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Effects of the surface layer structure of the heterogeneous ion-exchange membranes on their impedance

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ABSTRACT

Experimental details of measuring the impedance of heterogeneous membranes by the contact method with graphite electrodes in an aqueous medium were considered. It was shown that the inductive and capacitive components of the cell impedance lead to overestimation of the ionic resistance of heterogeneous and homogeneous membranes by 9% and 27%, respectively. Considering the physicochemical structure of heterogeneous membranes and proceeding from the Randles circuit, an equivalent electrical circuit capable of correct impedance description for heterogeneous membranes was proposed. The pressure effect on the membrane impedance was studied. An increase in the pressure on the electrodes to 2 MPa was shown to result in a considerable increase in the polarization resistance of heterogeneous membranes and decrease in the ionic resistance.

1. Introduction

Membrane technologies are utilized in many branches of industry. Approaches that use ion exchange membranes or membranes with an active ion exchange layer are among the most demanded ones. These types of membranes are widely used in water desalting [1,2] for alternative power generation [3,4] and for electrosynthesis [5,6].

Homogeneous membranes, which represent uniform ion exchange resin films, are used most often in fuel cells and in electrosynthesis. The manufacture of these membranes is complicated, and, therefore, they are expensive. Desalting is performed using much less expensive heterogeneous membranes, which are composites consisting of a reinforced polyethylene or polypropylene matrix and an ion exchange resin as a filler [7]. The surface of these membranes is made of an inert polymer by 80–90%, while the volume fraction of the ion exchange resin is about 60% [8]. The presence of a considerable amount of a non-conductive phase on the surface of heterogeneous ion exchange membranes was demonstrated by electron microscopy and by electrochemical methods [9,10].

Ionic conductivity, which is important for practical application of ion exchange membranes, is measured by impedance spectroscopy. Methods for measuring ionic conductivity of membranes can be classified into contact and difference ones. Contact methods imply the direct attachment of electrodes to the membrane; however, this brings about uncertainty in the membrane/electrode contact impedance, solution of which requires additional effort [11,12]. The contact measurement of the impedance of heterogeneous membranes is often performed in a mercury cell [13]. However, this method has some considerable drawbacks. At the time of measurement the membrane can be partially dehydrated [14], which is especially true for thin samples. Toxic mercury, which contaminates the membrane surface, is used as electrodes. Therefore, other types of electrodes and non-destructive measurements in contact with water could provide a good alternative.

This paper describes the details of measuring the impedance of heterogeneous membranes by the contact method with graphite electrodes in water. The effects of pressure on the electrodes and the surface inhomogeneity on the impedance of heterogeneous membranes are considered. The trends listed above are analyzed both qualitatively and quantitatively using the equivalent circuit method. For homogeneous membranes, the equivalent electrical circuit (EEC) was based on the Randles circuit, which we modified to obtain the EEC for heterogeneous membranes [15].

2. Experimental

2.1. Materials

We used heterogeneous membranes, MC-40 and AMEX, and a homogeneous membrane, MF-4SC. The membrane composition, manufacturers and other characteristics are summarized in Table 1.

2.2. Equipment and configuration of the measuring cell

The measuring cell used in our work was a symmetric system of a membrane, graphite electrodes, current-carrying copper electrodes,

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Table 1
Characteristics of the ion exchange membranes.

Membrane	MF-4SC	MC-40	AMEX
Manufacturer	JSC Plastpolymer	JSC Shchekinoazot	JSC Mega
Production method	Extrusion	Hot pressing	
Functional groups	$R\text{-}SO_3^-$		$R'\text{-}NR_3^+$
Polymer base of the ion exchange resin	Perfluorinated copolymer	Styrene divinylbenzene copolymer	
Type	Homogeneous	Heterogeneous	
Thickness in the wet state, μm	100	510	770
Inert base	—	Polyethylene	

and 10-mm thick organic glass plates anchored by a spring assembly to maintain a constant pressure. The whole system was immersed in deionized water to maintain a 100% humidity.

The impedance was measured using a 2B-1 impedance meter in the frequency range of $1–6\cdot10^6$ Hz and an AC voltage of 100 mV. The data were approximated using a ZView program package. The membrane thickness was measured by a Mitutoyo micrometer, series 293. Deionized water was obtained using a Millipore water treatment setup (18.2 MΩ·cm).

2.3. Procedures

All cation exchange and anion exchange membranes were conditioned according to standard procedures [16]. For conversion to the sodium and chloride forms, membranes were successively kept in 0.1 M NaCl solutions for an hour and washed with deionized water three times. For removing the surface layer, membranes were polished on both sides in the wet state with the G44H sandpaper (grit size P1200) and, after polishing, the treated membrane was washed in deionized water.

