

## A STUDY OF RECHARGEABLE ZINC ELECTRODES FOR ALKALINE CELLS REQUIRING ANODIC LIMITATION

L. BINDER, W. ODAR and K. KORDESCH

*Institute for Inorganic Chemical Technology, Technical University of Graz, A-8010 Graz, Stremayrgasse 16 III (Austria)*

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### Summary

A well known technology exists for the preparation of anodes for rechargeable alkaline cells in which the zinc capacity is far in excess of the cathodic capacity, as in AgO-Zn or Ni-Zn cells. However, in rechargeable alkaline zinc-air cells and zinc-manganese dioxide cells the zinc limits the discharge. Especially for the manganese dioxide cathode it is necessary to limit the discharge to a definite fraction (1/3) of its available capacity to obtain a good cycle life.

This study of alkaline zinc powder electrodes evaluates parameters such as cell geometry, electrolyte additives, and current collectors (see Table 1) and shows that it is a considerable achievement to obtain 50 - 100 cycles reliably under anode limiting conditions. It is this fact which has prevented the technology of alkaline MnO<sub>2</sub>-zinc cells from producing rechargeable batteries of consumer quality up to the present time.

### Zusammenfassung

Die Technologie zur Herstellung von Anoden für aufladbare alkalische Zellen, in denen die Zinkkapazität die Kathodenkapazität weit überschreitet, wie in AgO-Zn- oder Ni-Zn-Zellen, ist gut bekannt. In aufladbaren Zink-Luft-Zellen und in Zink-Braunstein-Zellen begrenzt das Zink die Entladung. Besonders für die Braunsteinkathode ist es notwendig, die Entladung auf einen Bruchteil (1/3) ihrer verfügbaren Kapazität zu begrenzen, um eine hohe Zyklenzahl zu erhalten.

Diese Studie von alkalischen Pulverzinelektroden überprüft nochmals den Einfluss von Zellgeometrie, verschiedenen Elektrolytzusätzen und der Stromableiter (siehe Tabelle 1) und findet, dass es einen beträchtlichen Erfolg bedeutet, 50 - 100 Zyklen unter limitierenden Bedingungen verlässlich zu erhalten. Diese Tatsache verhinderte bisher die Produktion aufladbarer alkalischer MnO<sub>2</sub>-Zn-Zellen von jener Güte, die der Konsument verlangt.

## Introduction

The use of zinc as dissolution electrode in galvanic cells goes back to Alessandro Volta [1]. About sixty years later G. Leclanché developed a cell which forms the technical basis of the modern dry-cell industry [2]. In Leclanché's cell a zinc rod served as the negative electrode.

Since that time zinc has continued to be the preferred electrode for use in both primary and rechargeable cells, since it offers an attractive combination of high specific power, high current drain, and low cost. The zinc-rod anode of the first Leclanché cells was soon replaced by a zinc can which also served as the cell container. The advantages offered by amalgamation of the zinc anode were recognized at an early date and this method of preventing zinc corrosion is still used today to ensure the shelf life of Leclanché cells.

In 1903 the first patent for a wet alkaline  $\text{MnO}_2$ -zinc cell was filed and about ten years later the first "dry cells" of the alkaline  $\text{MnO}_2$  type were patented. Forty years passed before the first commercial  $\text{MnO}_2$ -Zn cell appeared. It was the "crown" cell of W. S. Herbert, first described in 1952 [3]. However, the available current drain was still too low for many applications, but this changed with the use of large area zinc electrodes.

Much work on large area zinc electrodes had taken place in the meantime on the  $\text{HgO}$ -Zn cell and on the air-depolarized zinc cell. The  $\text{HgO}$ -Zn cell has a very stable voltage on discharge, a high specific energy, and 80 - 90% utilization of the active materials. However, in secondary operation the cell shows limited rechargeability and low specific power. The disposal of the cell can present problems because of the health hazard associated with mercury.

In air-depolarized cells zinc powder or porous zinc plates are used as anodes. During cell operation the zinc is converted to  $\text{ZnO}$  and the plates are recharged or replaced by new ones. Another construction uses a zinc-KOH slurry which is converted to a zinc oxide slurry as the cell discharges. The zinc oxide is reconverted to zinc outside the cell [4]. Short cycle life and low efficiency are the unresolved problems with this cell.

Silver oxide-zinc and Ni-Zn cells are usually designed with cathode limitation providing twice the anode discharge capacity; this enables them to have cycle lives of 100 - 150 cycles and over 250 cycles, respectively.

The formation of dendrites cannot be fully suppressed by the use of current collectors with large surface areas (grids, wire fabrics). However, using improved separators combined in multi-layer arrangements, the danger of short circuiting is reduced. Shape change, which involves the reduction of the geometric area of the zinc electrode on cycling, is much more difficult to prevent [5, 6]. The active material is removed from the electrode edges and agglomerates toward the plate center. If cycling continues for a sufficient time, the edge areas of the current collector are completely denuded of zinc. The result is a loss of capacity and reduction of the useful life of the cell. McBreen [6] found that the active zinc tended to move away from high current density areas. Recently, another mechanism has been proposed [7]

based on convection induced by electro-osmosis through the separator. Densification and loss of electrode porosity are often observed in electrodes that have undergone shape change. Passivation may accompany densification, resulting from increased current density caused by loss of zinc surface area.

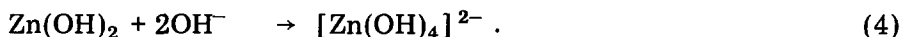
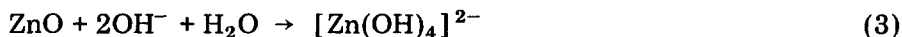
The phenomena associated with zinc limitation appear in air-zinc cells and in rechargeable  $\text{MnO}_2$ -zinc cells. Studies have shown that  $\text{MnO}_2$  is a good reversible electrode if it is discharged by not more than about 30% of the nominal  $1 e^-$  capacity. It suffers a permanent capacity loss below the level of  $\text{Mn}_3\text{O}_4$  (which cannot be recharged). To prevent irreversible damage to the  $\text{MnO}_2$  electrode, the capacity of the  $\text{MnO}_2$ -zinc cell must be limited by the amount of zinc.

