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The anodic behaviour of porous zinc electrodes

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The passivation of horizontal and vertical porous zinc (unamalgamated) electrodes in aqueous KOH solutions has been studied. The results are interpreted in terms of the formation of a soluble anodic product which decomposes within the electrode forming an insoluble deposit. The ohmic resistance of the insoluble anodic product provides the major component of the electrode polarization and determines the useful duration of discharge of the electrode.

Introduction

Interest in the electrochemical behaviour of zinc in aqueous alkali has increased in recent years because of the use of zinc, as the negative electrode, in battery systems possessing high energy and power to volume or weight ratios.

The transition between the active and passive states of the system Zn/Zn(II), OH^- has been intensively investigated [1]. Experiments have been mainly concerned with planar solid electrodes. Galvanostatically, transition times for passivation, τ, have been determined and attempts have been made to establish the relationship between the current density i, and τ. Whereas Sanghi and Wynne-Jones [2] concluded that there was no general relationship between τ and i, Landsberg [3], Eisenberg [4] and Hampson [5–8] and their co-workers showed that these parameters can be correlated thus:

$$(i-i_l)\,\tau^{\frac{1}{2}} = k \qquad (1)$$

where i_l is the limiting current below which passivation will not occur and k is a constant for a given electrolyte concentration, temperature and electrode disposition. The importance of free convection has been discussed by Eisenberg *et al.* [4, 9] who concluded that there was no theoretical justification for Equation (1) when convection occurred. Attempts have been made to minimize interference from convective mass transfer by shortening the transition time and optimizing cell design and electrode [4–9] configuration. Alternatively, it may be controlled by the use of a rotating disc electrode [10–12].

Work on porous zinc electrodes has been carried out by Breiter [13] who has compared $i-V$ curves for porous and smooth electrodes and found that only a small fraction of the interiors of porous electrodes participate in the electrochemical processes.

The object of the present investigation was to determine the transition times for porous electrodes using the galvanostatic technique. The data should form a comparison with similar data for smooth electrodes and provide information on the mode of passivation of porous zinc electrodes.

Experimental

Materials

All reagents were 'AnalaR' grade and bidistilled, deionised water was used throughout. KOH solutions were stored in 'hard' polyethylene containers, care being taken to exclude CO_2.

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Zinc anodes were prepared by the reduction of zinc oxide compacts on silver mesh grids in aqueous KOH (1 mol l^{-1}). After reduction the zinc sponge was freed from OH^- by washing and, after pressing, the electrodes were vacuum dried. The porous zinc electrodes had a large surface/weight ratio (~0·8 m^2 g^{-1}) and high porosity (72%). The zinc oxide content of the electrodes was ~2%.

Apparatus

Measurements were made with the anode in both horizontal and vertical configurations. This is shown, for the former case, in Fig. 1. The anode samples were supported by a zinc disc. The anode potential was measured with reference to an unpolarized zinc electrode in conjunction with a conventional Luggin capillary which was close to the anode surface. The overpotential measurements were made with a valve voltmeter, the circuit of which has been described previously [5]. Current measurements were made using a moving coil galvanometer (accuracy 1% of full scale deflection). The cathode was a platinum gauze.

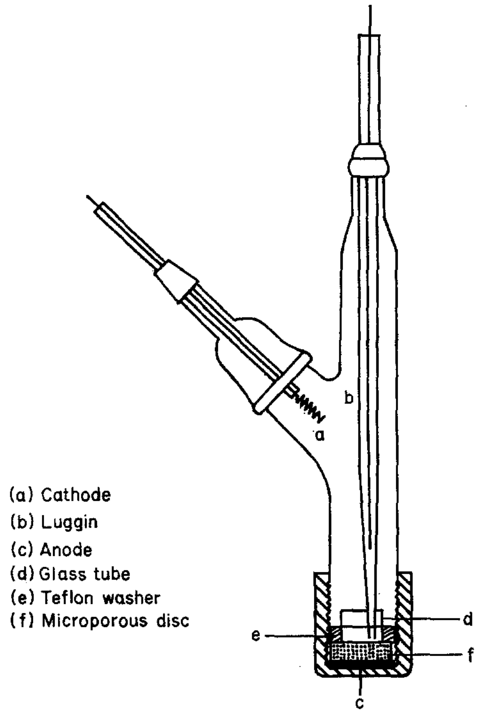

Fig. 1. Cells and electrode.

