Electrode-diaphragm assembly for alkaline water electrolysis

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Abstract. In connection with the development of hydrogen energy, special attention is currently being paid to the creation of highly efficient water electrolyzers, including electrolyzers with alkaline electrolyte. The main disadvantage of hydrogen production by water electrolysis is its high energy consumption. The present article shows that energy consumption can be reduced by changing of the electrodes and diaphragm layout. The phase inversion method used for the manufacture of polymer-based porous diaphragms for alkaline water electrolyzers made it possible to create an electrode-diaphragm assembly, where elements of electrode-diaphragm assembly represent a single element. The comparative research of electrolysis cells with different electrode-diaphragm assemblies and cells of the traditional "zero gap" was carried out.

1. Introduction
Alkaline water electrolysis (AWE) is one of the main methods of hydrogen generation for power engineering, metallurgy, glass and food industries. In recent years, new areas of alkaline water electrolysis application have appeared: small scale energy remote plants based on renewable energy sources; transport; astronautics [1, 2].

The energy consumption of alkaline water electrolyzers can be reduced by creating new electrocatalysts, diaphragm materials and changing the method of assembly of the diaphragm-electrode [3]. Traditionally, alkaline water electrolysis uses cells with a gap between the electrodes and the diaphragm and with a “zero gap”, in which the electrodes are pressed tightly against the diaphragm material. The advent of new polymer-based diaphragm materials has allowed the creation of an electrode-diaphragm assembly in which electrodes with catalytic layers and diaphragm material represent a single element. The technology of membrane-electrode blocks (MEB) is well known in electrolyzers and fuel cells with polymer electrolyte membrane (PEM). The development of electrode-diaphragm assemblies allows to reduce contact resistance at the diaphragm-electrode interface, and reduce the energy consumption of the electrolysis module.

2. Experimental
2.1. Electrodes of electrode-diaphragm assemblies
At the present work, electrodes with a porous coating [4, 5], modified by catalysts of cathodic and anodic processes of AWE were used. Expanded nickel grids with 1x2 mm rhombus meshes was used as a base of cathode and anode. Two types of porous coating were applied to the surface of the mesh.
Then, nickel or nickel-cobalt powder was suspended into the electrolyte in an amount of 10 g/l, and electrolytic coating was performed, current density 5 A/dm$^2$, temperature 60 °C, nickel anodes located on both sides of the expanded grid. During electrolysis co-deposition of a metal powder on a expanded grid surface and its fixation by galvanically deposited nickel or nickel-cobalt occurs.

The first type of porous coating - a commercially available nickel powder with a particle size of 2-4 microns, was applied from a suspension in a standard bath for nickel electroplating: nickel sulfate (NiSO$_4$·6H$_2$O) - 350 g/l; nickel chloride (NiCl$_2$·6H$_2$O) - 60 g/l; boric acid (H$_3$BO$_3$) 20-30 g/l; modifying additives, figure 1a.

The second type of porous coating - nickel-cobalt powder was applied from a suspension in an electroplating bath of the composition: nickel sulfate (NiSO$_4$·6H$_2$O) - 175 g/l; cobalt sulfate (CoSO$_4$·6H$_2$O); nickel chloride (NiCl$_2$·6H$_2$O) - 30 g/l; cobalt chloride (CoCl$_2$·6H$_2$O) - 30 g/l; boric acid (H$_3$BO$_3$) 20-30 g/l; modifying additives. Nickel-cobalt powder was prepared by thermal decomposition of mixed (1:1 molar ratio) nickel and cobalt formate in an inert argon environment. The synthesized powder is pyrophoric, which indirectly indicates the presence of nanosized particles and a large specific surface, Figure 1b.

Both types of porous coatings were modified with catalysts of cathodic and anodic processes. One of the most active and stable catalysts for the hydrogen evolution reaction (NiP$_x$) was carried out by reduction of sodium hyposphosphate from a solution of nickel chloride [6]. An aqueous solution of nickel chloride with acetate buffer was prepared; the composition of nickel sulfate NiSO$_4$·7H$_2$O was 30 g/l; sodium acetate CH$_3$COONa - 10 g/l; acetic acid CH$_3$COOH - 10 g/l. An electrode with a porous nickel coating was dipped into the solution and slowly heated. The formation of a finely dispersed catalytically active structure on the particles of the porous coating (Fig. 2a and 2b) occurs at a temperature of 30–40 °C.

