ELECTROCHEMICAL BEHAVIOUR OF ZINC IN ALKALINE SOLUTIONS

Part I. Constant Current Measurements

BY INDRA SANGHI* AND W. F. K. WYNNE-JONES
(Physical Chemistry and Coke Research Laboratories, King's College, University of Durham, Newcastle-on-Tyne)

Received November 4, 1957
(Communicated by Dr. K. S. G. Doss, F.A.SC.)

ABSTRACT

The cathodic and anodic polarization of zinc in different concentrations of alkaline solutions has been studied under constant-current conditions. The changes of zinc electrode-potential with reference to a Hg/HgO/KOH system have been measured both in KOH and zincate solutions using a "Luggin" capillary and a specially designed cell, current being drawn from an electronic current stabilizer. Time-potential curves have been plotted and it is found that the anodic zinc passivates at a certain stage showing a sudden rise in potential by as much as 3-4 volts. Before the passivation, the main electrode reaction is the formation of Zn++, while after the passivation it changes to gas evolution. No definite relationship as previously suggested by Muller, between the current density and the passivation time was found, perhaps due to migration and non-linear diffusion effects and other reasons discussed in the paper. It has been found that the behaviour of zinc differs in concentrated alkaline solutions (i.e., 0.5 N to 5 N) from that in dilute solutions (0.2 N to 0.01 N), in which case the open circuit rest-potential of zinc is indefinite and may vary by as much as 500-600 mV, while the maximum passivation jump in potential is about 2 volts only. Also the passivation and the decay of current on breaking the circuit are found to be slower than in the case of concentrated solutions. Colour changes of the zinc electrode, during the polarization, are also briefly described and discussed.

INTRODUCTION

In recent times there has been increased interest in the electrochemical behaviour of zinc owing to its potential applications in new types of storage batteries, electrolytic capacitors, semiconductors and rectifiers, etc. Various workers have studied different aspects of the behaviour of zinc in the past;

* Present Address: Senior Scientific Officer, Central Electrochemical Research Institute, Karaikudi, S. India.
but their approach has been rather limited in the sense that they were usually concerned with particular problems of plating and polarization, etc. For example, Morgan and Ralston,\textsuperscript{1} Tope,\textsuperscript{2} Baroch, Hilliard and Lang,\textsuperscript{3} Edward and Swanson,\textsuperscript{4} etc., have studied the possibility of depositing zinc from zinicate solutions. Abramson,\textsuperscript{5} Beklemysheva,\textsuperscript{6} Titov and Paleolog\textsuperscript{7} and Essin\textsuperscript{8} studied the cathodic polarization of zinc on various metals or streaming-mercury electrodes. Similarly, Clark and Akimov,\textsuperscript{9} Newbery,\textsuperscript{10} Muller,\textsuperscript{11} etc., have studied the anodic passivation of zinc, while Huber,\textsuperscript{12} Bieri\textsuperscript{13} and Laske\textsuperscript{14} have been mainly interested in the morphology of the anodic layers produced on zinc. Other workers such as Hoar,\textsuperscript{15} Evans,\textsuperscript{16} Vernon,\textsuperscript{17} Gilbert\textsuperscript{18} and Delahay\textsuperscript{19} et al. have concerned themselves with the corrosion and pitting of zinc. However, a co-ordinated picture of the whole phenomenon does not emerge from these studies. There are also several gaps in the existing information which it is now possible to fill in by the use of new instruments and techniques. It was therefore thought desirable to make a comprehensive and co-ordinated study of the various problems involved in anodic and cathodic polarization of zinc, particularly in alkaline solutions.

\textbf{EXPERIMENTAL}

\textit{Apparatus and materials}.—The method used was to record the potential changes at the individual electrodes while they were being polarized. The following polarizing and measuring circuits were used:—

\textit{Polarizing circuit}.—The source of polarizing current was an electronic current stabiliser similar to that described by Thirsk and Wynne-Jones.\textsuperscript{20} It employed ten EF 50 valves in parallel and an anode voltage of 500 volts. Its current range could be extended from 60 $\mu$A. to about 100 mA. but it was more stable in the range 100 $\mu$A. to 40 $\mu$A. when a current change of 0.5% required a change of about 300 V across the cell. The current could be set to desired values by means of appropriate resistances in the cathode line of the valves, in series with the cell. Two sets of cathode resistances could be used, either a set of variable resistances or a selected value from a set of fixed resistors.

