Effect of Surface Modification of Perfluorinated Membranes with Polyaniline on Their Polarization Behavior[1]

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Abstract—The possibility of obtaining composite membranes based on MF-4SK and polyaniline with an anisotropic structure and asymmetric current-voltage curves in an external electric field was considered. The polarization behavior of the obtained composite membranes was studied. As the current density increased during the synthesis of polyaniline, the conductivity of the membranes decreased; the hysteresis on the cyclic current-voltage curve, as well as the asymmetry of the parameters of the current-voltage curves, increased; and pseudolimiting current appeared due to the formation of a bipolar internal boundary.

Keywords: anisotropic composite ion-exchange membrane, synthesis of polyaniline, asymmetry of conductivity, current–voltage curve, limiting current

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INTRODUCTION

Composite materials based on polyaniline (PANI) and perfluorinated membranes are very promising for use in various electrochemical and sensor devices [1]. Various methods for the preparation of these materials were developed. They can be divided into two large groups: template synthesis of polyaniline directly in the matrix of the membrane and introduction of commercial polyaniline [2–5]. Both groups of methods have their own advantages and disadvantages. When commercial polymer is introduced in the membrane at the stage of its formation, for example, during film casting from a suspension containing polyaniline and an F-4SK solution, it is difficult to have polyaniline uniformly distributed in the membrane. Moreover, forming a continuous path of charge transfer along the chain of conjugated carbon–carbon bonds requires contact between the polyaniline particles. This can only be achieved by increasing the polyaniline content in the membrane phase, which adversely affects the strength characteristics of the composite material [6]. One of the advantages of this method is the optimum conductive properties of the modifier. Synthesis of polyaniline directly in the phase and/or on the membrane surface seems more promising. The oxidative polymerization of aniline directly in the transport channels of the membrane matrix creates conditions for a continuous path for electric- and masstransfer along the polyaniline chain across the membrane.

However, an obvious disadvantage of this group of methods is the impossibility of creating the conditions of synthesis that would provide the maximum electron conductivity of polyaniline [7, 8].

There are many variants of the template synthesis of polyaniline. An essential condition of this synthesis is monomer and oxidant concentration in the phase or near the membrane surface at which polymerization starts. This can be achieved in various ways: by keeping the membrane in solutions containing the monomer and oxidant in sequence [9]; sequential diffusion of the polymerizing solutions across the membrane into water; and counter-diffusion of the monomer and oxidant across the membrane [10]. To prepare composites with uniform distribution of PANI in the MF-4SK polymer base matrix, iron(III) chloride or ultraviolet radiation is used [11]. Materials in which polyaniline is distributed mainly on the surface of the composite are obtained by treatment with oxidants such as persulfate, permanganate, or bichromate anions, etc., which are co-ions relative to the MF-4SK membrane. Due to their anisotropic structure and asymmetric transport properties, these composites are most promising for use in various devices and electrochemical processes. The preparation of these materials in a concentration field using high reagent and supporting acid concentrations was described in [5]. It can be assumed that the use of an electric field will accelerate the preparation of the material and reduce the concentrations of the polymerizing solutions, as was the case with the preparation of bulk-modified composites in the presence of $FeCl_3$ [12].

The aim of this work was to examine the possibility of obtaining surface-modified composites based on the MF-4SK membrane and polyaniline under the

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Table 1. Conditions for the preparation of MF-4SK/PANI composites

Sample	Current density during PANI synthesis, A/m^2	Composition of polymerizing solutions in near-membrane chambers on the side of	
		cathode	anode
MF-4SK/PANI-1	246	0.002 M K$_2$Cr$_2$O$_7$ + 0.05 M HCl	0.01 M C$_6$H$_5$NH$_2$ + 0.05 M HCl
MF-4SK/PANI-100-1	100		
MF-4SK/PANI-200-1	200		
MF-4SK/PANI-300-1	300		
MF-4SK/PANI-100-2	100	0.005 M (NH$_4$)$_2$S$_2$O$_8$ + 0.05 M HCl	
MF-4SK/PANI-200-2	200		
MF-4SK/PANI-300-2	300		

conditions of an external electric field and to study their electrochemical behavior.

