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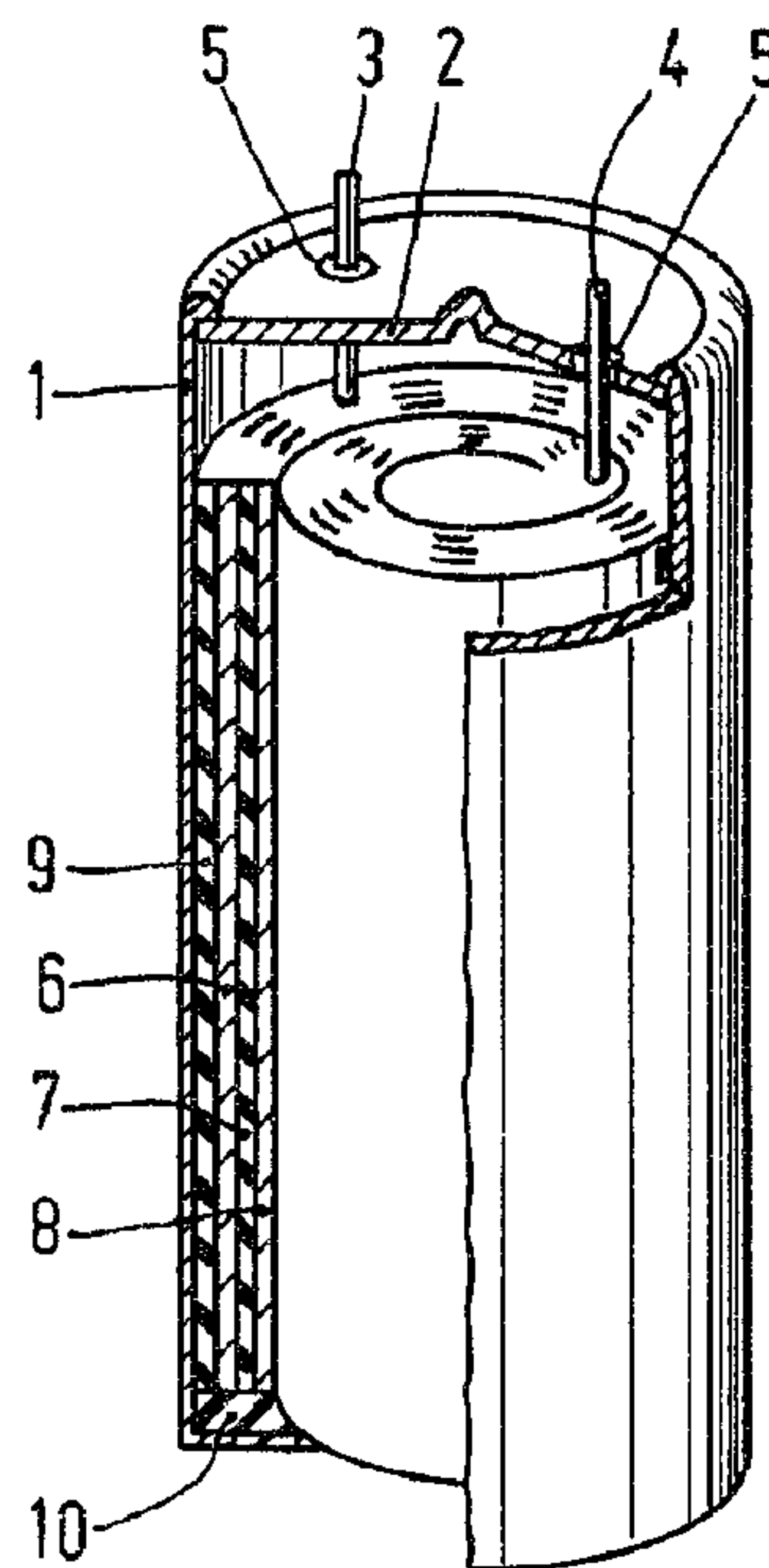
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(54) Titre : CELLULE ELECTROCHIMIQUE

(54) Title: ELECTROCHEMICAL CELL



(57) **Abrégé/Abstract:**

The invention relates to an electrochemical cell comprising a negative electrode of a stable hydride-forming material, in which a large loading capacity at low temperature is obtained by the addition of a catalytic material of the type DE_3 , wherein D is one or more of the elements selected from Cr, Mo and W, and wherein E represents Ni and/or Co. The catalytic material can be provided in the form of a eutectic segregation or it can be provided at the surface of powdered hydride-forming material by means of an electrochemical reaction.

