Current-voltage curves measurement

The voltammetric characteristics of the membranes were obtained using the rotating membrane disk method, which allows for setting a constant thickness of the diffusion layer while simultaneously determining the effective (Hittorf) transport numbers. Voltammetric measurements were performed in ternary solutions of $CaCl_2$ (0.015 mol-eq/L) + NaCl (0.015 mol-eq/L). The current density was varied stepwise. The flow rate of the solution into the cathode chamber was 7.5±0.1 ml/min. The composition of the initial solution in the anode chamber was kept constant.

The concentrations of Ca^{2+} and Na^+ cations in the cathode and anode chambers of the rotating membrane disk were determined using the Aquilon Stayer liquid ion chromatograph.

The transport numbers of ions were determined using the formula:

$$T_i = \frac{(c_i - c_i^0)v_i F}{I} \qquad (1)$$

where T_i is an effective transport number; c_i is an electrolyte concentration in the studied chamber, mol-eq/L; c_i^0 is an initial concnetration, mol-eq/L; v_i is a volume flow rate, L/s; I is a polarizing current, A; F is the Faradey constant, C/mol-eq.

Permselectivity coefficients were calculated based on effective transport numbers:

$$P_{1,2} = \frac{T_1 c_2^0}{T_2 c_1^0} \qquad (2)$$

where 1 refers to sodium ion, 2 refers to calcium ion.

Determination of Thermodynamic Equilibrium Constants

Membranes, converted to Ca^{2+} and Na^+ forms and rinsed with deionized water, were placed in solutions with different ratios of Ca^{2+} and Na^+ ion concentrations. The total ion concentration was maintained constant at 0.03 mol-eq/L. Once equilibrium was established, the equilibrium ionic composition of the solution was determined. By analyzing the changes in ion concentrations in the solution, the equilibrium concentrations of Ca^{2+} and Na^+ ions in the PFSA and MA-1 membranes were determined. Equilibrium ion concentrations in the solution were normalized to the total ion concentration in the solution, while ion concentrations in the membranes were normalized to the membrane exchange capacity.

The obtained relationships between the equivalent fraction of calcium ions in the membrane $\bar{\Theta}_1$ and the modifying film $\tilde{\Theta}_1$, and the fraction of calcium ions in the solution Θ_1, were used to construct the ion exchange isotherms (3) and Donnan sorption isotherms (4).

$$\frac{\bar{\Theta}_1^{1/z_1}}{\bar{\Theta}_2^{1/z_2}} = \bar{k}_{1,2}\frac{\Theta_1^{1/z_1}}{\Theta_2^{1/z_2}} \tag{3}$$

$$\frac{\tilde{\Theta}_1^{1/z_1}}{\tilde{\Theta}_2^{1/z_2}} = \tilde{k}_{1,2}\frac{\Theta_1^{1/z_1}}{\Theta_2^{1/z_2}} \tag{4}$$

where, $\tilde{\Theta}_j$, $\bar{\Theta}_j$ and Θ_j are the ratios of ions of j-type in the modifying layer, membrane-substrate and solution; z_1 and z_2 are ions charges.

Determination of Ion Diffusion Coefficients in Membranes

For cation-exchange PFSA films the diffusion coefficients of Ca^{2+} and Na^+ ions were calculated using the specific conductivity values of the membranes in Ca^{2+} and Na^+ forms. The specific conductivity of the membranes, $\bar{\kappa}_j$ ($j = Ca^{2+}$, Na^+), was determined by analyzing the electrochemical impedance spectra obtained in a mercury-contact cell. Membrane resistance was determined by extrapolating the measured complex impedance to infinite frequency. Frequency spectra of electrochemical impedance were acquired using a "Parstat 4000" potentiostat-galvanostat-impedance meter over the frequency range of 1 Hz – 500 kHz.

Based on the specific conductivity values of the studied membranes in monoionic forms and the membrane exchange capacity Q, the diffusion coefficients ($\bar{D}_j$) of calcium and sodium were calculated using Nernst-Einstein relation.

$$\bar{D}_j = \frac{\bar{\kappa}_j RT}{\bar{Q}F^2 z_j} \tag{5}$$

The integral (P_i) and then the differential (P_j^*) diffusion permeability coefficients of the anion-exchange films were calculated from the experimentally obtained concentration dependence of the diffusion flux (j). The diffusion coefficients of co-ions in the modifying layer were determined using the equation:

$$D_i^* = \left[\frac{P_i^*}{(1 + z_i)}\right]_{c=c_0} \tag{6}$$

The diffusion coefficients of Na^+ and Ca^{2+} ions in the MA-1 membrane were determined at a concentration of $c0 = 0.03$ mol-eq/L.

The system includes Ca^{2+} (1), Na^+ (2) and Cl^- (3) ions ($j = 1,2,3$). Two diffusion boundary layers (I and IV), modifying layer (II) and membrane (III).

