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(54) Title: COMPOSITE HYDROGEN STORAGE MATERIALS FOR RECHARGEABLE HYDRIDE ELECTRODES

(57) Abstract

A composite hydrogen storage material for a rechargeable hydride electrode comprises a major amount of a metallic component able to store hydrogen by absorption and being resistant to alkaline media and a minor amount of a nanocrystalline or amorphous surface activator having electrocatalytic characteristics for the major component.
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COMPOSITE HYDROGEN STORAGE MATERIALS FOR
RECHARGEABLE HYDRIDE ELECTRODES

TECHNICAL FIELD

This invention relates to composite hydrogen storage materials for hydride electrodes of hydride-based rechargeable cells and batteries and to cells or batteries employing such composite hydrogen storage materials.

BACKGROUND ART

Rechargeable nickel-metallic hydride batteries have been widely developed for numerous applications including the replacement of Ni-Cd batteries for consumer use.


1. High hydrogen storage capacity

The hydrogen storage capacity is mainly determined by the thermodynamic properties of the hydride. An alloy may be used as anode material in a hydride battery if the heat of formation of the hydride is in an optimal range of 8-10 kcal/mol. (M. A. Fetchenko, Electrochem. Soc. Proc., Vol. 92-5, P. 141 (1992)). This condition can be fulfilled by adjusting the composition of the alloy, i.e. the ratio between the metals forming stable hydrides (La, Zr, Ti, Mg, etc.) and those forming unstable hydrides (Ni, Co, Fe, Cu, etc.). For hydrides with optimal compositions, the hydrogen dissociation pressure at equilibrium should be in the range from 10^-3 atmosphere to a few atmospheres. Basically the hydride anode materials belong to two main classes:
(a) Intermetallic compounds of the LaNi₅ class. The following patents disclose material compositions and manufacturing procedures for AB₅ materials: U.S. Patents 5,284,619; 5,358,800; Japanese Patents 6,215,766; 6,145,850; 5,263,162; 5,051,695; 5,036,405; 4,253,158; 4,303,730; 3,289,042; 3,057,157; 1,253,159; 93,082,025; 61,019,061.

(b) AB₂ Laves phase materials based on Ti and Ni: U.S. Patents: 4,551,400; 4,623,597; 4,893,756; 4,637,967; 5,277,999.

2. High Corrosion Resistance and Stability

A high resistance to corrosion in alkaline solution and good mechanical stability to repeated charge/discharge are required, both of which guarantee a long cycling life. The corrosion stability of the material is ascribed to the formation of a passive film on the surface of the material, which can protect the interior of the material from being corroded during repeated charge/discharge. While this film is necessary to protect the bulk from further oxidation, it should not be so compact as to prevent hydrogen from diffusing to and out of the electrode. Good hydride electrode materials should not experience compositional changes due to such factors as the dissociation of certain elements during repeated electrode reaction.

The mechanical stability of the electrode is determined by the volume change of the electrode material due to hydrogen sorption/desorption and by the toughness or strength of the material which tends to retain the integrity of the material.

3. High electrocatalytic activity for electrochemical reduction and oxidation, which guarantees optimal kinetics of charge and discharge, and hence a high charging efficiency and a good rate capability of
the hydride electrode (M. Ciureanu et al, Electrochemical Soc. Proc., Vol. 94, 27 (1994)).

4. The hydrogen diffusion rate in the bulk material should be high enough to avoid large diffusion resistance. Also, the ohmic resistance of the electrode and connections should be low.

5. Easy activation of the freshly prepared electrodes.

6. High energy and power density.

7. Low self discharge rate: the electrode should not experience a large loss in capacity during prolonged storage. One of the techniques allowing a low self-discharge is to select a hydrogen storage alloy having a low equilibrium plateau pressure.


For a given electrode material it is difficult to obtain simultaneously all the performances mentioned above. Generally, the procedures used to improve the electrode characteristics optimize one property, while sacrificing another.

