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- (71) **Applicant:** UNIVERSITY OF IOWA RESEARCH FOUNDATION [US/US]; 2660 University Capitol Centre, Iowa City, Iowa 52242 (US).
- (72) **Inventors:** LEDDY, Johna; 905 S. Summit St., Iowa City, Iowa 52240 (US). REED, Jessica Jewett; 3821 41st St., Des Moines, Iowa 50310 (US).
- (74) **Agents:** RUTT, J. Steven et al.; The Marbury Law Group, PLLC, 11800 Sunrise Valley Drive, 15th Floor, Reston, Virginia 20191 (US).
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(54) **Title:** MAGNETICALLY MODIFIED METALS AND METAL ALLOYS FOR HYDRIDE STORAGE

(57) **Abstract:** A device comprising a magnetic element, which comprises a magnetic material, wherein the magnetic element is adapted to absorb hydrogen to form hydride. The magnetic aspect of the system enhances the hydrogen storage. Also disclosed is a metal hydride element comprising a magnetic material and absorbed hydrogen. The magnetic element and the metal hydride element can be an electrode. Further disclosed are methods for making and using the electrode.



MAGNETICALLY MODIFIED METALS AND METAL ALLOYS FOR HYDRIDE STORAGE

RELATED APPLICATIONS

This Application claims priority to US provisional application 61/617,508 filed 3/29/2012, which is incorporated herein by reference in its entirety.

FEDERAL FUNDING STATEMENT

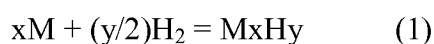
This invention was made with government support under Contract No. NSF0809745 awarded by the United States National Science Foundation. The Government has certain rights in the invention

BACKGROUND

Today efforts are being made by governments and researchers to transition away from an economy dependent on fossil fuels to alternative energies. Not only are alternative fuel sources necessary to relieve the burden of dwindling oil supplies, they are an answer to environmental sustainability woes. While hydrogen is still being explored as a commercial fuel, it is an attractive energy source for many reasons. Its natural abundance and straight forward synthesis make it a viable alternative to fossil fuels energy sources. In addition, hydrogen can be stored for a long time without significant degradation, unlike stored electrical charge. In principle, hydrogen fueled vehicles could emit only water from their exhaust systems. However, until better and efficient storage systems are created the use of hydrogen as a fuel is a concern of safety.

There are three types of hydrogen storage: gaseous, liquid, and solid state. A major drawback of gaseous and liquid storage is the relatively small amount of hydrogen that may be stored, even under high pressure. The sheer volume of hydrogen needed to give comparable energy density to gasoline is more than can currently be feasibly stored onboard a vehicle (Sandi, *Interface* 2004, 40-43). Solid state storage refers to the storage of hydrogen in metal hydrides and other nanostructured materials.

Metal hydrides form when hydrogen reacts with a metal or alloy to create a new hydrogen containing product. The reaction can be seen in Equation 1 where M represents the metal and H the hydrogen.



Metal hydrides show promise for solid state storage of hydrogen due to their ability to store large amounts of hydrogen in small volumes and their relative stability. Since metal hydrides are typically solids at ambient conditions, they are less volatile than compressed gas or liquid hydrogen, which is an important factor to consider for fuel containment in the event of a crash.

While this type of solid state storage is likely to be most suitable to meet the specifications for onboard vehicle hydrogen fuel storage, it suffers an energetic cost associated with electrochemically driving the hydrogen into and out of the storage material lattice. In addition to energetic costs, the absorption and release of hydrogen in the metal are kinetically rate limited at atmospheric pressure. This means that the release of the hydrogen fuel from the storage material is not rapid enough to meet consumer demands. The rate is so slow because of the energy tax associated with the interfacial kinetics for hydrogen atom transfer. The slow kinetics are manifest as a large energetic cost so that the value of hydrogen as a fuel is markedly diminished. Poor interfacial hydrogen atom transfer is an obstacle to hydrogen as a viable fuel source especially in portable applications.

Accordingly, there remains an unmet need in the art for improved hydride absorption in order to decrease the energetic cost of metal hydride formation, to increase the kinetics of the reaction, and to provide better solid state hydrogen storage devices. The energetic taxes are extracted for both hydrogen adsorption and hydrogen desorption. A process that overcomes the poor kinetics of both adsorption and desorption is particularly valuable.

SUMMARY

Embodiments described herein include articles, devices, and compositions, as well as methods of making and methods of using same.

Described here, for example, is a device comprising a magnetic element, which comprises a magnetic material, wherein the magnetic element is adapted to absorb hydrogen to form hydride.

In one embodiment, the magnetic element comprises a hydrogen-absorbing material different from the magnetic material.

In one embodiment, the magnetic material is a hydrogen-absorbing material.

In one embodiment, the magnetic element comprises a substrate and a coating disposed on the substrate, wherein: (i) the substrate comprises a hydrogen-absorbing material different from the magnetic material, and wherein the coating comprises the magnetic material, or (ii) the substrate comprises the magnetic material, and wherein the coating comprises a hydrogen-absorbing material different from the magnetic material.

In one embodiment, the magnetic element comprises a mixture of the magnetic material and a hydrogen-absorbing material different from the magnetic material.

In one embodiment, the magnetic element comprises metal.

In one embodiment, the magnetic element comprises Pd or an alloy thereof.

In one embodiment, the magnetic element comprises an AB₂ or AB₅ material.

In one embodiment, the magnetic material comprises Fe₃O₄, Fe₂O₃, NdFeB, SmCo₅, Sm₂Co₁₇, Sm₂Co₇, La_{0.9}Sm_{0.1}Ni₂Co₃, Ti_{0.51}Zr_{0.49}V_{0.70}Ni_{1.18}Cr_{0.12}, or a combination thereof.

In one embodiment, the magnetic material comprises Fe₃O₄, NdFeB, SmCo₅, or a combination thereof.

In one embodiment, the magnetic material comprises at least one magnetic particle, magnetic wire, or magnetic mesh.

In one embodiment, the magnetic material comprises at least one magnetic particle comprising a magnetic core and a protective coating.

In one embodiment, the magnetic material comprises at least one magnetic particle comprising a magnetic core and a silane protective coating.

In one embodiment, the magnetic material comprises at least one magnetic particle comprising a Fe₃O₄ magnetic core and a -Si-CH₃ protective coating.

In one embodiment, the magnetic material is not externally magnetized.

In one embodiment, the magnetic material is externally magnetized.

In one embodiment wherein the magnetic element comprises a substrate and a magnetic coating, the magnetic coating further comprises at least one polymer.

In one embodiment wherein the magnetic element comprises a substrate and a magnetic coating, the magnetic coating further comprises at least one ion exchange polymer or at least one conducting polymer.

In one embodiment wherein the magnetic element comprises a substrate and a magnetic coating, the magnetic coating further comprises at least one Nafion polymer or derivative thereof.

In one embodiment wherein the magnetic element comprises a substrate and a magnetic coating, the magnetic coating further comprises octadecyltrimethylammonium bromide Nafion or an alkyl ammonium modified Nafion.

In one embodiment, the magnetic element comprises metal, and wherein the presence of the magnetic material decreases the potential or energy tax/cost for electrochemically absorbing hydrogen to form metal hydride.

In one embodiment, the magnetic material increases the absorption rate of hydrogen into the magnetic element by at least 10%, or wherein the magnetic material increases the desorption rate of hydrogen into the magnetic element by at least 10%.

In one embodiment, the magnetic element is an electrode.

In one embodiment, the magnetic element comprises metal hydride.

In one embodiment, the device is a fuel cell.

Also described here is a metal hydride element comprising a magnetic material.

In one embodiment, the metal hydride element comprises a substrate and a coating disposed on the substrate, wherein: (i) the substrate comprises a metal hydride different from the magnetic material, and wherein the coating comprises the magnetic material, or (ii) the substrate comprises the magnetic material, and wherein the coating comprises a metal hydride different from the magnetic material.

In one embodiment, the metal hydride element comprises a mixture of the magnetic material and a metal hydride different from the magnetic material.

In one embodiment, the magnetic material is a metal hydride.

In one embodiment, the metal hydride element comprises Pd, an alloy thereof, or an AB₂ or AB₅ material.

In one embodiment, the magnetic material comprises at least one magnetic particle, magnetic wire, or magnetic mesh.

In one embodiment, the magnetic material comprises Fe₃O₄, Fe₂O₃, NdFeB, SmCo₅, Sm₂Co₁₇, Sm₂Co₇, La_{0.9}Sm_{0.1}Ni₂Co₃, Ti_{0.51}Zr_{0.49}V_{0.70}Ni_{1.18}Cr_{0.12}, or a combination thereof.

In one embodiment, the presence of the magnetic material decreases the potential for electrochemically absorbing hydrogen to form metal hydride.

In one embodiment, the metal hydride element is substantially free of any metal hydroxide.

Also described here is a fuel cell device comprising the metal hydride element as electrode.

Also described here is a nickel metal hydride battery comprising the metal hydride element of as electrode.

Further described here is a method for making the metal hydride element, comprising (i) contacting a magnetically-modified element with a hydrogen source, wherein the magnetically-modified element comprises a metal-based hydrogen-absorbing material and a magnetic material; and (ii) applying an electrochemical potential to form a metal hydride element.

Further described here is a method for making the metal hydride element, comprising contacting a magnetically-modified element with a pressurized hydrogen gas, wherein the magnetically-modified element comprises a metal-based hydrogen-absorbing material and a magnetic material.

Additionally described here is a method for using the device comprising the magnetic element described above, comprising absorbing hydrogen into the magnetic element, and optionally desorbing hydrogen therefrom. In one embodiment, the method further comprises demagnetizing the magnetic material to reduce desorption of the absorbed hydrogen.

Additionally described here is a method for using the metal hydride element described above, comprising desorbing hydrogen from the metal hydride element, and optionally resorbing hydrogen to form metal hydride. In one embodiment, the method further comprises using the desorbed hydrogen to generate energy.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 depicts hydrogen absorption in palladium. The hydrogen atoms occupy octahedral (O_h) and tetrahedral (T_d) sites in the palladium lattice.

Figure 2 shows cyclic voltammograms at a Pd electrode in 0.5 M H_2SO_4 at 298 K. Scan rate is 50 mV/s. The upper potential limit is fixed at 1.40 V while the lower limit is decreased to either ~ 0.22 or ~ 0.25 V to show H absorption into Pd.

Figure 3 shows the voltammetric profile for an unmodified Pd electrode versus SCE in 0.1 M HNO_3 . The electrode area is the same in all figures, Area = 0.438 cm^2 . Scan rate is 50 mV/s.

Figure 4 shows the comparison of voltammetric data for electrodes modified with a Nafion film and for a composite of Nafion and Bangs magnetic microparticles in 0.1 M HNO_3 at scan rate of 50 mV/s. The film was dried in an external magnetic field. Nafion film (gray, long-short dash) and composite (black, short dash) are shown. The voltammetric wave for the magnetically modified electrode is characteristic of faster kinetics than the simple Nafion film as shown by (e.g., 2 mA) for smaller voltage perturbations from approximately ~ -0.1 V on reduction and oxidation.

