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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 an additive which includes SnO_2. 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 relates generally to electrochemical cells including cathode additives and more particularly to primary alkaline electrochemical cells having cathodes formed of manganese dioxide, a tin dioxide additive, and other cathode components.

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

A primary goal in the design of alkaline batteries is to increase the service performance of the cell. The service performance is the length of time taken 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 which has been 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 provide for better utilization of the materials of the electrodes. This approach is taken in U.S. Patent No. 5,342,712, which discloses utilizing 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.

We have now discovered that the service performance of alkaline cells may be improved by the addition a tin dioxide additive to the active cathode material, i.e. the manganese dioxide (MnO_2). 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 tin dioxide (SnO_2).

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 SnO_2 additive constitutes from 0. 1 to 10 weight percent of said cathode, preferably from 1 to 5 weight percent of said cathode 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;

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; and

Figure 3 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 and preferred 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.

A cathode 20, preferably formed of a mixture of manganese dioxide, graphite, 45% potassium hydroxide solution, deionized water, a TEFLON™ solution, 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 71.76 to

81.66 weight percent MnO_2, about 8.52 weight percent graphite, about 7.87 weight percent alkaline solution, such as a 45% KOH solution, about 0.36 weight percent deionized water, about 1.49 weight percent binder material. such as a TEFLON™ solution, and approximately 0. 1 to 10 weight percent of a SnO_2 additive. More preferably, the weight percent of MnO_2 is between about 76.76 and 80.76 and the weight percent of the SnO_2 additive is between 1 and 5 such that the combined weight percent of MnO_2 and the SnO_2 additive is a constant of preferably approximately 81.76. The amount of alkaline solution used in the cathode varies according to cell size as does the amount of the binder material.

The cathode can be made by weighing out the needed materials and mixing the MnO_2, the SnO_2 additive, and the graphite and blending to obtain a homogeneous mixture. Then, the deionized water, the TEFLON™ solution and the KOH solution are 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 additive significantly increases the service performance of alkaline electrochemical cells. The following comparative examples illustrate the advantages obtained from practicing the present invention.

COMPARATIVE EXAMPLE 1

A control alkaline D-size cell was prepared as described above except no additive was included in the cathode and the weight percentage attributed to the additive was provided by additional MnO_2. Thus, the composition of the cathode in the control cell was approximately 81.76 weight percent MnO_2, 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. A first experimental D-size cell was prepared in the same way, except that some of the MnO_2 was replaced by SnO_2 to provide a cathode with 1.6 weight percent SnO_2. The two cells were continuously connected to a 1.0 Ohm load and the voltages of the cells were measured over a period of time. Figure 2 shows a graph of the time versus voltage discharge profiles of the two cells. At a cut-offvoltage of 0.75 volt, the first experimental cell including the SnO_2 additive exhibited a 24% increase in service performance over the control cell.

COMPARATIVE EXAMPLE 2

A control alkaline AA-size cell was prepared as described above using the same weight percentages as used for the control D-size cell except that no additive was included in the cathode and the weight percentage attributed to the additive was provided by additional MnO_2. A second experimental AA-size cell having a cathode with 1.6 weight percent SnO_2 was also constructed. The two cells were subjected to an IEC photoflash test by connecting the cells to a 1.8 Ohm load for cycles of fifteen seconds ON-and forty-five seconds OFF (i.e., each cycle equaling one minute) and the voltages of the cells were measured over a period of ON/OFF cycles. Figure 3 shows a graph of the cycle versus voltage discharge profiles of the two cells. At a cut-off voltage of 0.9 volt, the second experimental cell including the SnO_2 additive exhibited a 25% increase in service performance over the control cell.

Although the above comparative examples were restricted to D and AA-size cells, it will be appreciated by those skilled in the art that the increase in service performance may be obtained regardless of the size of the cell.

Claims

1. An electrochemical cell having an anode, a cathode, and an electrolyte, said cathode comprising a manganese dioxide active material and an additive comprising SnO_2.

2. An electrochemical cell according to claim 1, in which said anode includes zinc and said electrolyte is an alkaline electrolyte.