The force by which the spring pressed on the cell was found using a force gauge, one end of the spring being secured and the other end being attached to the gauge. The spring assembly was stretched to the measuring cell size. The measured force was 49 N and remained constant for several hours. The pressure on the electrodes was changed by varying the electrode surface area and calculated as the ratio of the applied force to the electrode surface area.

The membrane impedance Z was analyzed in two ways, namely, as the Nyquist plots representing the dependence of the impedance complex number Im(Z) on the real part Re(Z) and as Bode phase plot representing the dependences of the phase angle θ between the ac voltage applied and the ac current arising in the system on the logarithm of the ac current frequency log(f).

At frequencies above 100 kHz, the true impedance value can be distorted by the impedances of the connecting wires and the measuring cell. The inductive and capacitive components for the cell were found by measuring the impedance of short electrodes and electrodes separated by an insulator of the same thickness as the membrane, and the result was subtracted from the obtained membrane impedance according to [17] using formula (1).

$$Z_{true} = (Z_m - Z_s)/(1 - Z_m/Z_o) \quad (1)$$

where Z_{true} is the true membrane impedance, Z_s is the short-cell impedance, Z_o is the open-cell impedance, and Z_m is the measured impedance value.

3. Equivalent electrical circuit of a homogeneous membrane

There is no common approach to the design of equivalent electrical circuits (EEC) describing the impedance Nyquist plots for ion exchange membranes. This is largely caused by different methods for impedance measurement and, as a consequence, basically different resistances, capacitances, and inductances formed in the system. The greatest progress was made in the modeling of ion-exchange membrane impedance obtained by difference method, where the three-layer system consisted of a cation-exchange membrane and two adjoining diffusion layers was studied [18,19]. However, it is difficult to describe the contact impedance of membrane with the help of the above approaches without adjacent solutions obtained with ideally polarizable electrode. In order to compose an EEC for contact measurements for a heterogeneous membrane, we started out from the Randles circuit adjusted to a homogeneous medium with mainly ionic charge carriers [15] (Fig. 1a).

This circuit (Fig. 1a) reflects rather comprehensively the physical scheme of the cell. The ionic resistance of the sample is reflected by the resistive element (R_m), while the processes of electrical double layer (EDL) charge/discharge at the membrane – electrode boundary, dielectric relaxation of the sample, and diffusion toward the electrodes are represented by the capacitors C_d and C_g and by the Warburg element (W), respectively.

However, even for a model system, the EEC of a homogeneous medium with mainly ionic charge carriers (Fig. 1a) may lead to a faulty interpretation of approximation of experimental data, depending on the relationship between the ion mobility and concentration [15], because the equivalent circuit approach is not sufficiently rigorous. In practice, the behavior of the membrane is not ideal, which is related to the physicochemical inhomogeneity of both the test material bulk and the electrode/sample interface [20,21]. This brings about a poor approximation of experimental data.

Therefore, the electrode capacitor C_d and the Warburg element W are usually replaced by constant phase elements (CPEs) (Fig. 1b), whose impedance is determined from formula (2), or, alternatively, dispersion equations are used to find the relaxation time spectrum [22]. It is noteworthy that the "apparent" R_m value includes the contact resistance, which is determined by the quality of the contact between

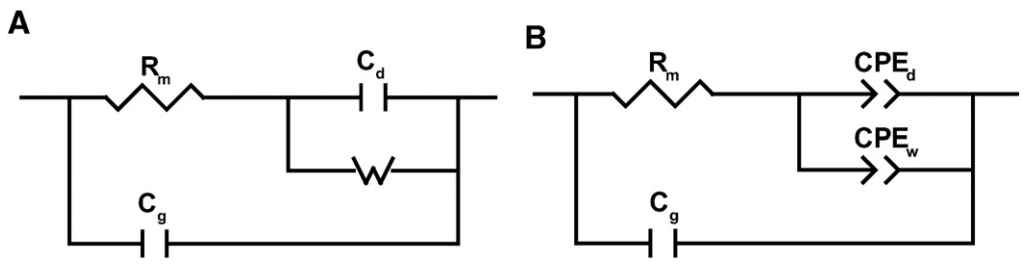

Fig. 1. (*a*) EEC for a conductor with predominantly ionic conduction, (*b*) EEC for a homogeneous membrane used in this work. (The ideal capacitor and the Warburg element were replaced by constant phase elements).