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AIR-DEPOLARIZED DEFERRED ACTION CELL

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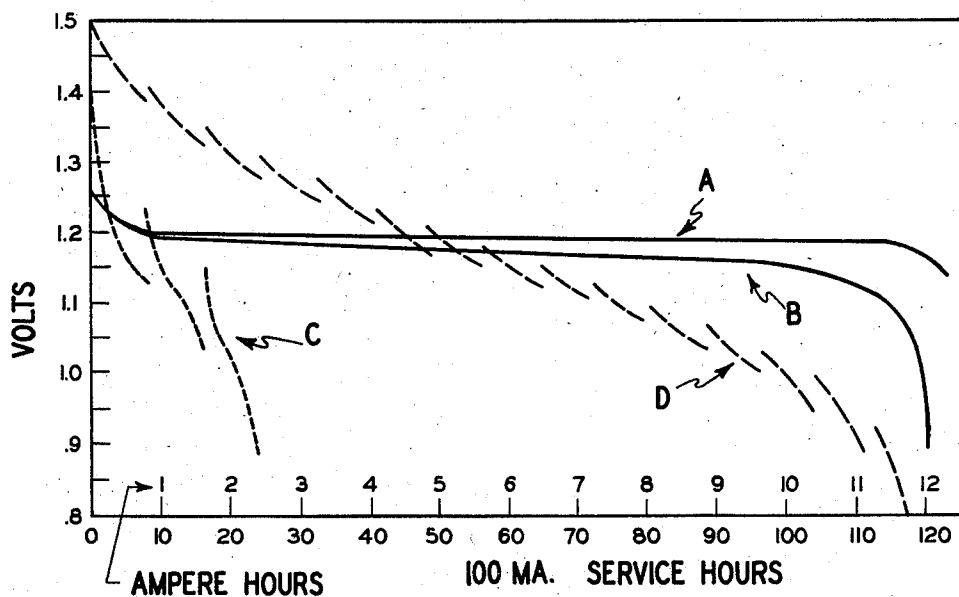
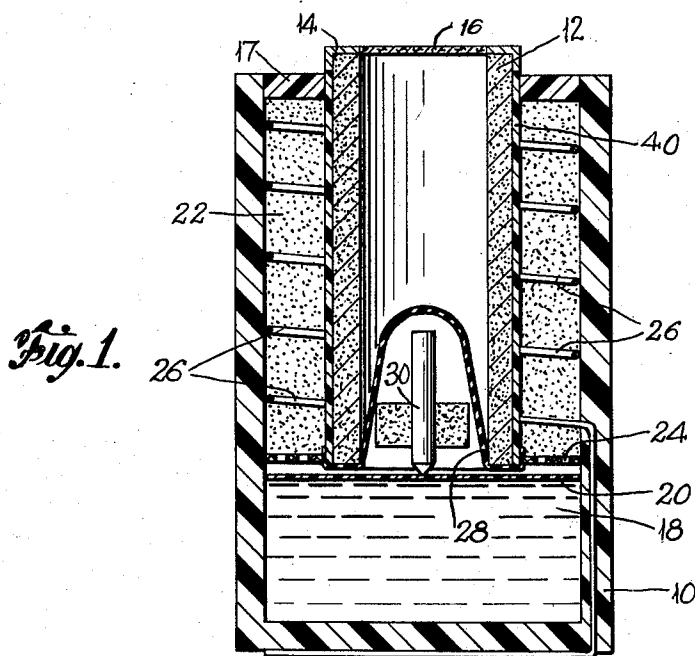


Fig. 2.

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AIR-DEPOLARIZED DEFERRED ACTION CELL

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5 Claims. (Cl. 136—86)

This invention relates to an air-depolarized deferred action cell employing an alkaline electrolyte in conjunction with a gelled anode.

The main object of this invention is to provide an air-depolarized deferred action cell operable at good currents, and satisfactory voltages, at temperatures as low as -20°C .

Another object of the invention is to provide a cell of the character described, which even after activation can have its energy withdrawn without appreciable loss over periods of several months.

These and other related objects, features and advantages of the present cell construction will become more apparent as the description thereof proceeds, particularly when taken in conjunction with the accompanying drawing wherein:

Fig. 1 is a front elevational view, broken away, of a cell in accord with the invention; and

Fig. 2 contains a series of curves showing the performance of such a cell, and of some comparable existing cells under identical conditions.

Referring now to Fig. 1, it will be seen that the cell of the invention comprises a plastic container 10 fabricated from polyethylene or methyl methacrylate. Centrally positioned in this container is a tubular carbon cathode 12, treated by either of the processes disclosed in the U.S. Patents 2,615,932 and 2,669,598, issued on October 28, 1952 and February 16, 1954 to A. Marko and K. Kordesch.

