



Effect of Polyaniline Coating on “Shape Change” Phenomenon of Porous Zinc Electrode

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Performance of porous zinc electrode in alkaline secondary battery systems suffers mainly from shape change and dendrite growth. Polyaniline coating in direct contact with porous zinc electrode was found to restrict zincate movement away from the test electrode, which otherwise may lead to a decrease in electrode surface area (shape change of the electrode) on repeated cycling. Constant current charge/discharge cycles of the blank and polyaniline-coated zinc electrodes have been carried out to assess the performance of the polymer film. It was found that a fibrous network of polyaniline coating allows OH⁻ ions and restricts the diffusion of zincate ions.

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Zinc is used as a negative electrode for many alkaline battery systems because of its low equilibrium potential reversibility, compatibility with aqueous electrolytes, low equivalent weight, high specific energy and volumetric energy density, abundance, low cost, low toxicity, and ease of handling.¹ Zinc anode secondary batteries (zinc/silver oxide) are potential candidates to fulfill the need for lightweight and high discharge rate application like missiles, torpedoes, and spacecrafts. Its widespread commercialization has been hindered by the short cycle life of the zinc electrode. In general, the shape change of zinc electrode and dendrite growth resulting from the high solubility of zinc discharge products in the electrolyte are the main problems. The deposition of zinc-active material during charging is nonuniform, and results in electrode shape change. Dendrite deposits are formed due to the high local current density. Attempts to reduce the solubility of zinc discharge products have included the use of additives either to the electrode²⁻⁶ or to the electrolyte.⁷⁻⁹ The use of additives will reduce the initial content of zinc-active species, and may lower the specific energy or specific power of the electrode. Separators provide a barrier to zinc dendrite growth, and can play an important role in determining the transport of species between the negative and positive electrode compartments. The rate of zinc material redistribution was slower in Zn/NiOOH cells using microporous separators, compared to cells using ion-exchange membranes.¹⁰ Suga et al.¹¹ proposed that anodes comprised of zinc-active material and a polymer layer which is permeable to oxygen formed in direct contact with the anode suppress dendrites growth and the shape change. Zinc ionomer¹² layers directly in contact with porous zinc electrode were found to impede the dissolution of the discharge products into the electrolyte.

Polyaniline is a stable, nontoxic, and easy to synthesize polymer. The general morphology of untreated, as synthesized, and untreated conducting polymer on a microscopic or nanoscopic scale, is fibril or globular.¹³ With the help of atomic force microscopy, Avlyanov et al.¹⁴ have shown that the “filmlike” conducting form of polyaniline obtained via in situ chemical polymerization is quite smooth, with a root-mean-square (rms) surface roughness ca. 3 nm, and is composed of aggregation of globules of ca. 50 nm diameter.

In this work, an attempt has been made to study the effect of polyaniline coating directly in contact with the porous zinc electrode on its performance as an alkaline secondary electrode. Hence, the effect of polymer coating on shape change of the electrode, dendrite formation, and cell capacity yield has been carried out by conducting a cycle life test of a zinc/silver oxide system.

Experimental

The test zinc electrodes were prepared by pressing the mixture of 95 wt % ZnO with 5 wt % polytetrafluoroethylene (PTFE) as binder onto a silver foil of 0.1 mm thickness with 40 × 45 mm dimen-

sions. The thickness of the working electrode was about 1.4 mm and the porosity was 0.6. Chemically synthesized polyaniline (1 wt %), prepared from distilled aniline (Aldrich), was dissolved in N-methyl pyrrolidone, and the same was applied as a thin layer of ~250 μm thickness onto the surface of zinc electrode. The porous zinc electrode was wrapped in nonwoven cellulose separator and sandwiched between two sintered silver electrodes. The silver electrodes were initially wrapped in nylon separator and then in four folds of cellophane separator. Two test cells were fabricated, one with blank zinc electrode (cell B) and the other with polyaniline-coated zinc electrode (cell P). Assembled cells were soaked in 6 M KOH solution for 17 h and then subjected to formation cycles. The cells were characterized by charge/discharge cycles, morphological, and Fourier transform infrared (FTIR) analysis. Charge/discharge experiments were carried out using Bitrode Fenton, model MCN16-2-12,LCN. Scanning electron microscopy (SEM) micrographs were taken by Hitachi, model 3000H. FTIR spectra were registered using a Perkin-Elmer Paragon-500 FTIR spectrometer using KBr pellets in the region between 400 and 4000 cm⁻¹. The analysis of zincate in the KOH electrolyte solution was carried out with a Varian atomic absorption spectrometer.

