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(54) **Alkaline cell having a cathode including an additive**

(57) A cathode for use in an electrochemical cell having an anode and an electrolyte. The cathode includes a manganese dioxide active material and a titan-

ate additive which preferably includes at least one of BaTiO₃ or K₂TiO₃. The cathode of the present invention is particularly adapted for use in an electrochemical cell having a zinc anode and an alkaline electrolyte.

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Description

The present invention generally relates to electrochemical cells including cathode additives and more particularly to primary alkaline electrochemical cells having cathodes formed of manganese dioxide, one or more titanate additives, and other cathode components.

A typical alkaline cell would comprise: a steel cylindrical can having a cathode comprising manganese dioxide as the active material, generally formed on the interior surface of the steel can; an anode comprising zinc, generally located in the centre of the cell; a separator located between the anode and the cathode; and an alkaline electrolyte simultaneously contacting the anode, cathode, and separator. A conductive anode current collector is inserted into the anode active material and a seal assembly closes the open end of the steel can.

A primary goal in designing alkaline batteries is to increase the service performance of the cell. The service performance is the length of time for the cell to discharge under a given load to a specific voltage at which the cell is no longer useful for its intended purpose. One approach taken to increase service performance was to increase the interior volume of the cell in order to increase the amount of active materials within the cell. However, the commercial external size of the cell is fixed, thereby limiting the ability to increase the amounts of active materials within the cell. In order to accommodate more active materials within the cell while maintaining the external size of the cell, the steel label of the conventional alkaline cell has been replaced with one made of thinner metalized plastic film. Thus, the steel can may be enlarged to provide a greater internal volume. By switching to a thinner plastic film label, the service performance of a typical alkaline cell was significantly increased.

Another approach taken to increase the service performance of a cell is to utilize an anatase titanium dioxide as an additive to a cathode having manganese dioxide as the active material.

Despite past increases in service performance, the need to find new ways to increase service performance remains the primary goal of cell designers.

The present invention improves the service performance of alkaline cells by the addition of one or more titanate additives to the active cathode material. Thus, the present invention consists in an electrochemical cell having an anode, a cathode, and an electrolyte, said cathode comprising a manganese dioxide active material and an additive comprising a titanate.

The titanate additive is preferably one or both of BaTiO_3 or K_2TiO_3 .

The cathode of the present invention is particularly adapted for use in an electrochemical cell having a zinc anode and an alkaline electrolyte.

In a preferred embodiment, the titanate additive constitutes from 0.1 to 10 weight percent of said cathode, preferably from 1 to 5 weight percent of said cath-

ode and more preferably from 1 to 2 weight percent of said cathode.

The invention is further illustrated by reference to the accompanying drawings, in which:

Figure 1 is a cutaway perspective view of an example of an electrochemical cell constructed in accordance with the present invention; and

Figure 2 is a comparative graph of the service performance of a standard alkaline cell having a cathode with no additives and electrochemical cells having cathodes with additives in accordance with the present invention.

Figure 1 shows a cutaway view of a typical cylindrical alkaline battery 10. Alkaline battery 10 includes a steel can 15 having a cylindrical shape and one open end. A metalized, plastic film label 16 is formed about the exterior surface of steel can 15 except for the ends of steel can 15. At the closed end of steel can 15 is a positive cover 17 preferably formed of plated steel. Film label 16 is formed over the peripheral edge of positive cover 17.

In the embodiment shown, a cathode 20 preferably formed of a mixture of manganese dioxide, graphite, 45% potassium hydroxide solution, deionized water, an aqueous TEFLON™ solution of 20% polytetrafluoroethylene, and an additive, is formed about the interior side surface of steel can 15. A separator 30, which is preferably formed of a non-woven fabric that prevents migration of any solid particles in the battery, is disposed about the interior surface of cathode 20. An electrolyte 40 formed of potassium hydroxide is disposed in the interior of separator 30. An anode 50, preferably formed of zinc powder, a gelling agent and other additives, is disposed within electrolyte 40 in contact with a current collector 60, which may be formed of brass.

