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(54) Title: ALLOYED ZINC POWDERS FOR ALKALINE BATTERIES WITH HIGH PYKNOMETER DENSITY

(57) Abstract: The invention describes alloyed zinc powders for alkaline batteries. The powders have a high pyknometer density as a consequence of the presence of only a limited quantity of pores. This high pyknometer density results in strongly reduced gassing after partial discharge of the powders. Also, a process for the manufacturing of a zinc alloy powder for alkaline batteries is disclosed, comprising the step of atomising a zinc alloy, characterised in that the atomising process has a flow rate of at least 700 kg/h, and preferably at least 1000, 1100 or even 1650 kg/h. In one embodiment, the atomising process is performed in a controlled atmosphere, wherein the oxygen content is less than 4 % by volume, and preferably between 0.2 and 3.5 %. The atomising process can be a centrifugal atomisation process. In the atomising process, the zinc alloy consists either of: a) 0.005 - 2 % by weight of indium, and 0.005 - 0.2 % by weight of either one of Al and Bi; or b) 0.005 - 2 % by weight of indium, and 0.005 - 0.2 % by weight of Bi, and 0.001 - 0.5 % of either one or both of Al and Ca; or c) 0.005 - 2 % by weight of either one or both of Bi and Al; and 0 - 0.5 % by weight of Pb, the remainder being zinc.

Alloyed zinc powders for alkaline batteries with high pyknometer density

The invention relates to alloyed zinc powders for alkaline batteries, and more particularly to zinc powders having a specific density as measured with a pyknometer, which allows to obtain superior properties.

Zinc alloy powders are used as anode active material in alkaline batteries. In these batteries, undesirable corrosion of zinc can lead to hydrogen formation, which is commonly referred to as 'gassing'. As the quantity of gas increases, the internal pressure inside the cells builds up with an ensuing risk for bulging or leaking. Moreover, gassing leads to increased cell impedance and to loss of capacity. For these reasons, battery producers require powders exhibiting the lowest possible gassing.

One must make a distinction here between two kinds of gassing: shelf life gassing and gassing after partial discharge.

Shelf life gassing is the kind of gassing which occurs in non-discharged batteries. This type of gassing can be measured by storing fresh cells for a certain time at a controlled temperature, and then opening the cells while collecting the hydrogen and determining its volume. An alternative method is to perform out-of-cell tests, in which non discharged zinc powders are brought in contact with alkaline electrolyte in special gassing vessels, whereby the gas generation is measured as a function of time. To accelerate these tests, they are performed at elevated temperature, usually at 45, 60 or 71 °C.

Partial discharge gassing, referred to as 'PD gassing', corresponds to gassing after partial discharge of the batteries. PD gassing can be measured by partly discharging a battery, storing it at for a certain time at a controlled temperature, and measuring the volume of gas that has formed. Here also, in- and out-of-cell tests can be used. One such method is described in US 5,364,715, which is incorporated here by reference. In this test, a zinc alloy anode is discharged under standardised conditions to 15% depth of discharge at 2.88 A for 161 minutes. The anode mix is then maintained at 71 °C for 24 h, whereupon its volume expansion, due to gas formation, is measured. The result is

expressed as a percentage of the original volume. This figure is further referred to as the 'gel expansion'.

Usually, the PD gassing rate is significantly higher than the shelf life gassing rate. This is for instance illustrated in Figure 1, which shows the influence of the discharge time on PD gassing for LR14 batteries. The chart shows gas volumes (in ml) measured in LR14 batteries after storage during 7 days at 71 °C versus the partial discharge time in hours. The upper line is for a Zn alloy with 500 ppm Pb and 500 ppm Bi, the middle line is for an alloy with 500 ppm Bi and 60 ppm In, the lower line is for an alloy with 500 ppm Bi, 500 ppm In and 70 ppm Al. The discharge time is expressed in hours of discharge over a 2-Ohm resistor, the gassing is expressed in ml of gas. Gassing after discharge is clearly much higher than gassing in the non-discharged state. For this reason, battery producers pay much attention to PD gassing, and consider the amount of PD gassing as a key parameter that is to be minimised.

