

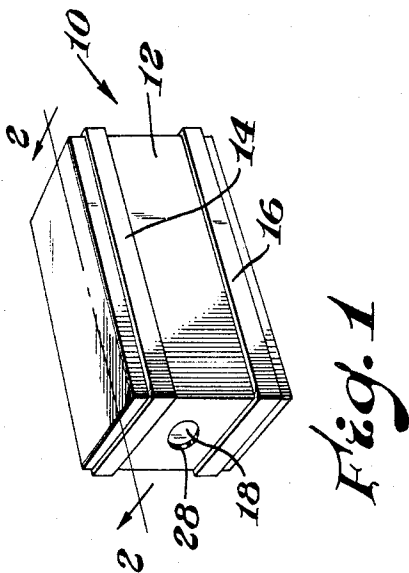
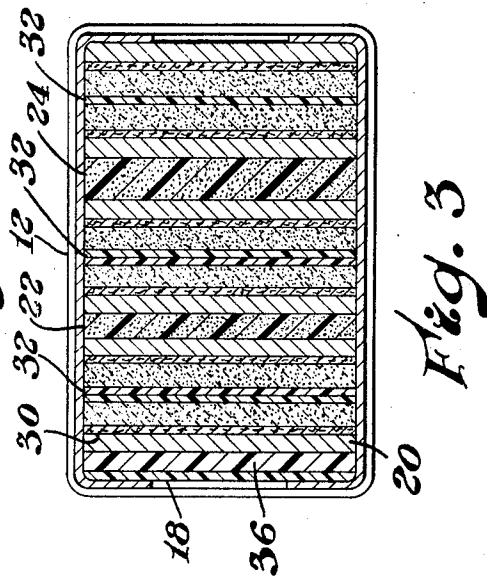
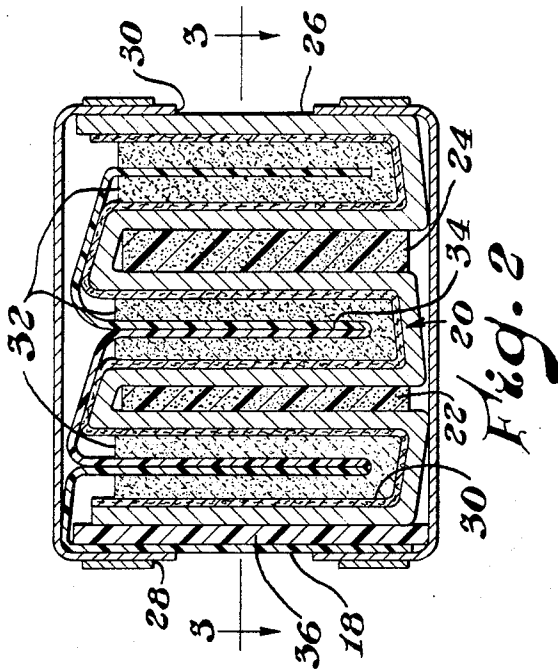
July 16, 1968

J. L. ROBINSON ET AL

3,393,097

PRIMARY CELL HAVING A FOLDED MAGNESIUM ANODE

Filed July 29, 1966



INVENTORS.
John L. Robinson
Earl D. Ayers
BY
Earl D. Ayers
AGENT

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3,393,097

PRIMARY CELL HAVING A FOLDED
MAGNESIUM ANODE

John L. Robinson, Freeland, and Earl D. Ayers, Auburn,
Mich., assignors to The Dow Chemical Company, Mid-
land, Mich., a corporation of Delaware
Continuation-in-part of application Ser. No. 469,446,
July 6, 1965. This application July 29, 1966, Ser.
No. 573,739

5 Claims. (Cl. 136—83)

This is a continuation-in-part of applicants' co-pending application, Ser. No. 469,446, filed July 6, 1965, now abandoned, for "Primary Cell Having a Folded Magnesium Alloy Anode."

The invention relates to improved flat primary cells and especially to such cells which employ magnesium or magnesium alloy anodes.

For the purposes of the specification and claims, magnesium and magnesium base alloys containing at least 70 percent of magnesium are hereinafter referred to as magnesium metal.