Current collector 60 contacts a brass rivet 70 formed at the open end of steel can 15. A nylon seal 71 is formed at the open end of steel can 15 to prevent leakage of the active ingredients contained in steel can 15. Nylon seal 71 contacts a metal washer 72 and an inner cell cover 74, which is preferably formed of steel. A negative cover 75, which is preferably formed of plated steel is disposed in contact with inner cell cover 74 and brass rivet 70, which contacts current collector 60 through a hole formed in nylon seal 71. Negative cover 75 is electrically insulated from steel can 15 by nylon seal 71.

The cathode of the present invention for a D-size cell is preferably composed of approximately 71.7 to 81.7 weight percent MnO_2 , about 8.5 weight percent graphite, about 7.9 weight percent of an alkaline solution, such as an aqueous 45% KOH solution, about 0.4 weight percent deionized water, about 1.5 weight percent binder material, such as an aqueous TEFLON™ solution of 20% polytetrafluoroethylene, and approximately 0.1 to 10 weight percent of an additive. More

preferably, the weight percent of MnO_2 is between about 76.8 and 80.8 and the weight percent of the additive is between 1 and 5 such that the combined weight percent of MnO_2 and the additive is a constant of preferably approximately 81.8. The amount of alkaline solution used in the cathode varies according to cell size as does the amount of the binder material. The additive is a titanate, preferably BaTiO_3 or K_2TiO_3 .

The cathode may be made by weighing out the needed materials and mixing the MnO_2 , the titanate additive, and the graphite and blending to obtain a homogeneous mixture. The deionized water, the TEFLON™ Solution, and the KOH solution are then mixed with the dry cathode components to form a homogeneous cathode mix. The cathode mixture is then placed in steel can 15 and moulded into an annular, cylindrical shape.

As stated above, it has been discovered that the addition of small amounts of the above listed additives significantly increases the service performance of alkaline electrochemical cells. The following example illustrates the advantages obtained from practicing the present invention.

EXAMPLE

Control alkaline D-size cells were prepared as described above except that no additive was included in the cathodes. Thus, the composition of the cathode in the cell of the present invention was approximately 80.16 weight percent MnO_2 , about 1.6 weight percent titanate, about 8.52 weight percent graphite, about 7.87 weight percent of a 45% aqueous solution of potassium hydroxide (KOH), about 0.36 weight percent deionized water, and about 1.49 weight percent of a TEFLON™ binder solution. In the control cell, the weight percentage of MnO_2 relative to the cathode was equal to the combined weight percentage of MnO_2 and the additive in the experimental cells. Experimental D-size cells having a BaTiO_3 additive and other experimental D-size cells having a K_2TiO_3 additive were constructed, along with control cells having no additive. Each cell was connected to a 2.2 Ohm load for one hour per day. Figure 2 shows the resulting time versus voltage discharge profiles for the cells. For a 1.00 volt cutoff, the experimental cells with the K_2TiO_3 additive showed an average 10% increase over the service performance of the control cell and the experimental cells having the BaTiO_3 additive exhibited an average 8% increase in service performance over the control cells. At a 0.80 volt cutoff, the experimental cells having the K_2TiO_3 additive had an average 13% increase in service performance over the control cells, while the experimental cells had an average 10% increase in service performance over the control cells.

As is apparent from the above example, significant increases in service performance of an alkaline electrochemical cell may be obtained using additives of BaTiO_3 and K_2TiO_3 .

Although the above example used D-size cells, it will be appreciated by those skilled in the art that the increase in service performance may be obtained regardless of the cell size. Because some of the above additives perform better than others in continuous tests while others perform better in intermittent tests, it may be desirable to combine such additives to enhance the overall service performance of an electrochemical cell for both continuous and intermittent use.

Claims

1. An electrochemical cell having an anode, a cathode, and an electrolyte, said cathode comprising a manganese dioxide active material and an additive, characterised in that the additive comprises a titanate.
2. An electrochemical cell according to claim 1, wherein said anode includes zinc and said electrolyte is an alkaline electrolyte.
3. An electrochemical cell according to claim 1, wherein said additive constitutes from 0.1 to 10 weight percent of said cathode.
4. An electrochemical cell according to claim 3, in which said additive constitutes from 1 to 5 weight percent of said cathode.
5. An electrochemical cell according to claim 4, in which said additive constitutes from 1 to 2 weight percent of said cathode.
6. An electrochemical cell according to any one of claims 1 to 5, in which the additive is BaTiO_3 .
7. An electrochemical cell according to any one of claims 1 to 5, in which the additive is K_2TiO_3 .