Several patents and patent applications claim powders showing low PD gassing, methods to make such powders, or cells containing them. In US 5,364,715, an electrochemical cell is disclosed containing a zinc gel showing a gel expansion of less than 25%. Preferably, the gel expansion should be lower than 20%, and even more preferably less than 15%. US 5,364,715 teaches that the lower the gel expansion, the lower the gassing in the cell and thus the longer the lifetime of the cell before leaking occurs.

Methods to make powders exhibiting low PD gassing are for instance given in WO 00/48260, describing centrifugal atomisation of Zn alloy powders, and in WO 2004/012886, describing impulse atomised powders. In US 2003/0203281 A1, a zinc powder or zinc alloy powder in which 60 to 100% of the particles have a diameter of from 40 to 140 µm is disclosed. According to the inventors, such powders show very good PD gassing. Several patents claim powder compositions showing low PD gassing. Pb, Bi, In, Al, Ca, Mg, Li, Ga are the alloying elements most often quoted, but alloys containing other elements are also claimed. Organic or inorganic additives can further improve PD gassing. Examples of such patents are EP 0457354, DE 4329431, WO 96/06196, and BE 1008715. As some impurities can increase gassing, several

patents such as EP 0500313, US 5,108,494, JP 05-166507, US 5,321,476, and US 5,425,798 claim low impurity levels.

Using or combining the methods described in the prior art, zinc powder producers
5 presently can make powders with an admissible PD gassing rate. However, many battery producers still strive to further decrease gassing, because they want to further limit the risk of cell leakage, while ensuring increased capacity in intermittent discharge regimes. From an alternative point of view, cheaper but less pure zinc could be tolerated if the intrinsic PD gassing of the powder is further reduced. Also, the use
10 of powders with lower PD gassing could allow decreasing or even eliminating additives to the anode. Some of these additives, like indium salts, are expensive indeed. Others, like organic additives, can impact negatively on battery capacity and shock resistance. For all these reasons, every further decrease in PD gassing is a technical improvement that can result in a better or cheaper battery.

15 The present invention provides for zinc alloy powders showing markedly improved PD gassing, based on a correlation between PD gassing and 'pycnometer density'. The density of a material is the ratio between the weight of that material and its volume. The weight of a subject can easily be measured. For complex shapes, like zinc
20 powders, a pycnometer is used to determine the volume. The measuring method is detailed further on. Knowing the weight and volume of zinc powder, its density can be calculated. This density is called the absolute pycnometer density.

The bulk density of massive zinc is 7.14 kg/l. Alloyed zinc powders for battery
25 applications usually only contain some hundreds of ppm of alloying elements. This does not significantly affect the density of the zinc. It was however found that the absolute pycnometer density of zinc powders is often significantly lower than the bulk density of 7.14 kg/l. This can be explained by the presence of closed pores in the zinc powder, and of irregularities on the surface of the zinc powder, called open pores,
30 which are not filled with water during the determination of the zinc powder volume. It is assumed that these pores play an important role in determining the electrochemical behaviour of the powders in batteries.

Instead of expressing the density in terms of the absolute pyknometer density, it is here preferred to express it as a relative figure, defined as the ratio of the absolute pyknometer density to the bulk density of zinc, expressed as percentage. For instance, if an absolute pyknometer density of 6.783 kg/l is measured, the (relative) pyknometer density is determined as 95.0%.

In this invention, a zinc-based alloy powder for alkaline batteries is disclosed, having a pyknometer density of more than 95% of the bulk density of the alloy. In preferred embodiments, the pyknometer density exceeds 96%, 97%, 98%, 98,5% or even 99%.