Results and Discussion

FTIR analysis.—Figure 1a and b shows the IR spectrum of the polymer film from the electrode surface, recorded before and after completing 100 cycles to confirm the presence of polymer network and recomplexing of zincate ions with the imine groups of the polymer. The peak at 750 cm⁻¹ in both the samples of the IR spectrum proves the presence of polymer network before and after 100 cycles; a redshift in the n(NH) vibration peak from 3377 cm⁻¹ (uncharged) to 3180 cm⁻¹ (after 100 cycles) indicates zincate recomplexing with imine groups of the polymer in the cycled electrode. The zincate complexing with polymer helps in retaining the zinc ions at the electrode vicinity.

Electrolyte analysis.—To analyze the quantity of diffused zincate across the polyaniline film, KOH electrolyte solution from cell P and cell B was analysed for zinc. The results showed that the diffusion of zinc in cell P was 24% less than cell B.

SEM analysis.—Figure 2a and b shows the electron micrographs of the surface and cross section of the polyaniline-coated zinc electrode, surface of blank zinc is shown in Fig. 2c before commencement of the charge/discharge cycles. The surface of the electrode shows aggregation of polyaniline globules linked together with fine fibrous structures. The cross section of the electrode shows fibrous network spread of ~250 μm thickness, on the electrode surface.

The fine fibrous network spread of polyaniline serves a dual purpose as follows: (i) it impedes the diffusion of zincate ions (discharge products) from the electrode vicinity; (ii) it permits the passage of OH⁻ ions through the polymer layer.

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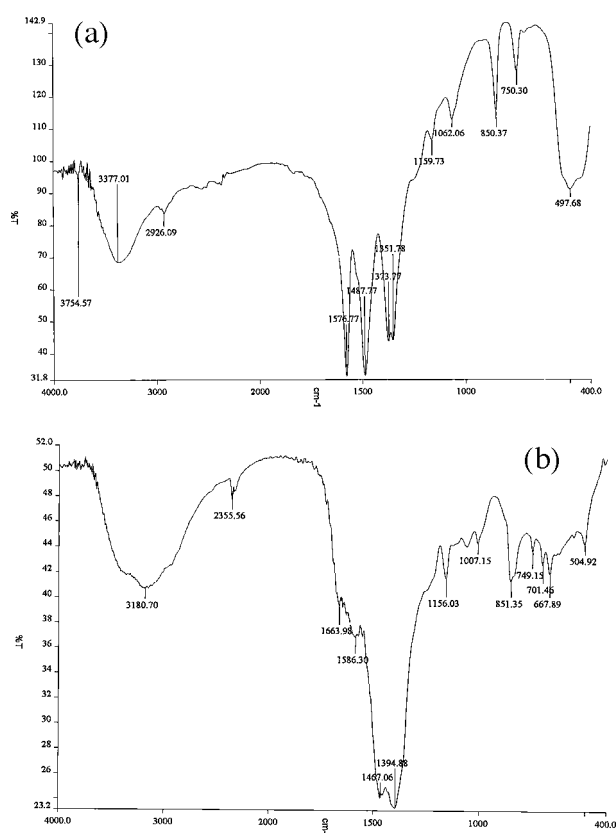


Figure 1. FTIR spectrum of polyaniline on zinc electrode (a) as prepared; (b) after 100 cycles.

