

ELECTROCHEMICAL STABILITY OF STRONG BASIC ANION EXCHANGE MEMBRANES IN CONDITIONS OF HIGH INTENSIVE ELECTRODIALYSIS PROCESS

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Abstract

A study of the stability of strongly basic anion-exchange membranes under intense current regimes. Studied in detail the process of dissociation of water molecules at current densities above the limit for commercially available strong base anion exchange membrane MA-41 (JSC "Schekino-Nitrogen", Russia) and AMH (the production of JSC "Mega", Czech Republic) in a high-intensity electrodialysis 0.01M sodium chloride. In current-limiting mode in the surface layer of strongly basic anion exchange membranes fixed thermohydrolysis process quaternary ammonium bases to form the catalytically active reaction of dissociation of water in the fixed amine.

Key words: anion exchange membrane, the dissociation of water, stability, thermal hydrolysis, transport of ions, the limiting current, current-voltage characteristics.

1. INTRODUCTION

The heightened interest of researchers to anion exchange membranes is caused not just by the fact that the functional groups of anion exchange membranes are less resistant during the electrodialysis process than the functional groups of cation exchange membranes, but also by the possibility of transformation of amino groups of membranes during their exploitation, which leads to changes in contributions of coupled effects of concentration polarization to mass transfer of salt ions and products of water dissociation. Moreover, the peculiarities of the ion transport through anion exchange membranes are also governed by the microrelief of their surface. As it was shown in majority of theoretic works [Nikonenko 2010], the typical for heterogeneous membranes alternation of areas of ion exchange material and insulating surface must aid to electroconvection, while its impact on general mass transfer may be dominating in case of size of these areas being comparable with diffusion layer thickness [Zabolotsky 1998]. On the other hand, the changes in alkaline properties of the amino groups of membranes leads to onset of the another effect of concentration polarization – water dissociation at membrane/solution interphase boundary [Rubinstein 2000]. Also it is important that the hydroxyl ions produced during the water dissociation are able to significantly change the structure and the chemical composition of surficial layer of the anion exchange membranes. It was previously shown [Chermit 2011] that the OH⁻ ions participate in thermal hydrolysis of quaternary ammonium bases, which occurs at the anion exchange membrane/solution boundary according to Hoffmann mechanism and changes the composition of surficial layer of an anion exchange membrane [Hwang 2006]. This explains high intensity of the water dissociation reaction on commercial strongly alkaline AMH and MA-41 anion exchange membranes, mostly containing quaternary ammonium groups which may not be active in the water dissociation reaction according to catalytic activity series of ion exchange groups presented in [Zabolotsky 1988].

This way the question about the ways of improving the chemical stability specifically of strongly alkaline anion exchange membranes under high current densities in membrane systems, and also the problem of searching for the novel methods to enhance the electrotransport and exploitation characteristics of these membranes, are still open.

The aim of this work was to study the stability of ion exchange membranes in conditions of intensive electrodialysis and to investigate the water dissociation process under current densities higher than the limiting current density using the commercial strongly alkaline MA-41 (ShchekinoAzot Ltd., Russia) and AMH (Mega a.s., Czech Republic) anion exchange membranes.

2. EXPERIMENTAL

2.1 Materials and methods

The subjects of study were heterogeneous MA-41 (ShchekinoAzot Ltd.), manufactured in Russia, and Ralex AMH (Mega a.s.), manufactured in Czech Republic, anion exchange membranes. The studies were conducted during the electrodialysis of 0,01 M NaCl solution in galvanostatic mode using the technique described previously described in details [Zabolotsky 2011], with universal flow rate through all cameras of 3 L per hour. For this task the electrochemical cell was assembled, the membrane stack of which contained 6 flow-through independent cameras: two investigation chambers (1 – concentration chamber (CC), 2 – desalination chamber (CO)), two buffer chambers (3 and 4), two electrode chambers (5 and 6). Intermembrane space was 1 mm and the polarized area was 30 cm². For the prevention of chlorine production and loss of solution caused by this process, sodium sulfate solution was used for the electrode chambers.

