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Electrodeposited Zinc Electrodes for High Current Zn/AgO Bipolar Batteries

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Electrodeposited zinc electrodes for high current zinc bipolar batteries have been prepared and studied on the basis of morphology, particle size, surface area, bulk density, current density, and specific energy density. Electrodeposition was performed in alkaline bath with copper as substrate. The material so developed was characterized by XRD, SEM, bulk density measurements, BET surface area and electrochemical discharge testing. The effect of ZnO and KOH concentrations, bath temperature, distance between electrodes and use of surfactants was studied on the morphology and electrochemical properties of the synthesized powders. Surfactant resulted in an increase in current density due to improved surface area. The discharge current capability upto 700mAcm^{-2} was achieved.

Keywords: Nanocrystalline zinc powder, Bipolar zinc electrodes, Triton X-100, Electrodeposition.

1. INTRODUCTION

Zinc is widely used as anode material in primary and secondary batteries like Zinc-MnO_2 [1], Zinc-AgO [2], Ni-Zn [3], Zn-HgO [4], Zn-air [5] etc due to relatively high electrode potential and low equivalent weight. Zinc is environmentally safer than other anode materials besides having high rate discharge performance [6, 7].

Zinc electrodes are prepared by variety of methods like paper making technology [8], electrodeposition [9], pasted zinc electrodes [10], thick film printed zinc electrodes [11] and pressed plate electrodes [12] etc. Among these deposited zinc electrodes gives higher current densities due to elimination of the binder during electrode manufacturing process. Various deposition methods employed for the synthesis of zinc powder include physical vapor deposition, chemical vapor deposition, zinc oxide deposition/ reduction and Electro-deposition [13]. Electrodeposition method is mostly preferred as it achieves better control over morphology, porosity and surface area of the electrode. Electrosynthesis methods are preferred as they are cheap and have better control due to variations in temperature, solution concentrations and current density etc [14]. Both acidic and alkaline baths have been used for the Electrodeposition of zinc but alkaline baths are preferred due to better control over the deposition distribution [15].

Electrodeposited electrodes present various inherent problems like dendrite formation, large particle size and low surface area [16, 17]. Large particles and low surface area is not suitable for high power batteries. Different additives like rare earth metals [18], tartaric acid [19], polyalcohols [20] and surfactants [21] were added to the deposition bath to improve the morphology of the deposited powders. Presence of fine zinc particles in the powder greatly improves the performance of the zinc electrodes [22].

Despite the advent of new battery systems such as lithium ion and metal hydride systems, zinc silver oxide is still the best in terms of power density [23, 24] This superiority makes zinc silver oxide system the top choice for applications where volume and weight are critical and high power output is required, such as the high power density pulse batteries [25]. These high power batteries require thin electrodes which cannot be manufactures by conventional pressing or pasting methods.

In this study we have prepared thin zinc electrodes by electrodeposition from alkaline bath. Various parameters which control morphology, particle size and surface area of the zinc powders have been optimized. The thin electrodeposited electrodes have been assembled into high power bipolar zinc batteries. Current densities upto 700mAcm^{-2} have been obtained.

2. EXPERIMENTAL

2.1. Electrode fabrication

All chemicals were of analytical grade and used without any further purification. Thin zinc electrodes with 0.4 mm thickness were prepared by electrodeposition from alkaline bath. Various bath compositions are shown in Table.1.

Required amount of Zinc oxide (99.5%, Acros) was dissolved in KOH (Merck) solution (Various molarity) with the help of gentle heating (70~ 80 °C). The solution was cooled to room temperature and filtered to remove any undissolved ZnO. Sodium dodecyl sulfate (Merck) and Triton X-100(Merck) were used as surfactants. Zn sheet (>99.9%) was used as anode(15cm x 10cm x 1cm) with copper disc (0.05mm thickness and 75cm^2 area) as substrate for the deposition. Copper foil was polished with zero grade emery paper and washed with acetone. The polished foil was immediately used for deposition to avoid surface oxidation. One side of the copper foil was coated with a paint (Berger supper gloss enamel), which was washed with acetone after deposition process to avoid the peeling of the paint layer at high current discharge due to heating. Thus only one side of the electrode was deposited with zinc and the other side used as current collector in bipolar cell assembly.