The processes claimed in the mentioned patents involve impregnating porous carbon with a solution containing at least one heat-decomposable salt of a heavy metal such as iron, cobalt, nickel, manganese, chromium, copper, silver, gold, platinum, vanadium, titanium, uranium, thorium and the rare earths, and at least one heat-decomposable salt of aluminum, the enumerated salts acting as oxidizing agents for carbon. Following impregnation with above-described solution, the treated carbons are heated to decompose the salts, thereby activating and catalyzing them. Following this treatment, the carbon contains within its pores and at the surface thereof a spinel type catalyst consisting of an oxide of the heavy metal and of aluminum oxide ($\text{RO} \cdot \text{Al}_2\text{O}_3$). This treatment will be more fully described hereinafter.

Surrounding the top of cathode 12 is a copper coated steel cap 14 serving as the top contact of the cell. A top seal 16 of plastic tape closes the cell to the air, and prevents the entrance of moisture therein. As shown, the length of the cathode is about $\frac{2}{3}$ that of the cell container, but its upper part protrudes above the container. The remaining $\frac{1}{3}$ of the container is a self-contained electrolyte reservoir 18 defined by the cell bottom and walls, and at its top by a frangible separation wall 20, such as a disk of vinyl resin about $\frac{1}{32}$ inch in thickness, inserted after the desired amount of electrolyte (KOH) is poured into the container.

After the above elements are in place, the anode mix 22 consisting of zinc powder coated with carboxy methyl

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cellulose is tamped in around the outside of the separator surrounded cathode. A perforated cardboard washer 24 holds the zinc powder in place. A copper wire spiral 26 surrounds the anode particles, and passes through the sides of the container to serve as the anode collector.

In the embodiment of the cell shown on Fig. 1, an elastic membrane 28 seals the cathode at its lower end, and serves as a gas vent after activation.

Activation of the present cell may be accomplished by first removing the plastic tape seal 16, and then applying downward pressure on the deformable membrane 28 with a pencil or any other hard cylindrical tool introduced into the cell through the open end of the carbon cathode 12, until the same meets the pin 30, thus breaking the wall 20, which may be scored to make it more readily frangible, permitting electrolyte to flow into the anode regions of the cell when the cell is inverted. More simply, the pin 30 can be dispensed with, and a pencil or other pointed instrument used to apply the necessary pressure through the membrane 28 to break the frangible wall 20. The membrane 28 must be strong enough not to be punctured during breakage of the electrolyte retaining frangible wall 20.

Cathode fabrication

The cathodes used in the cells of the invention are prepared from a mixture consisting of about 60 percent by weight of projector type carbon, about 40 percent by weight of soft pitch and about $1\frac{1}{2}$ percent by weight of fuel oil. Tubes having the desired dimensions are extruded from such a mix and baked at 1000°C . for about 6 hours. After this baking the tubes have a porosity of between 20 and 33 percent, using water saturation method measurements. The tubes are next heated in a CO_2 atmosphere between 850°C . to 950°C . for two hours to convert their hard and shiny skin to a surface having a dark black appearance. In this condition the carbon tubes are better able to absorb the catalyzing solution in which they will be immersed. Such a solution consists of an 0.1 molar solution of aluminum nitrate and cobalt nitrate containing 75 g. $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 29 g. $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ per liter. Generally one carbon cathode requires about 3 ml. of solution. Best results have been obtained by placing the carbon dioxide-treated carbon tubes, once cooled, in a container which is then evacuated. After obtaining a vacuum of about 20 millimeters of mercury, the catalyzing solution is allowed to enter the container, and to soak the electrodes. Upon restoring the air pressure, the solution is pressed into the pores of the tubes. The tubes are then dried at 100°C . for two hours, and heated again to 850°C . for two hours in carbon dioxide to decompose the metal nitrates to oxides. After this treatment a spinel of the formula $\text{CoO} \cdot \text{Al}_2\text{O}_3$ is formed from the catalyst mixture. The deposit is observable on the surface of the carbon tubes as a blue deposit. After cooling the carbon tubes in a carbon dioxide atmosphere, the vacuum operation and heating cycles are repeated to increase the activity of the carbon surface. A third cycle of treatment is not necessary, except for high current electrodes of a capacity of 100 milliamperes per centimeter squared, or more.

For best results the carbon electrode tubes should be wet-proofed. This can be achieved by immersing the tubes in a 1.5 percent paraffin petroleum ether solution for about five minutes. Following this the electrodes are air dried by passing air through their center. Wet-proofing affects the polarization of the electrode, but too much wet-proofing is detrimental to electrode life, since it permits accumulation of hydrogen peroxide, which accelerates carbon oxidation, and in some cases destroys the

wet-proofing agent (for example, paraffin can be oxidized to fatty acids by nascent oxygen in the presence of heavy metal catalysts). As an additional wet-proofing, a mixture of equal parts of nitro-benzene and kerosene is applied to the inside of the tubular carbon electrode. The very dense inner surface of the electrode does not take up an appreciable amount in a short time. However, the vapors of the compounds mentioned travel to the active outer surface, and are adsorbed there to give the desired degree of repellency.