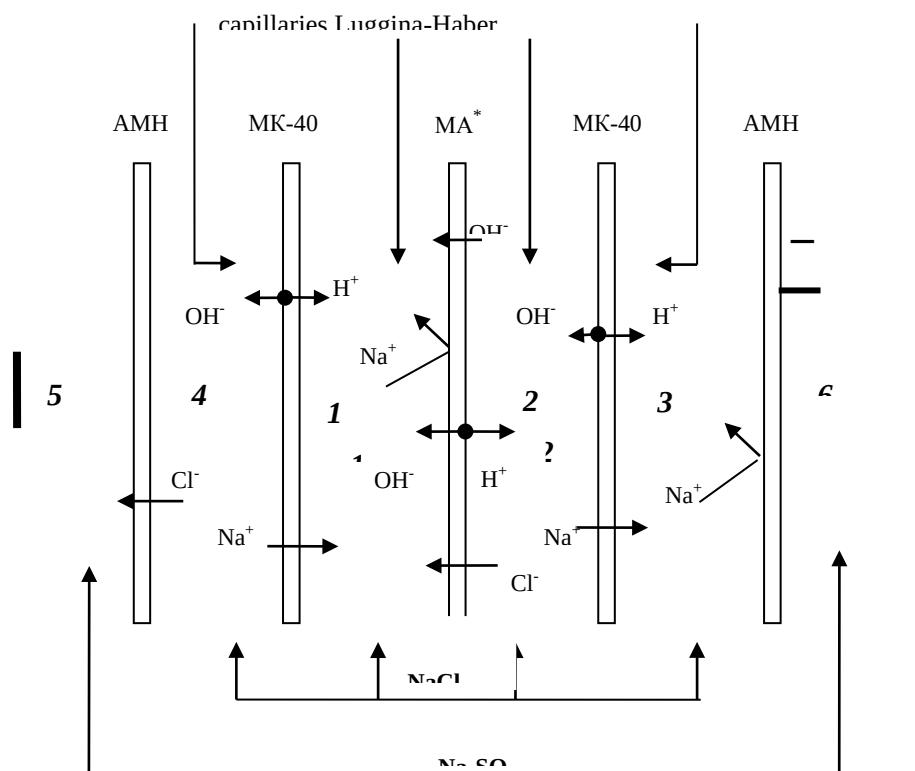


Fig. 1. The scheme of electrodialysis cell for desalination

* MA - investigated anion-exchange membrane

3. RESULTS AND DISCUSSION

Literature data analysis shows that the water dissociation reaction actively occurs at the commercial strongly alkaline MA-41 and AMH membranes [Zabolotsky 2012]. At the same time, this process is more intensive in case of AMH membrane, mainly containing quaternary ammonium bases, and the transport number of OH⁻ ions reach values as high as 0,38. For the MA-40 membrane, containing secondary and tertiary amines, the rate of water dissociation (transport number of OH⁻ reaches 0,25) is higher than for strongly alkaline MA-41 membrane (transport number of OH⁻ reaches 0,19).