Figure 5 shows an overlay of cyclic voltammograms from composite films of TMODA-Nafion and SiMAG particles. The electrolyte is 1.0 mM HNO_3 and scan rate is 50 mV/s. C1 (black, solid), C3 (pink, solid), C8 (blue, long dash), C18 (green, short dash).

Figure 6 shows an overlay comparing cyclic voltammograms for a blank TMODA-Nafion film, and composites of TMODA-Nafion with C1 or glass microbeads. The electrolyte is 1.0 mM HNO_3 and scan rate is 50 mV/s. Blank (blue, solid), C1 (pink, short dash), Glass microbeads (black, long dash).

Figure 7 shows an overlay of cyclic voltammograms comparing blank TMODA-Nafion to composites containing C1 microparticles. The magnetized C1 particles had been exposed to an external magnet for magnetic field alignment. The supporting electrolyte is 0.1M HNO_3 and scan rate is 50 mV/s. Blank (black, solid), Non-magnetized C1 (pink, solid), Magnetized C1 (blue, short dash). Both composites that contain C1 magnets yield higher current than the TMODA-Nafion film. The microstructure on magnetization will differ from the composite formed with magnetic particles that is not magnetized during formation of the composite on the electrode.

Figure 8 shows an overlay of cyclic voltammogram data for TMODA-Nafion film and composite films of TMODA and C1 particles at pH values of 5 and 10. The electrolyte was 0.1 M NaNO_3 and the scan rate was 50 mV/s. TMODA-Nafion film at pH 10 (black, solid),

TMODA-Nafion film at pH 5 (gray, long dash), C1 composite at pH 5 (pink, short dash), C1 composite at pH 10 (green, long dash- short dash).

Figure 9 shows one exemplary embodiment of the magnetic element described herein wherein the magnetic material is present in a coating.

Figure 10 shows one exemplary embodiment of the magnetic element described herein wherein the magnetic material is mixed with the hydrogen absorbing material.

DETAILED DESCRIPTION

INTRODUCTION

All references described herein are hereby incorporated by reference in their entireties.

Though magnetic modification of electrodes was previously shown to increase rates of electron transfer in the positive electrode of batteries (see US Patent 8,231,988, incorporated herein by reference in its entirety), its impact on atom transfer is unknown in the art. For example, in hydrides storage, proton (H^+) is first converted to hydrogen atom ($H\cdot$), which then cross the electrode interface to absorb into the electrode. This process allows storage of hydrogen as hydrogen radical also called hydrogen atom in the electrode as a hydride or metal hydride. More hydrogen can be stored as the hydride in palladium than as compressed hydrogen gas. The challenge of metal hydride storage is that the kinetics of getting the hydrogen in and out of the electrode is slow and therefore also energy intensive. As described herein, magnetic modification of electrodes significantly improves the rates of atom transfer and hydride storage. Such electrodes are particularly useful in fuel cells and Ni-MH batteries.

In an alternative embodiment, hydrogen storage in a material can be facilitated with magnetic modification where the material is not serving as an electrode. In the electrode configuration, the magnetically modified electrode can serve for hydrogen generation and storage where the electrode generates hydrogen in the electrolysis that contains hydrogen donors and stores the generated hydrogen as hydride in the electrode.

Magnetic materials are described in, for example, US Patent 8,231,988, US Patent 7,709,115 and US Patent 6,890,670, all of which are incorporated herein by reference in their entireties.

Fuel cells are described in, for example, US 2010/0021776; US 2010/0159365; US 3853628, and JP 2002198057, all of which are incorporated herein by reference in their entireties.

Ni-MH batteries are described in, for example, US Patent 7,709,115 and US Patent 6,890,670, both of which are incorporated herein by reference in their entireties.

MAGNETIC ELEMENT FOR HYDROGEN-STORAGE DEVICE

Many embodiments described herein relates to a device, such as a hydrogen-storage device, comprising a magnetic element. The magnetic element can comprise, for example, at least one magnetic material, wherein the magnetic element is adapted to absorb hydrogen via the formation of hydride.

The magnetic element can comprise, for example, a substrate and a coating disposed on the substrate, wherein the substrate comprises a hydrogen-absorbing material different from the magnetic material, and wherein the coating comprises the magnetic material, as shown in Figure 9.

The magnetic element can comprise, for example, a substrate and a coating disposed on the substrate, wherein the substrate comprises the magnetic material, and wherein the coating comprises a hydrogen-absorbing material different from the magnetic material.

The magnetic element can comprise, for example, a mixture of the magnetic material and a hydrogen-absorbing material different from the magnetic material, as shown in Figure 10. The mixture can be formed by, for example, melting the hydrogen-absorbing material and adding the magnetic material having a higher melting point. In other words, the magnetic material can be inserted into the bulk of the hydrogen-absorbing material rather than merely coated on its surface. When the matrix is formed by heating, it will be necessary to determine whether or not the magnetic component has been heated above a temperature (e.g., Curie temperature) so that the magnetic particles are demagnetized. If the magnetic particles are demagnetized on formation, it is necessary to re-magnetized the particles after the temperature has been lowered to allow solidification of the composite. Magnet incorporated conducting electrodes were formed previously where magnetic microparticles are disbursed in an electron conducting matrix of carbon particles. In a heterogeneous matrix composed of at least two components where one is the hydrogen absorbing media (e.g., palladium) and the other is a magnetic component, intimately mixed, the requirements for magnetic impact on hydrogen absorption are satisfied. A third component might provide

enhanced electron conduction in such a matrix should be hydride forming component also serve as an electrode. The third component might be for example a carbon particulate.

The magnetic element can comprise, for example, a metal or an alloy that is magnetic. In other words, the hydrogen-absorbing material itself can be rendered magnetic. For example, palladium is paramagnetic, which means it can support a magnetic field under externally applied field. But once the action field is removed, the magnetization of the palladium will dissipate. Materials that are ferrimagnetic or ferromagnetic or anti-ferromagnetic will support permanent magnetic field if they are of sufficient size. Some hydride forming materials such as AB₅ and AB₂, which are ferrimagnetic or ferromagnetic, may be able to support a permanent magnetic field.

The presence of the magnetic material in or near the magnetic element can, for example, decrease the potential for electrochemically absorbing hydrogen to form a metal hydride. The presence of the magnetic material in or near the magnetic element can, for example, decrease the energetic cost of metal hydride formation and increase the kinetics of the reaction.

Alternatively, the magnetic element can be described in its hydride state. For example, the magnetic element can be a metal hydride element comprising at least one magnetic material and at least one metal hydride, wherein the magnetic material can be different from or the same as the metal hydride. The presence of the magnetic material in the magnetic element can, for example, accelerate atom transfer. In one embodiment, the magnetic element is substantially free of any metal hydroxide such as nickel hydroxide.

A further alternative embodiment is where the hydride forming material is magnetically modified but the hydride is not part of an electrochemical circuit. In these embodiments, the hydride is loaded and released by changes in the external pressure of, for example, hydrogen gas at the surface of the hydride forming material that is magnetically modified. Magnetic modification can include either incorporation of magnetic materials as described in Figures 9 and 10 or magnetizing the metal hydride forming material that is either paramagnetic, ferrimagnetic or ferromagnetic.

The above embodiments apply to both adsorption of hydride and desorption of hydrogen radical. Both the processes of absorption and desorption are accelerated by the magnetic modification described herein. The acceleration in the kinetics corresponds to a

decrease in the overall energetic tax to drive storage of hydrogen as hydride and release of hydrogen as hydrogen radical.

HYDROGEN-ABSORBING MATERIAL

Hydrogen-absorbing materials suitable for the hydride storage device described herein include materials known in the art. The hydrogen-absorbing material can comprise, for example, a metal or an alloy thereof.

The hydrogen-absorbing material can comprise, for example, a transition metal. The hydrogen-absorbing material can comprise, for example, palladium. The hydrogen-absorbing material can comprise, for example, a palladium alloy such as silver or copper-modified palladium, or a palladium-modified lighter metal material. The hydrogen-absorbing material can comprise, for example, an alkaline earth metal such as Ca or Mg, or an alkali metal such as Na or Li. The hydrogen-absorbing material can comprise, for example, complex metals comprising sodium, lithium, or calcium. The hydrogen-absorbing material can comprise, for example, AB₅ or AB₂ materials common in nickel metal hydride batteries and other metal hydride batteries. In a preferred embodiment, the hydrogen-absorbing material comprises palladium.

Alternatively, the hydrogen-absorbing material can be described in its hydride state. The hydrogen-absorbing material can comprise one or more compounds selected from, for example, palladium hydride, MgH₂, NaAlH₄, LiAlH₄, LiH, LaNi₅H₆, Mg₂NiH₄, TiFeH₂, LiNH₂, LiBH₄ and NaBH₄, as well as the hydrides of AB₅ and AB₂ material.

MAGNETIC MATERIAL

Magnetic materials described herein are known in the art and include, for example, materials that develop a magnetic moment following exposure to a strong magnetic field for a sufficient period of time (See US Patent Nos. 8231988, 7709115 and 6890670). The magnetic material can comprise, for example, permanent magnetic materials, paramagnetic materials, superparamagnetic materials, ferromagnetic materials, ferrimagnetic materials, superconducting materials, anti-ferromagnetic materials, and combinations thereof.

In one embodiment, the magnetic material comprises at least one permanent magnetic material selected from, for example, samarium cobalt, neodymium-iron-boron, aluminum-nickel-cobalt, iron, iron oxide, cobalt, misch metal, ceramic magnets comprising barium ferrite and/or strontium ferrite, and mixtures thereof.

In one embodiment, the magnetic material comprises at least one paramagnetic material selected from, for example, aluminum, steel, copper, manganese, and mixtures thereof.

In one embodiment, the magnetic material comprises at least one ferromagnetic or ferrimagnetic or anti-ferromagnetic material selected from, for example, gadolinium, chromium, nickel, and iron, and mixtures thereof.

In one embodiment, a mixture of permanent magnetic materials (ferromagnetic and/or ferromagnetic) and paramagnetic materials is used.

In one embodiment, the magnetic material comprises at least one ferromagnetic or ferromagnetic material selected from, for example, iron oxides, such as Fe_3O_4 and Fe_2O_3 .

In one embodiment, the magnetic material comprises at least one ferromagnetic material selected from, for example, Ni-Fe alloys, iron, and combinations thereof.

In one embodiment, the magnetic material comprises at least one ferrimagnetic material selected from, for example, rare earth transition metals, ferrite, gadolinium, terbium, and dysprosium with at least one of Fe, Ni, Co, and a lanthanide and combinations thereof.

In one embodiment, the magnetic material comprises at least one superconducting composition comprising a suitable combination of, for example, niobium, titanium, yttrium barium copper oxide, thallium barium calcium copper oxide, and bismuth strontium calcium copper oxide.

In one embodiment, the magnetic material comprises at least one anti-ferromagnetic material selected from, for example, FeMn, IrMn, PtMn, PtPdMn, RuRhMn, and combinations thereof.

