Voltage decay at passivated zinc anodes

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A study has been made of the passivating process at a zinc electrode in KOH solutions. Zinc electrodes were passivated at a constant overpotential and the current response during passivation was measured. The potential response after the passivating potential was removed was also measured.

The current during passivation soon reached a semi-steady-state value which increased with increasing overpotential but varied only slightly with changing KOH concentrations.

When electrodes were passivated at overpotentials > 325 mV, the open circuit voltage decay showed an arrest, the duration of which decreased with increasing KOH concentration. This duration increased when ZnO was dissolved in the electrolyte, when the temperature was decreased, and when the passivating overpotential was increased.

The results are interpreted by assuming that passivation is due to the formation of a film, possibly $Zn(OH)_2$, which can dissolve in the electrolyte. The potential of the electrode is a mixed potential.

The anodic zinc electrode process in alkaline solutions has been studied in a variety of ways. Some studies used galvanostatic methods [1–6]; others used transient DC pulses [7–9]; the potentiostatic approach has also been used [10]. The process has been studied in dilute as well as in concentrated alkaline solutions. Both NaOH and KOH have been used as the electrolyte. Thus a good deal of experimental information is available.

The general conclusion of all this work is that the anodic process consists of the following steps.

1. The zinc is oxidized to form solid ZnO or $Zn(OH)_2$;
2. this ZnO or $Zn(OH)_2$ dissolves in the electrolyte to form $Zn(OH)_3^-$ or $Zn(OH)_4^=$, depending on the electrolyte concentration;
3. after a while the electrolyte can no longer dissolve the ZnO or $Zn(OH)_2$ that is produced by the charge transfer reaction, and then the solid ZnO or $Zn(OH)_2$ film remains on the electrode, passivating it. This represents the end of discharge in a zinc–alkaline battery.

While there is fairly general agreement on this three-step mechanism for the anodic behaviour, there is some difference of opinion concerning the details of the various steps. Part of this may be due to differences in experimental procedure and conditions. Euler [11] suggests that the parameters for the electrode process may depend on the purity of the zinc electrode.

Step 3 is the passivating process. Many attempts have been made to determine the time-dependence of this process. One relationship that has been observed [5, 7, 8, 12–14] is given in equation (1).

$$(i-a) \times t^{\frac{1}{2}} = k \tag{1}$$

where

i is the current density;

t is the time to reach passivation;

a is a constant, probably a limiting current density; and

k is a constant

This relationship was observed both for vertical and horizontal electrodes [14, 15], but the values of the constants are different.

This equation is similar to one for a diffusion-limited process. In this situation it could be the diffusion of zincate ions away from the electrode. If one uses the Sand equation [16], then

$$k = \frac{nFAD^{\frac{1}{2}} \pi^{\frac{1}{2}} C}{2} \qquad (2)$$

where

n is the valence of the diffusing ion;

F is the Faraday;

D is the diffusion coefficient of the diffusing ion;

C is the difference in concentration of the diffusing species at the electrode surface and in the bulk solution.

Application of equation (2) may not be easy in this situation. The diffusion coefficient of the zincate ion does vary with KOH concentration and there will be changes in OH^- ion concentration as current flows. Furthermore, convective processes will no doubt modify the diffusion process. However, if one assumes that the diffusion coefficient does remain constant, then the fact that k is experimentally a constant suggests that C remains constant throughout the anodic process.

Assuming an average value of 0·7 amp $sec^{\frac{1}{2}}/cm^2$ for k [15] and using 10^{-6} cm^2/sec as the value of the diffusion coefficient [21], then, at 25°C, the value of C is approximately 0·004 $moles/cm^3$ or 4 M. This is a solubility greater than that of stable ZnO but possibly that of the discharge reaction product. This value seems fairly reasonable considering the obvious approximations involved in making the calculations.

At higher current densities, a first order time dependence was found [5, 12]

$$(i - a') t = k' \qquad (3)$$

a' has been interpreted as a corrosion current density and k' as the number of coulombs needed to form a covering layer on the zinc electrode [12]. Others [6] could determine no relationship between current density and passivation time.

The general interpretation for these relationships is that a or a' corresponds to the rate at which the discharge product dissolves in the electrolyte. i, of course, is a measure of the rate at which the zinc is oxidized. Thus equations (1) and (3) provide a mathematical statement of the proposition that the time required for passivation depends on the net effect of two processes: the formation of the discharge

reaction product; and the dissolution of this product in the electrolyte. The greater the difference between these two processes, the faster the discharge reaction product will accumulate on the electrode surface and the shorter will be the time required for the electrode to be passivated. The term a can then be considered to be the maximum current density at which passivation will not occur [13]. However, these relationships have not yet served to clarify in detail the mechanism of these anode processes.