\textit{Measuring circuit}.—Three different arrangements to measure the potentials were used depending on the requirements of the measurements, \textit{e.g.},

\begin{enumerate}
\item To obtain the slow changing time-potential curves, a potentiometric circuit with a multi-range Pye Galvanometer was used.
\item To obtain more rapidly changing potentials, a sensitive Cambridge Galvanometer suitably shunted and calibrated was used. As used, it took only about 0.2 $\mu$A. per volt deflection of about 40 mm.
\end{enumerate}
Electrochemical Behaviour of Zinc in Alkaline Solutions—I

(c) For very rapid changes an oscilloscopic arrangement could be used to photograph the curves. But it was found that the oscilloscope needed a current of more than 2 µA. per volt deflection and it was coupled with a suitable single-valve cathode follower which reduced the intake of the current from the experimental cell to about 0.2 µA. only.

Cell.—The electrochemical cell used was of a special design similar to the one recently described by Jones, Lind and Wynne-Jones. It was fitted with a perspex top which held the experimental electrode in such a way as to allow it three independent movements, i.e., vertical, horizontal and rotational. The cathode and anode compartments were fully separated by a joining tube and were about 6" apart.

Reference electrode.—The Hg/HgO/N-KOH system was used as reference electrode. The actual construction of which was such as to avoid any external bridge while at the same time incorporating a "Luggin" capillary which could be placed quite close to the surface of the experimental electrode. It incorporated a small test-tube with a pin-hole blown in the side to allow electrical contact between the electrode and the main body of electrolyte. The whole assembly could easily go into a side limb of the cell by means of an ungreased ground glass joint. The tip of the capillary was placed in front of the experimental electrode as recommended by Sidney Bernart to give the best current distribution and potential measurement.

Bronsted and Ming Chow have evaluated the $E^\circ$ of the system Hg/HgO(S)-OH'/H2; Pt at 25° to be about 0.9264 volt. Employing the value of $E^\circ = 0.8280$ volt for OH'/H2; Pt half cell, we get Hg/HgO, OH' $E^\circ = 0.0984$.

Solutions.—All solutions were made from "Analar" KOH and ZnO in distilled water and were stored in Pyrex vessels, fitted with a U-tube containing "Sofnolite" to absorb CO2. Solutions could be taken out by pumping air through these "Sofnolite" tubes.

The electrolyte in the cell was changed every day and care was taken to see that the concentration of zincate ion did not materially change during the course of the experiment. However, during the experiment the solution was accessible to air and not stirred.

Zinc.—Two types of zinc were used:

(i) Containing 0.2% of Pb and 0.05% of Cd.

(ii) 99.99% pure zinc.
Temperature.—A thermostat maintained at 25°C. (± 0.1°C.) was used during all measurements of potential changes. Platinum foil was used as the auxiliary electrode.

Experimental technique.—It was decided, after some preliminary experiments, that pure zinc sheet electrodes of 99.99% purity would be the most convenient to use. The electrodes consisted of 1 × 1 × 0.3 cm.5 sheets, to the centre of one face of which a thick steel wire was firmly but carefully soldered so as not to affect the zinc as far as possible.

Preparation of electrode surface.—Factors affecting the choice and selection of electrode materials and of the methods of prepolarization-preparation and cleaning have been well discussed by Briggs.55 Clearly, the question of pretreatment of electrodes is very complex and complicated and no clear picture of all its effects is so far available. Some of the confusion and diversity of experimental data reported by various workers in the past might easily have been due to the different pretreatment techniques employed. The procedure adopted finally was to smooth out the flat face of the zinc electrode by rubbing down with six grades of "SIA" emery paper (from 0 to 6/0) lubricated with alcohol, and rotating the face by 90° between successive grades. A final treatment of rubbing with "diamantine powder" was tried but found to be unsatisfactory as diamantine tended to get embedded in the surface. The electrodes were, therefore, given a final rub first with plain parchment paper and then with "Selvyt" cloth lubricated with alcohol, before being put in the cell.

