



## Effect of alkaline electrolysis conditions on current efficiency and morphology of zinc powder

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### ABSTRACT

The deposition of electrolytic zinc from alkaline zincate solution was investigated and the effects of process parameters on current efficiency, morphology and specific surface area of zinc powders were analysed, based on excess potential and hydrogen release. Experiments were carried out with specific zincate and KOH concentrations under different current densities and current efficiencies were calculated based on powder weight. SEM imaging was used to study the effects of various conditions on powder morphology and the specific surface area was measured by BET. The highest specific surface area obtained was 9.14 m<sup>2</sup>/g.

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### 1. Introduction

Zinc has been an attractive material as an anode for secondary alkaline batteries which are widely used in aerospace, military, commercial and various other fields. It has a comparatively low cost, low equilibrium potential and good electrochemical reversibility (Wang et al., 2001; Zhang, 2006). The major difficulties in the expansion of these usages are corrosion and dendritic growth in secondary batteries, so there have been several attempts to modify zinc electrodes with rare earth films to protect them from corrosion (Zhu and Zhang, 2008; Zhu et al., 2009). Although some attempts have been made to improve the deposition process by means of surfactants, a single composition of the main electrolyte constituents is usually selected in research papers (Cheng et al., 2007; Zhang et al., 2008).

It is reported that porous zinc powder is produced in the presence of various organic additives from 12 M KOH solution and 4 wt.% ZnO when electrolyzed in a bath at a current density of 12 A/dm<sup>2</sup>. Zinc samples electrolyzed in the presence of cationic cetyl trimethyl ammonium bromide (Zn-CTAB) have a high corrosion rate and surface area. While zinc deposited with anionic surfactants, such as sodium dodecyl benzene sulfonate and sodium dodecyl sulfate exhibits high

dendritic and secondary growth (Ghavami and Rafiei, 2006). In other experiments, studies on the effect of organic acid additives in a solution of 8.5 M KOH containing 25 g/L ZnO found that hydrogen overpotential rose significantly, while dendrite formation was reduced to some extent. The order of increase in hydrogen overpotential was: tartaric acid > succinic acid > phosphoric acid > citric acid; while dendrite inhibition followed the order: citric acid > succinic acid > tartaric acid > phosphoric acid (Lee et al., 2006).

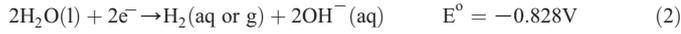
The effects of the addition of inorganic compounds like ZnO, V<sub>2</sub>O<sub>5</sub>, PbO, HgO, Sb<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and Pb<sub>3</sub>O<sub>4</sub> on the temperature and corrosion performance of solid porous zinc or paste electrodes have also been evaluated (Shivkumar et al., 1998; McBreen and Gannon, 1981; McBreen and Gannon, 1985). But the basic effect of electrolyte composition on the current efficiency of the alkaline zinc process, and the resultant morphological properties of the zinc powder, have not been reported quantitatively in the literature. Furthermore, in morphological studies, research has usually focused only on SEM images and battery outputs (Hu and Chang, 2004; Shivkumar et al., 1998).

In this research the alkaline electrowinning process focused on producing zinc powder and analyzing its morphological changes. The importance of such investigation is due to the usage of zinc powder in alkaline batteries which require a large specific surface area. Taking advantage of materials with a larger surface area will result in a lighter battery and better performance. By expanding the specific surface area, the contact between the effective mass of the electrode and the conduction grid will be enhanced, and the voltage loss of the battery during discharge will be diminished (Zhang, 1996).

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Two cathodic reactions can take place in alkaline zinc electrolysis:



Although it seems that Eq. (2) must take place first, in practice, Eq. (1) happens because of the hydrogen overpotential. The above  $E^\circ$  values are relevant to the release of hydrogen from a clean platinum electrode surface, whereas it is released from the surface of other metals at much higher potentials. Understanding the hydrogen release and overpotential phenomena is of great importance in the zinc deposition process. In different KOH concentrations, the overpotential of a Zn cathode is expressed by the Tafel equation (Eq. (3)).

