CERTAIN TRANSFER PARAMETERS IN FUEL-CELL ION-EXCHANGE MEMBRANES

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Experimental determinations were made of the electrical conductivity of ion-exchange membranes as a function of degree of hydration and temperature, as well as determinations of membrane moisture content as a function of the partial water–vapor pressure above the membrane and of temperature.

One promising type of electrochemical generator (ECG) involves the use of ion-exchange membranes (IEM), which serve as a quasisolid electrolyte. Mass-transfer processes in generators of this type have significant special features distinguishing them from generators with liquid and "matrix" electrolytes. One such feature results from the complex and little-studied character of the kinetic phenomena in IEM.

Homogeneous organic membranes have received greatest recognition, on the basis of their overall physicochemical and mechanical parameters. Such a membrane consists of a mechanically strong film fabricated from a water-insoluble high-molecular ionite consisting of three-dimensionally cross-linked polymer chains (the matrix) with active ionogenic groups rigidly attached to them. Theoretical calculation of transfer phenomena in such IEM entails considerable difficulties, resulting principally from the approximate character of current physical models of ionites [1, 2]. As numerous investigations have shown [1-4], the kinetic processes in IEM depend on many parameters: the structure of the matrix, the nature of the ionogenic groups, the degree of ionite cross-linkage, the type of counterions, etc.

There is at present no single generally accepted and experimentally grounded theory to account for the influence of these parameters on the thermodynamic functions of the processes occurring in IEM, particularly sorption processes. The mechanism by which water is sorbed on an ionite, which largely governs the transfer phenomena in IEM, has not been adequately studied. The contribution made to the thermodynamic functions by the processes that take place when the membrane absorbs water is not fully clear.

Specifically, in the case of the sulfo acid membrane in H^+ form used in fuel cells (FC) at complete dehydration the hydrogen ions are bound to the SO_3^- groups by strong ionic bonds. The $SO_3^-H^+$ group as a whole is therefore rather stable and undergoes little polarization. As the membrane absorbs water, the $SO_3^-H^+$ group is hydrated, being converted to $SO_3^-H_3O^+$, then to $SO_3^-H_5O_2^+$, etc.

As a result of this process, the groups in question begin to dissociate, the bonding between the hydrated hydrogen ions and the SO_3^- group becomes more flexible, and displacement of the hydrated counterions in an applied electric field is possible.

The electrical conductivity of IEM during the initial stage of hydration is rather well described by the following equation [5], which was derived on the basis of the theory of absolute reaction rates [6]:

$$\sigma = [Ce^2\lambda^2/h] \exp[-\Delta G/RT]. \tag{1}$$

The influence of moisture content is exerted primarily through the differential free activation energy ΔG, which decreases as the hydrate shell of the counterion becomes larger [3]. There should also be a rise in λ as IEM swell.

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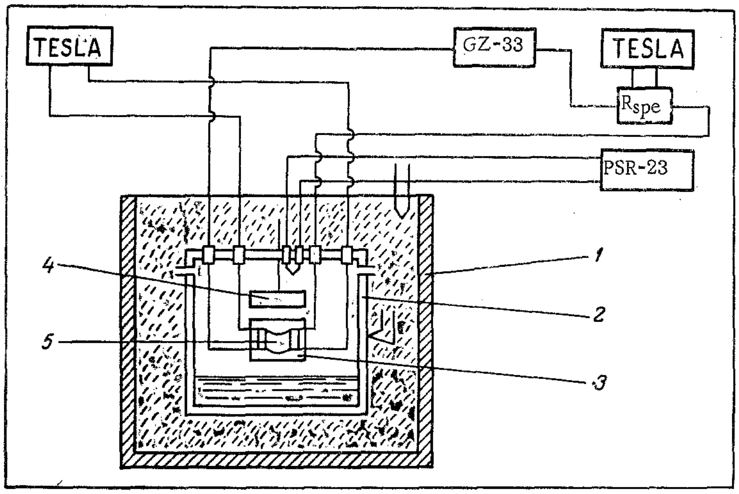

Fig. 1. Diagram of experimental apparatus.