EXPERIMENTAL

Preparation of Anisotropic MF-4SK/Polyaniline Composites Under the Conditions of an External Electric Field

The perfluorinated sulfocationite membrane MF-4SK (Plastpolymer) was the base membrane for the preparation of composites. The membrane was modified by synthesizing polyaniline on the membrane surface in a four-chamber cell while applying direct current. A 0.01 M aniline solution in 0.05 M HCl was fed into the cell chamber on the anode side and a 0.002 M potassium bichromate solution or a 0.005 M (NH$_4$)$_2$S$_2$O$_8$ solution in 0.05 M HCl was introduced on the cathode side. A 0.05 M HCl solution was fed in the near-electrode chambers. The synthesis was carried out at different polarization current densities (i, A/m^2) for 60 min (Table 1). The phenylammonium cations were transferred, in accordance with the direction of electric current, across the MF-4SK cation-exchange membrane into the concentration chamber (Fig. 1). The bichromate or persulfate anions, in turn, migrated to the membrane surface, where the oxidative polymerization of aniline occurred. Thus, a polyaniline layer formed on the membrane surface on the cathode side.

The green color typical for polyaniline in the form of emeraldine appeared after 20 min of synthesis when potassium bichromate was used and after 30 min in the case of ammonium persulfate.

All the composite membrane samples had different color intensities. Figure 2 shows the electronic absorption spectra of the samples, which exhibit absorption maxima typical for the emeraldine form of polyaniline: a maximum around 300 nm corresponding to the π−π* electron transitions in the benzene rings of polyaniline and a broad band at 800 nm corresponding

to the localized polarons or radical cations [13]. Visual comparison of the composites obtained in the presence of ammonium persulfate and potassium bichromate at the same current density showed that the intensity of coloring was higher for the latter in all cases. This is indirect evidence for the larger amount of polyaniline in the membrane when potassium bichromate is used as an oxidant that initiates polymerization of aniline, though its redox potential is smaller than that of ammonium persulfate. This assumption is confirmed by the fact that the optical density at the absorption maxima for the MF-4SK/PANI-100-1 composite is higher than for MF-4SK/PANI-100-2. This unexpected result can be explained by the fact that during the preparation of composites, synthesis of polyaniline occurs concurrently with its oxidative destruction [14]. In general, the yield of PANI depends on the rate ratio of these two processes. We can assume that under the action of a stronger oxidizer (ammonium persulfate), the destruction is much faster and the amount of PANI in the membrane ultimately decreases. A comparative study of composites based on carbon nanotubes and polyaniline obtained in the presence of sodium persulfate and potassium bichromate was performed in [15]; it was noted that the yield of PANI was higher in the
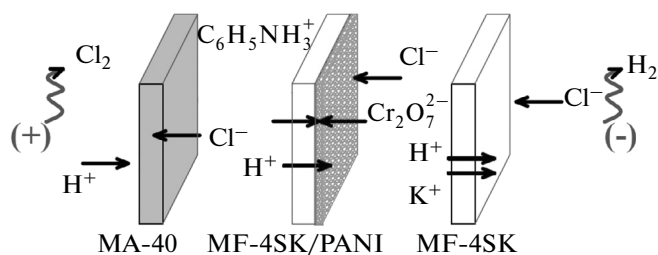

