JOURNAL OF APPLIED ELECTROCHEMISTRY **22** (1992) 95–98

Conductive fillers for immobilized alkaline zinc anodes

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Received 18 December 1990; revised 28 March 1991

Conductivity tests and cycling experiments have shown that the addition of a material which is conductive at its surface (not necessarily in the bulk) helps to improve the performance of a rechargeable powder-zinc anode gel. The most suitable geometry of the additive proved to be cylindrical with a length-to-diameter ratio of about 100 : 1 to 1000 : 1. A good material was short-cut polymer fibres which were metallized by means of an electroless plating process. In terms of accumulated cycle capacity an improvement of up to 20% could be achieved for a rechargeable alkaline C-size battery and even a simplification of the cell construction may be expected.

1. Introduction

In alkaline zinc/manganese dioxide batteries the useable cell capacity is exhausted as soon as the amount of metallic zinc in the anode gel decreases to about 30% weight [1, 2]. This point is indicated by a significant voltage drop of a cell under load.

Taking into account that the original anode gel contains 60% by weight, only one half of the zinc is consumed as an active electrode material. The remaining half of the zinc powder is disposed of, or collected for recycling, with the used battery.

With primary cells this may not be a big problem. Zinc powder is not expensive and the rejected fraction has done its work as an electronically conductive component of the anode mass.

The rechargeable version of the zinc/manganese dioxide-system requires a capacity limiting zinc anode which is only reliably working if a high and reproducible discharge process efficiency is guaranteed.

Establishing a conductive matrix in the anode space of the cell by admixing light-weight materials with good surface conductivity to the anode gel should improve the anode quality with respect to efficiency and cumulative capacity [3]. The conductive matrix may prevent the formation of isolated zinc particles without contact to the current collector during discharge (a function of particular importance in mercury-free cells) and on the other hand serve as a three-dimensional substrate for the zinc deposition on charge.

Geometries and materials (after suitable surface metallization) to be tested were: hollow microspheres and foamed grains (glass), short-cut staple fibres (glass, polymers), porous spheres or fibres (inorganic oxides).

2. Experimental details

2.1. *Preparation of conductive fillers*

The required surface conducting materials were prepared following [4–10]. In principle the non-conducting substrates (fibres, spheres, foam-balls) were degreased by treatment with dilute KOH, rinsed with water and activated with a solution of tin(II) chloride in a water/HCl mixture. The most common catalyst – palladium(II)chloride – was not applicable because of a possible contamination of the anode mixture with traces of this noble metal. Thus a complex solution of silver ions was used to catalyze the substrates. After this step of the plating process the materials were immersed in a solution consisting of a silver (ELS, electroless silver) or copper (ELC, electroless copper) salt, a complexing agent, HCHO and water. All these operations were performed in a simple beaker-cell equipped with a paddle stirrer.

Successful plating experiments could be obtained as indicated in Table 1.

The first inspection of the plated materials was done by checking the uniformity and brilliance of the

Table 1.

	Glass spheres	*Glass foam*	*Fibres made from*		
			Polyimide	*Polyester*	*Polyvinyl alcohol*
ELS	**	*	**	*	*
ELC	**	*	**	*	*

* Metal deposition of good quality
** Metal deposition of very good quality

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deposition under a stereo microscope (magnification up to 63 : 1). Simultaneously, the adherence of the produced metal coating to the substrate could be examined.

To determine the amount of metal in the final product small fractions of coated fibre were treated with nitric acid to dissolve the metal component. After adequate dilution the silver or copper concentration was measured by AAS. As a result of the low polymer densities, metal contents up to 81% were found.

2.2. *Conductivity tests*

The conductive materials were added to the commonly used anode mixture in amounts ranging from 0.1% to 2% and the conductivity of the paste obtained was measured using a test set up indicated in Fig. 1.

The final compositions were: zinc (Hoboken-Overpelt L305F/64, 3% Hg) + additive = 74%, zinc oxide = 4%, magnesium oxide = 0.7%, Carbopol = 1.3%, KOH (saturated with ZnO) = 20%.

