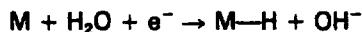


Description

The subject matter of this invention relates to the field of energy storage and utilization with an improved battery and to an electrode for use therein. More particularly, the invention relates to a battery having a mechanically self-supporting ribbon electrode using disordered active material which may be formed by rapid solidification. The battery electrode stores electrochemical energy for subsequent release to produce an electrical current while maintaining structural integrity during such a cycle.

Some research has been conducted involving hydrogen storage secondary batteries. However, a basic understanding resulting in a viable approach to optimizing such batteries has not been forthcoming in the scientific or patent literature. Examples of such efforts are U.S. Patents Nos. 3,669,745 and 3,824,131 and a technical paper entitled "A New Type of Reversible Negative Electrode for Alkaline Storage Batteries Based on Metal Alloy Hydrides," 1974, 8th International power Sources Conference. These research efforts have not resulted in widespread commercial utilization of this battery technology. In fact, the prior research suggests no significant improvement over conventional battery systems such as nickel cadmium. As a result, the hydrogen storage battery system has apparently been ignored or abandoned.

Secondary batteries using a hydrogen rechargeable electrode operate in a different manner than lead acid, nickel cadmium or other battery systems. The hydrogen storage battery utilizes an anode which is capable of reversibly electrochemically storing hydrogen and usually employs a cathode of nickel hydroxide material. The anode and cathode are spaced apart in an alkaline electrolyte. Upon application of an electrical current to the anode, the anode material (M) is charged by the absorption of hydrogen:



Upon discharge the stored hydrogen is released to provide an electric current:



The reactions are reversible and this is also true of the reactions which take place at the cathode. As an example, the reactions at a conventional nickel hydroxide cathode as utilized in a hydrogen rechargeable secondary battery are as follows:



The battery utilizing an electrochemically hydrogen rechargeable anode offers important potential advantages over conventional secondary batteries. Hydrogen rechargeable anodes should offer significantly higher specific charge capacities than lead anodes or cadmium anodes. Furthermore, lead acid batteries and nickel-cadmium type secondary batteries are relatively inefficient, because of their low storage capacity and cycle life. A higher energy density should be possible with hydrogen storage batteries than these conventional systems, making them particularly suitable for battery powered vehicles and other mobile applications. Hydrogen storage batteries have not lived up to their potential, however, because of the materials and mechanical structures used.

The materials used for the hydrogen rechargeable anode of the battery are of utmost importance since the anode must efficiently perform a number of functions within useful operating parameters in order to have an efficient charge/discharge cycle. The material must be capable of efficiently storing hydrogen during charging with insignificant self-discharge until a discharge operation is initiated. Since reversibility of the charge/discharge reactions is necessary, a highly stable bonding of hydrogen to the storage sites of the anode is not desired. On the other hand, it is also undesirable if the bonds between the hydrogen atoms and the anode material are too unstable. If the bonds are too unstable during charging, the dissociated hydrogen atoms may not be stored by the anode, but may recombine to form hydrogen gas such as in the electrolysis of water. This can result in low efficiencies, loss of electrolyte and inefficient charging.

Another important characteristic of the hydrogen rechargeable electrode is its structure. Prior art hydrogen storage materials use a binder material to physically hold the hydrogen storage material together and in electrical contact with a grid collector. Since the binder material is not itself an active hydrogen storage material, its use decreases the capacity of the cell. The increase in weight of inactive material also decreases the energy density of a cell using the electrode.

As an electrode charges and discharges, the hydrogen storage material expands and contracts. These volumetric changes can cause cracking and disintegration of the electrode's structural integrity. The electrode tends to fail if the hydrogen storage material loses electrical contact with, or falls away from, the collector grid. Using more binder material will delay this problem and extend cycle life of the cell, but the capacity of the cell decreases.

Another problem experienced by some hydrogen rechargeable electrodes is low charge and discharge rates. Increasing the surface area of an electrode shortens the hydrogen diffusion lengths and increases the charge and discharge rates. For prior art electrodes, increasing the surface area is achieved by increasing

the porosity. Increasing the porosity, however, allows the electrolyte to corrode and degrade the electrode's structural integrity. Again, this leads to early electrode failure as the material disintegrates and falls away from the grid collector. Attempts to alleviate this problem by coating the surface to prevent the active material from falling away is not helpful since any coating would decrease the needed porosity.

Many previous attempts to utilise hydrogen in secondary batteries have proven to be unsuccessful because of the limiting factors of structural and electrical integrity in using the hydrogen storage materials.

