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Lower rate of $H^+(OH^-)$ ions generation at an anion-exchange membrane in electrodialysis

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ABSTRACT

A way of improvement of electromembrane technology for water production required in heat-and-power engineering by applying modified anion exchange membranes is proposed. The novel membranes are produced by treatment of commercial Russian heterogeneous MA-40 membranes with a polyelectrolyte bearing quaternary ammonium groups. It is found that this modification results in lowering the rate of H^+ and OH^- ions generation (water splitting) at overlimiting currents and in a considerable increase in current efficiency due to the decrease in the OH^- ions transfer across the anion-exchange membrane. Moreover, we observed an increment in the salt counterion transfer through the membrane. The decrease in water splitting rate at the interface 'anion-exchange membrane/depleted solution' leads to increasing pH in the desalting compartment and decreasing pH in the concentrating one. As a consequence, the risk of the salt precipitation on the membrane surface in the concentrating compartment is reduced, and the removal of weak acids from the desalting water is found enhanced.

Keywords: Ion exchange membrane; Modification; Water splitting; $H^+(OH^-)$ ions generation; Electrodialysis; Hybrid baro-electromembane technologies

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1. Introduction

Economic and ecological problems caused by anthropogenic pollution of environment requires conversion of conventional technologies into the alternative ones like membrane technology characterized by low chemical consumption and resource saving [1]. The ways of membrane technology evolution, in particular, the technology of makeup water production for thermal power stations (TPS), in many aspects depend on the properties of the membranes [2].

The makeup water for TPS must not contain the salts of hardness and its pH should be alkalescent or, at least, neutral. In this case, it is possible to minimize the salt precipitation and extend the equipment's lifetime due to the removal of aggressive carbonic acid from water. Widely introduced today, the reverse osmosis (RO) plants are sufficiently advantageous, however, they require specially treated water and are characterized by low water recovery. Besides, when applying the pressure driven technologies, it is not

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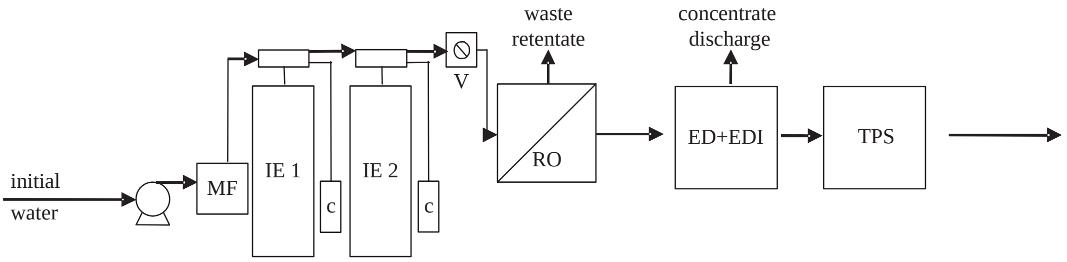

Fig. 1. Flowsheet of a membrane system for makeup water production for thermal power station.

possible in principle to achieve high concentrations of retentate because of the necessity to overcome the osmotic pressure difference (about 1 bar per 1 g salts/L). The incorporation of electromembrane modules into the systems for makeup water production for TPS improves the ecological impact of the technology. Fig. 1 depicts an example of such a system developed by ''Membrane Technology'' Innovation Enterprise (Krasnodar, Russia).

The parameters of raw artesian water and water after baromembrane and electromembrane modules are shown in Table 1. The hardness is eliminated by sodium cation-exchange (IE). The RO modules are used to obtain the demineralized water with concentration 10–50 mg/l. Residual ionic impurities are removed in an electrodialyzer with ion exchange bed (electrodeionizator) (EDI), which allows the simultaneous pH correction.

When a current normal to membrane surface is applied in an ED, the cations, C^+, and anions, A^-, migrate across cation-exchange (CEM) and anion-exchange (AEM) membranes, respectively (Fig. 2). pH of the desalted solution depends strongly on the rate of H^+ and OH^- ions generation at the interface of CEM and AEM in the desalination compartment (DC). If the rate is higher at the AEM, the outlet solution is acidified. Otherwise, the desalted solution becomes alkalinized.

