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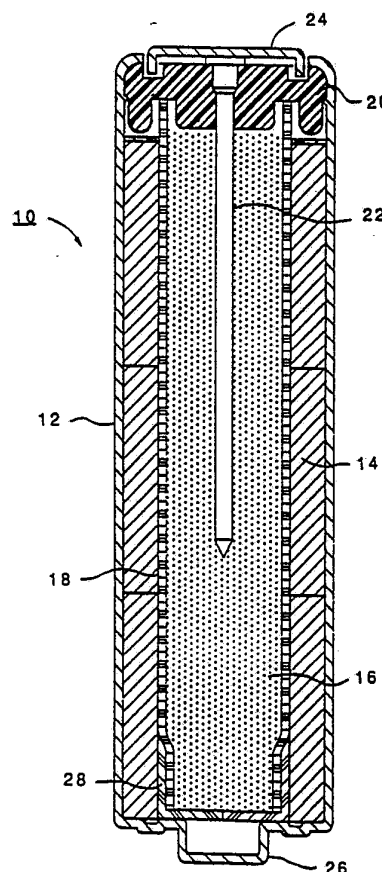
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(54) Title: HIGH CAPACITY RECHARGEABLE CELL HAVING MANGANESE DIOXIDE ELECTRODE

(57) Abstract

A rechargeable cell having a manganese dioxide positive electrode is provided, where the cell has high capacity, and high volumetric and gravimetric energy densities. The cell has an aqueous electrolyte, usually potassium hydroxide, but the electrolyte may also be acidic or a salt solution. The discharge capacity of the cell is determined by the theoretical one electron discharge capacity of the manganese dioxide -- since the manganese dioxide is considered to be reversibly charged and discharged only between its nominal status of MnO_2 and its fully discharged one electron status of Mn_2O_3 . The negative electrode is also rechargeable; and while it is usually zinc it may also be such as iron, lead, cadmium, hydrogen, or a metal hydride. The discharge capacity of the cell is limited as a consequence of the theoretical discharge capacity of the negative electrode or anode, which is in the range of from 60 % to 120 % of the theoretical one electron discharge capacity of the MnO_2 electrode.



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HIGH CAPACITY RECHARGEABLE CELL HAVING MANGANESE DIOXIDE ELECTRODE

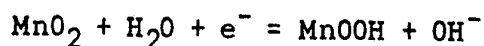
FIELD OF THE INVENTION:

This invention relates to rechargeable cells having manganese dioxide electrodes, and particularly cells which are substantively anode limited in respect of their discharge capacity. In that regard, the theoretical discharge capacity of the anode is in the range of from 60% to 120% of the theoretical one electron discharge capacity of the MnO_2 electrode. The usual embodiment may be the typical "bobbin" type cylindrical cell, however spirally wound cells, button or coin cells, and flat plate cells may be provided in keeping with the present invention.

BACKGROUND OF THE INVENTION:

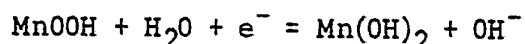
Manganese dioxide electrodes, when used as rechargeable cathodes in electrochemical cells, are known to be reversible only if the manganese dioxide is charged and discharged between its nominal status of MnO_2 and its fully discharged one electron status of Mn_2O_3 . For purposes of the present discussion, the discharge capacity of the MnO_2 electrode between the MnO_2 status and the Mn_2O_3 status is termed or designated as the theoretical one electron discharge capacity of the MnO_2 electrode. If the discharge process of the MnO_2 cathode continues beyond the Mn_2O_3 level, an irreversible phase change has been reported to occur, so that the manganese dioxide electrode is no longer fully rechargeable.

Specifically, the following equation is descriptive of the discharge reaction which takes place as the MnO_2 discharges towards its Mn_2O_3 one electron discharge level in the presence of an aqueous electrolyte.



However, it must not be overlooked that, during discharge, the structure or lattice of the MnO_2 electrode expands or at least tends to expand. Moreover, at a certain point of the discharge, the discharge mechanism changes; and after that point, the discharge

which is in the second electron discharge level of the MnO_2 electrode occurs following a heterogeneous phase reaction which is set forth as follows:



What the above reaction equation describes requires the dissolution of the MnOOH in the form of $\{\text{Mn(OH)}_4\}^+$, and assumes the presence of graphite within the MnO_2 matrix. The literature reports an electrochemical reduction on the graphite to $\{\text{Mn(OH)}_4\}^+$, and then there is a precipitation of Mn(OH)_2 from the latter phase. See, for example, Journal of Electrochemical Society, Volume 115, No. 4, pages 333 to 338 (1968); Boden et al, "The Alkaline Manganese Dioxide Electrode". See also Journal of Power Sources, 16, (1985), pages 1 to 43; Desai et al, "Manganese Dioxide - A Review of a Battery Chemical, etc."

However, particularly with reference to alkaline manganese dioxide/zinc cells, the second step described above occurs at a voltage which is too low to contribute significantly if at all to the service life of the cell, since it occurs below 0.9 volts. Generally, it is considered that the second discharge step described above is irreversible, thereby rendering the MnO_2 electrode to be non-rechargeable.

Particularly with respect to MnO_2/Zn cells, there have been a number of steps taken to ensure rechargeability; and specifically, steps have been taken to severely limit the discharge capacity of the anode, or to provide electronic means to preclude overdischarge of the MnO_2 cathode, so as to provide rechargeable MnO_2/Zn cells. This has been particularly of concern when it was intended to provide MnO_2/Zn cells in sufficient quantities as to make them commercially viable, meaning especially that ordinary commercially available battery grade manganese dioxide had to be relied upon.

Of course, it is generally to be noted, as well, that it is the MnO_2 electrode that provides the difficulty as to rechargeability; it being generally considered that it is the material of the anode that is reversible or rechargeable over most if not all of the cycle life of the cell.

Historically, rechargeable alkaline MnO_2/Zn cells that have been brought to the market in the late 1960's and early 1970's were not successful because of the constraints placed upon them. Those constraints were, as noted above, the use of electronic controls to determine the end of the discharge -- that is, to cut off the discharge at a certain point -- or even placing the onus on the user of the cell to keep records of the amount of use that the cells were put to and to place the cells in the charger for recharging at an appropriate time, which must be neither too early or too late. In general, such cells were merely modified primary alkaline MnO_2/Zn cells, and generally they had the same balance between the active materials in the anode and cathode as primary cells but merely employed additives to suppress gas formation, and of course improved separators to preclude the chance of shorting between the anode and cathode. Such cells were also quite low in respect of their energy densities: For example, a D cell may have been rated at only 2 Ah as a rechargeable cell, but could deliver only 6 Ah before the cell was completely exhausted and not further rechargeable. In such cells, the theoretical capacity of the zinc anode was generally set higher than that of the theoretical one electron discharge capacity of the MnO_2 , at about 130% to 135% of the theoretical one electron discharge capacity. A more full discussion of the above is found in FALK and SALKIND Alkaline Storage Batteries, published by John Wiley & Sons, New York, 1969, at pages 180 to 185, and also pages 367 to 370.

So as to overcome the limitations noted above, cells were developed by which the discharge capacity of the cell was limited by imposing anode limitation on the capacity of the cell -- by which it was made impossible to discharge the MnO_2 to more than a given amount because of the available capacity of the anode. Generally, that meant that the discharge capacity of the zinc anode was allowed to become no more than about 30% of the theoretical one electron discharge capacity of the MnO_2 cathode. This, at least, preserved the rechargeable characteristics of the cell, but resulted in a cell

having quite low deliverable energy capacity and density. Those limitations, understandably, mitigated against the commercial acceptability of such cells.

Reference is made to Amano et al U.S. Patent 3,530,496, issued September 22, 1970. Amano et al make a very strong statement of their intent to limit the depth of discharge of the MnO_2 electrode by providing an anode that has its capacity limited to between 20% to 30% of the MnO_2 electrode capacity. The available capacity of the MnO_2 depends on various parameters such as the drain rate, cutoff voltage, and whether the cell will be subjected to continuous or intermittent use. The available capacity of the MnO_2 electrode is neither clearly indicative nor clearly a measure of or a consequence of the balance of the cell, as discussed below. Generally, it can be assumed that limiting the available anode capacity to less than 30% of the available cathode capacity is equivalent to a theoretical anode capacity limitation of less than 30% of the theoretical one electron MnO_2 discharge capacity.

How Amano et al achieve their zinc anode limitations is that they provide cathodes having dimensions that are essentially equal to those of primary alkaline cells, and then reduce the zinc capacity of the anodes by placing an annular or hollow cylindrical gelled zinc anode adjacent to the MnO_2 cathode and separated from it by a suitable two component separator. Then, the center of the anode is filled with gelled electrolyte that does not have any active anode material added to it. Amano et al also prefer that amalgamated copper particles be included in the anode so as to enhance its conductivity. Moreover, Amano et al also provide a zinc oxide reserve mass, they employ PTFE as a binder, and they must use a perforated coated screen current collector rather than a single nail which would otherwise be used in a primary MnO_2/Zn alkaline cell.

