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Effects of additives on the suspension of products of discharge of zinc in alkaline solution

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The effects and theories explaining the mode of action of various additives which have been used to increase the amount of zinc which may be anodically dissolved into highly alkaline electrolytes are reviewed. This topic has applications for the improvement of the energy density of battery systems which rely on the fullest possible dissolution of zinc anodes.

1. Introduction

Several electrolyte additives have shown the ability to increase the amount of zinc that can be dissolved into alkaline solutions. Two classes of additives are apparent: (i) a type that produces suspensions of charged micelles of solid, and (ii) a type that stabilizes dissolved polymeric zincate. In addition to increasing the amount of zinc that may be anodically dissolved, these additives exhibit additional effects which provide evidence as to their mechanism of action. This paper reviews the existing literature, presents work performed at the Continental Group, Inc. (CGI) during 1980–81 and recent work at the Pinnacle Research Institute (PRI), and then attempts an overall explanation.

2. Anodic dissolution of zinc

It is well known that higher concentrations of zinc may be achieved by anodic dissolution into alkaline solution than by the simple chemical dissolving of ZnO. The solutions produced are complicated systems, reported to consist of three states: individual zincate ions, an unstable colloidal state involving zinc oxide or hydroxide, and a relatively stable, polymeric state [1]. The high levels of supersaturation achieved through anodic dissolution decay slowly over periods of weeks [1, 2]. Additives that apparently stabilize polymeric zincate also retard the decay of supersaturation.

The following physical observations are helpful. When zinc is discharged into KOH free of additives, a clear solution is produced which becomes full of white precipitate as anode passivity is approached. In the presence of additives stabilizing polymeric zincate this pattern is observed after a greater amount of current has passed. In the presence of additives producing a 'quasi-colloid' of suspended charged micelles, a blackened electrolyte, which cannot be clarified via conventional filtration, is produced and remains free of macroscopic particulates even to the point of anode passivity.

One battery system which relies on the fullest possible dissolution of zinc into alkaline solution is the circulating slurry system. In this system, depending on hydraulic design, 300 to $350\,\mathrm{g\,dm^{-3}}$ of particulate 100 mesh zinc is the limiting slurry composition found suspendable without undue difficulty. Assuming 90% may be utilized without severe loss of performance under best conditions this places a requirement that the electrolyte be able to dissolve between 221 and $258\,\mathrm{A\,h\,dm^{-3}}$ of zinc at rates corresponding to vehicle 'cruise' or higher (when cruise would generally be considered to be 80–$120\,\mathrm{mA\,cm^{-2}}$).

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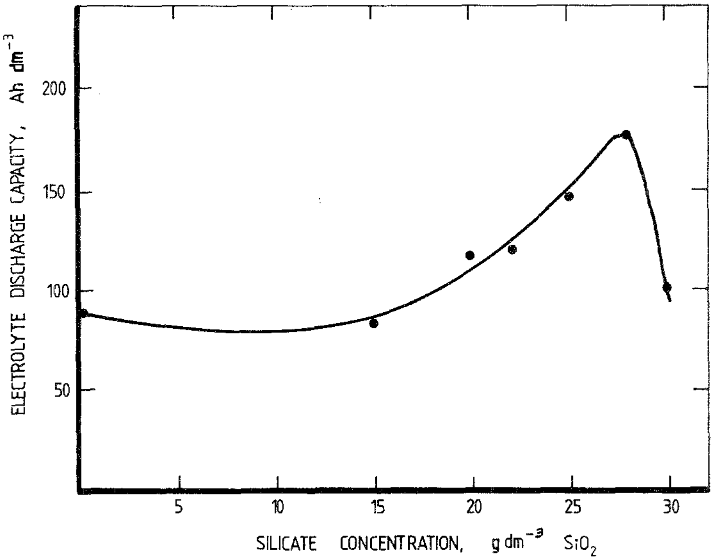

Fig. 1. The effect of the silicate ion on the 150 mA cm^{-2} discharge of slurry zinc–air cells in 12 M KOH at 55°C, using 300 g dm^{-3} 100 mesh zinc and 100 cm^2 cell.