The goal of our work is the improvement of the electrodialysis technology applied in desalination/deionization of diluted solutions, by means of surface modification of anion exchange membranes with a polyelectrolyte containing quaternary ammonium groups.

2. Experimental

It is known that commercial Russian heterogeneous MA-40 and MA-41 membranes (Schekinoazot, Russia) contain secondary and tertiary amino-groups with high catalytic activity regarding water dissociation reaction while MK-40 cation exchange membrane comprises sulfo-groups with low catalytic activity towards water dissociation reaction [3–5]. Therefore, generally,

Table 1
Main characteristics of raw and treated water

Chemical parameters	Artesian water	Water after reverse osmosis	Water after continuous EDI
Ca^{2+}, mg/l	41.4	3.0	Not detected
Mg^{2+}, mg/l	11.9	0.8	Not detected
Na^{+}, mg/l	90	0.7	Not detected
Fe^{2+}, mg/l	up to 0.1	<0.05	Not detected
Fe^{3+}, mg/l	up to 0.1	<0.05	Not detected
Ba^{2+}, mg/l	up to 1.0	Not detected	Not detected
Sr^{2+}, mg/l	up to 1.0	Not detected	Not detected
Cl^{-}, mg/l	11.0	1.8	<0.05
NO_3^{-}, mg/l	12.0	1.3	Not detected
F^{-}, mg/l	0.9	<0.19	<0.01
HCO_3^{-}, mg/l	137	6.1	Not detected
Si, mg/l	10.0	0.3	0.05
pH	8.0	5.6	7.0
ρ, MOhm·cm	0.001	0.2-0.25	10.5

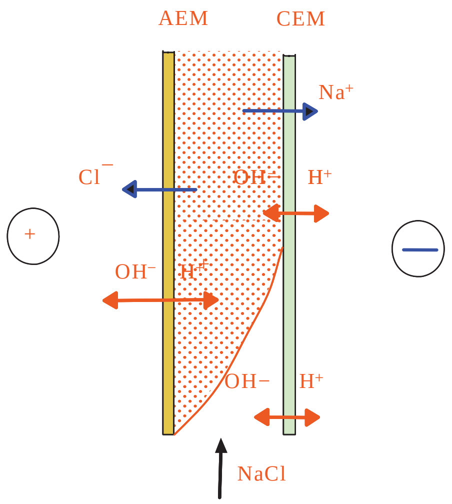

Fig. 2. Scheme of ion fluxes in the desalting compartment of a membrane stack.

the desalted solution is acidic. In order to increase the solution pH, it is sufficient to convert secondary and tertiary amines on AEM's surface into quaternary amines with low catalytic activity. For this purpose, a commercial MA-40 membrane was modified by a strong polyelectrolyte bearing the quaternary ammonium groups.

The pictures of membrane surface and cross-section were obtained with the help of scanning electronic microscope (SEM) combined with energy dispersive X-ray analysis. IR-spectra of the commercial MA-40 membrane and modified MA-40M membrane were recorded with the help of IR-spectrometer ''InfraLUM FT-0.2'' (Russia). Interpretation of the spectra was performed using the characteristic infrared absorption frequencies [6,7].

The concentration dependencies of membrane electrical conductivity in NaCl solutions were measured with an RLC MT 4080A immittance device (Motech Industries) at a frequency of 100 kHz by a differential method with a clip-cell [8]. Experimental data were treated by the microheterogeneous model [9] in order to reveal bulk morphology changes [10].

Current–voltage characteristics (CVC) and pH variation vs. potential drop across the membrane are obtained for commercial MA-40 and modified MA-40M membranes with the help of a setup providing laminar uniform flow of solution between the membranes [11]. Ion transport numbers across the membranes in desalination channel were measured by means of technique maintaining constant solution composition and pH [12]. For the formation of desalination channel commercial heterogeneous MK-40 membrane (Schekinoazot, Russia) and commercial homogeneous CMX membrane (Tokuyama Soda, Japan) were used. The experiments were performed in 0.005M NaCl solution.