DISCLOSURE OF THE INVENTION

The present invention seeks to provide a novel composite hydrogen storage material for hydride electrodes comprising two components. The first component, or major component, has high hydrogen storage capacity and good resistance to alkaline media, but typically has poor electrode kinetics. The second component, or minor component, is an alloy or mixture of alloys which functions as a surface activator and has a catalytic effect on the major component.

In accordance with the invention there is provided composite hydrogen storage alloys comprising: a) a major amount of a metallic component able to store hydrogen by absorption, said component being resistant to alkaline media, and b) a minor amount of a
nanocrystalline or amorphous metallic alloy, said alloy having electrocatalytic characteristics for said major metallic component.

The metallic component (major component) may be one having poor electrode kinetics or have difficulty in activation.

In particular, the alloy forming the minor component functions as a surface activator and is effective in lowering the overpotential of an electrode made from the composite in two processes. The first is the electro-reduction during charging of the electrode, whereby hydrogen absorption into said composite material is favored over hydrogen evolution and its surface. The second is for the electrochemical oxidation of hydrogen so that during discharge of the hydride electrode, the hydrogen stored in the composite can be withdrawn under appropriate current.

In especially advantageous embodiments the minor component can be an alloy which is able to store hydrogen.

More especially the alloy forming the minor component is a non-noble metal alloy.

In another aspect of the invention there is provided a rechargeable hydride cell or battery comprising an electrode made of the composite material of the invention, as the anode.

DESCRIPTION OF PREFERRED EMBODIMENTS

The invention more particularly concerns a new class of hydride electrode materials, based on composite alloys synthesized by mechanical alloying of two components: (1) a major component, having good hydrogen storage capacity and high corrosion resistance in alkaline solution; (2) one or more nanocrystalline or amorphous minor components acting as surface activator or catalyst for the major component. The
latter may be selected from alloys which have good hydrogen storage capacity, but cannot be used themselves as anode materials because of their low corrosion resistance or poor mechanical stability. The main advantage of the composite materials is that they combine the high storage capacity, corrosion resistance and stability of one component, with the good electrocatalytic activity and easy activation of the other, while not sacrificing any individual characteristics. Another important advantage is that the procedure can be used to improve the electrocatalytic activity of any traditional hydrogen storage material, with no restriction on composition and phase structure.

Also, since both components can be hydrogen absorbing materials, the composite may have both capacities, which increases the specific energy and power; this represents an important advantage over a purely electrocatalytic material, which improves the kinetics, but does not contribute to the hydrogen storage capacity (thus reducing the specific energy).

The major component is usually and preferably in nanocrystalline form as a result of ball milling to mix the two components, and this produces good mechanical resistance in the electrode on long term cycling. Employing the major component in nanocrystalline form also contributes to better rate capability of the electrode because the large density of grain boundaries enhances hydrogen diffusion.

The advantages over the existing alloys or techniques include:

(1) The second component which has catalytic effect on the other component does not need to contain precious metals, for example, Pd or Pt, as in previous
catalysts used for hydride electrodes, e.g. as described in U.S. Patent 4,859,413 (Harris et al).

(2) The second component can also be a hydrogen storage alloy, in this way the hydrogen storage capacity of both components can be used, giving advantages over existing catalysts such as Co, Co$_3$O$_4$ and RuO$_2$, etc. (Iwakura et al, J. Alloys Compds, 192 (1993) 152; Sakai et al, J. Alloys Compds., 192 (1993) 158), which can not reversibly absorb hydrogen so that the specific energy density of the electrode is reduced.

