

EXPERIMENTAL SURVEY OF RECHARGEABLE ALKALINE ZINC ELECTRODES

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Summary

Rechargeable alkaline zinc-air cells and zinc-manganese dioxide cells need zinc electrodes working for at least 100 cycles under anode limiting conditions. The discharge of the manganese dioxide cathode especially must be limited to a definite fraction (1/3) of its available capacity to obtain a good cycle life.

This study proposes a new test cell for investigations on pasted alkaline zinc powder electrodes. When, following experimentation, the value of the construction was established, a series of different electrode mixtures was cycled. It was found that 100 full discharges could be obtained with a zinc utilization of about 30% in the final cycles.

Zusammenfassung

Aufladbare alkalische Zink-Luft-Zellen und Zink-Braunstein-Zellen erfordern Zinkelektroden, die zumindest 100 Zyklen unter limitierenden Bedingungen zu geben imstande sind. Besonders die Entladung der Braunsteinelektrode muss auf einen Bruchteil (1/3) ihrer verfügbaren Kapazität begrenzt werden, um eine hohe Zyklenzahl zu erhalten.

Diese Studie stellt eine neue Versuchszelle für Untersuchungen an alkalischen Pulverzinelektroden vor. Nachdem sich die Konstruktion im Verlauf einiger Versuche als brauchbar erwiesen hatte, wurde eine Reihe von verschiedenen Elektrodenmischungen geprüft. Es wurde festgestellt, dass 100 Vollentladungen erreicht werden konnten, wobei die Zinkausnutzung während der letzten Zyklen etwa 30% betrug.

Introduction

Zinc electrodes for rechargeable alkaline MnO_2 -zinc cells must be capacity-limiting [1]. There is also a requirement to solve the most important problems (dendrite formation, shape change, passivation) characterizing the

cycling behaviour of zinc electrodes. In a previous investigation the influence of electrolyte additives and cell construction on the capacity loss of zinc electrodes during cycling has been examined [2]

Even the most refined cell construction techniques used for these experiments did not guarantee sufficiently uniform electrodes and a precisely flat separator. It therefore appeared reasonable to design and test a new cell.

Experimental

The first part of this paper deals with the construction and development of the test cell. The second part describes cycling tests using different zinc electrode mixtures.

Cell description

The cell consists of two cylindrical cases, two cell tops, a centre ring, and two pistons all made from polymethacrylate (Fig. 1).

The cell tops are removable and carry the adjustment screws. The O-ring-tightened-pistons can be moved forward inside the cell cases by turning these screws. The front planes of the pistons are fitted with current collectors of copper foil. To enlarge the surface area of the current collectors they were initially (first two cells) covered with copper wire mesh (wire diameter 0.2 mm, screen opening 0.45 mm). The copper wire mesh could be renewed after the experiment. (For experiments subsequent to No 3, the cell was used without the copper wire fabric.) The electrode space is limited by the current collector, the wall of the cylindrical case, and the separator.

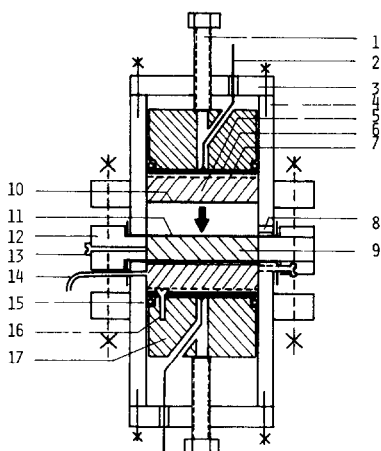


Fig 1 Longitudinal section of the test cell 1, Adjustment screw, 2, conductor, 3, cell top, 4, cell case, 5, electrode mixture, 6, copper foil, 7, copper wire mesh, 8, evacuation hole, 9, electrolyte, 10, felt, 11, separator, 12, centre ring, 13, sealing screw, 14, electrolyte bridge, 15, O-ring seal, 16, fastening screw, 17, piston

Experiment No 15 and subsequent experiments were conducted with a slightly modified cell made from polyamide. The reduced applied current density corresponds with the smaller electrode areas and increased distance between the electrodes.

