

The invention relates to a gas-tight alkaline battery of the round-cell type, having a positive nickel hydroxide electrode and a negative cadmium electrode, each of which has the form of a pressed-powder tablet in a metal wire cloth casing.

Round cells, in particular those of an Ni/Cd system, have a wide range of applications for supplying power to devices in the entertainment electronics field, for operating miniature motors, e.g. in electrical shavers, in hobby tools or in model building. As mass-produced items, they are nowadays subject to such highly rationalized production that desirable improvements in quality barely seem possible without the simultaneous burden of higher production costs. Moreover, the normal requirements of practice for currently commercially available round cells are not fulfilled satisfactorily.

In accordance with the present art, an Ni/Cd round cell has a housing cup with a positive pole and a cover with a negative pole, both the parts being produced from deep-drawn sheet steel, and being provided with a nickel coating approximately 5 μm thick. In the closure zone, formed by the cup edge or the cover edge being bent around, there is a sealing ring of plastics material, which also has the function of electrical insulation of the cup and the cover.

The housing interior is substantially filled by both mass electrodes, which are in the form of pressed tablets in a fine-mesh metal wire cloth, in particular a nickel wire cloth. Between the positive and the negative electrode tablet is the separator, of a plastics fleece, which is impregnated with alkaline electrolyte. The uniform contact resistance between the electrodes and the housing is maintained by a corrugated contact spring on the rear side of the negative electrode.

In order to prevent an accumulation of gas in the cell in the cyclical charging/discharging operation, the negative electrode is conventionally provided with a greater capacitance than the

positive electrode, which determines the useful capacitance of the cell. Part of the negative excess capacitance forms a so-called charge reserve comprising excess cadmium hydroxide which can be further charged to give metallic cadmium once the positive electrode is already fully charged, and the oxygen now evolved by the latter is taken up by the already charged part of the negative electrode, with the formation of $\text{Cd}/(\text{OH})_2$, at the same rate as new Cd_{met} is produced in the course of further charging from the charge reserve. The cell is thus protected against overcharging.

The other part of the negative excess capacitance is present in the normally discharged state of the cell, that is to say once the positive electrode has been fully discharged, as metallic cadmium and thus forms a negative discharge reserve which is still available. However, in parallel with its discharging, the current continuing to flow in the discharge direction would bring about an electrolytic water decomposition with the formation of H_2 in the positive $\text{Ni}(\text{OH})_2$ electrode which cannot be further reduced, that is to say instead of the nickel hydroxide electrode a hydrogen electrode would be produced whereof the potential is more negative than that of the cadmium electrode. In order to eliminate the inherent risk of polarity reversal of the cell and the build-up of gas pressure, the positive electrode mass is provided with an addition of $\text{Cd}(\text{OH})_2$ - a so-called antipolar mass - namely having a material which is capable of reduction at the same potential as that of the negative electrode and which has to be matched to the capacity for discharge of the negative electrode such that the latter is already exhausted and is evolving oxygen when part of the antipolar addition begins to be converted to Cd_{met} . In these circumstances, the oxygen can be reduced in a manner similar to that of overcharging with the $\text{Cd}/\text{Cd}(\text{OH})_2$ potential. The cell is thus also secured against polarity reversal.

Using a ratio between positive and negative total capacitance which is once set by appropriately pre-treating the electrode,

and with the aid of the mutually matched capacitance proportions for the charge reserve, the discharge and the non-polar mass, the gas-tight round cell can operate reliably in all conventional operating states, as long as this balance of the capacitance proportions, the so-called cell equilibrium, is not subsequently disturbed.

This is the case with extreme loads, for example in the event of rapid charging at high currents, since in the overcharging phase the oxygen conversion at the negative electrode lags behind the formation rate of the charged positive electrode, and the original equilibrium is shifted at the expense of the charge reserve.

In order to improve the oxygen reduction, an electrocatalytic active material in the form of an auxiliary electrode was associated with the negative electrode, for instance in accordance with DE-A-35 34 758. The use of an auxiliary electrode was not successful, however, if a complete consumption of the gas was to take place in the event of long-term charging as well. In the art of batteries, a requirement of this type has recently become particularly topical because of the use of cordless telephones, if these are to remain operable over a period of months.