To allow high currents to be drawn, in spite of the tendency of the zinc to passivate at high current densities, electrodes of large surface area have been designed. Zinc powder was pressed into the required anode shape and electrolyte was added. An electrolyte reserve was designed so that sufficient electrolyte was available for the reaction in the anode space. Another means of providing sufficient electrolyte and producing a reasonably flexible (extrudable) structure is to immobilise the electrolyte with a gelling agent and to add sufficient zinc particles to give it electronic conductivity. Such electrodes comprise 17 - 20 parts of alkali hydroxide (KOH), 50 - 70 parts of zinc, 6 - 10 parts of a gelling agent (*e.g.*, Na-CMC), 2 - 4 parts of ZnO, and the rest water [19]. The necessary current collector is usually made from copper or brass.

The work of Dirkse [8], Hampson [9], and Gerischer [10] confirmed that the discharge reaction of amalgamated zinc follows eqns. (1) - (4). The first step is the oxidation to solid ZnO or  $\text{Zn}(\text{OH})_2$ :



In a second step the dissolution and formation of zincate ions follows:

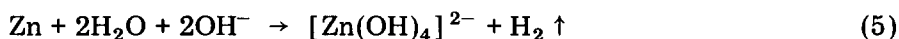


If the zincate concentration limit is exceeded, solid products may be reformed by reversal of reactions (3) and (4). Notably, Dirkse studied the properties of saturated [11] and supersaturated [12] solutions of ZnO in KOH.

Two different forms of passivation can stop the discharge of a zinc electrode before the active material is exhausted [13]. The "spontaneous" passivation occurs at high current densities within a few seconds. The "long-time" passivation is observed in the range 15 - 35 mA/cm<sup>2</sup> after some hours. Sanghi and Fleischmann [14] showed that the dissolution of zinc occurs with nearly the same overvoltage, independent of the degree of ZnO saturation. This is explained by the existence of supersaturated solutions of ZnO in KOH, which are normally quite stable, but if precipitation is induced by

any means (nucleation) solid products form immediately and passivate the electrodes.

The amalgamation of the zinc should reduce the loss of zinc by the reaction:



and prevent hydrogen gassing. Considerable efforts have been made to replace mercury by other metals or metal oxides [15 - 18].

In rechargeable alkaline  $\text{MnO}_2$ -zinc cells the effects of passivation and corrosion of the zinc electrode are of particular importance because the necessity for capacity limitation does not allow for the provision of any zinc reserve.

## Experimental

One part of our investigation examined the influence of electrolyte additives and cell construction on the capacity loss of limited zinc electrodes during cycling. The addition of complexing agents (*e.g.*, cyanide ions) should help to obtain zinc deposits with a large surface area on the current collector when the electrode is recharged. Such deposits reduce the probability of electrode passivation during the following discharge. Table 1 gives an overview of the different experiments undertaken.

The results were complemented by recording current-voltage diagrams for zinc electrodes within the potential range of passivation and of hydrogen evolution. It was possible to show the effect of some alkali salts on the area of the passivation peak of the zinc electrode. These measurements also confirmed the possibility of obtaining high hydrogen overvoltages on unamalgamated zinc by the addition of other metals.

### Zinc-zinc cells

The charging process needs special attention because the cycle life of the cell is largely determined by the properties of the redeposited zinc. It corresponds to the cathodic reduction of complex metal ions because, in a discharged cell, the zinc is available in hydroxo- or cyanocomplexes or as solid  $\text{ZnO}$ . It depends also on the concentration of the  $\text{KOH}$  used and on the type and concentration of complexing agents.

The cathodic discharging of complex metal ions has been thoroughly studied by Gerischer [20]. He stated that the predominating complex may not be directly discharged, but another complex (with lower coordination number, present only in small concentrations) could be first discharged. In the case of an alkaline Zn-cyanide containing electrolyte the process would include the following reactions:

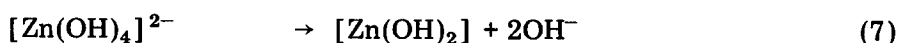
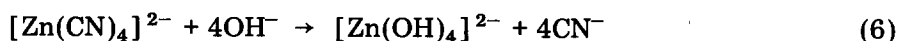


TABLE 1

Cell no.	Type	Electrolyte	Electrode gel	Current collector	Figure
1	1 (Fig. 1)	KOH	ZnO/Na-CMC/KOH	Brass wire fabric (amalgamated)	2
2	1	KOH + ZnO**	ZnO/Na-CMC/KOH	Brass wire fabric (amalgamated)	2
3	1	KOH + ZnO**	ZnO/Zn(CN) <sub>2</sub> / Na-CMC/KOH	Brass wire fabric (copper plated, amalgamated)	2
4	1	KOH + ZnO**	ZnO:Zn(CN) <sub>2</sub> = 3:2 ZnO:Zn(CN) <sub>2</sub> = 1:1	Brass wire fabric (copper plated, amalgamated)	2
5	1	KOH + ZnO** + Zn(CN) <sub>2</sub> **	ZnO:Zn(CN) <sub>2</sub> = 1:1	Brass wire fabric (copper plated, amalgamated)	3
6	1*	KOH + ZnO** + Zn(CN) <sub>2</sub> **	Zn(CN) <sub>2</sub> /Na-CMC/ KOH	Brass wire fabric (copper plated, amalgamated)	4, 6
7	1*	KOH + ZnO** + Zn(CN) <sub>2</sub> **	Na-CMC/KOH/ZnO/ Zn(CN) <sub>2</sub> (1:1)	Copper foil (silver plated)	6
8	1	KOH + ZnO** + Zn(CN) <sub>2</sub> **	Na-CMC/KOH/ZnO/ Zn(CN) <sub>2</sub> (1:1)	Brass wire fabric (silver plated)	4
9	2 (Fig. 7)	Pasted KOH (Na-CMC)	Zn***/ZnO/KOH/ Na-CMC	Copper wire fabric (silver plated)	4
10	2	Pasted KOH (Na-CMC)	Zn***/ZnO/Cu***/ PTFE***/HgO/KOH/ Na-CMC	Copper wire fabric (silver plated)	8
11	2	Pasted KOH (Na-CMC)	Zn***/ZnO/Cu***/ PTFE***/HgO/KOH/ Na-CMC	Copper wire fabric (silver plated)	8
12	2	Pasted KOH (Na-CMC)	ZnO replaced by Zn(OH) <sub>2</sub>	Copper wire fabric (silver plated)	8
13	2	Pasted KOH (Na-CMC)	as cell No. 11	Copper wire fabric (amalgamated)	4
14	3 (Fig. 10)	Pasted KOH (Na-CMC)	Zn/ZnO/HgO/KOH/ Na-CMC	Copper wire fabric (amalgamated)	4
15	3	Pasted KOH (Na-CMC)	Zn/ZnO/HgO/KOH/ Na-CMC	Copper wire fabric (amalgamated)	4

\* Additional test set up (Fig. 5(a), (b)).

