

This Sheet Has Been Replaced

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## Patent Claims

1. Gastightly sealed alkaline storage battery in the form of a button cell having positive and negative electrodes disposed in the cell casing and separated by a separator, characterized in that the mass mixture of the positive mass electrodes produced by dry pressing contains a nickel hydroxide having spherical particle shape and high solid-state density as active material.
2. Alkaline storage battery according to Claim 1, characterized in that it is a nickel/hydride storage battery.
3. Alkaline storage battery according to Claim 1 or 2, characterized in that the pycnometric density of the spherical nickel hydroxide is  $3.3 \text{ g/cm}^3$  to  $3.9 \text{ g/cm}^3$  and the size of the majority of its particles is in the range 5 to  $20 \mu\text{m}$ .
4. Alkaline storage battery according to one of Claims 1 to 3, characterized in that in addition to metallic nickel and cobalt as well as cobalt hydroxide, a powdered plastics binder is added to the active material of the positive mass electrodes.
5. Alkaline storage battery according to one of Claims 1 to 4, characterized in that the mass mixture for the positive electrode is pregranulated before dry pressing into tablets.
6. Alkaline storage battery according to Claim 5, characterized in that the granulated material has a particle size between  $100 \mu\text{m}$  and  $1000 \mu\text{m}$ .
7. Alkaline storage battery according to one of Claims 2 to 6, characterized in that the material of the negative electrode is a hydrogen storage alloy of the type  $\text{MmNi}$ , containing a misch-metal.
8. Alkaline storage battery according to one of

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- 2 -

Claims 1 to 7, characterized in that a microporous material whose pore diameter is less than the smallest particle size of the spherical nickel hydroxide is provided for the separator.



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A standard 1D barcode with vertical black bars of varying widths on a white background, positioned below the text 'This Sheet Has Been Replaced'.



**Gastightly sealed alkaline storage battery  
in the form of a button cell**

The invention relates to a gastightly sealed alkaline storage battery in the form of a button cell  
5 having positive and negative electrodes disposed in the cell casing and separated by a separator.

The casing of a button cell is formed by a basin-shaped lower section and a lid of nickel-plated sheet steel. The lower section receives the positive  
10 electrode, then follows an alkaline-resistant plastics material as separator; the negative electrode is situated on the latter. The electrodes and the separator are impregnated with electrolyte. Situated between negative  
15 electrode and the lid is a spring which produces an intimate contact of the electrodes with the cell container. The cell basin and the lid are insulated from one another by a plastics ring. A perfectly sealing closure is achieved by flanging over and squeezing the rim of the basin.

20 Apart from their special construction, which distinguishes them from cylindrical cells, button cells are always designed for low capacities of up to about 1 Ah. Owing to the small overall size, they find versatile use in the electronics industry.

25 The electrodes of button cells are typically mass electrodes. These are always based on a dry mixture of the respective active material - nickel hydroxide in the case of the positive electrode - optionally with additions of a conducting agent and a binder. Pressed  
30 powder tablets are produced from the dry mixture and, finally, as is known from button cells of the Ni/Cd type, these are pressed into a small basket of nickel wire gauze for the purpose of reinforcing the compact and improved current collection.

35 Whereas the progressive miniaturization in the case of the button cells is understandably also imposing higher requirements on the electrochemical storage capacity per unit volume, the Ni/Cd and Ni/metal hydride



button cells currently available are coming up against a limit to their possibilities in relation to the volumetric energy density. This is due to the fact that, because of its particle size and particle distribution, the nickel hydroxide used permits only a mass utilization of about 80% of the theoretical value, namely approximately 230 mAh/g compared with 289 mAh/g. Correspondingly, the volumetric utilization based on the electrode volume has only values of approximately 300 mAh/cm<sup>3</sup>.

The nickel hydroxide powder at present used in button cells is obtained from a precipitation and drying process as an initially lumpy material which yields a powder having a particle size distribution of 30 to 300  $\mu$ m after subsequent grinding.

Since the production of positive button-cell electrodes requires, in addition to nickel hydroxide as the actual active electrode mass, further additives whose mean particle size of 1 to 5  $\mu$ m is markedly below that of the nickel hydroxide particles, a uniform distribution of the density of all the components as a result of mixing and subsequent compacting by pressing is difficult.

US Patent Specifications 4,844,999 and 4,985,318 disclose a nickel hydroxide powder to be used for paste electrodes, which powder is said to have a total pore volume of only 0.05 ml/g, the pore radii of the powder being between 15 and 30 Å. A comparatively high density and fine division of this known material can be inferred from these data and from its specific surface of 15 to 30 m<sup>2</sup>/g.

However, it is also in accordance with experience that an increase in the mass utilization can be achieved by further postgrinding of a conventional nickel hydroxide powder to particle sizes of < 20  $\mu$ m by then distributing the powders admixed for the purpose of electron collection more finely and more uniformly so that the electronic binding of the Ni(OH)<sub>2</sub> mass particles is enhanced and, additionally, those regions in the



electrode are opened up which were otherwise not accessible to the electron transfer. At the same time, however, other disadvantages have to be accepted.