| Table 1 |

**Cathodic polarization**

<table>
<thead>
<tr>
<th>Room temperature</th>
<th>Potentials vs. Hg/HgO/N—KOH reference electrode in volts.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration of KOH</td>
<td>Initial Rest Potential</td>
</tr>
<tr>
<td>N</td>
<td>−1.35</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>N/100</td>
<td>−0.5</td>
</tr>
<tr>
<td>2.5 N</td>
<td>−1.36</td>
</tr>
<tr>
<td>N</td>
<td>−1.32</td>
</tr>
<tr>
<td>N/2</td>
<td>−1.28</td>
</tr>
<tr>
<td>N/5</td>
<td>Variable</td>
</tr>
<tr>
<td>N/10</td>
<td>−0.6 to 1</td>
</tr>
<tr>
<td></td>
<td>−1.2</td>
</tr>
</tbody>
</table>
Stopping off.—The rest of the electrode and the wire-lead were given two coats of either the commercial stopping-off compound "Lacomit" or a polystyrene cement.

Polarization procedure.—Two minutes after the electrodes were introduced into the cell, their potential with respect to the reference electrode was measured. By careful working and use of the above technique the reproducibility of this could be achieved within ± 5 millivolts. Only when this was achieved was the constant current from the stabilizer switched on and the polarization started. All current densities were estimated on the apparent area of the electrode surface.

In the following experiments, the solutions were not stirred.

RESULTS

(Note.—All potentials as given in this section are with respect to Hg/HgO/N KOH half-cell.)

Cathodic polarization

In 2.5 N—KOH saturated with ZnO.—on cathodic polarization, zinc deposits could easily be obtained from such solutions. At 20 mA./cm.² the initial potential of about −1.36 V. slowly became more negative by about 0.1 V. in half an hour, as the deposition proceeded.
In N-KOH saturated with ZnO.—Zinc deposits at 20 mA./cm.², the potential changing quickly at first from about —1·3 to —1·5 V. in 30 seconds, and then gradually becoming more negative by 50–60 mV. in 5 minutes or so.

In N-KOH.—The steady initial potential (without polarization) of zinc electrode was about —1·35 V. On commencing the polarization at a c.d. of 14 mA./cm.² the potential first jumped to about —1·58 V. and then gradually decreased to —1·66 in about 15 minutes. On switching off, the recovery was very rapid up to —1·36 V. followed by a slow rise to —1·35 V. in about 15 minutes. Working with the same electrode and varying the current density in the range 100 μA. to 40 mA./cm.² and allowing time for the potential to become sufficiently steady, it was found that the potentials obtained in the increasing and decreasing order of current densities were very similar, but it was easier and quicker to achieve steady values of potential in the decreasing order than in the increasing order of current densities.

The potential of the zinc electrode varied from —1·37 to —2·03 V. when the current density was varied from 100 μA. to 40 mA./cm.². On plotting the potential against the logarithm of the current density from the above preliminary results, all the points between current density 40 mA. to 500 μA./cm.² were found to lie on a straight line. Only the points corresponding to lower current densities were on a curve convex to the “log i” axis.

In 1·65N-KOH + 4 gm./lit. of ZnO.—The potential changes corresponding to cathodic polarization at various current densities are shown graphically in Fig. 2.

As shown there, the zinc electrode potential was found to oscillate at current densities of the order 10–20 mA./cm.². Also, on switching off the current the recovery of potential was very rapid.

The potential values corresponding to cathodic polarization at other current densities in some solutions are tabulated in Table I.

Anodic polarization

In 1·65N-KOH containing 4 gm./lit. of ZnO.—The potential changes at various current densities are shown graphically in Fig. 2.

The upper part of the diagram represents conditions of anodic polarization, while the lower part represents conditions of cathodic polarization. Each curve shows the potential changes at a particular value of the current density and where the potential change was too rapid to be followed accurately by the measuring arrangements (a) and (b) as described earlier, a broken
**Electrochemical Behaviour of Zinc in Alkaline Solutions—I**

**Fig. 2.** Potential—Time Curves for Zn in Alkaline Solutions.
line is shown on the curve. When the current was switched off the potential changed rapidly and this decay is indicated in each curve by an arrow pointing downwards on the anodic and upwards on the cathodic polarization curves.

