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**Patent Claims**

1. Alkaline accumulator, sealed in a gas-tight manner, in the form of a button cell having positive and negative electrodes arranged in the cell container and separated by a separator, characterized in that the support matrix and collector matrix of at least the positive electrode is formed by a porous metal foam or metal felt.
2. Accumulator according to Claim 1, characterized in that the metal on which the foam or felt is based, is nickel.
3. Accumulator according to Claim 1 or 2, characterized in that the foam structure has an open-cell porosity of from 85 to 97%, preferably of approximately 95%.
4. Accumulator according to any one of Claims 1 to 3, characterized in that the active material embedded in the support matrix is free of conducting-medium additions.
5. Accumulator according to any one of Claims 1 to 4, characterized in that the proportion of the metal foam of the electrode volume is approximately 5%.
6. Accumulator according to any one of Claims 1 to 5, characterized in that the specific volume capacity of the positive electrode is from 500 to 700 mAh/cm<sup>3</sup>.



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**Alkaline accumulator, sealed in a gas-tight manner,  
in the form of a button cell**

The invention relates to an alkaline accumulator, sealed in a gas-tight manner, in the form of a button cell having positive and negative electrodes arranged in the cell container and separated by a separator.

The container of a button cell is formed by a cup-shaped bottom section and a cover of nickeled steel sheet. The bottom section first accommodates the positive electrode, there then follows an alkali-resistant plastic material as the separator, on which the negative electrode lies. The electrodes and the separator are impregnated with electrolyte. Between the negative electrode and the cover there lies a spring which establishes an intimate contact of the electrodes with the cell container. The cell cup and the cover are insulated with respect to one another by a plastic ring. By means of the cup rim being flanged and pressed into place, satisfactorily sealed closure is achieved.

Apart from their special type of construction, which distinguishes them from round cells, button cells are always designed for small capacities up to approximately 1Ah. Whereas, furthermore, round cells are as a rule fitted with thin-film, flexible wound electrodes, the typical button cell electrodes are mass electrodes which consist of a dry mixture and are pressed to form pellets, and which are incorporated into the cell so tightly, that they are under a continuous areal pressure.

The dry mixture is composed of powdered active material ( $\text{Ni(OH)}_2$  in the case of the positive electrode), conducting medium such as Ni powder, and small amounts of a binder. For the purpose of establishing a discharge reserve in the cell, additions of metallic cobalt or cobalt oxide are also customary. Tableting of the mass mixture is effected during manufacture by means of rotary presses.

The finished pellets require, however, in addition to the conductive material already present in the

mass, a likewise conductive external reinforcement by a small basket of nickel wire fabric. After they have been inserted therein, the small basket must be closed by means of a small disc of the same wire fabric, by a rim projecting beyond the pellet above the covering disc being folded over. This once more requires the use of a press ram. A continuous production process is hindered by such operations.

A further factor is that additions of conducting medium, because of the poorly conductive active  $\text{Ni(OH)}_2$ , e.g. Ni powder, may form up to 30% by weight of the mass mixture and thus constitute a considerable ballast of inert material. For the necessary formation of a three-dimensional collector structure when the electrode is pressed, the use of this material is indispensable, however. The volume capacity of the electrode is thus distinctly limited. Typically, at most 450 mAh/cm<sup>3</sup> of electrode are attained.

A further process engineering drawback is that only those mixtures can be used in the electrode fabrication, which can be processed in a rotary press. This presupposes a granulable mass which at the same time exerts a certain lubricating effect on the stamping die and permits volumetric proportioning. Not every particle distribution and not every binder is suitable for this. This results in a low flexibility of the process in terms of formula changes, particle size changes and variations in the plastic binder addition.

The object of the invention is to provide a button cell on the basis of the alkali NiCd system or the NiH system, preferably comprising hydrogen storage alloys as the negative electrodes, which cell is substantially free of the drawbacks described.

The object is achieved by means of a button cell as defined in Claim 1.

According thereto, the use of positive pasted electrodes having a highly porous support matrix made of metal foam (foam electrode) or of a metal felt or metal batt (felt electrode) has been found to be very

advantageous. The metal forming the basis thereof is preferably nickel.

There are various techniques for generating a foamed metal. The starting material is usually a foamed plastic, e.g. polyurethane, of sponge-like, open-cell structure. This is plated with the metal in question, and the metal, to remove the plastic, is backed under inert gas. In the process, the plastic is decomposed thermally and, through pores in the nickel surface, passes into the gas phase. According to another process, the "plastic sponge" is filled with metal powder and the whole is sintered. A third method provides for a metal powder to be mixed with a pore former, the mixture to be sintered or melted, and remaining residues of the pore former to be removed by etching.

The metal felts are based on spun metallic fibre, usually strengthened by sintering in the manner of a bonded fibre web. Alternatively, they can also be obtained via bonded plastic fibre webs which are metallized and then heated under inert gas. According to a further known process, Ni is deposited from the gas phase on a bonded plastic fibre web. Such bonded fibre webs have pore sizes between 100 and 1000  $\mu\text{m}$ .

For the purpose of manufacturing positive electrodes according to the invention for button cells, a nickel foam e.g. having a porosity of from 85 to 97%, preferably of 95%, and having pore sizes between 50  $\mu\text{m}$  and 500  $\mu\text{m}$ , which foam is available as a strip or sheet material, is precompacted to a defined thickness, e.g. to 4 mm, and into this three-dimensional matrix a homogeneous aqueous paste of  $\text{Ni}(\text{OH})_2$  powder with various additions is introduced in a continuous or discontinuous process.

