

VARTA Batterie Aktiengesellschaft

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Patent Claims

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1. Gastightly sealed metal oxide/metal hydride storage battery having positive electrode which is disposed in the cell casing and comprises a metal oxide, having a negative electrode which comprises a hydrogen storage alloy, having a separator which is disposed between positive and negative electrode and contains an alkaline electrolyte, and having an auxiliary electrode which maintains the oxygen consumption and is in electrically conducting contact with the negative electrode, characterized in that the auxiliary electrode contains a hydrogen storage alloy as the agent which maintains the gas consumption in the event of overcharging and polarity reversal and in that the auxiliary electrode is connected in an electrically conducting manner to the negative electrode.
2. Gastightly sealed storage battery according to Claim 1, characterized in that the auxiliary electrode rests directly against the rear of the negative electrode.
3. Gastightly sealed storage battery according to Claim 1 or 2, characterized in that a hydrophobic binder is added to the alloy material of the auxiliary electrode and a hydrophilic binder is added to the alloy material of the negative electrode.
4. Gastightly sealed storage battery according to one of Claims 1 to 3, characterized in that, optionally, one of the conducting agents Cu powder, Ni powder or graphite is added to the alloy material of the negative electrode.
5. Gastightly sealed storage battery according to one of Claims 1 to 4, characterized in that, in addition to graphite and soot, PTFE is added to the alloy material



of the auxiliary electrode as binder.

6. Gastightly sealed storage battery according to one of Claims 1 to 5, characterized in that the mass mixture on which the auxiliary electrode is based is composed of 0 to 20% by weight of graphite, 0 to 20% by weight of soot, 0.5 to 10% by weight of PTFE, the remainder to 100% by weight being hydrogen storage alloy.

7. Gastightly sealed storage battery according to Claim 6, characterized in that the mass mixture on which the auxiliary electrode is based is composed of 0 to 4% by weight of graphite, 1 to 3% by weight of soot, 1 to 4% by weight of PTFE, the remainder to 100% by weight being hydrogen storage alloy.

8. Gastightly sealed storage battery according to one of Claims 1 to 7, characterized in that the mass mixture on which the negative electrode is based is composed of 10 to 50% by weight of Cu powder or Ni powder, 0 to 10% by weight of hydrophilic binder, the remainder to 100% by weight being hydrogen storage alloy.

9. Gastightly sealed storage battery according to Claim 8, characterized in that the mass mixture on which the negative electrode is based is composed of 20 to 40% by weight of Cu powder or Ni powder, 1 to 4% by weight of hydrophilic binder, the remainder to 100% by weight being hydrogen storage alloy.

10. Gastightly sealed storage battery according to one of Claims 1 to 7 characterized in that the mass mixture on which the negative electrode is based is composed of 0 to 20% by weight of graphite, preferably 10 to 15% by weight of graphite, 0 to 10% by weight, preferably 0.5 to 4% by weight, of hydrophilic binder, the remainder to 100% by weight being hydrogen storage alloy.



**Gastightly sealed metal oxide/metal hydride
storage battery**

The invention relates to a gastightly sealed metal oxide/metal hydride storage battery having positive
5 electrode which is disposed in the cell casing and comprises a metal oxide, having a negative electrode which comprises a hydrogen storage alloy, having a separator which is disposed between positive and negative
10 electrode and contains an alkaline electrolyte, and having an auxiliary electrode which maintains the oxygen consumption and is in electrically conducting contact with the negative electrode.

A preferred field of application of the invention are button cells of the Ni/metal hydride type because of
15 their efficiency and their established use in mains-independent appliances. However, their load-carrying capacity for high currents does not reach that of cylindrical cells. As a reason, a role may be played by the fact that the conductivity of the negative button-
20 cell electrode is relatively low. The lower conductivity is due to the proportion of a plastics binder in the mass mixture, which plastics binder is preferably composed of PTFE and may amount to 10%. On the other hand, the addition of the binder is necessary for reasons of
25 mechanical strength. It also imparts a hydrophobic nature to the mass and creates the condition for an adequate gas consumption in the event of overcharging and polarity reversal. Rechargeable, gastight metal
oxide/hydride button cells in accordance with the
30 definition of the generic class formulated at the outset must be both capable of overcharging and proof against polarity reversal.

During the overcharging, oxygen is generated at the positive electrode and has to be consumed to avoid an
35 unacceptably high internal pressure. The means suitable for this purpose is an auxiliary electrode which is usually composed of a mixture of soot, graphite and PTFE and which is situated on the rear of the negative main



electrode and is electrically short-circuited to the latter. The mechanism of the oxygen consumption can be described by the equation (1) $O_2 + 4e^- + 4 H_2O = 4 OH^-$.

5 A metal oxide/hydride button cell having an auxiliary electrode for the oxygen consumption can be found, for example, in German Offenlegungsschrift 39 29 306, Figure 4.

10 However, if a metal oxide/hydride storage battery enters polarity reversal after exhaustive discharge of the positive electrode, which generally limits the discharge, the positive electrode now develops hydrogen, which can be absorbed directly by the negative electrode, with conversion to metal hydride. However, this can take place only at a metallic surface which is in direct
15 communication with the gas phase. A liquid film at the metal surface impedes the hydrogen absorption considerably. The presence of a hydrophobic binder can keep the electrolyte away from parts of the electrode surface and thus facilitate the penetration of the
20 hydrogen into the interior of the negative mass.

German Offenlegungsschrift 40 29 503 also discloses an alkaline storage battery having a negative metal hydride electrode to whose active mass special catalysts composed of Raney nickel or Raney silver are
25 added specifically for the oxidation of the hydrogen produced in the event of polarity reversal.

Nevertheless, there remains the disadvantage of a reduced electrical conductivity, which is associated with the use of a hydrophobic binder. On the one hand,
30 in the case of mass electrodes, the binder ensures the cohesion and the hydrophobicity of the powder compact and, on the other hand, its action is that of an electrical insulator, with the result that a good protection against polarity reversal and a good current-
35 carrying capacity are mutually exclusive.

The object of the invention is to make available a storage battery, in particular in the form of a button cell, for the alkaline metal oxide/hydrogen system, which



storage battery can be operated even at high currents without limiting its gastight function.

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

According to the invention, the auxiliary electrode normally provided in a metal oxide/metal hydride cell for the oxygen consumption also takes over the rapid conversion of the hydrogen in the case of a
10 polarity reversal since, like the negative main electrode, it has a hydrogen storage alloy as main component and is connected in an electrically conducting manner to the negative electrode of the cell and, in particular, rests directly against the rear of the
15 negative main electrode. The auxiliary electrode according to the invention can advantageously be used in cylindrical cells and prismatic cells and is particularly suitable for use in button cells.

The auxiliary electrode according to the invention is produced by mixing the said hydrogen storage alloy with a carbon-containing and simultaneously hydrophobizing material, preferably a mixture of graphite, soot and PTFE, in a high-speed knife mill. The resultant mixture is extremely fine-grained and
25 homogeneous. On the one hand, this provides for a multiplicity of three-phase boundaries which are required for the oxygen consumption and, on the other hand, numerous surfaces without electrolyte coverage are also presented to the hydrogen and make it possible for it to
30 penetrate the alloy particles rapidly.

According to the invention it has furthermore proved advantageous to produce the negative main electrode from a powder which contains, in addition to the hydrogen storage alloy as the important component,
35 also nickel metal or copper metal in powdered form as highly conductive components. Graphite may also be used as alternative conducting agent.

Furthermore, to improve the mechanical robustness





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

According to the invention, the auxiliary electrode normally provided in a metal oxide/metal hydride cell for the oxygen consumption also takes over the rapid conversion of the hydrogen in the case of a
10 polarity reversal since, like the negative main electrode, it has a hydrogen storage alloy as main component and is connected in an electrically conducting manner to the negative electrode of the cell and, in particular, rests directly against the rear of the
15 negative main electrode. The auxiliary electrode according to the invention can advantageously be used in cylindrical cells and prismatic cells and is particularly suitable for use in button cells.