The specific structural characteristics of ionites, in which ions of one sign are attached to a polymer framework, and the sorption of water by ionites leads to the appearance of a convective conductivity component in IEM placed in a constant electric field, which causes an overall increase in conductivity. Since in a hydrogen–oxygen FC containing a cation-exchange membrane water is usually present only at the cathode and the counterions move from the anode to the cathode, it is possible for the portion of the IEM adjoining the anode to undergo some dehydration and for a corresponding moisture-content gradient to develop. However, development of the latter should cause a flow of water in the opposite direction to the flow of ions. Moreover, the distension pressure at the IEM surface adjoining the anode, where H^+ ions are formed, is apparently less than at the IEM surface adjoining the cathode, where H^+ ions are absorbed as a result of the basic current-generating reaction. Some compromise moisture distribution should eventually be established over the thickness of the IEM; its character is governed by many parameters. In addition, taking into account the elasticity of the IEM polymer framework, the presence of this distribution should obviously lead to distribution of the ionite-matrix pore volume over the thickness of the IEM.

Proceeding from the above characteristics of kinetic phenomena in IEM and taking into account the specific features of the operation of the FC under consideration, the transfer phenomena in an FC membrane can be described with the aid of the IEM model [1], in which the membrane lies between solutions of different concentrations and is exposed to a constant electric field. The movement of the H^+ ions is then described by the equation

$$\Phi_{\mathrm{H}^+} = -D^0_{\mathrm{H}^+}\left(\frac{C_{\mathrm{H}^+}}{RT}\,\mathrm{grad}\,\mu_{\mathrm{H}^+} + \frac{C_{\mathrm{H}^+}\mathrm{F}}{RT}\,\mathrm{grad}\,\varphi\right) + C_{\mathrm{H}^+}v, \tag{2}$$

where

$$D^0_{\mathrm{H}^+} = D_{\mathrm{H}^+}\left(1 + \frac{\partial \ln f_{\mathrm{H}^+}}{\partial \ln C_{\mathrm{H}^+}}\right);\; v = -\frac{1}{\rho_0\delta}\left(\frac{C_{\mathrm{SO}_3^-}\mathrm{F}}{\omega}\,\Delta\varphi + \Delta P\right).$$

The first term in the ion-flow equation (2) characterizes the diffusive flow component described in accordance with Fick's first law, while the middle term characterizes the ion flux developing as a result of the action of the electric field; the final term represents the convective ion-flux component. It must be noted that, under the conditions obtaining in the FC in question, all three components of the H^+ flux have the same direction.

The characteristics of membrane transfer phenomena described above must be taken into account in investigating the operation of an IEM-containing FC and an ECG based on it. A knowledge of the dependence of the kinetic phenomena in the IEM on the FC working parameters is required for selection of the method to be used to remove the water formed, for evaluation of the contribution made by each of the component polarization losses, for determination of the detailed mechanism of oxygen-electrode function, and for analysis of many other processes that, in aggregate, govern optimization of heat and mass transfer in the FC and hence affect the efficiency and stability of its operation.

We conducted an experimental investigation of the main IEM parameters influencing mass transfer in an FC as a function of temperature, moisture content, electrical conductivity, and partial water–vapor pressure above the IEM. Our study was made by the isopiestic method in the apparatus shown in Fig. 1.

The apparatus consisted of a controlled-temperature chamber 1 enclosing the hermetically sealed tank 2. Within the tank, over sulfuric acid solution, was a device holding the IEM test specimen. This device consisted of tank 3, with potential and current leads and hermetically sealed lid 4. Within the tank were the test specimen 5 and two lugs attached to opposite ends of the specimen.