Electrodeposition was carried out as function of current densities at 25 °C and 65 °C for 15 to 24 minutes to allow deposition of ~ 4g zinc powder. The time of deposition was calculated with the help of Faraday's law as follows;

$$m = Q/F \times M/z \qquad (i)$$

where;

m = mass of zinc deposited
Q = total electric charged involved in deposition
F = Faraday’s constant (F= 96485 coulombs)
M = Molar mass of zinc (65.38)
z = It is the electron transferred per ion (2 in case of Zn^{+2})
Q can be calculated from the formula;

$$Q = It \qquad (ii)$$

Where;
I = Current in Amperes (Get by multiplication of the current density x total area of electrode)
t = Time of deposition in seconds

Sponge zinc deposits were washed with deionized water until neutral, slightly rolled with acrylic rod to final thickness of 0.40mm and dried under vacuum at 50 °C for 24 Hours.

Figure.1 shows the electrochemical cell for zinc deposition

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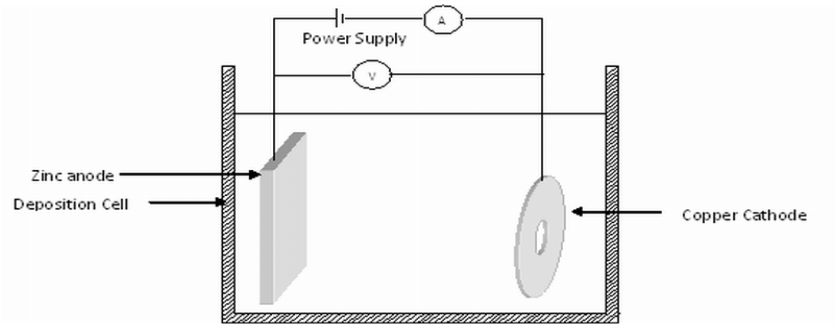

Figure 1. Zinc electrodeposition box

Table 1. Bath compositions

Bath ID	KOH (Molar)	ZnO (g/Lit)	Bath temperature (°C)	Deposition Time (minutes)	Current Density (mA/cm^2)	Surfactant	Distance (cm)
Zn-1	6	20	35~ 45	24	120	--	85.5
Zn-2	4	20	35~ 45	18	170	--	85.5
Zn-3	6	20	35~ 45	18	170	--	85.5
Zn-4	6	20	65~ 75	18	170	--	85.5
Zn-5	6	15	35~ 45	18	170	--	85.5
Zn-6	8	20	35~ 45	18	170	--	85.5
Zn-7	6	20	35~ 45	15	220	--	85.5
Zn-8	6	20	35~ 45	18	170	--	40
Zn-9	6	25	35~ 45	18	170	--	85.5
Zn-10	6	20	35~ 45	18	170	SDS	85.5
Zn-11	6	20	35~ 45	18	170	Triton x-100	85.5

2.2. Characterization of the deposited powders

The deposited powders were characterized with the help of XRD, SEM, BET surface area, bulk density followed by discharging at various loads.