3. Additives producing suspensions of charged micelles

The silicate ion is the best known and first discovered of the class of additives producing suspensions of negatively charged micelles*. The effect of silicate on the discharge of zinc into KOH was first shown by Flerov [3–5]. According to work performed by the author at CGI, the optimum amount of silicate to discharge maximum levels of zinc into 12 M KOH at 150 mA cm^{-2} and at 55° C in a slurry cell is a concentration expressed as 28 g dm^{-3} SiO_2 [6]. Both higher and lower concentrations are less effective (see Fig. 1.)

Silicate adsorbs on ZnO (and, thus, the zinc surface in aqueous solution because it is always covered with ZnO) possibly due to displacement of H_2O from the predominant aqueous ion, the tetrahedral species, $SiO_2(OH)_2^{2-}$ (the expression commonly used for silicate, SiO_3^{2-} is a simplification), which can leave an empty *sp*^{3} orbital for coordination with whatever lone pair electrons are available. The oxygen lone pairs of ZnO certainly qualify. This displacement of water and electronic rearrangement may be favoured in the case of ZnO, particularly since the complete *d*^{10} electron shell is very compact and probably withdrawn from possible coulombic repulsion. The ZnO forms a structure in which zinc is lodged in tetrahedral holes formed by the close packing of oxygen atoms (coincidentally also the preferred structure of silicates). As silicon exhibits one of the more extensive chemistries of oxygen-linked intermetallics, interaction is expected. Actual compound formation with Zn–O–Si bridging is known (e.g. willemite, hemimorphite).

The following discussion illustrates the interaction postulated. The adsorption of silicate on ZnO and its high negative charge leads to colloid formation due to repulsive forces between particles. Silicate is likely to be a highly effective stabilizer due to its potential coordination with each ZnO surface oxygen, and because of the high charge density it can impart a micelle. Flerov [3, 4] argued that a more extensive hydration sheath around silicates further isolated each micelle from the hydroxide ion and the free water needed to dissolve it.

Silicate does not colloidally suspend reagent ZnO added to strongly alkaline solution. Particles of ZnO must apparently be of sufficiently small size for coulombic forces to prevail over gravitation. Conductivity studies performed by Marshall *et al.* [7] conclude that the number of ZnO molecules per colloidal particle may be of the order of 5 or 6.

In fact, when reagent ZnO is dissolved in silicate-containing KOH, the reaction

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* The following discussion of micellular discharge product suspension relates to KOH concentrations greater than approximately 7 M. At lower concentrations (say 3 M) other unique effects of silicate are observed, as discussed later.

$$ZnO + H_2O + 2OH^- = Zn(OH)_4^{2-} \quad (1)$$

occurs to a lesser extent than without silicate. The 'solubility' of ZnO decreases. This may also be due to the adsorption of silicate on ZnO. A negatively charged layer is established on the ZnO surface which reduces the surface OH^- concentration as well as inhibits transport of OH^- to the ZnO and transport of $Zn(OH)_4^{2-}$ away. Fig. 2 illustrates this suppression of 'solubility' in 12 M KOH at 55°C (the data were taken after 2 h of interaction and do not necessarily reflect equilibrium).

Other additives have been identified at CGI which produce dark micellular suspensions of zinc discharge products in KOH. These are the structural analogies to silicate, stannate (SnO_3^{2-}) and titanate (TiO_3^{2-}).

It was hypothesized that the adsorption of a silicate ion on ZnO is due to its ability to lose a water from its tetrahedral coordination sphere and thus to leave an electronic configuration in which the two negative charges are retained, but with an empty sp^3 orbital left for coordination. The IVa family (s^2p^2) and the IVb family (d^2s^2) can produce such oxyanions in highly skilled alkaline solution. These may thus be rationalized to have the potential for producing negatively charged 'quasi-colloids" during the anodic dissolution of zinc.

