DIFFUSION OF ALKALI METAL THROUGH ZINC MEMBRANES

I. I. Astakhov and B. N. Kabanov

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In [1] it was reported that as a result of the discovery of diffusion through a metallic membrane it was shown for the first time by a direct method that alkali metals could penetrate into the body of solid electrodes to form intermetallic compounds with the electrode metal. Later the relationship between the diffusion rate and the nature of the alkali cation was investigated [2].

The present work is concerned with the investigation of some of the principles governing the penetration process using the same diffusion procedure. In its construction the apparatus used for measuring the diffusion of alkali ions through the membrane was similar to the well-known apparatus in which, for example, the diffusion of hydrogen through various metallic membranes is measured [3]. It consists of two cells—a "polarization" and a "diffusion" cell—connected to each other by ground-glass joints. The joints were smeared with a thin layer of vacuum grease, and a zinc membrane was fixed between the cells. Membranes of about 30-μ thickness were obtained by rolling zinc foil, and thinner membranes (down to 15-μ) were made by electropolishing the 30-μ membranes. A solution of alkali or alkali metal salt was placed in the polarization cell; a 10^{-3} N solution of potassium sulfate was placed in the diffusion cell, and a glass electrode for measuring the pH was introduced through an air-tight seal. The solution in the diffusion cell was stirred by a glass screw-type stirrer. In order to remove oxygen, electrolytic hydrogen was passed through the solution for a few hours. The alkali metal which penetrated the membrane during cathodic polarization diffused through the membrane and passed into the solution in the diffusion cell, making it alkaline. The amount of alkali metal which diffused through the membrane was calculated from the change in pH.

Preliminary tests on the measurement of diffusion through the membrane showed that with zinc the penetration rate, in accordance with the result obtained in [4], depended little on the surface treatment of the electrode. With membranes of the same thickness and under the same polarization conditions the penetration rate was approximately the same for simply rolled membranes, for membranes cleaned with glass powder, for electropolished membranes, and for membranes activated by a brief anodic treatment before testing. Evidently this may be due to the fact that zinc quickly recrystallizes even at room temperature [5].

To investigate the relationships governing the diffusion, the variation with time of the pH of the solution in the diffusion cell, with constant stirring, was determined. The tests were carried out with membranes 15 and 19 μ thick. The polarization cell contained 1 N potassium hydroxide solution, and the polarization potential was equal to -1.9 V against the normal hydrogen electrode. The results are given in Fig. 1, where the time from the beginning of polarization is plotted against the abscissa axis and the absolute amount of potassium which has diffused through unit area of membrane is plotted against the ordinate axis. The curves are displaced relative to each other by approximately 5 h, which corresponds to the time taken by the diffusion front to traverse a distance equal to the difference in thickness of the two membranes, i.e., 4 μ. On this basis the value of the diffusion coefficient can be determined [6]. The diffusion coefficient of potassium in zinc was found to be equal to approximately $5 \cdot 10^{-12}$ cm^2/sec. This result cannot be compared with any others since the literature contains no data on the diffusion on alkali metals in zinc. If the published data [7] on self-diffusion coefficients in zinc are extrapolated to room temperature, the value $7 \cdot 10^{-12}$ cm^2/sec can be obtained for the self-diffusion coefficient at the grain boundaries. The proximity of this value to the value of the diffusion coefficient of potassium in zinc shows that the result we obtained is reasonable, although the quantitative agreement is evidently accidental. The self-diffusion coefficient in monocrystalline zinc at room temperature is equal to approximately 10^{-18} cm^2/sec. Diffusion at the grain boundaries begins to predominate when $D_{bou}/D_{bod} > R_g/\delta$ [8], where D_{bou} and D_{bod} are the diffusion coefficients along the boundaries and in the body of the grains respectively, R_g is the mean diameter of the crystal grains, δ is the width of the grain boundary ($5 \cdot 10^{-8}$ cm). In our case $R_g = 2.7 \cdot 10^{-4}$ cm* and $R_g/\delta = 5 \cdot 10^3$. Consequently self-diffusion in zinc must occur predominantly along the grain boundaries.

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* The mean grain diameter was determined by means of an electron miscroscope.