The magnetic material can comprise one or more compounds selected from, for example, Fe_3O_4 , Fe_2O_3 , NdFeB alloys, SmCo_5 , $\text{Sm}_2\text{Co}_{17}$, Sm_2Co_7 , $\text{La}_{0.9}\text{Sm}_{0.1}\text{Ni}_2\text{Co}_3$, $\text{Ti}_{0.51}\text{Zr}_{0.49}\text{V}_{0.70}\text{Ni}_{1.18}\text{Cr}_{0.12}$. The magnetic material can comprise one or more compounds selected from, for example, Fe_3O_4 , NdFeB and SmCo_5 .

The magnetic material can comprise, for example, magnetic particles. The magnetic particles can be, for example, uncoated. The magnetic particles can comprises, for example, a magnetic core and at least one protective coating. The protective coating can comprise, for example, at least one inert material.

Other than magnetic particles, the magnetic material can be in the form of any type of microstructure materials, such as magnetic wires and magnetic meshes. In general, the magnetic material should be a small permanent magnet that can be incorporated into the magnetic element described herein. They do not have to be particles. In some embodiments, the electromagnets is part of the magnetic element.

Suitable inert materials for coating the magnetic particles include, for example, materials that do not adversely interact with the environment in which the particles are used. Such coatings can be used, for instance, to render the magnetic particles inert to corrosive effects of solvents and electrolytes such as acids, bases, and oxidants and reductions. Examples of suitable inert materials include, for example, substituted and unsubstituted polystyrenes, silanes and combinations thereof. Also, glasses, siloxanes, and other silicon containing materials can provide inert coatings.

In a particular embodiment, the inert material comprises one or more silanes. The silane can be, for example, represented by $-\text{Si}-(\text{CH}_2)_n-\text{CH}_3$. n can be, for example, 1-20, or 1-10 or 1-5, or 1-2, or about 1. In a particular embodiments of the present invention, the magnetic particles are silane-coated Fe_3O_4 or NdFeB .

Other suitable inert coating include polystyrene coatings, polystyrene over a silanes, and siloxanes.

The size of the magnetic particles are not particularly limited. The diameter of the magnetic particles can be, for example, 1 to 1000 microns, 1 to 100 microns, or 1 to 50 microns, or 1 to 20 microns, or 1 to 10 microns. In some embodiment, the magnetic particles have a diameter of at least 1 micron to sustain a permanent magnetic field. In some embodiment, the magnetic particles have a diameter of at least 0.5 micron to sustain a permanent magnetic field.

METHODS FOR MAKING

In some embodiments where the magnetic element comprises a substrate coated with a magnetic material, the magnetic element can be made by dispersing the magnetic material in a suspension, depositing the suspension onto the substrate, and drying the coated substrate.

The suspension can comprise, for example, at least one polymer binder. The suspension can comprise, for example, at least one ion exchange polymer. The suspension can comprise, for example, at least one Nafion® polymer or a sulfonic acid polymer or a carboxylic acid polymer derivatives thereof. The suspension can comprise, for example,

octadecyltrimethylammonium bromide (TMODA) modified Nafion or other alkyl-ammonium modified Nafion or other ion-exchange polymer.

In an alternative embodiment, the magnets may be held against the surface with an externally applied magnetic field and there is no binder present. Because this is an adsorption process, the binder is not rigorously required.

In one embodiment, the coated substrate is prepared in the presence of an external magnetic field, and the magnetic material is magnetized to sustain that magnetic field. In another embodiment, the coated substrate is prepared in the absence of an external magnetic field, and the magnetic material only sustain a residual magnetic field. The magnetic material may be magnetized prior to incorporation into the substrate coated.

In some embodiments where the magnetic element comprises a mixture of the hydrogen absorbing material and the magnetic material, the electrode can be made by melting the hydrogen-absorbing material and adding the magnetic material having a higher melting point.

The magnetic element described herein can be further processed to form a metal-hydride element by, for example, (i) contacting the magnetic element with a hydrogen source, wherein the magnetic element comprises a metal-based hydrogen-absorbing material and a magnetic material; and (ii) applying an electrochemical potential to form a metal hydride electrode.

The magnetic element described herein can be further processed to form a metal-hydride element by, for example, contacting a magnetic element with a pressurized hydrogen gas, wherein the magnetic element comprises a metal-based hydrogen-absorbing material and a magnetic material.

In some embodiments, the metal hydride element comprises a substrate and a magnetic coating disposed on the substrate, wherein the substrate comprises the metal hydride, and wherein the magnetic coating comprises the magnetic material. In some embodiments the magnetic coating is above the metal hydride forming material. In other embodiments, the magnetic material is below the metal hydride forming material. In other embodiments, the metal hydride electrode comprises a mixture of the metal hydride and the magnetic material.

METHOD OF USING

The metal hydride element described herein can be used in various energy-related applications. For example, hydrogen can be desorbed from the metal hydride element. The hydrogen desorbed can be used to, for example, generate energy such as electricity. Moreover, hydrogen can be resorbed into the element to form metal hydride, so that the hydride absorbing material can be used in multiple cycles.

The device comprising the magnetic element described herein can be used in various energy-related applications. For example, hydrogen can be absorbed into the magnetic element. Optionally, to reduce desorption of the absorbed hydrogen, the magnetic element can be demagnetized. Moreover, the absorbed hydrogen can be desorbed to generate energy..

PERFORMANCE

Compared to a conventional hydrogen absorbing element comprising hydrogen absorbing material but no magnetic material, the magnetic element described herein comprising the magnetic material can function to decrease the overpotential for electrochemically absorbing hydrogen to form metal hydride. For example, the presence of the magnetic material can increase the absorption rate of hydrogen into the hydrogen-absorbing material for at least 10%, or at least 100%, or at least 10 times, or at least 50 times. Further, the presence of the magnetic material can increase the desorption rate of hydrogen from the metal hydride element for at least 10%, or at least 100%, or at least 10 times, or at least 50 times.

Further, the amount hydrogen adsorbed at a given potential for a given period of time can be enhanced by, for example, at least 10%, or at least 100%, or at least 10 times, or at least 50 times. Additionally, that amount hydrogen desorbed at a given potential for a given period of time can be enhanced by, for example, at least 10%, or at least 100%, or at least 10 times, or at least 50 times.

Finally, the rate of atom transfer in the magnetic element and the metal hydride element described herein can be enhanced by, for example, at least 10%, or at least 100%, or at least 10 times, or at least 50 times.

APPLICATIONS

The magnetic element and the metal hydride element described herein can be used in a wide range of applications, including hydrogen-storage devices, hydrogen generation – storage devices, fuel cells, and batteries.

The magnetic element and the metal hydride element described herein can be used as electrode in, for example, a fuel cell. The magnetic element and the metal hydride element can be used in, for example, a fuel cell comprising hydride as the fuel storage matrix and possible the anode of the fuel cell. The magnetic element and the metal hydride element can be used in, for example, a proton exchange membrane (PEM) fuel cell.

The magnetic element and the metal hydride element described herein can be used as electrode in, for example, a battery. The magnetic element and the metal hydride element can be used in, for example, a nickel metal hydride battery. The magnetic element and the metal hydride element can be used in, for example, a nickel metal hydride battery, wherein the magnetic element and/or the metal hydride element is the counter-electrode that faces the $\text{Ni(OH)}_2/\text{NiOOH}$ electrode (*i.e.*, the negative electrode).

The magnetic element and metal hydride element described herein is used in, for example, a hydrogen storage device for absorbing hydrogen from pressurized hydrogen gas.

In some embodiments, the magnetic element and metal hydride element described herein can be used to isolate H_2 out of a reformat fuel stream (see Grashoff *et al.*, *Platinum Metals Rev.* 1983, 27(4), 157-169).

HYDROGEN/PALLADIUM SYSTEMS

Electrochemistry of Hydrogen in Palladium Systems

Palladium has an fcc structure with a lattice parameter of 0.3890 at 298 K (Flanagan *et al.*, *Annu. Rev. Mater. Sci.* 1991, 269-304). As hydrogen absorbs into the (111) face of the metal, the lattice undergoes an isotropic expansion while maintaining its fcc structure. A representation of the absorption of hydrogen into the palladium lattice is shown in Figure 1. The absorbed hydrogen atoms can occupy both tetrahedral and octahedral sites within the lattice. For palladium, both underpotential deposited hydrogen (H_{UPD}) and overpotential deposited hydrogen (H_{OPD}) can occur within the same potential window (Jerkiewicz, *Progress in Surface Science* 1998, 57, 137-186).

A proposed mechanism for the formation of the metal hydride is :



where *ads* and *abs* indicate adsorbed as to the surface and absorbed as into the bulk.

This mechanism describes a kinetically driven system in which absorption of hydrogen and creation of the hydride is limited by the formation of the surface adsorbate. Consider the palladium electrode. H^+ ions migrate to the surface of the electrode where an electron transfer occurs, yielding the adsorbed species. Note that the evolution of hydrogen gas at the electrode surface is not included in the mechanism as it is a side reaction not generated by the experiments herein. The kinetics of the absorption process are assumed to be relatively faster than the adsorption process, however, little is known about the actual kinetics of the reaction. The absorption process creates a metal hydride layer at the surface of the metal.

Cyclic Voltammetry

Cyclic voltammetry (CV) is an electrochemical technique in which current is measured as a potential range is scanned. CV provides unique information about the energetic costs of electroabsorbing hydrogen because the current output at the potential of absorption can be measured. To decrease energetic losses associated with electroabsorbing hydrogen, the increased current seen when hydrogen absorbs into the metal needs to occur at a lower potential than the potential for hydride formation in the absence of modification. The hydrogen absorption occurs on the forward sweep or the reductive wave of the voltammograms shown here.

Grden *et al.* has done extensive electrochemical research on the palladium and hydrogen system (Grden *et al.*, *Electrochimica Acta* 2008, 53, 7583-7598). Figure 2 shows CV data obtained by Grden *et al.* for a bare palladium electrode in 0.5 M H_2SO_4 electrolyte at scan rate 50 mV/s. These data were used as a reference standard for the studies herein. In order to determine that the experimental observations obtained demonstrated the absorption phenomena expected, comparisons between experimental results and the reference voltammogram were made. Note that the reference electrode in Grden is RHE and in the following working examples the reference is SCE, which is V vs NHE. These comparisons can be found in the Example 3.

WORKING EXAMPLES

EXAMPLE 1 – Electrodes and Instrumentation

The electrochemical cell is a three electrode cell. Measurements were made by cyclic voltammetry.

Working Electrode

The working electrode was a Pine Instruments palladium rotating disk electrode (RDE) with a Teflon shroud. All experiments were done on this one electrode. The electrode was of geometric area 0.438 cm^2 . A detailed cleaning procedure was employed between uses to ensure electrode surface reproducibility. First, the electrode was cleaned with an ethanol soaked Kimwipe to dissolve any remaining polymer deposits. Next, the electrode was polished by hand on a polishing pad with, successively, 3, 1, 0.3, and $0.05 \text{ }\mu\text{m}$ grit alumina oxide polishing powders (Buehler) in water slurry. The electrode was rinsed with water between different grits. Finally, the surface is rinsed thoroughly with distilled water and stored upright in a protective cylinder until ready for use.