Figure 3a and b shows the electron micrographs of polymer-coated and blank zinc electrode, after completing 100 cycles. The surface of blank zinc electrode shows large deposits of zinc on the separator, whereas polymer-coated electrode was free of zinc deposits but pores were observed on the surface of the polymer. Figure 3c shows the electron micrographs of the cross section of cycled polyaniline-coated zinc electrode. At higher magnification (Fig. 3d) needlelike ZnO crystals packed on the solid zinc surface along with zinc grains were observed. Such a porous passivating film facilitates the zinc ions to diffuse into bulk solution and the OH⁻ ions to penetrate onto the zinc surface. As a result, the anodic dissolution of zinc proceeds continuously until the zinc is consumed or the zinc surface is fully inhibited.

With discharge, due to the absence of polyaniline coating on blank zinc electrode, most of the zincate ions diffuse into the counter electrode compartment and deposit on the separator on charge. The zinc deposits grow as the cycle number increases. Zinc deposits were not observed on the separator of polymer-coated electrode, as diffusion of zincate ions was restricted by the polyaniline coating. The pores on the polymer surface may be due to weak sites of the polymer which had ruptured due to gas evolution from the electrode surface.

Analysis of charge/discharge profile.—Figure 4 shows the charge/discharge curves of cell P and cell B for 100 cycles. For cell B overpotential rise was observed between 2.2 and 2.7 V during the sixth cycle to the end of the 100th cycle, whereas for cell P, the overpotential rise was between 2.2 and 2.5 V during the 50th cycle to the 100th cycle. No potential rise was observed in cell P before the 50th cycle. The observance of overpotential rise is due to the poor recovery of coulombic charge applied during cell discharge. The internal resistance drop was 3 and 5 mΩ for cell P and cell B, respectively. In cell B the recovery of charge from the sixth cycle was declining due to gradual depletion of zincate ions at the vicinity

