Experimental optimization of alkaline zinc-silver oxide primary cell with respect to the zinc electrode preparation and composition

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The optimization of parameters controlling the fabrication of zinc electrodes, by the slurry paste method, has been carried out. The parameters varied were active material composition, applied compression and electrode thickness. The optimum values obtained by a factorial experimental programme were: a zinc material that contains 2–4 wt% HgO, 0·5–2% PVA, and 94–97·5% ZnO; a compression of 500–1500 psi applied to the zinc electrode; and an electrode thickness of 0·265–0·35 mm.

1. Introduction

The alkaline zinc—silver oxide system is unique as a power source because it has a watt-hour output per unit of weight or volume greater than that of most primary batteries. It can deliver this output at a high current rate and at a constant voltage level.

The aim of this project was to establish the optimum parameters for the fabrication of zinc electrodes used in an alkaline zinc—silver oxide primary battery. The optimization of the parameters, zinc electrode active material composition, compression applied to the electrode, and electrode thickness, was carried out by a factorial experimental programme. The zinc electrodes were fabricated by the slurry paste method.

Reactions at the zinc electrode in aqueous alkaline solutions has been the subject of extensive studies [1–16]. The electrochemical behaviour of porous zinc electrodes in aqueous KOH solutions has been studied by Elsdale *et al.* [17] and others [18–23].

2. Experimental

2.1. *Materials and chemicals*

The grid material of Exmet 5 Ag 6-3/0 expanded silver screen was supplied by Exmet Co Bridgeport, Connecticut, USA. The separator material of Viskon brand 3463 S-950-CLS was supplied by Chicopee Manufacturing Co Milltown, New Jersey, USA.

The zinc oxide, mercuric oxide, silver peroxide, potassium hydroxide, polyvinyl alcohol (PVA), sodium carboxylmethyl cellulose (CMC), sodium hydroxide, hydrochloric acid and all other chemicals used were of reagent grade. Solutions were made with distilled water.

The particle size of the ZnO powder was determined by transmission electron microscope (TEM) photographs ($\times$ 60 000). The average diameter of the particles was $8 \cdot 33 \times 10^{-5}$ cm ($0 \cdot 833\ \mu$m).

2.2. *Preparation of zinc electrodes*

About 1·2 g of zinc electrode mixture (the compositions will be specified later) were mixed in a mortar with PVA solution (or water) to form a paste. The paste was applied to a grid of 5·25 $\times$ 3·50 cm cut from the expanded silver screen. The pasted electrode was then dried at 75° C for about 4 hours, and subsequently was formed in a 5% KOH solution against a nickel counter-electrode at a rate of approximately 0·15 mA cm^{-2} for about 25 hours. After forming, the electrode was thoroughly washed in distilled water to remove the KOH. The formed electrode was pressed to the required thickness and then dried at about 55° C for a minimum time of 8 hours.

In order to evaluate the effect of amalgamation on the coefficient of use and the energy density of the zinc electrode, a number of zinc electrodes were constructed with the HgO content of the zinc electrode mixture being varied from 0–5 wt%, the PVA content was fixed at 2%, and the ZnO content was varied from 93–98% corresponding to the variations of HgO content. In all cases these zinc electrodes were pressed at 1500 lb to a thickness of 0·35 mm.

To evaluate the influence of the PVA content of the zinc active material on the energy density and the coefficient of use of the zinc electrode, a number of zinc electrodes were prepared where the PVA content was varied from 0–6·5 wt%, the HgO content was fixed at 2%, and the ZnO content was varied from 91·5–98% to correspond to the variations of PVA content. These electrodes were pressed at 1500 lb to a thickness of 0·35 mm.

To examine the effect of compression on the coefficient of use and on the energy density of zinc electrodes, 12 zinc electrodes were fabricated with a zinc active material containing 96 wt% ZnO, 2% HgO, and 2% PVA. All these electrodes were pressed to the same thickness of 0·35 mm. The applied compression was varied from 0–4000 psi.

To investigate the influence of electrode thickness on zinc electrode performance, nine special zinc electrodes were prepared with a zinc active material containing 96% ZnO, 2% HgO, and 2% PVA. The compression applied was 1500 psi, and the electrode thickness was varied from 0·265–0·56 mm.

A number of zinc electrodes were also fabricated according to the established optimum conditions: an active material having a composition of 96% ZnO, 2% HgO, and 2% PVA; a compression of 1500 psi applied to the zinc electrode; and an electrode thickness of 0·35 mm.