The experiment was conducted in the following manner. The weight and electrical resistance of the IEM specimen in the "absolutely" damp state were determined and the specimen was then fastened into tank 3 and placed together with it into tank 2. A sulfuric acid solution of the requisite concentration was first poured into tank 2. The latter was then hermetically sealed and lowered into controlled-temperature chamber 1. Establishment of the proper temperature in chamber 1 and tank 2 was monitored with thermocouples connected to a PSR-23 instrument. The scattering of temperature values did not exceed ±0.25°C. Periodic measurement of the electrical resistance of the specimens was employed to make certain that steady-state moisture-content conditions were established. These measurements were made by the four-probe method with high-frequency ac current. The high-frequency voltage source was a GZ-33 signal generator. The measurement frequency was 5000-7000 Hz. The voltage at the specimen and the current in the circuit were measured with a TESLA vacuum-tube millivoltmeter. The specimen resistance was measured to within 5%. It was assumed that the IEM specimen was steady-state with respect to moisture content when its electrical resistance remained constant for 4 or 5 h, and then the lid 4 of tank 3 was hermetically sealed and tank 2 was removed from chamber 1. Sealed tank 3 was then taken from tank 2 and weighed, the IEM specimen was removed from it, and it was again weighed. A correction was introduced for the weight of the water vapor in the tank. The accuracy of the weighing was ±5 mg. The weight difference thus yielded the weight of the IEM specimen being investigated. The specimen was then dried in a vacuum of $1.29 \cdot 10^{-3}$ N/m^2 for 10-12 h at room temperature. It was established that further drying did not reduce the weight of the IEM specimen. The specimen weight after vacuum drying was taken as the "absolutely" dry weight. The difference between the weight of the IEM specimen under given experimental conditions and the weight after vacuum drying yielded the amount of water sorbed by the IEM specimen under these experimental conditions.

Our investigation of the IEM specimens was conducted at temperatures of 40, 50, 60, and 70°C. In order to avoid the influence of destruction on the properties of the IEM, each specimen was utilized in only one experiment.

Since many researchers (e.g., [7, 8]) have demonstrated that the trend of the hydration and dehydration curves of IEM is not unambiguous, all other conditions being equal, we employed completely water-saturated specimens as the initial state of the IEM. Thus all the experimental points characterized the dehydration of the IEM investigated.

We studied the most common type of cation-exchange membranes: MPFS-26, FK-3, SKM-IXa, and MK-102. Our investigation yielded the experimental dependence of the electrical conductivity of the IEM on their degree of hydration at the above temperatures. This relationship is shown graphically in Fig. 2 for an MPFS-26 membrane. The conductivity σ of the IEM in $\Omega^{-1} \cdot \mathrm{cm}^{-1}$ is plotted along the ordinate and the amount of water in moles n_{H_2O} calculated in equivalents of polystyryl sulfo acid (PSSA) is plotted along the abscissa. The functions for different temperatures are given. The vertical line in Fig. 2 corresponds to the maximum possible distension of this type of IEM. The character of the relationship shown in Fig. 2 was qualitatively the same for all types of IEM. In all cases, there was an abrupt rise in the conductivity of the membrane during absorption of the first few moles of water. This sharp increase in σ usually terminated after sorption of about 10-15 molecules of water per molecule of PSSA. This quantity varied with the temperature and the type of IEM. The relationship obtained between σ and n_{H_2O} corresponded to the hydration mechanism described above for sulfo acid membranes. The first few moles of water absorbed by the membrane probably had specific properties (this was the hydrate or "bound" water). In particular, the packing of these moles in the hydrate layers was denser than in the $(H_2O)_n$ aggregates of pure water [9]. The unusual properties of the hydrate water can obviously explain the abrupt change in the kinetic parameters of the IEM on absorption of the initial, rather small amount of water. The absorbed water over the amount necessary for formation of the first hydrate layers ("free" water) probably has properties and structure analogous to those of pure water.

