ELECTROCHEMICAL PROPERTIES OF CATION-EXCHANGE MEMBRANES OF THE HOMOGENEOUS TYPE

N. I. Men'shakova, V. L. Kubasov, and L. I. Krishtalik

UDC 541.135.5

In an earlier communication [1] we had examined the effect of solution concentration and temperature on the swelling of the heterogeneous MK-40 membrane, and we also studied the absorption of solvent and electrolyte by the membrane. The figures obtained were compared with the membrane's electrochemical characteristics (electric conductivity, selectivity with respect to hydroxyl ions).

In the present paper we report the results obtained in similar studies involving a homogeneous cation-exchange membrane of the Nafion type, which is a perfluorinated polymer with ionogenic sulfo groups. In addition we compare the characteristics of homogeneous and heterogeneous membranes. The measuring methods have been described in [1]. The results of the measurements are presented in Figs. 1 to 4 and Table 1.

It is conspicuous to note at first that the homogeneous membrane swells much less than the heterogeneous membrane (Fig. 1). This difference primarily arises because these membranes differ substantially in their exchange capacity, which is 2.5 mg-eq/g of resin for MK-40 and 0.82 mg-eq/g of membrane for the Nafion membrane. In dilute solutions the relative swelling of the heterogeneous membrane is 1.5 to 2 times higher than that of the homogeneous membrane. Probably this is due to the voids between grains in the heterogeneous membrane, which can fill up with solution. In concentrated solutions the swelling is practically the same for both types of membrane when it is referred to the same number of membrane ions.

One could think that swelling in these solutions is determined to a substantial degree, both for the homogeneous and for the heterogeneous membrane, by hydration of the membrane ions, and that the importance of intergranular voids decreases because of membrane compressibility. The importance of the space between grains can also be seen from the data of Fig. 2, which shows the average concentration of the solution absorbed by the membrane; this was found from the amounts of alkali and water absorbed by the membrane. For the heterogeneous membrane, this concentration is lower than that of the external solution, but still of the same order of magnitude, and it changes in parallel with it. But for the homogeneous membrane, the average concentration of the absorbed solution is much lower than that of the external electrolyte, and it goes through a maximum, i.e., is basically determined by alkali absorption. The behavior found for the heterogeneous membrane reflects the contributions of two components, viz., the absorption of alkali and water within the ion-exchanger grains, and penetration of the solution into the space between grains.

TABLE 1. Results for Electrolyte Absorption by the Homogeneous Membrane

NaOH concentration, g/liter	Specific absorption by the membrane		Total amt. of ions, mg-eq/g of membrane	Current yield % (expt.)	Ratio betw. spec. absorpt. of water and spec. abspt. of alkali, mg-mole of H_2O/mg-eq of NaOH
	of NaOh, mg-eq/g of membrane	of H_2O, mg-mole/g of membrane			
0 (H_2O)	–	5,50	1,64	100	–
50	0,011	3,34	1,66	93	303,0
100	0,035	3,19	1,71	85	91,5
200	0,060	2,64	1,76	67	44,0
300	0,080	1,80	1,80	58	25,0
400	0,027	0,61	1,69	58	22,6
500	0,005	0,39	1,65	70	78,0

Moscow. Translated from Élektrokhimiya, Vol. 17, No. 2, pp. 275-278, February, 1981. Original article submitted June 3, 1980.

0038-5387/81/1702-0228$07.50

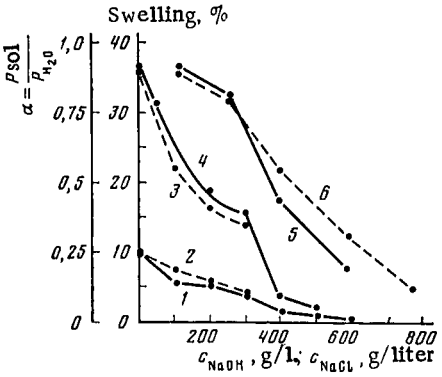

Fig. 1

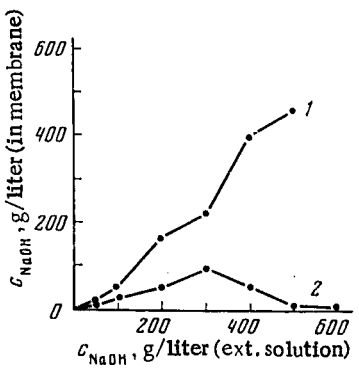

Fig. 2

Fig. 1. The swelling of Nafion (1, 2) and MK-40 (3, 4) membranes and the partial-pressure ratios of the NaOH solutions and H_2O (curve 5 at t = 20°C, curve 6 at t = 80°C) as functions of NaOH (1, 4, 5, 6) and NaCl (2, 3) solution concentration.

Fig. 2. The concentration of the alkali absorbed by membranes MK-40 (1) and Nafion (2) as a function of concentration of the external solution.