Procedure

The current collectors (wire mesh on the pistons) are amalgamated and the pistons inserted in the cases. The cell tops are screwed to the cases. The flexible pipe (PTFE) used as electrolyte bridge to the reference electrode (Hg/HgO) is filled with KOH. The electrode mixtures (Zn-electrode, ZnO-electrode, respectively) are weighed directly into the cell cases. The electrode mixture is slightly compressed, using an auxiliary piston and a round piece of cellulose felt, to form it into a cylinder. The felt prevents adhesion of the electrode mixture to the auxiliary piston. The centre ring is used to stretch a piece of wet separator over the opening of the cell case. The cell case is then fastened to the centre ring by three screws. Electrolyte (immobilized by 2% Na-CMC) is inserted into the electrode space through the evacuation hole. The piston is then moved toward the separator by turning the adjustment screw until the pasted electrolyte is pressed out again. The evacuation hole is closed by a screw. This operation prevents the presence of bubbles (air) between the electrode mixture and the separator. The second electrode is prepared similarly and also attached to the centre ring. The space between the separators is filled with 9M KOH containing 2% Na-CMC. The filling hole is closed by the sealing screw.

A constant current is applied and the cell is reversed automatically when the end of discharge (or charge) voltage step appears. During cell operation the voltage between the working electrode and the reference electrode (Hg/HgO) and the cell voltage are recorded.

A detailed description of the operational procedure can be found in a previous paper [2].

Results

The main purpose of the first experiment was to test the operation of the test cell itself. Technical problems concerning the prevention of electrolyte losses had to be solved. Figure 2 shows how the amount of reversibly reacting zinc diminished during cycling.

The recorded electrode voltages should give some information concerning the causes of capacity loss. At a voltage of -1.35 (vs Hg/HgO) of both electrodes the cell voltage was zero at the beginning of each cycle. When the electrochemical reactions proceeded, the voltage of the reducing electrode became more negative and the voltage of the oxidizing electrode became more positive. The difference in these voltages was the measured cell voltage.

