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PRIMARY CELL

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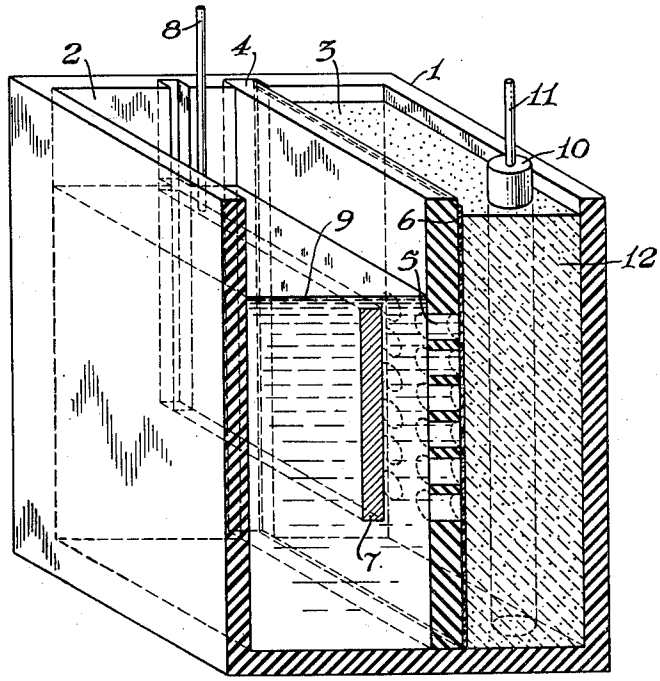


Fig. 1

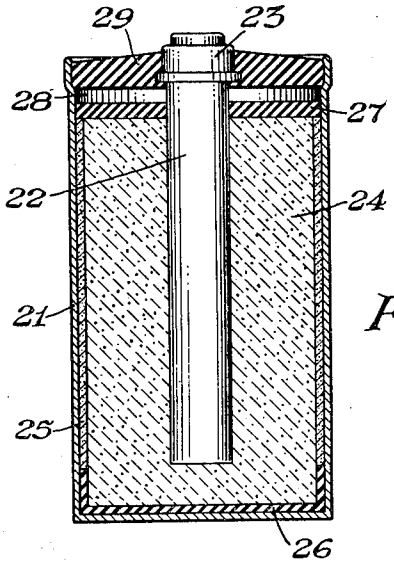


Fig. 2

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PRIMARY CELL

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The invention relates to an improved primary cell.

It more particularly concerns an improved primary cell utilizing as the anode material magnesium and alloys thereof in which magnesium is the predominant constituent.

Inasmuch as magnesium is an abundant and readily available metal high in the electromotive force series of the metals, it is a desideratum in the art to employ it as the anode material in primary cells, and numerous attempts at such use have been made. Nevertheless, insofar as we are aware, there are no commercially successful primary cells employing magnesium as anode material.

Accordingly, it is the principal object of the invention to provide an improved primary cell utilizing magnesium as the anode material, such object being attained by the means and in the manner described in the following specification and illustrated in the annexed drawing.

In said drawing:

Fig. 1 shows a cutaway isometric view of a "wet" cell assembled according to the invention;

Fig. 2 shows a vertical section of a "dry" cell embodying the invention.

In brief, the primary cell of the invention consists of a voltaic system employing an anode of magnesium or alloy thereof in which magnesium is the predominant material, a cathode of carbon depolarized with manganese dioxide, and an electrolyte of an aqueous solution of ammonium bromide which may advantageously contain a chromic acid salt of one of the alkali, alkaline earth metal, or ammonium bases to modify the corrosive action of ammonium bromide upon magnesium.

Referring more specifically to the elements of the cell, the anode may be formed of either pure metallic magnesium or of a magnesium-base alloy containing a major portion of the metal, all such materials being included with the term "magnesium" hereinafter employed. However, metallic magnesium of at least 99 5 per cent purity is to be preferred, and impurities such as iron, copper, and nickel, which increase the corrodibility of the magnesium, are preferably to be kept as low as reasonably possible, preferably below 0.002 per cent in the case of iron, below 0.01 per cent in the case of copper, and below 0.001 per cent in the case of nickel. The usual structural alloys are generally suitable as anode material, particularly the magnesium-base alloys in which the magnesium content exceeds about 80 per cent and which contain the usual amounts

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of manganese and either or both aluminum and zinc. Suitable proportions of these alloying elements are aluminum 2–9 per cent, zinc 0.5 to 3 per cent, manganese 0.1 to 0.5 per cent. The presence in the alloy of 0.05 to 0.5 per cent of calcium is also desirable. The anode material may be in any of the forms in which magnesium articles may be produced, such as rod, sheet, plate, and the like.