We can formulate a boundary value problem, considering that the competing ions function as counterions with respect to the initial membrane matrix and as co-ions in the modifying layer. Transport equations are formulated as Nernst– Planck equations in the steady state form. It is assumed that the electroneutrality condition holds and that thermodynamic equilibrium is maintained locally, i.e., at the interfaces. The effects that manifest at high current densities, dissociation of water molecules, appearance of space charge layer near the interfaces, and the exaltation effect, were not considered. Let the electrical current with density i flow normally to the surface of the modified membrane that is interposed between two identical electrolyte solutions I and IV with ion concentrations $c_j^I = c_j^{IV} = c_j^0$. Let us choose a space coordinate system so that its origin coincides with the left boundary of diffusion layer I ($x = 0$). The width of the entire system is indicated by $l = \delta + \tilde{d} + \bar{d} + \delta$.+

A boundary value problem for three ions $j = 1, 2, 3$ with concentrations $c_1(x)$, $c_2(x)$ and $c_3(x)$ in four layers $m = I, II, III, IV$ is formulated in a scaled form. The Nernst–Planck equation holds in all four layers:

$$j_j = \left[-D_j \left(\frac{dc_j}{dx} + \frac{z_j F}{RT} c_j \frac{d\varphi}{dx} \right) \right]_m, \ j = 1, 2, 3, \ m = I, II, III, IV \tag{1}$$

along with electroneutrality condition

$$\left[\sum_{i=1}^{3} z_i c_i \right]_m + Q_m = 0, \qquad m = I, II, III, IV \tag{2}$$

For the diffusion layers, $Q_I = Q_{IV} = 0$, and for the modifying film and the membrane, $\tilde{Q} = Q_{II}$ and $\bar{Q} = Q_{III}$. For the whole system, the condition for the flow of electrical current is

$$\sum_{j=1}^{3} z_j j_j = \frac{i}{F} \tag{3}$$

Local thermodynamic equilibrium is assumed to be maintained at the interfaces. The imposition of condition of local thermodynamic equilibrium (continuity of the electrochemical potential) for all the interfaces in the electromembrane system leads to six boundary conditions. For the first diffusion layerI/modifying layer II boundary, we write

$$\left(\frac{c_1^{1/z_j}}{c_j^{1/z_i}} \right)_{m=II} = k_{1,j}^{I,II} \left(\frac{c_1^{1/z_j}}{c_j^{1/z_i}} \right)_{m=I}, \qquad j = 2, 3 \tag{4}$$

For the modifying layer II/membrane III boundary,

$$\left(\frac{c_1^{1/z_j}}{c_j^{1/z_i}}\right)_{m=III} = k_{1,j}^{II,III}\left(\frac{c_1^{1/z_j}}{c_j^{1/z_i}}\right)_{m=II}, \qquad j=2,3 \tag{5}$$

For the membrane III/second diffusion layer IV,

$$\left(\frac{c_1^{1/z_j}}{c_j^{1/z_i}}\right)_{m=III} = k_{1,j}^{IV,III}\left(\frac{c_1^{1/z_j}}{c_j^{1/z_i}}\right)_{m=IV}, \qquad j=2,3 \tag{6}$$

where $(c_j)_m$ is the ion concentration at the interfaces; and a $k_{1,j}^{I,II}$, $k_{1,j}^{II,III}$ and $k_{1,j}^{III,IV}$ are local thermodynamic equilibrium constants at the diffusion layer I/modifying layer II, modifying layer II/substrate membrane III, and substrate membrane III/diffusion layer IV interfaces, respectively.

The thermodynamic equilibrium constant at the modifying layer II/membrane III interface is expressed through two other equilibrium constants:

$$k_{1,j}^{II,III} = \frac{k_{1,j}^{I,II}}{k_{1,j}^{III,IV}} \tag{7}$$

For counterions $j=1$ and $j=2$, boundary conditions (4)–(6) are described with an ion-exchange constant; and for counterion $j=1$ and coion $j=3$, they are described by the Donnan equation.

The concentrations of all ionic species are defined at the outer boundaries of diffusion layers I ($x=0$) and IV ($x=l$), which is a consequence of constancy of the ion concentrations in the solution bulk:

$$c_j(0) = c_j^0, \; c_j(l) = c_j^0. \tag{8}$$

In Eqs. (1)–(8), c_j^0 is the molar concentration of the j-th ionic species in the bulk of the solution on the left and right boundaries of the considered system; j_j is flux density of the j-th ionic species; $[c_j]_m$ are the boundary concentrations of the j-th ionic species in the m-th layer; z_j is the charge number of the j-th ionic species; $[D_j]_m$ are the diffusion coefficients of the j-th ionic species in the m-th layer; φ is the electric potential; $l = 2\delta + \tilde{d} + \bar{d}$ is the length of a multilayer system; δ is the thickness of diffusion layers; $\tilde{d}$ is the thickness of the modifying layer; $\bar{d}$ is the thickness of the substrate membrane; F, R, and T have their conventional meaning.

Simultaneous Eqs. (1) with additional conditions (2) and (3) and boundary value conditions (4)–(8) make up a boundary value problem describing a four-layer membrane system.

This boundary value problem has a physical meaning if the current does not exceed its limiting value ($i \leq i_{lim}$). For thickness of modifying layer $\tilde{d} = 0$ this problem transforms into a boundary value problem describing a three-layer system with an isotropic membrane.