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Fo 13120 DL/EP

The present invention concerns a method of manufacturing an electrode for an electrochemical generator, particularly but not exclusively an alkaline accumulator.

Two methods are mainly known to manufacture an electrode in an alkaline accumulator.

The first method consists in directly preparing the active material in the appropriate granulate form and in introducing it into tubes or pockets made of perforated metal sheets and acting as current collectors.

For certain applications implying very rapid discharges, the electrodes obtained by this method do not present sufficient electrical qualities as they do not comprise a conducting network integral with the active material.

The second method (see for example DE-A-3 015 981) allows to avoid this drawback, because it consists in introducing active material into a metal sponge constituted by a sintered support. To this end, the support is first made from a thin band of sheet which may be perforated, or from a metal fabric coated with a very fine metal powder. Nickel, iron etc. may be used. The coated band is put into an furnace and the sintering takes place at an elevated temperature (of about 1000°C under inert or reducing gas atmosphere, such that the metal powder grains become solded as well to adjacent grains as to the band.

Alternatingly, the pre-heated powder-coated band can be introduced for some seconds into a furnace equipped with high frequency (300 to 600 kHz) or medium frequency (1 to 10 kHz)

generators.

The sintered sponge resulting therefrom (which gives good conduction features to the electrodes) is impregnated with appropriate metal salts according to the electrode type concerned: for example nitrates, chlorides or sulfates of nickel and of cadmium. These salts are chemically transformed and they precipitate in the sintered support in the form of nickel hydroxide, cadmium hydroxide and so on. It is then necessary to eliminate the detrimental residual salts by chemical or electrochemical methods. After all these operations, an electrode is obtained, which is composed of a sintered metal support, the active material in the discharged state being integrated in the pores. It is evident that for obtaining this result, it has been necessary to implement complicated and expensive equipments as well as great energy quantities.

Finally, another method for manufacturing a small electrode in the shape of a pastille for a button type nickel cadmium accumulator is known from the Japanese patent application JP-A-57-189 455.

A mixture of nickel powder and of active material is prepared, and the sintering of the metal powder by an induction at 200 kHz during one second is performed.

This method cannot be used, if long electrodes are to be manufactured, conceived for example to be wound up. In fact, it is imperative in this case to integrate a metallic current collector into the powder mixture, and it has then been observed that the electrodes obtained by the preceding method crumble after some hours in the presence of an electrolyte.

The present invention aims to avoid these drawbacks and to

propose an efficient method allowing to obtain electrodes having performances similar to those of existing electrodes.

According to the present invention, a method of manufacturing an electrode for an electrochemical generator, according to which an intimate mixture of conductive metal powder and an active material in granular form is realised and the sintering of said metal powder is carried out by submitting it to a variable magnetic field, is characterized in that a metal current collector is integrated into the powder mixture, that the unit passes through said variable magnetic field induced by current pulse trains, the frequency of said pulses being chosen between about 1 MHz and 10 MHz, the duration of a pulse train being longer than 0,05 seconds and the interval between two successive trains being at least equal to the duration of a pulse train, so as to ensure the sintering of said metal powder without altering the active material grains.

The structure of that current collector may be a sheet of extended metal, a metal fabric, constituting a frame, a grid or equivalent. For example, steel or nickel-steel may be used.

In order to promote close contact between the metal grains and the active material grains, it is advantageous to compress the mixture onto said current collector. Such compression may take place prior to the real sintering operation or it may take place during the sintering operation in the intervals between two pulse trains.

It is preferable to perform the sintering under an inert or reducing atmosphere; the sintering gas may include water vapour.

The present invention also provides an electrode obtained by the above defined method; the mixture may comprise (by weight) 10% to 90% metal powder and 90% to 10% active material.

Advantageously, 0,05% to 0,15% (by weight) of graphite may be added to the mixture. Its function is to reduce the unwanted metal oxides which may appear when the active material is being heated and which may cover the surface of its grains.

The sintered mixture may be cut into any size according to any desired geometry; alternately, it may be used directly as an electrode.

Other features and advantages of the invention will appear during the following description of an embodiment of a nickel-hydroxide electrode for a nickel-cadmium accumulator. This example is made to illustrate but not to restrict the invention.

