



(22) Date de dépôt/Filing Date: 2004/01/22

(41) Mise à la disp. pub./Open to Public Insp.: 2005/07/22

(51) Cl.Int.⁷/Int.Cl.⁷ H01M 10/24, H01M 10/28, H01M 4/24

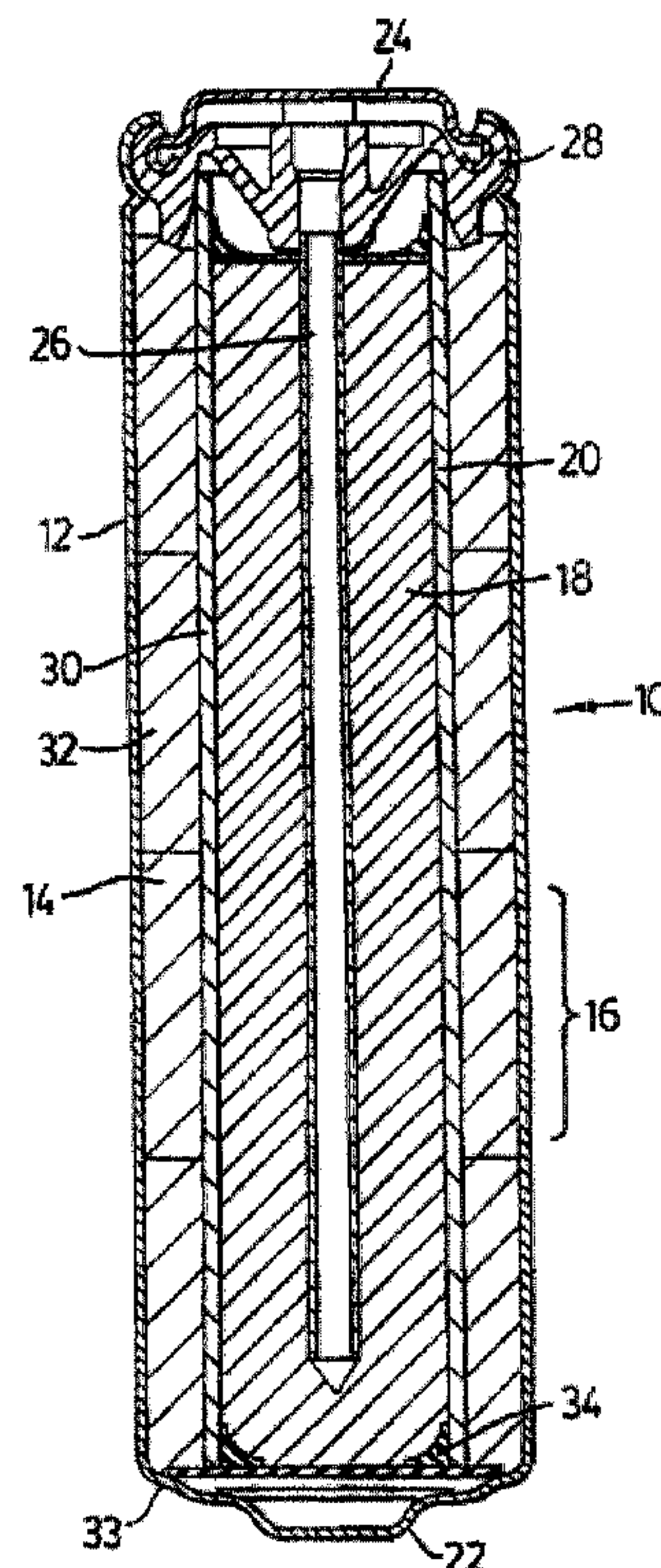
(71) Demandeur/Applicant:
PURE ENERGY VISIONS INC., CA