2.3. Preparation of silver oxide electrodes

The silver oxide electrodes used for this study were prepared by the slurry paste method. About 4 g of AgO was made into a paste with 1 ml of aqueous CMC solution (1% by weight). The paste was applied to a grid of 5·25 × 3·50 cm cut from the expanded silver screen. After drying at 70° C for about 2 hours, the electrode was pressed at 45 000 lb.

2.4. Test cell assembly and experimental procedure

A schematic diagram of the test cell assembly is shown in Fig. 1. There were two types of electrode assemblies used in the test cells:

(a) central zinc electrode wrapped in separator with an AgO electrode placed on each side;

(b) central AgO electrode wrapped in separator and a zinc electrode placed on each side.

The electrode assembly of type (a) was used for all the zinc electrode factorial evaluation studies. In the comparison between the performance of the zinc electrode fabricated by the optimized slurry paste method and those of the commercial zinc electrodes, the electrode assembly of type (b) was used for the conven-
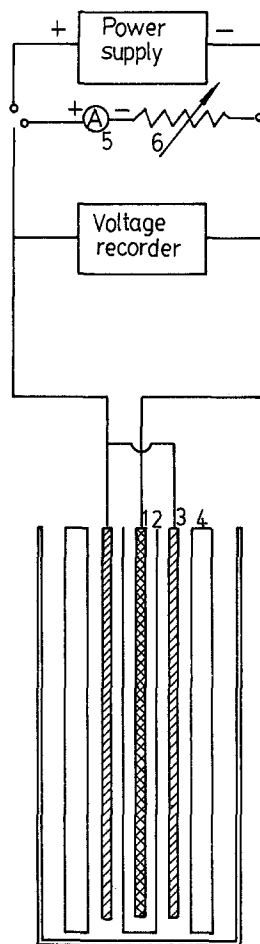

Fig. 1. Schematic diagram of test cell assembly and electrical circuit: (1) zinc negative (or AgO positive); (2) separator film; (3) AgO positive (or zinc negative); (4) acrylic sheet; (5) ameter; (6) variable resistor.

ience of arrangement of certain commercial electrodes.

In all cases the quantity of AgO present was well in excess of that required for a zinc electrode limited cell.

After inspection, the electrode assembly was installed in a rectangular acrylic case filled with 40 wt% KOH solution. The dimensions of the acrylic cell chamber were $8 \cdot 0 \times 7 \cdot 5 \times 2 \cdot 0$ cm. The cell was activated and discharged at a constant rate of 1 A at $28°$ C through a series of variable resistors. The terminating cut-off voltage was set at 1 V. Discharge curves were displayed using one Gould Brush 220 and two Linear Model 232 recorders. Constant currents and potentials were supplied by conventional regulated power supplies.

3. Results and discussion

The most desirable composition of the zinc active material, the optimum compression applied to the zinc electrode, and the optimum electrode thickness were determined separately based on the coefficient of use (COU) and the energy yield.

The actual energy yield and energy density of zinc electrodes were calculated as follows

$$E = \int P_t \, dt = \int V_t i_t \, dt$$

where E = energy (W h, or W min); P_t = instantaneous power (W); V_t = instantaneous voltage (V); i_t = instantaneous current (A). The energy density (ED) of the zinc electrodes was defined as

$$ED = \frac{E}{\text{weight of zinc electrode}}.$$

The coefficient of use of the zinc electrode was defined as the ratio of ampere-hours actually delivered to the theoretical equivalent ampere-hours per gram of zinc active material. A theoretical equivalent of $1 \cdot 22$ g zinc equal to 1 A h [25] was used in this calculation.

3.1. The optimum HgO content

The energy density and the coefficient of use of zinc electrode as functions of the HgO content are shown in Fig. 2.

An inspection of Fig. 2. shows that the optimum mercuric oxide content of the zinc active material is between 2–4%. Both the energy density and the COU of the zinc electrode reach their respective maximum at this range of concentration.

