Short Communication

Effects of lanthanum and neodymium hydroxides on secondary alkaline zinc electrode

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Abstract

Lanthanum and neodymium hydroxides coated on planar zinc electrodes, which are prepared by electrolysis, are found to lower the amount of zinc discharge products that are dissolved in an alkaline electrolyte. This reduces the dendritic growth and shape change of the zinc electrodes. The performance of these hydroxides has been assessed by cyclic voltammetry. Scanning electron microscopy is also applied to examine the morphology of the surface of the zinc electrodes before and after 50 charge/discharge cycles. © 1997 Elsevier Science S.A.

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1. Introduction

The performance of secondary cells that employ zinc negative electrodes is usually limited by the poor cycling characteristics of zinc. The high solubility of the zinc discharge products in KOH electrolyte results in the growth of dendrites which cause cell shorting, as well as electrode shape change which causes gradual capacity loss, and, therefore, curtails cycle life. One possible approach reducing the problem is to limit the solubility of discharge products in the alkaline solution, so that there are very few species available in the KOH electrolyte at the recharge stage. Successful attempts to reduce the solubility of zinc include the use of the additives in either the electrode [1–7] or the electrolyte [8–13].

A polymer film which is substantially in direct contact with the electrode has also been investigated [14,15]. The layer blocks the direct contact between the electrode and the electrolyte, which, to some degree, prevents the dissolution of zincate in the electrolyte. Nevertheless, the synthesis of the polymer is complicated.

It is well known that the discharge products $Cd(OH)_2$ or $Fe(OH)_2$, that form, respectively, on a cadmium or an iron anode, have a structure which allows passage of ions relating to the electrode reactions. That is to say, when recharging, the OH^- species are transported through the voids that are formed between the hydroxide particles.

Compounds of rare earth elements such as lanthanum oxide and cerium oxide, have been used as additives for the zinc electrode [16,17]. In the present work, two hydroxides of rare earth elements, viz., lanthanum hydroxide and neodymium hydroxide, have been studied. The hydroxides are coated on the surface of zinc anodes and are found to lower the solubility of the discharge products.

2. Experimental

2.1. Preparation of zinc electrode

A planar zinc (99.999%) electrode (Johnson Matthey Chemicals, Royston, UK) was used (apparent area: 1 cm × 1 cm). The electrodes were pretreated in acetone (degreasing) followed by a short immersion in 50% (v/v) (sp. gr. 1.18) HCl until a light, matt, clean surface was apparent [18].

2.2. Coating of hydroxides

The coating experiments were performed in a cell with a zinc electrode, a platinum sheet counter electrode and an electrolyte containing 0.045 M $La(NO_3)_3$ or 0.035 M $Nd(NO_3)_3$ (both of AR grade, Beijing Chemical Factory, Beijing, PR China).

The hydroxide coatings were prepared by applying a negative current through the zinc electrode; hydrogen evolution took place in concert with formation of the hydroxide coating [19]. The electrodes were then rinsed repeatedly with double-distilled water and were used immediately for cyclic voltammetry or charge/discharge experiments.

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2.3. Cyclic voltammetry

Cyclic voltammetry was carried out at 5 m V s^{-1} in a cell which was separated into two compartments by a Celgard microporous membrane (Hoechst Celanese Corporation, USA). The potential scans were applied with a RDE4 bipotentiostat (Pine Instruments, USA) that was connected to a Type 3086 x-y recorder (Yokogama Hokushin Electric, Tokyo, Japan). The cells contained a zinc electrode, a nickel sheet counter electrode, and a Hg/HgO reference electrode. The volume of electrolyte in cell was 5 ml. The sweep range was − 1.25 to − 1.65 V (versus Hg/HgO electrode).