3. Results

3.1. Surface morphology and chemical composition

Analysis of the SEM data showed that the surface and bulk morphology of the modified MA-40M membrane does not significantly change in comparison to the initial MA-40 membrane [13]. Results of probing X-ray microanalysis (Fig. 3a,c) lead to the conclusion that the polyethylene forming part of MA-40 as filler does not interact with the polyelectrolyte, but the reaction occurs with the ion exchange grains inside a surface layer of the membrane (Fig. 3b).

The comparison of the conductivity–concentration curves obtained for the unmodified and modified membranes has shown that the surface of MA-40M is enriched with quaternary amines [13]. IR-spectra

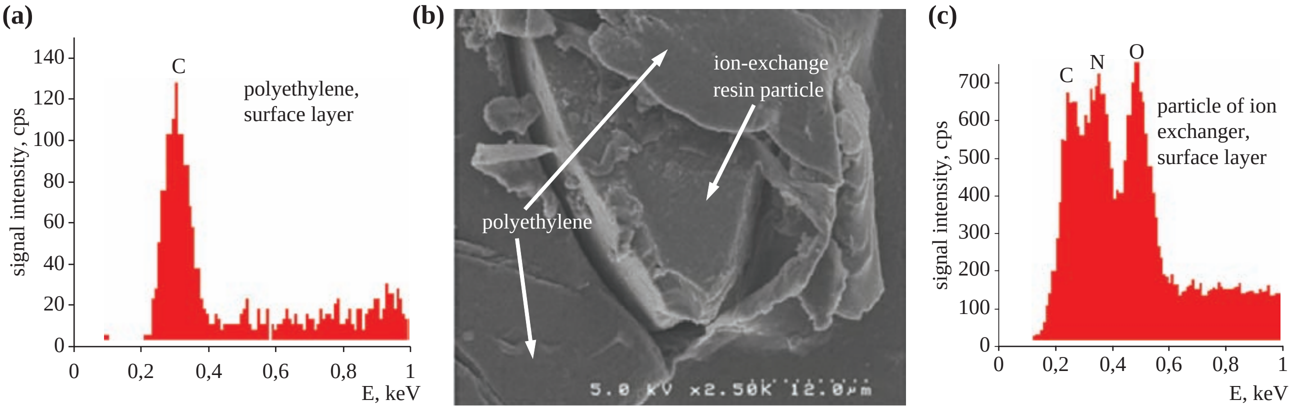

Fig. 3. Results of electronic scanning microscopy (b) combined with probing X-ray microanalysis of polyethylene (a) and ion-exchange resin particle (c) on the MA-40M membrane surface.

Table 2
Characteristic frequencies of the IR-spectra for MA-40 and MA-40M membranes

Membranes	cm^{-1}								
	ν –OH	ν $_{\text{Csp3–H}}$	δ –NH$_2$	δ $_{\text{Csp3–H}}$	δ $_{\text{Csp3–H}}$	ν –C≡N	ν $_{\text{as}}$ –COO$^-$	ν $_{\text{s}}$ –COO$^-$	δ –NH$_2$
MA-40	3427.17	2918-2851	1643	1474-1464	1385	–	–	–	874–656
MA-40M	3442.6	2924-2852	1664	1473-1463	1360	2241	1638	1358	1054–720

Type of vibration: ν – stretch, ν $_{\text{as}}$ – asymmetrical stretch, ν $_{\text{s}}$ – symmetrical stretch, δ – bend.

revealed the presence of –CH$_2$ and –OH groups both for commercial and modified membranes (Table 2). These groups belong to anion exchanger EDE-10P forming the conducting phase of the MA-40 membrane. The treatment of MA-40 by polyelectrolyte results in appearance of –C≡N and –COO$^-$ groups in the membrane (Table 2). These groups can interact with secondary and tertiary amines of MA-40 forming electrostatic and chemical bonds between the polyelectrolyte and ion exchange material.