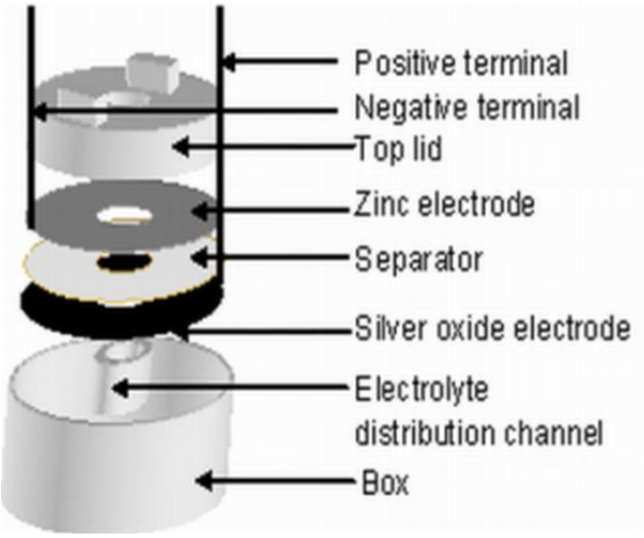

Figure 2. a) Electrochemical discharge box

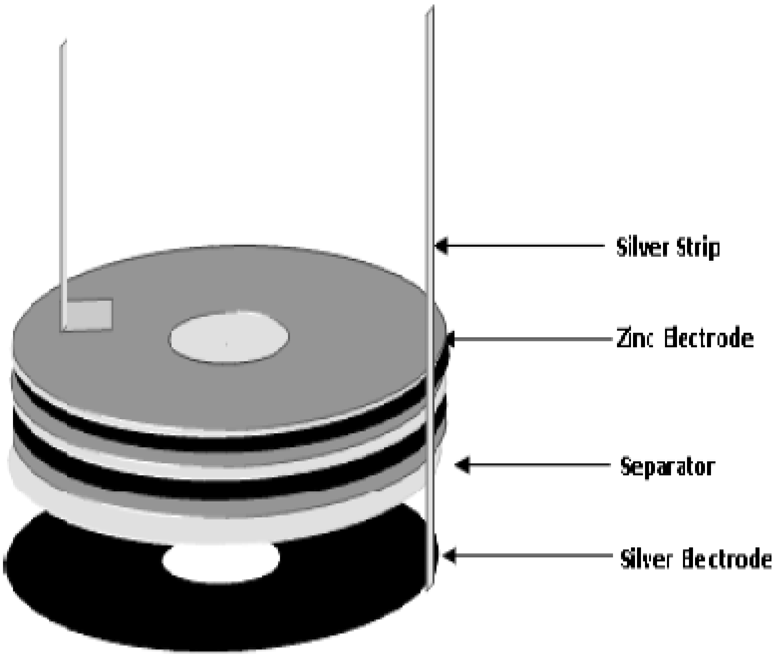

Figure 2. b) Bipolar cell assembly

Electrochemical cell assembly was made by taking the deposited electrode as working electrode and sintered silver oxide electrode (75cm^2 surface area) as counter electrode. Silver electrode was pre-electroformed to 2.3V, so as to convert all the silver powder to silver (II) oxide. 31% KOH solution was used as electrolyte with porous cotton paper separator. All the cells were soaked for 10 seconds before discharge testing. The cells were discharged in a Teflon test cell shown in Figure 2A. To check the performance of the Zinc electrodes in bipolar configuration, 3 electrodes were stacked in series (Figure 2B) against electroformed sintered silver electrodes. Cotton paper was used as separator.

3. RESULTS AND DISCUSSIONS

3.1 XRD analysis

Structural characterization of the deposited powder was performed by XRD measurement. The spectra were recorded on X-PERT PRO diffractometer using the Cu-Kα radiation. Intense diffraction peaks observed in Figures 3-6 indicate the crystalline nature of the material.

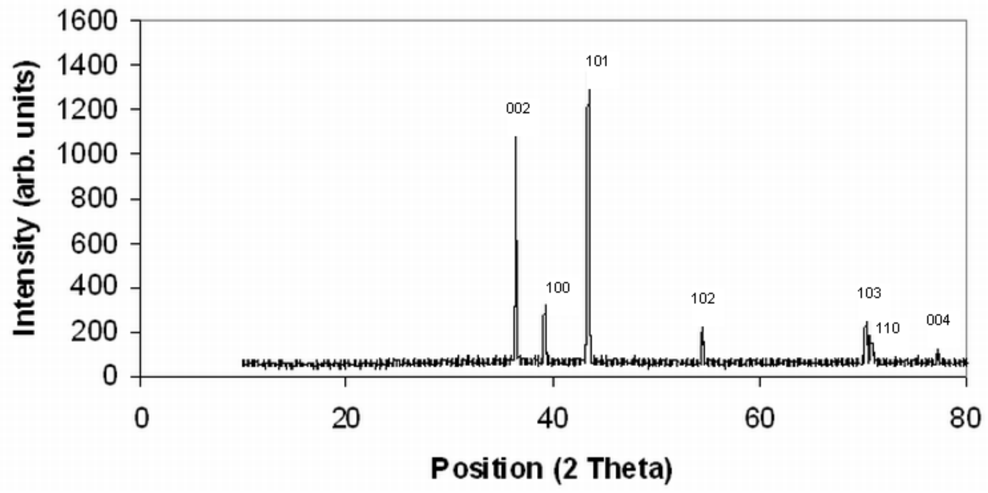

Figure 3. XRD pattern of Zinc powder (Zn-11)