(72) Inventeur/Inventor:
DANIEL-IVAD, JOSEF, CA

(74) Agent: ANISSIMOFF & ASSOCIATES

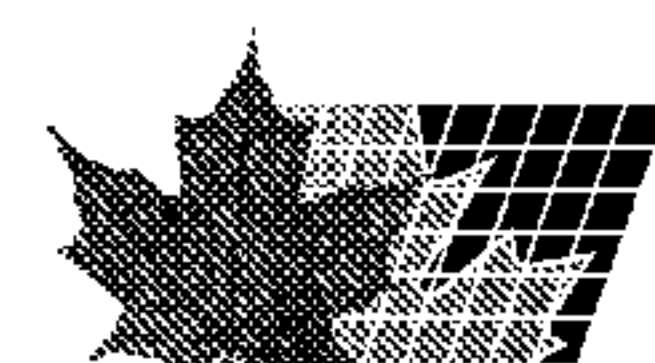
(54) Titre : PILE ALCALINE AU DIOXYDE DE MANGANESE AYANT UNE MEILLEURE TENSION DE CIRCUIT OUVERT

(54) Title: ALKALINE MANGANESE DIOXIDE CELL WITH IMPROVED OPEN CIRCUIT VOLTAGE



(57) Abrégé/Abstract:

An alkaline manganese dioxide cell exhibiting improved open circuit voltage (OCV) as a consequence of an oxidizing additive mixed to the manganese dioxide cathode material that does not have an adverse effect on the cell impedance. The manganese dioxide positive electrode includes up to 5% by weight of the manganese dioxide of an oxidizer selected from compounds of permanganate, peroxysulfate, or combinations thereof.



- 15 -

ABSTRACT

An alkaline manganese dioxide cell exhibiting improved open
circuit voltage (OCV) as a consequence of an oxidizing additive
mixed to the manganese dioxide cathode material that does not
have an adverse effect on the cell impedance. The manganese
dioxide positive electrode includes up to 5% by weight of the
manganese dioxide of an oxidizer selected from compounds of
permanganate, peroxy sulfate, or combinations thereof.

- 1 -

ALKALINE MANGANESE DIOXIDE CELL WITH IMPROVED OPEN CIRCUIT VOLTAGE

5 FIELD OF THE INVENTION

The invention relates to alkaline manganese dioxide cells, particularly to the use of an oxidizing additive to improve the open circuit voltage of such cells without adversely affecting the cell impedance.

10

BACKGROUND OF THE INVENTION

Primary (non-rechargeable) manganese dioxide-based alkaline cells are well known and include a positive electrode having manganese dioxide (MnO_2) as an active material, a negative electrode utilizing zinc as the active material, an aqueous solution of potassium hydroxide as electrolyte, and a separator between the positive and negative electrode.

One important parameter that is easily measured by the manufacturer and consumers is the Open Circuit Voltage (OCV) and the Closed Circuit Voltage (CCV). The OCV/CCV measurement is strongly dependent on the materials used in the cell. Generally, primary alkaline cells with an OCV of greater than 1.60V and a CCV of greater than 1.50V are considered good quality cells for certain applications. However, it is quite desirable to increase the OCV and expand the cell usage in numerous devices.

According to practical experience the open circuit voltage of cells having identical design depend on how the manganese dioxide cathode material was made. Even products of the same manufacturer having an identical product number but made at different times can produce different OCV values when used in cells. On the other hand, end users of cells prefer cells having largely uniform OCV values.

The primary active material to increase this voltage is the positive electrode, in this case, manganese dioxide. Numerous approaches have been proposed to increase the open circuit voltage (OCV) by employing various additives to the electrochemical cell or by producing an electrolytic manganese dioxide with greater potentials.

- 2 -

Magahed in U.S. Patent 4,397,925 issued August 9, 1983, describes button cells having cathodes, which are extended with high potential oxide. The cathode in this situation is a monovalent silver oxide (Ag_2O) extended with divalent silver oxide (AgO), mercury oxide (HgO), and/or permanganate compound (KMnO_4 , LiMnO_4 , BaMnO_4 ... etc.). These extended cathodes will show high OCV and impedance values in addition to two distinct plateaus of discharge. Magahed addresses the undesirable high voltage and high impedance levels by including in the electrolyte a reducing agent from the group of soluble complex hydrides. The reducing agent significantly lowers cell OCV and impedance that in turn offers a single voltage plateau discharge.

