

PATENT SPECIFICATION

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(54) IMPROVEMENTS IN OR RELATING TO DIVALENT SILVER OXIDE ELECTRICAL CELLS

(71) We, KABUSHIKI KAISHA DAINI SEIKOSHA, a Japanese company, of 31-1, 6-chome, Kameido, Koto-ku, Tokyo, Japan, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed to be particularly described in and by the following statement:-

This invention relates to divalent silver oxide electrical cells.

Divalent silver oxide electrical cells are capable of giving relatively large amounts of electrical energy per unit volume and are therefore particularly interesting and attractive for use as electrical power sources for driving small electronic apparatus, such as electronic wrist watches, and in other cases where the power supply cell must be as small as possible and yet have a long useful life over which it presents at least an approximately constant output voltage to its load. However, such cells, as at present in general use, have the serious defect that the curve of output voltage against extent of discharge shows two distinct steps or "plateaus", for the discharge potential difference to turn divalent silver oxide into monovalent silver oxide is approximately 0.3V. So relatively large a potential difference between "plateaus" is a serious defect when the cell is for use in an apparatus such as an electronic timepiece since it militates against obtaining the high degree of time-keeping accuracy which is desirable in an electronic timepiece.

One way of overcoming this defect is described in the specification of Japanese Patent Issued No. 48-32850 (Japanese Patent Issued No. 32850/1973). In the cell described in this specification the surface of a positive depolarising mix pellet made of divalent silver oxide is coated with a continuous layer of monovalent metal oxide such as monovalent silver oxide or silver itself. The disclosure in this specification has, however, the disadvantages that it involves a decrease in the quantity of divalent silver oxide which can be used in a cell of given size and complicates manufacturing production of the cell.

The present invention seeks to reduce these disadvantages.

According to this invention there is provided an electrical cell comprising, within a container constituting a positive terminal of the cell, a body of divalent silver oxide positive depolarising mixture having formed, on at least part of the surface thereof, a silver or monosilver oxide layer of at least 5% porosity.

At least part of the surface of the layer may be penetrated by monovalent silver oxide powder or a mixture of monovalent silver oxide powder and silver powder. Alternatively it may be formed into monovalent silver oxide by an electrolytic operation.

The invention is illustrated in the accompanying drawings in which:

Figure 1 is a longitudinal sectional elevation of one form of miniature divalent silver oxide cell embodying the invention; and

Figure 2 shows part of the anode constituted by the silver layer on the surface of the positive depolarising mix of the cell shown in Figure 1.

Referring to Figure 1, this shows a negative cap 1 which serves as the cathode terminal of the cell and in which is housed a negative depolarising mix 2 of amalgamated zinc. 3 is a separator and 4 is electrolyte absorbent material holding the electrolyte. 5 is a positive container which serves as the anode terminal of the cell and in which is housed a pellet of positive depolarising mixture 6. This pellet has a silver or monosilver oxide layer 7 which has been formed on the surface thereof. 8 is a packing spacer which separates and insulates the cathode and anode from one another and serves also to complete and seal the cell.

Manufacture: Example 1

After forming a body of positive depolarising mixture 6, mainly composed of divalent silver oxide, it is provided with a silver or mono silver oxide layer of at least 5% porosity over its upper and peripheral surfaces so that it is covered by the layer except for the bottom surface thereof. The thus covered positive depolarising mixture, which is pressed into a disc like pellet is then placed in the positive container 5 with its uncovered surface towards the base of the container as shown in Figure 2. The porous structure of the material used for the layer may have 85% to 98% porosity, for example, so that it is a sponge-like metal body with an apparent density of 1/7 to 1/50 of that of solid silver plate material. The porosity can be decreased as desired by compression and deformation and the flexibility is very good due to its original matrix structure. Advantage of these properties is taken by making a coated positive depolarising pellet structure as shown in Figure 2 by suitable applied pressure.

After inserting the coated pellet in the container the separator 3, the electrolyte absorbent material 4, the insulating packing spacer 8 are inserted, and the negative cap 1, previously filled with the negative depolarising mixture 2 is put in place (see Figure 1). Finally the cell is sealed by a caulking, pressing or swaging operation performed on the end portion of the positive cap 1, where it adjoins the spacer 8, and the open end of the container 5.

Manufacture: Example 2

As Example 1, except that, after providing the positive depolarising mixture pellet with its layer thereon, the upper surface of the pellet is penetrated with monovalent silver oxide powder before placing it in position and completing the other operations of making the cell.

