

Gas-tight alkaline accumulator

The invention relates to a gas-tight alkaline accumulator for the storage of electrical energy, having a positive electrode containing substantially nickel hydroxide as the active material, a negative electrode and a separator arranged between the electrodes in a sealed housing.

New techniques for preparing electrodes and the resulting electrode structures for gas-tight alkaline accumulators, on the one hand, afford improved electrochemical utilisation of the mass and, on the other hand, make for more rational cell production. Parallel measures are aimed at promoting gas consumption and achieving more reliable gas-tight functioning of the hermetically sealed accumulator cells.

The electrochemically active electrode materials, namely nickel hydroxide for the positive electrode, and cadmium hydroxide, iron hydroxide, zinc hydroxide and cobalt hydroxide for the negative electrode, still enjoy the status of classic materials for energy storage in the alkaline accumulator. Yet, as active materials for the negative electrodes, they have been supplemented by metals and metal alloys which have been enabled to store hydrogen. The gas-tight nickel-hydrogen accumulator has in this way joined the range of classic alkaline accumulators of the gas-tight type. Various construction forms of alkaline accumulator electrodes are currently used. The sintered type is particularly widespread for electrodes of both polarities. Electrodes produced by the sintering-impregnation process are regarded as robust, durable and highly resistant, but also as expensive on account of the number of steps involved in their manufacture. Sintered electrodes are being replaced today variously by electrodes of the pressed powder type. Their advantage lies in a greater utilisation capacity of the mass, with a smaller proportion of dead material in the conductive and support framework.

The negative electrodeposited electrode obtained by cathodic metal deposition from cadmium salt solutions represents a special construction form (in accordance with DE-OS 28 22 821).

A development which is still very new relates to electrode support frameworks of highly porous metal foam into which a slurry or a paste of a flowable active mass is introduced (cf. US-PS 4 251 603 or E-PS 185 830).

The patent literature also discloses examples of combinations of one type of electrode with the other in a gas-tight alkaline accumulator. For example, DE-OS 34 16 817 discloses the possibility of incorporating a negative, charged cadmium electrode of the electrodeposited type together with a positive, charged pressed powder electrode. According to E-PS 284 333, both of the electrode species of a gas-tight nickel/hydrogen battery are present in the form of the metal foam framework electrodes which have been mentioned.

The differences in mechanical and electrical characteristics between individual electrode constructions make it difficult to select from the range of types available a suitable electrode for a gas-tight alkaline cell of a particular design and having to meet specific operational demands.

The object of the invention is to provide a gas-tight alkaline accumulator cell which is equipped with electrodes which complement one another optimally as to energy storage capability and mechanical stability, and which can be manufactured by way of an inexpensive production process affording maximum automatability.

The object is achieved according to the invention by an accumulator such as that indicated in Claim 1.

According to this, the combination of a positive metal foam

framework electrode and a negative calender-coated electrode in a gas-tight alkaline accumulator proves to be very favourable. Not the least reason for this lies in the manufacturing technology. Because the majority of gas-tight accumulators are of the winding cell type, the novel electrodes which must be utilised for this are as a rule strip electrodes. High flexibility makes them equal to the particular mechanical stresses arising during the winding process.

The favourable combination of a positive metal foam framework electrode and a negative calender-coated electrode has a particularly advantageous effect in a gas-tight nickel/hydrogen accumulator. The positive electrode of such an accumulator according to the invention is thus based on a metal foam support, generally of nickel, which possesses an excellent electrical conductivity at extremely high porosity - its pore volume reaches at least 95%. The performance of a Co-coated nickel foam or a foam of an Ni/Co alloy is particularly favourable in this regard. The positive active mass, made into a slurry or a paste, is introduced into the open pore system of this framework body.

The principal constituent of the active mass is nickel hydroxide which according to the invention is accompanied by a fairly large quantity of powdered nickel metal and optionally further powdered metals from the series Co, Cu, Fe, Mo, W, Cr, Ti and Zn and a fairly small quantity of further metallic hydroxides, at least one hydroxide from the series $\text{Co}(\text{OH})_2$, $\text{Cd}(\text{OH})_2$, $\text{Zn}(\text{OH})_2$, $\text{Al}(\text{OH})_3$, $\text{Mg}(\text{OH})_2$, iron hydroxides and Mn hydroxides. The positive active mass is prepared starting from a dry mixture of the named constituents, wherein the proportion of nickel hydroxide should be from 75 - 90 wt-% of the dry mixture, the proportion of powdered metal from 5 to 25 wt-% and the proportion of foreign hydroxides from 1 to 10 wt-%.