3.2. Rate of H$^+$ and OH$^-$ ions generation

By means of registration of pH within the boundary layers of solutions near the membrane from its depleted and concentrated side, it is found that with the current growth, pH of the desalted solution close to the MA-40M surface decreases less than that near the MA-40 and the commercial homogeneous AMX membranes; the latter membrane is considered for comparison (Fig. 4). This observation testifies that the transformation of secondary and tertiary amino groups into quaternary ammonium bases lowers the rate of H$^+$ and OH$^-$ ion generation. The suppression of this reaction promotes development of electroconvection at the MA-40M membrane [14] resulting in intensive mixing of the solution near the membrane. The latter causes a higher decrease in the effective thickness of the depleted diffusion boundary layer near the modified membrane, in comparison to the original membrane, that leads to considerable augmentation of Cl$^-$ ion flux through the MA-40M membrane. As a result, at overlimiting currents, under the same voltages, the mass transfer across the modified membrane is higher in comparison with the original membrane (Fig. 4).

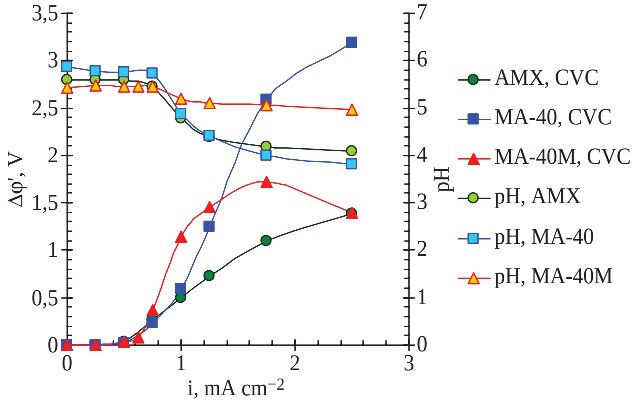

Fig. 4. Current–voltage curves and pH evolution of the solution adjacent to the depleted membrane surface vs. the current density. The concentration of NaCl feed solution $C = 0.005$ M; the intermembrane distance $h = 7$ mm; the active membrane area $S=2 \times 2$ cm^2 the flow velocity $V = 0.32$ cm s^{-1}.

In the DC formed with a MK-40 and a MA-40 membranes, the desalted solution is acidified due to a more intensive H$^+$ and OH$^-$ ion generation at the surface of anion exchange membrane in comparison with the cation-exchange one (Fig. 5). In a DC formed by a cation-exchange membranes with sulfonic groups (CMX, MK-40) and a MA-40M membrane, the desalted solution becomes more alkaline (CMX) or without pH changes (MK-40) at overlimiting currents at least up to $i/i_{\text{lim}} < 3$ (Fig. 5a) (or up to 8 V per cell pair, Fig. 5b) that testifies that the rate of H$^+$ and OH$^-$ ion generation reaction is higher at the CMX membrane and the same at MK-40 membrane in comparison with the MA-40M membrane.

3.3. Stability of modification

The properties of modified membrane are stable. It is found that the mass transfer characteristics and electrochemical properties of modified membranes do not change during at least 300 h of continuous exploitation in electrodialyzer (Fig. 6).

3.4. Advantages of electrodialysis with modified membranes

The following effects determine some economic benefits from the use of modified MA-40M membrane:

- An increase in current efficiency up to 20–30% at concentrations <0.01 M and a potential drop about 2 V or higher;
- A decrease in salt precipitation on the concentrating membrane surface due to the reduced water splitting rate at anion exchange membrane and elimination of