Procedure

Electrode potential measurements were made at convenient time intervals for different current densities with the test electrode in both horizontal and vertical orientations. Experiments were carried out in 1, 2, 5, 7, and 10 M KOH and in 7 M KOH containing different concentrations of zincate.

Interrupted polarization experiments in which the current was interrupted after flowing for a predetermined period were made on vertical orientated electrodes, in 7 M KOH electrolyte. After interruption, polarization was recommenced and continued until the electrode passivated.

Result and discussion

Zincate free electrolytes

During galvanostatic polarization at low overpotentials, gaseous hydrogen was evolved. This was probably due to the displacement of hydrogen retained (adsorbed possibly) within the porous structure of the electrode by the formation of the anodic product. (It should be noted that the Zn(II)/Zn electrode in alkali is 400 mV more negative than the potential of the reversible hydrogen electrode.)

Fig. 2 shows typical potential-time curves which are characterized by a nearly linear rise in overpotential, up to ~200 mV, followed by a steeper rise in the curve. Compared with planar

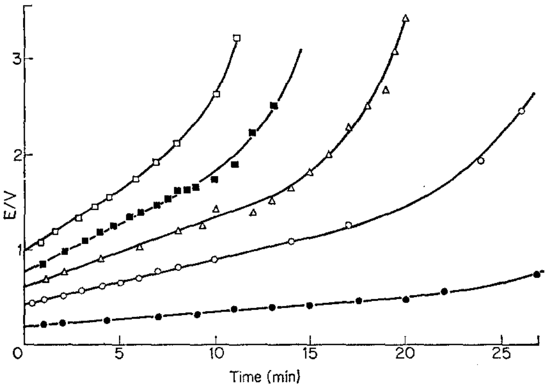

Fig. 2. potential time curves. 10 mol l^{-1}KOH; 23°C; vertical electrodes. □—1·82 A cm^{-2}; ■—1·66 A cm^{-2}; △—0·91 A cm^{-2}; ○—0.61 A cm^{-2}; ●—0.31 A cm^{-2}.

electrodes, passivation of porous electrodes is reflected by a more gradual increase in potential. (Even at quite high overpotentials (~1·8 V), possibly due to two simultaneous reactions, viz. oxygen evolution and anodic dissolution, the potential still continued to rise relatively slowly.) Consequently, in contrast to the planar zinc electrode, the time of passivation cannot be measured with any degree of accuracy without reference to the potential scale. The criterion used to define the termination of useful discharge was the attainment of a potential 0·3 V above the initial (on load) potential. The time when this occurred was defined as $t_{0\cdot3}$. Comparison of the times of polarization required to cause passivation in the case of smooth electrodes [5, 6], and microporous electrodes shows that at all current densities (above the limiting value in the case of vertically orientated systems) the active region of electrode discharge was considerably greater for microporous electrodes. Thus in 10 mol l^{-1}, at an apparent current density of 0·2 A cm^{-2}, 'vertical and horizontal' passivation times were respectively 65 sec and 40 sec for smooth electrodes compared with about 500 sec for both orientations of microporous electrodes. This confirmed the expected result that increasing the ratio true/apparent surface area increases the time of active anodic dissolution. The extent of the increase undoubtedly depends on the morphology of the electrode, for, whereas Breiter [13] reports that only a small part of the interior of the electrode participates in the electrochemical process, in the present case the contribution of the interior must be considerable.

The linear $i-\tau^{\frac{1}{2}}$ relationship which applies theoretically to a diffusion controlled passivation process is a consequence of solving the diffusion equation for the case of semi-linear infinite diffusion. A simple relationship also exists between the applied current density, i, and the time taken to reach a designated potential ΔV higher than the initial on-load potential, provided that the charge transfer overpotential and concentration overpotential remain constant (so that ΔV arises solely due to an increase in the ohmic resistance of the system). This is likely to be the case in a porous electrode system in which the anodic product remains as a solid phase on the electrode as is frequently the case with microporous zinc electrodes in alkali. The change in potential ΔV at $t_{\Delta V}$ due to the transfer of charge across the interphase is:

$$\Delta V = i \times \text{resistance } (R) \text{ of product layer.}$$

Since R is proportional to i,

$$\Delta V = \text{constant} \times i^2$$

Hence $t_{\Delta V}$ is proportional to i^{-2}.

