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Patent claims

1. Alkaline metal oxide/metal hydride battery,
10 having a positive electrode which contains a metal oxide,
and a negative electrode which is formed by a hydrogen
storage alloy material that comprises, in addition to
misch metal, the elements nickel and cobalt and has the
CaCu₅ type crystal structure, characterized in that a
15 part of the cobalt in the alloy is replaced by iron
and/or copper, and in that it has the composition

$MmNi_vAl_wMn_xCo_yM_z$ with Mm = misch metal, with M =
Fe and/or Cu and with the parameters

- 20 $0.2 \leq x \leq 0.4$
 $0.1 \leq z \leq 0.4$
 $0.2 \leq y \leq 0.4$
 $0.3 \leq w \leq 0.5$
 $4.9 \leq v + w + x + y + z \leq 5.1.$

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2. Alkaline metal oxide/metal hydride battery
25 according to Claim 1, characterized in that the misch
metal has an La content of from 25 to 60% by weight,
preferably from 40 to 60% by weight, the remainder to
100% by weight being predominantly Ce and other rare-
earth metals.
- 30 3. Alkaline metal oxide/metal hydride battery
according to one of Claims 1 to 2, characterized in that



the positive electrode is a nickel hydroxide electrode.

4. Alkaline metal oxide/metal hydride battery according to Claim 3, characterized in that the nickel hydroxide electrode is of the foamed-metal electrode type.

5. Process for the production of a negative hydrogen storage alloy electrode for an alkaline metal oxide/metal hydride battery according to Claim 1, characterized in that the molten alloy is atomized and the collected material is heat-treated and pulverized in subsequent steps and, if appropriate with the addition of a binder, is applied onto an electrode support.

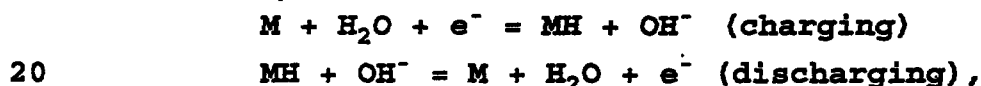
6. Process according to Claim 5, characterized in that the heat-treatment is carried out for 2 h to 4 h at 700°C to 900°C under vacuum.

Alkaline metal oxide/metal hydride battery

The invention relates to an alkaline metal oxide/metal hydride battery, having a positive electrode which contains a metal oxide, and a negative electrode which is formed by a hydrogen storage alloy material that comprises, in addition to misch metal, the elements nickel and cobalt and has the CaCu_5 type crystal structure.

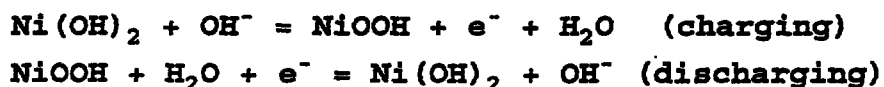
Cells of the rechargeable metal oxide/metal hydride system generally prove superior to conventional accumulator cells of the lead/acid or nickel/cadmium system. The superiority is primarily based upon the significantly better charge acceptance capability of the hydrogen storage negative electrode compared to that of a negative lead or cadmium electrode.

Hydrogen storage by the active material M of the negative metal hydride electrode takes place reversibly according to the scheme



a hydride MH being formed by the charging current with decomposition of water, whereas during discharging, hydrogen is liberated and binds to OH^- ions to form H_2O . A current flowing in the external circuit of the cell corresponds to the electron which is simultaneously released.

The positive partner of the negative hydrogen storage or metal hydride electrode is generally a nickel hydroxide electrode, at which the following reversible reactions take place:



Both electrodes are separated by a separator in the alkaline electrolyte.

In the multiplicity of metal oxide/metal hydride batteries which, in particular, are also included in the generic type formulated at the outset, the electrochemically active material of the negative
5 electrode is derived from an intermetallic compound LaNi_5 , in which both part of the lanthanum and part of the nickel is replaced by other metals, but without the ability to form a metal hydride being thereby reduced.

For example, a part of the lanthanum can be
10 replaced by other rare-earth metals, and a part of the nickel can be replaced by metals such as cobalt, aluminium, manganese, iron or chromium.

In the literature, all of these alloys are assigned, according to their representative, LaNi_5 , to an
15 AB_5 type. It has a CaCu_5 structure.

In contrast, other hydrogen storage alloys having titanium and/or zirconium and nickel as essential components belong to the AB and AB_2 types (TiNi and ZrNi_2).

