

ZINC ELECTRODE IN ALKALINE ELECTROLYTE

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The zinc electrode in alkaline electrolyte is unusual in that supersaturated zincate solutions can form during discharge and spongy or mossy zinc deposits can form on charge at low overvoltages. The effect of additives on regular pasted ZnO electrodes and calcium zincate electrodes is discussed. The paper also reports on *in situ* x-ray absorption (XAS) results on mossy zinc deposits.

INTRODUCTION

There are several reviews of the zinc electrode in alkaline electrolyte (1, 2). Recent fundamental work on the zinc electrode in alkaline electrolyte has focused on methods for reducing the solubility of ZnO, the mechanisms of formation and decomposition of supersaturated zincate electrolytes, the growth of mossy deposits on charge at low current densities, and the effect of additives and pulsed charging on the morphology of the zinc electrode.

Many of the problems of rechargeable zinc batteries are due to zinc electrode shape change and zinc dendritic growth. These problems can be traced to the high solubility of the discharge products of the zinc electrode. In the case of the silver-zinc battery there are very limited options for dealing with these problems because of the necessity of using $\approx 45\%$ KOH to suppress the solubility of Ag_2O . Sacrificial cellulosic separators are also necessary to inhibit migration of silver species to the zinc electrode. With the use of nickel, manganese dioxide or air positive electrodes there are many more options for the choice of separator and the electrolyte composition. This has led to many design changes and electrolyte formulations that improve the cycle life of the zinc electrode. The design changes can be classified as soluble zinc electrodes or zinc electrodes of limited solubility.

ZINC ELECTRODES

Soluble zinc electrodes: The equilibrium solubility of ZnO in KOH depends on the KOH concentration and increases from 6 g/l in 10% KOH to 53 g/l in 30% KOH. However, when a zinc electrode is discharged in an alkaline electrolyte supersaturated

zincate solutions can be formed. The zincate solubility can be as much as three times the equilibrium solubility. These solutions, however, are not supersaturated in the ordinary sense of the term. Neither seeding or shock causes precipitation of ZnO. Instead, the ZnO is precipitated slowly in a manner resembling a decomposition reaction. The presence of Li^+ , SiO_2^- or sorbitol retards the process. Depending on conditions, it can take anything from hundreds of hours to a year to reach the equilibrium solubility (3). Developers, such as Sorapec, have taken advantage of this and have developed nickel zinc batteries with the discharged product of the zinc electrode completely dissolved in the electrolyte (4).

Electrodes of limited solubility: The other approach to minimizing problems at the zinc electrode is to reformulate the electrode or electrolyte composition so as to reduce the ZnO solubility. This can be done either by incorporating $\text{Ca}(\text{OH})_2$ in the zinc electrodes or by use of electrolytes with minimal hydroxyl content containing highly soluble salts such as phosphate, borate carbonate or fluoride. The benefits of these approaches have been reviewed by Bass *et al.*(5).

Effect of additives: The two approaches for the zinc electrode, outlined above, increase the cycle life considerably if they are combined with the use of additives and/or special charging techniques. In conventional pasted zinc electrodes small amounts of additives such as HgO or PbO can have enormous effects on the zinc electrode. Additives such as HgO or Ga_2O_3 accelerate shape change and decrease cycle life, whereas additives such as Pb or mixtures of PbO and CdO are beneficial. Observations at Brookhaven National Laboratory (BNL) during the charging of pasted ZnO electrodes showed that beneficial additives promoted zinc deposition in the interior of the electrode in the vicinity of the grid current collector, whereas additives such as HgO or Ga_2O_3 promoted zinc deposition on the front of the electrode that abuts the separator. Additives such as PbO and $\text{In}(\text{OH})_3$ promote the formation of dense zinc deposits that increase the polarizability of the electrode. HgO and Ga_2O_3 on the other hand promote finely divide zinc deposits and electrodes with low polarizability and high rate capability.

Additives in calcium zincate electrodes: Additives such as PbO are particularly helpful in increasing the discharge capacity of electrodes of low solubility containing $\text{Ca}(\text{OH})_2$. Electrolytes of low solubility can lead to passivation of the zinc electrode on discharge. The effect of additives on the performance of calcium zincate electrodes has been examined at BNL.