Thus a plot of i versus $t^{-\frac{1}{2}}$ should be a straight line and the linear relationship would be expected to hold for all orientations of the electrode provided that no products leave the electrode. Fig 3 shows that linear i-$t_{0\cdot3}^{-\frac{1}{2}}$ plots are obtained for upward facing horizontally

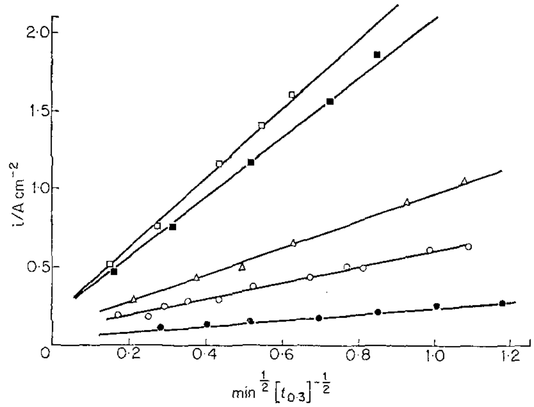

Fig. 3. i-$t_{0\cdot3}^{-\frac{1}{2}}$ Correlation—horizontal electrodes. ●—1 mol l^{-1}; ○—2 mol l^{-1}; △—5 mol l^{-1}; □—7 mol l^{-1}; ■—10 mol l^{-1} at 23°C.

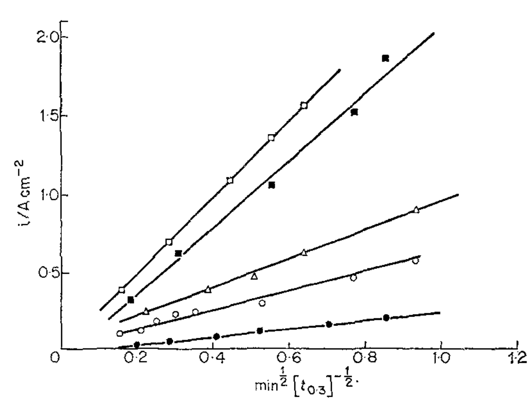

Fig. 4. i-$t_{0\cdot3}^{-\frac{1}{2}}$ Correlation—vertical electrodes. ●—1 mol l^{-1}; ○—2 mol l^{-1}; △—5 mol l^{-1}; □—7 mol l^{-1}; ■—10 mol l^{-1} at 23°C.

orientated electrodes although (as might be expected) the data are more scattered than those for smooth electrodes [5]. By extrapolating Fig. 4 to infinite time ($\tau^{-\frac{1}{2}} = 0$) for vertically orientated electrodes a significant limiting current density is indicated. However, these current densities are apparently proportionally less than those for similar systems with smooth electrodes [6] notwithstanding the very much increased active dissolution time. These results suggest that in the present experiments with vertically orientated electrodes a much larger proportion (in comparison with smooth electrodes) of the anodic product remains at the electrode. This is in agreement with the earlier assumption that the products of the anodic oxidation do not readily leave the microporous electrode. It is also interesting to note that the choice of other arbitrary cut-off potentials (ΔV) produce straight line plots. This gives general support to the ideas used in the interpretation of the experimental data since there is nothing special about the choice of any particular value of ΔV.

The extrapolation of the polarization curves (Fig. 2) to zero time yield values of η_0, the potential of the electrode at zero time. Attempts to correlate η_0 and i as conventional Tafel plots do not yield the expected linear relationship. Instead a straight line relationship between η_0 and i exists which extends well into the 'Tafel region'.

Since i_0 for the Zn(II)/Zn reaction in alkali is [14] ~300 mA cm^{-2} this latter observation tends to suggest that the main origin of the electrode polarization is ohmic.

At higher current densities potential oscillations are observed during the transition from active to passive states. These are similar to those reported by Breiter [13] who observed current oscillations during potentiodynamic experiments on the passive transition and attributed them to the buckling and tearing of the active film. Hull *et al.* [15] and Jones and Redfearn [16], the latter using similar electrodes to those used for the present investigation, observed oscillations at overpotentials of ~300 mV when zinc anodes were discharged at low temperatures in the region of −20°C. These may be caused by alternate passivation and depassivation of the zinc electrode.