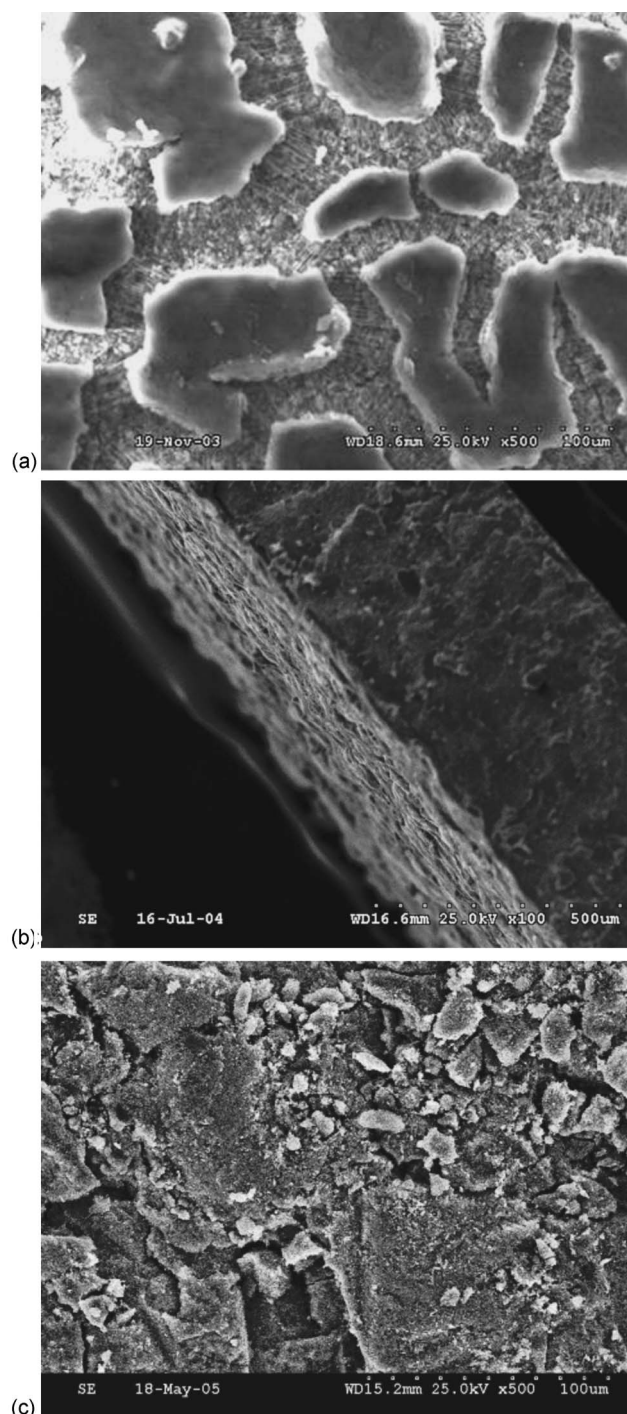


Figure 2. SEM of the fresh porous zinc electrode (a) surface of the polyaniline-coated zinc electrode, (b) cross section of the polyaniline-coated zinc electrode, (c) surface of the blank zinc electrode.

of the electrode, caused by the absence of polymer coating and later by passivation of the electrode. But, in cell P, the reason for poor recovery of charge after 50 cycles was the depletion of KOH solution in the pores of the electrode due to gradual pore plugging on repeated cycling. Pore plugging occurs in porous zinc electrodes¹⁵ due to differences in the molar volume of ZnO (14.51 cm³/mole) and zinc (9.15 cm³/mole).

Discharge curves of cell P and cell B are shown in Fig. 5. A potential plateau at 1.3 V was observed from the first to 50th cycle in cell P. This flat plateau indicates that the porosity of the electrode

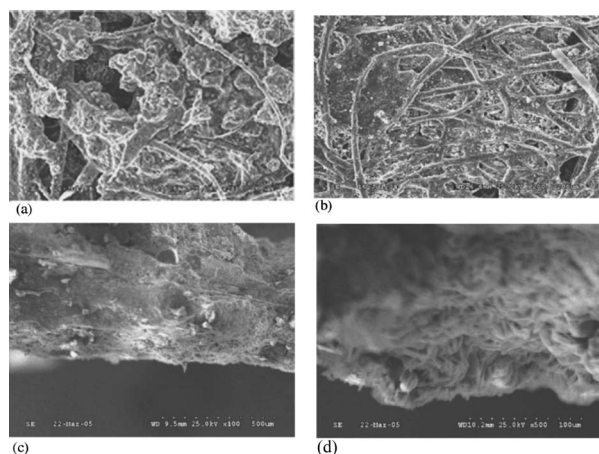


Figure 3. SEM of zinc electrode after 100 cycles; (a) polyaniline-coated zinc electrode, (b) blank zinc electrode, (c) cross section of the polymer-coated zinc electrode, and (d) polymer-coated zinc electrode surface magnified to show zinc needles.

is good and all the discharge products were retained at the electrode vicinity up to 50 cycles. After 50 cycles the discharge curves show an irregular potential rise or hump, which gradually increases due to gradual pore plugging of the electrode or minor rupturing of the polymer coating due to the pressure of the gases evolved.

In cell B, the hump or irregular potential drop was observed in almost all discharge curves because of the depletion of discharge products near the electrode.

The capacity versus cycle number for cell P and cell B are shown in Fig. 6. The anomalous capacity variation with cycling (*e.g.*, capacity decrease at the 30th cycle and then increase at the 35th cycle) is a unique feature of secondary alkaline zinc system.³ The cell capacity varied between 80 to 100% for cell B, and no frequent capacity variation was observed in cell P. After 80 cycles the capacity of both cells started degrading gradually. It can be assumed that at 80 cycles, the zinc electrode in cell P was partly passivated and the zinc in cell B was completely passivated.

Photographs of blank and polyaniline-coated zinc electrodes after 100 cycles are shown in Fig. 7a and b. The blank zinc electrode showed large quantities of zinc deposited in the central portion of the electrode, leaving the edges of the electrode bare. Polyaniline-coated zinc electrode showed uniform distribution of zinc on the current collector. In cell B, due to the absence of polymer layer,

