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(Received, 27 July, 1994  
Revised form, 7 March 1995)

## Electrochemical Behaviour of Zinc in Alkaline Carbonate Solutions

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### Abstract

Carbonation by atmospheric carbondioxide is a problem in affecting the performance of electrodes used in alkaline batteries. Zinc electrodes suffer loss of shelf-life, discharge capacity and cycle life when carbonates contaminate the electrolyte. Cyclic voltammetric studies on zinc in alkaline carbonate solutions revealed the formation of two types of passive films. Increase of carbonate and hydroxyl ion concentrations causes the dissolution of both these films. The enhanced dissolution is responsible for the loss of cycle life. Detailed mechanism of film-formation and dissolution is discussed.

### Introduction

Interest in the understanding of the passivation of zinc in alkaline carbonate solutions is raised, in particular with that of carbonate's deleterious effect in alkaline electrochemical cells while using zinc as a rechargeable anode. Carbonates slowly accumulate due to the absorption of atmospheric CO<sub>2</sub> or it is introduced with the tapping-up water. Excess amounts of carbonates in the electrolytes of Ni-Zn cells are known to have a detrimental influence on the cell performance; the cells become sluggish due to the decrease in conductivity [1]. However, a few studies were made on the effect of carbonates on the dissolution and passivation of zinc [2, 3, 4].

The chemical species likely to be formed by the oxidation of zinc in dilute alkali and alkaline carbonates solutions may be an amorphous form and six other crystalline forms designated as  $\alpha$ ,  $\beta_1$ ,  $\beta_2$ ,  $\gamma$ ,  $\delta$  and  $\epsilon$ . The most stable one is  $\epsilon$ -Zn(OH)<sub>2</sub> or several basic carbonates may be formed in addition to ZnCO<sub>3</sub><sup>2-</sup> species in excess carbonate solutions. Zn<sub>5</sub>(OH)<sub>6</sub>(CO<sub>3</sub>)<sub>2</sub> is well characterised among other basic carbonates. It occurs naturally as hydrozincite among other basic carbonates. It occurs naturally as hydrozincite which consists of Zn<sup>2+</sup> in coordination with 6 and 4 in the ratio of 2:3 [5].

It is also important to establish whether the formation ZnCO<sub>3</sub> involves the direct formation of a solid state oxidation or dissolution-precipitation.

### Experimental

Zinc electrode (99.999% purity) of 0.5 cm<sup>2</sup> area was used as working electrode. A large platinum and Hg | HgO | OH<sup>-</sup> electrodes were used as auxiliary and reference electrodes respectively. The solutions were deoxygenated by passing N<sub>2</sub> gas before the experiments. The Analar chemicals were dissolved in double-distilled water. Solutions of 0.1M to 6.0M KOH, and KOH solutions containing 10<sup>-1</sup>M to 8 x 10<sup>-1</sup>M K<sub>2</sub>CO<sub>3</sub> were used.

### Results

#### 1. Behaviour in alkali solutions

When polarised from -1500 mV to -900 mV an anodic peak appeared at -1200 mV (Figure 1). The reverse scan exhibited

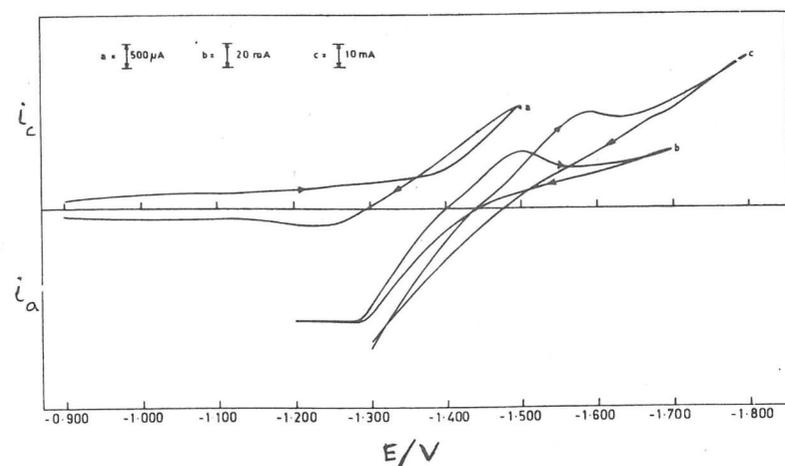


Fig.1: Typical cyclic voltammograms of zinc in KOH solutions at 50 mV/s

(a) 0.1M (b) 6.0M (c) 10.0M

a cathodic peak at -1350 mV, followed by hydrogen evolution in 0.1M KOH. The anodic peak potential was independent of sweep rate. The anodic peak currents decreased with sweep rate. This

is because the electrode surface is getting passivated. The passive film formation exceeds the dissolution of zinc in 0.1M KOH.