Electrolyte containing Zn(II)

Examination of the *i* v. ($t_{0\cdot 3}^{-\frac{1}{2}}$) plots shown in Fig. 5 for both horizontal and vertical electrodes indicates that the addition of Zn(II) to the electrolyte has little effect on the duration of the discharge. This suggests that the oxidation product is not zincate but probably ZnO or $Zn(OH)_2$ formed by the decomposition of the complex diaquotetrahydroxyl anion. This is further evidence for the dissolution-precipitation model, passivation being due to back precipitation from the electrolyte rather than the formation of an insoluble layer by direct oxidation of the zinc electrode.

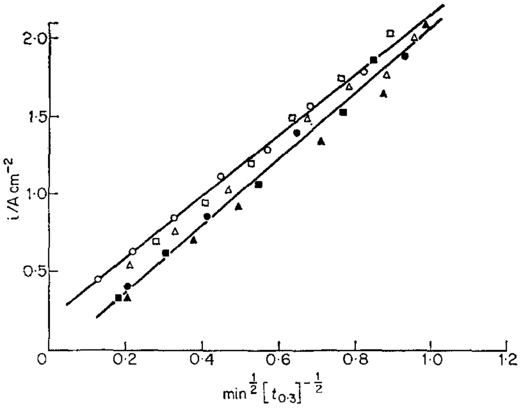

Fig. 5. Effect of [Zn(II)] on i-$t_{0\cdot 3}^{-\frac{1}{2}}$ curves horizontal and vertical electrodes. Open symbols: vertical systems at 23°C Closed symbols: horizontal systems. ○, ●—7·0 mol l^{-1} KOH; △, ▲—7·0 mol l^{-1} KOH + 1·2 mol l^{-1} ZnO; □, ■—7·0 mol l^{-1} KOH + 0·6 mol l^{-1} ZnO.

Interrupted polarizations

It has been demonstrated with a smooth electrode [6] that provided adequate time was allowed to elapse after an interruption in the polarization, the electrode returned to its unpolarized condition. That is, if the products of the electrode reaction were allowed to diffuse away from the electrode, then the system was unaffected. It was found that in the present series of experiments this is certainly not the case, as is shown in Fig. 6 which is typical of the systems tested. The longer the rest after a polarization has been commenced and interrupted, the shorter the time required for the complete termination

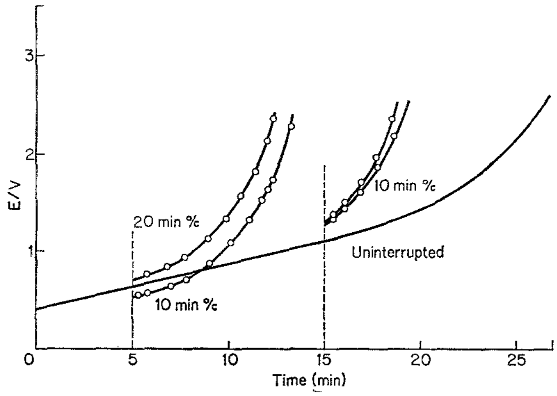

Fig. 6. Interrupted polarizations. 10 mol l^{-1} KOH; 23°C; vertical electrodes 0.61 A cm^{-2}. ‐ ‐ ‐ ‐ denotes start of interruption.

of the zinc dissolution reaction. These results can be interpreted if the initial product of the electrode reaction is $Zn(OH)_4^{2-}$ (probably hydrated), produced according to

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

which then decomposes within the pores of the electrode according to

$$\begin{aligned} Zn(OH)_4^{2-} &= ZnO + H_2O + 2OH^- \\ &\text{or} \\ &\quad Zn(OH)_2 + 2OH^-. \qquad (3) \end{aligned}$$

The results shown in Fig. 5 make it clear that this decomposition is a fairly slow reaction. That this reaction is indeed slow is supported by the findings of Hampson, Herdman and Taylor [7]. Some further support is also given to the diffusion-precipitation model by this behaviour.

Mechanism of discharge

The results strongly suggest that the normal processes of charge transfer and mass transfer in solution do not control completely the termination reaction in the present system. It seems likely that the reaction proceeds by the initial formation of a soluble zincate which then decomposes to give an oxide film within the pores of the electrode. This oxide film gives rise to a high ohmic component of the total electrode overpotential. It is suggested that this ohmic overpotential is the major factor which terminates the useful discharge of the porous zinc electrode.

Acknowledgments

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