The sample was inserted into a glass tube of known diameter and length, contacted with two piston-type electrodes and connected to a LCR-meter. The conductivities of pastes containing a conductive filler were compared with the conductivity of the standard mixture. One series of tests was conducted using anode mixtures before discharge and another series using exhausted ones.

It was expected that the effect of adding a conductive component to the mixture would be clearly visible in the case of the discharged anodes, where the contribution of zinc particles to the conductivity is dramatically reduced. Table 2 shows the results, confirming this assumption.

The most useful anode modification was done by adding copper or silver plated fibres. Glass spheres (GK), though perfectly metallized, showed a negative effect while foamed glass balls (Sikug) increased the conductivity of the mass significantly. This may be due to their high porosity, resulting in a quick uptake of electrolyte. The best geometry was represented by the fibres which were able to provide conductive links between zinc particles within a certain range.

2.3. *Cycling tests*

The positive effect of a conductive filler in a complete rechargeable manganese dioxide/zinc-cell had to be established by long term experiments. The most useful method of testing was cycling under the following conditions:

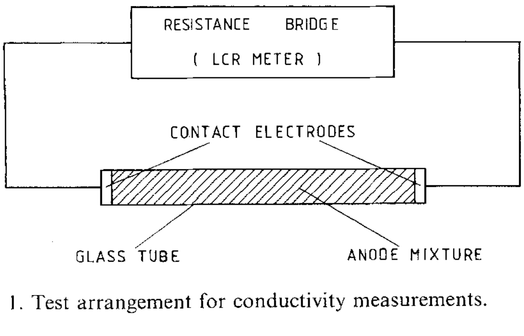

Fig. 1. Test arrangement for conductivity measurements.

Table 2.

Mixture	*Geometry*	*Conductivity* × 10^{-2} (Ω^{-1} cm^{-1})		
		After initial cycle	*After 35 cycles*	
Standard		4.3	2.9	C
			0.6	D
Lenz PI SC 5000 ELS	fibres	15.1		
Lenz PI SC 5000 ELC	fibres	13.6	8.9	C
(Conc.: 0.16%)			4.2	D
GK ELS (Conc.: 1.1%)	spheres	2.1		
GK ELC (1.1%)	spheres	1.8		
EMS PEs ELS (0.16%)	fibres	16.8		
Sikug ELC (2.15%)	foam	19.6		

C = Anode in charged condition; D = Anode in discharged condition.

Discharge: constant resistor load 3.9 Ω [11] cut-off voltage 0.9 V.
Charge: trickle charge, 1.72 V constant for 20 h.

The test cells were cylindrical LR-14 (C-size) batteries. The construction of these cells has been described elsewhere [12].

For reasons of test capacity cycling had to be limited to a period of about 40 days. The whole test program was done by a computer controlled device which was able to operate 48 batteries simultaneously. The charge/discharge currents and the cell voltages were measured every minute and the charge input/output was calculated subsequently. Any time when a battery was switched from charge to discharge or vice versa, a record of data concerning the charging/discharging procedure was printed.

3. Results and discussion

The results of the cycling tests are collected in Figs 2 to 8. The chosen form of presentation is a combination of plots of individual discharge capacities and cumulative discharge capacities versus cycle number.

These plots show clearly the effects of a variety of

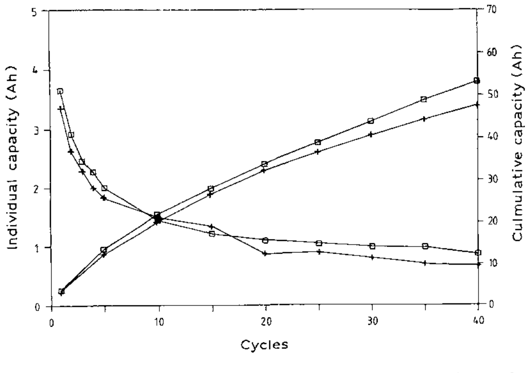

Fig. 2. Individual discharge capacity and accumulated (cumulative) cycle capacity against cycle number. (□) Batt. 275, std.; (+) batt. 289 GK. Additive: hollow glass spheres, copper plated; Conc.: 1.1% (GK ELC, standard).

