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Catalysis of water splitting reaction in asymmetric bipolar membranes with different chemical composition of cation-exchange layer

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ABSTRACT

The asymmetric bipolar membranes were prepared based on the heterogeneous anion-exchange membrane RALEX AMH and homogeneous perfluorocarbon cation-exchange film MF-4SC. A water-splitting catalyst was introduced into the cation-exchange layer of the membrane to investigate the course of the water-splitting reaction. The resulting membranes have been studied by electrochemical impedance and voltamperometry methods. Effective water-splitting constants were calculated using the mathematical model of heterolytic water-splitting reaction developed previously. It is shown that introduction of the catalyst significantly reduces the voltage on the bipolar region but simultaneously increases the co-ion leakage. It was found that it is possible to regulate the fluxes of salt ions and water-splitting products (hydrogen and hydroxyl ions) by changing the current density. Such an ability makes it possible to conduct a desalting process with simultaneous pH adjustment.

Keywords: Bipolar membrane; Water-splitting; Electrochemical impedance; Current-voltage characteristic; Ion transport numbers

1. Introduction

Bipolar membranes (BPM) are bilayer composites in which layers (cation- and anion-exchange) have ion-selective properties. The main feature of the BPMs is their ability to produce proton and hydroxyl ion from a water molecule, under the influence of an imposed electric current. Thus, a bipolar membrane can be regarded as an electrochemical reactor capable of separating reaction products and remove them from of the reaction zone [1]. Such properties allow creating a number of unique electro membrane processes using BPMs such as pH adjustment of the solutions without the addition of chemicals and the formation of by-products [2], the conversion of salt solutions into acids and bases, the separation of ions, the continuous electrochemical regeneration of ion exchangers in the production of ultra pure water, etc. Other applications and properties of the BPMs are subjects of the recent reviews [3–5].

The use of new bipolar membranes capable of ensuring the generation of hydrogen and hydroxyl ions at a given rate will lead to the creation of electro membrane devices and technologies for desalting, concentrating and adjusting the pH of solutions [2]. It is known that a salt ions leakage through a bipolar membrane exists at small currents. However, the current range, at which the noticeable transfer of salt ions and the generation of H+ and OH– ions flow simultaneously, is very low and does not allow to efficiently conduct the desalting process while simultaneous pH adjustment.

At the same time, it is possible to obtain a bipolar membrane in which the cation- or anion-exchange layers have

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different thicknesses [6]. The advantage of such membranes is the possibility to regulate the ratio of the salt ions transfer and the generation of water dissociation products by changing the thickness of one of the layers constituting the bipolar membrane.

A robust heterogeneous anion-exchange membrane and a Nafion (or its cheaper analog MF-4SC) solution can be used to obtain such membranes. The main disadvantage of these membranes is a low adhesion of the per fluorocarbon matrix of the cation-exchange film to the surface of the heterogeneous membrane-substrate, which does not allow them to be used in practice. The authors managed to solve this problem by creating an intermediate layer consisting of interlaced chains of polyethylene of a heterogeneous anion-exchange membrane and a per fluorocarbon matrix of the cation-exchange membrane [6].

The key features that determine the possibility of efficient use of a bipolar membrane are the over voltage of the bipolar region, the overall potential drop across the BPM, and the current efficiency of the water-splitting reaction. Improvement of the electrochemical characteristics of a bipolar membrane can be achieved by introduction of a catalyst onto the bipolar boundary. Introduction of a catalyst reduces the over voltage of the bipolar region and the total potential drop across the bipolar membrane [7].

The possibility to apply a thin layer to the membrane-substrate allows a relatively easy introduction of various catalyst additives, in the form of suspensions or sols of the catalyst inside the film applied to the substrate. Nano- or micro-sized particles of inorganic compounds [8–13], or functionalized polymers with a predetermined nature of ionogenic groups, have been proposed by various researchers as such catalysts [2,14–16].

This work aims to study the electrochemical characteristics of asymmetric bipolar membranes, both containing and not containing a water-splitting catalyst, in which a heterogeneous anion-exchange membrane was used as the substrate, and a homogeneous cation-exchange membrane was used as the cation-exchange layer.