Dhanji in U.S. Patent 4,555,457 issued November 26, 1985, describes a conventional magnesium-manganese dioxide cell comprising a combined cathode dry mix and electrolyte with the addition of 0.1 to 10% by weight of potassium monoperoxysulfate, 2KHSO_5 (OXONE® sold by Dupont) to the electrolyte, which consists of magnesium perchlorate $\text{Mg}(\text{ClO}_4)_2$ and lithium chromate Li_2CrO_4 for improving the open circuit voltage from 1.8 volts to 2.3 volts and capacity of the cell. It is important to note that the preferred embodiment of that patent incorporates a cathode and a non-alkaline electrolyte mix that has about 50% to 60% wetness, as required for the flow of current. In addition, in a comparison with the prior art as shown in Figure 11 of U.S. Patent 4,555,457, an improvement in the open circuit voltage also increases cell impedance. This increase is not beneficial for the cell capacity at different discharge rates.

As various additives, methods, and processes are employed to increase the OCV of primary electrochemical cells, there is a need for providing a means of regulating the OCV/CCV without adversely affecting (increasing) cell impedance.

SUMMARY OF THE INVENTION

The main object of the present invention is to provide an alkaline manganese dioxide-zinc cell incorporating suitable oxidizers as direct additives to the electrolytic manganese dioxide (EMD) that enhance the open circuit voltage (OCV) of the cell without adversely affecting cell impedance.

- 3 -

A further object of the invention is to enable production of cells with highly uniform open circuit voltages.

According to the present invention these objectives have been met by an alkaline manganese dioxide cell, wherein the positive electrode employs a variety of suitable oxidizing additives in an amount of less than 5% relative to the mass of the manganese dioxide, whereby the open circuit voltage increases and the cell impedance stays essentially the same.

The addition of the oxidizer occurs directly and not through the aqueous electrolyte as disclosed in the above referenced prior art patents, which increases the chance of cell shortages. The oxidizer can be added as a solid powder or an aqueous solution in potassium hydroxide directly to the cathode mass during the cathode powder processing.

The present invention increases the voltage potential of the EMD cathode material in a simple way and enables manufacturing of cells that precisely meet the final cell voltage requirements.

Cells according to the present invention may also have a number of additives for purposes of enhancing the conductivity and the structural integrity of the manganese dioxide positive electrode, or for enhancing hydrogen recombination at the electrode. For example, the manganese dioxide electrode may include at least one additive that comprises: graphite, carbon black, an inorganic binder, an organic binder, or a combination thereof.

Where the cells are intended for commercial use, the electrolyte may be a 4N to 12N aqueous solution of potassium hydroxide, optionally with ZnO dissolved in it. A separator between the zinc electrode and the manganese dioxide electrode and appropriate terminal means contacting the zinc electrode and manganese dioxide electrode are provided.

In keeping with the present invention, the positive manganese dioxide electrode includes an oxidizing additive. Any suitable oxidizing additive may be used. The oxidizing additive may comprise permanganate and/or peroxysulfate compounds in an amount of up to about 5%, preferably up to about 2.5%, by weight of the manganese

- 4 -

dioxide. Suitable permanganate and peroxy sulfate compounds may comprise potassium, barium, calcium, silver, copper, and/or lithium. Preferably, the oxidizing additive is potassium permanganate, potassium peroxy sulfate, or potassium peroxydisulfate.