In accordance with the present invention, a hydrogen storage electrochemical cell comprises

- (a) at least one hydrogen storage electrode comprising at least one self-supporting solid, metallic, amorphous electrochemically active body formed by rapid solidification from a melt thereby having a non-particulate, dimensionally anisotropic shape with a continuous amorphous structure throughout, the body having a composition comprising at least four elements, said elements being 40 to 75 atomic percent titanium, 15 to 55 atomic percent nickel, from trace amount to 15 atomic percent aluminium, and at least one of vanadium, hafnium, niobium, and zirconium each of the elements being present in an effective amount so that the electrode is capable of being electrochemically charged with hydrogen to store energy and capable of electrochemically discharging hydrogen and realising energy, while maintaining its structural integrity during electrochemical charge and discharge cycles;
- (b) at least one counter electrode for allowing the release of the energy stored in the hydrogen storage electrode, the counter electrode being positioned in the cell and spaced in operative relation with the hydrogen storage electrode; and
- (c) casing means having the hydrogen storage electrode and the counter electrode positioned therein.

The invention herein provides a new and improved cell having an electrode with an active material and mechanical structure allowing for high charge and discharge rates, efficient reversibility, high electrical efficiency, bulk hydrogen storage without substantial structural change of poisoning, mechanical integrity over long cycle life, and deep discharge capability.

The present invention includes an electrode using a disordered active material. The problems in prior art electrochemical cells as discussed above are obviated by the present invention, all with improved electrochemical performance of the cells.

The present invention provides an electrochemical cell containing an electrolyte wherein the electrode includes an active material which is substantially nonporous or impermeable to the electrolyte.

The electrochemical cell may be assembled using a self-supporting electrode which includes the steps of producing a disordered active material, aligning the material in a predetermined position in a cell casing and rapidly solidifying the disordered active material.

Some examples of hydrogen storage electrochemical cells according to the invention and methods for their manufacture will now be described with reference to the accompanying drawings, in which:-

Figure 1A is a cut-away side view of a flat cell;

Figure 1B is a side view of a battery using a plurality of the cells illustrated in Figure 1A;

Figure 1C is a side view of a jelly roll cell;

Figure 1D is a top view of a wound cell embodiment using an inventive electrode;

Figure 1E is a side view of a spool cell;

Figure 1F is a top view of a ribbon illustrating the spool cell components;

Figure 2 is a diagrammatic side view of an apparatus used in a rapid solidification process;

Figure 3 is a block diagram of an illustrative apparatus for depositing a collector on an electrode;

Figure 4 is a graph of cell capacity versus cycle life for a cell having a ribbon electrode with a titanium-nickel-aluminum-vanadium composition; and,

Figure 5 is a graph of cell capacity versus discharge rate for a number of cells having a ribbon electrode.

The present invention provides an electrode including a disordered active material formed by rapid solidification. The resultant material does not need a binder to be used as an electrode, and thus, is considered self-supporting. The material also is substantially nonporous and impermeable to an electrolyte. The composition of the material includes titanium, nickel and aluminum in combination with at least one other element such as zirconium, niobium, hafnium, or vanadium. Various counter electrode systems, and more particularly, electrolytes, may be used in an electrochemical cell containing the electrode. The electrodes of the invention provide greatly improved cycle life without a significant decrease in cell capacity. Without the need for an inactive electrode material such as a binder, the energy density of a cell containing the electrode is significantly increased.

In particular, the electrodes of the present invention provide a disordered material. The disordered material includes means for storing hydrogen and subsequently discharging at least a portion of the stored hydrogen to provide a supply of electrons. Such disordered materials have tailor-made local chemical environments which are designed to improve the electrochemical performance of the electrode by increasing the density of catalytically active sites for hydrogen dis-association and also of hydrogen storage sites.

Disordered materials are ideally suited for manipulation since they are not constrained by the symmetry of a single phase crystalline lattice or by stoichiometry. By moving away from the materials

having such restrictive single phase crystalline symmetry, it is possible to accomplish a significant alteration of the local structure and chemical environments involved in electrochemical hydrogen storage to greatly enhance the properties of the hydrogen storage electrode.

The types of disordered structures which provide the local structural chemical environments for the enhanced electrochemical hydrogen storage characteristics contemplated by the invention include:

1. Mixtures of polycrystalline or micro-crystalline and amorphous phases.
2. Amorphous materials containing one or more amorphous phases.

An advantage of the disordered materials is that their compositions can be varied over a substantially continuous range of percentages for the component elements to enhance the structural integrity of the material, and thus, the electrode. Providing a high degree of mechanical integrity to the structure of the electrode significantly extends its cycle life. Furthermore, the disordered material allows the flexibility to maximise the cell capacity while maintaining the structural integrity of the electrode.

After improving the capacity and cycle life of cells using the electrodes, the charge and discharge rate properties also may be optimised. These properties describe the relationship of voltage and time as a function of charge and discharge rates: The width and thickness of the electrodes can be adjusted to control the surface area to volume ratio and thus vary the charge-discharge rate properties.