2. Experimental

2.1. Objects of the study

The objects of the study were asymmetric bipolar membranes obtained according to the method described in [6]. Commercial heterogeneous anion-exchange membrane Ralex AMH-PES (produced by Mega a.s., Czech Republic) with a thickness of 450 µm (contain quaternary ammonium groups) was used as an anion-exchange layer. Sulphonated polytetrafluoroethylene film (MF-4SC) was used as the cation-exchange layer. The asymmetric bipolar membranes were obtained by casting a 5% solution of a sulfonated polytetrafluoroethylene in a solvent prepared by mixing isopropyl alcohol and pure acetic acid (1:1) on the surface of the membrane-substrate followed by evaporation of the solvent at 40°C for 6 h.

Samples were also obtained on the substrate surface of which a slurry consisting of a water-splitting catalyst and liquid MF-4SC was applied (Fig. 1). The thickness of the substrate membrane in the dry state was 450 ± 5 µm, the thickness of the MF-4SC film was 30 ± 5 µm.

A powder of phosphoric cation-exchanger was used as a catalyst. The mean size of the powder particles was 20 ± 2 µm, a small fraction (approx. 2% of the total number of particles) of bigger particles up to 100 µm was also presented in the powder.

The investigated asymmetric bipolar membranes received the following markings: asymmetric bipolar membrane without the catalyst – BM-a, the membrane with the catalyst – BM-ac.

2.2. Electrochemical measurements

Various methods can be used to study the process of water-splitting and ion transport in bipolar membranes. The most important ones are voltammetry [17], chronopotentiometry [18], the method of the frequency spectrum of electrochemical impedance [19], and measurement of the transport numbers of ions through membranes.

As a rule, for a comprehensive study of the water-splitting reaction and ions transport in an electro membrane system, it is necessary to use combination of different methods.

In this work the measurements were carried out in a four-compartment electrochemical cell (Fig. 2) with an active membrane area of 2.27 cm^2. The Haber-Lugginn capillaries connected to silver chloride electrodes were used to study the current-voltage characteristic and monitor the potential drop on the membrane during measurement of the transport numbers. The frequency spectrum of the impedance was measured with Pt/Pt electrodes made of platinum wire 0.1 mm in diameter. Pt/Pt electrodes and tips of the Haber-Lugginn capillaries were located 0.2 mm away from the membrane surface. The investigated membrane was separated from the polarizing platinum electrodes by auxiliary membranes to prevent its contact with the products of electrode reactions. The investigated membrane was in contact with 0.01 M hydrochloric acid solution from the side of the cation-exchange layer and with 0.01 M sodium hydroxide solution from the side of the anion-exchange layer. The solutions feed rate was 2 ml/min. Such set up is favoring the establishment of conditions similar to the working ones [19].

The solutions and the cell itself were thermostatted at 25 ± 0.1°C.

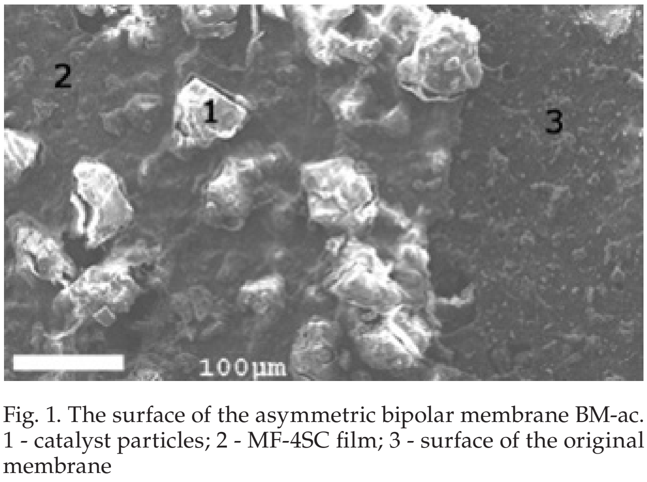

Fig. 1. The surface of the asymmetric bipolar membrane BM-ac. 1 - catalyst particles; 2 - MF-4SC film; 3 - surface of the original membrane