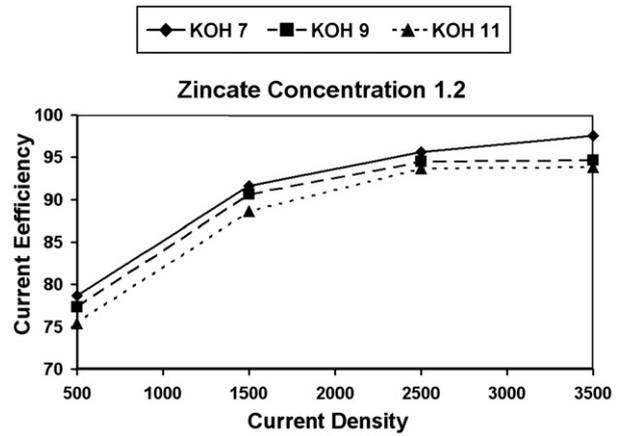
$$\eta = a - b \cdot \log i \quad (3)$$

where  $a$  and  $b$  are Tafel constants,  $\eta$  is the overpotential and  $i$  is current density.

The relevant data are tabulated by Sui and Evans (1999). This phenomenon makes alkaline electrolytes more appropriate than acidic electrolytes. The energy consumption of an acid process is about 35% of the cost of zinc powder production (Habashi, 1991), whereas the alkaline process consumes less energy due to the lower overpotential. Alkaline processes are also friendlier to the environment because they avoid the problem of iron dissolution and removal as jarosite in the acid processes (Lee and Piron, 1997).

**Table 1**  
Experimental conditions, powder weight, current efficiency and specific surface of powders.

Experiment Number	Electrolysis conditions			Powder weight (g)	Current efficiency (%)	Specific surface (m <sup>2</sup> /g)
	Current Density (A/m <sup>2</sup> )	Zincate (mole/L)	KOH (mole/L)			
1	500	1.2	7	2.9	79	3.2
2	1500	1.2	7	14.6	92	5.1
3	2500	1.2	7	17.6	94	7.4
4	3500	1.2	7	25.0	98	7.4
5	500	1.2	9	2.8	77	3.9
6	1500	1.2	9	14.5	91	5.3
7	2500	1.2	9	17.0	95	7.7
8	3500	1.2	9	24.2	95	7.9
9	500	1.2	11	2.8	75	3.9
10	1500	1.2	11	14.2	89	5.9
11	2500	1.2	11	17.1	94	7.8
12	3500	1.2	11	24.1	94	7.8
13	500	0.8	7	2.8	74	3.7
14	1500	0.8	7	13.7	86	5.2
15	2500	0.8	7	16.2	89	7.5
16	3500	0.8	7	23.5	92	7.6
17	500	0.8	9	2.7	73	3.9
18	1500	0.8	9	13.7	86	5.7
19	2500	0.8	9	16.1	88	7.8
20	3500	0.8	9	23.5	92	7.8
21	500	0.8	11	2.7	72	4.1
22	1500	0.8	11	13.3	83	6.0
23	2500	0.8	11	16.0	87	8.2
24	3500	0.8	11	23.0	90	8.1
25	500	0.5	7	2.6	71	3.9
26	1500	0.5	7	13.3	84	5.7
27	2500	0.5	7	15.7	86	8.4
28	3500	0.5	7	23.0	90	8.5
29	500	0.5	9	2.6	72	4.0
30	1500	0.5	9	13.1	82	5.9
31	2500	0.5	9	15.5	85	8.8
32	3500	0.5	9	22.5	88	8.9
33	500	0.5	11	2.6	70	4.4
34	1500	0.5	11	13	82	6.2
35	2500	0.5	11	15.5	85	9.1
36	3500	0.5	11	22.2	87	9.1