Fig. 1. Diagram of the formation of a polyaniline layer on the surface of the MF-4SK membrane under the conditions of an external electric field.
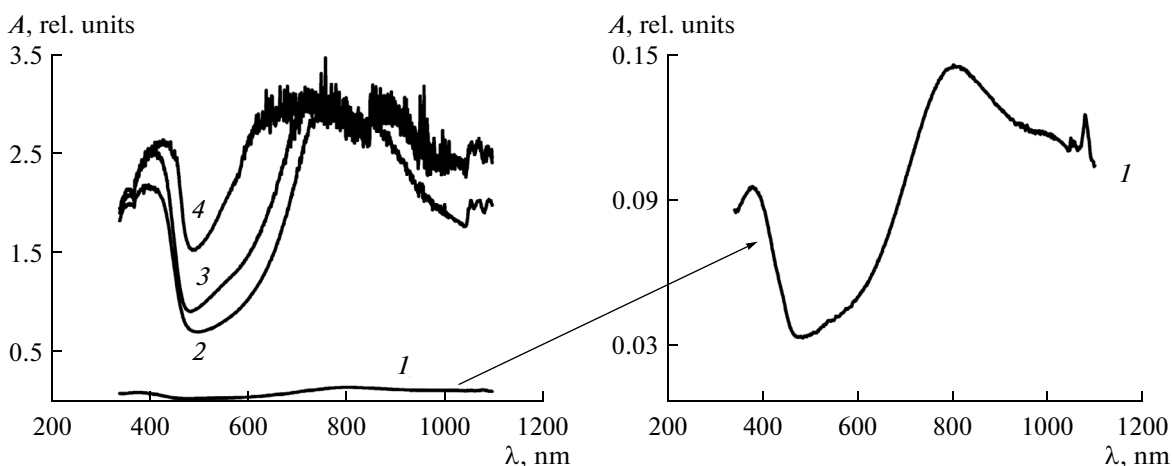
Fig. 2. Electronic absorption spectra of MF-4SK−PANI composites obtained under the conditions of an external electric field using (*1*)−(*3*) ammonium persulfate and (*4*) potassium bichromate as an oxidant of aniline: (*1*) MF-4SK/PANI-100-2, (*2*) MF-4SK/PANI-200-2, (*3*) MF-4SK/PANI-300-2, and (*4*) MF-4SK/PANI-100-1.

latter case. The authors explained this by the decomposition of sodium persulfate in water to thiosulfate, liberating molecular oxygen. However, it was also noted that the PANI layer obtained in the presence of sodium persulfate was more uniform and conductive compared with that synthesized in the presence of potassium bichromate.

In each series of MF-4SK/PANI composites, we visualized an increase in the color intensity at increasing current density in the course of their preparation. According to Fig. 2, the optical density at the absorption maxima on the electronic absorption spectra increases with the current density during the preparation of anisotropic cation-exchange composite membranes. According to the Bouguer−Lambert−Beer law, the optical density at the absorption maximum is proportional to the content of the corresponding component in the sample.

Thus, it was shown that a polyaniline layer can be obtained on the surface of the MF-4SK membrane under the conditions of an external electric field. The amount of polyaniline in the membrane increases with current density during the preparation of the composites irrespective of the nature of the oxidant. The use of the potassium bichromate oxidant allows synthesis of samples with deeper coloring and hence with a larger amount of polyaniline in the emeraldine form.

Polarization Behavior
of Anisotropic MF-4SK/PANI Composites

The current-voltage curves (CVCs) were measured in the same cell in which the composites were prepared. The cell (Fig. 3) consisted of two near-electrode chambers with platinum polarizing electrodes with an area of 7.1 cm^2 and two near-membrane chambers. To prevent the transfer of the electrolysis products from near-electrode to near-membrane chamber, we used auxiliary anion- and cation-exchange membranes to separate the membrane under study from the anode and cathode chambers, respectively. The given rate of electrolyte circulation in the chambers (14 mL/min) was maintained using a peristaltic pump. Direct current was applied at a specified scan rate to the polarizing electrodes using an Autolab pgstat302n potentiostat/galvanostat. The change in the potential difference on the membrane was recorded using Luggin−Haber capillaries connected with the membrane and the silver/silver chloride electrodes. The silver chloride electrodes were connected to the potentiostat/galvanostat, from which the signal was fed to a computer, which allowed real-time recording of the experimental ΔE value.