The auxiliary electrode according to the
20 invention is produced by mixing the said hydrogen storage alloy with a carbon-containing and simultaneously hydrophobizing material, preferably a mixture of graphite, soot and PTFE, in a high-speed knife mill. The resultant mixture is extremely fine-grained and
25 homogeneous. On the one hand, this provides for a multiplicity of three-phase boundaries which are required for the oxygen consumption and, on the other hand, numerous surfaces without electrolyte coverage are also presented to the hydrogen and make it possible for it to
30 penetrate the alloy particles rapidly.

According to the invention it has furthermore proved advantageous to produce the negative main electrode from a powder which contains, in addition to the hydrogen storage alloy as the important component,
35 also nickel metal or copper metal in powdered form as highly conductive components. Graphite may also be used as alternative conducting agent.

Furthermore, to improve the mechanical robustness





of the compact, the electrode mixture may contain a binder which is, however, hydrophilic, in contrast to the binder used in the auxiliary electrode, or at least has an only weakly expressed hydrophobic nature, for example
5 polyvinyl alcohol or polyethylene.

As a result of joining a hydrophobic auxiliary electrode formed from a hydrogen storage alloy to a negative main electrode composed of the same hydrogen storage alloy which has a high electrical conductivity
10 due to metal additives and an at least only weakly hydrophobic nature owing to a hydrophilic binder additive, an electrode combination is present which combines in itself the two capabilities, namely load-carrying capacity for high currents and prevention of a
15 pressure buildup after a polarity reversal.

In particular, the novel auxiliary electrode permits in this connection - in contrast to the oxygen-consumption electrodes present in conventional Ni/hydride and NiCd cells - the removal both of the oxygen and of
20 the hydrogen from the gas phase. A strong and permanent hydrophobic behaviour is indispensable for this dual function of the auxiliary electrode according to the invention.

It is based on a mass mixture of the following composition: 0 to 20% by weight of graphite, 0 to 20% by weight of soot, 0.5 to 10% by weight of PTFE, the remainder to 100% by weight being hydrogen storage alloy. A particularly advantageous mixture is composed of 0 to 4% by weight of graphite, 1 to 3% by weight of soot, 1 to
30 4% by weight of PTFE, the remainder to 100% by weight being hydrogen storage alloy.

The following mass mixtures are suitable for producing the negative main electrode:

1. 10 to 50% by weight, preferably 20 to 40% by weight, of Cu powder or Ni powder, 0 to 10% by weight, preferably 1 to 4% by weight, of hydrophilic binder, the remainder to 100% by weight being hydrogen storage alloy or
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2. 0 to 20% by weight, preferably 10 to 15% by weight, of graphite, 0 to 10% by weight, preferably 0.5 to 4% by weight, of hydrophilic binder, the remainder to 100% by weight being hydrogen storage alloy.

For the two alternative mass mixtures (metal powder or graphite as conducting agent), the content of alloy metal is approximately between 70 and 95% by weight.

Suitable as hydrogen storage material are alloys of the LaNi_5 type or TiNi type. Preferred are alloys of the LaNi_5 type in which lanthanum and/or other rare-earth elements form the misch-metal component of MmNi_5 alloys. An exemplary alloy has the composition $\text{MmNi}_{4.3-x}\text{Co}_x\text{Mn}_{0.3}\text{Al}_{0.4}$, where $0.2 < x < 0.7$.

Typical mass mixtures for the positive electrode contain, in addition to nickel hydroxide, metallic nickel and cobalt, graphite and cobalt oxide. These additives predominantly act as conducting material; the cobalt oxide additionally ensures an increase in the oxygen overvoltage at the positive electrode and consequently an increase in the charging efficiency.

The subject of the invention is explained in greater detail below by reference to the example of a button cell.

Figure 1 shows a Ni/hydride button cell according to the invention.

Figure 2 shows the surface structure of an auxiliary electrode according to the invention in an enlargement.

Figure 3 shows discharge capacities of button cells according to the invention compared with standard cells.

Figure 4 shows the establishment of the internal gas pressure of button cells according to the invention for different operating states.

According to Figure 1, the storage battery according to the invention does not differ in its





structure from a conventional Ni/hydride button cell having the casing can 1, the lid 2, the sealing ring 3, the positive nickel hydroxide electrode 4, the negative metal hydride electrode 5, the electrolyte-impregnated separator 6, the auxiliary electrode 7 for the oxygen consumption and the compression spring 8.

According to the invention and in contrast to the conventional design, the auxiliary electrode pressed against the back of the negative electrode is, however, also an alloy electrode and is strongly hydrophobic owing to a PTFE addition, whereas the negative electrode itself is hydrophilic.

The surface, shown enlarged in Figure 2, of the auxiliary electrode reveals individual metal hydride particles 9 which are partially wetted by an electrolyte film 10, but partially cemented to neighbouring particles by hydrophilic binder 11 (PTFE) and present large parts of their surface which are not covered by liquid electrolyte because of the water-repellent effect of the binder. At these points, H_2 can easily penetrate into the interior of the particles. It is absorbed by the alloy metal and thus removed from the gas space.

At other points, the conditions are in turn beneficial for an O_2 consumption as a result of the simultaneous presence of electrolyte, hydrophobic binder and exposed particle surface because said O_2 consumption is, in accordance with equation (1) in the introduction, this is possible only with the intervention of H_2O and in the electronic exchange with the solid alloy phase (three-phase relationship).

The superior high current-carrying capacity of button cells which are provided with negative electrodes according to the invention using Cu as conducting agent and with auxiliary electrodes according to the invention emerges from Figure 3.

The mass compositions of the test electrodes were within the scope of the formulations specified above. As is evident from the bar representations, the discharge





capacities K (in % of the nominal capacity NC) of the button cells (B) according to the invention were appreciably above those of standard production cells (A) at the high loads of $1C$ A and $2C$ A. An important reason
5 for the better high-current behaviour of the cells according to the invention is the lack of a hydrophobic binder in their negative electrodes, which is responsible for a more beneficial electronic conductivity.

Finally, the gas-consumption performance of the
10 novel auxiliary electrode is manifested in the behaviour of the internal cell gas pressure both in the case of overcharging and in the case of overdischarging. Thus, according to Figure 4, the internal pressure p [bar] of a 250 mAh button cell is only approximately 1 bar (curve
15 1) for an overcharging with $0.2C$ A. In the case of a polarity reversal, the internal pressure hardly exceeds 3 bar (curve 2) for the same current. Pressures of this magnitude are quite safe for the mechanical robustness of button cells.



Abstract

**Gastightly sealed metal oxide/metal hydride
storage battery**

In a gastightly sealed metal oxide/metal hydride button storage battery, in particular a nickel/metal hydride button cell, the active material of an auxiliary electrode is composed of the same hydrogen storage alloy as that of the negative electrode, to which the auxiliary electrode is electrically short-circuited. As a result, the auxiliary electrode can maintain both the oxygen consumption and, in the event of polarity reversal of the cell, the hydrogen consumption. As a result of a strongly hydrophobic adjustment of the auxiliary electrode and an only weakly hydrophobic or hydrophilic adjustment of the negative electrode by means of hydrophobic or hydrophilic binder additions, respectively, and as a result of adding highly conducting metal powder (Cu or Ni) to the mass of the negative electrode, a high gas-consumption rate in the event of overcharging and polarity reversal and simultaneously a good discharge capacity are obtained even at high currents (up to 2C A). The internal cell pressure of a 250 mAh button cell does not exceed 3 bar either during overcharging or during overdischarging at 0.2C A (= 50 mA) and is consequently not critical.