Ogawa et al, in U.S. Patent 3,716,411, issued February 13, 1973, teach a rechargeable alkaline manganese cell, the discharge capacity of the anode of which is controlled within such a range that the cathode can be recharged; and wherein the anode and cathode face each other through a gas permeable and dendrite impermeable

separator. However, the Ogawa et al cell is strictly anode limited in that the capacity of the anode is held to be not more than about 40% of the theoretical one electron discharge capacity of the manganese dioxide. Ogawa et al discuss the fact that if a zinc-manganese dioxide cell is discharged so that its terminal voltage reaches a voltage below 0.9 volts and down to about 0.75 volts, and where the capacity of the zinc negative electrode is about the same or slightly smaller than that of the manganese dioxide positive electrode, then the effect of the discharge on the manganese dioxide is such that it is non-reversible at least in part. Ogawa et al provide that under no conditions should the depth of discharge of the anode be permitted to exceed 60% of the theoretical one electron discharge capacity of the manganese dioxide cathode. Ogawa et al provide an alternative structure which comprises two positive electrodes, one on either side of the anode, and wherein the inner positive electrode is contained within a perforated nickel plate steel pocket or canister.

Kordesch, in U.S. Patent 4,091,178, issued May 23, 1978, also provides a rechargeable MnO_2/Zn cell where the theoretical discharge capacity of the anode is specifically limited to about 33% of the one electron discharge capacity of the cathode. However, Kordesch also provides a charge reserve mass in which a quantity of zinc oxide is placed that is equal to at least 50% of the discharge capacity of the anode. Because there is an excessive capacity of MnO_2 , as well as additional ZnO , the energy density of the Kordesch cell is quite low.

Tomantschger et al, in a commonly owned U.S. Patent Application No. 07/667,476 filed March 11, 1991, provide rechargeable alkaline manganese zinc cells that utilize an MnO_2 positive electrode and a zinc negative electrode, wherein the anode capacity of the zinc is limited to between 40% and up to 100% of the theoretical one electron discharge capacity of the MnO_2 . That provides a rechargeable alkaline manganese cell having higher capacity and higher energy density than has been available from the prior art cells.

The following discussion is directed to the manner in which the theoretical energy content, and its theoretical discharge capacity, may vary for any given electrode composition. Since, in most cells, the anode or negative electrode of the rechargeable cell is substantially completely reversible as to its charging and discharge characteristics, the following discussion is particularly directed to MnO_2 electrodes in the presence of alkaline electrolytes.

The drain rate of the active material of a cell, and particularly the cathode or positive electrode thereof, may be expressed in terms of milliamperes per gram (mA/g) of the active material of the electrode. However, that drain rate may change for any given electrode composition; and moreover, the nature of the utilization for which the cell is intended may also affect the design of the electrode and its composition. For example, the utilization of conductive additives, and the quantity thereof, the particle size of the active material, the electrolyte concentration within the cell, and so on, may have an effect on the manner in which the cell may be efficiently utilized.

Thus, a cell may be optimized for high drain rate or low drain rates, and that makes it necessary to perform tests over all of the drain rates that will be encountered in practical applications, using weighing factors for each drain rate as may be determined by the cell designer, so as to determine the best overall performance. It follows that, depending on the cell balance, the drain rate for the cell that is based on the active material content of the cell, will be different for different designs. A full discussion of a number of those factors is to be found in the commonly owned co-pending application of Tomantschger et al, U.S. Patent Application No. 07/667,476, noted above. That application shows the capacity in mAh/g of active material for MnO_2 electrodes in an alkaline electrolyte, as determined in half-cell experiments for various drain rates expressed in mAh/g. In the experimental work described in that application, it was demonstrated that even at low drain rates in continuous discharge experiments to a cut off of -435 mV vs. the

Hg/HgO reference electrode, only the first electron discharge capacity of the MnO_2 discharge is utilized. A similar discussion is made below.

There may be circumstances where, in respect of primary cells, at least a portion of the second electron discharge of the MnO_2 electrode can be utilized. However, these applications are typically limited to medium to low rate intermittent use, and to lower cut off voltages. For example, Barak in Electrochemical Power Sources, primary and secondary batteries, published by Institution of Electrical Engineers, London, 1980, at pages 95 and 96 describe the capacity yields of alkaline MnO_2 electrodes under various standardized application tests.

It is also to be remarked, however, that in addition to the capacity utilization consideration, primary alkaline cells contain a further additional amount of MnO_2 . This is to preclude the cell from leaking if it is left in an operating device and is utilized as an energy source for extended periods of time. A description of that circumstance is found in Leger, U.S. Patent 2,993,947, issued July 25, 1961.

What the present invention provides is cells which have a manganese dioxide electrode, a high capacity relative to prior art cells, and an aqueous electrolyte. A negative electrode or anode is, of course, provided, with a separator between the negative electrode and the MnO_2 electrode, and appropriate terminal means contacting the negative electrode and MnO_2 electrode so as to provide respective negative and positive terminals for the cell. The manganese dioxide of the MnO_2 electrode is capable of being reversibly charged and discharged between the nominal status of MnO_2 and the fully discharged one electron status of Mn_2O_3 ; the discharge capacity of the MnO_2 electrode between the MnO_2 status and the Mn_2O_3 status being the theoretical one electron discharge capacity of that electrode.

In its broadest terms, the present invention contemplates negative electrodes where the principal active component may be chosen from the group consisting of zinc, iron, lead, cadmium, hydrogen, and metal hydrides. The principal active component of the

aqueous electrolyte is chosen to accommodate the specific couple between the negative electrode and the positive MnO_2 electrode, and particularly may be chosen from the group consisting of alkali metal hydroxides -- e.g., KOH --, or an acid such as H_2SO_4 , H_3BO_3 , or H_3PO_4 , or a solution of salt which may be ZnCl , NH_4Cl , NaCl , or KCl . The negative electrode is, of course, rechargeable.

In keeping with the provisions of the present invention, the theoretical discharge capacity of the negative electrode is in the range of from 60% to 120% of the theoretical one electron discharge capacity of the MnO_2 electrode.

In a typical embodiment of cells according to the present invention, where the cells are intended for commercial exploitation, the active material of the negative electrode is zinc, and the electrolyte is 4N to 12N potassium hydroxide.

Cells according to the present invention may have a number of additives for purposes of enhancing the structural integrity of the MnO_2 cathode, or for inhibiting oxygen evolution or hydrogen evolution, and so on. For example, the MnO_2 electrode may include at least one additive which is chosen from the group consisting of 5% to 15% by weight of graphite, 0.1% to 15% by weight of carbon black, an inorganic binder, graphite fibres that are used as a fibrous reinforcing agent, and a hydrophobic organic binder chosen from the group consisting of PTFE, polypropylene, and polyethylene. The hydrophobic material may be present in the range of from 0.1% to 10% by weight of the MnO_2 electrode. The carbon black may be present as a porous additive in the MnO_2 electrode in the range of from 0.1% to 15% by weight thereof.

To promote hydrogen gas recombination within the cathode, the cathode composition may include hydrogen recombination catalysts such as those taught in commonly owned U.S. Patent application Serial No. 07/520,820, filed July 9, 1990. Still further, so as to provide for overcharge capability, an oxygen evolution catalyst as taught in commonly owned U.S. Patent 4,957,827, issued September 18, 1990, to Kordesch et al, may be utilized. Whatever catalyst is

selected, it is chosen so as to be stable over a wide voltage range -- typically from 0.9 volts versus Zn to 2.0 volts versus Zn -- and also over a wide temperature range -- typically from -40°C to $+70^{\circ}\text{C}$ -- without any significant deterioration in performance of the cell. Such catalysts may be oxides, spinels, or perovskites of nickel, cobalt, iron, manganese, chromium, vanadium, titanium, and silver. As taught in U.S. Patent 4,957,827, the oxygen evolution catalyst may be placed on the outer surface of the cathode, or they may be dispersed throughout the MnO_2 electrode.

So as to ensure hydrogen gas porosity of the cathode, and thereby access of hydrogen gas into the cathode where the hydrogen will be oxidized, the cathode composition preferably contains both carbon black as well as the hydrophobic binder. Still further, for purposes of hydrogen gas porosity and accessibility, the cathode composition may further comprise from about 0.1% to 5.0% of a hydrophobic material such as PTFE, polyethylene, or polypropylene, together with an additional porous additive such as from about 0.1% to 5.0% of carbon black. Such additives improve the gas transport characteristics of the cathode, and thereby enhance the hydrogen recombination rate of the cathode.

The MnO_2 electrode may comprise from 0.1% to 5% of a hydrogen evolution catalyst such as one chosen from the group consisting of silver, oxides of silver, silver salts, platinum, and compounds of silver and platinum.

