

Gas-tight nickel cadmium battery

The invention relates to a gas-tight nickel cadmium battery in the shape of a button with a positive electrode, a negative electrode, which is an electrode comprising an active mass pressed in the form of a tablet into a small nickel wire cloth basket, an intermediate separator and with a carbon layer bonded with synthetic material and electrically contacting the negative electrode, for catalytically supporting the oxygen reduction.

Gas-tight alkaline batteries of the button cell type can be recharged or overcharged with currents $i \geq 0.3$ CA solely with special safety precautions, since the resulting gas pressure threatens to burst the cell box.

Conventional nickel cadmium button cells contain negative electrodes, which have dimensions such that an uncharged material (Cd(OH)_2) is still present therein, if the positive electrode is already in the fully charged state and solely gaseous oxygen is liberated. This reaches the negative electrode, where it is reduced chemically or electrochemically. Consequently, when operating with low currents, the oxygen pressure remains in a range which is not harmful for the cell box. On the other hand, on account of its overrating as regards capacity, the so-called charging reserve, the negative electrode never reaches the fully charged state, so that a liberation of hydrogen is prevented. The established stationary equilibrium pressure moreover depends both on the electrode geometry as well as on the quantity of electrolyte and ambient temperature.

However, the wish for a more rapid charging ability, for which currents up to $i \geq 0.5$ CA would have to be used, overtaxes the reducing power for gaseous oxygen defined by the cell balance of conventional button cells. Under these circumstances, pressures of up to 20 bars may occur, which far exceed the bursting pressure of normal button cell boxes, which is about 10 bars.

Therefore, in order to make the consumption of gas more intensive, one has attempted to support the effectiveness of the negative electrode by the insertion of auxiliary electrodes, which are electrically connected in parallel with the cadmium electrode and preferably consist of catalytically active materials. In a known case according to DE-OS 2826780, an auxiliary electrode of this type consists of a gauze-reinforced active carbon layer, which is hydrophilic, and of a hydrophobic layer of porous polytetrafluoroethylene (PTFE), the active carbon

layer resting directly on the surface of the cadmium electrode, whereas the hydrophobic PTFE-layer is remote from the surface of the cadmium electrode.

In other cases (see J.MRHA et al., Journal of Power Sources, volume 8, No. 1, pages 3-8 (1982), Elsevier Sequoia, Lausanne (CH)), the auxiliary electrodes are composed for the most part of a mixture of active carbon and PTFE-bonded cadmium material, which is identical to the active material of the negative main electrode and are pressed as separate layers onto the side of the main electrode facing the gas chamber.

Cadmium electrodes are also known from US-A-3 438 812, which at the same place have only a thin surface coating of a catalytically active material, for example finely distributed platinum.

The electrocatalytically active material of an auxiliary electrode, even an oxygen consumption electrode, facilitates the electron exchange in the sense of the equation



and thus converts the oxygen gas occurring, electrochemically.

The object on which the invention is based consists of providing a nickel cadmium battery of the button cell type, in which a carbon coating of the negative electrode for the purpose of oxygen reduction is achieved in a particularly simple and rational manner as regards manufacturing techniques.

The object is achieved according to the invention by the means disclosed in the characterising part of Claim 1.

Accordingly, for its special purpose, the invention directly uses the small cloth baskets or their coverings of nickel wire cloth serving for reinforcing the pressed electrodes comprising an active mass for button cells. In the case of conventional mass production, both parts are stamped out of the endless cloth web first of all as circular blanks, occasionally also in oval shapes, one part is shaped to form a small basket open at the top and after the insertion of the electrode tablet previously pressed independently and of the small basket lid, the edge of the small basket projecting beyond the cover insert is flanged over towards the inside. The active

mass electrode is thus provided with a good electronic conductance and protected on all sides against oozing.

It is also possible to shape small nickel wire cloth baskets so that the upper part of the edge projects outwards and thus forms a peripheral flange, which overlaps the edge of a correspondingly cut lid part with a larger contour than that of the electrode tablet and then to close the small basket by a flanging operation including both edge parts.

According to the invention, there is now introduced into the nickel wire cloth at least of the small basket lid of the negative cadmium electrode, a mixture of active carbon, conducting graphite and a binding agent, preferably by rolling. Polyisobutylene for example is suitable as the binding agent, or on account of its resistance to oxidation, polytetrafluoroethylene (PTFE) is even better suited. The proportions of the three components of the carbonaceous mixture should be according to the invention 57-58% by weight active carbon, 8-12% by weight conducting carbon black and 22-28% by weight PTFE.

