

# Zinc deposition during charging nickel/zinc batteries

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## Abstract

A method of solving the classical problem of short cycle life with nickel/zinc secondary batteries is suggested by studying the effects of the negative electrode substrate on Zn deposition. The use of different coatings on the substrate, (the so-called current-collector) is studied by testing several working electrodes (Zn, Cd and Pb) in a zinc oxide saturated potassium hydroxide electrolyte. Cyclic voltammograms show that the nucleation potential of the Zn deposition on a Pb substrate is lower than that on Zn or Cd. Cathodic polarization curves at various temperatures are also obtained and reveal that slower electrode kinetics and more Cd or Pb coating can retard shape change and dendritic growth by leading to slow electrode kinetics and uniform current distribution. These coatings are applied to a Cu mesh and the effects of coating materials on the current-collector on Zn deposition in Ni/Zn secondary batteries are also studied. Application of Pb as a coating metal on the current-collector of negative electrode retards shape change and the dendritic Zn growth and, hence, increases cycle life.

*Keywords:* Zinc deposition; Nickel/zinc batteries; Current-collector; Cathodic polarization

## 1. Introduction

The nickel/zinc (Ni/Zn) battery is a power source that offers considerable advantages in terms of high specific energy and power. The nominal discharge voltage is 1.6 V per cell and the battery holds an almost constant voltage throughout most of the discharge period and exhibits voltage stability at different discharge rates. The system, however, can hardly complete more than 200 to 300 deep-discharge cycles before failing. The failure is usually caused by the negative electrode, which suffers from the following two phenomena: (i) Zn dendrite nucleation and growth leading to cell shorting, and (ii) redistribution of Zn material to cause a shape change that results in capacity loss. Recently, performances of more than 500 cycles have been achieved [1,2] by applying additives or multi-component electrolytes. In the authors' laboratory, an Ni/Zn secondary battery for electric vehicle is under development and 180 Ah capacity cells have been installed in a test vehicle and have given 300 cycles of deep-discharge with high specific energy and power [3]. Different cell sizes are also being developed for electric scooters and other applications.

Since the limitation of the Ni/Zn battery is due to negative electrode degradation, the deposition of zinc on the negative electrode has been of technological interest. The places where the reduced zinc is deposited are not only in the active material but also on the surface of the current-collectors. Thus,

investigation of the effect of the substrate on Zn deposition is of importance. The complex behaviour of Zn has been reported [4,5] and includes a few studies of the initial stage of deposition from a phenomenological point of view. The kinetics of electrocrystallization obtained from the potentiostatic deposition of foreign substrates have also been studied [6] and the relevant general electrocrystallization models [7] gave direct information as to the kinetics of nucleation and crystal growth in two or three dimensions. Research on an Ag substrate [8] showed that a monolayer of Zn was deposited by forming an alloy. More detailed studies on several kinds of substrate, including Cu, Au, Cd, Zn [9], Pb, Tl, Sr and In [10], also reported alloy formation on the deposits. Examination of the deposition of Zn on Sn, Pb and Ag showed that the best adherence is Pb in alkaline electrolyte [11]. Many effects of additives to the negative electrodes have been investigated and published or filed as patents by many investigators [12–15].

In the present work, the effects of Cd and Pb substrates are studied electrochemically and compared with a Zn substrate. In particular, it is examined whether these substrates retard shape change by leading to slow electrode kinetics and uniform current distribution when coated on the current-collector. It has also been examined whether these substrates can help lower the nucleation overpotential so that porous, mossy Zn deposits rather than dendritic growth are obtained. The techniques used are cyclic voltammetry and cathodic polariza-

zation measurement at various temperatures followed by scanning electron microscope (SEM) examination of the working electrode surface. Applications of this study to actual battery systems (3.5 Ah test cells) have also been performed and the negative electrodes examined in an X-ray radiograph after a number of cycles. The latter provides information on the redistribution of active materials before and after the substitution of coating materials on the current-collectors.