(3) The composite is formed by mechanically alloying the individual components in a ball mill. This has several advantages over existing techniques. First, the components are made independently and then mixed mechanically, which allows a free selection of each component in composition and amount, not limited by the phase rule or by solidification techniques as in multi-phase alloys from a direct cast of a melt containing all the elements, as described by Notten et al in J. Electrochem. Soc., 138 (1991) 1877, and by Ovshinsky et al in U.S. Patent 5,277,999. Secondly, the oxide films on the surface of individual components are broken down during the milling process and a close contact between the major component and second catalytic component is formed. As a result, the composite material can be used directly to make electrodes without further activation treatment, with a corresponding reduction in cost. The invention, surprisingly, permits the use as the second component of some metallic alloys which can absorb hydrogen but are otherwise unsuitable, for different reasons, as electrode materials of hydride cells or batteries.

The first role of the minor component is to enhance the transfer process of hydrogen from the
adsorbed state MH\text{ads} (formed by the reaction (1) of water electroreduction) into absorbed state MH\text{abs}, i.e. k\text{p} process in (2), lowering the accumulation of hydrogen at electrode surface and therefore the charging overpotential. This favors sorption of hydrogen into the bulk over recombination of the reduced hydrogen to molecular hydrogen (the forward reactions in (3) and (4)), which then bubbles off.

\[ M + H_2O + e^{-} \xrightarrow{k_v} OH^- + MH_{ads} \quad (1) \]

\[ MH_{ads} \xrightarrow{k_p} (MH_{abs})_{sub-surface} \xleftrightarrow{\text{diffusion}} (MH_{abs})_{bulk} \quad (2) \]

\[ MH_{ads} + H_2O + e^{-} \xrightarrow{k_h} H_2 + M + HO^- \quad (3) \]

\[ 2MH_{ads} \xrightarrow{} H_2 + 2M \quad (4) \]

The second role of the minor component is to enhance the electrochemical oxidation of hydrogen (backward reaction k\text{p} in (2)) and hence to lower the
overpotential during discharge of the electrode. This results in a higher discharge capacity at the same discharge current, i.e., a higher rate capability and a better utilization of the electrode material. Another important advantage of the lower discharge overpotential is that it allows the use of an alloy which forms more stable hydride (a lower equilibrium dissociation pressure) as anode material, favoring a high charge retention or a low self-discharge rate.

In a particular embodiment the composite of the invention is represented by:

$$A_xB_{1-x}$$

where A is the major metallic component with $X > 0.5$, more preferably in the range of $0.85 < X < 1.00$, B is the surface activator component represented by:

$$Ni_yM_{1-y}$$

where M is any element other than Ni, more preferably, M= Al, B, C, Ca, Co, Cr, Cu, Fe, Li, Mg, Mn, Mo, Na, Nb, O, P, Rare earth metals, Si, V, Y, Zn, Zr, or their combinations, $0.1 < X < 0.9$, more preferably $0.5 < Y < 0.9$.

As indicated above, the minor component of the composite functions as a surface activator which is effective to lower the overpotential for electrochemical reduction and oxidation of hydrogen in a hydride electrode containing the composite whereby hydrogen absorption into the metallic component (major component) is favored over hydrogen evolution at the surface of the metallic component.

In a particular embodiment the surface activator is one able to store hydrogen but is
otherwise unsuitable as the metallic component (major component) of a composite hydrogen storage material.

Most suitably the surface activator is a non-noble metal.

In a particular embodiment the surface activator is nanocrystalline or amorphous Ni$_y$Mg$_{1-y}$, where $0.1 < y < 0.9$.

A number of composites were synthesized by ball milling under argon atmosphere, using amorphous and nanocrystalline Mg-Ni alloys with or without LmNi$_5$ as minor component. LmM$_5$ is a conventional hydrogen storage intermetallic compound, with Lm=La-rich mischmetal and M is a mixture of Ni, Co, Mn and Al. The particular interest in the composite materials should be stressed. As mentioned previously, there are up to now a few studies reporting the effect of surface activators on the charge capacity, but the recommended effective additives are rare and expensive materials like Pd and Pt or alloys containing them. The present invention uses for the first time amorphous and nanocrystalline Mg-Ni alloy powders, an excellent hydrogen storage medium, but which cannot be used itself as an anode material owing to its low corrosion resistance. It undergoes a rapid decrease in discharge capacity during repeated charge-discharge, but it remains very stable as a minor component together with LmM$_5$ in the investigated composites. The reason for this behavior is not known, but implies that the performance of the two components is mutually enhanced.