Other wet-proofing agents can be used in addition to paraffin and petroleum ether. Thus chloronaphthalene and dibenzylether may be used.

Anode construction

To achieve the highest possible capacity in a given volume, a powder zinc anode is used. Thirty percent of the zinc particles in this powder should be between 20 and 30 mesh (Tyler) in size; 30 percent between 60 and 100 mesh; another 30 percent should be between 100 and 200 mesh, and the rest is through 200 mesh. This powder is first coated with sodium carboxymethyl cellulose in such a way that a zinc powder carboxymethyl cellulose-water gel is formed. The gel is pressed into thin rods, dried and crushed to a particle size of 12 to 20 mesh. This material is coarse enough to allow the electrolyte to penetrate between the particles. During activation with electrolyte, the carboxymethyl cellulose coating swells, and forms a homogeneous gel anode.

The zinc powder should be amalgamated with from 2 to 4 percent of mercury. Amalgamation is best carried out in a 5 percent ammonia solution by adding the necessary amount of mercury to zinc powder. Vigorous stirring facilitates fast and uniform amalgamation. Amalgamated zinc powder is then washed once or twice with water, and dried in a vacuum at a moderate temperature (40° to 50° C.).

Suitably, pieces of binding straw extending from top seal 17 to the perforated cardboard washer 24, may be placed in the zinc particles on either side of the cathode, to allow the escape of air when the cell is inverted to get electrolyte in place.

Electrolyte

Potassium hydroxide is the preferred electrolyte for the cells of the invention, especially in respect to low temperature service. Nine normal potassium hydroxide solution was found superior to six normal solution for such application.

Separator

A suitable separator 40 for this cell is regenerated cellulose on a vinyl chloride-vinyl acetate copolymer film base in a two-ply layer. Other suitable separator materials are copolymers of vinyl chloride and acrylonitrile, parchment paper and caustic-resistant cellophane.

Polystyrene, "Lucite," and similar plastic materials are best suitable as cell containers. For best results a plastic seal should be placed on top of the cell to prevent moisture from entering the same. Suitably such seals may be of the type disclosed and claimed in the co-pending application of P. A. Marsal, Serial No. 409,435, filed February 10, 1954.

Cell performance

Fig. 2 shows the performance of a D-size cell of the type above described on a drain of 100 milliamperes.

Curve of A represents the performance at the indicated drain of a deferred action cell of the invention discharged for eight hours daily on a five days per week continuous service basis. Curve B relates the same information after a delay over a three months period for the same cell. The difference between curves A and B then shows shelf losses in capacity after activation over the given period. The simple flat discharge curves at both periods of time should be noticed. It should be noted also that until nearly the total discharge of the cells occurs, the shelf loss in voltage is only a few millivolts. Curve C relates the performance of a standard D-size LeClanche type cell. Curve D relates the performance in the above indicated test of a D-size cell using MnO₂ depolarizer mix in conjunction with a zinc anode. It should be obvious from a comparison of the curves of Fig. 2, that the cells of the invention have a greater capacity and a greater keeping quality than those of the other systems.

What is claimed is:

1. A deferred action air-depolarized cell comprising a cupped container, the lower part of said container forming an electrolyte-containing reservoir defined by the container walls and bottom at its upper extremity, and by a frangible separation wall, a centrally-apertured tubular cathode composed of activated and catalyzed carbon, having in the pores and at the surface thereof a spinel type catalyst consisting of an oxide of a heavy metal and of aluminum oxide, said cathode extending from immediately above said separation wall to above the top of said container, said cathode being maintained in place at its lower extremity by a centrally apertured insulating washer; an anode gel between said container walls and said cathode; a separator consisting of alkali resistant material between said cathode and anode material, a metallic wire surrounding said anode material, and passing through the sides of said container to serve as the anode collector thereof, a top seal over said anode material below the top of said cathode, externally-actuated means in the central aperture of said cathode for rupturing said separation wall and a metallic cap surmounting the top of said cathode.

2. The cell of claim 1 wherein said anode consists of amalgamated zinc powder coated with sodium carboxymethyl cellulose.

3. The cell of claim 1 wherein said cathode is about two-thirds the length of said cell container.

4. The cell of claim 1 wherein said electrolyte is 9N potassium hydroxide.

5. The cell of claim 1 wherein metallic wire serving as the anode collector thereof is composed of copper.

References Cited in the file of this patent

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