The addition of HgO to the active material has the effect of increasing the hydrogen overvoltage and preventing the self-discharge of the zinc electrode [23, 24]. If the HgO content is too high, the
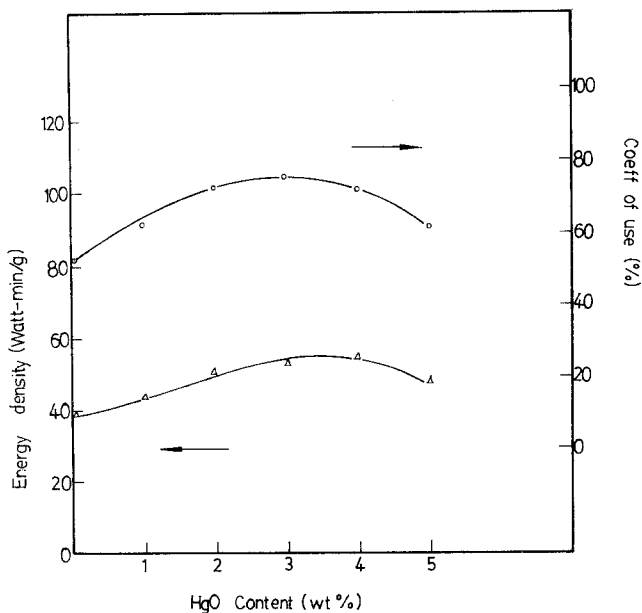

Fig. 2. Energy density and the coefficient of use of zinc electrode as a function of the HgO content in zinc active material.

proportion of area of the amalgamated material will be duly increased with a corresponding decrease in the contact area between the zinc material and the electrolyte, this will result in a decrease in the discharge performance of the zinc electrode. Snyder and Lander [23] found that the self-discharge rates of zinc electrodes can be rendered negligible by using a 40–45% KOH cell electrolyte and 2–4% HgO additions to the electrode. Gregory et al. [21] observed that the mercury content required to reduce the rate of hydrogen evolution to an acceptable level increases with increasing temperature and corresponds to 2–3 wt% Hg at 25° C, 3–4 wt% at 40° C, and 6–8 wt% at 60° C.

3.2. The optimum PVA content

The energy density and the coefficient of use of zinc electrodes as function of the PVA content are shown in Fig. 3. The results indicate that the optimum PVA content of the active material is about 0·5–2·0%. The COU and the ED of the zinc electrode obtained at this range of composition are both close to the maximum.

The main purpose of adding PVA to the zinc electrode mixture is to decrease zinc mobility and increase capacity retention [25]. A very low PVA content not only weakens the cohesive force of the

the zinc material but can also increase the internal resistance [20] and thus reduce the discharge performance of the zinc electrode. A PVA content that is too high can cause the reduction of the pore volume of zinc electrodes. This reduction in pore volume will lower the discharge efficiency of the electrode because of less OH^- and H_2O available for electrode reaction [1, 11–17].

The effect of PVA content in the zinc active material on the performance of the zinc electrodes may also be explained from the fact that PVA acts as a binder of the ZnO particles, and increasing the amount of PVA automatically results in the decreasing of the total ZnO content of the electrode, thus leading to a lower cell capacity. However, a minimum amount of PVA is necessary in order to maintain the physical integrity of the zinc electrode. Sulks [25] found that quantities from 1–5% are effective.

3.3 The optimum compression applied to the zinc electrode

The zinc active material was compressed around the silver mesh under high pressure in order to increase both the cohesive force of the material and the adhesion of the active material to the electrode grid. The amount of compression is also a function of the final porosity desired and the
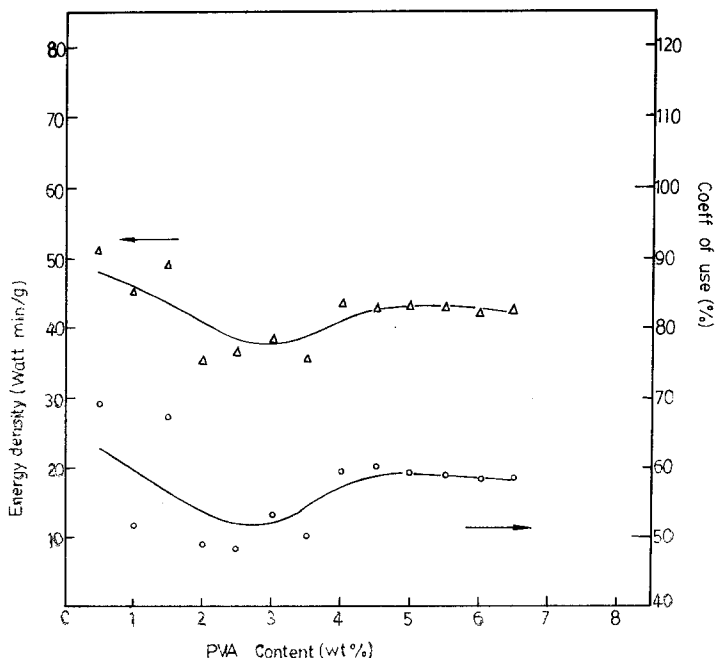

