"The advantage in using the proposed design will be an increase in the cycling life and reliability."

A New Silver-Zinc Battery Configuration: The Use of a Rotating Vertical Zinc Electrode in the Charging Cycle

by

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ABSTRACT

A new design of a silver-zinc cell is presented. The system consists of a circular zinc electrode disk (negative electrode) which is rotated on the perpendicular axis passing thru its center and two circular disks with porous silver oxide coating (positive electrode) sandwiching the negative electrode. The electrolyte is 40 percent potassium hydroxide solution. The cell is charged with both the zinc electrode being rotated in a set of runs and stationary in another set. The rotating electrode has a more uniform plating of zinc while the stationary electrode has dendritic and mossy growth and unevenly plated zinc. The performance of the cells at the two different conditions are nearly identical. Problems on the proper current distribution as well as electrical contact in the negative electrode were encountered. The design can help increase the number of charge-discharge cycles of the cell. However, the energy density is lower due to the space requirements of the rotating disk and accessories.

INTRODUCTION

Zinc's use in battery is favored both technologically and economically because of its low equivalent weight and high voltage – it has a high energy density. Historically, the Volta pile and the Daniel cell, and the LeClanche's cell (the present dry cell) which are all primary cells use zinc. On the secondary cells, the silver-zinc and the nickel-zinc cells, both alkaline, are the major cells using zinc as an electrode. In both these cells, problems are due to the dendritic growth of zinc and the shape change that occurs after several cyclings, thereby limiting the life of the cells. This paper presents a design that attempts to alleviate this problem – the use of a rotating vertical zinc electrode disk. While it may be true that the use of the design could solve some problems, there are also other disadvantages which may correspondingly result.

LITERATURE SURVEY

Alkaline-Zinc Battery Systems

The two major alkaline zinc cells are the nickel-zinc and the silver-zinc systems.

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The Nickel-Zinc Cells

This system utilizes $Ni(OH)_2$ as the active positive electrode and zinc as the negative electrode. It has a high discharge voltage of 1.60 to 1.65 V per cell and is capable of having a high, energy density (40-60 Wh/kg). The overall cell reaction is:

$$2\,NiOOH + Zn + 2H_2O \rightleftharpoons 2\,Ni(OH)_2 + Zn\,(OH)_2$$

Silver-Zinc Cells

Of all the rechargeable battery systems in use today, the silver zinc battery gives the highest energy density. The positive active material of this cell consists of Ag_2O_2, while the negative material, zinc hydroxide. The cell reaction consists of two steps:

$$Ag_2O_2 + Zn + H_2O \rightleftharpoons Ag_2O + Zn\,(OH)_2$$

$$Ag_2O + Zn + H_2O \rightleftharpoons 2\,Ag + Zn\,(OH)_2$$

The Silver Electrode

The silver oxide material has two forms: AgO and Ag_2O. The AgO has a voltage of 1.85V while the Ag_2O, 1.602V. The presence of two silver oxides gives the cell a two-level voltage discharge, which should be considered in the charging and discharging of cells. The base of the silver electrode is made of expanded silver sheet, silver wire mesh, perforated silver sheet, or silver plated copper sheet. For high coloumbic efficiency, the electrode should contain porous active material in the form of sintered, finely-divided silver powder with a porosity of 50-60 percent. Three methods are used in silver electrode fabrication.

1) The pasting of silver oxide to the base grid, drying, reducing, and sintering.
2) Pressing fine silver powder in a mold on the silver grid and sintering.
3) Imbedding the fine silver powder in a plastic binder such as polyethylene, pressing on the grid, and sintering.

The electrode may be sintered at 537°C for 30 minutes or 722°C for three minutes.

The Zinc Electrode

In alkaline zinc electrode processes, most considerations are made with respect to the oxides and hydroxides of the metal and its interaction with the strong electrolyte. Zinc hydroxide produces zincates, e.g., $Zn(OH)_3-/Zn(OH)_4^{-2}$, etc. Zincates are more soluble than the hydroxides, which allow for high discharge rates at the zinc electrode.

