Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2014.981930

56 (2015) 3207–3210
December

Taylor & Francis
Taylor & Francis Group

Chronopotentiometry and impedancemetry of homogeneous and heterogeneous ion-exchange membranes

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Received 28 July 2014; Accepted 7 October 2014

ABSTRACT

It is known that the behavior of a membrane with homogeneous and heterogeneous surface under the same current density is different. In order to find out this difference, a two-dimensional non-stationary model of mass transfer through electrically inhomogeneous surface of ion-exchange membrane under direct current is proposed. In this paper, the general formulation of the boundary conditions at the conductive sections has the form of the integral function of the local current density. The problem was solved by applying an electric current stream function, which is quite similar to the stream function in hydrodynamics. For the first time, it is proved that the distribution of current lines over the conductive sections of the membrane is not uniform. It is shown experimentally and theoretically that the shape of chronopotentiograms and electrochemical impedance spectra changes with changing conductive portion of the ion-exchange membrane surface.

Keywords: Mass transfer; Electromembrane system; Purification of water solutions; Water treatment; Mathematical modeling; Partial differential equations; Electrochemical impedance spectroscopy; Chronopotentiometry

1. Introduction

Non-stationary electrochemical methods of ion-exchange membrane investigation, such as chronopotentiometry [1–3] and electrochemical impedance spectroscopy [4], are effective tools for the determination of important characteristics such as the diffusion layer thickness [5], the rate of H^{+}, and OH^{-} ions generation [6]. Most of the mathematical models of ion transport in electrochemical systems are limited to a one-dimensional geometry [7]. The complexity of mathematical description dramatically increases when passing to the two-dimensional modeling. Nevertheless, the necessity

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

of understanding the role of the heterogeneous structure of the membrane surface is an important issue.

The mass transfer through the ion-exchange membrane with a heterogeneous surface was theoretically studied by Rubinstein et al. [8]. They have formulated and solved the boundary value problem for the stationary ion transport in diffusion boundary layer (DBL) near the heterogeneous surface. They have found that the limiting current density for this system is lower than for the homogeneous membrane. One of the basic assumptions was the condition of the uniform distribution of current density over the cross section of the conductive part.

2. Theory

In this paper, we propose a two-dimensional non-stationary model of ion transport through the membrane and two adjacent DBLs. Ion transport in the system is described by the Nernst–Planck and the material balance equations under the local electroneutrality assumption. A new formulation of the boundary conditions at the conductive areas is proposed. In our model, the current, which is the integral of the local current density, is given instead of uniform distribution condition of the current density at the conductive region:

$$j_{\mathrm{av}} = \frac{1}{L}\int_{0}^{L} j_x\left(t, -\delta^{I}, y\right)\mathrm{d}y = \frac{1}{L}\int_{0}^{L} j_x\left(t, \mathrm{d} + \delta^{II}, y\right)\mathrm{d}y = \mathrm{const.} \tag{1}$$

This condition is more general, because it does not impose any restrictions on the distribution of the local current density. Solution of the problem with the condition (1) is possible by using an electric current function η. For the first time, this concept was introduced by Taylor and Sharman [9] and used by Pismenskiy et al. [10] in the mathematical description of gravitational convection in the membrane system.

The membrane considered in this study is electrically heterogeneous from the side of desalination chamber (Fig. 1) and homogeneous from the other side.

The calculated concentration distribution near the surface of the membrane and the current lines are shown in Fig. 2. In the case of heterogeneous surface, electric current can flow only through conductive portions of the surface, whereby the local current density in these regions is much higher than the average current density. Moreover, there is irregular distribution of current lines inside the conductive regions: the current lines density is higher near the boundary of this region with a non-conductive surface section (Fig. 2(b)). The calculated distribution is significantly different from the distribution postulated in the work of Rubinstein et al. Considerable unevenness in the distribution of current density near the border between conducting and non-conducting regions causes a large value of the tangential component of the current, which can be essential in describing overlimiting current modes. Concentration of the solution near the surface of the conductive region is distributed more evenly than the current density (Fig. 2(a)) due to the contribution of the tangential component of the ion flux density.

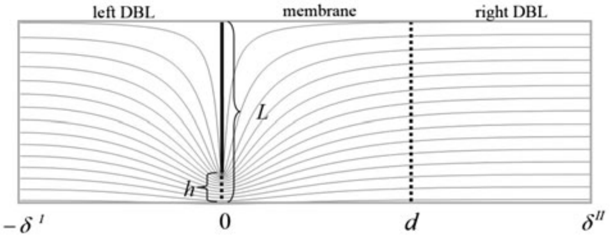

Fig. 1. Schematic representation of the system under study. Solid black line indicates the non-conductive surface portion (length h), dotted – conductive. The total length of the section is L. Calculated distribution of current lines shown by smooth curved lines.

If DBL (δ) in systems with heterogeneous and homogeneous membranes is the same, the concentration polarization in the case of a heterogeneous membrane will be higher: the boundary concentration near a conducting region is smaller (Fig. 2(a)), and the potential drop is higher.

