The disclosure describes a disposable anode package for use in mechanically rechargeable oxygen-depolarized metal-air batteries. The anode package includes a cellophane envelope which retains the flocculent discharged anode material. A pull tab at the top of the cellophane envelope allows the spent anode to be removed. Dependent on the thickness of the individual cells, nonreactive mesh or fiber separator materials are used to prevent the discharged flocculent matter from dropping to the bottom of the anode package.
1 DISPOSABLE ANODE PACKAGE

The invention described herein may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment of any royalties thereon or therefor.

This invention relates to mechanically rechargeable primary oxygen-depolarized batteries and, more particularly, to a disposable anode package which permits removal of a spent anode and recharging products. The invention includes an envelope which encases flocculent material formed at the anode and which prevents this material from sinking to the bottom of the cell where it will wedge the anode between the cathode walls. This envelope also serves as a separator which prevents anode ions from migrating to the cathode. Dendrite formation is thus inhibited. In one configuration, the separator is composed of a cellophane bag and spacing material placed between the bag wall and the anode to maintain the position of the flocculent material adjacent the place on the anode where it is formed. Removal of the anode, flocculent material, spacing material and envelope is accomplished by pulling up on a tab portion of the bag.

Metal-air cells have been used both as primary and secondary or rechargeable batteries. Examples of these batteries are shown in U.S. Pat. Nos. 3,457,115 to C. E. Kent, issued July 22, 1969; 3,436,270 to H. G. Oslin et al., issued Apr. 1, 1969; and 3,297,484 to L. W. Niedrach, issued Jan. 10, 1967. In the case of magnesium-air batteries, those that use a magnesium anode, electrical recharging is impractical due to the highly reactive nature of magnesium. Magnesium-air batteries may, however, be mechanically recharged by removing the spent anode and replacing it with a fresh anode. Additional electrolyte, usually a saline solution, is then added to the cell to complete the mechanical recharging process.

One of the major difficulties in mechanically recharging such a cell is the physical removal of the anode from the cell. Design restraints on light portable battery packs usually restrict cell thickness to the point that the spacing between the anode and the cathodes is on the order of a few centimeters. When magnesium anodes are used with a salt water electrolyte, magnesium hydroxide is produced which falls to the bottom of the cell. This wedges the anode between surrounding cathodes, causing the cell to rupture and making removal of the anode difficult in cells which are physically thin. In addition, flocculent material eventually will block off the operable surface of the anode as it falls to the bottom of the cell and will compact at the bottom of the cell such that electrolyte will be prevented from contacting the magnesium in the anode. This magnesium hydroxide must be removed prior to recharging to permit insertion of another anode as well as to prevent obscuring of the anode by the compacted flocculent material.

The subject invention contemplates encasing the anode in a cellophane envelope which will permit the flow of electrolyte through its walls while at the same time containing the flocculent material. When the anode is removed by extracting the cellophane bag, both the spent anode and the magnesium hydroxide are removed from the cell.

In addition, as part of the subject system, an expanded non-reactive mesh or fiber separator is used in combination with the cellophane bag to maintain this material at the place where it is generated so that compacting cannot occur. This permits the electrolyte to reach the anode. In the case of the fiber separator, capillary action also ensures that the electrolyte will be evenly distributed over the entire surface of the anode.

It is therefore an object of this invention to provide the anode of a metal-air cell with a microporous wettable envelope which has a high-electrolytic conductivity when wetted with the electrolyte. This system is used in the battery.

It is another object of this invention to provide means for containing flocculent material formed at the anode of a metal-air battery and for removing the anode and flocculent material when the anode is spent.

It is another object of this invention to provide the combination of a battery separator envelope and a flocculent material holding spacer for the anode of a mechanically rechargeable metal-air battery cell.

It is still another object of this invention to provide a disposable anode package for use in mechanically rechargeable metal-air battery cells which includes a metal anode, a baglike separator with a pull tab, and spacing material between the anode and the separator.

Other objects, advantages and novel features of the invention will become apparent from the following detailed description thereof when considered in conjunction with the accompanying drawings in which like numerals represent like parts throughout and wherein:

FIG. 1 is a diagram of a metal-air battery anode with an expanded rayon mesh spacer and cellophane separator bag.