The additional criteria of reasonable solubility, immunity to reduction upon battery recharge and inability to participate in a cementation reaction with zinc metal, place severe constraints. Only silicate, stannate and titanate apparently pass these tests.

In 12 M KOH at 55°C, stannate and titanate additions form weak colloids which extend the amount of zinc that can be anodically dissolved. (see Fig. 3 and Table 1). Experimentation over a greater range of concentrations is necessary to identify the optimum performance of these additives.

Silicate is apparently the most effective negative micellular stabilizer. This may be due to its higher absorbing power (possibly due to its greater ability to participate in metal–oxygen–metal bridging) which is attributed to the small size of silicon and hence propensity to pack into the tetrahedral holes in oxide structures.

The 'quasi-colloid' ages as ZnO particulates agglomerate. In the case of silicate approximately half has precipitated within 2 months and the rest is of filterable size.

4. Additives stabilizing polymeric zincate

Additives which stabilize polymeric zincate are typified by xylitol and molasses, and were first

Table 1. Discharge study of 200 cm² zinc–air cell in 1.2 dm³ 12 M KOH at 55°C using a rate of 200 mA cm⁻²

Additive	*Concentration ($g\,dm^{-3}$)*	*Resulting charge*[a] *($A\,h\,dm^{-3}$)*
No additives		
–	–	87
Colloid-producing additives		
titanate	(saturated)	102
stannate	(saturated)	139
silicate	25 SiO_2	154
Polymeric stabilizer additives		
sorbitol	10	124
sorbitol	15	141
sorbitol	20	107
sorbitol	25	99
aluminate	25	125
Combined effects		
sorbital +	15	
silicate	25 SiO_2	191

[a] Higher $A\,h\,dm^{-3}$ performance would be expected at lower discharge rates.

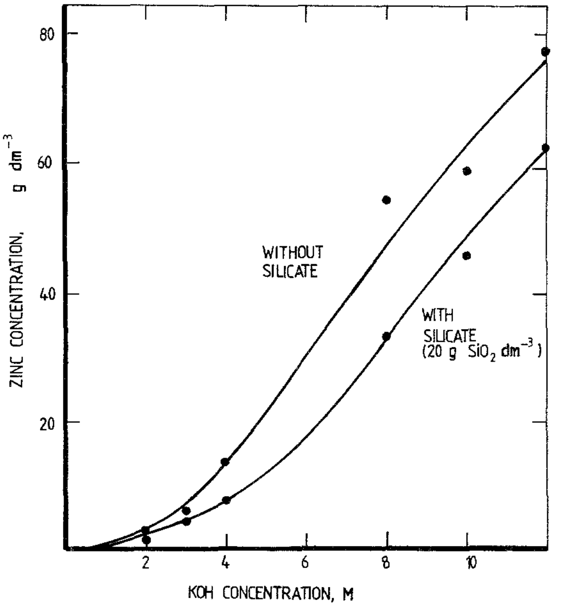

Fig. 2. The supression of zinc oxide 'solubility' by the silicate ion at 55°C, and 2 h equilibration times.

reported by Dmitrenko *et al.* [1]. It was suggested that the hydrogens of dissolved zincate may hydrogen-bond to zinc oxide nuclei such that further nucleation and growth is suppressed, with the net effect that a lace-like polymeric structure of zincate and zinc oxide remains in solution [1, 8–9]. Greatly enhanced hydrogen bonding (i.e. in pure water) has been confirmed in high concentration alkaline zincate solutions via IR spectroscopy [7].

For the polymeric zincate model to be correct, other additives (besides zincate) should be able to hydrogen bond to ZnO nuclei and achieve this dissolved polymeric state. Monosaccharides were selected by Dmitrenko *et al.* [1, 8, 9] to test this hypothesis because they have multiple proton-donating groups, are stable in concentrated alkali, and do not discharge in zinc dissolution. Further, and above all, the protons are not readily lost.