The parameters of CVCs were determined by the tangent method using numerical differentiation in the Microsoft Excel program. The tangent method is used to find the equations of linear regression of the sections corresponding to the ohmic, limiting, and overlimiting states of the electromembrane system (EMS) on the current-voltage curve. The slopes of the ohmic region, the limiting current plateau, and the overlimiting state region were determined as the coefficients a of the linear equations of the tangent lines of the form $y = ax + b$. The criterion of optimization of the number of points used for drawing the tangent lines was the accuracy of approximation (R^2). Then we determined all the characteristic points of CVCs by solving a set of two equations. These calculations were performed for all the curves in the series. The results of calculation were averaged and the confidence intervals and errors were determined for all quantities. Numerical differentiation was used because the differential curves for the CVCs of the membrane have a pronounced peak at currents close to the limiting current (i_{lim}) determined by the tangent method. Both methods allow us to determine i_{lim} with an error of less than 5%.
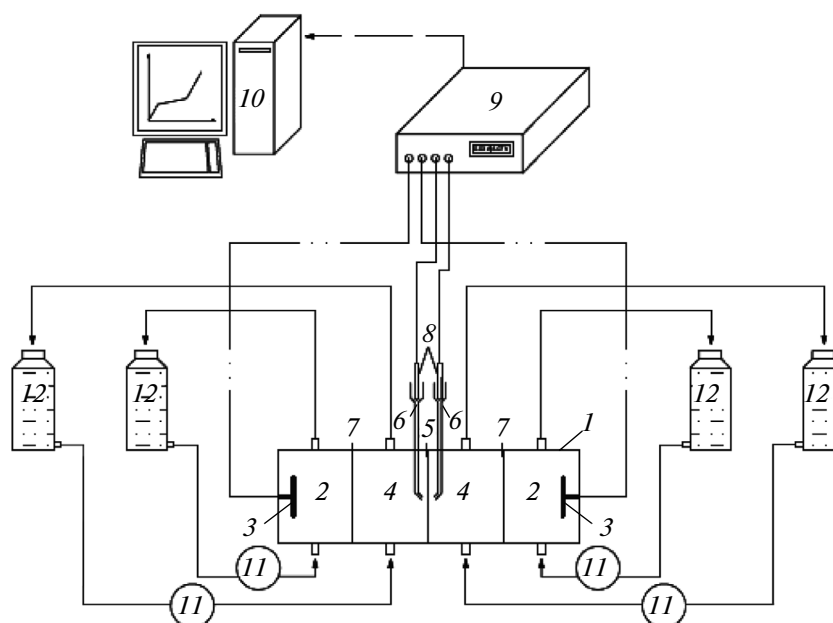
Fig. 3. Diagram of a unit for measuring the CVCs of the membrane system: (*1*) measurement cell, (*2*) near-electrode chambers, (*3*) platinum polarizing electrodes, (*4*) near-membrane chambers, (*5*) membrane under study, (*6*) Luggin−Haber capillaries, (*7*) auxiliary membranes, (*8*) silver/silver chloride electrodes, (*9*) Autolab pgstat302n potentiostat/galvanostat, (*10*) PC, (*11*) Heidolph pumpdrive 5101 peristaltic pump, and (*12*) vessels for solutions.

When studying the polarization behavior of the obtained composites, it was noted that the CVCs changed during the experiment. Based on the experimental data, the total charge to be passed through the EMS to obtain reproducible results was determined. According to Fig. 4, reproducible results can be obtained after the 12th measurement, which corresponds to 2000−2500 C. This charge can be passed through the EMS in the course of sequential measurements of CVCs and by preliminarily keeping the membrane at a certain current. For example, at $I = 200$ mA, the keeping time of the sample should be 3 h.

The measurement of cyclic CVCs at the standard scan rate usually used for measurements (1×10^{-4} A/s) showed that the polarization curves of the composites had a pronounced hysteresis, while the measurement of cyclic CVCs on the original MF-4SK membrane at the same scan rate had no such effect. The degree of this effect depends on the current density at which the samples were synthesized.

To determine the reason for the hysteresis, we studied the chronopotentiograms of the composites at different current densities (Fig. 5). An analysis of the results showed that the time of reaching the constant voltage drop on the composite membrane is at least 17 min. Therefore, to reduce the hysteresis, it is necessary to decrease the current scan rate during CVC measurements for membranes.

An analysis of the experimental CVCs measured at different scan rates of the polarizing current (Fig. 6) showed that the polarization behavior of the composites.

ite orientated by its nonmodified side toward the flow of counterions is independent of the scan rate of current in the range 0.4×10^{-5} to 4.6×10^{-5} A/s. However, when the composite is orientated by its polyaniline layer toward the flow of counterions, the shape and parameters of CVCs depend strongly on this value. The hysteresis of the polarization curve decreases with the scan rate. The hysteresis of CVCs was not com-
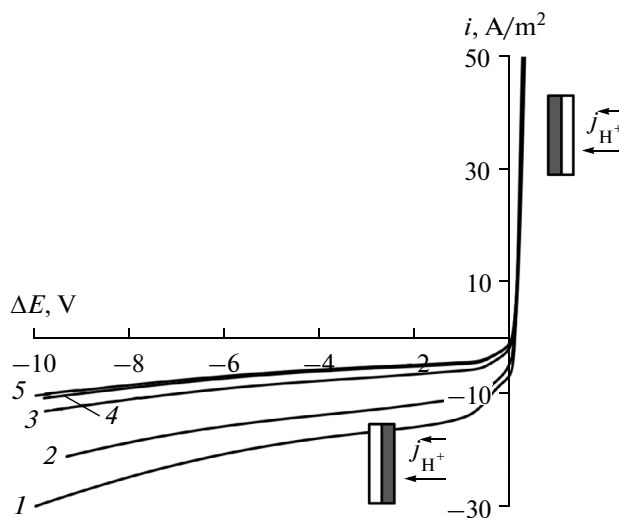

