Executive Summary

Introduction

The movement toward implementation of hydrogen as an alternate fuel has been an active goal among energy scientists and environmentalists since the 1973 "energy crisis". It is for this reason that the International Energy Agency (IEA) Agreement on the Production and Utilization of Hydrogen was established in 1974. After a quarter-century, the IEA Hydrogen Agreement continues to promote this same goal. In recent years, renewed support has come in the form of increasing interest from the industrial sector, in particular oil companies and automobile manufacturers. This trend seems to have at least three sources: (1) the technical successes of several new fuel-cell companies, (2) increasing movement toward efficient and clean vehicles, and (3) a growing scientific and political realization that the long suggested negative effects of greenhouse gases are likely real and pose very serious questions for our future. The renewed opportunity to participate in the practical implementation of "Hydrogen Energy" has been welcomed by all within the IEA Hydrogen Agreement family, but there are many technical and economic problems that remain. The IEA Hydrogen Agreement's Task 12, Hydrogen Storage in Metal Hydrides and Carbon, was specifically targeted towards addressing the problem of "solid-state" hydrogen storage.

On-board hydrogen storage remains an undisputed problem for hydrogen-fueled vehicles. Although recent progress in metal hydride batteries has been significant, little real progress has been made in efforts to advance the room-temperature hydrogen gas storage capacity of traditional hydrides over the last 30 years. At least this statement can be made relative to the present requirements for supplying PEM fuel-cell vehicles, where high gravimetric hydrogen-storage density is required and where hydrogen must be liberated at temperatures compatible with the waste heat of the fuel-cell (<100˚C). Alternatives to solid-state vehicular hydrogen storage exist, such as high-pressure gas, cryogenic liquids and onboard reforming of conventional liquid hydrocarbon fuels, but well-known disadvantages can be cited for each.

Something of a thermodynamic dilemma has evolved over the last 30 years when it comes to "conventional" metal hydride storage of hydrogen. Numerous hydrides with metallic bonding (e.g., those represented by $LaNi_5$ and TiFe) have been developed to reversibly store hydrogen at near-ambient temperatures, but they suffer from poor gravimetric capacity (typically no more than 2 wt.% H). At the other extreme, there are ionic- and covalent-bonded hydrides (e.g., Li- and Mg-based alloys, respectively) that have good gravimetric capacities (5-10 wt.% H), but require uncomfortably high temperatures (>250˚C) to release the stored hydrogen at positive pressure. There are very few known hydrides between these two extremes.

The basic hydride problem was recognized by the IEA Hydrogen Agreement Executive Committee and led to the creation of Task 12 in 1995 to seek new and different storage possibilities. Thus, the Task focused new hydride storage R&D on non-traditional hydrides. In addition, carbon hydrogen-storage media were incorporated into the Task in response to reports of new promising results. This Final Report for Task 12 thoroughly summarizes the extensive solid-state hydrogen-storage R&D work completed on behalf of IEA during the period 1995-2000.

Duration

Task 12 was formed October 1995, with William Hoagland (USA) as the charter Operating Agent. Gary Sandrock replaced Mr. Hoagland in late 1996. Originally, Task 12 was chartered for the period Oct. 1995 – Sept. 1998, but positive results led to its extension to Sept. 2000. Originally aimed solely at metal hydride R&D, carbon was added in 1998.

Targets

The Task took aims at the following two technical targets:

1. The identification of a formulation technique for a metal hydride or carbon material that is capable of 5 wt.% hydrogen capacity with a desorption temperature of less than 100˚C and a desorption pressure of at least 1 atmosphere absolute.

2. The development of a metal hydride surface treatment such that high-efficiency, reversible electrochemical reactions can be accomplished over thousands of cycles.

Target 1 centered on the potential application of metal hydrides or carbon as hydrogen-storage media for PEM fuel cell vehicles, although other applications could also use such properties. Originally the temperature target was set at 150˚C, but that was virtually met and superseded by a new target of 100˚C during the course of the Task. Most of the Task activities were aimed toward Target 1. Target 2 concerned itself with electrochemical applications, for example electric storage batteries.

National Participations

The countries that participated in Task 12, along with the associated IEA Hydrogen Agreement Executive Committee (ExCo) members, are listed in Table I. Multiple ExCo names indicate a succession of individuals during the Task duration. Norway did not participate for the full five years of the Task. The European Commission intended to participate in the area of carbon, but its contribution was brief and never formalized.

