

The invention relates to a gastightly sealed alkaline storage battery in button-cell form having a porous positive electrode, a porous negative electrode, an auxiliary electrode which maintains the oxygen consumption and is in electrically conducting contact with the negative electrode, and a separator which is disposed between the main electrodes, essentially no free electrolyte being present.

The field of application of the invention primarily covers button cells of the Ni/Cd type and Ni/hydride type, but also includes other rechargeable alkaline systems, such a Ni/Zn or AgO/Zn.

A very frequent cause of the premature failure of rechargeable alkaline button cells is separator drying-out, which interrupts the ion-conduction path between the electrodes. There are two reasons for the electrolyte loss of the separator which is observed after continuous cyclic charge/discharge operation or continuous overcharging: one is the swelling of the electrodes in contact with the separator on either side and the other is an electrolyte depletion due to an internal corrosion which consumes water.

The swelling of positive nickel hydroxide electrodes, which is due to a crystal-chemistry phase change during the electrical cyclic treatment, as a result of which nickel hydroxide phases with larger volume requirements are produced, is generally known.

The electrode swelling is also accompanied by an increase in the internal pore volumes of the electrodes. At the beginning of the cycle life, 100 % of the pore volumes of the two electrodes is filled. At the same time, the separator has a degree of filling of 70 to 90 %. Since, at 5 μm to 50 μm , the pore diameters in the electrodes are markedly less than those of a standard separator at 100 μm to 300 μm and, in addition, the fibres, of which the latter is formed, have predominantly hydrophobic properties, a swelling of the electrodes mainly operates in the direction of a depletion of the electrolyte content in the separator. In this way, the

capillary competition can result in a complete drying-out of the separator. This manifests itself at first in a rise in the internal resistance of the cell, and falling load capacity and reduced voltage level associated therewith.

Added to the drying-out effect of the swelling, is the drying-out already mentioned which is due to electrolyte depletion as a consequence of internal corrosion. This takes place at corrodible substances such as, for example, metallic nickel, which is added in powdered form to the active material of the positive electrode in order to improve the electrical conductivity.

Particularly susceptible to corrosion because of their readily oxidisable alloy components, in particular those from the group comprising the rare earths are hydrogen storage alloys which are used in nickel/hydride cells as negative electrodes.

Because of the reaction



they remove water from the electrolyte. In addition to the oxidation of the metal, a gradual mechanical breaking-up of the alloy structure is produced as a result of the incorporation and removal of hydrogen, in which breaking-up the porosity increases, particularly in the microregion. These micropores also contribute to the comparatively much coarser pores of the separator being sucked empty as time elapses. The electrolyte is "redistributed" at the expense of the separator.

German Patent Specification 2 838 857 discloses a storage battery of the Ni/H₂ type having a multiplicity of positive and negative electrodes in a stacked arrangement in which two different types of separators are involved, of which one type has a very low gas permeability or high electrolyte affinity and thus prevents, as insulation between positive electrode and negative electrode, a contamination, in particular, of

the sensitive metal hydride electrode with the oxygen gas produced at the positive electrode, while the other type of separator, a coarse-pore nonwoven material, makes it possible for the oxygen to escape in the opposite direction to an oxygen reduction electrode which is also inserted in the stack between each pair of positive electrodes.

In the metal oxide/hydrogen storage battery according to German Offenlegungsschrift 3 929 306, to protect the negative electrode, a sheathing of the metal hydride particles by a metal with low oxygen affinity is provided. The oxygen flow in the cell is additionally deflected from the negative electrode by placing the auxiliary electrode for the oxygen consumption, which is also present in this case, outside the ion path between positive electrode and negative electrode. In this cell, a normal, homogeneous nonwoven separator is used for electrode insulation.

The object of the invention is to provide a button cell having a high service life which is little impaired by swelling of the electrodes and by corrosion of the electrode materials.

According to the invention, the object is achieved by a storage battery as defined in Patent Claim 1.

According to a subfeature of the claim, the separator used in the button-cell storage battery is microporous and, because of a mean pore size or a mean pore diameter which is less than the mean pore diameter of the electrodes, it has a strong electrolyte retaining capacity, and this expresses itself in a very low gas permeability in the ready-to-operate cell, i.e. the cell filled with electrolyte. This automatically results from the high degree of filling of the fine pores with capillary action, which permits gas passage only under high pressure.