The ratio by weight of nickel to the sum of the other metals in the

powdered metal constituent may vary within the limits 1 : 1 and 1 : 20.

The foreign hydroxides, for example $\text{Co}(\text{OH})_2$, $\text{Zn}(\text{OH})_2$ or $\text{Mg}(\text{OH})_2$, may advantageously be already contained in the nickel hydroxide if the latter has been obtained by simultaneous precipitation. The dried precipitation product should then comprise from 85 to 98 wt-% $\text{Ni}(\text{OH})_2$ and from 12 to 15 wt-% foreign hydroxides.

In order to prepare the coatable paste of active mass, the dry mixture described hereinabove is stirred into an aqueous dispersion of a plastifying binder and a thickener. This dispersion forms the "aqueous phase" of the ready paste or slush, accounting for approximately 30% of the weight thereof.

Suitable binders are polyethylene, polypropylene, acrylic acid esters, polybutadiene, polyvinyl alcohol, polyvinyl acetate, polytetrafluoroethylene and polyvinylidene chloride, and acrylic acid ester copolymers, with the commercial product Mowilith VDM 758 (ex Farbwerke Hoechst AG, Frankfurt-Höchst) having proved a particularly valuable member of the latter group of substances.

In order to prepare the dispersion, the binders and the thickener are weighed out and mixed with water in quantities such that this mixture contains approximately 4.5 wt-% binder and approximately 0.8 wt-% thickener.

The active mass for the positive electrode of the accumulator cell according to the invention is consequently prepared in a very simple manner, namely from starting substances which, being completely normal commercial products, are readily obtainable, by way of straightforward and easily automated weighing and mixing processes.

The morphological characteristics of the solid constituents also

exert a considerable influence on the quality of the paste of active mass in terms of the criteria of good electrochemical utilisation capacity and a low tendency of the finished electrode to swell. It is thus favourable if the particles of the nickel hydroxide utilised, into which optionally foreign hydroxides (from a simultaneous precipitation) are incorporated, are of spherical form and are between 3 μm and 70 μm in size. The powdered nickel metal should preferably be a Mond nickel having a particle size of around 0.1 to 3 μm .

The paste is now introduced, by coating on both sides, into a highly porous foamed nickel structure which has, for example, a pore volume of 97%, a thickness of 1.7 mm and a mass per unit area of 35 to 65 mg/cm². More advantageously, this process may take the form of continuous paste introduction, by means of an application device through which the metal foam framework is guided in the form of a strip.

A highly advantageous post-treatment of the finished, dried electrode material consists of nickel or cobalt salt impregnation in a bath, followed by exposure to a precipitating alkali. This results in post-coating of the pore system of the electrode with nickel hydroxide or cobalt hydroxide, thus improving substantially the electrochemical utilisation capacity and the electrical loading capacity.

A similarly favourable outcome may be achieved if the nickel hydroxide particles are provided with a thin metallic layer of cobalt or nickel before mixing.

The negative counterelectrode to the metal foam framework electrode in an accumulator according to the invention results from calender coating the active material dry on to a support material, optionally with the aid of a binder. The active material is generally one of the usual metallic hydroxides $\text{Cd}(\text{OH})_2$, $\text{Fe}(\text{OH})_2$,

$\text{Zn}(\text{OH})_2$ or $\text{Co}(\text{OH})_2$. In gas-tight alkaline accumulators of the classic type, they are supplemented with additional active components which form a discharge reserve or, as a constituent of the positive active mass, afford protection from pole reversal. These include auxiliary agents which are known per se in the role of supporting oxygen consumption and improving electrical conductivity. The support material comprises a fine-meshed metallic net or an expanded metal of nickel, iron, copper or silver. For reasons of economy, nickel-plated or silver-plated iron or copper material may be used in place of solid nickel or silver wire netting. In the case of all the support materials named, currentless or galvanic cobalt-plating before the electrode mass is calender-coated affords advantages in terms of electrochemical utilisation capacity and loading capacity.