3. Results and discussion

Comparison of calculated chronopotentiogramms for the case of homogeneous and heterogeneous membranes is shown in (Fig. 3(a)). Curve 1 is calculated for the case of homogeneous membrane having the DBL thickness of 240 μm, and concentration of salt (NaCl) in a solution bulk of 0.1 M. Calculations for heterogeneous membrane was conducted using two models (Fig. 3(b)): one-dimensional (curve 1) and two-dimensional (curve 2).

In order to superpose the calculated and experimental values of the stationary potential drop using a one-dimensional model, one has to use the value of δ equal to 325 μm, which, evidently, does not meet the actual conditions of the experiment. To achieve the same goal by using a two-dimensional model, the value of δ has been taken equal to 240 μm, which is in good agreement with those obtained for the AMX membrane. Electrical heterogeneity of the membrane

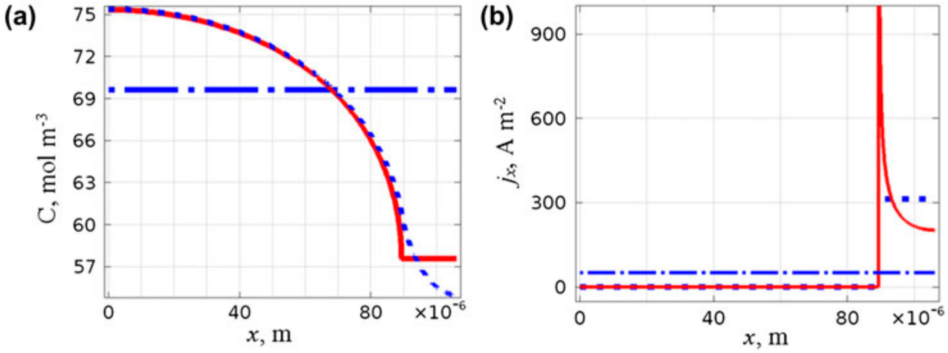

Fig. 2. The concentration distribution (a) and normal (b) current density calculated by the model with integral condition (1) (solid line) and Rubinstein model with the uniform distribution of current density (dotted line) on the conductive portion of the membrane. Dot-dashed lines show the concentration distribution and the current density at the surface of a homogeneous membrane.

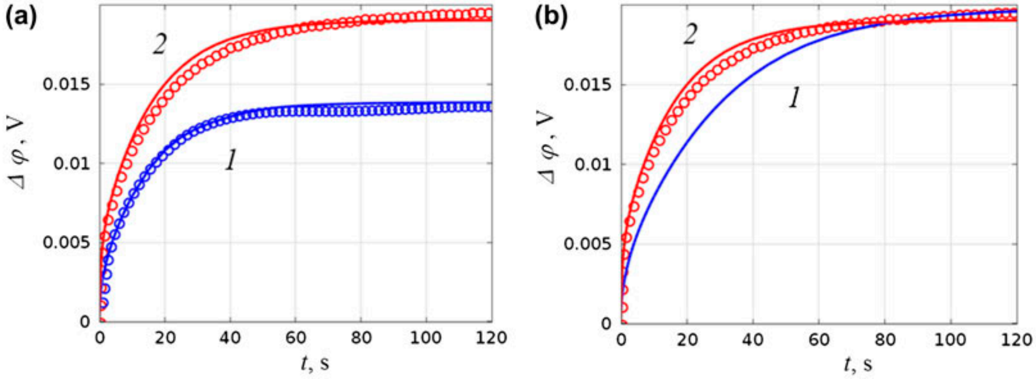

Fig. 3. Experimental (dots) and calculated (lines) chronopotentiograms for membranes (a) AMX (1) and MA-41 (2), (b) MA-41 in 0.1 M NaCl solution at constant current density $j = 50$ A m^{-2}. Curves were calculated using a one-dimensional (1) and two-dimensional (2) models.

MA-41 was characterized by parameters $h = 15$ μm and $h/L = 0.21$, which are close to the estimates given by Volodina et al. [1].

3.1. Two-dimensional modeling of heterogeneous membrane impedance spectra

The method of theoretical description of impedance spectra using the numerical solution of transient transport equations proposed in [11], as well as the above-described two-dimensional transport model with an integral assigning of the current density were used to calculate the impedance spectra of the heterogeneous membrane.

It is shown that the form of calculated impedance spectra is qualitatively different from the Warburg type spectrum for the finite length diffusion (Fig. 4). The reason for this deviation could be the contribution of the solution close to the surface of the membrane where cylindrical diffusion takes place. As this area is relatively small to the entire diffusion layer, the change in its relaxation time affects only the high-frequency domain of the spectrum.

