IN THE UNITED STATES DISTRICT COURT
FOR THE DISTRICT OF MASSACHUSETTS

01 11247 MEL

KAPLESH KUMAR, **Plaintiff**	
v.	**Civil Action No.**
OVONIC BATTERY COMPANY, LLC, **ENERGY CONVERSION DEVICES, INC.,** **STANFORD OVSHINSKY,** **Defendants**	

JUL 19 1 45 PM '01

COMPLAINT FOR PATENT INFRINGEMENT

Plaintiff, Dr. Kaplesh Kumar (hereinafter "Kumar") sues Defendants Ovonic Battery Company, LLC (hereinafter "OBC"), Energy Conversion Devices, Inc. (hereinafter "ECD"), and Stanford Ovshinsky (hereinafter "Ovshinsky") for infringing United States Letters Patent No. 4,565,686 (hereinafter "the '686 patent"), and alleges as follows:

PARTIES

1. Plaintiff, Dr. Kaplesh Kumar, a citizen of the Commonwealth of Massachusetts residing at 25 Redwing Road, Wellesley, MA 02481, is inventor and Exclusive Licensee of the '686 patent. He has a Doctor of Science degree in Materials Science from the Massachusetts Institute of Technology and a Juris Doctor Magna Cum Laude degree from the New England School of Law. Dr. Kumar is employed as an engineer, and is also registered as a patent attorney with the United States Patent and Trademark Office (hereinafter "USPTO").

RECEIPT # 32541
AMOUNT $ 150
SUMMONS ISS. yes
LOCAL RULE 4.1
WAIVER OF SERV.
MCF ISSUED
AO 120 OR 121
BY DPTY CLK. E.O.M.
DATE 07-19-01

(1)

2. Upon information and belief, Defendant ECD is a corporation and Defendant OBC is a Limited Liability Company, both duly organized and existing under the laws of the state of Michigan, and OBC is a subsidiary of ECD.

3. Upon information and belief, Defendant Stanford Ovshinsky is founder and Chief Executive Officer of OBC and/or ECD.

JURSIDICTION AND VENUE

4. This is an action for pecuniary relief from patent infringement arising under the Patent Laws of the United States, Title 35 of the United States Code.

5. The subject matter jurisdiction of this Court is founded on 28 U.S.C. § 1331 and 28 U.S.C. §1338. Venue is proper pursuant to 28 U.S.C. § 1391.

6. This Court has jurisdiction over Defendants ECD, OBC, and Ovshinsky, because they have committed acts of patent infringement during the course of their business and activities in this District.

THE PATENTS IN SUIT

7. On 21 January, 1986, United States Letters Patent No. 4,565,686 (the '686 patent), entitled "Method of Storing Hydrogen Using Nonequilibrium Materials and System," was duly and legally issued to Kaplesh Kumar, who assigned his rights in the '686 patent to The Charles Stark Draper Laboratory, Inc. (hereinafter Draper), a nonprofit corporation based in Cambridge, Massachusetts. On or about October, 2000, Draper granted Dr. Kumar an Exclusive License for the '686 patent with sole rights to sublicense and enforce it for past and ongoing infringement. A copy of the '686 patent is attached as Exhibit A.

8. Upon information and belief, ECD is assignee of United States Letters Patent No. 4,623,597, issued 18 November 1986 (hereinafter "the '597 patent") and filed more than one year after the filing of the Kumar '686 patent; and OBC is assignee of United States Letters Patent No. 5,840,440, issued 24 November 1998 and filed 20 November 1995 (hereinafter "the '440 patent"). Copies of the '597 patent and the '440 patent are attached as Exhibits B and C.

BACKGROUND

9. In the February 1980 issue of the prestigious Journal of Applied Physics, Dr. Kaplesh Kumar published the pioneering discovery responsible for the commercial viability of Nickel Metal Hydride (hereinafter "NiMH") batteries: nonequilibrium samarium (rare earth)-cobalt (transition metal) alloys store more hydrogen than their equilibrium crystalline counterparts, and are immune to physical degradation from cyclic hydrogen storage, unlike the prior art equilibrium crystalline material. (Exhibit D) Dr. Kumar applied for a patent in January 1981 (which finally issued as the '686 patent) with material, process, and system claims based on nonequilibrium amorphous and metastable crystalline hydrogen storage alloys. The USPTO Examiner objected to the amorphous alloy claims, but eventually allowed them as part of system and method claims based on rare earth-transition metal alloy compositions. The Examiner extracted from the patentee the surrender of nonequilibrium metastable crystalline alloy material, system, and method claims, all of which were patentable and allowed to later inventors as in the '597 and '440 patents.

10. In or about September 1994, Draper learned of ECD's work in hydrogen batteries through an article in the popular press. Draper counsel contacted ECD and/or OBC and offered the '686 patent for licensing, to which ECD and/or OBC professed no interest, stating that its batteries

did not use the amorphous or rare earth-transition metal materials claimed in the '686 patent. These communications between ECD and/or OBC and Draper, as well as other later ones between ECD and/or OBC and Dr. Kumar are included as Exhibits E-I.

11. In or about late 1999, Dr. Kumar discovered ECD's and/or OBC's website www.ovonic.com and its claim that virtually all NiMH battery manufacturers were producing NiMH batteries for portable electronics and electric vehicles under license from OBC and/or ECD. The licenses had been granted under ECD's hydrogen storage battery '597 patent, which had issued in November 1986. (See Exhibits J-L from Ovonic website.) Upon information and belief, ECD had applied for the '597 patent in April 1982, and its sole claim to novelty was use of nonequilibrium amorphous and/or metastable crystalline alloys (described as "disordered" in the '597 patent) for the negative electrode.

12. Through Dr. Kumar, Draper procured several portable electronics' NiMH batteries commercially and had them analyzed by an expert in the field. Of the almost two dozen batteries examined, all but one had negative electrodes composed of rare earth-transition metal alloys, significant and varying portions of which were amorphous and the remainder were metastable crystalline.

13. Upon information and belief, Defendant Stanford Ovshinsky, listed as an inventor on the '597 and '440 patents, has initiated and/or actively assisted ECD and/or OBC in licensing the '597 and/or the '440 patents to battery companies in the United States and worldwide, with distribution, use and/or selling rights in the United States; and Defendants Ovshinsky, ECD and/or OBC have secured other United States Patents derived from the '597 and/or '440 patents and licensed them as well.

14. On or about November 2000, through counsel, Dr. Kumar contacted ECD's and/or OBC's in-house counsel and again offered the '686 patent for licensing under the Exclusive License grant from Draper. ECD and/or OBC, through their in-house counsel, yet again showed no interest in licensing the '686 patent, and instead referred Plaintiff to the earlier communication with Draper in respect of said patent.

15. On or about December 2000, Plaintiff's counsel contacted ECD and/or OBC yet again and informed them of Plaintiff's awareness that ECD and/or OBC had licensed a large number of companies the '686 patented technology to manufacture NiMH batteries in which the negative electrodes were composed of rare earth-transition metal materials. Defendants were also informed that the '440 patent obtained by OBC closely described and claimed what the Kumar '686 patent had already disclosed and/or patented, and that it appeared that ECD and/or OBC had failed to disclose the '686 patent to the USPTO although the examiner of the '440 patent would have likely found the '686 patent highly material. ECD's and/or OBC's counsel failed to respond to this communication.

16. The sole invention in the NiMH batteries produced under license from ECD and/or OBC is the use of a hydrogen absorbing negative electrode made from the nonequilibrium amorphous and metastable crystalline materials that the Kumar '686 patent had disclosed and patented, or had sought to patent. In other respects, upon information and belief, the NiMH battery construction is virtually identical to that of the prior art nickel-cadmium (Ni-Cd) battery.

17. The Kumar '686 patent is a pioneer patent, per the U. S. Supreme Court's definition. <u>Boyden Power-Brake Co. v. Westinghouse,</u> 170 U.S. 537, 561-562 (1898). In the NiMH battery, it allows retrievable hydrogen storage in the electrode material without its degradation, thus providing "a function never before performed . . .." It also is the critical essential enabling

technology uniquely responsible for the NiMH battery's commercial viability, and is thus "one of such novelty and importance as to [have made] a distinct step in the progress of the art . . .."

INFRINGEMENT OF THE '686 PATENT

16. ECD, OBC, and Ovshinsky have infringed and continue to infringe; have induced and continue to induce others to infringe; have committed and continue to commit acts of contributory infringement of one or more claims of the '686 patent. The Defendants' infringing activities in the United States and this district include development, manufacture, use, sale, and/or offer for sale, as well as licensing others for the development, manufacture, use, sale, and/or offer for sale of certain NiMH batteries having negative electrodes containing rare earth-transition metal alloys in their nonequilibrium amorphous and metastable crystalline states. Such infringing activities constitute a violation of 35 U.S.C. § 271. Upon information and belief, such infringement has been, and continues to be willful.

17. As a consequence of the infringing activities of the Defendants regarding the '686 patent, as complained of herein, Dr. Kaplesh Kumar has suffered significant monetary damages in an amount yet to be determined, and will continue to suffer such damages unless and until this Court grants Plaintiff the relief requested herein.

UNFAIR COMPETITION, M.G.L. c. 93A, §§ 2 and 11

18. Through their conduct and actions, as detailed above and in the attached exhibits, Defendants OBC, ECD, and Ovshinsky have engaged in unfair methods of competition and unfair or deceptive acts or practices in the conduct of trade or commerce, and thereby violated M.G.L. c. 93A, §§ 2 and 11, which unfair competition has and will continue to result in injury to Plaintiff.

REQUESTED RELIEF

WHEREFORE, the Plaintiff Dr. Kaplesh Kumar prays for judgment against Defendants ECD, OBC, and Ovshinsky and requests this Honorable Court to:

A. Declare that ECD, OBC, and Ovshinsky have infringed and continue to infringe, induced others to infringe and continue to induce others to infringe, and/or committed and continue to commit acts of contributory infringement with respect to one or several claims of the '686 patent;

B. Declare that ECD and OBC, and Ovshinsky have engaged in unfair dealing, bad faith negotiations, and unfair methods of competition and unfair or deceptive acts or practices in the conduct of trade or commerce, in violation of M.G.L. c. 93A, §§ 2 and 11, and assess and award damages, treble damages, attorneys fees and costs as provided in c. 93A, §§ 2 and 11;

C. Order that ECD, OBC, and Ovshinsky account for and pay to Dr. Kaplesh Kumar damages including license fees, royalties, and other all such amounts due or collected from all ECD and/or OBC licensees making, using, importing, or selling NiMH batteries, directly or through third parties, as well as any lost royalties, lost license fees, and lost profits on account of past or ongoing infringement, inducement infringement, and/or contributory infringement activities in which the Defendants have engaged;

D. Grant Plaintiff pre-judgment and post-judgment interest on the damages resulting from ECD's, OBC's, and/or Ovshinsky's past and ongoing infringement, inducement infringement, or contributory infringement of the '686 patent;

E. Order that ECD's and/or OBC's '597 and '440 patents be canceled because of ECD's and/or OBC's misuse in the licensing of the '597 patent, and OBC's and/or ECD's inequitable conduct in withholding highly relevant '686 patent information from the USPTO Examiner during the prosecution of the '440 patent;

F. Declare this to be an "exceptional case" pursuant to 35 U.S.C. § 285, and order ECD, OBC, and/or Ovshinsky to pay Plaintiff's attorneys fees and costs; and

G. Grant such other and further relief as the case may require and the Court may deem just and proper.

JURY DEMAND

PLAINTIFF KAPLESH KUMAR DEMANDS A JURY TRIAL ON ALL ISSUES TRIABLE TO A JURY IN THIS MATTER.

Respectfully Submitted,

Kaplesh Kumar, BBO No. 636289
25 Redwing Road
Wellesley, MA 02481
(781) 283-5755

Dated: 19 July, 2001

EXHIBIT A

United States Patent [19]

Kumar

[11] **Patent Number: 4,565,686**

[45] **Date of Patent: Jan. 21, 1986**

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[54] **METHOD OF STORING HYDROGEN USING NONEQUILIBRIUM MATERIALS AND SYSTEM**

[75] Inventor: **Kaplesh Kumar**, Wellesley, Mass.

[73] Assignee: **The Charles Stark Draper Laboratory, Inc.**, Cambridge, Mass.

[21] Appl. No.: **502,535**

[22] Filed: **Jun. 13, 1983**

Related U.S. Application Data

[63] Continuation of Ser. No. 226,927, Jan. 21, 1981, abandoned.

[51] **Int. Cl.⁴** **C01B 6/24**
[52] **U.S. Cl.** .... 423/644; 148/403; 420/435; 420/455; 420/900; 422/129; 422/139; 423/648 R
[58] **Field of Search** .... 420/435, 455, 900; 148/403; 422/129, 139; 423/644, 648 R, 645

[56] **References Cited**

U.S. PATENT DOCUMENTS

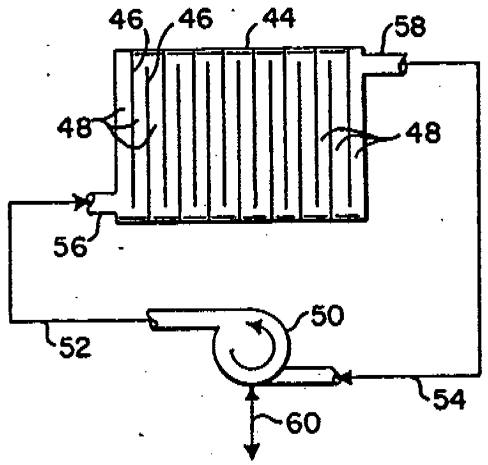
4,116,682	9/1978	Polk et al.	75/170
4,242,315	12/1980	Bruning et al.	423/645

Primary Examiner—R. Dean
Attorney, Agent, or Firm—Weingarten, Schurgin Gagnebin & Hayes

[57] **ABSTRACT**

A nonequilibrium state material, typically a rare-earth-transition metal, for reversible hydrogen storage. A rare earth-transition metal such as a rare earth cobalt alloy, like a samarium-cobalt or a lanthanum-nickel alloy, is provided in the amorphous or metastable crystalline state as a hydrogen absorbing material, particularly for use in a hydrogen storage and retrieval system, such as a fluidized bed or stacked plate hydrogen storage cell. The rare-earth-transition metal material is rapidly cooled from the liquid state to avoid the transition to a full crystalline state thereby obtaining an amorphous or quasi-stable crystalline state material which has the property of enhanced hydrogen storage capacity as well as being substantially immune to fracturing.

8 Claims, 4 Drawing Figures



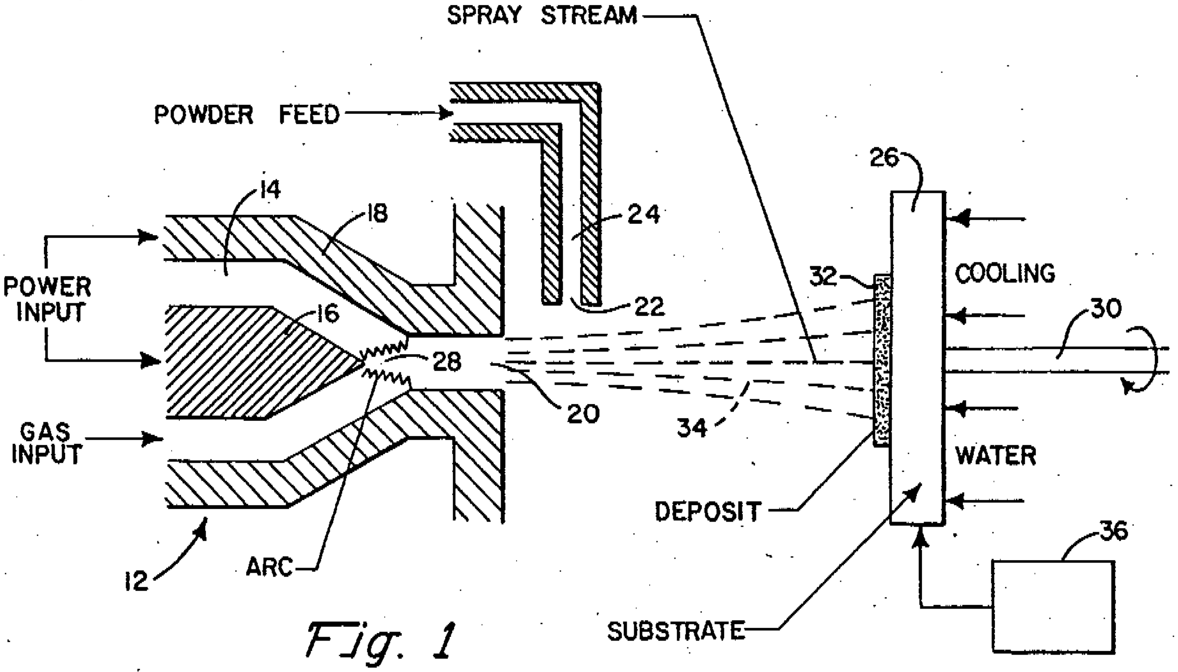


Fig. 1

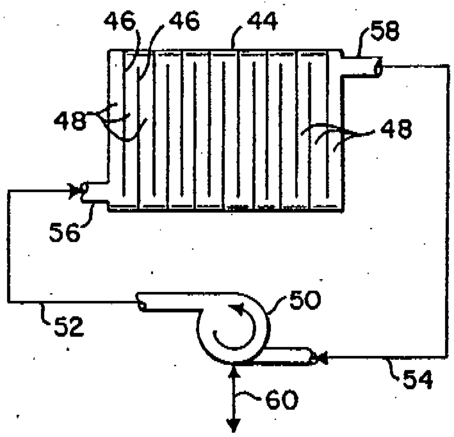


Fig.3

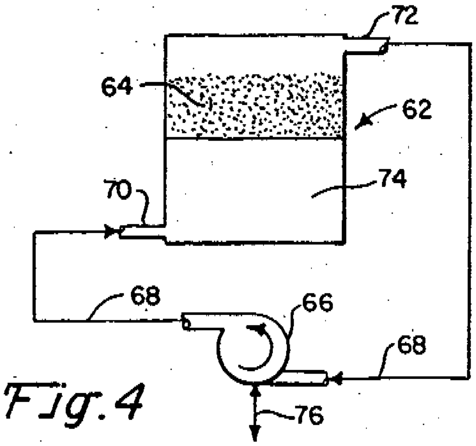


Fig.4

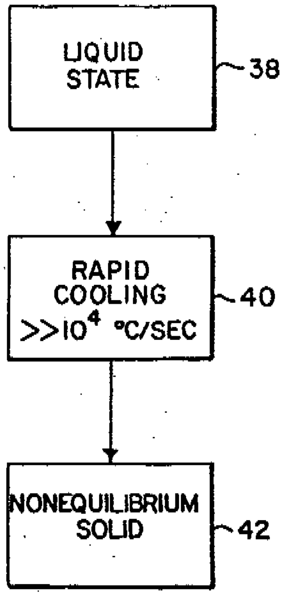


Fig.2

METHOD OF STORING HYDROGEN USING NONEQUILIBRIUM MATERIALS AND SYSTEM

This application is a continuation of application Ser. No. 226,927, filed on Jan. 21, 1981, abandoned.

FIELD OF THE INVENTION

The present invention relates to materials for reversible hydrogen storage and in particular to nonequilibrium state rare earth-transition metal materials for such application.

BACKGROUND OF THE INVENTION

The high density storage of hydrogen as a fuel for controlled release and combustion with oxygen to provide energy is of current interest. Conventional high pressure storage in the compressed gas or liquidized state is undesirable because of the high pressure involved, the bulk weight of the containers, and inherent danger in pressurized systems. Other techniques for hydrogen storage have included the utilization of material having the chemical binding capability for reversibly storing, and therefore releasing, hydrogen gas at relatively low temperatures and pressures. A number of materials have evolved for this purpose including certain rare earth-transition materials and in particular samarium-cobalt, $SmCo_5$ and lanthanum-nickel, $LaNi_5$. One of the serious limitations in the previous use of samarium-cobalt and similar materials is their structural instability over repeated absorption/desorption cycles of hydrogen storage and release.

Samarium-cobalt and similar rare earth-transition metal materials have a crystalline atomic structure characterized by a systematized arrangement of atoms within a lattice structure which differs from material type to material type. Recent investigations point to the existence of crystal structure strains resulting from repeated absorption and desorption of hydrogen gas as being at least partially responsible for the fracturing of the hydrogen storage material under such repeated cycling.

The results of such fracturing impair the use of the material in a hydrogen storage cell. In the case where such material is used as a plurality of exposed sheet surfaces in a labyrinth of passages through which hydrogen is pumped, the fracturing would clearly destroy the physical and mechanical integrity of the cell. In other cases in which a fluidized bed of particulate material is employed, the particle size is important to proper aeration of the fluidized bed whereas repeated fracturing results in particles of such small size that they pack in dense clumps which can not be effectively fluidized thereby greatly reducing the effective storage capacity of the cell.

BRIEF SUMMARY OF THE INVENTION

In accordance with the teaching of the present invention, samarium-cobalt, lanthanum-nickel and other rare earth-transition metal materials as well as other alloys useful for reversible hydrogen storage are produced in a nonequilibrium structural state such as an amorphous or metastable crystalline state. The nonequilibrium state materials are used as a hydrogen absorbing material in a cell for the reversible storage of hydrogen gas which in turn serves as an energy generating fuel supply. The nonequilibrium state material eliminates the tendency to fracture characteristic of crystalline state rare earth-transition metal materials and possesses an enhanced hydrogen storage capacity for the same bulk of material.

Samarium-cobalt, lanthanum-nickel and other rare earth-transition metal materials when cooled from a high temperature, liquid state assume a crystallized state of a predetermined atomic lattice nature dependent upon the material involved and characteristic of the low or room temperature phase of the material. The avoidance of a crystallization transformation from the liquid state as the rare earth-transition metal material is cooled can not be achieved by normal techniques insofar as it requires rapid cooling rates. Rates are required substantially in excess of 10^4 degrees centigrade per second, typically in the range of 10^6 to 10^8 degrees centigrade per second. When special steps are taken to produce such rapid cooling, the transformation to the low temperature crystalline phase is suppressed to produce either a completely amorphous, solid state, rare earth-transition metal material characterized by the random atomic structure of the liquid state from which cooling commences or to a partially crystallized or metastable crystalline state depending upon the specific cooling rate utilized. Samarium-cobalt and lanthanum-nickel materials thus produced are configured into a form in which they are then used for hydrogen storage with the improved storage capacity and fracture immunity necessary to make a commercially successful fuel storage cell.

BRIEF DESCRIPTION OF THE DRAWING

These and other features of the present invention are more fully set forth below in the following detailed description and accompanying drawing of which:

FIG. 1 is a schematic diagram of apparatus useful in producing nonequilibrium state rare earth-transition materials for use as hydrogen storage media in accordance with the present invention;

FIG. 2 illustrates the process of nonequilibrium state material formation for use in accordance with the present invention;

FIG. 3 is a schematic diagram of first reversible hydrogen storage apparatus for use in the present invention;

FIG. 4 is a schematic diagram of second apparatus for use in providing reversible hydrogen storage in accordance with the present invention.

DETAILED DESCRIPTION

The present invention contemplates a nonequilibrium state material, particularly a rare earth-transition metal material such as a rare earth-cobalt or a rare-nickel alloy like samarium-cobalt and lanthanum-nickel for use in reversible hydrogen storage in a hydrogen fuel cell. Other crystalline materials, such as iron-titanium alloys, previously used for hydrogen storage in the crystalline state, may also be provided in a nonequilibrium state and used thus more advantageously for reversible hydrogen storage.

Materials such as the alloys of a rare earth and transition metal and certain other alloys have long been known for having a capacity to reversibly store, and therefore release, a substantial amount of hydrogen at relatively low pressures and temperatures. U.S. Pat. Nos. 4,036,944 and 4,133,426 show representative examples of this technology. In particular the U.S. Pat. No. 4,036,944 recognizes the well known deficiency of such materials in that they tend to fracture after repeated cycles of storage and release of hydrogen gas, eventually reducing the effectiveness of the cell as a storage mechanism to the point of uselessness. Such a deficiency is a serious limitation in the commercial or industrial application of such hydrogen storage cells. Recent investigations of rare earth-metal alloys has led to the discovery that the production of the alloy in an amorphous state, characterized by a random atomic orientation, as opposed to the regular lattice structure of the crystalline state, produces a material capable of absorbing substantially larger quantities of hydrogen without any tendency to fracture over repeated absorption/desorption cycles.

The production of nonequilibrium state rare earth-transition metal materials requires that the normal transformation to a room temperature crystal phase material be suppressed. This typically involves cooling the material from a liquid state in a very rapid manner, above 10^4 degrees centigrade per second, typically within the range of 10^6 to 10^8 degrees centigrade per second in the case of samarium-cobalt. Such rapid quenching can not readily be achieved without the use of special techniques. One such technique is illustrated with respect to FIG. 1 showing an apparatus for plasma spraying a earth-transition metal powder. It is to be noted that FIG. 1 represents an exemplary approach to producing the amorphous material for use in the present invention, other techniques being possible. In the apparatus of FIG. 1 the sprayed powder is converted into a liquid by a plasma torch and directed at a cooled substrate which accomodates the required rapid cooling to a solid, nonequilibrium state material. In particular, in FIG. 1 a plasma torch **12** has a gas supply annular passage **14** surrounding a central electrode **16** and contained within an outer housing **18** acting as an electrode. The gas applied through the annular passage **14** exits through a gas nozzle **20** directly above which is a material feed nozzle **22** that applies a rare earth-transition metal powder through a channel **24** to the gas from the gas nozzle **20**. The combined gas and rare earth-transition metal material is directed toward a cooled substrate **26** for deposition in a nonequilibrium, amorphous or metastable crystalline phase.

Liquification of the powdered, rare earth-transition metal material is achieved by heating and ionizing the gas supplied through the annular channel **14** by an arc discharge **28** between the electrode **16** and the surrounding housing electrode **18**. Passage through the nozzle **20** permits the gas to be accelerated toward the substrate **26**. The powdered, rare earth-transition metal material injected through the nozzle **22** is picked up by the plasma gas and uniformly liquified and homogenized in temperature to form a plasma flame **34** directed at deposition layer **32** on the substrate **26** where the liquified rare earth-transition metal material collects for instant cooling. This rapid cooling avoids the transition to a crystallized state characteristic of low temperature rare earth-transition metal alloys.

The substrate **26** may be mounted on a shaft **30** for rotation during the deposition of the layer **32** to improve the homogeneity of the deposit. A use of a particle size of substantial uniformity is desirable along with relatively short nozzle **20** to substrate **26** distances in the range of 2 to 20 centimeters. This insures a homogeneous liquified condition to the deposited material as it strikes the layer **32**. A particle size of 40 microns plus or minus 20 microns is typical in the case of samarium-cobalt either as $SmCo_5$ or Sm_2Co_{17}.

The substrate **26** is preferably of a high thermal conductivity material such as copper and the rotation rate, where employed, is preferably a few hundred revolutions per minute. In addition, a scanning mechanism **36** may be utilized to oscillate substrate **26** in amplitudes that increase with thickness of layer **32** thereby insuring more uniform cooling by reducing the deposition rate with increasing deposit thickness and therefore with increasing thermal resistance between the hot deposition and the cool sink of the substrate **26**. The substrate **26**, typically using a water cooling circulation, is maintained well below the crystallization temperature for the rare earth-transition metal material. The crystallization temperature is approximately 500 degress centigrade in the case of samarium-cobalt. The deposition apparatus of FIG. 1 is substantially as shown in copending, commonly assigned U.S. patent application Ser. No. 138,650, filed Apr. 8, 1980.

FIG. 2 illustrates the typical process of nonequilibrium state rare earth-transition metal material formation for use in the present invention and in essence requires the material start in a liquid state as illustrated in step **38** and experience a rapid cooling well in excess of 10^4 degrees centrigrade per second in a cooling step **40** to result in a nonequilibrium solid formation step **42** which is completely stable not only chemically but physically after repeated cycles of hydrogen absorption and release. The cooling step **40** typically occurs at a rate of 10^6 to 10^8 degrees centrigrade per second in the case of samarium-cobalt. The more rapid rate produces a totally amorphous state material from complete suppression of the transformation to the low temperature crystalline phase. A partially crystallized or metastable crystalline state in which some crystalline forms, occurs from a less rapid cooling in step **40**. The metastable condition nevertheless lacks the overall crystallized condition which leads to fracturing from the stresses of repeated cycles of hydrogen storage and release.

A first cell for the reversible storage of hydrogen using nonequilibrium state material such as provided above is illustrated with respect to FIG. 3. As shown there a container **44** includes a plurality of plates **46** emanating from opposite inner walls of the container **44** in an interlocking comb pattern to define a elongated or labyrinth set of passages **48** through the container **44**. The plates **46** contain deposits of nonequilibrium state material, the rare earth-transition metal material formed above as deposits **32**. These are formed in sheets of up to 5 mm thickness and typically backed by a substrate on which the deposit **32** forms to provide mechanical structure to the plates **46**. Hydrogen gas is typically cycled through the channels **48** by a pump **50**, forming a closed loop through conduits **52** and **54**, inlet **56** and outlet **58**. A hydrogen supply or extraction conduit **60** is provided to apply hydrogen to the storage cell for absorption by the rare earth-transition metal material on the plates **46** or for release therefrom.