The materials of the present invention may have anisotropic dimensions which means that the material exhibits lengths of different values when measured along axes in different directions. Thus, the material will generally have different length, width and thickness dimensions or at least length and width dimensions which are significantly greater than the thickness of the material. Examples of suitable anisotropic material are a ribbon, wire, or sheet. These examples, however, are not meant as limitations. The dimensions and configurations of an electrode and a battery made from such an electrode are dependent upon the application and can be of any size, shape, capacity, etc. as required. Preferably, the thickness of the material is less than about 50 microns (μm). The material can be made in a continuous fashion with the length cast or cut in lengths of a predetermined value.

Powder electrodes of the prior art must rely upon porosity and particle size to improve charge-discharge rate properties. The present invention is not limited by these constraints and does not increase the porosity of the material to increase the charge-discharge rates. The problem of corrosion and structural degradation is minimized by not increasing the porosity. The material used as the electrodes of the present invention can be made substantially nonporous and impermeable to the electrolyte and thus minimize the corrosion problem. Hence, the structural integrity of the material is preserved to insure long cycle life.

The porosity of the material can also be considered in terms of the mean pore size of the material which in the case of the present invention is less than 0.001 microns (μm). Alternatively, the total porosity of the material measured by any conventional method, such as the Mercury Intrusion Method, would be less than approximately 5% by volume of the material.

It is important to distinguish between the porosity of the material and the void space which may exist in the materials. Porosity describes the property of containing pores which are minute channels through a solid or open spaces in a solid. Porosity also can be used to describe the total volume occupied by such pores. Void spaces differ in that the spaces in a solid are closed and do not exist as channels through the solid. Although void space may affect the density of the material, porosity is unaffected.

Preferably, the electrode is formed with an irregular surface having ridges, wrinkles, and/or holes through the material which result in anisotropic tensile properties. These holes or any other macroscopic passages in the material are to be distinguished from the pores discussed above.

The density of the materials used to make the electrodes and the bulk density of the electrode are significantly greater than many of the materials or fabricated electrodes of the prior art. Preferably, the density of the material of the electrode is not less than 5 g/cc (cm^3) nor greater than 8 g/cc (cm^3). Optimally, the density of the material of the electrode is in the range of about 6 to 7.5 g/cc (cm^3). The materials of the present invention preferably have a density greater than about 90% of the density of the mixed phase polycrystalline ingot form of the material. The bulk density of the electrode is determined by the density of the active material and the packing density of the multiple layers or windings of the active material. Packing density is the percentage of electrode space filled by the active material instead of other electrode material such as a binder, for example, or space in the form of voids and/or pores. A packing density of 80% or greater is possible with the invention.

The present invention contemplates compositions of disordered materials which charge by absorbing and storing hydrogen and subsequently discharge at least a portion of the stored hydrogen to provide a supply of electrons. Suitable compositions include titanium, nickel and aluminium with at least one other element selected from a group consisting of zirconium, vanadium, niobium, and hafnium.

Preferably, the amount of titanium is between about 44 and 60 atomic percent; the amount of nickel between about 35 and 40 atomic percent; and the amount of aluminium between about 3 and 5 atomic percent.

The present invention also includes at least one counter electrode providing for the release of the energy stored in the electrode. The counter is spaced in operative relation with the electrode. The cell also includes a casing which has the electrode and the counter electrode positioned therein. The counter electrode includes an electrolyte placed in operative contact with the electrode. A plurality of these cells may be assembled to produce a battery. Specifically, a hydrogen storage battery may be formed if each cell

includes at least one anode means for efficient reversible hydrogen absorption and desorption. At least one cathode means is provided for reversible oxidation.

Referring to Fig. 1A, a flat cell 10 is illustrated which uses a plurality of substantially flat sheets 15 of the material described above. Interleaved between the sheets 15 is a plurality of flat tabs 20 which extend beyond the edges of the sheets 15 so that a buss tab 25 may be used to electrically contact each of the tabs 20. The buss tab 25 may then be physically crimped to compress the sheets 15 and tabs 20 together. The tabs 20 and buss tab 25 may be made of suitably conductive metals such as nickel. The flat cell 10 includes a counter electrode 30 which is substantially flat and aligned to be in operative contact with the plurality of sheets 15. A separator 35 is disposed between the counter electrode 30 and the sheets 15.

A second plurality of substantially flat sheets 40 may be spaced in operative contact with the counter electrode 30 on the side opposite the first plurality of flat sheets 15. Similarly interleaved between the sheets 40 is a second plurality of flat tabs 45 which extend beyond the edges of the sheets 40 so that a second buss tab 50 may be used. A second separator 55 is disposed between the second plurality of sheets 40 to electrically contact each of the tabs 45 and the counter electrode 30.