Modification of the porous nickel or nickel-cobalt coating with a catalyst for the oxygen evolution reaction by nickel-cobalt spinel was carried out by direct thermal decomposition. A solution of nickel nitrate Ni(NO$_3$)$_2$ 2 - 2 g/l; cobalt nitrate Co(NO$_3$)$_2$ 2-4 g/l; ammonium chloride NH$_4$Cl - 0.3 g/l in a mixture of butanol - 24 g/l and isopropanol - 24 g/l was prepared. An electrode with nickel coating was immersed in the resulting solution for 20 minutes. Nickel-cobalt spinel was synthesized by thermal decomposition in a vacuum, raising the temperature from room to 250 °C at a rate of 4 °C per 20 minutes and subsequent processing at 400 °C in air atmosphere. The micrograph of the obtained anodes is shown in Figure 3.

2.2. The diaphragms forming solution for electrode-diaphragm assemblies

The diaphragm is a porous matrix based on a polysulfone filled with hydrophilic agent (titanium dioxide, TiO$_2$) and reinforced with a polyamide network [7-9]. To prepare the forming diaphragm solution, a suspension of titanium dioxide dried in an oven was prepared in dimethylacetamide using an ultrasonic disperser. The resulting suspension was filtered through a sieve with a polymer mesh size 0.5 μm. Polysulfone was added to the obtained filtrate, and placed in an oven (t = 60 °C). Three types of diaphragms were investigated as the basis of the electrode-diaphragm assembly: 1 - the diaphragm contains 33 mass.% polysulfone and 67 wt.% titanium dioxide, the forming diaphragm solution contained pore-forming agent polyvinylpyrrolidone, 15 wt.% by weight of the polymer; 2 - the diaphragm contains 33 mass.% polysulfone and 67 wt.% titanium dioxide, no pore-forming agent was added; 3 - the diaphragm contains 40 mass.% polysulfone and 60 wt.% titanium dioxide, no pore-forming agent was added.

2.3. The formation of the electrode-diaphragm assembly

As it is known from the technology of membrane-electrode blocks for fuel cells and electrolyzers with polymer electrolyte membranes, the catalytic layers on the membrane surface are formed by sputtering a suspension of the catalyst in a membrane solvent. In article [3] an attempt to form an electrode-diaphragm assembly for an alkaline water electrolyser by spraying a suspension of Raney nickel in dimethylacetamide (polysulfone solvent) is described. The results presented by the authors showed that a cell with such an electrode-diaphragm assembly is characterized by a voltage 30% higher than with nickel fibers tested in the same work.
In the present work, a similar attempt was made, but with a suspension of nickel-cobalt powder in dimethylacetamide, and the conductivity of the catalytic layers was also insufficient.

The formation of the electrode-diaphragm assembly was carried out as follows - a diaphragm forming solution was applied to a reinforcing mesh 500 μm thick (section 2.2), the electrodes were pressed on both sides and the resulting element was immersed in a coagulation bath with a temperature of 4 °C containing 50 masses. % dimethylacetamide and 50 wt.% water [10].

3. Results and discussion

3.1. Electrodes

Figure 1 shows microphotographs of a porous coating deposited from a suspension of nickel powder in galvanic nickel plating bath (Figure 1a) and a suspension of nickel-cobalt powder obtained by thermal decomposition of mixed nickel-cobalt formate (Figure 1b). The difference in the morphology of the coatings is clearly visible, nickel particles have a cubic face-centered lattice, and nickel-cobalt powder particles are characterized by a much smaller cross section and have a needle structure.

![Figure 1](image1.png)

**Figure 1.** Electrodes with porous coating, formed from a galvanic bath: a - precipitated commercial nickel powder; b - precipitated nickel-cobalt powder obtained by thermal decomposition of mixed nickel-cobalt formate.

Figure 2. shows microphotographs of a porous coating modified by chemical deposition of a NiPₓ catalyst of hydrogen evolution reaction. It have to be noticed, that the deposited NiPₓ alloy repeats the initial structure of the porous coating particles, face-centered cubic (Figure 2a) and needle-like (Figure 2b).

![Figure 2](image2.png)

**Figure 2.** A porous coating modified by a NiPₓ cathodic process catalyst: a — surface of a nickel powder; b - the surface of the particles of nickel-cobalt coating.
Figure 3 shows microphotographs of a porous coating modified by chemical deposition of the NiCo$_2$O$_4$, catalyst of oxygen evolution reaction. The results of microscopic investigations correlates well with the results of poresimetry, carried out by the contact-reference porosimetry method.

![Figure 3](image1.png)

**Figure 3.** A porous coating modified by an anodic process catalyst, NiCo$_2$O$_4$: a - surface of nickel powder; b - the surface of nickel-cobalt particles.