Dry cells which employ magnesium as the anode metal are desirable because such dry cells having equivalent capacity to dry cells containing zinc provide a higher voltage potential, are lighter in weight, and are smaller in size.

Problems arise in constructing and operating magnesium anode type primary cells because of physical expansion within the cell as the anode decomposition product forms as the cell is used.

Economic problems exist also, because of the relative cost of production of magnesium anode type primary cells as compared to the cost of producing other primary cells.

Further, there is a continuing need for primary cells having improved current delivering capacity per unit of volume and weight of the cell or cell pack.

The solution of some of the above problems, however, prove helpful in constructing cells using other than magnesium as the anode material.

Accordingly, a principal object of this invention is to provide an improved primary cell.

Another object of this invention is to provide an improved primary cell which is readily adaptable to automated manufacturing techniques.

A further object of this invention is to provide an improved primary cell utilizing a magnesium alloy anode.

A still further object of this invention is to provide an improved anode-separator assembly for use in primary cells.

Yet another object of this invention is to provide an improved magnesium anode primary cell having large current delivering capacity in relation to its size.

An ancillary object of this invention is to provide an improved primary cell which has means therein for compensating for expansion within the cell assembly as anode decomposition product is formed.

An additional object of this invention is to provide means for preserving the moisture balance within the cell within operable limits during the use of the cell.

In accordance with this invention, there is provided a primary cell assembly in which the anode is formed from a single sheet of metal into a generally accordion folded configuration in which the adjacent folds are spaced from one another. Sheets of compressible material are inserted between some of the folds along the anode, and an ionically conductive but substantially electronically non-conductive separator adheres to one side of said anode sheet. Cathode mix is inserted between adjacent folds on the side of the anode having the separator adhering thereto, and a sheet-like cathode electrode is inter-

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leaved into the various adjacent anode folds which contain cathode mix. The assembly is disposed in a suitable housing and held under sufficient pressure to insure a low internal resistance in the cell. The cells may be connected in parallel or in series to form battery packs delivering needed voltages and current capacities, as is well known in the art.

The invention, as well as additional objects and advantages thereof, will best be understood when the following detailed description is read in connection with the accompanying drawing, in which:

FIG. 1 is an isometric view of a cell in accordance with this invention;

FIG. 2 is a sectional view taken along the line 2—2 of FIG. 1, and

FIG. 3 is a sectional view taken along the line 3—3 of FIG. 2.

Referring to the drawing, there is shown a primary cell, indicated generally by the numeral 10, enclosed in a suitable outer casing 12 and provided with pressure bands 14, 16 which may be disposed either as shown or around an inner casing, if any, for example. A terminal, such as the terminal 18, for example, is disposed at each end of the cell.

Referring especially to FIGS. 2 and 3, as well as to FIG. 1, the cell 10 has a folded anode, indicated generally by the numeral 20, made of a sheet of magnesium alloy, for example. The anode, as shown, has five folds and is in an accordion-like configuration with space between each of the folds. A sheet of compressible material 22, 24 is disposed between spaced apart pairs of the folds in the anode in the part of the cell which is remote from the ends of the cell.

The surface 26 of one end face of the anode 20 serves as a terminal of the cell 10. Access to the terminals 18, 26 are through the apertures 28, 30, respectively, in the casing 12.

A porous separator 30 which adheres to the anode 20 is folded to shape (usually) as the anode is folded. Paper is commonly used as the separator material, although other material which is ionically conductive but electronically non-conductive may be used. The separator 30 is on the side of the anode faces which face the cathode mix 32 in the cell.

The cathode electrode 34 is a sheet of conductive material, such as carbon loaded vinyl plastic material, for example, or graphite cloth, as another example.

The electrode 34 is inserted into the cathode mix 32 in the various anode folds and is looped over the end of the cell 10 within the casing 12 to constitute the terminal 18.

The cathode electrode is separated by means of an insulating sheet 36 from the end of the anode 20.