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Fig. 2

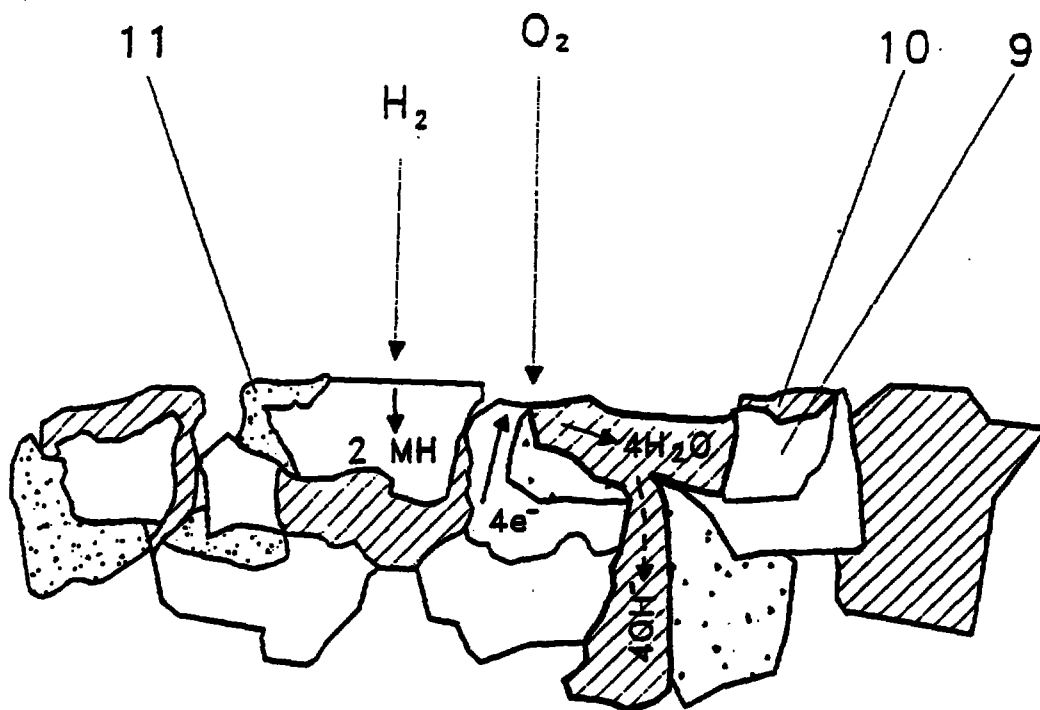
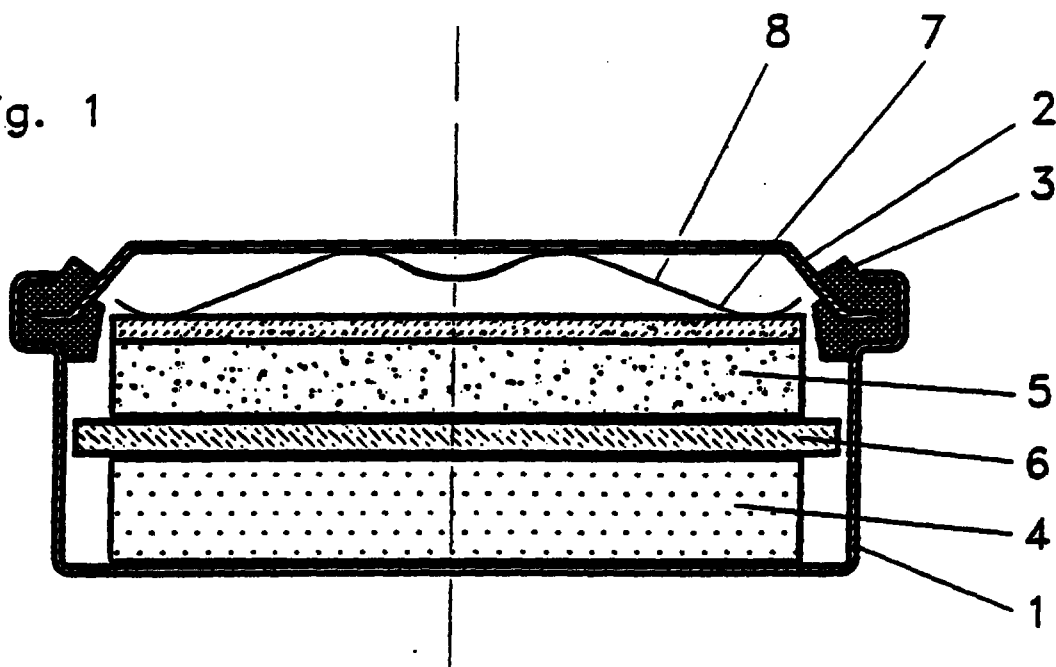


Fig. 1



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Fig. 3

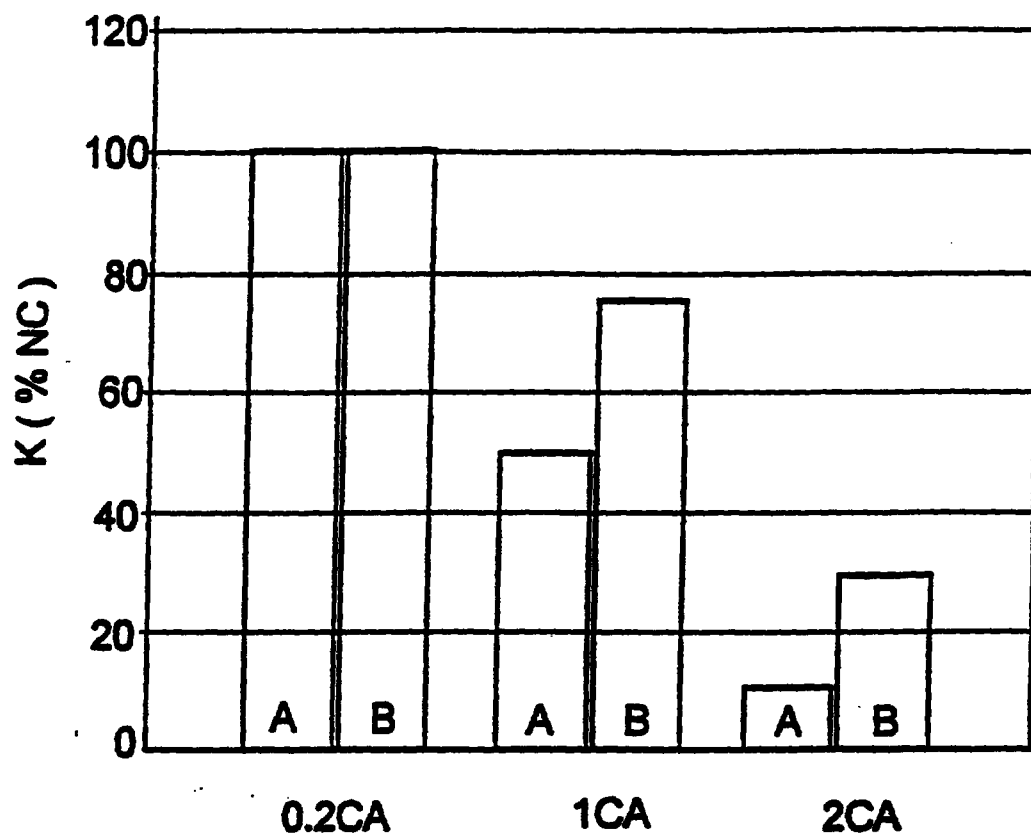
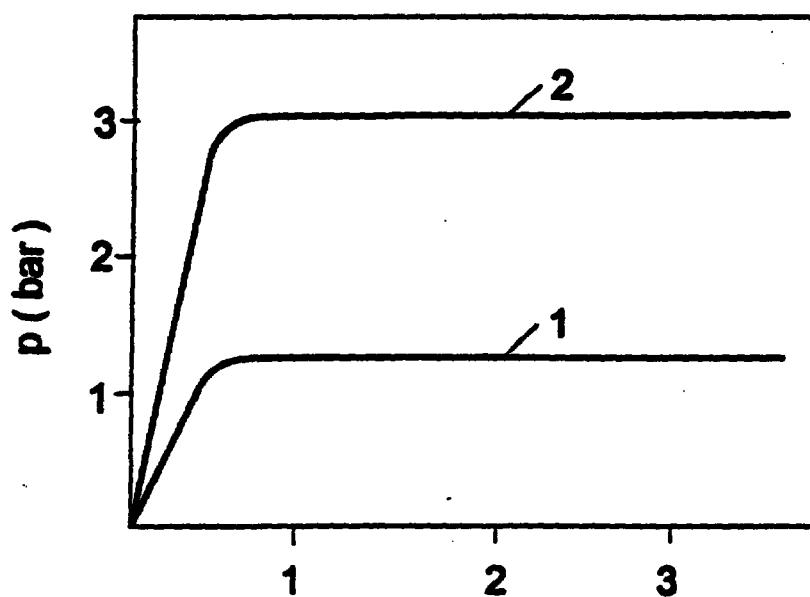