Anodic Processes in Alkaline Electrolyte

Several theories have been proposed regarding the anodic processes at the zinc electrode. As observed in early work involving galvano-state measurementon zinc sheets, at a particular current, the overpotential remains relatively constant or increases slightly for some time. With the start of zinc passivation, a rapid increase in overpotential sets in. From voltage sweep techniques, visual and microscopic observations, x-ray diffraction and the ring disc technique, three types of processes have been observed to inhibit zinc dissolution in alkaline electrolytes:

1) At an overvoltage of 30 mV a monolayer passive film can form and inhibit dissolution.
2) On continued dissolution, this film becomes thicker and tends to crack and peel off.
3) In quiescent electrolyte, a deposit of zinc oxide can form on the electrolytic side of this thick film.

In alkaline solution, the length of the discharge process is directly determined by the ability of the electrode to remain "active" for the dissolution process. Although experimental conditions vary from one experiment to another, it is known that the major part of the passivating film is ZnO. In porous zinc electrode, the discharge processes are very similar to those observed in sheet zinc in quiescent electrodes.

Cathodic Processes at the Zinc Electrode

Zinc deposition, hydrogen evolution, and oxygen reduction are the important cathodic processes at the zinc electrode. Vital to long cell life is controlled zinc deposition during the charge-discharge cycle. The dissolved zinc should deposit adherently and uniformly on the surface of the substrate. When zinc is deposited from alkaline solutions, three types of deposits form: a) smooth deposits at low overvoltage and stirred electrolytes; b) mossy deposits in still electrolyte and low overvoltage, c) dendritic deposits at high overvoltage. The transition from moss to dendrites corresponds to the onset of mass transport control and is characterized by a critical current density that is dependent on temperature and very dependent on the hydrodynamic conditions at the electrode surface.

Hydrogen evolution is not a major problem in alkaline zinc cells. Mercury or lead additives decrease the rate of hydrogen evolution. Some studies have demonstrated that oxygen reduction occurs rapidly on zinc electrodes in alkaline electrolyte. This reduction yields large amounts of peroxides that can oxidize organic separators.

Problems in the Cycling Behavior of Zinc Electrodes

The low cycle life of zinc has limited its use as the negative active material in storage batteries. Concentrated alkaline electrolytes are used to increase zincate solubility to prevent passivation during discharge. This high zincate solubility, however, permits the zinc to be deposited in a dendritic or non-adherent form during charging. Moreover, overcharge for zinc electrodes is not desirable since it promotes dendritic growth. Generally, dendritic growth, deposit adherency, and gross zinc redistribution are all capable of causing cell failures such as zinc dezinsification and passivation.

Actually, the problem is how to improve the throwing power of zinc (uniform plating of the zinc). It boils down to considering the current distribution in the cell. At areas of high current density, uneven deposits (dendrites and moss) form. At areas of low current density, loose or less deposits form. Normal deposits form at intermediate current density. The morphology change from one cycle to the next may not be much, but after several cycles, the effect is cumulative and the electrode shape would have changed very much, affecting its performance. This situation, plus dendritic growths will easily cause short circuit.

Together with the problem of current distribution is the concentration gradient of the electrolyte from the top to the bottom of the cell. In vented cells, hydrogen evolution occurs and water has to be added from time to time, normally added from the top with the electrolyte not being mixed. Therefore, in charging, the morphology changes with more efficient plating and at regions with high ion concentration.

Shape change involves the reduction of the zinc electrode geometry area on cycling, where the zinc electrode active material is removed from the electrode edges and agglomerates toward the plate center. In this process the edge areas of current collector are completely denuded of zinc. Once activated, the movement of zinc progresses as cycling continues and results in a reduction of capacity and useful life of the cell.

Several theories have been proposed on the cause of problems in zinc cycling. A discussion of all these will cause confusion. Apparently, these problems, inherent with zinc, can be mitigated but not totally eliminated.

Some Solutions and Recent Advances

Several proposed solutions with the aim of increasing the cycle life of zinc cells have appeared in the literature. Only a few will be presented here.

When zinc electrodes are brought to fully charged conditions, dendritic growth is promoted. The capacity of the cell is improved if the zinc is completely discharged on each cycle. However, the effect is limited.

To improve zinc morphology, the use of electrolyte additives such as lead, tin, and organic electrolytes produces desirable effects although not entirely satisfactory. Lead and tin can be displaced by zinc while the organic additives are rapidly oxidized.

Some researchers claim that various charging methods such as pulse currents, periodic reversals, half wave rectifiers, among others, have beneficial effects. However, these are not promising.

Several methods have been used to mitigate shape changes: 1) addition of binders such as polytetraflouroethylene or polyvinyl alcohol to the zinc electrode, 2) the extension of negative plate beyond the edges of the positive plate, 3) the use of contoured electrodes with extra ZnO at the electrode edges or 4) zinc electrodes that are thicker at the plate top than at the bottom.