Experimental

The work described and reported here was undertaken to gather more information about this passivating process at the zinc anode.

The cell case and arrangement were the same as that used in earlier work [17]. The working electrode was the cross-sectional area (0·018 cm^2) of a 99·999% zinc wire. The reference electrode was an amalgamated zinc wire, and the counter electrode was zinc sheet. The electrolyte was aqueous KOH ranging from 10 to 45% KOH by weight. Two types of electrolyte were used: (1) plain KOH solutions; and (2) these same KOH solutions saturated with ZnO.

A Wenking potentiostat was used to impress the anodic potential upon the electrode. This potential was applied and removed by means of a mercury-wetted contact relay. The voltage–time trace was obtained on an X–Y plotter using an electrometer having an input resistance of 10^{14} ohms. Such traces were made at 25°C and at −3°C. All measurements were made in unstirred solutions.

Results

The anodic potential was impressed for different lengths of time up to 6 minutes. Typical current flow during that time is shown on Fig. 1. At anodic potentials of 100 mV or greater, the current behaviour was the same as that shown on Fig. 1 for 200 mV. The current reaches a somewhat steady state after about 20 seconds. This semi-steady-state current varied with the impressed potential as shown on Fig. 2, and also slightly with KOH concentration (Fig. 3). There
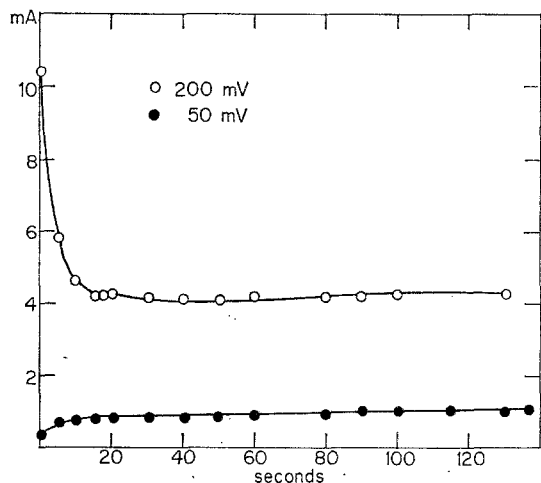
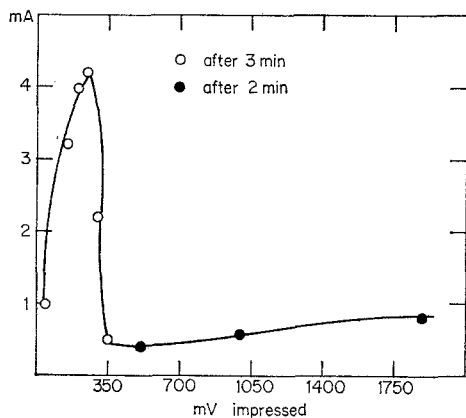Fig. 1. Current-time traces during voltage decay in 20% KOH at 0°C.

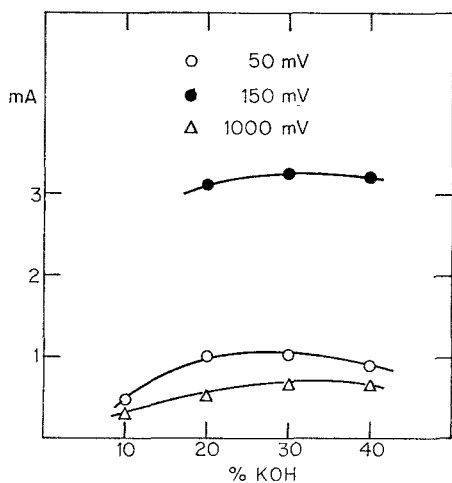Fig. 2. Steady state current in 30% KOH at 0°C while voltage is impressed for the time indicated.

Fig. 3. Steady state current at 25°C.

was no oxygen evolution under any of the experimental conditions used.

In some instances the current oscillated during the anodization period. This was noted in 30 and 40% KOH and occurred when the impressed potential was about 300 mV. These oscillations appeared sometime during the first 200 seconds, and lasted at least a half minute. In one instance the oscillations continued for about 5 minutes. The current range during the oscillations varied from 1 to 8 mA.