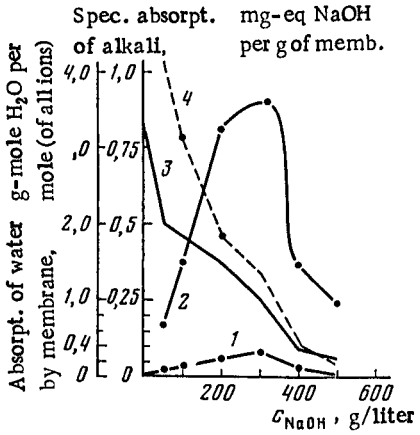

Fig. 3. The specific absorption of alkali (1, 2) and the absorption of water (3, 4) of membranes Nafion (1, 3) and MK-40 (2, 4) as functions of concentration of the external solution.

A decrease of membrane swelling with increasing solution concentration [2] is due to falling water activity in the alkali solution. One can in fact see from Fig. 1 (curves 5 and 6) that water activity falls markedly with increasing alkali concentration, and this drop, like that of water absorption by the membrane, is most pronounced in the NaOH concentration range between 300 and 400 g/liter. However, the change of membrane swelling which occurs as a function of alkali concentration is more drastic than that of water activity. The water in the membrane is in equilibrium with the solution, so that its activity is the same as that in the solution. However, the activity coefficient of water in the membrane seems to depend somewhat differently on the concentration of ions in the phase within the membrane than does that of the water in the external solution on its concentration.

In the range of alkali concentrations above 300 g/liter, the water content in the membrane becomes smaller than one mole per mole of all sorts of ion (Fig. 3, curves 1 and 2) for both types of membrane. It follows that in such membranes, part of the ions effectively are not hydrated. Related to this situation one finds a drastic change in all membrane proper-

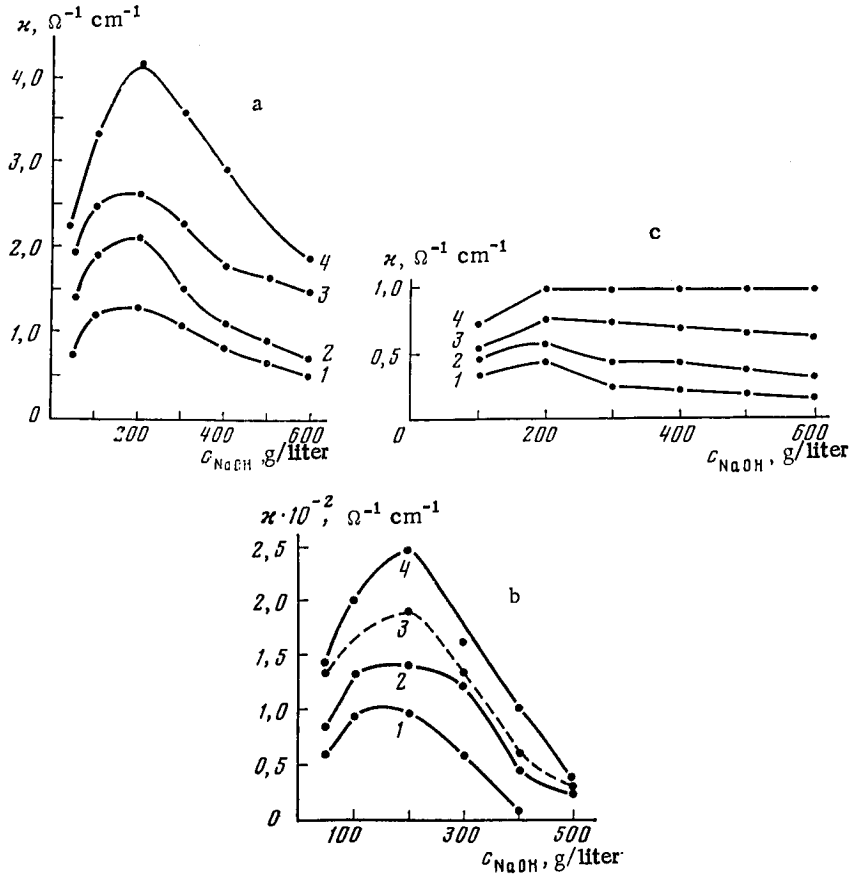

Fig. 4. The specific electric conductivity of membranes MK-40 (a) and Nafion (b) and of alkali solutions (c) as functions of concentration of the external solution and of temperature: 1) 25°C, 2) 40°C, 3) 60°C, and 4) 80°C.

ties. At concentrations above 300 g/liter, the amount of superequivalent alkali absorbed in the membrane begins to fall (Table 1; Fig. 3, curves 3 and 4). In the external solution, the concentration and, therefore, the activity of alkali increases, but in the membrane, the NaOH concentration falls, despite the fact that it should increase owing to the Donnan equilibrium [3]. This drop may be caused by rapid increase of the NaOH activity coefficient in the membrane, since the ions are substantially less hydrated than in the solution. As a result, the NaOH activity in the membrane increases despite decreasing NaOH concentration (Fig. 2). In the heterogeneous membrane, in addition to the alkali absorbed by the ion exchanger there is a certain amount of electrolyte in the space between grains. It is obvious that this electrolyte, which moreover may have a composition somewhat different from that of the external solution, does not contribute decisively to the total amount of alkali absorbed, since the total alkali absorption still decreases.