The effect of additives on zinc utilization was determined by tests in 1 Ah nickel-zinc cells with two electrodes. The zinc electrodes (7.62 x 5.08 cm) were prepared by mixing 3 g of PTFE bonded ZnO with 3 g of $\text{Ca}(\text{OH})_2$ and an additive and pressing the mix on to a silver grid. The cells were wet down with 20% KOH containing 11 g LiOH + 30 g ZnO/l. After soaking overnight the cells were charged at 75 mA for 17 h. The zinc utilization was determined by discharging the cells at 500 mA (C/2 rate) till the zinc

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electrode reached -1.0 V vs. a Hg/HgO reference. The results are shown in Fig. 1. It is clear that additives can have a beneficial or detrimental effect on the zinc utilization in zinc electrodes with limited solubility. Additions of PbO and Cu powder are especially helpful.

Additives in pasted ZnO electrodes: Work at BNL (6-8) and the work of Himy, Wagner (9) and others indicate that additives, either added singly or in combination, can have an enormous effects on the rate of electrode shape change and the polarizability of the electrode. Additives such as HgO and Ga_2O_3 decrease the electrode polarizability and accelerate shape change. Additives like PbO and $\text{In}(\text{OH})_3$ increase the electrode polarizability and inhibit shape change. The addition of CdO has a minimal effect on electrode polarizability. The best compromise between cycle life and high rate performance is to add combinations of additives such as PbO + CdO.

Mechanism of the effect of additives: The mechanism by which additives work in pasted zinc electrodes is not fully understood. The work of McBreen and Gannon indicates that additives do affect the zinc morphology and the distribution of zinc within the pores of the electrode and across the surface of the electrode (6-8). One unexpected finding on additives in pasted ZnO electrodes was that on the first charge the oxide additives were often quantitatively deposited as the metal prior to the onset of zinc deposition (6). This was true for both HgO and Tl_2O_3 . It is difficult to envision how an additive of limited solubility can be quantitatively reduced in a non-conducting matrix such as ZnO. The fact that this occurs and that the effect of the additive persists throughout cycling indicates that the additive effect may be a substrate effect that controls zinc nucleation and morphology. The effect of additives on zinc utilization in electrodes of limited solubility is even more mysterious. The effect of the Cu powder can be rationalized by the fact that Cu substrates promote the growth of finely divided deposits that inhibit passivation on discharge. However, PbO is known to promote dense deposits so a decrease in zinc utilization would be expected.

MOSSY ZINC DEPOSITS

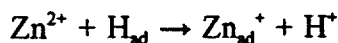
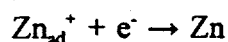
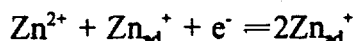
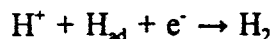
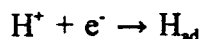
Mechanisms for formation of mossy zinc deposits: Zinc deposition from alkaline zincate electrolytes is unusual in that finely divided spongy or mossy deposits are formed at low current densities (10). In the case of other metals finely divided deposits are only formed at very high current densities (11). Three types of mechanisms have been proposed to explain the anomalies in zinc deposition. These are:

1. Zinc deposition through surface oxide films (12-14).
2. Instabilities due to multiple steady states caused by autocatalytic processes (15, 16).

3. Stabilization of dendrites and superlattices by codeposition of adsorbates such as hydrogen (17).

Wiert and co-workers have proposed that at low overvoltages zinc deposition occurs through a non stoichiometric ZnO film on the zinc surface (12-14). This is illustrated in Fig. 2. This model was developed to account for the polarization curves, ac impedance measurements, and morphological features in scanning electron micrographs. To explain all the observed phenomena they also postulated the following. Parts of the film are insulating and block the surface; the remainder has both ionic and electronic conductivity which permits deposition. The thickness of the film can be affected by potential, Pb additives and the presence of anodically generated zincate species. The latter promote the growth of spongy zinc by decreasing the film thickness.