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ABSTRACT:

"Electrochemical cell."

The invention relates to an electrochemical cell comprising a negative electrode of a stable hydride-forming material, in which a large loading capacity at low temperature is obtained by the addition of a catalytic material of the type DE_3 , wherein D is one or
5 more of the elements selected from Cr, Mo and W, and wherein E represents Ni and/or Co.

The catalytic material can be provided in the form of a eutectic segregation or it can be provided at the surface of powdered hydride-forming material by means of an electrochemical reaction.

Fig.

"Electrochemical cell."

The invention relates to an electrochemical cell comprising a negative electrode whose electrochemically active material consists of an intermetallic compound which forms a hydride with hydrogen and which has the CaCu_5 -structure, and of a catalytic
5 material at the surface of which hydrogen exhibits a large electrochemical activity.

The invention also relates to an electrochemically active material for use in such a cell and to a method of manufacturing such a material.

10 The electrochemical cell may be in open communication with the atmosphere or may be sealed from the atmosphere. A cell which is sealed from the atmosphere may comprise a valve which is dimensioned such that it becomes operative at a predetermined pressure.

In a rechargeable cell of the sealed type, the
15 electrochemically active part of the positive electrode consists of, for example, nickel hydroxide, silver oxide or manganese oxide, nickel hydroxide being generally preferred for practical reasons.

An electrolyte is used in the cell, which generally consists of an aqueous solution of one or more alkali hydroxides such
20 as lithium hydroxide, sodium hydroxide and potassium hydroxide, having a pH in excess of 7.

The cell may further comprise a separator which separates the electrodes electrically, but permits transport of ions and gas. The separator may consist of synthetic resin fibres
25 (woven or non woven), for example, of polyamide fibres or polypropylene fibres.

Such an electrochemical cell is described in European Patent Application EP-A1-0251384. In said Application, one or more of the metals Pd, Pt, Ir and Rh are added to the electrochemically active
30 material to improve the loadability at low temperature and the activation speed of the cell.

A disadvantage of the known cell is that it requires the use

of a relatively large quantity of a noble metal. When the noble metal is used in the form of a monolayer on the grains of the hydride-forming material, as is also described in EP-A1-0251384, a smaller quantity of the noble metal is required, but in this case, however, a labour-intensive electrochemical treatment is necessary to apply the monolayer. Moreover, for some applications it is desirable to further increase the loadability of the cell, in particular at low temperatures.

One of the objects of the invention is to provide an electrochemical cell and an electrochemically active material having a large loadability also at a low temperature, for use in such a cell. The aim of the invention is to achieve this by adding a material which has a catalytic effect on the formation and conversion of atomic hydrogen. The capacity of the cell to be manufactured should be as large as possible while preserving the other favourable properties of the cell. For this reason, it is desirable to achieve said purpose with the smallest possible quantity of the additive if the catalytic material is of a type in which no hydrogen is stored. A further object of the invention is to provide an electrochemical cell and an electrochemically active material which can meet the requirements without using noble metals.

An additional object of the invention is to provide a method of manufacturing the electrochemically active material in which the catalytic material is optimally distributed.

These objects are achieved according to the invention by an electrochemical cell and an electrochemically active material as described in the opening paragraph, which are characterized in that the catalytic material is of the type DE_3 , wherein D is one or more of the elements selected from Cr, Mo and W, and wherein E is one or more of the elements selected from Ni and Co. In a preferred embodiment of the electrochemical cell according to the invention, the catalytic material comprises the compound $Mo(Co, Ni)_3$, wherein Co and Ni may be present separately or together in any ratio.

The catalytic material is very effective, both in the electrochemical cell and in the electrochemically active material, if it is located on the grain boundaries of the intermetallic compound having the $CaCu_5$ -structure. This is the case, in particular, when the

average crystallite size of the intermetallic compound is less than 30 μm .

The use of the catalytic material is very advantageous with stable hydride-forming materials as described in, for example, 5 United States Patent Specification US 4487817. In said Specification, the intermetallic compound having the CaCu_5 -structure is of the type having the compositional formula: AB_mC_n , wherein $m + n$ ranges between 4.8 and 5.4, wherein n has a value from 0 to 0.6, wherein A consists of Mischmetall or of one or more elements selected from the 10 group consisting of Y, Ti, Hf, Zr, Ca, Th, La and the other rare earth metals, wherein B consists of two or more elements selected from the group consisting of Ni, Co, Cu, Fe and Mn, and wherein C consists of one or more elements selected from the group consisting of Al, Cr and Si.