When the applied potential was removed, the voltage of the zinc electrode dropped immediately. However, as the applied potential increased, this rapid drop on open circuit voltage was followed by a slower drop (Fig. 4). After this there was a rapid drop to a value near that of the open circuit voltage (before any anodic potential was applied). This slower decay in voltage, a–b in Fig. 4, has been associated with the formation of a film of zinc peroxide on the zinc electrode [18]. Experiments were carried out in which repeated passivation–depassivation cycles were made on the same electrode without removing it from the electrolyte. These cycles gave substantially the same results provided the electrode was allowed to relax to its original equilibrium potential before it was repassivated.

The variation of the length of this slower voltage decay portion a–b was measured. A summary of the results is shown in Fig. 5–8. The variation of a–b with KOH concentration is
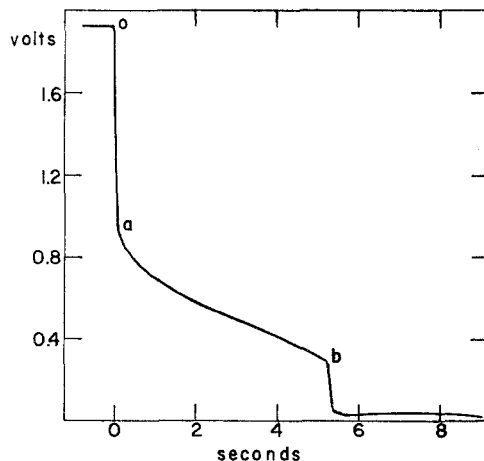

Fig. 4. Voltage decay at 25°C in 30% KOH saturated with ZnO after a voltage of +1900 mV had been impressed for 3 mins.
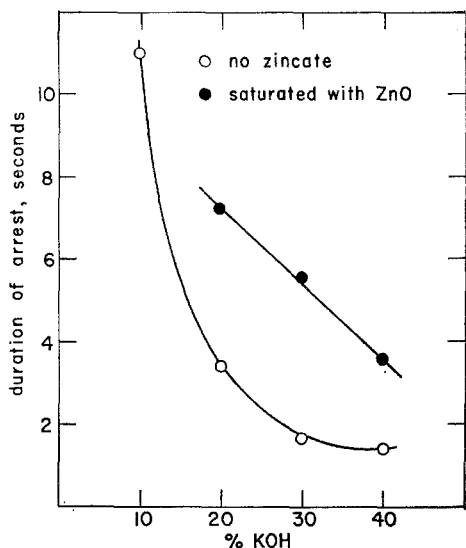
C

Fig. 5. Duration of voltage arrest at 25°C after impressing +1900 mV for 2 mins.

shown in Fig. 5: the length of a–b decreases rapidly with increasing KOH concentration, the presence of zincate ion serves to increase the length and when solutions containing higher zincate concentrations (obtained by electrolytically generating it) were used, the length of a–b increased still further. One solution containing electrolytically generated zincate behaved somewhat differently than other electrolytes that were used. This was a 30% KOH solution containing
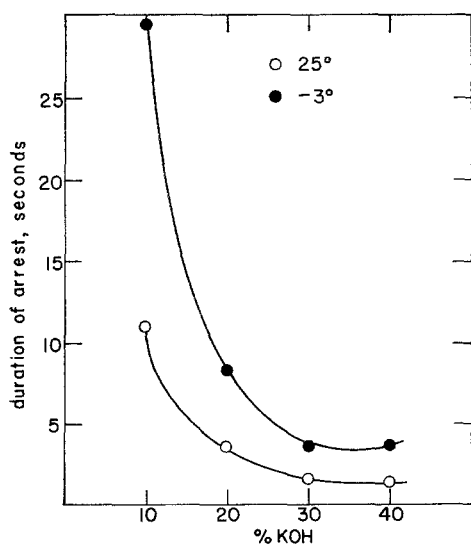

Fig. 6. Duration of voltage arrest in zincate-free solutions after impressing +1900 mV for 2 mins.

11% dissolved ZnO. For this solution the length of a–b increased continually with the length of time the anodic voltage was impressed (up to 6 minutes) The other electrolytes showed the kind of behaviour illustrated in Fig. 8.