Table I
IEA H_2 Annex 12 Participating Countries
and Executive Committee Members

Country	ExCo Member
Canada	N. Beck
European Commission [1]	A. Bahbout, G. Tartaglia
Japan	K. Hayashi, Y. Tokushita
Norway [2]	T. Riis
Sweden	W. Raldow, L. Vallander, K. von Kronhelm
Switzerland	G. Schriber
United States	N. Rossmeissl

[1] never formalized
[2] participated for first three years only

The minimum level of effort required was 1.0 person-year/year (py/y). The actual levels of effort varied slightly from time to time, but can reasonably be represented in py/y as follows: Canada=1.0, Japan=3.0, Sweden=1.0, Norway=1.0, Switzerland=2.0, and USA=2.8.

Official Experts and Institutions

The roster of Task participants and institutions (Table II) covers a large spectrum of experience, expertise, reputation and experimental capability in the field of metal hydrides and carbon-hydrogen interactions. Those skilled in the art will recognize most of the names and institutions listed in Table II. In addition to the designated Official Experts listed in Table II, there were many other staff members, graduate students and postdoctoral scientists involved in the work. The individuals are too numerous to be mentioned here; see the List of Publications and Presentations. Note that Bogdanovic' (Germany) and

Verbetsky (Russia) participated unofficially because their countries were not formal participants in Task 12. However, they did have limited financial support from Sweden and Switzerland, respectively, as well as the IEA.

Table II
Participating Task 12 Experts and Institutions

Canada:	R. Chahine*, University of Quebec A. Zaluska*, McGill University
(European Commission*):	(P. Bernier*, University of Montpellier)
Japan:	E. Akiba, National Institute of Materials & Chemical Research S. Suda, Kogakuin University I. Uehara*, Osaka National Research Institute N. Kuriyama*, Osaka National Research Institute
Norway:	A. Maeland*, Institute for Energy Technology
Sweden:	D. Noréus, Stockholms University (B. Bogdanovic', Max-Planck-Institute für Kohlenforschung)
Switzerland:	L. Schlapbach, University of Fribourg K. Yvon, University of Geneva (V. Verbetsky, Moscow State University)
United States:	M. Heben*, National Renewable Energy Laboratory C. Jensen, University of Hawaii R. Loutfy*, MER Corporation F. Lynch*, Hydrogen Components Inc. R. Murphy*, Oak Ridge National Laboratory G. Sandrock, SunaTech, Inc. G. Thomas, Sandia National Laboratories

* indicates not involved for full 5 years; ( ) indicates unofficial

Projects

Task 12 consisted of a series of R&D projects aimed at particular materials and approaches toward achieving one of the Task Targets. Table III lists the 20 projects (16 hydride and 4 carbon). Each Project had a Leader and was funded mainly by the Leader's country. However, most of the projects involved international collaborations beyond the Leader's home country or institution. All projects were experimental in nature except Project 7, which was a data compilation and public on-line database activity.

The projects listed in Table III are generally in order of initiation, with subdivision only as to hydride and carbon. It is useful though to group the projects into more specific categories to better explain their purposes:

Projects 5, 6, 10, 11, 14 and 15 can be collectively described as projects on complex hydrides involving mixtures of ionic species and covalently bonded complexes of hydrogen and non-transition or transition metals. Projects 5, 6, 10, 14 and 15 involve the family of non-transition metal complexes called the alanates, principally catalyzed $NaAlH_4$. The catalyzed alanates were brought into Task 12 as a result of the pioneering discovery of this new class of exciting materials by Prof. B. Bogdanovic' of Germany. Project 11 has searched for new transition metal complexes using high-pressure techniques. Project 16 can perhaps also be included in this category because it resulted in the discovery of a new class of hydrides based on the Zintl phase, a kind of hybrid among ionic, complex and metallic hydrides.

Projects 1, 2, 8, 9 and 12 all look at materials based on Mg_2NiH_4 or Mg_2NiH_4-containg alloys. Mg_2NiH_4 can also be classified as a transition metal complex and has been known as a classic Mg-based hydride since 1968. These projects have examined some new ways to improve Mg_2NiH_4 properties and understanding by thermomechanical means (1), mechanical milling (8, 9, and 12) or vapor-phase synthesis (2). Although Project 12 started out to improve the hydriding and dehydriding properties of the Mg_2NiH_4-Mg eutectic alloy by ball milling and fluorination, it evolved into a project examining the catalytic properties of the material on the hydrolysis-driven liberation of H_2 from $NaBH_4$ complex solutions.

Projects 4 and 13 studied the relatively unexplored area of Ca-based alloys and intermetallic compounds. Project 3 discovered a new AB_2 Laves-phase hydride.

Projects C-1, C-2, C-3 and C-4 widely addressed the newly active area of hydrogen in/on carbon. C-1 focused on single-wall nanotubes with an emphasis on optimizing synthesis and cutting for the purposes of hydrogen storage. C-3 and C-4 surveyed a range of available carbons relative to gaseous and electrochemical hydrogen storage, respectively. C-2 studied the potential of storing and liberating covalent-bonded hydrogen on fullerene carbons.