Short circuiting in zinc cells can be minimized by the use of separators, organic (such as cellophane and other plastics) or inorganic (such as $KTiO_3$ and ZnO_2). They appear to improve the electrolyte wetability through loosely bound water which facilitates proton transfer.

A zinc-nickel oxide cell using a revolving thin-apertured shutter-separator has been reported. The zinc electrode does not suffer from shape change, retaining its performance on repeated deep discharges. This is attributed to the shutter rotation which agitates the electrolyte and prevents dendritic formation and unequal zinc distribution.

A recent approach used is by vibrating the zinc electrode in the cell during recharging (at 50 Hz). This results in a flat dense deposit without shape change. A plastic net around the nickel electrode is provided so that the formation is avoided. It has a disadvantage of having a reduced energy density in a volume basis and increased cost.

PROPOSED DESIGN

For the purpose of increasing the cycling life of the zinc cell by improving the throwing power and minimizing the effect of the concentration gradient from the top to the bottom of the cell, a rotating vertical disc electrode is proposed.

The discs are placed alternately with the positive electrodes and the system immersed in the electrolyte. The discs are rotated during the charging process. In this manner, the deposition of zinc will be uniform since the concentration gradient from top to bottom will have little effect on the disc; rotation means that any point on the radius will be passing thru both a high and a lower concentration at a constant speed. Moreover, the rotation will create turbulence and mixing in the electrolyte.

MATERIALS AND METHODS

Electrode Base Material

The following material was used as electrodes: copper screen 1mm thick with 4 mm x 0.5 mm size of opening (10 openings per mm). The electrodes were discs 10 cm in diameter. The negative electrode has a 4 mm x 0.8 mm diameter hollow shaft through the center. The positive electrode was slit 1.5 mm in one radius and the opposite side has a 4 cm x 3 cm extension to act as the positive terminal. Two of these plates sandwich the negative electrode. Both electrodes were electroplated with 0.25 mm thick silver. For good contact, the shafting of the negative electrode was clad with pure silver and two silver wires were coiled on the shaft to act as the conducting material for the negative terminal (see Figures 1 and 2).

Preparation of the Active Positive Electrode

Fine silver oxide powder was mixed with water to form a slurry paste. The material was pasted on the electrode plate and dried at 80°C in a shelf drier. The plate was then sintered at 537°C for 30 minutes in a furnace. The final plate thickness was 3 mm.

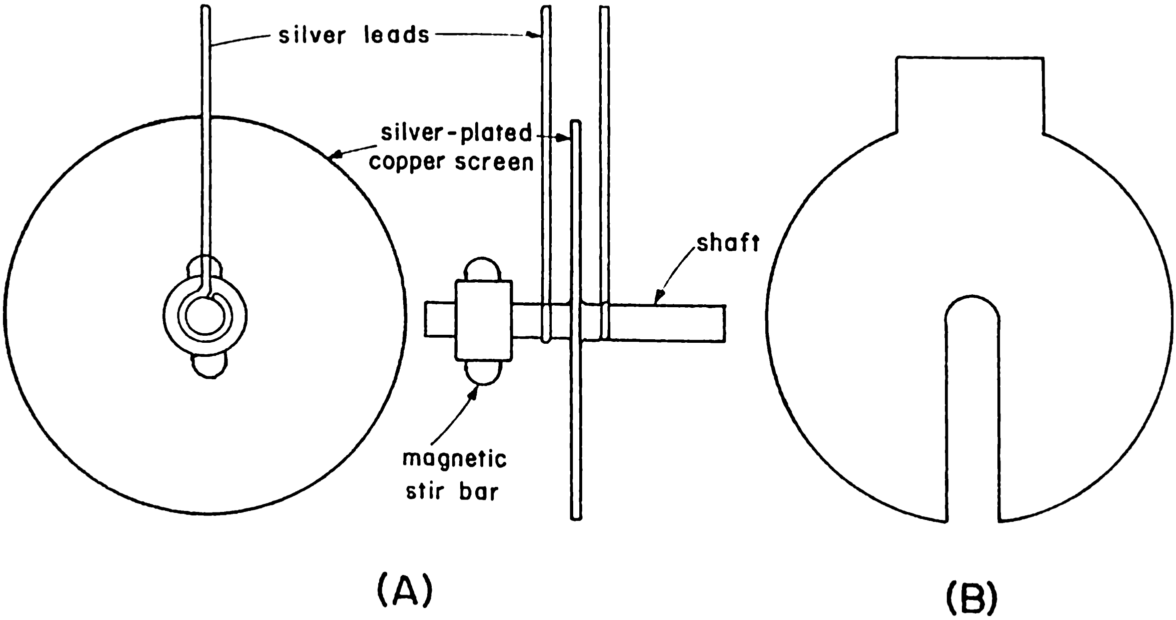

Figure 1. (A) The negative electrode assembly.
(B) The positive electrode.