Counter and Reference Electrodes

The counter electrode consisted of high surface area platinum mesh with a geometric area of approximately one inch squared. The electrode was cleaned by soaking in concentrated HNO_3 for five minutes and rinsed with distilled water prior to use. A saturated calomel electrode (SCE) with standard potential -0.2412 V vs. NHE served as the reference electrode. The SCE was cleaned by a brief rinse with distilled water prior to use and blotted dry with a Kimwipe.

Voltammetry

A CHI 1030 potentiostat from CH Instruments, Inc. was used to collect all cyclic voltammetric data. Voltammograms were typically recorded at various scan rates between 25 to 150 mV/s . The scans were taken with scan rate order randomized to eliminate scan rate bias and possible changes associated with extra electrochemical events. To be consistent with literature data, scans were commonly taken at a scan rate of 50 mV/s . The electrolyte and pH varied and are noted in each case. Common electrolytes were 0.1 M NaNO_3 (Fisher) and 1.0 mM HNO_3 (Fisher). Electrolyte solutions were purged with nitrogen gas for 15 minutes before experimental tests. All experiments were conducted at room temperature. Voltammetric data were analyzed by macros created in Microsoft Excel.

EXAMPLE 2 – Magnetic Particles

Magnetic microparticles were obtained from several sources. The most effective microparticles were coated magnetite microparticles, SiMAG®, from commercial distributor Chemicell (Germany). The particles consist of a single core of magnetite (Fe_3O_4) encapsulated in a thin silane coat. The silane coat makes the magnetite chemically inert but is sufficiently thin to establish a magnetic field at the electrode surface. These particles have different chain length in the silane surface coatings and are named as C_n for $-\text{Si}-(\text{CH}_2)_{n-1}\text{CH}_3$ silane coatings. The names are listed in Table 1. The particles are identified by their short name throughout this section.

Commercial Name	Functional Group Coating	Short Name
SiMAG-Methyl	$-\text{Si}-\text{CH}_3$	C1
SiMAG-Propyl	$-\text{Si}-(\text{CH}_2)_2\text{CH}_3$	C3
SiMAG-Octyl	$-\text{Si}-(\text{CH}_2)_7\text{CH}_3$	C8
SiMAG-Octadecyl	$-\text{Si}-(\text{CH}_2)_{17}\text{CH}_3$	C18

Table 1. Properties and naming of commercial Chemicell magnetite particles.

Properties in common for the SiMAG particles regardless of silane chain length include average size of $1\ \mu\text{m}$, surface area of approximately $100\ \text{m}^2/\text{g}$, and density of $2.25\ \text{g}/\text{cm}^3$. Also, the number of particles is constant at $1.8 \times 10^{12}/\text{g}$.

The magnetic susceptibility of the commercial SiMAG particles from Chemicell was previously determined in the same lab and summarized in Table 2. It is of note that the expected pattern of increasing chain length of coating decreasing the magnetic field strength is not consistently observed. The C18 particles have higher magnetic field strength measurements than C8 particles. Otherwise, the shorter chain lengths have stronger magnetic fields.

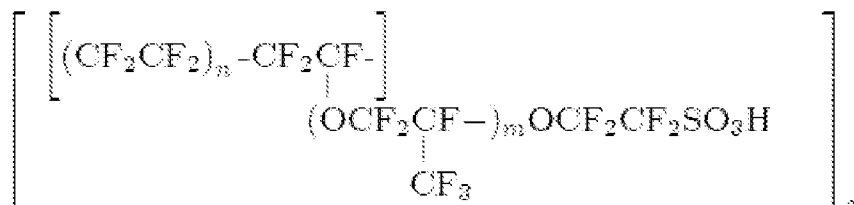
Volume magnetic susceptibility (c.g.s)	
C1	5.39×10^{-5}
C3	2.39×10^{-5}
C8	8.60×10^{-6}
C18	1.96×10^{-5}
water	-1.06×10^{-6}

Table 2. Volume magnetic susceptibilities in centimeter-gram-second units for SiMAG particles.

Other microparticles included polymer magnetite composites from Bangs Laboratories, Inc. (ProMag PMC3N). These particles have an average size of $2.70\ \mu\text{m}$ and density of approximately $1.22\ \text{g}/\text{cm}^3$. Based on density, the magnetic content is less than the Chemicell particles.

EXAMPLE 3 – Nafion and Nafion Composite Modified Electrode

One of the ion exchange polymer coatings used in these experiments was Nafion®. Developed by scientists at DuPont, Nafion consists of a Teflon-like fluorocarbon backbone with side chains that terminate in sulfonic acid sites (Zook *et al.*, *J. Anal. Chem.* 1996, 68, 3793-3796). The chemical structure of Nafion is:



where m is usually 1; $5 \leq n \leq 7$.

The proton from the sulfonic acid group can easily exchange cationic species from solution, including other protons from solution, such as HNO_3 . Nafion, an ion conducting polymer, serves as a membrane film with high proton concentration between the electrode and electrolyte solution. Nafion is used to support micro-magnets on the electrode surface. Thus, simple Nafion films serve as controls for the magnetic composite films. Prior studies showed that Nafion films and Nafion films with low loading of polystyrene particles ($\leq 5\%$) have the same cyclic voltammetric response (Minteer, S. D. Magnetic Field Effects on Electron Transfer Reactions, Ph.D. thesis, University of Iowa, 2000). In general, addition of nonmagnetic microparticles either yields the same cyclic voltammetric response as simple Nafion films or occasionally degrades performance relative to Nafion.

Preparation of Nafion and Composite Films

The Nafion films cast on the electrode are prepared from a commercial Nafion suspension (Ion Power, Inc.). The commercial suspension is 5% weight Nafion in a mixture of alcohols and water. The palladium working electrode is modified with either (a) a Nafion film; (b) a composite of Nafion and magnetic microparticles with no external magnetic field applied; or (c) a composite of Nafion and magnetic microparticles formed under an external magnetic field. All composites are 15% wt/wt magnetic particles.

The simple Nafion film preparation consists of depositing 5 μL of the Nafion suspension on the surface of the electrode via pipette.

For composite films, the Nafion suspension and microparticles are mixed in a centrifuge tube and then vortexed briefly to suspend microparticles. The suspension is used

immediately to form composite modified electrodes. In composite cases, a 5 μ L aliquot of Nafion and magnetic microparticles is applied to the electrode. When composites are aligned in the magnetic field, a NdFeB ring magnet encompassing the electrode surface is used. The ring magnet has outer diameter of 7.5 cm, inner diameter of 5 cm, and height of 1 cm. To magnetize the composite, the electrode modified by the suspension is centered inside a hollow cylinder and magnet. The field strength of the external magnet is sufficient to magnetize and align the microparticles. Once magnetized by an external field, the microparticles are able to sustain that magnetic field. Without magnetization by the external magnet, the microparticles may sustain a residual magnetic field. No attempt to demagnetize microparticles was made.

In all cases, the modified electrode was air dried in an upright position for 30 minutes before being placed in a vacuum desiccator to ensure complete evaporation of solvent. Vacuum drying times varied for composite and Nafion films. Interactions between the magnetic particles and the Nafion shorten the useable lifetime of the composite if the film is dried too long. Composite films are dried for 50 minutes whereas simple Nafion films are dried for upwards of 2 hours.

EXAMPLE 4 – TMODA and TMODA Composite Modified Electrode

A modified Nafion suspension, octadecyltrimethylammonium bromide (TMODA, Sigma) Nafion, was employed as a less harsh alternative to pure Nafion.

TMODA Chemistry and Preparation

The TMODA solution was prepared in the laboratory following the procedure outlined by Klotzbach *et al.*, *Membrane Sci.* 2006, 276-283. TMODA Nafion is formed by exchanging the proton of Nafion with the TMODA cation. The TMODA modified Nafion has a lower ion exchange capacity because the film volume increases and is less acidic than a pure Nafion film. The milder environment is less likely to dissolve the magnetic microparticles and their coatings than the highly acidic proton exchanged Nafion.

Preparation of TMODA and Composite Films

The TMODA films cast on the electrode are prepared from TMODA modified Nafion. Prior to use, the suspension is vortexed approximately 15 seconds to ensure effective mixing of the Nafion and TMODA. The palladium working electrode was modified with either (a) a TMODA film; (b) a composite of TMODA and magnetic microparticles with no external magnetic field applied; (c) a composite of TMODA and magnetic microparticles

formed under an external magnetic field; or (d) a composite of TMODA and 3 to 10 μm glass beads with density 2.5 g/cm^3 (Polysciences, Inc.).

The simple TMODA film was prepared by depositing 5 μL of the TMODA suspension on the surface of the electrode with a pipette.

For composite films, a 5 μL aliquot of TMODA and magnetic microparticles is applied to the electrode. The composite mixture was 50 mg microparticles per mL suspension. The composite suspensions were vortexed briefly to suspend microparticles prior to use and were refrigerated when not in use. A NdFeB ring magnet was used for magnetic field alignment (Figure 4).

In each case, the modified electrode was air dried in an upright position for 30 minutes prior to being placed in a vacuum desiccator. All TMODA films were dried in a vacuum desiccator for 50 minutes.

The density of TMODA is not readily determined and varies with preparation of each new batch of TMODA modified Nafion, thus film thicknesses for TMODA and composite films are unknown. It is assumed that thicknesses are comparable to those of the Nafion films.

EXAMPLE 5 – Nafion Results

Comparison to literature studies

In order to verify the response seen from the reductive wave as actual hydrogen absorption, the unmodified palladium electrode was tested in acidic solution. Figure 3 shows a voltammetric profile for the bare, unmodified Pd electrode in 0.1 M HNO_3 at scan rate of 50 mV/s.

The results seen on the bare electrode are similar to that of the bare electrode in sulfuric acid as witnessed by Jerkiewicz, *Progress in Surface Science* 1998, 57, 137-186. The reductive wave in shows a reduction of surface oxides followed by steep take off of the hydride absorption. The oxidative wave shows a large peak around 0 V corresponding to the desorption of hydrogen.

Composite Films of Nafion and Magnetic Particles

Initial tests of composite Nafion films were done with Bangs PMC3N magnetic microparticles. The composite film was dried within the field of a NdFeB ring magnet. An overlay of voltammetric data comparing the Nafion film with the composite can be seen in

Figure 4. The magnetic particles show enhanced current output at lower overpotential during the absorption process. It is unclear as to why the desorptive wave is so much larger for the blank Nafion film than for the composite. The acidity of Nafion does not appear to be ideal for the polymer coated Bangs microparticles, thus they were not used in further experiments.

EXAMPLE 6 – TMODA Results

The following details the results of the composite films made with TMODA.

SiMAG Particles

The SiMAG particles were the only magnetic microparticles used in composites with TMODA-Nafion because of their strong field strength and acid resistant silane coating. Figure 5 displays the cyclic voltammogram overlay of the SiMAG particles and TMODA-Nafion composite in 1.0 mM HNO₃ electrolyte with scan rate of 50 mV/s. It is apparent that the C1 particles show greater current gains compared to the other SiMAG particles. This is likely due to the short silane chain length of the particle coating. Therefore, C1 particles were the choice magnetic particles for remaining trials.