The anode configuration used, with the folds being slanted rather than square, permits the compression of the sheets 22, 24 to take place while maintaining substantially uniform pressure across the surface of the anode and cathode electrodes. Under pressure the anode tends to be displaced slightly upwards or downwards as well as inwardly, thus tending to keep the spacing equal as the accordion folded anode is compressed or expanded as anode decomposition product forms.

The magnesium metal anode 20 may be formed of any suitable magnesium alloy, for example, the quick acting alloy containing aluminum and minor amounts of indium. Examples of suitable alloys are described in U.S. Patents 2,934,583 and 3,038,019.

The cushioning means 22, 24 are formed of any compressible non-conductive material which exhibits substantial compression strength, but is yieldingly compressible. While a pad formed of jute or sisal fibers, horsehair,

shredded rubber or latex impregnated natural fibers may be used, it is preferred to use a material which exhibits a relatively high threshold resistance to compression, yet a relatively constant progression in resistance to compression, once threshold pressure is exceeded, until the material has undergone a very substantial reduction in thickness, e.g., 75 to 90 percent reduction. Therefore, the ratio of total void space to volume occupied by solid matter in the material is preferably quite high, e.g., at least 4:1. Preferably, the material exhibits a resilient resistance to compression such that it is not compressed more than one-third under a load of 25 to 50 pounds per square inch. It is also desirable to use a material which will not take up moisture from the mix cake.

The materials which appear to best exhibit the foregoing desired properties are the resilient expanded, or foamed, synthetic plastics, e.g., Pelsapan expanded polystyrene, or expanded plasticized polyvinyl chloride. Such expanded plastics are cellular, generally having closed or substantially closed cells. Brittle materials are generally to be avoided as they tend to compress irreversibly or to simply break down into particulate material. In general, those expanded plastics which are so brittle or rigid that a layer of the material will break or crack when bent over a mandrel having a radius ten times the thickness of the layer may be usable for batteries in very light service, but will not withstand normal or heavy service involving moderate to rough handling or jarring.

Generally, a layer of compressible material at least one-sixteenth inch thick must be used with each anode assembly. A layer of about one-eighth to one-quarter inch thick for each anode assembly is suitable for most batteries. A layer thicker than about one-quarter inch may be used where space requirements permit, but the additional thickness is of no marked advantage.

The cathode mix 32 may be made up of any suitable composition normally employed for primary dry cells having magnesium anodes. Such mix is also known as a depolarizing mass. The mix cake is usually made up from a mixture of manganese dioxide and carbon black which is readily compressed or molded into cake form after being moistened with the electrolyte. A suitable mixture contains from 75 to 95 percent by weight manganese dioxide and the balance carbon black. A desirable mixture consists of 90 percent by weight MnO_2 (gold coast ore) and 10 percent acetylene black. Organic cathode depolarizing mixtures and electrolytes of the type disclosed and claimed in U.S. Patent No. 3,231,427 to R. C. Kirk et al. may also be used, for example.

Cathode mixes utilizing various aromatic nitro compounds may also be used, as disclosed in the article "Dry Cells Containing Various Aromatic Nitro Compounds as Cathode Materials" by Morehouse and Glicksman, *Journal of the Electrochemical Society*, volume 105, pp. 306-311.

Any suitable electrolyte may be used. A suitable electrolyte may be prepared by dissolving an alkali metal bromide, alkaline earth metal bromide or ammonium bromide in water in a concentration between about 30 grams per liter and that producing a nearly saturated solution at ordinary temperatures. The actual concentration used does not appear to be critical, although for best results certain concentrations are to be preferred depending upon the particular bromide or combination of bromides used. For example, preferred concentrations of the alkali metal bromides are from about 150 to 500 grams of the salt per liter of solution. Of the alkali metal bromides, lithium bromide produces the most desirable results, particularly in concentrations of about 300 grams per liter. Similar concentrations may be used with the alkaline earth metal bromides, which include the bromides of magnesium, calcium, barium and strontium. Of these, magnesium bromide is to be preferred. Its most effective concentration is about 300 grams per liter of solution.

While a single bromide may be used as the electrolyte, better results are had with combinations of the aforesaid bromides, particularly combinations of an alkali metal bromide with an alkaline earth metal bromide, such better results being manifested in greater shelf life and high capacity.