At higher KOH concentrations (1.0M to 6.0M KOH) the anodic peak potential and anodic peak current varied linearly with  $\sqrt{v}$  [sweep rate<sup>1/2</sup>], suggesting that the diffusion of zinc ions in the solution is slow.

Log anodic peak currents varied with log a<sub>OH<sup>-</sup></sub> ions. A value of 0.72 was observed in the concentration range of 0.1M to 1.0M suggesting the partial coverage of the surface by OH<sup>-</sup> ions, while complete coverage of the surface by OH<sup>-</sup> ions occurred in 1.0M to 6.0M KOH solutions, as indicated by a value of 0.89.

#### 2. Behaviour in alkaline carbonate solutions

##### A. 0.1M KOH + H<sub>2</sub>CO<sub>3</sub> solutions

Figure 2 presents the electrochemical spectrum in 0.1M KOH containing K<sub>2</sub>CO<sub>3</sub> solutions. In 0.1M KOH + 0.1M K<sub>2</sub>CO<sub>3</sub>

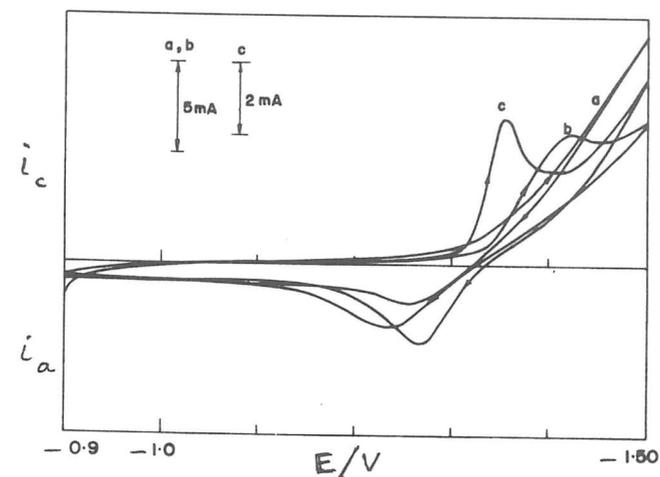


Fig.2: Typical Cyclic Voltammograms of zinc in 0.1M KOH solution containing (a) 0.1M K<sub>2</sub>CO<sub>3</sub>, (b) 0.3M K<sub>2</sub>CO<sub>3</sub>, (c) 0.5M K<sub>2</sub>CO<sub>3</sub>. E<sub>λ,a</sub> = -0.9V; E<sub>λ,c</sub> = -1.5V; V=5 mV s<sup>-1</sup>

solutions, anodic peak appeared at -1234 mV in the forward scan and the current had fallen to a low value suggesting the passivation of the surface. A single cathodic peak appeared at -1424 mV.

The anodic peak potential became noble with sweep rate with  $[dE_{p,a}/d \log v]_{OH^-} = 40 \pm 10 \text{ mV/decade}$ . The anodic peak potentials varied with carbonate ion concentrations. At constant  $OH^-$  ions and sweep rate,  $[dE_{p,a}/d \log a_{CO_3^{2-}}] = 30 \text{ mV decade}^{-1}$ . The variation of  $\log i_{p,a}$  with  $\log$  carbonate at a constant sweep rate in the sweep rate range of 5 to 10  $\text{mV s}^{-1}$  gave a value of 0.5. This suggests that there is a hindrance to the dissolution of zinc by carbonate ions and that diffusion of the carbonate in solution is slow. However above 10  $\text{mV s}^{-1}$ , a value of 0.78 suggests that adsorption of  $CO_3^{2-}$  ions on the surface takes place and with time the carbonates diffuse inside the passive film. In all carbonate solutions, the variation of  $Q_a$  (charge flowed under an anodic peak) with sweep rate suggests that the passivation is predominant for short periods and with the passage of time the passive film dissolves in the presence of excess carbonates.

B. 1.0M KOH +  $K_2CO_3$  solutions

Figure 3 presents the cyclic voltammogram of zinc in 1.0M KOH solutions containing  $K_2CO_3$ . When polarised from -1500 mV, the forward scan revealed two anodic peaks at -1240 mV followed by a sharp peak at -1100 mV. Complete passivation was observed upto -900 mV. Beyond -900 mV, the current began to rise. On the reverse scan a cathodic peak appeared at -1417 mV and this was followed by hydrogen evolution.