5 The object of the invention is to provide an alkaline button cell, in particular of the Ni/hydride system, which has a markedly improved storage capacity compared with currently commercially available button cells of the same construction.

10 According to the invention, this object is achieved with a nickel hydroxide powder which has spherical particle shape and high solid-state density and which is pressed in the dry state and forms the active material of the positive electrode.

15 The pycnometric density of the nickel hydroxide powder of the invention is preferably above  $3.3 \text{ g/cm}^3$ , with an upper limit of  $3.9 \text{ g/cm}^3$ . Most of the particle sizes are distributed over the range 5 to 20  $\mu\text{m}$ , in the most favourable case over the range 10  $\mu\text{m}$  to 15  $\mu\text{m}$ . They consequently achieve virtually the same order of  
20 magnitude of the particle sizes of the additives already mentioned, which are 1 to 5  $\mu\text{m}$ . As a result, when mixed with the latter, a more homogeneous distribution and better space utilization is achieved.

Suitable as negative electrode materials for the  
25 Ni/hydride button cells preferred according to the invention are, in particular, hydrogen storage alloys, including those of the  $\text{LaNi}_3$  type or  $\text{TiNi}$  type. Preferred are alloys of the  $\text{LaNi}_3$  type in which lanthanum and/or other rare-earth elements form the misch-metal component  
30 of  $\text{MmNi}_3$  alloys. An exemplary alloy has the composition  $\text{MmNi}_{4.3-x}\text{Co}_x\text{Mn}_{0.3}\text{Al}_{0.4}$ , where  $0.2 < x < 0.7$ .

Typical mass mixtures for the positive electrode contain, in addition to nickel hydroxide, metallic nickel and cobalt, graphite and cobalt oxide. These additives  
35 predominantly act as conducting material; the cobalt oxide additionally provides for an increase in the oxygen overvoltage at the positive electrode and consequently for an increase in the charging efficiency.



In order to improve the mechanical strength when the dry mass is pressed, a powdered plastics binder, for example polytetrafluoroethylene (PTFE), polyethylene (PE), polypropylene (PP) or polyvinylidene fluoride (PVDF) is advantageously added in addition.

A typical mass mixture is composed, for example, of:

- 3 to 10% by weight of CoO
- 2 to 10% by weight of Co<sub>met.</sub>
- 20 to 50% by weight of Ni<sub>met.</sub>
- 0.5 to 3% by weight of plastics binder
- Remainder to 100% by weight of Ni(OH)<sub>2</sub>

The range of variation of the Ni(OH)<sub>2</sub> component ranges approximately from 40% by weight to 70% by weight.

As a result of a nickel hydroxide having spherical particle shape and simultaneously high solid-state density (preferably, > 3.5 g/cm<sup>3</sup>) it is possible, according to the invention, to achieve a high packing density owing to the uniform and smooth particle surfaces and owing to optimum particle size distribution.

In view of the processability of the masses, it is particularly advantageous to granulate the abovementioned mass mixtures before dry pressing into tablets. This produces mass conglomerates which have the particle size 100 µm to 1000 µm and which can be excellently dispensed because of their flowability. In addition, the larger particles prevent mass leaking as slurry from the small nickel-gauze basket. The danger of penetration of the separator is also reduced.

Similar success cannot be achieved with a commercial nickel hydroxide powder having the particle size 50 to 300 µm even if the latter is postground to a particle fineness of approximately 20 µm because the particles of the postground product still have irregular surfaces with the result that they resist an optimum space filling during compacting. The success of the use



of a positive mass postground from coarse-grained standard material for electrodes having high density and high capacity per unit volume consequently remains limited.

5           It is true that a certain increase in the mass utilization is possible as a result of said postgrinding of the standard nickel hydroxide powder; the spacing between the electrochemically active parts and the metallic conducting matrix also becomes smaller and the  
10   load-carrying capacity consequently becomes better during the production of the electrode masses. In the case of cells containing such a nickel hydroxide powder with a particle spectrum from 50 to 300  $\mu\text{m}$ , however, an irreversible decline in capacity sets in if they are  
15   stored under short-circuit conditions for a prolonged period, particularly at high temperatures. The capacity loss is absent only in the case of the use of nickel hydroxide powder having particle sizes  $< 20 \mu\text{m}$ .

          In conflict with the advantages of finely ground  
20   standard nickel hydroxide, however, is the danger that, during the operation of the cell, in particular during cyclical charge/discharge treatment and during persistent overcharging, individual mass particles detach themselves from the positive electrode and in this way slowly build  
25   up a short-circuit connection to the negative electrode. An approximately 0.2 mm thick, open-pore separator composed of a fibrous nonwoven material and having a pore size of approximately 100 to 300  $\mu\text{m}$ , such as is at present normally used in button cells, is incapable of  
30   preventing this migration of the mass particles, with the result that failure of the cell occurs.