Oxidizing additives may be present in an amount of from about 0.05 to 5.0%, preferably about 0.1% to 0.75%, by weight of manganese dioxide.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG.1 is a cross-sectional view of a cell according to the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS:

As shown in Figure 1, an embodiment of a primary alkaline manganese dioxide-zinc cell 10 comprises the following main units: a steel can 12, optionally coated with a conductive coating on the inside of the can, defining a cylindrical inner space, a manganese dioxide cathode 14 formed by a plurality of hollow cylindrical pellets 16 pressed in the can, a zinc anode 18 made of an anode gel and arranged in the hollow interior of the cathode 14, and a cylindrical separator 20 separating the anode 18 from the cathode 14. The ionic conductivity between the anode and the cathode is provided by the presence of potassium hydroxide, KOH, electrolyte added into the cell in a predetermined quantity.

The can 12 is closed at the bottom, and it has a central circular pip 22 serving as the positive terminal. The upper end of the can 12 is hermetically sealed by a cell closure assembly which comprises a negative cap 24 formed by a thin metal sheet, a current collector 26 attached to the negative cap 24 and penetrating deeply into the anode gel to provide electrical contact with the anode, and a plastic top 28 electrically insulating the negative cap 24 from the can 12 and separating gas spaces formed beyond the cathode and anode structures, respectively.

The material of separator 20 may consist of a single non-woven layer or a cellophane layer or combinations thereof. Typically the separator material is a

- 5 -

conventional ion permeable absorbent membrane comprising non-woven materials including polyamide, polyvinyl alcohol, rayon or cellulosic (rayon) fibers. A micro-porous cellophane film layer may be incorporated to prevent shorting of the cell due to the formation of zinc dendrites during discharge.

5 The separator **20** is wound to form a cylindrical tube of two or three turns, which results in multiple layers separating the anode from the cathode, and is placed into the hollow cylindrical cathode structure.

 As illustrated in Figure 1, one method of achieving sealing of the separator bottom is by means of a hot-melt bead **34**, which is used to seal the separator **20** to a washer **33** in
10 the cell. In another variation the washer is omitted and hot-melt adhesive only is used. Furthermore, bottom seal cups may be employed without the use of a hot-melt adhesive.

 The negative zinc electrode comprises powdered metallic zinc or zinc alloys and optionally zinc oxide together with a suitable gelling agent such as carboxymethyl cellulose, polyacrylic acid, starches, and their derivatives.

15 The electrolyte is an aqueous alkaline solution of usually 4N to 12N potassium hydroxide. The electrolyte may contain additives, such as dissolved zinc oxide (ZnO), so as to reduce the gassing of the active zinc within the negative electrode, and so as to permit overcharge of the cell without damaging it.

 A suitable manganese oxide positive electrode comprises electrolytic or
20 chemically synthesized manganese dioxide containing typically over 90% of four valent manganese and minor amounts of lower valence oxides. The oxidizing additives are added to the manganese dioxide powder in the dry process of blending the positive electrode materials. Depending on the nature of the cell, the positive electrode may be molded into pellets and inserted into the can, followed optionally by re-compaction.
25 Otherwise, the positive electrode may be extruded directly into the can, or it may be rolled or cast as a flat positive electrode for use in flat plate cells, button or coin cells.

 As discussed above, it has been found that the addition of oxidizing additives to the cathode material produces a higher open circuit voltage of the cell without increasing the cell impedance. The additives comprise permanganate and peroxysulfate compounds,
30 preferably 0.05% to 5% by weight of manganese dioxide, more preferably 0.1% to 0.75%

- 6 -

by weight of manganese dioxide. The compounds are present in the cell preferably in the form of potassium permanganate or potassium peroxydisulfate. The amount of various additive compounds will vary depending on the size or format of the cell.

As noted, the present invention is applicable not only to bobbin type cells, but also to spirally wound cells, button or coin cells, and to flat plate cells. The invention is applicable to both primary and rechargeable alkaline cells.

The following examples will assist those skilled in the art to better understand the invention and its principles and advantages. It is intended that these examples be illustrative of the invention and not limit the scope thereof.

Example 1:

Alkaline AA-size cells were prepared according to the above description of Figure 1 with variations in the cathode formulation due to the addition of the appropriate oxidizing agent. In all cases, the oxidizer replaced part of the active electrolytic manganese dioxide (EMD) material in a way that the volume of the total cell materials was maintained at a constant level.

