

[72] Inventors Toshiso Kamai;
Sumio Uchida, both of Ibaraki, Japan
[21] Appl. No. 874,994
[22] Filed Nov. 7, 1969
[45] Patented Nov. 2, 1971
[73] Assignee Hitachi Makuseru Kabushiki Kaisha, also
known as Hitachi Maxell, Ltd.
Osaka Prefecture, Japan
[32] Priority Aug. 12, 1965
[33] Japan
[31] 40/49310
Continuation-in-part of application Ser. No.
571,907, Aug. 11, 1966, now abandoned.

[50] Field of Search..... 136/30, 31,
102, 107, 125-127, 6, 14, 111, 20, 95, 120, 64

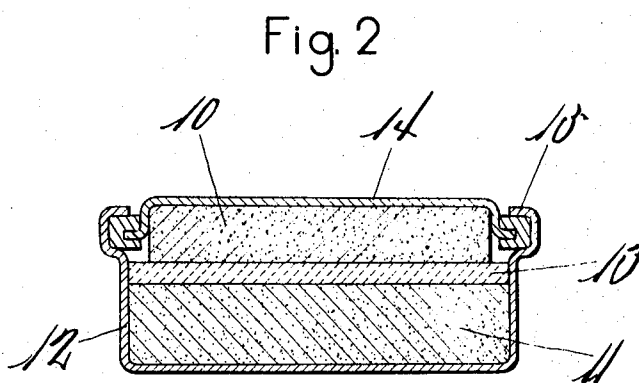
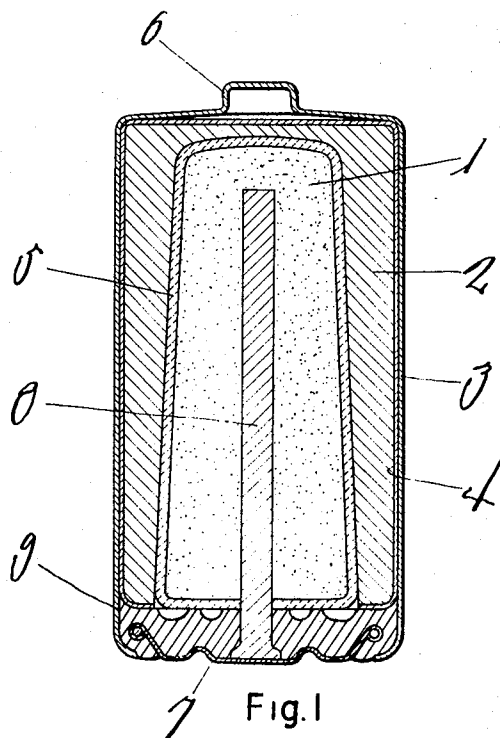
References Cited			
UNITED STATES PATENTS			
2,422,045	6/1947	Ruben	136/107
2,862,987	12/1958	Morgan	136/111
2,945,078	7/1960	Chapman et al.	136/30 X
3,253,959	5/1966	Jones	136/107
3,288,651	11/1966	Linton	136/107
3,367,801	2/1968	Kreiselmaier	136/125 X

Primary Examiner—Winston A. Douglas
Assistant Examiner—A. Skapars
Attorney—Wenderoth, Lind and Ponack