\*\* Saturated.

\*\*\* Powdered.



The effects of colloidal organic compounds (*e.g.*, gelatine) are well known in electroplating processes. Other chemicals of this type (*e.g.*, starch, Na-CMC) are often used in battery production. They block the active spots of the current collector and prevent crystallization in preferred directions (formation of dendrites).

Another factor of great importance is the cell geometry. The different current densities on small surface elements are a function of their location,

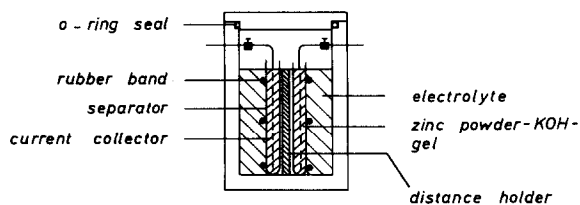


Fig. 1. Design of zinc/zinc cells with liquid electrolyte.

because short distances mean low electrolyte resistance. This effect is partly compensated for by the local overvoltage which is increased at high current density spots.

To obtain information on the effects of electrolyte composition, cell geometry, design, and current collector material, special cells and test methods have been developed.

### Cell description

Measurements were carried out on cells with a cylindrical case made from polyacrylate. The inside diameter of 30 mm and its height of 60 mm corresponded to commercial D-size cells. The cell tops were removable and the cells could be made gastight by means of an O-ring seal.

The cells (as shown in Fig. 1) were fitted with current collectors of amalgamated brass wire fabric (wire diameter 0.2 mm, screen opening 0.45 mm).

The basic idea was to undertake measurements on cells where both electrodes were equal. At the starting point one electrode was to be in the charged, the other in the discharged condition. One current collector (size: 25 × 50 mm) was electroplated with 120 mg of zinc layered with zinc oxide gel, the other collector was covered with a gel mixture of zinc oxide only. The surface of the electrodes was protected by a thin layer of acetylcellulose, then they were enclosed in pieces of regenerated cellulose, separated by strips of polyvinylchloride and held tightly together by rubber bands. The electrode package was inserted into the cell case and covered with electrolyte.

A constant current of 100 mA was applied. The cell voltage was recorded. First, the zinc electrode was oxidized until the current collector was completely denuded of zinc. At this point a voltage step of about 1 V was recorded. Theoretically, the same amount of zinc was deposited on the other current collector simultaneously. The cell was reversed when the voltage step appeared and the ampere hour capacity was calculated. The time between reversing points became shorter with increasing number of cycles, this means that the amount of reversibly reacting zinc diminished also. The capacity decrease was clearly related to the visibly deteriorating quality of the zinc deposits on the collector. The cycling was continued until the capacity loss amounted to 50%.

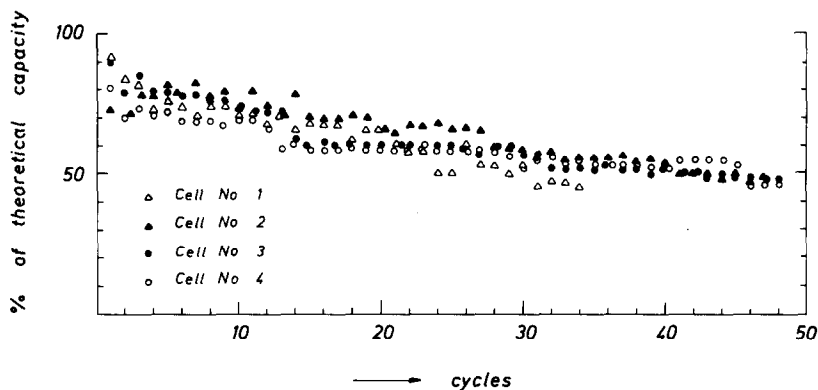


Fig. 2. Capacity loss of zinc/zinc cells during cycling. Cells Nos. 1 - 4.

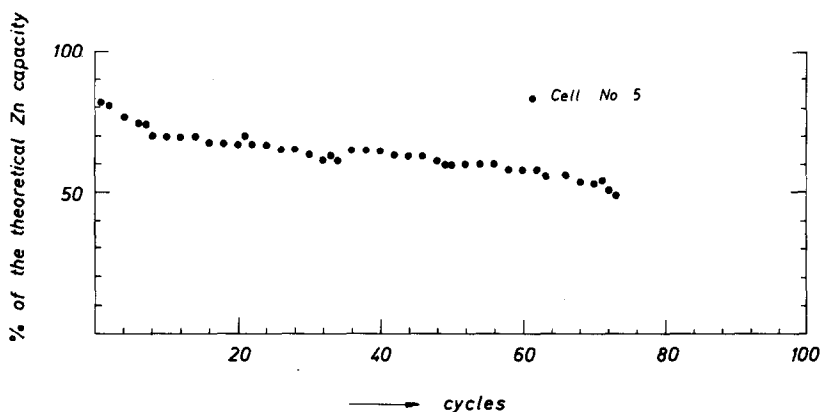


Fig. 3. Capacity loss of zinc/zinc cells during cycling. Cell No. 5.