Each AA-size cell contained 3 cathode pellets weighing approximately 3.3 to 3.5 g. The cathode formulation typical of primary alkaline cell consists about 88 to 92 wt % EMD, 4.5 to 9.0 wt % conductive powder, and the remainder being other additives such as binders and electrolyte including the oxidizing agent that are blended and pressed into a cathode pellet. As referenced above, the oxidizer agent, in this example, potassium permanganate (KMnO_4) was added by adjusting the amount of EMD accordingly. Furthermore, in this example, the EMD was supplied by Delta Limited and the KMnO_4 addition is expressed in weight % based on EMD in the cathode formulation.

Test cells (50 cells per group) were tested for the basic electrical tests. These tests include open circuit voltage (OCV), closed circuit voltage (CCV) carried out at 500mA for 200 msec. load, short circuit current (SCC), and the impedance (IMP).

Table 1 shows the basic electrical tests of the test cells with the addition of various levels of KMnO_4 using Delta Ltd. EMD.

Table 1: Basic Electrical Tests of AA Test Cells with Various Levels of KMnO₄ Employing Delta Ltd. EMD

Test Cell Group	KMnO ₄	OCV (mV)	dVocv (mV)	CCV (mV)	dVccv (mV)	SCC (A)	IMP (m)
Control	0%	1597		1524		15.7	102
#1	0.25%	1616	17	1542	18	15.2	107
#2	0.6%	1623	26	1551	27	16.5	98
#3	0.9%	1656	59	1571	47	15.2	109
#4	1.2%	1684	85	1614	90	20.3	83
#5	2.4%	1750	153	1619	95	17.4	100
#5b	4.8%	1760	163	1640	116	15.5	110

5

The results of Table 1 clearly show the increase in the OCV/CCV ratio with an increase in KMnO₄. However, surprisingly, the impedance value, unlike the data disclosed in the prior art, is not negatively affected by the addition of the oxidizer. In addition, prior art incorporates the electrolyte as a vehicle for the addition of the oxidizer to the manganese dioxide. Here, in a simple and cost effective way, the oxidizer is directly added to the manganese dioxide.

10

Example 2:

To demonstrate the effect of a different EMD type, alkaline AA-size cells were prepared as in Example 1 but with EMD supplied by Xiangtan Electrochemical Company and three different levels of potassium permanganate. Once again, test cells were tested for the basic electrical tests; OCV, CCV, SCC, and IMP.

15

Table 2 shows the basic electrical tests of the test cells with the addition of various levels of KMnO₄ using Xiangtan Electrochemical Company EMD.

20

- 8 -

Table 2: Basic Electrical Tests of AA Test Cells with Various Levels of KMnO_4 Employing Xiangtan Electrochemical Company EMD

Test Cell Group	KMnO_4	OCV (mV)	dVocv (mV)	CCV (mV)	dVccv (mV)	SCC (A)	IMP (m)
Control	0%	1574		1498		14.8	106
#6	0.25%	1593	19	1517	19	15.7	101
#7	0.5%	1605	31	1529	31	16.2	99
#8	0.75%	1673	99	1596	98	19.3	87

Once again, Table 2 clearly shows the voltage improvement by applying permanganate to an alternative EMD supplier, Xiangtan Electrochemical Company. In addition, it can be seen as in Table 1, that the IMP (cell impedance) is not negatively affected by the addition of KMnO_4 in the practical range for application in alkaline cells. However, there is a surprising trend to higher SCC and lower IMP values with increasing KMnO_4 addition.

The OCV maximum according to the International Standard IEC 60086 for primary alkaline cells is set at 1.65V. Therefore, the maximum practical amount of KMnO_4 additive will depend on this IEC maximum limit value and on the EMD type used. Tests similar to those made in Examples 1 and 2 and illustrated in Tables 1 and 2 can be made when a new type or batch of manganese dioxide material is bought, and based on the tested values the amount of the oxidizing additive should be chosen to ensure the desirable OCV value.