FIG. 4 illustrates a second, alternative cell for reversibly storing hydrogen in nonequilibrium state in accordance with the present invention and includes a fluidized bed chamber **62** having therein a supply of powdered, nonequilibrium state rare earth-transition metal material typically produced in accordance with the apparatus and process illustrated above and and subsequently ground to a desired particle size as known in the art. A pump **66** is provided which, by means of conduits **68** and inlet **70** and outlet **72**, applies a stream of hydrogen gas through the fluidized bed **64**, typically after distribution through a collimation apparatus 74. Supply and exhaust conduit 76 is similarly provided so that the hydrogen can be applied to or retrieved from the storage chamber 62. Apparatus using crystalline state material for providing fluidized bed storage and release of hydrogen material of the type illustrated in FIG. 4 are known in the art. The cells of both FIGS. 3 and 4 are typically operated at several atmospheres of pressure.

The above described invention provides for an efficient and effective reversible hydrogen storage cell with improved hydrogen storage capacity and material fracture immunity. Alterations and improvements to the specific example illustrated above are contemplated within the scope of the invention as only limited in the following claims.

What is claimed is:

1. A system for retrievably storing hydrogen comprising:

an amorphous rare earth-transition metal alloy material;

a container for said material, and

means for supplying hydrogen to said material and exhausting hydrogen from said material for respective absorption and desorption thereby.

2. The system of claim 1, wherein said amorphous rare earth-transition metal alloy material is selected from the group consisting of rare earth-cobalt alloys, rare earth-nickel alloys, and combinations thereof.

3. The system of claim 1, wherein said amorphous rare earth-transition metal alloy material is selected from the group consisting of samarium-cobalt, lanthanum-nickel, and combinations thereof.

4. The system of claim 1, wherein said amorphous rare earth-transition metal alloy material is in the form of a plurality of sheets within said container.

5. The system of claim 1, wherein:

said amorphous rare earth-transition metal alloy material is in a particulate form within said container; and

said container further comprises fluidized bed apparatus.

6. A process for reversibly storing hydrogen in an amorphous rare earth-transition metal alloy material comprising the steps of:

supplying hydrogen to amorphous rare earth-transition metal alloy material in a closed system, cycling said hydrogen over said alloy material to cause hydrogen to be stored in said alloy material; and

withdrawing hydrogen from said system to retrieve the stored hydrogen.

7. The process of claim 6, wherein said rare earth-transition metal alloy material is selected from the group consisting of rare earth-cobalt alloys, rare earth-nickel alloys, and combinations thereof.

8. The process of claim 6 wherein said rare earth-transition metal alloy material is selected from the group consisting of samarium-cobalt, lanthanum-nickel and combinations thereof.

* * * * *

EXHIBIT B

United States Patent [19]

Sapru et al.

[11] **Patent Number: 4,623,597**

[45] **Date of Patent: * Nov. 18, 1986**

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[54] **RECHARGEABLE BATTERY AND ELECTRODE USED THEREIN**

[75] Inventors: **Krishna Sapru**, Troy; **Benjamin Reichman**; **Arie Reger**, both of Birmingham; **Stanford R. Ovshinsky**, Bloomfield Hills, all of Mich.

[73] Assignee: **Energy Conversion Devices, Inc.**, Troy, Mich.

[*] Notice: The portion of the term of this patent subsequent to Dec. 11, 2000 has been disclaimed.

[21] Appl. No.: **801,545**

[22] Filed: **Nov. 25, 1985**

Related U.S. Application Data

[63] Continuation of Ser. No. 614,273, May 25, 1984, abandoned, which is a continuation of Ser. No. 372,693, Apr. 28, 1982, abandoned.

[51] **Int. Cl.**^{4} **H01M 4/02**; H01M 10/36

[52] **U.S. Cl.** **429/101**; 429/209; 429/218; 429/223; 420/900

[58] **Field of Search** 429/209, 218, 101, 57, 429/40, 223; 420/900

[56] **References Cited**

U.S. PATENT DOCUMENTS

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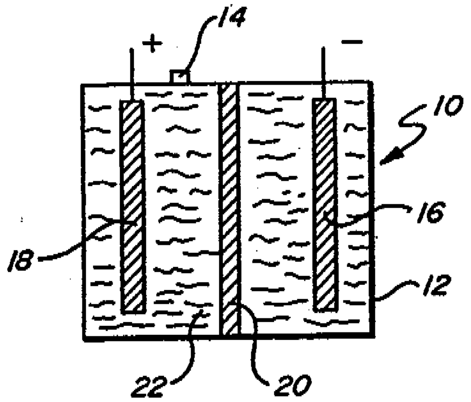
3,824,131	7/1974	Beccu	429/223
3,874,928	4/1981	Will	429/57
3,980,501	9/1976	Feder et al.	429/218
4,107,405	8/1978	Buegen et al.	429/218
4,216,274	8/1980	Bruning et al.	429/101
4,430,391	2/1984	Ovshinsky et al.	429/40
4,431,561	2/1984	Ovshinsky et al.	420/900
4,487,818	12/1984	Ovshinsky et al.	429/44

Primary Examiner—Donald L. Walton
Attorney, Agent, or Firm—James D. Ryndak; Lawrence G. Norris; Richard M. Goldman

[57] **ABSTRACT**

An improved battery utilizing a hydrogen rechargeable anode of a disordered non-equilibrium multicomponent material including one or more elements forming a host matrix and at least one modifier element incorporated therein. The anode is capable of electrochemically absorbing hydrogen from an electrolyte during application of a charging current thereto. The hydrogen is stored in the anode bulk until discharge is initiated, whereupon an electrical current is produced when the hydrogen is released. The superior battery of the invention has attained high density energy storage, efficient reversibility, high electrical efficiency, bulk hydrogen storage without structural change or poisoning and hence long cycle life and deep discharge capability.

32 Claims, 6 Drawing Figures



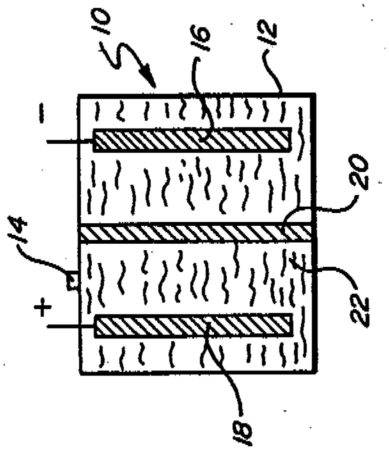

10
16
12
-
20
14
+
22
18

FIG. 1

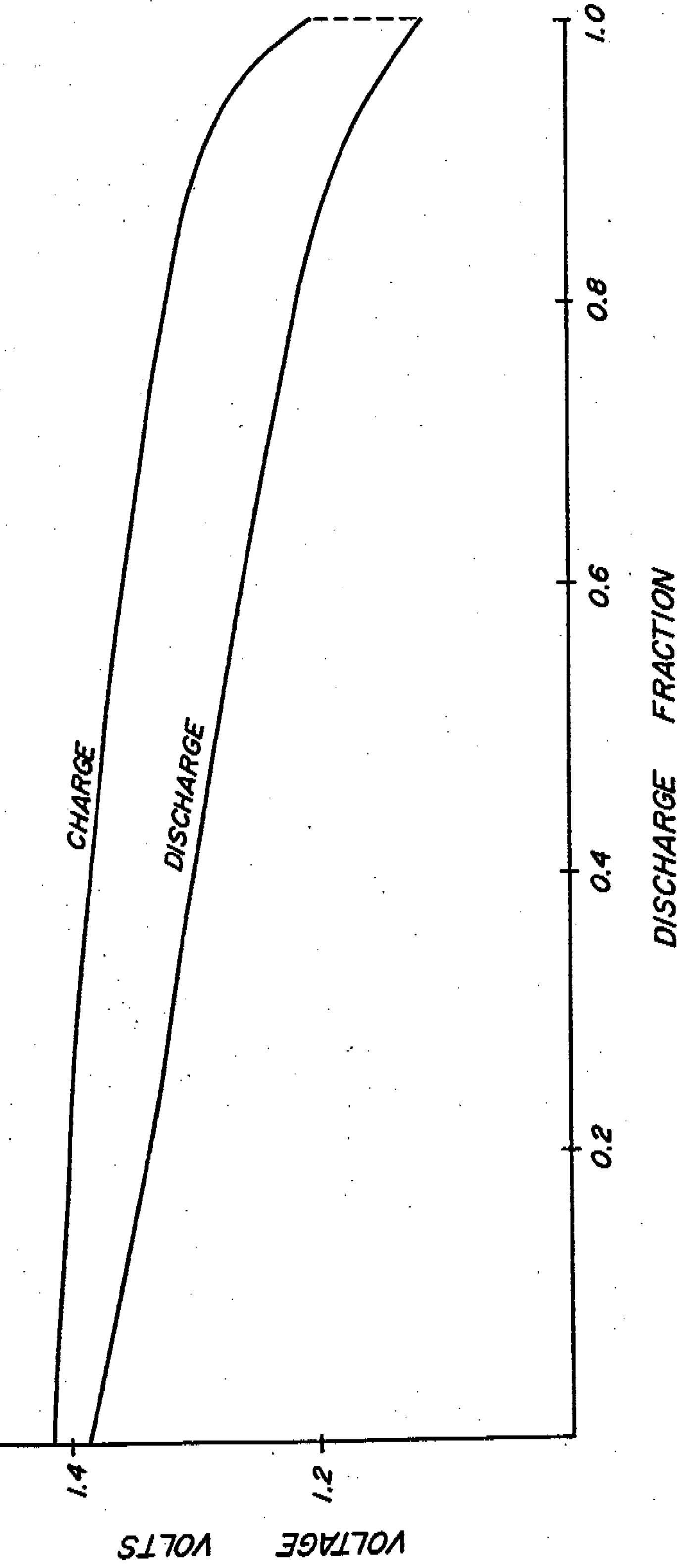
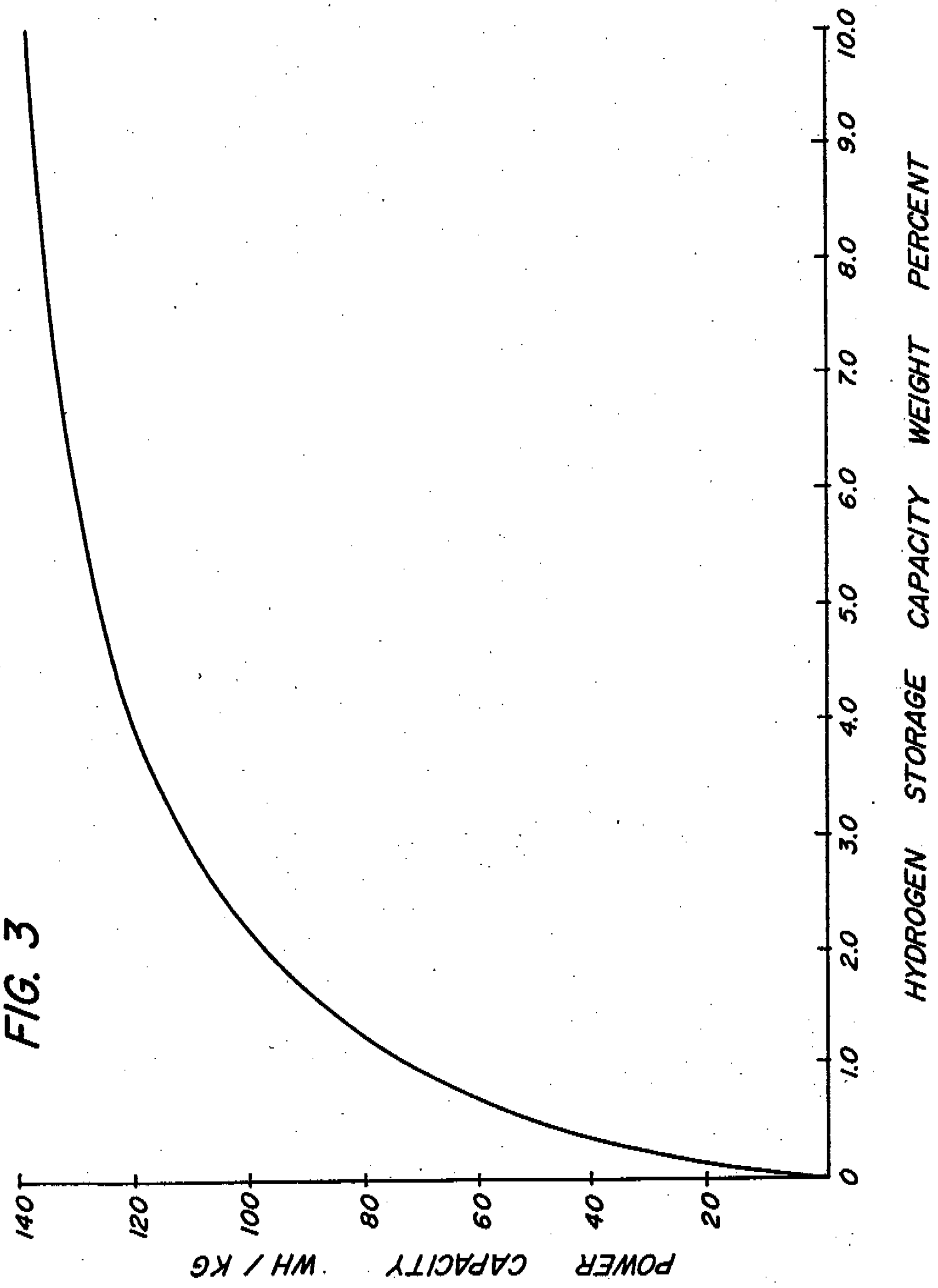

CHARGE
DISCHARGE
1.4
1.2
VOLTAGE VOLTS
0.2
0.4
0.6
0.8
1.0
DISCHARGE FRACTION

FIG. 2

FIG. 3


POWER CAPACITY WH / KG
140
120
100
80
60
40
20
HYDROGEN STORAGE CAPACITY WEIGHT PERCENT
0
1.0
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7.0
8.0
9.0
10.0

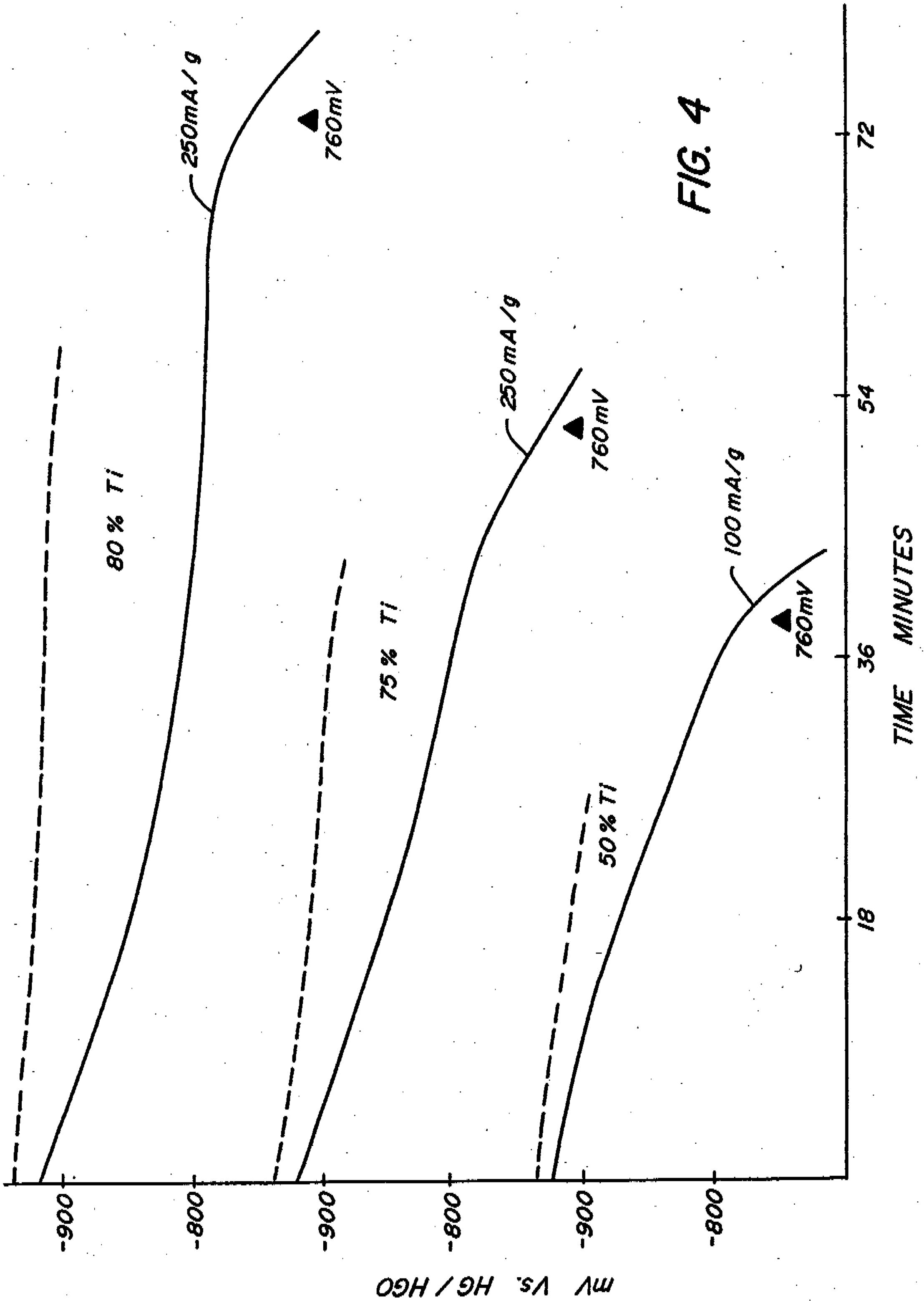
250mA/g
760mV
80% Ti
250mA/g
760mV
75% Ti
100mA/g
760mV
50% Ti
18
36
54
72
TIME MINUTES
-900
-800
-900
-800
-900
-800
mV vs. HG/HGO

FIG. 4

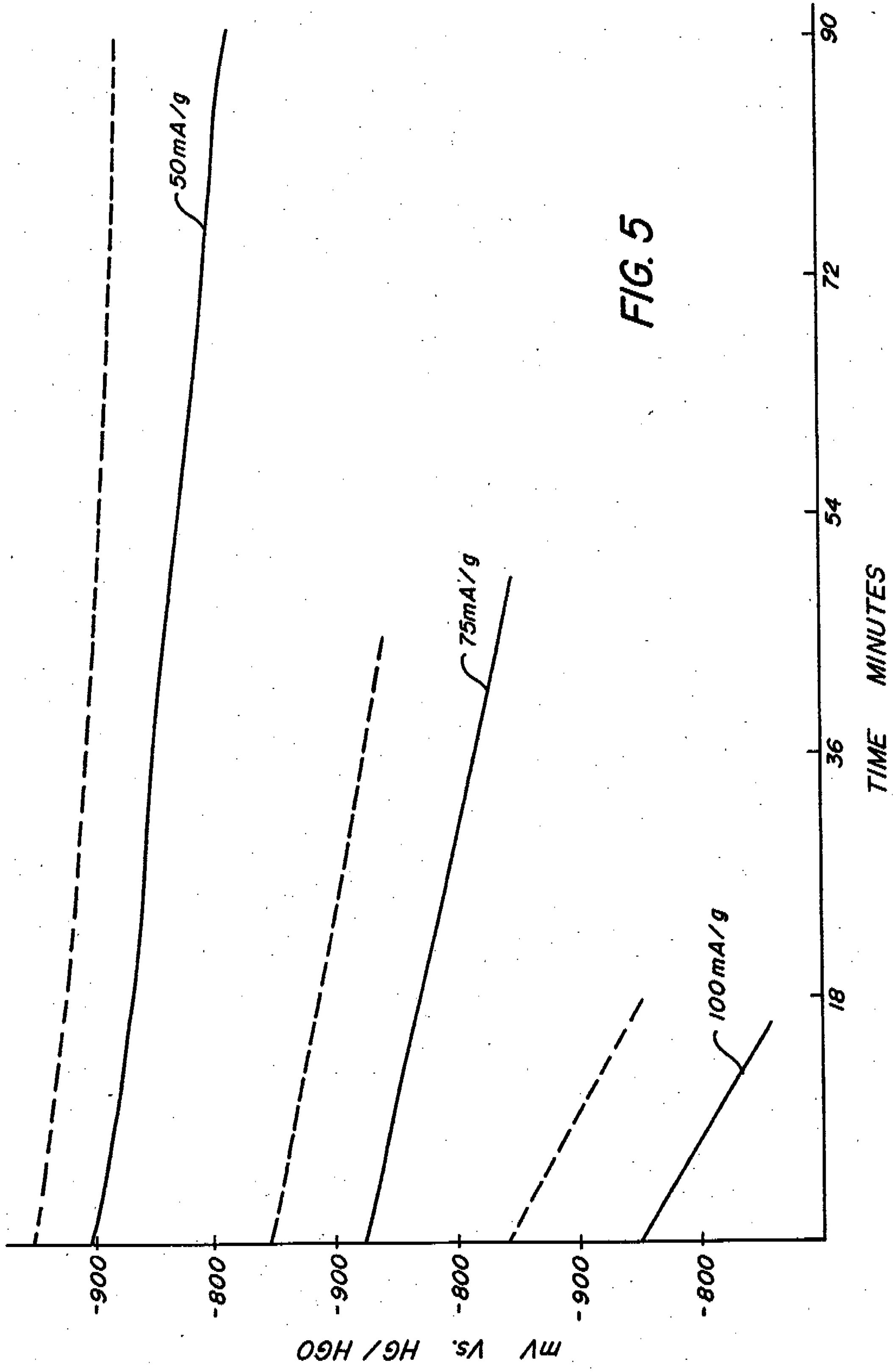
50mA/g
75mA/g
100mA/g
90
72
54
36
18
TIME MINUTES
-900
-800
-900
-800
-900
-800
mV vs. HG/HGO

FIG. 5

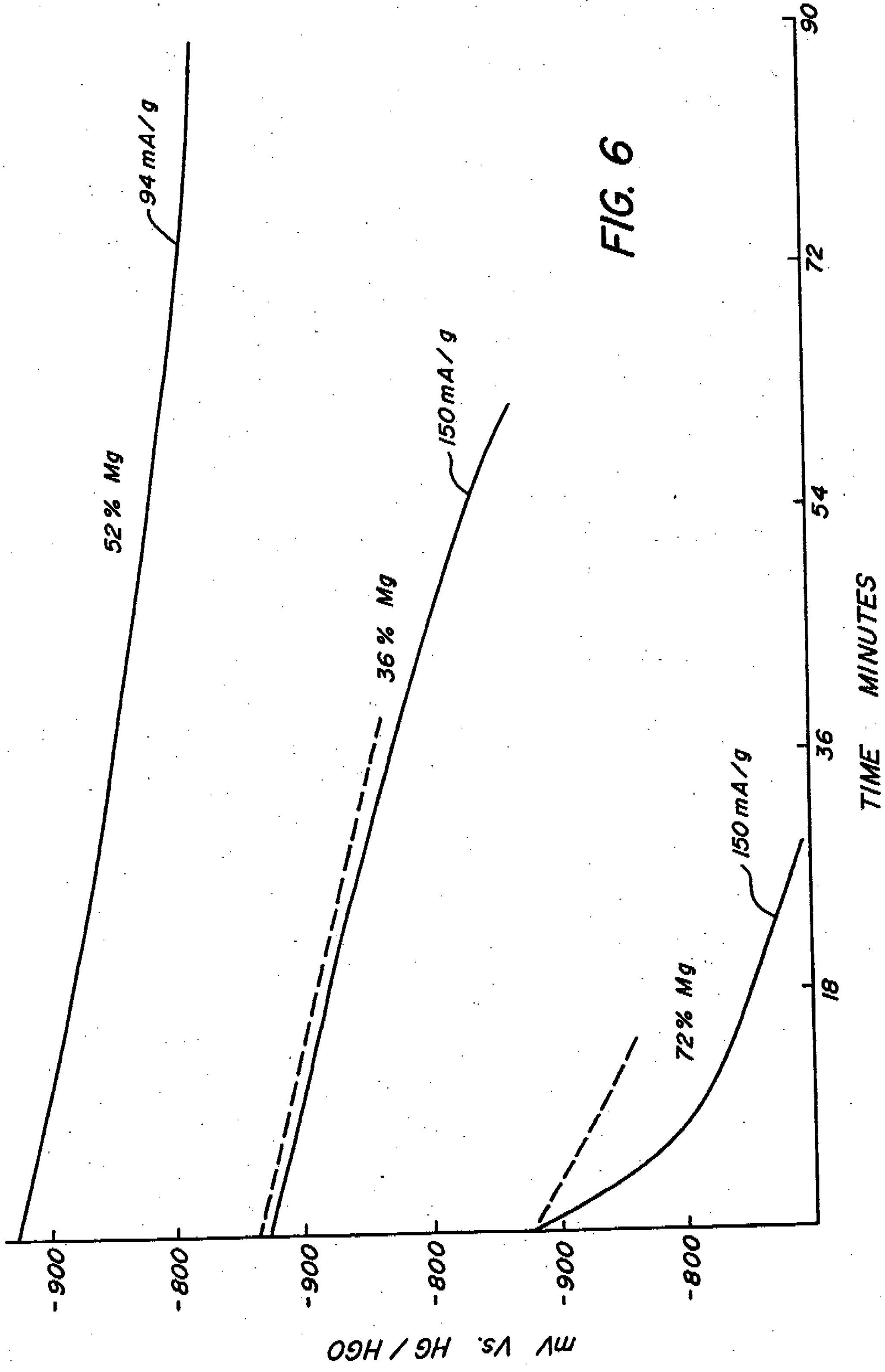
52 % Mg
94 mA/g
36 % Mg
150 mA/g
72% Mg
150 mA/g
-900
-800
-900
-800
-900
-800
mV Vs. HG / HGO
18
36
54
72
90
TIME MINUTES

FIG. 6

RECHARGEABLE BATTERY AND ELECTRODE USED THEREIN

RELATED APPLICATIONS

This is a continuation of application Ser. No. 614,273 filed May 25, 1984, now abandoned, which is a continuation of application Ser. No. 372,693 filed Apr. 28, 1982, entitled "Improved Rechargeable Battery and Electrode Used Therein," now abandoned.

BACKGROUND OF THE INVENTION

The subject matter of this invention relates to the field of energy storage and utilization and in particular to an improved battery and to a rechargeable electrode for use therein. More particularly, the invention relates to a battery having an anode formed from a primarily non-equilibrium disordered material designed to have a large number of catalytically active sites and also a large number of storage sites to store a substantial amount of hydrogen with the chemical bonding designed to efficiently store and release the hydrogen. The battery anode is charged to store hydrogen and discharged to release the stored hydrogen to produce an electrical current.

The present invention frees the anode material design from the limits of crystalline stoichiometry and compositions and allows a whole range of reversible hydrogen storage bonding in the material. The superior battery of the invention has attained a high density energy storage, efficient reversibility, high electrical efficiency, bulk hydrogen storage without substantial structural change or poisoning and hence long cycle life and deep discharge capability. The disordered material preferably is formed from lightweight materials to give a high storage capacity and is made from low cost materials. Thus, for the first time a quantum step forward in battery performance has been attained.

The storage of energy has been one of the great scientific, technological and economic problems in the energy field and most particularly the storage of electrical energy.

The demand for the storage of electricity is increasing at a rapid rate as the world becomes increasingly more dependent on electricity generated from both large base load plants and from renewable, but variable energy sources. It has been estimated that the total energy storage required in the United States by the year 2000 will be about 200 trillion Wh (watt-hours). Batteries have particular advantages for storage applications since:

(1) they store and release electric energy,

(2) they are portable and modular and hence have very flexible uses,

(3) they are relatively easy to manufacture,

(4) they are relatively compact,

(5) they are compatible with and have the ability to follow efficiently the instantaneous variations in the demand for electricity, while at the same time providing regulation of the output, and

(6) they provide local storage and hence reduce transmission and distribution costs.

While each of the above advantages of batteries potentially are available, there remain many problems with conventional batteries. For example, conventional batteries containing lead, mercury or cadmium are environmental contaminants, and therefore cannot easily be disposed of. Conventional batteries have serious materials problems which effect shelf life and cycle life and make them uneconomical for many applications.

The battery field has long been recognized as being a field of slow development rather than the quantum leap forward necessary to permit cost effective use of batteries on a truly large scale basis. It has been stated that "Battery technology is a classic example of an evolving process. We take one step back for every two forward. Most systems that are receiving attention today have been around for decades, and you really can't point to any breakthroughs." A battery, both primary and secondary, with high energy and power density, low cost and long life with many rechargeable cycles is necessary to answer the needs for energy storage and portability which are basic requirements for energy storage. Because of the failure to achieve breakthroughs to solve critical problems in existing battery technology, batteries have achieved only a small fraction of their true potential use.

The applications and potential applications for batteries are too numerous and familiar to enumerate, but some applications are of particular interest for secondary batteries. A secondary battery is a battery which is capable of being recharged after use so that it can be used again to supply electrical energy. Secondary batteries have particular utility in portable applications, such as portable electronic devices, and are particularly suitable for the utilization of solar energy and other electricity generators, such as thermoelectric generators, especially for remote use. It is estimated that the size of the battery market for solar energy applications and the market for electric vehicle batteries will be in the hundreds of gigawatt hours by the year 2000. While great progress has been made in the photovoltaic conversion of solar energy into electricity, there has been little progress in the companion or supporting technology for storage of electrical energy. The development of a truly cost effective technology for storing electrical energy in a convenient reversible form would expand enormously the potential for the utilization of photovoltaic power generation.