Fig. 4



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**Gastightly sealed metal oxide/metal hydride
storage battery**

The invention relates to a gastightly sealed metal oxide/metal hydride storage battery having positive
5 electrode which is disposed in the cell casing and comprises a metal oxide, having a negative electrode which comprises a hydrogen storage alloy, having a separator which is disposed between positive and negative electrode and contains an alkaline electrolyte, and
10 having an auxiliary electrode which maintains the oxygen consumption and is in electrically conducting contact with the negative electrode.

A preferred field of application of the invention are button cells of the Ni/metal hydride type because of
15 their efficiency and their established use in mains-independent appliances. However, their load-carrying capacity for high currents does not reach that of cylindrical cells. As a reason, a role may be played by the fact that the conductivity of the negative button-
20 cell electrode is relatively low. The lower conductivity is due to the proportion of a plastics binder in the mass mixture, which plastics binder is preferably composed of PTFE and may amount to 10%. On the other hand, the addition of the binder is necessary for reasons of
25 mechanical strength. It also imparts a hydrophobic nature to the mass and creates the condition for an adequate gas consumption in the event of overcharging and polarity reversal. Rechargeable, gastight metal oxide/hydride button cells in accordance with the
30 definition of the generic class formulated at the outset must be both capable of overcharging and proof against polarity reversal.

During the overcharging, oxygen is generated at the positive electrode and has to be consumed to avoid an
35 unacceptably high internal pressure. The means suitable for this purpose is an auxiliary electrode which is usually composed of a mixture of soot, graphite and PTFE and which is situated on the rear of the negative main

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electrode and is electrically short-circuited to the latter. The mechanism of the oxygen consumption can be described by the equation (1) $O_2 + 4e^- + 4 H_2O = 4 OH^-$.

5 A metal oxide/hydride button cell having an auxiliary electrode for the oxygen consumption can be found, for example, in German Offenlegungsschrift 39 29 306, Figure 4.

10 However, if a metal oxide/hydride storage battery enters polarity reversal after exhaustive discharge of the positive electrode, which generally limits the discharge, the positive electrode now develops hydrogen, which can be absorbed directly by the negative electrode, with conversion to metal hydride. However, this can take place only at a metallic surface which is in direct
15 communication with the gas phase. A liquid film at the metal surface impedes the hydrogen absorption considerably. The presence of a hydrophobic binder can keep the electrolyte away from parts of the electrode surface and thus facilitate the penetration of the
20 hydrogen into the interior of the negative mass.

German Offenlegungsschrift 40 29 503 also discloses an alkaline storage battery having a negative metal hydride electrode to whose active mass special catalysts composed of Raney nickel or Raney silver are
25 added specifically for the oxidation of the hydrogen produced in the event of polarity reversal.

Nevertheless, there remains the disadvantage of a reduced electrical conductivity, which is associated with the use of a hydrophobic binder. On the one hand,
30 in the case of mass electrodes, the binder ensures the cohesion and the hydrophobicity of the powder compact and, on the other hand, its action is that of an electrical insulator, with the result that a good protection against polarity reversal and a good current-carrying capacity are mutually exclusive.
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The object of the invention is to make available a storage battery, in particular in the form of a button cell, for the alkaline metal oxide/hydrogen system, which

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storage battery can be operated even at high currents without limiting its gastight function.

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

According to the invention, the auxiliary electrode normally provided in a metal oxide/metal hydride cell for the oxygen consumption also takes over the rapid conversion of the hydrogen in the case of a
10 polarity reversal since, like the negative main electrode, it has a hydrogen storage alloy as main component and is connected in an electrically conducting manner to the negative electrode of the cell and, in particular, rests directly against the rear of the
15 negative main electrode. The auxiliary electrode according to the invention can advantageously be used in cylindrical cells and prismatic cells and is particularly suitable for use in button cells.

The auxiliary electrode according to the invention is produced by mixing the said hydrogen storage alloy with a carbon-containing and simultaneously hydrophobizing material, preferably a mixture of graphite, soot and PTFE, in a high-speed knife mill. The resultant mixture is extremely fine-grained and
20 homogeneous. On the one hand, this provides for a multiplicity of three-phase boundaries which are required for the oxygen consumption and, on the other hand, numerous surfaces without electrolyte coverage are also presented to the hydrogen and make it possible for it to
25 penetrate the alloy particles rapidly.

According to the invention it has furthermore proved advantageous to produce the negative main electrode from a powder which contains, in addition to the hydrogen storage alloy as the important component,
35 also nickel metal or copper metal in powdered form as highly conductive components. Graphite may also be used as alternative conducting agent.

Furthermore, to improve the mechanical robustness



of the compact, the electrode mixture may contain a binder which is, however, hydrophilic, in contrast to the binder used in the auxiliary electrode, or at least has an only weakly expressed hydrophobic nature, for example polyvinyl alcohol or polyethylene.

As a result of joining a hydrophobic auxiliary electrode formed from a hydrogen storage alloy to a negative main electrode composed of the same hydrogen storage alloy which has a high electrical conductivity due to metal additives and an at least only weakly hydrophobic nature owing to a hydrophilic binder additive, an electrode combination is present which combines in itself the two capabilities, namely load-carrying capacity for high currents and prevention of a pressure buildup after a polarity reversal.

In particular, the novel auxiliary electrode permits in this connection - in contrast to the oxygen-consumption electrodes present in conventional Ni/hydride and NiCd cells - the removal both of the oxygen and of the hydrogen from the gas phase. A strong and permanent hydrophobic behaviour is indispensable for this dual function of the auxiliary electrode according to the invention.

It is based on a mass mixture of the following composition: 0 to 20% by weight of graphite, 0 to 20% by weight of soot, 0.5 to 10% by weight of PTFE, the remainder to 100% by weight being hydrogen storage alloy. A particularly advantageous mixture is composed of 0 to 4% by weight of graphite, 1 to 3% by weight of soot, 1 to 4% by weight of PTFE, the remainder to 100% by weight being hydrogen storage alloy.

The following mass mixtures are suitable for producing the negative main electrode:

1. 10 to 50% by weight, preferably 20 to 40% by weight, of Cu powder or Ni powder, 0 to 10% by weight, preferably 1 to 4% by weight, of hydrophilic binder, the remainder to 100% by weight being hydrogen storage alloy or

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2. 0 to 20% by weight, preferably 10 to 15% by weight, of graphite, 0 to 10% by weight, preferably 0.5 to 4% by weight, of hydrophilic binder, the remainder to 100% by weight being hydrogen storage alloy.