In all the experimental groups above, permanganate addition has been extensively tested and has not shown detrimental effects on other battery performance parameters such as shelf-life, capacity retention and electrolyte leakage/leaktightness. Tables 3 and 4 show the service time for three selected tests to two voltage levels for cells made in experiments 1 and 2.

- 9 -

TABLE 3a: Service Time in Hours for Cells of Experiment 1

	KMnO ₄	3.9Ω to 1.1V	3.9Ω to 0.8V	10Ω to 1.1V	10Ω to 0.9V	500mA to 1.1V	500mA to 0.8V
Control	0%	4.05	7.08	14.75	20.22	1.13	2.95
#1	0.25%	4.53	6.93	15.57	18.87	1.48	2.72
#2	0.60%	4.00	7.50	15.18	19.75	1.15	3.03
#3	0.90%	4.05	7.17	15.05	20.12	1.20	3.20
#4	1.20%	4.20	7.05	15.08	19.70	1.20	3.12
#5	2.40%	3.63	7.30	15.13	19.60	1.37	3.00
#5b	4.80%	4.00	6.95	14.68	19.05	1.20	2.85

TABLE 3b: Relative Service Time for Cells of Experiment 1

	KMnO ₄	3.9Ω to 1.1V	3.9Ω to 0.8V	10Ω to 1.1V	10Ω to 0.9V	500mA to 1.1V	500mA to 0.8V
Control	0%	100%	100%	100%	100%	100%	100%
#1	0.25%	112%	98%	106%	93%	131%	92%
#2	0.60%	99%	106%	103%	98%	101%	103%
#3	0.90%	100%	101%	102%	100%	106%	108%
#4	1.20%	104%	100%	102%	97%	106%	106%
#5	2.40%	90%	103%	103%	97%	121%	102%
#5b	4.80%	99%	98%	100%	94%	106%	97%

5

TABLE 4a: Service Time in Hours for Cells of Experiment 2

	KMnO ₄	3.9Ω to 1.1V	3.9Ω to 0.8V	10Ω to 1.1V	10Ω to 0.9V	500mA to 1.1V	500mA to 0.8V
Control	0%	3.63	6.97	13.78	19.87	0.88	2.72
#6	0.25%	3.83	6.98	13.50	19.62	1.25	2.75
#7	0.50%	3.75	7.05	13.68	19.78	1.22	2.63
#8	0.75%	3.70	7.02	13.53	19.68	1.27	2.75

- 10 -

TABLE 4b: Relative Service Time for Cells of Experiment 2

	KMnO ₄	3.9Ω to 1.1V	3.9Ω to 0.8V	10Ω to 1.1V	10Ω to 0.9V	500mA to 1.1V	500mA to 0.8V
Control	0%	100%	100%	100%	100%	100%	100%
#6	0.25%	106%	100%	98%	99%	142%	101%
#7	0.50%	103%	101%	99%	100%	138%	97%
#8	0.75%	102%	101%	98%	99%	143%	101%

As can be seen from tables 3 and 4, the service time is not negatively affected by the addition of KMnO₄. In fact, especially at the higher rate of 500 mA, the performance to the higher voltage level of 1.1 V is significantly improved over no KMnO₄ addition, up to 43% improvement were measured depending on EMD grade and level of addition.

Example 3:

To demonstrate the effect of other oxidizer additives, potassium peroxodisulfate, K₂S₂O₈, was evaluated in alkaline AA-size cells, which were prepared as in Example 2 with EMD supplied by Xiangtan Electrochemical Company and two different levels of potassium peroxodisulfate (K₂S₂O₈). The separator used in this experiment was different, therefore, control cells that had no K₂S₂O₈ addition were prepared as well for comparison. Once again, test cells were tested for the basic electrical tests; OCV, CCV, SCC, and IMP.