According to the invention, the mean pore diameter of the separator should be 0.05 μm to 10 μm , preferably, however, 0.1 μm to 3 μm , and its thickness

should be 0.05 mm to 0.3 mm, preferably between 0.1 mm and 0.2 mm.

In principle, any fine-pored material can be used for the separator provided it is resistant to
5 hydroxide solution and meets the specified conditions.

Particularly advantageous, however, is a plastics membrane, preferably composed of polyethylene (PE) or polypropylene (PP). Such a membrane is obtained in multifarious ways, for example by stretching a suitable
10 film material. According to another method of production, a plastics material, which is blended with a finely powdered pore-forming agent, is formed into a membrane, for example by extrusion or rolling and the pore forming agent is then dissolved out of it. In this case,
15 stretching is omitted.

Radiation-crosslinked polymer films are also suitable for the purpose according to the invention.

Because of its high surface forces, such a separator always has a very high degree of electrolyte
20 filling from 95 to 100 % and as a result of this, and also because of its low pore diameter, it is virtually unpassable for oxygen, which is produced at the positive electrode during the overcharging. It consequently forms an effective oxidation protection for the negative
25 electrode, in particular for the sensitive H₂ storage alloy of a nickel-hydride cell, of which the fibrous non-woven separators normally used in alkaline cells are not capable. With pore diameters of about 100 μ m to 300 μ m, the latter exert only relatively low capillary forces,
30 the degree of filling being about 50 to 80 %, with the result that the O₂ overcharging pressure produced in the cell is sufficient to overcome the surface tension of the hydroxide solution electrolytes (5N to 8N KOH).

The separator according to the invention therefore
35 remains protected against the danger of drying-out.

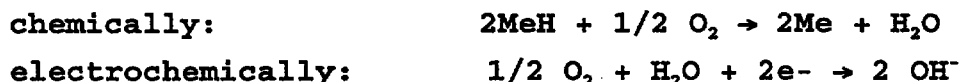
In a tightly sealed storage battery, the oxygen liberated by the positive electrode must, however, reach the negative electrode or an auxiliary electrode which is at the same potential in order to be consumed there, and

this is described, depending on the type of cell, by the following equations:

Ni/Cd



Ni/H



10 According to the invention this is achieved in that the auxiliary electrode is disposed outside the ion-conduction path between positive electrode and negative electrode, which path usually extends through the separator. It is advantageous, in particular, to dispose an auxiliary electrode short-circuited to the negative
15 electrode inside a button cell housing on its freely accessible rear side.

Due to the use of a microporous membrane separator having a certain pore characteristic which protects it from premature drying-out, the rechargeable
20 alkaline button cell according to the invention proves to have a surprisingly long life in continuous cyclic operation. The gastight operation of the cell is ensured by the trouble-free, direct transfer of the oxygen from the positive electrode to the rear side of the negative
25 electrode, where it is electrochemically converted at high reaction rate at a consumption electrode.

In principle, any electrode from known alkaline secondary systems are available for selection as electrode materials for the cell, nickel hydroxide and
30 silver oxide, however, being preferred on the positive side. For the negative side, cadmium, zinc and, in the case of Ni/hydride storage batteries, the particularly preferred hydrogen storage alloys of the AB₅ type (LaNi₅) or of the AB₂ type (NiTi₂) are suitable.

35 The invention is illustrated below by a number of figures and an exemplary embodiment.

Figure 1 shows a button-cell storage battery according to the invention in section.

Figure 2 shows the capacity behaviour over a prolonged cycling time (number of cycles n).

5 Figure 3 shows discharge curves in the case where a conventional separator is used.

Figure 4 shows discharge curves according to Figure 3 in the case where a separator according to the invention is used.

10 Figure 5 shows changes in the cell height for continuous overcharging.

Figure 1 shows the basic structure of a storage battery according to the invention with its essential parts, the positive electrode 1, which is always present
15 in tablet form with wire fabric sheathing, negative electrode 2, the microporous separator 3 and the auxiliary electrode 4 (oxygen reduction electrode). In this case, the auxiliary electrode is formed by rolling a mixture of active carbon, conducting soot and PTFE into
20 a nickel gauze and, particularly advantageously, it is integrated in the nickel fabric sheath of the negative electrode. This provides a very reliable electron-conducting contact at the same time.