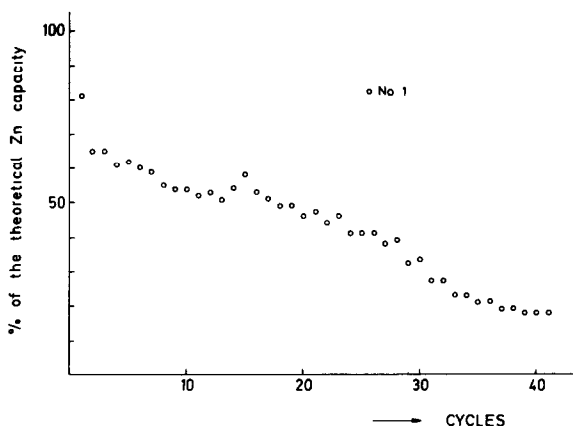


Fig 2 Capacity loss of zinc/zinc cells during cycling Experiment No 1

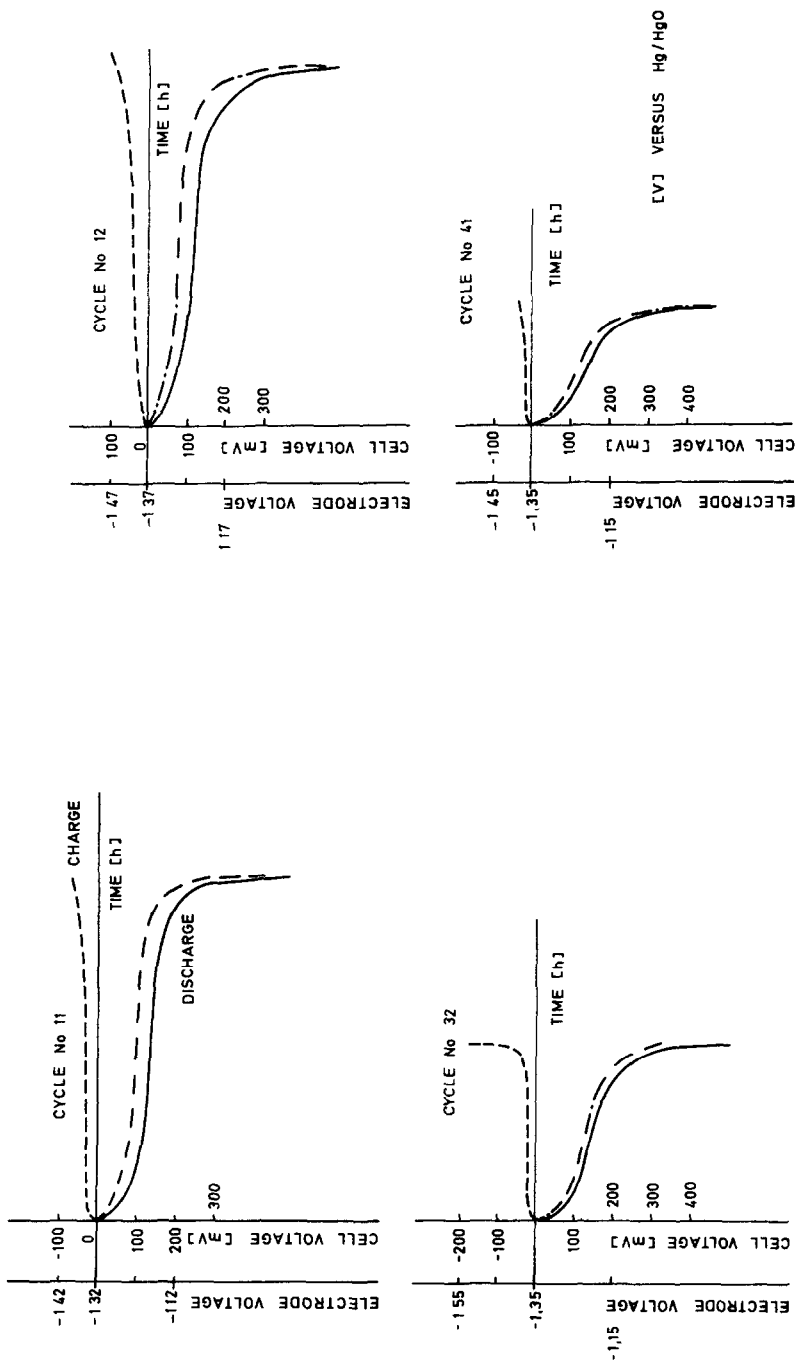
It was expected that the significant voltage step at the end of each cycle would be mainly caused by the final dissolution of metallic zinc or by its passivation. This was confirmed during the first cycles (Fig 3, cycles Nos 11, 12). When the number of cycles increased, the contribution to the cell voltage step of the reducing electrode voltage became more important (Fig 3(a), cycle No 32). Finally, changes occurred, and at the end of the last cycle (Fig 3(b), cycle No 41) the voltage step was mainly caused by the oxidizing electrode.

An additional observation was made when we carried out these measurements. The electrodes of the cell showed different voltage characteristics when the cell was cycled; they were different for an electrode which started as a zinc electrode from one which started as a zinc oxide electrode. The "history" of the electrode was of importance even after a large number of cycles. This observation agreed with earlier experiments on cells of different construction [2].

With increasing amount of zinc electrode mixture, the thickness of the cylindrical shaped electrodes and the distance between the current collectors also increase. This leads to a higher ohmic resistance of the cell and increases the probability of non-adherent zinc deposits. Therefore experiments Nos 2 - 5 were used to determine the optimum amount of zinc electrode mixture for this cell. It can be seen (Fig 4, Fig 5, Table 1) that the experiments should not commence with a zinc capacity much greater than 1 A h.

The addition of MgO was an attempt to prevent electrode shape change by blocking the movement of materials formed during the electrochemical processes [3]. Figure 5 shows the results of experiments Nos 6 and 7 (with MgO, see Table 1) compared with experiment No 5 (without MgO). The improved performance of the cell after addition of MgO to the electrode mixtures was the reason for using this additive throughout the program.

The results after addition of K_2SO_4 to the electrode mixtures [4] did not seem as clear as those with MgO. This series was stopped after three



(b)

(a)

Fig 3 Electrode voltage and cell voltage during cycling Experiment No 1.