FIG. 2 is a diagram of a metal-air battery anode with a fiber spacer and cellophane separator bag.

FIG. 3 is a cross section of a metal-air cell in which a bagged anode has been inserted showing the collection of flocculent material at the bottom of the separator envelope.

FIG. 4 is a partial cross section of a metal-air cell anode and separator showing flocculent material held in place by a spacer; and

FIG. 5 is a cut away diagram of a metal-air battery showing the position of the anode package in an individual cell as well as a series of cells which, when wired in series, completes the battery.

Referring to FIGS. 1 and 2, anode plates 1 and connector clips 2 are shown encased in cellophane envelopes or bags 3 which have pull tabs and are securing at the top in back of the anode. The front portions of envelopes 3 terminate below the level of electrolyte at edges 5. The wall portions of the envelopes are sealed in any convenient manner with the exception that holes 6 are left in the bottom of the bags to permit hydrostatic pressure of the electrolyte on either side of the envelopes to equilibrate. This pressure occurs once these anode packages are inserted into a cell shown in FIG. 3 and the electrolyte is added to the cell. These holes are, however, sufficiently small to prevent flocculent material from falling through. In one operative embodiment, holes having a mean diameter of one-eighth inch were used. It will be appreciated that these holes may also be located on the sides of the envelope as well as at the bottom for rapid equilibration. Clips 2, in the configuration shown, protrude over edges 5 of the envelopes in any manner which will enable a solid contact with the cathode connector of the next cell in a cell series or with a terminal connection (not shown). In one embodiment, the anode is made of a flat sheet of magnesium to which clips 2 are bonded.

It will be appreciated that this envelope will be effective in any mechanically rechargeable metal-air battery cell in which flocculent material, sometimes called sludge, is produced. The envelope may be made from any material which is microporous and wettable with a high-electrolytic conductivity when wetted with the electrolyte used in the battery. The material must not react with the active constituents of the battery and must have enough structural stability to prevent rupture when the anode package is removed. Cellophane sausage casing, such as that manufactured by Union Carbide, which has been deglycerinated and which contains only small amounts of sulfur has proved satisfactory. Radiation grafted polyethylene which has been treated so that it is wettable, swellable and microporous is also acceptable for use as an envelope. In general, any battery grade cellophane having a thickness of one or two mils, whether glycerinated or not, will be acceptable material for the envelope.

In FIG. 1, a spacing material of an expanded rayon mesh 8 is shown. This mesh may be made of any nonreactive material such as polyethylene and functions to hold any flocculent material produced by the anode in place. It also serves as a damping mechanism to the sloshing of electrolyte within the envelope. In FIG. 2, the separating material 9 is fibrous which,
in addition to holding flocculent material, also serves as a wick to bring electrolyte into contact with the anode as can be seen in FIG. 3, no spacing material need be used in the envelope. In this case, the envelope serves its primary function of providing an efficient method of removing sludge and anode from the battery cell.

FIG. 3 is a cross-sectional view of a complete metal-air cell. Here anode 1 encased by envelope 3 is shown inserted into a cell composed of air cathodes 10 supported by rigid metal casing members 11. The air cathode structure is shown and explained in U.S. Pat. No. 3,297,489 to L. W. Niedrach, issued Jan. 10, 1967. These cathodes are generally microporous material which will maintain electrolyte on one side while permitting a gas to come through from the other side to react with the electrolyte. More basically, the cathode must be nonwettable and provide a catalyst to the oxygen in the air. The most common air cathode materials are platinum, palladium, silver and some types of activated carbon plated on a cathode matrix of stainless steel, nickel mesh or any material that will not react with the electrolyte at a high rate. Pore size in the cathode is in the hundred to thousand micron range. The cathode is usually made by bonding a mixture of Teflon and metal powders to the screen to provide bonding and nonwettability. Connector clip 2 extends beyond the cell casing and rests on a rubber insulating cap member 13 which is slotted to receive the anode and envelope and which limits the insertion of the anode so that it will not contact casing member 11. When fully inserted, clip 2 also extends beyond envelope 3. Female connector 12 is shown mounted on the casing and is configured to receive the anode connector clip from another cell. The battery is shown filled with a salt water electrolyte 14 to a level above envelope edge 5. Flocculent material 15, which in this case is magnesium hydroxide, is shown at the bottom of the envelope. In the embodiment shown in FIG. 3, no spacing material is used.

