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Patent Claims

1. Electric accumulator having a positive nickel-hydroxide electrode, a negative electrode which comprises a hydrogen storage alloy, a separator situated inbetween, and an alkaline electrolyte, characterized in that the nickel hydroxide mass of the positive electrode is admixed with an oxidation-resistant graphite as a conducting medium.
2. Electric accumulator according to Claim 1, characterized in that the graphite has a high degree of crystallinity, the crystallite size (stack height) L_c being at least 180 nm.
3. Electric accumulator according to Claim 2, characterized in that the crystallite size (stack height) L_c is at least 200 nm.
4. Electric accumulator according to any one of Claims 1 to 3, characterized in that the ash content of the graphite is less than 0.5%.
5. Electric accumulator according to any one of Claims 1 to 4, characterized in that the proportion by weight of the graphite of the mass mixture of the positive electrode is between 1 and 25%.
6. Electric accumulator according to any one of Claims 1 to 5, characterized in that the proportion by weight of the graphite of the mass mixture of the positive electrode is approximately 15%.
7. Electric accumulator according to any one of Claims 1 to 6, characterized in that the cell components are arranged in a button cell container.



* C L M S *



Electric accumulator

The invention relates to an electric accumulator having a positive nickel-hydroxide electrode, a negative electrode which comprises a hydrogen storage alloy, a separator situated inbetween, and an alkaline electrolyte.

It is known that numerous metals and alloys, by forming metal hydrides, are able to absorb and store significant amounts of hydrogen. This ability is the basis for an energy storage system which, in addition to the conventional Ni/Cd accumulator or the lead-acid battery, has recently encountered a great deal of interest, namely the Ni/metal hydride accumulator.

Positive and negative electrode of this secondary system are arranged so as to be separated from one another, in an alkaline electrolyte, as is usual in other cases. In this arrangement, the positive electrode in principle corresponds to the positive nickel hydroxide electrode of the Ni/Cd accumulator.

According to the current standard, e.g. in accordance with US Patent 4935318, the active mass of the electrode contains, in addition to nickel hydroxide as the main component, a conducting medium in the form of nickel metal powder, also cobalt metal powder, certain foreign hydroxides, especially cobalt hydroxide, and a binder. The constituents are mixed in the dry state, the mixture is then pasted with water and spread into a highly porous three-dimensional nickel matrix.

When an electric current is applied to the negative electrode of an Ni/metal hydride secondary cell (Ni/MH), the active material thereof, the metal or the alloy M capable of absorbing hydrogen, is charged by the absorption of hydrogen:



During discharging, the stored hydrogen is

released, so that an electric current is generated:



Both reactions are reversible.

5 A similar situation applies to the reactions taking place at the positive nickel hydroxide electrode.

Charging: $\text{Ni}(\text{OH})_2 + \text{OH}^- \rightarrow \text{NiOOH} + \text{H}_2\text{O} + e^-$

Discharging: $\text{NiOOH} + \text{H}_2\text{O} + e^- \rightarrow \text{Ni}(\text{OH})_2 + \text{OH}^-$

10 Because of the environment-friendly energy source hydrogen, which here is used in conjunction with the well-established, in principle identical positive electrode of the Ni/Cd accumulator, Ni/metal hydride batteries even today offer distinct advantages compared to conventional secondary batteries.

15 Ni/metal hydride batteries are gas-tight, maintenance-free, and, thanks to a well-advanced electrode fabrication technology, already attain energy densities of 50 Wh/kg. Here, the quality of the positive electrode plays a particularly important part, since it
20 limits the capacity.

Prior to the introduction of rapidly chargeable Ni/Cd button cells, the conducting medium used in nickel hydroxide electrodes, instead of the nickel powder customary today, was graphite. For the positive
25 electrode, mainly consisting of mercury(II) oxide, however, of a metal oxide/hydrogen experimental cell, German Patent 1771420 likewise proposed a graphite addition to improve the conductivity.