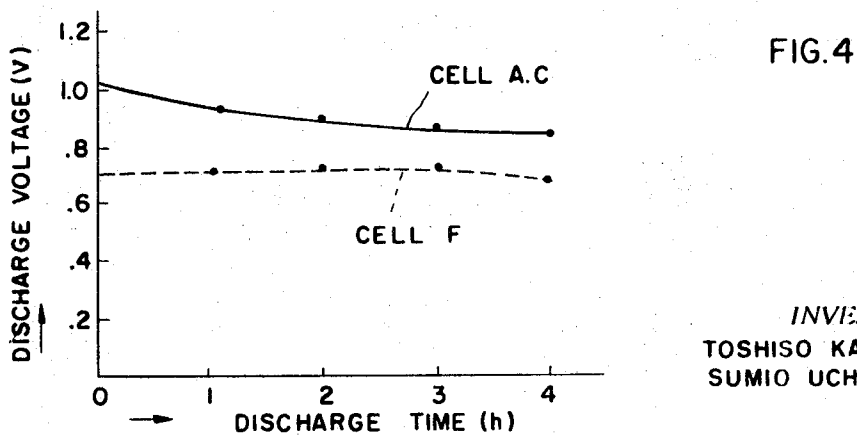
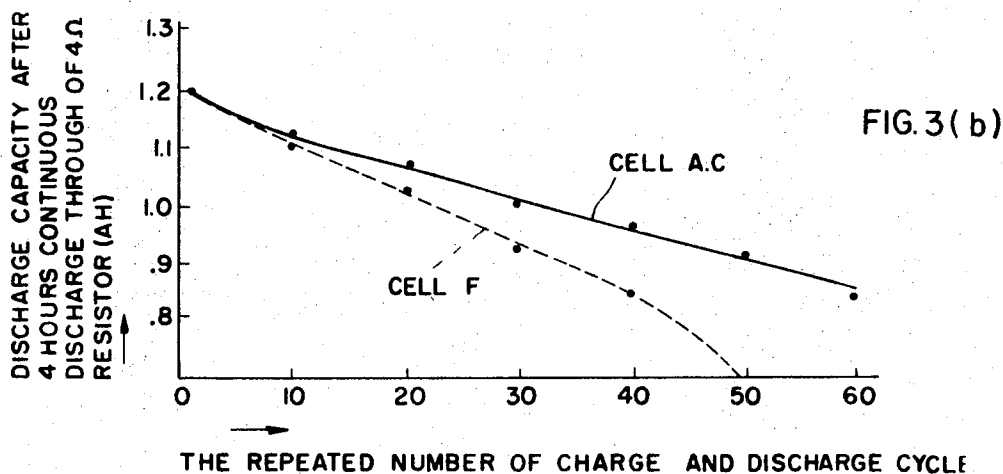
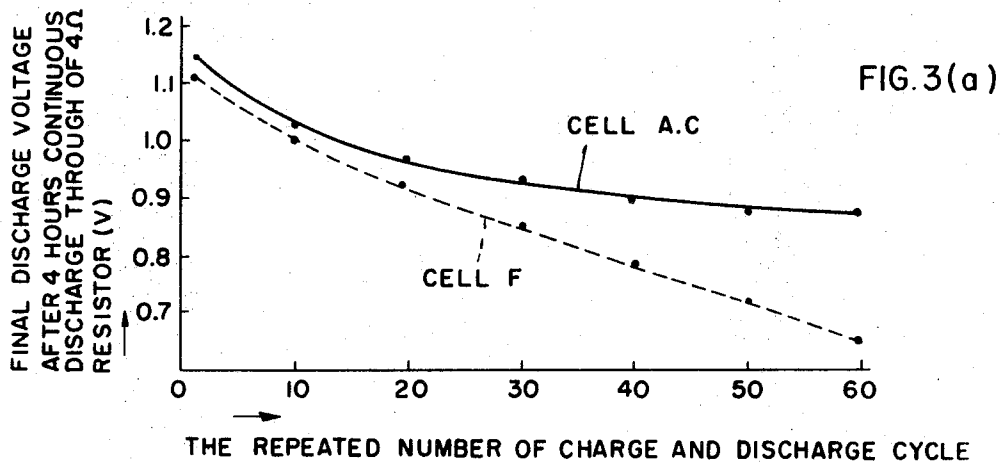
[54] ZINC ALKALINE SECONDARY CELL
6 Claims, 14 Drawing Figs.
[52] U.S. Cl..... 136/30,
136/107, 136/111, 136/125
[51] Int. Cl.....H01m 43/02

ABSTRACT: Improved zinc-alkaline secondary cells are provided by distributing throughout a zinc amalgam anodic body a substance selected from the group consisting of gold, silver, tin, alloys thereof, gold and silver oxides and hydroxides and mixtures of said substances.

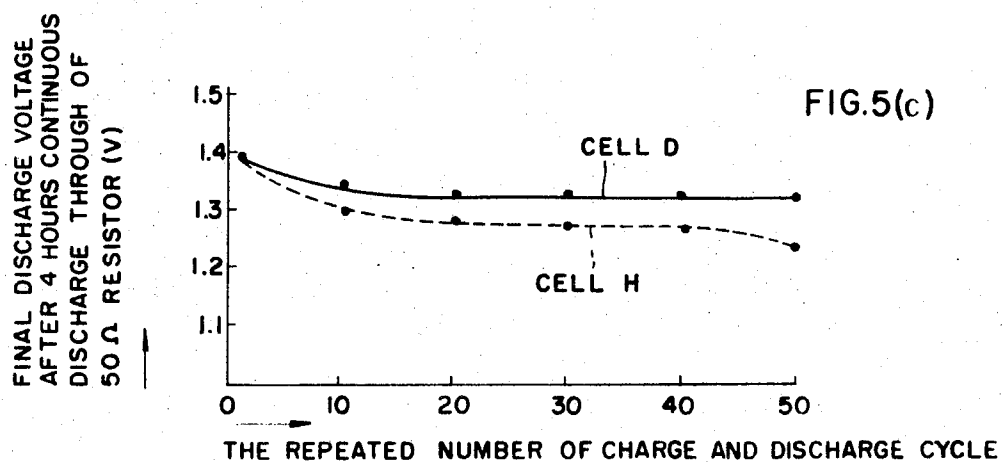
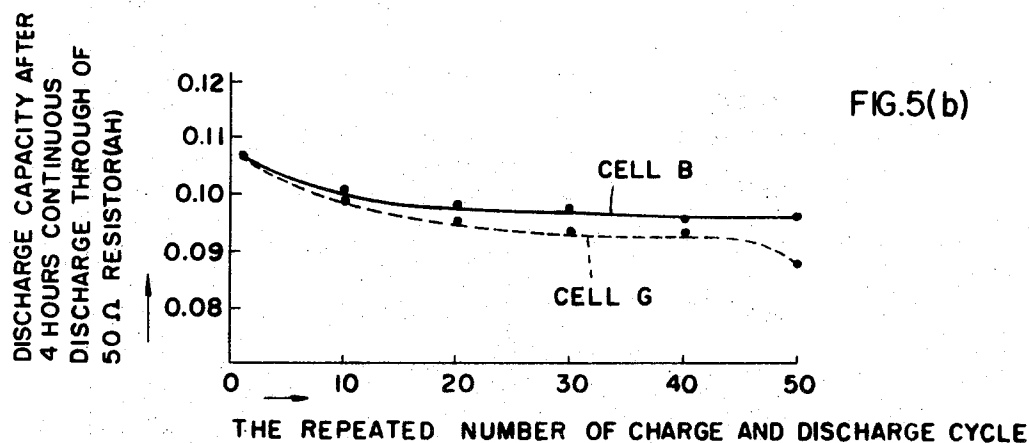
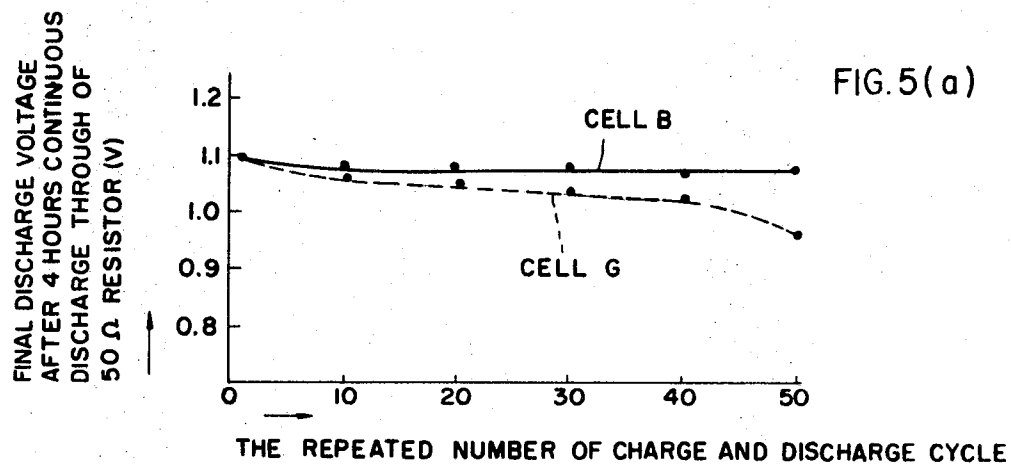
SHEET 1 OF 5