In 10 M KOH, ZnO concentrations of 180 g dm^{-3} (148 A h dm^{-3}) and 160 g dm^{-3} (132 A h dm^{-3}) were achieved with molasses and xylitol, respectively, after 4 days of concentration decay [1]. (Initial concentrations, which should be higher were not reported.) A concentration of 140 g dm^{-3} (115 A h dm^{-3}) was reported with no additives after 4 days.

In work at CGI, aluminate ion additions produced capacity extensions without colloid

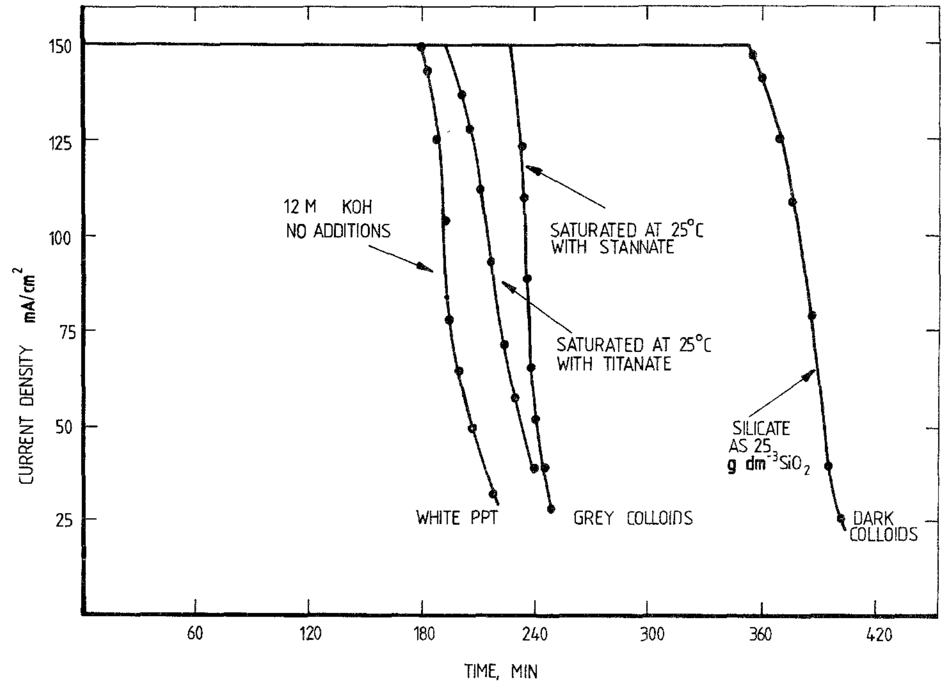

Fig. 3. Comparison of the effects of additions of stannate, titanate and silicate in constant current zinc–air discharge at 55°C using 300 g dm^{-3} 100 mesh zinc, 100 cm^2 cell, 1.2 dm^3 volume.