Another distinct manifestation of the structural changes occurring in the ion exchanger at high concentrations of the external solution is the conductivity change exhibited by it. Both for the heterogeneous and for the homogeneous membrane, the conductivity maximum is at a concentration of about 200 g/liter (Fig. 4, parts a and b), i.e., close to the concentration where one observes the conductivity maximum of the free solution (Fig. 4c). However, the conductivity decrease following the maximum is more drastic in the membranes than in solutions of the same concentration, particularly in the homogeneous membrane. At the same total concentration of ions in the membrane (this is attained at concentrations of the external solution of about 100 and 400 g/liter), membrane conductivity is substantially lower in the more concentrated solution, i.e., in the less hydrated state. It had been pointed out in [1] that this is evidence for stronger binding of the mobile ions by the matrix at lower water contents in the matrix. The maximum present in the curve of alkali absorption not due to exchange leads to a minimum in the alkali current yield obtained with Nafion mem-

branes in the concentration range of 300 to 400 g/liter, but for MK-40 membranes, such a minimum is not observed. The matter obviously has to do with the fact that current transport across the heterogeneous membrane is a more complicated process, since the current can pass, both through the grains and through the solution in the intergranular space. The importance of the latter ought to increase with increasing concentration of the external solution, since the resistance of the grains increases strongly under these conditions. Moreover, the mobility ratio of Na^+ and OH^- ions should change owing to the small amount of water present in the bulk of the membrane, and this influences the relation between current yield and NaOH concentration.

It has been pointed out above that the intergranular electrolyte has no decisive effect on the amount of alkali absorbed by the MK-40 membrane without exchange. Hence one can compare the amounts of alkali absorbed by different membranes while assuming that they are determined by the ion exchanger itself. One can see from Fig. 3 that for membrane MK-40, the amount of alkali absorbed is tens of times larger. The exchange capacity of this membrane is approximately three times as high as that of the homogeneous membrane. On the assumption of equal NaOH activity coefficients in the ion exchanger, one ought to expect the opposite relation, i.e., lower absorption for the MK-40. It follows that the activity coefficient of the electrolyte in the homogeneous membrane is much higher; this is due to the lower water content of the membrane and, possibly, to the more rigid polymer structure.

It must be stressed in conclusion that the kinetic and equilibrium properties of membranes in a substantial way depend on the degree of membrane hydration. When the amount of absorbed water is reduced to levels below one molecule per ion, particularly drastic changes result, and in particular, a nonmonotonic behavior of most membrane characteristics with changing concentration of the external solution.

LITERATURE CITED

1. N. I. Men'shakova, L. I. Krishtalik, and V. L. Kubasov, Élektrokhimiya, 14, No. 3, 356 (1978).
2. D. Bergner, Chemiker Z., 101, No. 10, 433 (1977).
3. B. N. Laskorin, N. I. Smirnova, and M. N. Gantman, Ion-Exchange Membranes and Their Application [in Russian], Gosatomizdat, Moscow (1961).

PHOTOELECTROCHEMICAL PRECIPITATION OF MnO_2 ON A POLYCRYSTALLINE TiO_2 ELECTRODE

T. V. Dzhavrishvili, A. L. Asatiani, and Z. A. Rotenberg

UDC 541.138

During the last years the photocatalytic properties of TiO_2 have attracted an ever-increasing interest of the researchers [1, 2]. This is due in the first instance to the fact that electrodes made of TiO_2 or other titanium compounds [3, 4] can be used in photoelectrochemical elements for the decomposition of water. The main purpose of creating such elements is the preparation of hydrogen. Besides this, processes can be carried out in such a system, where substances are formed on the anode under the action of light which are even more important than hydrogen. In our opinion, the realization of such photoelectrochemical systems is a very important task.

In the present work we have investigated the photooxidation of Mn^{2+} on TiO_2 with the aim to obtain MnO_2 which, as is well known, is used as an oxidant in chemical current sources. Polycrystalline rutile was used as the electrode, obtained by oxidation of Ti at 700°C in an oxygen atmosphere. The procedure for the measurement of photocurrents was in principle the same as the one described in [5]. The measurements were carried out in 1 N H_2SO_4 containing different amounts of $MnSO_4$.

Institute of Inorganic and Electrochemistry, Academy of Sciences of the Georgian SSR, Tbilisi. Translated from Élektrokhimiya, Vol. 17, No. 2, pp. 278-281, February, 1981. Original article submitted June 3, 1980.

0038-5387/81/1702-0231$07.50