Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2014.980975

56 (2015) 3228–3232
December

Taylor & Francis
Taylor & Francis Group

The influence of activation of heterogeneous ion-exchange membranes on their electrochemical properties

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Received 28 July 2014; Accepted 7 October 2014

ABSTRACT

The aim of this work was to find optimal conditions of activation of heterogeneous ion-exchange membranes. Commercial both cation-exchange and anion-exchange membranes were used in this study. The activation procedure consists in alternating immersion of a heterogeneous membrane into aqueous solutions of 1 M HCl and 1 M NaOH. The activation procedure of cation-exchange membranes consists in a multiple conversion of the Na^+ membrane form to the H^+ form and back and that of anion-exchange membranes in a multiple conversion of the Cl^- membrane form to the OH^- form and back. An efficient activation of anion exchange membranes strongly depends on the total time of treatment and on the number of exchange steps and requires at least a 5-d treatment and two exchanges of ions or 4.5 h treatment and four exchanges of ions. An efficient activation of cation exchange membranes is a rather fast process requiring about 3.5 h and three exchanges of ions.

Keywords: Heterogeneous ion-exchange membranes; Electrochemical properties; Activation

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1. Introduction

Heterogeneous ion-exchange membranes are used in various applications such as electrodialysis, electrophoresis, and electrodeionization [1–4]. The heterogeneous ion-exchange membrane consists of an ion-exchange resin, a polymer binder and a reinforcing fabric. An ion-exchange resin gives the membrane the required electro-chemical properties, a polymer binder gives the membrane good mechanical properties and a reinforcing fabric ensures dimensional stability of membranes during swelling and also improves membrane mechanical properties.

Commonly used ion-exchange resins consist of a cross-linked polymer matrix with anion or cation-active groups which are uniformly distributed in the matrix. A strongly acidic cation-exchange resin contains negatively charged SO_3^- groups which are fixed to the polymer matrix and exchangeable cations. A

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Presented at the MELPRO 2014 Conference Membrane and Electromembrane Processes, 18–21 May 2014, Prague, Czech Republic

strongly basic anion-exchange resin consists of fixed quaternary ammonium groups and exchangeable anions. Commercial ion-exchange resins differ in the type and concentration of ion-exchange groups and the degree of crosslinking [5]. They are mainly supplied in the form of small beads that are not suitable for the production of heterogeneous membranes. The suitable form is a fine powder which can be obtained by grinding of beads. The powdered resin is mixed into a melted polyolefin binder and the mixture is extruded into the shape of a flat membrane and reinforced with a fabric [6,7].

Heterogeneous ion-exchange membranes must be activated before their insertion in an application device. The activation is carried out by immersions, in turns, in aqueous solutions of acids and bases. During the activation, membranes swell and ion exchange groups dissociate. If the activation process is not complete, a part of the ion-exchange groups are not dissociated and cannot participate in the transfer of ions [8].

The swelling of an ion exchange resin and ion exchange kinetics depend on the degree of crosslinking and on the type of ion exchange groups [9–11]. Some producers of ion-exchange membranes use the same process of activation for the cation- and anion-exchange membranes and do not respect the different procedural and time requirements for each type of membrane that are required for complete dissociation of the functional groups.

The aim of this work was to find the optimal conditions of the activation process to achieve the perfect opening structure of heterogeneous cation- and anion-exchange membranes and to achieve optimal electrochemical properties in the shortest possible time.

2. Experimental

2.1. Materials

Heterogeneous cation-exchange membranes CM-PES and anion-exchange membranes AMH-PES (both MEGA a.s., Czech Republic) were used in this study. CM-PES membranes comprised a finely ground strongly acidic gel ion exchanger, based on sulphonated styrene–divinylbenzene copolymer, polyethylene binder and a polyester fabric reinforcement. AMH-PES membranes comprised a finely ground gel type 1 strong-base anion exchanger, based on styrene–divinylbenzene copolymer with quaternary ammonium groups, polyethylene binder and a polyester fabric reinforcement.