15 To obtain a compound within the existence range of the intermetallic compound having the CaCu_5 -structure, the overall atomic quantity of the elements Y, Ti, Hf and Zr preferably amounts to less than 40% of A.

In order to obtain an electrochemically stable material, the 20 maximum atomic quantity per gram atom of A is for Ni : 3.5, for Co : 3.5, for Cu : 3.5, for Fe : 2.0 and for Mn : 1.0.

In order to obtain a corrosion-resistant material, n preferably has a value of at least 0.05. In this case, C consists of one or more of the elements selected from the group consisting of Al, 25 Cr and Si in the atomic quantities indicated, Al : 0.05-0.6, Cr : 0.05-0.5 and Si : 0.05-0.5.

According to the invention, the object of providing a method of manufacturing an electrochemical material is achieved by a method in which the intermetallic compound having the CaCu_5 -structure 30 is ground to obtain a powder, after which the grains thus formed are provided electrochemically with a layer of the catalytic material. Electrochemical methods are to be understood to include a galvanic method, a currentless deposition method and an exchange method. A particular advantage of this method is that it permits a maximum 35 quantity of catalytic material to be applied to the powder surface. In an optimum situation, the layer of the catalytic material is not thicker than a monolayer, so that the overall quantity of the hydride-

forming intermetallic compound is as large as possible and the hydrogen can diffuse to the intermetallic compound via a short path.

A simple and little labour-intensive alternative method of manufacturing an electrochemical material, in which the catalytic material is located on the grain boundaries of the intermetallic compound having the CaCu_5 -structure is characterized according to the invention in that a non-stoichiometric melt is made of the elements A, B and C, the composition being selected such that it is outside the existence range of the compound AB_mC_n , and a part of the elements B being replaced by one or more elements D, the melt being cooled while forming a two-phase material consisting of the compound having the CaCu_5 -structure and of the catalytic material. In this case, an excess of the elements B is used for the quantity of element E which is necessary for the catalytic material DE_3 . This means that in the preferred compositions indicated the composition of the melt corresponds to the compositional formula AB_pC_n , wherein $p + n$ is larger than 5.4.

In the above-described stable hydride-forming materials which are known per se, an increased corrosion resistance and electrochemical stability is attained (during a large number of charging and discharging cycles) by means of substitutions and additions to the generic LaNi_5 -compound, which is partly at the expense of the capacity of the cell to be manufactured. The sometimes adverse consequences hereof can be overcome partly by the larger loadability attained according to the invention.

The catalytic activity for the formation of hydrogen can be measured by means of the exchange current density J_0 which is higher for the noble metals Pt, Pd, Rh and Ir than for Co, Ni, W and Mo, see an article by S. Trasatti in J. Electroanal. Chem. 39, pages 163 to 184 (1972), in particular Figs. 3 and 4 on pages 173 and 175. Consequently, it is surprising that compounds of Co and/or Ni with W and/or Mo render an at least equally good result, all the more because these compounds, unlike Pt and Pd, do not form hydrides with hydrogen themselves. In an article by M.M. Jaksic in Electrochimica Acta, 29 (11), pages 1539 to 1550 (1984) the catalytic activity of compounds such as MoCo_3 , WNi_3 and MoNi_3 is attributed to a synergetic effect. From said article it can be derived that besides W

and Mo also Hf and Zr, and besides Ni and Co also Fe may be candidates for the formation of compounds which are catalytically active for the formation of hydrogen. With respect to LaNi_5 , it has been established in experiments leading to the invention that the life of the

5 electrochemical cell and the corrosion resistance of the electrochemically active material are insufficient for practical use.

The use of said catalytic materials in an electrochemical cell and an electrochemically active material according to the invention has the additional advantage that few new elements are
10 introduced into the overall composition. According to the invention, a small addition of Mo and/or W and an increase of the quantity of Ni and/or Co relative to La and the other rare earth metals is sufficient.

The invention will be explained in greater detail by means of exemplary embodiments and with reference to a drawing, in
15 which the only

Figure is a partly sectional and partly elevational view of a sealed rechargeable electrochemical cell according to the invention.