Epelboin *et al.* proposed the following reaction mechanism to explain S shaped polarization curves and inductive loops in ac impedance curves, during zinc deposition (15). The reaction scheme involves an autocatalytic step. This reaction scheme has been slightly modified by Lee and Jorné (16) and is as follows:



The autocatalytic step can yield multiple steady states and instabilities. It can also induce an inverse relationship between the rate of zinc deposition and zinc ion concentration. Epelboin postulated that these instabilities were the cause of mossy deposits.

Clarke and co-workers have reported on a very interesting *in situ* high resolution x-ray diffraction study of dendritic zinc deposition from a ZnSO₄ electrolyte (17). The x-ray diffraction data displayed extra peaks in addition to the strongest expected zinc reflections. The spacing and symmetry of the additional peaks indicated a $\sqrt{3} \times \sqrt{3}$ superlattice ordering in the basal plane of zinc. They proposed a "keystone" model to explain the formation of superlattices. The model is illustrated in Fig. 3. The model depends on the codeposition of an adsorbate which interferes with normal epitaxial deposition. They postulate that the most likely adsorbate is hydrogen. This is supported by pyrolytic analysis of the deposit which indicates a hydrogen content as large as 1.7%

by weight. This exceeds the hydrogen content of FeTiH_2 . A similar mechanism may result in moss formation.

XAS studies of deposition of mossy zinc: The zinc deposition studies were carried out in the cell shown in Fig. 4. XAS spectra were recorded for the zincate electrolyte, prior to zinc deposition. Zinc was deposited under potentiostatic conditions (-45 mV or -65 mV vs. a Zn wire reference) in a thin cavity (~0.5 mm). After sufficient zinc was deposited to fill the cavity above the level of the x-ray window, transmission XAS measurements were made, with the electrode still under potential control.

Figure 5 shows a comparison of the Fourier transform of the EXAFS for a zinc foil and a mossy zinc deposit at -65 mV. There is no evidence for a Zn-O contribution at 1.5 Å. This indicates that the electrolyte within the electrode pores is completely exhausted of zincate and is essentially a pure KOH solution. Also there is no evidence for significant adsorbed oxide on the zinc deposit. The first Zn-Zn peak for the mossy deposit is much lower than that found for the metal foil. The data for this peak could be fitted to a single Zn-Zn coordination shell with a coordination number of 4.09 and a bond distance of 2.63 Å. The nearest coordination shell for bulk zinc has 6 atoms at 2.67 Å and 6 others at 2.89 Å. If the zinc deposit was oriented with the c-axis parallel to the lines of current, then only the nearest neighbors in the basal plane would be observed; that is 6 atoms at 2.67 Å. This is due to the polarization of the x-ray beam in the plane of the synchrotron ring. Such effects have actually been reported for single crystal zinc (18). This could partially explain the result. However, the calculated coordination number is considerably lower than six. Clarke, on the basis of x-ray diffraction results has reported that mossy zinc is a nanophase material with a crystallite size of ≈ 20 Å (25). The very low coordination number would be consistent with this. All of this indicates that mossy zinc is a very unusual material.

Figure 6 shows Fourier transforms of the EXAFS for zinc moss at -45 mV, zinc foil, and 8.4 M KOH + 0.74 M KOH. At -45 mV there is a large Zn-O contribution. This is either due to the presence of zincate in the electrode pores or the presence of the Zn_xO_y films, postulated by Wiart and co-workers (12-14). Because of the presence of two types of zinc species qualitative analysis of the spectra was impossible.

CONCLUSIONS

The work discussed above indicates that the electrochemistry of zinc deposition in alkaline electrolyte is exceedingly complex. The same is true for the discharge process. The formation and stability of the supersaturated zincate solutions remains an enigma. The work of Clarke, a physicist, has revealed complexities in zinc moss deposition that were hitherto unknown. All of this indicates the need for an interdisciplinary approach to the study of the zinc electrode. There are apparently autocatalytic processes involved

in both the deposition process on charge and the precipitation of ZnO on discharge. This means that on charge zinc prefers to deposit at sites where there is zinc and on discharge ZnO precipitates preferentially at sites where there is ZnO. This could account for some of the instability of the electrode on cycling.

