ion-exchange membranes for electrochemical reactor with reduced energy consumption”, *IOP Conference Series: Earth and Environmental Science,* vol.1348, 012058. https://doi.org/10.1080/1755-1315/1348/1/0112058

About the authors

Nefedov Volodymyr, Doctor of Technical Sciences (D.Sc.), Professor, Head of the Research Laboratory of Battery Systems and Energy in Ukrainian State University of Science and Technologies, Leading Researcher, M.S. Poliakov Institute of Geotechnical Mechanics of the National Academy of Sciences of Ukraine (IGTM of the NAS of Ukraine), Dnipro, Ukraine, vnefedov@i.ua ***(Corresponding author)***, ORCID ***0009-0001-5335-7738***

Bichai Artem, Bachelor’s Degree, Ukrainian State University of Science and Technologies, Dnipro, Ukraine, artembichai@gmail.com, ORCID ***0009-0000-5883-1120***

Polishchuk Yuliya, Candidate of Technical Sciences (Ph.D), Assistant professor, Director of the Scientific Center for Innovative Materials and Technologies Ukrainian State University of Science and Technologies, Dnipro, Ukraine, yu.v.polishchuk@gmail.com, ORCID ***0000-0003-1552-4117***

АНАЛІЗ РОБОТИ ЕЛЕКТРОЛІЗЕРА ДЛЯ ОТРИМАННЯ ВОДНЮ З РОЗЧИННИМ ЗАЛІЗНИМ АНОДОМ ЗА ДОПОМОГОЮ МАТЕМАТИЧНОЇ МОДЕЛІ

Нефедов В., Бічай А., Поліщук Ю.

Анотація. Отримання хімічно чистого водню електрохімічним методом має обмеження через високу вартість електролізу водних розчинів. Для зниження напруги на електролізері запропоновано замінити анодний процес виділення кисню (стандартний потенціал у кислому середовищі плюс 1,23 В) розчиненням анода з електронегативних металів. Такими металами можуть бути алюміній та залізо – найпоширеніші конструкційні матеріали. Відходи цих металів у вигляді брухту або стружки досить дешеві та можуть бути використані у вигляді засипного електрода. Стандартний потенціал заліза становить мінус 0,44 В, а алюмінію в кислому середовищі мінус 2,30 В. При підключенні до анода електрода (катода) з низькою перенапругою виділення водню, з'являється можливість отримувати водень із одночасною генерацією електроенергії. При використанні залізного анода напруга на комірці знижується до 0,5–0,6 при густині струму близько 0,1А/см^2. Проведені розрахунки та попередні експерименти показали, що для зменшення поляризаційних опорів виділення водню та розчинення заліза склад аноліту та католіту має бути різним. Для зниження поляризаційних та омічних опорів при електролізі були обрані 1М розчин HCl як католіт і 5М розчин NaCl як аноліт. Тому анодна та катодна камери електролізера мають бути розділені. Для розділення електродних камер можуть використовуватись як пористі діафрагми, так і аніонообмінні мембрани. Для діафрагм були оцінені товщина, пористість, протікання та коефіцієнти звивистості доби. Властивості діафрагм визначають як енергетичні витрати на електроліз (процеси переносу зарядів), а й процеси переносу речовини. Для обґрунтованого вибору матеріалів діафрагм та аналізу процесів переносу речовини в електролізері запропоновано математичну модель, за допомогою якої оцінено значення дифузійних та міграційних потоків у реакторі. Крім того, запропоновано оптимізований склад аноліту та католіту, який забезпечує протікання електродних процесів з мінімальними енергетичними витратами; підтримку заданого складу розчинів та можливість подальшого очищення від продуктів електролізу.

Ключові слова: водень, електроліз, залізний розчинний анод, міграція, дифузія, математична модель