The cell 10 depicted in Fig. 1A may be sealed in a suitable material, such as a plastic wrap 60, which does not deteriorate in contact with the electrolyte used and allows venting of the cell 10 should it gas during operation. The first and second buss tabs 25, 50 are electrically connected to first set of leads 65 which extends outside of the cell plastic 60. Likewise, a second lead 70 electrically connects to the counter electrode 30 and extends outside of the cell plastic 60.

A plurality of cells similar to the cell 10 illustrated in Fig. 1A may be assembled as a battery 75 depicted in Fig. 1B. A battery casing 80 contains the individual cells, collectively numbered as 85. The casing 80 includes a venting means 90 should any of the cells 85 excessively gas during operation. Since the cells 85 are already sealed in plastic 60, there is no need for forming individual cell walls with the casing 80, thus reducing the space and weight of the casing 80. The casing 80 may be a rigid material or a settable material, such as an epoxy. The cells 85 are easily stacked together and placed in a mold (not shown) into which a setting material is introduced around the circumference of the stacked cells 85. The first and second lead 65, 70 extend through the casing 80 available for external connection.

Fig. 1C illustrates a jelly roll cell 100 which is made by spirally winding a flat cell about an axis 105. The jelly roll cell may then be placed in a can which contains a conductive adhesive (not shown) contacts the tabs 110 interleaved with a plurality of sheets 115 of the material described above. A separator 120 is spaced between the sheets 115 and a counter electrode 125.

Another cell embodiment is illustrated in Fig. 1D which depicts a wound cell 150 including a flat rectangular counter electrode 155. A separator 160 covers the counter electrode 155. Wound around the counter electrode 155 is the material in ribbon form 165. The configuration of the winding is a double diagonal wind in the directions illustrated by the arrows 170. This winding allows the cell 150 to bend without unraveling the winding, instead it tightens upon itself. To prevent the ribbon 165 from buckling on the edges 175 of the counter electrode 155, a sawtooth configuration 180 allows the ribbon 165 to squarely rest on the edges 175. Other suitable embodiments would use a flat edge on non-diagonal windings.

Fig. 1E illustrates a spool cell 200 which includes a rod-like counter electrode 205. A separator 210 covers the counter electrode 205. The inventive material is formed as a plurality of washer-like bodies 215, each having a hole 220. The counter electrode 205 is inserted through the hole 220 of each body 215 which stack upon one another. The washer-like bodies 215 may be stamped out of the material formed as a ribbon 225 as illustrated in Fig. 1F. The bodies 215 may be connected at point 230 and then folded upon one another before inserting the counter electrode 205 through the holes 220.

The disordered materials are preferably prepared by rapid solidification. Rapid solidification refers to methods and processes for rapidly quenching a material from the liquid state into the solid state at a quench rate sufficiently high to freeze the positions of the atoms in the atomic arrangement of the material in a variety of non-equilibrium arrangements. As previously discussed, the disordered material so produced may be one of many types of structures. The structure is either substantially amorphous or a multiphase material generally amorphous in character without long range atomic disorder, but also containing some localised atomically ordered structures such as microcrystalline and/or polycrystalline inclusions. Specifically, amorphous refers to an alloy or material which has long range disorder, although it may have short or intermediate order or even contain at times some crystalline inclusions.

The material is typically ejected in its liquid state into a high quench environment such as onto a chill wheel where it solidifies before complete crystallization can begin. Generally, the rapid solidification processes are to be contrasted to the thin film deposition processes such as sputtering or vacuum deposition which are conducted at low rates of particle transfer or to a substrate to form a thin film. preferably, the rapid solidification processes commonly referred to as melt spinning, jet casting, multiple jet casting, or planar flow casting are used. These rapid solidification processes may be used regardless of the particular apparatus used or details of the process itself. The present invention is not limited to a particular structure nor material made by the following methods. Additionally, any electrode made by these methods may initially be in either the charged or discharged state.

In particular, Fig. 2 shows a diagrammatic side view illustrating an apparatus used in a rapid solidification process. The chill surface 250, here illustrated as a wheel, travels in the direction of the arrow in close proximity to a nozzle orifice 255. The disordered material described above is heated to a molten

state in a crucible 260 by an induction heater 265. The crucible 260 is further equipped with means 270 for pressurizing the molten disordered material contained therein to effect expulsion through the nozzle orifice 255. The molten disordered material may be agitated in order to maintain uniformity of dispersion. In operation, the molten disordered material is maintained under pressure in the crucible 260 and ejected through the nozzle orifice 255 onto the surface of the rotating chill wheel 250, whereupon it immediately solidifies to form the material having anisotropic dimensions, otherwise referred to as a ribbon 275. The ribbon 275 is directed into a collection area 280 as either a continuous strip or it may be cast to a predetermined length as it is removed from the chill wheel 250. The apparatus may use a plurality of gas jets 285 to direct an inert gas, such as argon, onto the ribbon before it leaves the chill wheel. This allows control of the quench duration. Other means for aiding the solidification of the molten material may be used.