Another important result on Mg-Ni alloys is that their catalytic activity remains unchanged as a minor component.

As major component of the composites a wide range of hydrogen storage alloys may be used, which are known to have good hydrogen storage capacity and high
corrosion resistance in alkaline media. These may be, for example, conventional hydride electrode materials like ZrNi_{1.2}Mn_{0.3}Cr_{0.2}V_{0.3}, but also materials formerly considered to be unsuitable as hydride electrode materials like Zr(FeCr)₂.

Typical intermetallic compounds which may be employed as the major component include: LaNi₃.₅Co₀.₇Al₀.₈, ZrNi₁.₂Mn₀.₃Cr₀.₂V₀.₃, ZrCrNi, ZrFeCr (i.e., Zr(FeCr)₂), Zr₇Ni₁₀, Zr₇Ni₉V, YCo₃ and Ti₇Mo₃.

LaNi₃.₅Co₀.₇Al₀.₈ and ZrNi₁.₂Mn₀.₃Cr₀.₂V₀.₃ are conventional hydride electrode materials selected from AB₅ and AB₂ classes.

The materials employed as the minor component in the invention more especially are amorphous powders or nanocrystalline powders having a grain size in the range of about 1 to 100 nm, especially 10 to 60 nm, more especially 15 to 50 nm. For both amorphous and nanocrystalline minor components, the powder size was typically smaller than 50 micrometers, more especially in the range of 1 to 27 micrometers. Suitably the composite may contain 50% to 99% by weight of the major component, more especially 85% to 99%, with the balance being the minor component to a total of 100%.

a) Material Preparation

Both new and conventional hydrogen storage materials as major component (1) and nanocrystalline and amorphous Mg-Ni alloys, or a 1:1 mixture of Mg-Ni alloys and LmM₅ (LmNi₃.₇Co₀.₇Mn₀.₃Al₀.₃) as minor component (2) were prepared. The ingots of component (1) and LmM₅ were obtained by arc-melting the mixture of component elements according to the specific compositions under an argon atmosphere. The nanocrystalline and amorphous Mg-Ni alloys were synthesized by mechanically alloying pure Mg and Ni,
Mg$_2$Ni and Ni, or MgNi$_2$ and Mg in a SPEX-8000 vibrator ball mill for not less than 18 hours under an argon atmosphere. The composite materials were obtained by mixing the components together and grinding the mixture in the ball mill for different periods of time of 15 to 60 minutes at room temperature, also under argon.

Some materials were sieved through a 300 mesh screen.

The samples of composite materials were checked for crystallinity by X-ray diffractometry. The structure of component (1) was found to be nanocrystalline in all cases, as the diffraction satellites were broadened as a result of the ball milling. A fitting program was used in the case of Zr(FeCr)$_2$ to calculate the grain size; it was found that the grains were 30-50 nm for samples which were ball milled for 15 minutes and 15-30 nm for those ball milled for 40-60 minutes.

