JOURNAL OF APPLIED ELECTROCHEMISTRY 7 (1977) 271–273

SHORT COMMUNICATION

The point of passivation of a zinc electrode in alkali

A. MARSHALL

Ciba-Geigy Ltd, Simonsway, Manchester, UK

N. A. HAMPSON

Chemistry Department, The University, Loughborough, Leicestershire, UK

Received 28 October 1976

Confirmatory evidence is provided that at the point of passivation of solid zinc in alkali there is no free OH^- in the reaction layer at the electrode.

---

1. Introduction

A number of workers [1] studying the anodic behaviour of polycrystalline zinc in KOH solutions have established that after a period of active dissolution the electrode becomes passive, caused by a layer of oxy-products based on Zn(II) covering the electrode surface. Investigations [2–4] of the anodic behaviour using galvanostatic polarization have been unable to yield information about the actual mechanism by which the passive layer is formed. Powers and Breiter [5] and Powers [6] have made L.S.V. measurements coupled with simultaneous microscopic examination of the working electrode. Two processes were identified, both of which engendered the formation of an electrode film. The formation of $Zn(OH)_2$ on the electrode via back-precipitation from a supersaturated solution and the formation of ZnO directly from the lattice were observed [5]. Dirkse and Hampson [7] also used L.S.V. in KOH solutions ranging in concentration from 1–13 mol dm^{-3} to obtain information on the mode of passivation and concluded that this back-precipitation was the most likely process of electrode blocking.

A knowledge of the composition of the electrolyte layers next to the electrode is clearly of some importance since this composition becomes critical at the point of passivation. It was suggested [4] on the basis of a large number of passivation experiments in concentrated alkaline zincate electrolyte that passivation occurs when the Zn(II) concentration at the anode is equal to a half of the hydroxyl concentration in the bulk. This communication confirms that conclusion.

2. Experimental

Current-bias potential curves were obtained using a scanning potentiostat (Kemitron 0·5A) and recorded on an *X–Y* recorder (Bryans 26000A4) or photographed from the screen of an oscilloscope (Hewlett-Packard 130C).

Electrolyte solutions were prepared from AnalaR grade reagents and bidistilled de-ionized water. The reference was the Hg/HgO electrode, which was separated from the main cell by a closed liquid seal tap in conjunction with a Luggin capillary system. The zinc working electrode was prepared from zinc rod (Johnson Matthey 99·999%) mounted in polythene and sectioned at right-angles to the long axes. The counter electrode was a large area platinum gauze.

3. Results

Typical current–potential L.S.V. curves showed the characteristic maximum now recognized as typical of this system [5, 6]. Fig. 1 shows plots of peak height versus Zn(II) concentration for the linear potential sweep of polycrystalline zinc in two alkaline solutions. Extrapolation of the curves to the Zn(II) concentration axis yields a value of approximately a half of the hydroxyl concentration

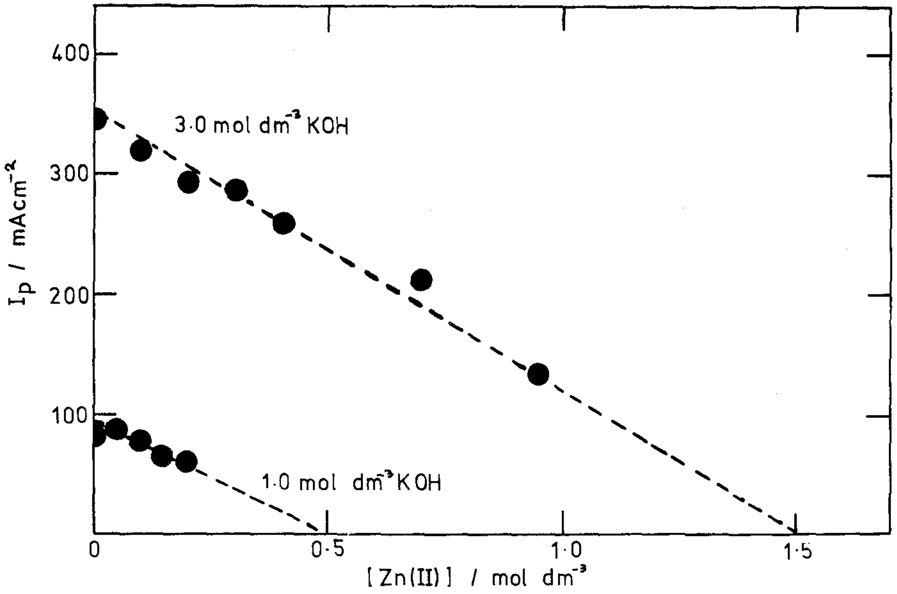

Fig. 1. Current maxima in the L.S.V. curve for a zinc electrode in alkaline zincate solutions. Sweep rate = 0·030 V s^{-1}; temperature = 23° C.