The cell contains essentially no freely mobile
25 electrolyte except in the pores of the electrodes and the separator.

Exemplary embodiment:

The mode of operation of the arrangement described above is shown using the example of a
30 nickel/hydride button cell.

Composition of the cell components:

a) Positive electrode

Ni(OH) ₂	:	66 % by weight
Ni _{met}	:	30 % by weight
Co _{met}	:	3 % by weight
CoO	:	1 % by weight.

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This material is pressed into a tablet and then provided, on the entire outside surface, with a nickel gauze which ensures the electrical collection.

b) Negative electrode

5 H-storage alloy: 94.5 % by weight
 conducting soot: 2 % by weight
 graphite: 2 % by weight
 PTFE powder: 1.5 % by weight

10 As in the case of the positive electrode, a weighed amount of this material is pressed into a tablet and placed in a small basket of Ni gauze. The O₂-consuming auxiliary electrode is placed on the rear side of the electrode. For permanent mechanical fixing and electrical contact, the projecting edge of the small
15 basket is flanged over.

c) Separator

 The separator used in the exemplary embodiment is a PP membrane produced from stretched plastics material and the pore diameter is in the order of
20 magnitude of 2 μ m to 10 μ m.

 Due to the microporous separator, electrical measurements carried out on finished cells yielded an outstanding cycle endurance in the case of the Ni/hydride button cell. Whereas the capacity values C[mAh] of a cell
25 equipped with a conventional separator drops abruptly after approximately 80 cycles (curve 1), the cell equipped with the microporous separator mentioned has hitherto been stable over 200 cycles (curve 2).

 The microporous separator also has a favourable
30 effect on the load capacity of the cell. Compared with cells containing a conventional separator (Figure 3), cells according to the invention (Figure 4) exhibit a markedly higher voltage level for the respective discharge currents of 50 mA (curve 1) and 120 mA (curve
35 2).

Finally, Figure 5 shows the outstanding overcharge capacity due to the use of the O_2 -consumption electrode. Despite overcharging for more than 30 days with a two-hour current (0.5 CA), the cell vessel
5 exhibits no deformations, which would first manifest themselves in an increase in the cell height (h). In this connection, curve 1 relates to an overcharge current of $i = 0.5$ CA, while curve 2 relates to an overcharge current of $i = 0.2$ CA.

Patent Claims

1. Gastightly sealed alkaline storage battery in button-cell form having a porous positive electrode, a porous negative electrode, an auxiliary electrode which
5 maintains the oxygen consumption and is in electrically conducting contact with the negative electrode, and a separator which is disposed between the main electrodes, the storage battery essentially containing no free electrolyte, characterised in that the separator is
10 composed of a microporous material with low gas permeability in the operating state of the cell, in that the mean diameter of the separator pores is less than the mean diameter of the pores in the positive electrode and the negative electrode, and in that the auxiliary
15 electrode is disposed outside the ion-conduction path between positive electrode and negative electrode.
2. Storage battery according to Claim 1, characterised in that the microporous separator is a plastics membrane having pore diameters between 0.05 μm and 10 μm ,
20 preferably 0.1 μm and 3 μm .
3. Storage battery according to Claim 2, characterised in that the plastics membrane is produced by stretching a plastics film.
4. Storage battery according to Claim 2, characterised in that the plastics membrane is produced by
25 forming a plastics material mixed with a pore forming agent and washing out the pore forming agent.
5. Storage battery according to Claim 2, characterised in that the plastics membrane is a radiation-crosslinked polymer film.
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6. Storage battery according to one of Claims 2 to 5, characterised in that the thickness of the plastics membrane is 0.05 mm to 0.3 mm, preferably 0.1 mm to 0.2 mm.
- 35 7. Storage battery according to one of Claims 2 to 6, characterised in that the membrane material is polyethylene (PE) or polypropylene (PP).
8. Storage battery according to one of Claims 1 to



7, characterised in that the auxiliary electrode is disposed at the side of the negative electrode remote from the positive electrode.

9. Storage battery according to one of Claims to 8,
5 characterised in that the auxiliary electrode is composed of a mixture of active carbon, conducting soot and PTFE rolled into a nickel wire gauze.