## 2. Experimental

Cyclic voltammetric and cathodic polarization curves were obtained with a potentiogalvanostat using Zn, Cd and Pb as a working electrodes, a Hg/HgO electrode as a reference electrode, and nickel as a counter electrode. All electrode potentials are reported with respect to the Hg/HgO electrode. The working electrodes (Zn, Cd and Pb) were obtained as 99.99% pure rods (Aldrich, USA). The latter were cut into pellets and mounted in epoxide resin. The exposed area of the electrodes was 1 cm<sup>2</sup> after repeated polishing. Prior to each run, the working electrodes were ground with 600 grit silicon carbide followed by further polishing with 0.05 μm alumina powder. The electrolyte was zincate saturated (5 wt.%) 8.6 M KOH solution, which was prepared from reagent grade 80% KOH hydrated (Shinyo, Japan) and ZnO (Hanil, South Korea) with distilled deionized water.

Electrochemical data were obtained with a potentiogalvanostat (EG&G Princeton Applied Research, M273). The cyclic voltammetry studies were made in voltage envelopes of -0.2 to -1.8 V at a scanning rate of 10 mV s<sup>-1</sup>. Cathodic polarization curves were obtained by potentiodynamic method, at a sweep rate of 0.2 mV s<sup>-1</sup>. The potential was scanned while the temperature was held at 25, 40, 50 or 60 °C. As Zn is deposited on each substrate, the surfaces of the electrodes were rinsed, dried and examined by SEM (JEOL). In order to prevent additional surface oxidation, the specimens were kept in an argon-purged container.

Polymer-binded ZnO powder was roll-pressed on to a Cd-coated Cu mesh in the dry state to obtain a negative electrode. Copper meshes coated with Pb and Sn were also utilized. Sintered nickel hydroxide electrodes prepared on an expanded Ni screen were assembled with several layers of organic microporous film and filled with electrolyte in a test cell. These test cells (3.5 Ah) were cycled at a C/12 charge rate and a 5C/18 discharge rate. Redistribution of Zn-active materials was examined at different states of cycling by an X-ray radiograph (Hitachi 160 KVP).

## 3. Results and discussion

### 3.1. Cyclic voltammograms

The cyclic voltammogram of the Zn redox reaction on a Zn working electrode is shown in Fig. 1 and is compared with

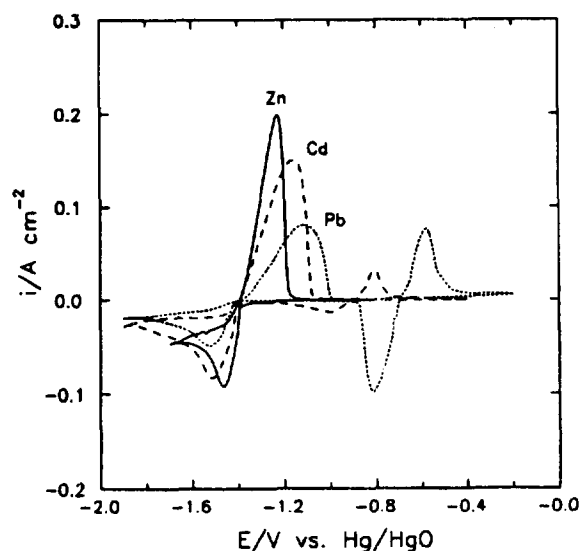


Fig. 1. Cyclic voltammograms of Zn in zincate saturated KOH on Zn, Cd and Pb substrates.

plots obtained from Cd and Pb working electrodes. These plots present typical cathodic and anodic peaks that represent Zn deposition and dissolution. In the cathodic loop of the Zn substrate, especially, Zn reduction is shown. This is caused by the zincate dissolving in the electrolyte followed by nucleation at -1.386 V and growth of Zn deposits. In the final stages of Zn deposition, i.e., as the potential reaches -1.6 V, hydrogen starts to evolve from the surface of the Zn substrate.