20 Example of a rechargeable cell construction.

The cell (as shown in the Figure), which is sealed from the air and which is manufactured by means of a suitable housing 1 of metal, such as stainless steel, having a cover 2 in which apertures are formed for conductors 3 and 4. Said conductors are insulated from
25 the metal housing 1, 2 by means of synthetic resin rings 5. The outside diameter of the house may be, for example, 22 mm and the height may be 41 mm. A roll of a negative electrode 6, a separator 7 and a positive electrode 8 are accommodated in the space inside the housing, the assembly being surrounded by an electrically insulating synthetic
30 resin foil 9 of, for example, polyvinyl chloride, and supported by a disc 10 of an electrically insulating material such as polyvinyl chloride.

The negative electrode 6 consists of a hydride-forming intermetallic compound as described hereinbefore and is connected to
35 the conductor 3. The negative electrode 6 is manufactured by fusing suitable quantities of the relevant elements, pulverizing the intermetallic compound thus formed and applying it to a nickel

carrier, for example, by means of a polymer binder material such as polyvinyl alcohol. The intermetallic compound can be pulverized, for example by grinding, to a grain size of approximately 40 μm . When the cell is activated by repeated hydrogen adsorption and desorption the grain growth is further reduced to the order of magnitude of 1 to 5 μm .

The positive electrode 8 is a nickel hydroxide electrode of the conventional sintered type which is connected to the conductor 4. A 6 N potassium hydroxide solution in water is used as the electrolyte. The electrolyte is absorbed in the separator 7 and is in wetting contact with the electrochemically active material of the two electrodes. The separator 7 is in the form of a non-woven membrane of polyamide fibres.

The free gas space in the cell is approximately 5 cm^3 . A sealed cell of this type has an EMF of between 1.2 and 1.4 V. The cells according to the invention can be assembled in a conventional manner to form batteries comprising, for example, several series-arranged cells.

Comparative example A, not according to the invention.

An electrochemically active material for the negative electrode, having the composition $\text{La}_{0.8}\text{Nd}_{0.2}\text{Ni}_{2.5}\text{Co}_{2.4}\text{Si}_{0.1}$ is prepared by mixing the necessary quantities of the various components, after which they are fused, cooled, ground and pulverized by repeated hydrogen adsorption and desorption. The powder formed has a surface area of approximately 0.25 m^2/g . Subsequently, an electrode is formed and incorporated in a cell, for example, as described hereinabove.

The loadability of the negative electrode is determined at 25°C by measuring the storage capacity of the cell in charging and discharging cycles at a rate of 2.0 C, i.e. at a rate of charging and discharging which would supply to or extract from the cell 2.0 times the nominal capacity of the cell in 1 hour. The nominal capacity of a cell is the capacity at a low charging and discharging rate.

The loadability after 10 charging and discharging cycles is 30% of the maximum value, after 20 cycles it is 90%, after 30 cycles it is 100% and after 300 cycles it is 95%.

At 0°C, the loadability after a great number of cycles is only 50% of the value at 25°C. If the discharging rate is increased to 3.0 C, the loadability at 0°C is only 35% of the value at 25°C. The exchange current density J_0 is measured after more than 100 cycles and at a degree of loading of 15%, and is 190 mA/g.

Comparative example B, not according to the invention.

An electrochemical cell is manufactured as described in comparative example A, using a composition of the melt according to the formula $\text{La}_{0.8}\text{Nd}_{0.2}\text{Ni}_{3.0}\text{Co}_{2.4}\text{Si}_{0.1}$. This composition is outside the existence range of the intermetallic compound having the CaCu_5 -structure. For this reason, a second phase is formed, during cooling, on the grain boundaries in addition to the intermetallic compound. Said second phase consists of Ni and Co, having a composition near $\text{NiCo}_{2.8}$. This material, in which no hydrogen is stored, acts catalytically on the formation of hydrogen.

When the melt is cooled slowly, crystallites having dimensions of 60 to 100 μm are formed. In the electrode manufactured, the loadability at 3.0 C and 0°C is 50% of the value at 25°C. The exchange current density is 287 mA/g.

When the melt is cooled rapidly, crystallites are formed having dimensions of 10 to 30 μm . In this case, the loadability at 3.0 C and 0°C is 70% of the value at 25°C. The exchange current density is 338 mA/g.

Comparative example C, not according to the invention.