In the case of the preferred accumulator according to the invention, namely the nickel/hydrogen accumulator or metallic hydride accumulator, the calender-coating mixture for the negative electrode is likewise formed substantially from a dry powder mixture with a small quantity of pulverulent plastics. The active material, which at the same time forms the principal constituent of the latter dry powder mixture, is in this case a powdered metal or metal alloy in powder form, which is capable of absorbing and storing hydrogen electrochemically. These materials store electrochemical energy by a process in which a proton is discharged from the electrolyte, close to the surface, to a neutral hydrogen atom which is subsequently stored in the interior of the metallic solid body.

When the cell is in the discharged state, the active material is preferably supplemented with an additional quantity of the metal or the metal alloy in the form of hydride, hence it possesses a discharge reserve.

For the purpose of improving the electrical conductivity, there are

furthermore admixed to the active material metallic powders of nickel, cobalt or copper, and, if desired, also graphite and conductive carbon black. Finally, alongside the active material, there are provided oxygen-consuming agents in the form of a carbonaceous mixture. The components thereof are conductive carbon black, activated carbon and polytetrafluoroethylene which are in an approximate mutual ratio by weight of from 3 to 20 wt-%, preferably 7.5 wt-%, conductive carbon black, from 50 to 80 wt-%, preferably 75 wt-%, activated carbon and from 10 to 30 wt-%, preferably 17.5 wt-%, polytetrafluoroethylene.

This mixture may either be calender coated on to the finished electrode in a thin layer or be mixed already into the dry powder mixture as a constituent of the latter.

Plastics from the series polyethylene, polypropylene, polytetrafluoroethylene, polyvinylidene fluoride, polyvinylidene carbonate, polyvinyl alcohol, polyisobutylene and polyacrylonitrile are considered as the binder for the negative electrode.

In this instance also, intensive intermixing first of all the components of the dry powder mixture, followed by separate admixture of the binder to the latter, is recommended.

The finished calender-coating mixture then comprises from 60 to 80 wt-% metal or metal alloy capable of hydrogen storage, from 5 to 20 wt-% of the same active material in the form of hydride, from 10 to 35 wt-% powdered metal or from 1 to 6 wt-% carbon black and graphite as the conductive agents, from 1 to 6 wt-% binder and from 1 to 8 wt-% carbonaceous mixture for oxygen consumption.

In this way the negative coated electrode is preferably obtained as a result of dry calender coating on to a support material, wherein it is favourable to pre-calender coat the calender-coating mixture to form a laminate from 0.3 to 0.8 mm thick before application to

a fine-meshed metallic net or expanded metal.

In the case of both the positive metal foam framework electrode and the negative calender-coated electrode, it has proved to be favourable to cobalt-plate the support by currentless or galvanic treatment in a cobalt salt-containing bath liquid prior to introducing the mass or prior to the calender coating process, because this increases the electrical loading capacity.

The operations for preparing both electrode species are once more explained by reference to two schematic Figures, in which

Figure 1 shows the preparation of the positive metal foam framework electrode, and

Figure 2 shows the preparation of the negative calender-coated electrode.

According to Figure 1, the solid constituents of the paste of active mass to be prepared, namely nickel hydroxide 1 (optionally with inclusion of foreign hydroxides), powdered metal additives 2 and added metallic hydroxides 3, excluding Ni(OH)_2 , and the constituents of the "liquid phase", namely the binder 4 and water 5, are in each case mixed discretely in the dry mixer 6 or in the stirred vessel 7. The solid and the liquid mixed products are then supplied together to the mixing vessel 8 and are stirred to form the coatable paste 9. The paste passes thence to the coating device 10 through which there passes the metal foam support strip 11, with the pore system thereof absorbing the paste. The filled support strip finally passes through a drying zone 12.

According to Figure 2, weighed quantities of a hydrogen storage alloy 13, a powdered alloy 14 which is identical but charged with hydrogen, a conductive material 15 (powdered metal or carbon black/graphite mixture), an organic binder 16 and a carbonaceous

mixture 17 as the oxygen-consuming agent are mixed in the dry mixer 18. In the calender 19 this dry mixture is pre-calendered to a 0.3 to 0.5 mm-thick strip 20 which is then coated in the calender 21 on to a reticular support strip 22. The calender-coated electrode strip may also undergo subsequently a post-treatment (not illustrated), for example plastics coating by immersion in 5 to 15% dispersions of polyethylene, polytetrafluoroethylene or acrylic acid compounds, as a result of which the mechanical stability of the strip is increased, or the oxygen-consuming component 17 is omitted from the calender-coating mixture and is applied by calender coating only once the electrode strip is finished. This measure ensures that the oxidation-sensitive hydrogen-storage alloy is largely spared any contact with oxygen. Oxygen consumption is displaced into the outer region of the electrode surface, which is advantageous for the cyclic stability of nickel/hydrogen cells.