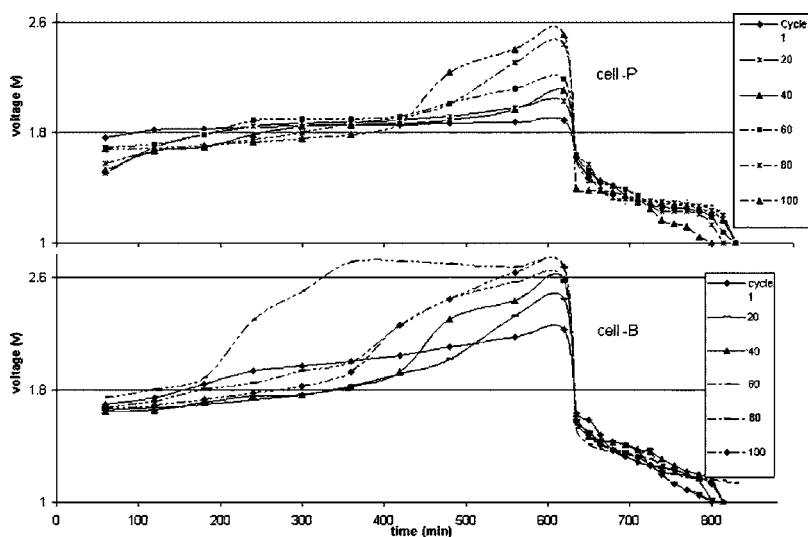


Figure 4. Charge/discharge curves of cell P and cell B.

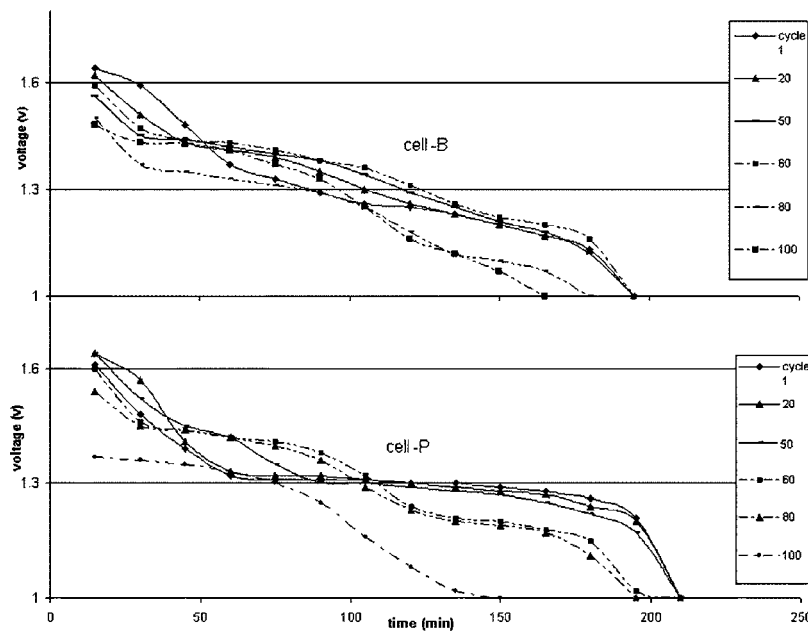


Figure 5. Discharge curves of cell B and cell P.

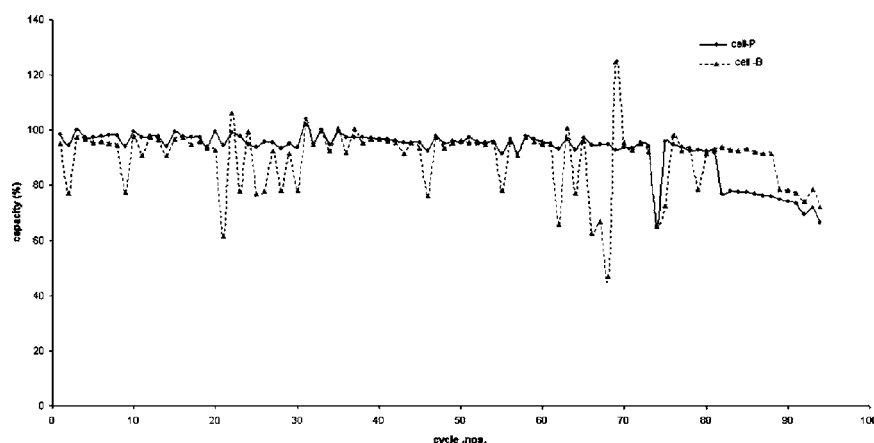


Figure 6. Capacity of blank zinc and polyaniline-coated zinc.