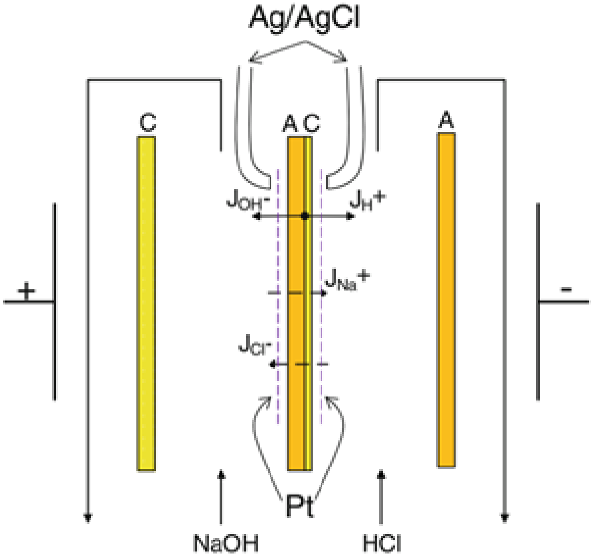

Fig. 2. The scheme of the experimental cell and ion fluxes through the membrane under investigation. C – cation-exchange membrane MF-4SC; A – anion-exchange membrane MA-41; AC – asymmetrical bipolar membrane under investigation.

2.2.1. Voltammetry

The method of volt-amperometry makes it possible to qualitatively study the process of ion transport through the BPM, in those cases when it is not necessary to know the over voltage on each of the layers composing the BPM. The type of the current-voltage characteristic is determined by the structure of the membrane and by the nature of the processes occurring in it under polarization by an electric current. The potential drop on the membrane is the sum of several components: the Donnan potentials at the membrane-solution boundaries, the ohmic voltage drop across the mono polar layers, which is determined by the membrane structure and the type of charge carrier; potential drop at the bipolar boundary.

In the study of asymmetric bipolar membranes, a dynamic method of measuring the current-voltage characteristics was used. The test membranes were pre-conditioned for 30–40 min in an electrochemical cell (Fig. 2) with the pump on and without current. After that, a linearly increasing current was applied to the cell with the help of a Potentiostat/Galvanostat/EIS Analyzer Parstat 4000, and the current-voltage characteristic was recorded. As it was shown in [20] the sweep rate of the perturbing signal must be low enough such that quasi-steady-state conditions are reached. In our work the current sweep rate was set at 2×10^{-5} A/s.

2.2.2. Transport numbers

Non-selective transfer of ions through the membrane is carried out by two mechanisms: diffusion and migration. As a first approximation, it was assumed that the electro migration transport number t_i^m is averaged over the thickness of the membrane and does not depend on the current density. The permeability coefficient P_i was also assumed to be independent of the current density. Then the equation of the flux of hydrogen or hydroxyl ions will be written as:

$$J_i = J_{dif,i} + J_{mig,i} = P_i \Delta c_i + \frac{iS}{F} t_i^m \qquad (1)$$

where J_i – total flux, mol/s; $J_{dif,i}$, $J_{mig,i}$ – diffusion and migration component of the total flux, mol/s; P_i – coefficient of permeability by acid or alkali, L/s; Δc_i – the difference in the concentrations of acid or alkali in the depth of the solution on both sides of the membrane, mol/L; F – Faraday constant, 96485 C/mol; i – current density, applied to the cell, A/cm^2; S – membrane area, cm^2.

Efficient ion transport number of hydrogen or hydroxyl can be calculated by the formula:

$$T_i = \frac{Fc_i V}{iS\tau} \qquad (2)$$

where V – volume of the solution, L; τ– sample collection time, s.

And the flux of ions according to the equation:

$$J_i = \frac{iT_i}{F} \qquad (3)$$

where T_i – effective transport number.

Combining Eqs. (1)–(3), we can obtain the dependence of the effective transfer number on the diffusion and migration components:

$$T_i = t_i^m + \frac{P_i \Delta c_i F}{iS} \qquad (4)$$

Thus, the calculation of the average value of migration transport number of the hydrogen or hydroxyl ions through the membrane and the acid or alkali permeability coefficient reduces to determining the coefficients in the equation of the linear dependence of T_i on the inverse current density i^{-1}.

In this study, a modified Hittorf method adapted for measuring transport numbers in membranes was used. The essence of the method is to determine the total flux of sodium cations into the acid from alkali and total flow of chlorine anions into the alkali from acid.

At each investigated current density, the membrane was held for 60 min at a given current density to achieve a steady state. Every 15–20 min then sampled acid and alkali at the outlet of the cell.