First anodic peak:

The anodic peak potential varied with  $\log v$  with a value of 40  $\text{mV decade}^{-1}$ . The anodic peak potential and peak current varied with  $\sqrt{v}$  linearly, suggesting that the diffusion of carbonate ions or  $OH^-$  ions is rate-controlling. The anodic peak potential varied with  $\log$  carbonate ion concentration suggesting the participation of carbonate ions, and the value of 30  $\text{mV decade}^{-1}$ . The electrons may involve stepwise electron transfer and a chemical step succeeding the electrons transfer is slow.

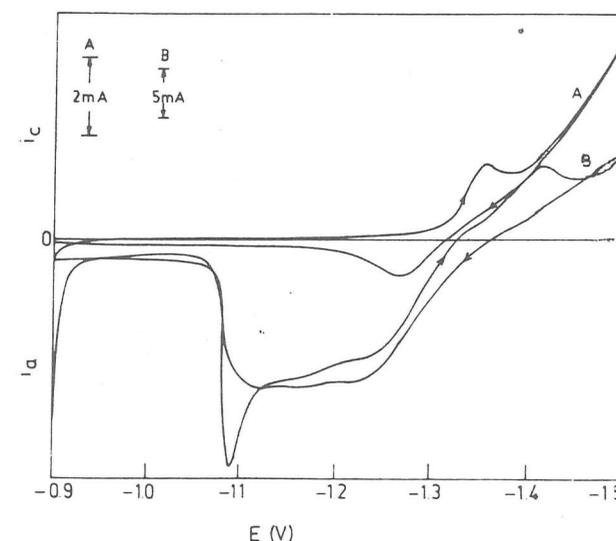


Fig.3: Typical Cyclic Voltammograms of zinc in KOH solutions containing 0.5M  $K_2CO_3$ . (A) 0.1M KOH (B) 1.0M KOH  
 $E_{\lambda,a} = -0.9V$ ;  $E_{\lambda,c} = -1.5V$ ;  $v = 5 \text{ mV s}^{-1}$ .

The anodic peak currents decreased with carbonate ion concentration and

$$\left[ \frac{d \log i_{p,a}}{d \log a_{CO_3^{2-}}} \right]_{v, OH^-} = -0.5$$

This suggests that the dissolution of  $Zn^{2+}$  ions outside the metal is hindered while the passive film containing carbonate formation is facilitated. The anodic charge ( $Q_a$ ) decreased with  $v$ . The flow of metal ions leaving the lattice was facilitated with the passage of time.

At constant sweep rate the increase of  $Q_a$  with carbonate ion concentration may be due to the dissolution of  $Zn(OH)_2$  in presence of carbonates.

Second anodic peak:

The anodic peak potential varied with  $\log v$  with a slope of 70  $\text{mV/decade}$ , and with carbonate ions with a slope of 30  $\text{mV decade}^{-1}$ . These suggest the participation of carbonate ions and incorporation of carbonates in the passive film formation and dissolution. At higher  $v$ ,

$$\left\{ \frac{d \log i_{p,a}}{d \log CO_3^{2-}} \right\}_v = 0.33$$

was observed, which became one at low sweep rate. This is because of the time dependency of the adsorption of carbonate ions and migration inside the film.

C. 6M KOH + K<sub>2</sub>CO<sub>3</sub> solutions

Figure 4 presents the cyclic voltammogram of zinc in 6M KOH containing K<sub>2</sub>CO<sub>3</sub> solutions. Even in the presence of carbonates, the E<sub>p,a</sub> shifted towards active direction with v, suggesting that the dissolution of zinc as zincate or zinc hydroxy carbonates is favoured. The carbonates did not influence the dissolution as evidenced by the independency of E<sub>p,a</sub> with CO<sub>3</sub><sup>2-</sup> ions concentration. In solutions containing > 0.3M K<sub>2</sub>CO<sub>3</sub> the anodic peak current decreased with v. This suggests that there is a competition between OH<sup>-</sup> ions and CO<sub>3</sub><sup>2-</sup> ions for the dissolution and passivation respectively.