In the first experiments (cell No. 1) we employed 9 - 10M pure KOH. The performance improved when the electrolyte was saturated with ZnO (cell No. 2). In the subsequent experiments the effect of  $\text{Zn}(\text{CN})_2$  addition to the electrolyte gel was studied. Initially ZnO and  $\text{Zn}(\text{CN})_2$  were used in a ratio of 3:1. These cells reached a cycle life of only 15. The amount of  $\text{Zn}(\text{CN})_2$  was then raised to a ZnO:  $\text{Zn}(\text{CN})_2$  ratio of 3:2 (cell No. 3) and finally to 1:1 (cell No. 4). The results can be seen in Fig. 2.

In cell No. 5 the electrolyte was saturated with ZnO and  $\text{Zn}(\text{CN})_2$ . It had the best cycling properties, as shown in Fig. 3. Control cell No. 6 was constructed with an electrode gel containing only  $\text{Zn}(\text{CN})_2$  and without ZnO. It resulted in fewer cycles (Fig. 4). Cell No. 8 was the last in this series of cells with liquid electrolyte. It was free from mercury and had current collectors made from silver-plated copper wire fabric. As shown in Fig. 4, the cell behaved erratically. The amount of reversibly reacting zinc dropped slowly over 10 cycles from 90% to 70%. Then a sudden drop took place followed by a recovery after four cycles. The capacity did not fall below 50% for about 25 cycles.

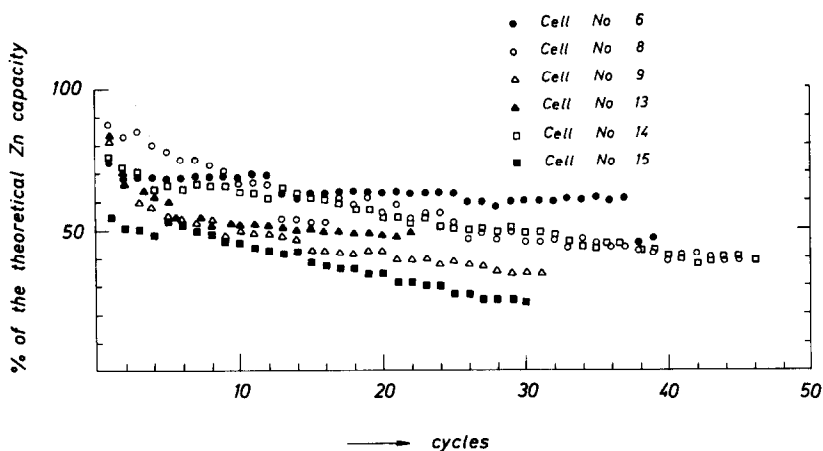


Fig. 4. Capacity loss of zinc/zinc cells during cycling. Cells Nos. 6, 8, 9, 13, 14, 15.

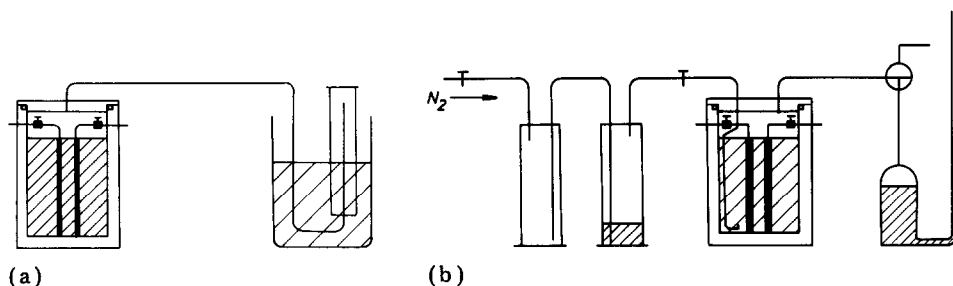


Fig. 5. (a) Device to observe gas evolution from the cell. (b) Apparatus to determine the amount of the evolved gas.

The next test series served to determine the amount of hydrogen evolved to determine whether the losses were (partly) caused by the zinc corrosion. To detect whether any gas was evolved from the cell the first device was sufficient (Fig. 5(a)), but to determine the amount of the gas additional equipment was necessary (Fig. 5(b)).

The gassing tests commenced with cell No. 6 and continued with cell No. 7, a cell free from mercury and fitted with current collectors made from silver-plated copper foil. In Fig. 6 the observed pressures are plotted *versus* the hours of operation.

A changed cell construction (Fig. 7) was required for the pasted electrolyte cells, Nos. 9 - 13. Cell No. 9 (see Fig. 4) contained KOH gel only. Cells Nos. 10 - 13 were used to test the effect of the addition of copper powder and PTFE\* to the KOH gel. Figure 8 shows that the cells Nos. 10 - 12 produced nearly uniform cycles. The rapid drop of the capacities in the early

\*PTFE = polytetrafluorethylene.



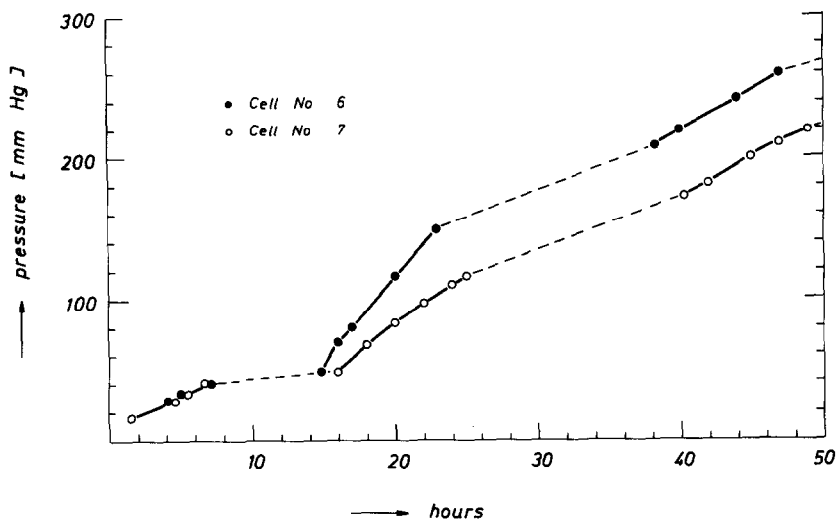


Fig. 6. Correlation between gas pressure and the length of cell operation. Cells Nos. 6, 7.