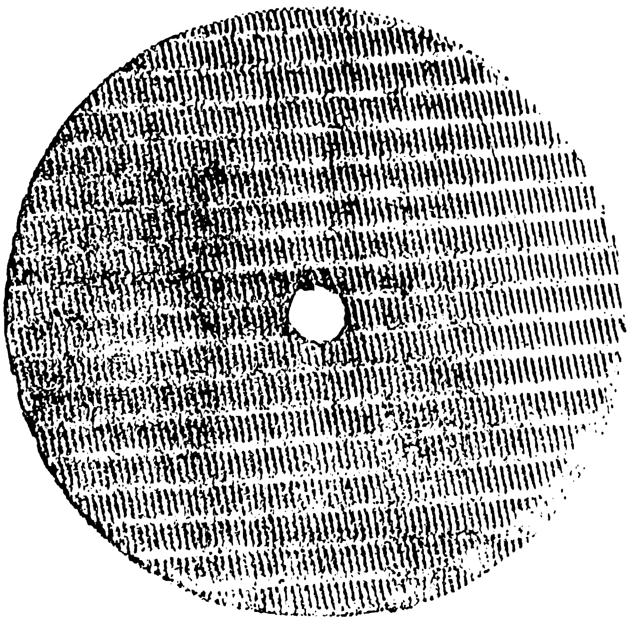

Figure 2. Photograph of a cut copper screen used as the electrode.

Preparation of the Negative Electrode

The zinc electrode was made using the electroformed process. Finely divided zinc oxide, U.S.P. was mixed in a solution containing 40 percent KOH to form a thick paste (50g/100g solution). Using the silver electrode as the anode, the zinc was electroplated on the prepared rotating disc.

Assembly of the Cell

The cell body was made of acrylic plates ("plexiglass") 1/4 in. thick, machined and glued together using chloroform to form a rectangular box measuring 3" x 4" x 4". A plexiglass rod was used as the shaft for the rotating electrode with a magnetic bar attached perpendicularly near one end. When properly supported in the box the negative electrode can be rotated using a magnetic stirrer. The two positive electrodes are place 1 cm away from both sides of the negative electrode (see Figure 3). The electrolyte was prepared by dissolving 500 g of KOH in 750 ml of distilled H_2O.

Charging and Discharging of the Cell

A regulated power supply (commercially available kit) 1.25 to 25 V DC, 3 amp was used to charge the cell. Charging was done with the current maintained at 0.5 amperes for 15 hours. The speed of rotation of the negative electrode was 20 rpm. Since at such a low speed, the torque produced by a magnetic stirrer is not sufficient to move the electrode, a gear motor with a magnetic bar attached perpendicularly to the shaft was used and was able to rotate the disc during the entire charging times.