The Zn nucleation potential on a Pb substrate is relatively lower than those on Cd or Zn. This indicates that the Pb substrate is less facile to the deposition of Zn than either the Cd or the Zn substrate. The potential of the anodic peak from the dissolution of the deposited Zn increases in the order: Zn < Cd < Pb. This indicates the order of increasing deposit adherency. The hydrogen gas starts to evolve at a much lower potential for the Pb and Cd substrates compared with the Zn substrate. Voltammograms for Cd and Pb show secondary anodic peaks of substrate dissolution at -0.8 and -0.6 V, respectively, and the cathodic counterparts for deposition of the dissolved Cd or Pb ions.

### 3.2. Cathodic polarization curves

The cathodic polarization curves of zinc on the Zn, Cd and Pb substrates at four different temperatures are presented in Fig. 2. Nucleation and dissolution potentials, Tafel slopes and equilibrium potentials obtained from the room temperature test and cyclic voltammograms are listed in Table 1. The relatively lower value of the Tafel slope on Pb compared with Zn and Cd explains the slower kinetics due to high overvoltage for zinc reduction. Thus, a uniform current distribution is expected, which is beneficial in preventing the negative electrode from suffering dendritic growth of Zn deposition.

The rate of Zn deposition from the zincate solution was determined. Using the current density from the cathodic