Fig. 4. CVCs of the MF-4SK/PANI-1 composite in 0.05 M HCl measured in sequence; measurement no. (*1*) 1, (*2*) 5, (*3*) 10, (*4*) 12, and (*5*) 13.
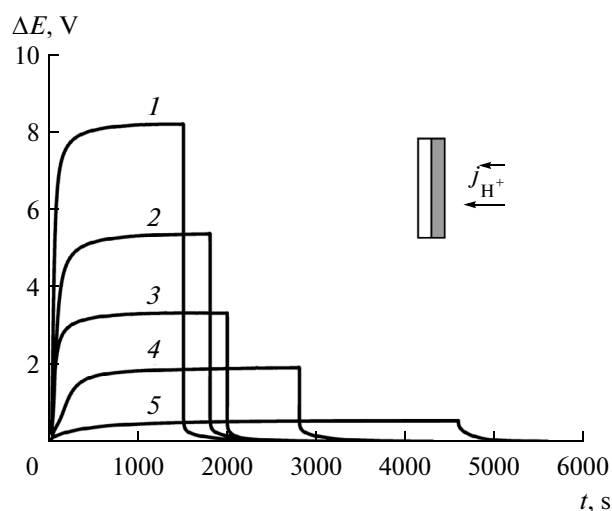
Fig. 5. Chronopotentiograms of the MF-4SK/PANI-1 anisotropic composite measured in 0.05 M HCl at different porarizing currents i, A/dm^2: (*1*) 11.3, (*2*) 7.0, (*3*) 6.5, (*4*) 2.8, and (*5*) 1.3.

sured using the current scan rates from 0.9×10^{-5} to 4.6×10^{-5} A/s depending on the sample preparation conditions. The scan rate can be higher (4.6×10^{-5} A/s) for the samples obtained at the minimum current density (100 A/m^2), but minimum (0.9×10^{-5} A/s) for the samples with the densest polyaniline layer obtained at the maximum current density (300 A/m^2) and having the most pronounced hysteresis of CVCs.

The developed procedure was used to study the polarization behavior of a series of anisotropic composites MF-4SK/PANI obtained at current densities of 100, 200, and 300 A/m^2. According to the data presented in Fig. 7, the CV curves are asymmetric for all the samples depending on the orientation of the modifying polyaniline layer relative to the counterion flow. If the counterion flow meets the polyaniline layer, the limiting current and the conductivity of the EMS decrease in all cases, while the potentials of the start of the overlimiting state increase compared with that for the original membrane. For the reverse orientation of membranes, an increase in the current to 100 A/m^2 did not lead to the limiting condition in the EMS and its conductivity was higher than in the case with the counterion flow meeting the modified composite surface. A similar form of polarization curves was observed for the anisotropic composites obtained by sequential diffusion of polymerizing solutions across the membrane into water [5, 10].

pletely eliminated during the experiment because of high time consumption. Thus, at a scan rate of 0.4×10^{-5} A/s, the total time of measurement of one cyclic CVC was ~7 h. Therefore, in further experiments, we used the range of scan rates that allowed the minimum hysteresis on the CVC.