In order to obtain the disordered materials desired by the present invention, the surface of the chill wheel 250 must ordinarily be able to obtain quench rates in the area of at least 10^4 °C. Significantly lower quench rates (5^{-1}) per sec. will result in crystalline ribbons. In order to obtain a sufficiently high quench rate to make a disordered material, a 10-inch (25.4 cm) diameter chill wheel must ordinarily revolve between 2,000 and 3,000 rpm (rotations per minute). The chill wheel 250 may be optionally provided with cooling means (not shown) such as a circulating cooling liquid through its interior. The process of the present invention is usually carried out in a controlled atmosphere.

The width and thickness of the ribbon produced by the rapid solidification process can be readily adjusted by changing the interrelationship between the volumetric flow rate, the diameter of the nozzle orifice 255, and the chill wheel's surface velocity. Generally, the nozzle orifice has a diameter of about 0.0635 to 0.114 cm. and is located approximately 1—2 mm. above the chill wheel 250. The axis through the crucible 220 is tilted at an 88° angle from the horizontal in the plane of the chill wheel 250. As a general proposition, it can be stated that an increase in the chill wheel surface velocity results in production of a thinner strip and, conversely, that a reduction of the velocity results in a thicker strip.

The method also may include placing a collector in electrical contact with the material so as to collect the electrons produced during the operation of the electrode. The collector may be continuously deposited onto the material in the fashion generally depicted in Fig. 3. Referring to that figure, a block diagram of a system apparatus is illustrated. Although this process could be performed on a batch basis, continuous processing is preferred. Thus, the collector is deposited on the material in the application chamber 300. A roll of the material 305 is fed off of a payout reel 310 into and through the chamber 300 where the collector is deposited. After the collector has been deposited, the material 305 moves to a take-up reel 315. The process may be observed through a viewing port 320 or through monitoring or control instrumentation.

An additional step which is contemplated is abrading the ribbon for operative contact with an electrolyte. Such an abrading process removes any foreign matter on the surface of the material which may interfere with the contact between the material and the electrolyte.

Another means for removing foreign matter from the surface of the material is to chemically etch the material's surface. Any suitable solution such as equal parts of nitric acid and HF mixed in a 1:25 ratio with water may be used.

One may coat the electrode once the foreign matter has been removed. Such a coating could prevent the reformation of a detrimental surface layer and yet not interfere with the function of the electrode. A coating also could effect the characteristics of the active material. For example, sputter coating the inventive material with nickel appears to enhance the desorption kinetics of the material. Suitable coatings also include titanium/nickel and palladium. The coating may include other means for increasing the rate of exchange of electrons between the surface of the material and the remainder of the material relative to a material having no such coating.

Another method is the assembling of an electrochemical cell using a self-supporting electrode. This method includes the steps of producing a disordered material previously described herein preferably by rapid solidification. The method further includes aligning the electrode in the predetermined position in a cell casing. Because of the structural integrity exhibited by the inventive electrodes even on extended cycling, the electrodes may be aligned immediately after formation in a cell casing. There is no need to add binder material or any special mechanical structure in order to support the electrode in the casing. Such a self-supporting electrode allows for ease of and inexpensive manufacture and assembly.

These methods not only avoid the use of a binder during the formation of electrodes, but also do not require that the electrodes be sintered. Sintering is often undesirable because of a decrease in the charge/discharge rates corresponding to the inherent decrease in the surface area caused by sintering.

The method may further include abrading or etching the material to remove surface contamination for operative contact with an electrolyte as previously discussed. Cleaning of the material to expose the material directly for operative contact with the electrolyte also is contemplated.

Additionally, the method may include placing a collector in electrical contact with the material so that electrons produced during the operation of the electrode may be collected. Again, coating the electrode is contemplated to alleviate the problems previously discussed.

Examples 1—6

The apparatus employed is similar to that depicted in Fig. 2. The chill wheel used has a diameter of 10 inches (25.4 cm), is one inch (2.54 cm) wide and is made of copper. It is rotated at a speed of about 2500 rpm. A nozzle with an orifice having a diameter of 0.0889 cm. is mounted perpendicular to the direction of movement of the peripheral surface of the chill wheel. The axis through the crucible is at an 88° angle measured from the horizontal in the plane of the chill wheel axis. The gap between the orifice and the surface of the chill wheel is 0.159 cm. Materials having the compositions set out in Table I below were employed. A manifold having a plurality of openings expels argon gas in such a manner that the gas pressure enhances the contact between the ribbon and the chill surface. The manifold is located parallel to the chill wheel surface and extends from top dead center to a point 45 after top dead center. A flow of argon at a pressure of 20 psi. is normally used. The details of the rapid quench techniques used in the present invention are discussed in the articles "Production of Amorphous Alloy Ribbons and Effects of Apparatus Parameters on Ribbon Dimensions" by Liebermann, et al., IEEE Transactions on Magnetics, Vol. MAG-12, No. 6, Nov. 1976, and "The Dependence of the Geometry of Glassy Alloy Ribbons on the Chill Block Melt-Spinning Process Parameters" by Liebermann, 43 Materials Science and Engineering 203—210, 1980, which are hereby incorporated by reference.