The electrolyte comprises an aqueous solution of ammonium bromide. The concentration does not appear to be critical and may range from about 30 grams per liter to amounts producing nearly saturated solutions. A generally useful range of concentration is between about 100 and 300 grams per liter, 200 grams per liter being preferred.

For some purposes, as when the cells are to remain for long periods on open circuit or are to be used intermittently over long periods, it is desirable to reduce the rate at which the anode material is corroded by the electrolyte. This may be accomplished by including in the electrolyte a chromic acid salt of a base of the alkali, alkaline earth, and ammonium bases, such as Na_2CrO_4 or $Na_2Cr_2O_7$, Li_2CrO_4 or $Li_2Cr_2O_7$, $CaCrO_4$ or $CaCr_2O_7$, $(NH_4)_2CrO_4$ or $(NH_4)_2Cr_2O_7$ for example, in corrosion-inhibiting concentrations such as from about 0.01 to 25 grams per liter of solution.

The cathodes used according to the invention are similar to those heretofore used in standard Leclanché cells. They consist of carbon rods or plates or other suitable form of the material embedded in a depolarizer mass consisting of a mixture of manganese dioxide and finely divided carbon, preferably acetylene black, moistened with the electrolyte. The proportions of manganese dioxide to the finely divided carbon are preferably in the range of 75 to 95 per cent MnO_2, the balance being finely divided carbon. Best results appear to be obtained with 90 per cent MnO_2 and 10 per cent acetylene black.

The three elements of the cell are arranged in a suitable manner to provide a voltaic system in which the anode is separated from the cathode and the electrolyte provides a path for the passage of electrical current between them as in conventional cell construction.

The invention may be further explained and illustrated with reference to the aforesaid drawing.

Fig. 1 of the drawing represents a "wet" cell assembled in accordance with the invention, cut away to show internal structure. A container or

jar 1 of insulating material, such as glass or molded plastic, is divided into an anode compartment 2 and a cathode compartment 3 by means of a partition 4. Partition 4 consists of a board or plate of insulating material, such as glass or plastic, which is conveniently molded of phenol-formaldehyde resin. It is provided with a plurality of perforations 5, arranged in a regular pattern, to permit the passage of current through the electrolyte between the electrodes. On the cathode side of partition 4 is a porous filter medium 6 such as a sheet of filter paper, which serves as a liquid-permeable retainer for the contents of the cathode compartment. In compartment 2 is disposed an anode 7 consisting of a plate of magnesium to which is secured a terminal rod 8, the rod being immersed in a body of liquid electrolyte 9 consisting of an aqueous solution of ammonium bromide to which may be added, if desired, corrosion-inhibiting amounts of a chromic acid salt of an alkali metal, alkaline earth metal or ammonium. Cathode 10 in compartment 3 is a carbon rod having terminal 11, which is embedded in a mass 12 of a depolarizer mix composed of manganese dioxide and finely divided carbon moistened with the electrolyte.

The "dry" cell shown in Fig. 2 comprises the container 21, which is a cup formed of magnesium and serves as the anode. Cathode 22 is a carbon rod with terminal cap 23, packed in a bobbin 24 of depolarizer mass of manganese dioxide and carbon moistened with an electrolyte of the same composition as that already mentioned. Between depolarizer 24 and the sides of the cup is a body of gelled electrolyte 25. An insulating disc 26 of waxed paper, paper board, or the like separates the depolarizer bobbin from the bottom of the cup 21, and a similar disc 27 covers the top of the bobbin. A vent space 28 is provided above disc 27, which is closed by a vented insulating cover 29 of wax or resin.

TABLE I

D size dry cells

Cell No.	Electrolyte, Grams per Liter		Capacity	
	Salt	Inhibitor	Hours' Continuous Discharge to 1.13 Volt	Flash Light Test—Days to 0.935 Volt
1	150 NH_4Br	10 $(NH_4)_2CrO_4$	211	23.9
2	175 NH_4Br	do	257	22.9
3	200 NH_4Br	do	237	23.5
4	225 NH_4Br	do	265	24.0
5	175 NH_4Br	5 $(NH_4)_2CrO_4$	265	20.7
6	do	15 $(NH_4)_2CrO_4$	265	22.1
7	do	25 $(NH_4)_2CrO_4$	265	16.1
8	200 NH_4Br	do	274	24.6
9	175 NH_4Br	5 Na_2CrO_4	250	15.4
10	do	10 Na_2CrO_4	234	17.0
11	do	15 Na_2CrO_4	239	19.8
12	do	25 Na_2CrO_4	248	22.1
13	200 NH_4Br	do	274	23.8
14	175 NH_4Br	5 $(NH_4)_2Cr_2O_7$	311	17.4
15	do	10 $(NH_4)_2Cr_2O_7$	271	20.6
16	do	15 $(NH_4)_2Cr_2O_7$	262	21.2
17	150 NH_4Br	10 $(NH_4)_2Cr_2O_7$	257	17.0
18	do	25 $(NH_4)_2Cr_2O_7$	245	13.3
19	do	10 $(NH_4)_2CrO_4$	171	12.8

