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PATENT SPECIFICATION

NO DRAWINGS.

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COMPLETE SPECIFICATION

Electrodes and their production

We, UNION CARBIDE CORPORATION, of 270, Park Avenue, New York, State of New York, United States of America, a Corporation organised under the laws of the State of New York, United States of America (Assignee of RALPH MARTIN FOCKING and DEMETRIOS VASILIOS LOUZOS), 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:—

The present invention relates to negative electrodes for use in alkaline cells and to process for the manufacture thereof.

Various prior art techniques are known which can be used for the manufacture of alkaline cell electrodes having improved properties due to increased porosity, i.e. increased electrode surface area.

These prior art techniques deal mainly with the compression molding of finely divided mixtures of conductive materials and negative active materials and require either that specific crystalline types of material be employed or that more than one type of negative active material be present in the mixture.

For example, it has been proposed to prepare electrodes by compressing a mixture of dendrites of needle-like crystals of a conductive material, such as copper, and a negative active material such as cadmium hydrate. The use of the aforementioned crystal types is required in this process in order to produce a desired interlocking therebetween to thus provide a porous electrode structure. In addition to requiring particular crystalline materials it is also necessary in this known process that special care be taken in handling the mixed materials in order to preserve the original crystalline structure. Moreover, the cohesion provided by the interlocking of the crystals is not always sufficient to prevent softening of the electrode and loss of capacity.

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In another known process, the use of the special crystalline forms is not considered essential, however, the use of more than one type of negative active material is necessary in order to provide suitable porosity in the electrode.

It can thus be seen that heretofore, in order to provide an electrode having increased porosity, it has been found necessary to use special materials and at times special processing and handling techniques. Moreover, the degree of porosity provided by these procedures did not always prove to be entirely satisfactory for the intended use.

It is therefore the object of the present invention to provide an electrode for a secondary alkaline cell having a high surface area and increased porosity which can be manufactured simply and without the need for special materials.

Accordingly, the present invention provides a negative electrode for use in an alkaline cell which comprises a compressed mixture of a conductive metal powder, a negative active material and solid potassium hydroxide or solid sodium hydroxide.

This electrode when placed in contact with the electrolyte of an alkaline cell develops a high porosity upon dissolution of the solid KOH or NaOH contained in the electrode. This high porosity condition is achieved without the use of special materials or special processing.

It is preferred to use KOH and, for the sake of convenience the present invention will be described in detail with reference thereto.

In the practice of the present invention, a finely divided mixture of conductive material, negative active material, and solid KOH, is prepared and subsequently compression molded, preferably, but not necessarily, on a conductive support. The crystalline structure and sizing of the particles in the mixture is not critical, it being important only that, after compression molding, the packing of the com-

pressed mixture be between about 45 per cent and 80 per cent and preferably between 60 per cent and 80 per cent. (By "% packing" we mean the ratio X100 of the weight of the mixture in a given volume divided by the maximum possible weight of said mixture in the same volume). Mixing of the solid particles and simultaneous size reduction of the KOH, which is most conveniently added as pellets or flakes, may be accomplished in any one of several types of mills, e.g. a muller, swing hammer, or rotating knife type. Simple blending is sufficient if the KOH is initially finely divided.

With regard to the mixture constituents, the conductive material can for example be nickel powder such as derived from nickel carbonyl decomposition and the negative

active material can be CdO or $\text{Cd}(\text{OH})_2$ when producing uncharged electrodes. Iron powder can also be used as the conductive material.

In general, the conductive material may be present in the mixture in amounts of up to 50 per cent by weight and the amount of negative active material can vary from 40 to 95 per cent by weight. The usual range for KOH is from 5 to 25 per cent by weight of the electrode mix.

Specific proportions of mixture constituents which have been tested and which provide a suitable uncharged electrode are shown in Table I. These mixtures were compression molded on a metal screen at a pressure of about 8 tons per in^2 and used as electrodes in open beaker trials and in sealed Ni-Cd constructions.

TABLE I

Negative Active Material Per cent by weight	Conductive Material Per cent by weight	KOH Powder Per cent by weight
54.5 CdO	36.3 Ni or Fe	9.2
49.6 CdO	33 Ni	17.4
26.3 CdO		
30.0 $\text{Cd}(\text{OH})_2$	35 Ni	8.7

With regard to the formation of the electrode, conventional compression molding techniques using the usual equipment and pressures from about 3 tons to 20 tons per in^2 are considered to be suitable in the practice of the present invention.

The electrode of the present invention is self-supporting, i.e. it does not shed, and it can be charged completely or partially either outside the cell or after the cell is assembled and sealed.

Thus, a reserve Ni-Cd cell can be made with the water left out during shelf storage. The water can be added through a suitable seal when needed for service.

When the electrode of this invention comes into contact with aqueous KOH electrolyte during electroforming, the solid KOH contained in the electrode dissolves with the consequent formation of electrolyte channels in the electrode structure which provide a suitable ratio of pore volume to apparent electrode volume for high rate service. Also, the dissolution of the solid KOH, in addition to providing a porous, high-surface area article suitable for use as an electrode also furnishes additional caustic for recycling.