The use of carbon fibres, as well as the use of hydrophobic binders, will ensure that hydrogen gas within the cell will have access in to the cathode, where the hydrogen is oxidized. An additional 0.1% to 5% of hydrophobic binder such as PTFE, polyethylene or polypropylene, together with the porous additive such as 0.1% to 5% of carbon black, may be incorporated into the cathode to further improve the gas transport characteristics thereof, and thereby to enhance the hydrogen recombination rates.

Depending on the nature of the cell, the cathode may be molded into pellets and inserted into the can, followed optionally by recompaction. Otherwise, the cathode may be extruded directly into

the can, or it may be rolled or cast as a flat cathode for use in flat plate cells or even in respect of button or coin cells.

BRIEF DESCRIPTION OF THE DRAWINGS:

The present invention is described hereafter, in association with the accompanying drawings, in which:

Figure 1 is a typical cylindrical cell in which the present invention may be embodied;

Figure 2 shows curves comparing the capacity of active material of manganese dioxide cathodes and zinc electrodes intended for use in cells according to the present invention, where the data were determined in half cell tests;

Figures 3 to 8 are graphical representations of the capacity of test cells against the capacity of a control cell, where the test cells all have different balances of the active materials of the positive and negative electrodes, and wherein the test cells are charged and discharged according to a particular test regimen and the control cell is charged and discharged according to standard test procedures; and

Figure 9 shows the results of cycling tests using deep discharge cycles, for two different cell configurations having differing ratios of anode capacity to cathode capacity.

DESCRIPTION OF THE PREFERRED EMBODIMENTS:

Referring to Figure 1, a typical cylindrical cell is shown at 10. The cell comprises a container 12, within which is a cathode 14 and an anode 16. Between the cathode and the anode there is located a separator 18. The cell is closed by the closure member 20, through which a current collector 22 extends into the anode 16. The current collector or nail 22 contacts a metal negative cap 24 which is placed or welded across the head of the nail, and across the closure member 20, thereby providing a negative terminal for the cell 10. At the other end of the cell there is formed a pip 26, and it provides the positive terminal for the cell. It is evident that the can 12 contacts the cathode 14 whereas only the cap 24 through nail 22 contacts the

anode 16. To preclude short circuit within the cell, the pip 26 is insulated from the anode 16 by an insulating washer or bottom cup 28.

It is evident that similar or appropriate structures, providing negative and positive electrodes respectively connected to negative and positive terminals for the cell, and separated by an appropriate separator, may be provided in spirally wound cells, flat plate cells, and button or coin cells.

Within the cell, an aqueous electrolyte is provided so as to flood the cell and contact and provide ionic paths so that the cell may be charged and discharged.

The separator 18 may be permeable to the passage of gases such as hydrogen or oxygen that are produced within the cell on overcharge, standby, or overdischarge conditions. The cell may comprise an absorber made from rayon or polyvinylalcohol fibres, and a barrier which may consist of cellulose, CELLOPHANE (TM), polyamide or polyethylene, or the like. The separator is such that the cell will not be shorted because of zinc dendrite growth through the separator. Other appropriate separator materials such as those sold in association with the trademark CELGARD (TM) and PERMION (TM) may be used, as well as multi-component designs, the use of several laminates, and so on.

Typically, the electrolyte is alkaline metal hydroxide such as 4N to 12N potassium hydroxide. It may, as appropriate, contain various additives including dissolved zinc oxide. Other aqueous electrolytes may be utilized, as noted above.

The choice of the material of the negative electrode is usually zinc, but it may also be iron, lead, cadmium, hydrogen, or a metal hydride. Accordingly, the choice of the aqueous electrolyte may expand, depending on the couple between the negative electrode and the MnO_2 cathode, to include other alkaline metal hydroxides, acids such as H_2SO_4 , H_3BO_3 and H_3PO_4 , or aqueous solutions of salts such as $ZnCl$, NH_4Cl , $NaCl$, and KCl .

It is desirable that energy densities of different cells might be compared in actual discharge experiments. However, in practice, difficulties in making such comparisons are encountered. For example, it is well known that the drain rate of a cell, expressed for example as mA/g of active material, may affect the utilization of the theoretical one electron energy capacity for a given MnO_2 electrode composition. In essence, the practical capacity of an electrode approaches the theoretical capacity of the electrode only in circumstances where a very low drain rate can be maintained. Such circumstances may be, for example, electrical clocks where the clock runs continuously for a long period of time on a single AA cell; but most battery powered devices such as radios, tape players, electric toys, and the like, require considerably higher drain rates.

The degree of utilization of the electrode also depends on the composition of the electrode; for example, whether the electrode includes conductive additives, as well as the particle size of the active material of the electrode, the electrolyte concentration, and so on. Thus, specific cells can be designed and optimized for high drain rate circumstances, or for low drain rate circumstances. Moreover, the degree of utilization, and the specific cell design, may be predicated upon the configuration of the cell -- which may be a coin or button cell, or a flat plate cell, rather than a more typical cylindrical or bobbin type cell.

That fact that different cell designs will accommodate different drain rates thereby makes it necessary to perform tests on commercially available cells over all drain rates that may be encountered in practical applications; and then to apply weighting factors for each drain rate so as to attempt to determine which cell has demonstrated the best overall performance. However, depending on the cell balance, the drain rate that is based on the active material content of the electrodes of the cell, will be different for different designs.

A specific example follows:

Example I:

The following compositions were used to construct half-cells, both as to the MnO_2 electrode composition and the anode composition. Each cell is expressed in parts by weight:

Table 1: Composition of MnO_2 and Zn Electrodes Used in the Half Cell Tests

<u>Cathode Composition</u>		<u>Anode Composition</u>	
MnO_2	84.5	$\text{Zn}(3\% \text{Hg})$	65.50
Graphite	9.00	CMC/CARBOPOL*(1/1)	1.00
9N KOH	6.50	9N KOH, 5% ZnO	33.50

*(TM)

Half cell experiments were then carried out, at various drain rates expressed in terms of mA/g. The capacity of the active material for the zinc and the manganese dioxide was determined in mAh/g, at various drain rates. The results are shown in Figure 2, where curve 40 shows the theoretical two electron zinc capacity and curve 42 shows the actual determined capacity of zinc to a cutoff voltage of -435 mV versus a Hg/Hg0 reference electrode voltage. Likewise, curve 44 shows the theoretical capacity of manganese dioxide for the one electron ($1e^-$) discharge, and curve 46 shows the measured capacity at various drain rates to a cutoff voltage of -435 mV versus a Hg/Hg0 reference electrode voltage. It is clear from Figure 2 that only the theoretical energy content or capacity of respective cells provides a reliable means of comparing cell designs.

Example II:

Having determined that the best comparison between cell designs is only in respect of their theoretical energy capacity, various cell designs of AA test cells were fabricated in keeping with the teachings of two prior art patents that are noted above. Then, their theoretical energy capacities were analyzed, with the result being shown in Table 2, below. It should be noted that the comparisons are made on the basis of each of the cells having a volume of 7.5 ml, a weight of 22.5 g, and an average discharge voltage of 1.25 volts. The theoretical capacities are in practise, and

as discussed above, achievable only at low discharge rates. Table 2 also provides the theoretical gravimetric and volumetric energy densities of the respective prior art cells; and included in Table 2 in all categories shown in that Table is a cell in keeping with the present invention.

Table 2: AA Cell Design Comparisons

	<u>Amano</u> <u>3,530,496</u>	<u>Kordesch</u> <u>4,091,178</u>	<u>Ogawa</u> <u>3,716,411</u>	<u>Present</u> <u>Design</u>
MnO ₂ {Ah} 1e ⁻	2.234	2.261	2.136	2.136
Zn{Ah} 2e ⁻	0.670	0.746	1.282	2.136
Cell{Ah}	0.670	0.746	1.282	2.136
Zn:1e ⁻ MnO ₂ Ratio	0.30	0.33	0.60	1.00
Capacity (Wh)	877.5	932.5	1602.5	>2670
theor. Energy Density (Wh/kg) (Wh/l)	<39 <117	41 124	<71 <214	>119 >356

Table 3, below, is the composition of the cathode and anode used in the cell of the present invention as specified in Table 2 above.

Table 3: Composition of Present Design Test Cells Used in Example II

<u>Cathode Composition</u>		<u>Anode Composition</u>	
MnO ₂	79.01	Zn	56.95
Graphite, Carbon, }	14.49	CARBOPOL	0.52
PTFE, Ag ₂ O		ZnO	9.00
9N KOH	6.50	9N KOH, 5% ZnO	33.53

A principal feature of the present invention is that the theoretical discharge capacity of the negative electrode is in the range of from 60% to 120% of the theoretical one electron discharge capacity of the MnO₂ electrode. However, in order to determine that range, a number of experiments were undertaken, as described below and as illustrated in Figures 3 to 8.