The use of electric vehicles to replace fossil fuels is very important. It has been estimated that more than twothirds of all our energy, for example, from automobile exhausts or power plants, is wasted and given off to the environment. The Canadian House of Commons' Special Committee on Alternative Energy and Oil Substitution has stated: "The main problem with developing a practical and competitive electrical vehicle has been the inability to produce inexpensive, reliable, lightweight, energy-dense and durable batteries. A large variety of battery systems is presently being tested but none has emerged which completely overcomes all of these difficulties. Analysts continue to say a quantum leap in battery technology must be made before electrical vehicles become competitive with conventional cars in the automobile market."

The Department of Energy (DOE) has developed target goals for electric vehicles. The 1982 goal is to obtain a battery capacity of 56 Wh/kg which would power an electric vehicle for 100 miles. The best commercially attainable capacities are for lead acid and nickel cadmium batteries which are reported as 37 Wh/kg and 39 Wh/kg, which are well below the 1982 DOE goal. These two types of batteries account for about ninety percent of the secondary battery market. While it has been estimated that a 100 mile range would take care of about ninety percent of the driving needs of the urban population, a recent survey made for DOE shows that consumers are not likely to purchase electric vehicles in large quantities until their range is extended to 200 miles. This figure is beyond the range of existing batteries, but is within the capability of the battery of the present invention. For example, the battery of the present invention can be greatly reduced in size and weight while still producing the desired power, because of the high energy storage density. This greatly increased density gives rise to new battery applications which previously were prohibited, because sufficient power was not available for a given battery size and weight.

The components of a conventional secondary battery such as a nickel-cadmium cell are the anode formed from a cadmium material, and the cathode formed from a nickel hydroxide material. The anode and cathode typically are spaced apart in the cell containing an alkaline electrolyte, such as KOH. The battery is charged upon application of an electric current to the anode as shown in the following equation:

$$Cd(OH)_2+2e^- \rightarrow Cd+2OH^-$$

When the battery is utilized (discharged) the reverse reaction occurs to provide a supply of electrons:

$$Cd+2OH^- \rightarrow Cd(OH)_2+2e^-$$

Over the years, many different electrochemical systems have been developed for battery applications. Such systems, such as zinc-chloride, nickel-zinc, lithium-metal sulfide and nickel-hydrogen have been explored, but have only found limited and specialized applications. The nickel-zinc system has a low cycle life and is expensive. The zinc-chloride battery operates with hazardous chemicals and has a very complex recharging system along with being expensive. Most lithium-metal sulfide systems operate at only very high temperatures of above 350° C. The nickel-hydrogen system is a high pressure, large and expensive system utilized for some specialized space applications.

Each of the available systems provides one or more significant impediments to widespread use, such as low energy density, high operating temperatures, hazardous and/or toxic chemicals, expensive materials or operating procedures. Lead and cadmium systems, for example, both present disposal problems and neither system meets even the 1982 DOE goals. Further, battery electrodes are notorious for their susceptibility to corrosion which limits life time and cycling life for secondary batteries. The large-scale utilization of batteries for storage of electricity has remained blocked because of the fundamental limitations in the technology.

Some research has been conducted involving hydrogen rechargeable 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. One example of such efforts is U.S. Pat. No. 3,874,928. These research efforts have not resulted in any commercial utilization of this battery technology. As a matter of fact, the prior research results have suggested no significant improvement over the conventional nickel cadmium system and hence have resulted in the hydrogen storage battery techniques apparently being ignored or abandoned.

Secondary batteries using a hydrogen rechargeable electrode operate in a different manner than the lead acid and other prior systems. The battery utilizes an anode which is capable of reversibly electrochemically storing hydrogen and employs a cathode of nickel hydroxide material which is used in a conventional secondary battery. 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:

$$M+H_2O+e^- \rightarrow M-H+OH^-$$

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

$$M-H+OH^- \rightarrow M+H_2O+e^-$$

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:

Charging: $Ni(OH)_2+OH^- \rightarrow NiOOH+H_2O+e^-$

Discharging: $NiOOH+H_2O+e^- \rightarrow Ni(OH)_2+OH^-$

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, however, prior anodes have not levied up to that potential because of the limitations of the materials utilized. Thus more electrical energy per unit weight should be possible with such batteries making them particularly suitable for battery powered vehicles and other mobile applications. Furthermore, lead acid batteries and nickel-cadmium type secondary batteries are relatively inefficient, because of their low storage capacity and cycle life.

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 complete 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.

The materials for storing hydrogen which have been proposed in the prior art for use as a hydrogen chargeable anode for secondary batteries have generally been limited to materials which are primarily crystalline structures. In crystalline materials the catalytically active sites result from accidently occurring, surface irregularities which interrupt the periodicity of the crystalline lattice. A few examples of such surface irregularities are dislocation sites, crystal steps, surface impurities and foreign absorbates.

A major shortcoming with basing such anode materials on crystalline structures is that irregularities which result in active sites typically only occur in relatively few numbers on the surface of a crystalline material.

This results in a density of storage sites which is relatively low. Of equal importance is that the type of sites available are of an accidental nature and are not designed into the material as are those of the present invention. Thus, the efficiency of the material for the storage of hydrogen and the subsequent release to form water is substantially less than that which would be possible if a greater number and variety of sites were available.

All of the previous attempts to utilize hydrogen in secondary batteries have proven to be unsuccessful, because the crystalline materials have one or more limiting factors which prevent commercialization. The invention herein provides a new and improved battery having an electrode formed from disordered non-equilibrium material which does not suffer from the disadvantages and limitations of the prior art batteries containing crystalline electrode materials.

SUMMARY OF THE INVENTION

The limitations of the prior art, and in particular those which have blocked large scale utilization of hydrogen rechargeable batteries are overcome by greatly improving and expanding in a unique and fundamental way, both qualitatively and quantitatively, the characteristics of the hydrogen electrode by providing disordered materials which can be tailor-made to greatly increase the reversible hydrogen storage characteristics which are required for efficient and economical battery applications. The superior battery of the invention has attained high density energy storage, efficient reversibility, high electrical efficiency, bulk hydrogen storage without structural change or poisoning and hence long cycle life and deep discharge capability. These essential battery attributes are unique to the present invention.

The disordered electrode materials are formed from lightweight, low cost elements by any number of techniques, which assure formation of primarily non-equilibrium metastable phases resulting in the desired high energy and power densities and low cost. The resulting low cost high energy density disordered material allows the batteries to be utilized most advantageously as secondary batteries, but also as primary batteries.

The materials of the present invention have a greatly increased density of catalytically active sites and storage sites when compared to single phase crystalline materials and other prior art materials, which improves the electrochemical charging/discharging efficiencies and provides a greater electrical energy storage capacity. The materials are tailored to allow bulk storage of the dissociated hydrogen atoms at bonding strengths within the range of reversibility suitable for use in secondary battery applications. Tailoring of the local structural ahd chemical order of the materials of the present invention is of great importance to achieve the desired characteristics.

The improved characteristics of the anodes of the present invention are accomplished by manipulating the local chemical order and hence the local structural order by the incorporation of selected modifier elements into a host matrix to create a desired disordered material. The disordered material has the desired electronic configurations which result in a large number of active sites. The nature and number of storage sites can be designed independently from the catalytically active sites. The desired multicomponent disordered material can be amorphous, polycrystalline (but lacking long range compositional order), or microcrystalline in structure or an intimate mixture of any combination of those phases. The ability to have a large number of sites and to simultaneously control the type of the active sites is also unique to the anodes of the present invention.

The framework for the active battery materials of the present invention is a host matrix of one or more elements. The host elements are chosen in general to be hydride formers and can be lightweight elements. The host matrix element or elements are modified by incorporating selected modifier elements, which may or may not be hydride formers. The modifiers also can be lightweight elements and enhance the disorder of the material, thus creating a greater number and spectrum of catalytically active and hydrogen storage sites. Multiorbital modifiers, for example transition elements, provide a greatly increased number of storage sites due to various bonding configurations available, thus resulting in an increase in energy density. The technique of modification to provide a non-equilibrium material having a high degree of disorder provides unique bonding configurations, orbital overlap and hence a spectrum of bonding sites. Due to the different degrees of orbital overlap and the disordered structure, an insignificant amount of structural rearrangement occurs during charge/discharge cycles or rest periods therebetween resulting in long cycle and shelf life.

The hydrogen storage and other characteristics of the disordered materials of the present invention can be controllably altered depending on the selected host matrix and modifier elements and their relative percentages to allow the tailor-making of the anode materials. The anodes are resistant to degradation by poisoning due to the increased number of selectively designed storage and catalytically active sites which also contribute to long cycle life. Also, some of the sites designed into the material can bond with and deactivate poisonous species without effecting the active hydrogen sites. The materials thus formed have a very low self discharge and hence good shelf life.

The disordered materials can be utilized for anodes of various configurations and designs. The materials can be deposited by vacuum deposition, spraying techniques, melt spinning and other similar rapid quenching techniques or can be manufactured in powder form.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic illustration of an embodiment of the battery of the present invention.

FIG. 2 shows a representative charge/discharge cycle of the battery.

FIG. 3 shows a power vs. storage capacity curve of the battery.

FIG. 4 shows several discharge potential vs. time curves with open circuit voltage curves for certain disordered Ti-Ni anode materials of the present invention.

FIG. 5 shows several discharge potential vs. time curves with open circuit voltage curves for a prior art crystalline Ti-Ni anode material.

FIG. 6 shows several discharge potential vs. time curves with open circuit voltage curves for various MgNi materials of the present invention.

DETAILED DESCRIPTION

The battery of the present invention is a basic and unique approach to the electrical energy storage problem and has attained high density energy storage, efficient reversibility, high electrical efficiency, bulk hydrogen storage capacity without substantial structural change or poisoning and hence long cycle life and deep discharge capability. The improved battery includes disordered electrode materials having tailor-made local chemical environments which are designed to yield high electrochemical charging and discharging efficiency and high electrical charge output. The manipulation of the local chemical environments of the materials is made possible by utilization of a host matrix which can, in accordance with the present invention, be chemically modified with other elements to create a greatly increased density of catalytically active sites for hydrogen dissociation and also of hydrogen storage sites.

The disordered electrode materials, unlike the specific and rigid structure of crystalline materials, are ideally suited for manipulation since they are not constrained by the symmetry of single phase crystalline lattice or by stoichiometry. By moving away from materials having such restrictive single phase crystalline symmetry it is possible by selectively modifying in accordance with the present invention to accomplish a significant alteration of the local structural and chemical environments involved in electrochemical hydrogen storage to greatly enhance the properties of the anode materials.

The disordered materials of the present invention are designed to have unusual electronic configurations, which result from the varying 3-dimensional interactions of constituent atoms and their various orbitals. The disorder comes from compositional, positional and translational relationships of atoms that are not limited by crystalline symmetry in their freedom to interact. Selected elements can be utilized to further modify the disorder by their interaction with these orbitals so as to create the desired local chemical environments. These various configurations generate both a large number of catalytically active sites and hydrogen storage sites not only on the surface but throughout the bulk of the material. The internal topology that is generated by these configurations also allows for selective diffusion of atoms and ions. The invention that we described makes these materials ideal for the specified use since one can independently control the type and number of catalytically active and storage sites. All of the aforementioned properties make not only an important quantitative difference, but qualitatively change the materials so that, as shown by the results, unique new materials ensue.

The disorder in the modified material can be of an atomic nature in the form of compositional or configurational disorder provided throughout the bulk of the material or in numerous regions of the material. The disorder also can be introduced into the host matrix by creating microscopic phases within the material which mimic the compositional or configurational disorder at the atomic level by virtue of the relationship of one phase to another. For example, disordered materials can be created by introducing microscopic regions of a different kind or kinds of crystalline phases, or by introducing regions of an amorphous phase or phases, or by introducing regions of an amorphous phase or phases in addition to regions of a crystalline phase or phases. The interfaces between these various phases can provide surfaces which are rich in local chemical environments which provide numerous desirable sites for electrochemical hydrogen storage.

The disordered materials of the present invention all have less order than the highly ordered crystalline structures which provide the single phase materials such as used for many of the anodes of the prior art. The types of disordered structures which provide the local structural chemical environments for improved hydrogen storage characteristics in accordance with the present invention include multicomponent polycrystalline materials lacking long range compositional order, microcrystalline materials, amorphous materials having one or more phases or multiphase materials containing both amorphous and crystalline phases or mixtures thereof.

An advantage of employing these disordered materials is that with such materials storage sites can be distributed throughout the bulk of the material. Also, the disordered materials can be designed to have the desired porosity, which can further increase the storage capacity and charge/discharge rate. In a crystalline structure the storage sites are limited to a relatively few accidentally occurring irregularities appearing on the surfaces of the material. In a modified disordered material the locations of storage sites are not limited to just the surfaces of the material. In contrast to crystalline structures, the materials of the present invention have three dimensional disorder with storage sites distributed throughout the bulk of the material. They provide a substantially increased surface area which does not depend merely on the presence of cracks, voids and grain boundaries. The disordered materials of the present invention have a greatly increased density of storage and catalytically active sites which provide a significant improvement of hydrogen absorption and desorption in both amount of hydrogen stored and the efficiency of storage during charging. The catalytically active sites reduce the charging and discharging overvoltage and hence substantially the entire energy utilized during charging efficiently results in hydrogen stored in the bulk of the material. The density of storage sites is a major factor in enabling relatively high hydrogen storage capacity for electrochemical charging making these materials suitable for high energy density applications, such as for powering battery operated transportation vehicles.

Another advantage of the disordered materials of the present invention is that they are much more resistant to poisoning. As stated before, the materials of the present invention have a much greater density of catalytically active sites. Thus, a certain number of such sites can be sacrificed to the effects of poisonous species while the large number of unpoisoned active sites still remain to continue to provide the desired completely reversible hydrogen storage characteristics. Also, some of the poisons are inactivated by being bonded to other sites without effecting the hydrogen catalytic storage sites.

Another advantage of the host matrix of the present invention is that it can be modified in a substantially continuous range of varying percentages of modifier elements. This ability allows the host matrix to be manipulated by modifiers to tailor-make or engineer hydrogen storage materials with all the desirable characteristics, i.e., high charging/discharging efficiency, high degree of reversibility, high electrical efficiency, long cycle life, high density energy storage, no poisoning and minimal structural change. This is in contrast to multicomponent single phase crystalline materials which generally have a very limited range of stoichiometry available. A continuous range of control of chemical and structural modification to optimize performance characteristics of such crystalline materials therefore is not possible.

Referring now to FIG. 1, a schematic representation of a battery **10** of the present invention is illustrated. The battery **10** includes a casing **12** which can be hermetically sealed and/or can include a vent **14**. The battery **10** includes an anode **16** formed from the disordered materials of the present invention and a cathode **18** which can be a conventional nickel hydroxide cathode. The anode **16** and cathode **18** are separated by a separator **20**, which also can be a conventional separator such as utilized in the nickel cadmium systems. The battery **10** also contains an electrolyte **22** such as KOH. The dimensions and configurations of the battery **10** and electrodes **16** and **18** are dependent upon the application and can be of any shape, size, capacity, etc. as desired.

A representative charge/discharge cycle of the battery **10** is illustrated in FIG. 2. The difference between the charge and discharge voltages at each depth of discharge shows a remarkably good charging efficiency. For example, at a 40% depth of discharge (0.4), the difference is only about 0.075 volts. It should be noted that the discharge cycle can be at any rate, depending upon the desired application and here was chosen to be 50 mA/gr. The charge rate is, however, chosen to maximize the efficiency of hydride formation and was chosen to be 25 mA/gr, which is a very high charging rate.

FIG. 3 illustrates a calculated theoretical power capacity of the battery **10** vs. the storage capacity of the anode **16** when utilizing a conventional cathode **18**. Since the efficiency of the nickel cathode does not change, it becomes the limiting factor in the battery **10**. Nonetheless, only a three percent storage capacity anode **16** is capable of achieving a power capacity of 114 WH/kg. The materials of the present invention can be expected to exceed such a power capacity value which is sufficient to power a vehicle over 200 miles.

ANODE MATERIAL PREPARATION

A number of anodes **16** were prepared in accordance with the teachings of the present invention. The method selected for initial material screening was cosputtering. The cosputtering method is advantageous for material optimization since it is a relatively fast method of producing different kinds of modified materials to thereby allow a fast screening of the various materials to determine their characteristics. Sputtering also can be a desirable method for preparing the materials, because it lends itself to the production of the non-equilibrium disordered materials and allows an intimate mixing of the host matrix element and modifier elements on an atomic scale so that local order chemical modification can readily take place. Although sputtering techniques are described in detail, any of the allied rapid quenching, bulk and powder techniques which result in the desired non-equilibrium disordered materials are also applicable and within the scope of the invention.

The materials were prepared utilizing either a R.D. Mathis Sputtering Unit or a Sloan SL 1800 Magnetron Sputtering System. An advantage of the particular Sloan system over the Mathis unit, is that it can accommodate more then one target and thus each element sputtered can have a separate dedicated target. The Mathis unit is a single target unit and to accomplish sputtering of more than one element, the target was comprised of multiple elements. Thus, the Mathis target

was comprised of a host element base with sections of desired modifier elements attached to the base.

One or more thin nickel substrates were positioned in the vacuum chamber of the sputtering machine employed. It is noted that other suitably conductive substrates such as titanium, graphite, mild steel, nickel plated mild steel or other materials can also be utilized. During deposition the substrates were maintained at a relatively cool temperature, 130° C. to 150° C., to ensure production of the desired disordered materials. The chamber was evacuated to a background pressure of typically approximately 1×10^{-6} torr. Typically, argon gas was introduced into the chamber at a partial pressure of approximately 6.0×10^{-3} torr. It is noted, however, that reactive sputtering in a gas containing hydrogen, for example 1% to 5% hydrogen, may be advantageous. The relative percentages of elements contained in the materials co-deposited on the substrate were controlled in a different manner depending upon the sputtering machine used. On the Sloan machine, the relative percentages were controlled by varying the magnitude of magnetic flux associated with each target and with the Mathis the composition of the materials was controlled by their position relative to the target.

A number of the materials were tested for utilization as the hydrogen rechargeable anodes **16** in batteries having various configurations, but substantially equivalent in operation to the battery **10**. Further, anode tests were also performed in a half cell utilizing a 4M KOH electrolyte at room temperature, unless otherwise noted. The anodes were electrochemically charged with hydrogen by holding the electrode potential at approximately −1.2 volts vs. an Hg/HgO reference electrode for approximately 10 minutes. After charging the anode was disconnected and the cell open circuit voltage was measured. A constant discharge anodic current, such as 0.1 mA was caused to pass through the electrode and the anode's voltage vs. the reference electrode was recorded during the discharge period. When the electrode potential dropped to less than −0.76 volts the discharge cycle was terminated. The cutoff voltage of −0.76 was arbitrarily chosen, but it is noted that many applications for secondary batteries will have some similar lower voltage limit below which operation will cease thereby necessitating a recharging before further utilization of the battery.

Based upon these measurements the electrical storage capacity of each anode was calculated. Furthermore, since the discharge potentials were measured over a period of time the kinetics of the discharge were determinable. In addition to the electrical tests, other measurements were made. These included the hydrogen storage capacity by weight percent of the charged materials which were computed by dividing the weight of the hydrogen stored, by the sum of the weight of the material and the hydrogen stored therein, Also, the chemical compositions of the anode materials were determined by energy dispersive spectroscopy. All chemical composition are given in atomic percentages.

TABLE I

Composition	Performance of Various Anodes At Room Temperature Current Density mA/gr.	 Specific Capacity mAh/gr.	% H Stored by Weight
$Ti_{80}Ni_{20}$	250	300	1.1

TABLE I-continued

	Performance of Various Anodes At Room Temperature		
Composition	Current Density mA/gr.	Specific Capacity mAh/gr.	% H Stored by Weight
$Ti_{75}Ni_{25}$	250	188	.69
$Ti_{69}Ni_{31}$	167	154	.58
$Ni_{65}Mg_{35}$	88	143	.52
$Ni_{55}Mg_{45}$	50	199	.73
$Mg_{52}Ni_{48}$	94	161	.60
$Ni_{52}Mg_{48}$	50	566	2.1

Table I shows the test results of some representative examples of the anode materials of the present invention. One series of materials utilized a titanium host matrix modified by the incorporation of nickel. A typical open circuit voltage for these materials was found to be −0.93 volts vs. Hg/HgO. As can be seen, the materials with the highest Ti content provided the highest specific capacities and hydrogen storage percentages for this series. It is noted that none of the materials of the tested series approached the theoretical limit of two hydrogen atoms per Ti atom thereby showing that further increased storage capacity is possible in optimizing these materials, such as by the addition of low weight modifier elements as enumerated hereinafter. The specific capacity was taken by discharging to −0.76 volts as previously mentioned. Higher specific capacities can be generated just by discharging to a lower voltage.

Several discharge curves are shown in FIG. 4 for three TiNi materials of the present invention. Increased performance of the materials in terms of current density and discharge cycle length, are seen with increased Ti content. The unoptimized materials of the present invention provided long operating cycles at high current densities. The dashed lines represent the open circuit voltages at various depths of discharge and show very stable performance. Further and of great importance, the materials are shown to have excellent polarization characteristics which are substantially uniform. Each of the materials had a very small millivolt difference between the initial discharge voltage and the open circuit voltage. This very low overvoltage illustrates the very efficient operation of the anodes due to the high density of catalytically active sites.

For reference, the TiNi system of FIG. 4 can be compared to the prior art at TiNi crystalline material illustrated in FIG. 5. The prior art anode at a 100 mA/gr current density operated at relatively low voltages which fell from about 840 mV to about 760 mV in less than 15 minutes. In comparison, the unoptimized $Ti_{80}Ni_{20}$ material of the present invention provided a current density two and one half times as large, operated at higher voltages which decreased more gradually, and provided a voltage of greater than 760 mV for about 80 minutes which is over five times as long as the prior art anode discharged at 100 mA/gr. A comparison of FIGS. 4 and 5 also shows the improved polarization of the materials of the present invention. The prior art materials show a much higher overvoltage at even a 50 mA/g discharge rate which increases dramatically as the discharge rate is increased to 100 mA/g. The catalytic inefficiency of the prior art materials is thus dramatically illustrated.

Table I also shows a series of NiMg materials formed with varying Mg content which also provided excellent results. The first three representative materials were prepared in the manner described above, however, the fourth material exhibited the best result. This material was prepared in a manner to result in a highly disordered substantially amorphous structure, which was achieved by depositing the material at a substrate temperature substantially below 50° C. This results in a substantial increase in the density of storage sites. The open circuit voltages of the NiMg materials were also quite good, approximately −0.93 volts vs. the Hg/HgO reference electrode. Discharge curves for certain of the NiMg disordered materials are shown in FIG. 6. These materials also have dramatically better polarization characteristics than the prior art materials. The 52% Mg curve was a continuous dischrage curve without open circuit voltage readings.

Other materials tested also showed suitability for use as an anode material for the hydrogen rechargeable battery. For example, a V host matrix modified with nickel provided an open circuit voltage of approximately −0.93 volts vs. Hg/HgO. Other host elements which may be particularly suitable for the anode materials of the invention include Zr, Nb, La, Si, Ca, Sc and Y. Each of the host element or elements preferably should be a hydride former and can also be lightweight elements. A "lightweight element" as used herein includes any of those elements which have an atomic number of 22 or less. Modifiers added to the host element or elements can include Cu, Mn, C, Fe, Ni, Al, Co, Mo, W, Li and Re. The modifiers also can be hydride formers.

Furthermore, while the representative materials tested are binary compositions the materials of the invention are not so limited and multi-element combinations of three or more elements can also be formed such as MgNiCu, TiNiCu, TiNiMg, MgFeAl, etc. The modifiers selected to increase the disorder of the host matrix elements, can be lightweight elements, and increase the number of catalytically active and storage sites and hence increase resistance to poisoning. This alloying results in more disorder, both positional and translational, neither of which is possible in a stoichiometrically bound or periodically constrained material. Excellent charging/discharging efficiencies were also found possible during testing of the materials of the present invention. For example, an anode material of approximately $Mg_{40}Ni_{60}$ composition was charged utilizing an applied voltage of 1.43 volts. The open circuit voltage resulting from the charging voltage of 1.43 was 1.4 volts, thus further evidencing the very high charging efficiency of the battery.

Certain of the materials of the present invention were tested at an elevated electrolyte temperature of 70° C. At the higher temperature the electrochemically induced storage capacity was increased and discharge performance was found to be improved. More importantly, operation at higher temperatures showed that the materials have a broad temperature operating range and are capable of much higher storage capacities and improved charge/discharge performance. For example, a $Ti_{75}Ni_{25}$ material having a specific capacity of 188 mAh/gr at 20° C., showed an increase to 475 mAh/gr at 70° C. Also, the $Mg_{52}Ni_{48}$ example was also tested at 50° C. and exhibited an increase in specific capacity to 240 mAh/gr. Thus by optimizing the materials using the modification technique, further improvements in battery performance can be attained. The battery 10 thus also has a wide temperature operating range in contrast to lithium systems which generally are high temperature systems and nickel-cadmium systems which generally operate below 50° C.

It should be noted that testing at 70° C. also gives an indication of very good shelf life of the anodes since operating at elevated temperatures would normally accelerate degradation of conventional battery electrodes. The highly disordered materials of the present invention, however, showed no signs of degradation after testing at 70° C. The 70° C. temperature was arbitrarily selected and is not an upper performance limit. The chemical stability of the disordered materials of the present invention is also excellent since the electrodes tested in the KOH electrolyte indicate no signs of degradation after numerous charge/discharge cycles. The resistance to degradation is attributed to the disordered structure of the materials as well as their ability to accommodate charge/discharge cycling without structural change. Some of the batteries were discharged substantially to zero potential, and were then recharged showing no permanent degradation and deep discharge potential.

It is also noted that the materials of the present invention are capable of absorbing hydrogen by subjecting the electrode to a gaseous hydrogen atmosphere at elevated temperatures. The gaseous hydrogen is catalytically dissociated and chemically bonded to the active storage sites. The charged/disordered anode material thus formed can then be discharged in a battery to provide a supply of electrons as discussed previously in detail. This method of charging the electrode can offer some operational advantages.

Although the anodes described ar formed from substantially homogeneous disordered material bodies, the anodes also can be formed in a multilayer structure. The anode structure can include a bulk formed from a disordered material having a large number of storage sites with a thin outer layer, such as 1 to 5 microns, of a second disordered material. The outer layer material is designed to have a substantial number of catalytically active sites to provide a low overvoltage during charge/discharge cycles.

Furthermore, due to the completely reversible nature of the battery, the hydrogen absorption and desorption characteristics remain substantially constant. The battery potential at any point in each desorption or discharge cycle is directly related to the state of charge of the battery, since the potential changes throughout the desorption cycle. Therefore, the amount of charge remaining in the battery is readily obtained.

While the present invention has been described in conjunction with specific embodiments, those of normal skill in the art will appreciate that modifications and variations can be made without departing from the scope of the present invention. Such modifications and variations are envisioned to be within the scope of the appended claims.

What is claimed and desired to be secured by Letters Patent of the United States is:

1. A hydrogen battery comprising:

at least one anode for reversibly electrochemically charging and discharging hydrogen, said anode comprising a disordered multicomponent material, said disordered multicomponent material having at least one structure selected from the group consisting of: amorphous, microcrystalline, polycrystalline lacking long-range compositional order with three or more phases of said polycrystalline structure and any combination of said amorphous, microcrystalline and polycrystalline structures;

a casing having said anode positioned therein;

at least one cathode capable of reversible oxidation positioned within said casing and spaced from said anode;

a separator separating the cathode and said anode; and

an electrolyte in contact with both said cathode and said anode.

2. The battery of claim 1 wherein said anode material reversibly stores said hydrogen without degradation.

3. The battery of claim 1 wherein said anode material provides local chemical environments that include sites for selectively inactivating poisonous species.

4. The battery of claim 1 wherein said anode material is capable of inhibiting poisoning of the hydrogen absorption and desorption characteristics.

5. The battery of claim 1 wherein said anode material is capable of charging and discharging hydrogen at low overvoltages.

6. The battery of claim 1 wherein said anode material is capable of charging a large amount of hydrogen under one polarity and for discharging a desired amount of hydrogen under the opposite polarity.

7. The battery of claim 1 wherein said anode material is capable of reversibly deep discharging charged hydrogen.

8. The battery of claim 1 wherein said anode material includes at least one lightweight element.

9. The battery of claim 1 wherein said disordered material has an internal porosity to enhance the hydrogen absorption and desorption characteristics.

10. The battery of claim 1 wherein said disordered material has an internal topology to enhance the hydrogen absorption and desorption characteristics.

11. The battery of claim 1 wherein said anode material comprises at least one host matrix material selected from the group consisting of Mg, Ti, V, Zr, Nb, La, Si, Ca, Sc and Y.

12. The battery of claim 1 wherein said anode material includes at least one modifier element for said host matrix material selected from the group consisting of Cu, Mn, Fe, Ni, Al, Mo, W, Ti, Re or Co.

13. The battery of claim 1 wherein said anode material comprises a host matrix material and modifier element, said host matrix material selected from the group consisting of Mg, Ti, V, Zr, Nb, Si, Ca, Sc, Y, and combinations thereof and said modifier element is selected from the group consisting of Cu, Mn, C, Fe, Ni, Al, Co, Mo, W, Li, Re and combinations thereof.