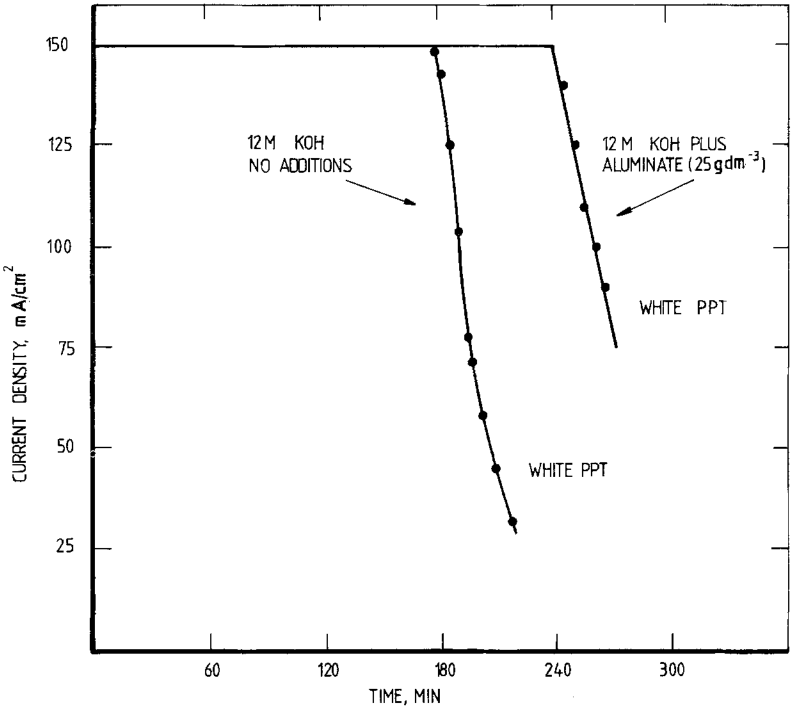

Fig. 4. The effect of the addition of aluminate ion in constant current zinc–air discharge at 55°C using 300 g dm^{-3} 100 mesh zinc, 100 cm^2 cell, 1.2 dm^3 volume.

formation (see Fig. 4). Given the fixed hydrogens, this may help confirm the possibility of polymeric zincate stabilization through hydrogen-bonded lace structures.

At the Pinnacle Research Institute it was suspected by the author that the micellular and polymeric stabilization mechanisms are sufficiently different in character that they might function simultaneously. To this end an experiment was performed adding silicate (expressed as 25 g dm^{-3} SiO_2) and 15 g dm^{-3} sorbitol. A significant increase in electrolyte discharge capacity over the effects of the additives taken individually was observed and is noted in Table 1 [10]. These experiments were performed at 55°C using a 200 cm^2 zinc–air cell submersed in 1.2 dm^3 of a slurry of 12 M KOH and 300 g dm^{-3} of particulate zinc.

This result is important in that it opens a new avenue to optimization of electrolyte discharge capacity. Were these data to be taken at lower discharge rates (80–120 mA cm^{-2}), it is possible that discharge capacities well suited to the needs of recirculating slurry zinc–air batteries may be found.

Dmitrenko *et al.* [1] have proposed that if terminal –OH groups work due to their proton-donating capabilities, terminal –SH groups should work better due their even greater proton-donating ability. A possible problem area is that actual ionization in highly alkaline media may occur and interfere with the hydrogen bonding process.

Thio-sugars and starting materials for these are not readily available. However, an analogue may be synthesized without too much difficulty; 1, 2, 5, 6, 9, 10-hexabromododecane is available and very inexpensive. It may be converted to the thiol via nucleophilic displacement by a large excess of hydrosulphide in ethanol. The resulting compound should be soluble in alkaline solution and provide multiple hydrogen-bonding sites. Such an experiment was beyond the scope of the present investigation at PRI.

5. Effects of silicate additions at low KOH concentrations

In 1974 Drury *et al.* [11] reported conditions of KOH concentration, silicate concentration, electrolyte flow and current density such that 'possibly infinite' amounts of zinc may be anodically dissolved without leading to passivation. The

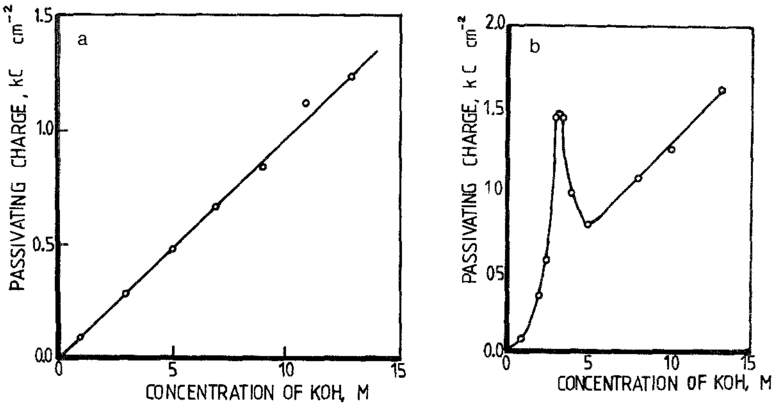

Fig. 5(a) The effect of KOH concentration on passivating charge at a constant current density of $33\,\mathrm{mA\,cm^{-2}}$ at 23°C [10]. (b) The effect of KOH concentration on passivating charge with the addition of 2 vol % potassium silicate solution at a constant current density of $33\,\mathrm{mA\,cm^{-2}}$ at 23°C [10].

phenomena has been reported in subsequent literature [12–15].