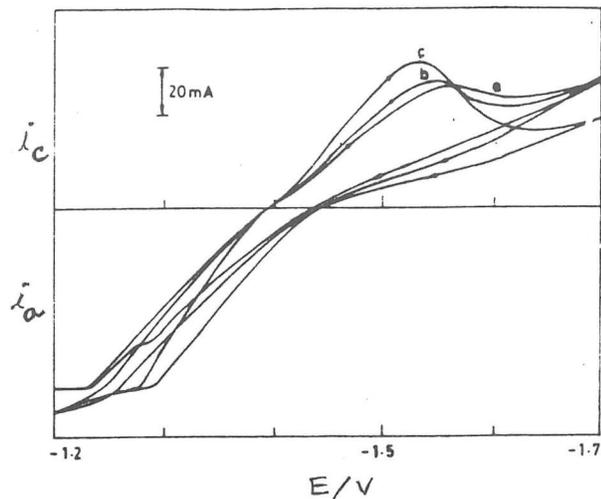


Fig.4: Typical Cyclic Voltammograms of Zinc in 6.0M KOH solutions containing: (a) +0.1M K<sub>2</sub>CO<sub>3</sub>; (b) +0.3M K<sub>2</sub>CO<sub>3</sub>; (c) +0.5M K<sub>2</sub>CO<sub>3</sub>.  
E<sub>λ,a</sub> = -1.2 mV; E<sub>λ,c</sub> = -1.7 mV; V = 5 mV s<sup>-1</sup>.

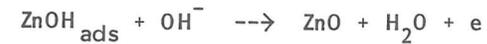
Discussions

Most of the literature on the mechanism of passivation suggest an adsorption model or a model involving the nucleation and growth of a two dimensional layer, though a dissolution-precipitation mechanism was the earliest one known [6-9].

In 0.1M KOH, the E<sub>p,a</sub> was invariant with sweep rate suggesting



and the blocking of the active sites caused a decrease of dissolution current. This adsorbed intermediate rejects a proton at the critical potential to form a passive oxide layer. The log i<sub>p,a</sub> vs log a<sub>OH<sup>-</sup></sub> variation with a slope of 0.72 suggests the fractional coverage by ZnO which may be a loose flocculant film.



In higher concentrations of alkali, a value of

$$\left[ \frac{d \log i_{p,a}}{d \log a_{OH^-}} \right]_v = 0.89$$

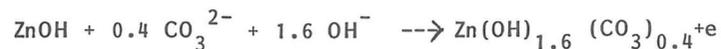
suggests that the passivation may be due to the formation of a monolayer phase resulting from the nucleation growth and overlap of two dimensional oxide clusters.

An underlying layer of Zn(OH)<sub>2</sub> with an overlayer of ZnO may be formed in 0.1M to 1.0M KOH solution. The presence of overlayer may result from the ageing of the Zn(OH)<sub>2</sub> film or from field effects to produce a more compact ZnO structure [10].

In the presence of carbonates, the dense film on zinc was not stable [11] and higher anodic polarisation causes the adsorption of CO<sub>3</sub><sup>2-</sup> ions. If the adsorption obeys Langmuir isotherm[12]

$$E_{p,a} = \frac{RT}{\alpha_a F} \ln \left[ \frac{\gamma \alpha_a F}{KRT} \right] + \frac{RT}{\alpha_a F} \ln v$$

The [d E<sub>p,a</sub> / d log v] would give the anodic Tafel slope of the dissolution reaction. The observed Tafel slope of 35 ± 10 mV decade<sup>-1</sup> suggests that



Then,

$$i_a = K_2 K_1 (\text{Zn})(\text{OH}^-)^{2.6} (\text{CO}_3^{2-})^{0.4} \exp(1 + \beta) F \Delta \phi / RT$$

When the concentration of  $\text{OH}^-$  ions was raised to 1.0M, the  $E_{p,a}$  was dependent on the  $\text{CO}_3^{2-}$  ion and  $[dE_{p,a}/d \log a_{\text{CO}_3^{2-}}]_v = 30 \text{ mV decade}^{-1}$ .

This suggests that



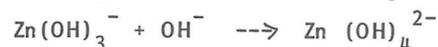
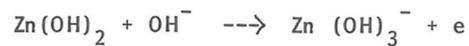
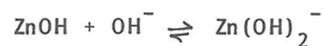
Nernst equation gives

$$E_e = E_{e^0} - 2.303 RT/2F \log [\text{CO}_3^{2-}]$$

The formation of  $\text{ZnCO}_3$  occurs via the migration and diffusion of  $\text{CO}_3^{2-}$  ions inside the  $\text{Zn(OH)}_2$  film and migration of  $\text{Zn}^{2+}$  ions from  $\text{Zn}^{2+}$  rich layer outside. The outgoing  $\text{Zn}^{2+}$  ions react with  $\text{CO}_3^{2-}$  ions resulting in the formation of dense  $\text{ZnCO}_3$  film outside.