14. The battery of claim 13 wherein said anode material is amorphous.

15. The battery of claim 1 wherein said anode material comprises a host matrix material and a modifier element, said host matrix material selected from the group consisting of Ti, Mg and V and said modifier element is Ni.

16. The battery of claim 15 wherein said anode material is amorphous.

17. The battery of claim 13 wherein said anode material comprises titanium and nickel.

18. The battery of claim 13 wherein said anode material has a composition in the range of from about $Ti_{69}Ni_{31}$ to about $Ti_{80}Ni_{20}$.

19. The battery of claim 18 wherein said anode material is amorphous.

20. The battery of claim 13 wherein said anode material has a composition of about $Ti_{80}Ni_{20}$.

21. The battery of claim 13 wherein said anode material has a composition in the range of from about $Mg_{52}Ni_{48}$ to about $Mg_{35}Ni_{65}$.

22. The battery of claim 13 wherein said anode material comprises vanadium and nickel.

23. A rechargeable hydrogen storage battery electrode comprising a disordered multicomponent material for reversibly, electrochemically charging and discharging hydrogen without forming hydrogen gas, said material including a host matrix selected from the group consisting of Mg, Ti, V, Zr, Nb, La, Si, Ca, Sc and Y, and combinations thereof and at least one modifier element selected from the group consisting of Cu, Mn, C, Fe, Ni, Co, W, Li, Re and combinations thereof, said material having at least one structure selected from the group consisting of amorphous, microcrystalline, polycrystalline lacking long-range compositional order with three or more phases of said polycrystalline structure and any combination of said amorphous, microcrystalline and polycrystalline structures.

24. The electrode of claim 23 wherein said material is amorphous.

25. The electrode of claim 23 wherein said host matrix material is selected from the group consisting of Ti, Mg, V and combinations thereof and said modifier is nickel.

26. The electrode of claim 25 wherein said electrode is amorphous.

27. The electrode of claim 23 wherein said host matrix is titanium and said modifier is nickel.

28. The electrode of claim 23 wherein said host matrix material is titanium and said modifier element is nickel, the composition of said electrode being in the range of from about $Ti_{69}Ni_{31}$ to about $Ti_{80}Ni_{20}$.

29. The electrode of claim 27 wherein said electrode is amorphous.

30. The electrode of claim 27 wherein said composition of said electrode is about $Ti_{80}Ni_{20}$.

31. The electrode of claim 23 wherein said host matrix is magnesium and said modifier is nickel.

32. The electrode of claim 23 wherein said host matrix is vanadium and said modifier is nickel.

* * * * *

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United States Patent [19]

Ovshinsky et al.

[11] **Patent Number: 5,840,440**

[45] **Date of Patent: Nov. 24, 1998**

[54] **HYDROGEN STORAGE MATERIALS HAVING A HIGH DENSITY OF NON-CONVENTIONAL USEABLE HYDROGEN STORING SITES**

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[73] Assignee: **Ovonic Battery Company, Inc.**, Troy, Mich.

[21] Appl. No.: **560,612**

[22] Filed: **Nov. 20, 1995**

[51] **Int. Cl.^{6}** **H01M 10/34**

[52] **U.S. Cl.** **429/60**; 429/59; 429/101; 429/218; 420/900; 420/417; 420/421; 420/422; 204/293

[58] **Field of Search** 420/900, 422, 420/417, 421; 429/218, 59, 101, 60; 204/293

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Primary Examiner—Bruce F. Bell
Attorney, Agent, or Firm—David W. Schumaker; Marvin S. Siskind; Marc J. Luddy

[57] **ABSTRACT**

Disordered multicomponent hydrogen storage material characterized by extraordinarily high storage capacity due to a high density of useable hydrogen storage sites (greater than 10^{23} defect sites/cc) and/or an extremely small crystallite size. The hydrogen storage material can be employed for electrochemical, fuel cell and gas phase applications. The material may be selected from either of the modified $LaNi_5$ or modified TiNi families formulated to have a crystallite size of less than 200 Angstroms and most preferably less than 100 Angstroms.

57 Claims, 5 Drawing Sheets

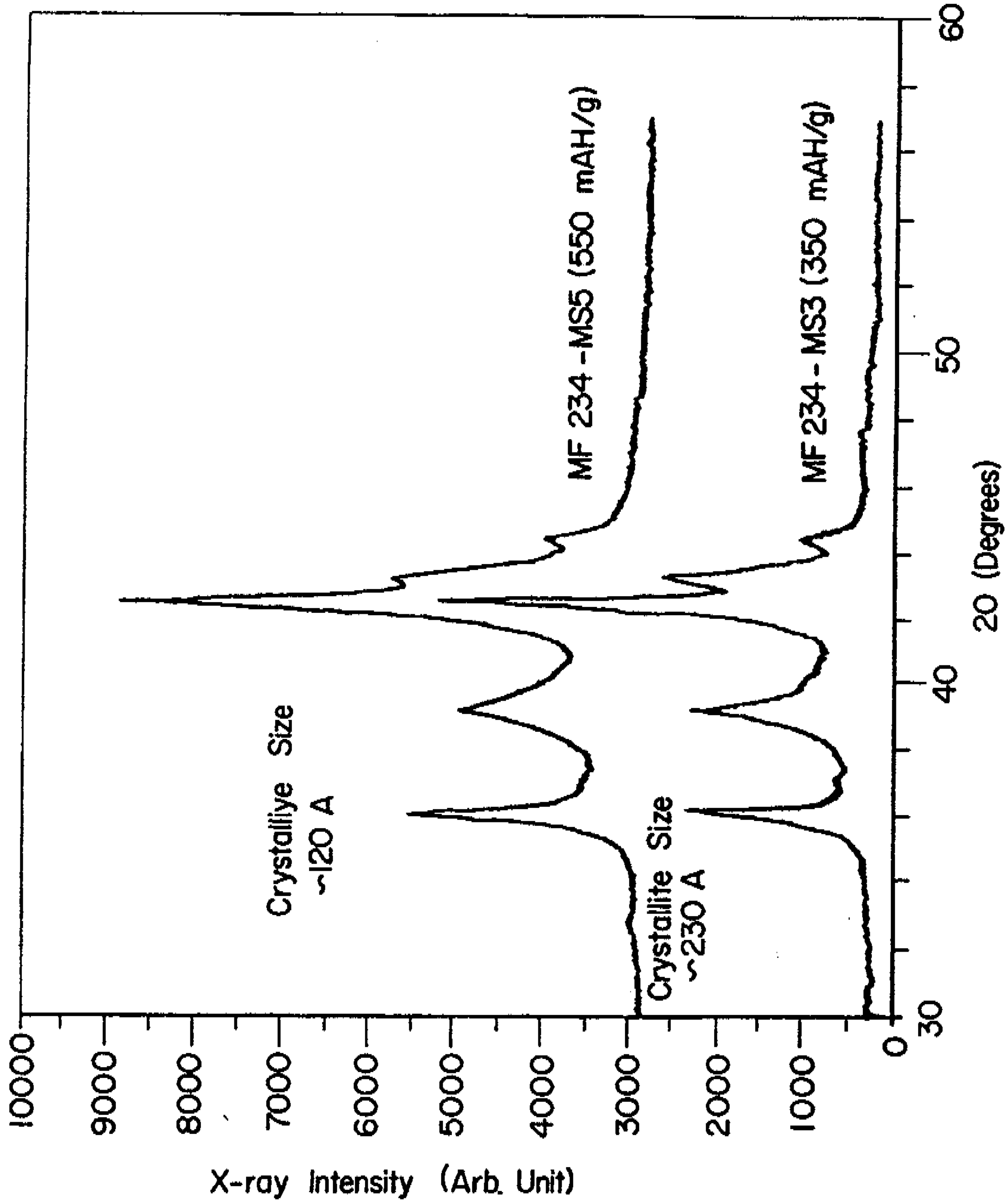
MF 234 -MS5 (550 mAH/g)
MF 234 - MS3 (350 mAH/g)
Crystalliye Size
~120 A
Crystallite Size
~230 A
X-ray Intensity (Arb. Unit)
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
30
40
50
60
2θ (Degrees)

FIG-1

FIG-2A

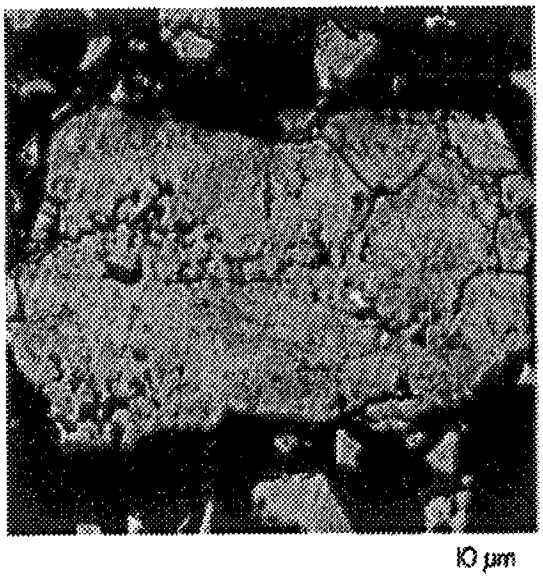

FIG-2B


V₁Ti₉Zr₃₃Ni₃₈Cr₁Co₄Mn₃
Ti₇Zr₄₁Ni₃₉Co₁Mn₃
10 nm
MS234 - SS (RIBBON)

FIG-3

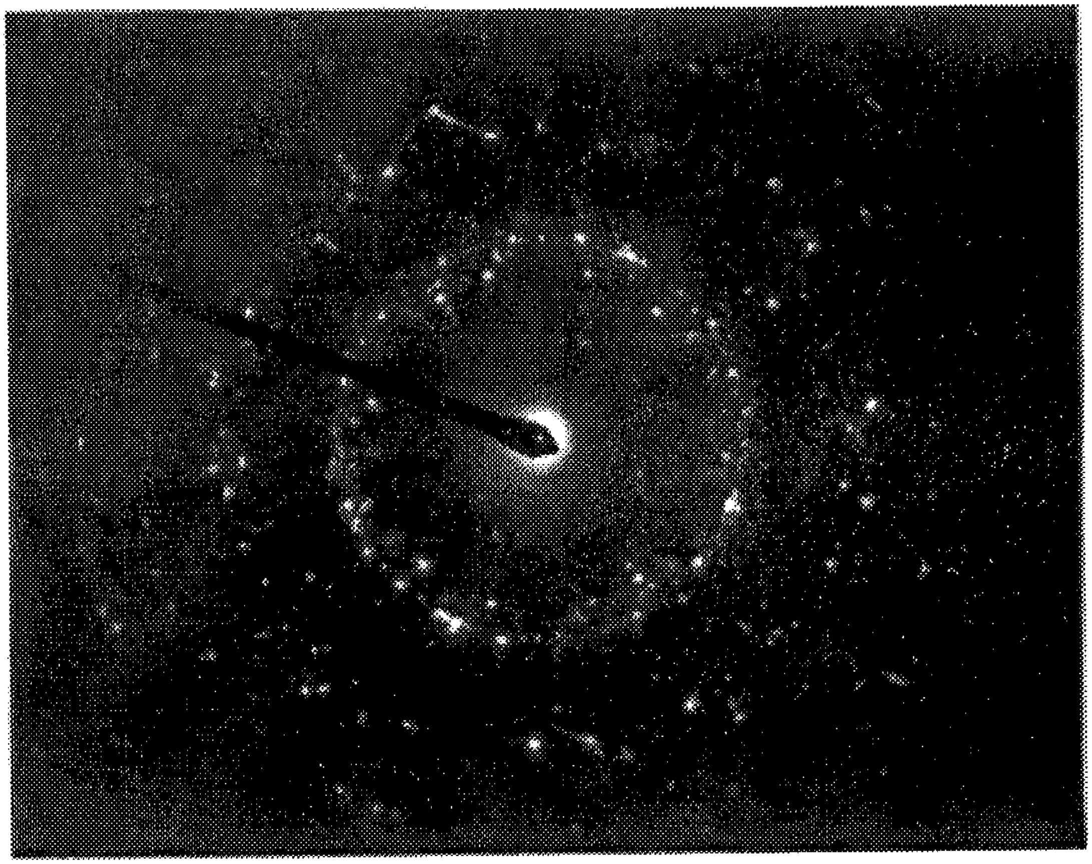

FIG-4

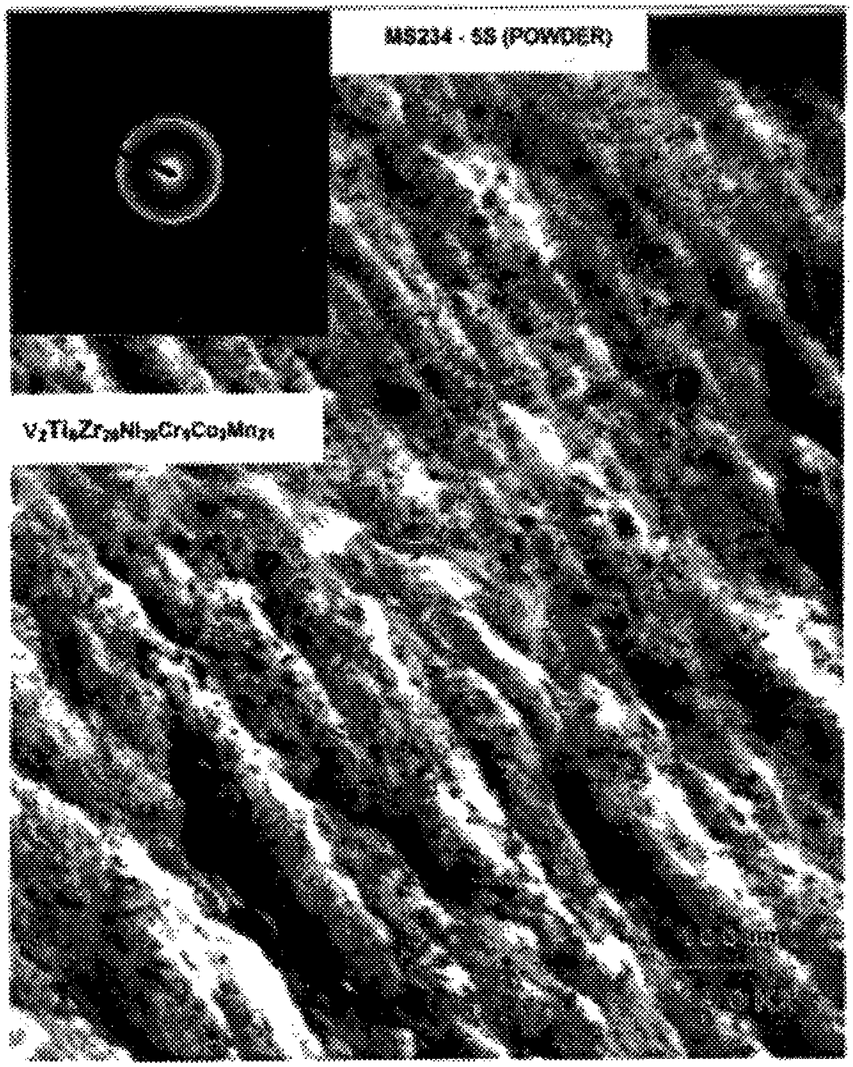

FIG - 5

HYDROGEN STORAGE MATERIALS HAVING A HIGH DENSITY OF NON-CONVENTIONAL USEABLE HYDROGEN STORING SITES

FIELD OF THE INVENTION

The present invention relates to disordered hydrogen storage materials characterized by an extraordinarily high density of useable hydrogen storing sites characterized by unusual local order, said material particularly applicable for use in electrochemical rechargeable nickel metal hydride batteries.

More particularly, in a preferred embodiment, the invention relates to nickel metal hydride (Ni-MH) rechargeable batteries having disordered negative electrodes formed of highly modified $LaNi_5$ and highly modified TiNi based electrochemical hydrogen storage alloys. In addition to very high hydrogen storage capacity, batteries that incorporate the alloys of the instant invention have electrochemical performance characteristics, such as cycle life, charge retention, low temperature, and energy density, that are as good as or better than known rechargeable cells nickel metal hydride batteries. The relatively flat PCT curves make variants of these hydrogen storage alloys promising candidates for the gas phase storage and release of hydrogen.

BACKGROUND OF THE INVENTION

In rechargeable alkaline cells, weight and portability are important considerations. It is also advantageous for rechargeable alkaline cells to have long operating lives without the necessity of periodic maintenance. Rechargeable alkaline cells are used in numerous consumer devices such as portable computers, video cameras, and cellular phones. They are often configured into a sealed power pack that is designed as an integral part of a specific device. Rechargeable alkaline cells can also be configured as larger cells that can be used, for example, in industrial, aerospace, and electric vehicle applications.

The materials proposed in the prior art for use as hydrogen storage negative electrode materials for secondary batteries are materials that primarily have simple crystalline structures. In simple crystalline materials, the catalytic and storage active sites result from accidently occurring, surface irregularities which interrupt the periodicity of the crystalline lattice. A few examples of such surface irregularities are dislocation sites, crystal steps, surface impurities and foreign absorbates. For more than three decades, virtually every battery manufacturer in the world pursued such crystalline electrode materials for electrochemical applications, but none produced a commercially viable nickel metal hydride battery until after the publication of U.S. Pat. No. 4,623,597 (the '597 patent) to Ovshinsky, et al, which disclosed Ovshinsky's fundamentally new principles of electrode material design that commercial electrochemical products began to appear.

As taught in the '597 patent (the contents of which are incorporated by reference), a major shortcoming of basing negative electrode materials on simple ordered crystalline structures is that irregularities which result in the aforementioned catalytically active sites occur relatively infrequently. This results in a relatively low density of catalytic and/or storage sites and consequently poor stability. Of equal importance is that the type of catalytically active sites available are of an accidental nature, relatively few in number and are not designed into the material as are those of the present invention. Thus, the efficiency of the material in storing hydrogen and its subsequent release is substantially less than that which would be possible if a greater number and variety of sites were available.

Ovshinsky's fundamental principles overcome the limitations of the prior art by improving the characteristics of the negative electrode through the use of disordered materials to greatly increase the reversible hydrogen storage characteristics required for efficient and economical battery applications. By applying the principles of disorder, it has become possible to obtain a high energy storage, efficiently reversible, high electrical efficient battery in which the negative electrode material resists structural change, poisoning, resistance to the alkaline environment, good self-discharge characteristics and hence low cycle life and deep discharge capabilities. The resulting disordered negative electrode materials are formed from lightweight, low cost elements by techniques that assure formation of primarily non-equilibrium metastable phases resulting in high energy and power densities and low cost. These non-equilibrium, metastable phases assure the formation of localized states where a special degree of disorder, if properly fabricated, can come from the structural and compositional disorder of the material.

The materials described generally in the '597 patent have a greatly increased density of catalytically active sites providing for the fast and stable storage and release of hydrogen. This significantly improved the electrochemical charging/discharging efficiencies and also showed some increases in hydrogen storage capacity. Generally, this was accomplished by the bulk storage of hydrogen atoms at bonding strengths within the range of reversible electromotive force suitable for use in secondary battery applications. More specifically, such negative electrode materials were fabricated by manipulating the local chemical order and hence the local structural order by the incorporation of selected modifier elements into the host matrix to create the desired disorder, type of local order and metal hydrogen bond strengths. The resulting multicomponent disordered material had a structure that was amorphous, microcrystalline, multiphase polycrystalline (but lacking long range compositional order), or a mixture of any combination of these structures.

The host matrix of the materials described in the '597 patent were formed from lightweight elements that are hydride formers. This host matrix was modified by incorporating selected modifier elements that could also be hydride formers. These modifiers enhanced the disorder of the final material, thus creating a much greater number and spectrum of catalytically active sites and some increase in the number of hydrogen storage sites. Multiorbital modifiers (such as transition elements) provided the greatly increased number of sites due to various bonding configurations available. For reasons explained in greater detail hereinbelow, the resulting increase in useable capacity was primarily due to the formation of the aforementioned increase in catalytic sites which more efficiently store and release hydrogen. Because of this more efficient storage and release of hydrogen and because of the higher density of the catalytic sites, the hydrogen more readily found a storage site. Unfortunately, there remained, until the instant invention, an insufficient density of new hydrogen storage sites formed due to disorder to significantly increase the hydrogen storage capacity of the material.

The '597 patent describes the use of, inter alia, rapid quench to form disordered materials having unusual electronic configurations, which results from varying the three-dimensional interactiors of constituent atoms and their various orbitals. Thus, it was taught that the compositional, positional and translational relationships of the constituent atoms were not limited by crystalline symmetry in their freedom to interact. Selected elements could be utilized to further control the disorder of the material by their interaction with orbitals so as to create the desired local internal chemical environments. These various and at least partially unusual configurations generate a large number of catalytically active sites and hydrogen storage sites not only on the surface but throughout the bulk of the material. The internal topology generated by these various configurations allowed for selective diffusion of hydrogen atoms.

In general, disorder in the modified material can be of an atomic nature in the form of compositional or configurational disorder provided throughout the bulk of the material or in numerous regions or phases of the material. Disorder can also be introduced into the host matrix by creating microscopic phases within the material which mimic the compositional or configurational disorder at the atomic level by virtue of the relationship of one phase to another. For example, disordered materials can be created by introducing microscopic regions or phases of a different kind or kinds of crystalline phases, or by introducing regions of an amorphous phase or phases, or by introducing regions of an amorphous phase or phases in addition to regions of a crystalline phase or phases. The types of disordered structures that provide local structural chemical environments for improved hydrogen storage characteristics include amorphous materials, microcrystalline materials, multicomponent multiphase polycrystalline materials lacking long range composition order or multiphase materials containing both amorphous and crystalline phases.

Short-range, or local, order is elaborated on in U.S. Pat. No. 4,520,039 to Ovshinsky, entitled Compositionally Varied Materials and Method for Synthesizing the Materials, the contents of which are incorporated by reference. This patent discloses that disordered materials do not require periodic local order and how spatial and orientational placement of similar or dissimilar atoms or groups of atoms is possible with such increased precision and control of the local configurations that it is possible to produce qualitatively new phenomena. In addition, this patent discusses that the atoms used need not be restricted to "d band" or "f band" atoms, but can be any atom in which the controlled aspects of the interaction with the local environment and/or orbital overlap plays a significant role physically, electronically, or chemically so as to affect physical properties and hence the functions of the materials. The elements of these materials offer a variety of bonding possibilities due to the multidirectionality of f-orbitals, d-orbitals or lone pair electrons. The multidirectionality ("porcupine effect") of d-orbitals provides for a tremendous increase in density of sites, the spectrum of types of sites and hence the presence of active storage sites. Following the teaching can result in a means of synthesizing new materials which are disordered in several different senses simultaneously.

The '597 patent is described in detail above because this patent represents a starting point for the investigation that resulted in the present invention. Ovshinsky's '597 patent introduced the concept of making negative electrode material for nickel metal hydride batteries from multicomponent disordered alloys. This teaching was diametrically opposed to the conventional "wisdom" of battery manufacturers at the time. It was not until this concept was adopted in production processes by said manufacturers that negative electrode materials with an increased number of catalytically active sites were produced and nickel metal hydride batteries became commercially viable. In capsule form, the '597 patent taught that significant additional sites for hydrogen catalysis (to allow the rapid storage and release of hydrogen and greatly improve stability) were formed and made available by purposely fabricating disordered negative electrode material (as opposed to the homogeneous, ordered polycrystalline material of the prior art). The '597 patent also proposed that the use of disorder could be employed to obtain additional hydrogen storage sites. However, it was not appreciated that in order to obtain a substantial increase in hydrogen storage capacity from such non-conventional storage sites, it would be necessary to increase the number of storage sites by approximately 3 orders of magnitude.

Not only was the teaching of the Ovshinsky patent adopted by all nickel metal hydride manufacturers, but in recent years some of these manufacturers have begun to use rapid solidification techniques (as taught by Ovshinsky) to increase the degree of disorder within a negative electrode alloy formula. For instance, Japanese companies have even gone so far as to rapidly quench highly-modified $LaNi_5$-type electrochemical negative electrode material. By employing nonequilibrium processing techniques, the resulting negative electrode material includes hydrogen storage phases and catalytic phases on the order of 2000 Angstroms in average dimension. The hydrogen storage capacity of the negative electrode material does not improve significantly, but the catalytic activity is greatly improved as evidenced by improved rate capability and stability to oxidation and corrosion resistance is improved resulting in increased cycle life.

As mentioned above, certain battery companies have recently begun to investigate the use of rapidly-quenched, highly modified $LaNi_5$ type hydrogen storage materials for electrochemical applications. For example, in Phys. Chem 96 (1992) No. 5 pp. 656–667, P. H. L. Notten, et al of Philips Research Laboratories presented a paper entitled "Me t-Spinning of AB_{55}-Type Hydride Forming Compounds and the Influence of Annealing on Electrochemical and Crystallographic Properties." In this paper, non-stoichiometric modified $LaNi_{55}$ materials, $La_6Nd_2Ni_3Co_{24}Si_1$ and $La_6Nd_2Ni_{26}Co_{24}Mo_1$ were rapidly spun These non-stoichiometric materials were compared to their stoichiometric counterparts with the result being that the non-stoichiometric materials demonstrated good, but not unusual hydrogen storage capacity. However, the non-stoichiometric compounds did show the presence of additional volume percents of a catalytic phase, which phase, as predicted by the '597 patent, was responsible for the improved electrochemical properties as compared to the properties found in the examples of stoichiometric material. Once again, and importantly, no significantly higher density of non-conventional hydrogen storage sites were obtained.

In research and development activities at Energy Conversion Devices, Inc. with highly modified TiNi-type electrochemical negative electrode materials, such as described in U.S. Pat. No. 4,637,967 entitled Electrodes Made With Disordered Active Material And Methods Of Making Same, (the disclosure of which is incorporated herein by references rapidly quenched electrode materials were melt spun. The work resulted in having oxidation and corrosion resistance was dramatically improved and cycle life was improved by a factor of five. On the other hand and as was true in the case of the aforementioned Japanese work, no significant increase in hydrogen storage capacity was demonstrated and the phases of the negative electrode material present were also relatively large.

Therefore, while the teachings of the '597 patent were revolutionary for those of ordinary skill in the art in learning to apply Ovshinsky's principals of disorder to negative electrode materials to obtain commercial batteries with commercially viable discharge rates and cycle life stabilities while maintaining good hydrogen storage capacity, the '597 patent provided for the most part generalities to routineers concerning specific processes, processing techniques, alloy compositions, stoichiometries in those compositions, etc. regarding how to further significantly increase the hydrogen storage capacity (as opposed to the catalytic activity). It was not until the subject invention that a teaching was presented of the nature and quantification of additional active storage sites required to significantly increase the hydrogen storage capacity of the negative electrode material through the deliberate introduction of defect sites and the presence of other concurrent non-conventional and/or conventional storage sites.

Despite the exceptional electrochemical performance now provided by current highly disordered nickel metal hydride systems (twice the hydrogen storage capacity of conventional NiCd systems) consumers are demanding increasingly greater run times, safety and power requirements from such rechargeable battery systems. No current battery system can meet these demands. Accordingly, there exists a need for a safe ultra high capacity, high charge retention, high power delivery, long cycle life, reasonably priced rechargeable battery system.

SUMMARY OF THE INVENTION

There is disclosed herein a hydrogen storage material that is characterized by a density of hydrogen storage sites of greater than 1.2×10^{23}/cc and more preferably greater than 1.5×10^{23}/cc, corresponding to a specific capacity which is far in excess of conventional hydrogen storage materials. The material can be used as an electrochemical electrode, a gas phase storage alloy or a fuel cell.

There is also disclosed an improved hydrogen storage material formed from an alloy that is selected from the group consisting of alloys represented by the formula $ZrMn_wV_xM_yNi_z$, where M is Fe or Co and w, x, y, and z are mole ratios of the respective elements where $0.4\leqq w\leqq 0.8$, $0.1\leqq x\leqq 0.3$, $0\leqq y\leqq 0.2$, $1.0\leqq z\leqq 1.5$, and $2.0\leqq w+x+y+z<2$ 4, alloys corresponding substantially to the formula $LaNi_5$ in which one of the components La or Ni is substituted by a metal M selected from Groups Ia, II, II, IV, and Va of the Periodic Table of the Elements other than lanthanides, in an atomic proportion which is higher than 0.1% and lower than 25%; alloys having the formula $TiV_{2-x}Ni_x$, where $x=0.2$ to 0.6; alloys having the formula $Ti_aZr_bNi_cCr_dM_x$, where M is Al, Si, V, Mn, Fe, Co, Cu, Nb, Ag, or Pd, $0.1\leqq a\leqq 1.4$, $0.1\leqq b\leqq 1.3$, $0.25\leqq c\leqq 1.95$, $0.1\leqq d\leqq 1.4$, $a+b+c+d=3$, and $0\leqq x\leqq 0.2$; alloys having the formula $ZrMo_dNi_e$ where $d=0.1$ to 1.2 and $e=1.1$ to 2.5; alloys having the formula $Ti_{1-x}Zr_xMn_{2-y-z}Cr_yV_z$ where $0.05\leqq x\leqq 0.4$, $0<y\leqq 1.0$, and $0<z\leqq 0.4$; alloys having the formula LnM_5 where Ln is at least one lanthanide metal and M is at least one metal chosen from the group consisting of Ni and Co; alloys comprising at least one transition metal forming 40–75% by weight of said alloys chosen from Groups II, IV, and V of the Periodic System, and at least one additional metal, making up the balance of said electrochemical hydrogen storage alloy, alloyed with the at least one transitional metal, this additional metal chosen from the group consisting of Ni, Cu, Ag, Fe, and Cr—Ni steel, and alloys comprising a main texture of an Mm—Ni system; and a plurality of compound phases where each compound phase is segregated in the main texture, and wherein the volume of each of the compound phases is less than about 10 μm^3. The improvement in the aforementioned hydrogen storage materials comprises providing a crystallite size of less than about 200 Angstroms and more particularly less than about 100 Angstroms, where the small crystallite size, in a preferred embodiment is achieved via rapid solidification with a significant increase in the density of active hydrogen storage sites present in the resultant ground powder which is believed to be due, at least in part, to a high defect density in the melt spun ribbon. Therefore, the improved hydrogen storage materials of the present invention have achieved higher hydrogen storage via a microcrystalline, nanocrystalline, and/or an amorphous microstructure as opposed to the conventional polycrystalline embodiments of these allows currently employed by all other nickel metal hydride battery manufacturers.