Table III
List of Task 12 Projects and Leaders

No.	Title	Lead Expert	Lead Country
1	Destabilized magnesium nickel hydride	D. Noréus	Sweden
2	Vapor phase synthesized Mg_2Ni	G. Thomas	USA
3	Fine-structured $RE(Mn,Al)_2$ alloys	L. Schlapbach	Switzerland
4	Laves phase $CaAl_{2-b}X_b$ alloys with substitutional and interstitial elements X	I. Uehara	Japan
5	Preparation and characterization of titanium-aluminum alloys as potential catalysts for reversible alkali metal-aluminum hydrides	A. Maeland	Norway
6	Structural investigations of intermediates and end products in the synthesis of Ti-doped alkali metal-aluminum hydrides	D. Noréus	Sweden
7	Comprehensive hydride review and associated IEA databases	G. Sandrock	USA
8	Mechanical destabilization of metal hydrides	A. Zaluska	Canada
9	Ball milling under reactive atmosphere	E. Akiba	Japan
10	Application of polyhydride catalysts to Na-Al hydrides	C. Jensen	USA
11	High-pressure synthesis of new hydrogen storage materials	K. Yvon	Switzerland
12	Ball milling effects during fluorination of the eutectic alloy $Mg-Mg_2Ni$	S. Suda	Japan
13	Ca-based ternary alloys	N. Kuriyama	Japan
14	Catalytically-enhanced sodium aluminum hydride	C. Jensen	USA
15	Metal hydride safety testing	F. Lynch	USA
16	Synthesis and structural analysis of new ternary hydrides based on hydride-fluoride similarity	E. Akiba	Japan
C-1	Optimization of single-wall nanotube synthesis for H_2-storage	M. Heben	USA
C-2	Hydrogen storage in fullerene-related materials	R. Loutfy	USA
C-3	Assessment of hydrogen storage on different carbons	R. Chahine	Canada
C-4	Hydrogen-carbon, hydrogen-metals	L. Schlapbach	Switzerland

Communications

The keys to a successful Task are interactions, collaborations and communications among the participants. For Task 12, this was accomplished in two ways. First, every two months or so, Project Leaders provided short progress reports that were then assembled and distributed by e-mail.

The second method of communication was in the form of Experts' Workshops that were held about twice per year, on the average. Table IV lists the official Experts' Workshops held throughout the duration of Task 12. The first three listings represent Planning Workshops held before the formal start of the Task. Often Workshops were held in conjunction with international meetings to minimize extra travel and maximize IEA participation. The Workshops usually covered two areas: (1) necessary information transfer and (2) technical reviews of all the projects by the Leaders or their representatives. Attendance at the Workshops was excellent. In almost all cases, good direct or proxy presentations were made and all Experts were encouraged to interact and provide advice and comments. International collaborations were reinforced or newly established. The spirit of the IEA Workshop was fulfilled in all cases.

Table IV
List of Experts' Workshops

Dates	Location
21 March 1994	Washington, D.C., USA
12 October 1994	Miami Beach, USA
17-18 July 1995	Henniker, USA
27-28 September 1995	Kjeller, Norway
27 August 1996	Les Diablerets, Switzerland
13 March 1997	Alexandria, USA
14 July 1997	Henniker, USA
26 January 1998	West Palm Beach, USA (carbon only)
9-10 March 1998	Davos, Switzerland
30 September – 1 October 1998	Tokyo, Japan
20-21 July 1999	Henniker, USA
2-3 March 2000	Davos, Switzerland
6-7 October 2000	Noosa, Australia

Summary of Results Achieved

The overall result of the Task was significant measurable progress toward Target 1, as well as general progress in the understanding of metal hydrides and carbon as hydrogen-storage media. This will be only a brief summary of the principal results, project by project. Each of these projects is presented in some detail later in the form of individual Project Reports, the main summary mechanism of this Final Task Report. In addition, Publications and Presentations resulting from each Project are listed in order for interested parties to pursue even more details.

The closest approach to achieving the 100˚C, 5 wt.% hydrogen-storage target resulted from the sodium alanate (hydride complex) projects. Sequential Projects 10 and 14 studied the catalyzing of $NaAlH_4$ by mechanical (ball milling) methods using liquid and solid catalyst precursors. Preliminary determinations of engineering behavior and properties were made. By the end of the Task, 4-4.5 wt.% at 125˚C was routinely demonstrated with reasonable hydriding and dehydriding rates. This is close to the target and represents a hydride capacity-temperature combination never achieved before. Related work showed the

validity of the two-step $NaAlH_4$ reaction and determined the structure of the important intermediate phase Na_3AlH_6 (Project 6). The exact catalyst(s) influencing the alanate reactions have not been determined, but Project 5 examined the possible structural and reaction roles of Ti_3Al hydrides as catalysts. A much needed safety study of $NaAlH_4$ was started in Project 15, but, unfortunately, was not completed. As a measure of the progress made in the IEA alanate efforts, distinct interest has resulted from outside of the IEA, including commercial interest among automotive and fuel cell companies. An example of increased national interest can be seen by the fact that Japan's WE-NET project has begun the funding of independent alanate work by one of the IEA alanate Experts.