In addition to the uncharged electrodes previously described, the present invention also contemplates the production of charged cadmium electrodes prepared in the same

manner as uncharged electrodes except that Cd metal is used as the negative active material. Approximately the same proportions of conductive material and KOH can be used for preparing charged and uncharged electrodes. A charged electrode in accordance with this invention was formed of a mixture of 54.4 per cent by weight Cd, 36.5 per cent by weight Ni, 9.1 per cent by weight KOH.

In the present invention, the use of flakes or pellets of KOH in the fabrication of the electrode provides a further advantage in that the KOH, while in the solid state, acts as a binder, in addition to being a fugitive material. While the binding force of the KOH is relatively weak, it is nevertheless significant. Since the usual fugitives require washing of the electrode prior to use, and even then remain to some extent as an impurity, and since the usual binders take up considerable space and consequently lower volumetric efficiencies, it can be seen that the combined non-contaminating fugitive binder of this invention represents a substantial industrial benefit.

Although the preferred embodiment is as heretofore described, it is possible in some instances to employ substitute materials. For example, NaOH may be substituted for KOH if performance at low temperature is not required. Similarly, zinc or zinc oxide may be

- substituted for cadmium or cadmium oxide if shorter cycle life is acceptable in a secondary cell. Zinc may be also substituted for cadmium in making a charged negative electrode for a primary alkaline cell, e.g. of the reserve type.

WHAT WE CLAIM IS:—

1. A negative electrode for use in an alkaline cell which comprises a compressed mixture of a conductive metal powder, a negative active material and solid potassium hydroxide or solid sodium hydroxide.
2. An electrode as claimed in claim 1, in which the conductive metal powder is nickel or iron powder.
3. An electrode as claimed in claim 1 or 2, in which the negative active material is cadmium, cadmium oxide, cadmium hydroxide, zinc or zinc oxide.
4. An electrode as claimed in any of claims 1 to 3, in which the conductive metal powder is present in the mixture in an amount of up to 50 per cent by weight, the negative active material is present in an amount of from 40 to 95 per cent by weight and the potassium hydroxide or sodium hydroxide is present in an amount of from 5 to 25 per cent by weight.
5. A negative electrode for use in an alkaline cell substantially as hereinbefore particularly described.
6. A process for the production of a negative electrode as claimed in claim 1 which comprises preparing a finely divided mixture of the metal conductive powder, the negative active material and solid potassium hydroxide or solid sodium hydroxide and then com-

pression molding said mixture.

7. A process as claimed in claim 6 in which the mixture is compression molded on a conductive support.

8. A process as claimed in claim 6 or 7 in which, after compression molding, the packing of the compressed mixture is between 45 and 80 per cent.

9. A process as claimed in claim 8 in which, after compression molding, the packing of the compressed mixture is between 60 and 80 per cent.

10. A process as claimed in any of claims 6 to 9 in which a pressure of 3 to 20 tons per square inch is used in the compression molding.

11. A process as claimed in any of claims 6 to 10 in which the conductive metal powder is nickel or iron powder.

12. A process as claimed in any of claims 6 to 11 in which the negative active material is cadmium, cadmium oxide, cadmium hydroxide, zinc or zinc oxide.

13. A process as claimed in any of claims 6 to 12 in which the finely divided mixture is composed of up to 50 per cent by weight of the conductive metal powder, from 40 to 95 per cent by weight of the negative active material and from 5 to 25 per cent by weight of potassium hydroxide or sodium hydroxide.

14. A process for the production of a negative electrode substantially as hereinbefore particularly described.

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WHAT WE CLAIM IS:—

1. A negative electrode for use in an alkaline cell which comprises a compressed mixture of a conductive metal powder, a negative active material and solid potassium hydroxide or solid sodium hydroxide.
2. An electrode as claimed in claim 1, in which the conductive metal powder is nickel or iron powder.
3. An electrode as claimed in claim 1 or 2, in which the negative active material is cadmium, cadmium oxide, cadmium hydroxide, zinc or zinc oxide.
4. An electrode as claimed in any of claims 1 to 3, in which the conductive metal powder is present in the mixture in an amount of up to 50 per cent by weight, the negative active material is present in an amount of from 40 to 95 per cent by weight and the potassium hydroxide or sodium hydroxide is present in an amount of from 5 to 25 per cent by weight.
5. A negative electrode for use in an alkaline cell substantially as hereinbefore particularly described.
6. A process for the production of a negative electrode as claimed in claim 1 which comprises preparing a finely divided mixture of the metal conductive powder, the negative active material and solid potassium hydroxide or solid sodium hydroxide and then com-

pression molding said mixture.

7. A process as claimed in claim 6 in which the mixture is compression molded on a conductive support.

8. A process as claimed in claim 6 or 7 in which, after compression molding, the packing of the compressed mixture is between 45 and 80 per cent.

9. A process as claimed in claim 8 in which, after compression molding, the packing of the compressed mixture is between 60 and 80 per cent.

10. A process as claimed in any of claims 6 to 9 in which a pressure of 3 to 20 tons per square inch is used in the compression molding.

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