The concentration of chloride ions in a solution of sodium hydroxide was determined by potentio metric titration with a solution of silver nitrate, previously neutralizing the alkali with nitric acid. The concentration of sodium ions in the hydrochloric acid solution was determined by direct potentiometry with a sodium-selective electrode.

Effective transport numbers were calculated by the following equations:

$$T_{\mathrm{Na^+/Cl^-}} = \frac{\left(C_{\mathrm{Na^+/Cl^-}} - C^0_{\mathrm{Na^+/Cl^-}}\right)WF}{iS} \qquad (5)$$

$$T_{\mathrm{H^+/OH^-}} = 1 - \left(T_{\mathrm{Cl^-}} + T_{\mathrm{Na^+}}\right) \qquad (6)$$

where $c_{\mathrm{Na^+/Cl^-}}$ and $c^0_{\mathrm{Na^+/Cl^-}}$ – concentrations of ions in solution, at the outlet the cell, and in feed solution, mol/L;

W – volume flow rate, L/s; T_{Na^+/Cl^-} – effective transport numbers of sodium or chloride ions; T_{H^+/OH^-} – effective transport numbers of H^+ and OH^- ions. For simplicity we consider transport numbers for hydrogen and hydroxyl ions the same. However, one must bear in mind that hydrogen ions can pass only through cation-exchange layer and hydroxyl ions – through anion-exchange layer.

2.2.3. Electrochemical impedance spectroscopy

The method of the frequency spectrum of electrochemical impedance was first used to study processes in bipolar membranes in the work of Sheldeshov, Gnusin, and Zabolotsky [21]. The installation proposed in this work allows obtaining of the most complete information on the processes of ion transport through bipolar membranes under conditions when a direct current flows through the membrane.

Example of electrochemical impedance spectrum of bipolar membrane is shown in (Fig. 3).

The limit of the frequency spectrum of the bipolar membrane impedance (Fig. 3) on the axis of active resistances at $\omega \to \infty$ is $R\infty$ (point A) - the resistance which includes the monopolar regions of the bipolar membrane, the resistance of the solution between the membrane surface and the measuring electrode, and also the resistance of the electrodes themselves And all the intermediate resistances associated with the wires and their connections. The second limit is the point B in which $\omega \to 0$ and the active resistance (R_0) includes, in addition to the above, also the resistance caused by the slow chemical reaction at the bipolar boundary. The emergence of this resistance causes the appearance of the potential "excess" (overvoltage) of the bipolar region and leads to the bipolar membrane CVC deviation from linearity. The resistance of the bipolar region can be found as:

$$R_b = R_0 - R_\infty \tag{7}$$

Integrating the resulting dependence of R_b from the current density one can build the partial CVCs of the bipolar region (η_b), which cannot be obtained by other means.

$$\eta_b = \int_0^i R_b di \tag{8}$$

To compare the efficiency of different catalysts with each other, it was suggested in [22] to use the value of the effective rate constant of the water dissociation reaction in the bipolar region ($k\Sigma$). This value can be found using the experimentally obtained dependence of the partial current on the dissociation products of water on the magnitude of the over voltage of the bipolar region, found from the electrochemical impedance of the membrane. Based on the obtained experimental data, using the Eqs. (9)–(11) (a detailed derivation of these equations can be found in [22]), the effective water-splitting rate constant ($k\Sigma$) in the reaction layer was calculated by minimizing the residual dispersion of the experimental points with respect to the calculated curve.

$$i_{H^+/OH^-} = k_\Sigma \frac{\varepsilon\varepsilon_0}{\beta}\Big(\exp\big(\beta E_m(\eta_b)\big) - \exp\big(\beta E_m(0)\big)\Big) \tag{9}$$

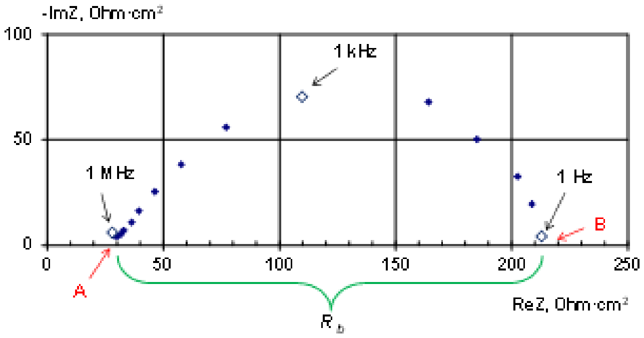

Fig. 3. Electrochemical impedance spectra of bipolar membrane under DC polarization with superimposed AC amplitude (example based on the real spectrum obtained for The BM-ac membrane under conditions described in this section).