SiMAG Particle in Film	Current (mA) at -1.0 V
C1	0.4065
C3	0.1682
C8	0.1683
C18	0.1583

Table 3. Current output based on magnetic particle type in the film at -1.0 V potential during the reductive scan.

The current output based on SiMAG particle type in the composite at -1.0 V potential during hydrogen absorption is shown in Table 3. At this arbitrary potential it is clear that C1 magnetic microparticles outperform the other SiMAG magnetic particles by nearly three times the current output.

To confirm that the effect of increased current at a lesser potential was due exclusively to the magnetic property of the particles, and not general particulate matter effects in the film, a composite film of TMODA-Nafion containing glass microbeads was cast and tested in 1.0 mM HNO₃ electrolyte. Figure 6 shows an overlay of the CV data obtained for a blank TMODA-Nafion film, a composite of TMODA-Nafion and C1, and a composite of TMODA and glass microbeads. The glass microbeads showed similar performance to that of the blank thus confirming that the increased current observed is due solely to the presence of the magnetic microparticles and not to general particulate species.

The question arose as to whether field alignment of the magnetic microparticles had any influence on current gains. Figure 7 displays an overlay of cyclic voltammograms of blank TMODA, and composites containing C1 microparticles that are either magnetized or nonmagnetized. The magnetized composite film was exposed to an external magnetic field while drying. It is found that the non-magnetized composite outperforms the magnetized version. Table 4 displays data describing the current output at -1.0 V on the reductive wave. The nonmagnetized C1 particles outperform the magnetized C1 particles with approximately 1.5 times more current at the same overpotential. The composite films both outperform the blank TMODA-Nafion film, but the nonmagnetized C1 particles provide 2.7 times more current output than the blank, whereas the magnetized C1 particles provide 1.8 times more current. This raises the question as to why not externally magnetizing the microparticles shows greater current gains than the magnetized particles. This is likely due to a better distribution of the magnetic field on the surface of the electrode in the nonmagnetized case where the particles have a residual magnetic field. Placing the electrode in an external magnetic field to magnetize the microparticles causes the particles to align and form pylons on the electrode surface. This causes a less well distributed magnetic field on the electrode surface with less magnetic particles immediately at the electrode surface.

Film Composition	Current (mA) at -1.0 V
Blank TMODA	0.118
Magnetized C1 particles in TMODA	0.216
Non-magnetized C1 particles in TMODA	0.321

Table 4. Current output based on film composition at -1.0 V potential during the reductive scan.

pH Effects

The effect of pH was studied in order to determine how the system responds to changes in the concentration of H^+ in solution.

The location of the hydride desorption peak was not well defined in supporting literature, causing uncertainty about the large broad peak occurring on the oxidative wave. To verify that this peak is that of hydride desorption, the C1 and TMODA composite film was tested in 1.0 M $NaNO_3$ electrolyte at pH 5.16 and pH 10.01. NaOH was added to the electrolyte solution to achieve pH 10.01. An increase in pH caused a decrease in the oxidative wave, indicative of lower H^+ ion concentration rather than an oxide stripping wave. The

TMODA-Nafion film was also tested in the 1.0 mM NaNO₃ electrolyte at pH 10. Figure 8 shows an overlay of the CV data collected at pH 5 and pH 10.

Examination of Figure 8 revealed that the blank TMODA-Nafion electrode in pH 5 electrolyte performed similarly to the composite film in pH 10. Thus, it took five orders of magnitude decrease in the concentration of H⁺ for the magnetic microparticles to give current output comparable to an electrode without magnets. The absorption take-off peak in the reductive scan for C1 at pH 5 occurs several hundred millivolts before that of the blank films. The blank TMODA film modified electrodes can be thought of as the traditional palladium hydride system. Therefore, by adding magnetic microparticles to the traditional palladium hydride system, the overpotential required to electrochemically absorb hydrogen is decreased.

Table 5 displays the current output for the blank films and composite films at pH values of 5 and 10. The blank TMODA films perform similarly regardless of H⁺ concentration. The magnetic C1 microparticles give nearly twice as much current output as the blank film in pH 5 solution, thus indicating that the magnetic particles are inducing the increased current output. This means that the absorption rate of hydrogen into the metal is increased by adding magnetic microparticles to the surface of the electrode.

Film Composition	Current (mA) at -1.0 V
Blank TMODA, pH 5	0.110
Blank TMODA, pH 10	0.082
C1 particles in TMODA, pH 5	0.193
C1 particles in TMODA, pH 10	0.124

Table 5. Current output based on film composition and pH of electrolyte at -1.0 V potential during the reductive scan.

WHAT IS CLAIMED IS:

1. A device comprising a magnetic element, which comprises a magnetic material, wherein the magnetic element is adapted to absorb hydrogen to form hydride.
2. The device of claim 1, wherein the magnetic element comprises a hydrogen-absorbing material different from the magnetic material.
3. The device of claim 1, wherein the magnetic material is a hydrogen-absorbing material.
4. The device of claim 1, wherein the magnetic element comprises a substrate and a coating disposed on the substrate, wherein:
 - (i) the substrate comprises a hydrogen-absorbing material different from the magnetic material, and wherein the coating comprises the magnetic material, or
 - (ii) the substrate comprises the magnetic material, and wherein the coating comprises a hydrogen-absorbing material different from the magnetic material.
5. The device of claim 1, wherein the magnetic element comprises a mixture of the magnetic material and a hydrogen-absorbing material different from the magnetic material.
6. The device of claim 1, wherein the magnetic element comprises metal for hydrogen absorption.
7. The device of claim 1, wherein the magnetic element comprises Pd or an alloy thereof.
8. The device of claim 1, wherein the magnetic element comprises an AB₂ or AB₅ material.
9. The device of claim 1, wherein the magnetic material comprises Fe₃O₄, Fe₂O₃, NdFeB, SmCo₅, Sm₂Co₁₇, Sm₂Co₇, La_{0.9}Sm_{0.1}Ni₂Co₃, Ti_{0.51}Zr_{0.49}V_{0.70}Ni_{1.18}Cr_{0.12}, or a combination thereof.
10. The device of claim 1, wherein the magnetic material comprises Fe₃O₄, NdFeB, SmCo₅, or a combination thereof.
11. The device of claim 1, wherein the magnetic material comprises at least one magnetic particle, magnetic wire, or magnetic mesh.
12. The device of claim 1, wherein the magnetic material comprises at least one magnetic particle comprising a magnetic core and a protective coating.

13. The device of claim 1, wherein the magnetic material comprises at least one magnetic particle comprising a magnetic core and a silane protective coating.
14. The device of claim 1, wherein the magnetic material comprises at least one magnetic particle comprising a Fe_3O_4 magnetic core and a $-\text{Si}-\text{CH}_3$ protective coating.
15. The device of claim 1, wherein the magnetic material is not externally magnetized.
16. The device of claim 1, wherein the magnetic material is externally magnetized.
17. The device of claim 4, wherein the magnetic coating further comprises at least one polymer.
18. The device of claim 4, wherein the magnetic coating further comprises at least one ion exchange polymer or at least one conducting polymer.
19. The device of claim 4, wherein the magnetic coating further comprises at least one Nafion polymer or derivative thereof.
20. The device of claim 4, wherein the magnetic coating further comprises octadecyltrimethylammonium bromide Nafion or an alkyl ammonium modified Nafion.
21. The device of claim 1, wherein the magnetic element comprises metal, and wherein the presence of the magnetic material decreases the potential or energy tax/cost for electrochemically absorbing hydrogen to form metal hydride.
22. The device of claim 1, wherein the magnetic material increases the absorption rate of hydrogen into the magnetic element by at least 10%, or wherein the magnetic material increases the desorption rate of hydrogen into the magnetic element by at least 10%.
23. The device of claim 1, wherein the magnetic element is an electrode.
24. The device of claim 1, wherein the magnetic element comprises metal hydride.
25. The device of claim 1, wherein the device is a fuel cell.
26. A metal hydride element comprising a magnetic material.
27. The metal hydride element of claim 26, wherein the metal hydride element comprises a substrate and a coating disposed on the substrate, wherein:
 - (i) the substrate comprises a metal hydride different from the magnetic material, and wherein the coating comprises the magnetic material, or

(ii) the substrate comprises the magnetic material, and wherein the coating comprises a metal hydride different from the magnetic material.

28. The metal hydride element of claim 26, wherein the metal hydride element comprises a mixture of the magnetic material and a metal hydride different from the magnetic material.

29. The metal hydride element of claim 26, wherein the magnetic material comprises metal hydride.

30. The metal hydride element of claim 26, wherein the metal hydride element comprises Pd, an alloy thereof, or an AB₂ or AB₅ material.

31. The metal hydride element of claim 26, wherein the magnetic material comprises at least one magnetic particle, magnetic wire, or magnetic mesh.

32. The metal hydride element of claim 26, wherein the magnetic material comprises Fe₃O₄, Fe₂O₃, NdFeB, SmCo₅, Sm₂Co₁₇, Sm₂Co₇, La_{0.9}Sm_{0.1}Ni₂Co₃, Ti_{0.51}Zr_{0.49}V_{0.70}Ni_{1.18}Cr_{0.12}, or a combination thereof.

33. The metal hydride element of claim 26, wherein the presence of the magnetic material decreases the overpotential for electrochemically absorbing hydrogen to form metal hydride.

34. The metal hydride element of claim 26, wherein the metal hydride element is substantially free of any metal hydroxide.

35. A fuel cell device comprising the metal hydride element of claim 26 as electrode.

36. A nickel metal hydride battery comprising the metal hydride element of claim 26 as electrode.

37. A method for making the metal hydride element of claim 26, comprising (i) contacting a magnetic element with a hydrogen source, wherein the magnetic element comprises a metal-based hydrogen-absorbing material and a magnetic material; and (ii) applying an electrochemical potential to form a metal hydride element.

38. A method for making the metal hydride element of claim 26, comprising contacting a magnetic element with a pressurized hydrogen gas, wherein the magnetic element comprises a metal-based hydrogen-absorbing material and a magnetic material.

39. A method for using the device of claim 1, comprising absorbing hydrogen into the magnetic element, and optionally desorbing hydrogen therefrom.

40. The method of claim 39, further comprising demagnetizing the magnetic material to reduce desorption of the absorbed hydrogen.
41. A method for using the metal hydride element of claim 26, comprising desorbing hydrogen from the metal hydride element, and optionally resorbing hydrogen to form metal hydride.
42. The method of claim 41, further comprising using the desorbed hydrogen to generate energy.