The zinc-based alloy powder according to the invention is characterised in that it contains 0.005% - 2% by weight of one or more of Pb, Bi, In, Al, Ca, Mg, and Ga. Preferably the zinc alloy contains 0.005 - 0.05% by weight of one or more of Pb, Bi, In, Al, Ca, Mg, Ga. The most preferred zinc alloys contain only Bi and In, preferably combined with Al.

In another embodiment, an alkaline battery is claimed containing a zinc-based alloy powder according to the invention as described above.

Also, a process for the manufacturing of a zinc alloy powder for alkaline batteries is disclosed, comprising the step of atomising a zinc alloy, characterised in that the atomising process has a flow rate of at least 700 kg/h, and preferably at least 1000, 1100 or even 1650 kg/h. In one embodiment, the atomising process is performed in a controlled atmosphere, wherein the oxygen content is less than 4% by volume, and preferably between 0.2 and 3.5%. The atomising process can be a centrifugal atomisation process.

In the atomising process, the zinc alloy consists either of:

- (a) 0.005 - 2% by weight of indium, and 0.005 - 0.2% by weight of either one of Al and Bi; or
- (b) 0.005 - 2% by weight of indium, and 0.005 - 0.2% by weight of Bi, and 0.001 - 0.5% of either one or both of Al and Ca; or
- (c) 0.005 - 2% by weight of either one or both of Bi and Al; and 0 - 0.5% by weight of Pb, the remainder being zinc.

In another embodiment, a zinc alloy powder for alkaline batteries is claimed, in particular having pyknometer densities cited above, and comprising 0.005 - 2% by weight of In, 0.005 - 0.2% by weight of Al, 0.005 - 0.2% by weight of Bi, and 0.0025 - 0.5% by weight of Pb, the remainder being zinc, which is characterised in that the gel expansion of a zinc alloy anode of an alkaline battery comprising said powder, which is discharged to 15% depth at 2.88 A for 161 minutes and thereafter stored for 24 h at 71 °C, is less than 2.7%, and preferably less than 2.5%, expressed as a percent of the original volume.

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Similarly, for a zinc alloy powder comprising 0.005 - 2% by weight of In, 0.005 - 0.2% by weight of Bi, and 0.0025 - 0.0050% by weight of Pb, the remainder being zinc, a gel expansion of a zinc alloy anode of less than 5.5%, and preferably less than 5.2% is claimed.

15 Also, for a zinc alloy powder comprising 0.005 - 2% by weight of In, 0.005 - 0.2% by weight of Al and 0.005 - 0.2% by weight of Bi, the remainder being zinc, a gel expansion of a zinc alloy anode of less than 1.5%, and preferably less than 1.35% is claimed.

20 For each of the zinc alloy powders cited hereabove, preferably they comprise less than 500, or even less than 250 ppm of each of Bi, In and Al.

Surprisingly, the inventors found that a higher pyknometer density entails a lower PD gassing for a given alloy composition and particle size distribution. The zinc powder producer thus must use suitable conditions to produce powders with high pyknometer density, which is a measure for the presence of closed or open pores in the Zn powders. To reach this goal, the manufacturer can optimise different atomising techniques (air atomisation, centrifugal atomisation, gas atomisation with controlled gas composition), and atomisation conditions (shape and configuration of atomisation equipment, flow rate of gas and zinc alloy, temperature of zinc alloy and gas, cooling conditions) in known ways.

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Some alloying elements increase pyknometer density, and, by this, lower PD gassing. It has however to be kept in mind that alloying elements may also impact PD gassing through electrochemical mechanisms. Thus the combination of the impact of alloying element on soundness of structure and on hydrogen overvoltage has to be considered.