Removal of the anode and flocculent material is accomplished by pulling on tab 4. In addition to aiding in the removal of the sludge produced, it prevents magnesium ions and hydrogen produced in the reaction process from reaching the cathode.

FIG. 4 is a cross-sectional view of a portion of the metal anode 1, the envelope 3, expanded rayon mesh 8 and flocculent material 15. The addition of the mesh to the cell shown in FIG. 3 prevents the flocculent material from compacting at the bottom of the envelope, thus obscuring a portion of the anode. When the flocculent material is caught in the mesh, it is not sufficiently dense to block the electrolyte from reaching the anode. A like effect can be obtained with the aforementioned fibrous spacing material.

FIG. 5 is a cut away diagram of a partially completed metal-air battery 20 made up of serially connected metal-air cells 21. Cell 21a is cut away to show the insertion of removable anode package 22. In order to mechanically recharge the battery, spent anodes are removed by pulling the tab on the envelopes and new anodes inserted as shown at 21a. Electrolyte is then added to each cell. This recharging process requires little or no skill, no danger to personnel and may be accomplished in the most remote of locations. If the metal-air cell utilizes a magnesium anode, it may be recharged by dipping the entire battery with new anode packages in salt water.

This invention is not, however, limited to magnesium-air batteries. Disposable anode packages of the type described may be used to advantage in mechanically rechargeable cells whenever anodes are to be removed or whenever flocculent sludge is produced at the anode-electrolyte interface.

What is claimed is:

1. Apparatus for containing and removing flocculent material surrounding the anode of a primary battery which is recharged by the removal of a spent anode therefrom and by the insertion of both a fresh anode and fresh electrolyte into each of the cells of said battery comprising:

- an electrolyte-wettable nonreactive microporous cellophane envelope surrounding and spaced from said anode at its side and bottom portions and having a tab portion formed as an extension of one of the side portions of said envelope, said tab portion projecting above said anode to facilitate removal of said envelope and anode such that whenever said anode is in its operating position within any of said cells it may be removed by means of said tab portion, whereby any flocculent material formed at the anode-electrolyte interface is contained within said envelope and is removed with the removal of said envelope and anode,

the bottom portion of said envelope having openings of a size sufficient to permit said electrolyte to rapidly enter and small enough to prevent said flocculent material from passing therethrough; and

- a nonreactive separator placed between said anode and the interior wall portions of said envelope to maintain said flocculent material in the position at which it is formed on the surface of said anode,

whereby any flocculent material formed at the anode-electrolyte interface is contained within said envelope and is removed with the removal of said envelope and anode, and the electrolyte in each of said cells is allowed to equilibrate on both sides of the wall portions of the envelopes inserted in said cells.

2. The apparatus as recited in claim 1 wherein said separator is an expanded rayon mesh.

3. The apparatus as recited in claim 2 wherein said separator is formed from fibrous cellulose material.

4. In an oxygen-depolarized metal-air cell of the type wherein a metal anode is inserted in an open-ended cavity formed by a gas-permeable air cathode and wherein an electrolyte is added to said cavity, a disposable anode package for use in mechanically recharging said cell comprising:

- a highly reactive metal anode adapted to fit within said cavity; and

an electrolyte-wettable nonreactive microporous cellophane envelope surrounding the side and bottom portions of said anode and having a tab portion integrally formed therewith as an extension of one of the side portions of said envelope, said tab portion extending above the top portion of said anode and protruding through the open end of said cavity to facilitate removal of said anode and envelope from said cell when said anode is spent, said envelope having openings at the bottom portion thereof of a size sufficient to permit the electrolyte carried within said cell to rapidly enter said envelope and small enough to prevent any flocculent material formed at the anode-electrolyte interface from passing therethrough whereby the electrolyte is allowed to equilibrate on both sides of the wall portions of said envelope, and wherein said disposable anode package further includes a nonreactive separator placed between said anode and the interior wall portions of said envelope to maintain said flocculent material in the position at which it is formed on the surface of said anode,

whereby any flocculent material formed at the anode-electrolyte interface is a byproduct of the electrochemical reaction in said cell is removed with the removal of said envelope and anode from said cell.

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