For the two alternative mass mixtures (metal powder or graphite as conducting agent), the content of alloy metal is approximately between 70 and 95% by weight.

- 10 Suitable as hydrogen storage material are alloys of the LaNi_5 type or TiNi type. Preferred are alloys of the LaNi_5 type in which lanthanum and/or other rare-earth elements form the misch-metal component of MmNi_5 alloys. An exemplary alloy has the composition $\text{MmNi}_{4.3-x}\text{Co}_x\text{Mn}_{0.3}\text{Al}_{0.4}$, where $0.2 < x < 0.7$.

- 15 Typical mass mixtures for the positive electrode contain, in addition to nickel hydroxide, metallic nickel and cobalt, graphite and cobalt oxide. These additives predominantly act as conducting material; the cobalt oxide additionally ensures an increase in the oxygen overvoltage at the positive electrode and consequently an increase in the charging efficiency.

- 20 The subject of the invention is explained in greater detail below by reference to the example of a button cell.

25 Figure 1 shows a Ni/hydride button cell according to the invention.

- Figure 2 shows the surface structure of an auxiliary electrode according to the invention in an enlargement.

30 Figure 3 shows discharge capacities of button cells according to the invention compared with standard cells.

- Figure 4 shows the establishment of the internal gas pressure of button cells according to the invention for different operating states.

35 According to Figure 1, the storage battery according to the invention does not differ in its



structure from a conventional Ni/hydride button cell having the casing can 1, the lid 2, the sealing ring 3, the positive nickel hydroxide electrode 4, the negative metal hydride electrode 5, the electrolyte-impregnated separator 6, the auxiliary electrode 7 for the oxygen consumption and the compression spring 8.

According to the invention and in contrast to the conventional design, the auxiliary electrode pressed against the back of the negative electrode is, however, also an alloy electrode and is strongly hydrophobic owing to a PTFE addition, whereas the negative electrode itself is hydrophilic.

The surface, shown enlarged in Figure 2, of the auxiliary electrode reveals individual metal hydride particles 9 which are partially wetted by an electrolyte film 10, but partially cemented to neighbouring particles by hydrophilic binder 11 (PTFE) and present large parts of their surface which are not covered by liquid electrolyte because of the water-repellent effect of the binder. At these points, H_2 can easily penetrate into the interior of the particles. It is absorbed by the alloy metal and thus removed from the gas space.

At other points, the conditions are in turn beneficial for an O_2 consumption as a result of the simultaneous presence of electrolyte, hydrophobic binder and exposed particle surface because said O_2 consumption is, in accordance with equation (1) in the introduction, this is possible only with the intervention of H_2O and in the electronic exchange with the solid alloy phase (three-phase relationship).

The superior high current-carrying capacity of button cells which are provided with negative electrodes according to the invention using Cu as conducting agent and with auxiliary electrodes according to the invention emerges from Figure 3.

The mass compositions of the test electrodes were within the scope of the formulations specified above. As is evident from the bar representations, the discharge



capacities K (in % of the nominal capacity NC) of the button cells (B) according to the invention were appreciably above those of standard production cells (A) at the high loads of $1C$ A and $2C$ A. An important reason
5 for the better high-current behaviour of the cells according to the invention is the lack of a hydrophobic binder in their negative electrodes, which is responsible for a more beneficial electronic conductivity.

Finally, the gas-consumption performance of the
10 novel auxiliary electrode is manifested in the behaviour of the internal cell gas pressure both in the case of overcharging and in the case of overdischarging. Thus, according to Figure 4, the internal pressure p [bar] of a 250 mAh button cell is only approximately 1 bar (curve
15 1) for an overcharging with $0.2C$ A. In the case of a polarity reversal, the internal pressure hardly exceeds 3 bar (curve 2) for the same current. Pressures of this magnitude are quite safe for the mechanical robustness of button cells.



Patent Claims

1. Gastightly sealed metal oxide/metal hydride storage battery having positive electrode which is disposed in the cell casing and comprises a metal oxide, having a negative electrode which comprises a hydrogen storage alloy, having a separator which is disposed between positive and negative electrode and contains an alkaline electrolyte, and having an auxiliary electrode which maintains the oxygen consumption and is in electrically conducting contact with the negative electrode, characterized in that the auxiliary electrode contains a hydrogen storage alloy as the agent which maintains the gas consumption in the event of overcharging and polarity reversal and in that the auxiliary electrode is connected in an electrically conducting manner to the negative electrode.
2. Gastightly sealed storage battery according to Claim 1, characterized in that the auxiliary electrode rests directly against the rear of the negative electrode.
3. Gastightly sealed storage battery according to Claim 1 or 2, characterized in that a hydrophobic binder is added to the alloy material of the auxiliary electrode and a hydrophilic binder is added to the alloy material of the negative electrode.
4. Gastightly sealed storage battery according to one of Claims 1 to 3, characterized in that, optionally, one of the conducting agents Cu powder, Ni powder or graphite is added to the alloy material of the negative electrode.
5. Gastightly sealed storage battery according to one of Claims 1 to 4, characterized in that, in addition to graphite and soot, PTFE is added to the alloy material





of the auxiliary electrode as binder.

6. Gastightly sealed storage battery according to one of Claims 1 to 5, characterized in that the mass mixture on which the auxiliary electrode is based is composed of 0 to 20% by weight of graphite, 0 to 20% by weight of soot, 0.5 to 10% by weight of PTFE, the remainder to 100% by weight being hydrogen storage alloy.

7. Gastightly sealed storage battery according to Claim 6, characterized in that the mass mixture on which the auxiliary electrode is based is composed of 0 to 4% by weight of graphite, 1 to 3% by weight of soot, 1 to 4% by weight of PTFE, the remainder to 100% by weight being hydrogen storage alloy.

8. Gastightly sealed storage battery according to one of Claims 1 to 7, characterized in that the mass mixture on which the negative electrode is based is composed of 10 to 50% by weight of Cu powder or Ni powder, 0 to 10% by weight of hydrophilic binder, the remainder to 100% by weight being hydrogen storage alloy.

9. Gastightly sealed storage battery according to Claim 8, characterized in that the mass mixture on which the negative electrode is based is composed of 20 to 40% by weight of Cu powder or Ni powder, 1 to 4% by weight of hydrophilic binder, the remainder to 100% by weight being hydrogen storage alloy.

10. Gastightly sealed storage battery according to one of Claims 1 to 7 characterized in that the mass mixture on which the negative electrode is based is composed of 0 to 20% by weight of graphite, preferably 10 to 15% by weight of graphite, 0 to 10% by weight, preferably 0.5 to 4% by weight, of hydrophilic binder, the remainder to 100% by weight being hydrogen storage alloy.