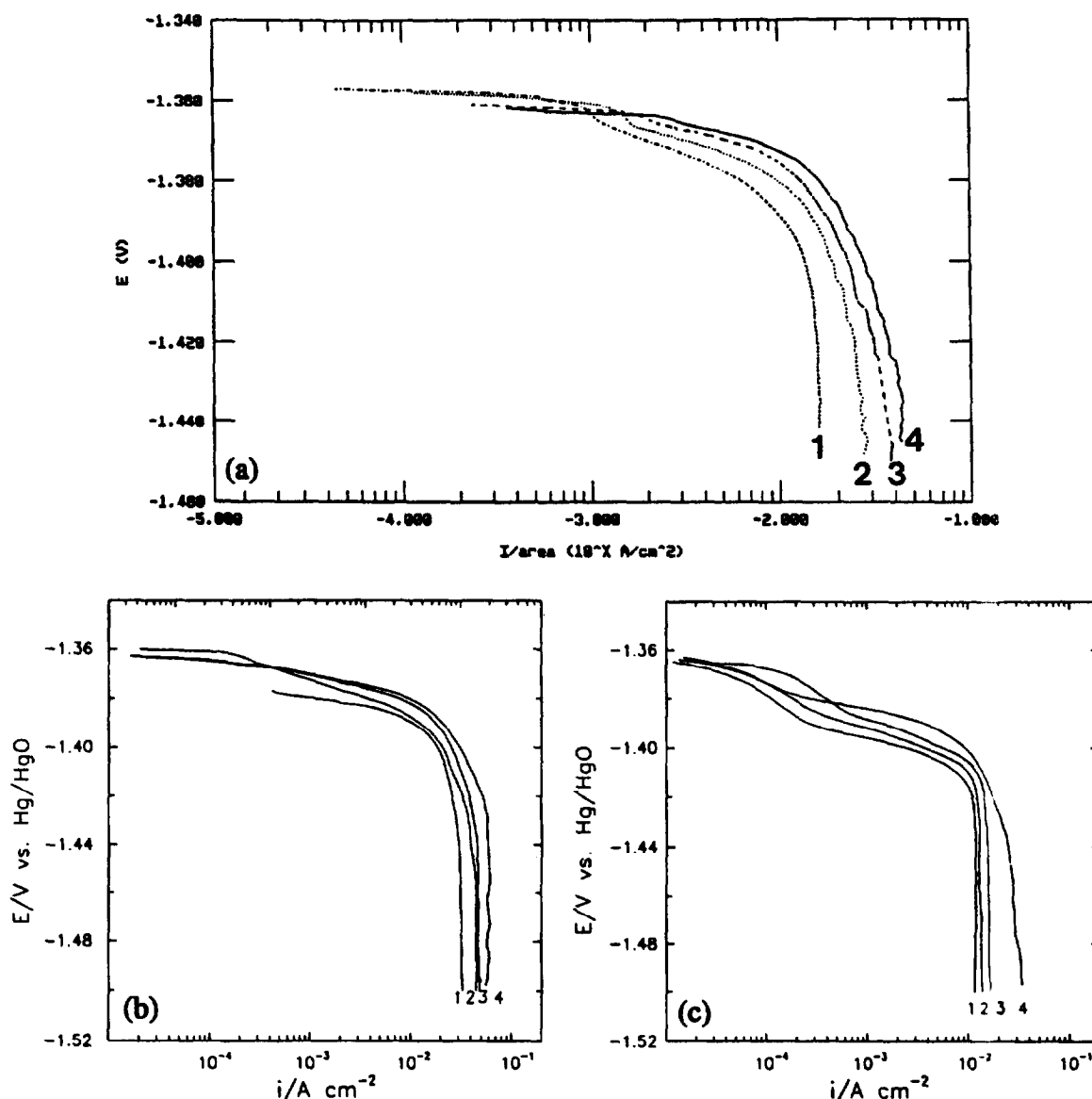


Fig. 2. Cathodic polarization of Zn on (a) Zn, (b) Cd and (c) Pb at various temperatures: (1) 25 °C; (2) 40 °C; (3) 50 °C; and (4) 60 °C.

Table 1  
Test results of cyclic voltammetry and cathodic polarization at 25°C

Substrate	Nucleation potential (V)	Dissolution potential (V)	Tafel slope (V/decade)	Equilibrium potential (V)
Zn	-1.386	-1.226	-0.018	-1.357
Cd	-1.381	-1.151	-0.016	-1.377
Pb	-1.414	-1.120	-0.009	-1.363

polarization curve, the weight gain by the deposition per time per unit area can be calculated. Faraday's law may conveniently be summarized by

$$W = itA/zF \quad (1)$$

where  $W$  is the weight of the deposition in g;  $i$  is the deposition current density in  $A\ cm^{-2}$ ;  $t$  is the elapsed time in s;  $A$  is the atomic weight of the reduced substance in g/mol;  $z$  is the number of charges involved;  $F$  is the Faraday constant. Now, the deposition rate can be calculated using this equation

$$R = 1.21I \quad (2)$$

where  $R$  is the rate of deposition in  $mg\ h^{-1}\ cm^{-2}$ ; the constant 1.21 is calculated for a Zn substance;  $I$  is the current density given in  $mA\ cm^{-2}$ . Assuming that most of the deposition is accomplished before the transient current density, where the reaction is controlled by charge transfer, the deposition rates of Zn on three kinds of substrate at four different temperatures are plotted in Fig. 3. These follow an Arrhenius plot.

When Zn is reduced and deposited on Zn, Cd and Pb substrates, the slopes of the Arrhenius plots are -1.14,

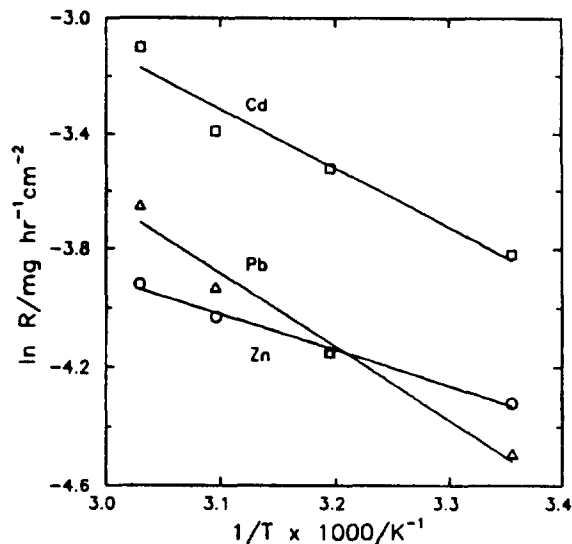


Fig. 3. Arrhenius plot of Zn deposition.