There is further disclosed herein a hydrogen storage material having a high density of useable hydrogen storage sites. This high density is created through the use of non-conventional hydrogen storage sites in combination with conventional hydrogen storage sites. That is, the non-conventional hydrogen storage sites substantially contribute to the total hydrogen storage capacity of the alloy (when compared to the cast alloys). Preferably the non-conventional hydrogen storage sites contribute to at least 5 or 10% of the total hydrogen storage capacity of the material. More preferably, the non-conventional hydrogen storage sites contribute to at least 20 or 33% of the total hydrogen storage capacity of the material. Most preferably, the non-conventional hydrogen storage sites contribute to at least 50% of the total hydrogen storage capacity of the material.

The non-conventional hydrogen storage sites are preferably created by rapidly solidifying a molten material, such as a molten hydride forming alloy material, and thereafter grinding the solidified material to a powder. The non-conventional sites may also be created by other rapid quench techniques such as plasma spraying in which metastable phases and small particle size with a high ratio of surface states to bulk states is present. The hydride forming alloy may be either stoichiometric or non-stoichiometric and may be either a TiNi type alloy or a $LaNi_5$ type alloy. The alloys typically will contain both hydride-forming elements and modifier elements.

For a typical TiNi type alloy, the hydride-forming elements may be selected from the group consisting of Ti, V, Zr and mixtures or alloys thereof and the modifier elements may be selected from the group consisting of Ni, Cr, Co, Mn, Mo, Nb, Fe, Al, Mg, Cu, Sn, Ag, Zn, or Pd and mixtures or alloys thereof. Alternatively, for a typical $LaNi_5$ type alloy, the hydride-forming elements may be selected from the group consisting of Sc, Y, La, Ce, Pr, Nd, Sm, Mm and mixtures or alloys thereof and the modifier elements may be selected from the group consisting of Ni, Cr, Co, Mn, Fe, Cu, Sn, Al, Si, B, Mo, V, Nb, Ta, Zn, Zr, Ti, Hf, W and mixtures or alloys thereof.

The hydride forming alloy may further include at least one glass forming element selected from the group consisting of Al, B, C, Si, P, S, Bi, In, Sb and mixtures or alloys thereof.

The hydrogen storage material is preferably a compositionally and/or structurally disordered, multi-component material having a crystalline size on the order of less than about 200 Å. More preferably the crystallites are on the order of less than about 150 Å. Most preferably the crystallites are on the order of less than about 100 or 75 Å. The hydrogen storage material preferably is multi-phase and contains both catalytic phases and hydrogen storage phases which are most preferably in close proximity to each other. Some or all of these phases are preferably characterized by a substantially higher density of active hydrogen storage sites which may be, a least in part, attributed to a high defect density in addition to conventional hydrogen storage sites and catalytically active sites, such that the total amount of active hydrogen storage sites is significantly higher than that expected from conventional hydrogen storage sites and exemplified eletrode material having much higher specific capacity and small crystallite sites as compared to conventional polycrystalline electrode materials.

The hydrogen storage material of the present invention preferably includes minimal phases of hydride forming elements that do not form active hydride storage sites and substantially no phases of hydrides with incorrect bond strengths for use in electrochemical applications.

There is additionally disclosed a rapidly solidified hydrogen storage alloy ribbon, said ribbon characterized by a defect density of at least 5×10^{21}/cc, preferably at least 1×10^{22}/cc and most preferably at least 5×10^{22}/cc. Such defect density provides for the ribbon to fracture, when ground, into the very small nanocrystalline crystallite sizes referenced herein so as to allow for the extraordinarily high surface to bulk ratio of hydrogen bonding sites.

There is further disclosed a rapidly solidified hydrogen storage alloy having the composition: (Ovonic Base Alloy)$_a$M$_b$

where

Ovonic Base Alloy represents an Ovonic alloy that contains 0.1 to 60 atomic percent Ti, 0.1 to 50 atomic percent Zr, 0.1 to 60 atomic percent V, 0.1 to 60 atomic percent Ni, and 0.1 to 56 atomic percent Cr, as described above;

a is at least 70 atomic percent;

M represents at least one modifier chosen from the group consisting of Co, Mn, Al, Fe, W, La, Mo, Cu, Mg, Ca, Nb, Si, and Hf;

b is 0 to 30 atomic percent;

b>0; and

a+b=100 atomic percent.

The alloy is characterized by a 5% greater hydrogen storage capacity than the same material in cast form. Preferably the increase is 10, 20, 33 or even 50% greater than cast. The preferred composition is, in atomic percent, 0.5–2.0% V; 7.0–8.5% Cr; 6.0–8.0% Ti; 20–35% Zr; 0.01–0.5% Fe; 15–25% Mn; 1.5–3.0% Co; 25–40% Ni; and 0.01–2.0% Mg.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 plots x-ray diffraction patterns for melt spun hydrogen storage materials, the upper plot teing for a material within the scope of the instant invention and the lower plot being for a material outside the scope of the instant invention;

FIGS. 2(A) and (B) are a side by side comparison of SEM photographs of melt spun hydrogen storage materials, the left photograph being for a material outside the scope of the invention and the right photograph being for a material within the scope of the invention;

FIG. 3 is a highly magnified TEM-bright field photograph of a melt spun ribbon flake of a hydrogen storage material of the instant invention, specifically shown is the intimately striated catalytic and storage phases of the material;

FIG. 4 is an electron diffraction pattern of the material of FIG. 3, this figure indicates the extremely high density of defects in the material; and

FIG. 5 is an TEM-dark field photograph of a powdered hydrogen storage material of the instant invention, specifically illustrating the high uniformity of the material.

DETAILED DESCRIPTION OF THE INVENTION

The instant inventors have developed a hydrogen storage material which is characterized by a uniquely high hydrogen storage capacity created by non-conventional storage sites as well as conventional storage sites and whereby the non-conventional hydrogen storage sites substantially contribute to the total hydrogen storage capacity. While all storage materials have both conventional hydride storage sites and non-conventional storage sites, typically the non-conventional storage sites are accidental artifacts within the crystalline lattice constraints of the material and are insignificant in number and/or density to affect the overall storage capacity of the electrode material. Therefore, hydrogen storage capacity due to the non-conventional storage sites is not significant when compared with storage due to conventional sites. However, in the materials of the instant invention, the non-conventional storage sites substantially contribute to the total hydrogen storage capacity thereby achieving remarkably high and unexpected hydrogen storage capacity.

To elaborate, the total number of conventional hydride sites for a typical electrochemical hydrogen storage material (such as a highly ordered polycrystalline material) is generally limited to about one hydrogen atom per hydridable metal atom and may be on the order of about 1×10^{23} sites/cc. The conventional hydride storage sites are locations in the material's structural lattice at which a hydrogen atom bonds into the electronic lattice in a low energy state. There are, for any particular material, a number of these conventional sites that are proportional to the formula and microstructure of the alloy and are dependent upon the amount of hydride forming elements in the formula as well as the bond strengths of constituent phases. For example, whereas $LaNi_5$ type alloys are usually denoted as $LaNi_5H_6$, i.e., one hydrogen atom per one metal atom, VTiZrNi type alloys may have up to 1–1.4 hydrogen atoms per each metal atom. The constraint comes not only from the crystalline structure, but also from the shrinkage of adjacent prospective sites when a hydrogen atom occupies a particular site. Consequently, the typical hydrogen/metal ratio of the best of conventional materials is only about 1 to 1.4.

In the materials of the instant invention the available or useable hydrogen storage sites has been increased to much greater than 1×10^{23} to even as high as $1.5–1.8\times10^{23}$. Also, the ratio of hydrogen to metal is much greater than expected as per the explanation set forth in the preceding paragraph.

Though not wishing to be bound by theory, it should be noted that in the prior art hydrogen storage materials, whether electrochemical or thermal, the total number of defect sites may be on the order of 10^{14} sites/cc. These defect sites are typically due to lattice defects such as steps, dislocations, surface impurities, crystalline plane dislocations, foreign adsorbate dislocations, surface states, etc. Although not initially apparent, the reader should note that each of these defect sites may create as many as 1000 active hydrogen storage sites as the affect of the defect reverberates throughout the lattice. Thus, 10^{15} defect sites/cc are theoretically capable of creating as many as 10^{19} active hydrogen storage sites. However, since the number of conventional hydrogen storage sites is on the order of 10^{23} sites/cc, the number of active sites due to convention defects is inconsequential in comparison. In order to obtain a meaningful contribution from defects that can serve as additional active hydrogen storage sites, it is necessary to deliberately increase the density of non-conventional sites to about 10^{19} sites/cc. In this manner, the 1000 fold increase in active hydrogen storage sites could reach the 10^{22}–10^{23} level and contribute significantly to higher useable storage capacity. It should be readily apparent that the typical number of accidental lattice defect sites is extremely small when compared with the number of conventional hydrogen storage sites by several orders of magnitude.

In contradistinction to the orior art hydrogen storage materials, the number of defect sites of the hydrogen storage materials of the instant invention is much higher. Specifically, the instant inventors have produced materials having a higher density of defect sites than the number of active storage sites present in most previously produced materials (reaching defect densities up to 5×10^{21}/cc, 1×10^{22}/cc and even 5×10^{22}/cc). There are two possible mechanisms through which this extremely high density of defect states can contribute to the hydrogen storage sites of the material. The first, as implied above, is that hydrogen is stored directly in the defects themselves. This storage mechanism is straight forward and easy to understand. The hydrogen merely finds these low energy defect sites in the lattice structure and uses them as it would for conventional low energy lattice sites.

However, it should be noted that the high level of defects sites is noted in the melt spun ribbon. It is unclear if these defects sties remain in the ground powder (at least in large enough numbers to account for the instant materials which receive 5, 10, 20, 33, even 50% of their total hydrogen storage capacity (compared with cast) by storage of hydrogen at non-conventional storage sites.) It is possible that once the ribbons are ground into powder, many of the lattice defects will be translated into crystallite surface states. That is, as the ribbons are ground, the material is fractured along the defects and these will no longer be internal crystallite defects, but will now be a massive amount of new crystallite surfaces, i.e., the ratio of surface sites to bulk sites become similar.

Therefore, another means to explain the extremely high number of non-conventional hydrogen storage sites is by the greatly increased number of and reduced size of the crystallites. The small size of the crystallites increases the number of surface states of the material. These surface states in turn can account for the non-conventional storage sites. That is, these surface sites, because they are not bound by additional crystalline lattice have more room to expand, and thus are not confined by nearby bound hydrogen. Therefore, these surface sites that conventionally would have been precluded from storing hydrogen (because they would have been inside a crystallite) are now capable of storing hydrogen. Most importantly, such surface sites the degree of local disorder presented by a surface state is much different than that presented by a bulk state. The degree of freedom, the possible unusable bonding configurations and the type of orbital overlaps change the nature of surface defects in a dramatic fashion. It is possible that the bonding options offered by the small crystallite surface states of the instant invention are the most energetic possible and that is the reason for the remarkably high hydrogen storage capacity demonstrated herein.

As alluded to above, the materials of the present invention are preferably prepared by rapidly solidifying a molten material using melt spinning and thereafter grinding the solidified material to a powder. A preferred melt spinning apparatus employs a boron nitride crucible and a copper beryllium chill wheel contained in an evacuated chamber continuously filled with argon at a rate of 1–10, preferably 2–8, or most preferably 3–5 liters per minute. Once the desired quantities of alloy components have been added to the boron nitride crucible, the crucible is heated to a temperature of 1000°–2100° C., preferably 1200°–1900° C., or most preferably 1450°–1800° C.

The size of the orifice of the crucible, the wheel speed, the chill rate, and the pressure under which the melt is forced from the crucible are all interrelated, and control the formation of the microstructure in the materials of the present invention. Generally, these factors must be chosen so that the melt is sufficiently cooled while on the wheel to produce the desired high defect microstructure. It is envisioned that rapid solidification processes other than melt spinning may allow the formation of the high defect microstructure necessary to create the hydrogen storage material of the instant invention having the requisite particle size and density of catalytic and hydrogen storage sites. For example, gas atomization, planar flow casting, plasma spray, and other accelerated quenching processes may be substituted for melt spinning and hence are well within the spirit and scope of this invention.

The temperature of the chill wheel can be any temperature from −273° to 90° C., preferably 0° to 75° C., and most preferably 10° to 25° C. The wheel itself preferably has a copper beryllium surface, although any high hardness, high melting point material unreactive to the molten stream may be used.

The preferred hydrogen storage materials of the instant invention are hydride forming alloys. The hydride forming alloy may be either stoichiometric or non-stoichiometnc and may be either TiNi type alloys, $LaNi_5$ type alloys or mixtures thereof. While the alloys can be of any known prior art composition, typically they will contain both hydride-forming elements and modifier elements.

For a typical TiNi type alloy, the hydride-forming elements may be selected from the group consisting of Ti, V, Zr and mixtures or alloys thereof and the modifier elements may be selected from the group consisting of Ni, Cr, Co, Mn, Mo, Nb, Fe, Cu, Sn, Ag, Zn, or Pd and mixtures or alloys thereof. Alternatively, for a typical $LaNi_5$ type alloy, the hydride-forming elements may be selected from the group consisting of Sc, Y, La, Ce, Pr, Nd, Sm, Mm and mixtures or alloys thereof and the modifier elements may be selected from the group consisting of Ni, Cr, Co, Mn, Fe, Cu, Sn, Mo, V, Nb, Ta, Zn, Zr, Ti, Hf, W and mixtures or alloys thereof.

The hydride forming alloy may further include at least one glass forming element selected from the group consibting of Al, B, C, Si, P, S, Bi, In, Sb and mixtures or alloys thereof. Specifically useful alloy compositions may include alloys selected from the group consisting of:

alloys represented by the formula $ZrMn_wV_xM_yNi_z$, where M is Fe or Co and w, x, y, and z are mole ratios of the respective elements where $0.4\leqq w\leqq 0.8$, $0.1\leqq x\leqq 0.3$, $0\leqq y\leqq 0.2$, $1.0\leqq z\leqq 1.5$, and $2.0\leqq w+x+y+z\leqq 2.4$;

alloys corresponding substantially to the formula $LaNi_5$ in which one of the components La or Ni is substituted by a metal M selected from Groups Ia, II, III, IV, and Va of the Periodic Table of the Elements other than lanthanides, in an atomic proportion which is higher than 0.1% and lower than 25%;

alloys having the formula $TiV_{2-x}Ni_x$, where x=0.2 to 0.6;

alloys having the formula $Ti_aZr_bNi_cCr_dM_x$, where M is Al, Si, V, Mn, Fe, Co, Cu, Nb, Ag, or Pd, $0.1\leqq a\leqq 1.4$, $0.1\leqq b\leqq 1.3$, $0.25\leqq c\leqq 1.95$, $0.1\leqq d\leqq 1.4$, $a+b+c+d=3$, and $0\leqq x\leqq 0.2$;

- alloys having the formula $ZrMo_dNi_e$ where d=0.1 to 1.2 and e=1.1 to 2.5;
- alloys having the formula $Ti_{1-x}Zr_xMn_{2-y-z}Cr_yV_z$ where $0.05\leqq x\leqq 0.4$, $0<y\leqq 1.0$, and $0<z\leqq 0.4$;
- alloys having the formula LnM_5 where Ln is at least one lanthanide metal and M is at least one metal chosen from the group consisting of Ni and Co;
- alloys comprising at least one transition metal forming 40–75% by weight of said alloys chosen from Groups II, IV, and V of the Periodic System, and at least one additional metal, making up the balance of said electrochemical hydrogen storage alloy, alloyed with the at least one transitional metal, this additional metal chosen from the group consisting of Ni, Cu, Ag, Fe, and Cr—Ni steel;
- alloys comprising a main texture of an Mm—Ni system; and a plurality of compound phases where each compound phase is segregated in the main texture, and wherein the volume of each of the compound phases is less than about 10 μm^3; and
- alloys having a the composition: (Ovonic Base Alloy)$_aM_b$; where
  - Ovonic Base Alloy represents an Ovonic alloy that contains 0.1 to 60 atomic percent Ti, 0.1 to 50 atomic percent Zr, 0.1 to 60 atomic percent V, 0.1 to 60 atomic percent Ni, and 0.1 to 56 atomic percent Cr, as described above;
  - a is at least 70 atomic percent;
  - M represents at least one modifier chosen from the group consisting of Co, Mn, Al, Fe, W, La, Mo, Cu, Mg, Ca, Nb, Si, and Hf;
  - b is 0 to 30 atomic percent;
  - b>0, and
  - a+b=100 atomic percent.

Alloys of the invention were prepared having the specific formulae set forth below in Table 1, which are covered by the generic composition in atomic percent: 0.5–2.0% V; 7.0–8.5% Cr; 6.0–8.0% Ti; 20–35% Zr; 0.01–0.5% Fe; 15–25% Mn; 1.5–3.0% Co; 25–40% Ni; and 0.01–2.0% Mg.

TABLE 1

Alloy	Alloy Compositions in Atomic Percent								
Number	V	Ti	Zr	Ni	Co	Cr	Fe	Mg	Mn
1	1.4	7.5	28.9	31.8	2.5	7.7	0.13	0.7	19.3
2	1.3	7.8	29.2	31.6	2.4	7.8	0.12	0.3	19.3
Conventional Cast	1.4	7.5	28.9	32.7	2.5	7.7	—	—	19.3

EXAMPLE

Bulk negative electrode materials according to the present invention were rapidly solidified by melt spinning. Raw materials in powder form following the compositions set forth above in Table 1 were put into a boron nitride crucible heated to a temperature of about 1050° C. This crucible had a 0.97 mm orifice through which the melt was injected onto a fast spinning copper beryllium wheel (turning at around 26 m/s). The wheel was cooled by continuously running water at 17° C. The crucible and wheel where enclosed in a chamber that was pumped down and then filled with argon supplied at the rate of 3–5 L/min.

The resulting ribbons and flakes collected at the bottom of the chamber. These were ground for 30–90 minutes. The final powder has a particle size of about 200 mesh. These materials were then pressed onto a nickel wire screen and compacted to form disordered negative electrodes. These disordered negative electrodes were assembled into cells. These cells were cycled and the results are presented in Table 2, below and compared to the same alloy (as above) prepared by conventional casting.

TABLE 2

Alloy Number	initial capacity (mAh/g)	cycling capacity (mAh/g)
1	317	322
2	535	556
Conventional Cast	340	340

As can be seen from a perusal of Table 2, not all melt spun alloys exhibit the greatly increased capacity. When analyzed, the alloy materials having greatly enhanced storage capacity where shown to have many differences from those having "normal" capacity. Samples 1 and 2 have been chosen for comparison due to their essentially identical composition.

One such difference can be seen in the crystallite size of the materials. The microstructure of these materials was analyzed using x-ray diffraction (XRD). Comparison of the crystallite sizes of the samples 1 and 2 (as derived from the XRD plots of FIG. 1) shows that the material of sample 1 has an average crystallite size of about 230 Å, while the material of sample 2 has an average crystallite size of about 120 Å. Additional data from SEM indicates that the crystallite size of the powder may be even smaller than 120 Å and may be as low as 50 Å or even less. As discussed above, this difference in crystallite size may have a substantial effect on storage capacity. It may be that these small crystallites contribute non-conventional storage sites (i.e. surface state sites, crystallite boundary sites, etc.). Therefore, the hydrogen storage material of the instant invention is preferably a compositionally or structurally disordered, multi-component material having a crystalline size on the order of less than about 200 Å. More preferably the crystallites are on the order of less than about 150 or 125 Å. Most preferably the crystallites are on the order of less than about 100 or 50 Å. This nanocrystalline microstructure exhibits useful intermediate range order.

Another difference may be see by comparison of scanning electron microscope (SEM) pictures of particles of samples 1 and 2 seen in FIG. 2. In FIG. 2 the SEM picture on the left is that of the sample 3 material, while the SEM picture on the right is that of sample 2. Comparison dearly indicates that the material of sample 1 is phase segregated (i.e. the catalytic and storage phases are separated in relatively large dumps), while the material of sample 2 is highly uniform with both catalytic and storage phases intimately mixed throughout. This high uniformity allows for better utilization of the storage material. Therefore, the hydrogen storage material of the instant invention is preferably multi-phase and contains both catalytic phases and hydrogen storage phases which are intimately mixed in close proximity to each other. It is also possible that the more uniform microstructure indicates more uniform cooling and possibly a higher defect density than sample 1.

FIG. 3 is an TEM-bright field photograph of the melt spun ribbon (before grinding) of sample 2. The different phases (i.e. catalytic and storage) can clearly be seen as light and dark bands striated throughout the material. Also, the figure shows the very high defect state of the ribbon material. FIG. 4 is an electron diffraction pattern of the material of FIG. 3

(i.e. sample 2). The relative randomness and multitude of dots on the pattern are an additional indication of the extremely large defect density of the material. In fact, the technical experts who assisted in performing analysis of the material indicated that it has the highest defect density of any material that has ever been seen! This extremely high defect density appears to be, in one way or another, the main contributor to the greatly increased capacity of the material.

FIG. 5 is an TEM-dark field photograph of the alloy material of sample 2 after it has been ground into powder. As can be seen, the material is still highly uniform. It should also be noted that since the material has such as high density of defects, it is easily ground into a powder and need not be pre-hydrided to increase its friability.

Finally, two other notable properties of the hydrogen storage material of the instant invention are that the material preferably includes substantially no phases which include hydride forming elements but do not form hydride storage sites and substantially no phases which include hydrides with incorrect bond strengths.

Therefore, it can clearly be seen that the hydrogen storage materials of the present invention show tremendous promise for commercial, industrial and consumer uses. These materials may be used for gas phase hydrogen storage, as well as, electrochemical applications and are particularly well suited for use in nickel hydride batteries.

While the present invention has been described in conjunction with specific embodiments, those of normal skill in the art will appreciate that modifications and variations can be made without departing from the scope of the present invention. Such modifications and variations are envisioned to be within the scope of the appended claims. Particularly included within the scope of said claims are hydrogen storage materials for non-electrochemical applications, such as thermal hydrogen storage or heat pump applications.

We claim:

1. A high capacity hydrogen storage material characterized by a density of hydrogen storage sites of greater than 1.2×10^{23}/cc.

2. The hydrogen storage material of claim 1, wherein the density of hydrogen storage sites is greater than 1.5×10^{23}/cc.

3. The hydrogen storage material of claim 2, wherein said material is an electrochemical electrode.

4. The hydrogen storage material of claim 2, wherein said material is a gas phase storage material.

5. The hydrogen storage material of claim 1, wherein said density of storage sites are obtained from conventional storage sites and defect storage sites.

6. The hydrogen storage material of claim 1, wherein said density of storage sites are obtained from conventional storage sites and crystallite surface storage sites.

7. The hydrogen storage material of claim 1, wherein said density of storage sites are obtained from conventional storage sites, crystallite surface storage sites and defect storage sites.

8. An improved high capacity hydrogen storage material formed from an alloy is selected from the group consisting of:

- alloys represented by the formula $ZrMn_wV_xM_yNi_z$, where M is Fe or Co and w, x, y, and z are mole ratios of the respective elements where $0.4\leqq w\leqq 0.8$, $0.1\leqq x\leqq 0.3$, $0\leqq y\leqq 0.2$, $1.0\leqq z\leqq 1.5$, and $2.0\leqq w+x+y+z\leqq 2.4$;
- alloys corresponding substantially to the formula $LaNi_5$ in which one of the components La or Ni is substituted by a metal M selected from Groups Ia, II, III, IV, and Va of the Periodic Table of the Elements other than lanthanides, in an atomic proportion which is higher than 0.1% and lower than 25%;
- alloys having the formula $TiV_{2-x}Ni_x$, where x=0.2 to 0.6;
- alloys having the formula $Ti_aZr_bNi_cCr_dM_z$, where M is Al, Si, V, Mn, Fe, Co, Cu, Nb, Ag, or Pd, $0.1\leqq a\leqq 1.4$, $0.1\leqq t\leqq 1.3$, $0.25\leqq c\leqq 1.95$, $0.1\leqq d\leqq 1.4$, $a+b+c+d=3$, and $0\leqq x\leqq 0.2$;
- alloys having the formula $ZrMo_dNi_e$ where d=0.1 to 1.2 and e=1.1 to 2.5;
- alloys having the formula $Ti_{1-x}Zr_xMn_{2-y-z}Cr_yV_z$ where $0.05\leqq x\leqq 0.4$, $0\leqq y\leqq 1.0$, and $0<z\leqq 0.4$;
- alloys having the formula LnM_5 where Ln is at least one lanthanide metal and M is at least one metal chosen from the group consisting of Ni and Co;
- alloys comprising at least one transition metal forming 40–75% by weight of said alloys chosen from Groups II, IV, and V of the Periodic System, and at least one additional metal, making up the balance of said electrochemical hydrogen storage alloy, alloyed with the at least one transitional metal, this additional metal chosen from the group consisting of Ni, Cu, Ag, Fe, and Cr—Ni steel, and
- alloys comprising a main texture of an Mm—Ni system; and a plurality of compound phases where each compound phase is segregated in the main texture, and wherein the volume of each of the compound phases is less than about 10 μm^3; said improvement comprising in combination:

the crystallite size is less than 200 Angstroms.

9. The hydrogen storage material of claim 8, wherein the crystallite size is less than about 100 Angstroms.

10. The hydrogen storage material of claim 9, wherein said material is an electrochemical electrode.

11. The hydrogen storage material of claim 9, wherein said material is a gas phase hydrogen storage material.

12. A hydrogen storage material, said material characterized by a hydrogen storage capacity created by non-conventional hydrogen storage sites as well as conventional hydrogen storage sites, whereby said non-conventional hydrogen storage sites substantially contribute to the total hydrogen storage capacity of the alloy.

13. The hydrogen storage material of claim 12, wherein said non-conventional hydrogen storage sites contribute to at least 5% of the total hydrogen storage capacity of the material.

14. The hydrogen storage material of claim 13, wherein said non-conventional hydrogen storage sites contribute to at least 10% of the total hydrogen storage capacity of the material.

15. The hydrogen storage material of claim 14, wherein said non-conventional hydrogen storage sites contribute to at least 20% of the total hydrogen storage capacity of the material.

16. The hydrogen storage material of claim 15, wherein said non-conventional hydrogen storage sites contribute to at least 33% of the total hydrogen storage capacity of the material.

17. The hydrogen storage material of claim 16, wherein said non-conventional hydrogen storage sites contribute to at least 50% of the total hydrogen storage capacity of the material.

18. The hydrogen storage material of claim 12, wherein said non-conventional hydrogen storage sites are created by rapidly solidifying a molten material and thereafter grinding the solidified material to a powder.

19. The hydrogen storage material of claim 18, wherein said molten material is a molten hydride forming alloy material.

20. The hydrogen storage material of claim **19**, wherein said hydride forming alloy is a stoichiometric TiNi alloy.

21. The hydrogen storage material of claim **20**, wherein said hydride forming alloy includes both hydride-forming elements and modifier elements.

22. The hydrogen storage material of claim **19**, wherein said hydride forming alloy is a non-stoichiometric TiNi alloy.

23. The hydrogen storage material of claim **22**, wherein said hydride forming alloy includes both hydride-forming elements and modifier elements.

24. The hydrogen storage material of claim **23**, wherein said hydride forming alloy includes hydride-forming elements selected from the group consisting of Ti, V, Zr and mixtures or alloys thereof and modifier elements selected from the group consisting of Ni, Cr, Co, Mn, Mo, Nb, Fe, Cu, Sn, Ag, Zn, Pd and mixtures or alloys thereof.

25. The hydrogen storage material of claim **24**, wherein said material further includes at least one glass forming element selected from the group consisting of Al, B, C, Si, P, S, Bi, In, and mixtures or alloys thereof.

26. The hydrogen storage material of claim **19**, wherein said hydride forming alloy is a stoichiometric $LaNi_5$ alloy.

27. The hydrogen storage material of claim **26**, wherein said hydride forming alloy includes both hydride-forming elements and modifier elements.

28. The hydrogen storage material of claim **27**, wherein said hydride forming alloy includes hydride-forming elements selected from the group consisting of Sc, Y, La, Ce, Pr, Nd, Sm, Mm and mixtures or alloys thereof and modifier elements selected from the group consisting of Ni, Cr, Co, Mn, Fe, Cu, Sn, Mo, V, Nb, Ta, Zn, Zr, Ti, Hf, W and mixtures or alloys thereof.

29. The hydrogen storage material of claim **28**, wherein said material further includes at least one glass forming element selected from the group consisting of Al, B, C, Si, P, S, Bi, In, Sb and mixtures or alloys thereof.