The electrode species utilised in the production of an accumulator cell according to the invention are adjusted as to thickness such that the ratio of area-related capacity of the negative electrode to area-related capacity of the positive electrode is between 1.2 and 2.

For cells of the AA version having an effective capacity of 1050 mAh (0.2 CA) the electrode dimensions which follow are favourable.

Positive metal foam framework electrode:

Length:	64	mm		
Breadth:	41	mm	Capacity:	1050 mAh
Thickness:	0.75	mm		

Negative calender-coated electrode:

Length:	90	mm	Capacity:	1660 mAh
Breadth:	41	mm	Discharge reserve:	450 mAh

Thickness: 0.45 mm Charge reserve: 160 mAh

The two electrodes are separated one from the other in the discharged state by a polyethylene, polyamide or polypropylene fibre nonwoven, and they are helically wound. An aqueous 5 to 8 N KOH solution having LiOH additions of from 0.3 to 2 N is used as the electrolyte. The cells are set in operation by charging with a 10-hour nominal current and discharging with a 5-hour current, after they have been activated by temperature-controlled storage at 45°C to 80°C for a period of from 1 to 14 days. After completion of two such cycles the cells have reached their full electrical loading capacity.

Claims

1. Gas-tight alkaline accumulator for the storage of electrical energy, having a positive electrode containing substantially nickel hydroxide as the active material, a negative electrode and a separator arranged between the electrodes in a sealed housing, characterised in that the positive electrode is formed by impregnating a highly porous metal foam support framework with an aqueous paste of active mass, and the negative electrode is formed by applying a plastics-bound active material on to a reticular support framework by calender coating.
2. Gas-tight alkaline accumulator according to Claim 1, characterised in that it is a nickel/hydrogen accumulator.
3. Gas-tight alkaline accumulator according to Claim 2, characterised in that the paste of active mass is formed by mixing an aqueous binder dispersion with a dry mixture of nickel hydroxide, powdered nickel metal and at least one further powdered metal selected from the group comprising the metals Co, Cu, Zn, Fe, Mo, W, Mn, Cr and Ti.
4. Gas-tight alkaline accumulator according to Claim 2, characterised in that the active material of the negative electrode contains a hydrogen-storing metal or a hydrogen-storing alloy.
5. Gas-tight alkaline accumulator according to Claim 3, characterised in that the dry mixture contains additionally one or more hydroxides selected from the group comprising $\text{Co}(\text{OH})_2$, $\text{Cd}(\text{OH})_2$, $\text{Zn}(\text{OH})_2$, $\text{Mg}(\text{OH})_2$, $\text{Al}(\text{OH})_3$, iron hydroxides and Mn hydroxides.
6. Gas-tight alkaline accumulator according to Claim 3 or 5, characterised in that the proportion by weight of nickel hydroxide in the dry mixture is from 75 to 90%, and the proportion by weight of the metallic components is from 5 to 25%.



7. Gas-tight alkaline accumulator according to one of Claims 3, 5 or 6, characterised in that the binder is selected from the substance group comprising acrylic acid esters, polybutadiene, polyvinyl alcohol, polyvinyl acetate, polytetrafluoroethylene and polyvinylidene chloride.

8. Gas-tight alkaline accumulator according to Claim 4, characterised in that the active material contains an additional quantity of storage alloy in the form of hydride when the cell is in the discharged state.

9. Gas-tight alkaline accumulator according to Claim 4 or 8, characterised in that the active material contains as further components conductive agents and/or oxygen-consuming agents.

10. Gas-tight alkaline accumulator according to Claim 9, characterised in that the oxygen-consuming agent comprises a mixture of conductive carbon black, activated carbon and polytetrafluoroethylene, which is incorporated into the active material during mixing or is applied in the form of a thin layer to the surface of the electrode by calender coating.