Table 5 shows the basic electrical tests of the test cells with the addition of various levels of K₂S₂O₈ using Xiangtan Electrochemical Company EMD.

- 11 -

**Table 5: Basic Electrical Tests of AA Test Cells with Various Levels of $K_2S_2O_8$,
Employing Xiangtan Electrochemical Company EMD**

Test Cell Group	$K_2S_2O_8$	OCV (mV)	dVocv (mV)	CCV (mV)	dVccv (mV)	SCC (A)	IMP (m)
Control	0%	1.580		1.504		18.7	84
#9	0.75%	1.584	4	1.504	0	17.8	89
#10	1%	1.589	9	1.511	7	17.9	89

Once again, Tables 5 shows the voltage improvement by applying persulfate to EMD supplied by Xiangtan Electrochemical Company. In addition, it can be seen as in Tables 1 and 2, that the IMP is not negatively affected by the addition of $K_2S_2O_8$. However, when compared to Experiment 2, at the same level of additive addition, potassium permanganate is a more powerful oxidizing agent and would be preferred. Tables 6a and 6b show the service time for three selected tests to two voltage levels for cells made in experiments 3.

TABLE 6a: Service Time in Hours for Cells of Experiment 3

	$K_2S_2O_8$	3.9 Ω to 1.1V	3.9 Ω to 0.8V	10 Ω to 1.1V	10 Ω to 0.9V	500mA to 1.1V	500mA to 0.8V
Control	0%	3.94	7.61	14.22	20.61	1.31	2.88
#9	0.75%	4.00	7.35	13.88	20.31	1.25	2.71
#10	1%	3.69	7.05	14.12	20.38	1.26	2.65

TABLE 6b: Relative Service Time for Cells of Experiment 3

	$K_2S_2O_8$	3.9 Ω to 1.1V	3.9 Ω to 0.8V	10 Ω to 1.1V	10 Ω to 0.9V	500mA to 1.1V	500mA to 0.8V
Control	0%	100%	100%	100%	100%	100%	100%
#9	0.75%	101%	97%	98%	99%	96%	94%
#10	1%	94%	93%	99%	99%	97%	92%

- 12 -

As can be seen from tables 6a and 6b, the service time is not significantly affected by the addition of $K_2S_2O_8$.

CLAIMS

1. An alkaline electrochemical cell with improved open circuit voltage, comprising a manganese dioxide cathode, a separator, an anode and an aqueous alkaline electrolyte,
5 said cathode including an oxidizing additive of less than 5 weight% relative to the mass of said manganese dioxide for increasing the open circuit voltage without adversely affecting the cell impedance.
2. A cell as claimed in claim 1, wherein said oxidizing additive comprises a
10 permanganate compound, a peroxysulfate compound, or a combination thereof.
3. A cell as claimed in claim 2, wherein said permanganate compound is selected from the group consisting of potassium, barium, calcium, silver, copper, and lithium permanganate.
15
4. A cell as claimed in claim 2, wherein said peroxysulfate compound is selected from the group consisting of potassium, barium, calcium, silver, copper, and lithium peroxysulfate.
- 20 5. A cell as claimed in claim 2, wherein said permanganate compound is potassium permanganate.
6. A cell as claimed in claim 2, wherein said peroxysulfate compound is potassium peroxodisulfate.
25
7. A cell as claimed in any one of claims 1 to 6, wherein the amount of said oxidizing additive relative to the manganese dioxide material is less than 2.5%..
8. A cell as claimed in any one of claims 1 to 7, wherein said cathode includes said
30 oxidizing additive in an amount from about 0.1% to about 0.75% by weight of manganese dioxide.

- 14 -

9. A cell as claimed in any one of claims 1 to 8, wherein said manganese dioxide cathode material is electrolytic manganese dioxide.

5 10. A cell as claimed in any one of claims 1 to 9, wherein said cathode is pressed from a powder mix comprising said manganese dioxide and said oxidizing additive.