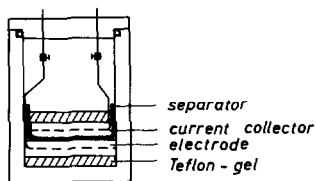


Fig. 7. Construction of cells with pasted electrolytes.

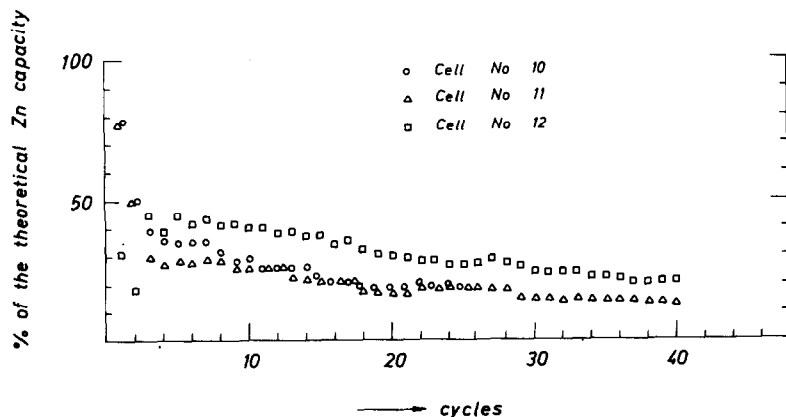


Fig. 8. Capacity loss of zinc/zinc cells during cycling. Cells Nos. 10 - 12.

cycles is beneficial for rechargeable  $\text{MnO}_2$  cells: from the third cycle on the capacity is quite uniform.

Commencing with cell No. 13, current collectors were made from amalgamated copper wire fabric. Cell No. 13 unexpectedly demonstrated that the two electrodes behaved unequally (Fig. 9). The cell voltages of the even

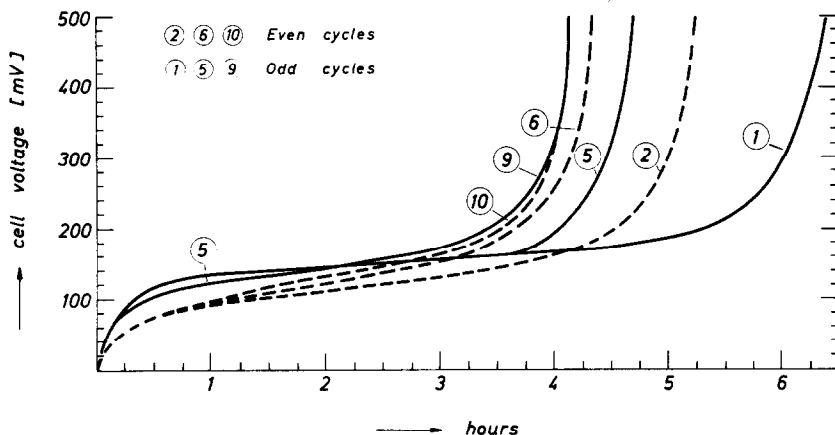
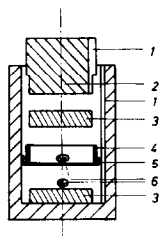


Fig. 9. Performance curves of cell No. 13, showing the voltage differences between even and odd numbered cycles.



- 1 notch for the conductor
- 2 piston
- 3 electrodes
- 4 hollow cylinder
- 5 separator
- 6 Na-CMC-KOH-gel

Fig. 10. Improved construction of zinc/zinc cells.

numbered cycles were initially 40 mV lower, but the odd cycles had a longer life. The decrease of the available zinc capacity during cycling of cell No. 13 is plotted in Fig. 4.

A more refined cell construction (Fig. 10) was designed to give more uniform electrodes and assure an exactly flat separator. The piston (2) should prevent any deformation of the electrodes (3). The hollow cylinder (4) should tighten the separator and contain the upper electrode. The results were not convincing, as seen from the performances of cells Nos. 14 and 15, also plotted in Fig. 4.

### Current-voltage functions

Current-voltage diagrams of zinc electrodes were recorded with an apparatus which consisted of two cylindrical cell compartments set in a water cooled (-heated) box, made from polyacrylate. One contained the "working"

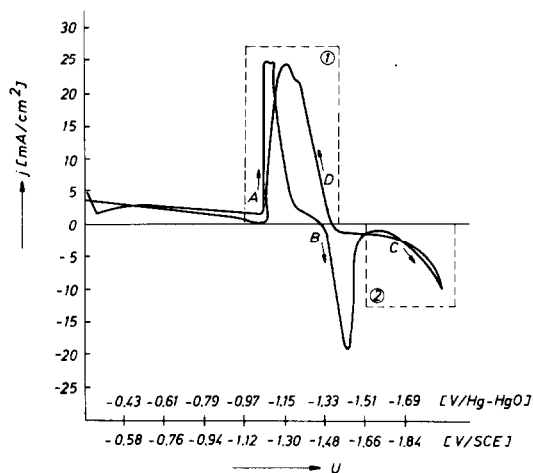


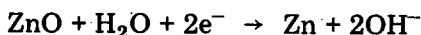
Fig. 11. Current-voltage diagram of a zinc electrode in 1M KOH.

zinc electrode, the other the inert counter electrode (Pt, Ag). A Haber-Luggin capillary was attached to the surface of the zinc electrode and an electrolyte bridge connected to the reference electrode (calomel or Hg/HgO). These electrodes were linked by a Wenking potentiostat (G. Bank Elektr. 7114 SMP 66). The potential/time curve was of triangular form and the sweep rates were 20 mV/min and 60 mV/min. The current flowing between the working electrode and the counter electrode was recorded with a Goerz Servogor recorder, type RE 512. Similar studies of zinc electrodes are reported in the literature [21 - 23].