An electrochemical cell is manufactured as described in example A, the composition of the electrochemically active material for the negative electrode being represented by the compositional formula $\text{La}_{0.8}\text{Nd}_{0.2}\text{Ni}_{2.5}\text{Co}_{2.0}\text{Pd}_{0.4}\text{Si}_{0.1}$. In the cell manufactured, the loadability at 3.0 C and 0°C is more than 90% of the value at 25°C. The exchange current density is approximately 500 mA/g.

35 Example 1.

An electrochemical cell is manufactured as described in example A, the composition in the melt corresponding to the formula

La_{0.8}Nd_{0.2}Ni_{3.0-x}Mo_xCo_{2.4}Si_{0.1}. An optimum composition is attained when x has a value of approximately 0.1. In conformity with example B, a second phase is formed during cooling. The dimensions of these eutectic segregations is in the order of magnitude of 1 to 2 μm ,
5 at an average crystallite size of the intermetallic compound having the CaCu₅-structure of 30 μm . The second phase consists of MoCo₃ with a small quantity of Ni. The composition can be represented by the formula Mo(Co, Ni)₃. MoCo₃ and MoNi₃ can be mixed in wide ratios and each form compounds having a small existence range, i.e., the
10 ratio Mo to Co and/or Ni is always fairly accurately 1 : 3. In conformity with example B, the crystallite size can be influenced advantageously as well as the dimension of the eutectic segregations by the choice of the cooling rate.

When the material is pulverized by means of repeated
15 hydrogen adsorption and desorption, particles having dimensions of approximately 1 μm are formed. To obtain a proper distribution of the catalytic material in the electrochemically active material it is useful to cool the melt rapidly so that a small average crystallite size is obtained, preferably smaller than 30 μm .

20 In the electrochemical cell manufactured, the loadability at 3.0 C and 0°C is 90% of the value at 25°C. The exchange current density is 585 mA/g.

The electrochemically active material which is used according to the present example is sufficiently resistant to
25 corrosion. After more than 100 charging and discharging cycles the capacity of the electrochemical cell was 91% of the maximum value.

Example 2.

An electrochemical cell is manufactured as described in
30 example A, the composition of the electrochemically active material also being the same. After the melt has cooled, the material is ground to a grain size of approximately 40 μm . By means of electrodeposition a layer of MoNi₃ is formed at the surface. Instead of MoNi₃, WNi₃ can also suitably be used.

35 The results obtained are at least just as good as when Pd-containing materials are used having a Pd content of 0.4 in the compositional formula of the intermetallic compound having the CaCu₅-structure.

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THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. An electrochemical cell comprising a negative electrode which electrode comprises an electrochemical active material consisting of an intermetallic compound of the formula AB_mC_n wherein m plus n is between 4.8 and 5.4, n has a value of up to 0.6 and greater than 0, A is a Mischmetall or at least one element of the group consisting of Y, Ti, Hf, Zr, Ca, Th, La and the remaining rare earth metals, B is at least two elements selected from the group consisting of Ni, Co, Cu, Fe and Mn and C consists of at least one element selected from the group consisting of Al, Cr and Si, and has a $CaCu_5$ structure, and a catalytic material at the surface of which hydrogen exhibits a large electrochemical activity, said catalytic material having a composition of formula DE_3 wherein D is at least one element selected from the group consisting of Cr, Mo and W and E is at least one element selected from the group consisting of Ni and Co.

2. An electrochemical cell as claimed in claim 1, characterized in that the catalytic material comprises the compound $Mo(Co, Ni)_3$.

3. The electrochemical cell as claimed in claim 2, characterized in that the catalytic material is located at the grain boundaries of the intermetallic compound having the $CaCu_5$ -structure.

- 10 -

4. An electrochemical cell as claimed in claim 1, characterized in that the catalytic material is located at the grain boundaries of the intermetallic compound having the CaCu_5 -structure.

5. A negative electrode comprising an electrochemically active material consisting of an intermetallic compound of the formula AB_mC_n wherein m plus n is between 4.8 and 5.4, n has a value of up to 0.6 and greater than 0, A is a Mischmetall or at least one element of the group consisting of Y, Ti, Hf, Zr, Ca, Th, La and the remaining rare earth metals, B is at least two elements selected from the group consisting of Ni, Co, Cu, Fe and Mn and C consists of at least one element selected from the group consisting of Al, Cr and Si, and has a CaCu_5 -structure, and a catalytic material at the surface of which hydrogen exhibits a large electrochemical activity, said catalytic material having a composition of formula DE_3 wherein D is at least one element selected from the group consisting of Cr, Mo and W and E is at least one element selected from the group consisting of Ni and Co.