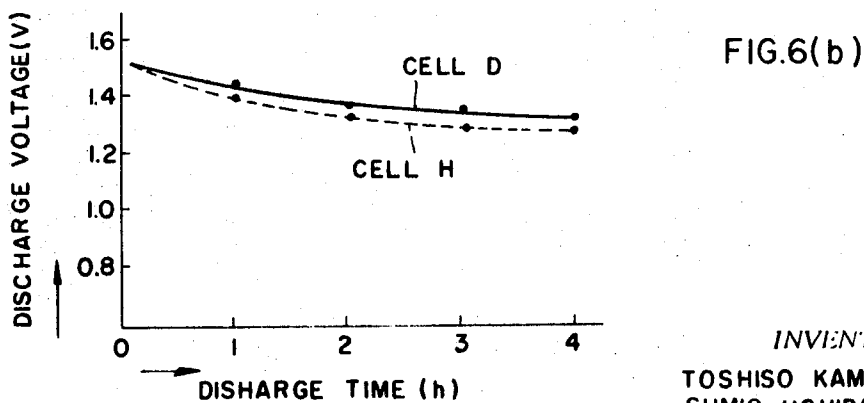
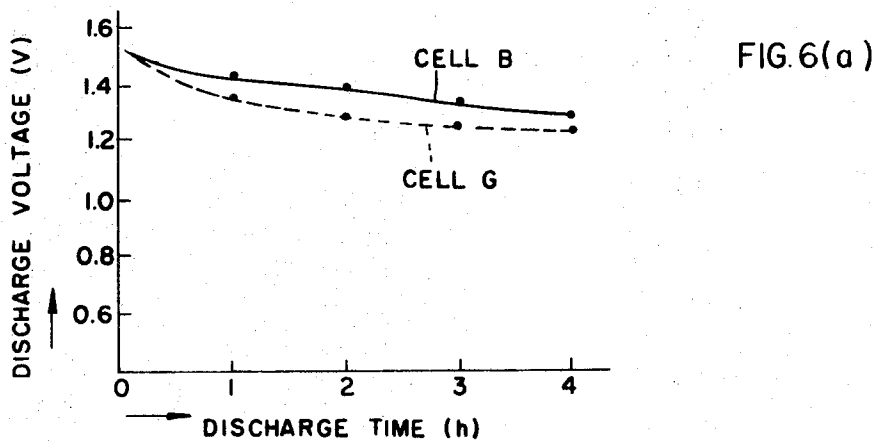
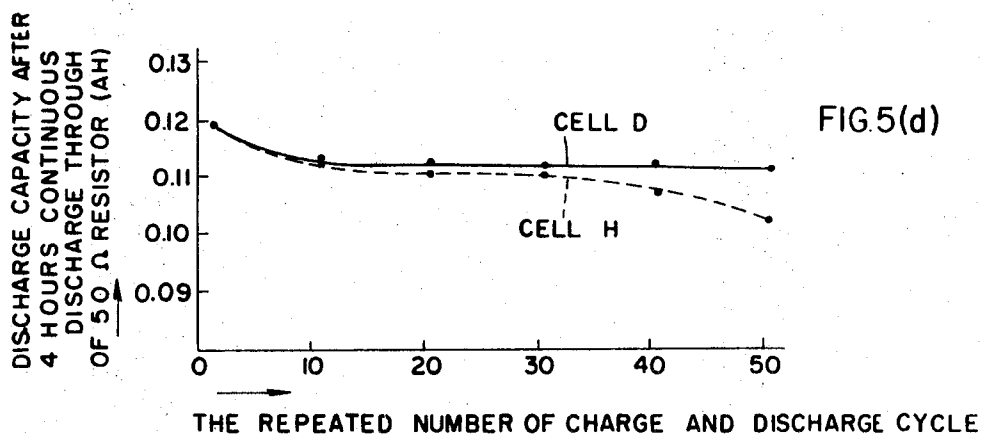
INVENTOR S
BY Toshiso Kamai
Sumio Uchida