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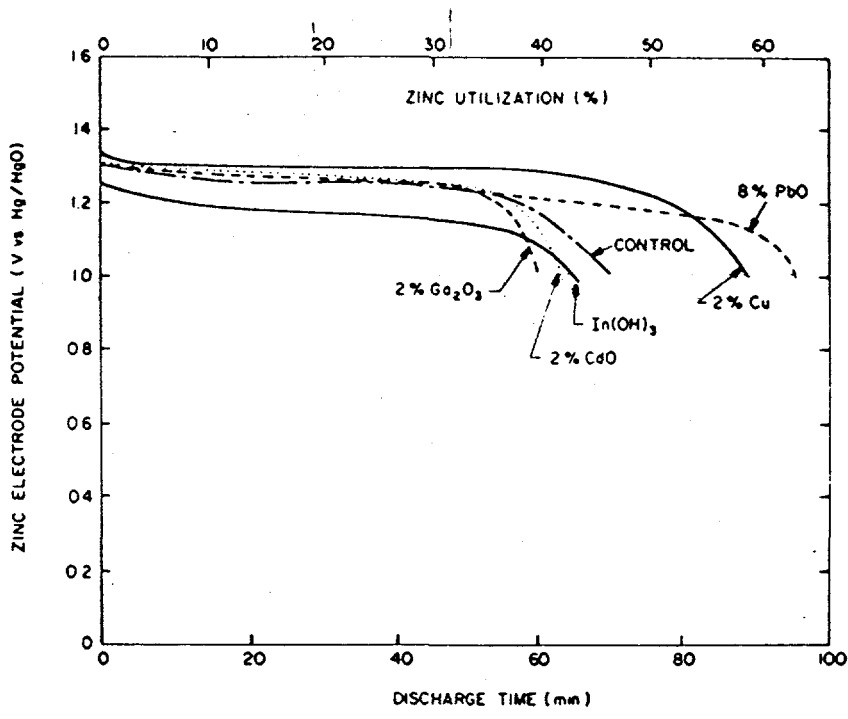


Fig. 1. Zinc utilization for calcium zincate electrodes with various additives. The control had no additive. The additions were 2% for Ga(OH)₂, CdO, In(OH)₃, and Cu. The PbO addition was 8%.

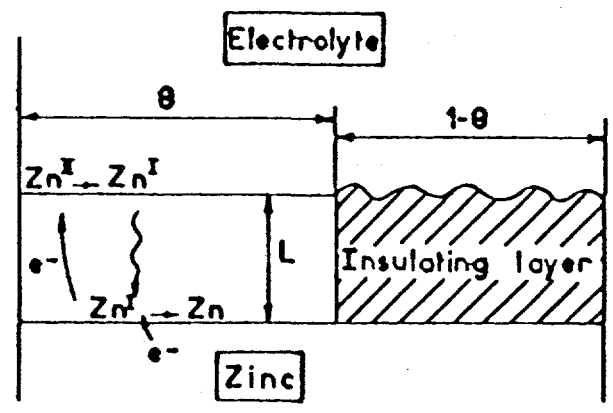


Fig. 2. Model for zinc deposition through an oxide film at low overvoltages (14).

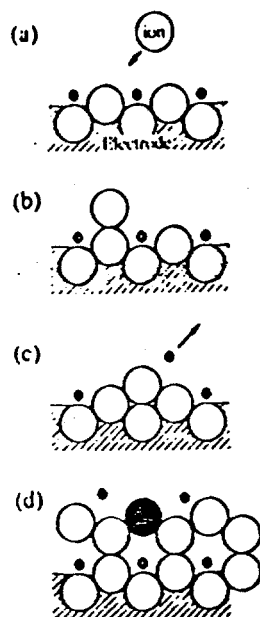


Fig. 3.

The "keystone" model to explain formation of superlattice structures (17). The large circles indicate zinc, both before and after incorporation into the lattice. The small circles indicate an adsorbate such as hydrogen. Without interference from the adsorbate the result is compact epitaxial deposition, as shown in (c). With adsorption of hydrogen at the energetically favorable sites, deposition can occur at other sites such as in (b). This type of deposition and the deposition of "keystone" atoms (the dark circle) (see (d)) produces a $\sqrt{3}\times\sqrt{3}$ superlattice when the growth is in the [110] direction.