Without silicate ion in solution the charge passed to reach anode passivation at constant current density for a given electrolyte volume increases linearly from KOH concentrations of 1 M to 14 M (see Fig 5a) [13]. Analysis of the final electrolytes from these experiments reveals a linear increase of dissolved zinc with increasing KOH concentration. At 14 M KOH and a silicate concentration of 0.15 M, these authors reported that a concentration of 4.9 M Zn^{2+} may be formed by anodic dissolution at $33\,\mathrm{mA\,cm^{-2}}$. This represents a charge passed of $263\,\mathrm{A\,h\,dm^{-3}}$, which may be the highest ever reported for anodic dissolution of particulate zinc electrodes.

With the addition of silicate, a very sharp peak in the charge-to-passivation curve is observed at approximately 3 M KOH (see Fig. 5b.) Analysis of centrifuged electrolyte showed ZnO to be formed in this region, with a corresponding deviation from linearity in the increase of dissolved zinc with increasing KOH concentration. The solutions in this region are described as milk-white throughout the length of the discharge. As much as $242\,\mathrm{A\,h\,dm^{-3}}$ of zinc was dissolved before passivation at $33\,\mathrm{mA\,cm^{-2}}$ (without silicate, only $48\,\mathrm{A\,h\,dm^{-3}}$ may be passed).

The amount of charge to passivation in this region was found to be greater for vertically oriented planar zinc electrodes than for anodes of fluidized particulates. This was explained by a reduction of shearing flow experienced by the zinc surface in slurry systems, and the build-up of oxide that insulates the particles from the current collector.

The existence of such a 'window' of silicate concentration, KOH concentration and current density conditions can be explained in terms of the anodic dissolution process.

Electron transfer:

$$\mathrm{Zn} = \mathrm{Zn}^{+} + e \qquad (2)$$

$$\mathrm{Zn}^{+} = \mathrm{Zn}^{2+} + e \qquad (3)$$

Chemical steps:

$$\mathrm{Zn}^{2+} + 2\mathrm{OH}^{-} = \mathrm{ZnO} + \mathrm{H_2O} \qquad (4)$$

$$\mathrm{ZnO} + 2\mathrm{OH}^{-} + \mathrm{H_2O} = \mathrm{Zn(OH)}_4^{2-} \qquad (5)$$

At low KOH concentrations, insufficient hydroxide ion is present to rapidly dissolve the discharge products to zincate. Zinc hydroxide or zinc oxide is the primary product. Oxide is formed on the electrode surface (within the adsorbed silicate layer) and passivation is observed.

At slightly higher hydroxide ion concentrations, say 3 M, a balance exists wherein sufficient hydroxide ion is present within the silicate layer to transport some zincate ion out, but not enough to prevent a great deal of dissolved zinc being transported through the silicate layer as Zn^{2+}. This then forms ZnO, but only at some distance from the electrode such that passivation of the electrode does not occur.

Obviously, this balance is affected by current density, so that at higher rates of anodic dissolution the electroneutrality requires so much additional hydroxide ion to intrude into the silicate layer that passivation by ZnO formation becomes possible. This is consistent with the observation of the peak in passivating charge only at low current densities (e.g. $30\,\mathrm{mA\,cm^{-2}}$).