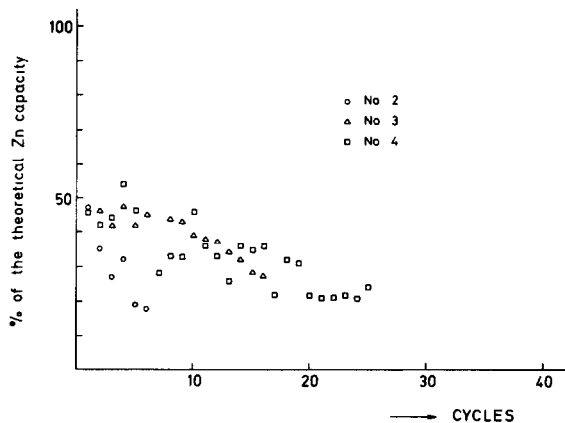


Fig 4 Capacity loss of zinc/zinc cells during cycling Experiments Nos 2 - 4

TABLE 1

Experiment no	Composition of electrodes no	Current density (mA/cm ²)	Theoretical capacity (A h)	Cycles recorded	Remarks
1	1	10	—	41	
2	1	11	3 0	6	
3	1	11	1 5	16	
4	1	7	1 5	25	
5	1	7	2 3	11	
6	2	7	1 4	22	
7	2	7	0 78	37	
8	3	7	0 79	22	
9	3	7	1 4	35	
10	3	7	1 75	30	
11	4	7	1 12	35	*
12	4	7	1 16	28	
13	4	6 3	1 11	34	
14	5	6 7	0 92	29	
15	5	3 8	1 02	32	
16	6	3 8	0 69	20	
17	6	3 8	0 57	20	
18	7	4 4	0 83	13	**
19	8	3 1	0 95	66	
20	7	3 1/2 5	0 91	43	***
21	9	3 3	0 96	36	
22	10	2 5	0 81	98	
23	10	2 5	0 8	47	

* The last 2 cycles at 11 mA/cm²

** The experiment was stopped by a breakdown of the automatic control

*** 2 5 mA/cm² from cycle No 6 onwards

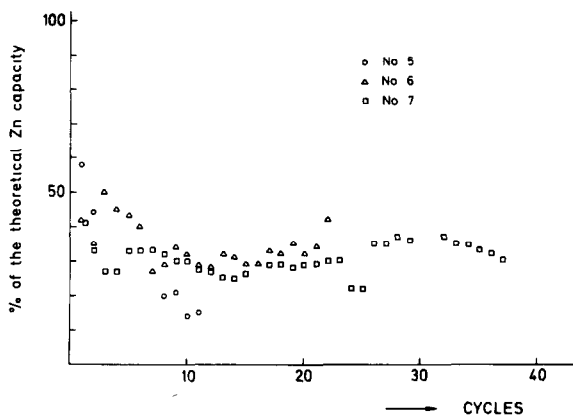


Fig 5 Capacity loss of zinc/zinc cells during cycling Experiments Nos 5 - 7

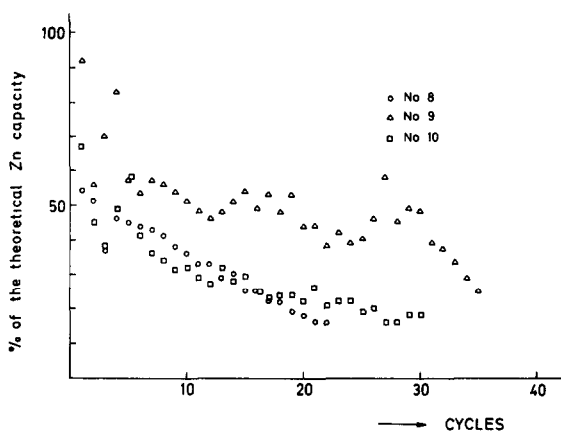


Fig 6 Capacity loss of zinc/zinc cells during cycling Experiments Nos 8 - 10

experiments (Fig. 6) Non-amalgamated zinc powder was used to prepare the zinc electrode for experiments Nos 11 - 13. The zinc oxide electrodes did not contain any HgO and the current collectors were silver plated. In place of mercury, sodium stannate and lead oxide were added to the electrode mixtures (see Table 2, comp No 3). The uniformity of the cycles up to No 33 shown by experiment No 11 (see Fig 7) is an indication that this might be a future development.