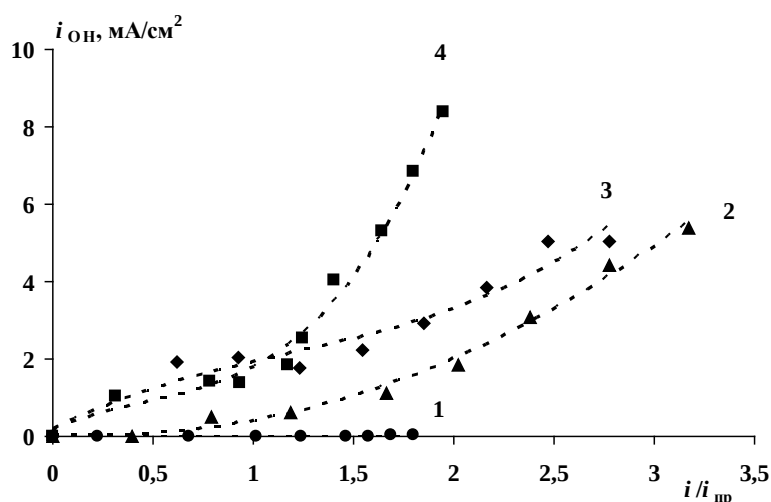


Fig. 2 Partial CVC by hydroxyl ions for membranes

MA-40M (1), MA-41 (2), MA-40 (3) и AMH (4) in 0.01 M NaCl

at the rotational speed of the membrane disk 100 rev / min

At the first look, these data are inconsistent with series of catalytic activity of ionogenic groups in water dissociation reaction [Zabolotsky 1988]. However it was found that during the dissociation reaction the produced hydroxyl ions cause hydrolysis of quaternary ammonium bases in surficial layer of membrane [Shaposhnik 2008, Choi 2003, Sata 1996].

As a result of this reaction, the catalytically active ionogenic groups containing tertiary amines are formed, and under the harsher condition the loss in exchange capacity of membrane can be observed. Basing on analysis of the cited works it may be suggested that the thermal hydrolysis of the quaternary ammonium bases occurs in surficial layer of membranes under the intensive current modes, forming the fixed amino groups catalytically active in water dissociation reaction [Zabolotsky 2012].

To assess the stability of the anion exchange membranes, their current-voltage characteristics (CVC) were measured after the electro dialysis with the current three times higher than the limiting current density lasting 3 hours. Plots illustrate the CVC of virgin MA-41 membranes (Fig. 3, curve 1) and after its work in electro dialysis under the current density of 10 mA/cm² (Fig 3, curve 2), and also of channels formed by MK-40 and MA-41 membranes before and after their work under current (Fig. 4). The decrease in plateau length can be observed in CVC of MA-41 membrane, indicating the partial transformation of the quaternary ammonium bases in the tertiary amino groups, which catalyze the water dissociate, hence hastening the onset of overlimiting conditions, during the thermal hydrolysis.

The limiting current density was determined for MA-41 membrane during the electro dialysis desalination of 0,01 M NaCl solution: it was 3,36 mA/cm² for virgin membrane and 4,45 mA/cm² for the membrane which received the extra treatment for 3 hours.

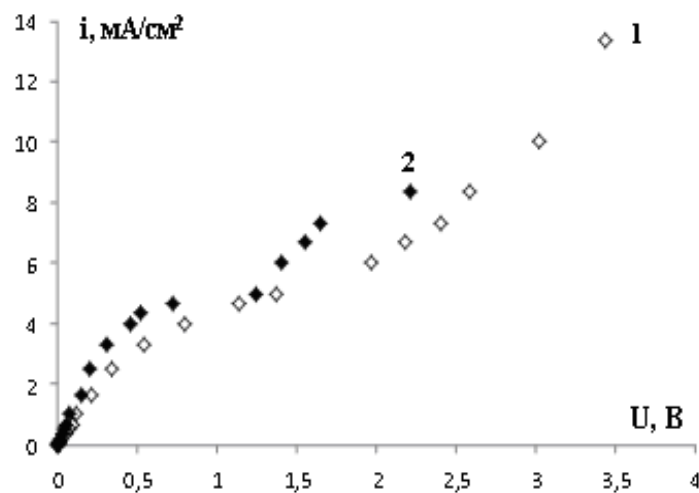


Fig. 3 General CVC membrane MA-41

1 - initial membrane 2 - membrane after polarization treatment for 3 hours

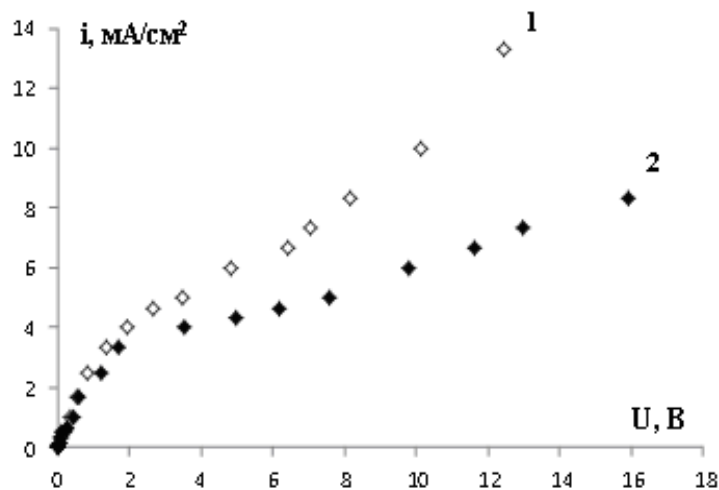


Fig. 4 The CVC of desalting chambers containing:

1 – initial membranes MK-40 and the initial membrane MA-41,
2 - membranes MK-40 and MA-41, after polarization treatment for 3 hours

The similar study was conducted for Ralex AMH membrane as well (Fig. 5 and 6). By determination of limiting current it was found that, in contrast to MA-41 membrane, the limiting current density is not affected that strongly during the electrodialysis desalination – it was 4,15 mA/cm² before and 3,9 mA/cm² after treatment.

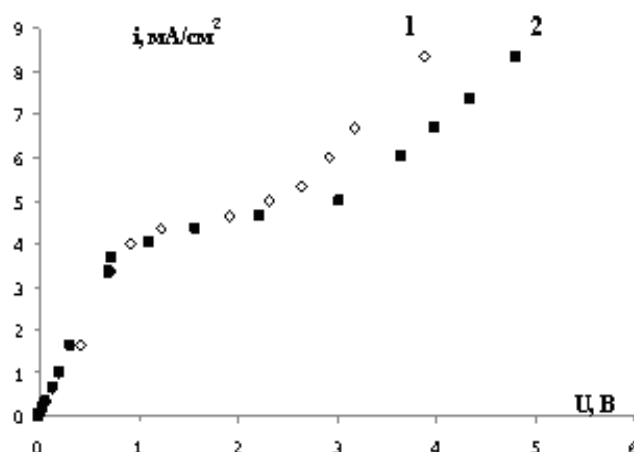


Fig. 5. The general CVC of membrane AMH

1 - initial membrane 2 - membrane after polarization treatment for 3 hours

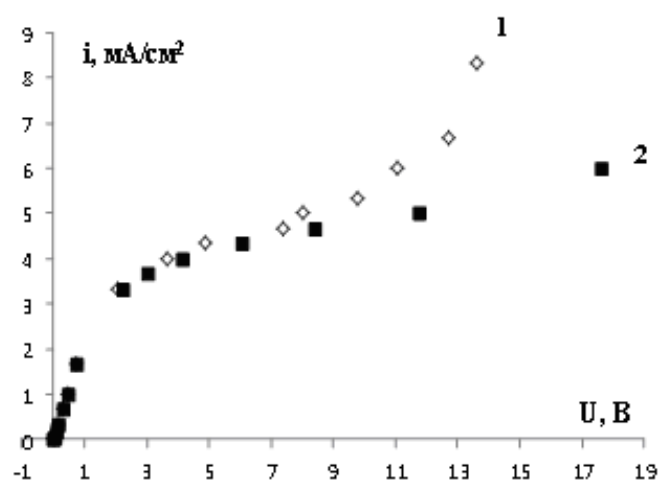


Fig. 6. The CVC of desalting chambers containing:

1 – initial membranes MK-40 and the initial membrane AMH,

2 - membranes MK-40 and AMH, after polarization treatment for 3 hours

The similar pattern is also observed for the dependences of pH from current density (Fig. 7). The increase in pH of treated solution is observed for chambers formed by MK-40 membrane and MA-41 membrane after the electrodialysis treatment (curves 3 and 4), compared to chambers formed by MK-40 and virgin MA-41 (curves 1 and 2).