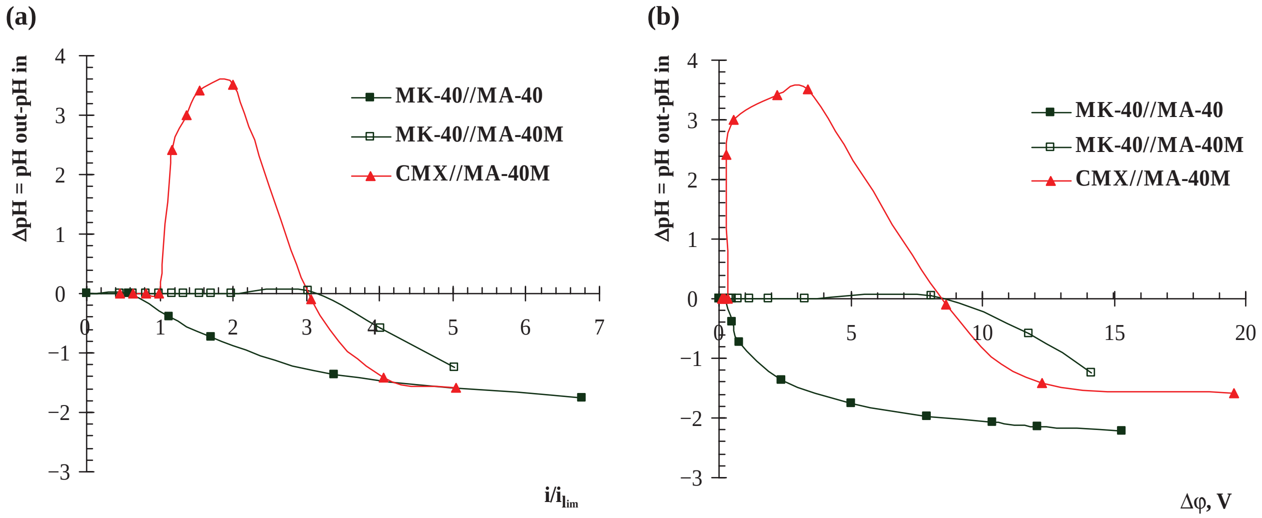

Fig. 5. Difference of pH in the outlet and inlet solutions of the desalination channel vs. the total current divided by the limiting current (a) and potential drop over a cell pair (b). $C = 0.005$ M; $h = 1$ mm; $S = 3 \times 3$ cm^2 $V = 1.6$ cm s^{-1}.

pH growth on the concentrating side of the membrane;

- A growth in the pH of desalted solution that leads to an increase in the dissociation of weak acids, such as carbonic and silicic acids, and enhances the rate of their removal during ED/EDI.

At lower rate of membrane scaling in concentrating compartment, the frequency of acid rinsing of electrodialyzers' compartments is reduced. This leads to an increase in working hours and in annual output of the plant as well as to a decrease in water discharge. The membrane lifetime increases as well that result in reducing the number of membrane replacements.

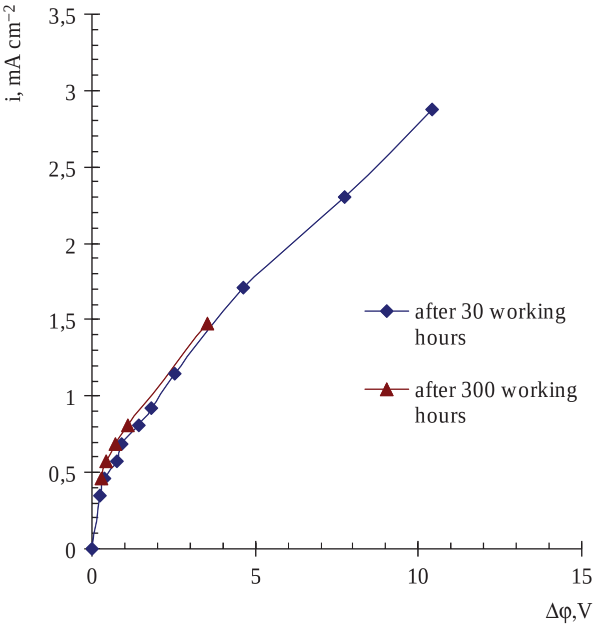

Fig. 6. Current–voltage curves of the desalination channel with SMX and MA-40M membranes. $C = 0.002$ M; $h = 1$ mm; $S = 3 \times 3$ cm^2 $V = 1.6$ cm s^{-1}.