![Figure 4](image2.png)

**Figure 4.** Differential pore radius distribution obtained by contact-reference porosimetry: 1 - porous coating obtained by deposition of nickel-cobalt powder, modified by NiP$_x$; 2 - porous coating obtained by the deposition of nickel powder, modified by NiP$_x$; 3 - porous coating obtained by precipitation of nickel-cobalt powder, modified by precipitation of NiCo$_2$O$_4$.

The porous coating obtained by the deposition of nickel-cobalt powder and modified by NiP$_x$ (1) is characterized by the most developed specific surface, both macro- and nanosized pores are available for the reaction. A wide range of pore distribution to radii has a positive effect on the transport of hydrogen gas bubbles, thereby reducing spurious ohmic losses, by reducing the shielding of the electrode surface by the generated gases. The porous coating obtained by the deposition of nickel powder (2) is characterized by a lower specific surface, and the main pore radii are in the range of 150-500 nm. The largest pore radii and the smallest specific surface are characteristic of a porous coating modified with an anode process catalyst - nickel-cobalt spinel (3), which can be explained by a fundamentally different way of modifying the surface of a porous coating. It have to noticed that investigations of electrode processes kinetics shows that the specific surface area plays a smaller role in the reactions of oxygen evolution reaction, in comparison with hydrogen evolution reaction.

The following are the polarization curves of the electrodes with catalysts of the cathode (Figure 5) and anode (Figure 6) processes.
Figure 5. Polarization curves of electrodes with catalysts of cathodic processes: 1 - smooth nickel grid; 2 - nickel grid with nickel powder; 3 - nickel grid with nickel-cobalt powder; 4 - nickel mesh with nickel powder modified by NiP<sub>x</sub>; 5 - nickel grid with nickel-cobalt powder modified by NiP<sub>x</sub>.

Figure 6. Polarization curves of electrodes with catalysts of anode processes: 1 – smooth nickel grid; 2 - nickel grid with nickel powder; 3 - nickel mesh with nickel-cobalt powder; 4 - nickel grid with nickel powder modified by NiCo<sub>2</sub>O<sub>4</sub>; 5 - nickel mesh with nickel-cobalt powder modified by NiCo<sub>2</sub>O<sub>4</sub>.

A porous nickel coating formed with nickel and nickel-cobalt powder allows reducing the overvoltage of hydrogen evolution reaction up to 190-210 mV and the overvoltage of oxygen evolution reaction up to 260-300 mV at a current density of 300 mA/cm<sup>2</sup> compared to a smooth nickel grid. Modification of the porous coating with a catalyst (NiP<sub>x</sub>) can further reduce the overvoltage of hydrogen evolution up to 100-130 mV, and with an anode process catalyst (NiCo<sub>2</sub>O<sub>4</sub>) up to 120-170 mV. It is characteristic that during the deposition of a porous coating and its modification, the Tafel
slope of the polarization curves changes, which may indicate a change in the reaction mechanism. Same time, the Tafel slope of the polarization curves of porous electrodes formed on the basis of nickel and nickel-cobalt powder practically do not differ.

3.2. Diaphragm

Figure 7 shows typical microphotographs of the diaphragm.

![Microphotographs of the diaphragm](image)

**Figure 7.** Microphotographs of the diaphragm: polysulfone - 33 mass. %, titanium dioxide - 67 mass. %, blowing agent polyvinylpyrrolidone, 15 wt.% by weight of the polymer.

Figure 8 shows the integral curve of the diaphragm pores to the radii distribution.

![Integral curve of the distribution of pores](image)

**Figure 8.** Integral curve of the distribution of pores of the diaphragm material along the radii:
1 - the diaphragm contains 33 mass.% polysulfone and 67 wt.% titanium dioxide, the forming diaphragm solution contained pore-forming agent polyvinylpyrrolidone, 15 wt.% by weight of the polymer; 2 - the diaphragm contains 33 mass.% polysulfone and 67 wt.% titanium dioxide, no pore-forming agent was added; 3 - the diaphragm contains 40 mass.% polysulfone and 60 wt.% titanium dioxide, no pore-forming agent was added.