At somewhat higher KOH concentration the amount of negative charge within the adsorbed silicate layer is no longer sufficient to keep hydroxide ion out. Thus one would expect anomalies, due to the proportion of silicate and hydroxide ion adjacent to the electrode, to occur at lower KOH concentrations (such as 3 M). If OH^- can no longer be partially excluded from the electrode surface, ZnO formation can take place within the silicate layer, and passivation occurs. These arguments rely on a higher stability of Zn^{2+} in the region of high silicate concentration than that outside it.

The amount of charge passed per litre of electrolyte to achieve passivation again increases at much higher OH^- concentration when, firstly, more zincate ion formation can occur (a second order function with OH^- concentration) and, secondly, when disproportionation of zincate to ZnO produces nucleating particulates of the 5 to 6 ZnO size in the bulk electrolyte which silicate adsorption can suspend colloidally.

Two cautionary notes are needed concerning the practical utility of the discovery of the 'silicate window' in 3 M KOH by Drury *et al.* [11]. The rates of discharge used in the characterization of the amount of charge which could be passed without passivation were low. The rate used ($33\,mA\,cm^{-2}$) is not close to the range of 80–120 $mA\,cm^{-2}$ necessary as a 'cruising power output' current density for electric vehicle batteries.

Secondly, it was recognized by Marshall *et al.* [14] that the vapour pressure of water above 3 M KOH electrolyte is so high that electrolytes based on this composition would rapidly lose water through evaporation and active transport through air electrodes under the 50–60°C temperature conditions of practical use. These authors studied lowering the vapour pressure to approximately 8 M KOH (where conductivity is at maximum and water is neither rapidly lost nor gained) through the addition of 4 M KF. It was concluded the increased viscosity of these compositions made them unsuitable for flowing electrolyte batteries, although large capacity extensions due to silicate were still observed.

These considerations have cast doubt on a low KOH concentration approach to improving electrolyte discharge capacity unless significant improvements can be found.

6. Additional additive and effect

Lithium hydroxide additions have shown the ability to extend the amount of zinc which can be anodically dissolved into KOH [13]. Studies of electrode capacitance via cyclic voltammetry at potentials of zinc dissolution show that lithium ions are not adsorbed on zinc; such studies confirm that silicate ions are absorbed because capacitance is greatly reduced in their presence [15]. The energy of hydration of the lithium ion is greater than that of the potassium ion due to its small size. If lithium ions do replace potassium ions from the interior of the nuclei of ZnO (for whatever reason), it is possible that less water is available in the immediate neighbourhood of the particulate (or polymer) for dissolution of ZnO via the reaction pathway of Equation 5. The function of hydration sheaths about the nuclei remains unclear at present.

7. Additive effects on voltammetric behaviour

The effect of silicate ion on voltammetric studies of the passivation of zinc anodes in 8 M NaOH containing 1 M zincate at room temperature was studied by Lewis and Turner [15]. Dramatic differences with and without the presence of a small amount of silicate were apparent.

It was seen that silicate ion does not delay the active to passive transition in anodic sweeps, as usually expected of a passivation inhibitor. In fact, the active to passive transition occurred sooner (i.e. at lower potentials). Silicate ion adsorption apparently exerts a catalytic influence on the dissolution of zinc. The presence of a strongly negative layer of adsorbed silicate alters the potential of the double layer and reduced its hydroxide ion content such that the current density corresponding to diffusion layer electrolyte saturation was reached earlier in an anodic scan.

Upon cathodic scan, wildly fluctuating currents were observed as reactivation of the passive zinc electrode occurred. This effect may be due to uneven film composition as a result of adsorption of silicate ions on preferred sites. Also, as the passive film is decomposed in reactivation, displaced silicate may adsorb to an increasing extent on progressively less and less oxide. Such rapid current fluctuations are not observed in reactivation of passivated zinc electrodes in the absence of silicate. Thus, silicate and probably the other classifications of additives discussed do not act as conventional passivation inhibitors.

There appears to be great scope for additional research in the area of the effects of additives on the anodic dissolution of zinc in alkaline systems.

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