Fig. 2

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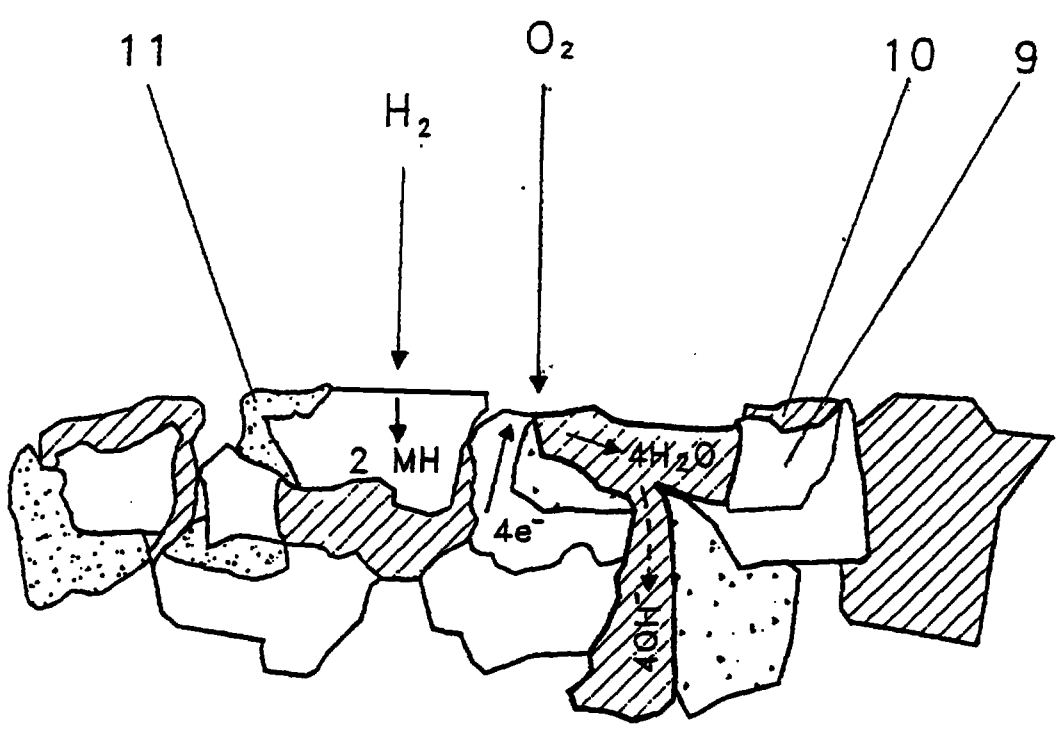


Fig. 1

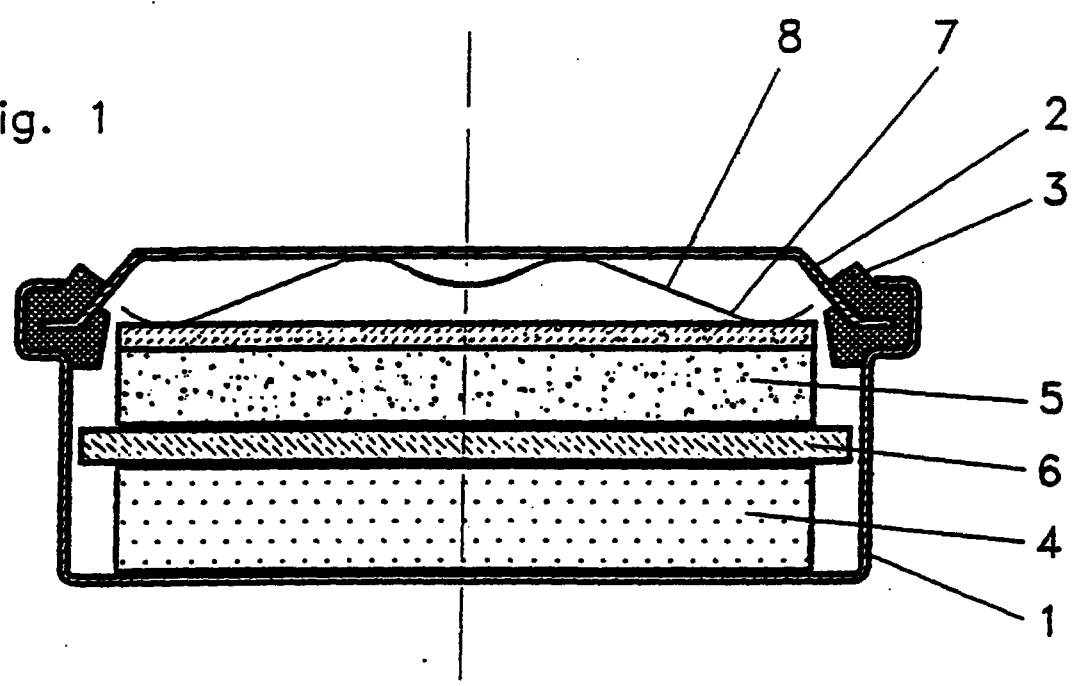


Fig. 3

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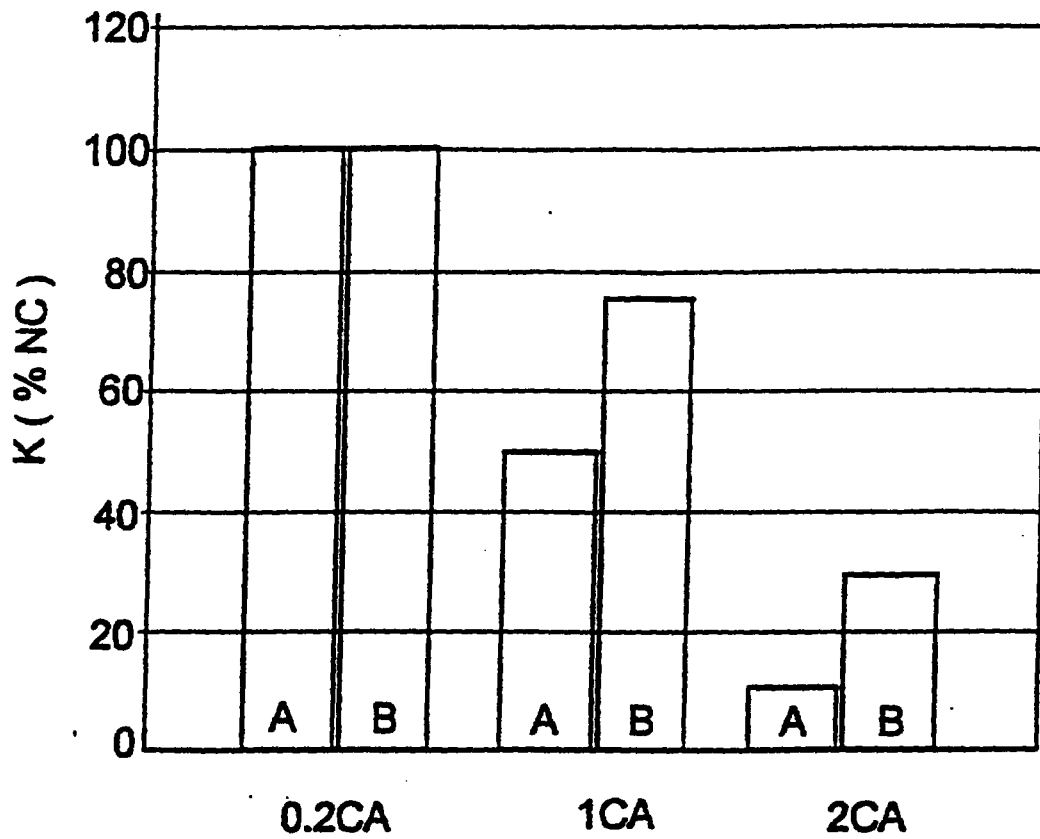
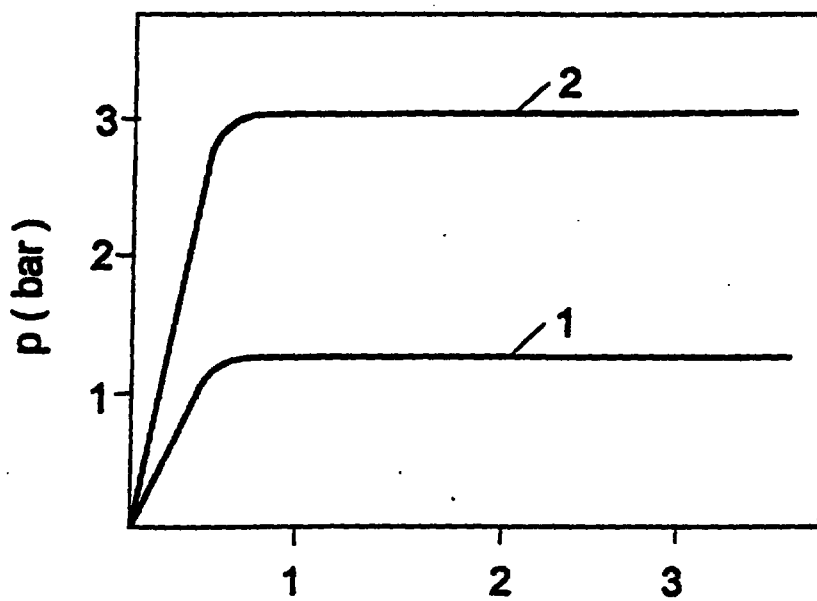