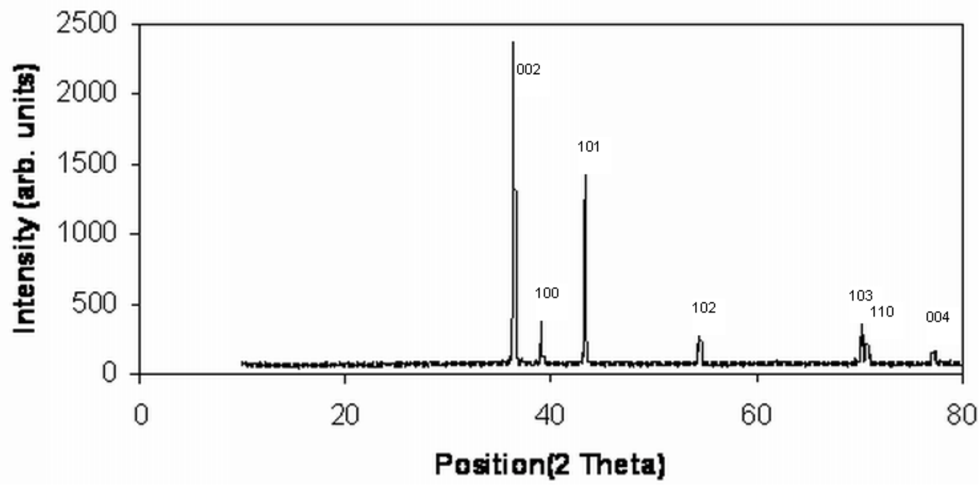

Figure 4. XRD pattern of Zinc powder (Zn-4)

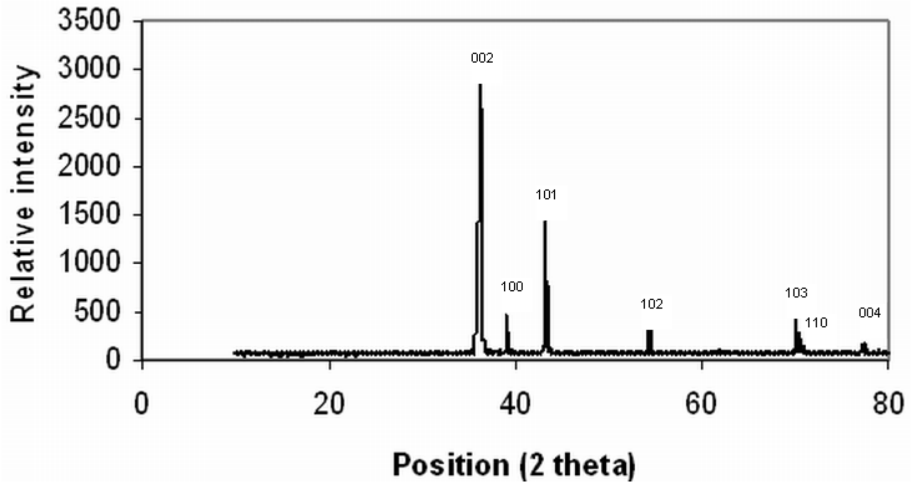

Figure 5. XRD pattern of Zinc powder (Zn-10)