In each of Figures 3 to 8, the discharge capacity is on the vertical axis, and is measured in mAh. The horizontal axis shows the number of cycles to which the control and test cells have been subjected, and in each case only six cycles of data are shown. The first bar is indicated at 31C, or 41C, 51C . . . 81C, and is indicative of the characteristic of the control cell for the cell of the given balance between the active materials of the positive and negative electrodes of the cell, as they vary through Figures 3 to 8. The remaining five pairs of bars compare the discharge capacity of the control cell in each of cycles 2 through 6 at 32C, 33C, 34C, 35C and 36C for Figure 3 (and likewise 42C . . . 46C, 42C . . . 46C for Figure 4), and so on. The measured capacity of the test cells in keeping with the test procedures described below, is shown in Figure 3 at 32T, 33T, 34T, 35T, and 36T, and in the other figures at 42T . . . 46T, 52T . . . 56T, and so on. The tables, below, further provide the capacities of the control and test cells, all as described below.

The balance of the test cells and the control cells in Figure 3 is that the theoretical capacity of the zinc electrode is 80% of the theoretical one electron discharge capacity of the MnO_2 electrode. The balance in Figure 4 is 90%; the balance in Figure 5 is 100%, the balance in Figure 6 is 110%, the balance in Figure 7 is 120%, and the balance in Figure 8 is 130%. All of the tests are in respect of cylindrical AA alkaline MnO_2/Zn cells, and are indicative of the general nature of the effect of cell balance of the theoretical discharge capacity of the negative electrode with respect to the theoretical one electron discharge capacity of the MnO_2 electrode in all cases.

The tests were conducted as follows:

A plurality of cylindrical AA alkaline MnO_2/Zn cells were manufactured and tested. The cells were balanced, as noted above, by limiting the theoretical discharge capacity of the zinc electrode to 80%, 90%, 100%, 110%, 120%, or 130% of the theoretical one electron capacity of the MnO_2 electrode of the respective cells.

Then, one set of cells from each of the balance sets was tested by continuously discharging the cell on a 10 ohm load resistor to a cutoff voltage of 0.9 volts.

A second set of cells was assembled into a four cell battery pack, in series. The battery pack was connected to a 39 ohm load resistor for one week. It should be noted that this test is considered to be abusive, and that in general the useful cell capacity of the cells is considered to have been exhausted within the first 15 hours of discharge. At that time, the voltage of the battery pack will drop significantly, and at the end of the test following one week of discharge, the voltage of the battery pack is about 0 volts.

Because all of the cells are probably not substantially or specifically equivalent to one another, it is evident that by the end of the test some of the cells within the battery pack will have typically reversed and have been driven to negative voltages by the other cells in the set. As noted, however, the average of the cells and the terminal voltage of the four cell battery pack at the end of the one week test is substantially 0 volts.

After the test, each battery pack is dis-assembled, and each of the cells is recharged and then cycled on a ten ohm load to 0.9 volts cutoff, to determine the degree of recovery of the cells. Each of the bars showing the results of the test cells in Figures 3 through 8, and in each case in cycles 2 through 6, represents an average of four cells per test.

Referring now to Figures 3 through 8, the following tables set forth the capacity of the control cell after the first cycle, and after each of the second through the sixth cycles, for each set of control and test cells having balances of the theoretical capacities of the zinc electrode to the theoretical one electron discharge capacity of the MnO_2 electrodes, as shown. The tables also show the average discharge capacity of the four test cells for each set of tests having specified balance of the theoretical capacity of the zinc electrode with respect to the theoretical one electron discharge capacity of the MnO_2 electrode.

Thus, the results of Figures 3 through 8, shown in tabular form, are as follows:

Figure 3 Results:

Balance {Zn:MnO₂ 1e⁻} = 80%
Capacity in mAh²

	<u>Control Cell</u>	<u>Average of Four Test Cells</u>
Cycle 1	1353	-
2	998	862
3	917	793
4	879	783
5	845	728
6	805	663

Figure 4 Results:

Balance {Zn:MnO₂ 1e⁻} = 90%
Capacity in mAh²

	<u>Control Cell</u>	<u>Average of Four Test Cells</u>
Cycle 1	1473	-
2	1079	1048
3	983	820
4	948	839
5	879	753
6	828	676

Figure 5 Results:

Balance {Zn:MnO₂ 1e⁻} = 100%
Capacity in mAh²

	<u>Control Cell</u>	<u>Average of Four Test Cells</u>
Cycle 1	1547	-
2	1135	1310
3	1013	989
4	972	847
5	873	750
6	792	696

Figure 6 Results:

Balance {Zn:MnO₂ 1e⁻} = 110%
Capacity in mAh²

	<u>Control Cell</u>	<u>Average of Four Test Cells</u>
Cycle 1	1571	-
2	1139	800
3	1029	665
4	987	620
5	903	588
6	847	524

Figure 7 Results:

Balance {Zn:MnO₂ 1e⁻} = 120%
Capacity in mAh²

	<u>Control Cell</u>	<u>Average of Four Test Cells</u>
Cycle 1	1583	-
2	1113	262
3	1004	257
4	961	251
5	860	247
6	787	244

Figure 8 Results:

Balance {Zn:MnO₂ 1e⁻} = 130%
Capacity in mAh

	<u>Control Cell</u>	<u>Average of Four Test Cells</u>
Cycle 1	1614	-
2	1143	165
3	998	180
4	933	183
5	843	167
6	775	169

From a review of the above tables, and as graphically illustrated in Figures 3 through 8, it is evident that up to a balance of somewhat less than 120% of the theoretical discharge capacity of the negative electrode compared to the theoretical one electron discharge capacity of the MnO₂ electrode, full recovery of the MnO₂ electrode is observed. Over 120%, there is only limited recovery.

Thus, it is apparent that substantially up to a balance of 120% theoretical discharge capacity of the negative electrode with respect to the theoretical one electron discharge capacity of the MnO₂ electrode, cells according to the present invention will provide useful capacity, and are rechargeable.

Example III:

Using the cathode and anode compositions as described above with respect to Example II, the present invention was applied to AAA, AA, C, and D cells having conventional cylindrical cell configurations. The capacity in ampere-hours of cells in each size was determined, as noted below in Table 4, and the cells were constructed having the respective ratios of the zinc anode to the MnO₂ cathode as noted in Table 4.

Table 4: Energy Densities of Cylindrical RAM Cells
According to the Present Design

	AAA	AA	C	D
Capacity [Ah]	1.02	1.93	5.73	12.75
Zn:1e ⁻ MnO ₂	0.95	0.70	0.64	0.61
Ratio * Zn:PAM MnO ₂	0.70	0.52	0.47	0.45
theor. Energy Density {Wh/kg}	116	107	116	116
{Wh/l}	364	322	311	332

* Primary Alkaline MnO₂

The theoretical energy densities, both gravimetric and volumetric were then determined, as also noted in Table 4. It will be seen that the gravimetric energy densities generally range from about 100 Wh/kg to about 120 Wh/kg; and that the volumetric energy densities generally ranged from about 300 Wh/litre to about 375 Wh/litre.

Example IV:

Finally, cells in keeping with the present invention and having cathode and anode compositions as noted below in Table 5 were constructed. However, one set of AA cells was constructed having an anode to one electron MnO_2 discharge capacity ratio of about 42%; and the other set of AA cells was constructed having an anode to one electron MnO_2 discharge capacity ratio of about 100%. Those cells were then subjected to deep discharge tests at 3.9 Ohms, to a 0.9 volt cutoff. The results of those tests are shown in Figure 9.

Table 5: Composition of Present Design Test Cells used in Example IV

<u>Cathode Composition</u>		<u>Anode Composition</u>	
MnO_2	83.03	Zn, ZnO	65.00
Graphite, Carbon, } PTFE, Ag_2O	10.47	CARBOPOL	0.50
9N KOH	6.50	9N KOH, 5% ZnO	34.50

It will be seen from Figure 9 that the cells having an anode to one electron MnO_2 discharge capacity ratio of 41% are shown in curve 50; and cells having an anode to one electron MnO_2 discharge capacity ratio of 100% are shown in curve 52. The average cell life of the cells shown in curve 50 was 8 cycles above the 300 mAh capacity cutoff. It will also be noted that the cumulative capacity of the cells in curve 52 for the first 25 cycles was about 15.2 Ah; whereas the cumulative capacity for the first 25 cycles of the cells in curve 50 was only 8.8 Ah. Thus, over the first 25 cycles, the cumulative capacity of cells in keeping with the present invention and having an anode to one electron MnO_2 discharge capacity ratio of 100% as compared with cells having an anode to one electron MnO_2

discharge capacity ratio of 41%, was exceeded by more than 70%. Clearly, the cells with an anode to one electron MnO_2 discharge capacity ratio of 41% are emulative of prior art cells, particularly such as those taught by Amano et al and Kordesch, as discussed above.

As noted, the present invention is applicable not only to conventional bobbin type cells, but it may also be applied to button or coin cells, and to flat plate cells.