Fig. 1 is a very diagrammatic view of a portion of an electrode according to the invention.

Fig. 2 is a diagram on an enlarged scale depicting the powder mixture of the electrode shown in fig. 1.

Fig. 3 is a very simplified diagram of a device for manufacturing the electrode of fig. 1.

Fig. 1 shows a diagram of a portion of a nickel-hydroxide electrode. It comprises a band of metal latticework 1 made of nickel or nickel-steel, covered on both sides by a mixture of nickel powder, nickel hydroxide powder and graphite in the proportion ranges specified above.

Fig. 2 shows the nickel grains 2, the nickel hydroxide grains 3 and the flakes of graphite 4. After having been compressed, the electrode 15 is disposed in an induction furnace as shown in fig. 3.

The furnace wall 10 is surrounded by an inductor 13 which produces an electric field at about 1 MHz. An inlet 11 and an outlet 12 are provided in the furnace wall 10 for circulating a light gas which may be reducing or neutral in character, for example hydrogen. The gas fills the furnace, expelling the air contained therein, and escapes via an overflow tube.

A varying magnetic field is applied for as short as possible a period compatible with the sintering of the grains of nickel without altering the grains of nickel hydroxide. Thus, pulse trains of a duration of 0,1 second separated by intervals of 10 seconds, are realised.

During the application of the field, the conductive bodies of the mixture (nickel and graphite powder) heat up, since eddy currents are induced therein. The intervals between pulse trains allow the energy released by sintering the nickel to be dissipated and thus avoid overheating of the nickel hydroxide grains.

A suitable degree of sintering is obtained after applying ten pulse trains of 0,1 second duration each.

In a variant implementation, the reducing gas contains water vapour. It has been observed that this improves the electrical efficiency of the nickel hydroxide.

Due to the method according to the invention, an electrode with its active material integrated in a sintered support can

be obtained directly. All the impregnation and chemical treatment operations are avoided.

Naturally, the method just described can be modified. For example, cooling could be improved by a flow of coolant gas derived from a cooling coil or other suitable means.

Clearly, the mixture can be compressed either by means of rollers or else by means of a press, and according to another variant of this method, compression steps may be inserted in between successive sintering and cooling steps.

Any other shape of the current collector may be used.

The invention is not restricted to an electrochemical generator of the alkaline accumulator type. By way of example, the active material can be chosen from the group consisting of the oxides of lead, iron, cadmium and zinc and the hydroxides of cadmium and nickel.

The metal powder may be chosen from the group consisting of nickel, lead, cadmium, iron, copper, silver and zinc.

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# CLAIMS

1. A method of manufacturing an electrode for an electrochemical generator, according to which an intimate mixture of conductive metall powder and an active material in granular form is realized and the sintering of said metal powder is carried out by submitting it to a variable magnetic field, characterized in that a metallic current collector is integrated into the powder mixture, that the unit passes through said variable magnetic field induced by current pulse trains, the frequency of said pulses being chosen between about 1 MHz and 10 MHz, the duration of a pulse train being longer than 0,05 seconds and the interval between two successive trains being at least equal to the duration of a pulse train, so as to ensure the sintering of said metal powder without altering the active material grains.
2. A manufacturing method according to claim 1, characterized in that the structure of said collector is chosen amongst a tape, a sheet of extended metal, a metal fabric, bars constituting a frame or a grid.
3. A method according to one of claims 1 and 2, characterized in that said mixture is compressed onto said collector.
4. A method according to claim 3, characterized in that said compression is performed between two pulse trains.
5. A method according to claim 1, characterized in that the sintering is carried out under inert or reducing atmosphere.
6. A method according to claim 5, characterized in that the sintering gas contains water vapour.



7. An electrode obtained by means of the method according to one of the preceding claims, characterized in that said mixture comprises by weight:

- 10 to 90% metal powder (2)
- 90 to 10% active material (3).

8. An electrode according to claim 7, characterized in that graphite (4) is added to said mixture in a weight proportion comprised between 0,05% and 15%.

9. An electrode according to claim 7, characterized in that said active material is chosen amongst the oxides of lead, iron, cadmium, zinc, and the hydroxides of cadmium and nickel, and that said metal powder is chosen amongst nickel, lead, cadmium, iron, copper, silver, zinc.