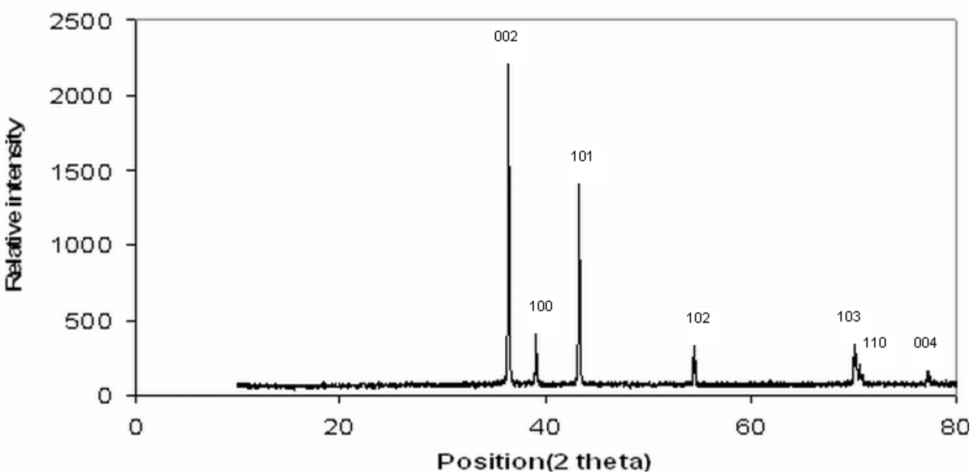

Figure 6. XRD pattern of Zinc powder (Zn-3)

The characteristic zinc peaks (101), (100), (002), (102), (103) and (110) are present in the X-ray diffractograms with no extra peaks ruling out the possibility of impurities. The crystallite sizes calculated from the Scherer formula are presented in Table 2. Nano sized crystallites were obtained in the presence of surfactants. This shows that presence of surfactant protects the crystallites from crystal growth and agglomeration. The presence of nanocrystallites increases the surface area and thus producing improved current density.

3.2. SEM analysis

Morphology of the deposited powders was studied with the help of Scanning electron microscopy. Irregular shaped micrometer sized particles were deposited in the absence of surfactants. Well defined leaves like nano sized structures were developed with Tritone X-100 (Fig 7). When sodium dodecyl sulfate was used as surfactant rod like submicron sized structures were produced (Fig. 8).

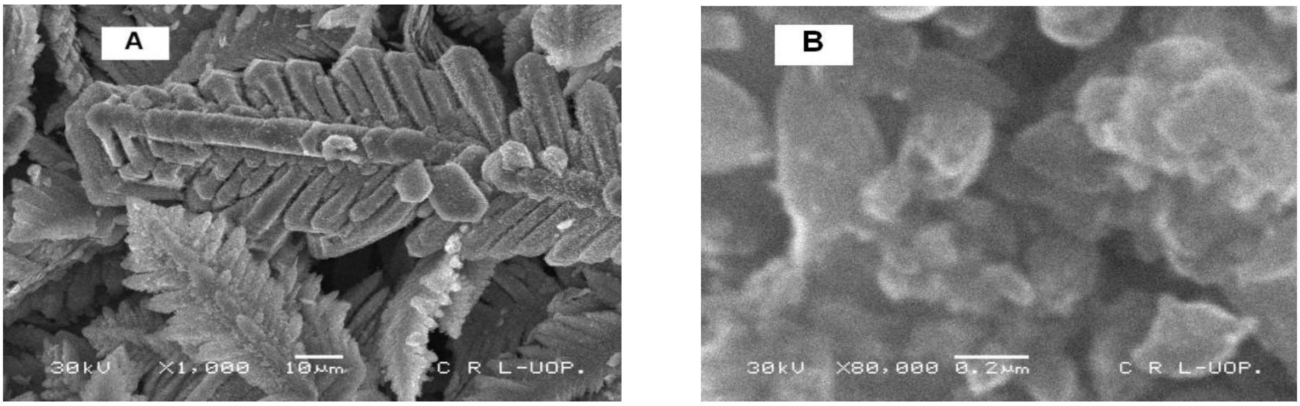

Figure 7. SEM of Zinc powder deposited in presence of Triton X-100 (Zn-11) a) Low magnification showing the microstructure of the deposited powders b) High magnification, each microstructure consisting of nano particles