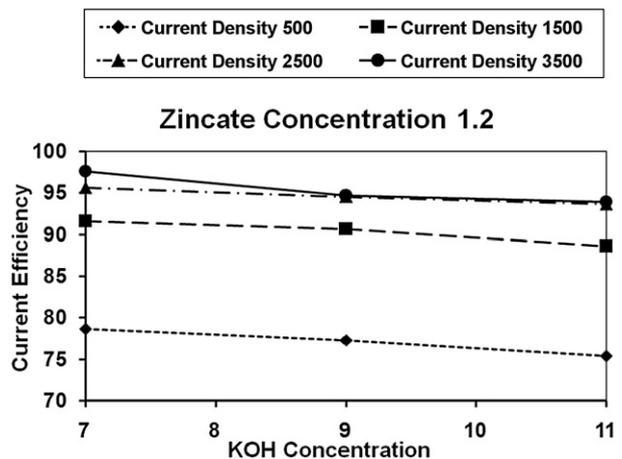


**Fig. 1.** Variation of current efficiency according to current density and KOH concentration with 1.2 M zincate.

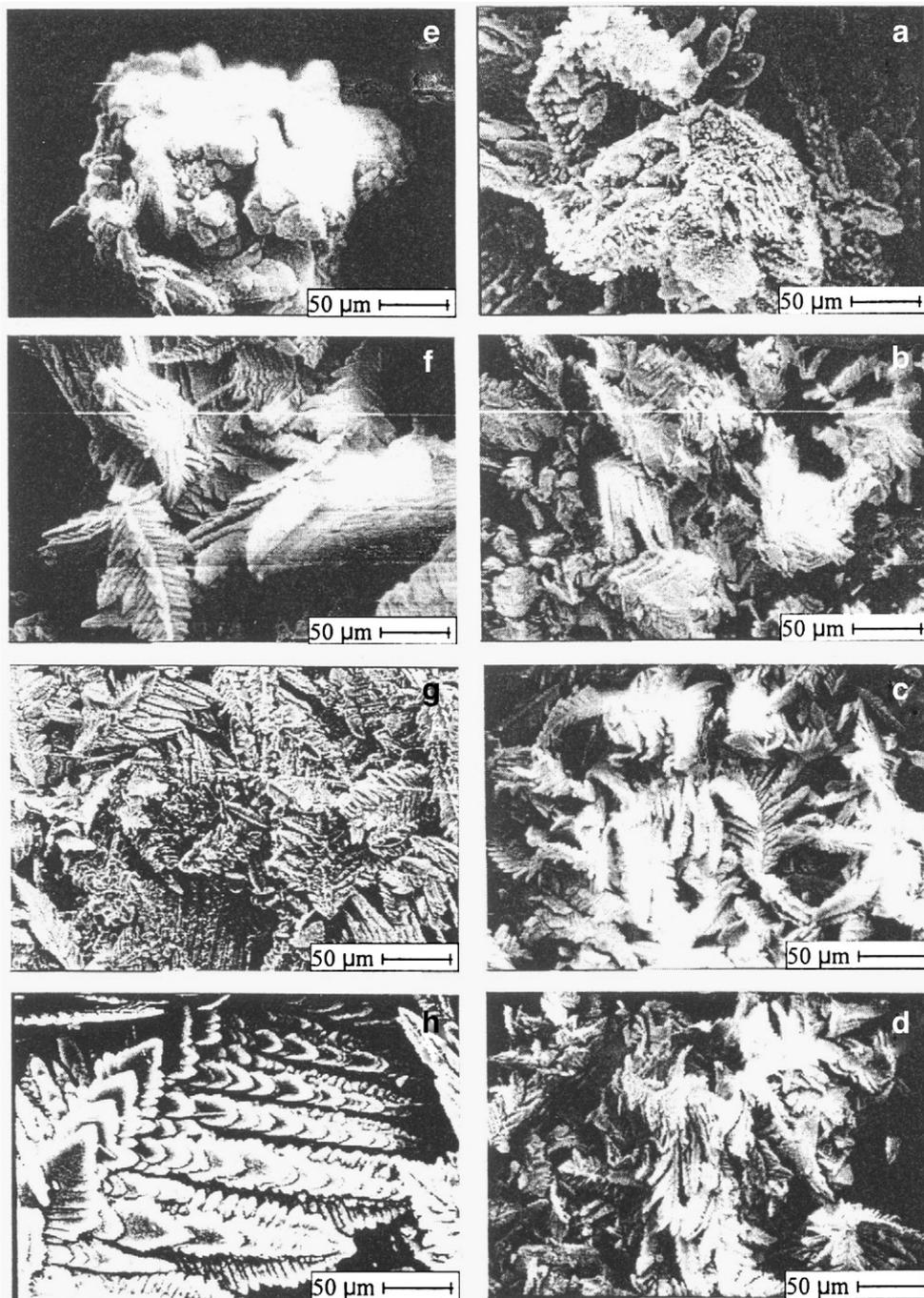
The hydrogen gas released at the cathode also affects the morphology of the powder. In the case of industrial applications, larger electrodes are used and the gas release is more evident and important. In the first stages of deposition, when the reaction area of zinc deposition is small, the release of hydrogen bubbles will cause parasites or dendrites and potential oscillation in the cell (Zhang et al., 2008). Furthermore, the electrode undergoes corrosion and forms holes in the zinc due to hydrogen evolution (Hu and Chang, 2004; Lee et al., 2006).