2.4. Charge/discharge experiments

An analog cell (flooded electrolyte) with a zinc anode ('blank' or coated with hydroxide) and an NiOOH cathode was used. The electrolyte was 40% KOH saturated with zincate. The latter was prepared by dissolving ZnO powder (AR grade, Chengdu Chemical Reagent Factory, Chengdu,

Fig. 1. Electron micrograph of hydroxide layer coating on zinc electrode.

China) in 40% KOH; the amount was sufficient to saturate the solution with zincate. The cells were discharged at 60 mA cm^{-2} for 5 min followed by charging at 30 mA cm^{-2} for
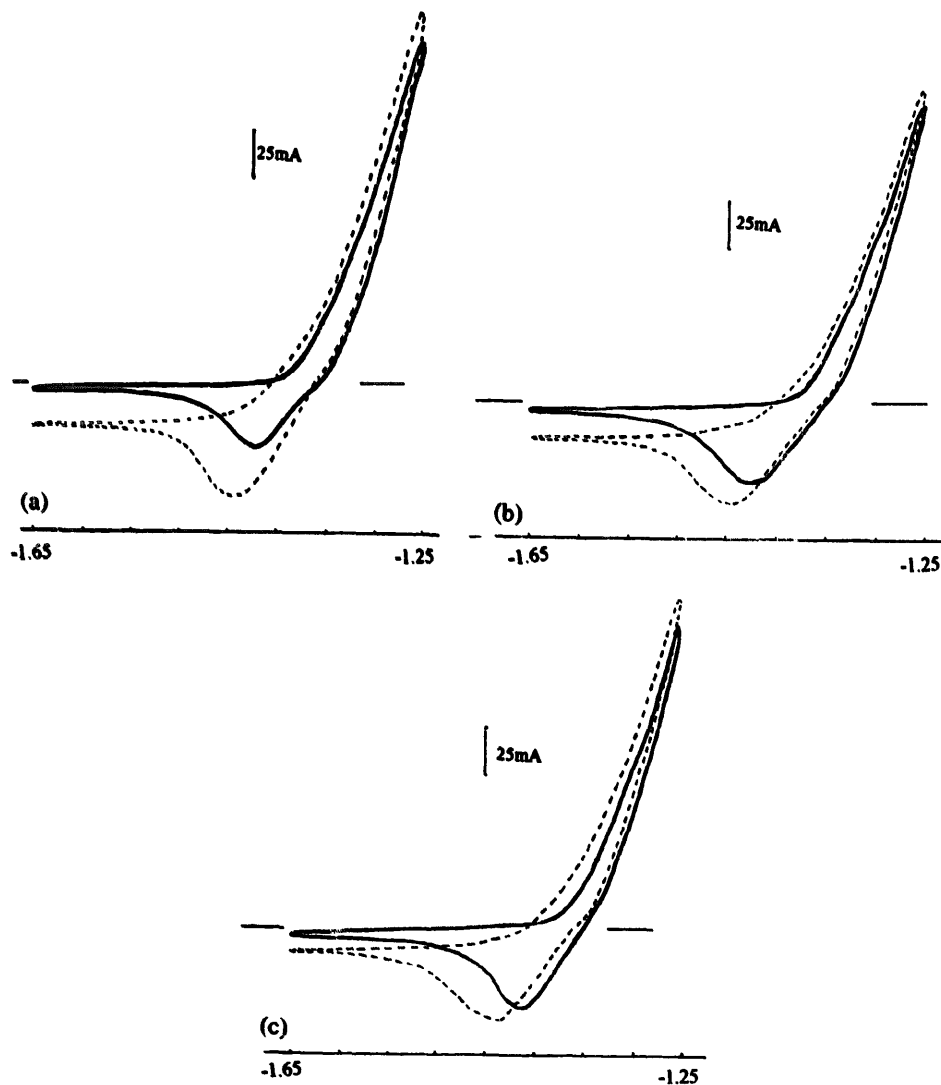
Fig. 2. Voltammograms for the zinc electrode in 40% KOH on (———) 1st and (— — —) 25th scan: (a) with no coating; (b) with coating of La(OH)$_3$, and (c) with coating with Nd(OH)$_3$.