Several electrodes weighing in the range of 0.15g to 0.35g were cut from the ribbon. A nickel tab was used as an electron collector crimp connected to the ribbon electrode. The counter electrode was a nickel blank electrode. Each electrode was cycled in 4M KOH electrolyte at a charge rate of 250 mA/g for 2 hours and a discharge rate of 50 mA/g to -0.7V Hg/HgO reference electrode.

In these Examples ribbon electrodes were formed based upon the quaternary composition of titanium, nickel, aluminium, and either vanadium or zirconium. Although several electrodes of each composition were tested for electrochemical performance, only the highest capacity of any electrode measured during the first seven cycles is reported in Table I.

TABLE I

Example	1	2	3	4	5	6
Ti (atm.%)	55	55	50	50	45	45
Ni (atm.%)	35	30	35	35	35	35
Al (atm.%)	5	10	5	10	10	10
V (atm.%)	5	5	10	5	10	
Zr (atm.%)						10
Chill Wheel (rpm)	3500	2500	3000	2500	2500	2500
Orifice Dia. (cm)	.089	.089	.10	.10	.089	.089
Ribbon Thickness (microns)	40	45	38	45	38	38—50
Ribbon Width (cm)	.227	.221	.237	.169	.283	.151
Capacity (mAh/g)	191	169	235	172	222	142

The charge-discharge cycling test was extended for Example 3 to measure the cycle life of the electrode. Figure 4 illustrates that the capacity did not significantly decrease even after 315 cycles were completed. In fact, the capacity decreased only about 13% comparing cycles 93—103 to cycles 305—315. For each cycle the charge rate was 250 mA/g for two hours and the discharge rate was 50 mA/g to -0.7 volts. For the first 93 cycles, the electrode was charged to 56% of full capacity and thereafter, to full capacity. The test was terminated on cycle 316.

The density of Example 3 was calculated by measuring the weight of the ribbon in air and subsequently in a fluid of known density. Specifically, isopropyl alcohol was used as the fluid. The density of the ribbon was calculated to be approximately 5.9 g/cc (cm³).

Examples 7—9

The procedure of Examples 1 to 6 was repeated to form ribbon electrodes based on the composition of titanium, nickel aluminium and niobium. In Example 9 vanadium was added. The same equipment was

employed and any change in the process conditions is noted in Table II below. Although several electrodes of each composition were tested for electrochemical performance following the procedure in Examples 1 to 6, only the highest capacity of any electrode measured during the first seven cycles is reported in Table II.

TABLE II

Example	7	8	9
Ti (atm.%)	44	55	45
Ni (atm.%)	40	30	40
Nb (atm.%)	11	10	5
Al (atm.%)	5	5	5
Zr (atm.%)			
V (atm.%)			5
Hf (atm.%)			
Chill Wheel (rpm)	2500	2500	2500
Orifice Dia. (cm)	.089	.089	20
Ribbon Thickness (microns)	25—32	25—50	40—50
Ribbon Width (cm)	.194	.115—.188	.138
Capacity (mAh/g)	260	250	202

The half cell capacity of Example 9 was measured at varying discharge rates and illustrated in Figure 5. The first discharge rate was measured for ten cycles; each subsequent discharge rate was measured for seven cycles. The data points are the average of the three electrodes and last five cycles.

As illustrated by these examples, a number of advantages result from use of the electrodes. Since the electrodes are self-supporting, there is no need to use binder material to impart structural integrity to the electrode. This results in an immediate gain in energy density for the electrode since less inactive material is being used. The cell capacity can be increased without a concomitant increase in porosity which would otherwise lead to corrosion and degradation of the structural integrity of the electrode material. The electrochemical performance of the electrodes indicates enhanced cycle life without a significant decrease in cell capacity.

Having a material which maintains its structural integrity during cycling, the material allows flexibility in maximizing the cell capacity. The structure of the electrode also allows for repeated volumetric expansion and contraction without structural degradation during the absorption and desorption of hydrogen. The electrode allows the optimization of charge and discharge rates since the surface area to volume ratio can be controlled by changing the thickness and width of the electrode itself.

Generally, the electrodes are flexible allowing easy alignment in a battery casing. Without the need for binder material or special structural devices for their alignment, using the inventive electrodes to assemble a battery is inexpensive and simple.