At current densities higher than 10 mA./cm.² the zinc electrode seems to be clearly characterized by a well-defined passivation stage, when the potential may suddenly jump as much as 4 volts or so depending on the conditions of polarization. At current densities of the order of 15–20 mA./cm.² the passivation may occur at any time between 2½ and 4 hours of polarization. Within this range the actual passivation time was not found to be reproducible. At 40 mA./cm.² the passivation may set in within 10–15 minutes of polarization while the maximum potential reached may only be about +1.9 V. The relation between the current density and the time taken for passivation under these conditions was not found to be a simple or definite one. The potential of the passive electrodes may vary from +1.85 to +2.7 V, and is not exactly reproducible, although it obviously depends on the current density to some extent and approximately lies in the same region under similar conditions. At 20 and 40 mA./cm.² the zinc electrode potential was found to oscillate and fluctuate with time, although it is difficult to say how far this phenomenon was truly periodic in nature, as the matter was not investigated in detail. However, it may be of some interest to note that Schwabe²⁸ quite recently published his study of true periodic phenomena on zinc electrodes in chloride, sulphate, nitrate and perchlorate solutions. The decay of potential on switching off the current was very rapid in all these cases.

In 5 N-KOH containing 20 gm./lit. ZnO.—No passivation occurs even after 5 hours and at a current density of 50 mA./cm.² while at 100 mA./cm.² partial passivation occurs in about 30 minutes or so, when an electro-polishing effect is obtained at a slightly fluctuating potential of about +2.05 V. Decay of potential on switching off the current is rapid in these cases also.

In 2.5 N-KOH saturated with ZnO.—Zinc does not passivate when polarised at current densities lower than 40 mA./cm.² Even at 40 mA./cm.² it freely goes into solution with an overvoltage as low as about 50 mV, and is not found to passivate upto 3 hours. However, above 55 mA./cm.² passivation is found to occur in about 40–60 minutes when the potential suddenly rises to about +2.3 V.

In N-KOH saturated with ZnO.—At 10 mA./cm.² it takes about 2–3 hours before zinc passivates suddenly and the potential rises from the initial value of about −1.3 to +2.4 V. However, within a few minutes the potential
falls again slightly and then becomes steady at about $+2.0\text{ V}$. At 20 mA./cm.$^2$ the potential first slowly rises to about $-1.15\text{ V}$. in 18-20 minutes when it suddenly passivates and the potential jumps to $+2.0\text{ V}$. At 40 mA./cm.$^2$ the passivation is almost immediate.

If after passivation, the current is switched off and the decay followed, it is found that the potential very rapidly falls from $+2.0\text{ V}$. to about $0\text{ V}$. and then gradually falls to about $-0.7\text{ V}$. in about 3 minutes or so when it either becomes steady, or further falls towards the equilibrium potential depending on the history of polarization.

In N-KOH solutions the pre-polarization rest potential is $-1.34$ to $-1.35\text{ V}$. When an anodic current of 14 mA./cm.$^2$ is switched on it jumps to $-1.28\text{ V}$. and then slowly rises to $-1.24\text{ V}$. in about 15 minutes. On switching off, the decay is very rapid and the electrode almost regains its rest potential.

In 0.5 N-KOH.—A 2 mA./cm.$^2$ the potential varies only slightly (about 50 mV.) in 4-5 hours, when there is sudden passivation and the potential jumps to about $+2.0\text{ V}$. and then changes little. However, at 5 mA./cm.$^2$ the passivation is gradual and sets in within a few minutes as shown in Fig. 2. During this time a thin greyish film is formed on zinc which slowly turns into a dark blue anodic layer. This layer can be peeled off by making the electrode cathodic for a few minutes at a current density of about 200 $\mu\text{A}$.

In 0.5 N-KOH saturated with ZnO.—No passivation occurs within 20-30 minutes at 2 mA./cm.$^2$, but if the current density is then raised to 5 mA./cm.$^2$ passivation quickly sets in and the potential jumps to somewhere in the region of $+2.5\text{ V}$. or more depending on the nature and time of previous treatment of the electrode. However this jump is not very reproducible. Also, the decay of the potential, when the current is switched off after the passivation, is not immediate but gradual and there is an arrest in the potential region of $-0.5\text{ V}$. 