- 5 To illustrate this, the addition of Bi was investigated. In a certain range of concentrations, Bi lowers the pyknometer density, but nevertheless a decreased PD gassing is observed: the electrochemical effect of Bi, greatly increasing the hydrogen overvoltage in the considered range of concentrations, predominates.
- 10 Other elements like Fe, Sb, As, Ge and other well known impurities in zinc do not influence pyknometer density in their usual concentrations, but do increase gassing by lowering the hydrogen overvoltage. Preferably, the zinc powder producer will use zinc with a very low content of these impurities to obtain powders with low PD gassing. From another point of view however, the zinc powder producer might use less pure
- 15 and thus less expensive zinc by using the present invention, and yet obtain an acceptable PD gassing level.

The invention will now be illustrated by the following examples. Zinc powders were made by air atomisation, atomisation with gas with controlled oxygen content (% O₂)

20 and centrifugal atomisation (CA) using SHG zinc of 99.995% purity suitable for battery applications according to the prior art. Alloying elements like Bi, In, Al, Ca or combinations of them of the same or higher purity level were added. After atomisation, the powders were sieved to take away the coarse fraction, typically using a sieve of 420, 500 or 720 µm. Some of the powders were also sieved on a fine sieve (25, 45, 87

25 or 106 µm).

PD gassing was measured using the method described in US 5,364,715, and expressed as percent gel expansion. Pyknometer density was measured using a 100 ml pyknometer flask with ground-in thermometer and capillary side tube, as sold by VWR

30 International (under ref. brnd43438). Figure 2 shows a schematic drawing of such a pyknometer, wherein A is a flask of 100 ml approximately, B a thermometer, F a ground glass cover, and G a socket. Densities were measured at 20 °C, using the following two steps.

1. Determination of the pyknometer volume (V_p) using de-aerated distilled water. According to ASTM D854-02, density of this water at 20 °C is 0.99821 kg/l. The volume of the pyknometer thus can be determined by weighing it on an analytical balance before and after filling it with water, and dividing the weight difference by the
5 density of the water.

2. Determining the pyknometer density of a zinc powder as follows:

- Weighing the empty pyknometer (W_1);
- Adding approximately 45 g of the zinc powder into the pyknometer and weighing (W_2);
- 10 - Filling the pyknometer with water to above the zinc powder level and stirring the content of the pyknometer to remove entrapped air;
- Fully filling the pyknometer with water and weighing (W_3).

The weight of the zinc powder is $W_2 - W_1$; the total weight of the water is $W_3 - W_2$;
15 the total volume taken by this water is $V_w = (W_3 - W_2) / 0.99821$.

The absolute pyknometer density is calculated as $(W_2 - W_1) / (V_p - V_w)$; the (relative) pyknometer density, defined as a percentage of the bulk density of zinc, is $(W_2 - W_1) / (V_p - V_w) / 7.14 * 100$.

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Example 1

Zinc powders with 230 ppm Bi and 160 ppm In were atomised with a mixture of N_2 and O_2 containing 0.6 or 2.35% O_2 , and with air (20.9% O_2). Before atomising, the gas mixture was blown sufficiently long in the atomising chamber to obtain a gas
25 composition corresponding with the composition of the atomising gas. The flow rate of the zinc alloy was 720 kg/h. In Table 1 the obtained pyknometer density and gel expansion are given.

Table 1: Pyknometer density and gassing for alloy with, in ppm, 230 Bi and 160 In

% O_2	0.6	2.35	20.9
Pyknometer density (%)	97.9	94.3	93.3
Gel expansion (%)	2.47	5.48	26

It is obvious from this example that choosing atomising conditions that yield a high pyknometer density results in powders with low PD gassing.