          Owing to their fineness, the spherical particles of the nickel hydroxide used according to the invention are no more prevented by conventional separators from  
35   penetrating them than the postground standard material. In both cases, an effective remedy has proved to be a microporous separator material in the form of PE or PP membranes whose open pores have a smaller diameter than



the particle sizes which are between 5 and 20  $\mu\text{m}$ . The positive nickel hydroxide electrodes composed of finely divided material are therefore preferably used in conjunction with a short-circuit-proof microporous separator. At the same time, owing to its better space utilization, the combination of such a separator with the finely divided spherical  $\text{Ni}(\text{OH})_2$  is substantially more advantageous than the corresponding combination with a postground standard material.

The advantageous properties of a button cell storage battery having positive electrodes composed of spherical nickel hydroxide powder are elucidated with reference to some figures.

Figure 1 shows an Ni/hydride storage battery in accordance with the invention in section.

Figure 2a shows diagrammatically a standard production-type nickel hydroxide powder and

Figure 2b shows a nickel hydroxide powder having spherical particles.

Figure 3 shows a particle-size distribution of nickel hydroxide powder having spherical particles.

Figure 4 shows specific volumetric capacities of pressed powder electrodes composed of nickel hydroxide with spherical particles and of conventional nickel hydroxide.

According to Figure 1, the conventionally constructed button storage battery 1 comprises the basin-shaped lower section 2 containing the positive electrode 3 with nickel hydroxide of spherical particle shape, the lid section 4 which, in addition to a contact spring 6, receives the negative electrode 5 composed of a pressed alloy powder having hydrogen storage capacity, a sealing ring 7 and a separator 8.

Figures 2a and 2b reveal the influence of the morphology of the nickel hydroxide particles on the space filling of the positive pressed powder tablet, the figures showing the subregion Z of the positive electrode of Figure 1 on a considerably enlarged scale.



Because of the irregular shape of the particles in the nickel hydroxide normally used (Figure 2a), a dead volume remains in the positive electrode 3 after pressing.

5 In contrast, the uniform and smooth shape of the spherical particle surfaces, combined with an optimally adjusted particle-size distribution, favours a high packing density (Figure 2b). As a result of the use of spherical nickel hydroxide particles, the electrode  
10 volume is therefore substantially better utilized than is possible with an  $\text{Ni}(\text{OH})_2$  material having irregular particle surface.

In the volume distribution diagram according to Figure 3, the cumulative curve 1 shows the breakdown of  
15 the total volume of the spherical  $\text{Ni}(\text{OH})_2$  powder (cumulative distribution Q3) as a function of particle size  $x$  [ $\mu\text{m}$ ]. The fraction of the total volume which is occupied by particles which are equal to this size or smaller is deduced from the curve for each particle size  
20  $x$  selected. Thus, it can also be seen that the spherical powder as a whole is composed only of particles whose size does not exceed 30  $\mu\text{m}$ .

The curve 2, derived from the cumulative curve 1, of the particle-size distribution has a maximum in the  
25 range 10 to 20  $\mu\text{m}$  and has a width at half maximum of likewise approximately 10 to 20  $\mu\text{m}$ . This signifies a frequency maximum of the spherical particles within this narrow size spectrum. Substantial requirements for an optimum packing density, i.e. also for an optimum space  
30 utilization, therefore exist.

The extremely favourable volumetric capacity of a button-cell electrode used according to the invention and composed of spherical nickel hydroxide powder compared with a conventional pressed powder electrode is  
35 revealed by Figure 4. In the latter, the specific capacities  $K_v$  [ $\text{mAh}/\text{cm}^3$ ] based on the volume unit are made obvious by means of bar diagrams for the state immediately after filling the cell with electrolyte (a)



and after 100 cycles (b), respectively.

In contrast to the electrodes used according to the invention, the pressed electrodes composed of conventional nickel hydroxide (particle size 50 to 300  $\mu\text{m}$ ) are subject to a spontaneous swelling as soon as they come into contact with the electrolyte. The filling of their pore system with electrolyte effects an increase in the electrode height amounting to up to 25%, which results in a corresponding drop in the volumetric capacity. Whereas the volumetric capacity of the fresh conventional electrode has already dropped to approximately 300  $\text{mAh}/\text{cm}^3$  at the beginning of the cyclic operation ((a), right-hand bar), the initial capacity of the positive electrode composed of  $\text{Ni}(\text{OH})_2$  powder is virtually 400  $\text{mAh}/\text{cm}^3$ .

After 100 cycles, the volumetric capacity of the conventional electrode has dropped further to approximately 270  $\text{mAh}/\text{cm}^3$  ((b), right-hand bar). On the other hand, the electrode in accordance with the invention remains virtually unaltered at the high capacity level of 400  $\text{mAh}/\text{cm}^3$ , which is at the same time evidence of their dimensional stability, which is explained by the better space utilization of the spherical particles or their lower volume requirement.

Because of the absence of a tendency to swell, the pressed electrode composed of spherical particles provides an important precondition for increasing the volumetric capacity in a button cell.

On the other hand, allowance must be made for the increase in volume which occurs in the case of nonspherical standard material even in constructing the cell. An externally specified volume can accordingly be utilized only to a rather small extent.