INVENTORS
TOSHISU KAMAI
SUMIO UCHIDA

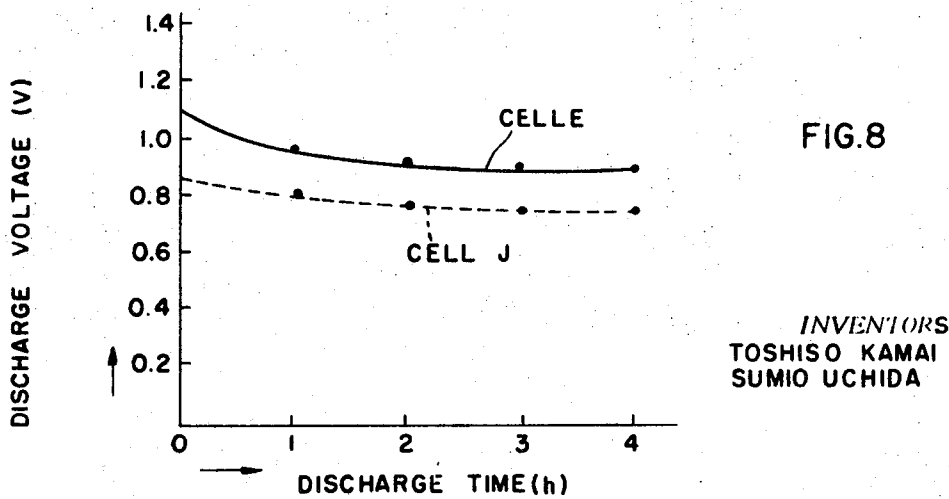
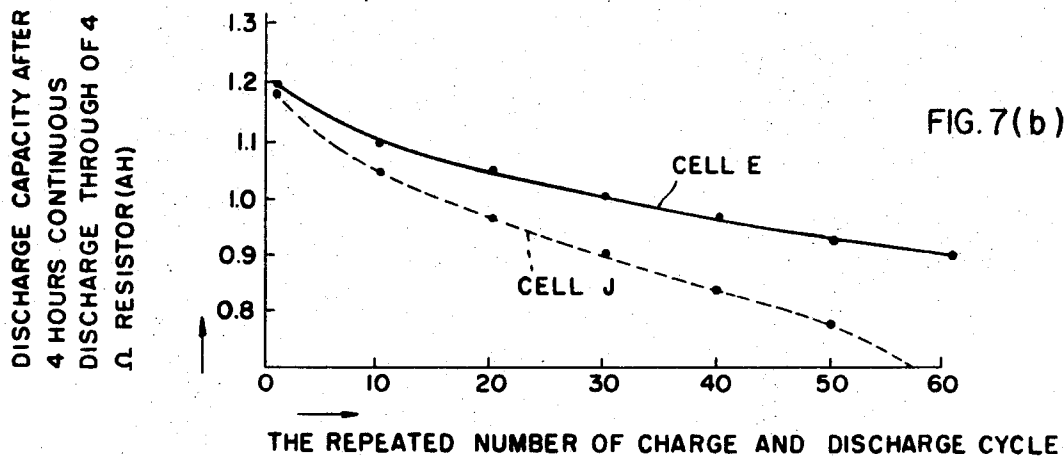
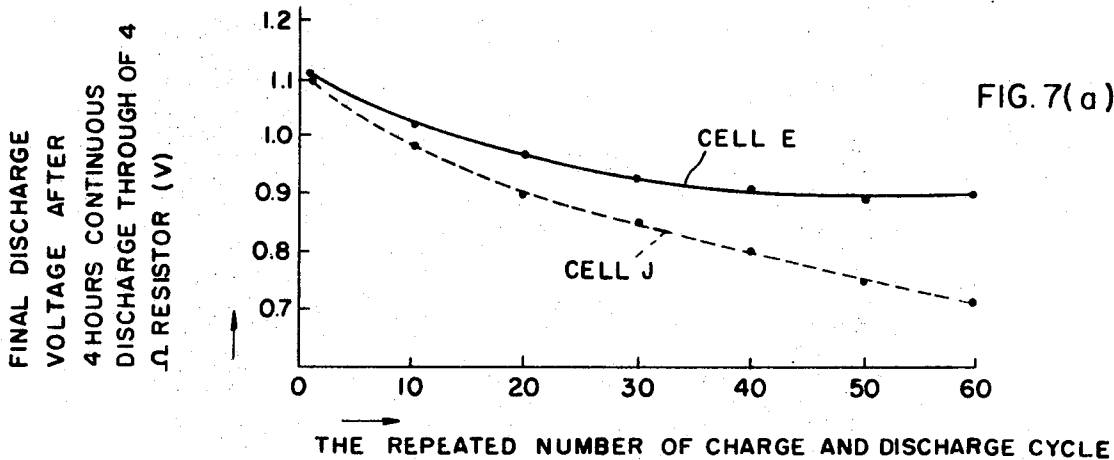