10 min and were reversed automatically when the time set for discharge (or charge) was completed.

2.5. Scanning electron microscopy

The preparation of samples for study by scanning electron microscopy (SEM) was as follows: the zinc electrodes (50th cycle charged state) were removed immediately from the electrolyte, washed repeatedly with double-distilled water, rinsed in acetone, and dried in air.

3. Results and discussion

3.1. Coating of hydroxides

The hydroxide coatings on the zinc anode have good mechanical stability, i.e., when washed in a stream of water, the hydroxide remains in contact with the electrode. The particles are formed into layers, see Fig. 1. (Note, the cracks in the micrograph are formed during drying of the electrode.) The OH⁻ ions pass through voids between the particles when the electrode reaction takes place. When a negative current is passed through the zinc anode, the pH value near the electrode surface increases due to hydrogen generation. At this stage, a uniform layer of hydroxide is formed on the zinc electrode.

The hydroxides are sparingly soluble in the battery electrolyte, the concentrations of La^{3+} and Nd^{3+} are as follows [20]:

$$\log[La^{3+}] = 23.02 - 3pH$$

$$\log[Nd^{3+}] = 21.25 - 3pH$$

The standard reduction potential of $La(OH)_3$ and $Nd(OH)_3$ is -2.90 and -2.72 V, respectively [21]. Thus, the hydroxides are not oxidized or reduced in the operational voltage range of the battery.

The hydroxide may be either anhydrous or hydrated; this is difficult to determine. Because of the high water content in the hydroxide (not dried), it has a high ionic conductivity. The thickness of the hydroxide layer is determined by the current density, the time of electrolysis, the concentration and pH of the electrolyte, and the temperature.

3.2. Cyclic voltammetry

Cyclic voltammograms of zinc electrodes with coatings of different hydroxides were obtained in 40% KOH between -1.65 and -1.25 V (Fig. 2). Two conversion reactions of zinc species take place in this potential range, namely:

$$Zn \rightarrow Zn(OH)_2 \ (or \ ZnO) \tag{1}$$

$$Zn(OH)_2 \ (or \ ZnO) \rightarrow Zn \tag{2}$$

The area of the anodic peak on the cyclic voltammogram corresponds to the quantity of charge due to zinc oxidation

when reaction (1) takes place, the area of the cathodic peak corresponds to the charge due to reduction of $Zn(OH)_2$ (or ZnO) which is generated in reaction (1) but undissolved in the electrolyte. If the amounts of $Zn(OH)_2$ (or ZnO) retaining in the electrode are more, that is to say, the dissolved amount of $Zn(OH)_2$ is less, then the area of the cathodic peak would be correspondingly larger.

On the initial scan (see solid lines, Fig. 2), the areas of the cathodic peaks (Fig. 2(b) and (c)) are larger than that for an uncoated electrode (Fig. 2(a)). This indicates that the amounts of the electrodes with coating are more than that in an uncoated zinc electrode after the oxidation reaction took place. Because the area of the cathodic peak on the cyclic voltammogram for zinc electrodes can present the amounts of $Zn(OH)_2$ (or ZnO) retaining with electrode, therefore, if the amounts of $Zn(OH)_2$ (or ZnO) are more, then the area of the cathodic peak would be correspondingly larger.

There is little change in the area of cathodic peaks after 25 scans (see dashed lines, Fig. 2), but all the peaks are shifted by ~ 25 mV towards more negative potentials. Limiting diffusion currents, which indicates the concentration of $Zn(OH)_4^{2-}$ in the electrolyte, are reached between -1.65 and -1.60 V approximately (see dashed lines, Fig. 2). The limiting diffusion current can be determined from the difference in value between the baseline and the straight line part on the dashed lines at potentials between -1.65 and -1.60 V. On the 25th cycle, the reduced materials include $Zn(OH)_2$ (or ZnO) which are retained in the zinc electrode, and $Zn(OH)_4^{2-}$ which is dissolved in the electrolyte. Both species give rise to the cathodic peak, but the zincate results in