Examples of primary cells made in accordance with the invention and of the design shown in Fig. 2 are set forth in Table I. In Table I the cells were conventional D size (flash light cells) "dry" cells. Cells numbered 1 to 18 inclusive employed as the anode material a magnesium-base alloy having the nominal composition: 3 per cent Al, 1 per cent Zn, 0.2 per cent Mn, remainder commercial magnesium. In cell number 19, 0.2 per cent of calcium was added to the anode material, which was otherwise of the same composition as that of the other cells. The anodes were drawn cans made from rolled sheet 0.032 inch thick of the aforesaid alloys. The electrolytes in each case had the composition shown in the table, and were gelled by mixing with 15 grams of cornstarch and 5 grams of wheat flour per 120 c. c. of solution. The cathodes of each cell consisted of a carbon rod packed in a depolarizing mass composed of 90 per cent by weight MnO_2 (gold coast ore) and 10 per cent acetylene black moistened with the electrolyte. The cells were subjected to two capacity tests. The one, "Hours' continuous discharge," consisted in determining the number of hours required for the cell voltage to drop to 1.13 volts on being continuously discharged through a resistance of 83⅓ ohms. The other, "Flash light test," consisted in determining the number of elapsed days for the cell voltage to drop to 0.935 volt when discharged through a resistance of 6⅔ ohms for 4 minutes of each ½ hour through 10 hours of each day for 5 days a week.

TABLE II

Wet cells

Cell No.	Electrolyte, Grams per Liter		Anode Composition	Ampere Hours to 1 Volt
	Salt	Inhibitor		
1	NH_4Br, 150	$(NH_4)_2CrO_4$, 15	M1	17
2	do	do	AZ31	16
3	NH_4Br, 200	$(NH_4)_2CrO_4$, 10	AZ31	19

Wet cells made up in accordance with the invention and of the design shown in Fig. 1 are set forth in Table II. The cells held 300 c. c. of electrolyte of the composition indicated in Table II and the anodes were plates 3½" x 2" x ¼" of the composition indicated. In the table, "M1" is the A. S. T. M. designation of a magnesium-base alloy having the nominal composition of 1.5 per cent manganese, the balance commercial magnesium; "AZ31" is the A. S. T. M. designation of a magnesium-base alloy whose nominal composition is: 3 per cent aluminum, 1 per cent zinc, 0.3 per cent manganese, remainder commercial magnesium. The cathode mix in the cathode compartment consisted of 90 per cent by weight of manganese dioxide (gold coast ore) and 10 per cent of acetylene black. In determining the capacity of these cells they were discharged through a resistance which was adjusted to a value such that the current density initially was 6 amperes per square foot of anode surface facing the cathode compartment. The number of ampere hours produced by the cell discharging through the said resistance until the voltage dropped to 1 volt was measured and is set forth in the last column.

In operation, cells made according to the invention constitute a unique voltaic system inasmuch as the cathode is depolarized by manganese dioxide which operates in an alkaline medium. Very soon after current is drawn from the cells it is found that the pH initially at about 6.6 quickly enters the range of about 7.5 to 8.3, the latter pH being the maximum attained. Within this pH range most of the energy of the cell is delivered. Attempts heretofore to utilize manganese dioxide as a depolarizer in an aqueous alkaline medium have been unsuccessful. For

example, the zinc Leclanché cell becomes useless when the electrolyte becomes alkaline, due to the resulting drop in voltage of the cell. In contrast with this, in operation the electrolyte of our cells exhibits a pH of about 7.5 to 8.3, a pH range at which conventional cells using a manganese dioxide-depolarized cathode do not function.

It is to be understood that the foregoing description is illustrative rather than strictly limitative, and that other embodiments of the new cell are possible within the spirit of the invention and the scope of the following claims.

We claim:

1. A primary cell comprising a magnesium anode, a manganese dioxide-depolarized cathode, and an electrolyte comprising an aqueous solution of ammonium bromide.

2. A primary cell comprising a magnesium anode, a manganese dioxide-depolarized cathode, and an electrolyte comprising an aqueous solution of ammonium bromide, and corrosion-inhibiting amounts of a chromic acid salt of a base selected from the group consisting of the alkali metal, alkaline earth metals, and ammonium bases.