30. The hydrogen storage material of claim **19**, wherein said hydride forming alloy is a non-stoichiometric $LaNi_5$ alloy.

31. The hydrogen storage material of claim **30**, wherein said hydride forming alloy includes both hydride-forming elements and modifier elements.

32. The hydrogen storage material of claim **31**, wherein said hydride forming alloy includes hydride-forming elements selected from the group consisting of Sc, Y, La, Ce, Pr, Nd, Sm, Mm and mixtures or alloys thereof and modifier elements selected from the group consisting of Ni, Cr, Co, Mn, Fe, Cu, Sn, Mo, V, Nb, Ta, Zn, Zr, Ti, Hf, W and mixtures or alloys thereof.

33. The hydrogen storage material of claim **32**, wherein said material further includes at least one glass forming element selected from the group consisting of Al, B, C, Si, P, S, Bi, In, Sb and mixtures or alloys thereof.

34. The hydrogen storage material of claim **21**, wherein said hydride forming alloy includes hydride-forming elements selected from the group consisting of Ti, V, Zr and mixtures or alloys thereof and modifier elements selected from the group consisting of Ni, Cr, Co, Mn, Mo, Nb, Fe, Cu, Sn, Ag, Zn, Pd and mixtures or alloys thereof.

35. The hydrogen storage material of claim **34**, wherein said material further includes at least one glass forming element selected from the group consisting of Al, B, C, Si, P, S, Bi, In, Sb and mixtures or alloys thereof.

36. The hydrogen storage material of claim **12**, wherein said material is a compositionally or structurally disordered, multi-component material.

37. The hydrogen storage material of claim **36**, wherein said material contains crystallites on the order of less than 200 Å.

38. The hydrogen storage material of claim **37**, wherein said material contains crystallites on the order of less than 150 Å.

39. The hydrogen storage material of claim **38**, wherein said material contains crystallites on the order of less than 125 Å.

40. The hydrogen storage material of claim **39**, wherein said material contains crystallites on the order of less than 100 Å.

41. The hydrogen storage material of claim **40**, wherein said material contains crystallites on the order of less than 50 Å.

42. The hydrogen storage material of claim **36**, wherein said material is a multi-phase material containing both catalytic phases and hydrogen storage phases.

43. The hydrogen storage material of claim **42**, wherein said catalytic phases and said hydrogen storage phases are intimately mixed in close proximity to each other.

44. The hydrogen storage material of claim **12**, wherein said material includes substantially no phases which include hydride forming elements but do not form hydride storage sites.

45. The hydrogen storage material of claim **12**, wherein said material includes substantially no phases which include hydrides with excessive bond strengths.

46. The hydrogen storage material of claim **12**, wherein said material is formed from an alloy is selected from the group consisting of:

alloys represented by the formula $ZrMn_wV_xM_yNi_z$, where M is Fe or Co and w, x, y, and z are mole ratios of the respective elements where $0.4 \leqq w \leqq 0.8$, $0.1 \leqq x \leqq 0.3$, $0 \leqq y \leqq 0.2$, $1.0 \leqq z \leqq 1.5$, and $2.0 \leqq w+x+y+z \leqq 2.4$;

alloys corresponding substantially to the formula $LaNi_5$ in which one of the components La or Ni is substituted by a metal M selected from Groups Ia, II, III, IV, and Va of the Periodic Table of the Elements other than lanthanides, in an atomic proportion which is higher than 0.1% and lower than 25%;

alloys having the formula $TiV_{2-x}Ni_x$, where $x=0.2$ to 0.6;

alloys having the formula $Ti_aZr_bNi_cCr_dM_x$, where M is Al, Si, V, Mn, Fe, Co, Cu, Nb, Ag, or Pd, $0.1 \leqq a \leqq 1.4$, $0.1 \leqq b \leqq 1.3$, $0.25 \leqq c \leqq 1.95$, $0.1 \leqq d \leqq 1.4$, $a+b+c+d=3$, and $0 \leqq x \leqq 0.2$;

alloys having the formula $ZrMo_dNi_e$ where $d=0.1$ to 1.2 and $e=1.1$ to 2.5;

alloys having the formula $Ti_{1-x}Zr_xMn_{2-y-z}Cr_yV_z$ where $0.05 \leqq x \leqq 0.4$, $0 \leqq y \leqq 1.0$, and $0 < z \leqq 0.4$;

alloys having the formula LnM_5 where Ln is at least one lanthanide metal and M is at least one metal chosen from the group consisting of Ni and Co;

alloys comprising at least one transition metal forming 40–75% by weight of said alloys chosen from Groups II, IV, and V of the Periodic System, and at least one additional metal, making up the balance of said electrochemical hydrogen storage alloy, alloyed with the at least one transitional metal, this additional metal chosen from the group consisting of Ni, Cu, Ag, Fe, and Cr—Ni steel; and

alloys comprising a main texture of an Mm—Ni system; and a plurality of compound phases where each compound phase is segregate In the main texture, and wherein the volume of each of the compound phases is less than about 10 μm^3.

47. A rapidly solidified hydrogen storage alloy ribbon, said ribbon characterized by a defect density of at least $5\times10_{21}$/cc.

48. The rapidly solidified hydrogen storage alloy ribbon of claim **47**, wherein said defect density is at least 1×10^{22}/cc.

49. The rapidly solidified hydrogen storage alloy ribbon of claim **47**, wherein said defect density is at least 5×10^{22}/cc.

50. The rapidly solidified hydrogen storage alloy ribbon of claim **47**, further characterized by a crystallite size of less than 200 Å.

51. The rapidly solidified hydrogen storage alloy ribbon of claim **47**, further characterized by a multi-phase structure containing both catalytic phases and hydrogen storage phases.

52. A rapidly solidified hydrogen storage alloy, said alloy having a the composition: (Ovonic Base Alloy)$_a$M$_b$

where

Ovonic Base Alloy represents an Ovonic alloy that contains 0.1 to 60 atomic percent Ti, 0.1 to 50 atomic percent Zr, 0 1 to 60 atomic percent V, 0.1 to 60 atomic percent Ni, and 0.1 to 56 atomic percent: Cr, as described above;

a is at least 70 atomic percent;

M represents at least one modifier chosen from the group consisting of Co, Mn, Al, Fe, W, La, Mo, Cu, Mg, Ca, Nb, Si, and Hf;

b is 0 to 30 atomic percent;

$b>0$; and

$a+b=100$ atomic percent;

said alloy being characterized by a 5% greater hydrogen storage capacity than the same material in cast form.

53. The rapidly solidified hydrogen storage alloy of claim **52**, wherein said alloy has a 10% greater hydrogen storage capacity than the same material in cast form.

54. The rapidly solidified hydrogen storage alloy of claim **53**, wherein said alloy has a 20% greater hydrogen storage capacity than the same material in cast form.

55. The rapidly solidified hydrogen storage alloy of claim **54**, wherein said alloy has a 33% greater hydrogen storage capacity than the same material in cast form.

56. The rapidly solidified hydrogen storage alloy of claim **55**, wherein said alloy has a 50% greater hydrogen storage capacity than the same material in cast form.

57. The rapidly solidified hydrogen storage alloy of claim **52**, wherein said alloy has the composition, in atomic percent: 0.5–2.0% V; 7.0–8.5% Cr; 6.0–8.0% Ti; 20–35% Zr, 0.01–0.5% Fe; 15–25% Mn; 1.5–3.0% Co; 25–40% Ni; and 0.01–2.0% Mg.

* * * * *

Role of atmosphere in the crystallization of amorphous plasma-sprayed Sm-Co deposits

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Thick, machinable, and amorphous 1Sm-5Co plasma-sprayed deposits show a high resistance to magnetization and demagnetization at room temperature. This behavior is believed to be related to large internal stresses and variations in chemical composition present in the as-sprayed material. Thermal treatments of these deposits, in argon, at temperatures substantially lower than those required for crystallization, produce little change in their magnetic behavior. Similar treatments in hydrogen, however, result in an easy approach to saturation and very low coercivity values. This different response of the material to hydrogen has been attributed to an increased mobility of the atoms in hydrogen, which permits sufficient rearrangement of the atoms so that high magnetization and low coercivity are achieved in the amorphous state. Use of a hydrogen atmosphere also results in a considerable increase in the temperature required for crystallization. Whereas crystallization occurs at about 500 °C in argon, temperatures of about 700 °C are needed to produce similar effects in hydrogen. The suppression of the crystallization processes in hydrogen has been attributed to a deposit-hydrogen chemical interaction at the low temperatures. The results of this study indicate that amorphous 1Sm-5Co is probably more suited for use as a means for storing hydrogen than is crystalline $SmCo_5$ material.

PACS numbers: 64.80. – v, 75.50.Kj, 82.65.Nz

I. INTRODUCTION

$SmCo_5$ (like several other rare-earth–transition-metal compounds) is known to reversibly absorb and desorb large quantities of hydrogen at low temperatures.[1,2] The extent of hydride formation at a given temperature is a function of the pressure of the hydrogen gas that surrounds the sample. Pressed powder samples of $SmCo_5$ have been observed to release almost all of the hydrogen, at room temperature, in about 2 h simply by releasing the hydrogen gas pressure surrounding the samples.[3] With increases in sample exposure temperature a slight increase in hydrogen solubility is observed and higher gas pressures are required for formation of the second (hydride) phase.[1] Repeated cycles of hydrogen absorption and desorption usually lead to severe cracking and fracturing of the material, possibly due to the generation of large internal stresses related to the hydrogen absorption and hydride formation processes.

Part of the earlier interest in the interaction of hydrogen with $SmCo_5$ dealt with development of efficient procedures for storing hydrogen for subsequent use as a fuel.[4,5] Recently, however, the effect of hydrogen on the sintering of Sm-Co magnets was also investigated as an alternative to the more conventional inert-gas atmosphere that is employed commercially.[6] The beneficial effects of using hydrogen were evident in the higher-density higher-energy product material that was produced at the lower sintering temperatures (where relatively poor properties were measured for the argon sintered material). Because hydrogen appeared to have aided in the atomic rearrangement process necessary for high-temperature sintering, we have ventured to examine (in this study) the effects of the environment (argon and hydrogen) on the low-temperature crystallization and annealing behavior of amorphous plasma-sprayed deposits of close-to-$SmCo_5$ stoichiometry. Several interesting observations have been made and are reported in this paper.

II. EXPERIMENTAL METHODS

Amorphous plasma-sprayed disk-shaped samples, about 0.1 in. thick and 0.2 in. in diameter, were heat treated for 16 h in flowing argon or hydrogen, at each of the several temperatures indicated in Sec. III, with gas pressures only slightly raised above atmospheric. After exposure to temperature, the samples were allowed to cool inside the furnace at low rates of cooling. The atmosphere (in which the heat treatment was performed) was maintained throughout this cooling cycle. The exposed samples were measured for specific heat C_p within a few hours of removal from the furnace using a differential scanning calorimeter. Virtually no change in the value of C_p was observed for periods in excess of 24 h following sample removal from the furnace. Most of the magnetic data reported in this paper was collected on the heat-treated samples at room temperature with the aid of high-strength magnets capable of applied static magnetic fields of up to 140 kOe.

III. RESULTS AND DISCUSSIONS

Over 0.1-in.-thick amorphous plasma-sprayed deposits (with an overall composition close to that of stoichiometric $SmCo_5$) were fabricated using techniques described previously.[7] The amorphous nature of the deposits was confirmed by observing broad unresolved peaks in the x-ray-diffraction patterns of these samples. Resistivity values measured on the as-sprayed amorphous samples were about three to four times higher than those measured for the sprayed material in its crystalline state. The amorphous material was also quite machinable (unlike the commercial sin-

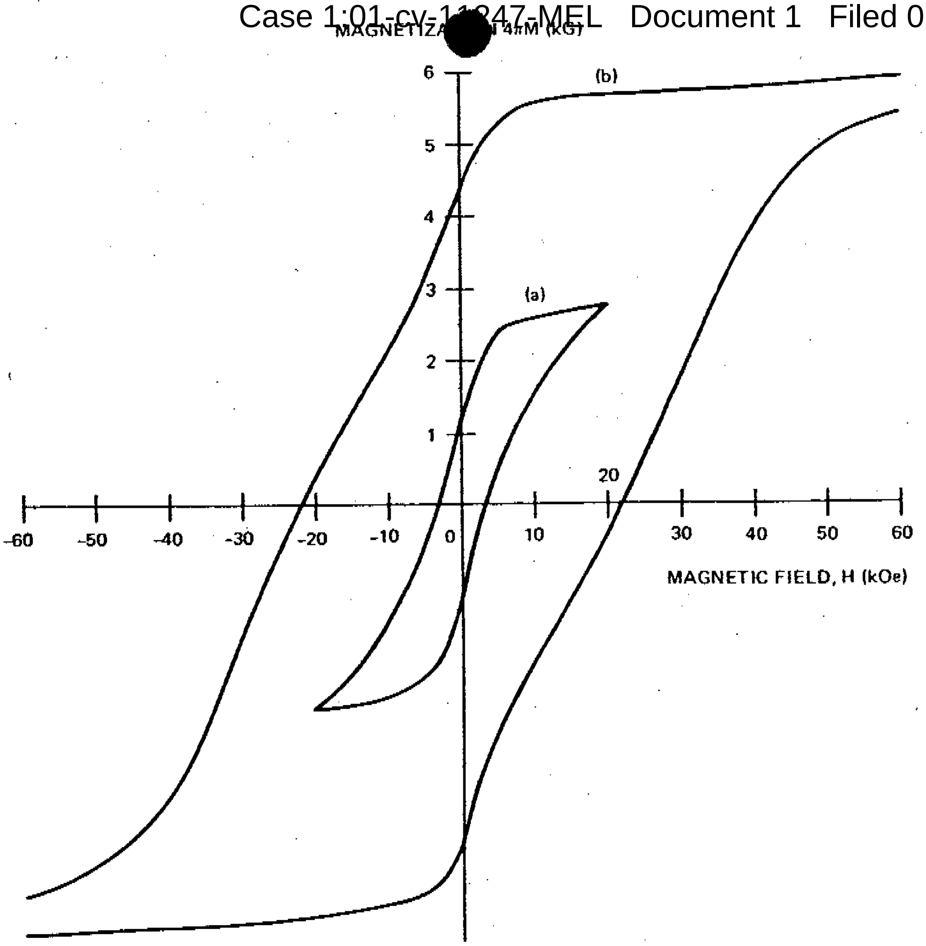

FIG. 1. $4\pi M$-vs-H loops obtained on as-sprayed amorphous deposits for magnetizing fields of (a) 20 kOe and (b) 140 kOe.

tered variety) with lathe-machining characteristics similar to those from cast iron. Single-point carbide tooling was used to check the machinability of this material.

$4\pi M$-vs-H plots obtained on the sprayed amorphous material for large (140 kOe) magnetizing fields were qualitatively similar to those reported earlier for these materials.[8] The as-sprayed amorphous deposits were difficult to magnetize and showed high intrinsic coercivity H_{ci} values of about 20 kOe for magnetizing field strengths of 140 kOe. For lower magnetizing fields of 10–20 kOe, H_{ci} values of less than 5 kOe were observed. $4\pi M$-vs-H curves obtained with 20- and 140-kOe magnetizing field strengths on an as-sprayed amorphous sample are shown in Fig. 1. These observations were unexpected since amorphous material produced elsewhere by sputter deposition had shown H_{ci} values of less than 300 Oe and a quick approach to saturation at modest values of the applied field.[9] This radically different behavior of the thick sprayed amorphous material was, therefore, interpreted as resulting from large internal stresses and nonuniformity in composition present in the as-sprayed condition. On this basis it was concluded that thermal treatment of these deposits, at temperatures below those required for rapid crystallization, would yield easily saturating low-coercivity amorphous Sm-Co material similar in properties to that produced by sputter deposition.

Crystallization temperatures of slightly over 500 °C were reported earlier for heat treatments conducted on sputtered deposits in vacuum. We, therefore, subjected the sprayed amorphous material to temperatures in the range 400–500 °C under argon and studied the effects of these thermal treatments on the magnetic properties. The results were disappointing in that only marginal changes were observed. The effects of these heat treatments are shown in Table I. Here $4\pi M_D$ refers to the $4\pi M$ values at 20-kOe field strength on the demagnetization portion of the hysteresis curve (after magnetization at 140 kOe). The marginal response to heat treatment in argon was attributed to the very low mobility of the atoms at these low temperatures. The low mobility of the atoms was also noted in efforts made to crystallize sputtered amorphous deposits at similar temperatures.[9] An alternate approach was, therefore, adopted to speed up the kinetics of

TABLE I. Response of amorphous material to 16-h treatments in argon and hydrogen.

Sequence	Heat treatment	Atmosphere	C_p (cal/g °K)	$4\pi M_D$ (G)	H_{ci} (kOe)
A	As-sprayed	···	0.088	~ 5600	~20.0
B	A +450 °C	Argon	0.087	5850	20.0
C	B +500 °C	Argon	0.086	5700	22.0
D	A +450 °C	Hydrogen	0.095	9000	0.7
E	D +500 °C	Hydrogen	0.099	10 000	0.3

TABLE II. Effects of argon treatments on hydrogen-treated samples. Time at temperature: 16 h.

Sequence	Heat treatment	Atmosphere	C_p (cal/g °K)	$4\pi M_D$ (G)	H_{ci} (kOe)
A	As-sprayed	···	0.086	~5600	~20.0
B	A +400 °C	Hydrogen	0.095	7850	3.5
C	B +450 °C	Hydrogen	0.094	8150	0.8
D	C +350 °C	Argon	0.091	8500	1.1
E	D +400 °C	Argon	0.092	8400	1.1
F	E +450 °C	Argon	0.088	8000	1.1
G	F +500 °C	Argon	0.089	7650	5.5

the atomic rearrangement processes that were considered necessary to achieve high $4\pi M$ and low H_{ci} in the amorphous plasma-sprayed material. Because hydrogen had been observed elsewhere to accelerate sintering kinetics in powder compacts of Sm-Co, it was hoped that use of hydrogen might also prove beneficial in the low-temperature annealing of sprayed amorphous Sm-Co material. A sample (similar to the one treated in argon) was, therefore, heated at 450 °C in hydrogen. The data in Table I shows that in line with our expectations the values of $4\pi M$ and C_p registered a large increase and H_{ci} registered a large decrease with this treatment. The shape of the $4\pi M$-vs-H loop was also observed to approach rectangularity because of the resulting high susceptibility to magnetization. The increase in C_p was believed to result from an as yet unidentified deposit-hydrogen interaction. Since no significant change was observed in the room-temperature value of C_p for periods greater than 24 h, it was assumed that the reaction product was quite stable. It was, therefore, concluded that not all of the hydrogen was released upon exposing the sample to the ambient air environment following the high-temperature exposure to hydrogen.

To confirm that the high $4\pi M$ and low H_{ci} values were a consequence of atomic rearrangement and were not directly related to the retention of hydrogen in the material, a separate similarly prepared amorphous sample was subjected to a variety of heat treatments, first in hydrogen and next in argon, and its properties measured after each treatment (see Table II). The increases in C_p and $4\pi M$ and the decreases in H_{ci} (with exposure to hydrogen at 400 and 450 °C) were in agreement with the above noted observations. When this hydrogen treated sample was subsequently sequentially exposed to temperatures of 350, 400, and 450 °C in argon, a gradual decrease in C_p was observed with apparently no significant change in the shape of the demagnetization curve and in the values of $4\pi M_D$ and H_{ci}. The decrease in C_p, with extended exposure to argon, was interpreted as reflecting a reduced hydrogen presence in the material. The value of C_p measured after the 450 °C argon exposure was quite similar to those measured earlier for the as-sprayed and the argon heat-treated deposits, indicating that much of the hydrogen (introduced in the sample from the hydrogen treatments) had been removed. It was noted that the $4\pi M_D$ and H_{ci} values remained virtually unchanged with the exclusion of hydrogen and the demagnetization loop retained its rectangularity, clearly demonstrating that the atomic rearrangement that was desired had in fact been achieved. The value of H_{ci} was, therefore, found not be directly dependent on the amount of hydrogen in the amorphous sample, as had been observed elsewhere at room temperature for powder compacts of crystalline $SmCo_5$ material.[3] When this sample was given an additional exposure to 500 °C, also under argon, the $4\pi M_D$ value decreased, H_{ci} increased, and the demagnetization curve lost its rectangular appearance. All of this indicated the onset of crystallization at 500 °C. This temperature was quite similar to those reported earlier for sputtered amorphous Sm-Co deposits crystallized in vacuum.[9] Representative curves obtained after a variety of treatments of these deposits are shown in Fig. 2.

Another similarly prepared sprayed amorphous sample was sequentially subjected to a series of temperatures exclusively in a hydrogen atmosphere, and measurements were made for both C_p and $4\pi M$. In line with the other observations, both $4\pi M_D$ and C_p were found to increase and H_{ci} was found to decrease with increasing temperatures up to 600 °C. Table III shows that unlike the samples treated in argon, crystallization of this material did not occur until about 700 °C in hydrogen (as was interpreted from the loss in rectangularity of the demagnetization curve, the decrease in $4\pi M_D$ and C_p, and the increase in H_{ci} with this treatment). The $4\pi M_D$ value following the 700 °C treatment was still quite high, indicating only partial crystallization of the material. This gradual increase in crystallinity (as observed from the reasonably high $4\pi M_D$ values measured for the 500 °C argon- and 700 °C hydrogen-treated samples) is interpreted to illustrate that the crystallization process in this

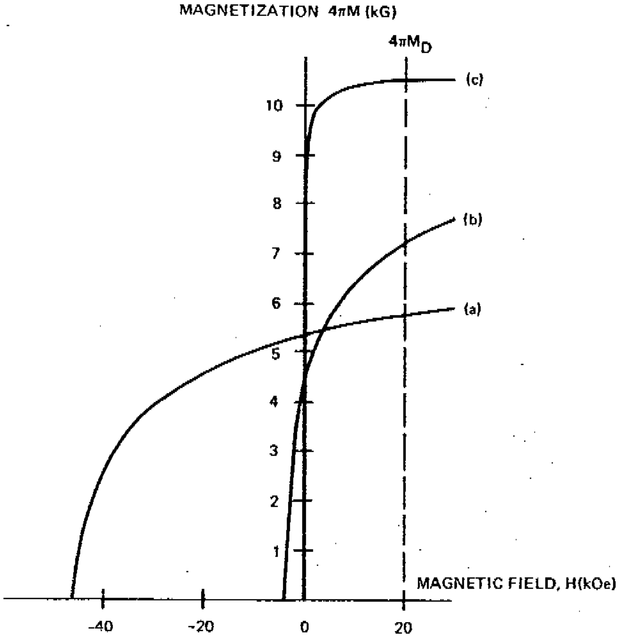

FIG. 2. Typical demagnetization curves obtained on samples after a variety of heat treatments. (a) $SmCo_5$ magnet after 1000 °C for 2 h; 900 °C for 3 h; (b) sample in Table III after sequence G; (c) sample in Table I after sequence E.

TABLE III. 16-h treatments of amorphous depos[illegible] hydrogen.

Sequence	Heat treatment	C_p (cal/g °K)	$4\pi M_D$ (G)	H_{ci} (kOe)
A	As-sprayed	0.086	~5600	~20.0
B	A +400 °C	0.095	7550	4.5
C	B +450 °C	0.094	8400	1.0
D	C +600 °C	0.115	9750	0.2
E	D +700 °C	0.088	7250	3.5
F	E +600 °C	0.089	7200	3.7
G	F +500 °C	0.095	7300	3.8

material proceeds by nucleation and growth of the crystallites.

To ensure that crystallization of the 700 °C sample had indeed occurred and that the observations were not the direct result of a reduced deposit-hydrogen interaction (possibly because of a thermodynamic instability of the various hydrides at 700 °C), this sample was subjected to two additional heat treatments, in hydrogen, at 600 and 500 °C, respectively. It was found that even though the value of C_p increased with these additional treatments (indicating more hydrogen pickup), the values of $4\pi M_D$ and H_{ci} were largely unaffected, therefore demonstrating that the observations were indeed a result of deposit crystallization. These measurements also showed that wholly crystallized or partly crystallized material could not be made amorphous by subjecting it to heat treatments similar to those used in this study in hydrogen. The dependence of the crystallization temperature on the atmosphere used for heat treatment was intriguing. Even though hydrogen increased the mobility of the atoms to yield the desired atomic rearrangement processes for achieving high $4\pi M$ and low H_{ci}, it also resulted in increasing the temperature required for crystallization. This was attributed to the possible formation of reasonably stable compounds (resulting from the interaction of the deposit with hydrogen at temperatures lower than those required for crystallization of the amorphous material). The chemical interaction of the gas with the deposit was, therefore, believed to have suppressed the crystallization process. The room-temperature stability of the products formed from this deposit-hydrogen interaction was indicated in the close-to-constant C_p values measured on the several samples for periods in excess of 24 h after sample removal from the furnace.

This study was also extended to include the effects of low-temperature treatments in hydrogen on crystalline isotropic Sm-Co material. Sprayed magnets, treated earlier for 2 h at 1000 °C followed by 3 h at 900 °C under argon, were exposed to hydrogen at 500 °C. Of the four crystalline samples that were exposed, all except one (unlike similar amorphous samples) were found to crumble to a coarse powder with this treatment. Aside from a decrease in H_{ci}, no other notable changes in the magnetic properties were found for the single-crystalline sample that retained its physical integrity after the 500 °C hydrogen exposure. $4\pi M_D$ for this hydrogen-treated crystalline sample was measured as 5600 G and H_{ci} as 13 kOe. The values of $4\pi M_D$ and H_{ci} prior to the hydrogen exposure were 5700 G and 45 kOe, respectively. The lack of change in th[illegible]lues of $4\pi M_D$ from the 500 °C hydrogen treatments for this sample and for the hydrogen-treated partially crystallized sample (discussed above) was expected from earlier observations on powder compacts, which showed that exposure to hydrogen has minimal effect on the value of the magnetocrystalline anisotropy.[3]

The value of C_p measured for the 500 °C hydrogen-treated crystalline sample was 0.091 cal/g °K. This value was substantially higher than values of close to 0.085 cal/g °K that were typically measured on well-crystallized annealed high-temperature argon-treated samples and indicated a definite interaction of the crystalline material with the hydrogen gas. It was, however, interesting to note that this value of 0.091 cal/g °K was lower than the 0.095 measured on the partially crystallized sample after an identical exposure at 500 °C (in Table III), which, in turn, was lower than the 0.099 measured after a similar exposure for the amorphous sample in Table I. These higher values of C_p associated with a greater amorphous character to the deposit might well indicate a higher hydrogen-storage capability. The higher resistance to physical degradation, in addition to the higher C_p values observed for the amorphous Sm-Co materials, suggest that amorphous Sm-Co (as also possibly other rare-earth–cobalt) materials may be more suited to storing hydrogen than are the crystalline materials that have been examined so far. These studies showed that the measured value of C_p following exposure of the material to hydrogen could possibly be used as a measure of the extent of crystallization in the sprayed amorphous deposits.

IV. SUMMARY

(1) $4\pi M$-vs-H curves obtained on thick plasma-sprayed amorphous deposits showed a high resistance to magnetization and demagnetization for this material. This was attributed to large internal stresses and variations in composition present in the as-sprayed condition.

(2) Thermal treatment of these deposits in an argon atmosphere, at temperatures lower than those required for crystallization, had little effect on the magnetic behavior of the material. Samples exposed to a hydrogen atmosphere, however, showed development of high magnetization and low coercivity from treatments at temperatures similar to those used with argon. It was determined that the changes in the magnetic response of the material were not related to hydrogen retention in the samples but resulted from rearrangement of the different atomic species. The value of the specific heat C_p was used to indicate the amount of hydrogen retained in the samples.

(3) Use of a hydrogen atmosphere was found to increase the temperature required for rapid crystallization of the amorphous material. Whereas temperatures of about 500 °C were found to be adequate for crystallization of the deposits in argon, temperatures of close to 700 °C were required for generating similar effects in hydrogen. The suppression of the crystallization process in hydrogen was thought to have resulted from the formation of reasonably stable compounds (between hydrogen and the deposit) at the lower temperatures. The process of crystallization in this material was in-

terpreted as proceeding by nuclea[illegible] and growth of the crystallites.

(4) When wholly crystallized and partially crystallized sprayed Sm-Co samples were subjected to low-temperature treatments in hydrogen, no apparent change was observed in the $4\pi M$ behavior of the material. These studies showed that it is not possible to convert wholly or partially crystallized Sm-Co material into the amorphous state by subjecting it to 16-h 500 °C treatments in hydrogen, at close-to-atmospheric pressures. The data also indicated the possibility that amorphous 1Sm-5Co material was more suited for storage of hydrogen than is crystalline $SmCo_5$.

ACKNOWLEDGMENTS

The authors wish to thank the staff of the Francis Bitter National Magnet [illegible]oratory (which is supported at MIT by the National Science Foundation) for making their high-strength magnets available for magnetic measurements.

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EXHIBIT F

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September 7, 1994

Mr. Marvin Siskind, Esq.
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Dear Mr. Siskind:

We provide intellectual property counselling to The Charles Stark Draper Laboratory (Draper) and have reviewed a recent article entitled "Energizing the Batteries for Electric Cars" published in Mechanical Engineering, July 16, 1993, pages 73-75. This article indicates that the Ovonic Battery Co. has recently developed a nickel-metal hydride battery that uses a specially engineered "amorphous" negative electrode that allows for hydrogen storage and retrieval.