For the following experiments commercial battery grade zinc powder, amalgamated with 6% of mercury was used. The addition of 2% of graphitized carbon fibres to the electrode mixtures was an attempt to improve the conductivity of the pasted electrodes and to provide a large area of substrate for the redeposition of zinc (Fig 8, experiments Nos 14, 15).

The high starting capacity values of experiments Nos. 16 and 17 (Fig 9) are due to a conductive matrix of copper powder, 7.5% added. The first discharge of experiment No 17 showed a zinc utilization of more than 90%.

TABLE 2

Composition of electrode mixtures

No	Zinc electrode		Zinc oxide electrode	
1	Zn(4% Hg)	54 3%	ZnO	62 5%
	KOH gel*	34 8%	KOH gel	31 3%
	ZnO	10 9%	HgO	6 2%
2	Zn(4% Hg)	60%	ZnO	62%
	KOH gel	30%	KOH gel	30%
	ZnO	6%	HgO	4%
	MgO	4%	MgO	4%
3	Zn(4% Hg)	55%	ZnO	58%
	KOH gel	35%	KOH gel	32%
	ZnO	3%	HgO	4%
	MgO	5%	MgO	4%
	K ₂ SO ₄	2%	K ₂ SO ₄	2%
4	Zn(Hg free)	55%	ZnO	58%
	KOH gel	35%	KOH gel	32%
	MgO	5%	MgO	4%
	Na ₂ SnO ₃	3%	Na ₂ SnO ₃	4%
	PbO	2%	PbO	2%
5	Zn(6% Hg)	52%	ZnO	56 5%
	KOH gel	37%	KOH gel	34 5%
	MgO	9%	MgO	3 5%
	Carbon fibers	2%	HgO	3 5%
6	Zn(6% Hg)	46 5%	ZnO	49%
	KOH gel	38 5%	KOH gel	36 5%
	MgO	7 5%	MgO	3 5%
	Copper powder	7 5%	HgO	3 5%
			Copper powder	7 5%
7	Zn(6% Hg)	39 5%	ZnO	45%
	KOH gel	35 5%	KOH gel	32 5%
	MgO	7%	HgO	6 5%
	Copper powder	10 5%	Copper powder	9 5%
	Carbowax ^R	7 5%	Carbowax ^R	6 5%
8	Zn(6% Hg)	43%	ZnO	45 5%
	KOH gel	36%	KOH gel	32%
	MgO	7%	MgO	3%
	Copper powder	7%	HgO	6 5%
	Carbowax ^R	7%	Copper powder	6 5%
9	Zn(6% Hg)	42%	ZnO	45%
	KOH gel	35 5%	KOH gel	32%
	MgO	6 5%	HgO	6 5%
	Copper powder	9 5%	Copper powder	10%
	Carbowax ^R	6 5%	Carbowax ^R	6 5%
10	Zn(3% Hg)	40 5%	ZnO	45%
	KOH (9M)	34 5%	KOH (9M)	32%
	Rice starch	3%	Rice starch	3%
	MgO	6%	HgO	3 5%
	Copper powder	9 5%	Copper powder	10%
	Carbowax ^R	6 5%	Carbowax ^R	6 5%

