

SPECIFICATION

Preparation of negative sintered foil electrodes for gas-tight Ni/Cd storage batteries or cells

The invention relates to the preparation of negative sintered foil electrodes for incorporation into gas-tight Ni/Cd storage batteries or cells (hereinafter referred to as batteries), the electrodes containing a discharge reserve.

In order to operate a gas-tight Ni/Cd storage battery safely without any danger of over-charging and polarity reversal, its electrodes must be such that after full charging and also after drawing the total useful electrical capacity any current that continues to flow will produce exclusively oxygen gas at one of the two electrodes, the oxygen being consumed by reduction at the other electrode. Since in general the positive electrode determines the useful capacity, the negative electrode may, if the battery is fully charged, not yet have reached its full charge capacity, but it must still contain a certain amount of chargeable mass, i.e. cadmium hydroxide, as charge reserve, which prevents the formation of hydrogen during further charging of the battery, which is tightly sealed.

Moreover, the negative electrode requires, on account of its comparatively greater charge dependence, a larger amount of charged negative mass than the charged positive mass, this difference being known as the discharge reserve.

The establishment of the negative discharge reserve was hitherto effected by a method known as "open formation", wherein the positive and negative electrodes were charged together in the storage battery, prior to sealing of the storage battery, until after the start of the formation of oxygen at the positive electrode, the negative electrode, which has a higher charge capacity, taking an additional amount of charge. After sealing the storage battery, when the battery is discharged until the useful capacity, which is governed by the positive electrode, has been exhausted, a charge excess of unoxidised cadmium remains on the negative electrode as a discharge reserve. This discharge reserve should remain constant in amount during further use of the storage battery, apart from unavoidable ageing effects.

This open formation has disadvantages since the batteries cannot be assembled ready for use and sealed in one operation. Extraction devices have to be used to remove the alkaline mist that is unavoidably formed during overcharging.

It is known, e.g. from U.S. Patent Specification 3,297,433, to prepare active cadmium powder chemically in a wet manner by reducing a cadmium compound with aluminium or zinc and to compact the resultant powder into

dischargeable cadmium electrodes.

According to German Offenlegungsschrift 2,361,905, another chemical preparation of the active mass consists of thermally decomposing a mixture of cadmium and nickel formates in a stream of hydrogen, thereby obtaining a dischargeable mass which likewise contains metallic cadmium.

In all these cases the chemical preparation results in the complete conversion of a cadmium compound to cadmium metal. Since this cadmium metal is active, it may in principle be added to an existing active mass as a defined discharge reserve.

In practice however the establishment of the discharge reserve is beset by difficulties since an oxidation-free drying of the active cadmium cannot always be effected satisfactorily and the active material used as the basic mass is itself subject to considerable tolerance problems as regards the electrochemical current efficiency.

An object of the invention is to provide a method for the preparation of negative sintered foil electrodes for gas-tight Ni/Cd storage batteries, which method will permit the establishment of a discharge reserve in an industrially simple and controllable manner.

In accordance with the present invention, there is provided a method for preparing a negative sintered foil electrode for incorporation into a gas-tight Ni/Cd storage battery, the electrode containing cadmium hydroxide as active mass and a discharge reserve constituted by metallic cadmium, wherein the cadmium is produced by a partial chemical reduction of the cadmium hydroxide.

Preferably, the sintered foil electrode is treated, by immersion or spraying, with a solution of a reducing agent in an inorganic or organic solvent to subject the electrode to said partial chemical reduction. Particularly suitable for the reduction treatment is a negative sintered foil which does not have a wide range of variation as regards capacity rating and dimensions. With such a foil, the partial chemical reduction can also be regulated and monitored as necessary in accordance with specific empirical values. Theoretically, the reducing agent used must have an appropriate reduction equivalent in order to obtain the desired discharge reserve. However, a partial self-decomposition, which reduces the range of application, must be taken into account. This self-decomposition rate is dependent on the concentration and temperature of the solution.

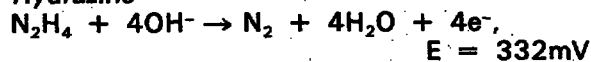
In principle, all those substances that are readily soluble in water or inert organic solvents and are converted to their oxidation products at a potential that is lower than the Cd/Cd^{++} redoxpotential, are suitable as reducing agents for use in the method of the invention. Such substances also include nascent hydrogen, since the potential of the normal hydrogen electrode in alkaline solution

pH) is 20 mV more negative than the potential of the reaction $\text{Cd}(\text{OH})_2 + 2\text{e}^- \rightleftharpoons \text{Cd} + 2\text{OH}^-$.