b) Electrode Preparation and Discharge Capacity of the Electrode

The electrode used for capacity measurement was constructed by cold pressing a mixture of the active materials and copper or nickel powder into a pellet. The measurements were carried out using a counter electrode NiOOH/Ni(OH)$_2$ and an electrolyte of 6M KOH. The charging current was for 3 to 3.5 hours at 100 mA/g-active material and a short circuit was applied every half an hour, in order to discharge the impurities deposited on the negative electrode (mainly Cd from the commercial positive Ni hydroxide electrode). The discharge current was 37.15 to 40 mA/g-active material and the cut-off voltage for the discharge was 0.95 V. The mass of the counter electrode was in large excess compared with the test electrode, and therefore the discharge capacity was negative electrode (the test electrode) limited.
In all cases, the composites yielded a significant increase in capacity as compared with the major component (1), as seen in Table 1. Thus, for Ni$_{10}$Zr$_7$, the capacity increased from 80 mAh/g to 180 mAh/g (composite with 5 wt % amorphous Mg$_{50}$Ni$_{50}$ alloy which is hereafter called MgNi); for Zr$_7$Ni$_9$V$_1$ the capacity increased from 130 mAh/g to 180 mAh/g (composite with 5 wt % MgNi and LmM$_5$); for YCo$_3$ the capacity increased from 92 to 228 mAh/g (Composite with 5 wt % MgNi and 5 wt % LmM$_5$); for ZrCrNi the capacity increased from 300 mAh/g to 380 mAh/g (composite with 5% Mg$_{40}$Ni$_{60}$).
### Table 1 Experimental results of other alloys and their composites

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<th>Electrode</th>
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<th>Disch. capacity, mAh/g</th>
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<tr>
<td>Zr(FeCr)₂</td>
<td>Mechanically ground</td>
<td>40</td>
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<tr>
<td>Zr(FeCr)₂ + 5%MgNi</td>
<td>Ball milling, 15 min.</td>
<td>200</td>
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<tr>
<td>Zr(FeCr)₂ + 5%MgNi + 5%MnM₃</td>
<td>Ball milling 15 min.</td>
<td>230</td>
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<tr>
<td>Zr(FeCr)₂ + 5%MgNi + 5%MnM₃</td>
<td>Ball milling 40 min.</td>
<td>260</td>
</tr>
<tr>
<td>ZrMe₂</td>
<td>mechanically ground</td>
<td>187</td>
</tr>
<tr>
<td>ZrMe₂ + 3%MgNi</td>
<td>Ball milling, 5 Min.</td>
<td>225</td>
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<tr>
<td>ZrMe₂ + 5%MgNi + 5%MnM₃</td>
<td>Ball milling, 15 Min.</td>
<td>258</td>
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<tr>
<td>ZrMe₂ + 5%MgNi + 5%MnM₅</td>
<td>Ball milling, 40 Min.</td>
<td>288</td>
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<tr>
<td>ZrCrNi</td>
<td>Activated in hot KOH</td>
<td>300</td>
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<tr>
<td>ZrCrNi + 5%Mg₉₀Ni₅₀</td>
<td>Ball milling, 20 Min.</td>
<td>380</td>
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<td>Zr₇Ni₁₀</td>
<td>Ball milling, 15 min.</td>
<td>80</td>
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<tr>
<td>Zr₇Ni₁₀ + 5%MgNi</td>
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<tr>
<td>Zr₇Ni₁₀ + 5%MgNi + 5%MnM₅</td>
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<tr>
<td>LaMₛ</td>
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<tr>
<td>LaMₛ + 5%MgNi</td>
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<tr>
<td>Y₂Co₃</td>
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<tr>
<td>Y₂Co₃ + 5%MgNi + 5%MnM₅</td>
<td>Ball milling, 15 Min.</td>
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<td>Ti₇Mo₃</td>
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<td>Ti₇Mo₃ + 5%MgNi</td>
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<td>130</td>
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<tr>
<td>Ti₇Mo₃ + 5%MgNi + 0%MnM₅</td>
<td>Ball milling 15 Min.</td>
<td>114</td>
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\[\text{Me}_2 = \text{Ni}_{1.2}\text{Mn}_{0.3}\text{Cr}_{0.2}\text{V}_{0.3}\]
\[\text{MI} = \text{Ni}_{0.7}\text{Al}_{0.6}\text{Co}_{0.14}\]
\[\text{MgNi} = \text{Mg}_{0.9}\text{Ni}_{0.1}\]