## 2. Experimental

Three main parameters were chosen as variables, current density (C.D.), zincate concentration and electrolyte KOH concentration. Other parameters such as temperature and distance between electrodes were kept constant. KOH (7, 9, and 11 M) was dissolved in distilled water, then zincate (0.5, 0.8, and 1.1 M) was dissolved in each of the above solutions to produce nine different solutions which were filtered prior to use in the electrolysis bath. A 0.1 × 6 × 8 cm Zn plate was applied as the central cathode and two 0.2 × 6 × 8 cm Ni plates were used as anodes on both sides of the Zn plate. They were set parallel and immersed vertically in the bath. Nickel was chosen for its corrosion resistance and to avoid contamination of the electrolyte and zinc powder.



**Fig. 2.** Variation of current efficiency with KOH concentration at various current densities with 1.2 M zincate.



**Fig. 3.** Right column – SEM images of produced Zn powder from 0.5 M zincate 11 M KOH and current densities of (a) 500 A/m<sup>2</sup> (b) 1500 A/m<sup>2</sup> (c) 2500 A/m<sup>2</sup> (d) 3500 A/m<sup>2</sup>. Left column – Zn powder from 0.8 M zincate, 7 M KOH and current densities of (e) 500 A/m<sup>2</sup> (f) 1500 A/m<sup>2</sup> (g) 2500 A/m<sup>2</sup> (h) 3500 A/m<sup>2</sup>.

Current densities of 500, 1500, 2500 and 3500 A/m<sup>2</sup> were tested for each electrolyte, thus Zn powder was made under 36 different conditions as summarised in Table 1. The temperature was kept between 25 °C and 30 °C in a water bath and all experiments were completed in a one hour period. The resultant cathode powders were submerged and washed in distilled water several times until the left-over alkali deposits were cleansed from the powder. This was proved by the addition of a few droplets of phenolphthalein to the abluition water. After this, the powders were dried for 2 h at 80 °C and all powder samples were sieved by a 140 mesh.

A different weight of Zn powder was obtained in each experiment; therefore the electrolysis current efficiency was calculated by Eqs. (4) and (5).

$$m_t = \frac{Alt}{nF} \quad (4)$$

$$C.E = \frac{m_e}{m_t} \quad (5)$$

where  $m_e$  is measured weight of powder produced in 1 h;  $A$  is atomic weight of Zn (65.37 g/mol);  $I$  is current in ampere;  $t$  is time of operation equal to 3600 s,  $n$  is zinc valence which is 2 and  $F$  is Faraday constant.

The morphology and shape of the produced powders were studied by SEM imaging. Finally, the specific surface areas of the powders were measured by nitrogen adsorption method with a BET Quanta-chrome AS-MP 1 apparatus.