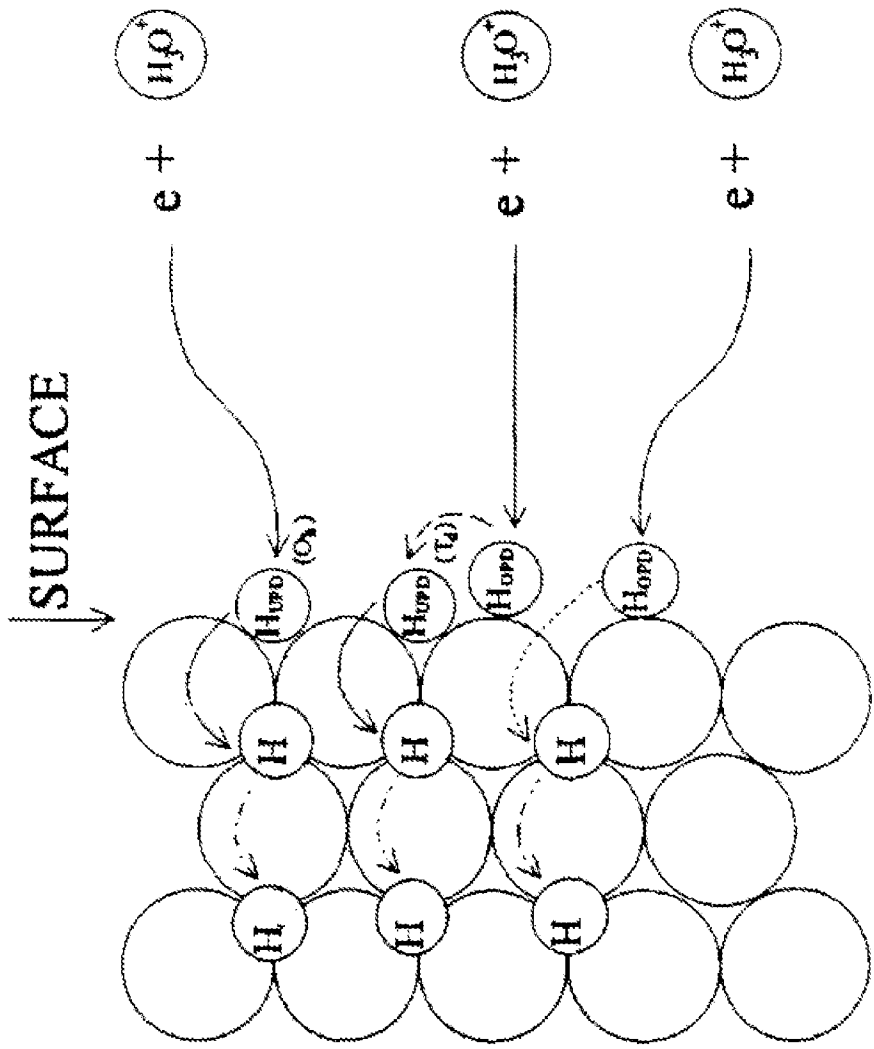


FIGURE 1

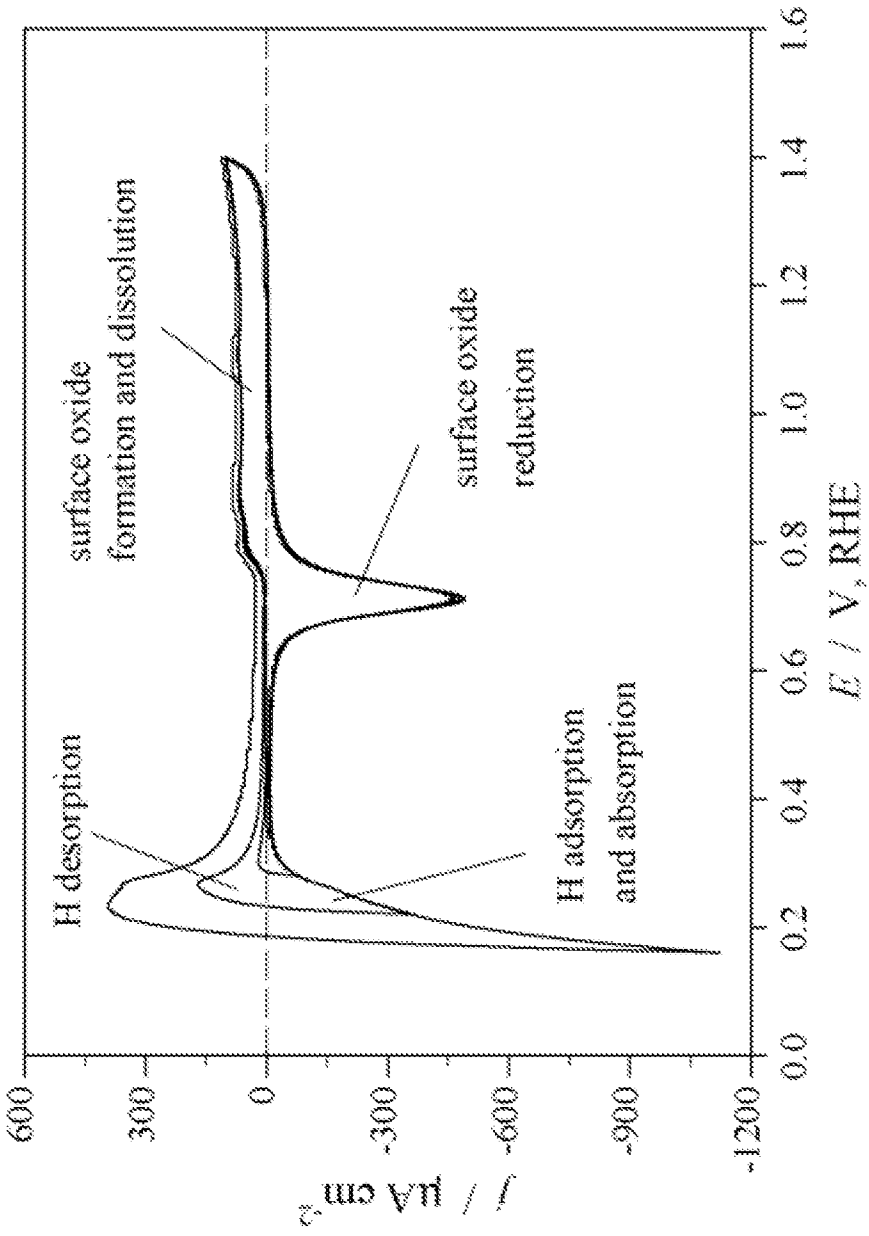


FIGURE 2

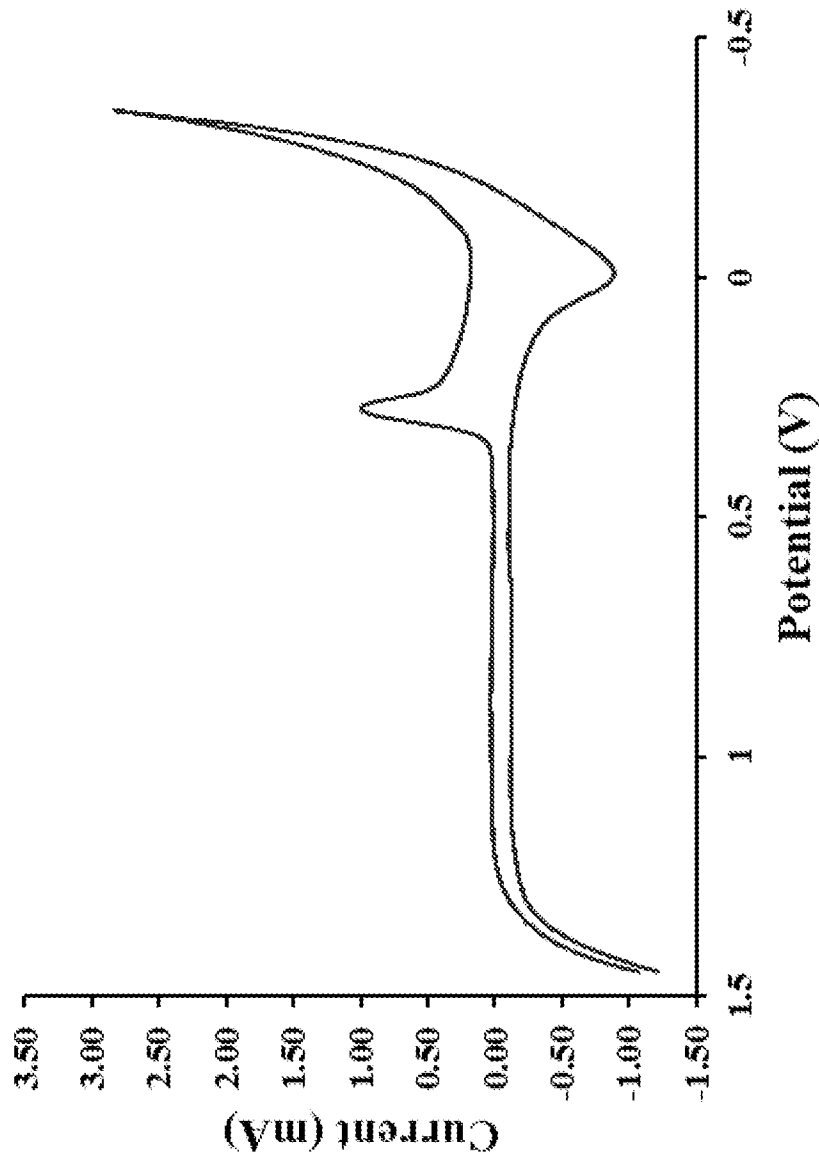


FIGURE 3

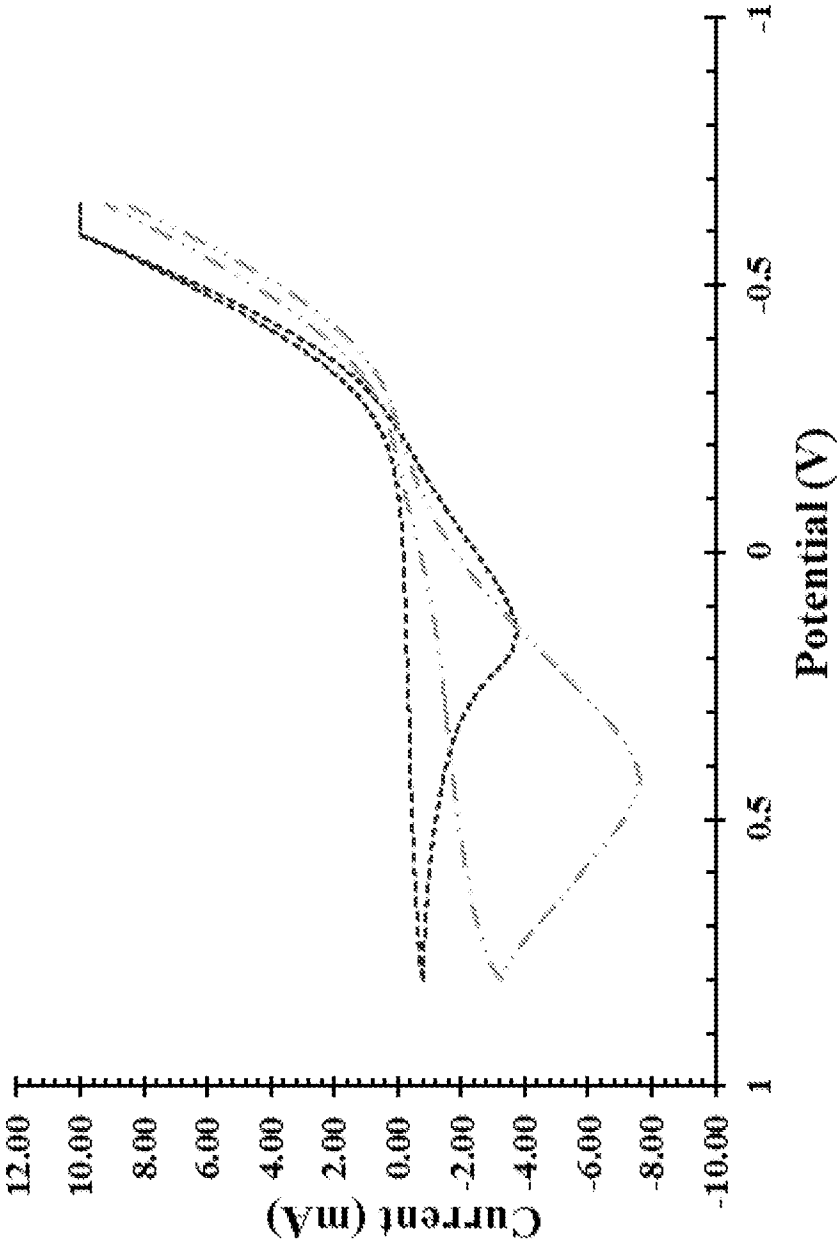


FIGURE 4

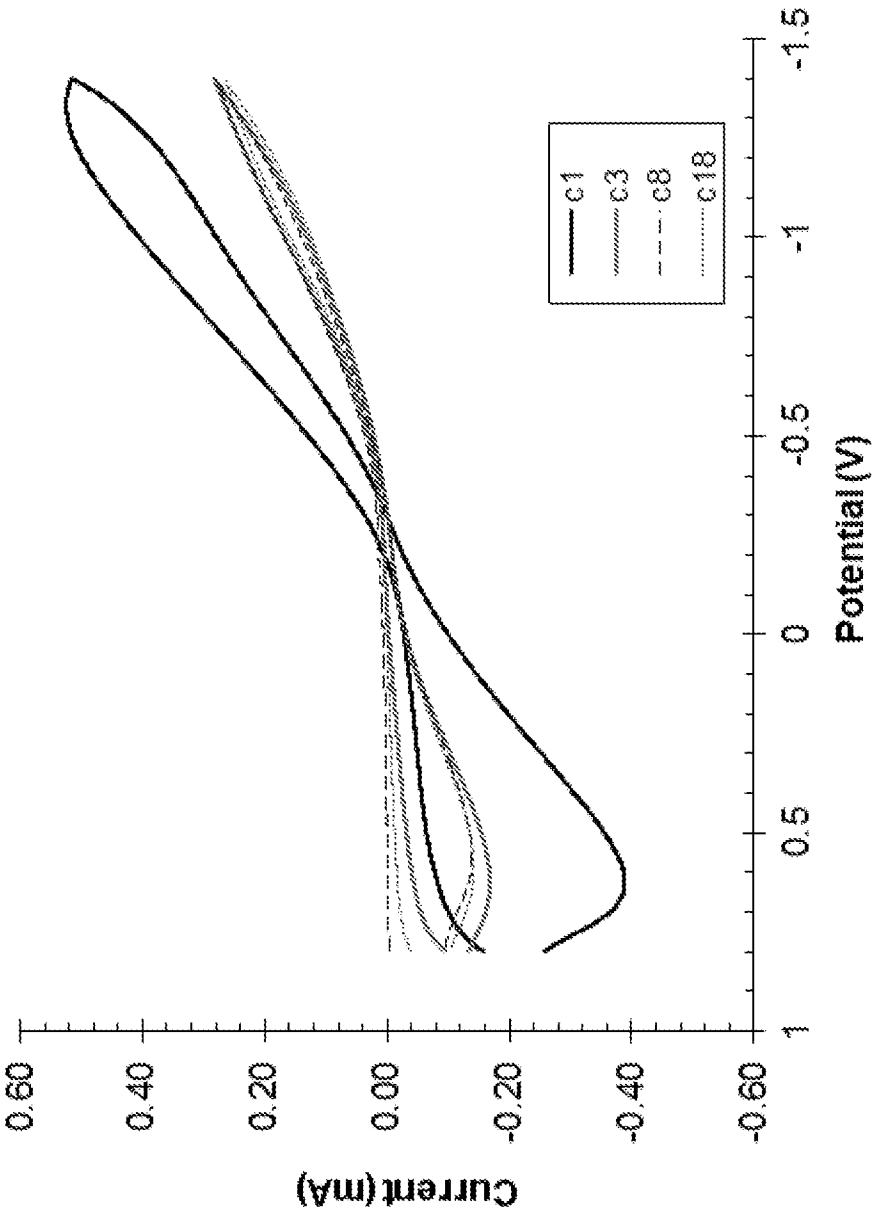


FIGURE 5

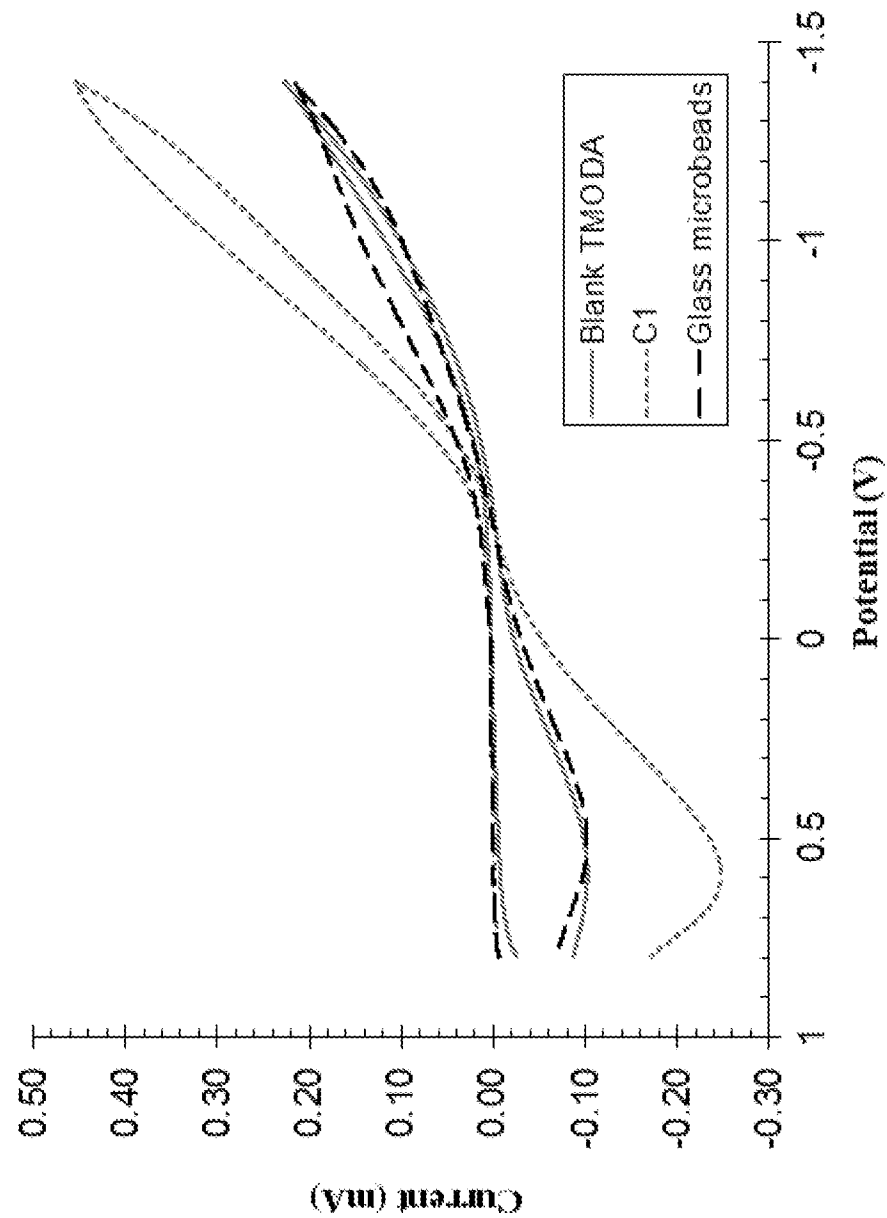


FIGURE 6

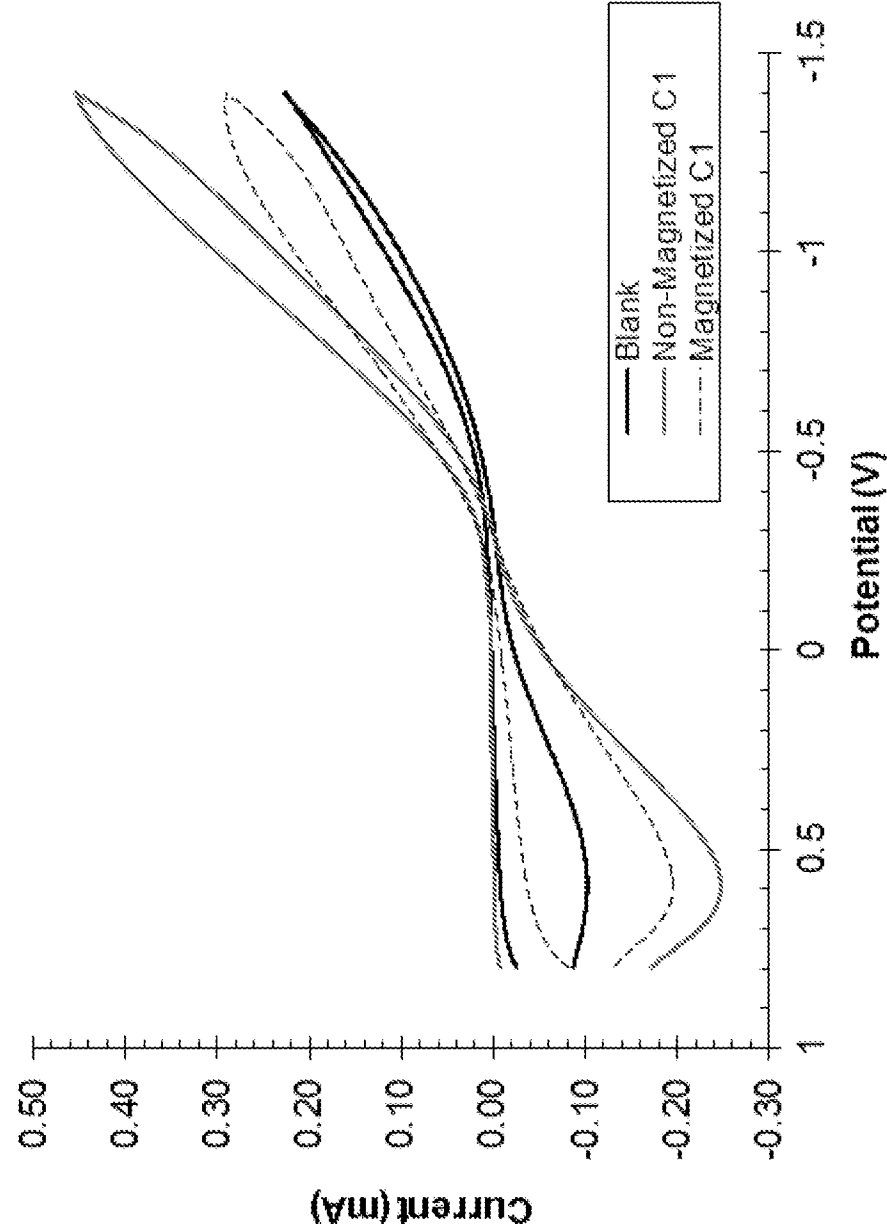


FIGURE 7

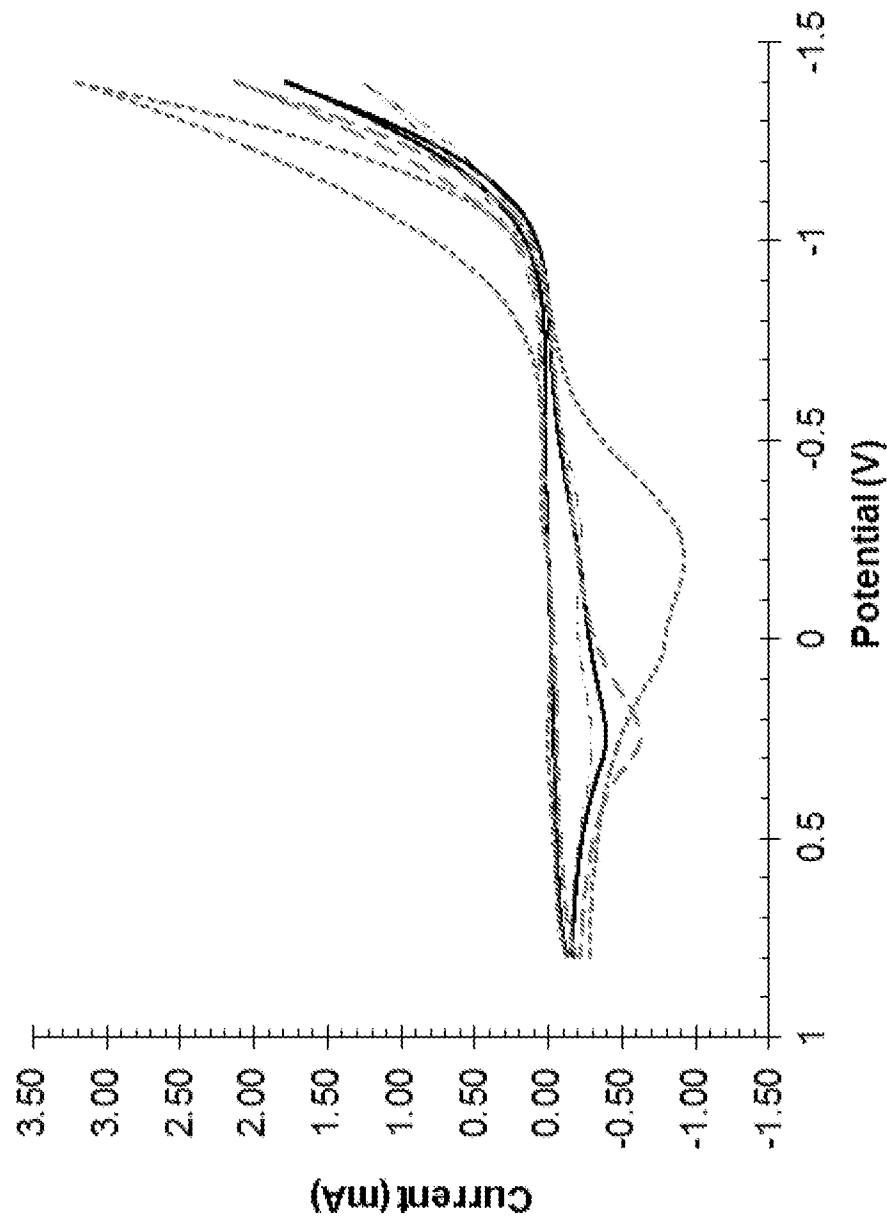


FIGURE 8

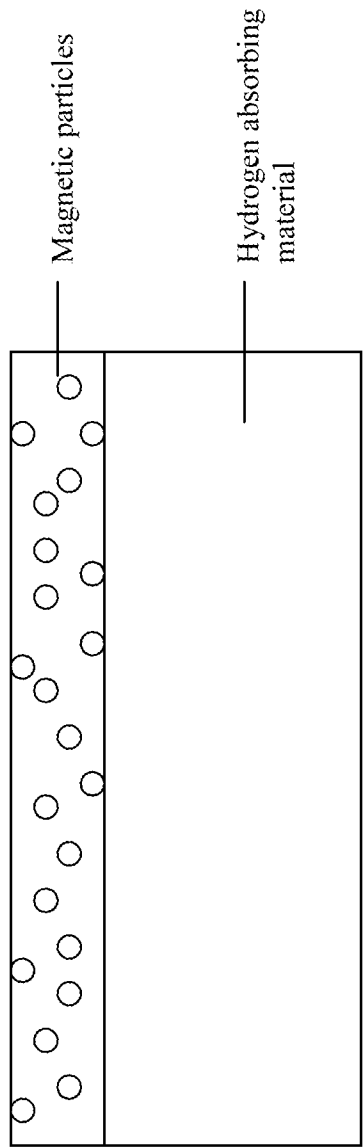


FIGURE 9

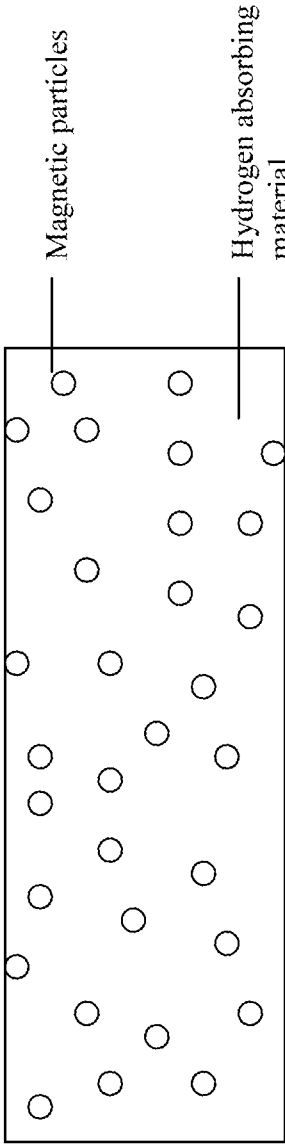


FIGURE 10

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2013/032666

A. CLASSIFICATION OF SUBJECT MATTER
INV. C01B3/00
ADD.

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)
C01B 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 practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	KHRUSSANOVA M ET AL: "Hydriding of mechanically alloyed mixtures of magnesium with MnO ₂ , Fe ₂ O ₃ and NiO", MATERIALS RESEARCH BULLETIN, ELSEVIER, KIDLINGTON, GB, vol. 26, no. 7, 1 July 1991 (1991-07-01), pages 561-567, XP024079779, ISSN: 0025-5408, DOI: 10.1016/0025-5408(91)90098-7 [retrieved on 1991-07-01] figures 1,3; table 1	1,2,5,6, 8-11,15, 21,22, 26,29, 31-33, 35-41
X	US 4 613 362 A (WELTER JEAN-MARIE [DE] ET AL) 23 September 1986 (1986-09-23) column 2, line 15 - line 65 ----- -/-	1,2,4-6, 8-11,15, 21,22, 26-29, 31-41



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

18 July 2013

Date of mailing of the international search report

26/07/2013

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Cristescu, Ioana

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/032666

