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Electrochemical study of ion transfer in ion-exchange membrane systems: Experiments and interpretation

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Recently, the interest to the mechanism of ion transfer and concentration polarisation in ion-exchange membrane (IEM) systems, especially at intensive currents, has increased. It is due, firstly, to attempts to optimise electrodialysis of dilute solutions where its rate is low, and, secondly, to expend research of nano- and microfluidic systems. In both cases there is a strong coupling between charge and volume transfer [1, 2], and the mechanism of this phenomenon is under high attention.

To attain a better understanding of these interfacial phenomena, both accurate experiment and advanced mathematical modelling are needed. In this paper we present the results of voltammetry, chronopotentiometry and impedance spectroscopy measurements of several IEMs differing in their surface properties. It is found that the limiting current density, $i_{\lim}^{\exp}$, determined by the intersection point of tangents depends on the membrane surface properties. It increases with the surface hydrophobicity and is a function of electrical and geometrical surface heterogeneity. In several cases $i_{\lim}^{\exp}$ is essentially higher than its "theoretical" value $i_{\lim}^{theor}$ found using a 2D convection-diffusion model based on the NERNST-PLANCK and NAVIER-STOKES equations under electroneutrality assumption (NP-NS model); the solution is reduced to the LÉVÊQUE equation for short desalination channels.

I-V and chronopotentiometric curves were computed after solving the set of NERNST-PLANCK, POISSON and NAVIER-STOKES equations in an ED diluate channel where a solution flows between an anion- and a cation-exchange membranes under a fixed applied voltage. Even for smooth homogeneous membranes, the calculated current density corresponding to the tangents intersection point (hence, to $i_{\lim}^{\exp}$) is higher than $i_{\lim}^{theor}$. Electro-convective vortices appear when the current density is lower than $i_{\lim}^{\exp}$.

Fig. 1 shows experimental and calculated current-voltage curves (CVC). The ratio $i / i_{\lim}^{theor}$ is presented as a function of the "*corrected*" potential difference (*pd*) equal to the measured *pd* reduced by the ohmic *pd*. The surface properties of the studied membranes differ by electric and geometric heterogeneity and by the degree of hydrophobicity. The last property seems to have a quite important role: the measured limiting current density $i_{\lim}^{\exp}$ increases with increasing surface hydrophobicity.

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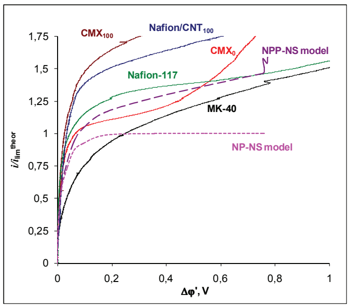

Fig. 1. Ratio $i / i_{\lim}^{theor}$ as a function of the “corrected” *pd*. Experimental data for different CEMs (heterogeneous MK-40, homogeneous Nafion®-117 and CMX, Nafion®-117 covered with carbon nanotubes (CNT), and calculations according to the NP-NS and the NPP-NS models. The subscript shows the number of hours of membrane treatment at an overlimiting current. A part of experimental data is taken from [3]

Concentration profiles and fluid and electric current streamlines in a diluate ED channel calculated according to the NPP-NS model are shown in Figs. 2 and 3. In all cases, a 0.01 mol dm^{-3} NaCl solution is considered as a feed solution. The channel length and height are 2 and 0.5 mm, respectively. The forced flow average velocity is 0.1 mm s^{-1}.

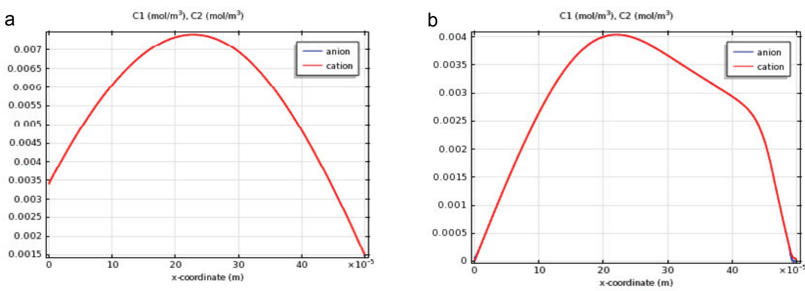

Fig. 2. Concentration profiles calculated according to the NPP-NS model at a current density close to $i_{\lim}^{theor}$ (a) and at $i > i_{\lim}^{theor}$ (b) in a desalination channel. An AEM is on the left, and a CEM, on the right.

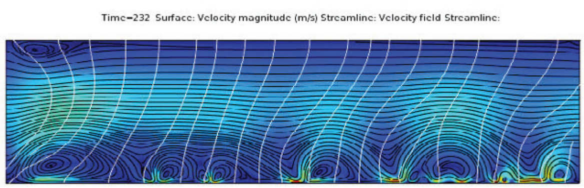

Fig. 3. Velocity and electric current streamlines calculated according to the NPP-NS model at an overlimiting current. Vortices arise at the CEM situated at the bottom. Gravitational forces have been neglected.

Acknowledgments

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