### 3. Results and discussion

The results of the current efficiency and specific surface area measurements are depicted in Table 1. The details of these results and a discussion about the effect of the parameters on the final products are as follows.

#### 3.1. Effect of current density C.D.

Changes of current efficiency due to C.D. variations in different zincate and electrolyte concentrations can be seen in Table 1. Fig. 1 shows the trend of changes in current efficiency due to current density for 1.2 M zincate which is the same for other zincate concentrations. The current efficiency increases with C.D. with all zincate and electrolyte concentrations; although the increase is less at higher current densities and plateaus when it reaches 2500 A/m<sup>2</sup>. Clearly, the overpotential of zinc deposition is less than the overpotential for hydrogen release at all current densities and zinc deposition is easier when the difference is greater (Diggle, 1973).

#### 3.2. Effect of electrolyte concentration

The trend in current efficiency against KOH electrolyte concentration is plotted in Fig. 2 for 1.2 M zincate concentration. According to Table 1, at all current densities and zincate concentrations, the current efficiency decreases when increasing the KOH electrolyte concentration. Here, the changes can be assumed to be linear due to increasing hydrogen evolution. The proposed mechanism of hydrogen release from the alkaline zincate solution is:



By adding more KOH to the solution, the potassium ion concentration rises and Eq. (6) goes to the right, producing more

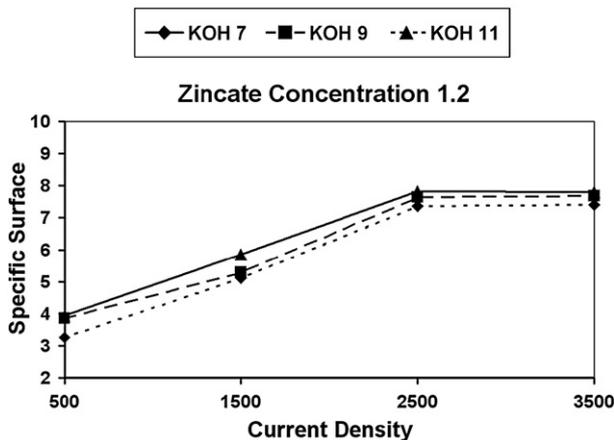


Fig. 4. Variation of specific surface areas with respect to C.D and KOH concentration with 1.2 M zincate.

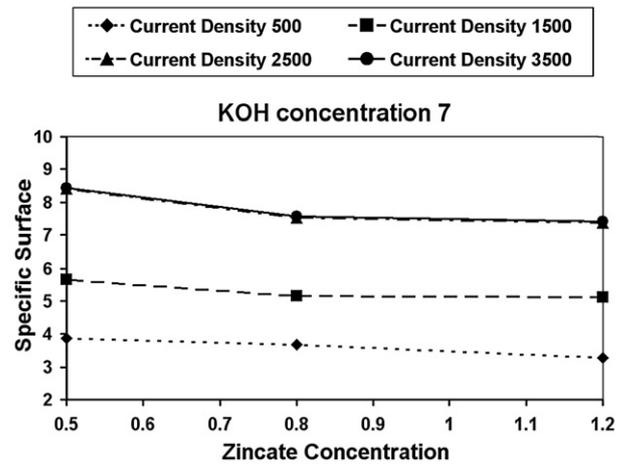


Fig. 5. Variation of specific surface areas due to C.D and zincate concentration in 7 M KOH. Specific surfaces at 2500 and 3500 A/m<sup>2</sup> are nearly overlapped.

KZn. As a result, hydrogen generation will increase via Eqs. (7) and (8) (Ravindran and Muralidharan, 1995). This phenomenon makes zinc deposition more difficult, therefore lessening the zinc deposition rate.