Fig. 4





**Gastightly sealed metal oxide/metal hydride
storage battery**

In a gastightly sealed metal oxide/metal hydride button storage battery, in particular a nickel/metal hydride button cell, the active material of an auxiliary electrode is composed of the same hydrogen storage alloy as that of the negative electrode, to which the auxiliary electrode is electrically short-circuited. As a result, the auxiliary electrode can maintain both the oxygen consumption and, in the event of polarity reversal of the cell, the hydrogen consumption. As a result of a strongly hydrophobic adjustment of the auxiliary electrode and an only weakly hydrophobic or hydrophilic adjustment of the negative electrode by means of hydrophobic or hydrophilic binder additions, respectively, and as a result of adding highly conducting metal powder (Cu or Ni) to the mass of the negative electrode, a high gas-consumption rate in the event of overcharging and polarity reversal and simultaneously a good discharge capacity are obtained even at high currents (up to 2C A). The internal cell pressure of a 250 mAh button cell does not exceed 3 bar either during overcharging or during overdischarging at 0.2C A (= 50 mA) and is consequently not critical.

Figure 1

Gastightly sealed metal oxide/metal hydride
storage battery

The invention relates to a gastightly sealed metal oxide/metal hydride storage battery having positive
5 electrode which is disposed in the cell casing and comprises a metal oxide, having a negative electrode which comprises a hydrogen storage alloy, having a separator which is disposed between positive and negative electrode and contains an alkaline electrolyte, and
10 having an auxiliary electrode which maintains the oxygen consumption and is in electrically conducting contact with the negative electrode.

A preferred field of application of the invention are button cells of the Ni/metal hydride type because of
15 their efficiency and their established use in mains-independent appliances. However, their load-carrying capacity for high currents does not reach that of cylindrical cells. As a reason, a role may be played by the fact that the conductivity of the negative button-
20 cell electrode is relatively low. The lower conductivity is due to the proportion of a plastics binder in the mass mixture, which plastics binder is preferably composed of PTFE and may amount to 10%. On the other hand, the addition of the binder is necessary for reasons of
25 mechanical strength. It also imparts a hydrophobic nature to the mass and creates the condition for an adequate gas consumption in the event of overcharging and polarity reversal. Rechargeable, gastight metal oxide/hydride button cells in accordance with the
30 definition of the generic class formulated at the outset must be both capable of overcharging and proof against polarity reversal.

During the overcharging, oxygen is generated at the positive electrode and has to be consumed to avoid an unacceptably high internal pressure. The means suitable for this purpose is an auxiliary electrode which is usually composed of a mixture of soot, graphite and PTFE and which is situated on the rear of the negative main electrode and is electrically short-circuited to the latter. The mechanism of the oxygen consumption can be described by the equation (1) $O_2 + 4e^- + 4 H_2O = 4 OH^-$.

10 A metal oxide/hydride button cell having an auxiliary electrode for the oxygen consumption can be found, for example, in German Offenlegungsschrift 39 29 306, Figure 4.

However, if a metal oxide/hydride storage battery enters polarity reversal after exhaustive discharge of the positive electrode, which generally limits the discharge, the positive electrode now develops hydrogen, which can be absorbed directly by the negative electrode, with conversion to metal hydride. However, this can take place only at a metallic surface which is in direct communication with the gas phase. A liquid film at the metal surface impedes the hydrogen absorption considerably. The presence of a hydrophobic binder can keep the electrolyte away from parts of the electrode surface and thus facilitate the penetration of the hydrogen into the interior of the negative mass.

German Offenlegungsschrift 40 29 503 also discloses an alkaline storage battery having a negative metal hydride electrode to whose active mass special catalysts composed of Raney nickel or Raney silver are added specifically for the oxidation of the hydrogen produced in the event of polarity reversal.

Nevertheless, there remains the disadvantage of a reduced electrical conductivity, which is associated with the use of a hydrophobic binder. On the one hand, in the case of mass electrodes, the binder ensures the cohesion and the hydrophobicity of the powder compact and, on the other hand, its action is that of an electrical insulator, with the result that a good protection against polarity reversal and a good current-carrying capacity are mutually exclusive.

10 The object of the invention is to make available a storage battery, in particular in the form of a button cell, for the alkaline metal oxide/hydrogen system, which storage battery can be operated even at high currents without limiting its gastight function.

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

 According to the invention, the auxiliary electrode normally provided in a metal oxide/metal hydride cell for the oxygen consumption also takes over the rapid conversion of the hydrogen in the case of a polarity reversal since, like the negative main electrode, it has a hydrogen storage alloy as main component and is connected in an electrically conducting manner to the negative electrode of the cell and rests directly against the rear of the negative main electrode.

 The auxiliary electrode according to the invention can advantageously be used in cylindrical cells and prismatic cells and is particularly suitable for use in button cells.

30 The auxiliary electrode according to the invention is produced by mixing the said hydrogen storage alloy with a carbon-containing and simultaneously

hydrophobizing material, preferably a mixture of graphite, soot and PTFE, in a high-speed knife mill. The resultant mixture is extremely fine-grained and homogeneous. On the one hand, this provides for a multiplicity of three-phase boundaries which are required for the oxygen consumption and, on the other hand, numerous surfaces without electrolyte coverage are also presented to the hydrogen and make it possible for it to penetrate the alloy particles rapidly.

10 According to the invention it has furthermore proved advantageous to produce the negative main electrode from a powder which contains, in addition to the hydrogen storage alloy as the important component, also nickel metal or copper metal in powdered form as highly conductive components. Graphite may also be used as alternative conducting agent.

Furthermore, to improve the mechanical robustness of the compact, the electrode mixture may contain a binder which is, however, hydrophilic, in contrast to the binder used in the auxiliary electrode, or at least has an only weakly expressed hydrophobic nature, for example polyvinyl alcohol or polyethylene.

As a result of joining a hydrophobic auxiliary electrode formed from a hydrogen storage alloy to a negative main electrode composed of the same hydrogen storage alloy which has a high electrical conductivity due to metal additives and an at least only weakly hydrophobic nature owing to a hydrophilic binder additive, an electrode combination is present which combines in itself the two capabilities, namely load-carrying capacity for high currents and prevention of a pressure buildup after a polarity reversal.

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In particular, the novel auxiliary electrode permits in this connection - in contrast to the oxygen-consumption electrodes present in conventional Ni/hydride and NiCd cells - the removal both of the oxygen and of the hydrogen from the gas phase. A strong and permanent hydrophobic behaviour is indispensable for this dual function of the auxiliary electrode according to the invention.

It is based on a mass mixture of the following composition: 0 to 20% by weight of graphite, 0 to 20% by weight of soot, 0.5 to 10% by weight of PTFE, the remainder to 100% by weight being hydrogen storage alloy.

A particularly advantageous mixture is composed of 0 to 4% by weight of graphite, 1 to 3% by weight of soot, 1 to 4% by weight of PTFE, the remainder to 100% by weight being hydrogen storage alloy.

The following mass mixtures are suitable for producing the negative main electrode:

1. 10 to 50% by weight, preferably 20 to 40% by weight, of Cu powder or Ni powder, 0 to 10% by weight, preferably 1 to 4% by weight, of hydrophilic binder, the remainder to 100% by weight being hydrogen storage alloy or
2. 0 to 20% by weight, preferably 10 to 15% by weight, of graphite, 0 to 10% by weight, preferably 0.5 to 4% by weight, of hydrophilic binder, the remainder to 100% by weight being hydrogen storage alloy.