6. The negative electrode as claimed in claim 5, characterized in that the catalytic material is located on the grain boundaries of the intermetallic compound having the CaCu_5 -structure.

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7. The negative electrode as claimed in claim 6, characterized in that the average crystallite size of the intermetallic compound is less than 30 μm .

8. The negative electrode as claimed in claim 7, characterized in that the intermetallic compound having the CaCu_5 -structure is of the type having the compositional formula AB_mC_n , wherein m plus n ranges between 4.8 and 5., wherein $0 < n \leq 0.6$, wherein A consists of Mischmetall or of one or more of the elements selected from the group consisting of Y, Ti, Hf, Zr, Ca, Th, La and the other rare earth metals, wherein B consists of two or more elements selected from the group consisting of Ni, Co, Cu, Fe and Mn, and wherein C consists of one or more of the elements selected from the group consisting of Al, Cr and Si.

9. The negative electrode as claimed in claim 5, characterized in that the intermetallic compound having the CaCu_5 -structure is of the type having the compositional formula AB_mC_n , wherein m plus n ranges between 4.8 and 5.4, wherein $0 < n \leq 0.6$, wherein A consists of Mischmetall or of one or more of the elements selected from the group consisting of Y, Ti, Hf, Zr, Ca, Th, La and the other rare earth metals, wherein B consists of Ni, Co, Cu, Fe and Mn, and wherein C consists of one or more of the elements selected from the group consisting of Al, Cr, and Si.