In more dilute solutions.—Time potential curves for some more dilute solutions are shown in Fig. 3. The decay of potentials, on switching off, is also shown. A few main potential values at some polarization stages are also given in Table II.

In all solutions, with or without ZnO, of concentration 0.2 N-KOH or lower, the equilibrium rest potential of an unpolarized electrode is often found to lie in the region of $-0.5\text{ V}$. although it may vary and in some cases even tend towards $-1.2\text{ V}$. depending on the conditions of the electrode surface, amount of oxide formed or present and the dynamics of corrosion


### Table II

**Anodic polarization**

<table>
<thead>
<tr>
<th>Concentration of KOH</th>
<th>Initial Rest Potential</th>
<th>c.d. mA/cm.²</th>
<th>Passivation Time</th>
<th>Potential Before Passivation</th>
<th>Potential After Passivation</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>-1.35</td>
<td>14.0</td>
<td></td>
<td>-1.24</td>
<td></td>
<td>Does not passivate for several hours</td>
</tr>
<tr>
<td>N/2</td>
<td>-1.3</td>
<td>5.0</td>
<td>About 5 minutes</td>
<td>+1.5</td>
<td>+1.85 V in 60 minutes</td>
<td>Potential continues to rise slowly and reaches +1.85 V in 60 minutes</td>
</tr>
<tr>
<td>N/10</td>
<td>Variable</td>
<td>2.0</td>
<td>4.5 hours</td>
<td>-1.3</td>
<td>+2.0</td>
<td>Gradual passivation</td>
</tr>
<tr>
<td></td>
<td>-1.2 to 0</td>
<td>0.1</td>
<td>About 5 minutes</td>
<td>Variable</td>
<td>+1.7</td>
<td></td>
</tr>
<tr>
<td>2.5-N</td>
<td>-1.36</td>
<td>10.0</td>
<td></td>
<td>-1.34</td>
<td></td>
<td>No passivation even in 3 hours</td>
</tr>
<tr>
<td></td>
<td></td>
<td>40.0</td>
<td></td>
<td>-1.32</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>55.0</td>
<td>50-60 minutes</td>
<td>-1.25</td>
<td>+2.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.5-3 hours</td>
<td></td>
<td>+2.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>-1.32</td>
<td>10.0</td>
<td></td>
<td>-1.15</td>
<td>+2.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>20.0</td>
<td>18-20 minutes</td>
<td>-1.15</td>
<td>+2.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>40.0</td>
<td>immediate</td>
<td>+2.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N/2</td>
<td>-1.32</td>
<td>5.0</td>
<td>0-1 minutes</td>
<td>+2.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>50.0</td>
<td>immediate</td>
<td>Above</td>
<td>+2.8</td>
<td></td>
</tr>
<tr>
<td>Saturated with ZnO</td>
<td></td>
<td>2.2</td>
<td>1-5 minutes</td>
<td>Slowly rises</td>
<td>+1.4</td>
<td>Gradual passivation</td>
</tr>
<tr>
<td>N/10</td>
<td>-1.2 to 0</td>
<td>1.0</td>
<td>0-5 minutes</td>
<td>+1.7</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Taking place. The passivation at current densities 2 mA/cm.² and lower, is gradual and can often be followed through all its stages. It may take 1-5 minutes to passivate completely and reach a peak voltage of about +1.5 V. Similarly, the decay is also gradual and there is a potential arrest in the region of -0.5 V.
GENERAL OBSERVATIONS

(a) In dilute solutions, if a good anodic passive layer has initially been formed by polarizing at 5 mA./cm.² or higher for some time and then the current is reduced, the potential falls only slightly at first but the electrode may become active again if left for a long time and if the current density is very low.

(b) However, if the current is reversed and made cathodic at 50–100 μA./cm.², after passivation, a significant amount of coulombic capacity can be observed for a time comparable to the anodic polarization time, before the potential reaches the −1.0 V. mark. Then on switching off the cathodic current, the potential tends to rise again and may reach a value of up to −0.5 V. This shows that under these conditions, it might be possible to
carry out, to a certain extent, some electrochemical oxidation or reduction entailing one of the following processes:

(i) oxidation and reduction of zinc oxide layers;
(ii) deposition and dissolution of zinc;
(iii) growth and dissolution of anodic layers;
(iv) evolution of oxygen or hydrogen.