Fig. 3. Energy density and the coefficient of use of zinc electrode as a function of the PVA content in zinc active material.
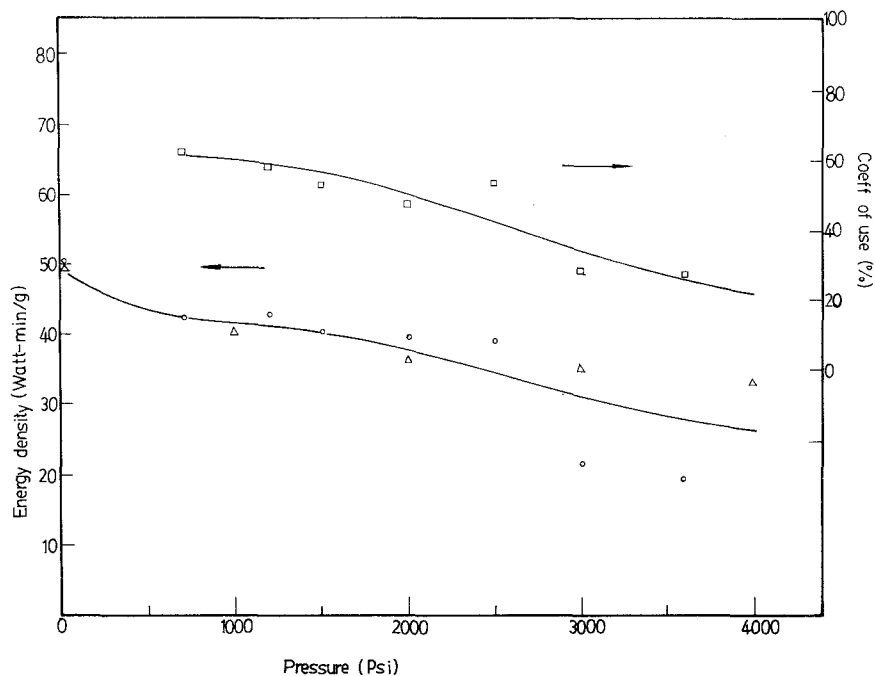
Fig. 4. Energy density and the coefficient of use of zinc electrode as a function of compression applied to the electrode.

characteristics of the zinc electrode mixture employed. For high rate electrodes, porosities in the range 80–90% by volume are desired. When high discharge rates are not required, porosity can be reduced to 30–40% [26] and higher energy density electrodes result.

The results shown in Fig. 4. indicate that compression should be kept to a minimum for the greatest discharge efficiency, because ED and COU decrease steadily, within experimental error, from 0 psi. In reality a minimum applied compression is required in order to obtain the proper mechanical strength and physical integrity of the zinc electrode. It was observed that the optimum compression applied to the zinc electrode is 500–1500 psi.

There are two sets of experimental points associated with the energy density curve shown in Fig. 4. The two sets of points (denoted by circles and triangles) corresponding to the ED curve were obtained from two separate series of experiments. However, these two series of experiments were carried out under the same conditions, and it can be observed that these two sets of points follow the same trend.

3.4. Performance of zinc electrodes as a function of electrode thickness

The performance of the zinc electrode as a function of electrode thickness is shown in Fig. 5. It can be seen that the highest energy density and the greatest coefficient of use of the zinc electrodes occur at an electrode thickness of 0·265–0·35 mm (the lower range of electrode thickness), and both the COU and the ED of the zinc electrode decrease continuously with increasing electrode thickness. This result is qualitatively in agreement with the conclusions reached theoretically by Kosholkin and Ksenzhek [27]. According to their report, the accessibility of the electrodes for an electrochemical reaction can be regarded as uniform if its thickness does not exceed $0·5\ X_e$ [28], where