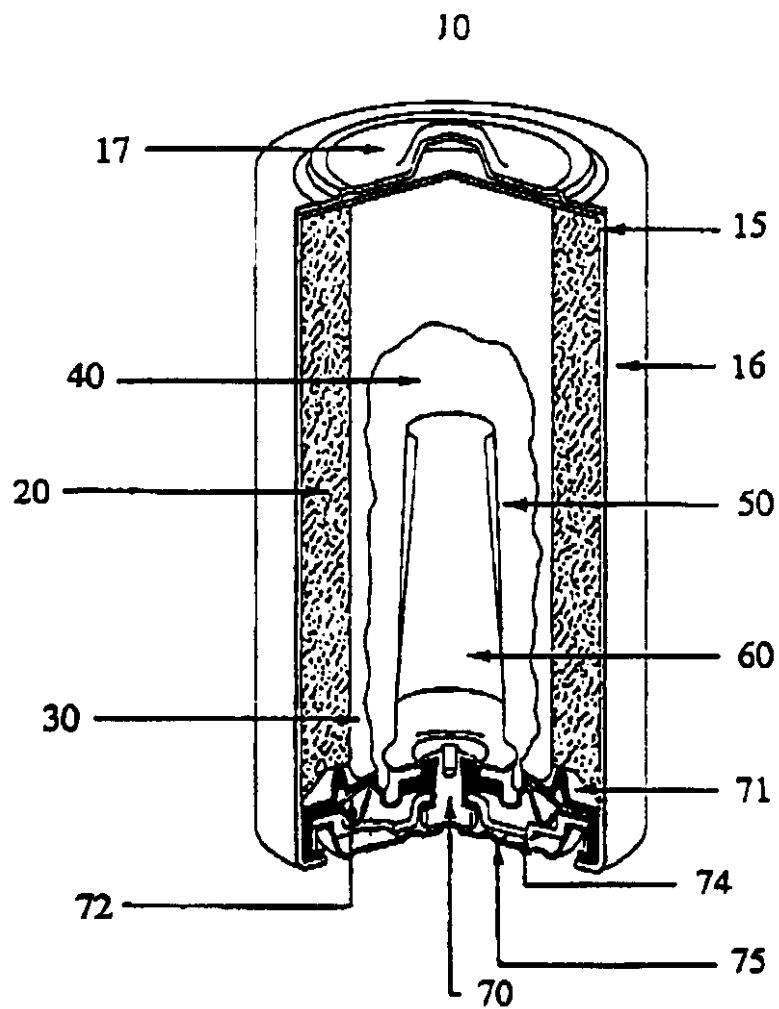
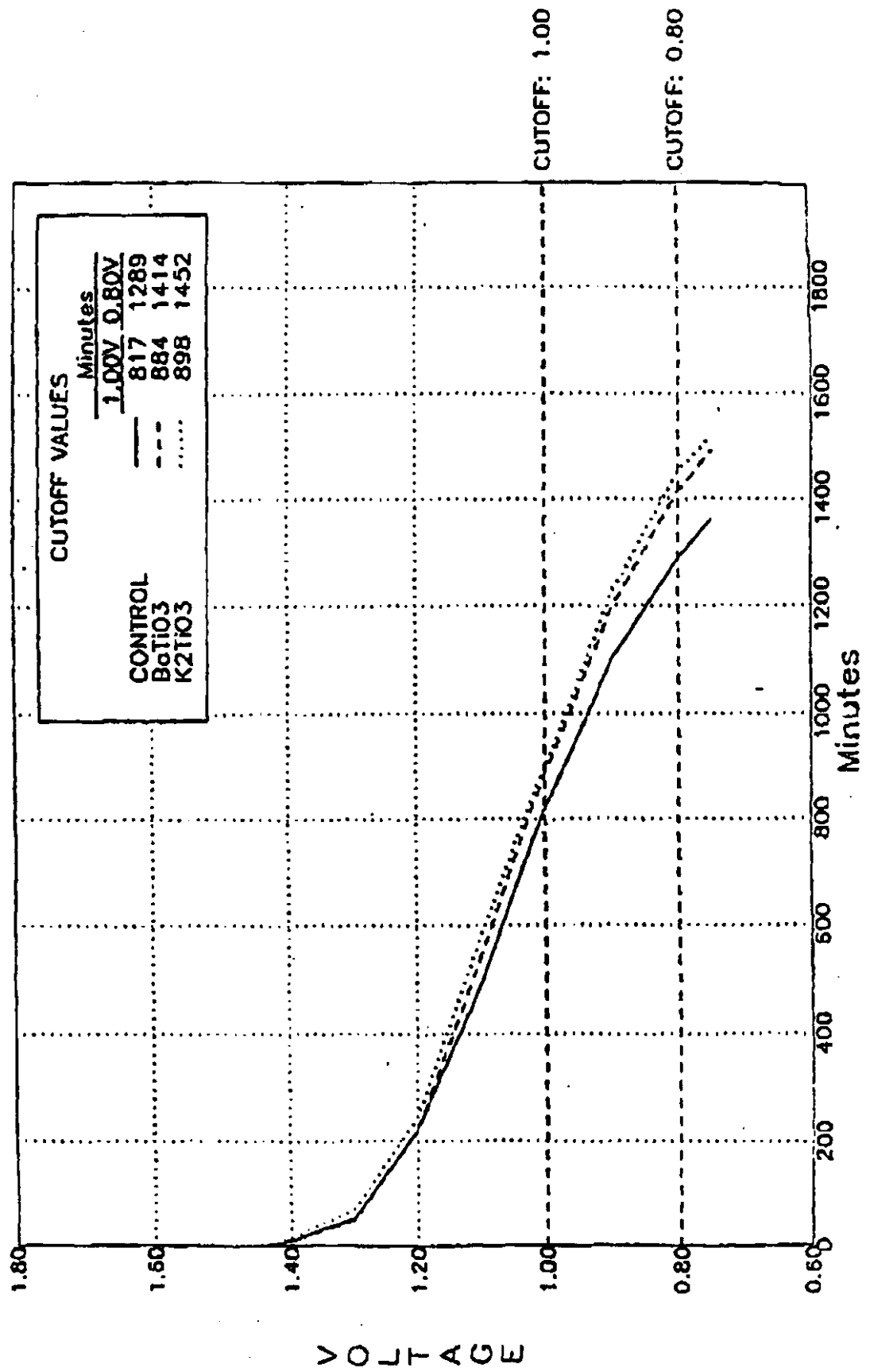


FIG. 1

FIG. 2





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EUROPEAN SEARCH REPORT

Application Number
EP 96 30 4260

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	US-A-4 465 747 (EVANS WILLIAM P) 14 August 1984 * claims 1-3 *	1,3-7	H01M4/50 H01M4/62
X	US-A-4 478 921 (LANGAN RICHARD A) 23 October 1984 * claims 4,5 *	1,3-7	
A	PATENT ABSTRACTS OF JAPAN vol. 014, no. 142 (E-0904), 16 March 1990 & JP-A-02 007368 (JAPAN STORAGE BATTERY CO LTD), 11 January 1990, * abstract *	1,2,7	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			H01M
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 17 September 1996	Examiner D'hondt, J
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons Δ : member of the same patent family, corresponding document			

EPO FORM 1501 03.82 (P0403)

具有一種包括添加劑的陰極的碱性電池

- 5 一種用於具有陽極和電解質的電化學電池中的陰極，包括二氧化錳活性材料和鈦酸鹽添加劑，該鈦酸鹽添加劑最好是包括 BaTiO_3 或 K_2TiO_3 中至少一種的化合物。本發明的陰極特別適合用在一種具有鋅陽極和碱性電解質的電化學電池中。

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