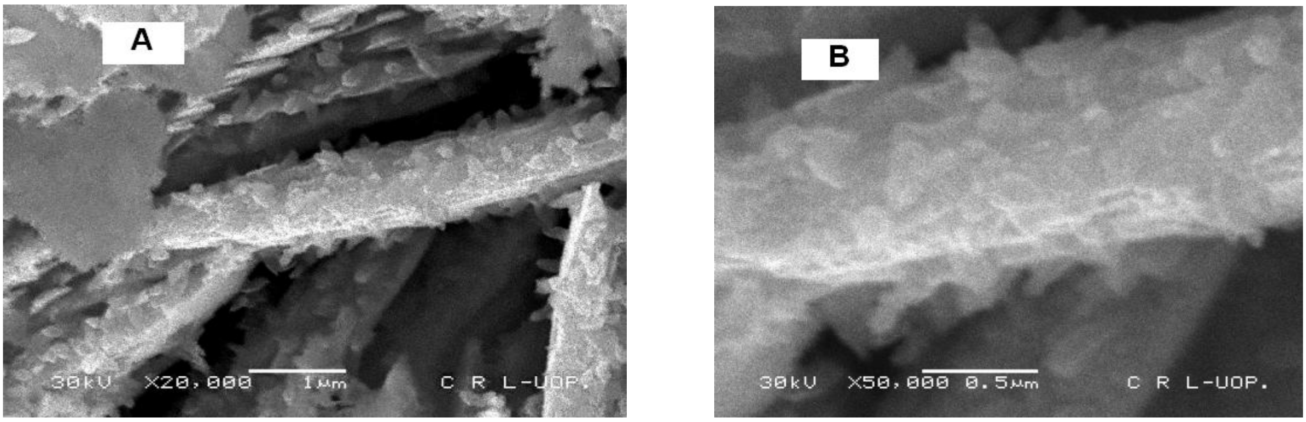

Figure 8. SEM of Zinc powder deposited in presence of sodium Dodecyl sulfate a) Low magnification showing the microstructure of the deposited powders b) High magnification, each microstructure consisting of submicron particles

In absence of surfactant the particle are dendritic in nature and have variable particle size The Nanocrystalline deposits have higher surface area (Table. 2) which results in better discharge performance (Fig.9).

3.3. Bulk density

Bulk densities of various samples measured by density cup method [26] are presented in Table.2. An increase in density was observed with increase in the concentration of KOH, increase in temperature, increase in the concentration of ZnO and increase in distance between the electrodes. Increase in bulk density resulted in decreased high load performance. This behavior can be explained on the basis that low surface area powders have high bulk densities and thus poor high current performance.