Figure 3 gives the specific resistance as a function of the number of moles of sorbed water for these membranes at 50°C; if $n_{H_2O} \leq 5$, the σ curves all run very close together, because the ionic groups in these sulfonate membranes are then similar in number and identical in form, and they are closely described

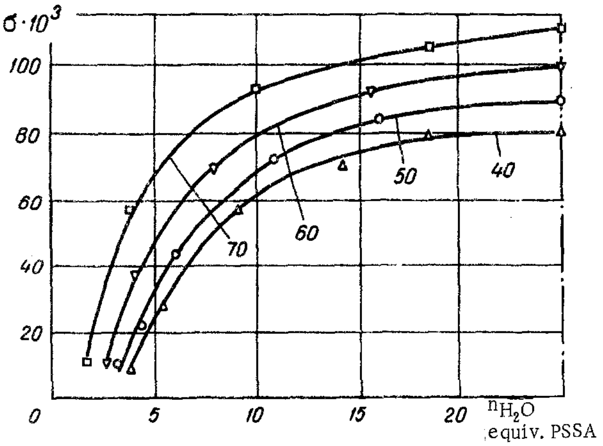

Fig. 2

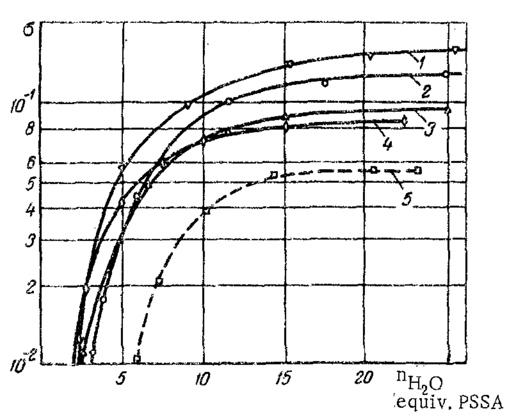

Fig. 3

Fig. 2. Electrical conductivity of type MPFS-26 IEM (σ, $\Omega^{-1}\cdot\text{cm}^{-1}$) as a function of degree of hydration n_{H_2O}/equiv. PSSA (number of moles of water per equivalent of polystyryl sulfo acid) and temperature (°C).

Fig. 3. Electrical conductivity σ ($\Omega^{-1}\cdot\text{cm}^{-1}$) of IEM of types FK-3 (1), MK-102 (2), MPFS-26 (3), SKM-IXa (4), and C-60 (5, from data of [5] for $t = 28°C$) as a function of degree of hydration n_{H_2O}/equiv. PSSA (number of moles of water per equivalent of polystyryl sulfo acid) at $t = 50°C$.

by (2), in accordance with the sorption theory for hydration water, which shows that the electrical conductivity increases with λ, which is due to the reduced influence of the fixed ions on the counterions. Also, λ should increase as the membranes swell. The water content affects the electrical conductivity mainly via the differential free energy of activation ΔG. The broken line in Fig. 3 gives results [5] for $t = 28°C$, which agree qualitatively with ours.

It can be seen from Fig. 3 that the curves began to diverge on further distension ($n_{H_2O} > 5$). However, the increase in σ slowed down at $n_{H_2O} \approx 7$ for type MPFS-26 IEM and at $n_{H_2O} \approx 9$-10 for FK-3, MK-102, and SKM-IXa IEM. The increase in σ on further distension of the membranes was due primarily to an increase in the convective conductivity component, which, all other conditions being equal, resulted for the most part from the influence and structural characteristics of the IEM gel matrix.