3. An electrochemical cell according to claim 1 or claim 2, in which 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 having an anode, a cathode, and an electrolyte, said cathode comprising a manganese dioxide active material and an additive comprising SnO_2, characterised in that the additive is present in an amount of from 1 to 2 weight percent of the cathode.

7. An electrochemical cell according to claim 6, in which said anode includes zinc and said electrolyte is an alkaline electrolyte.

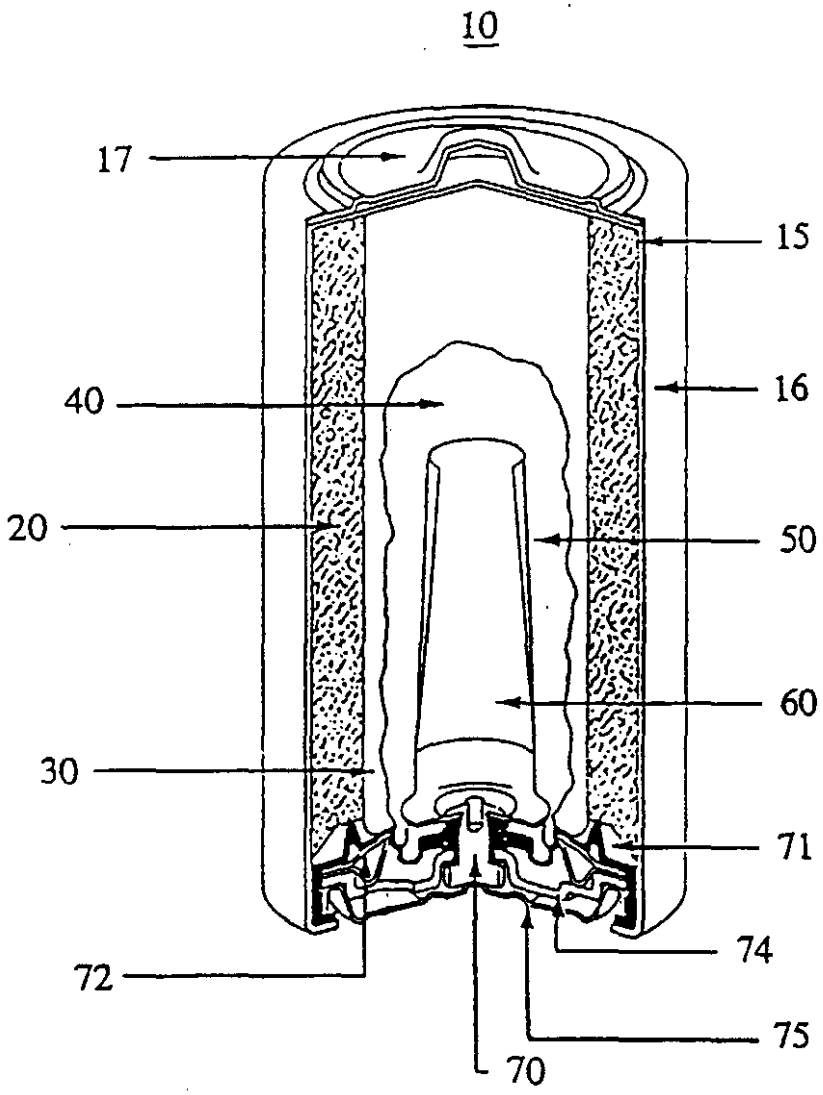
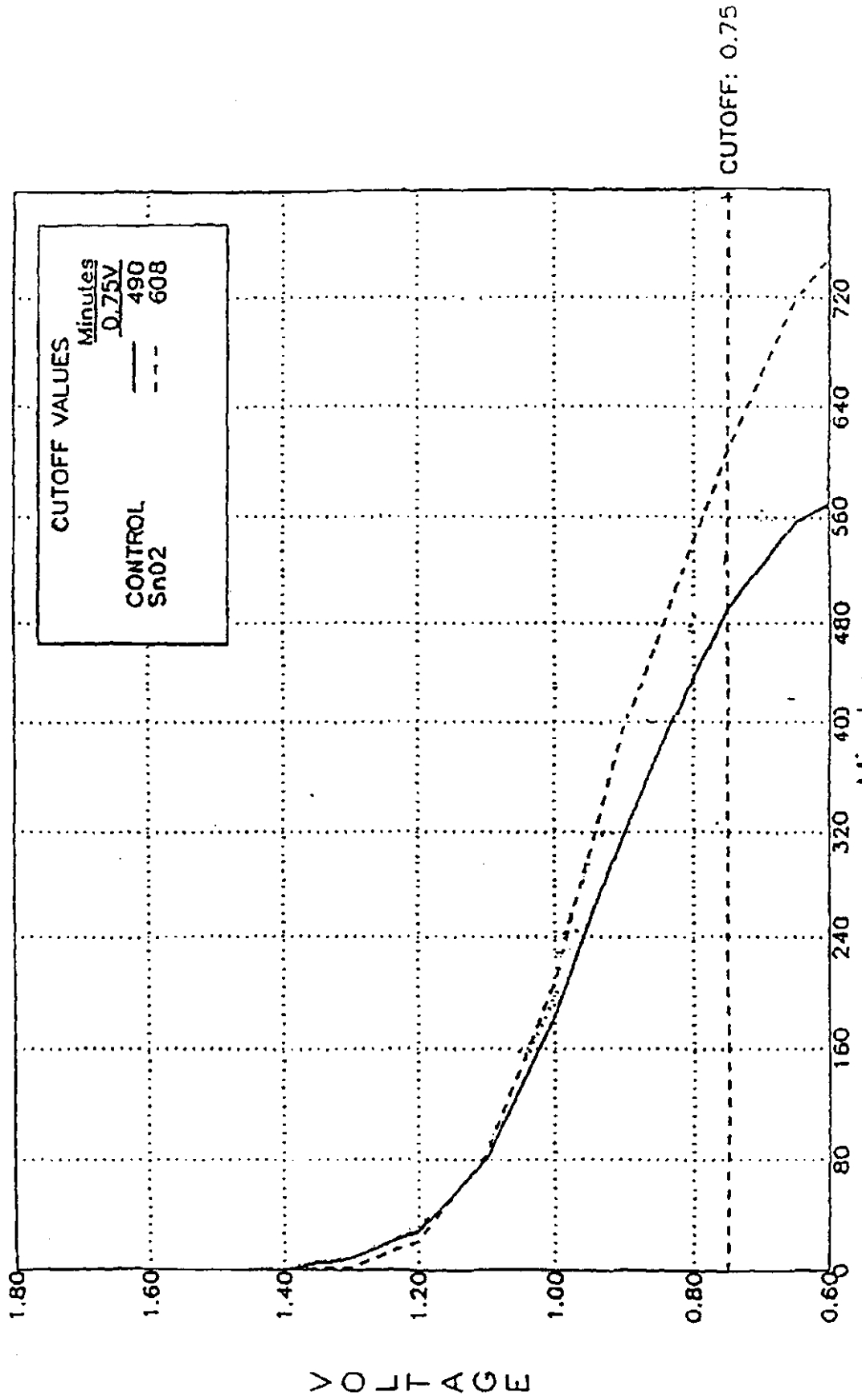