–1.96 and –2.34, respectively, and yield activation energies of 9.31, 16.05 and 19.23  $\text{J mol}^{-1} \text{K}^{-1}$ . As with the Tafel slopes, it is found that a lower activation energy is required for Zn deposition on the Zn substrate than on Cd and Pb substrates. By contrast, higher activation energy is required for the electrode reaction on the Pb substrate.

Thus, an improvement of the battery properties is anticipated if a material that can lead to slow kinetics, like Pb, is

applied to the negative electrode active material or to the surface of the current-collector in the Ni/Zn secondary battery. During charging, the reduced Zn ions from the electrolyte are transferred to the surface planes of the conductive mass of the electrode, and then diffuse along the surface to the growth sites. The Pb metal substrate can provide the nucleation and growth sites and this leads to lower current density and causes a uniform current distribution on the whole surface of the negative electrode.

### 3.3. Micrographs and radiographs

The morphologies of Zn deposition on Cd and Pb are quite different, as shown in Fig. 4. It has also been reported [10] that the basal plane of the Zn deposits on Zn is parallel to the substrate, but grown perpendicular to the Pb substrate. Thus, it is thought that the slower kinetics of Zn deposition on a Cd or a Pb substrate are related to the morphology of the growth of the Zn deposits. Zinc deposits on a Zn substrate at fast kinetics result in dendritic growth (Fig. 4(a)). As expected from the electrochemical data, a Cd or a Pb substrate induces lamellar type growth of the Zn deposit (Fig. 4(b) and (c)) and this will elongate the cycle life of Ni/Zn batteries.

Similarly, the current-collector coated with Pb and Cd gives uniform current distribution on charging, so that it causes a uniform redistribution of Zn-active material during

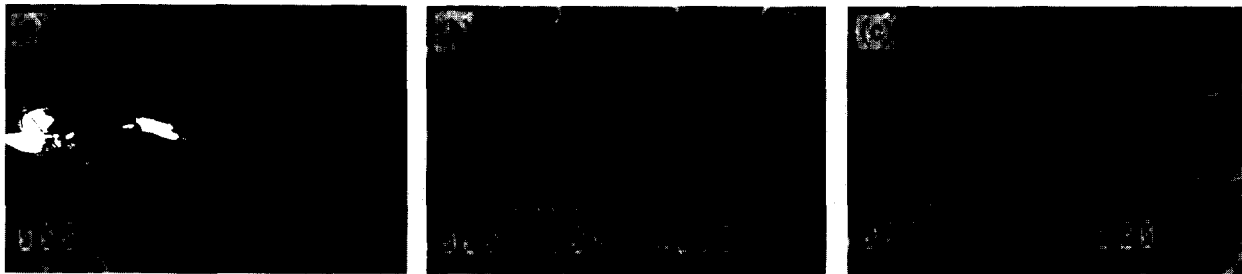


Fig. 4. SEM micrographs of Zn deposition on: (a) Zn substrate; (b) Cd substrate, and (c) Pb substrate.