Draper is the assignee of U.S. Pat. No. 4,565,686 (copy enclosed) which describes methods of hydrogen storage using crystallographic and amorphous (nonequilibrium) state materials. This patent indicates that alloys of rare earth-transition metals may be produced in an nonequilibrium structure, and that the nonequilibrium structures are useful for enhanced reversible hydrogen storage. The patent further discloses that other alloys, such as iron-titanium, may be provided in a nonequilibrium state, and that they are also useful for hydrogen storage and retrieval.

It appears that the electrode developed by the Ovonic Battery Co. uses hydrogen storage methods and materials that are very similar to those described in the above-cited U.S. patent to Draper. In particular, the nonequilibrium iron-titanium alloy disclosed in the Draper patent is specifically included in the amorphous negative electrode described in the above article. We therefore believe that it would be in our mutual best interest to discuss these issues further and arrive at some amicable and fair agreement concerning the licensing of this technology.

Sincerely yours,

Charles L. Gagnebin III

CLG/caa
Enclosures
37124
bcc: John A. Nelson
Kaplesh Kumar

EXHIBIT F

Energy Conversion Devices, Inc.

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Troy, Michigan 48084
Telex 230648
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Telephone 313/280-1900

RECEIVED
By
OCT 3 1 1994
WEINGARTEN, SCHURGIN,
GAGNEBIN & HAYES

October 26, 1994

Charles L. Gagnebin III
Ten Post Office Square
Boston, Massachusetts 02109

Dear Mr. Gagnebin:

We are in receipt of your letter of October 11, 1994 concerning your client's U.S. patent number 4,565,686 (the" '686 patent").

We have carefully reviewed the claims and specification of the '686 patent. It is clear that neither the battery electrodes nor any other product made by Ovonic Battery Company ("OBC") are covered by such claims. Without going into the specific details of our electrochemical electrode materials, processing methods and products, Claim 1 (we assume you are not attempting to assert Claim 6) of the '686 patent has four specific restrictions that find no response in OBC's battery electrodes. These claim restrictions are as follows:

1. "System for retrievably storing hydrogen". The hydrogen storage system disclosed in the '686 patent is fundamentally different from the electrochemical system used by OBC. Worldwide patent and trademark offices, including the United States Patent and Trademark Office, have distinguished the critical differences between thermal hydride systems and electrochemical hydride systems. OBC's electrochemical hydride materials employ an energy storage system that splits water into hydrogen and hydroxyl ions. This electrochemical system is distinctly and functionally different than the thermal system described in the '686 patent that splits molecular hydrogen into atomic hydrogen.

2. "Amorphous". OBC's battery electrode materials do not use amorphous materials, but rather employ disordered multiphase polycrystalline electrode materials. (The 1993 Mechanical Engineering article is in error when it describes OBC's electrode material as amorphous.)

3. "Rare-earth-transition metal alloy". OBC uses absolutely <u>no</u> rare earth elements in its battery electrode materials.

Charles L. Gagnebin II
October 26, 1994
Page Two

4. "Means for supplying hydrogen...and exhausting hydrogen...for absorption and desorption". In contrast to hydrogen storage systems, electrochemical devices such as batteries have no such hydrogen supplying and exhausting means.

In summary, not only does the '686 patent fail to cover OBC's battery electrode materials (or methods of making same), but the functional inapplicability of the subject matter set forth in the claims to electrochemistry merely mirrors the inherent impossibility of attempting to have thermal hydrogen storage system language cover electrochemical systems. Discussion of licensing the '686 patent is unnecessary.

For your information, a recent article in Science, copy enclosed, provides a general description of our technology in much greater depth than the erroneous description provided in Mechanical Engineering.

Very truly yours,

Marvin S. Siskind

Marvin S. Siskind
Vice President - Patent Counsel

cc: S. R. Ovshinsky
M.A. Fetcenko

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SCIENCE

A Nickel Metal Hydride Battery for Electric Vehicles

S. R. Ovshinsky, M. A. Fetcenko, and J. Ross

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Widespread use of electric vehicles can have significant impact on urban air quality, national energy independence, and international balance of trade. An efficient battery is the key technological element to the development of practical electric vehicles. The science and technology of a nickel metal hydride battery, which stores hydrogen in the solid hydride phase and has high energy density, high power, long life, tolerance to abuse, a wide range of operating temperature, quick-charge capability, and totally sealed maintenance-free operation, is described. A broad range of multi-element metal hydride materials that use structural and compositional disorder on several scales of length has been engineered for use as the negative electrode in this battery. The battery operates at ambient temperature, is made of nontoxic materials, and is recyclable. Demonstration of the manufacturing technology has been achieved.

The interest in electrically powered vehicles extends nearly as far back as interest in vehicles powered by hydrocarbon fuels. Throughout this period, however, there has been a major technological barrier to the development of practical electric vehicles (EVs) that can compete in performance and cost with those that use internal combustion (IC) engines. This barrier has been the lack of an economical battery with sufficient energy density and other essential performance criteria. In this article, we describe the science and technology of a nickel metal hydride (NiMH) battery that will permit future EVs to replace IC-powered vehicles in many applications.

Recently, U.S. federal and state governments have been providing an impetus for the development of an EV industry through legislation aimed at increasing national energy independence and reducing the impact of automobile emissions on the environment. California has passed laws that demand that 2% of new cars sold in 1998 be emission-free, and this percentage is slated to grow to 10% by the year 2003; 12 eastern states are planning similar laws. A comprehensive energy bill passed by Congress contains a tax credit for EV buyers. This bill also requires state and federal governments to purchase alternative-fuel fleet vehicles, with the percentage of new, cleaner fuel vehicles growing to 90% by the year 2000. It is expected that EVs will make up an increasing portion of alternative fuel vehicles as the market grows.

There are several important advantages of EVs compared with IC-powered vehicles. First, EVs are emission-free: they produce no pollution during operation. This quality is particularly important in city centers where congested automobile traffic is the primary source of local air pollution. The overall unwanted emissions that result from combustion of fossil fuels for the generation of electricity are also far less per mile of EV travel than the emissions produced directly by a fossil fuel–powered car. This fact, discussed in detail in a study by the Electric Power Research Institute (EPRI) (1), results from the sophisticated emissions controls that can be used economically by large, efficient, central power-generation facilities. Second, the EPRI study also details how the primary energy efficiency of electric transportation can exceed the efficiency of gasoline-powered vehicles in many instances. For example, the study shows that electric-powered commercial fleet vans that are used in urban areas have a significant advantage in energy efficiency over their gasoline-powered counterparts, traveling about 1100 miles per barrel of oil consumed at the power plant compared with 620 miles per barrel of oil refined into gasoline. This difference results primarily from the higher energy efficiency of power plant combustion—approximately twice as high as combustion of gasoline in an IC engine in urban traffic. Third, conversion from cars directly powered by fossil fuel to ones powered by electricity can shift the choice of hydrocarbon fuels that are consumed in the United States from oil to coal and gas. This change could possibly reduce the oil imports and, consequently, reduce the U.S. trade imbalance and the strategic vulnerability of its energy supply. Photovoltaic and other renewable energy sources are

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also increasingly available to generate pollution-free electricity for EVs.

In response to the need to develop a practical battery for EVs, the U.S. federal government authorized the establishment of the U.S. Advanced Battery Consortium (USABC) in 1990. Under the aegis of the Department of Energy, USABC brings together Chrysler, Ford, General Motors (GM), and EPRI to sponsor research and development of EV batteries. Although energy density is one of the most important requirements for an EV battery system, USABC has identified a number of other battery criteria as necessary for the development of economically viable EVs (Table 1 provides the primary midterm goals of USABC). Ovonic Battery Company (OBC), a subsidiary of Energy Conversion Devices, has received the first contract from USABC toward the continued development and fabrication of the company's proprietary NiMH batteries and has agreed to establish EV battery production facilities.

In this article, we describe the science and technology of the Ovonic NiMH battery, with emphasis on the materials science aspects of the metal hydride (MH) electrode and their effect on battery performance (2). The MH electrode offers an important opportunity for materials engineering and optimization when compared with negative electrodes for other nickel-based battery systems. In these other systems, the negative electrode (Cd, Zn, or Fe) is typically fabricated from relatively pure elemental metals, and the oxidation-reduction reactions associated with battery charge and discharge convert the electrode back and forth between a metal and a metal oxide that is a poor electric conductor. This type of chemical reaction can be undesirable in a practical battery design because of accompanying changes in the physical properties of the electrode. Changes in the mechanical integrity and surface morphology of the electrode as a result of dissolution and recrystallization and of its reduced electrical conductivity in the oxidized state are sources of many of the performance deficiencies in these systems.

The MH electrode, by contrast, uses a chemical reaction that reversibly incorporates hydrogen into a metal alloy. In this oxidation-reduction reaction both chemical states are metallic, and so electrical conductivity is high in both the charged and discharged states. Furthermore, the small size of the hydrogen atom allows it to enter the metal lattice during formation of the hydride (reduced) state with only about 10% volumetric expansion and without the changes in crystallography associated with oxidation and reduction of the Cd, Zn, or Fe electrodes.

In effect, the MH negative electrode can be regarded as a matrix for the chemical incorporation of the hydrogen atom. In the Ovonic NiMH battery, we have exploited the ability of this matrix to be engineered through the use of multi-element alloys, using compositional and structural disorder to produce materials with desirable battery properties.

Cell Reactions

The NiMH battery, which has a nominal voltage of 1.2 V, stores hydrogen as a reaction product in the solid hydride phase, unlike the nickel-hydrogen battery that stores hydrogen as a high-pressure gas. The negative electrode of a conventional NiMH battery consists of a hydrogen storage material (3–5) that can allow electrochemical storage and release of hydrogen during battery charge and discharge processes. The nickel hydroxide positive electrode (6–9) is electrochemically reversible between $Ni(OH)_2$ and nickel oxyhydroxide, usually written as NiOOH. At both electrodes, oxidation-reduction reactions take place in an alkaline medium consisting of 30% by weight KOH in water. During charge, the $Ni(OH)_2$ electrode is oxidized and the MH electrode is reduced. As a result, water is separated into hydrogen and hydroxyl ions, with hydrogen reacting with the metal in the negative electrode to form MH. At the positive electrode, the hydroxyl ion reacts with the $Ni(OH)_2$ electrode to form NiOOH. This reaction results in a change in the Ni oxidation state from +2 to +3. The half-cell reactions on charge and discharge of the battery can be written as

$$M + H_2O + e^- \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftarrows}} MH + OH^- \qquad (1)$$

$$Ni(OH)_2 + OH^- \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftarrows}} NiOOH + H_2O + e^- \qquad (2)$$

As a consequence of reactions 1 and 2, there is no net change in electrolyte quantity or concentration over the charge-discharge cycle. This result contrasts with other alkaline electrolyte systems such as NiCd where water is generated at both electrodes during charge and consumed at both electrodes during discharge. Although transient electrolyte concentration gradients can occur in the NiMH battery, its constant average concentration has the important consequences of good overall performance in gas recombination, kinetics, high- and low-temperature operation, and resistance to cycle-life limitations produced by corrosion and swelling.

Material Requirements

The MH materials used for an NiMH battery electrode must satisfy an extensive list of requirements. Above all, the amount of hydrogen that the MH material can absorb determines the electrochemical storage capacity of the electrode and, consequently, the energy storage capacity of the battery. It is desirable to have high electrode storage capacity that is electrochemically reversible. To ensure reversibility, an important aspect of the MH design is the range of metal-to-hydrogen bond strengths, which must be about 6 to 12 kcal mol^{-1}. If the bond strength is too weak, hydrogen will not react with the alloys and will be evolved as a gas. If the bond strength is too large, the MH electrode is extensively oxidized and does not store hydrogen reversibly.

Even with an optimally adjusted metal-hydrogen bond strength, the problem of electrode oxidation in the MH battery

Table 1. Primary USABC midterm performance goals for the EV battery and actual performance of the current OBC NiMH battery. DOD, depth of discharge.

Property	USABC	OBC
Specific energy (Wh kg^{-1})	80 (100 desired)	80*
Energy density (Wh per liter)	135	215*
Power density (W per liter)	250	470
Specific power (W kg^{-1}) (80% DOD in 30 s)	150 (>200 desired)	175
Cycle life (cycles) (80% DOD)	600	1000
Life (years)	5	10
Environmental operating temperature	−30° to 65°C	−30° to 60°C
Recharge time	<6 hours	15 min (60%) <1 hour (100%)
Self discharge	<15% in 48 hours	<10% in 48 hours
Ultimate projected price (dollars per kWh) (10,000 units at 40 kWh)	<$150	$200

*A specific energy of 80 Wh kg^{-1} and an energy density of 215 Wh per liter have been achieved in a laboratory prototype, with 50-Ah cells under a discharge rate at which the battery energy capacity is exhausted in 3 hours.

remains. The NiMH battery operates in a strongly oxidizing medium composed of a high-concentration alkaline electrolyte. Because many chemical elements react to form oxides in an alkaline electrolyte, it follows that if these elements are used as electrodes, they will oxidize and fail to store hydrogen reversibly. In addition, MH electrodes are typically designed for use in totally sealed batteries where oxygen recombination occurs at their surfaces. In this aggressively oxidizing environment, oxidation and corrosion resistance of MH electrode materials is critical. Because some oxidation at the metal-electrolyte interface is inevitable and because both passivation and corrosion can have adverse effects on battery performance, these unwanted processes must be controlled in a practical NiMH electrode design.

Another consideration in the use of hydride materials in NiMH batteries relates to electrochemical kinetics and transport processes. The power output of the battery depends critically on these processes. During discharge, hydrogen stored in the bulk metal must be brought to the electrode surface by diffusion. The hydrogen must then react with hydroxyl ions at the metal-electrolyte interface. As a consequence, surface properties such as oxide thickness, electrical conductivity, surface porosity and topology, surface area, and degree of catalytic activity affect the rate at which energy can be stored in and removed from the NiMH battery.

For the battery to operate as a sealed system, it must also tolerate the consequences of chemical reactions that occur during cell overcharge and overdischarge. In overcharge, oxygen gas is generated at the $Ni(OH)_2$-positive electrode and must recombine with hydrogen at the MH electrode to form water. In overdischarge, which occurs when a low-capacity cell in a series-connected string is subjected to reverse polarity, hydrogen is generated at the $Ni(OH)_2$ electrode and must be recombined at the surface of the MH electrode to form water. In a sealed system, these gas recombination reactions must occur at sufficient rates to avoid pressure buildup. This condition requires adequate electrode area, a thin electrolyte film, and, for the hydrogen absorption process, catalytic activity at the MH electrode surface to promote rapid dissociation of hydrogen.

Chemical and Structural Disorder in Engineered Materials

The diverse properties required for a superior MH battery electrode can be attained by the engineering of new hydrogen storage materials on the basis of the concepts of structural and compositional disorder (*2, 10–13*). Compositional and structural disorder is designed into the new MH materials on three different length scales through the use of elemental composition and processing techniques of alloys and electrodes. The length scales over which disorder is created can be designated: local (or atomic), which comprises regions with dimensions up to a few nearest-neighbor atomic distances; intermediate range, which comprises regions typically about 10 to 20 nm and extending up to about 100 nm; and long range, which involves regions with a dimension larger than about 100 nm. Disorder on each of these length scales is used to achieve different goals in the engineered alloys.

This approach allows one to consider a range of alloys for electrode materials containing elements that, if used alone, would be unacceptable for thermodynamic reasons, in particular oxidation or corrosion. Among the elements that become available for alloy formation in disordered electrode materials are Li, C, Mg, Al, Si, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Y, Zr, Nb, Mo, Sn, La, W, and Re. The list contains elements that can increase the number of hydrogen atoms stored per metal atom (Mg, Ti, V, Zr, Nb, and La). Other elements allow the adjustment of the metal-hydrogen bond strength (V, Mn, and Zr); provide catalytic properties to ensure sufficient charge and discharge reaction rates and gas recombination (Al, Mn, Co, Fe, and Ni); or impart desirable surface properties such as oxidation and corrosion resistance, improved porosity, and electronic and ionic conductivities (Cr, Mo, and W). The wide range of physical and chemical properties that can be produced in these alloys allows the MH battery performance to be optimized.

Compositional and structural disorder on a long-range length scale is used in the bulk of Ovonic MH alloys to give considerably higher hydrogen storage and better kinetics than possible in the conventional MH alloy structures, which are compositionally ordered and crystalline. The processing of disordered alloys can be optimized to produce polycrystalline, compositionally multiphase material. Figure 1 shows a scanning electron micrograph of a representative bulk region of a typical V, Ti, Zr, Ni, and Cr Ovonic MH alloy. Electron backscattering imaging was used to produce visual contrast between regions of the alloy that have different elemental compositions. This material contains five major distinct compositional phases as determined by energy-dispersive x-ray analysis. In addition, it has been determined separately by x-ray diffraction that the alloy contains three crystal structures: body-centered-cubic (bcc), hexagonal, and ^{14}C Laves crystal structures. From synthesis and characterization of separate, individual phases of a particular alloy, we conclude that the bcc structure can react to store large quantities of hydrogen (2.5% by weight) but lacks sufficient catalytic activity to be discharged at the required rates for battery applications. On the other hand, surrounding phases that may store less hydrogen but exhibit greater catalytic activity can effectively "channel" the hydrogen for rapid electrochemical discharge (*12*).

Intermediate-range structural and chemical disorder plays a number of important roles, primarily at interfaces both within the bulk of the MH electrode and at the electrode-electrolyte interface. Formation of the polycrystalline, compositionally multiphase bulk alloy gives rise to a high density of grain boundaries between com-

Fig. 1. Scanning electron micrograph of a bulk region of an Ovonic MH battery electrode that shows compositionally and structurally disordered multiphase alloy regions. Scale bar, 10 µm.

Fig. 2. Scanning transmission electron micrograph of the metal-electrolyte interface of an Ovonic MH battery electrode that shows the structure of the engineered multiphase bulk alloy and surface oxide.

positional and structural phases (for example, Fig. 1). The intermediate-range disorder that occurs at the grain boundaries increases surface area, which can greatly increase the density of catalytic sites. At the electrode-electrolyte interface, disorder on a length scale of approximately 10 to 100 nm is created during electrode processing and activation by the exploitation of chemical properties that are traceable to the elemental constituents of the MH alloy. The high-magnification scanning transmission electron micrograph of the electrode-electrolyte interface in Fig. 2 shows the presence of disorder on all three length scales but is particularly useful in illustrating the intermediate-range structural and compositional disorder that occurs in the engineered oxide layer that forms on the Ovonic MH electrode.

The basic Ovonic MH electrode typically contains elements such as V, Ti, Zr, Ni, and Cr. Although the alloy is a system with many characteristics such as MH bond strength that depend on interactions among the elemental constituents, some alloy properties are influenced by the chemistry of individual components. The primary role of V, Ti, and Zr in the alloy is hydrogen storage. All three elements, rather than just the least expensive (Ti), are used in the alloy for several reasons. Titanium and Zr form thick, dense, passive oxides in alkaline solutions, whereas V forms soluble oxides. These chemical characteristics are used in the preparation of the Ovonic MH electrode during the electrochemical activation step in which soluble oxides are intentionally corroded to produce intermediate-range structural disorder. This change gives rise to increased electrode surface area and microporosity and thereby increases charge acceptance. Chromium is used to limit the unrestrained corrosion of V and to control the alloy microstructure.

Zirconium contributes the important property of controlled hydrogen embrittlement, which leads to high surface area and, hence, to fast cell reactions. However, because excessive embrittlement can produce mechanical disintegration of the electrode that leads to poor electrical conductivity, high polarization, and low charge-recharge cycle life, one must control this property carefully in designing the electrode alloy.

Nickel serves several functions in the alloy. First, NiH has a weak bond strength. The bond strengths of elemental Ti, Zr, and V with hydrogen are too high for electrochemical applications. However, formation of alloys from these elements in various concentrations with Ni allows control of the alloy bond strength as was discussed earlier. Second, Ni is a catalyst for dissociation of H_2 and subsequent absorption of atomic H into the alloy. Third, Ni is resistant to oxidation. The combination of Ni with Zr, V, and Ti makes the alloy more resistant to oxidation and produces oxide films at the electrode-electrolyte interface that contain regions of metallic Ni. These regions help provide the necessary electrical conductivity and catalytic activity in the oxide film. The interface is characterized by a heterogeneous oxide region (Fig. 2) rather than a sharply defined homogeneous oxide film. We believe that this disordered oxide region is microporous and contains electrically conductive Ni regions that can catalyze the electrochemical discharge reaction (14).

Compositional disorder on the atomic scale is used to increase hydrogen storage capacity and improve catalytic activity through the incorporation into the M alloy of elements that generate new chemically active sites. These sites offer an increased variety of hydrogen bonding possibilities and enhanced rates as a result increased catalysis. Incorporation of elements with multidirectional *d* orbitals increases the range of stereochemical possibilities for bonding hydrogen, as confirmed b the increased amount of hydrogen absorbe and by increased catalytic activity. Thes effects also occur to a lesser extent wit elements containing *f* orbitals that exten in still more directions than *d* orbitals bu that are closer to the nucleus of the meta atom and, therefore, are less accessible.

Local compositional disorder is also use to adjust the metal-hydrogen bond strengt in the MH alloy. Measurements of equilibrium hydrogen pressure versus MH hydrogen concentration at 30°C are shown in Fig. 3 for a series of multicomponent MH alloys in which the ratio of V to Zr is systematically varied. The equilibrium hydrogen pressure, *p*, in these measurement is related to the change in Gibbs free energy, ΔG, which occurs for the reaction between gaseous hydrogen and the hydrogen storage alloy to form MH. This value can be written:

$$\Delta G = \Delta H - T\Delta S = RT \ln p \qquad (3)$$

Because the entropy term, $T\Delta S$, is small at room temperature compared with the enthalpy change, ΔH largely determines ΔG. Thus, determination of p provides a measure of ΔH, which is related to the metal-hydrogen bond strength. In Fig. 3, variations in the ratio of V to Zr give rise to the observed changes in p for a given hydrogen concentration in the MH alloy. This result indicates that these compositional variations have changed the metal-hydrogen bond strength.

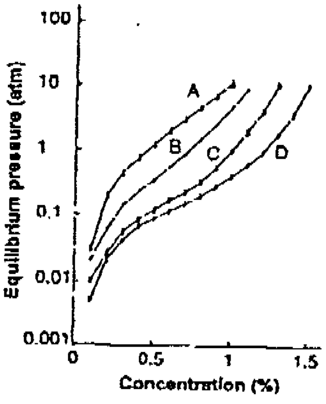

Fig. 3. Equilibrium hydrogen pressure versus hydrogen concentration (percent by weight) at 30°C for a series of Ovonic MH electrode alloys. Data show how variation in alloy composition may be used to control metal-hydrogen bond strength. The MH alloy compositions shown here, expressed as atomic percent, are **(A)** ($V_{21}Ti_{15}Zr_{15}Ni_{31}Cr_6Co_6Fe_6$), **(B)** ($V_{15}Ti_{15}Zr_{21}Ni_{31}Cr_6Co_6Fe_6$), **(C)** ($V_{18}Ti_{15}Zr_{18}Ni_{31}Cr_6Co_6Fe_6$), and **(D)** ($V_{15}Ti_{15}Zr_{20}Ni_{28}Cr_5Co_5Fe_6Mn_5$).

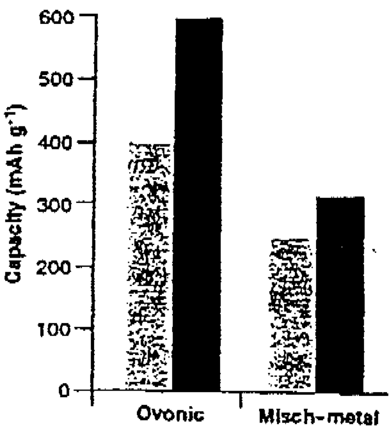

Fig. 4. Comparison of the charge storage capacity of present (shaded bars) and projected (solid bars) Ovonic MH battery and misch-metal ($LaNi_5$) electrodes.

Status of the Ovonic Battery

The storage capacity of current and future Ovonic MH electrodes is shown in Fig. 4, along with the storage capacity of current and improved conventional $LaNi_5$, or "misch-metal," MH electrodes. The latter materials are frequently referred to as misch metal because they are traditionally made from a mixture of naturally occurring rare-earth elements that can include Ce, La, Nd, and Pr. The data for current electrodes were obtained from electrochemical half-cell measurements of commercial Ovonic and misch-metal battery electrodes, as described in (11). Data for projected misch-metal electrodes are from (15) and are based on electrochemical half-cell measurements of prototype materials. Data for projected Ovonic MH electrodes are based on electrochemical measurements of advanced laboratory thin-film materials.

The USABC contract contains three main program goals: a scale-up from small portable cells (1 to 5 Ah) to large EV cells (50 to 250 Ah), an increase in energy density from 56 to 80 Wh kg^{-1}, and the construction of series-connected battery modules to produce the voltages required for EV propulsion (180 to 320 V). The performance capabilities of the present Ovonic NiMH technology are shown in the second column of Table 1. To a large extent, prototype batteries of several designs and sizes have demonstrated performance characteristics that satisfy or exceed individual USABC midterm goals shown in the first column. Efforts to optimize all performance characteristics within a particular cell design are an ongoing activity. Another program objective, scale-up of cell size, has also been achieved. The ability to manufacture batteries with this technology has been demonstrated by OBC and several of its licensees who have been producing small portable batteries since 1987. Series-connected battery modules up to 40 V have been constructed by OBC and are under test. A 12-V, 3-kWh module is shown in Fig. 5.

Comparison with Other Candidates for EV Batteries

Battery characteristics have a dominant influence on overall EV performance. For example, battery-specific energy (in watt-hours per kilogram) controls vehicle range. Similarly, battery power (in watts per kilogram) translates into vehicle acceleration. The Bertone Blitz, a high-performance prototype EV sports car (*16*), has achieved an impressive acceleration of 0 to 100 km per hour (0 to 62 miles per hour) in 6 s, in part through the use of Ni-Cd batteries with high peak power. Some candidate battery technologies for EV applications are listed in Fig. 6, which shows a comparison plot of peak power versus depth of discharge. These measurements were made independently at Argonne National Laboratories (*17*). High peak power (>150 W kg^{-1}), as required by the USABC goals shown in Table 1, must be maintained over the entire depth of discharge of the battery for satisfactory vehicle performance. The Ovonic NiMH battery provides the highest peak power and can maintain it over almost the full range of discharge.

Although Ni-Cd is a rechargeable battery technology with high peak power that is extensively used in consumer products such as electronic devices and power tools, its energy density does not meet USABC requirements, it uses toxic materials (Cd), and in the large sizes used for EVs, it is not a totally sealed system.

The Na-S battery has a high energy density, but its low peak power is a significant deficiency. In addition, the operating temperature of the battery is approximately 300°C, which must be maintained at all times because the battery can withstand only a few cycles of cooling and heating. The presence of molten sodium and sulfur is potentially hazardous, and corrosion has limited the reliability and life of prototype batteries.

Of the remaining batteries shown in Fig. 6, only the Pb-acid battery has been tested sufficiently to serve as a practical, immediate candidate for EV applications. However, its typical energy density of 30 Wh kg^{-1} is substantially below USABC requirements, and its limited cycle life would force it to be replaced every 32,000 km (20,000 miles).

Long cycle life is a feature of the Ovonic NiMH battery technology that will have economic consequences for EVs. Over 1000 charge-discharge cycles at 100% depth of discharge have been demonstrated (*13*) with Ovonic batteries. Under conditions of 30% depth of discharge, Ovonic NiMH cells designed for aerospace applications have demonstrated (*18*) a lifetime of more than 10,000 cycles. It is expected that in EV applications, batteries will experience a typical depth of discharge of about 80%. Under these conditions the cycle life of the Ovonic NiMH battery is projected to be 2000 to 3000 cycles, according to a numerical model (*18*).

Battery cycle life can be converted into EV battery-life driving range when the characteristics of the EV are specified. For example, in a GM Impact-type vehicle, replacement of the Pb-acid battery with an Ovonic NiMH system of the same volume increases its range to 480 km (300 miles). For 80% depth of discharge [385 km (240 miles)], even a conservative estimate of 500 cycles for the battery life will give a 200,000-km (120,000-mile) battery-life driving range. The electrical energy necessary to provide the 385-km range per charge costs only $2.32 at $0.08 per kilowatt-hour, compared with approximately $14 worth of gasoline needed to provide the same range for a typical IC-powered vehicle. Lifetime EV maintenance costs will also be smaller than for typical IC-powered vehicles. Therefore, EVs that are powered by batteries with long cycle lives and that meet the USABC initial cost goal of $150 per kilowatt-hour can be economically competitive on a lifetime basis.

Technology Improvements

The range of an EV will depend on many factors besides battery energy density, such as vehicle weight, tire rolling friction, and electric motor efficiency. Information published by GM on its pioneering Impact vehicle can be used to establish a benchmark for conversion of battery energy density to vehicle range (*19*) for EVs of this type. The data from GM show that their vehicle will travel 180 km (113 miles) with a battery that stores 13.5 kWh. For a battery of the same weight, the current Ovonic NiMH technology will, therefore,

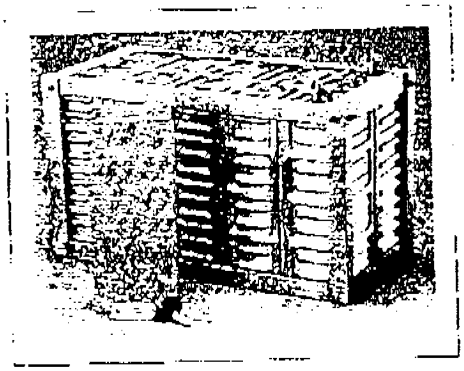

Fig. 5. A 3-kWh, 12-V series-connected Ovonic NiMH battery module and 250-Ah Ovonic NiMH single cell.