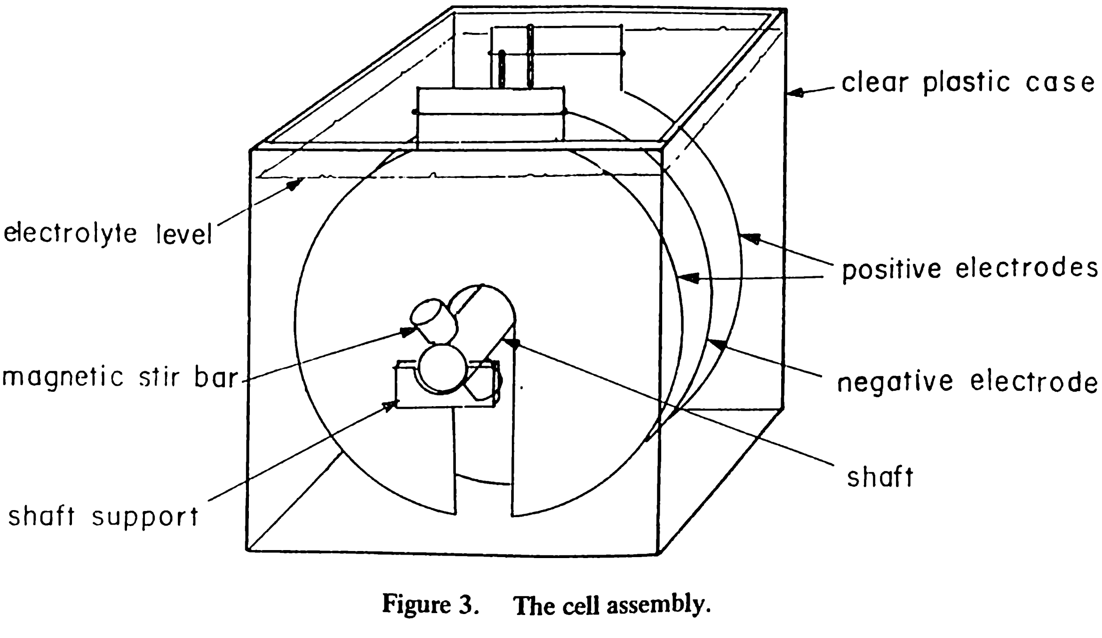

Figure 3. The cell assembly.

The cells were discharged at different times with different values of resistance. The current was obtained using a GE ammeter while the voltage was registered using a Simpson Multitester. The readings were taken every 30 minutes. Figure 4 shows the experimental setup.

The runs were divided into two groups: one with the negative electrode rotating and the other with the negative electrode stationary.

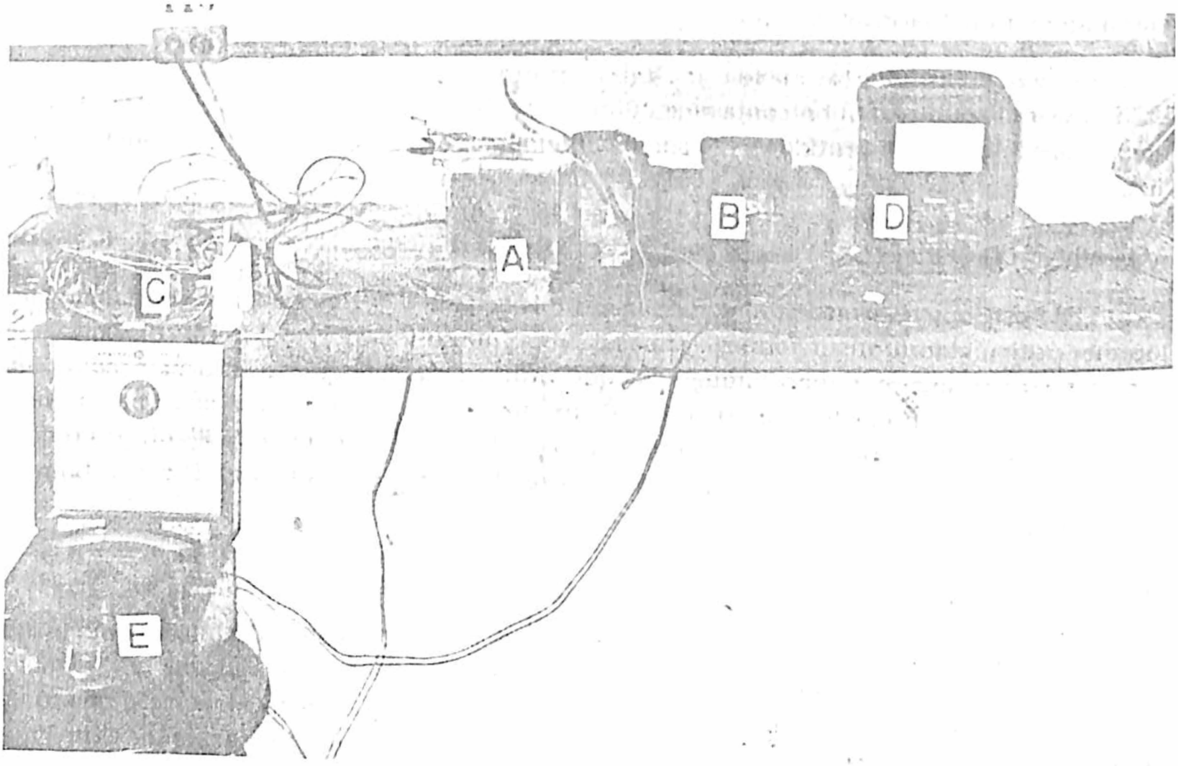

Figure 4. Photograph of the experimental set up; A, cell; B, motor; C, charger; D, voltmeter; and E, ammeter.