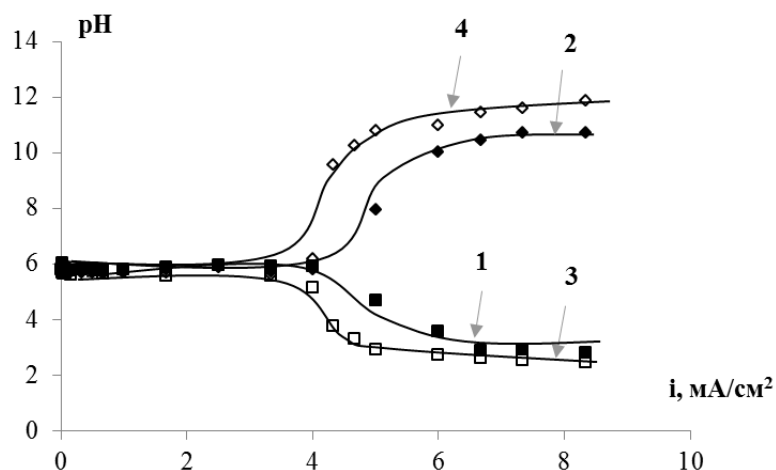


Fig. 7 The pH vs. current density for the MA-41

1 and 2 - the pH of the solution in chambers of electro dialysis cell with initial membrane,
3 and 4 - the pH of the solution in chambers of electro dialysis cell with membrane after polarization treatment for 3 hours at a current density of 10 mA/cm^2

In the electro dialysis cell chambers formed by MK-40 and AMH membranes a similar process is observed as in the case of the membrane pair formed by MK-40 and MA-41 membranes (Fig. 8).

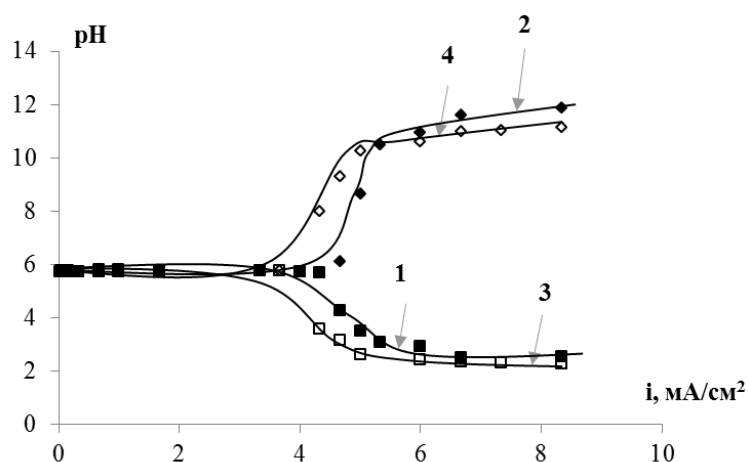


Fig. 8 The pH vs. current density for the Ralex AMH

1 and 2 - the pH of the solution in chambers of electro dialysis cell with initial membrane,
3 and 4 - the pH of the solution in chambers of electro dialysis cell with membrane after polarization treatment for 3 hours at a current density of 10 mA/cm^2

4. CONCLUSIONS

The chemical stability of strongly basic anion-exchange membranes MA-41 and Ralex AMH was investigated during electro dialysis desalination of 0.01 M sodium chloride solution.

Chemical stability evaluation was conducted based on the current-voltage and mass transfer characteristics of the initial membranes and the membranes subjected to the processing at a current density three times higher than the limiting current density ($i_{\text{lim}} = 4 \text{ mA/cm}^2$).

It was established that the limiting current density during electrodialysis desalination of 0.01M sodium chloride solution for the initial MA-41 membrane was 3.36 mA/cm^2 and for the membrane which has undergone additional polarization treatment for 3 hours - 4.45 mA/cm^2 . In addition, the current-voltage characteristics of the treated membrane MA-41 shows a decrease in the length of the limiting current plateau, indicating a partial transition of quaternary ammonium bases as a result of thermal hydrolysis into tertiary amino groups which will cause more rapid onset of the overlimiting state (intense water dissociation reaction occurs at the membrane / solution interface).

In contrast to the MA-41 membrane, the limiting current density on the Ralex AMH membrane during electrodialysis desalting changes insignificantly - from 4.15 mA/cm^2 to 3.9 mA/cm^2 before and after polarization treatment. Higher mass transfer coefficient of salt ions on the Ralex AMH compared with the MA-41 is associated with a greater proportion of a conducting surface.

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