Referring to Fig. 11, the characteristics of such a diagram may be described as follows: The experiment was started at a potential of  $-0.4$  V *vs.* the saturated calomel electrode (SCE) and  $-0.25$  V *vs.* the Hg/HgO electrode. At this time the electrode must be considered to be covered with a spontaneously formed surface layer of ZnO or Zn(OH)<sub>2</sub>. The potential was then changed to more negative values with a sweep rate of 60 mV/min. Initially, only a small current (leakage current) flowed. When the potential was reached where the reaction



started, the current increased significantly (Fig. 11A). After reaching a maximum value the current fell and reached zero at the equilibrium potential of the working electrode. When the potential became more negative, the reaction



(reverse of reaction (1)) took place and the previously formed surface layer was dissolved (Fig. 11B). At the end of this reaction the current was very small until it finally rose to a value where hydrogen evolution started (Fig. 11C). If the sweep direction was reversed and the same potential range

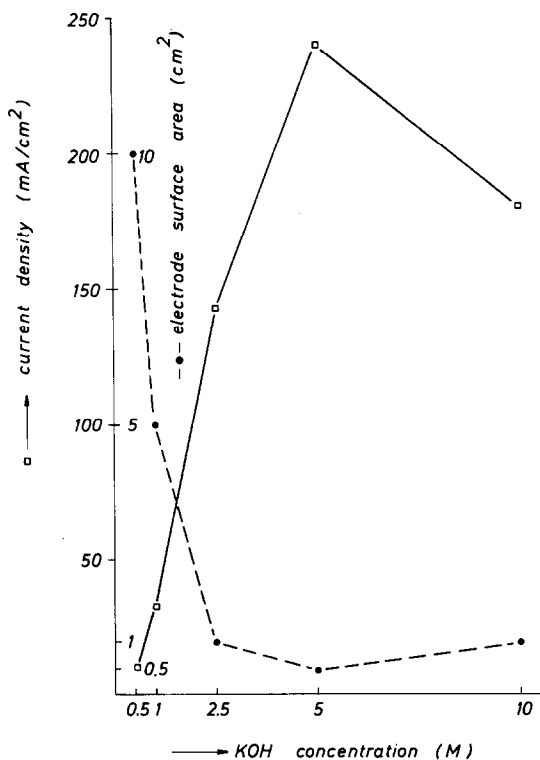


Fig. 12. The dependence of zinc passivation on KOH concentration, zinc electrode surface area, and current density.

traversed again, the positive current maximum of a newly built surface layer was obtained (Fig. 11D).

These experiments were intended to provide information about the effect of additives on zinc gel anodes. Two potential ranges were of particular interest: Range (1) in Fig. 11 would show the effect of chemicals on the formation of a surface layer (passivation). In the range of hydrogen evolution ((2) in Fig. 11) additives for increasing the hydrogen overvoltage on zinc could be evaluated.

The correlations between the KOH concentration, the electrode surface areas, and the maximum value of the current density (where passivation occurs) are indicated in Fig. 12. To demonstrate that some chemicals influence the formation of a passivation layer (limit the thickness ?) on the zinc electrode, the area of the "passivation peak" before and after the addition of some alkali salts was determined. The area measured in pure KOH served as the reference (100%). Figure 13 shows a typical series of passivation peaks recorded with a 1 cm<sup>2</sup> zinc electrode in potassium hydroxide (2.5 mole/l) after addition of 1, 2 and 3 wt.% potassium sulfate. The results of these investigations are collected in Fig. 14.

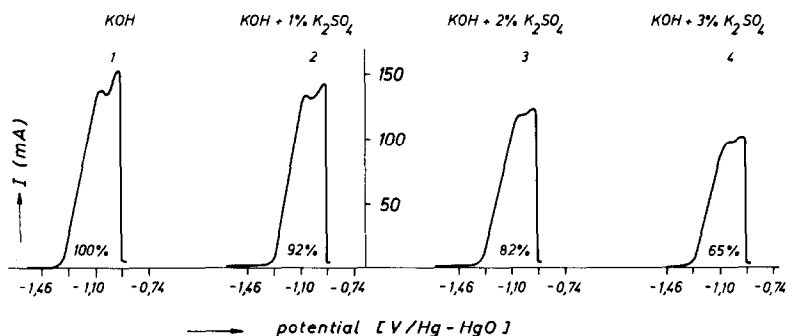


Fig. 13. A typical series of passivation peaks.

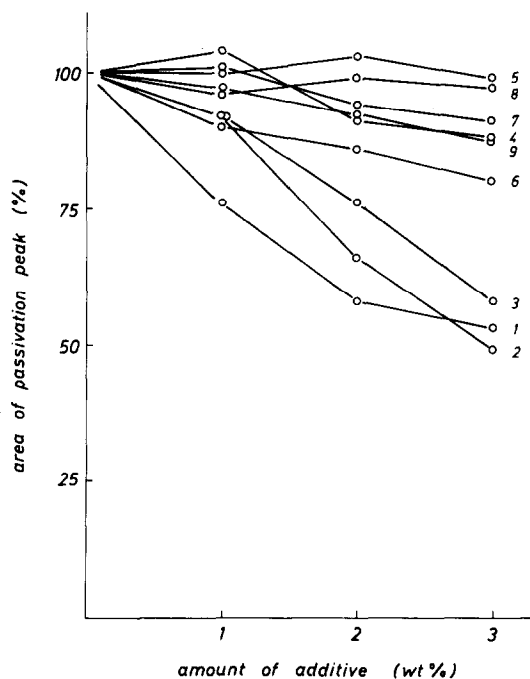


Fig. 14. The effect of some electrolyte additives on the area of the passivation peak. 1, potassium sulfate in 0.5M KOH; 2, potassium sulfate in 1M KOH; 3, potassium sulfate in 2.5M KOH; 4, potassium thiocyanate in 0.5M KOH; 5, EDTA in 0.5M KOH; 6, sodium acetate in 1M KOH; 7, potassium nitrate in 1M KOH; 8, potassium chloride in 1M KOH; 9, distilled water (10, 20, 30 ml) in 1M KOH.