$$Em(\eta_b) = \sqrt{\frac{2FN_+N_-(\Delta\varphi_o + \eta_b)}{\varepsilon\varepsilon_o(N_+ + N_-)}} \tag{10}$$

$$\Delta\varphi_o = \frac{RT}{F}\ln\left[\frac{N_+N_-}{K_W}\right] \tag{11}$$

where k_Σ – the total effective rate constant of the pseudo-mono molecular water dissociation reaction in the space charge region 2–4 nm thick in the absence of an electric field; E_m – the electric field strength at the interface between phases, which depends on the over voltage of the bipolar region of the membrane, E_0 – the electric field strength at this boundary at zero over voltage at the bipolar region; β – the entropy factor; ε – relative permittivity in the space charge region; ε_0 – absolute dielectric constant of vacuum, N_+, N_- – ion-exchange capacity of the cation- and anion-exchange layers, mol/L; $\Delta\varphi_o$ – equilibrium potential of a bipolar boundary, B; K_W – ionic product of water.

Electrochemical impedance frequency spectra measurements were carried out in the frequency range of alternating current from 1 Hz to 1 MHz distributed uniformly in logarithmic scale. The amplitude of the AC signal was 200 mV.

The ohmic contribution of total impedance of the cell itself is equal to 4 Ω·cm² for real and imaginary parts of impedance. The relative error magnitude of impedance measurements was less than 1 %.

3. Results and discussion

Despite the small thickness of the cation-exchange layer the value of the limiting current density for the asymmetric bipolar membrane decreases by more than an order of magnitude compared with the anion-exchange membrane-substrate (Fig. 4). It can be explained by the fact that chlorine anions penetrate into the cation-exchange film as co-ions hence their concentration in the layer will be substantially lower than in the bulk of the solution. As a result, the concentration of co-ions (anions) at the interface boundary of the cation-exchanger/anion-exchanger reaches zero at lower current compared with the anion-exchange membrane/solution boundary. Thus, we can say that the control of the electro diffusion kinetics passes from the diffusion

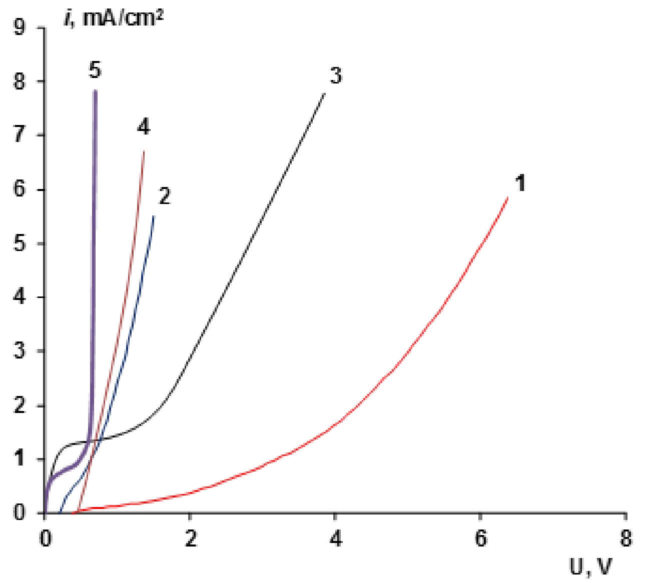

Fig. 4. General current-voltage characteristics. 1 – BM-a; 2 – BM-ac; 3 – anion-exchange membrane-substrate Ralex AMH; 4 – bipolar membrane MB-3 (measured in 0,5 M NaCl); 5 – bipolar membrane BP-1 measured in 2 M NaCl (adapted from [24]).