2.2. Membrane activation

The membrane samples were subjected to an activation process prior to electrochemical properties measurement [12]. The activation procedure consisted in an alternating conversion of the cation-exchange membrane to the H^+ and Na^+ form or the anion-exchange membrane to the OH^- and Cl^- form by exposing it to aqueous solutions of 1 M HCl and 1 M NaOH for a given time. The ratio of the membrane volume to the volume of reagent solution was 1:20. The activation was carried out so that the cation-exchange membranes ended in the H^+ form and the anion-exchange membranes ended in the Cl^- form. Six different procedures differing in a number and time of steps were applied to the examination of anion-exchange membranes (Table 1) and six different procedures were also applied to the examination of cation-exchange membranes (Table 2).

2.3. Electrical resistance measurement

The membranes after activation were equilibrated in 0.5 M KCl solution for 24 h. The anion-exchange membranes were in Cl^- form and cation-exchange membranes were in K^+ form. The membranes were placed in a thermostatic two-compartment cell. The cell was filed with 0.5 M KCl solution. The temperature of the cell was maintained at 25°C. The four-electrode method was used for determination of the membrane resistance. Electrical conductivity of the membranes was measured by the conductometer Philips PW9527 at 4 kHz of alternating current (AC) and subsequently at direct current (DC) 10 mA that was generated by the source of stabilized constant current of own production. The current was supplied to the measuring cell by a pair of working platinum electrodes. The active area of Pt electrodes was 1 cm^2. The DC was measured by Multimeter Hewlett Packard 34401A. The potential drop across the membrane at current was recorded using standard electrodes Ag/AgCl in saturated KCl and measured by the digital voltmeter Meratronik V544. The effective membrane area (A) in the measuring cell was 0.7854 cm^2, so that the current density was 12.7 mA/cm^2. Areal resistance (R_A) in 0.5 M KCl solution was calculated from measured data according the equations:

$$R_M = R_{(M+S)} - R_S \tag{1}$$

$$R_A = R_M \times A \tag{2}$$

Table 1
The scheme of activation of anion-exchange membranes

	Time					
Reagent	(min)	(min)	(min)	(min)	(min)	(min)
H_2O	10	10	30	30	60	1,440
1 M NaOH	10	10	30	30	60	1,440
H_2O	10	10	30	30	60	1,440
1 M HCl	10	10	30	30	60	1,440
H_2O	10	10	30	30	60	1,440
1 M NaOH		10		30		
H_2O		10		30		
1 M HCl		10		30		
H_2O		10		30		
Total time of activation	50	90	150	270	300	7,200

Table 2
The scheme of activation of cation-exchange membranes

	Time					
Reagent	(min)	(min)	(min)	(min)	(min)	(min)
H_2O	10	10	30	30	60	1,440
1 M HCl	10	10	30	30	60	1,440
H_2O	10	10	30	30	60	1,440
1 M NaOH	10	10	30	30	60	1,440
H_2O	10	10	30	30	60	1,440
1 M HCl	10	10	30	30	60	1,440
H_2O	10	10	30	30	60	1,440
1 M NaOH		10		30		
H_2O		10		30		
1 M HCl		10		30		
H_2O		10		30		
Total time of activation	70	110	210	330	420	10,080

where R_M is the membrane resistance, R_S is the solution resistance, $R_{(M+S)}$ is the resistance of membrane and solution.

3. Results and discussion

3.1. Anion-exchange membranes

The dependence of areal resistance of the anion-exchange membranes on the total time of their activation is shown in Figs. 1 and 2. From the viewpoint of efficiency of membranes, it is desirable to achieve the lowest resistances possible. It can be seen that the resistances depend considerably on the time of activation. Their lowest values were obtained with a rather long total time of activation of 7,200 min (5 d). However, the values of areal resistance depend not only on the total time of activation but also on the number of activation steps: the membranes activated with nine steps (four exchanges of ions: $Cl^- \rightarrow OH^- \rightarrow Cl^- \rightarrow OH^- \rightarrow Cl^-$) exhibit resistances lower than those with five steps (two exchanges of ions: $Cl^- \rightarrow OH^- \rightarrow Cl^-$) and the virtually same time.