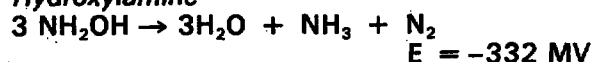
Reducing agents that can be oxidised at a standard potential lower than the normal hydrogen electrode and can thus be easily removed, in most cases forming gaseous reaction products, include those specified below together with their decomposition reactions.

The potentials E refer to N_2 in the same solution.

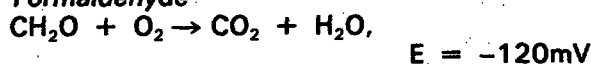
Hydrazine



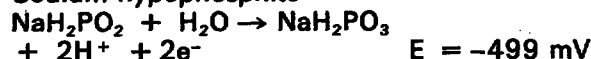
Hydroxylamine



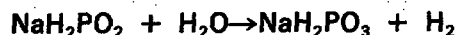
Formaldehyde



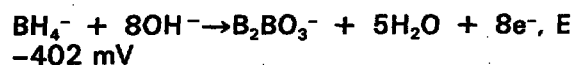
Sodium hypophosphite



Nascent hydrogen is also involved as an additional reducing agent when the above reducing agents are used, and is for example formed in the self-decomposition of sodium hypophosphite according to the equation

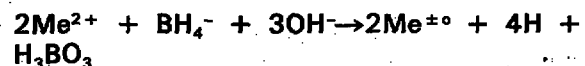


The partial chemical reduction of sintered foil electrodes is carried out particularly advantageously according to the invention using an alkali boronate. To this end, the very low normal potential $E_0 = -1.23\text{V}$ (alkaline solution) of the reaction



meets an essential prerequisite. The reducing effect is however also present in neutral, aqueous media, and is greater the more dilute the solution.

Since the atomic hydrogen produced at the metal Me (Cd or Ni) according to the equation



recombines more quickly to form H_2 on Ni than on Cd , on account of the lower deposition overvoltage, the presence of a fairly large amount of Ni in addition to Cd in the sintered foils means that part of the alkali boronate employed for the reduction of the $\text{Cd}(\text{OH})_2$ is not available. This is however no disadvantage since only a partial reduction of the cadmium hydroxide is intended and the metallic sin-

tered structure is very largely covered by the incorporated active mass.

The reduction treatment by immersion or spraying according to the invention can be very easily incorporated into continuous manufacture of the sintered foil electrodes by drying a sintered strip, impregnated with active mass (cadmium hydroxide), after it has passed through a precipitation bath and then passing the strip through a further bath containing the reducing solution. The length of this bath is such that for a given rate of movement the residence time of the strip is sufficient to be able to regulate the reducing effect via the bath concentration and temperature.

During the immersion or spray treatment a reduced pressure is produced in order to ensure that all the pores of the strip are completely filled with the reducing liquid. To this end, the bath is in the form of a closed chamber and simply has at its ends slits for the incoming and outgoing strip, which can be sealed against the external atmosphere e.g. by means of rubber sleeves.

The above concentration is preferably chosen so that the amount of solution filling the pore volume is theoretically sufficient to react completely with the cadmium hydroxide. In this way it is of course not possible to convert all the impregnated cadmium hydroxide to metallic cadmium, only a partial conversion into metallic cadmium being possible.

The partially reduced sintered strip is washed with the pure solvent which is the same as the solvent of the reducing solution. In the simplest case, the solvent is completely desalinated water. Non-aqueous solvents are however preferred since, on account of their volatility, they can be removed with less expenditure of heat in the subsequent drying, examples being trichloroethylene (B.P. = 87°C) and isopropyl alcohol (B.P. = 82.3°C).

In the drying stage the dischargeable cadmium formed is permanently fixed and at the same time preserved by producing an extremely thin oxide covering layer on the cadmium, for example by means of an accurately measured amount of oxygen, which layer protects the active material against further oxidation during assembly of the battery. By drying under defined conditions as regards duration, temperature and moisture content of the drying atmosphere as well as its gaseous composition, it is possible according to the method of the invention to establish accurately a desired discharge reserve.

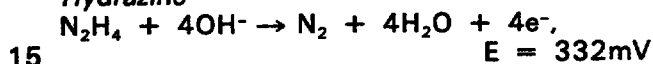
CLAIMS

1. A method for preparing a negative sintered foil electrode for incorporation into a gas-tight Ni/Cd storage battery, the electrode containing cadmium hydroxide as active mass and a discharge reserve constituted by metallic cadmium, wherein the cadmium is pro-

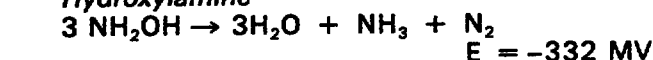
pH) is 20 mV more negative than the potential of the reaction $\text{Cd}(\text{OH})_2 + 2\text{e}^- \rightleftharpoons \text{Cd} + 2\text{OH}^-$.