Claims

1. A hydrogen storage electrochemical cell comprising:

- (a) at least one hydrogen storage electrode (15, 115, 165, 225) capable of being electrochemically charged with hydrogen to store energy and capable of electrochemically discharging hydrogen and realising energy, while maintaining its structural integrity during electrochemical charge and discharge cycles; and comprising at least one self-supporting solid, metallic, amorphous electrochemically active body formed by rapid solidification from a melt and having a non-particulate, dimensionally anisotropic shape with a continuous amorphous structure throughout, the body having a composition comprising at least four elements, said elements being 40 to 75 atomic percent titanium, 15 to 55 atomic percent nickel, from trace amount to 15 atomic percent aluminium, and at least one of vanadium, hafnium, niobium, and zirconium;

employed and any change in the process conditions is noted in Table II below. Although several electrodes of each composition were tested for electrochemical performance following the procedure in Examples 1 to 6, only the highest capacity of any electrode measured during the first seven cycles is reported in Table II.

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Orifice Dia. (cm)	.089	.089	20
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The half cell capacity of Example 9 was measured at varying discharge rates and illustrated in Figure 5. The first discharge rate was measured for ten cycles; each subsequent discharge rate was measured for seven cycles. The data points are the average of the three electrodes and last five cycles.

As illustrated by these examples, a number of advantages result from use of the electrodes. Since the electrodes are self-supporting, there is no need to use binder material to impart structural integrity to the electrode. This results in an immediate gain in energy density for the electrode since less inactive material is being used. The cell capacity can be increased without a concomitant increase in porosity which would otherwise lead to corrosion and degradation of the structural integrity of the electrode material. The electrochemical performance of the electrodes indicates enhanced cycle life without a significant decrease in cell capacity.

Having a material which maintains its structural integrity during cycling, the material allows flexibility in maximizing the cell capacity. The structure of the electrode also allows for repeated volumetric expansion and contraction without structural degradation during the absorption and desorption of hydrogen. The electrode allows the optimization of charge and discharge rates since the surface area to volume ratio can be controlled by changing the thickness and width of the electrode itself.

Generally, the electrodes are flexible allowing easy alignment in a battery casing. Without the need for binder material or special structural devices for their alignment, using the inventive electrodes to assemble a battery is inexpensive and simple.

Claims

1. A hydrogen storage electrochemical cell comprising:

- (a) at least one hydrogen storage electrode (15, 115, 165, 225) capable of being electrochemically charged with hydrogen to store energy and capable of electrochemically discharging hydrogen and realising energy, while maintaining its structural integrity during electrochemical charge and discharge cycles; and comprising at least one self-supporting solid, metallic, amorphous electrochemically active body formed by rapid solidification from a melt and having a non-particulate, dimensionally anisotropic shape with a continuous amorphous structure throughout, the body having a composition comprising at least four elements, said elements being 40 to 75 atomic percent titanium, 15 to 55 atomic percent nickel, from trace amount to 15 atomic percent aluminium, and at least one of vanadium, hafnium, niobium, and zirconium;



- (b) at least one counter electrode (30) for allowing the release of the energy stored in the hydrogen storage electrode, the counter electrode being positioned in the cell and spaced in operative relation with the hydrogen storage electrode; and
- (c) casing means having the hydrogen storage electrode (15, 115, 165, 225) and the counter electrode (30) positioned therein.
2. A hydrogen storage electrochemical cell according to claim 1, wherein the active body has a composition comprising, on an atomic basis, of from about 44% to about 60% titanium, from about 35% to about 40% nickel and from about 3% to about 5% aluminum.
3. A hydrogen storage electrochemical cell according to claim 2, wherein the composition of the active body further comprises from about 5% to about 11% niobium on an atomic basis.
4. A hydrogen storage electrochemical cell according to any of the preceding claims, wherein the hydrogen storage electrode and the counter electrode are spirally wound about an axis in a jelly-roll configuration.
5. A hydrogen storage electrochemical cell according to any of the preceding claims, wherein the hydrogen storage electrode comprises the active body present as a substantially flat sheet and the counter electrode comprises at least one substantially flat sheet.