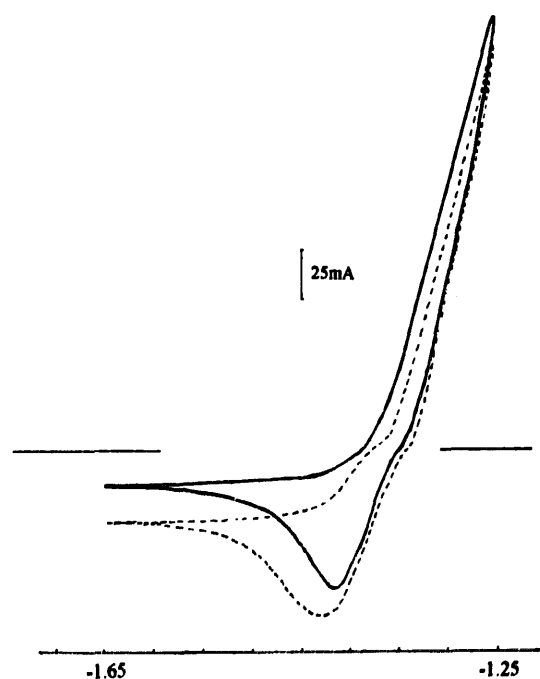25mA

-1.65   -1.25

Fig. 3

Fig. 3. Voltammograms for zinc electrode ('blank') on the 1st scan in electrolytes containing zincate: (———) mixed solution of zincate saturated 40% KOH and 40% KOH without zincate (1:1 v/v), and (– – –) 40% KOH saturated with zincate.

the occurrence of the limiting diffusion current. In essence, the larger the limiting diffusion current, the higher the concentration of $Zn(OH)_4^{2-}$ in the electrolyte, which means lesser amounts of $Zn(OH)_2$ (or ZnO) are retained in the zinc electrode. This also indicates that a coating of lanthanum or neodymium hydroxide on the zinc electrode can lower the amount of the zinc discharge products.

In order to confirm further the above findings, other cyclic voltammetric experiments were performed in an electrolyte that contains zincate. Fig. 3 presents cyclic voltammograms for a zinc electrode ('blank') on the first scan in 40% KOH saturated with zincate and in an electrolyte which was prepared by mixing zincate-saturated 40% KOH and 40% KOH without zincate (1:1 v/v). It can be seen that the limiting diffusion current occurred at potentials between −1.60 and −1.65 V in both solutions. Moreover, the limiting diffusion current obtained in the mixed solution is smaller. Apparently, this is strongly linked to the difference in concentration of $Zn(OH)_4^{2-}$ in the two solutions. It indicates that the value between the baseline and the straight line in the potential range between about −1.60 and −1.65 V, namely the limi-

ting diffusion current, increases with the increase in the concentration of zincate. There is also a little difference in the area of cathodic peaks.

3.3. Scanning electron microscopy

SEM graphs of zinc electrodes after 50 charge/discharge cycles (in charged state) are shown in Fig. 4. With an uncoated ('blank') electrode the zinc is deposited as an irregular sponge to give a three-dimensional structure (Fig. 4(a)). The shape change of this zinc electrode is severe. Large, multi-faceted crystallites are revealed by a high magnification (Fig. 4(b)).

The morphology of the electrode coated with $La(OH)_3$ is shown in Fig. 4(c). (Note, some of the coating layers were washed off during electrode treatment, as mentioned in Section 2.5.) A moderate granular deposit is observed.