Thus, in order to obtain reproducible results with a minimum hysteresis, the following procedure for measuring the CVCs of composite membranes was suggested. After the synthesis, direct current with a density of 280 A/m^2 should be passed through the system for 3 h. Thereafter, the CV curves should be mea-

Thus, for the anisotropic MF-4SK/PANI samples, the general tendency of polarization behavior is the asymmetry of CVCs irrespective of the conditions of their synthesis and the oxidant used. We assumed that the reason for this is the presence of two layers formed in accordance with the asymmetric conditions of synthesis in the modified sample. Polyaniline having
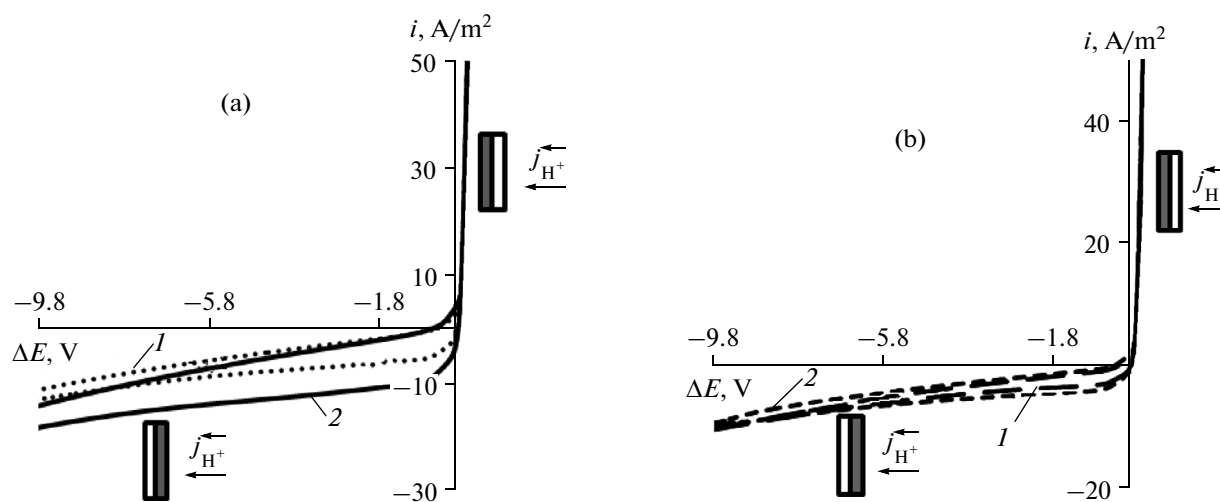