5 Example 2

Zinc powders with 40 ppm Pb, 100 ppm Bi, 200 In and 100 ppm Al were atomised with a mixture of N₂ and O₂ containing 0.6% O₂ and 2.35% O₂. The flow rate of the zinc alloy was 750 kg/h. The atomising conditions were the same as in Example 1. The following results were obtained:

10

Table 2: Pyknometer density and gassing for alloy with, in ppm, 40 Pb, 100 Bi, 200 In and 100 Al

% O ₂	0.6	2.35
Pyknometer density (%)	99.5	98.1
Gel expansion (%)	1.94	2.91

Again, the choice of atomising conditions that increases the pyknometer density decreases PD gassing. Moreover, a comparison of the results obtained in Examples 1 and 2 teaches that choosing an alloy that yields a higher pyknometer density for the same atomising conditions results in a lower gel expansion.

20 Example 3

Zinc powders with 230 ppm Bi and 160 ppm In were atomised by centrifugal atomisation (CA). Process variables were flow rate of zinc (700 - 1000 kg/h) and percent oxygen in the atomising chamber (1.5 - 2% O₂). Table 3 below summarises the results obtained. An increase in zinc flow rate, and a decrease in oxygen content increase pyknometer density, and as a result decrease PD gassing. This example shows that it is possible of obtaining a pyknometer density of at least 98% for zinc powders that are only alloyed with Bi and In.

Table 3: Pyknometer density and gassing for alloy with, in ppm, 230 Bi and 160 In

Flow rate	Pyknometer density (%)		Gel expansion (%)	
	1.5% O ₂	2% O ₂	1.5% O ₂	2% O ₂
700 kg/h	98.4	97.7	4.99	7.87
1000 kg/h	99.2	98.75	4.90	6.77

Example 4

- 5 Zinc powders with 40 ppm Pb, 100 ppm Bi and 160 ppm In were atomised by CA in an atmosphere with 2% oxygen at flow rates of zinc of 700 and 1000 kg/h. Table 4 shows the results obtained.

Table 4: Pyknometer density and gassing for alloy with, in ppm, 40 Pb, 100 Bi and 160 In

Flow rate	Pyknometer density (%)	Gel expansion (%)
700 kg/h	97.6	7.87
1000 kg/h	98.7	6.27

Again, an increased flow rate leads to a higher pyknometer density and a lower gel expansion. The example shows that it is possible of obtaining a pyknometer density of at least 97.5% for zinc powders which are only alloyed with Pb, Bi and In.

Example 5

Zinc powders with 40 ppm Pb, 160 ppm Bi and 160 ppm In were atomised by CA in an atmosphere with 2.45% O₂, at flow rates of zinc of 1100 and 1650 kg/h. The following results were obtained.

Table 5: Pyknometer density and gassing for alloy with, in ppm, 40 Pb, 160 Bi and 160 In

Flow rate	Pyknometer density (%)	Gel expansion (%)
1100 kg/h	98.4	7.15
1650 kg/h	99.1	5.69

Here also, an increased flow rate leads to a higher pyknometer density and a lower gel expansion.

5 Example 6.

Zinc powders with 100 ppm Bi and 160 ppm In were atomised by CA in an atmosphere with 2.45% oxygen at flow rates of 1100 and 1650 kg/h. Table 6 summarises the results obtained.

10 Table 6: Pyknometer density and gassing for alloy with, in ppm, 100 Bi and 160 In

Flow rate	Pyknometer density (%)	Gel expansion (%)
1100 kg/h	98.7	10.59
1650 kg/h	99.1	9.22

Again, an increased flow rate leads to a higher pyknometer density and a lower gel expansion.

15 Example 7

Zinc powders with 40 ppm Pb, 100 ppm Bi and 160 ppm In were atomised by CA in an atmosphere with 2.45% oxygen at flow rates of 1100 and 1650 kg/h. Table 7 summarises the results obtained.

20 Table 7: Pyknometer density and gassing for alloy with, in ppm, 40 Pb, 100 Bi and 160 In

Flow rate	Pyknometer density (%)	Gel expansion (%)
1100 kg/h	99.1	8.63
1650 kg/h	99.5	5.17

In this experiment also, an increased flow rate leads to a higher pyknometer density and thus to a lower gel expansion.