JA-A-60/124368 discloses positive electrodes for nickel/cadmium batteries which have a metal foam support structure which is impregnated with nickel hydroxide and for example 5 to 20% by weight of nickel powder and 3-7% by weight of cadmium powder. As a result of the metal foam structure, such electrodes have a better intrinsic conductivity than pressed-powder electrodes.

The object of the invention is to make available a round cell which meets the requirements of virtually unlimited long-term overcharging at high current, in that it does not suffer any but negligible reduction in its usable capacitance as a result of this treatment, and moreover has a better temperature behaviour

as well as improved high-current loading capacity.

In accordance with the invention, the object is achieved by the means specified in Claim 1.

It has been found that an Ni/Cd round cell has a substantially increased protection against overcharging with improved high capacitance if, in addition to a negative electrode provided with an auxiliary electrode, it has a positive electrode having a particular mass composition. The positive mass according to the invention in fact contains, instead of the conductive graphite in conventional masses, exclusively nickel powder. INCO nickel powder 255, for example, is of a suitable quality.

In accordance with the invention, the powder mixture of the positive electrode has a composition of 45 to 55% by weight of nickel hydroxide, 28 to 35% by weight of nickel, 8 to 12% by weight of cadmium hydroxide and 6 to 10% by weight of cadmium. Preferably, the proportions are 48 to 52% by weight of nickel hydroxide, 28 to 32% by weight of nickel, 10 to 12% by weight of cadmium hydroxide and 8 to 10% by weight of cadmium. A particularly advantageous mixture has approximately 49% by weight of nickel hydroxide, 31% by weight of metallic nickel, 11% by weight of cadmium hydroxide and 9% by weight of Cd_{met} .

The negative electrode has a conventional mass composition of calcium hydroxide, 15 to 25% by weight of cadmium and 8 to 12% by weight of nickel powder. However, a coating comprising a mixture of activated carbon, conductive carbon black and a hydrophobic binder is applied to the cover of its nickel wire cloth basket, which is of the same metal wire. As a result of the direct electron-conductive contact with the main electrode, this layer acts as an auxiliary electrode whereof the virtually polarization-free surface is the preferred site for oxygen consumption.

The operating reliability of the cell according to the invention

is, as also in other round cells, ensured by a certain cell equilibrium. In this case, it has proved to be particularly favourable to make the negative electrode capacitance approximately twice as large as the useful capacitance of the positive electrode. With this arrangement, of the negative capacitance excess 50% falls to the charge reserve and 50% to the discharge reserve. The positive electrode, for its part, is increased by the antipolar Cd/Cd(OH)_2 mass, whereof the capacitance is 30 to 50%, relating to the positive useful capacitance.

However, in order to prevent bulging as a result of the build-up of an extremely high internal pressure in the event of a malfunction of the round cell according to the invention, there is provided on the housing a predetermined break point in a manner known per se. It comprises a groove-type weakening in the housing wall, approximately in the centre of the base or cover, and is at the same time preferably formed as a polarity sign, (+ sign) or company symbol.

In accordance with what has been found, because of the measure according to the invention, that is to say by means of an auxiliary electrode which is known per se and which is electrically short-circuited to the negative main electrode in combination with a novel positive electrode, round cells can now be overcharged at length for a virtually unlimited period using currents in the order of magnitude of the 5-hour current. Hitherto, it was only possible to load round cells using an approximately 10-hour current to give an overcharge duration of at most 1000 hours (approximately 42 days) without their suffering damage. Furthermore, the permissible temperature range for discharge could be extended upwards by 10 degrees, namely to -20°C to $+60^\circ\text{C}$. The permissible temperature range during charging, on the other hand, extends from 0°C to 45°C , as in the case of known round cells, and the self-discharge is 15%/month.

The proof of the superiority of round cells according to the

invention with respect to the capacitance behaviour during long-term overcharging by comparison with Ni/Cd round cells in accordance with the present production standard was provided by a test in which commercially available cells having a nominal capacitance of 250 mAh (250 short-term loading) alongside cells modified in accordance with the invention (novel composition of the positive electrode tablets, basket cover of the negative electrode prepared as auxiliary electrode) were exposed to long-term overcharging using a five-hour current over 12 months. The cell housings were identical for both series of tests, and their dimensions (diameter x height) were 25.1 x 8.8 mm.