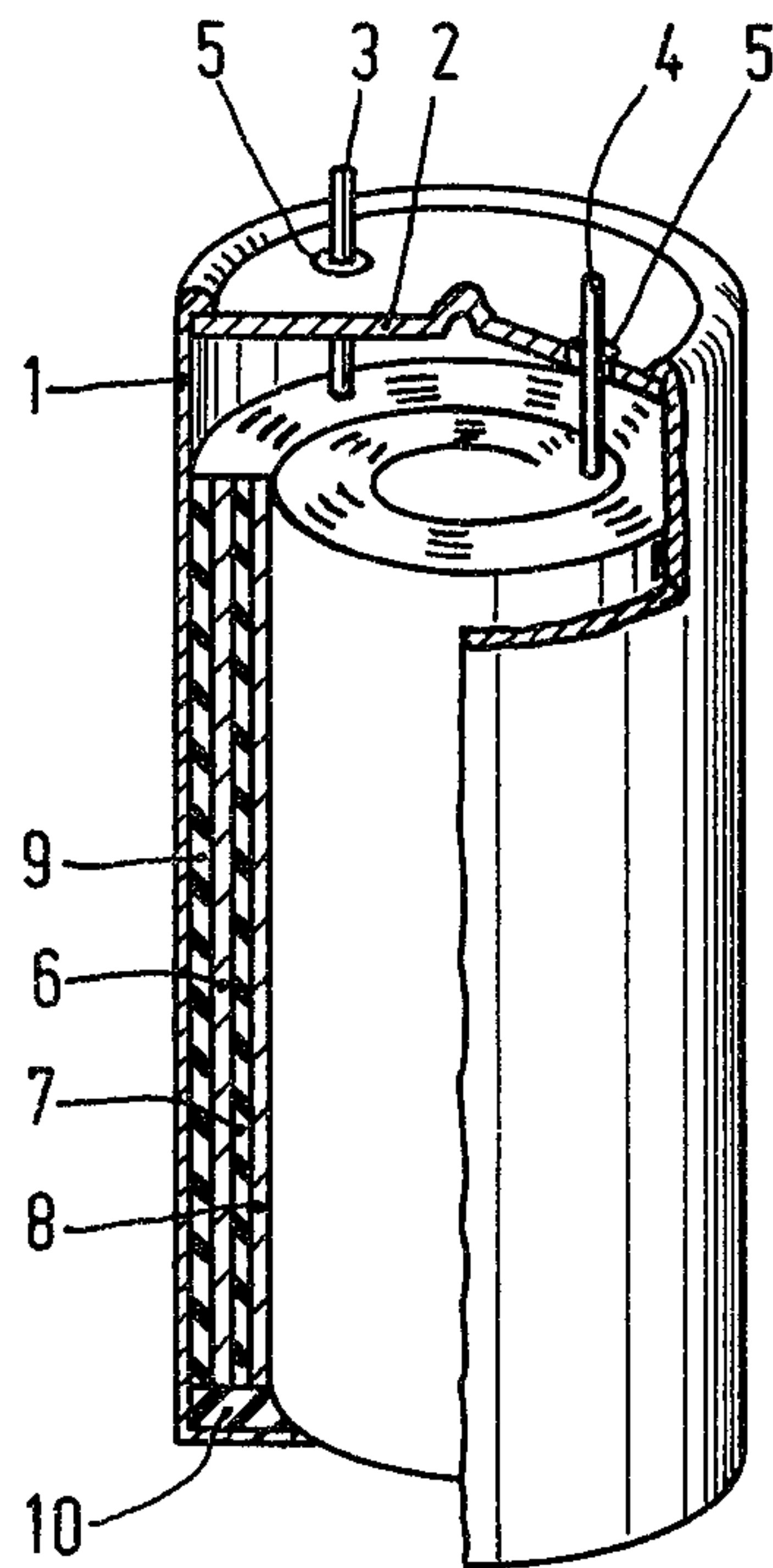
10. The negative electrode as claimed in claim 9, characterized in that the overall molar amount of the elements Y, Ti, Hf, Zr is less than 40% of A.
11. The negative electrode as claimed in claim 9,
5 characterized in that, per mole of A, the maximum quantity for Ni is 3.5 mole, the maximum quantity for Co is 3.5 mole, the maximum quantity for Cu is 3.5 mole, the maximum quantity for Fe is 2.0 mole and the maximum quantity for Mn is 1.0 mole.
12. The negative electrode as claimed in claim 11,
10 characterized in that the value of n is at least 0.05.
13. A method of manufacturing the negative electrode as claimed in claim 5, characterized in that the intermetallic compound having the CaCu_5 -structure is ground to form a powder, after which the grains thus formed are electrochemically
15 provided with a layer of the catalytic material.
14. An electrochemically active material consisting of an intermetallic compound of the formula AB_mC_n wherein m plus n is between 4.8 and 5.4, n has a value of up to 0.6 and greater than 0, A is a Mischmetall or at least one element of the group
20 consisting of Y, Ti, Hf, Zr, Ca, Th, La and the remaining rare earth metals, B is at least two elements selected from the group consisting of Ni, Co, Cu, Fe and Mn and C consist of at least one element selected from the group consisting of Al, Cr and Si, and has a CaCu_5 -structure, and a catalytic material at
25 the surface of which hydrogen exhibits a large electrochemical activity, said catalytic material having a composition of formula DE_3 wherein D is at least one element selected from the group consisting of Cr, Mo and W and E is at least one element selected from the group consisting of Ni and Co.

15. An electrochemically active material as claimed in claim 14, characterized in that C consists of one or more of the elements selected from the group consisting of Al, Cr and Si in the indicated mole percentages Al: 0.05-0.6, Cr: 0.05-0.5
5 and Si: 0.05-0.5.

16. A method of manufacturing an electrochemically active material consisting of an intermetallic compound of the formula AB_mC_n wherein m plus n is between 4.8 and 5.4 and wherein $0 < n \leq 0.6$, A is a Mischmetall or at least one element selected
10 from the group consisting of Y, Ti, Hf, Zr, Ca, Th, La and the remaining rare earth metals, B is at least two elements selected from the group consisting of Ni, Co, Cu, Fe and Mn and C is at least one element selected from the group consisting of Al, Cr and Si, said intermetallic compound having a $CaCu_5$ -
15 structure and a catalytic material, at the surface of which hydrogen exhibits a large electrochemical activity, said catalytic material having a composition of the formula DE_3 wherein D is at least one element selected from the group consisting of Cr, Mo and W and E is at least one element
20 selected from the group consisting of Ni and Co and said catalytic material is located on grain boundaries of the intermetallic compound having the $CaCu_5$ -structure, said method comprising forming a non-stoichiometric melt of the formula AB_pC_n wherein A, B, C and n have the meanings stated in claim 1,
25 p plus n is larger than 5.4 and a portion of the elements B is replaced by at least one of the elements D, and cooling said melt to thereby form a two-phase material consisting of the compound having the $CaCu_5$ -structure and the catalytic material.

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