The morphology of the electrode coated with $Nd(OH)_3$ is shown in Fig. 4(b). An integrated coating layer can be clearly seen (the cracks are formed during drying of the electrode).
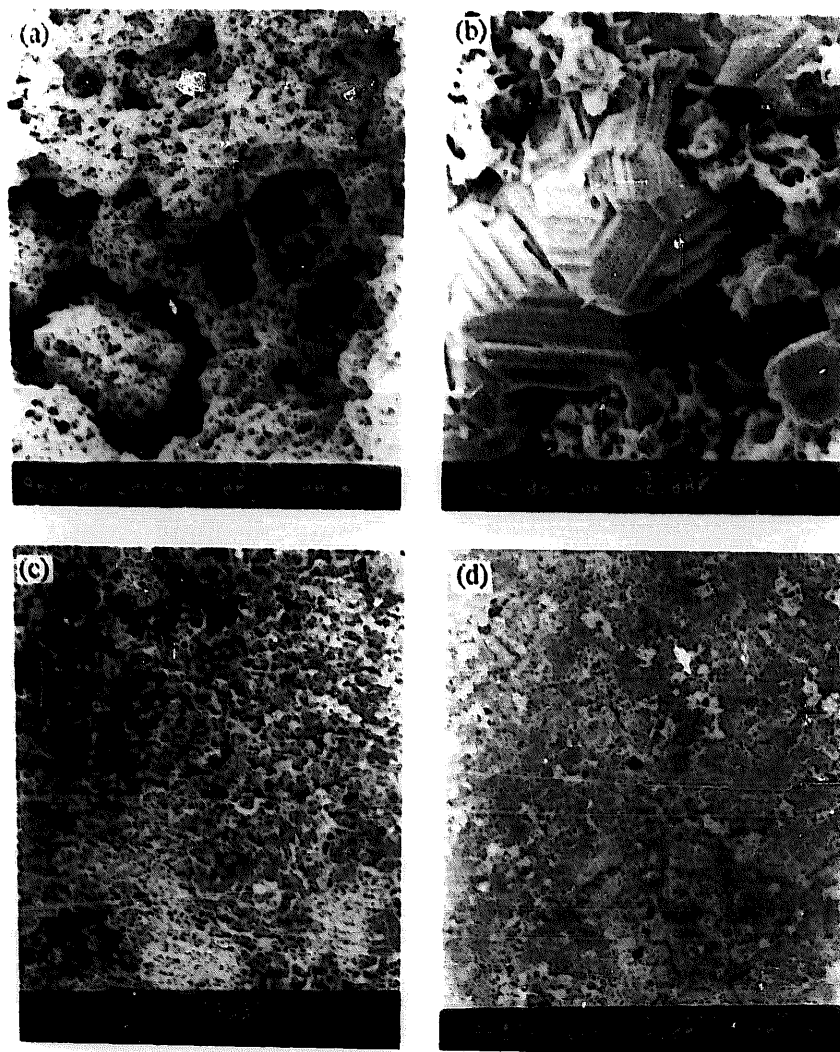

Fig. 4. Electron micrographs of zinc electrodes after 50 charge/discharge cycles: (a) no coating; (b) no coating (high magnification); (c) coating of $La(OH)_3$, and (d) coating of $Nd(OH)_3$.

The deposit is smooth and dense; it is composed of fine crystallites.

4. Conclusions

The effectiveness of coatings of lanthanum and neodymium hydroxides on zinc electrodes has been examined. In essence, it would appear that these coatings can impede the movement of zinc species (in the form of $Zn(OH)_4^{2-}$) away from the electrode, and thus minimize the amount of $Zn(OH)_2$ or ZnO that dissolves in the electrolyte. This, in turn, brings about a significant improvement in deposit morphology, which leads to a smoother surface and the prevention of dendrite growth and shape change. In particular, $Nd(OH)_3$ is found to be very effective.

The benefit of applying this type of hydroxide coating to secondary zinc electrodes is clear. The sparing solubility in alkaline electrolyte and the inertness in the charging/discharging voltage range of the battery guarantees its stability on prolonged cycling. Further work on the effects of other hydroxides of rare earth elements on planar and porous zinc electrodes is in progress.

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