Fig. 6. CVCs of the MF-4SK/PANI-1 anisotropic composite measured in 0.05 M HCl at (a) high ((*1*) 1.5×10^{-5} A/s and (*2*) 4.6×10^{-5} A/s) and (b) low ((*1*) 0.4×10^{-5} A/s and (*2*) 0.8×10^{-5} A/s) scan rates of the polarizing current.
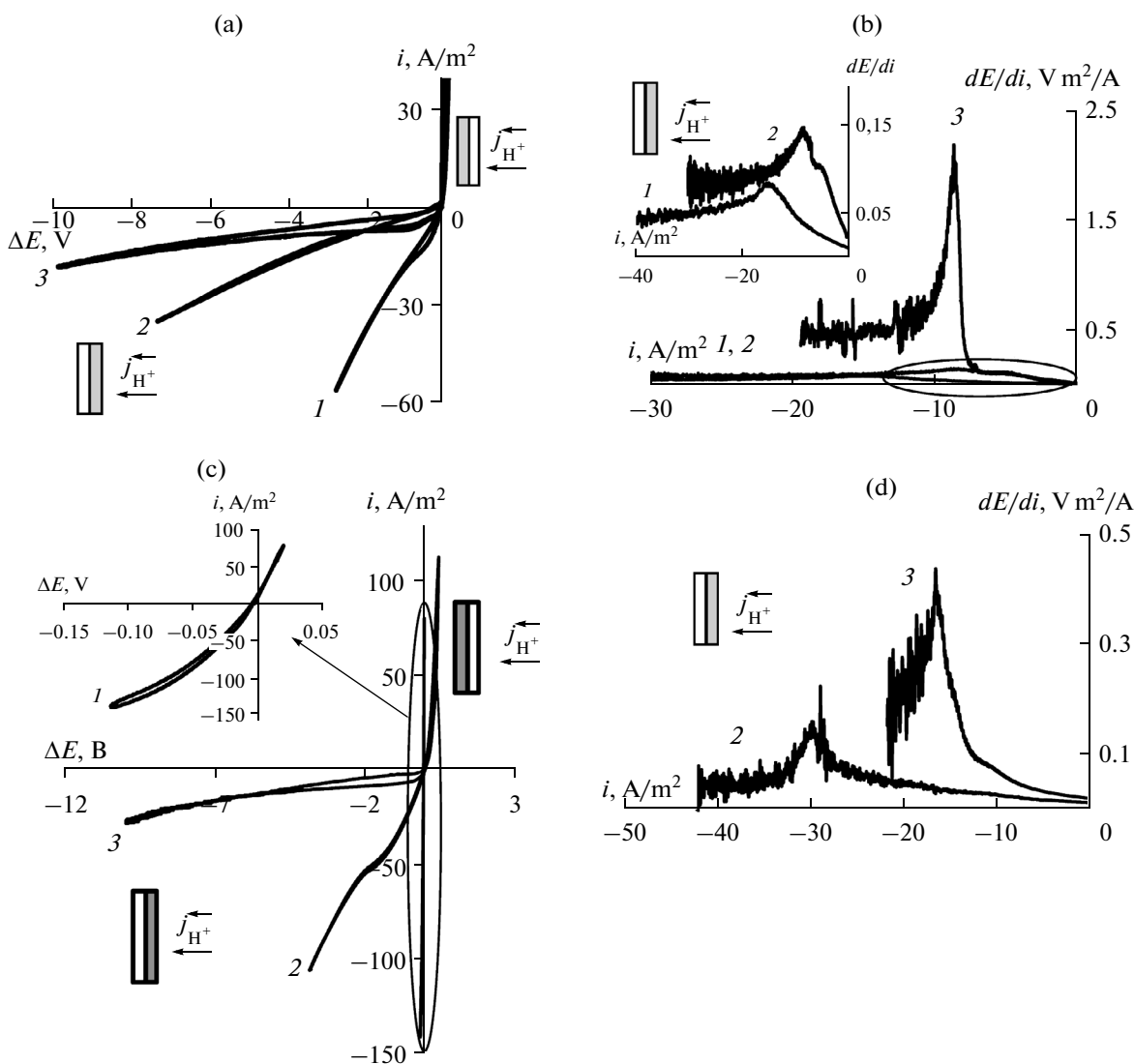
Fig. 7. (a), (c) Integrated and (b), (d) differential CVCs of the MF-4SK/PANI composites in 0.05 M HCl obtained at different current densities using (a), (b) potassium bichromate and (c), (d) ammonium persulfate as an oxidant of aniline. Current densities during the synthesis of the composites, A/dm^2: (*1*) 100, (*2*) 200, and (*3*) 300.

anion-exchange properties [16] is mainly localized in the surface layer of the sulfocationite membrane. This system is similar to the polyethylene terephthalate track membrane described in [17] and modified in aniline plasma under the conditions with only one open side of the membrane during plasmochemical polymerization in discharge. In this case, a gradient of thickness of the deposited polyaniline layer appears in the pore channels, and carboxyl cationite–anionite layers with bipolar conductivity are formed. The formation of an internal bipolar boundary between the cation- and anion-exchange layers in a perfluorinated membrane can lead to catalytic dissociation of water. When the membrane is orientated toward the counterion flow by its polyaniline layer, the counterions cease to participate in current transport because they are partially neutralized by hydroxyl ions generated on the

bipolar boundary, which should lead to the appearance of a quasilimiting state in the EMS (Fig. 8).

This is confirmed by a detailed analysis of the region of small displacements of the potential from equilibrium (from 0 to 100 mV) on the CV curve. The effect of the appearance of the quasilimiting state and of the second inflection on the CV curve at low potentials (Fig. 7b) is directly related to the emergence of a PANI layer on the membrane surface. The higher the current density used in the PANI synthesis, the larger the second inflection on the CV curve and hence the greater the role of the internal bipolar boundary in the composite membrane. For the samples obtained at the minimum current density of 100 A/m^2, this effect is not observed on the polarization curves.