4. Conclusion

From the practical point of view, the surface modification of MA-40 anion exchange membrane described above is of a great interest. First, the current efficiency increases considerably, in the considered case about 20–30% at the concentrations <0.01 M and the potential drops close to 2 V per cell pair, – due to the decrease in OH^- ion transport through the anion-exchange membrane. Second, the mass transfer of salt counterions grows because of decrease in the rate of H^+ ions generation (water splitting) that leads to increasing electroconvection. Besides, the membrane modification diminishes the salt precipitation on the concentrating membrane surface due to reducing the pH at this interface. As a result, the frequency of acid rinsing of electrodialyzers' channels and the water discharge decrease and the membrane lifetime increases. Finally, lower rate of H^+ and OH^- ions generation at anion-exchange membrane results in a growth of desalting solution pH that leads to an increase in dissociation degree of weak acids, e.g. carbonic and silicic acids. The last effect is very important for water deionization by electrodialysis.

Acknowledgement

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References

[1] R. Singh, Production of high-purity water by membrane processes, Desalination Water Treat., 3 (2009) 99–110.

[2] R.K. Nagarale, G.S. Gohil and K. Shahi Vinod, Recent developments on ion-exchange membranes and electro-membrane processes, Adv. Coll. Interf. Sci., 119 (2–3) (2006) 97–130.

[3] R. Simons, Electric field effects on proton transfer between ionizable groups and water in ion exchange membranes, Electrochim. Acta, 29(2) (1984) 151.

[4] G.Z. Nefedova, Z.G. Klimova and G.S. Sapozhnikova, Ion-exchange membranes. Granules. Powders. Catalogue (in Russian)/ed. A.B. Pashkov, Moscow, 1977.

[5] V.I. Zabolotskii, N.V. Shel'deshov and N.P. Gnusin, Dissociation of water molecules in systems with ion-exchange membranes, Russ. Chem. Rev., 57 (1988) 801–808.

[6] L.J. Bellamy, The Infrared Spectra of Complex Molecules, Chapman and Hall, 1980, pp. 299.

[7] V.A. Uglyanskaya, G.A. Tchikin, V.F. Selemenev and T.A. Zaviyalova T.A. Infrared spectroscopy of ion exchange materials, Voronezh: VGU, 1989, pp. 208.

[8] N.N. Belaid, B. Ngom, L. Dammak, C. Larchet and B. Auclair, Conductivité membranaire: interprétation et exploitation selon le modèle à solution interstitielle hétérogène, Eur. Polym. J., 35(5) (1999) 879–897.

[9] V.I. Zabolotsky and V.V.Nikonenko, Effect of structural membrane inhomogeneity on transport properties, J. Membr. Sci., 79 (1993) 181–198.

[10] N.P. Gnusin, N.P. Berezina, N.A. Kononenko and O.A. Dyomina, Transport structural parameters to characterize ion exchange membranes, J. Membr. Sci., 243 (1–2) (2004) 301–310.

[11] E. Volodina, N. Pismenskaya, V. Nikonenko, C. Larchet and G. Pourcelly, Ion transfer across ion-exchange membranes with homogeneous and heterogeneous surfaces, J. Coll. Interf. Sci., 285 (2005) 247–258.

[12] V.I. Zabolotsky, V.V. Nikonenko and N.D. Pismenskaya, On the role of gravitational convection in the transfer enhancement of salt ions in the course of dilute solution electrodialysis, J. Membr. Sci., 119 (2) (1996) 171–181.

[13] G.Yu. Lopatkova, E.I. Volodina, N.D. Pis'menskaya, Yu.A. Fedotov, D. Cot and V.V. Nikonenko, Effect of chemical modification of ion-exchange membrane MA-40 on its electrochemical characteristics, Russ. J. Electrochem., 42(8) (2006) 847–854.

[14] E.I. Belova, G.Yu. Lopatkova, N.D. Pismenskaya, V.V.Nikonenko, C. Larchet and G. Pourcelly, Effect of anion-exchange membrane surface properties on mechanisms of overlimiting mass transfer, J. Phys. Chem. B, 110(27) (2006) 13458–13469.