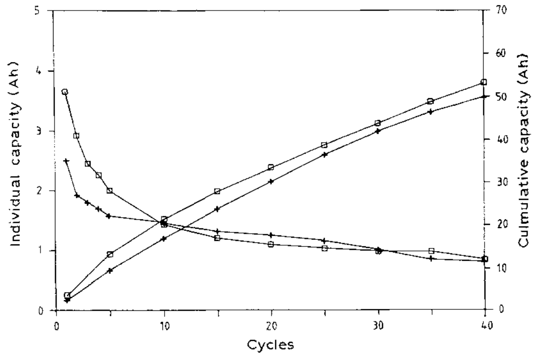

Fig. 3. Individual discharge capacity and accumulated (cumulative) cycle capacity against cycle number. (□) Batt. 275, std.; (+) batt. 287, SIKUG. Additive: glass foam balls, copper plated; Conc.: 4.0% (SIKUG ELC, standard).

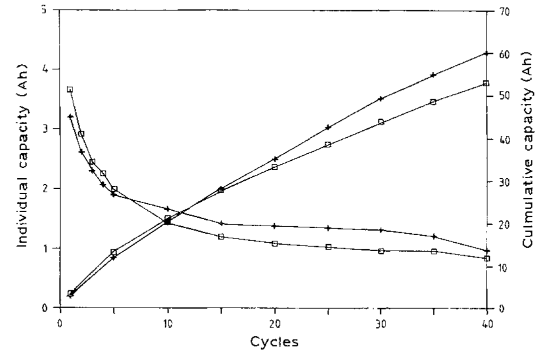

Fig. 4. Individual discharge capacity and accumulated (cumulative) cycle capacity against cycle number. (□) Batt. 275, std.; (+) batt. 283, PI fibres. Additive: polyimide fibres, silver plated; Conc.: 0.3% (PI fibres ELS, standard).

conductive fillers applied in different concentrations in the anode gel. The results of a cell with standard anode are given for comparison.

The least effective additives were silver or copper plated glass spheres (GK ELS, GK ELC), and copper plated glass foam balls (Sikug ELC) in concentrations up to 4% (Figs 2 and 3). A negligible improvement was given by 0.16% of silver plated polyester fibres (EMS PEs ELS).

The first positive results were obtained by adding 0.16% of silver or copper plated polyimide fibres (PI ELS, PI ELC). The nature of the metal used for metallization of the polmer seemed to be without visible influence.

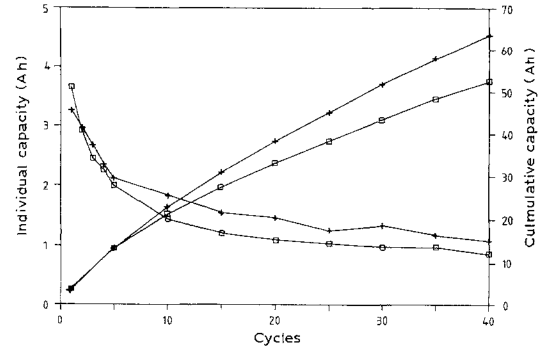

Fig. 5. Individual discharge capacity and accumulated (cumulative) cycle capacity against cycle number. (□) Batt. 275, std.; (+) batt. 285, PI fibres. Additive: polyimide fibres, copper plated; Conc.: 0.3% (PI fibres ELC, standard).

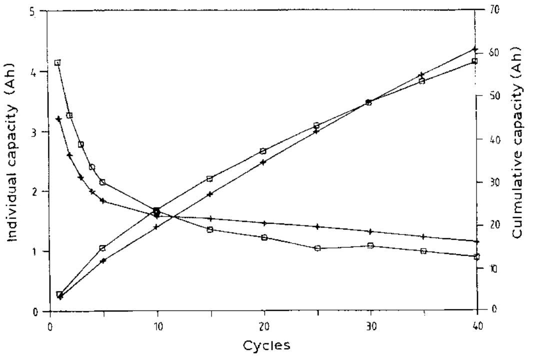

Fig. 6. Individual discharge capacity and accumulated (cumulative) cycle capacity against cycle number. (□) Batt. 291, std.; (+) batt. 293, PI fibres. Additive: polyimide fibres, silver plated; Conc.: 0.3% (PI fibres ELS, standard). No copper cage current collector.