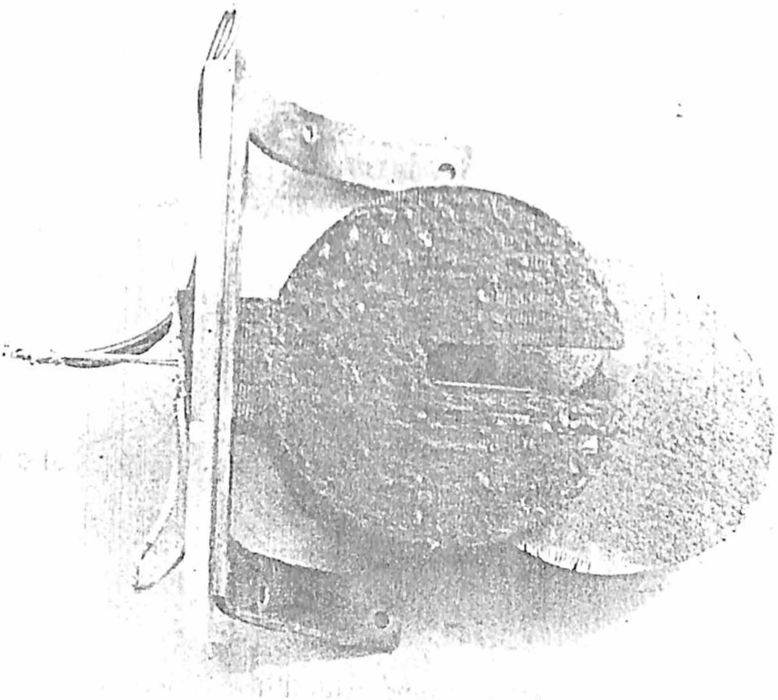

Figure 5. A photograph of the electrode assembly removed from the cell after a charging cycle.

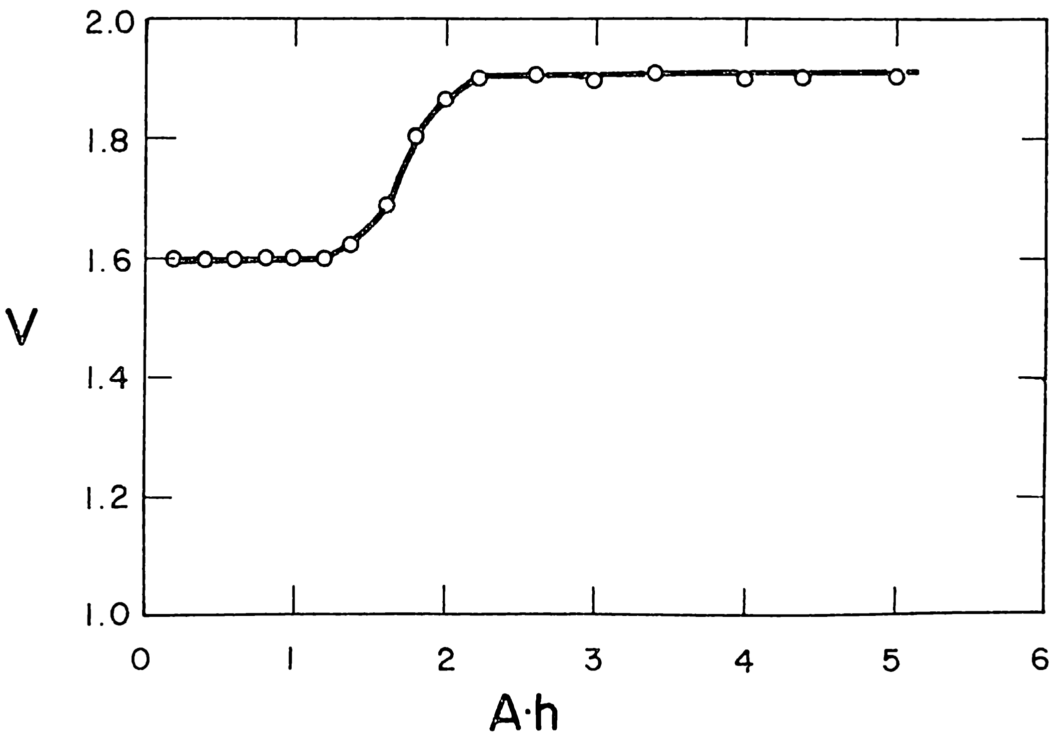

Figure 6. Charge curve for the silver-zinc cell with rotating negative electrode at a constant current of 0.5 ampere. The curve for the cells run with the stationary negative electrode is similar.