Lowering the temperature also increases the length of a–b (Fig. 6). The length of a–b increases with the value of the anodic potential that is
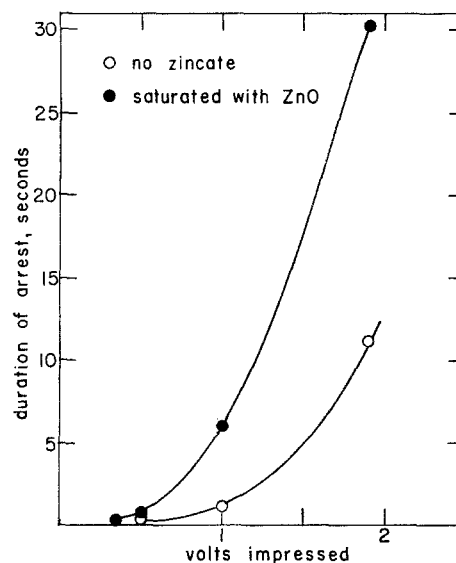

Fig. 7. Duration of voltage arrest at 0°C in 20% KOH after impressing an anodic potential for 2 mins.
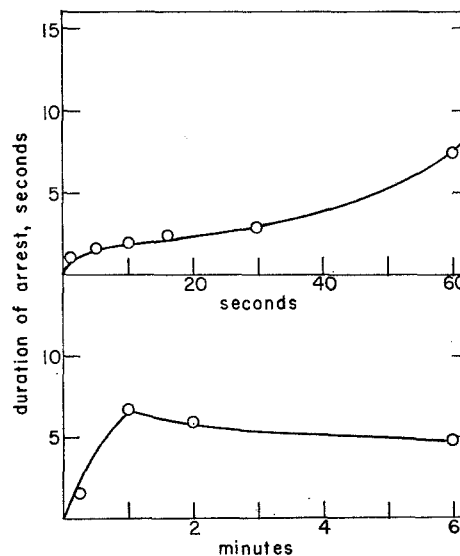

Fig. 8. Duration of voltage arrest at 0°C in 20% KOH saturated with ZnO as a function of the time a potential of +1000 mV was impressed.

applied to the electrode (Fig. 7) and also with the time the anodic potential is applied (Fig. 8). However, the maximum length of a–b is realized when the anodic potential is applied for about 1 minute. As the time is increased beyond this, a–b decreases a little in length. The portion a–b (Fig. 4) was not observed when the impressed anodic potential was less than 325 mV.

Discussion

The results presented here can be explained qualitatively in terms of the formation of a passivating film on the zinc electrode. This film is unstable with respect to the electrolyte either because it dissolves or because it may undergo a phase change to ZnO, for example.

We may assume that the voltage arrest shown in Fig. 4 is due to such a passivating film without specifying the precise nature of the film. These arrests were obtained only when the impressed voltage was greater than 325 mV. At potentials greater than this the final current during anodization is rather small, suggesting that passivation or film formation has taken place, Fig 2. The length of the voltage arrest should then coincide with the length of time the film remains on the electrode. The film is removed by dissolving in the electrolyte, as shown by the results of repeated passivation-depassivation cycles with the electrode relaxing to the original equilibrium condition within a short time (~ 10 min) after the current was interrupted. The variation of the length of the voltage arrest should then vary with the rate of dissolution of the film in the electrolyte. The length of the voltage arrest decreases with increasing KOH concentration. This is consistent with the fact that ZnO and $Zn(OH)_2$ have increased solubilities at increased KOH concentrations.

The length of the voltage arrest increases in the presence of zincate ions. This too is consistent with a dissolving process because ZnO and $Zn(OH)_2$ would dissolve less readily in solutions already containing zincate than in solutions containing no zincate.

Further, the length of the voltage arrest is greater at lower temperatures. One would also expect the rate of dissolving to decrease as the temperature is lowered.

The length of the voltage arrest is also related to the magnitude of the applied potential and its duration, Figs. 7 and 8. If the film forms a resistive layer on the electrode, then increasing the potential would allow an increased current to flow (Fig. 2) and this would result in a thicker film or one which takes longer to dissolve.

Likewise, allowing the potential to be applied for a longer time would lead to a thicker film which takes longer to dissolve. However, some of this film may begin to dissolve while the electrode is still being anodized and, consequently, the length of the voltage arrest (the amount of film) need not be directly related only to the potential and length of anodization.

As mentioned earlier, it has been suggested that the film is ZnO_2 [18]. This was suggested because the voltage level of the arrest is about 500 mV anodic to that of the open circuit voltage of a zinc electrode in a zincate solution. No thermodynamic data are available for ZnO_2 so it is impossible to calculate a theoretical potential value for an electrode involving this substance.

The voltage arrest appears in some instances when the applied potential is only 325 mV anodic to the zinc/zincate potential. It seems unlikely that this potential would be sufficient to produce a peroxide. Nor can this be accounted for by the presence of an oxygen gas potential since in these experiments the electrode potential was not high enough to bring about the evolution of oxygen.

