

The invention relates to a galvanic primary cell of acid type, having a zinc anode containing metal additives which suppress zinc corrosion and improve mechanical dimensional stability, a depolarizing cathode and a gel electrolyte.

Application of the invention extends substantially to acid zinc/manganese dioxide cells (Leclanché) and zinc/oxygen cells.

In cells of this type, the zinc electrode is conventionally constructed as a cup or hollow cylinder which receives all the other active cell constituents (a manganese dioxide/soot mixture pressed around a carbon rod current collector as the cathode, electrolyte paste with separator as a carrier) in itself, and more rarely is constructed as a flat sheet in a layered cell structure.

According to R. Huber, "Trockenbatterien [dry batteries]", page 29 (VARTA Technical Handbook Series, Volume 2, 1972), the anode sheet is alloyed, in dependence on its type of preparation, with various quantities of lead and cadmium, it being possible for the lead content to reach 0.6%. The alloyed lead increases the ductility during the rolling and extrusion procedure, and in addition has a slightly inhibiting action on zinc corrosion. The addition of cadmium improves the mechanical strength of the shaped zinc parts during the battery manufacturing process.

As a typical soluble electrode, the zinc metal is dissolved in the battery on current removal in a manner increasing with duration of use.

In addition to this "useful" dissolution, however, merely with relatively long storage and to a greater extent with increased temperature, a slight self-dissolution of the zinc takes place. This is caused by the fact that, although the exchange of acid oxygen by zinc is kinetically inhibited, the separation of hydrogen takes place at too low a potential for dissolution to be halted. The gradual accumulation of hydrogen in the interior

of the cell results in an increase in pressure which, in unfavourable cases, results in deformations or even the emergence of electrolyte.

If hydrogen evolution and the dissolution of the zinc anode in the unloaded state are not suppressed, then in addition an undesirable loss of capacitance occurs.

The previously proven means of suppressing zinc corrosion and hydrogen evolution by increasing the hydrogen separation voltage is the addition of mercury to the zinc. However, this increases the number of elements contained in the zinc which are to be regarded as toxic and pollutant, together with the lead and cadmium already mentioned, to three.

For this reason, there has been no lack of proposals which intended to provide a substitute for at least the particularly toxic metals Hg and Cd. Thus, DE-B 1 086 309 describes a soluble electrode of high-grade zinc with the addition of indium metal, or DE-A 3 229 703 describes the use of indium and gallium as metals alloyed with the zinc.

JP-A 60-170751 (Toshiba Denchi K.K.) mentions the addition of Pb and Li to the zinc, while JP-A 60-32249 (Touhou Aen. K.K.) recommends alloying the zinc with at least 0.01% of Ag and further metals.

DE-A 3 605 718 discloses a primary cell of the type formulated at the outset, which contains a zinc anode made of high-grade zinc with an alloying additive of up to 0.6% of Pb.

Finally, JP-A 58-3204 provides a choice of a total of 14 elements, including lead, as alloying additives, without however mentioning certain elements or combinations thereof with others as being preferred, let alone specifying useful concentrations.

Taking into account a range of known alloy compositions of zinc

electrodes, which is summarized only incompletely here, the object of the invention is to improve the above-mentioned primary cell with the aid of non-toxic additives in particular to the zinc electrode such that it is of equal value with a conventional acid primary cell whereof the proper electrical functioning and electrode quality is achieved by accepting toxic means.

According to the invention, the object is achieved by means of a primary cell as specified in Claim 1.

In accordance with this it has been found that on the one hand the inhibiting effect of mercury can also be achieved if, instead of it, the metals indium and bismuth are added individually or in combination to the zinc, or salts thereof are added to the electrolyte solution, and if on the other hand the cadmium to which the zinc electrode owes its mechanical stability is replaced by magnesium and/or lithium. The doping metals can for this reason be both depositions on the zinc surface or, and indeed preferably, alloy constituents. The negative electrode of the primary cell according to the invention is thus made, in its general construction, of high-grade zinc with additives of at least one of the metals In and Bi and at least one of the metals Mg and Li.

However, it has proved to be advantageous if the zinc sheet additionally contains Pb, whereof the quantity is within the framework of the range figures specified by Huber for individual cup alloys. According to the invention, the anode zinc should contain 0.01 to 0.6% of Pb, preferably 0.02 to 0.1% of Pb.

Regardless of the optional addition of Pb, the other metal contents contained in the zinc should in accordance with the invention in each case lie within the following limits:

0.003 to 0.03% of In;
0.001 to 0.01% of Bi;
0.0001 to 0.002 of Mg;

0.001 to 0.01% of Li.