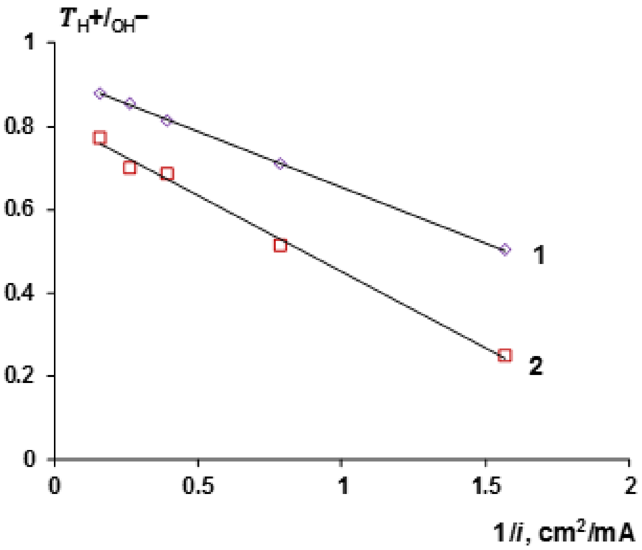

Fig. 5. The dependence of the transport numbers of dissociation products of water on the reverse current density for BM-a (1), BM-ac (2).

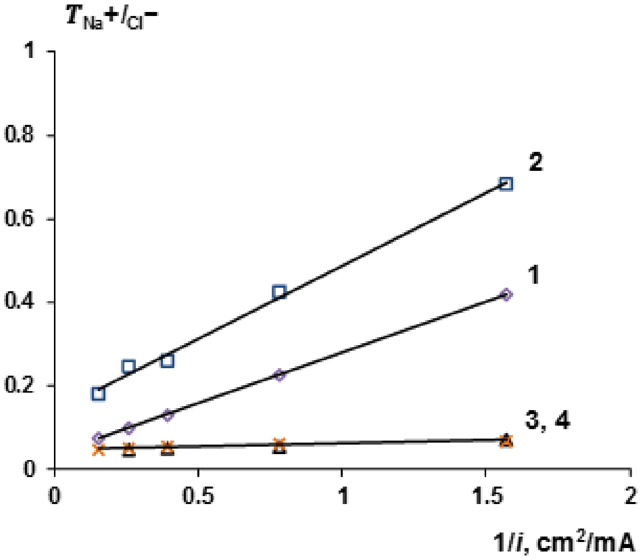

Fig. 6. Transport number of chloride ions (1, 2) and sodium ions (3, 4) via the BM-a (1, 3), BM-ac (2, 4) vs reverse current density

boundary layer in the solution to the cation-exchange layer, which acts as a diffusion layer of constant length.

The further buildup of the current density leads to the formation of a space charge region at the bipolar boundary and the beginning of the water-splitting reaction. The appearance of a new charge carriers (hydrogen and hydroxyl ions) in the bipolar boundary leads to a deviation of the shape of the current-voltage characteristic from the linearity of the limiting current plateau. The following rise of current appears exclusively due to the water-splitting reaction and can be addressed to the fluxes of H^+ and OH^- ions [23].

The introduction of the catalyst (Fig. 4, curve 2) significantly reduces the operating voltage of the asymmetric bipolar membrane. The current-voltage characteristic of the BM-ac membrane is close to the current-voltage characteristic of the MB-3 membrane [22]. Both membranes contain phosphoric ion-exchange groups in the cation-exchange layer, which explains the similarity of their features. The appearance of the limiting current on the general current-voltage characteristic of the BM-ac membrane can be explained by the co-ion leakage through the catalytically active cation-exchange layer. In the case of a MB-3 membrane (Fig. 4, curve 4), the ohmic region and the plateau of the limiting current are absent, due to high activity towards water-splitting, especially in dilute solutions. In case of solutions with high concentration (1 M and higher), the limiting current plateau can manifest even for the very selective BP-1 membrane (Fig. 4, curve 5).

A direct comparison of BPMs with high water-splitting activity (BM-ac, MB-3, BP-1) is not possible because the conditions in which curves 3 and 4 were obtained are significantly different compared with the conditions for curve 5 (Fig. 4).

Lesser selectivity of the BM-ac compared with the unmodified asymmetric bipolar membrane is confirmed by direct measurement of ion transport numbers (Fig. 5, curves 1, 2). This effect can be explained by the fact that in the case of BM-ac part of the volume of the cation-exchange film is occupied by less selective catalyst particles, which leads to an increase in the transport number of anions (Fig. 6, curves 1 and 2) due to the appearance of additional non-selective transport paths. At the same time, the thick membrane-substrate prevents the transfer of sodium ions (Fig. 6, curves 3, 4).