*KOH gel = 9M KOH + 4% Na-CMC

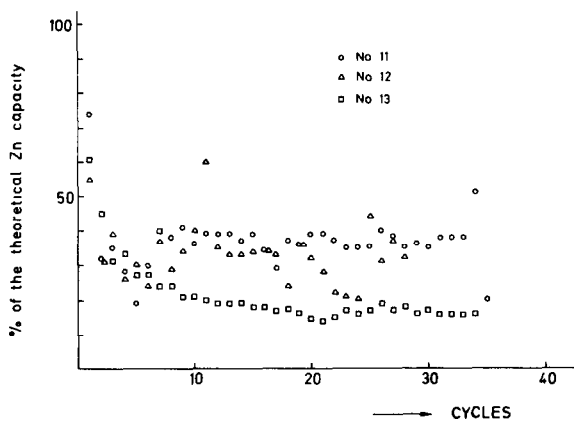


Fig 7 Capacity loss of zinc/zinc cells during cycling Experiments Nos 11 - 13

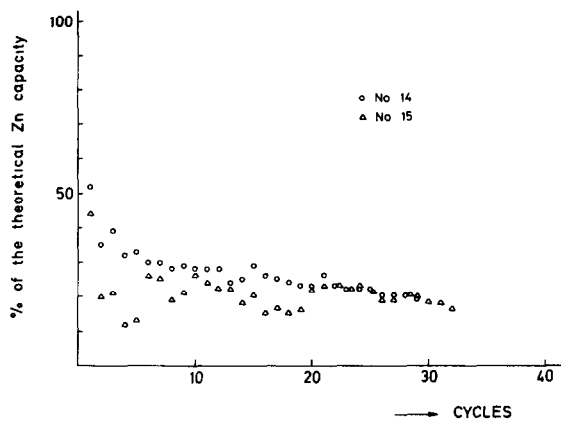


Fig 8 Capacity loss of zinc/zinc cells during cycling Experiments Nos 14 and 15

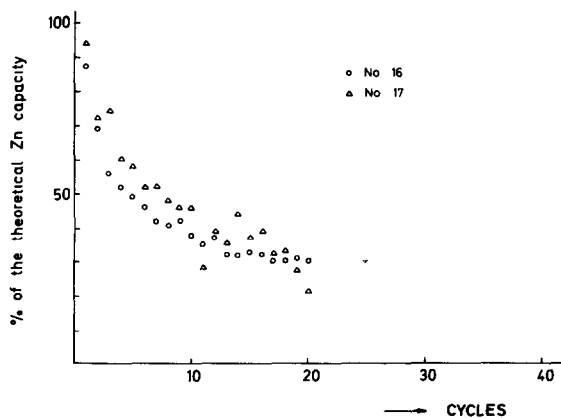


Fig 9 Capacity loss of zinc/zinc cells during cycling Experiments Nos 16 and 17

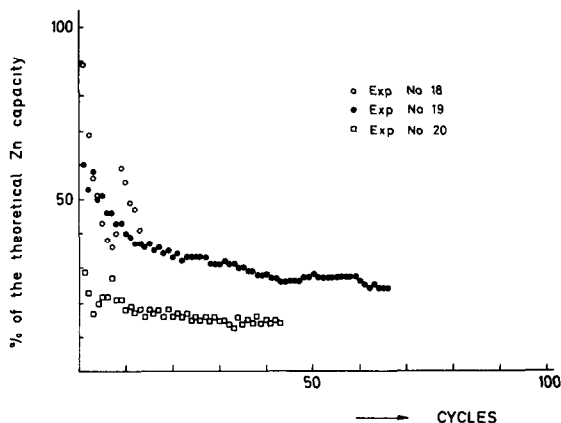


Fig 10 Capacity loss of zinc/zinc cells during cycling Experiments Nos 18 - 20

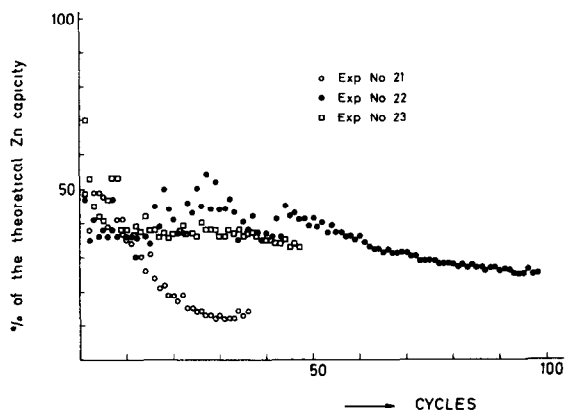


Fig 11 Capacity loss of zinc/zinc cells during cycling Experiments Nos 21 - 23

of the theoretical value. It was not possible to hold this level during the following cycles. Another additive enhancing the effect of the copper powder seemed to be necessary. This chemical could be chosen from a large variety of inorganic or organic compounds. Finally Carbowax (R) 200, a polyethylene glycol with a molecular weight of 200 was considered as useful. The high starting value of experiment No 17 was not reached again but it was possible to obtain a larger number of uniform cycles (Figs 10 and 11).

For experiments Nos 22 and 23, powdered rice starch was used as a gelling agent in place of Na-CMC. The electrodes of these experiments had the best cycling properties over a relatively long period (Fig. 11).