Figure 5 presents a schematic diagram showing the appearance of  $\text{ZnCO}_3$  on the film/solution interface.

In high alkali solutions ( $> 1.0\text{M KOH}$ ) it was pointed out earlier [13] that zinc dissolves as



In the presence of  $\gg 0.3\text{M K}_2\text{CO}_3$  solutions the  $i_{p,a}$  decreased with  $v$  suggesting the competition between  $\text{OH}^-$  and  $\text{CO}_3^{2-}$  ions for dissolution.

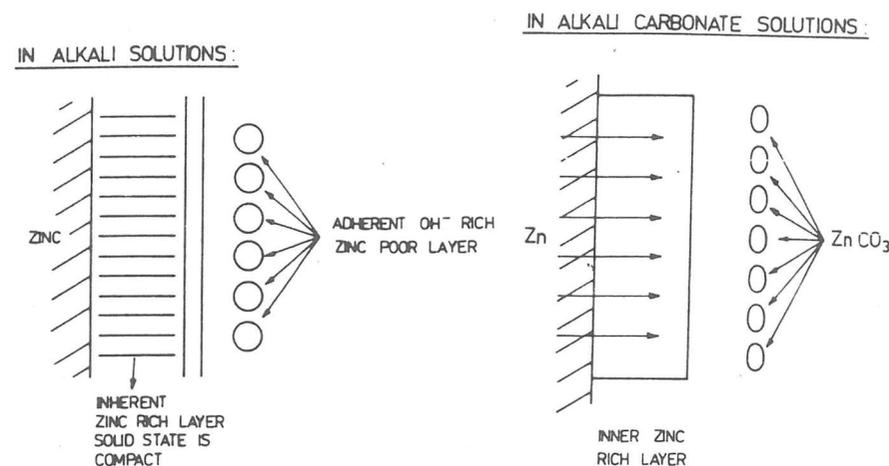
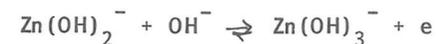
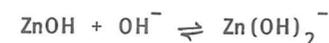


Fig.5: Schematic diagram showing the nature of passive films formed in both alkali and alkali carbonate solutions.



The carbonate film is formed by the dissolution of zinc and by the precipitation as  $\text{ZnCO}_3$ .

### Conclusions

In dilute alkali solutions the formation of  $\text{ZnCO}_3$  by the migration and diffusion of  $\text{CO}_3^{2-}$  ions inside  $\text{Zn(OH)}_2$  film. Increase of alkali concentration caused the formation of  $\text{Zn(OH)}_3^-$  which subsequently reacted with carbonates to form  $\text{ZnCO}_3$ .

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(Received, 25 October 1994  
Revised form, 9 March 1995)

## IONIC SOLVATION

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### Abstract

The concept of ionic solvation and the way it has been presented in the literature is critically discussed.

### Key words

Ionic solvation, ionic hydration, electrolytes

### The evolution of the concept of ion solvation

The concept of ionic hydration, an example of ionic solvation, where the solvent is water, was firstly introduced when Kablukow [1] said, in 1891: "In my opinion, water, as it decomposes the molecules of the dissolved substance, forms with the ions unstable compounds which exist in a dissociated state".

MacInnes [2] in 1939 defines solvation as:

"...complex formation between the solute and the solvent. With aqueous solutions it is called *hydration*. ..."

When defining total ionic solvation as a set of predominantly coulombic interactions between the solvent molecules and a certain ion, Bockris [3], in 1949 admits two types of solvation, primary and secondary:

"Acceptance of a coulombic view of the solvation of a simple ion does not suffice for a satisfactory definition of solvation. It follows from the Born-Fajans concept that a certain number of solvent molecules will be firmly attached to the ion and that a further ion-dipole interaction takes place involving solvent molecules outside the inner ion-solvent entity. It may be suggested that the term "primary solvation" is used in reference to the attachment of solvent molecules to ions in solution for which (i) the ion and its attached solvent molecules move together as one entity during electrolytic transport; (ii) the solvent ions have completely lost their own separate translational degrees of freedom. "Secondary solvation" may be suggested as the term referring to all electrostatic interactions which are not included in the definition of primary solvation given above. The term "total solvation" would then refer to the sum of these two types of solvation. ..."