It is desirable to include in electrolytes an alkali metal, alkaline earth metal or ammonium salt of chromic acid in corrosion inhibiting amounts, such as from 0.01 gram per liter of solution to concentrations producing saturation. A preferred concentration of the chromic acid salt is 0.05 to 2 grams per liter of solution. A number of suitable electrolyte compositions are set forth in U.S. Patents 2,547,907 and 2,547,908. In addition, chloride electrolytes of the type disclosed and claimed in John L. Robinson's co-pending application Ser. No. 386,781, filed July 31, 1964, now abandoned, for "Chloride Electrolyte for Magnesium Primary Cells," may be used.

Other examples of suitable electrolytes are disclosed and claimed in John L. Robinson et al. U.S. Patent 3,258,368, and in John L. Robinson U.S. Patent No. 3,258,367, entitled, "Organic Electrolyte for Magnesium Primary Cells" and "Electrolyte for Magnesium Primary Cells," respectively. Perchlorate electrolytes of the type disclosed and claimed, for example, in U.S. Patent No. 2,993,946 to Lozier may also be used.

Any electrolyte used should, of course, be compatible with the type of cathode mix used, as is well known in the art.

The porous separator 30 may be formed, for example, of a layer of blotter-like material, such as a Kraft paper about 6 to 12 mils thick which is highly porous and of a type normally used in such battery construction. A thicker layer of separator material may be used if desired.

The porous separator is thoroughly wetted with electrolyte and serves as an electrolyte bridge between the immediately adjacent metal anode and the mix cake.

Primary cells made in accordance with this invention are simple to construct by automated means. The anode, with separator 20 adhering thereto, may be stamped from sheet stock, bent to shape, and inserted in open top casing with the sheets 22, 24 of the compressible material between appropriate folds of the anode.

Cathode mix including electrolyte is then introduced and tamped. Following this, the sheet-like cathode electrode 34 is forced into the mix 32 and along the end of the casing where the electrode 34 forms the terminal 18.

Precise spacing between electrodes may easily be achieved.

While the invention has been described in connection with magnesium anode primary cells, the anode assembly consisting of the anode 20 and separator 30 may be used in other types of primary cells.

What is claimed is:

1. A primary cell comprising an anode of magnesium alloy, said anode being sheet-like in form and folded back and forth upon itself with the folds spaced apart from one another and with the part of the anode connecting adjacent folds being disposed non-perpendicularly with respect to said folds, an ionically conductive electronically insulating porous separator, said separator is thoroughly wetted with electrolyte and adhering to one side of said anode, at least two plate-like compressible elements, each of said compressible elements being disposed between adjacent folds of anode intermediate of the end folds of said anode, a plurality of batches of cathode depolarizing mix and electrolyte, one of said batches being disposed between each pair of adjacent folds of said anode on the side of the anode to which the separator adheres, a sheet-like cathode electrode, said cathode electrode being formed into spaced apart continuous folds, one of said folds being disposed into each batch of cathode depolarizing mix, and being generally parallel to and equally spaced from said adjacent anode folds and another fold of said cathode electrode being

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disposed adjacent to but spaced from one end of said anode on the side of said anode which faces away from said batches of cathode depolarizing mix and electrolyte, insulating means disposed between said last mentioned fold of said cathode electrode and said end of said anode, moisture-resistant housing means surrounding said anode, cathode electrode and depolarizing cathode mix, and electrolyte wetted-separator, and means in said housing for making electrical contact with said anode and with said cathode and for maintaining the cell under compression.

2. A primary cell in accordance with claim 1, wherein said cathode electrode is a sheet of carbon loaded vinyl plastic.

3. A primary cell in accordance with claim 1, wherein said separator is made of paper.

4. A primary cell in accordance with claim 1, wherein

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said anode folds with which said cathode electrode is aligned are substantially parallel one with another.

5. A primary cell in accordance with claim 1, wherein said cathode electrode is made of carbonaceous cloth.

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WINSTON A. DOUGLAS, *Primary Examiner*.

15 ANTHONY SKAPARS, *Assistant Examiner*.