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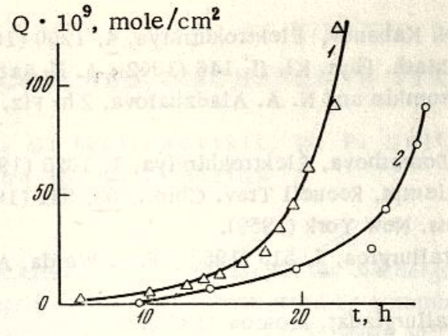

Fig. 1. Variation with time of amount of potassium (Q) diffusing through membrane with thickness 15 μ (1) and 19 μ (2).

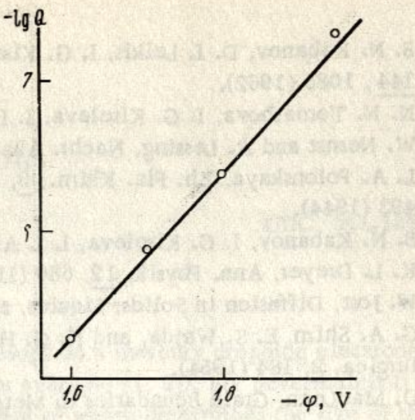

Fig. 2. Logarithm of amount of potassium diffusing through membrane in 22 h as function of polarization potential.

With the diffusion of potassium in zinc, like self-diffusion, the difference in the diffusion rates along the grain boundaries and within the grains is determined mainly by the difference in the structure of the crystal lattice of zinc at the boundaries and in the body of the grains. In this case diffusion of potassium in zinc at room temperature should also occur predominantly along the grain boundaries. It is moreover likely in our case that in order for this to take place it would be sufficient for the diffusion coefficient along the grain boundaries to exceed the diffusion coefficient in the body of the grain not by 10^7, as occurs with self-diffusion, but by only 10^4 times.

To investigate the dependence of the diffusion rate on the polarization potential of the membrane, the amount of potassium which diffused through a membrane 20 μ thick in 22 h was determined. The polarization cell contained 1 N potassium hydroxide solution. The results are shown in Fig. 2. As seen from the graph, the logarithm of the amount of potassium diffusing through the membrane increases linearly with the cathode polarization potential. This effect is fairly great: When the potential of the membrane is changed by 0.18 V, the amount of potassium diffusing through the membrane increases by 10 times. If it is assumed that the diffusion rate through the membrane is determined by the penetration rate, the penetration rate of potassium into the surface of the membrane should also clearly increase. At a potential of about −1.9 V against the normal hydrogen electrode the penetration rate is equal, as seen from Fig. 2, to approximately 10^{-7} mole/cm² in 22 h. This would correspond to the formation of approximately 100 monolayers of intermetallic compound per hour if the penetration were uniform. However, it was found earlier that about an hour was required to form a continuous monolayer of intermetallic compound on the electrode surface at the same potential, which indicates a much lower penetration rate leading to coverage of the surface [9].

In order to explain this apparent contradiction it is necessary to take into consideration the fact that diffusion through the membrane occurs along the grain boundaries. Consequently diffusion measurements can only be used to assess the penetration rate at points where the grain boundaries reach the surface. Since the grain boundaries occupy a very small part of the electrode surface, it is natural that this process can hardly increase the hydrogen overvoltage. Coverage of the electrode surface with intermetallic compound and the resulting increase in hydrogen overvoltage results from penetration of alkali metal into the surface of the grains and not into the points where the grain boundaries enter the surface.

It was suggested earlier [4] that the basic event in the penetration process consists of the migration of a discharging alkali ion from the outer layer of the double layer to a vacancy on the electrode surface and that the penetration rate is determined by the concentration of surface vacancies. In such a case the increase in the penetration rate with increased potential must signify that the electrode polarization increases the concentration of vacancies at its surface. The concentration of vacancies increases exponentially with decrease in their formation energy [10], while the vacancy formation energy is to a first approximation related linearly with the surface tension of the electrode metal [11]. When the electrode potential changes, the surface tension changes according to the electrocapillarity laws. If, as in the case of zinc for example, the electrocapillary curve maximum lies at a less negative potential than the polarization potential, the surface tension of the electrode metal decreases with increase in the cathode potential. Consequently the vacancy formation energy decreases and the penetration rate increases. Similar concepts were employed previously by Polukarov [12], who explained the increase in the defect disappearance rate in an electrolytic copper deposit during cathodic polarization by a decrease in the surface tension with increase in the potential.

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