The measurements in the hydrogen evolution range show that some metals or metal compounds should be able to replace mercury in the anodes of rechargeable cells. The differences between the hydrogen overvoltage on a pure zinc electrode in pure KOH and the hydrogen overvoltage on a modified zinc electrode or in a modified electrolyte were determined (Fig. 15). From these curves the hydrogen overvoltages could be found by the usual tangent construction method. The large differences in effectivity of

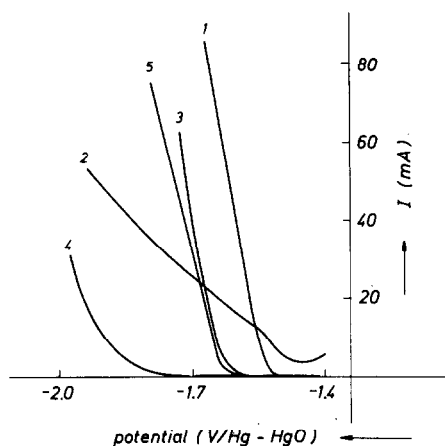


Fig. 15. Typical current-voltage diagrams recorded in the hydrogen evolution range. 1, pure zinc, pure KOH (9 - 10M); 2, pure zinc, KOH with 0.23 wt.% Pb; 3, pure zinc, KOH with 0.11 wt.% Sn; 4, pure zinc, KOH with 0.006 wt.% In; 5, amalgamated zinc, pure KOH.

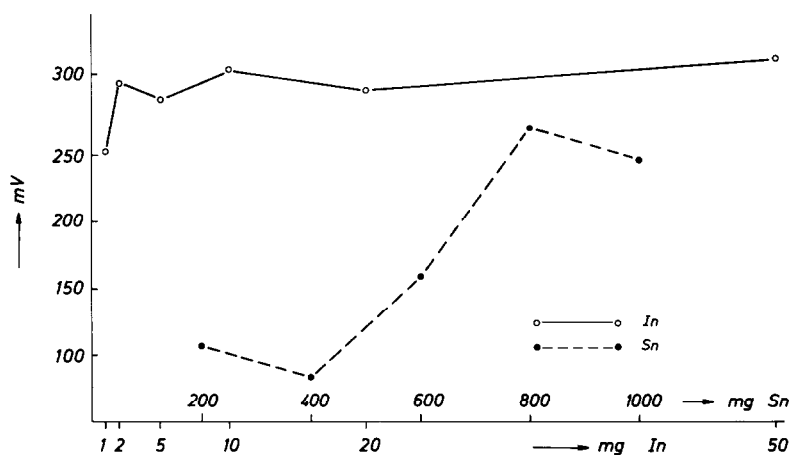


Fig. 16. Differences in the overvoltage (mV) between a zinc electrode in pure KOH and a zinc electrode in KOH containing small amounts of Sn and In.

some additives are evident. The most interesting additives seemed to be Sn and In. In Fig. 16 the changes of hydrogen overvoltage with increasing amount of metal additives are plotted.

## Discussion

Rechargeable alkaline  $\text{MnO}_2$ -zinc cells need reproducible, capacity-limiting anodes. This demand increases the number of problems characterizing the cycling behaviour of zinc electrodes. The efficient redeposition of

zinc upon the current collector in a ZnO saturated KOH solution is of particular importance.

The experiments were arranged to study simple facts; they began with liquid KOH electrolytes to investigate passivation phenomena and zinc (dis-solution) losses. The (purposely) small amounts of zinc, equivalent to about 0.1 A h, demanded a very uniform plating of the current collectors and a very accurate cell geometry. Different current collectors had to be tested in view of later technology.

Cell No. 1 used pure 9 - 10M KOH as electrolyte. When this cell was inspected after 32 cycles, the expected amount of deposited ZnO had visibly diminished. To counteract this loss of ZnO, the electrolyte of the following cell (No. 2) was saturated with ZnO. The result was as expected, an increase in the number of cycles (Fig. 2).

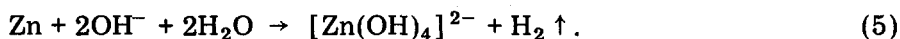
We next added  $\text{Zn}(\text{CN})_2$  to the electrode covering gel, and later also to the electrolyte itself. The expected positive effect of this addition — according to a patented process [24] — was obtained with a ZnO:  $\text{Zn}(\text{CN})_2$  ratio of 3:2 (cell No. 3).

It is a reasonable assumption that the addition of  $\text{Zn}(\text{CN})_2$  is effective only when a minimum concentration of  $[\text{Zn}(\text{CN})_4]^{2-}$  in the electrolyte is exceeded. At the start of this test series the minimum concentration was not reached and no effect was visible. The following cells, Nos. 3 and 4, had a cycle life of nearly 50 in which the greatest loss of capacity took place during the early cycles; afterwards the cells lost only about 10% of their theoretical capacity in the course of 32 cycles. The formation of  $[\text{Zn}(\text{CN})_4]^{2-}$  ions from the  $\text{Zn}(\text{CN})_2$  needs time, and so the stabilization of the cell occurs after about 10 cycles.

Considering this, the next cell (No. 5) was filled with KOH saturated with ZnO and  $\text{Zn}(\text{CN})_2$ . This provision resulted in a performance of about 70 cycles (Fig. 3). The cell still needed about 8 cycles to stabilise. Proceeding along this line, a cell was made using only  $\text{Zn}(\text{CN})_2$  for the electrode gel (cell No. 6, Fig. 4). The diagram shows that the capacity loss of this cell was nearly zero during the time of operation. A larger capacity loss was observed only after periods when the cell was not operating. The rapid decline in the early part of the capacity loss curve — well known from the other cells — was not observed here.

The fact that greater capacity losses were observed when the cell was idle led to the speculation that these losses were the result of zinc corrosion. However, this could not be verified by gas pressure measurement or by determining the amount of evolved hydrogen. Zinc oxidation due to air access is another possible explanation. Copper would catalyze this reaction.

The tests were carried out with cells Nos. 6 and 7. The reason for a lower gas evolution from cell No. 7 than from cell No. 6 may be due to the use of a silver plated current collector in this cell. Though cell No. 7 was free from mercury, the loss of zinc caused by corrosion was very much smaller than the loss calculated from the time of cell operation (Fig. 6), in other words, the loss of zinc capacity cannot entirely be accounted for by the reaction:



The largest part of the "lost" zinc stays in the electrode gel as passivated metallic zinc, in the form of unreacting ZnO, and as particulate metallic zinc without electronic contact with the current collector.

These effects became much more obvious with cells containing pasted electrolyte. Dendritic short-circuits and insufficient contact between separator and electrode gel turned out to be additional problems.