The additions of cobalt and cobalt oxides,
30 which only later became customary in addition to nickel metal powder as the conducting material, promote, owing to their conductivity, the mass utilization of the nickel hydroxide electrode. They additionally serve to set a discharge reserve on the negative electrode,
35 inasmuch as, during the first charging of the cell,



prior to the oxidation of the $\text{Ni}(\text{OH})_2$, stable conductive cobalt oxides (CoOOH) are formed whose oxidation potential is lower than that of NiOOH . They therefore no longer take part in the subsequent reaction scenario in the cell, if the end-of-discharge voltage does not drop significantly below 1V, and the total charge supplied once to form them is then retained by the negative electrode as a capacity excess (discharge reserve) with respect to the positive electrode. Under extraordinary operating conditions (e.g. polarity reversal, exhaustive discharge) the conductive matrix may, however, be destroyed reductively.

Most commercial Ni-metal hydride accumulators, whether they are round cells, prismatic cells or those of the button cell type, present a serious problem inasmuch that they do not, as a rule, withstand a high temperature short circuit (HTSC) test, which is performed by the battery customers from industry. In this test, the cells in the discharged state are provided with a load resistor of 2Ω and stored for 3 days at 65°C . Then a capacity test is carried out by means of a few charging/discharging cycles at room temperature. The test simulates the long-term short-circuit behaviour in electronic appliances, the high temperature shortening the test duration. In so doing, massive irreversible losses in capacity are found which are due to the reductive destruction of the CoOOH conductive matrix as a result of the negative potential of the metal hydride electrode being impressed on the positive electrode during the short circuit.

The object of the invention is to provide an alkaline Ni/metal hydride accumulator which stands up to the HTSC test.

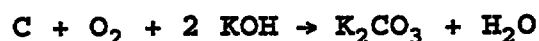
The object is achieved according to the invention by an accumulator as defined in Patent Claim 1.

It was found that accumulator failure hitherto had obviously been caused by the positive electrode, but that this can be stabilized if it is manufactured from a mass mixture of nickel hydroxide powder and an



oxidation-resistant graphite as the conducting medium. Thus it is no longer the reduction-prone CoOOH conductive matrix which acts as the main conductive matrix, but instead the inert graphite.

5 Admittedly, the addition of graphite in the field of the Ni/Cd cells has been known for a long time, as already mentioned above. The previously available graphite grades, however, were only conditionally suitable, because in alkaline cells they are subject to
10 oxidation according to:



The less oxidation-resistant the graphite is, the more K_2CO_3 is formed eventually. In the case of Ni/Cd cells, this reaction manifests itself by a stepped voltage
15 drop being produced. A possible cause is the shift of the potential-forming reaction from $\text{Cd}/\text{Cd}(\text{OH})_2$ to Cd/CdCO_3 . In addition, as more K_2CO_3 is formed, the electrolyte conductivity deteriorates. For these two
20 reasons, the use of Ni powder, in Ni/Cd button cells, as the conducting material instead of graphite has become generally established.

In contrast to Ni/Cd cells, Ni/metal hydride cells are not affected by the said voltage drop, since the formation of K_2CO_3 does not enter the negative
25 electrode reaction $\text{M} + x\text{H} \rightleftharpoons \text{MH}_x$ (M = hydrogen-storing alloy). Only the ion conductivity of the electrolyte is adversely affected as more K_2CO_3 is formed.

By means of employing, according to the invention, an oxidation-resistant graphite, this drawback,
30 too, could be overcome, however, so that said graphite becomes an advantageous alternative conducting material for the positive electrode masses in Ni/metal hydride accumulators.

The particular chemical resistance of this
35 graphite is predominantly based on its high degree of crystallinity. According to the invention, it has crystallite sizes of at least 180 nm, preferably of at



least 200 nm.