3.2. Cation-exchange membranes

The dependence of areal resistance of the cation-exchange membranes on the total time of their activation is shown in Figs. 3 and 4. Here again, the shortest activation time (70 min) is insufficient to achieve optimal electrochemical properties of membranes. Cation-exchange membranes need however much shorter times to attain equilibrium values: the total activation time of 210 min with three exchanges of ions ($Na^+ \rightarrow H^+ \rightarrow Na^+ \rightarrow H^+$) is quite sufficient. The number of activation steps plays here a small role.

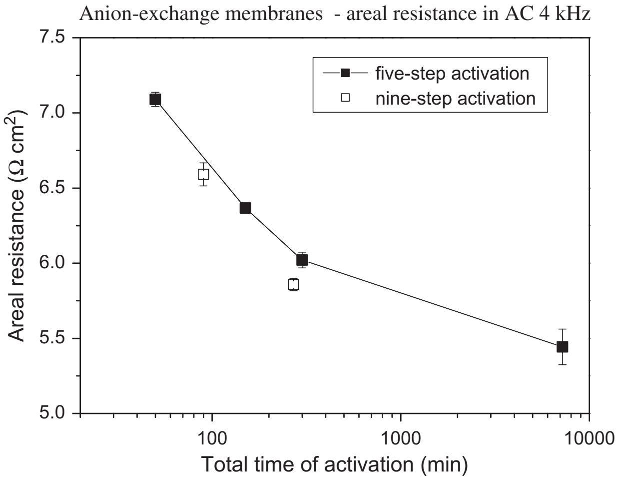

Fig. 1. Dependence of the areal resistance in AC 4 kHz on total time of activation of anion-exchange membranes.

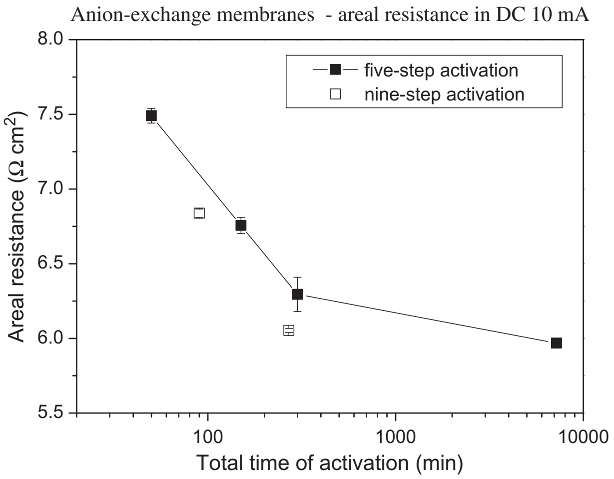

Fig. 2. Dependence of the areal resistance in DC 10 mA on total activation time of anion-exchange membranes.

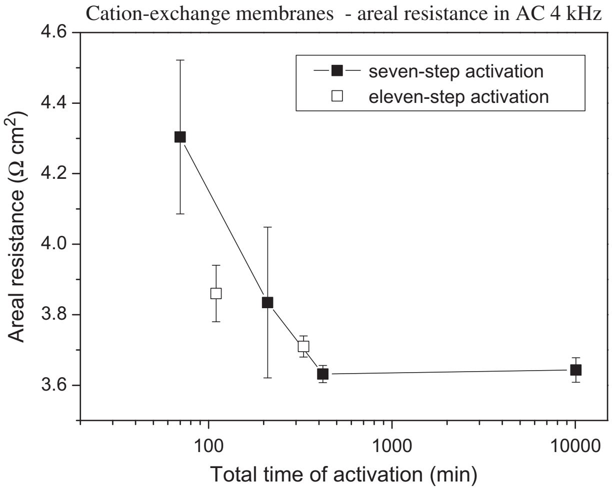

Fig. 3. Dependence of the areal resistance in AC 4 kHz on total time of activation of cation-exchange membranes.