The capacity is referred to the capacity per gram of the composite material.
The most spectacular improvement was observed in the case of a composite based on the Laves phase alloy Zr(FeCr)\(_2\), which is known as a good storage material for gaseous hydrogen, but with poor electrocatalytic properties for hydrogen reduction. The latter property makes this material as-fabricated unsuitable for hydride electrode material, with a discharge capacity of only 40 mAh/g after more than 100 charge discharge cycles. But in the presence of 5 wt % MgNi this capacity was raised to 200 mAh/g and with 5 wt % MgNi + 5 wt % LmM\(_5\) to 230 mAh/g; by decreasing the grain size of the composite by longer ball milling from 30-50 nm to 15-30 nm, the capacity was further increased to 260 mAh/g.

Another interesting result was obtained for the composite based on ZrNi\(_{1.2}\)Mn\(_{0.3}\)Cr\(_{0.2}\)V\(_{0.3}\). The basic material intermetallic compound is known to have high capacity only after thermal treatment and activation procedure; in the absence of such treatment, the capacity of the material was rather low. In the presence of 5 wt % MgNi and 5 wt % LmM\(_5\) the capacity was found to be 288 mAh/g.

An increase in capacity with increasing time of ball-milling was noted for the composites based on Zr(FeCr)\(_2\) and ZrNi\(_{1.2}\)Mn\(_{0.3}\)Cr\(_{0.2}\)V\(_{0.3}\). The significant increase of capacity observed for composites as compared with the basic component can be explained in terms of the important increase of the exchange current for hydrogen evolution.

**BRIEF DESCRIPTION OF DRAWINGS**

**Figure 1** is a plot of discharge capacity of hydride electrodes made of Zr(FeCr)\(_2\)-based composites vs cycle number -

1. Zr(FeCr)\(_2\)
2. Zr(FeCr)₂ + 5 wt % MgNi, ball-milling 15 min.

3. Zr(FeCr)₂ + 5 wt % MgNi + 5 wt % LmM₅, ball-milling 15 min.

4. Zr(FeCr)₂ + 5 wt % MgNi + 5 wt % LmM₅, ball-milling 60 min.;

**Figure 2** is a plot of discharge capacity of hydride electrodes made of ZrNi₁.₂Mn₀.₃Cr₀.₂V₀.₃-based composites vs cycle number -

1. ZrNi₁.₂Mn₀.₃Cr₀.₂V₀.₃

2. ZrNi₁.₂Mn₀.₃Cr₀.₂V₀.₃ + 5 wt. % MgNi, ball-milling 5 min.

3. ZrNi₁.₂Mn₀.₃Cr₀.₂V₀.₃ + 5 wt. % MgNi, + 5 wt % LmM₅, ball-milling 15 min.

4. ZrNi₁.₂Mn₀.₃Cr₀.₂V₀.₃ + 5 wt. % MgNi, + 5 wt % LmM₅, ball-milling 40 min.

**Figure 3** is a schematic representation of a battery or cell of the invention.

**DESCRIPTION OF PREFERRED EMBODIMENTS WITH REFERENCE TO THE DRAWINGS**

c) Cycling Behavior

In all cases except YCO₃, the composites showed excellent cycling behavior. Little or no decrease of the capacity was observed after more than 100 cycles. Typical plots of discharge capacity vs number of cycles are presented in **Figure 1** for Zr(FeCr)₂-based composites and in **Figure 2** for ZrNi₁.₂Mn₀.₃Cr₀.₂V₀.₃-based composites. Although the stability is mainly determined by the major component, it is found that the composites with MgNi+LmM₅ have better cycling behavior than those only with MgNi.

Another practically important feature for the composites is that while the basic compounds need several tens of, sometimes even more than 100, cycles to reach the maximum capacity, the composites need only 2-3 cycles or even reach their maximum at the first cycle as seen in **Figure 1** and **Figure 2**. The easy
activation represents another important advantage of using the composite hydrogen storage materials for hydride electrodes, especially for those materials like the AB\textsubscript{2}-based material, which can be used as hydride electrode material only after various activation steps.