The rate of water evaporation from the IEM was governed principally by the difference in the water–vapor partial pressures over the surface of the IEM and in the FC gas chambers. An ideal IEM (in the sense of retention of its moisture content and hence of its electrophysical properties) would be a membrane having a minimum water–vapor partial pressure over it, for which a small change in the moisture content would cause a substantial decrease in the water–vapor partial pressure above its surface. Our experiments

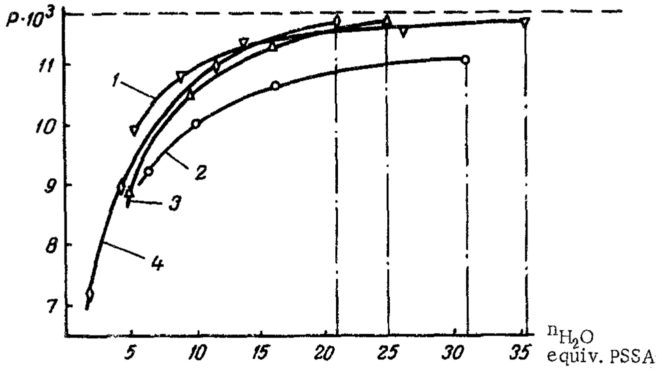

Fig. 4. Dependence of partial water–vapor pressure P (N/m^2) over IEM of types FK-3 (1), MK-102 (2), MPFS-26 (3), and SKM-IXa (4) on degree of hydration n_{H_2O}/equiv. PSSA (number of moles of water per equivalent of polystyryl sulfo acid) at $t = 50°C$.

showed that the qualitative character of the dependence of thewater–vapor partial pressure over the IEM (P) on the degree of hydration at different temperatures was the same for all the types of IEM investigated. During the initial period of drying, which corresponded rather well to the region of "free" water removal, P decreased very slightly and it was close to the water–vapor pressure over pure water at the same temperature. Further drying of the membrane led to an abrupt drop in P. The region where P depended only slightly on the moisture content was related to the temperature variation and its extent decreased as the temperature was raised. Comparison of the dependence of P on moisture content showed that the lowest values of P were displayed by IEM of the MK-102 type, as can be seen from Fig. 4, which illustrates the function in question for all the types of IEM studied at a temperature of 50°C. The horizontal dashed line in Fig. 4 corresponds to the vapor pressure of pure water at 50°C, while the vertical dashed lines correspond to the maximum water contents of the corresponding types of IEM.

Thus, without taking into account the mechanical properties, thermostability, or chemical stability of IEM, we can conclude that the best membranes from the standpoint of H^+ ion conductivity are those of the FK-3 type, while the best membranes from the standpoint of resistance to dehydration during operation in an FC are those of the MK-102 type, which have the lowest water–vapor partial pressure over the entire moisture-content range investigated. We established that a considerable proportion of the water absorbed by a membrane (from 40 to 60%, depending on the type of IEM and the temperature) is in the "free" capillary state.

Dehydration of the membranes within this moisture-content region did not lead to a material change in the IEM parameters investigated.

NOTATION

C_{H^+}, $C_{SO_3^-}$, C_{H_2O}	are the concentrations of H^+ ions, SO_3^- sulfo ions, and water, respectively;
ΔG	is the effective free activation energy;
λ	is the effective distance between functional groups;
σ	is the electrical conductivity;
P	is the water–vapor partial pressure;
T, t	are the temperature values;
Φ_{H^+}	is the total H^+ ion flux through IEM;
f_{H^+}	is the activity constant;
μ_{H^+}	is the chemical potential;
D_{H^+}	is the kinematic diffusion constant;
$D^0_{H^+}$	is the diffusion constant;
ΔP	is the difference in distention pressure at boundaries of IEM;
φ	is the potential;
$\Delta\varphi$	is the potential difference at the boundaries of IEM;
ρ_0	is the resistance to motion of an element of water volume produced by the IEM matrix;
ω	is the proportion of the pore volume in IEM;
v	is the average rate of movement of a water–volume element through IEM;
δ	is the thickness of the IEM;
n_{H_2O}	is the number of moles of water;
e	is the charge of the electron;
F	is the Faraday number;
h	is Planck's constant;
R	is the gas constant.

Subscripts

$+$, $-$	denote the sign of the ion charge;
H^+, SO_3^-, H_2O	indicate that the quantities in question pertain to hydrogen and sulfo ions and to water, respectively.

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