$$X_e = \sqrt{(r_0 k_0^e a_s/2)}$$

where X_e is the effective depth of penetration of the electrochemical process; X is the current coordinate; r_0 is the pore radius of the most frequently encountered pores; k_0^e is the specific conductivity of the electrolyte in the pores; and a_s is the true polarization coefficient. The
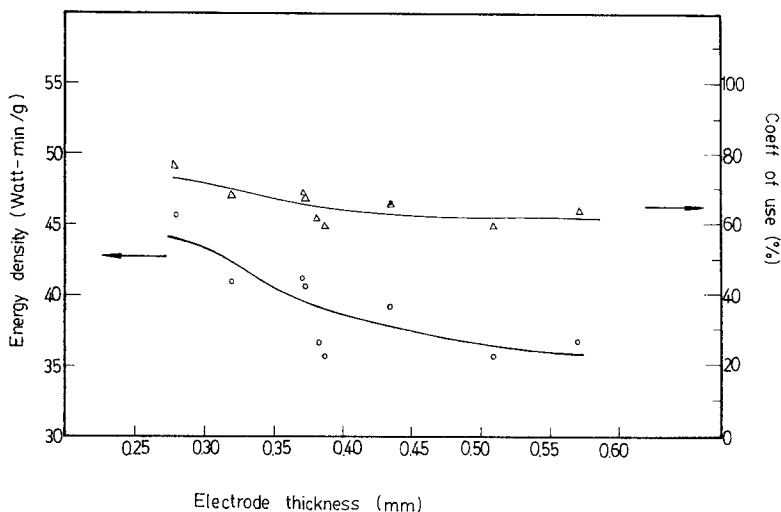
Fig. 5. Energy density and the coefficient of use of zinc electrode as a function of electrode thickness.

effective depth of penetration of the process for accumulator electrodes has been calculated to be 0·01–2·0 mm.

3.5. *The performance tests of zinc electrodes fabricated by the optimized slurry paste method*

Fig. 6. presents the results of the discharge performance tests on the zinc electrode fabricated by the optimized slurry paste method and those on the commercial zinc electrodes. These results indicate that the discharge performance of the

zinc electrode fabricated by the optimized slurry paste method (as shown by the discharge Curve D) was better than that of the commercial zinc electrodes tested (as shown by the discharge Curves A, B, and C). The fabrication method and the dimensions of these three commercial zinc electrodes were the same as those of the zinc electrodes prepared in this work. However, the exact active material formulation and specific fabrication conditions of these commercial zinc electrodes were not known.
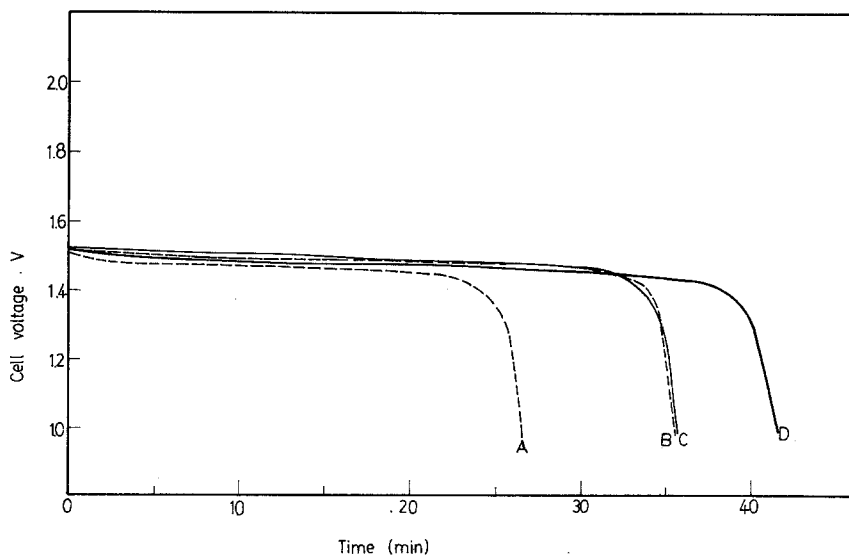

Fig. 6. Discharge curves of zinc electrodes at a constant current of 1 A at 28° C: Curves A, B, C, commercial zinc electrodes; Curve D zinc electrode made by the optimized slurry paste method.

4. Conclusions

The optimization of the alkaline zinc–silver oxide primary cells with respect to the parameters for the fabrication of zinc electrodes by the slurry paste method such as zinc active material composition, applied compression, and the electrode thickness showed that the optimum values of these parameters are: a zinc active material that contains 2–4 wt% HgO, 0·5–2% PVA, and 94–97·5% ZnO; a compression of 500–1500 psia applied to the zinc electrode; and an electrode thickness of 0·265–0·35 mm.

Acknowledgements

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