INVENTORS
TOSHISO KAMAI
SUMIO UCHIDA



INVENTORS

TOSHISO KAMAI
SUMIO UCHIDA



ZINC ALKALINE SECONDARY CELL

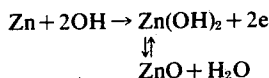
This application is a continuation in part of copending application Ser. No. 571,907, filed Aug. 11, 1966, now abandoned. This invention relates to a zinc alkaline secondary cell using zinc powder as an anode, and relates particularly to the active substance of the zinc anode. Its object is to provide a zinc alkaline secondary cell, the reversibility of the zinc anode of which on charge and discharge is excellent, and which has a long cycle life for charge and discharge of the cell and always maintains a high discharge capacity and a low cell inner resistance on charge and discharge cycle.

Zinc alkaline secondary cells using manganese dioxide as a depolarizer have already been proposed. The cell, made by an ordinary technique, however, involved many unresolved problems, and the cycle life for charge and discharge was insufficient. Ordinary zinc alkaline secondary cells include such defects as that the zinc for the anodic active substance grows coarse and the effective reactive area decreases on repeated charge and discharge cycles, and that discharge capability lowers with gradually increasing inner resistance; occasionally, during the charge of the cell, a separator is broken with zinc grown in dendrite shape; and the depolarizer and the anodic body form a short circuit, so that the cell life is entirely lost. Also, on discharge reaction, zinc in the anode is converted into an undissolved substance such as zinc hydroxide or zinc oxide, and the inner resistance in the anodic body gradually increases, so that there exists the defect that sufficient discharge capability is not realized. As a means to resolve this, a large amount of mercury has previously been added to the zinc anodic active substance in zinc amalgam form, and when the zinc is converted into zinc hydroxide or zinc oxide by reaction, it is allowed to act as an electric conductible auxiliary agent by depositing mercury. In such a method, however, the expected effect was not realized as the deposited mercury particles aggregated readily and grew coarse because of the high surface tension.

Another technique, as set forth in Morgan, U. S. Pat. No. 2,862,987, attempts to prevent hydrogen from being produced by employing a layer of tin solder at the anodic surface to protect the anodic body from the electrolyte. This method takes advantage of the higher overpotential of tin as versus zinc. This method, however, does not prevent deposition of mercury particles as discussed above and as will be discussed in detail below.

The object of the present invention is to eliminate the defects inherent in ordinary zinc alkaline secondary cells by adding (a) metallic powder such as gold, silver or tin, which does not dissolve in alkaline solution and which gives a high hydrogen overvoltage, or (b) a powder of alloy made from two or more of these metals, or (c) a suitable amount of said metals by plating zinc powder to the zinc anodic active substance, while pulverizing the alloy which is made up by alloying zinc of anodic reaction substance and said metals and using them as an anodic active substance. Details are illustrated below.

If a discharge reaction starts in a conventional zinc alkaline secondary cell by the following reaction at the anode:



zinc hydroxide or zinc oxide is produced from the surface of amalgamated zinc particles, while mercury which constitutes an alloy with the zinc begins to deposit as mercury particles. The electric resistance of the anodic active substance does not show any remarkable increase until these mercury particles grow coarse, but as the discharge reaction progresses and zinc hydroxide or zinc oxide accumulates, the mercury particles gradually aggregate to one another and grow coarse, so that the resistance of the anodic active substance suddenly increases. On increase of this resistance, it is impossible to maintain the plateau of the discharge curve characteristic of the al-

kaline secondary cell, so that with the elapse of discharge time, the terminal voltage will drop. However, if metallic particles such as gold, silver or tin, which do not dissolve in alkaline solution and have a high hydrogen voltage and an extremely lower electric resistance, are mixed in, the mercury is converted into an alloy by amalgamating with the said metals, and this does not allow the grain of these alloys to become coarse and it helps to maintain always a stable and lower electric resistance. Although the mixture of these metallic powders is effective in discharge as set forth, a peculiar effect is revealed particularly in the charge of the cell.

