

The invention relates to a gastight alkaline storage battery for storing electrical energy, having a positive electrode essentially comprising nickel hydroxide as active material, a negative electrode and a separator disposed between the electrodes in a closed casing.

In the field of gastight alkaline storage batteries, the recent technical development has concentrated mainly on the improvement of the electrode construction and on measures for promoting the gas consumption in order to make the gastight function still more reliable. This has now given rise to a wide variety of types among the electrodes, whose actual, electrochemically active material is nevertheless still composed of the conventional substances, namely nickel hydroxide in the case of the positive electrode and cadmium hydroxide, iron hydroxide, zinc hydroxide or cobalt hydroxide in the case of the negative electrode. Most of the commercially available gastight alkaline storage batteries are accordingly also based on the conventional alkaline battery systems, to which the hydrogen-storage systems must also be added.

Among the electrode types in gastight alkaline storage batteries, the sintered type is particularly common. In gastight wound cells, both electrode polarities belong to this type. In button cells, both electrode polarities are usually present as pressed-powder tablets mounted in a woven nickel-wire basket. In the case of other pressed electrodes, the active mass is pressed onto strip-type metal support gauzes.

A special type of negative electrode is the so-called electrodeposit electrode, which is obtained by cathodic metal deposition from cadmium salt solutions (German Offenlegungsschrift 28 22 821).

According to a still very recent development, a metal-foam matrix whose pore systems the active material takes up in pasty form [sic] forms the support and collector both for a positive (US Patent Specification 4 251 603) and for a negative electrode (European Patent

Specification 185 830).

Examples of various combinations of electrode types in gastight alkaline storage batteries can also be found in the patent literature. Thus, in a known nickel/hydrogen battery in accordance with European Patent Specification 284 333, both electrode species are present in the form of the metal-foam matrix electrodes mentioned. German Offenlegungsschrift 34 16 817 suggests the combination of a cadmium electrode of the electrode-deposited type with a positive, charged, pressed-powder electrode. Published European Specification 28 072 discloses the combination of a positive pressed electrode with negative sintered electrodes.

The object of the invention is to provide a gastight alkaline storage battery which is fitted with electrodes which supplement one another ideally in relation to energy storage capability and mechanical robustness and which can be produced by means of an inexpensive manufacturing process which is as automatable as possible.

The object is achieved, according to the invention, by a gastight alkaline storage battery as specified in Patent Claim 1.

In accordance therewith, both the positive and the negative electrodes of the storage battery according to the invention belong to the rolled-electrode type. This electrode type has gained a certain dissemination only very recently as a result of advances in rolling technology. In this connection, because of their mechanical strength and flexibility, rolled electrodes can readily be used in wound cells. Their production, in which a mixture essentially containing the active material and a powdered plastics binder is rolled onto a metallic support material, may preferably be carried out by belt conveyance. The preparation of the rolling mixture itself by dry mixing of the weighed, exclusively powdered components is problem-free and affords an efficient manufacturing operation.

Positive and negative rolled electrodes can be

combined particularly advantageously in a nickel/hydrogen storage battery.

Its positive electrode is based on an Ni gauze, a nickel-plated perforated strip, an Ni expanded metal or a nickel-fibre matrix as support material. The rolling mixture applied thereto is composed of a dry mixture comprising nickel hydroxide as active material and nickel-metal powder, according to the invention, and at least one further metal powder from the group comprising Co, Cu, Fe, Mo, W, Mn, Cr, Ti and Zn as conducting agent and of a plastics binder. In addition, an addition of 5 to 12% by weight of graphite and/or soot to the dry mixture is possible. According to the invention, the amount [sic] of metal powder should enter into the dry mixture in an amount of 5 to 25% by weight and the nickel hydroxide in an amount of 75 to 90% by weight (i.e. the totality of all the mixture components with the exception of the binder). The nickel powder alone should be in a weight ratio to the amount of the other metal powders of 1:1 to 1:20. According to the invention, a particularly advantageous dry mixture contains, in addition to nickel hydroxide, also smaller amounts of further hydroxides, at least one, however, from the series comprising $\text{Co}(\text{OH})_2$, $\text{Cd}(\text{OH})_2$, $\text{Zn}(\text{OH})_2$, $\text{Al}(\text{OH})_3$, $\text{Mg}(\text{OH})_2$, iron hydroxides and Mn hydroxides. These additives improve the continuous load carrying capacity of the electrode when operated cyclically and ensure a good charging efficiency. Instead of being included as separate additives in the dry mixture, they may also already be included in the nickel hydroxide provided they are produced as products of a simultaneous precipitation from a solution of corresponding metal salts together with the nickel hydroxide. In both cases, the proportion of foreign hydroxides in the nickel hydroxide present in the dry mixture should be 12 to 15% by weight.