The crystallite size L_c , also called stack height, is determined by X-ray powder diffraction on the basis of the Scherrer equation $D = K \times \lambda / \beta \times \cos \delta$. Here, $D (=L_c)$ is the edge length of the crystallite in its principal direction (in graphite the c axis), K is a constant with a value of ~ 1 , β is the half-intensity width, after elimination of experimental effects, of a selected reflex, the reflexes 002 and 004 being used as the basis of the calculation for the graphite.

A further criterion of the oxidation-resistant graphite is its ash content. This should be less than 0.5%, preferably less than 0.3%. The BET area of the material should be less than $6 \text{ m}^2/\text{g}$. Oxidation-resistant graphites of the quality required for use according to the invention have recently become commercially available, e.g. the type Lonza SFG 75.

The weight ratio of the constituents of the novel positive mass according to the invention should be from 75 to 90% of $\text{Ni}(\text{OH})_2$, preferably approximately 85%, and from 1 to 25% of graphite, preferably approximately 15%. In principle, higher graphite proportions up to 35% by weight are also possible.

It is possible to demonstrate by an experiment the beneficial effect of the measure according to the invention. To this end, in two test series, button cells were selected because they are readily fitted.

The positive electrodes of the one test series consisting of 6 cells were prepared from a mixture, according to the invention, of 85% by weight of $\text{Ni}(\text{OH})_2$ and 15% by weight of oxidation-resistant graphite. In addition, a second test series of 6 cells was involved, whose positive electrodes comprised a mass mixture, based on the prior art, of 66% by weight of $\text{Ni}(\text{OH})_2$, 30% by weight of Ni , 3% by weight of CoO and 1% by weight of Co (standard cells).

The negative electrodes used were, in all cases, compacted-powder pellets made of a hydrogen



storage alloy.

All the positive electrodes were stored overnight, prior to the cell assembly, in Co-containing aqueous KOH at 80°C. After cell assembly, the cells were put into service as usual, the charging/discharging current being 50 mA, and the end-of-discharge voltage being set to 0.7 V, but after the 6th cycle they were subjected to the HTSC test. Then the initial cyclic treatment was continued for a further 5 cycles, in order to determine the effect of the high-temperature short circuit test on the capacity behaviour.

The figure, in a comparative representation of curves, shows the capacity development ($C[Ah]$ as a function of the cycle number n) of Ni/hydride cells according to the invention and of standard cells under the influence of the HTSC test. Both curves in each case are averaged from the measured data of the one and the other group.

As can be seen, the HTSC test for the standard cells (curve 1) results in a serious drop in capacity, from which they do not recover in the further course of the cyclic treatment.

In contrast, not only does a sharp decline in capacity in the "graphite cells" according to the invention (curve 2) turn out to be smaller, but within 2 to 3 subsequent cycles a recovery does take place with which the original capacity is attained once more. The test result confirms that the capacity loss is due to the positive electrode. A possible explanation could be that in the cobalt-containing positive electrodes of conventional cells, the first charging operation builds up a stable conductive matrix of $\beta\text{-CoOOH}$, which surrounds the poorly conductive nickel hydroxide particles like a net. Under the conditions of the HTSC test, however, the potential of the positive electrode can be shifted so strongly to negative values, that the $\beta\text{-CoOOH}$ network structure is reduced to $\beta\text{-Co(OH)}_2$ and is thus destroyed. Owing to the absence of inherent

conductivity, the original conductive matrix is no longer able to reactivate nickel hydroxide which has likewise been discharged to the oxidation state of Ni^{2+} and which in any case is non-conductive and, owing to its crystal habit being low in water, is inactive.

A stable electrode matrix which, however, is obviously capable of said reactivation and which, insofar, behaves similarly to a stable sintered body, is therefore present in the novel graphite material having the specified characteristics.

The figure also shows that the "graphite cells" according to the invention, although cobalt is not an essential constituent of their positive electrode mass, are at least the equals of the conventional "cobalt cells" in terms of normal capacity behaviour.

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