It would be of great interest and practical importance from the alkaline accumulator viewpoint if the first of the above processes could be carried out electrochemically. However, our later experiments (under publication) tend to show that the first process is not very easy and is, in any case, improbable between $-0.5$ V. and $1.0$ V. Similarly the second process has also been shown to be inefficient and is improbable under these conditions so that finally a choice between the third and the fourth processes is left. It is very difficult to prove or disprove either of these two conclusively with the data available at the moment. However, constant overvoltage experiments do indicate that in cathodic reduction under the above conditions, most probably hydrogen is evolved on the zinc oxide surface which covers the electrodes in the potential regions of $-0.5$ V., in dilute solutions.

However, another disadvantage from the accumulator viewpoint is that the potential is not very constant and that there is no definite arrest. On the one hand, under passive conditions the anodic potential may wander between $+1.5$ V. and $+2.8$ V. depending on the concentration and current density, and on the other, under cathodic polarization it drops suddenly to $-1.3$ V. or lower in concentrated solutions, when zinc may be deposited or hydrogen evolved depending on the availability or otherwise of zincate ions. In dilute solutions, although the potential variation is not so large, the tendency for gas evolution on the Zn/ZnO/KOH surface also becomes more pronounced and oxygen may be given off below $+1.5$ V. while hydrogen evolution starts between $-0.5$ V. and $1.0$ V. Thus, although apparently the decay of potential is slow, in reality it does not involve any electrochemical reduction of the zinc oxide electrode.

(c) In all solutions if after passivation, the current density is gradually reduced the potential of the electrode gradually falls till either with increasing time or falling current density it ultimately becomes active again. However once passivated, the electrode potential does not fall back to the active region as soon as the current density is reduced below 20 mA./cm.$^2$, as suggested by Newbery.$^{20}$ There is a time lag depending on the previous history and conditions of the polarization of the electrode.
(d) A very large variety of anodic layers of different colours and appearance may be formed on zinc in alkaline solutions. The main influencing factors seem to be (i) current density, (ii) concentration of electrolyte, (iii) composition of electrolyte, i.e., presence of zincate, etc., (iv) nature of electrode surface and purity of material and (v) duration of polarization. It seems that factors (ii) and (iii) exert their influence mainly by the variation of the dissolving effect of the electrolyte on the anodic layers, e.g., layers are darker when the solutions are concentrated or no zincate is present than in weaker or zincate solutions. This is presumably due to the formation of excess interstitial zinc ions in the layers which are thereby rendered dark, when the solution exerts a significant dissolving effect.

However no detailed study of the colour and morphology of these layers was made in our experiments as Huber and his co-workers have already investigated this aspect.

**DISCUSSION OF PASSIVATION CURVES IN CONCENTRATED SOLUTIONS**

Various reasons for sudden passivation have already been discussed by Muller. In addition the following may also be considered:

(a) Phase changes on the surface which may involve sudden changes in the internal potential drops between metal/oxide, oxide/solution and across the oxide layer.

(b) Change in mode of conduction, i.e., from ionic to electronic (through interstitial ions, etc.) leading to change in the nature of reaction on the electrode.

It is difficult to decide and specify how far and which one of the above possibilities applies to a particular case. It is now realized that, in fact, measurements based on constant current methods alone are probably not sufficient to conclusively differentiate between the above. It is felt that in the case of constant current methods all the various stages of gradual polarization and passivation may not be observed due to the artificial necessity of forcing a predetermined current through the electrode. For example, observations on a fixed current density could only show those points of a potential current curve which lie on the co-ordinates of the current density being forced through. Such observations would therefore essentially be discontinuous. This may also be the reason why the potential after passivation wanders over such a wide range, i.e., $+1.5$ to $+2.8$ V., even though the basic reaction is the same, i.e., gas evolution. Thus, these passivation potentials only indicate the potential at which a particular current density can be sustained under the experimental conditions.
The slight gradual fall of potential after the initial passivation jump has been observed in some other cases also. Efforts have been made to explain this on the basis of:

(a) Recrystallisation or phase changes on the electrode surface.

(b) Breakdown of one dielectric and the establishment and stabilisation of another.

(c) Phenomena of nucleation and nucleus growth.