Patentansprüche

1. Eine Wasserstoff einlagernde elektroklinische Zelle, gekennzeichnet durch
- (a) mindestens eine Wasserstoff einlagernde Elektrode (15, 115, 165, 225), die zur Energiespeicherung elektrochemisch mit Wasserstoff geladen werden kann und die zur Wiedergewinnung dieser Energie elektrochemisch Wasserstoff abgeben werden kann, wobei ihre Struktur während des elektrochemischen Ladens und Entladens beibehalten wird, und die mindestens einen selbsttragenden festen, metallischen, amorphen elektrochemisch aktiven Körper aufweist, der durch schnelle Verfestigung einer Schmelze zu erhalten ist und eine ungeordnete, in ihrer Dimension eine isotropische Form mit einer durch und durch kontinuierlich amorphen Struktur hat, wobei der Körper eine Zusammensetzung hat, die mindestens vier Elemente umfaßt, diese Elemente aus 40 bis 75 Atomprozent Titan, 15 bis 55 Atomprozent Nickel, Spuren Mengen bis 15 Atomprozent Aluminium und mindestens eines der Elemente Vanadium, Hafnium, Niob und Zirkonium bestehen,
- (b) mindestens eine Gegenelektrode (30) aufweist, die die in der Wasserstoffspeicherlektrode gespeicherte Energie abzugeben erlaubt, wobei die Gegenelektrode in der Zelle vorgesehen ist und in geeigneter Relation zu der Wasserstoffspeicherelektrode angeordnet ist und
- (c) ein Gehäuse, in dem die Wasserstoffspeicherelektrode (15, 115, 165, 225) und die Gegenelektrode (30) vorgesehen ist.
2. Eine elektrochemische Wasserstoffspeicherzelle gemäß Anspruch 1, dadurch gekennzeichnet, daß der aktive Körper eine Zusammensetzung hat, die auf atomarer Basis etwa 44 bis etwa 60% Titan, etwa 35 bis etwa 40% Nickel und etwa 3 bis etwa 5% Aluminium aufweist.
3. Eine elektrochemische Wasserstoffspeicherzelle gemäß Anspruch 2, dadurch gekennzeichnet, daß die Zusammensetzung des aktiven Körper weiter etwa 5 Atomprozent bis etwa 11 Atomprozent Niob umfaßt.
4. Eine elektrochemische Wasserstoffspeicherzelle gemäß irgendeinem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß die Wasserstoffspeicherelektrode und die Gegenelektrode spiralförmig um eine Achse in einer gelförmigen Rollenkonfiguration aufgewickelt ist.
5. Eine elektrochemische Wasserstoffspeicherzelle gemäß irgendeinem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß die Wasserstoffelektrode aus einem aktiven Körper besteht, der als eine im wesentlichen flache Folie ausgebildet ist und daß die Gegenelektrode mindestens eine im wesentlichen flache Folie darstellt.

Revendications

1. Cellule électrochimique à stockage d'hydrogène, comportant:
- (a) au moins une électrode (15, 115, 165, 225) de stockage de l'hydrogène, pouvant être chargée d'hydrogène par voie électrochimique pour stocker de l'énergie et pouvant décharger l'hydrogène par voie électrochimique et libérer l'énergie, tout en conservant son intégrité de structure au cours des cycles de charge et de décharge électrochimiques, comprenant au moins un corps autoportant, solide, métallique, amorphe électrochimiquement actif, formé par solidification rapide à partir d'un bain de fusion et présentant une forme non particulière, dimensionnellement anisotropique, ayant entièrement une structure amorphe continue, ce corps ayant une composition constituée d'au moins quatre éléments, lesdits éléments étant 40 à 75 atomes pour-cent de titane, 15 à 55 atomes pour-cent de nickel, une quantité d'atomes d'aluminium allant de traces à 15 pour-cent et d'au moins l'un des éléments suivants, vanadium, hafnium, niobium et zirconium.



(b) au moins une contre-électrode (30) pour permettre la libération de l'énergie stockée dans l'électrode de stockage de l'hydrogène, la contre-électrode étant placée dans la cellule et à distance de fonctionnement de l'électrode de stockage de l'hydrogène; et

(c) une enceinte dans laquelle sont placées l'électrode (15, 115, 165, 225) et la contre-électrode (30).

2. Cellule électrochimique à stockage d'hydrogène selon la revendication 1, dans laquelle le corps actif a une composition constituée, sur la base des atomes, d'environ 44% à environ 60% de titane, d'environ 35% à environ 40% de nickel et d'environ 3% à environ 5% d'aluminium.

3. Cellule électrochimique à stockage d'hydrogène selon la revendication 2, dans laquelle la composition du corps actif est en outre constituée d'environ 5% à environ 11% de niobium, sur la base des atomes.

4. Cellule électrochimique à stockage d'hydrogène selon l'une quelconque des revendications précédentes, dans laquelle l'électrode de stockage de l'hydrogène et la contre-électrode sont enroulées en spirale autour d'un axe, selon la configuration d'un gâteau roulé.

5. Cellule électrochimique à stockage d'hydrogène selon l'une quelconque des revendications précédentes, dans laquelle l'électrode de stockage de l'hydrogène est constituée du corps actif présent sous forme d'une feuille sensiblement plane et dans laquelle la contre-électrode est constituée d'au moins une feuille sensiblement plane.