To demonstrate the effectiveness of the alloying additives according to the invention, test cells (A,B,C,D,E) were produced and subjected to various tests together with conventional or conventionally produced comparison cells (F,G). In the test cells, in accordance with the possible combinations specified in accordance with the invention, the following anode alloys were provided:

- A) Zn + 0.01% of In + 0.0005% of Mg
- B) Zn + 0.005% of In + 0.001% of Bi + 0.0003% of Mg
- C) Zn + 0.025% of Pb + 0.01% of In + 0.0003% of Mg
- D) Zn + 0.1% of Pb + 0.01% of In + 0.005% of Li
- E) Zn + 0.005% of Bi + 0.1% of Pb + 0.003% of Li

The comparison cells had an anode zinc comprising

- F) Zn + 0.25% of Pb + 0.06% of Cd
- G) Zn + 0.6% of Pb

The cathode materials, comprising electrolyte manganese dioxide, acetylene soot, zinc oxide and zinc chloride solution, were the same in all cells.

The separation between the anode and the cathode was provided by a conventional paper separator coated with gel.

The favourable result of the tests is expressed in four figure illustrations.

Figure 1 shows the resistance of cylindrical anode parts made of zinc alloys according to the invention, on mechanical deformation.

Figures 2, 3 and 4 show capacitance values of primary cells having zinc anodes according to the invention, under various

discharge conditions.

In detail, the bar chart according to Figure 1 illustrates the reduction in diameter which an anode annular cylinder for a primary cell having the IEC designation R 20 ($h = 61.5$ mm, $\phi = 34.2$ mm) undergoes under the mechanical energy effect of 0.5 joule (white bars) and 1.0 joule (hatched bars) respectively. The designations A to D and F, G relate to the zinc alloys defined above. The figures 0 to 80 marked on the Y axis of the chart show the degree of deformation D in %.

It can be seen from the bar lengths that the low-toxicity alloys A to D according to the invention are only negligibly inferior in their mechanical strength to the conventional alloys F and G.

In the bar charts 2 to 4, the designations A to G relate to test cells which differ only in the specified alloy compositions of their zinc anodes.

The capacitances K in Ah drawn are illustrated in dependence on the discharge process, namely

in Figure 2 a continuous 5.1 ohm discharge until a final voltage of 1.0 volts is achieved,

in Figure 3 a discharge in accordance with LIFT (Light Industrial Flashlight Test, i.e. 4 minutes per hour, 8 hours per day) of 2.2 ohms until a final voltage of 0.1 volts is reached, and

in Figure 4 an intermittent discharge of 4 h per day and 20 ohms until a final voltage of 0.9 volts is reached.

Here, all the white bars apply to freshly produced cells, and all the hatched bars apply to cells which are stored for 3 months at 45°C before the discharge tests.

As a whole, the electrical tests show that the low-toxicity

primary cells A to E according to the invention are at least equal to the comparison cells F and G with production zinc anodes as regards their capacitances. Consequently, it is possible to avoid not only mercury but, including already known Hg-free zinc alloys, also the highly toxic cadmium as an alloy metal, since according to the invention the corrosion-preventing role of mercury can be provided by indium and/or bismuth and the element-specific properties of cadmium and lead, which are more responsible for the mechanical behaviour of the zinc during processing, can be provided by magnesium and/or lithium. Here, a small remaining quantity of lead in the high-grade zinc, other than the stated replacement metals, can be advantageous.

The test results reproduced here could in principle be confirmed using further cells which, instead of the ZnCl_2 electrolyte, contains an NH_4Cl electrolyte, and whereof the cathode, instead of electrolyte manganese dioxide, was of natural manganese dioxide, so that what has been said in respect to the zinc alloys applies generally to all acid primary cells, whether zinc chloride or Leclanché cells.

Thus, the invention makes available an anode zinc which is comparable with the previous standard of quality as regards electrical power and storage capacity but which is "environment-friendly" as a result of the lack of toxic constituents.



Claims

1. Galvanic primary cell of acid type, having a zinc anode containing metal additives which suppress zinc corrosion and improve mechanical dimensional stability, a depolarizing cathode and a gel electrolyte, characterized in that the anode is made of high-grade zinc to which, instead of mercury, at least one of the metals indium and bismuth and, instead of cadmium, at least one of the metals magnesium and lithium is added, the quantities added respectively being:

0.003 to 0.03 % of indium

0.001 to 0.01 % of bismuth

0.0001 to 0.002 % of magnesium and

0.001 to 0.01 % of lithium.

2. Primary cell according to Claim 1, characterized in that lead is additionally added to the high-grade zinc as an alloy.

3. Primary cell according to Claim 1 or 2, characterized in that the quantity of lead additionally added to the high-grade zinc as an alloy is 0.01 to 0.6 %, preferably 0.02 to 0.1 %.