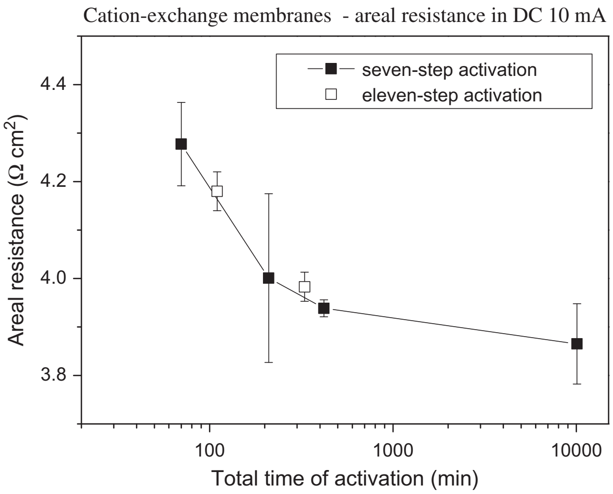

Fig. 4. Dependence of the areal resistance in DC 10 mA on total activation time of cation-exchange membranes.

4. Conclusions

The efficiency of the activation procedure of heterogeneous anion-exchange membranes by multiple immersions of membranes into aqueous solutions of 1 M HCl and 1 M NaOH strongly depends on the total time of treatment and on the number of exchanges of ions. An efficient activation of heterogeneous anion-exchange membranes requires at least a 5-d treatment and two exchanges of ions ($Cl^- \rightarrow OH^- \rightarrow Cl^-$) or 4.5 h treatment and four exchanges of ions ($Cl^- \rightarrow OH^- \rightarrow Cl^- \rightarrow OH^- \rightarrow Cl^-$).

An efficient activation of heterogeneous cation-exchange membranes is a rather fast process. It requires about 3.5 h treatment and three exchanges of ions ($Na^+ \rightarrow H^+ \rightarrow Na^+ \rightarrow H^+$).

Acknowledgments

This work was supported by Ministry of Industry and Trade of the Czech Republic under the project number FR-TI4/507 the grant program TIP.

References

[1] H. Strathman, Ion-exchange membrane separation processes, Membr. Sci. Technol. 9 (2004) 1–348.

[2] H. Strathman, Electromembrane processes: Basic aspects and applications, Compr. Membr. Sci. Eng. 2 (2010) 391–429.

[3] V.V. Nikonenko, N.D. Pismenskaya, A.G. Istoshin, V.I. Zabolotsky, A.A. Shudrenko, Description of mass transfer characteristics of ED and EDI apparatuses by using the similarity theory and compartmentation method, Chem. Eng. Process. 47 (2008) 1118–1127.

[4] V.K. Shahi, B.S. Makwana, S.K. Thampy, R. Rangarajan, A novel electrodialyzer for the production of demineralized water by electrodialysis, Desalination 151 (2002) 33–42.

[5] J. Naveh, Y. Marcus, The dependence of the swelling of ion-exchange resins on their crosslinking, J. Chromatogr. 148 (1978) 495–499.

[6] J. Křivčík, J. Vladařová, J. Hadrava, A. Černín, L. Brožová, The effect of an organic ion-exchange resin on properties of heterogeneous ion-exchange membrane, Desalin. Water Treat. 14 (2010) 179–184.

[7] K. Bouzek, S. Moravcová, J. Schauer, L. Brožová, Z. Pientka, Heterogeneous ion-selective membranes: The influence of the inert matrix polymer on the membrane properties, J. Appl. Electrochem. 40 (2010) 1005–1018.

[8] F. Karas, J. Hnát, M. Paidar, J. Schauer, K. Bouzek, Determination of the ion-exchange capacity of anion-selective membranes, Int. J. Hydrogen Energy 39 (2014) 5054–5062.

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

[10] N.P. Berezina, N.A. Kononenko, O.A. Dyomina, N.P. Gnusin, Characterization of ion-exchange membrane materials: Properties vs structure, Adv. Colloid Interface Sci. 139 (2008) 3–28.

[11] V.V. Nikonenko, N.D. Pismenskaya, E.I. Belova, P. Sistat, P. Huguet, G. Pourcelly, C. Larchet, Intensive current transfer in membrane systems: Modelling, mechanisms and application in electrodialysis, Adv. Colloid Interface Sci. 160 (2010) 101–123.

[12] W. Garcia-Vasquez, R. Ghalloussi, L. Dammak, C. Larchet, V. Nikonenko, D. Grande, Structure and properties of heterogeneous and homogeneous ion-exchange membranes subjected to ageing in sodium hypochlorite, J. Membr. Sci. 452 (2014) 104–116.