When zinc hydroxide or zinc oxide is reduced electrolytically and metallic zinc deposits during the charge of the ordinary zinc alkaline secondary cell, the mercury particles deposited at discharge or the particles amalgamated with zinc, which do not yet react and remain as metallic particles, act as a nucleus. As set forth above, however, if the mercury particles deposited grow coarser, the total number of zinc nuclei deposited decreases and as the charge time becomes longer, the zinc deposited grows coarser and the reactive surface area decreases, so that satisfactory discharge capability of the cell is not obtainable, or sometimes the separator is broken with zinc deposited in dendrite shape, so that it may cause a short circuit accident. But since most stable nuclei always exist if the aforesaid metallic powders are mixed in, the coarse growth of zinc particles will not occur and zinc in uniform size will deposit. Also, since the metallic grains in the anodic body are in good contact and the electric resistance is always kept at a low value, the time needed for charge of the cell becomes shorter. Moreover, if metallic powder scatters uniformly in anodic body, the mercury deposited on discharge allows such metal powder to amalgamate immediately, and a metal-mercury alloy having a high hydrogen overvoltage is formed and the metal which has locally a low hydrogen overvoltage and is not amalgamated decreases, and therefore evolution of gas remarkably decreases.

The objects of this invention are met by distributing the gold, silver, tin, alloys thereof, gold and silver oxides, hydroxides and mixtures thereof throughout the amalgamated zinc anodic active body. Of course, it is most desirable to insure uniform distribution of gold, silver and tin throughout the anodic body, but than perfect uniformity will produce superior and unexpected results in comparison with prior art cells, e.g. as in Morgan, discussed above wherein the tin is merely present as a solder at the anodic surface to protect the anodic body from the electrolyte.

Any method of distributing the above metals, oxides and hydroxides throughout the zinc amalgam is suitable e.g. plating, alloying or admixing is suitable. By plating, any method which takes advantage of the difference in potential between the plating material and the material to be plated is suitable.

The objects will be entirely understood from the following detailed description of actual embodiments thereof, with reference to the accompanying drawings.

FIG. 1 shows a sectional view of a cell A according to one embodiment of the present invention.

FIG. 2 is a sectional view of cell B according to another embodiment of the present invention.

FIGS. 3a and 3b show the characteristic curves of the charge and discharge cycles of cells A and C according to the present invention, and of an ordinary cell F. Curves (a) show the relation between the number of repeated charge and discharge cycles and the final discharge voltage (v), and curves (b) show the relation between the number of repeated charge and discharge cycles and the discharge capacity (AH).

FIG. 4 shows the continuous discharge curves of said cells A, C and F.

FIGS. 5a and 5d show the characteristic charge and discharge curves of the cells B and D, according to the present invention, and of ordinary cells G and H. Curves (a) show the relation between the number of repeated charge and discharge cycles and the final discharge voltage (v) of said cells B and G; curves (b) show the relation between the

number of repeated charge and discharge cycles and the discharge capacity (AH) in said cells B and G; curves (c) show the relation between the number of repeated charge and discharge cycles and the final discharge voltage (v) in said cells D and H, and curves (d) show the relation between the number of repeated charge and discharge cycles and the discharge capacity (AH) in said cells D and H.

FIG. 6 (a) shows the continuous discharge curve of said cells B and G, and FIG. 6 (b) shows the continuous discharge curve of said cells D and H.

FIGS. 7(a) and 7(b) show the characteristic curves of a cell E according to the present invention and of an ordinary cell J. Curves (a) show the relation between the number of repeated charge and discharge cycles and the final discharge voltage (v) in said cells E and J, and curves (b) show the relation between the number of repeated charge and discharge cycles and the discharge capacity (AH) in said cells E and J.

FIG. 8 shows the continuous discharge curves of said cells E and J.

Specific embodiments of the present invention are illustrated as follows:

EMBODIMENT 1 (FIG. 1)

4 percent-amalgamated 40-80 mesh zinc powder is mixed with 100-200 mesh silver powder in an amount of 8 wt. percent relative to the zinc powder. 35 percent aqueous potassium hydroxide solution is mixed with carboxymethyl cellulose sodium salt in an amount of 5 wt. percent relative to the aqueous solution to give a paste. Both the powder mixture and the paste are kneaded to produce a zinc anode active substance containing an electrolytic solution. The zinc anode active substance is left to stand for 24 hours to be "aged;" whereby a part of the zinc powder is dissolved and goes into the electrolyte solution to make the latter nearly saturated with zincate, so that evolution of gas during use is retarded.

An alkaline secondary cell using this zinc anodic active substance is shown in FIG. 1. A depolarizing compound 2 made by mingling manganese dioxide and artificial graphite is previously pressed into the same cup shape as the cathodic cup shaped inner can 4, and then the supporting portion, to rest on packing 9, is formed by bending the open edge of cathodic inner can inwards to an extent equal to the adjacent thickness of the depolarizing compound 2. Next, the separator 5 is inserted into the hollow portion of the cuplike depolarizing compound 2 in order to allow it to closely contact, with its inner wall, the zinc anodic active substance 1 which is closely packed so as to leave no hollow space, the open edge of the separator 5 being bent inwards and a cover 7 being provided to prevent zinc particles from floating or moving in the cell. Thus, the cathodic inner can 4 including the depolarizing compound 2, the separator 5 and the zinc anodic active substance 1 are closely inserted into the cathodic outer can 3 having the cathodic terminal element 6, and the anodic cover plate 7 which is integrated, by welding, to the anodic electron collecting rod 8 is closely mounted through the packing 9, and then the cell is completed by bending the open edge of the cathodic outer can 3 inwards and by sealing it in liquid-tight manner. This zinc alkaline secondary cell is denoted as cell A.