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.: 1, 3, 11, 15, 23-26, 29, 31, 35-37, 39, 41, 42(all partially)
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2013/032666

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2009/018821 A2 (FRAUNHOFER GES FORSCHUNG [DE]; STEPHANI GUENTER [DE]; ROENTZSCH LARS []) 12 February 2009 (2009-02-12) page 4, line 5 - line 35 -----	1,2,4-7, 9,11,12, 15,21, 22,26, 28, 30-34, 38-42
X	EP 2 153 482 A1 (TOYOTA MOTOR CO LTD [JP]) 17 February 2010 (2010-02-17) -----	1-6,8, 10-12, 16, 21-25, 29,35-37
Y	paragraph [0041] - paragraph [0046]; figure 2 -----	13,14, 17-20
Y	WO 2011/000828 A1 (FRAUNHOFER GES FORSCHUNG [DE]; POPALL MICHAEL [DE]; OLSOWSKI BIRKE-ELI) 6 January 2011 (2011-01-06) claims 1-4 -----	13,14, 17-20
T	Dietrich Berndt ET AL: "Batteries" In: "Ullmann's Encyclopedia of Industrial Chemistry", 15 June 2001 (2001-06-15), Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, XP055071720, ISBN: 978-3-52-730673-2 DOI: 10.1002/14356007.a03_343, page 108 - page 111 -----	

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2013/032666

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4613362	A	23-09-1986	DE 3147839 A1 16-06-1983
		EP 0083735 A1 20-07-1983	
		JP S58110401 A 01-07-1983	
		US 4613362 A 23-09-1986	

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		WO 2009018821 A2 12-02-2009	

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		WO 2008142515 A1 27-11-2008	

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		DE 102009036945 A1 24-03-2011	
		EP 2449616 A1 09-05-2012	
		JP 2012531516 A 10-12-2012	
		KR 20120110088 A 09-10-2012	
		US 2012100428 A1 26-04-2012	