At the same time, the potential drop over this solution becomes much higher due to the local increase in current density and the concentration reduction, which greatly affects the total system resistance. Thus, the entire diffusion layer can be divided into flat and spherical diffusion sections connected in series, and the total system impedance represented as the sum of two impedances:

$$Z_{\text{total}} = Z_{\text{flat diffusion}} + Z_{\text{cylindrical diffusion}} \quad (2)$$

From the point of view of the numerical experiment method, with a decrease in the conductive surface portion when δ/L ratio is fixed, the total resistance of the system becomes larger, and therefore the modulus

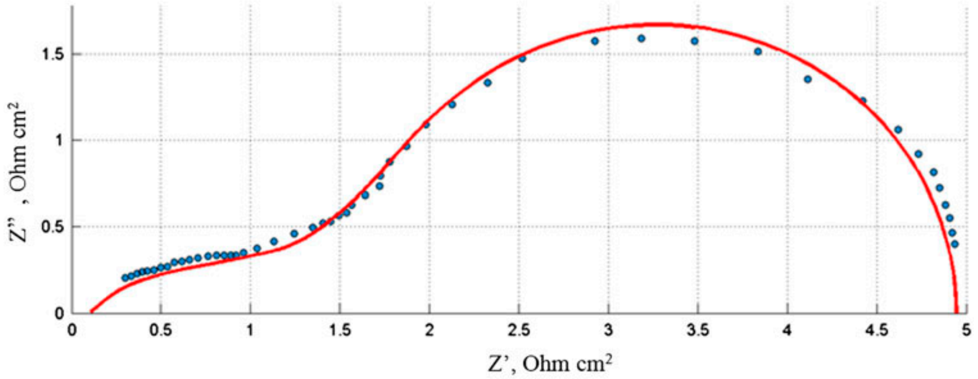

Fig. 4. Experimental (dots) and theoretical (line) spectra of a heterogeneous MK-40 membrane in NaCl solution (20 mol m^{-3}) $j = 0.06$ mA cm^{-2}.

of impedance increases and the phase angle α decreases due to the decrease in transition time.

The comparison of calculated and experimental spectra was carried out. It is found that by changing the degree of electrical heterogeneity of the membrane system and the DBL thickness, a good agreement between theoretical and experimental data can be achieved (Fig. 4).

Acknowledgments

Part of the work was carried out within the framework of joint French-Russian laboratory "Ion-Exchange Membranes and Related Processes." The authors are grateful to the CNRS, RFBR (Grant No. 14-08-31462-mol-a, 14-08-31451-mol-a), and FP7Marie Curie Actions "CoTraPhen" Project PIRSES-GA-2010-269135.

References

[1] E. Volodina, N. Pismenskaya, V. Nikonenko, C. Larchet, G. Pourcelly, Ion transfer across ion-exchange membranes with homogeneous and heterogeneous surfaces, J. Colloid Interface Sci. 285 (2005) 247–258.
[2] J.J. Krol, M. Wessling, H. Strathmann, Chronopotentiometry and overlimiting ion transport through monopolar ion exchange membranes, J. Membr. Sci. 162 (1999) 155–164.
[3] J.H. Choi, S.H. Kim, S.H. Moon, Pore size characterization of cation-exchange membranes by chronopotentiometry using homologous amine ions, J. Colloid Interface Sci. 191 (2001) 225–236.
[4] E. Barsoukov, J.R. Macdonald, Impedance Spectroscopy, Wiley, New York, NY, 2005, 595 pp.
[5] A.E. Kozmai, V.V. Nikonenko, N.D. Pismenskaya, S.A. Mareev, E.I. Belova, P. Sistat, Use of electrochemical impedance spectroscopy for determining the diffusion layer thickness at the surface of ion-exchange membranes, Pet. Chem. 52(8) (2012) 614–624.
[6] A. Alcaraz, P. Ramírez, S. Mafé, H. Holdik, A simple model for AC impedance spectra in bipolar membranes, J. Phys. Chem. 100 (1996) 15555–15561.
[7] A.J. Bard, L.R. Faulkner, Electrochemical Methods. Fundamentals and Applications, second ed., Wiley, New York, NY, 2001, pp. 161–164.
[8] I. Rubinstein, B. Zaltzman, T. Pundik, Ion-exchange funneling in thin-film coating modification of heterogeneous electrodialysis membranes, Phys. Rev. E. 65 (2002) 41507.
[9] G.I. Taylor, C.F. Sharman, A mechanical method for solving problems of flow in compressible fluids, Proc. R. Soc. London, Ser. A 121 (1928) 194–217.
[10] A.V. Pismensky, M.K. Urtenov, V.V. Nikonenko, P. Sistat, N.D. Pismenskaya, A.V. Kovalenko, Model and experimental studies of gravitational convection in an electromembrane cell, Russ. J. Electrochem. 48(7) (2012) 756–766.
[11] S.A. Mareev, V.V. Nikonenko, A numerical experiment approach to modeling impedance: Application to study a Warburg-type spectrum in a membrane system with diffusion coefficients depending on concentration, Electrochim. Acta 81 (2012) 268–274.