The nickel hydroxide, optionally containing inclusions of foreign hydroxides, is preferably based on spherically shaped particles having particle diameters of between 3 and 300 μm . Separately added foreign hydroxides

may have particle sizes of between 3 and 70 μm .

The particles of the metal powders are preferably also spherically shaped and have particle sizes of between 0.1 and 50 μm .

5 After all the components of the dry mixture have been thoroughly premixed, the plastics binder, composed of polyethylene, polypropylene, a polyester or polyvinyl alcohol, is finally added to the dry mixture in an amount of 2 to 10% by weight and the entire mixture is then
10 finally ground to produce the finished rolling mixture. All the mixing operations are advantageously carried out, in mixing devices having intensive comminution effect, for example in knife mills running at high speed. In particular, a very uniform distribution of the binder
15 materials is thereby achieved, said materials forming thin filaments which permeate the entire powder bed in a network-like fashion. Said rolling mixture is then prerolled at high pressure in a calender to form a laminate 0.5 to 0.8 mm thick and then rolled onto the
20 support material.

 In the case of the preferred storage battery according to the invention, namely of the nickel/hydrogen storage battery or metal hydride storage battery, a dry powder mixture also essentially forms, in addition to a
25 small amount of powdered plastics material, the rolling mixture for the negative electrode. Here the active material, which is also the main constituent of this dry powder mixture, is a metal powder capable of electrochemically absorbing and storing hydrogen or a metal
30 alloy in powder form. In the case of these materials, the electrochemical energy storage consists in the subsurface discharge of a proton from the electrolyte to form a neutral hydrogen atom and in the subsequent storage of said hydrogen atom in the interior of the
35 metallic solid.

 The active material is preferably supplemented by an additional amount of the metal or of the metal alloy in hydride form and consequently has a discharge reserve.

 For the purpose of improving the electrical

conductivity, metal powders composed of nickel, cobalt or copper, optionally also graphite and conductive soot are furthermore added to the active material. Finally, in addition to the active material, oxygen-consuming agents in the form of a carbon-containing mixture are provided. The components of the latter are conductive soot, active carbon and polytetrafluoroethylene and are approximately in a weight ratio of 3 to 20% by weight, preferably 7.5% by weight conductive soot, 50 to 80% by weight, preferably 75% by weight active carbon and 10 to 30% by weight, preferably 17.5% by weight polytetrafluoroethylene.

Said mixture can either be rolled onto the finished electrode in a thin layer or already be added to said electrode as a constituent of the dry powder mixture.

Suitable as binders for the negative electrode are plastics from the series comprising polyethylene, polypropylene, polytetrafluoroethylene, polyvinylidene fluoride, polyvinylidene carbonate, polyvinyl alcohol, polyisobutylene and polyacrylonitrile.

In this case, too, it is advisable to mix all the constituents of the dry powder mixture thoroughly first and then to add the binder to the latter separately.

The finished rolling mixture is then composed of 60 to 80% by weight of metal or metal alloy capable of storing H_2 , 5 to 20% by weight of the same active material in hydride form, 10 to 35% by weight of metal powder or 1 to 6% by weight of soot and graphite as conductive agent, 1 to 6% by weight of binder and 1 to 8% by weight of carbon-containing mixture for the oxygen consumption.

The negative rolled electrode is consequently also preferably produced by dry rolling onto a support material, it again being advantageous to carry out [sic] the rolling mixture to form a laminate having a thickness of 0.3 to 0.8 mm before application to a fine-mesh metal gauze or expanded metal.

The support material is nickel, iron, copper or silver. For cost-saving reasons, a silver-plated or

nickel-plated iron or copper material may also be used instead of the solid nickel or silver gauze.

A cobalt plating of the support by electroless treatment or electrodepositing treatment in a bath liquid containing cobalt salts prior to the rolling-on process has proved advantageous both in the case of the positive and in the case of the negative rolled electrode since this increases the current carrying capacity. The weight of the cobalt coating relative to the support may be 1 to 25%.

The figure shows diagrammatically the production cycle of rolled electrodes according to the invention, the working steps of which cycle are in principle the same for positive and negative electrodes.