Manufacture: Example 3

As Example 1 except that, after providing the positive depolarising mixture pellet with its layer thereon, the surface thereof, or at least the upper surface thereof, is oxidized positively by an electric resolving operation to form a mono-silver oxide layer there, i.e. is formed into silver oxide by an electrolytic operation.

The open circuit voltage and the internal resistance of a cell in accordance with this invention depend to a large extent on the pressure used during the press-forming operation on the coated positive depolarising mix and foamed silver. For a cell made in accordance with Example 1 typical values are shown in Table I below, in which t/cm² is tons per square centimetre.

Table I

Forming Pressure	Open Circuit Voltage	Internal Resistance
0.5t/cm ²	1.75V	45
2.0t/cm ²	1.65V	123
4.0t/cm ²	1.61V	125
8.0t/cm ²	1.61V	135

The figures in the above table are mean figures obtained after testing 50 cells each of 7.9mm overall diameter and 3.6 mm overall height.

As will be obvious from Table I, the voltage and resistance values obtained depend on the forming pressure used for the anode. The open circuit voltages increased with decrease in pressure until a maximum voltage of about 1.8V was reached.

A similar table (Table II) of open circuit voltages and internal resistances of cells made in accordance with Example 2 appears below:

Table II

Forming Pressure	Open Circuit Voltage	Internal Resistance
0.5t/cm ²	1.63V	28
2.0t/cm ²	1.61V	21
4.0t/cm ²	1.61V	15
8.0t/cm ²	1.61V	12

It will be seen that the values in Table II are generally somewhat better as regards open circuit voltages and internal resistances than those in Table I.

The final density of the positive depolarising mixture is dependent on the pressure applied during press-forming, and it will be appreciated that, in both Examples 1 and 2, a pressure of 8t/cm² or so is the best value to choose from the range of pressures covered by Tables I and II.

The layer is, of course, required to have a certain necessary minimum porosity, but in the case of Example 1, the values of internal resistance show a tendency to become high with decrease of the porosity of the layer below 10%. The method of Example 2 is therefore preferred because of the reduction of the effects of decrease of porosity due to the penetration of the layer with monovalent silver oxide powder. Instead of simple monovalent

silver oxide powder mixtures of silver powder with monovalent silver oxide powder could be used as penetrating material.

A table similar to Tables I and II, of open circuit voltages and internal resistances, but for cells in accordance with Example 3, appears below as Table III.

Table III

Forming Pressure	Open Circuit Voltage	Internal Resistance
4.0t/cm ²	1.61V	25
8.0t/cm ²	1.61V	38

The open circuit voltages decreased to a minimum of 1.6V and the internal resistance values were lower than in Tables I and II. The method of Example 3, compared with that of Example 2, is regarded as somewhat better because it does not involve the step of penetrating monovalent silver oxide into the layer. However, care must be taken to select a suitable oxidising treatment which will maintain the conductivity of the silver or monosilver oxide layer and not form a non-conductive monovalent silver oxide layer all over the surface of the former layer.

It is known in a divalent silver oxide electrical cell to form a divalent silver oxide electrode with a porous silver layer.

WHAT WE CLAIM IS:

1. An electrical cell comprising, within a container constituting a positive terminal of the cell, a body of divalent silver oxide positive depolarising mixture having formed on at least part of the surface thereof, a silver or monosilver oxide layer of at least 5% porosity.

2. A cell as claimed in claim 1 wherein at least part of the surface of the layer is penetrated by monovalent silver oxide powder or a mixture of monovalent silver oxide powder and silver powder.

3. A cell as claimed in claim 1 wherein at least part of the surface of the layer is formed into monovalent silver oxide by an electrolytic operation.

4. A cell as claimed in any of the preceding claims wherein the body of positive polarising material is formed as a compressed pellet having the layer formed thereon.

5. A cell as claimed in any of the preceding claims 1 to 4 and made substantially in accordance with Manufacture Example 1 set out herein.

6. A cell as claimed in any of the preceding claims 1 to 4 and made substantially in accordance with Manufacture Example 2 set out herein.

7. A cell as claimed in any of the preceding claims 1 to 4 and made substantially in accordance with Manufacture Example 3 set out herein.

8. Divalent silver oxide electrical cells substantially as herein described with reference to the accompanying drawings.

9. A divalent silver oxide cell comprising to form a silver layer using foamed silver having more than 5 percent porosity on either over all the surface of depolarizing mixture or the one portion thereof.

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6. A cell as claimed in any of the preceding claims 1 to 4 and made substantially in accordance with Manufacture Example 2 set out herein.

7. A cell as claimed in any of the preceding claims 1 to 4 and made substantially in accordance with Manufacture Example 3 set out herein.

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