#### 3.3. Effect of zincate concentration

According to Table 1, for all C.D.s and electrolyte concentrations, the current efficiency increases with zincate concentration. The increase in current efficiency is linear in the tested zincate concentration region because in the presence of zincate ions, Eq. (7) changes to Eq. (9) (Piron, 1991):



By increasing the zincate concentration and its reaction with KZn, the reduction of water and release of hydrogen is eliminated and therefore zinc deposition and current efficiency increases. As seen in Table 1, the greatest current efficiency occurs at C.D. of 3500 A/m<sup>2</sup>, with 1.2 M zincate and 7 M KOH concentration. An increase in C.D. to more than 3500 A/m<sup>2</sup> results in a significant temperature increase and serious electrical power loss.

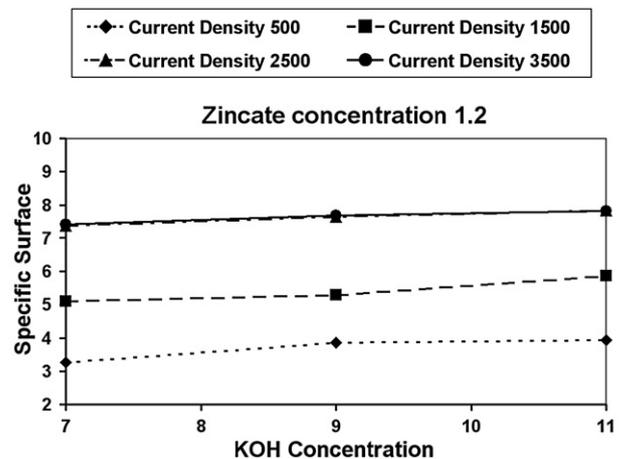


Fig. 6. Variation of specific surface areas with KOH concentration with 1.2 M zincate. Specific surfaces at 2500 and 3500 A/m<sup>2</sup> are nearly overlapped.

### 3.4. Morphology and specific surface measurements

For all conditions, an increase in C.D. changes the shape of the Zn powder and the morphology goes from dense and uniaxial to disperse and dendritic (Fig. 3). When the C.D. changes from 500 A/m<sup>2</sup> to 2500 A/m<sup>2</sup>, the specific surface area rises linearly, but up to 3500 A/m<sup>2</sup>, there is no further significant change (Fig. 4 and Table 1). At low current densities, zinc deposition is comparatively slow; consequently, dense and spherical depositions will be produced. By augmentation of C.D. and increasing the rate of deposition, dendritic growth is facilitated. It can also be seen in SEM images that by reducing the zincate concentration, the aggregation of dendritic deposits diminish. This is because in low zincate concentrations, more hydrogen gas is released.

Some measured specific surface areas are plotted against zincate and KOH concentrations in Figs. 5 and 6 which show that in lower zincate concentrations, the specific surface area is higher – in agreement with SEM observations. These changes in specific surface areas are greater at a C.D of 2500 and 3500 A/m<sup>2</sup>. This relation with C.D. can be seen in Fig 3 for two electrolyte conditions of 0.5 M zincate in 11 M KOH and 0.8 M zincate in 7 M KOH. SEM images, however, show no notable changes in powder morphology by augmentation of the electrolyte concentration, although there is a slight increment in the specific surface area of Zn powders.

### 3. Conclusions

Electrolytic zinc powder was produced by electrolysis of alkaline zincate solution. In this process, current efficiency increases with increasing current density under all concentrations tested and the zinc powder morphology changes from uniaxial and dense, to dendritic and loose. The specific surface area is also augmented. The current efficiency also goes up upon incrementing the zincate concentration from 0.5 to 1.2 M or when the KOH electrolyte concentration is decreased from 11 to 9 M. In this case, the zinc powder morphology changes from dendritic to uniaxial and the specific surface area decreases. The effect of zincate concentration is more considerable than KOH concentration. Dendritic zinc powder has a higher specific surface area and is better suited for use in batteries. The highest current efficiency of 97.6% was obtained at 3500 A/m<sup>2</sup> in 7 M KOH and 1.2 M zincate electrolyte, but the highest surface area zinc was

9.14 m<sup>2</sup>/g which was obtained at 3500 A/m<sup>2</sup> in 11 M KOH and 0.5 M zincate electrolyte.

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