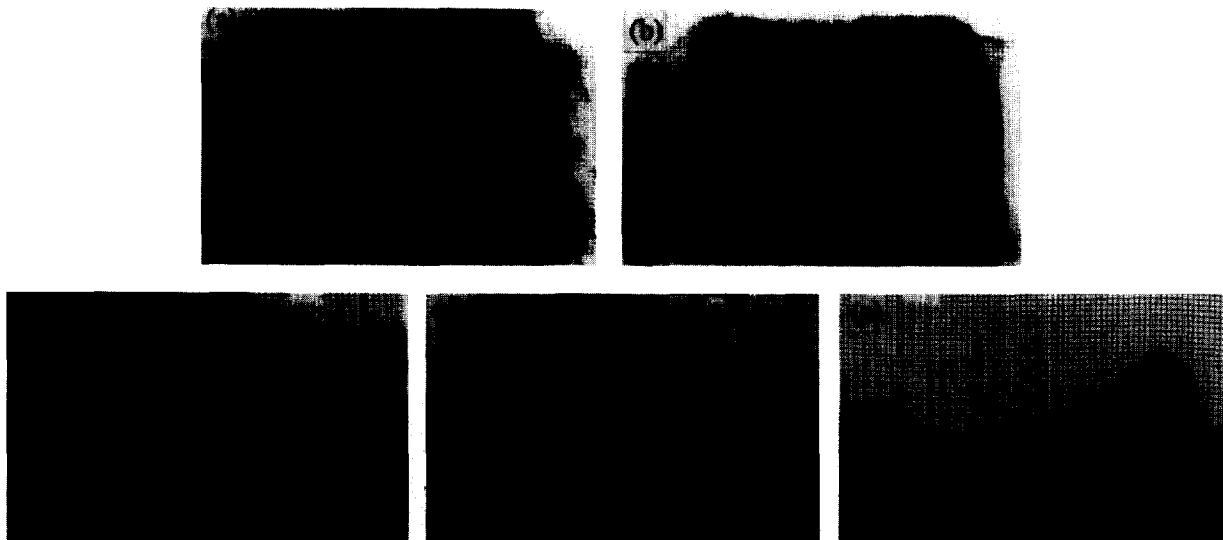


Fig. 5. X-ray radiographs of Zn electrodes with different coatings on Cu mesh current-collector: (a) Pb coating after 150 cycles; (b) Cd coating after 150 cycles; (c) Pb coating after 300 cycles; (d) Cd coating after 300 cycles, and (e) Sn coating after 300 cycles.

cycling in 3.5 Ah Ni/Zn test cells. This is demonstrated by X-ray images of the negative electrodes, see Fig. 5(a) and (b). The images show that shape changes are not so severe even after 150 charging/discharging cycles in highly alkaline electrolyte. After 300 cycles, however, the active materials are precipitated in different shapes according to the type of coating metals. In the case of a Cd-coated current-collector (Fig. 5(d)), more than 50% of Zn moves to the lower part of the electrode and forms a thick layer of active material and causes a significant loss in discharge capacity. Tin coating (Fig. 5(e)) promotes a more serious, shape change. The Pb coating (Fig. 5(c)) also suffers severe shape change, but it appears to be the best of all. A relatively large area of active materials is maintained in the original place and the test cell can discharge more than 60% of the nominal capacity after 300 cycles. These results suggest that a Pb coating on the current-collector can retard the progress of shape change of Zn electrodes in Ni/Zn batteries.

#### 4. Conclusions

When Zn is reduced and deposited on a Zn, Cd or Pb substrates, the nucleation potentials in the zincate saturated alkaline solution decrease in that order. The dissolution potential increases in the same order. Cathodic polarization curves show that the Tafel slope of Zn deposition on a Pb substrate is lower than that on either Zn or Cd. The activation energy calculated from these curves and measured at various temperatures also reveals that Pb has slower deposition kinetics than Zn or Cd. Practical application of coatings of Pb, Cd and Sn on the Cu mesh and charge/discharge cycle tests

demonstrate the potential of Pb coating for extending the cycle life of Ni/Zn batteries.

Thus, retarding the dendritic growth and shape change by the redistribution of Zn-active material is expected for the case of utilizing Pb as a coating metal for the current-collector of the negative electrode in Ni/Zn secondary batteries.

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