Any electrode involving $Zn(OH)_2$, Zn, or $Zn(OH)_4^=$ would not have a potential much more anodic than that of a zinc/zincate system unless the activities of the reacting species were extremely high or low. Thus there is no known chemical system involving zinc and oxygen that could give the potential associated with the voltage arrest.

An alternative explanation for the voltage arrest is that it is due to the diffusion of ions into and out of the double layer. However, if this were so one would not expect the sudden drop in voltage at point b of Fig. 4. This rapid drop suggests that a reactive species disappears and that the potential is then set by another system. This latter system is undoubtedly the zinc/ zincate system because the level of potential is

practically equal to that of open circuit as measured before the anodic potential was impressed.

Still another explanation is that during the passage of anodic current previous to the voltage decay measurements, it is possible that a film of $Zn(OH)_2$ is produced on the electrode surface [19]. During this time OH^- ions accumulate at the electrode surface [19]. The charge transfer reaction is

$$Zn(OH)_2^= \rightarrow Zn(OH)_2 + 2e \qquad (4)$$
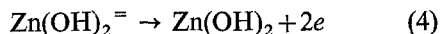
and the potential determining reaction during open circuit may be this system. At the moment the circuit is opened, the relative activities of the reacting species are such that the electrode potential is somewhat more anodic than that for the $Zn/Zn(OH)_2$ or $Zn/Zn(OH)_4^=$ systems. The $Zn(OH)_2^=$ may break up during the open circuit period and the $Zn(OH)_2$ will dissolve in the electrolyte. When the $Zn(OH)_2^=$ is gone, then the system will have the potential of the $Zn/Zn(OH)_2$ or $Zn/Zn(OH)_4^=$ couples which are rather close to each other in value. This assumption suggests then that the voltage-arrest is determined by the adsorbed $Zn(OH)_2^=$ species.

Some generalizations with respect to the length of the initial voltage drop, O–a in Fig. 4, may provide a clue.

1. For very short times of anodization, O–a increases as the time of anodization decreases.
2. O–a increases with increasing KOH concentration
3. O–a decreases with increasing zincate concentration.

Observation (1) suggests that the level of the voltage arrest is time-dependent. As the time of anodization increases the level of the voltage-arrest rises. This may be related to the change in activity of reacting species at the electrode surface.

Observations (2) and (3) show that the voltage level of the arrest increases with decreasing KOH concentration and with increasing zincate concentration. This suggests that reaction (4) is not the potential-determining process.

A more plausible explanation is as follows. The equilibrium potential (ocv) at a zinc electrode is the mixed potential involving the reduction of hydrogen, or, if zincate ions are present, it is the potential of the zinc/zincate system. The difference here is about 20 to 50 mV.

After the electrode has been polarized to passivation, the zinc is covered with a passivating film, perhaps $Zn(OH)_2$. Consequently, the ocv is now determined by the film and perhaps the oxygen evolution reaction. As the electrode remains on open circuit the film begins to dissolve or undergo a phase change. When either or both of these processes have proceeded to such an extent that zinc metal is exposed to the solution, then the potential of the system will fall to, and be set by, the zinc/zincate level.

This explanation is supported by the fact that this overvoltage decreases with increasing KOH concentration and with decreasing zincate ion concentration.

Another contributing factor is the nature of the passivating film that is formed, e.g., its compactness, or composition. This, too, may change with changing electrolyte concentrations. Such changes in physical nature may also govern the type of mixed potential that exists at the electrode.

The matter of oscillations has been dealt with recently by Degn [20]. His approach can also account for the oscillations we have observed. The passivation potential for the zinc electrode is somewhat less than 300 mV. At impressed voltages equal to or greater than this, the electrode becomes passive and the current falls. At this low current rate little reaction takes place and the concentration polarization is reduced. This allows more current to flow. Because of an external resistance (external to the electrode) in the system, this IR drop increases as the potential of the zinc electrode falls: $E_{el} = E_{imp} - IR$. Finally, E_{el} decreases to the point where the electrode again becomes active.

At higher values of E_{imp} the IR term does not become large enough to reduce E_{el} to a value below the passivation value. However, if E_{imp} is reduced, this value is reached and the electrode becomes active again.

Thus, the results of this work strongly suggest that the anodic passivation of the zinc electrode in KOH solutions is due to film formation on the electrode. The nature of this film cannot be unequivocally described from these results.

However, it does appear to have the solubility characteristics of $Zn(OH)_2$.

Acknowledgment

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