- 5 Reducing agents that can be oxidised at a standard potential lower than the normal hydrogen electrode and can thus be easily removed, in most cases forming gaseous reaction products, include those specified below together with their decomposition reactions.
- 10 The potentials E refer to NH_2 in the same solution.

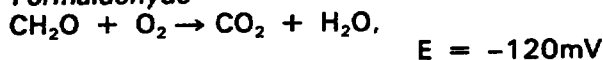
Hydrazine



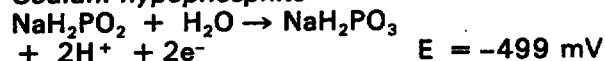
Hydroxylamine



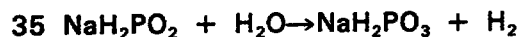
Formaldehyde



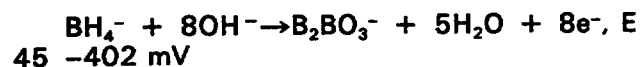
25 *Sodium hypophosphite*



- 30 Nascent hydrogen is also involved as an additional reducing agent when the above reducing agents are used, and is for example formed in the self-decomposition of sodium hypophosphite according to the equation

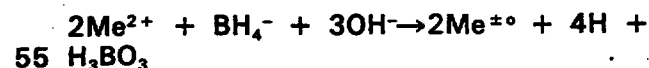


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- meets an essential prerequisite. The reducing effect is however also present in neutral, aqueous media, and is greater the more dilute the solution.
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Since the atomic hydrogen produced at the metal Me (Cd or Ni) according to the equation



- recombines more quickly to form H_2 on Ni than on Cd, on account of the lower deposition overvoltage, the presence of a fairly large amount of Ni in addition to Cd in the sintered foils means that part of the alkali boronate employed for the reduction of the $\text{Cd}(\text{OH})_2$ is not available. This is however no disadvantage since only a partial reduction of the cadmium
- 60
- 65 hydroxide is intended and the metallic sin-

tered structure is very largely covered by the incorporated active mass.

- The reduction treatment by immersion or spraying according to the invention can be very easily incorporated into continuous manufacture of the sintered foil electrodes by drying a sintered strip, impregnated with active mass (cadmium hydroxide), after it has passed through a precipitation bath and then passing the strip through a further bath containing the reducing solution. The length of this bath is such that for a given rate of movement the residence time of the strip is sufficient to be able to regulate the reducing effect via the bath concentration and temperature.
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- During the immersion or spray treatment a reduced pressure is produced in order to ensure that all the pores of the strip are completely filled with the reducing liquid. To this end, the bath is in the form of a closed chamber and simply has at its ends slits for the incoming and outgoing strip, which can be sealed against the external atmosphere e.g. by means of rubber sleeves.
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- The above concentration is preferably chosen so that the amount of solution filling the pore volume is theoretically sufficient to react completely with the cadmium hydroxide. In this way it is of course not possible to convert all the impregnated cadmium hydroxide to metallic cadmium, only a partial conversion into metallic cadmium being possible.
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- The partially reduced sintered strip is washed with the pure solvent which is the same as the solvent of the reducing solution. In the simplest case, the solvent is completely desalinated water. Non-aqueous solvents are however preferred since, on account of their volatility, they can be removed with less expenditure of heat in the subsequent drying, examples being trichloroethylene (B.P. = 87°C) and isopropyl alcohol (B.P. = 82.3°C).
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- In the drying stage the dischargeable cadmium formed is permanently fixed and at the same time preserved by producing an extremely thin oxide covering layer on the cadmium, for example by means of an accurately measured amount of oxygen, which layer protects the active material against further oxidation during assembly of the battery. By drying under defined conditions as regards duration, temperature and moisture content of the drying atmosphere as well as its gaseous composition, it is possible according to the method of the invention to establish accurately a desired discharge reserve.
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CLAIMS

- 125 1. A method for preparing a negative sintered foil electrode for incorporation into a gas-tight Ni/Cd storage battery, the electrode containing cadmium hydroxide as active mass and a discharge reserve constituted by metallic cadmium, wherein the cadmium is pro-
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duced by a partial chemical reduction of the cadmium hydroxide.

2. A method according to claim 1, wherein the electrode is treated with a solution of a reducing agent to subject the electrode to said partial chemical radiation.
3. A method according to claim 2, wherein the reducing agent is an alkali metal boronate.
- 10 4. A method according to claim 2 or 3, wherein after the electrode has been subjected to said partial chemical reduction, the sintered foil electrode is washed and then dried.
- 15 5. A gas-tight Ni/Cd storage battery comprising a negative sintered foil electrode prepared by a method according to any preceding claim.

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