It is known that phosphoric acid ionogenic groups that, on the one hand, have high catalytic activity in the water-splitting reaction, and on the other lose their selectivity (the ability to retain anions) when they enter the acid medium [1]. The reason for the decrease in the selectivity is the protonation of phosphoric acid groups at low pH values, according to the reactions:

$$-PO_3^{2-} + H_2O \xrightleftharpoons[k_{-1}=10^8 \div 10^{10}\, L/(mol \cdot s)]{k1=10^1 \div 10^3\, S^{-1}} -PO_3H^- + OH^- \qquad (12)$$

$$-PO_3\text{H}^-\ H_2O \xrightleftharpoons[k_{-1}=10^8 \div 10^{10}\, L/(mol \cdot s)]{k1=5 \cdot 10^{-3} \div 5 \cdot 10^{-1}\, S^{-1}} -PO_3H_2 + OH^- \qquad (13)$$

The equation of the current-voltage characteristic of the space-charge region proposed in [22] is equally applicable to both bipolar and asymmetric bipolar membranes (Fig. 7).

Comparison of the values of the parameter $k\Sigma$ for the obtained asymmetric bipolar and industrial bipolar membranes (Table 1) shows that the asymmetric membranes occupy an intermediate position between the membranes MB-2 and MB-3. The higher value of the $k\Sigma$ for the BM-a membrane compared to MB-2 can be explained by the different nature of the anion-exchange layers in these membranes and the content of ionogenic groups that determine the rate of dissociation of water molecules. For a membrane with a catalyst, the over voltage of the bipolar region (Fig. 7, curve 2) and the overall operating voltage (Fig. 4a curve 2) is lower than for industrial bipolar membranes MB-1 and MB-2 [22], which allows using them instead of industrial ones when processing dilute solutions.

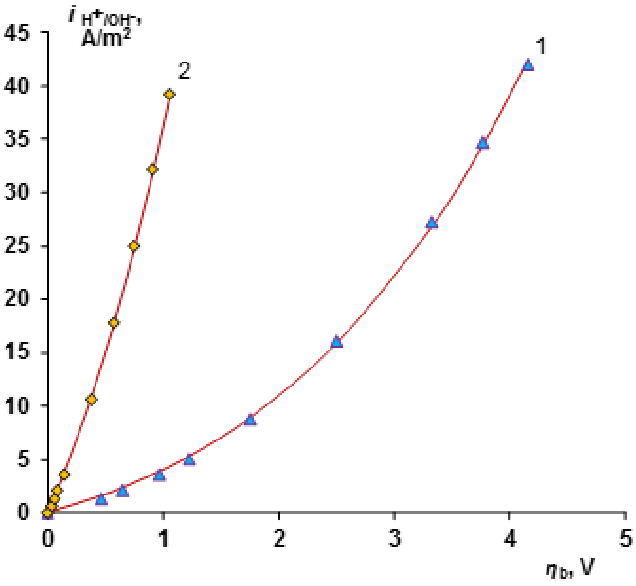

Fig. 7. Dependence of the current density for H^+ and OH^- ions on the over voltage of the bipolar region for BM-a (1) and BM-ac (2). The points are experimental data; the lines are calculated with Eq. (5).

Table 1
Effective water splitting rate constant calculated for asymmetric and industrial bipolar membranes

	k_Σ, 1/s
BM-a	3.75
BM-ac	20.3
MB-1 [22]	8.95
MB-2 [22]	0.401
MB-3 [22]	248

4. Conclusions

The resulting asymmetric bipolar membranes have a more pronounced dependence of the transport numbers of the protons and hydroxyl ions on the current density than industrial bipolar membranes. For example, in 0.01 M solutions of acid and alkali, when the current density varies from 0.05 to 1 A/dm^2, the transport numbers of the protons and hydroxyl ions for the MB-1 varies insignificantly from 0.90 to 0.97 [1]. Under the same conditions the transport numbers for the BM-ac membrane varies from 0.4 to 0.7. This strong dependence makes it possible to vary the amount of transfer of the chloride ion through the membrane from 0.55 to 0.25. The transport number of sodium ion through the asymmetric bipolar membrane under these conditions is small and varies insignificantly from 0.07 to 0.05.

The ability to regulate the transfer numbers of salt, hydrogen and hydroxyl ions by changing the current density makes it possible to conduct a controlled process of desalting solutions of electrolytes with simultaneous pH adjustment.

Acknowledgement

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