In general, especially in respect of cells that are placed into cylindrical containers the container or can 12 is a nickel plated deep drawn steel can, although other suitable metal cans may be used. So as to improve the contact and conductivity between the cathode 14 and the can 12, and thereby so as to reduce the internal resistance of the cell, the internal surface of the container 12 may be coated with a conductive coating such as LONZA (TM). Moreover, by using the conductive coating on the interior surface of the container 12, the risk of iron leaching from the can into the cell, which could result in increased hydrogen gassing, is reduced.

When the cell is a typical cylindrical cell, the cathode 14 may be placed into the container 12 by such ordinary cell manufacturing techniques as by being molded into discrete pellets, by being molded into discrete pellets and then recompactd after placement in the container 12, or by being extruded into the container.

Moreover, the closure member 20 is normally formed of a thermoplastic material, and contains a safety vent (not shown) which may be simply a rupturable membrane, or a resealable vent. The plastic closure member is molded from a thermoplastic material having enhanced hydrogen permeation rates, such as polypropylene, talc filled polypropylene, and nylon.

The scope of the present invention is defined by the appended claims.

WHAT IS CLAIMED IS:

1. A rechargeable electrochemical cell comprising a negative electrode, a positive MnO_2 electrode, a separator between said negative electrode and said MnO_2 electrode, terminal means contacting said negative electrode and said MnO_2 electrode to provide respective negative and positive terminals for said cell, and an aqueous electrolyte;

wherein the principal active component of said MnO_2 electrode is manganese dioxide which is capable of being reversibly charged and discharged between the nominal status of MnO_2 and the fully discharged one electron status of Mn_2O_3 , and wherein the discharge capacity of said MnO_2 electrode between the said MnO_2 status and the said Mn_2O_3 status is the theoretical one electron discharge capacity of said MnO_2 electrode;

wherein the principal active component of said negative electrode is chosen from the group consisting of zinc, iron, lead, cadmium, hydrogen, and metal hydrides;

wherein the principal active component of said aqueous electrolyte is chosen from the group consisting of alkali metal hydroxides, an acid chosen from the group consisting of H_2SO_4 , H_3BO_3 and H_3PO_4 , and a solution of a salt chosen from the group consisting of ZnCl , NH_4Cl , NaCl , and KCl ;

wherein said negative electrode is a rechargeable electrode;

and wherein the theoretical discharge capacity of said negative electrode is in the range of from 60% to 120% of the theoretical one electron discharge capacity of said MnO_2 electrode.

2. The rechargeable electrochemical cell of claim 1, wherein said negative electrode is zinc and said electrolyte is 4N to 12N potassium hydroxide.

3. The rechargeable electrochemical cell of claim 2, wherein said MnO_2 electrode includes at least one additive chosen from the group consisting of 5% to 15% by weight of graphite, 0.1% to 15% by weight of carbon black, an inorganic binder, graphite fibres as a fibrous reinforcing agent, and a hydrophobic organic binder chosen from the group consisting of PTFE, polypropylene, and polyethylene.

4. The rechargeable electrochemical cell of claim 3, wherein said MnO_2 electrode includes from 0.1% to 10% of said hydrophobic material chosen from the group consisting of PTFE, polypropylene, and polyethylene.

5. The rechargeable electrochemical cell of claim 4, wherein said MnO_2 electrode further comprises as a porous additive said 0.1% to 15% by weight of carbon black.

6. The rechargeable electrochemical cell of claim 3, wherein said MnO_2 electrode further comprises from 0.1% to 5% of a hydrogen recombination catalyst chosen from the group consisting of silver, oxides of silver, silver salts, platinum, and compounds of silver and platinum.

7. The rechargeable electrochemical cell of claim 3, further comprising an oxygen evolution catalyst chosen from the group consisting of at least an oxide of nickel, a perovskite of nickel, a spinel of nickel, and combination thereof, cobalt, iron, manganese, chromium, vanadium, titanium, and silver.

8. The rechargeable electrochemical cell of claim 7, wherein said oxygen evolution catalyst is placed on the outer surface of said MnO_2 electrode.

9. The rechargeable electrochemical cell of claim 7, wherein said oxygen evolution catalyst is dispersed throughout said MnO_2 electrode.
10. The rechargeable electrochemical cell of claim 2, wherein said electrolyte has a small quantity of zinc oxide dissolved therein.
11. The rechargeable electrochemical cell of claim 2, wherein said current collector is a single nail extending into said negative electrode.
12. The rechargeable electrochemical cell of claim 2, wherein the manganese dioxide of said positive electrode comprises electrolytic manganese dioxide, together with a hydrogen recombination catalyst.
13. The rechargeable electrochemical cell of claim 2 when placed into a cylindrical metal container, wherein said MnO_2 positive electrode is placed into said container by being molded into discrete pellets, by being molded into discrete pellets and then recompacted after placement in said container, or by being extruded into said container.
14. The rechargeable electrochemical cell of claim 13, wherein said metal container is a nickel plated steel can.
15. The rechargeable electrochemical cell of claim 14, wherein said container is coated on its interior surface with a conductive coating.
16. The rechargeable electrochemical cell of claim 13, wherein said cell is sealed by a closure element which has a safety vent formed therein; and wherein said closure element is made from a material which is chosen from a group of thermoplastic materials having enhanced hydrogen permeation characteristics consisting of polypropylene, talc filled polypropylene, and nylon.

17. The rechargeable electrochemical cell of claim 13, wherein said separator is a complex flexible structure which is gas permeable at least to gaseous hydrogen and oxygen, but impermeable to zinc dendrites.