In the case of alloys derived from LaNi_5 , the La
20 is customarily replaced by a so-called misch metal (Mm) which contains, in particular, La, Ce and other rare-earth metals. The substitution of nickel by other metals is usually carried out with the purpose of reducing the equilibrium pressure of hydrogen in the cell.

A plurality of such alloys is already known from
25 the patent literature. For example, US Patent 5008164 discloses an alloy of general composition $\text{MmNi}_a\text{Co}_b\text{Mn}_c$, in which $2.5 < a < 3.5$. By partial replacement of one of the substituents to form an alloy $\text{MmNi}_a\text{Co}_b\text{Mn}_c\text{X}_d$, it being
30 possible to select X from the group Fe, Cu, Mo, W, B, Al, Si and Sn, a 5-component B-part of the AB_5 alloy is formed from the 4-component B-part.

A large number of concrete examples for alloy compositions can be found in EP-A-206,776 (for example
35 $\text{MnNi}_{3.7}\text{Co}_{0.5}\text{Mn}_{0.6}\text{Al}_{0.2}$) or in EP-B-271,043 (for example $\text{MnNi}_{3.95}\text{Al}_{0.3}\text{Co}_{0.75}$). An alloy which likewise belongs to the prior art and is used in practice has the composition $\text{MmNi}_{4.3-y}\text{Co}_y\text{Al}_{0.4}\text{Mn}_{0.3}$ ($0.3 \leq y \leq 0.7$).

Finally, a preparation process, referred to as

gas atomization, for a hydrogen storage alloy powder is also disclosed in EP 420,669. In this process, argon gas jets from nozzles are directed perpendicularly against a pressurized liquid jet of the alloy that flows out of a melting vessel. The result is atomization of the molten material to form spherical particles, the surfaces of which can cool in a free environment and are collected at the bottom of a cooling chamber.

The problem underlying the invention is that, although known storage alloys with low cobalt contents do have a good current-loading capacity, even at low temperatures, a high cycle lifetime can, however, only be achieved with higher cobalt content. The scarcity and high price of this raw material constitutes a difficulty in this regard.

The object of the invention is therefore, starting from the latter alloy composition, to make available a modified alloy material which leads to a lengthening of the cycle lifetime while containing the lowest possible proportion of cobalt.

The object is achieved according to the invention with a metal oxide/metal hydride battery having a hydrogen storage alloy as active material of the negative electrode, as it is defined in Patent Claim 1.

Accordingly, these expectations are fulfilled by an alloy



in which Mm is a misch metal having an La content of from 25 to 60% by weight, preferably from 40 to 60% by weight, the remainder to 100% by weight being predominantly Ce, and M is one of the metals Cu or Fe, or mixtures thereof. According to the invention, the proportions of the individual components can vary within the limits

$0.1 \leq z \leq 0.4$; $0.2 \leq y \leq 0.4$; $0.3 \leq w \leq 0.5$;
 $0.2 \leq x \leq 0.4$ and $4.9 \leq v + w + x + y + z \leq 5.1$.

In addition to lanthanum, the misch metal contains, in particular, Ce (more than 25% by weight) as well as Pr and Nd. When Cu and Fe are used, the preferred Cu/Fe ratio is in the range of $0.5 \leq \text{Cu/Fe} \leq 2$.

5 As has been ascertained in tests with the alloy series



the cycle lifetime of cells can, if an alloy material with the substituents Cu and/or Fe for part of the cobalt
10 is used for their negative electrode, be considerably increased compared to a conventional hydrogen storage alloy $\text{MmNi}_{4.3-y}\text{Co}_y\text{Al}_{0.4}\text{Mn}_{0.3}$ ($0.3 \leq y \leq 0.7$) which has the same low cobalt content $y = 0.3$. The use of Si, V, Sn or Cr instead of Fe or Cu results in low capacities or
15 shorter cycle lifetimes.

It is particularly advantageous to produce the alloys according to the invention by atomization of the molten alloys and subsequent heat-treatment and pulverization. The heat-treatment is preferably carried
20 out with temperatures of 700°C to 900°C for a period of several hours, for example 2 h to 4 h.

Size AA Ni/H cells were used for electrical tests and alloys with composition according to the invention were used for their negative electrodes. Cells for
25 comparison contained negative electrodes made from the conventional alloy.

The alloy samples were produced either according to the conventional scheme: melting the starting metals, casting 12 h heat-treatment at 1000°C in a vacuum
30 furnace, pulverizing, < 75 μm particle-size screening, or according to the invention by atomization of the molten alloy, heat-treatment and pulverization. According to their X-ray diffraction patterns, all samples are shown to be monophase and exhibit exclusively the typical peaks
35 of the CaCu_5 structure.