Project 16 discovered a new family of hydrides based on the Zintl-phases, e.g. $SrAl_2$ and $SrAl_2H_2$, both of which are Zintl-phases. These new hydrides have certain similarities to the mixed ionic-covalent alanates and may offer an exciting new "nonconventional" area for future catalyzed hydride R&D.

Project 11 opened the stage for extending the catalyzed alanate work to transition metal complexes. It reported the discovery of a number of new complex hydrides. One of the most promising for future attempts at catalyzing is Mg_3MnH_7.

Five projects revisited the old and classic complex hydride Mg_2NiH_4 with aims at destabilizing it, i.e., making hydrogen desorption easier at lower temperatures. Projects 1 and 2 showed it was possible to destabilize Mg_2NiH_4 by lower temperature synthesis (avoiding microtwinning), mechanical working and controlling phase impurities like Mg. It also identified for the first time color and electrical resistivity changes that may have practical applications. Project 2 was performed in close conjunction with Project 1 using a newly developed method of synthesizing single-phase Mg_2NiH_4 by a Mg-vapor process. Projects 8 and 9 studied the effects of ballmilling. Project 8 showed that the temperature of hydrogen desorption could be synergistically lowered by ball milling mixtures of Mg_2NiH_4 and MgH_2. Project 9 examined the ball milling of Mg_2Ni in an H_2 atmosphere (i.e., the formation of Mg_2NiH_4 while milling). Although finer products resulted, the hydride phase structure was similar to static hydriding. In summary, the four projects cited immediately above resulted in significant improvements in hydriding/dehydriding kinetics and modest increases of equilibrium plateau pressures. In general, hydrogen liberation temperatures above 200˚C were still practically required, so the Task Target was not approached as nearly as the alanate work.

Project 12 was the only project in Task 12 that did not involve reversible hydriding and dehydriding. Instead it focused on the irreversible liberation of H_2 by the catalyzed hydrolysis of $NaBH_4$ solutions. It found ball milled and fluorinated $Mg\text{-}Mg_2Ni$ eutectic alloy (and its hydrides) to be promising hydrolysis catalysts.

Projects 4 and 13 searched for new Ca-based alloys and intermetallic compounds. Although several were identified, they seem to be highly prone to disproportionation and unlikely to provide much practical hope of achieving the Task Target. Similarly, Project 3 reported on the discovery of a new AB_2 Laves-phase CeMnAl. It does not seem to offer practical hydrogen-storage properties, but may be useful as a hydrogen getter.

The four projects on carbon storage media provided mixed results. Projects C-3 and C-4 surveyed a number of commercially and experimentally available materials with regard to gaseous and electrochemical hydrogen storage, respectively. Although some hydrogen storage was measured, results of these two projects fell well short of confirming the high levels of hydrogen storage often noted in the literature. In distinct and credible contrast to this, Project C-1 showed promising levels of hydrogen storage in single-wall carbon nanotubes that had been properly synthesized, purified and cut by mechanical/chemical processing. Levels of around 6.5 wt.% H_2 were shown, with some of that hydrogen coming off room temperature and the rest in the 200-400˚C range. Next to the alanate results, this project comes closest to meeting the technical Task Target of 5 wt.% H_2 at 100˚C.

Project C-2 studied chemisorbed hydrogen on fullerenes, i.e., fullerene hydrides. Because of the relatively strong H=C bonding, fullerene hydrides are a thermodynamic challenge for practical hydrogen

storage. However, like the catalyzed alanates, promising catalyst results were shown in the project, along with possibilities for metal atom substitution.

Finally, Project 7 (the only non-experimental project) resulted in an extensive series of on-line hydride databases (URL: http://hydpark.ca.sandia.gov). The hydride data are far more complete than any printed resource. It has become a widely used Internet resource by hydride scientists and engineers.

Future Work

The ExCo, Task 12 Experts and Operating Agent all agreed that the results of the Task 12 work were promising enough to construct a new and broader hydrogen storage task. The new proposed Task, Solid and Liquid State Hydrogen Storage Materials, has been approved and is being finalized for startup about May 2001. It will be broader in the sense that it will consider other solid and liquid storage media beyond nonconventional hydrides and carbon. It will also involve more than experimental projects, in particular theoretical, modeling and engineering activities. Additional countries, organizations and Experts will participate.

Acknowledgements

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