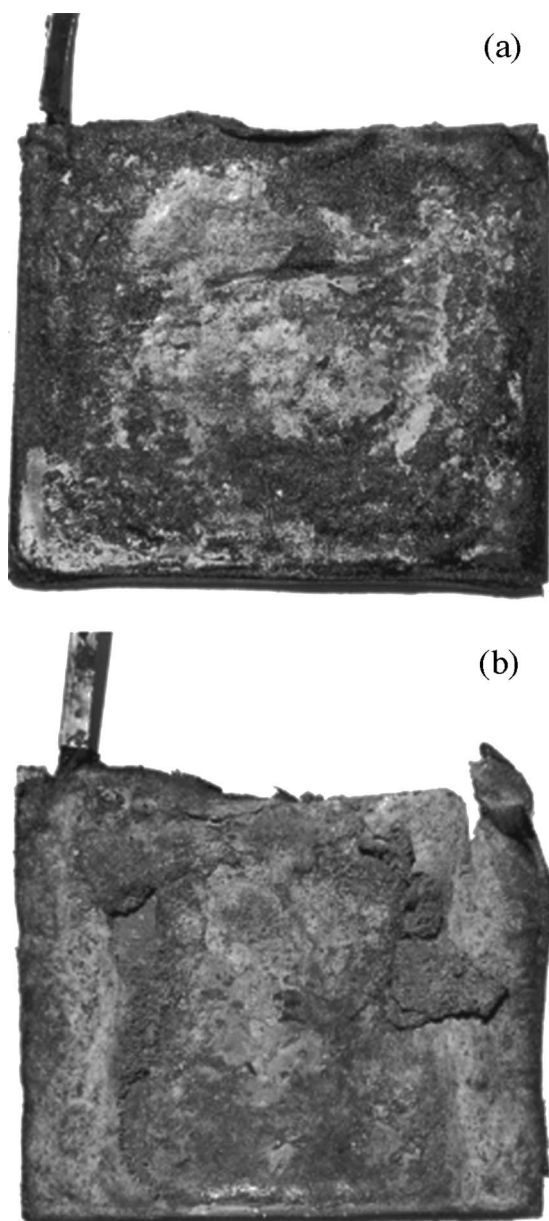


Figure 7. Photographs of zinc electrodes after 100 cycles: (a) blank zinc electrode; (b) polyaniline-coated zinc electrode.

redistribution of solid zinc and zinc oxide from one part of the electrode to the other (or shape change of the electrode) occurred through the movement of zincate ions.

Interaction of polyaniline film with zinc surface to produce needlelike crystallites is difficult to explain. In the previous studies of the passivation mechanisms of zinc anode, it was suggested that electrochemical dissolution of zinc anode takes place as a first step to produce $\text{Zn}(\text{OH})_2$, which dissolves immediately in alkaline solution to form zincate ions. As the zincate ions reach saturation concentration, the precipitation of solid zincate occurs to form a loosely adherent porous film in the vicinity of the zinc surface. When the electrochemical oxidation continues, a dense film is formed on the zinc surface due to the depletion of OH^- ions at the surface region.

In polyaniline-coated zinc the zincate ions formed in alkaline solution coordinate with the cationic groups of the polymer and form a complex. Apparently this complex formation may also be an important cause for spatial inhibition for the formation of dense passive film.

Conclusion

The fibrous network spread of polyaniline allows OH^- ions to pass through but impedes zincate ions due to its fine porous structure. The zincate ions recomplex with imine groups of the polymer and are retained at the electrode surface.

Due to this effect

1. Shape change of the electrode can be minimized;
2. Dendrite growth can be retarded; and
3. Uniform cell capacity can be achieved.

Hence, a polyaniline-coated zinc electrode is a better choice over the blank zinc electrode. Further research is in progress to stop or delay the process of pore plugging of the polymer-coated electrode and enhance the cycle life of the cell.

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