The purpose of the precompaction is an exact setting of the weight per unit area across the electrode thickness within a tolerance band of  $\pm 0.01$  mm.

The additions comprise, both, binders in solid, liquid or dispersed form, and Co powder,  $\text{CoO}$  or  $\text{Co}(\text{OH})_2$  powder, as well as, occasionally, compounds of Zn or Cd,

with the exception, however, of the conducting media otherwise customary in button cell electrodes.

The excess paste remaining on the substrate surface is then skimmed off, and the electrode strip is  
5 dried at elevated temperature up to approximately 150°C in a continuous through-type oven or alternatively in batches.

This is followed by the dried strip being compacted by rollers or by means of a static press, in order  
10 to ensure intimate contact of the individual powder particles. The electrode thickness is thus reduced from 4 mm to 2 mm, and such electrodes can be incorporated into button cells having, for example, a diameter of 25.1 mm and a height of 6.7 mm (series 170 Dk).

15 In a last conditioning step, circular, rectangular or hexagonal individual electrodes are punched from the strip, the punching tool being designed in such a way that the punching wastage is as low as possible.

The advantages of alkaline button cells being  
20 fitted with electrodes according to the invention result from the foam matrix, in contrast to the mass electrode, requiring no additions whatsoever of conducting media such as Ni powder. Their function is taken on by the three-dimensional sponge structure of the support, which  
25 structure in this arrangement takes up only about 5% of the total electrode volume. In the case of mass electrodes (compacted-powder pellets), the proportion by volume of the conductive material is between 3 and 15%, and its proportion by weight can reach up to 30%. In a  
30 particularly advantageous case it is also possible to dispense with the small nickel basket which encloses the positive electrode as a collector.

As a consequence of the particularly light, beneficial sponge structure of the foamed-metal support,  
35 the result for the button cell electrodes according to the invention is that of extraordinarily favourable specific volume capacities of from 500 to 700 mAh/cm<sup>3</sup>, up to 800 mAh/cm<sup>3</sup> being achievable optimally. The same applies to metal felt electrodes. In contrast, the

capacities in the conventional button cell electrodes are only approximately 450 mAh/cm<sup>3</sup>.

5 In a particularly advantageous embodiment of the button cell according to the invention, the up to 90% higher capacity of the positive individual electrode can be balanced by a negative electrode, likewise of the foam type, and it is possible to achieve, using this electrode combination, an increase of the cell capacity by approximately 40%. This only makes sense, though, in conjunction  
10 with the negative electrode of an NiCd button cell. In the intrinsically conductive, negative alloy electrodes of NiH cells, an additional conductive matrix is unnecessary.

The foam collector matrix is also mechanically  
15 more stable than the three-dimensional collector structure in a mass electrode which owes its coherence to the compaction pressure prevailing in each case, but eventually disintegrates noticeably under the influence of the volume changes of the nickel hydroxide, which occur  
20 in the cyclic charging/discharging operation. The decoupling, typically arising as a consequence in positive mass electrodes at high cycle numbers, of subsections of the active mass as a result of loss of contact between particles of the collector structure is not  
25 possible in the case of the foam electrodes to be used according to the invention in button cells.

Consequently, the foam electrode has a significantly higher cycle stability, compared to the mass electrode, so that, in the case of 1-hour charging and  
30 discharging, more than 1000 cycles can be achieved.

Two figures clarify the invention.

Figure 1 shows a sectional view of a button cell accumulator according to the invention.

35 Figure 2 shows the comparative capacity and lifetime behaviour of a button cell accumulator according to the invention and a conventional button cell accumulator.

According to Figure 1, the container of the button cell 1 is formed by the cup-shaped bottom section

2 and the cover 3 made of nickeled steel sheet. The cup-shaped bottom section contains the positive  $\text{Ni(OH)}_2$  electrode 4 having a collector structure according to the invention composed of an open-cell nickel foam 5, whereas the cover section accommodates the negative electrode 6 composed of, depending on the electrochemical system forming the basis,  $\text{Cd(OH)}_2$ , for example, or preferably of a hydrogen storage alloy.

The electrodes are electrically insulated with respect to one another by the interposed plastic separator 7, and the container is hermetically sealed by the cup rim being crimped against the cover rim. A plastic ring 8 simultaneously serves as a sealing ring and to insulate the cup with respect to the cover.

In Figure 2, the capacities C, in mAh, for a button cell according to the invention having a positive foam electrode (curve 1) and a conventional button cell (curve 2) are plotted against the cycle number n, the curves in each case representing average values for a group of a plurality of test cells. In all cases, NiH cells are involved. Each charging operation took place at a charging time of 4 h and at 100 mA, each discharging operation likewise at 100 mA up to the end-of-discharge voltage of 0.8 V.

It was found that the cells having positive foam electrodes are clearly superior to the cells having conventional positive mass electrodes, both in terms of capacity and with respect to the lifetime behaviour.

Finally, the pasted foam electrode, compared to the mass electrode or compacted-powder electrode, affords process engineering advantages which lie in, firstly, no account having to be taken, with respect to the formula for the active material, of mechanical processability in a rotary press. Thus, the morphology and particle size distribution of the  $\text{Ni(OH)}_2$  used, and of the other pulverulent additions, can be chosen freely. With the plastic binders, a completely free choice is possible between liquid, pulverulent and dispersed types; the concentration of these binders is likewise freely

selectable within wide limits.

Secondly, as a result of this flexibility in terms of the materials used, the capacity, the stability under load, and the cycle stability of the button cell  
5 can be significantly improved.