1 / 5

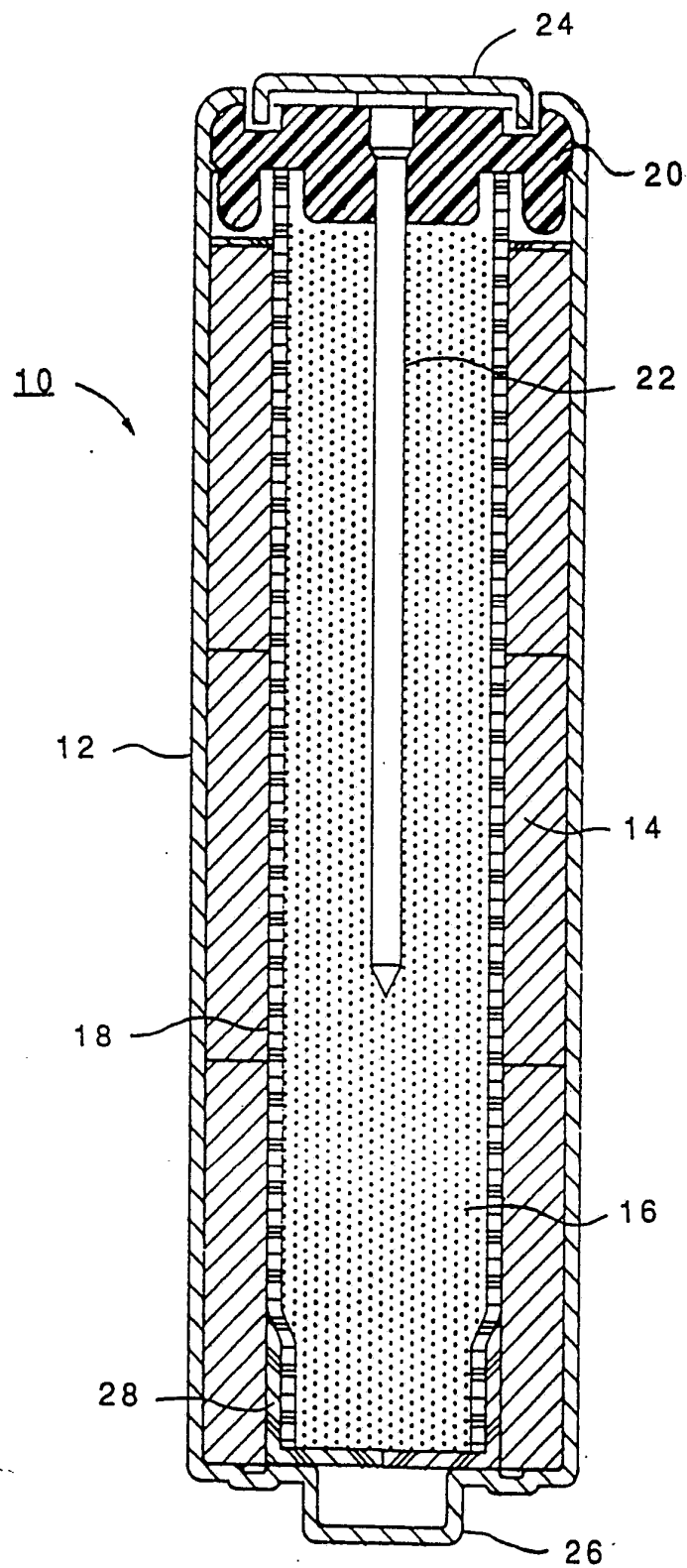


FIG. 1

2 / 5

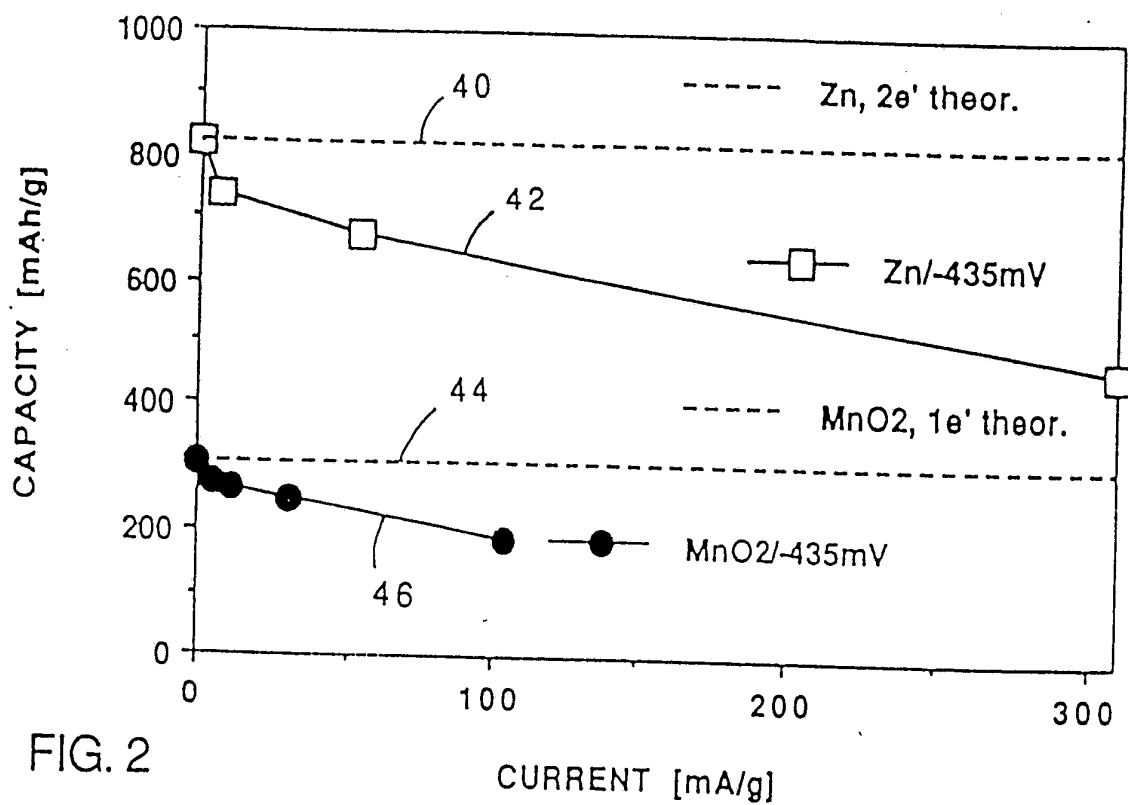


FIG. 2

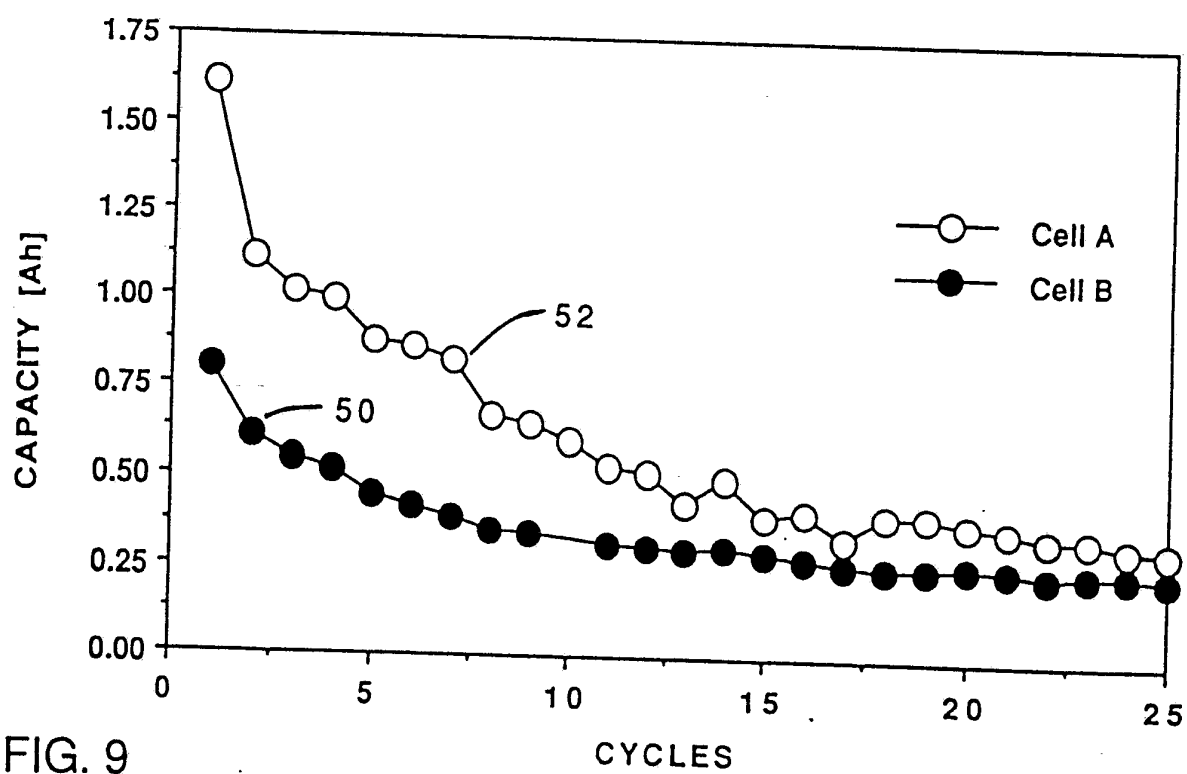


FIG. 9

3 / 5

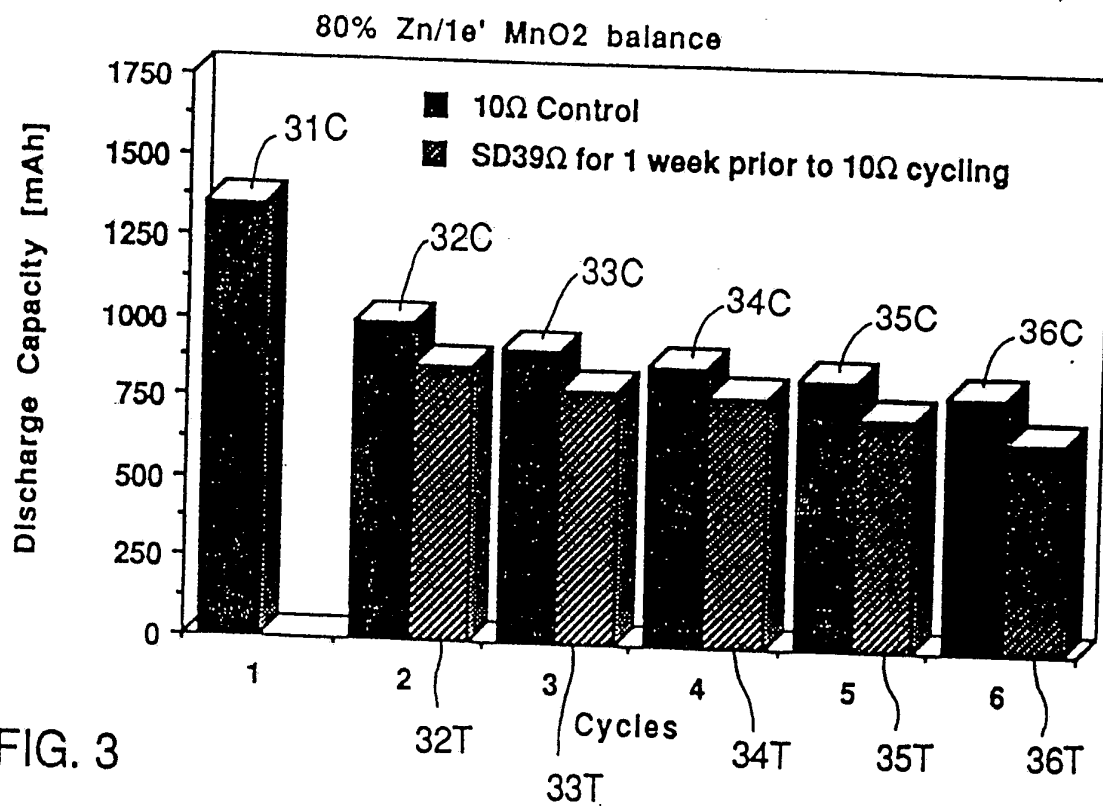


FIG. 3

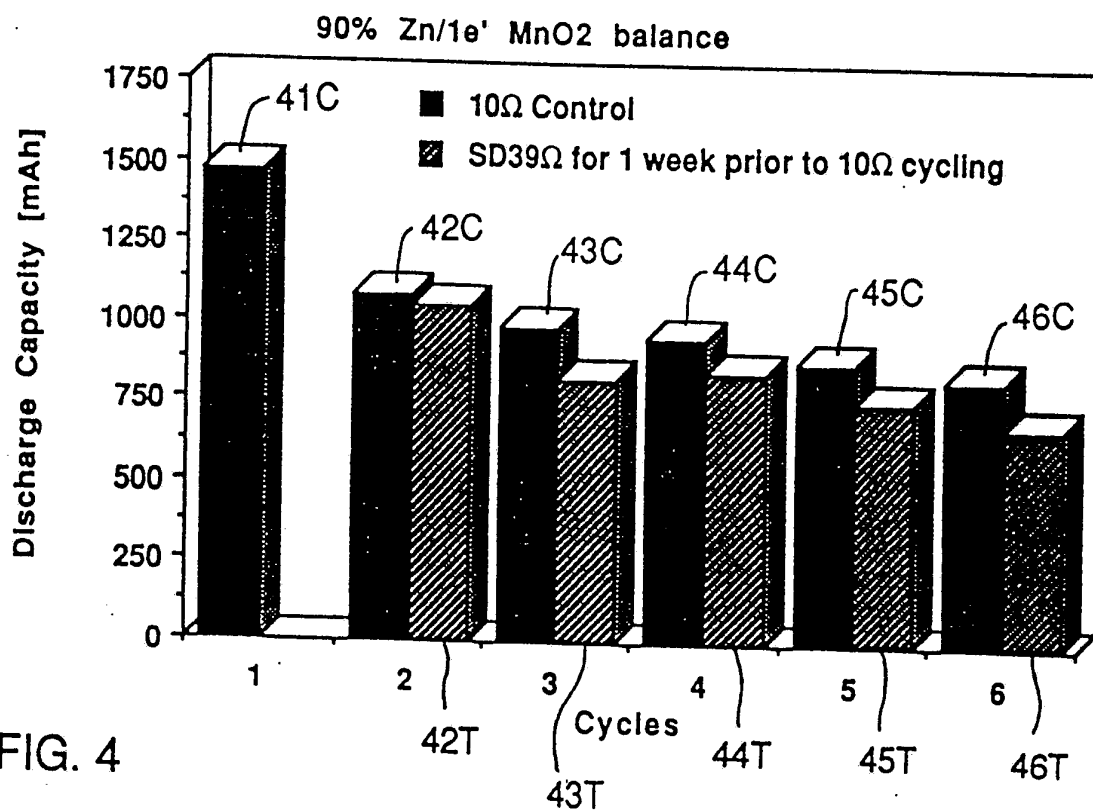


FIG. 4

4 / 5

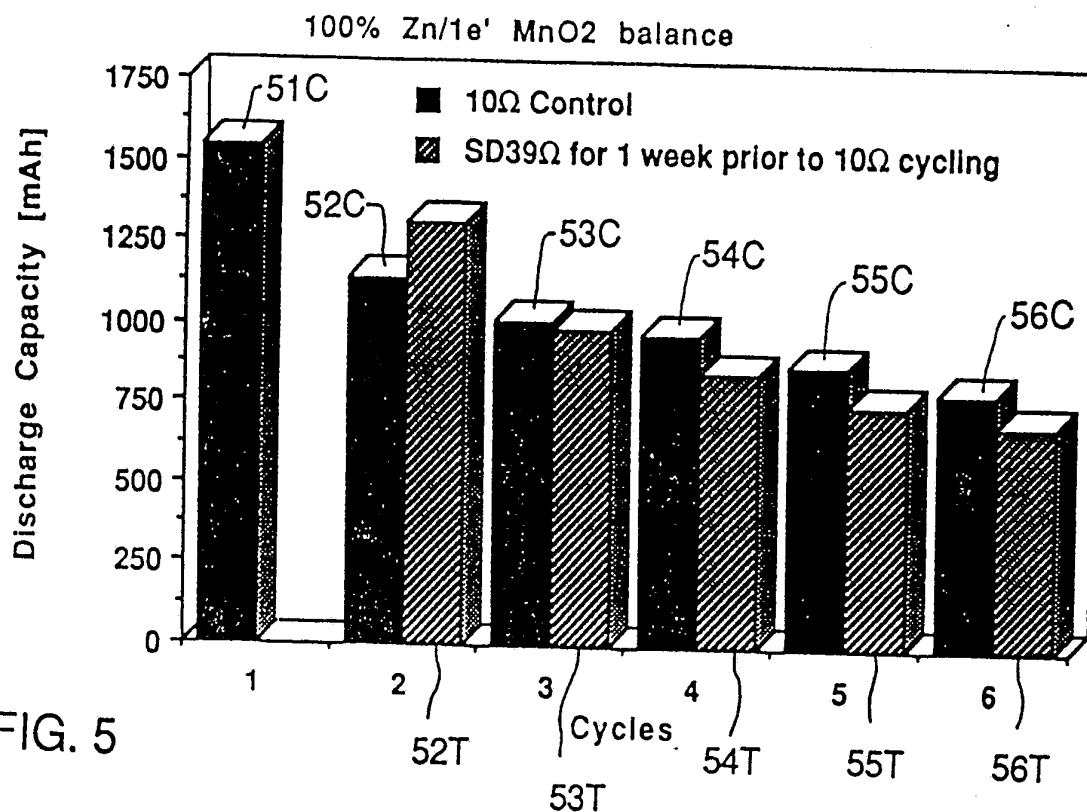


FIG. 5

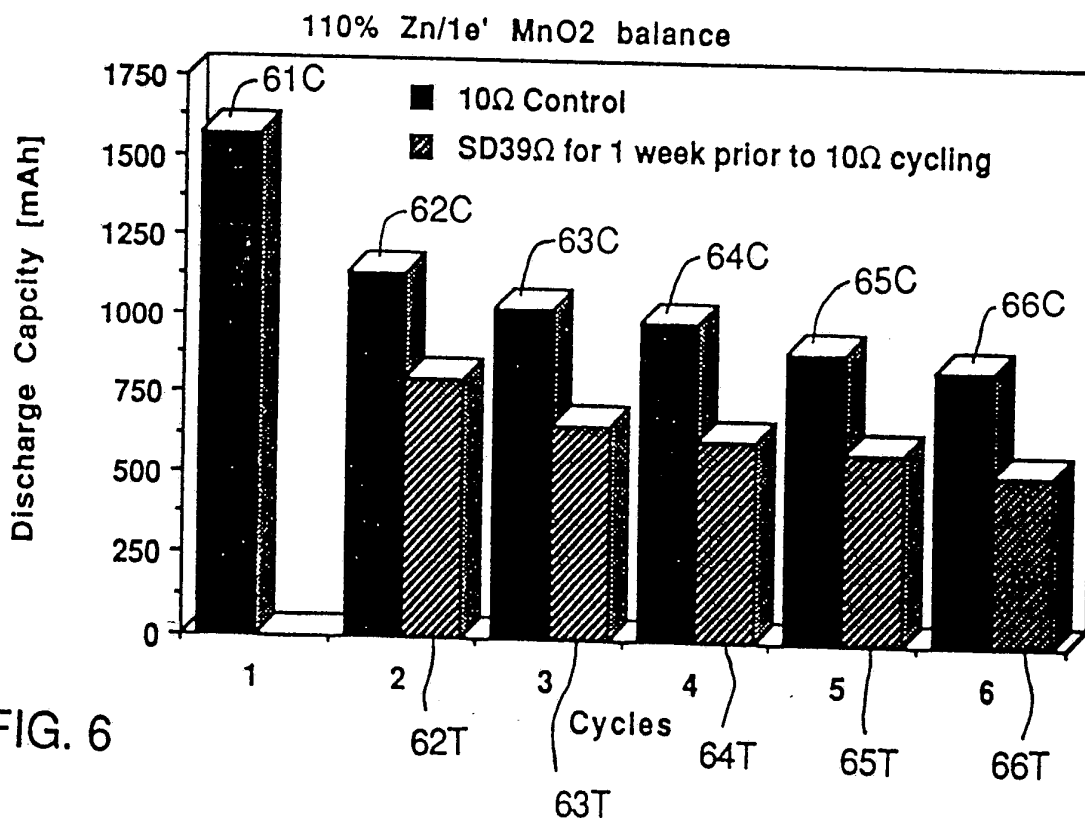


FIG. 6

5 / 5

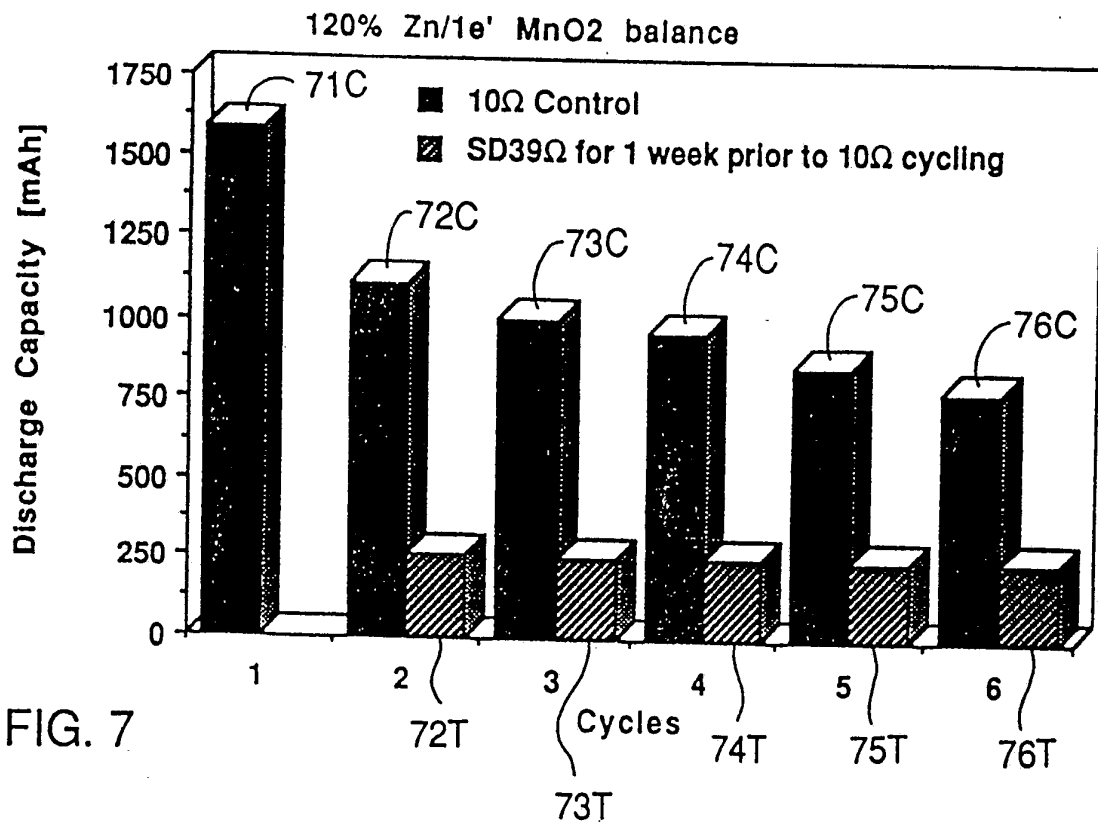


FIG. 7

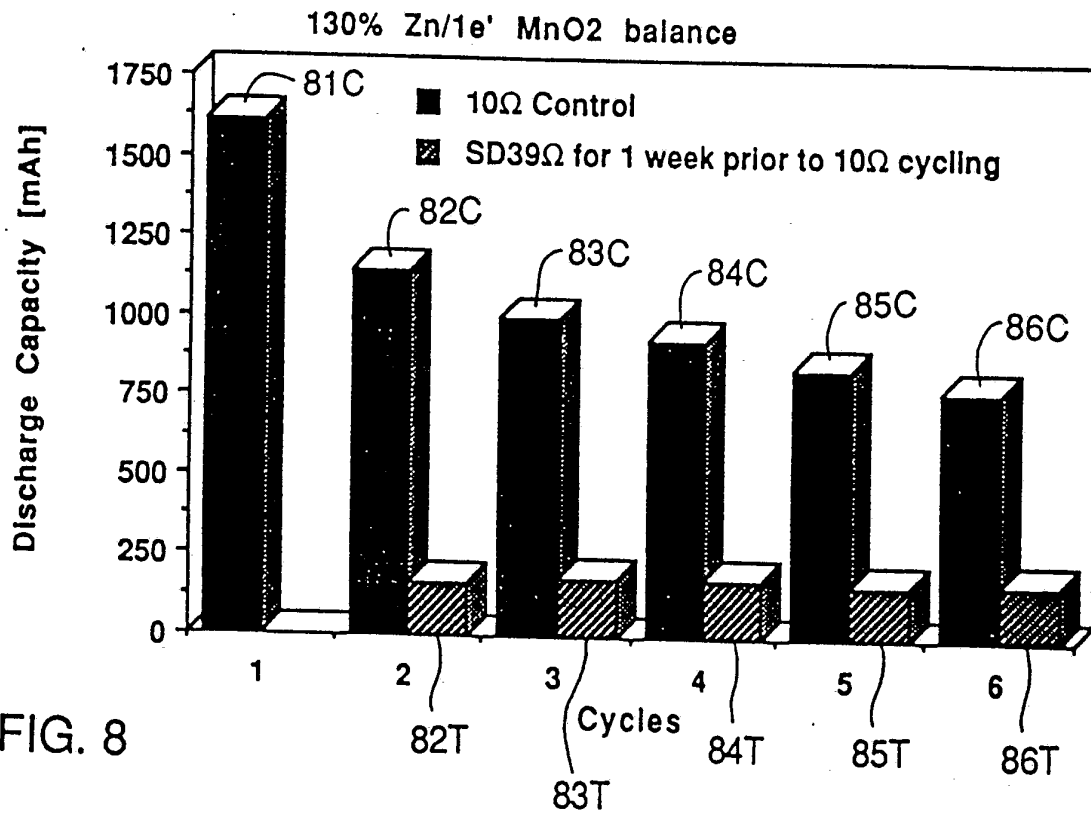


FIG. 8

INTERNATIONAL SEARCH REPORT

International Application No

PCT/CA 92/00101

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) *		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC ⁵ : H 01 M 10/36, H 01 M 10/34, H 01 M 10/24, H 01 M 4/50		
II. FIELDS SEARCHED		
Minimum Documentation Searched †		
Classification System	Classification Symbols	
IPC ⁵	H 01 M	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched *		
III. DOCUMENTS CONSIDERED TO BE RELEVANT*		
Category *	Citation of Document, † with indication, where appropriate, of the relevant passages ‡	Relevant to Claim No. ‡
A	K.V. Kordesch "Batteries", vol. 1, MARCEL DEKKER INC. "Manga- nese Dioxide", published 1974, New York, pages 281-291, see especially pages 286-289. ---	1, 2, 3, 10, 16, 17