FIG. 1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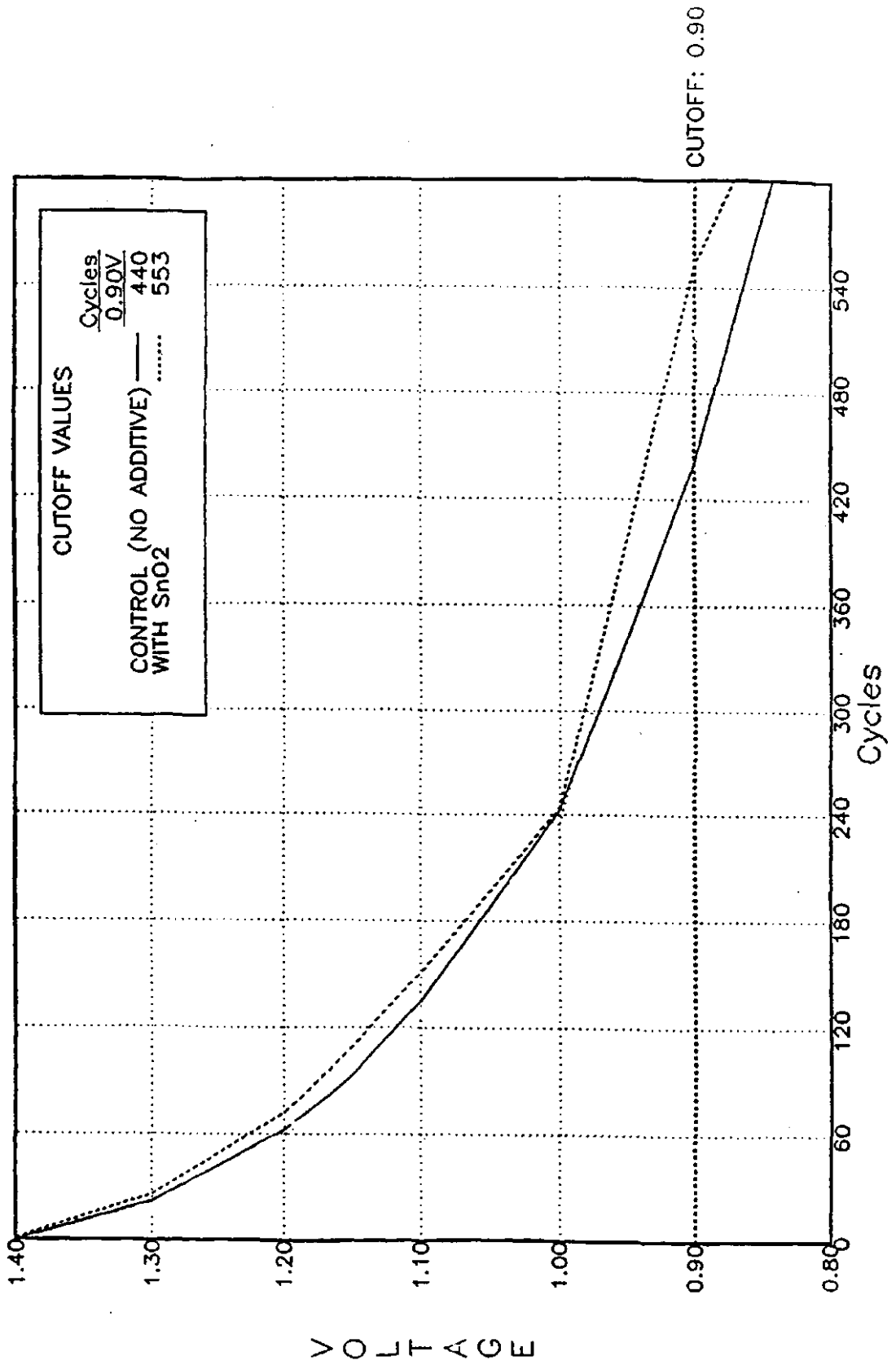
Minutes
VOLTAGE

FIG. 2

FIG. 3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240
300
360
420
480
540
Cycles

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EUROPEAN SEARCH REPORT

Application Number
EP 96 30 4264

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)
P,X	US-A-5 516 604 (MIECZKOWSKA JOLA E ET AL) 14 May 1996 * claims 1,4; example 5 * * column 6, line 6 - line 28; table 1 *	1-7	H01M4/50
X	US-A-4 549 943 (MELLORS GEOFFREY W) 29 October 1985 * column 4, line 44 - line 59; claims 1,7; example 3; tables I,II *	1,2	
X	DATABASE WPI Section Ch, Week 8128 Derwent Publications Ltd., London, GB; Class A85, AN 81-50867D XP002012847 & JP-A-56 061 771 (NIPPON ELECTRIC KK) , 27 May 1981 * abstract *	1	
A	US-A-4 207 391 (CHURCH PETER K ET AL) 10 June 1980 * column 1, line 7 - line 13; claims 1,2 *		TECHNICAL FIELDS SEARCHED (Int.Cl.6) H01M

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	17 September 1996	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
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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

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)

HP2614 説 明 書 摘 要

具有一種包括添加劑的陰極的碱性電池

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一種添加劑，該添加劑包括 SnO_2。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。