Effect of ionic strength on the passivation of zinc electrodes in KOH solutions

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Times to passivation have been measured for zinc electrodes in KOH–KF solutions at room temperature. A linear relationship between i and $t^{-\frac{1}{2}}$ was obtained. The intercept of these lines is interpreted to be a limiting current density. This limiting current density reaches a maximum in solutions 5M in KOH. Beyond this concentration the limiting current density decreases. This phenomenon is explained in terms of the loss of unbound water as the ionic strength of the solution increases.

Introduction

Passivation studies of zinc electrodes in KOH solutions have been an active area of research in recent years because of the importance of this system in the development of high energy density batteries. Passivation studies of vertically oriented electrodes introduce complications arising from convection, except at short passivation times. These considerations are minimized when the electrodes are oriented horizontally [1]. However, the vertical orientation is more common in practical storage cells.

Previous investigations of vertically oriented zinc electrodes in KOH solutions [2] have shown that Equation (1) holds for solutions ranging from

$$(i-a) = kt^{-\frac{1}{2}} \qquad (1)$$

1 to 13·8M KOH. i is the current density, t is the time to passivation, and a and k are constants; the former is probably a limiting current density below which passivation will not occur. Values of a and k were obtained from i v. $t^{-\frac{1}{2}}$ plots. The values of k varied with KOH concentration and reached a maximum at about 8·5M KOH [2]. A plot of a v. KOH concentration produced a similar curve with a maximum

at about 8M KOH. These results indicate that there are opposing factors influencing the values of a and k. The purpose of the present investigation was to determine whether the ionic strength of the electrolyte is one of the factors affecting the values of these constants for vertically oriented zinc electrodes. KF was chosen to maintain the ionic strength because the F^- ion is isoelectronic with the OH^- ion and therefore it is likely to have the same hydration number.

Experimental

The cell used was the one described earlier [2]. All electrodes (counter, reference, working) were of 99·999% zinc. The working electrode was oriented vertically and had an area of 3·46 cm². Before each run this electrode was etched in 50% nitric acid and then thoroughly rinsed with deionized water.

The solutions were made by weight and volume from analytical reagent grade KOH and KF, and deionized, double distilled water. Each solution was prepared by dissolving solid KF in aqueous KOH.

Time to passivation was measured on a clock accurate to 0·01 minute which was started simultaneously with the passage of current

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through the cell by means of a double pole switch. Passivation was indicated by a rapid rise in anode potential as shown on a Moseley Model 680 voltage-time plotter connected between the reference electrode and the working electrode. The current was measured with a Weston Model 1 ammeter. All measurements were made at room temperature, $22 \pm 1°C$.

Results

Typical plots of i v. $t^{-\frac{1}{2}}$ are shown on Fig. 1. The lines depart from linearity somewhat at
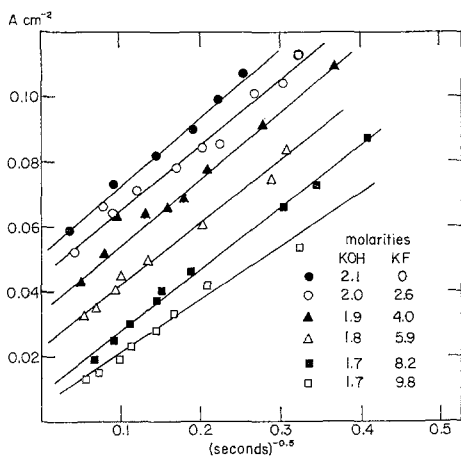

Fig. 1. Plot of i v. $t^{-\frac{1}{2}}$ for time to passivation studies of a zinc electrode in KOH solutions at room temperature.

longer passivation times in KOH solutions more concentrated than 7M, Fig. 2. For this reason, data from the longer passivation times were not used in calculating k and a in equation (1). For solutions more concentrated than 10M, only passivation times of less than 130 seconds were used. Hampson et al. [2] have suggested that such deviations from linearity are due to the downward flow of zinc-rich electrolyte over the face of the anode, its effect becoming more pronounced at longer passivation times.

Values of k and a, Equation (1), were calculated from the plots such as given in Figs. 1 and 2 by the method of least squares. Fig. 3 shows the values of k as a function of ionic strength. The dashed lines connect points of approximately equal OH^- ion concentration. Increasing ionic strength caused a decrease in the value of k. In F^--free KOH solutions the value of k is a
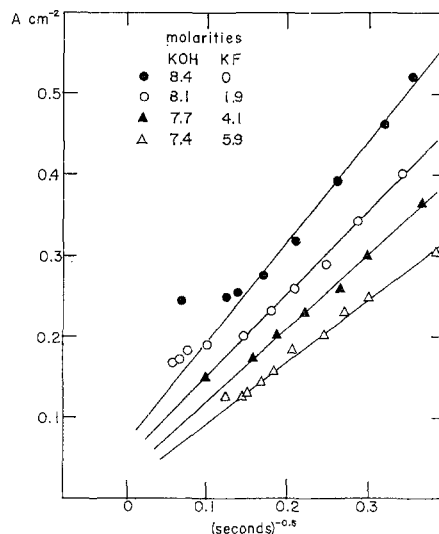

Fig. 2. Plot of i v. $t^{-\frac{1}{2}}$ for time to passivation studies of a zinc electrode in KOH solutions at room temperature.
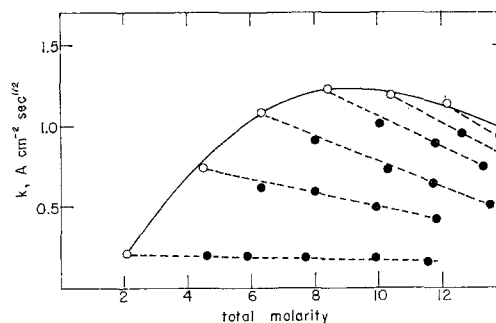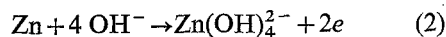

Fig. 3. Values of k as a function of ionic strength in KOH–KF solutions. Open symbols, F^--free solutions; closed symbols, KOH–KF solutions.

maximum in approximately 9M KOH.