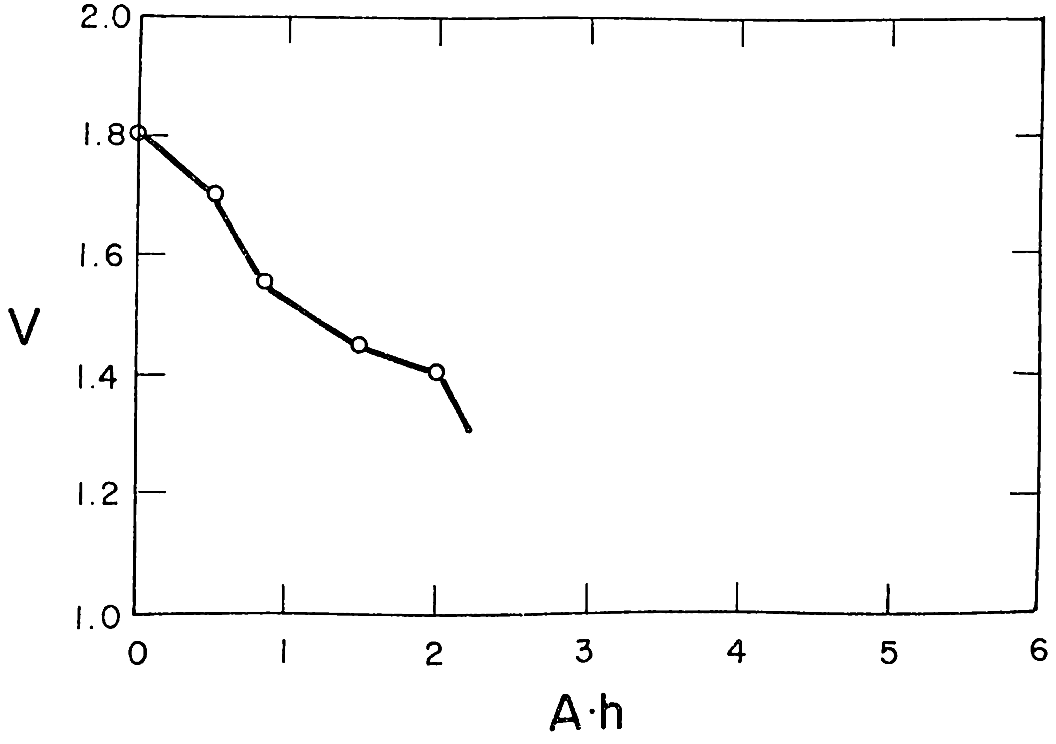

Figure 7. Discharge curve for the cell with the negative electrode rotated during charging.