With the coating of the small basket lid consisting of the Ni-cloth, by the active carbon mixture indicated, there is added to the negative cadmium electrode of the gas tight battery according to the invention, an auxiliary electrode for the oxygen consumption which is as simple as it is effective, whose incorporation in the conventional production sequence of the button cell necessitates no additional assembly stages. Under the aforementioned current conditions for rapid charging, a critical rise in pressure on account of sluggish gas consumption no longer takes place.

It is particularly advantageous if, with regard to the troublefree gas consumption, which necessitates the existence of three-phase limits, a highly porous PTFE-film is associated externally with the small basket lid. It is appropriately laid on the carbon-coated small basket lid at the time of assembly and is fixed to the lid jointly at the time of turning-over or flanging-over the projecting edge of the small basket. As has been shown, on account of its hydrophobic nature, in addition to the PTFE already existing in the carbon coating, the PTFE-film exerts an increased repellant effect on the electrolyte liquid, which is fixed substantially in the separator and in the porous electrodes. In this way, flooding of the layer containing carbon is reliably prevented in the case of excessive electrolyte dosing and the gas consumption is maintained.

In a further advantageous embodiment of the invention, the negative cadmium electrode, either in addition to the aforescribed PTFE-film or alone, can be provided with an ion exchange membrane, which is located between the electrode tablet and the coated small basket lid. A three-layer arrangement then possibly exists with this membrane, the carbon-coated small basket lid and the PTFE-film. The ion exchange membrane is impermeable for cadmium possibly escaping from the electrode tablet, thus prevents a separation of the metal in the region of the active carbon layer and protects its catalytic effectiveness.

The measures according to the invention are illustrated by two drawings.

Figure 1 shows a nickel cadmium battery of the button cell type according to the invention, in section.

Figure 2 shows the pressure development in a 250 DK nickel cadmium cell with and without the equipment according to the invention.

According to Figure 1, in the housing cup 2 with lid 3, which are insulated from each other and sealed by the synthetic seal 4, the button cell 1 contains a positive Ni O OH-electrode tablet 5 and a negative Cd-electrode tablet 6, both reinforced by a small basket 7 and small basket lid 8 of nickel wire cloth, furthermore a fleece separator 9, together with an electrolyte reservoir, a base insert 10 as well as a contact spring 11.

In a first embodiment of the invention (left-hand half of Figure 1), the small basket lid 8 of the cadmium electrode is provided with an active carbon layer 12 rolled into the nickel wire cloth and bonded with PTFE. In a second, preferred variation of the invention (right-hand half of Figure 1), the active carbon layer is supplemented both externally by a highly porous PTFE-film 13 as well as internally by an ion exchange membrane 14.

Numerical values of Table 1 form the basis of the curves of Figure 2, which values were found by pressure measurements on button cells of the 250 DK type (K = 250 mAh) with (curve A) and without gas consumption according to the invention (curve B). The measurements were carried out at an ambient temperature of 20°C during the 53rd charging cycle with a charging current $i = 0.5 \text{ CA}$ (125 mA).

Table 1

Internal pressures P of DK 250 Ni/Cd-button cells in bars

Charging duration (hrs)	Conventional cell	Cell according to the invention
1	0	0
2	1.9	0.3
3	8.5	0.6
4	13.0	1.0
5	16.0	1.2
6	17.4	1.4
7	18.0	1.4

The favourable effect of the active carbon layer according to the invention operating as a gas consumption electrode is in this case evident. With its presence, a constant gas pressure lying far below the bursting limit of approximately 10 bars is established. Carrying out the tests in a pressure vessel prevented bursting of the conventional comparison cell, which would occur after a charging duration of approximately 3.5 hours. Curve B therefore shows no interruption at this point.

Patent Claims

1. Gas-tight nickel cadmium battery in the shape of a button with a positive electrode, a negative electrode, which is an electrode comprising an active mass pressed in the form of a tablet into a small nickel wire cloth basket, an intermediate separator and with a carbon layer bonded with synthetic material and electrically contacting the negative electrode, for catalytically supporting the oxygen reduction, characterised in that forming the basis of the carbon layer is a mixture of 58 to 72% by weight active carbon, 8 to 12% by weight conducting carbon black and 22 to 28% by weight polytetrafluoroethylene, which is introduced into the nickel wire cloth material of the small basket lid and that located between the electrode tablet and the carbon-coated small basket lid is an ion exchange membrane.

2. Nickel cadmium battery according to Claim 1, characterised in that the carbon-coated small basket lid is provided on the outside with a hydrophobic membrane.

3. Nickel cadmium battery according to Claim 2, characterised in that the hydrophobic membrane is a polytetrafluoroethylene film.