The variation of a with ionic strength is given on Fig. 4. A maximum is obtained in about a 5M solution. For solutions more concentrated than this, a varies as a function of total ionic strength, independent of the contribution of KOH or KF.

Discussion

Although the actual steps in the zinc anode mechanism have not been definitely established [4, 5], the overall reaction may be represented as

$$Zn + 4 OH^- \rightarrow Zn(OH)_4^{2-} + 2e \qquad (2)$$

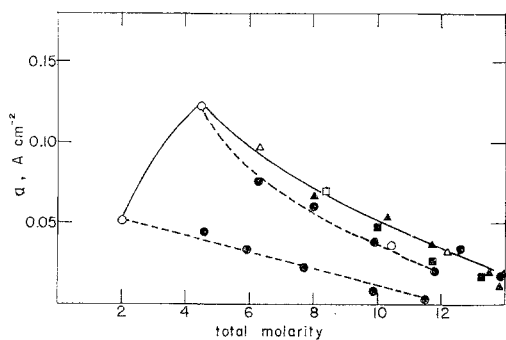Clearly then, the ability of the OH^- ion to reach

Fig. 4. Values of a as a function of ionic strength in KOH–KF solutions. Open symbols, F^--free solutions; closed symbols, KOH–KF solutions.

the electrode surface will influence the amount of current that can be supported without passivation. The effect of ionic strength on the mobility of the OH^- ion may explain the dependence of a on the ionic strength, and this is the approach we are presenting here.

We assume a to be a limiting passivation current density. Initially, it rises with increasing KOH concentration because there is a greater number of OH^- ions available to support a larger current without passivation. For solutions above 5M, apparently, the OH^- ion cannot reach the surface as readily, and this decrease in mobility results in a lower limiting current density. Adding KF to the KOH solution is likely to change only the concentration of 'free', i.e. non-bound water, by removing the water of hydration. The amount of 'free' water in solution, then, is determined by the total ionic strength. This may influence the value of a because of its effect on the mobility of the OH^- ion.

This dependence of the mobility of the OH^- ion on the amount of 'free' water can be explained by invoking a Grotthus-type mechanism for the transport of the OH^- ion in aqueous solutions. It has been proposed that the abnormally high mobility of H^+ and OH^- ions in water is due to an interchange between the ions and the solvent molecules with the result that the ion appears to travel much further than its true mean path [6]. Water molecules are hydrogen-bonded to each other. The force holding each hydrogen atom in the water molecule is greatly reduced by the approach of two other water molecules to the electron pairs of the oxygen

atom. An OH^- ion can easily be incorporated into the tetrahedral hydrogen-bonded structure of water [7]. The OH^- ion, having been incorporated into this structure can then leave as a molecule of water by removing one of the hydrogen atoms in the tetrahedral water complex. Fig. 5 illustrates, on a two-dimensional
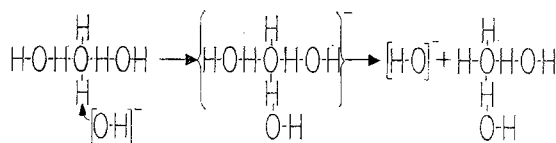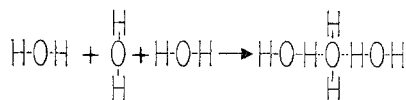

Fig. 5. Suggested mechanism for the transport of OH^- ions in aqueous solutions.

scale, the suggestion of Huggins [8] for this process. The centre of charge (OH^- ion) moves much further in this interchange than did the original OH^- ion. The rotation of water molecules to a favourable orientation appears to be the rate-determining step in this transfer mechanism [9]. It is evident that the probability of this transference will decrease as the number of 'free' water molecules decreases. Bound water molecules will not so easily be able to assume the proper orientation for this charge transference. Conductance measurements of concentrated KOH solutions [10] are consistent with this transference mechanism. Lown and Thirsk [10] conclude that as the concentration of KOH increases the percentage contribution of this charge transference mechanism decreases (from about 63% for 1M KOH at 25° and 1 atm to 0% at about 7M KOH), and that the OH^- ion conductance is increasingly due to a hydrodynamic mechanism. Their results give further evidence that the amount of 'free' water in solution affects the mobility of the OH^- ion.

In conclusion, the addition of KF to KOH solutions reduces the limiting passivation current density of the zinc electrode because the KF removes the 'free' water molecules by hydration, and this loss of 'free' waters lowers the mobility of the OH^- ions. Thus the effect of ionic strength on the value of a is due to the decrease in 'free'

water. The maximum on Fig. 4 can thus be explained as the net effect of two processes:

(a) as the KOH concentration increases, more OH^- ions are available and higher passivation currents can be tolerated;

(b) as the KOH concentration increases (increasing ionic strength), the concentration of 'free' water molecules decreases making it more difficult for the OH^- ions to participate in the electrode reaction.

This explanation may also account for the variation of k, Equation (1), in the KOH–KF mixtures, Fig. 3. However, because the physical significance of k is uncertain, no attempt is made here to develop such an explanation.

Acknowledgment

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