Thus in accordance with the invention:

i) a new class of composite hydride electrode material is proposed. The composites are synthesized by mechanical alloying of two components: a major component having high hydrogen storage capacity and a minor component with good electrocatalytic activity;

ii) a new type of surface activator as minor component is proposed, which may itself be a hydrogen storage material. Using as minor component nanocrystalline or amorphous Mg-Ni alloys or a mixture of the Mg-Ni alloys and LnM\textsubscript{5}, a spectacular increase of capacity was observed for a number of composites as compared with the major component. This increase is the result of an enhancement of the electrocatalytic activity of the material surface for charging. The proposed activators are cheap and easy to purchase, as compared to those previously proposed;

iii) the capacity increase observed with non-conventional basic components (having rather low electrochemical capacities in pure state) demonstrates that the proposed activators may be used in composites with any hydrogen storage material as major component, including those which, owing to their low electrocatalytic activity, have low capacities when used alone;

iv) the proposed minor component materials were used in the form of nanocrystalline or amorphous powders, which is believed to produce high electrocatalytic activity; and
v) the composite materials are easier to activate than the basic component and show a low self-discharge rate.

In a rechargeable electrolytic cell or battery the composite hydrogen storage material of the invention functions as the anode.

The anode may be a sintered electrode consisting of the hydrogen storage material with or without the addition of any suitable conducting material powder such as nickel, copper or carbon sintered together, with a current collector made of any suitable metal such as nickel. The anode may also be a non-sintered electrode fabricated by applying a paste which comprises the hydrogen storage material, binder medium such as polytetrafluoroethylene, carboxymethyl-cellulose, or polyvinyl alcohol etc., and a conducting material such as nickel, copper, carbon powder, etc., on to a current collector made of a suitable metal such as nickel.

The cell or battery additionally includes a cathode, and a separator which contains an electrolyte and separates the anode and the cathode. The anode, cathode and electrolyte are typically contained in a housing having a positive terminal electrically connected to the cathode. The terminals provide for out-flow of electric current developed by the electrochemical reaction in the housing.

The cathode may be, for example, a nickel electrode. Such a cathode may be formed by applying a paste of nickel hydroxide and a binding medium to a conductive core; suitable binding agents include polyacrylates, for example, sodium polyacrylate and ammonium polyacrylate, carboxymethyl cellulose and fluoro resins such as polytetrafluoroethylene, or mixtures of these agents. The paste may also contain a
conductive material, for example, carbon black, graphite or metal powder. The conductive core may be a metal.

The cathode may also be a sintered nickel electrode or a silver electrode, i.e., Ag/AgO electrode.

The anode and cathode are suitably separated by a separator, for example, a non-woven, non-electrically conducting cloth soaked with the electrolyte solution. One suitable separator is non-woven Nylon (Trade Mark) cloth.

The electrolyte is suitably an aqueous alkaline electrolyte solution, for example, an aqueous solution of KOH, LiOH or a solution of both.

With further reference to Figure 1, a battery includes a plurality of anodes 12 and cathodes 14 in a housing 16.

The anodes 12 and cathodes 14 form electrode pairs 20, each pair comprising an anode 12 and an adjacent cathode 14, in spaced apart relationship.

A cloth separator 18 impregnated with aqueous alkaline electrolyte solution is disposed between each adjacent pair 20.

Electrical conducting leads 34 electrically connect the anodes 12 to a negative terminal 26.

Electrical conducting leads 22 electrically connect the cathodes 14 to a positive terminal 24. The positive and negative terminals 24 and 26 are electrically insulated from housing 16 by insulators 28 and 30, respectively.

The anodes 12 are formed from the composite hydrogen storage material of the invention. The cathodes 14 are typically nickel electrodes.