A	US, A, 3 530 496 (YASUJI AMANO et al.) 22 September 1970 (22.09.70), see claims 1, 5 (cited in the application). ---	1, 2
A	US, A, 4 957 827 (KORDESCH et al.) 18 September 1990 (18.09.90), see claims 1, 3-6, 10, 11; fig. 1 (cited in the application). ---	1, 2, 3, 6, 7, 10, 11, 14, 16
A	WO, A1, 91/17 581	1, 2, 3,
* Special categories of cited documents: † "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "Z" document member of the same patent family		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
06 November 1992	20 NOV 1992	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	LUX e.h.	

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, " with indication, where appropriate, of the relevant passages	Relevant to Claim No.
	(BATTERY TECHNOLOGIES) 14 November 1991 (14.11.91), see claims; fig. 1 (cited in the application). -----	6,7-17

ANHANG

zum internationalen Recherchen-
bericht über die internationale
Patentanmeldung Nr.

ANNEX

to the International Search
Report to the International Patent
Application No.

ANNEXE

au rapport de recherche inter-
national relatif à la demande de brevet
international n°

PCT/CA92/00101 SAE 57040

In diesem Anhang sind die Mitglieder
der Patentfamilien der im obenge-
nannten internationalen Recherchenbericht
angeführten Patentedokumente angegeben.
Diese Angaben dienen nur zur Unter-
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This Annex lists the patent family
members relating to the patent documents
cited in the above-mentioned inter-
national search report. The Office is
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La présente annexe indique les
membres de la famille de brevets
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Im Recherchenbericht angeführtes Patentedokument Patent document cited in search report Document de brevet cité dans le rapport de recherche	Datum der Veröffentlichung Publication date Date de publication	Mitglied(er) der Patentfamilie Patent family member(s) Membre(s) de la famille de brevets	Datum der Veröffentlichung Publication date Date de publication
US A 4957827	18-09-90	AU A1 38789/89 CA A1 1295364 EP A1 389578 WO A1 9000818	05-02-90 04-02-92 03-10-90 25-01-90
WO A1 9117581	14-11-91	keine - none - rien	
US A 3530496	22-09-70	DE A 1771292 DE B 1771292 DE C3 1771292 FR A 1572618	01-04-71 22-06-72 08-02-73 27-06-69