Example 8

Zinc powders with 40 ppm Pb, 100 ppm Bi, 200 ppm In and 100 ppm Al were atomised by CA in an atmosphere with oxygen ranging from 1 to 6.25%, at a flow rate of 1650 kg/h. Table 8 summarises the results.

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Table 8: Pyknometer density and gassing for alloy with, in ppm, 40 Pb, 100 Bi, 200 In and 100 Al

% O ₂	1.0	1.75	2.45	3.25	4.0	4.75	5.5	6.25
Pyknometer density (%)	99.3	98.6	97.9	97.8	97.3	97.1	96.5	96.4
Gel expansion (%)	0.68	1.35	2.47	3.07	5.61	9.16	17.62	30.91

A decrease in oxygen content leads to an increased pyknometer density, and to a decreased PD gassing.

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Example 9

Zinc powders with 100 ppm Bi, 200 ppm In and 90 ppm Al were atomised by CA in an atmosphere with oxygen ranging from 1 to 5.5%, at a flow rate of 1650 kg/h. Table 9 summarises the results.

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Table 9: Pyknometer density and gassing for alloy with, in ppm, 100 Bi, 200 In and 90 Al

% O ₂	1.0	1.75	2.45	3.25	4.0	4.75	5.5
Pyknometer density (%)	99.8	99.2	99.0	99.1	98.9	98.6	98.7
Gel expansion (%)	1.07	1.32	1.32	3.34	10.73	17.69	20.05

A decrease in oxygen content leads to an increased pyknometer density, and to a decreased PD gassing.

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Claims

1. A zinc-based alloy powder for alkaline batteries having a pyknometer density of more than 95% of the bulk density of the alloy.
- 5 2. A zinc-based alloy powder according to claim 1, having a pyknometer density of more than 96% of the bulk density of the alloy.
3. A zinc-based alloy powder according to claim 2, having a pyknometer density of more than 97% of the bulk density of the alloy.
- 10 4. A zinc-based alloy powder according to claim 3, having a pyknometer density of more than 98% of the bulk density of the alloy.
- 15 5. A zinc-based alloy powder according to claim 4, having a pyknometer density of more than 99% of the bulk density of the alloy.
6. A zinc-based alloy powder according to anyone of claims 1 - 5, characterised in that the zinc alloy contains 0.005% - 2% by weight of one or more of Pb, Bi, In, Al, Ca, Mg, and Ga.
- 20 7. A zinc-based alloy powder according to claim 6, in which the zinc alloy contains 0.005 - 0.05% by weight of one or more of Pb, Bi, In, Al, Ca, Mg, Ga.
- 25 8. A zinc-based alloy powder according to claims 6 or 7, in which the zinc alloy is alloyed with only Bi and In, and preferably also Al.
9. Alkaline battery containing a zinc-based alloy powder according to anyone of claims 1 to 8.
- 30 10. A process for the manufacturing of a zinc alloy powder for alkaline batteries, comprising the step of atomising the zinc alloy, characterised in that the atomising process has a flow rate of at least 700 kg/h.