The effects of the addition of copper powder and PTFE to the electrode gel are of technical importance. It was expected that the copper powder would bring about a good electronic contact between all the zinc particles and the current collector by the simple effect of increasing the amount of metallic particles. Another reason for the desirability of copper powder in the zinc anodes is the necessity for the presence of an oxide-forming metal if the cell is overdischarged. Copper also serves as a transfer aid for the oxygen recombination cycle on overcharge. The hydrophobic properties of agglomerated PTFE particles should provide the immobilized electrolyte with a certain plasticity and porosity, preventing settling out of zinc and loss of electrolyte.

Cells Nos. 10 - 12 showed nearly uniform cycles after a rapid drop of capacity at the second cycle (Fig. 8). The insulating effect of the PTFE may be responsible for this behaviour, because no pressure was used to shape the anodes. Though the zinc utilization is low, the uniformity of the following cycles may be seen as a beneficial effect. PTFE is technically used as a binding agent for compressed zinc powder electrodes and no reduction of zinc utilization has been observed. Rampel described a PTFE-bonded zinc electrode which had 70 - 75% of its initial capacity after 50 cycles [25]. Another PTFE-bonded ZnO/Zn electrode was described by Vielstich [26]. It still had a zinc utilization of 61% after 300 cycles.

The differences in voltage levels of the cycles with even and odd numbers (Fig. 9) become smaller with increasing number of cycles; the curves actually cross over. It simply shows that the two electrodes are working at different overvoltages during the same electrode reaction (*e.g.*, oxidation). Different local current densities may cause different utilization. To explain this effect we may consider the unequal starting conditions of the electrodes: one as zinc metal, the other as ZnO.

The recording of current-voltage diagrams for passivation studies was started with 0.01M KOH. When the concentration of KOH was increased to 1M, the geometrical zinc electrode area of the experimental cell (10 cm<sup>2</sup>) had to be decreased to achieve passivation within the desired (constant) current ranges. At positive potentials (*vs.* the equilibrium potential of zinc) the zinc hydroxide dissolves (to hydroxozincate) faster than it can form a surface layer. The poor solubility of passivating deposits was described by Powers and Breiter [27]. At negative potentials the redeposition of zinc superseded the start of hydrogen evolution. In the case of 1M KOH a passivation was reliably achieved at a current density of 30 mA/cm<sup>2</sup> (electrode area:



5 cm<sup>2</sup>). Figure 12 gives the correlation between the KOH concentration of the electrolyte, the electrode areas, and the recorded maximum current densities. In the literature [28] it is reported that the maximum current density is achievable at an electrolyte concentration of 7.5M KOH. The fact that the current density needed for passivation decreases again at higher KOH concentrations is now confirmed for ZnO-free KOH.

If the area of the passivation peak (Fig. 11, ①) is proportional to the amount of the oxidation products of zinc, then it must be also proportional to the thickness of the surface layer, if the electrode area remains constant. The determination of the area of the passivation peak can therefore be used to show that some chemicals affect the formation of this surface layer. The requirement for a constant surface area of the electrode indicates the limitation of this method. At KOH concentrations of 5M and 10M, this constancy of electrode area cannot be assured. Figure 14 does not include KOH molarities over 2.5 because a considerable corrosion of the electrode occurs with higher concentrations, the zinc is roughened and the surface area increases. Consequently, the passivation peaks also become larger with increasing time of electrode exposure to the electrolyte. Moreover, the solubility of the additives in electrolytes of high KOH concentration is low and leads to the precipitation of an unknown amount of the added chemical. The diagram (Fig. 14) indicates that potassium sulfate had the largest depassivation effect. A similar observation was made in the course of other experiments [29].

The purpose of recording accurate current-voltage diagrams in the hydrogen evolution range was to confirm that some metals increase the hydrogen overvoltage of zinc to the same extent as mercury. In principle, this has been reported before [17, 18] but we had to remove some uncertainties concerning the efficiency of different additives at various concentrations (Fig. 15). It has been pointed out by Lee [15, 16] that the potential of the reversible hydrogen electrode in 9M KOH is  $-0.93$  V *vs.* the Hg/HgO electrode. The hydrogen overpotential on zinc depends on the applied current density and attains the value of 1 V at about 70 mA/cm<sup>2</sup>. The different curves of Fig. 15 must be compared with curve No. 1 which represents pure zinc in an electrolyte of KOH (9 - 10M) without additives. The addition of potassium stannate (0.11 wt.% Sn) to the electrolyte had nearly the same effect as the 4% amalgamation of the zinc electrode. The addition of larger amounts of lead ( $> 0.23$  wt.%) had no beneficial, but rather a detrimental effect. The most pronounced effect was produced by the addition of very small amounts of In (0.006 wt.%) (Fig. 16).

## Conclusion

A capacity limiting zinc anode is required for rechargeable alkaline MnO<sub>2</sub>-zinc cells because the MnO<sub>2</sub> electrode must be protected against being discharged below MnO<sub>1.5</sub>. Such a zinc electrode is different from

those used in AgO-Zn cells or Ni-Zn cells because the cycling of these cells is usually done with cathodic limitation.

A zinc electrode with the required properties can be achieved with the following provisions: an electrode gel is formed with zinc powder, KOH, and a gelling agent; copper powder and/or PTFE may be added; ZnO is added, acting as zinc reserve; other additives can prevent premature passivation and increase the hydrogen overvoltage; precautions must be taken to provide sufficient electrolyte during cycling; the electrode contains a current collector made from silver plated or amalgamated copper wire fabric. The addition of  $\text{Zn}(\text{CN})_2$  to the electrode gel gives good capacity and less cycling loss.

It is important to bear in mind that the results presented for the zinc test cell may differ from the results obtained with commercial rechargeable  $\text{MnO}_2$ -Zn cells [30] because the zinc cell test conditions are more stringent. Full discharge during each cycle is not common practice with commercial cells, and 50 complete discharge cycles are at least a good starting point for a proposed low cost cell [31].

Separator problems do not appear to be serious up to 200 cycles and the  $\text{MnO}_2$  cathode seems to tolerate more than 200 cycles at a 25% depth of discharge [32]. Complete cells containing zinc electrodes made in accordance with the best of our results have been built.

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