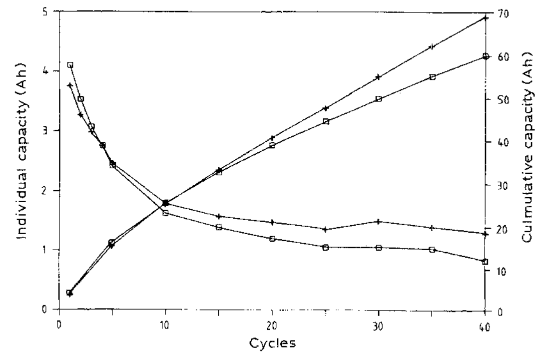

Fig. 7. Individual discharge capacity and accumulated (cumulative) cycle capacity against cycle number. (□) Batt. 301, std.; (+) batt. 300, PI fibres. Additive: polyimide fibres, silver plated; Conc.: 0.6% (PI fibres ELS, standard). No copper cage current collector.

Doubling the amount of conductive filler in the anode mass did not lead to a significant improvement in the case of the silver-plated material (Fig. 4). The effect of the copper-plated product was slightly increased (cumulative capacity) by this action (Fig. 5).

Encouraged by these observations an attempt was made to build a cell without the usual copper cage as the current collector [11]. It was shown that an amount of 0.3% of metal plated fibre was not sufficient to make the cell significantly better than the standard (Fig. 6).

As soon as the concentration of the metallized polymer (polyimide) fibre in the anode gel was raised to

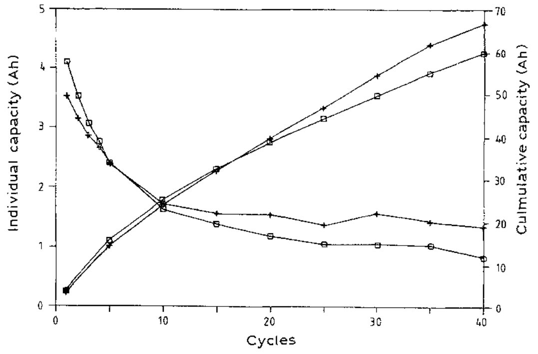

Fig. 8. Individual discharge capacity and accumulated (cumulative) cycle capacity against cycle number. (□) Batt. 301, std.; (+) batt. 298, PI fibres. Additive: polyimide fibres, copper plated; Conc.: 0.6% (PI fibres ELC, standard). No copper cage current collector.

0.6% the best results were achieved and the complicated copper cage-collector became obsolete (Fig. 7). Plating the fibres with copper instead of silver and applying the material in the same concentration resulted in a similar cell performance (Fig. 8).

Three different standards, batteries 275, 291 and 301 were chosen for comparison because the construction of the produced cells was changing with time and the actual standard should reflect the most recent developments.

4. Conclusion

Experimental work for increasing the anode gel conductivity in a rechargeable alkaline MnO_2/zinc cell has to deal with the following parameters: material and geometry of the additive, amount or concentration of additive, and the applied plating metal to give a sufficiently high surface conductivity.

Among these only the geometry and the concentration of the added particles were found to be important for the battery performance. The other parameters are only determining the production process. Conductivity tests and cycling experiments showed that the major influence is the geometry.

Metallized glass foam balls had to be supplied with a concentration of 2.15% while only 0.16% of metal covered fibres were used to achieve about the same conductivity in the anode mass (see Table 2).

Electrically conductive filaments showed the best ability to interconnect zinc particles in the anode gel thereby reducing the sensitivity of the anode efficiency on the applied discharge current density [1]. The result was a higher individual cycle capacity and a better accumulated discharge capacity with progressing cycle number.

Acknowledgement

The supply of fibre materials by Lenzing AG/Austria, EMS-Chemie AG/Switzerland, Steen & Co GmbH/Germany, and with glass particles by Schott AG/Germany is gratefully acknowledged.

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