11. A cell as claimed in any one of claims 1 to 10, wherein said cell is a primary cell.

10 12. A cell as claimed in any one of claims 1 to 10, wherein said cell is a rechargeable cell.

13. A method for manufacturing alkaline cells as claimed in any one of claims 1 to 12 , comprising the steps of: obtaining said manganese dioxide cathode material of a predetermined type in a quantity sufficient for producing a large number of cells; in
15 separately produced test cell, testing the open circuit voltage as a function of said oxidizing additive prior to said manufacturing; determining the percentage quantity of said additive to provide a pre-determined uniform open circuit voltage; and, manufacturing said cells by using said pre-determined quantity of said oxidizing additive.

20

14. A method as claimed in claim 13, wherein said predetermined uniform open circuit voltage is about 1.65V.

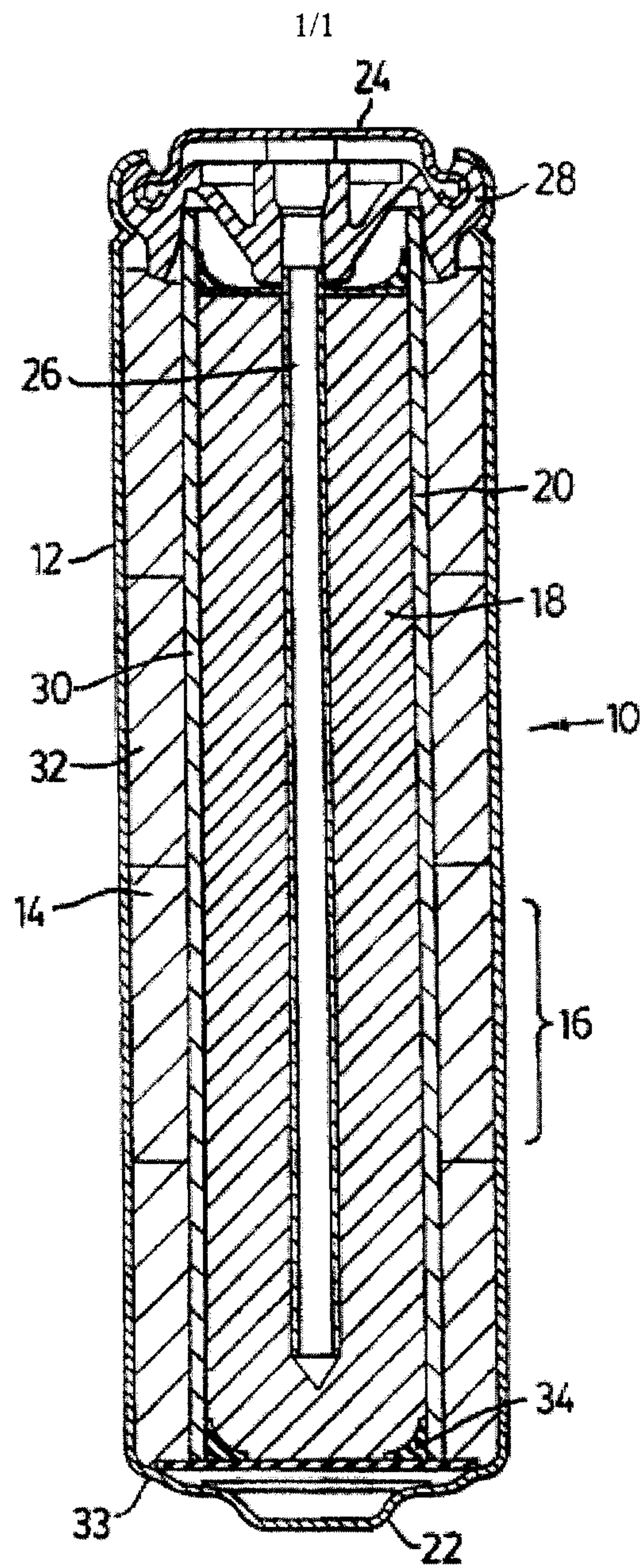


FIG. 1