For the two alternative mass mixtures (metal powder or graphite as conducting agent), the content of alloy metal is approximately between 70 and 95% by weight.

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Suitable as hydrogen storage material are alloys of the LaNi_5 type or TiNi type. Preferred are alloys of the LaNi_5 type in which lanthanum and/or other rare-earth elements form the misch-metal component of MmNi_5 alloys.

5 An exemplary alloy has the composition $\text{MmNi}_{4.3-x}\text{Co}_x\text{Mn}_{0.3}\text{Al}_{0.4}$, where $0.2 < x < 0.7$.

Typical mass mixtures for the positive electrode contain, in addition to nickel hydroxide, metallic nickel and cobalt, graphite and cobalt oxide. These additives
10 predominantly act as conducting material; the cobalt oxide additionally ensures an increase in the oxygen overvoltage at the positive electrode and consequently an increase in the charging efficiency.

The subject of the invention is explained in
15 greater detail below by reference to the example of a button cell.

Figure 1 shows a Ni/hydride button cell according to the invention.

Figure 2 shows the surface structure of an auxiliary
20 electrode according to the invention in an enlargement.

Figure 3 shows discharge capacities of button cells according to the invention compared with standard cells.

25 Figure 4 shows the establishment of the internal gas pressure of button cells according to the invention for different operating states.

According to Figure 1, the storage battery according to the invention does not differ in its
30 structure from a conventional Ni/hydride button cell having the casing can 1, the lid 2, the sealing ring 3, the positive nickel hydroxide electrode 4, the negative metal hydride electrode 5, the electrolyte-impregnated

separator 6, the auxiliary electrode 7 for the oxygen consumption and the compression spring 8.

According to the invention and in contrast to the conventional design, the auxiliary electrode pressed
5 against the back of the negative electrode is, however, also an alloy electrode and is strongly hydrophobic owing to a PTFE addition, whereas the negative electrode itself is hydrophilic.

The surface, shown enlarged in Figure 2, of the
10 auxiliary electrode reveals individual metal hydride particles 9 which are partially wetted by an electrolyte film 10, but partially cemented to neighbouring particles by hydrophilic binder 11 (PTFE) and present large parts
15 of their surface which are not covered by liquid electrolyte because of the water-repellent effect of the binder. At these points, H_2 can easily penetrate into the interior of the particles. It is absorbed by the alloy metal and thus removed from the gas space.

At other points, the conditions are in turn
20 beneficial for an O_2 consumption as a result of the simultaneous presence of electrolyte, hydrophobic binder and exposed particle surface because said O_2 consumption is, in accordance with equation (1) in the introduction, this is possible only with the intervention of H_2O and in
25 the electronic exchange with the solid alloy phase (three-phase relationship).

The superior high current-carrying capacity of button cells which are provided with negative electrodes according to the invention using Cu as conducting agent
30 and with auxiliary electrodes according to the invention emerges from Figure 3.

The mass compositions of the test electrodes were within the scope of the formulations specified above. As

is evident from the bar representations, the discharge capacities K (in % of the nominal capacity NC) of the button cells (B) according to the invention were appreciably above those of standard production cells (A) at the high loads of $1C$ A and $2C$ A. An important reason for the better high-current behaviour of the cells according to the invention is the lack of a hydrophobic binder in their negative electrodes, which is responsible for a more beneficial electronic conductivity.

10 Finally, the gas-consumption performance of the novel auxiliary electrode is manifested in the behaviour of the internal cell gas pressure both in the case of overcharging and in the case of overdischarging. Thus, according to Figure 4, the internal pressure p [bar] of a

15 250 mAh button cell is only approximately 1 bar (curve 1) for an overcharging with $0.2C$ A. In the case of a polarity reversal, the internal pressure hardly exceeds 3 bar (curve 2) for the same current. Pressures of this magnitude are quite safe for the mechanical robustness of

20 button cells.

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Patent Claims

1. Gastightly sealed metal oxide/metal hydride
10 storage battery having positive electrode which is
disposed in the cell casing and comprises a metal oxide,
having a negative electrode which comprises a hydrogen
storage alloy, having a separator which is disposed
15 between positive and negative electrode and contains an
alkaline electrolyte, and having an auxiliary electrode
which maintains the oxygen consumption and is in
electrically conducting contact with the negative
electrode, characterized in that the auxiliary electrode
contains a hydrogen storage alloy as the agent which
20 maintains the gas consumption in the event of
overcharging and polarity reversal and in that the
auxiliary electrode is connected in an electrically
conducting manner to the negative electrode and further
in that the auxiliary electrode rests directly against
25 the rear of the negative electrode and in that a
hydrophobic binder is added to the alloy material of the
auxiliary electrode and a hydrophilic binder is added to
the alloy material of the negative electrode.
2. Gastightly sealed storage battery according to
30 Claim 1, characterized in that, optionally, one of the
conducting agents Cu powder, Ni powder or graphite is
added to the alloy material of the negative electrode.
3. Gastightly sealed storage battery according to
Claim 1 or 2, characterized in that, in addition to
35 graphite and soot, PTFE is added to the alloy material of
the auxiliary electrode as binder.





4. Gastightly sealed storage battery according to one of Claims 1 to 3, characterized in that the mass mixture on which the auxiliary electrode is based is composed of 0 to 20% by weight of graphite, 0 to 20% by weight of soot, 0.5 to 10% by weight of PTFE, the remainder to 100% by weight being hydrogen storage alloy.
5. Gastightly sealed storage battery according to Claim 4, characterized in that the mass mixture on which the auxiliary electrode is based is composed of 0 to 4% by weight of graphite, 1 to 3% by weight of soot, 1 to 4% by weight of PTFE, the remainder to 100% by weight being hydrogen storage alloy.
6. Gastightly sealed storage battery according to one of Claims 1 to 5, characterized in that the mass mixture on which the negative electrode is based is composed of 10 to 50% by weight of Cu powder or Ni powder, 0 to 10% by weight of hydrophilic binder, the remainder to 100% by weight being hydrogen storage alloy.
7. Gastightly sealed storage battery according to Claim 6, characterized in that the mass mixture on which the negative electrode is based is composed of 20 to 40% by weight of Cu powder or Ni powder, 1 to 4% by weight of hydrophilic binder, the remainder to 100% by weight being hydrogen storage alloy.
8. Gastightly sealed storage battery according to one of Claims 1 to 7, characterized in that the mass mixture on which the negative electrode is based is composed of 0 to 20% by weight of graphite, preferably 10 to 15% by weight of graphite, 0 to 10% by weight, preferably 0.5 to 4% by weight, of hydrophilic binder, the remainder to 100% by weight being hydrogen storage alloy.



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Abstract

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In a gastightly sealed metal oxide/metal hydride button storage battery, in particular a nickel/metal hydride button cell, the active material of an auxiliary electrode is composed of the same hydrogen storage alloy as that of the negative electrode, to which the auxiliary electrode is electrically short-circuited. As a result, the auxiliary electrode can maintain both the oxygen consumption and, in the event of polarity reversal of the cell, the hydrogen consumption. As a result of a strongly hydrophobic adjustment of the auxiliary electrode and an only weakly hydrophobic or hydrophilic adjustment of the negative electrode by means of hydrophobic or hydrophilic binder additions, respectively, and as a result of adding highly conducting metal powder (Cu or Ni) to the mass of the negative electrode, a high gas-consumption rate in the event of overcharging and polarity reversal and simultaneously a good discharge capacity are obtained even at high currents (up to 2C A). The internal cell pressure of a 250 mAh button cell does not exceed 3 bar either during overcharging or during overdischarging at 0.2C A (= 50 mA) and is consequently not critical.

Figure 1