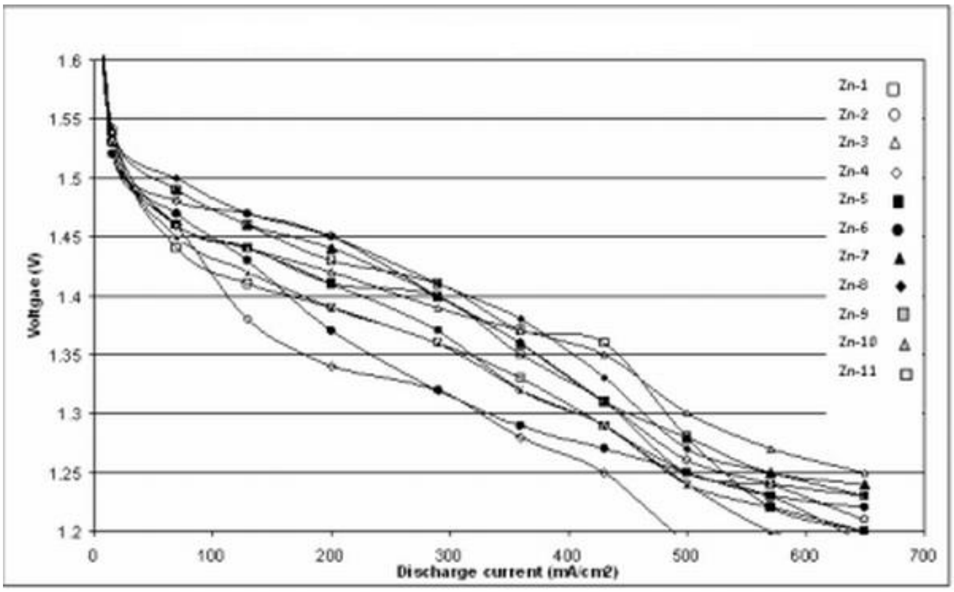

Figure 9. Discharge performance of various zinc samples at different loads

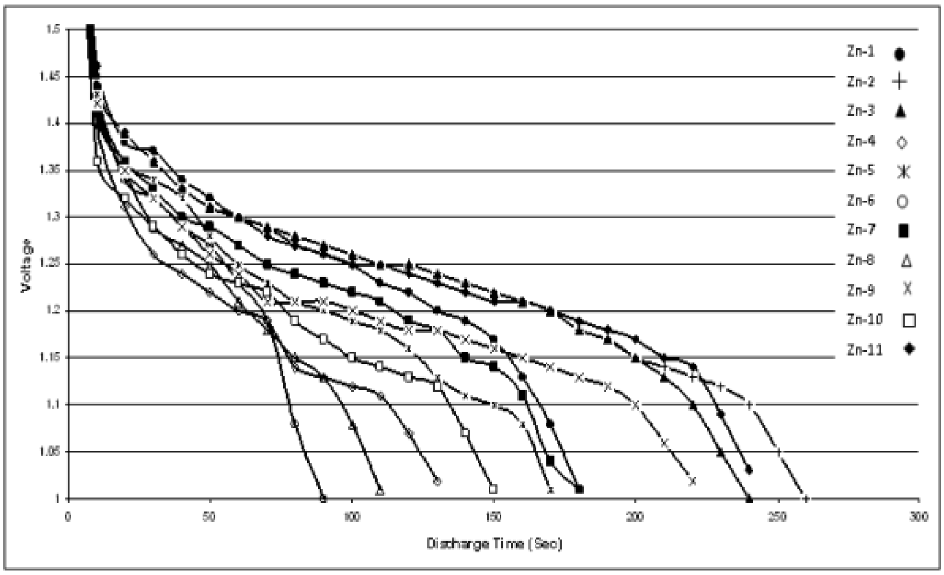

Figure 10. Discharge performance of various zinc samples at 220mAcm^{-2}

3.4. Surface area

The BET surface area of various samples is shown in Table.2. An increase in BET surface area was observed with increase in the concentration of KOH or increasing current density. Surface area decreased with increase in distance between the electrodes and increase in ZnO concentration.

Surfactants increased the surface area. Highest surface area was observed with Triton x-100. It is clear from Table-2 that Zn-11 has the highest electrode surface area and power density.

3.5. Electrochemical performance

The discharge performance of various electrodes at various current densities is shown in Fig.9. Open circuit voltages of the cells are in the range of 1.83V to 1.84V. It is clear from the discharge curves that the powders with low surface area have poor high rate performance.

At high discharge currents (Fig.9) high surface area samples Zn-3, Zn-8 and Zn-11 showed good performance. Good performance was observed at moderate discharge rates (Fig.10) for Zn-2, Zn-3, and Zn-11.