By carrying out discharge tests on cells which were taken from the test at monthly intervals, were discharged using the five-hour current to a discharge final voltage of 1V and were then re-charged using the five-hour current, the capacitance development of these cells under the influence of the (five-hour) long-term overcharging current of the same size was followed.

As the criterion for successfully withstanding the long-term overcharging test, a capacitance limit of 200 mAh was set, which the cell was not to fall below before a year had passed. Furthermore, a change in height in the cell as a result of accumulated internal pressure should not go beyond the tolerance limit of production in an any but negligible way, and this was ensured at least in the case of the test cells according to the invention.

The result of the long-term overcharging test is shown in the figure in the form of a graph.

Here, the cell capacitance C in mAh (valid for the discharge current at the level of the five-hour current) is shown over the overcharging time t in months with a long-term current at the level of the five-hour current. Curve 1, comprising the average values of the discharge tests in comparison cells of 250 short-term loading produced in the conventional way shows the fall in

capacitance thereof as a result of gradual gas consumption, since the reduction in oxygen at the negative cadmium electrode is not capable of keeping up with its rate of formation in the case of the five-hour overcharging current, and so the cell equilibrium originally set is lost. Even after being long-term overcharged for $\frac{1}{4}$ year, the cells no longer meet the predetermined capacitance requirement, and are totally unusable after 1 year. It is not possible then even to carry out re-charging.

The round cells according to the invention are represented by the capacitance curve 2, having an almost unchanged horizontal profile. In accordance with this, thanks to the collective effect of the negative auxiliary electrode and the modified positive mass, these cells are shown to be fully able to cope with the large gas quantity to be converted. In addition, the charge take-up as such is greatly improved by the combination of measures according to the invention, since the electrochemical conversion of the positive material in the presence of an exclusively metallic conductor powder is kinetically inhibited to much less of an extent and is thus more efficient.

Curve 2 also shows clearly the ability of Ni/Cd round cells according to the invention - here of the 250 short-term loading format - to maintain their output capacitance for a virtually unlimited period under long-term charging conditions at a relatively high current (five-hour current). The required minimum capacitance of 200 mAh is at least still reliably available after 12 months with a five-hour discharge.

Tests regarding the capacity for cycling of the novel round cell have shown that at least the same cycle life time is achieved as that of known comparable round cells.

Finally, as a further advantage of the invention, it should be emphasized that its "packaging", that is to say cell housing and design, is unchanged by comparison with the round cells available on the market in accordance with the most recent prior art, and

the equipping in accordance with the invention of the cadmium electrode with the gas consumption electrode and the modification of the positive electrode to the novel mass recipe requires only a minimal additional expense from a production point of view.

Claims

1. Gas-tight alkaline battery of the round-cell type, having a positive nickel hydroxide electrode and a negative cadmium electrode, each of which has the form of a pressed-powder tablet in a metal wire cloth casing, characterized in that the powder material of the positive electrode is a mixture comprising 45 to 55% by weight of nickel hydroxide, 28 to 35% by weight of nickel, 8 to 12% by weight of cadmium hydroxide and 6 to 10% by weight of cadmium, and in that the negative electrode is coupled to an auxiliary electrode for the purpose of electrochemically releasing the oxygen pressure.
2. Battery according to Claim 1, characterized in that the powder mixture of the positive electrode has a composition of approximately 49% by weight of nickel hydroxide, 31% by weight of nickel, 11% by weight of cadmium hydroxide and 9% by weight of cadmium.
3. Battery according to Claims 1 and 2, characterized in that the material of the negative electrode is a conventional cadmium hydroxide mass having 15 to 25% by weight of cadmium and 8 to 12% by weight of nickel powder proportions.
4. Battery according to Claim 3, characterized in that the auxiliary electrode is formed by a coating of the lid, comprising metal wire cloth, of the casing of the negative electrode with a mixture of activated carbon, conductive carbon black and a hydrophobic binder.
5. Battery according to one of Claims 1 to 4, characterized in that there is provided on the round-cell housing a predetermined break point in the form of a groove-type weakening in the housing wall.