The influence of the internal bipolar contacts on the polarization behavior of the MF-4SK/PANI com-
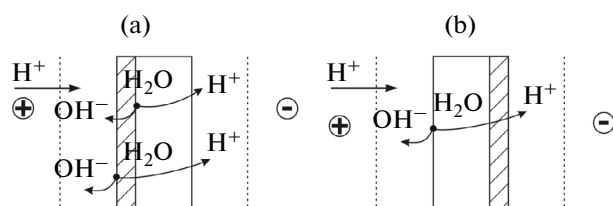
Fig. 8. Diagram of H^+ and OH^- ion flows that appear in the EMS with the membrane orientated by its modified layer toward the (a) anode and (b) cathode (the modified layer is hatched).

posite membrane was analyzed in [18]. The appearance of "fast ions" in the system due to the catalytic dissociation of water was confirmed by analyzing the frequency impedance spectrum.

The evaluation of the conductivity of the EMS from the slope of the ohmic region of CVCs showed that the asymmetry of this parameter is observed regardless of the measurement mode of the polarization curve, the orientation of the anisotropic membrane playing the determining role. Table 2 shows the calculated angular slopes of the ohmic region of CVCs and the asymmetry coefficients found as their ratio. According to Table 2, the EMS conductivity is lower when the modified side of the membrane is directed toward the counterion flow. This effect is consistent with the data of [10, 19] for the composite membranes obtained during the diffusion of the polymerizing solutions. The different conductivities of the membrane system can be explained by different concentration profiles formed in this bilayer membrane. The concentration of counterions on the internal interface is higher when the counterion flow meets the nonmodified side of the membrane. Hence, the electric conductivity of the less conductive modified layer will be higher in this case. For the opposite orientation, the

resistance of the modified layer and hence of the whole system is higher because of the lower concentration of counterions.

The asymmetry of conductivity was described in the literature, for example, for metal–polymer composite membranes [20]. The authors of [17, 20, 21] noted a relationship between the straightening effect similar to the $p–n$ transition in semiconductors and the change in the pore geometry of the membrane after the deposition of a modifier on one of its surfaces. As a result, a bipolar interface is formed between the initial membrane and the deposited layer, which have oppositely charged functional groups in electrolyte solutions. This diode effect or the effect of EMS conductivity switching was also found in the present study for composite anisotropic membranes prepared in an external electric field. The asymmetry coefficient of the slope of the ohmic region of the CVC was considerably higher for the samples obtained by using potassium bichromate (Table 2).

According to Table 2, as the current density increases during the synthesis of composite membranes orientated by their PANI layer toward the counterion flow, their conductivity at first decreases and then begins to increase if potassium bichromate is used. This may be due to the appearance of a contribution of the intrinsic conductivity of PANI to the total conductivity of EMS. For the composites obtained in the presence of ammonium persulfate, however, the conductivity only decreased as the current density increased during the synthesis of PANI irrespective of the membrane orientation. One possible explanation for these differences in the polarization behavior of the composites is the fact that for the samples obtained at the same current densities, the amount of PANI in the composites is lower in the case of ammonium persulfate used as an oxidant than in the case of potassium bichromate.

Table 2. Effect of current density during the synthesis of composite membranes on the angular slope of the ohmic segment of the CV curve

Sample	Angular slope of ohmic segment, $A/(V\,m^2)$		Asymmetry coefficient
	nonmodified side directed toward the counterion flow	modified side directed toward the counterion flow	
MF-4SK/PANI-100-1	1207	48	25
MF-4SK/PANI-200-1	475	15	32
MF-4SK/PANI-300-1	475	38	12
MF-4SK/PANI-100-2	3490	2050	1.7
MF-4SK/PANI-200-2	690	42	16
MF-4SK/PANI-300-2	205	30	7

CONCLUSIONS

Composite membranes based on MF-4SK and polyaniline with an anisotropic structure and asymmetric current-voltage curves can be obtained under the conditions of an external electric field. An analysis of various regions of the CVC curve of the composite membranes showed that as the current density increases during the synthesis of polyaniline, their conductivity decreases, the hysteresis on the cyclic current-voltage curve and the asymmetry of the CVC parameters increase, and the pseudolimiting current appears due to the appearance of an internal bipolar boundary. Based on the analysis of the polarization behavior of the samples, we can determine their effective applications in various electrochemical devices. Materials with moderate asymmetry of the current-voltage curve and sufficiently high density of the limiting current are promising for use in electrodialysis because, as is known, modification of perfluorinated membranes with polyaniline increases their selectivity and reduces the diffusion and electroosmotic permeability [22—24]. Anisotropic composite membranes with a diode-like effect may be used as membrane switches or relays.

ACKNOWLEDGMENTS

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