3. A primary cell comprising an anode of a magnesium-base alloy containing from about 2 to 9 per cent of aluminum, 0.5 to 3 per cent of zinc, 0.1 to 0.5 per cent of manganese, the balance being magnesium, a manganese dioxide-depolarized cathode, and an electrolyte comprising an aqueous solution of ammonium bromide.

4. A primary cell comprising an anode of a magnesium-base alloy containing from about 2 to 9 per cent of aluminum, 0.5 to 3 per cent of zinc, 0.1 to 0.5 per cent of manganese, 0.05 to 0.5 per cent of calcium, the balance being magnesium, a manganese dioxide-depolarized cathode, and an electrolyte comprising an aqueous solution of ammonium bromide.

5. A primary cell comprising an anode of a magnesium-base alloy containing from about 2 to 9 per cent of aluminum, 0.5 to 3 per cent of zinc, 0.1 to 0.5 per cent of manganese, the balance being magnesium, a manganese dioxide-depolarized cathode, and an electrolyte comprising an aqueous solution of ammonium bromide, and corrosion-inhibiting amounts of a chromic acid salt of a base selected from the group consisting of the alkali metal, alkaline earth metals, and ammonium bases.

6. A primary cell comprising an anode of a magnesium-base alloy containing from about 2 to 9 per cent of aluminum, 0.5 to 3 per cent of zinc, 0.1 to 0.5 per cent of manganese, 0.05 to 0.5 per cent of calcium, the balance being magnesium, a manganese dioxide-depolarized cathode, and an electrolyte comprising an aqueous solution of ammonium bromide, and corrosion-inhibiting amounts of a chromic acid salt of a base selected from the group consisting of the alkali metal, alkaline earth metals, and ammonium bases.

7. A primary cell comprising a magnesium anode, a manganese dioxide-depolarized cathode, and an electrolyte comprising an aqueous solution of ammonium bromide, and corrosion-inhibiting amounts of ammonium chromate.

8. A primary cell comprising an anode of a magnesium-base alloy containing from about 2 to 9 per cent of aluminum, 0.5 to 3 per cent of zinc, 0.1 to 0.5 per cent of manganese, the balance being magnesium, a manganese dioxide-depolarized cathode, and an electrolyte comprising an aqueous solution of ammonium bromide, and corrosion-inhibiting amounts of ammonium chromate.

9. A primary cell comprising an anode of a magnesium-base alloy containing from about 2 to 9 per cent of aluminum, 0.5 to 3 per cent of zinc, 0.1 to 0.5 per cent of manganese, 0.05 to 0.5 per cent of calcium, the balance being magnesium, a manganese dioxide-depolarized cathode, and an electrolyte comprising an aqueous solution of ammonium bromide, and corrosion-inhibiting amounts of ammonium chromate.

10. A primary cell comprising a magnesium anode, a manganese dioxide-depolarized cathode, and an electrolyte comprising an aqueous solution of ammonium bromide, said electrolyte having a pH between about 7.5 and 8.3.

11. A primary cell comprising an anode of a magnesium-base alloy containing from about 2 to 9 per cent of aluminum, 0.5 to 3 per cent of zinc, 0.1 to 0.5 per cent of manganese, the balance being magnesium, a manganese dioxide-depolarized cathode, and an electrolyte comprising an aqueous solution of ammonium bromide, said electrolyte having a pH between about 7.5 and 8.3.

12. A primary cell comprising a magnesium anode, a manganese dioxide-depolarized cathode, and an electrolyte comprising an aqueous solution of ammonium bromide, and corrosion-inhibiting amounts of ammonium chromate, said electrolyte having a pH between about 7.5 and 8.3.

13. A primary cell comprising an anode of a magnesium-base alloy containing from about 2 to 9 per cent of aluminum, 0.5 to 3 percent of zinc, 0.1 to 0.5 per cent of manganese, the balance being magnesium, a manganese dioxide-depolarized cathode, and an electrolyte comprising an aqueous solution of ammonium bromide, and corrosion-inhibiting amounts of ammonium chromate, said electrolyte having a pH between about 7.5 and 8.3.

14. A primary cell comprising an anode of a magnesium-base alloy containing from about 2 to 9 per cent of aluminum, 0.5 to 3 per cent of zinc, 0.1 to 0.5 per cent of manganese, 0.05 to 0.5 per cent of calcium, the balance being magnesium, a manganese dioxide-depolarized cathode, and an electrolyte comprising an aqueous solution of ammonium bromide, and corrosion-inhibiting amounts of ammonium chromate, said electrolyte having a pH between about 7.5 and 8.3.

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