Table 1 shows the total porosity and specific ionic conductivity of the diaphragms used to form the electrode-diaphragm assemblies. As can be seen from the table, the diaphragm synthesized with the addition of a pore-forming agent has the highest porosity and specific ionic conductivity. The decrease in the content of the pore-forming agent reduces the total porosity, the average radius of the pores and, accordingly, the specific ionic conductivity.
Table 1. Specific electrical conductivity and total porosity of the diaphragms.

| Diaphragm                                                                 | Specific ionic conductivity $\sigma$, Ohm$^{-1}$·cm$^{-1}$ | Total porosity cm$^3$/cm$^3$ |
|--------------------------------------------------------------------------|-------------------------------------------------------------|-------------------------------|
| 1 33 mass.% polysulfone and 67 wt.% titanium dioxide, the forming diaphragm solution contained pore-forming agent polyvinylpyrrolidone, 15 wt.% by weight of the polymer | 2.78                                                        | 0.460                         |
| 2 33 mass.% polysulfone and 67 wt.% titanium dioxide, no pore-forming agent was added | 2.57                                                        | 0.410                         |
| 3 40 mass.% polysulfone and 60 wt.% titanium dioxide, no pore-forming agent was added | 2.49                                                        | 0.360                         |

3.3. Electrode-diaphragm electrochemical performances

Figure 9 shows the i-V curves of an alkaline water electrolyser cell with an electrode-diaphragm assembly and “zero gap” at 90 °C, atmospheric pressure and electrolyte 39 mass.% KOH solution. The composition and layout method of Electrode-diaphragm assembly are shown in table 2.

![Figure 9. Typical i-V curves found in electrode-diaphragm assembly.](image-url)
Table 2. Composition and layout method of an alkaline electrolyser cells.

| Curve number in figure 9 | Layout method | Diaphragm | Electrodes |
|--------------------------|---------------|------------|------------|
| 1                        | Electrode-diaphragm assembly | 33 mass.% polysulfone and 67 wt.% titanium dioxide, the forming diaphragm solution contained pore-forming agent polyvinylpyrrolidone, 15 wt.% by weight of the polymer | Porous coating from nickel-cobalt powder suspension, modified by (NiPₓ) and (NiCo₂O₄). |
| 2                        | Electrode-diaphragm assembly | 33 mass.% polysulfone and 67 wt.% titanium dioxide, no pore-forming agent was added | Porous coating from nickel-cobalt powder suspension, modified by (NiPₓ) and (NiCo₂O₄). |
| 3                        | Zero gap      | 33 mass.% polysulfone and 67 wt.% titanium dioxide, no pore-forming agent was added | Porous coating from nickel-cobalt powder suspension, modified by (NiPₓ) and (NiCo₂O₄). |
| 4                        | Electrode-diaphragm assembly | 40 mass.% polysulfone and 60 wt.% titanium dioxide, no pore-forming agent was added | Porous coating from nickel-cobalt powder suspension, modified by (NiPₓ) and (NiCo₂O₄). |
| 5                        | Zero gap      | 40 mass.% polysulfone and 60 wt.% titanium dioxide, no pore-forming agent was added | Porous coating from nickel-cobalt powder suspension, modified by (NiPₓ) and (NiCo₂O₄). |
| 6                        | Electrode-diaphragm assembly | 40 mass.% polysulfone and 60 wt.% titanium dioxide, no pore-forming agent was added | Porous coating from nickel powder, modified by (NiPₓ) and (NiCo₂O₄). |

As can be seen from Figure 9, the cell with the electrode-diaphragm assembly (1) is characterized by the lowest voltage. However, investigations have shown that the purity of the generated gases sharply decreases from 99.86% to 97-98% H₂ at current densities above 400 mA/cm². Also, a decrease in the purity of the generated gases was noted for the electrode-diaphragm block (2), at current densities above 600 mA/cm². At the same time, a cell with the same diaphragm, but “zero gap” layout (3) shows a decrease in gas purity at current densities above 900 mA/cm². The decrease of the generated gases purity in the electrode-diaphragm assembly can be explained by the fact that the polymer matrix blocks the removal of generated gases from the surface of the electrode in contact with it.

Further investigations were carried out with a diaphragm with a minimum amount of hydrophilic filler and without a pore-forming agent. An electrolysis cell with an electrode-diaphragm assembly (4) shows a voltage lower than a cell with the same elements, but with a “zero gap” (5). The highest voltage is shown by the electrode-diaphragm block (6), which included electrodes with a porous coating formed from a suspension of commercially available nickel powder.

4. Conclusion

As a result of the research, an electrode-diaphragm assemblies for alkaline water electrolyser was created. When using the same diaphragm materials and electrodes, the layout of the electrolysis cell with the electrode-diaphragm assembly allows to reduce the energy consumption for hydrogen production, compared with the traditional "zero gap". This can be explained by a decrease in contact resistance at the electrode-diaphragm interface. On the other hand, blocking a part of the electrode surface with a diaphragm material leads to the need to reduce the gas permeability of the diaphragm material, primarily due to the reduction of pores of large radii and total porosity. As a result of the work, a new type of porous coating was also created for the cathodes and anodes of alkaline
electrolyzers, which made it possible to increase the specific surface and reduce the overvoltage of hydrogen and oxygen evolution.

5. References

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