		WO 2011000828 A1 06-01-2011	

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box II.2

Claims Nos.: 1, 3, 11, 15, 23-26, 29, 31, 35-37, 39, 41, 42(all partially)

Independent claims 1, 26 and 37 are directed to materials that comprise a magnetic material and a metal hydride and to a method for making the hydride respectively. Nickel is a material widely known and employed as metal hydride in the electrodes of batteries and is also a well-known ferromagnetic material.

The initial phase of the search revealed a very large number of documents relevant to the issue of novelty. So many documents were retrieved that it is impossible to determine which parts of the claims 1, 3, 11, 15, 23-26, 29, 31, 35-37, 39, 41 and 42 may be said to define subject-matter for which protection might legitimately be sought (Article 6 PCT). For these reasons, the search was performed taking into consideration the non-compliance in determining the extent of the search of claims 1, 3, 11, 15, 23-26, 29, 31, 35-37, 39, 41 and 42. In addition, present independent claims 1 and 26 relate to an extremely large number of possible compounds. Support in the sense of Article 6 PCT is to be found however in the description (examples) for only the compounds wherein the hydrogen-absorbing material is different from the magnetic material.

The search of claims was restricted to a device comprising a magnetic element comprising a magnetic material and a hydrogen-absorbing material different from the magnetic material.

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guidelines C-IV, 7.2), should the problems which led to the Article 17(2) declaration be overcome.