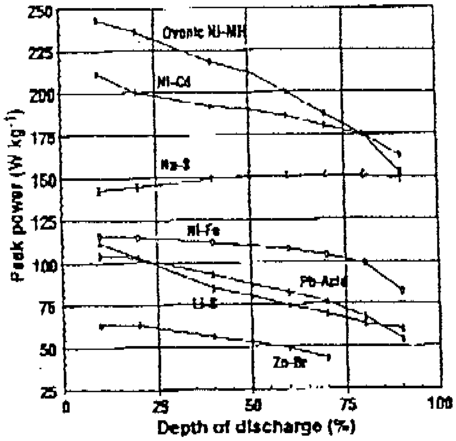

Fig. 6. Peak power versus depth of discharge, as measured (*17*) at Argonne National Laboratories, for a number of candidate EV battery technologies.

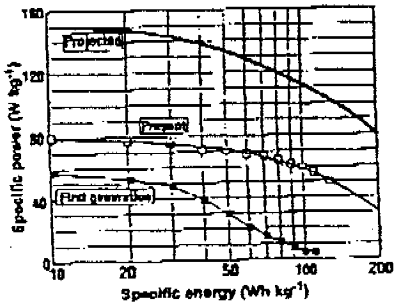

Fig. 7. Specific energy versus specific power for first-generation, present, and projected Ovonic NiMH batteries. Data shown for first-generation devices were obtained from 4-Ah "C" size cells; data for present devices were obtained from 50-Ah prismatic cells.

provide 31.6 kWh of energy storage, which will provide a vehicle range of 415 km (264 miles). For the same battery volume, the Ovonic NiMH battery will increase the range per charge to 480 km (300 miles). The environmental impact of eventual disposal of the Ovonic NiMH battery has also been studied (*20*). Knoll and colleagues concluded that, according to existing Environmental Protection Agency regulations, batteries that use this technology can be safely disposed of in landfills. It has also been shown (*21*) that with existing technology, Ovonic batteries can be recycled into metallurgical additives for cast iron, stainless steel, or new Ovonic NiMH battery electrodes. The commercial viability of each of these technologically feasible recycling programs will depend on process economics.

Future developments of Ovonic NiMH batteries will include improvements through the continued optimization of the MH materials and electrodes as well as improvements to the positive electrode and cell design (*2*). For example, some of the ongoing research at OBC focuses on application of the company's synthetic materials techniques to the development of an improved positive electrode with enhanced storage capacity through the use of engineered valence control. The chemical reaction that occurs during the charge of a conventional $Ni(OH)_2$ electrode involves transfer of one electron per Ni atom. We are developing materials that use the exchange of up to two electrons per atom. In addition, MH alloys with twice the storage capacity of first-generation materials have been measured in the laboratory, and cell designs in which lightweight substrates, current collection components, and containers are used are now being developed. Because the overall energy density of the battery is determined by the entire system, these combined approaches are targeted at the fabrication of batteries with both an energy storage density of 150 Wh kg^{-1} and the characteristics shown in Fig. 7.

Conclusion

In the development of the Ovonic NiMH battery, we have used aspects of physics, chemistry, metallurgy, and materials science. In particular, materials concepts (*10–13*) were focused on structural and compositional disorder to develop an NiMH battery with the characteristics necessary for practical EV use in the near, middle, and distant future.

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22. We thank the research staff at Energy Conversion Devices–OBC, particularly S. Venkatesan, for their contributions to the developments described in this article and S. J. Hudgens for his critical comments and helpful suggestions during preparation of the manuscript.

EXHIBIT G

LAMBERT & ASSOCIATES

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REGISTERED PATENT ATTORNEYS

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TELEPHONE: 617.720.0091
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www.pat-law.com

NEW HAMPSHIRE OFFICE
147 MAIN STREET, NASHUA, NH 03060-5592
TELEPHONE: 603.882.7316
FACSIMILE: 603.882.6557

November 20, 2000

Mr. Stanford R. Ovshinsky, CEO
Ovonic Battery Company, Inc.
1707 Northwood Drive
Troy, MI 48084-5524

Re: U.S. Patent No. 4,565,686 for Method of Storing Hydrogen Using Nonequilibrium Materials and System

Dear Sir:

I represent Dr. Kaplesh Kumar, the inventor and exclusive licensee of the subject pioneer patent, a copy of which is attached, with sole rights to enforce and sublicense it.

My client is interested in licensing this technology on fair and reasonable terms. The technology was initially offered for licensing to your company, or its predecessor in interest, in 1993. No response was received to that communication, indicating a lack of interest in the technology offered and forcing us to conclude that the technology was not relevant to your needs.

A recent investigation has revealed that the Nickel Metal Hydride batteries being manufactured and/or marketed by your company use my client's patented invention as the critical enabling technology.

In light of these findings, we are hopeful that your company will seriously consider licensing my client's pioneering patented technology.

We look forward to an equitable and mutually agreeable agreement with your company, and hope to hear back within two weeks from the date of this letter. If we do not receive any response, we will assume that you have no interest in engaging in negotiations and will proceed accordingly.

Very truly yours,

Gary E. Lambert, Esq.
Direct Dial: 617-742-8782

Enclosure

EXHIBIT H

ECD

Energy Conversion Devices, Inc.

1675 West Maple Road
Troy, Michigan 48084
Telephone 248/280-1900
Fax 248/280-1456

December 6, 2000
Via Facsimile - 1-617-227-0313

Gary E. Lambert, Esq.
Lambert & Associates
92 State Street
Boston, MA 02109-2004

Re: U.S. Patent No. 4,565,686

Dear Mr. Lambert:

Mr. Ovshinsky has forwarded your letter of November 20, 2000 to my attention for response.

We have, once again, reviewed the '686 patent of your client, Mr. Kumar. Contrary to your assertions, we are not using the invention set forth in the claims thereof nor do we have any plans to use that invention. Accordingly, no license is necessary.

Very truly yours,

Marvin S. Siskind

Marvin S. Siskind
Vice President-Patent Counsel

COPY SENT TO CLIENT
ON 12-6-2000

fax to 781-283-5784

Ovonics

EXHIBIT I

LAMBERT & ASSOCIATES

REGISTERED PATENT ATTORNEYS

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December 12, 2000

Marvin S. Siskind
Vice President – Patent Counsel
Energy Conversion Devices, Inc.
1675West Maple Road
Troy, MI 48084

Re: Licensing of U.S. Patent 4,565,686

Dear Mr. Siskind,

We are seriously disappointed at what appears as a casual dismissal of our offer to OBC to license the subject patent.

In your October 24, 1994 response to Mr. Charles Gagnebin, you listed four "specific restrictions" that you claimed "found no response in OBC's battery electrodes." We have never found persuasive your assertions as to items 1 and 4 of that letter, dealing with system for retrievably storing hydrogen and means for supplying and exhausting hydrogen. Indeed, we have concluded that they are universally found in all Nickel Metal Hydride batteries from manufacturers worldwide, including Ovonic.

Your other two assertions that OBC's battery electrodes do not use either amorphous materials or rare earth-transition metal (hereinafter RETM) alloy, merit closer consideration and are brought in serious question in view of information that has recently come to our attention.

Virtually all manufacturers, with isolated exceptions including Ovonic, fabricate their electrode materials from RETM-based compositions. It is our understanding from information available at Ovonic's website that the vast majority of these manufacturers are Ovonic or ECD licensees. Thus, Ovonic and/or ECD has licensed technology that implicitly or explicity uses my client's patented RETM compositions.

We also note that Ovonic has recently sought and obtained one or more United States patents that includes in its claims my client's RETM composition. U.S. patent 5,840,440 (hereinafter '440) issued to OBC in November 1998 not only describes RETM alloys produced by a process that mirrors the process described in my client's subject patent, it also includes these alloys in its claims. Interestingly, the OBC patent admits that there is no significant difference between the the Ti-based alloys from OBC and the RETM alloys from the other manufacturers, contrary to the impression left in the 1994 response to Mr. Gagnebin.

As stated previously, the fabrication technology described in U.S. patent '440 largely mirrors that of my client's. Indeed my client's process, plasma spraying, has been stated to be within the patent's ambit. Surprisingly, especially in view of OBC's awareness of my client's subject patent dating at least to 1994, the OBC patent simply ignores mention or discussion of my client's subject patent, which a reasonable examiner would have found highly relevant to the evaluation of the technology disclosed. The '440 OBC patent claims to break new ground in advancing the hydrogen storage capability of the electrode materials, while claiming materials and structures already disclosed and patented by my client.

We are hopeful that upon further closer examination you will conclude that it is in the interest of both parties to quickly enter into a fair and reasonable licensing agreement for my client's pioneering technology.

I look forward to an early favorable response.

Sincerely,

Donald J. MacDonald

Donald J. MacDonald, Esq.
LAMBERT & ASSOCIATES, PLLC
Direct Dial: 617-742-8714

EXHIBIT J

INFORMATION TECHNOLOGIES

Optical Memory Materials

Manufacturing and Sales

Licensees:

- Sony
- Matsushita
- Toray
- Asahi Chemical
- TDK Corp.
- Hitachi
- Toshiba
- Polaroid
- Teijin
- Plasmon
- IBM
- ITRI
- Others in negotiation

Products and Major Markets

- CD-RW optical disks
- DVD-RAM and DVD-RW optical disks
- PD optical disks

Patents: 15 U.S. and 58 foreign

Microelectronics

Ovonyx, Inc., joint venture with Tyler Lowrey to commercialize Ovonic thin-film, nonvolatile semiconductor memory and logic devices:

- Ovonic Unified Memory to replace DRAM, SRAM and Flash EEPROM
- Neural networks
- Thin-film logic
- Thin-film AMLCD pixel addressing

Patents: 28 U.S. and 101 foreign

ENERGY GENERATION

Photovoltaics

Manufacturing and Sales

Joint ventures:

- United Solar (with Canon Inc.)
- Sovlux (KVANT and Minatom in Russia)

Licensee:

- Canon

Products and Major Markets

- Solar roofing—solar shingles and metal roofing
- Remote power for developing nations
- Battery charging—marine applications and portable electronics
- Telecommunications and space applications
- Stand-by power
- Grid-connected distributed power
- Centralized (utility) power generation

Inventors of roll-to-roll continuous-web, triple-junction manufacturing technology.

Patents: 165 U.S. and 622 foreign

U.S. DEPARTMENT OF COMMERCE • PATENT & TRADEMARK OFFICE

ENERGY STORAGE

Nickel Metal-Hydride Batteries

Manufacturing and Sales

Ovonic Battery Company, an ECD subsidiary, is responsible for formation of strategic alliances, battery packs, materials development and electrode manufacturing.

Joint ventures:

- GM Ovonic (EV and HEV batteries)
- Sovlux (all batteries)

Licensees for portable electronics batteries:

- Hitachi-Maxell
- Canon
- Walsin
- Varta
- Matsushita/Panasonic (limited license)
- Three other major Japanese manufacturers
- Harding Energy
- LG Chemical
- Furukawa
- Samsung
- GP Batteries
- Eveready
- Japan Storage

Licensees for EV and HEV batteries:

- GM Ovonic
- Sanyo (limited to Japan)
- Nan Ya Plastics
- Hyundai
- Sanoh (HEVs in Japan)
- Saft
- Walsin

Products and Major Markets

- Portable electronics
- Electric vehicles (EVs)
- Hybrid electric vehicles (HEVs)
- Backup power
- Telecommunications
- Utility storage
- Electric scooters and bicycles
- Lawn and garden products
- Various other industrial, commercial and residential applications

Patents: 53 U.S. and 233 foreign

MACHINE AND MANUFACTURING TECHNOLOGY

Design and fabricate production equipment, pilot production lines, R&D equipment, coating machinery and hydride storage containers for in-house use, commercial customers, licensees, joint ventures (United Solar and GM Ovonic) and other strategic partners.

Patents: 68 U.S. and 179 foreign

Energy Conversion Devices, Inc. Power to Change the World™

Ovonic Battery Company

Portable Electronic Batteries

Electric Scooters

Electric Vehicles

Ovonic nickel metal-hydride (NiMH) rechargeable battery technology is being developed and commercialized through Ovonic Battery Company, a subsidiary of Energy Conversion Devices, Inc., formed in 1982.

The Ovonic NiMH battery uses proprietary electrode materials and cell designs to achieve widespread commercial use and acceptance as the technology of choice in laptop computers, cellular phones and video cameras. Today, battery manufacturers throughout the world license Ovonic technology and produce almost 1 billion NiMH batteries annually.

NiMH -- the next generation battery -- enables automotive manufacturers to offer electric vehicles with performance that satisfies customer demands in the marketplace.

In the News

- ECD Grants Patent License to Chinese Company
- Ovonic NiMH Batteries Lead American Tour de Sol for Seventh Consecutive Year
- CARB Battery Panel Report Shows Technology Ready, Realistic - Biggest Problem : No Cars Available
- ECD/Ovonic Battery Begin Major Battery Project in China
- Ovonic Battery Achieves ISO 9002 Quality Certification

Ovonic Battery Overview

We invite you to view a video overview regarding Ovonic Battery.

Download the FREE Windows Media Player if needed
Select Your Modem Speed : 56K or lower; ISDN or higher

Ovonic Battery Company 1707 Northwood ◆ Troy, Michigan 48084
Telephone: 248.362.1750 ◆ Fax: 248.362.9921
Email ovonicbattery@ovonic.com
For comments on our site, please contact the webmaster.

ECD Home | Hydrogen Technology | Info Storage | Lab Services | Manufacturing Technology | Ovonic Battery | Ovonyx | United Solar

EXHIBIT L

High Performance Zr-based Metal Hydride Alloys For Nickel Metal Hydride Batteries

R.C. YOUNG, S.R. OVSHINSKY, B. HUANG, B.S. CHAO, and Y. LI
Energy Conversion Devices, Inc, 1675 West Maple Road, Troy, MI. 48084

Abstract

Based upon Ovonic's multi-element, atomic engineering approach, two families of alloys are being used in commercial Nickel Metal Hydride (NiMH) rechargeable batteries, i.e. the mischmetal (Mm) based AB_5 and Zr based AB_2 alloys. While Mm based alloys are faster to activate, are limited by a discharge capacity of only 320-340 mAh/g. The Zr based alloy, although slightly slower to activate, provides a much higher discharge capacity.

In this paper, we first discuss the use of Ovonic's multi-element approach to generate a spectrum of disordered local environments. We then present experimental data to illustrate that through these atomically engineered local environments, we are able to control the hydrogen site occupancy, discharge capacity, kinetics, and surface states. The Zr based alloy with a specific discharge capacity of 465 mAh/g and excellent rate capability has been demonstrated.

Introduction

Since its commercialization in the early 90's, the performance of the Nickel Metal Hydride (NiMH) battery has continuously been improved. For example, a 4/3 Af NiMH cell in 1991 had a capacity of 2300 mAh (56 Wh/kg, 180 Wh/L). Today, several NiMH manufacturers provide commercial product in excess of 3500 mAh (90 Wh/kg and 300Wh/L). Due to its superior performance compared to NiCd and its favorable environmental attributes and a much lower $/Ah compared to Li-ion, the market for NiMH has been and will continue to enjoy a very healthy growth.

In recent years, increased environmental concerns and the awareness of the rapid depletion of non-renewable petroleum reserves have compelled the automotive and motorcycle industries worldwide to take electric propulsion seriously. The leading choice for electrically powered EV (Electric Vehicle) and HEV (Hybrid Electric Vehicle) today is the NiMH battery.

Unlike most of the traditional batteries such as NiCd, NiZn, NiFe where the negative electrode utilizes only a single element, the metal hydride electrode in the NiMH battery is based upon the concept of disordered, multi-element, atomically engineered materials patented by S. R. Ovshinsky et.al. in 1986[1]. Ovshinsky et.al illustrated that in a complex rechargeable battery system, the single element approach could no longer satisfy the various high performance criteria required for an advanced battery. Therefore, a multi-element approach must be taken from which a variety of randomly distributed local environments and/or phases are created. Only through these specially designed local environments and phases, it is possible to independently, and yet, coherently control the various properties, such as the discharge capacity, kinetics, corrosion resistance, surface catalytic activity, self-discharge, and cycle life.

Two families of metal hydride alloys are commercially being used in the NiMH battery i.e. the mischmetal (Mm; a mixture of La, Ce, Pr and Nd) based AB_5 and the Zr based AB_2 type of alloys. In both cases, multi-element, atomic engineering approaches have been adapted in the alloy design and optimization. Currently, all manufacturers of NiMH batteries are licensed under the fundamental basic patent by Ovshinsky et al. [1].

In this paper, we compare these two families of alloys in terms of crystal structure with emphasis on the local environment, discharge capacity, discharge rate, and activation.

Disordered Local Environment

Using atomic engineering to create a disordered local environment to improve specific properties of material and alloys is pioneered by Ovshinsky [2] and has been the foundation of the material design principle of the company since then, particularly for energy storage devices. This principle has lead to the commercialization of NiMH batteries and has now being applied to Li-ion batteries as well.

In the intermetallic AB_5 and AB_2 metal hydrides, the A site atoms, such as La, Mm, Zr, Ti etc., are the so called "hydride formers", which have a high affinity for hydrogen and tend to donate electrons for bonding with hydrogen. Therefore, as pointed out by Ovshinsky [1-4], the design and control of the A site elements and their surrounding environment is particularly important because they dictate not only the hydrogen site, but the absorption/desorption kinetics, the thermodynamic properties, the catalytic activity and other properties.

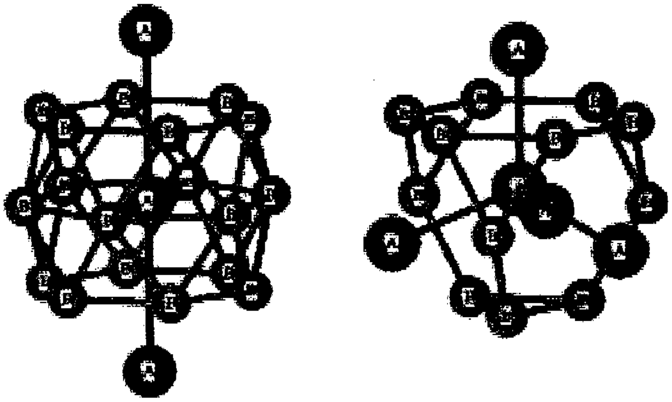

Figure 1. Local environment of A atom in hexagonal AB_5 (left) and Laves Phases AB_2 system (right)

Figure 1 shows the local environment of the A atom in the AB_5 and AB_2 systems. Typically, in the AB_5 system, the A site atoms are a mixture of La, Ce, Pr, and Nd, the so called mischmetal, and the B site atoms are Al, Mn, Co and Ni. In the AB_2 system, the A site atoms are a mixture of Ti and Zr, and the B site elements are V, Cr, Mn, Co and Ni. In most cases, these elements are randomly distributed in their respective lattice sites [5]. As a result, a variety of local environments with different nearest neighbor configurations are created that distort the bond length and bond angle, and alter both the size of interstitial volume and the hydrogen bond strength. In other words, a spectrum of disordered local environments is generated. This phenomenon of disordered local environments can be best illustrated from pressure-composition isotherms (PCT).

The plateau pressure of the PCT curve is usually governed by two factors; the size of the hydrogen sites and the hydrogen bond strength, which can be correlated with the free cell volume and electronegativity of the alloy respectively. Generally speaking, smaller free cell volumes and/or the weaker bonds will give rise to higher plateau pressures [6,7]. Alloy with a homogeneous local environment throughout the crystal will exhibit flat plateau pressures. Figure 2 shows the PCT curve of a commercial multi-element $MmNi_5$ alloy and two advanced Ovonic alloys. As can be seen from these curves, none of these alloys exhibit a flat plateau pressure. The steep slope of pressure-composition isotherms provides a clear indication of the disordered nature of the alloys. XRD spectra and the lattice parameters of Ov313 and 372 are shown in figure 3. Both samples exhibit a near single C14 structure. The Chemical Composition, average electronegativity and the cell volume of the alloys are given in Table 1. Ov372 has a smaller cell volume and a higher electronegativity than Ov313, therefore, it shows a higher plateau pressure.

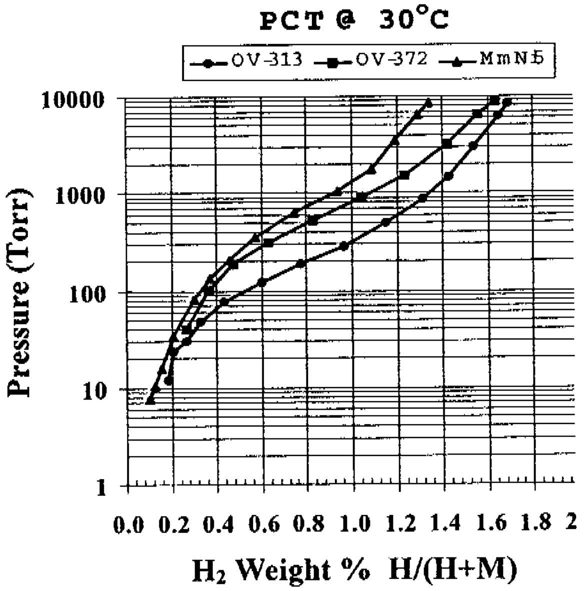

Figure 2. PCT curve of Ov313, Ov372, and a commercial $MmNi_5$ alloy

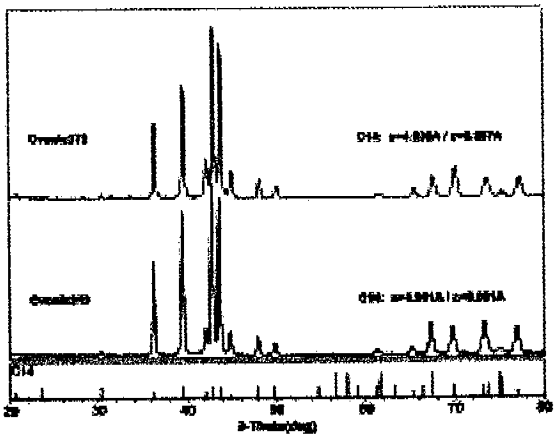

Figure 3. XRD spectra of Ov313 and Ov372

	Zr	Ti	V	Cr	Mn	Ni	χ	ν (Å³)
Ov313	19	14.5	12	10	10	34.5	1.652	171.8
Ov372	15	18.5	12	10	10	34.5	1.660	169.4

Table 1. Chemical Composition in atomic %, electronegativity (χ) and cell volume (ν) of Ov313 & Ov372

Hydrogen site occupancy and discharge capacity

As mentioned previously, in the intermetallic metal hydride alloys, hydrogen occupies the interstitial sites, i.e., the octahedral and tetrahedral interstitials. Octahedral sites are larger in volume and will typically be the first sites to be occupied. There are two size constraints for hydrogen occupancy: (1) the H-H distance must be > 2.1 Å. and, (2) the diameter of the interstitial volume must be > 0.8 Å.

In the AB_5 structure, there are 3 octahedral and 6 tetrahedral interstitial sites. Because of the size constraints, only 3 octahedral and 3 tetrahedral can be occupied by the hydrogen. Therefore, the maximum hydrogen site occupancy in the AB_5 structure is AB_5H_6, which corresponds to a discharge capacity of 375 mAh/g. The commercial alloys, typically demonstrated a discharge capacity in the range of 320-340 mAh/g. This discharge capacity reflects approximately 90% of the maximum capacity. Therefore, there is little room to make further improvement.

In the C_{14} and C_{15} Laves phases, there are 17 tetrahedral sites including 12 A_2B_2 sites, 4 A_1B_3 sites and 1 B_4 site. Again, because of the size constraints, the highest demonstrated hydrogen occupancy in the Laves phase is $ZrV_2H_{5.3}$ [8]. However, this alloy is not suitable for battery applications. The advanced Ovonic battery alloy, such as Ov212 ($Zr_{25}Ti_{8.5}V_8Cr_{20}Mn_{13}Ni_{24.5}Pd_1$) has demonstrated a discharge capacity of 465 mAh/g (see Figure 4), which is equivalent to $AB_2H_{3.3}$. We believe that, in this family of alloys, there is still much opportunities for further improvement.

Discharge kinetics

The basic charge-discharge reaction the NiMH battery can be written as:

Positive electrode: $Ni(OH)_2 \Leftrightarrow NiOOH + H^+ + e^-$ (1)

Negative electrode: $M + H^+ + e^- \Leftrightarrow MH$ (2)

These charge-discharge reactions are very similar to the Li-ion battery, with the exception that a proton rather than Li-ion is being transferred. It is obvious from this reaction, that the kinetics of the NiMH battery are governed by the electronic and ionic conductivity. Because of the metallic nature of the metal hydride and the excellent rate of proton diffusion in the solid, the charge-discharge kinetics of the metal hydride electrode can hardly be limited by either of these mechanisms.

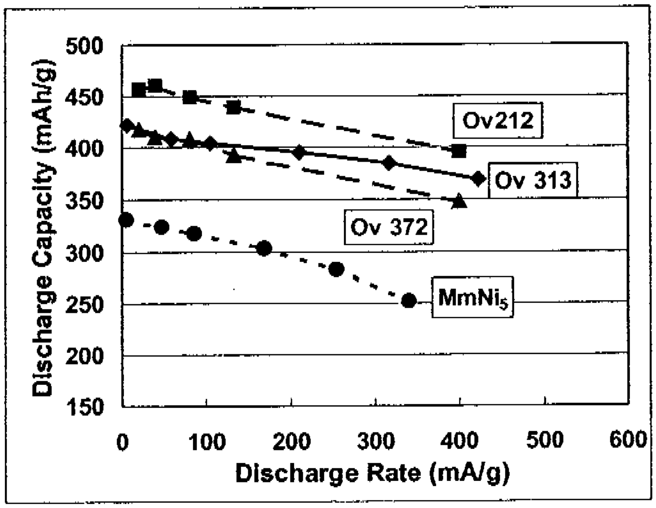

Figure 4. Comparison of the discharge capacity as a function of discharge rate of advanced Ovonic alloys (Ov212, 313, 371), and a commercial $MmNi_5$ alloy

As we pointed out in the next section, surface catalytic activity and the type of oxide formed on the alloy surface also play a crucial role in the charge-discharge kinetics. Because of the surface state, earlier generations of Zr based alloys exhibit high discharge capacity, however, limited rate capability and slower in activation. By using Ovonic proprietary atomic engineering approach, we have developed new advanced alloys to improve these properties. Figure 4 shows a comparison of the discharge capacity as a function of discharge rate of advanced Ovonic alloys, and a commercial $MmNi_5$ alloy. From the figure, the Ovonic alloys not only have a much higher discharge capacity but also superior rate capability. It is also interesting to point out that these two families of alloys exhibit similar slopes of decreasing capacity as a function of discharge rate, which suggests that they have similar rate-limiting mechanisms.

Activation

In addition to the control of the local environment in the bulk of the alloy, we also emphasize the control of the surface oxide and its catalytic activity. In Zr based alloys, the formation of a thin layer of dense Zr oxide on the surface leads to a requirement for a special activation process to remove the oxide.

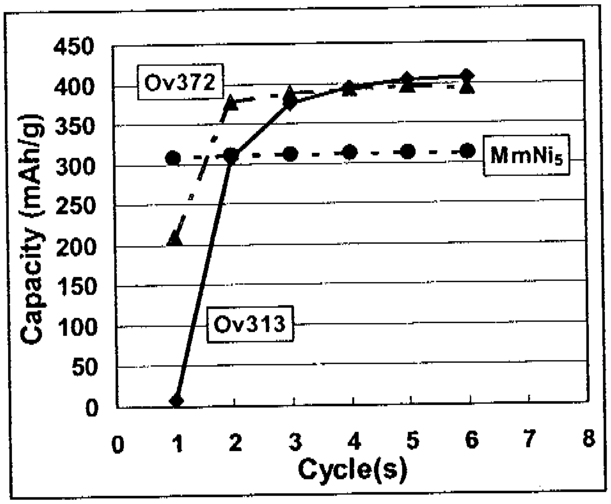

Figure 5. Comparison of the discharge capacity as a function of activation cycles of Ov313, Ov372 and $MmNi_5$ alloys (@ 50 mAh/g discharge rate)

Figure 5 shows a comparison of the discharge capacity as a function of activation cycles of Ov313, Ov372 and the $MmNi_5$ alloys. No treatment was given to these samples before the electrochemical cycles. This figure clearly indicates that the $MmNi_5$ alloy needs no activation process and that full discharge capacity can be realized in the first cycle. On the other hand, Ov372 activates easier than Ov313. Both alloys are stoichiometric compound with the same B site composition but different surface oxide characteristics. Special designed oxides on the surface allow for improved surface catalytic activity for hydrogen recombination and easier activation of the hydride material.

In summary, we have demonstrated that by using Ovonic's atomic engineering approach, a new generation of the Zr and Ti based metal hydride alloys has been developed. The alloys possess high discharge capacity, excellent kinetics, and easier activation. We believe, there is much opportunities for further optimization and improvement.

Acknowledgements:

The authors gratefully acknowledge L. Cantrell , S. Venkatesan and S. Dhar for critical review of this manuscript. This research is partially supported by NIST ATP program.

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