In the further processing to form negative electrodes, the alloys were rolled on an Ni perforated

plate after admixing carbon and a polytetrafluoroethylene binder.

Ni foam electrodes, which were obtained by pasting nickel hydroxide into an Ni foam frame were used
5 as positive electrodes. The paste was composed of 90% spherical nickel hydroxide and, for the remaining part, of CoO, binder (polytetrafluoroethylene) and water.

The separators were commercially available types made of, for example, polyamide nonwoven.

10 The electrolyte consisted of 6.5 molar KOH and 0.5 molar LiOH solution, in a proportion of 2.1 ml/cell.

At the start of the actual cycling, all of the cells were conditioned (run in) under the following conditions:

15 1 x (Charging for 15 h with 0.1 C; storage for 24 h at 60°C; discharging with 0.2 C to final voltage 1 V).

3 x (Charging for 7 h with 0.2 C; waiting for 0.25 h. Discharging with 0.2 C to final voltage 0.9 V).

20 The result of the cycling tests is recorded in a figure which shows the discharging capacities C (Ah) as a function of the cycle number n.

The curve referenced 1 relates to a conventional alloy with cobalt content Co_{0.3}, and the curve referenced 2 relates to another conventional alloy with cobalt
25 content Co_{0.7}. The clearly very good cycle lifetime of this known material is, however, obtained at the cost of using a correspondingly large amount of cobalt.

Alloys a (with M = Cu) or b (with M = Fe) according to the invention are clearly superior to the
30 known alloy 1 with regard to the lifetime behaviour.

Moreover, alloys according to the invention have cycle lifetimes very close to the conventional, Co-rich alloy 2, even in spite of their low cobalt content, if gas atomization is employed in their production and they
35 are subjected to the following process steps: melting, atomization, < 125 µm screening of the spherical particles

thus obtained, 3 h heat-treatment at 800°C in a vacuum furnace, pulverization. In this case it is essential according to the invention that the atomization be carried out in conjunction with the following steps of heat-treatment and pulverization. Curves A (M = Cu) and B (M = Fe) relate to alloys which indeed have this particularly advantageous production method.

Both the atomization and the subsequent heat-treatment and pulverization contribute considerably to the capacity and cycle lifetime, and because of these treatment steps the cycle lifetime is considerably higher than in the case of the conventionally produced samples a and b.

The special nature of the alloys produced according to the invention by atomization, heat-treatment and pulverization resides in the fact that their powder particles are spherically shaped and, under a scanning electron microscopy (SEM), exhibit a cell-type substructure. The substructures are separated from one another by boundary regions. These boundary regions, which constitute up to approximately 20% by volume of a particle, differ significantly in chemical composition (and probably also in crystallographic ordering) from the substructures. It is suspected that the boundary regions only have a low hydrogen storage capacity. The effect of the heat-treatment is to decompose the boundary regions to some extent by diffusion processes, which is probably the reason for the increase in capacity. The effect of pulverizing the heat-treated spherical particle is that the spherical shape is broken up. The particles in the electrodes therefore have better electrical contact with one another with the result of more efficient use of material and therefore further increased capacity.

The essential advantage of the invention is therefor that expensive cobalt can be replaced when using the new Cu- or Fe- containing hydrogen storage alloys. Ni/H cells equipped with this negative electrode material can achieve virtually the same cycle lifetime (approximately 1000 cycles) as cells with conventional

alloys, the cobalt content of which is approximately twice as great. With conventional alloys which contain approximately the same low quantity of Co as the alloys according to the invention, it is only possible to
5 achieve cycle lifetimes in the region of approximately 400 cycles. This is not sufficient for commercial application. On the other hand, the practical requirements for loading capacity of the cells are fully satisfied by the conventional alloys with low cobalt
10 content. The alloys according to the invention are in no way inferior to them in this regard, i.e. partial substitution of the cobalt by Cu or Fe does not necessarily lead to losses in capacity at higher loading. As measurements of the discharge capacities under
15 different loading levels from 1 C to 5 C have shown, at higher loadings levels (around 3 C) these capacities are in fact approximately 10% higher than the capacity values which are achieved with conventional alloys. Alloys according to the invention have a less sensitive reaction
20 in regard to their capacity behaviour to loading changes. Other properties such as self-discharge or pressure behaviour are also not detrimentally affected compared to conventional alloys.