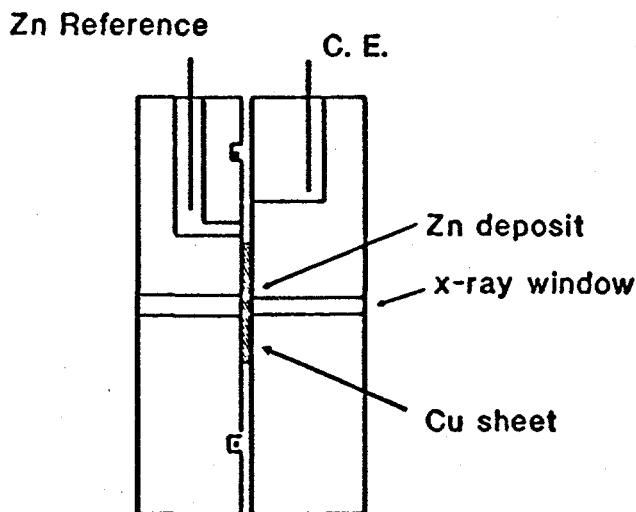


Fig. 4.

Cell for *in situ* XAS studies of deposition of zinc moss.

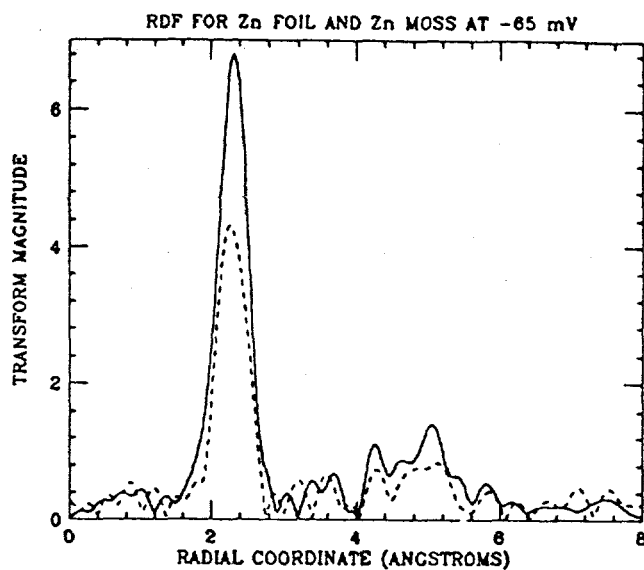


Fig. 5. Fourier transforms of the EXAFS for zinc foil (—) and zinc moss at -65 mV (---).

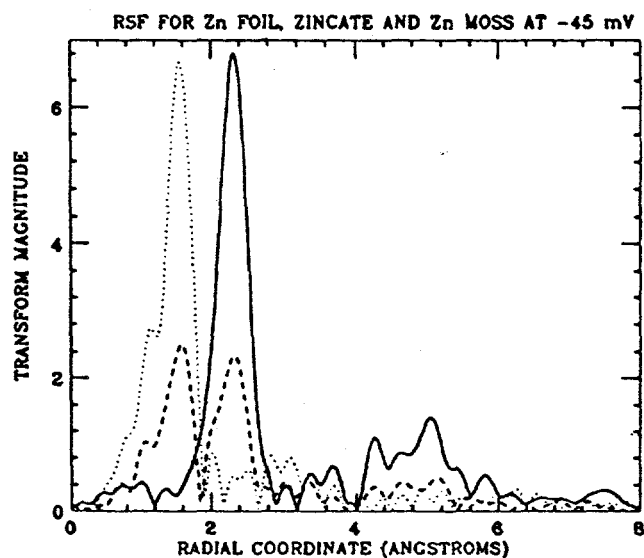


Fig. 6. Fourier transforms of the EXAFS for zinc foil (—), zinc moss at -45 mV (---) and an 8.4 M KOH + 0.74 M ZnO electrolyte (···).