11. A process according to claim 10, wherein the atomising process has a flow rate of at least 1000 kg/h.
- 5 12. A process according to claim 11, wherein the atomising process has a flow rate of at least 1100 kg/h.
13. A process according to claim 12, wherein the atomising process has a flow rate of at least 1650 kg/h.
- 10 14. A process according to anyone of claims 10 - 13, wherein the atomising process is performed in a protective atmosphere, wherein the oxygen content is less than 4% by volume.
- 15 15. A process according to claim 14, wherein the oxygen content is between 0.2 and 3.5% by volume.
16. A process according to claims 14 or 15, wherein the atomising process is a centrifugal atomisation process.
- 20 17. A process according to anyone of claims 10 - 16, wherein the zinc alloy consists either of
- (a) 0.005 - 2% by weight of In, and 0.005 - 0.2% by weight of either one of Al and Bi; or
- 25 (b) 0.005 - 2% by weight of In, and 0.005 - 0.2% by weight of Bi, and 0.001 - 0.5% of either one or both of Al and Ca; or
- (c) 0.005 - 2% by weight of either one or both of Bi and Al;
- and 0 - 0.5% by weight of Pb, the remainder being zinc.
- 30 18. A zinc alloy powder for alkaline batteries, in particular according to anyone of claims 1 to 5, comprising 0.005 - 2% by weight of In, 0.005 - 0.2% by weight of Al, 0.005 - 0.2% by weight of Bi, and 0.0025 - 0.5% by weight of Pb, the remainder being zinc, characterised in that the gel expansion of a zinc alloy anode of an alkaline battery

comprising said powder, which is discharged to 15% depth at 2.88 A for 161 minutes and thereafter stored for 24 h at 71 °C, is less than 2.7%, and preferably less than 2.5%, expressed as a percent of the original volume.

- 5 19. A zinc alloy powder for alkaline batteries, in particular according to anyone of claims 1 to 5, comprising 0.005 - 2% by weight of In, 0.005 - 0.2% by weight of Bi, and 0.0025 - 0.0050% by weight of Pb the remainder being zinc, characterised in that the gel expansion of a zinc alloy anode of an alkaline battery comprising said powder,
10 24 h at 71 °C, is less than 5.5%, and preferably less than 5.2%, expressed as a percent of the original volume.

20. A zinc alloy powder for alkaline batteries, in particular according to anyone of claims 1 to 5, comprising 0.005 - 2% by weight of In, 0.005 - 0.2% by weight of Al
15 and 0.005 - 0.2% by weight of Bi, the remainder being zinc, characterised in that the gel expansion of a zinc alloy anode of an alkaline battery comprising said powder, which is discharged to 15% depth at 2.88 A for 161 minutes and thereafter stored for 24 h at 71 °C, is less than 1.5%, and preferably less than 1.35%, expressed as a percent of the original volume.