EMBODIMENT 2 (FIG. 2)-

4 percent-amalgamated 60-100 mesh zinc powder is mixed with 150 mesh tin powder in an amount of 10 wt. percent relative to the zinc powder, and 0.6 gram of the mixture is molded under a pressure of 30-50 kg/cm² into a disk of 10 mm in diameter. The obtained disk is used as a zinc anode active substance 10.

A mixture of mercury oxide and artificial graphite is moistened with an alkaline electrolyte solution, and the mixture is kneaded to produce a depolarizing compound 11. 2.5 grams of the depolarizing compound is shaped by pressing under a pressure of about 50-100 kg/cm² on the bottom of a cuplike cathodic can 12 made of steel 0.3 mm. thick, which is 16 mm. in outer diameter and 8 mm. in height.

On the upper side of depolarizing compound 11 is mounted the separator 13, whose diameter is equal to the inner diameter of the steel cathodic can 12 and whose thickness is about 1.5 mm., and which is made of alkaline treated natural fiber impregnated with 35 percent potassium hydroxide, which contains zincate of nearly saturated value by dissolving zinc oxide therein. Then, after said shaped zinc anodic active substance 10 is mounted on the separator, a cell is made up by mounting dishlike steel anodic cover 14 having a polyethylene packing 15 which is U-shaped in section on its periphery at the open portion of the steel cathodic can, by bending the open periphery inwards and by sealing it tightly. If necessary, it is possible to seal by applying a liquid such as polyisobutylene at the contact face between the packing and the cathodic can or the anodic cover in order to further increase preventive characteristic of leakage of the alkaline electrolyte. This zinc alkaline secondary cell is denoted as cell B.

EMBODIMENT 3

Nonamalgamated zinc powder of 150-200 mesh size is immersed into a solution having the following composition:

grams		
Gold cyanide	(AuCN)	6
Silver cyanide	(AgCN)	40
Potassium cyanide	(KCN)	50
Sodium carbonate	(Na ₂ CO ₃)	28
Water	(H ₂ O)	1,500

and gold-silver alloy is plated on the zinc surface. Although the plating time varies somewhat with the temperature of the bath at from 40° to 70° C., the layer of gold-silver alloy is plated on the zinc powder surfaces within about 30 seconds. The composition of the plated layer obtained by said plating solution is nearly in a ratio of four silver to one gold, but it is not always necessary to hold this composition. Even if a somewhat smaller amount of added gold is plated, it will not influence the capability of the cell.

Then, the zinc anodic active substance is produced by adding the zinc powder plated with gold-silver alloy at 10 wt. percent to 40-80 mesh zinc powder, by warming, stirring and amalgamating them in 10 percent potassium hydroxide solution with addition of mercury. Using this anodic active substance, a cell is made up by the same method as in embodiment 1. This zinc alkaline secondary cell is denoted as C.

EMBODIMENT 4

A mixture of zinc and silver in an amount of 8 wt. percent relative to the zinc is melted at about 500° C., and then quenched to make zinc-silver alloy base metal. The base metal is crushed into powder grains of 50 mesh size, and the powder grains are amalgamated by being warmed and stirred in 8 percent aqueous sodium hydroxide solution with the addition of mercury thereto.

A mixture of silver oxide and artificial graphite is used as the depolarizing agent, and a 25 percent aqueous sodium hydroxide solution which is nearly saturated with zincate is used as the alkaline electrolyte solution.

By the employment of said elements, a cell is made up in the same construction as in embodiment 2. This zinc alkaline secondary cell is denoted as cell D.

EMBODIMENT 5

Silver-tin alloy consisting of 60 wt. percent of silver and 40 wt. percent of tin is crushed into 150 mesh powder. 5 percent-amalgamated 40-80 mesh zinc is mixed with the silver-tin alloy powder. Zinc oxide is added to 35 percent aqueous potassium hydroxide solution so that the latter is nearly saturated with zincate, and carboxymethyl cellulose sodium salt in an amount of 4 wt. percent relative to the aqueous potassium hydroxide solution is further added thereto to give a paste.

Both the metal mixture and the paste are kneaded to produce a zinc anodic active substance containing an electrolyte.

Manganese dioxide and mercury oxide are mixed together at the rate of four to one by weight, followed by addition of artificial graphite, as an electric conductive agent, to the mixture to produce a depolarizing compound.

Thereafter, a cell of the same construction as in embodiment 1 is made up. This zinc alkaline secondary cell is denoted as cell E.

In the five embodiments mentioned above, the embodiments of methods in which one or two members selected from the group consisting of gold, silver and tin were added to the zinc anodic active substance are described. It was confirmed that an equivalent effect was obtained even if, instead of gold or silver, oxide or hydroxide thereof was used. If the oxide or hydroxide of gold or silver is added to the zinc anodic active substance, zinc reduces these particles, allowing gold or silver to deposit in metallic state, and the zinc itself is oxidized into zinc oxide, which remains in the anodic active substance. Therefore, in the case of addition of oxide or hydroxide of gold or silver, an effect equivalent to that given by adding gold or silver, is obtained. In contrast with this, since tin oxide or tin hydroxide converts into stannate ion SnO_3^{2-} and completely dissolves in alkaline solution, it cannot exist as a solid metal such as gold or silver, so that it does not show an equivalent effect to metallic tin.