In accordance therewith, the rolling mixture is first prepared and is composed in each case of the active material 1, active additives 2 (metal hydroxides in addition to $\text{Ni}(\text{OH})_2$ in the case of a positive electrode, H_2 -storage alloy in hydride form in the case of a negative electrode), metallic additives 3, carbon-containing material 4 (O_2 -consuming agents in the case of the negative electrode, optionally conductive soot or graphite in the case of the positive electrode) and binder 5. The components corresponding to items 1 to 4 are expediently premixed separately and the resultant dry powder mixture is combined with the binder 5 in the high-speed dry mixer 6. In the calender 7, the finished rolling mixture is then prerolled to form a laminate or strip 8 and the latter is rolled onto a gauze-like support strip 10 in the calender 9.

An advantageous aftertreatment of the positive rolled electrode (not shown) may consist in exposing it to a solution of nickel or cobalt salts and then immersing it with pores still filled in an NaOH or KOH solution, as a result of which a hydroxidic film is deposited on the mass particles of the electrode and contributes to an improvement in the electrical characteristics.

A similar success is provided by an electrodepositing aftertreatment which is such that the

electrode material is immersed in a solution containing nickel and cobalt salts and that metallic nickel and cobalt are deposited. The amount of the material deposited in total is between 3 and 25% of the electrode weight.

As a result of immersion treatment in 5 to 15%-strength dispersions composed of polyethylene, polytetrafluoroethylene or acrylic acid compounds, negative rolled electrodes can acquire a plastics coating which gives them a better mechanical robustness.

Gastight alkaline cells can be constructed particularly advantageously from the positive and negative electrode material produced by rolling as described. Depending on electrode type, the electrode thicknesses are adjusted during the production so that the ratio per unit area of the total capacity of the negative electrode to the total capacity of the positive electrodes is between 1.2 and 2. Both electrodes are separated from one another in the discharged state by a nonwoven material composed of PE, PA or PP fibres and are spirally wound. An aqueous 5 to 8 N KOH solution containing 0.3 to 2 N LiOH additives is used as electrolyte. The cells are commissioned by charging with a 10-hour rated current and discharging with a 5-hour current after they have undergone an activation as a result of a high-temperature ageing at 45°C to 80°C for a period of 1 to 14 days. After completing two such cycles, the cells have reached their full electrical load-carrying capability.

Patent Claims

[lacuna] Gastight alkaline storage battery for storing electrical energy, having a positive electrode essentially comprising nickel hydroxide as active material, a negative electrode and a separator disposed between the electrodes in a closed casing, characterized in that both the positive electrode and the negative electrode are formed by rolling a dry powder mixture containing the respective active material and a plastics binder onto a metallic support material.

2. Gastight alkaline storage battery according to Claim 1, characterized in that it is a nickel/hydrogen storage battery.

3. Gastight alkaline storage battery according to Claim 2, characterized in that the rolling mixture for the positive electrode is formed by mixing a powdered plastics material with a dry mixture of nickel hydroxide, nickel-metal powder and at least one further metal powder from the group comprising the metals Co, Cu, Fe, Mo, W, Mn, Cr, Ti and Zn.

4. Gastight alkaline storage battery according to Claim 2, characterized in that the rolling mixture for the negative electrode is formed by mixing a powdered plastics material with a dry powder mixture essentially composed of a hydrogen-storing metal or a hydrogen-storage alloy.

5. Gastight alkaline storage battery according to Claim 3, characterized in that the dry mixture additionally contains one or more hydroxides from the group comprising Co(OH)_2 , Cd(OH)_2 , Zn(OH)_2 , Mg(OH)_2 , Al(OH)_3 , iron hydroxides and Mn hydroxides.

6. Gastight alkaline storage battery according to Claim 3 or 5, characterized in that the proportion by weight of the nickel hydroxide in the dry mixture is 75 to 90% and the proportion by weight of the metallic components 5 to 25%.

7. Gastight alkaline storage battery according to one of Claims 3, 5 or 6, characterized in that the



plastics binder is polyethylene, polypropylene, a polyester, polyvinyl alcohol or polytetrafluoroethylene.

8. Gastight alkaline storage battery according to Claim 4, characterized in that the dry powder mixture
5 contains an additional amount of the hydrogen-storing metal in hydride form.

9. Gastight alkaline storage battery according to Claim 4 or 8, characterized in that the dry powder mixture contains one or more metal powders from the group
10 comprising Ni, Co, Cu as conductive agent.

10. Gastight alkaline storage battery according to one of Claims 4, 8 or 9, characterized in that a mixed mass comprising conductive soot, active carbon and polytetrafluoroethylene is added to the dry powder
15 mixture as oxygen-consuming agent.