In a commercially preferred battery, the anode and cathode are separated from each other by the
separator which contains the electrolyte, and the anode, cathode and separator are spiraled and contained in a cylinder housing.
CLAIMS

1. A composite hydrogen storage material for a hydride electrode of a rechargeable electrolytic cell or battery comprising:
   a) a major amount of a metallic component able to store hydrogen by absorption, said metallic component being resistant to alkaline media, and
   b) a minor amount of a component selected from nanocrystalline surface activators, amorphous surface activators, and combinations thereof, said surface activator component having electrocatalytic characteristics for said metallic component.

2. A composite according to claim 1, which is represented by:

   \[ A_xB_{1-x} \]

   where \(A\) is the major metallic component with \(X > 0.5\) and \(B\) is the surface activator component represented by:

   \[ Ni_yM_{1-y} \]

   where \(M\) is any element other than \(Ni\), more preferably, \(M=Al, B, C, Ca, Co, Cr, Cu, Fe, Li, Mg, Mn, Mo, Na, Mb, O, P,\) Rare earth metals, \(Si, V, Y, Zn, Zr\), or their combinations, \(0.1 < Y < 0.9\).

3. A composite according to claim 1 or 2, wherein \(0.85 < X < 1.00\).
4. A composite according to claim 1, 2 or 3, wherein 0.5 < Y < 0.9.

5. A composite according to claim 1, 2, 3 or 4, wherein said surface activator is effective to lower the overpotential for electrochemical reduction and oxidation of hydrogen in a hydride electrode containing the composite, whereby hydrogen absorption into said metallic component is favored over hydrogen evolution at the surface of the metallic component.

6. A composite according to claim 1, 2, 3 or 4, wherein said surface activator is able to absorb hydrogen by absorption but is otherwise unsuitable as the major metallic component of a composite hydrogen storage material.

7. A composite according to claim 1, 2, 3 or 4, wherein said surface activator is of non-noble metal.

8. A composite according to claim 1, 2, 3 or 4, wherein said surface activator is nanocrystalline or amorphous Ni\textsubscript{y}-Mg\textsubscript{1-y}, where 0.10 < Y < 0.90.

9. A composite according to claim 2, wherein M is Mg.

10. A composite according to claim 1, wherein a) is Zr(FeCr)\textsubscript{2} and b) is MgNi.

11. A composite according to claim 1, wherein a) is Zr(FeCr)\textsubscript{2} and b) is MgNi and LnNi\textsubscript{3.7}Co\textsubscript{0.7}Mn\textsubscript{0.3}Al\textsubscript{0.3}.

12. A composite according to claim 1, wherein a) is ZrCrNi and b) is Mg\textsubscript{40}Ni\textsubscript{60}. 
13. A composite according to claim 1, where a) is ZrCrNi and b) is Mg$_{50}$Ni$_{50}$.

14. A composite according to claim 1, where a) is ZrCrNi and b) is Mg$_{50}$Ni$_{50}$ and Lm$_{3.7}$Co$_{0.7}$Mn$_{0.3}$Al$_{0.3}$.

15. An electrode made of a composite hydrogen storage material according to claim 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 11, 12, 13 or 14.

16. A rechargeable electrolytic cell containing an electrode according to claim 15.

17. A rechargeable battery comprising:

a) housing,

an anode and a cathode within said housing in spaced apart relationship with a separator containing an electrolyte therebetween,

a positive terminal electrically connected to the cathode and a negative terminal electrically connected to the anode,

said anode comprising a composite hydrogen storage material according to any one of claims 1 to 14.

18. A battery according to claim 17, comprising a plurality of pairs of electrodes in said housing, each pair comprising a said anode and a said cathode in said spaced apart relationship.
### INTERNATIONAL SEARCH REPORT

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC 6 H01M4/38 C01B3/00

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

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Further documents are listed in the continuation of box C.

patent family members are listed in annex.

**Date of the actual completion of the international search**

24 July 1997

**Date of mailing of the international search report**

05. 08. 97

Name and mailing address of the ISA

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Authorized officer

Andrews, M
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