The charge and discharge characteristics and the other various characteristics of the cells, which are made up according to the embodiments described above and those according to the usual cells, are illustrated in FIGS. 3 to 8.

FIGS. 3(a) and 3(b) show the battery characteristics obtained according to the number of repeated charge and discharge cycle of the cells A and C and an ordinary cell F, in which only amalgamated zinc is used for the zinc anodic substance. From the above-mentioned, it is clear that the dropping in the cell voltage is larger and the decrease in the discharge capacity of the cell is more remarkable in the ordinary type.

FIG. 4 shows a continuous discharge curve obtained through a resistor of 4Ω in 51 st charge from 50 times of the charge and discharge cycles repeated, and from this it is shown that the discharge capacity for the ordinary cell F is no more than 77 percent in comparison with the cell according to the present invention.

FIGS 5(a) to 5(d) show the charge and discharge characteristics of cells B and D, and mercury oxide cell G and silver oxide cell H of an ordinary type, and it is clear that the cell according to the present invention is more excellent. Particularly, it is very suitable for high precision instruments owing to its little drop of the cell voltage after repeated charge and discharge cycles.

FIGS. 6(a) and 6(b) show a discharge curve obtained from 31st discharge through a constant resistor of 50Ω after 30 repeated charge and discharge cycles.

FIGS. 7(a) and 7(b) show the charge and discharge cycle characteristics of cell E and cell J which uses as the depolarizing compound the substance formed by adding, as an electric conductive auxiliary agent, artificial graphite to the mixture in which manganese dioxide and mercury oxide are mingled in weight ratio of four to one, and uses an ordinary anode.

FIG. 8 shows a continuous discharge curve obtained in 51 st charge through a constant resistor of 40Ω , following 50 charge and discharge cycles for these cells. As seen in this figure, it is due to an addition of mercury oxide as the depolarizing compound that the drop in the cell voltage with discharge is flatter in comparison with that in FIG. 4. Moreover, the influence due to an addition of powder of silver-tin alloy to the zinc anodic active substance is more remarkable. The tables below show the results obtained by disassembling 20 cells and examining their average gas volume accumulated, which cells have been subjected to 50 repeated charge and discharge cycles for the cell A, C made up according to the embodiments of the invention and the ordinary cells

P, J, and with thirty repeated charge and discharge cycles for the cells B, D made up according to embodiments of the invention and the ordinary cells G, H, respectively. Since this gas volume accumulated is obtained from subtracting the gas volume contained in the making process, it is an absolute value evolved only by repeating the charge and discharge cycles.

Gas volume (milliliters) accumulated after repeating 50 charge and discharge cycles

Sort of cell	Maximum	Minimum	Average
Cell A	8.7	3.1	5.4
Cell C	7.8	5.2	6.0
Cell E	6.8	4.4	5.1
Ordinary dry cell F, J			

Gas volume (milliliters) accumulated after repeating 30 charge and discharge cycles

Sort of cell	Maximum	Minimum	Average
Cell B	0.98	0.37	0.63
Cell D	0.89	0.41	0.57
Ordinary cell G, H	2.05	1.33	1.76

As seen from above explanation, the alkaline secondary cell according to the present invention has an excellent life of charge and discharge cycle, and keeps a high discharge capacity and a low inner resistance during its charge and discharge, moreover accumulated gas volume never influences its capability in comparison with the conventional cells. Namely, the gas evolution can be practically prevented.

What is claimed is:

1. In a zinc-alkaline secondary cell comprising in combination a container, a cathode comprising a depolarizing material including an electrically conductive agent, an anode, an alkaline electrolyte and a separator interposed between said cathode and said anode; the improvement wherein said anode comprises as an anodic active body, amalgamated zinc and distributed throughout said anodic active body a substance selected from the group consisting of gold, silver, tin, alloys thereof, gold and silver oxides and hydroxides and mixtures of said substances.

2. A cell as in claim 1 wherein the substance distributed throughout said anodic active body is gold, silver, tin alloys and mixtures thereof.

3. A cell as in claim 1 wherein the substance distributed throughout said anodic active body is gold and silver oxides, hydroxides and mixtures thereof.

4. In a zinc-alkaline secondary cell comprising in combination, a container, a cathode comprising an admixture of graphite and a member selected from the group consisting of manganese dioxide, mercury oxide, silver oxide and mixtures thereof, an anode, an alkaline electrolyte consisting essentially of an aqueous solution of an alkali metal hydroxide substantially saturated with zincate, and a separator interposed between said cathode and said anode, said anode the improvement wherein comprises as an anodic active body, amalgamated zinc and distributed throughout said anodic active body a substance selected from the group consisting of gold, silver, tin, alloys thereof, gold and silver oxides and hydroxides and mixtures of said substances.

5. A cell as in claim 4, wherein the substance distributed throughout said anodic active body is gold, silver, tin, alloys and mixtures thereof.

6. A cell as in claim 4, wherein the substance distributed throughout said anodic active body is gold and silver oxides, hydroxides and mixtures thereof.

* * * * *

5

10

15

20

25

30

35

40

45

50

55

60

65

70

75