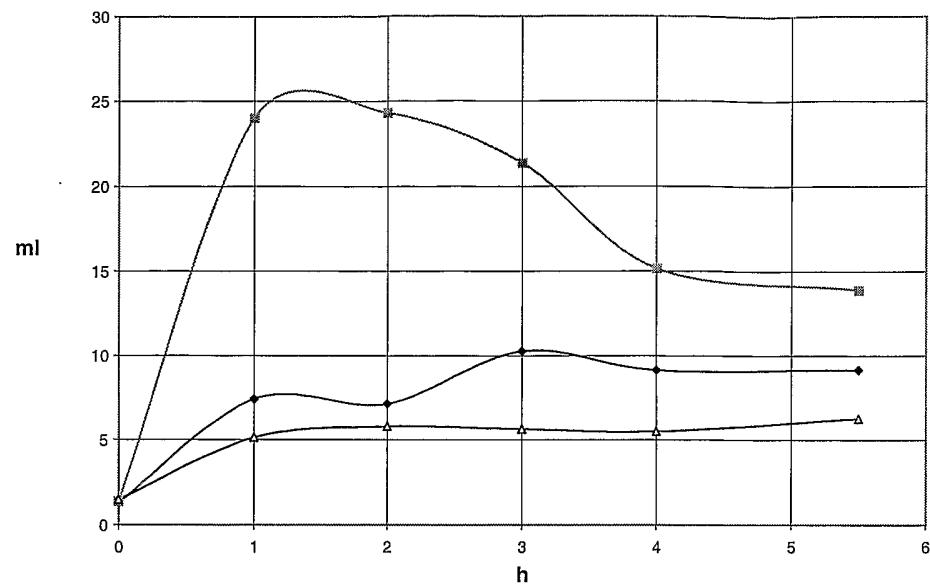


Fig. 1

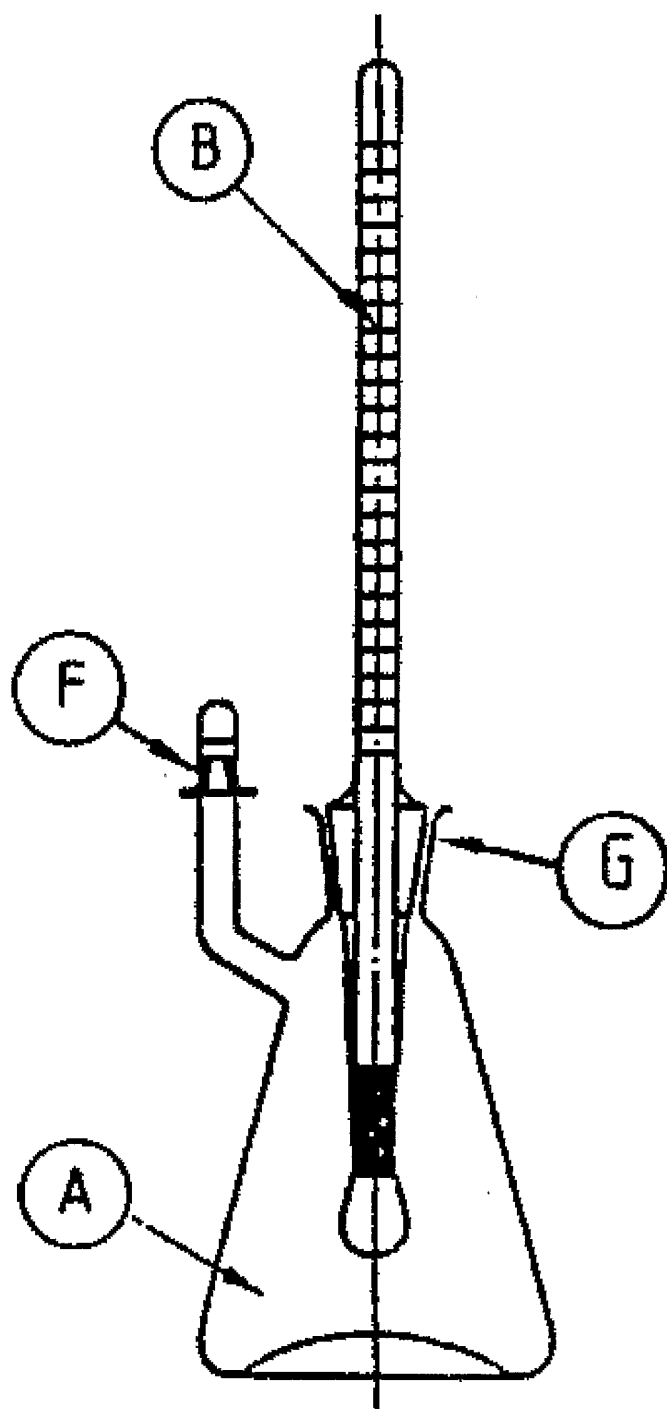


Fig. 2

INTERNATIONAL SEARCH REPORT

International application No
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A. CLASSIFICATION OF SUBJECT MATTER H01M4/42 H01M4/24 B22F9/10 B22F9/08		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) H01M B22F		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, PAJ, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 07 245103 A (MITSUI MINING & SMELTING CO LTD) 19 September 1995 (1995-09-19) paragraphs '0019!', '0029!', '0042!; table 1 -----	1-20
X	US 2004/115532 A1 (MALSERVISI MARTIN ET AL) 17 June 2004 (2004-06-17) paragraphs '0017!', '0024!; tables 1-3,6 -----	1-9, 18-20
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☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
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Date of the actual completion of the international search 2 March 2006		Date of mailing of the international search report 13/03/2006
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