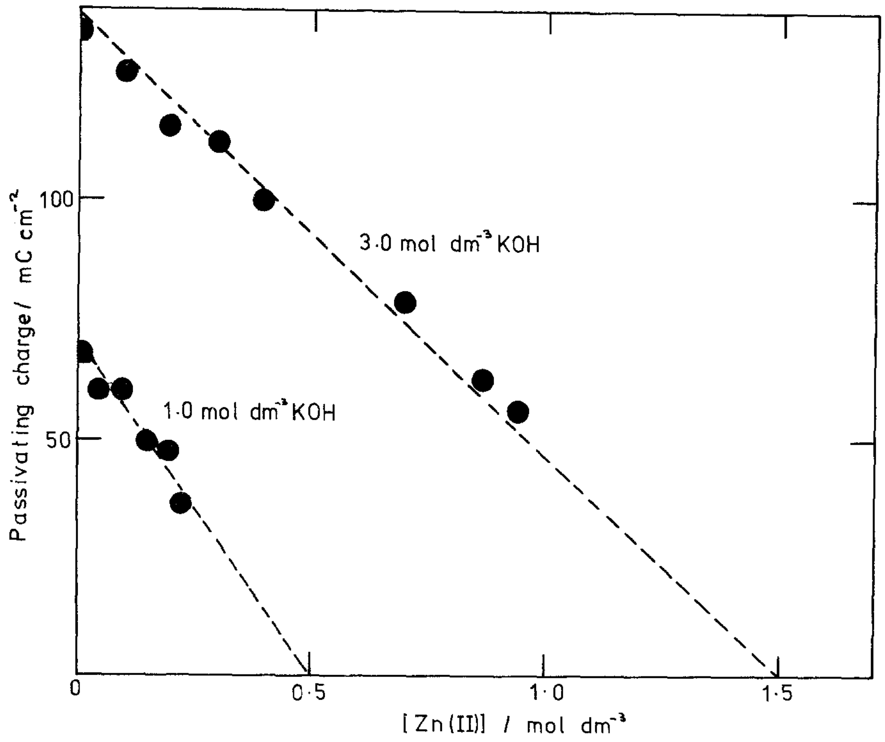

Fig. 2. Passivating charge for the passivation of zinc in alkaline zincate solutions. Sweep rate = 0·030 V s^{-1}; temperature = 23° C.

for the electrode/electrolyte system displaying maximum passivity. Similar extrapolations can be made for the passivating charge versus Zn(II) concentration plots (Fig. 2).

4. Discussion

The results obtained for KOH solutions are in agreement with the findings of Powers and Breiter [5], who concluded that the oxidation of zinc in KOH solution could take place via a dissolution–precipitation process, at potentials below the critical value for the initiation of the solid-state reaction. Assuming a high degree of reversibility in the electron transfer step, the concentration implied by the Nernst equation will result in an exceeded solubility product as the potential is made more positive. A progressive precipitation of Zn(II) will then occur in the electrode layer. Archdale and Harrison [8] have described the mechanism by which this solution-formed solid material may find its way back to the electrode surface. The initial film was found to be white, loose and flocculant, being predominantly $Zn(OH)_2$. A more compact greyish-black film of ZnO was observed at more positive potentials; this was formed by the solid-state oxidation of the zinc surface.

When the concentration of Zn(II) equals a half that of the OH^-, Figs. 1 and 2 indicate that the passivating charge (and maximum current) is zero. Hence the earlier suggestion [4] is confirmed.

The passivating process in the present experiments is, therefore, that of a build-up of Zn(II) in the anodic layers to a considerable degree of supersaturation corresponding to $2OH^- \equiv Zn(II)$. When no further OH^- is available (to form $Zn(OH)_2$) the electrode passivates.

References

[1] N. A. Hampson, 'Zinc-Silver Oxide Batteries,' (ed. A. Fleischer and J. J. Lander) Ch. 5, Electrochemical Society Inc., Wiley, New York (1971) pp. 37–61.
[2] M. Eisenberg, H. F. Bauman and D. M. Brettner, *J. Electrochem. Soc.* **108** (1961) 909.
[3] N. A. Hampson and M. J. Tarbox, *ibid* **110** (1963) 95.
[4] N. A. Hampson, P. E. Shaw and R. Taylor, *Brit. Corros. J.* 4 (1969) 207.
[5] R. W. Powers and M. W. Breiter, *J. Electrochem. Soc.* **116** (1969) 685.
[6] R. W. Powers, *ibid* **118** (1971) 685.
[7] T. P. Dirkse and N. A. Hampson, *Electrochim. Acta.* **117** (1972) 135.
[8] G. Archdale and J. A. Harrison, *J. Electroanal Chem.* **34** (1972) 21.