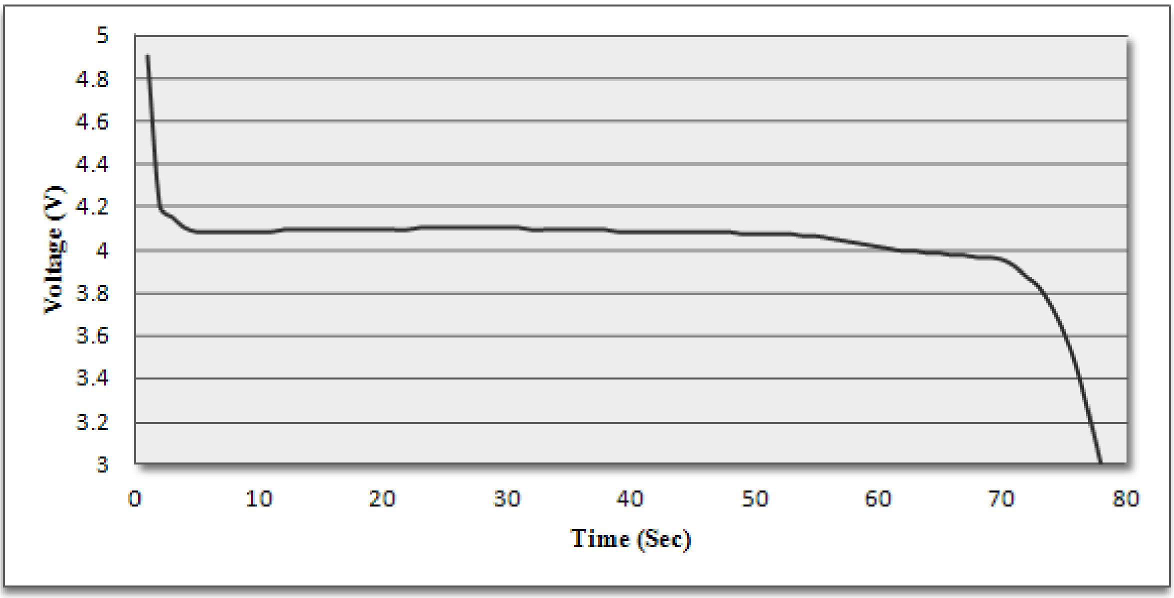

Figure 11. Discharge performance of a 3 Cell bipolar assembly at 500mA/cm^2

It is observed in Fig.10 that an increase in KOH concentration results in a decrease in energy density. Zn-2 with 4M KOH concentration has highest energy density while Zn-6 with 8M KOH concentration has lowest energy density.

Decrease in distance between electrodes during deposition process results in decrease in specific energy density. Zn-2, Zn-3 and Zn-11 are best in term of energy density.

The as prepared Zinc electrodes show excellent performance when used in bipolar cell configuration (Fig11).

Open circuit voltage upto 1.65/Cell was obtained in the bipolar configuration with Zn-2 as anode and electroformed sintered silver electrodes as cathode. The pack operated for 80 seconds at 500mA/cm2.

Table 2. Physical Parameters of Zinc powders

Zinc ID	Average Particle Size SEM	Average crystallite Size XRD (nm)	Powder deposited (grams)	Density (g/cm^3)	Surface area (m^2/g)	Totals surface area (m^2)	Morphology of particles
Zn-1	1~2µm	100 ~ 500	3.98	0.59	4.10	16.318	Dendritic
Zn-2	1~2 µm	150 ~ 500	4.05	0.57	4.22	17.09	Dendritic
Zn-3	1~2 µm	140 ~ 450	4.03	0.67	4.11	16.44	Dendritic
Zn-4	1~2 µm	200 ~ 600	4.05	0.91	2.55	10.32	Dendritic
Zn-5	1~2 µm	80 ~ 400	4.03	0.56	4.31	17.36	Dendritic
Zn-6	1~2 µm	130 ~ 440	4.06	0.64	4.41	17.90	Dendritic
Zn-7	1~2 µm	150 ~ 550	4.10	0.73	4.58	18.77	Dendritic
Zn-8	1~2 µm	110 ~ 430	4.07	0.62	5.06	20.52	Dendritic
Zn-9	1~2 µm	140 ~ 480	4.04	0.79	2.31	9.33	Dendritic
Zn-10	0.1 ~ 2 µm	30 ~ 110	4.08	0.93	2.65	10.81	Rods
Zn-11	0.1~0.2µm	15 ~ 85	4.05	0.66	5.11	20.69	Leaf structure

4. CONCLUSION

Zn-3 and Zn-11 with the highest surface area are good for high discharge performance and Zn-2, Zn-3 and Zn-11 are best in term of specific energy densities. The thin deposited electrodes thus obtained can be used for compact zinc bipolar batteries for high current applications.

ACKNOWLEDGMENT
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