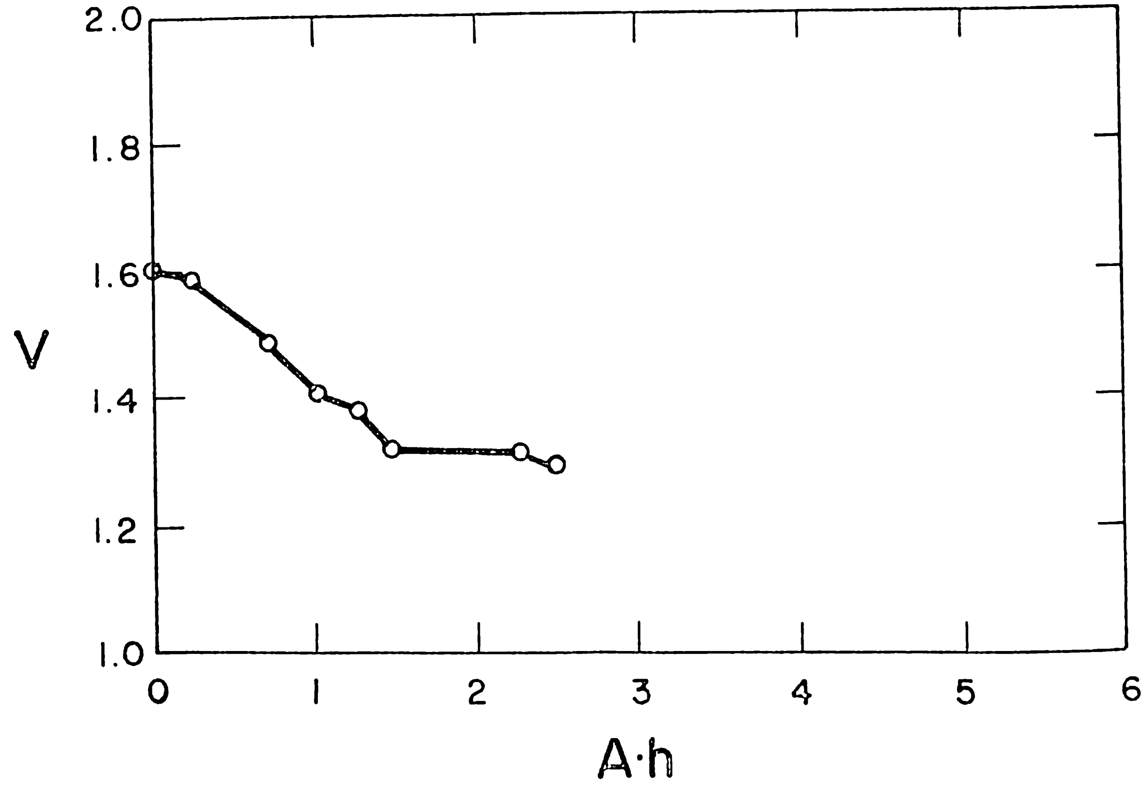

Figure 8. Discharge curve for the cell without rotating the negative electrode during charge.

RESULTS AND DISCUSSION

Figure 6 shows the charge curve (voltage versus ampere-hours) for the case where the negative electrode was rotated. The charging was done at a constant current of 0.5 amperes and the typical two-level curve was exhibited. The first level, at 1.60 V reflects the transformation of silver metal to monovalent silver oxide. A sharp rise to 1.90 V corresponds to the formation of the divalent silver oxide. The charging curves for the rotating and the stationary electrodes are similar.

Figure 7 shows a typical discharge curve when the cell was charged with the negative electrode rotating. Figure 8, on the other hand, shows the typical discharge curve for a stationary negative electrode during charging. The two curves are similar. The shape of these curves shows some anomaly. Typical discharge curves for Ag-Zn cells show the flattest curve of any battery system known. Examination of the cell after charging showed that the zinc plating was mossy and did not adhere well to the electrode. Therefore, during discharging, the voltage obtained was not flat as it should be. The problem is due to poor electrical contact between the silver leads and the rotating electrode, resulting in an uneven current distribution in the negative electrode. During discharge, some of the zinc just sloughed off, hence a poor discharge curve was exhibited.

Examination of the point of contact between the silver leads and the rotating electrode showed a very small area handling the current flow with the contact point varying during the rotation. Good electrode conductivity is a requirement for a battery and therefore, the cell's performance would be impaired. To remedy the situation, several contact points should be provided. They could be near the circumference of the electrode and at a circle near the shaft. Springs should be used to assure constant contact. A stronger magnet should also be provided for a more uniform rotation. For cells consisting of several electrode pairs, the rotation can be effected by using gears.

CONCLUSION AND RECOMMENDATIONS

This study tries to offer a method of lengthening the life of silver-zinc batteries. In actual cell assembly, after several charge-discharge cycles, the non-uniformity in zinc plating results in short circuiting of electrodes, shortening the life of the cell. With the movement of the negative electrode while charging, a higher throwing power (more uniform plating) will result in cells that could operate up to 300 cycles. This is due to solving the problem of non-uniformity of the electrolyte concentration. However, as the results show, a new problem arises, that is, the insufficiency of electrical contacts which, however, is a technical problem that could be solved.

The advantage to be gained in using the proposed design will mainly be an increase in the cycling life and reliability. However, several disadvantages aside from the electrical conductivity are foreseen. First, it is not guaranteed that the shape will not change, although radially, the disc will be symmetrical. Second, the cell will definitely take more space reducing the energy density (on a volume basis). Third, the cost of construction and operation will be higher.

Although the suggestion may not be promising and the model may not be feasible commercially, the idea could be useful in the study of electrode processes.

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