(d) Changes in the dissolving power of the electrolyte in contact with the anodic layer.

Hunter et al., have shown that in the case of porous anodic layers in general and for aluminium oxides in particular, the temperature and concentration of the electrolyte in the pores are very different from those of the bulk. If the case of zinc is taken to be similar, it may be assumed that when the resistance suddenly changes thereby causing the potential to jump, within a few seconds the heat produced in the pores and on the oxide-solution interface increases the solubility of the oxides slightly thereby reducing the layer thickness and allowing the potential to fall accordingly till a new equilibrium is established.

Passivation time.—Considerable efforts have been made to establish a relation between passivation time and current density, etc. But, it appears that there are many more variables involved than appear superficially or have so far been taken into account. For example, as not much attention was paid in the past to the pre-polarization preparation and surface conditions of the electrode, the results of various workers cannot be properly co-related and co-ordinated. Moreover, recent efforts to verify Muller’s equation have taken into consideration only short passivation times of the order of a few seconds at high current densities. It is therefore not surprising that under the conditions of our study we did not find passivation times to be reproducible presumably due to the convection and non-linear diffusion effects interfering. This was perhaps the case in Bieri’s experiments as well.

Discussion of Results in Dilute Solutions

In dilute or saturated zincate solutions the time-potential curves obtained are significantly different from those in concentrated alkaline solution, the main reason probably being that the dissolution rate of anodic layers is much larger in concentrated solutions. Saturation with zincate reduces the dissolving power but can by no means stop it completely as it has been
shown that even such saturated solutions can always take up more zinc which goes in as a complex and is then slowly precipitated out. The solubility may also be enhanced by the local increase of pH at the anode due to migration of OH\textsuperscript{-} ions.

But obviously the complex ion formation is much slower in dilute KOH and saturated zincate solutions thereby encouraging other reactions, e.g., layer formation and growth and ultimately passivation and gas evolution to compete more favourably.

Thus, in the interpretation and discussion of time-potential curves in dilute solutions, the only significant point is that the pre-polarization or post-polarization rest potential tends to stay in the region of $-0.5\, \text{V}$ and that even if a cathodic current of $100\, \mu\text{A./cm.}^2$ is passed the potential does not drop below $-1.0\, \text{V}$. Now we know that the hydrogen discharge or reduction potential of zinc oxide on zinc surface is mostly below $-1.3\, \text{V}$. So either of these processes are not very probable if the surface of the electrode is metallic zinc. But there is reason to believe that zinc is often covered with a very thin oxide film (Raether, Huber, Bieri, Laske, etc.) which may be dissolved by concentrated solutions but remains more or less unaffected in dilute solutions. So the potential that is being measured in dilute solutions is not Zn/electrolyte but Zn/ZnO/electrolyte potential. It is on the surface of this thin, adherent, covering layer of oxides, that both zinc deposition from zincate solutions, and hydrogen evolutions from pure alkali solutions can take place. Between $-0.5$ and $-1.2\, \text{V}$, it appears that only hydrogen evolves, the rate and the potential depending on the current density used.

Clark and Akomov\textsuperscript{9} have also observed that the open circuit potential tends to become slightly more positive with time. The reason why we find only a pseudo arrest with a varying potential range and not a particular fixed potential value corresponding to Zn/ZnO/KOH may be that in open circuit the potential tends to accommodate itself according to the corrosion balance in which $H_2$ evolution rate $=$ zinc corrosion rate and the electrons produced in the reaction

$$Zn \rightarrow Zn^{++} + 2\, e$$

are exactly equal to those used up in

$$2\, H^+ + 2\, e \rightarrow H_2.$$

Our constant potential results tend to confirm the above explanation and conclusively show that hydrogen can be deposited on ZnO at potentials $+\, ve$
to the equilibrium rest potentials. These observations are in conformity with those reported by Vermilyea\textsuperscript{30} in the case of tantalum.

ACKNOWLEDGEMENT

One of the authors (I. S.) wishes to thank the Electricity Research Council of the Central Electricity Authority, U.K., for their interest and support to this work.

REFERENCES

5. Abramson \ldots Bull. Acad. Sci., URSS, 1938, 1209.
7. Titov and Paleolog \ldots Khimi Referat. Zhur., 1941, 4, 84.