Discussion

The cycling of rechargeable zinc electrodes is known as a process having particular problems in each phase. If the charging step is considered to be

the first phase, a large area current collector must be provided. To obtain a zinc deposit of high activity and adherence to the current collector, several electrolyte additives are recommended in the literature to depress dendrite formation and short circuits. The kinetics of zinc electrodeposition and the morphology of the deposits have been thoroughly studied [5 - 7].

At the end of charge, the deposited zinc must be protected from the corrosive attack of the electrolyte (second phase). The classical method of amalgamation has been discredited in recent years on account of the environmental hazards of mercury. A number of other metals or metal compounds has been proposed to take its place.

The third phase of the cycling process is the redissolution of zinc on discharge and the formation of soluble and insoluble oxidation products. The main difficulty here is to obtain high currents without passivation of the zinc electrode. This is necessary to prevent severe zinc capacity losses in the cell. On the other hand, it is desirable to immobilize the oxidation products in the electrolyte to reduce the detrimental effect of shape change.

The considerable efforts to solve these problems are reflected in the electrode mixtures listed in Table 2. Starting with a composition without additives we soon arrived at very complex electrode mixtures. The beneficial effect of MgO has already been mentioned. The addition of potassium sulfate should prevent premature passivation of the zinc electrode. The positive results of other experiments [2] could not be verified over a longer cycling period.

Some experiments with non-amalgamated zinc showed the possibility of using electrodes free from mercury. Following the suggestions of Lee [8, 9], Povey and Turner [10], Himy and Wagner [11, 12], and McBreen and Gannon [13], lead was incorporated. The second additional component was sodium stannate. Different compounds of lead and tin are known for their ability to increase the hydrogen overvoltage of zinc. During the charging period, when zinc ions are reduced to metallic zinc, lead ions are also reduced and particles of metallic lead form a network having electric conductivity. The active area of the current collector is enlarged by this simple procedure. The oxides of cadmium and thallium which have also been proposed [11 - 13, 16] have not been tested because they seemed to be subject to similar objections to those of mercury.

To prevent a too wide expansion of the field of variable parameters we returned to the use of amalgamated zinc (6% Hg) and attempted to improve the electrodes by the addition of 2% of graphitized carbon fibres. This material was chosen because of its low specific weight and because it supposedly does not show substrate effects [14]. The results have not been very encouraging and, with regard to the results of other experiments [15], this development was stopped.

In place of graphite, copper powder was used for subsequent experiments. The use of powdered copper oxide or metallic copper was proposed by Kordesch [17] to increase the low temperature conductivity and rechargeable characteristics of zinc anodes for alkaline cells. His experiments showed

that metallic copper provided an even better matrix than lead for the redeposition of zinc when the cell was recharged. However, in experiment No 17, only the first discharge showed the expected high performance

Experiment No 18 and subsequent experiments were made with electrodes containing polyethylene glycol (Carbowax (R) 200) as an additional component. This chemical was found to depress dendrite formation and to give zinc deposits with good properties for use in rechargeable cells [18]. Other compounds belonging to this group showed similar effects. Recently, a detailed investigation of the electrochemical behaviour of ethylene glycol and its oxidative derivatives has been published [19, 20]

The addition of polyethylene glycol lowered the starting values and increased the number of discharges without a significant loss of capacity. Therefore this component was used for experiments 18 - 23, the last one of this series

Two further modifications were tested in experiments Nos 22 and 23 powdered rice starch was substituted for Na-CMC as a gelling agent, and the mercury content was lowered to 3% (based on zinc). The results can be seen in Fig 11. Other gelling agents with a sufficiently high stability (resistance to oxidation) are still under consideration.

Conclusion

The experiments confirmed that the proposed test cell was a workable instrument for testing zinc electrode mixtures. The test conditions are similar to the function of zinc electrodes in commercial rechargeable MnO_2 -Zn cells [21] with the exception that full discharge during each cycle is not common practice with commercial cells.

Considering the very stringent test conditions of complete discharge, the result of experiment No 22 (98 cycles) may be seen as promising for future developments.

In a series of 100 discharges, the cycling capacity of the MnO_2 cathode is only half used if the depth of discharge is limited to 25% [22]

Complete cells containing zinc electrode mixtures made in accordance with the tested compositions (Table 2) have been constructed.

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