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Hydrogen Storage Materials
— Key Technology for The Wide Use of Fuel-cell-powered Vehicles —

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7.1 Introduction

Hydrogen is considered to be the ultimate clean energy. In 2002, the Japanese government purchased the first automobiles equipped with fuel cells in order to promote the propagation of fuel cells that use hydrogen as fuel. Furthermore, in order to construct the basis for the introduction of automobiles equipped with hydrogen fuel cells, NEDO (See Footnote 1) plans to start a project in 2003 that aims at the development of basic technology for the safe use of hydrogen. Why have fuel-cell-powered vehicles been introduced onto the market despite the fact that the technology is not yet mature and the business is not generating income? It is felt that there is a strong intention to consider the future of the automobile industry that gave rise to the prosperity of the Japanese economy in the past, in addition to the purpose of searching for measures to reduce the generation of carbon dioxide (CO_2) that causes global warming and for an alternative energy for fossil fuels. Therefore, from the viewpoint of the future industry relating to hydrogen energy, this report summarizes technology issues related to hydrogen storage materials that are considered to hold the key to the success of hydrogen fuel cells.

While hydrogen reacts with oxygen to generate water, it is also considered as a medium for converting energy. It is converted to heat energy when it is simply burnt, to mechanical energy when used for internal combustion engines such as hydrogen engines, and directly to electric energy when used for fuel cells. In any of these processes, the reaction between hydrogen and oxygen generates only water and does not emit CO_2 that causes global warming. Since hydrogen is a secondary energy that can be produced by such methods as the electrolytic decomposition and thermal decomposition of water, by combining with renewable energies such as sunlight, it is possible to construct a hydrogen energy cycle based on the hydrogen generated from water as an ideal clean energy system that is not affected by resource restrictions and also decreases the environmental burden[1]. This is the reason why hydrogen is called the ultimate clean energy. Because hydrogen is a material, it is superior to electricity in that it can be stored in large quantities, and this fact provides the unique feature of hydrogen as a chemical energy (see Supplement).

To realize hydrogen energy systems, it is a premise to develop elemental technologies related to the production, transportation, storage, and utilization of hydrogen and to build the social infrastructure. In the issue No.7 of this bulletin, trends in the development of major production technologies and their problems were analyzed focussing on “Non-fossil-resources-based Hydrogen Production Technology” as a key technology for the building-up of sustainable hydrogen energy systems. In that report, it was pointed out that hydrogen energy systems must be discussed in the total framework including technologies for production, transportation, storage, and utilization.

Hydrogen is utilized in many application fields including the chemical industry such as the synthesis of ammonia and methanol and desulfurization refining of petroleum, the metal

Footnote 1:
New Energy and Industrial Technology Development Organization.

Supplement – Basic properties of hydrogen

Hydrogen is a gas under ordinary temperature and normal pressure. It is known as the lightest gas and highly flammable. The following are the characteristics of hydrogen related to the use for hydrogen fuel-cell-powered vehicles and hydrogen supply stations:

(1) Hydrogen provides clean energy that does not disrupt the environment, because the product of reaction with oxygen is water.

(2) Hydrogen is a secondary energy produced by such methods as the electrolytic decomposition of water. Since the raw material is water and it can be produced by making use of various kinds of renewable energy, there is no restriction from the viewpoint of resources.

(3) Although hydrogen is a gas at ordinary temperature and normal pressure, it becomes a liquid at an extremely low temperature that is lower than its boiling point (–253℃ at normal pressure).

(4) Because hydrogen is a material unlike electricity and heat, it is suitable for storing in large amounts.

(5) Hydrogen can be used as a cooling medium because the specific heat is as high as 14.9 J/g • K at 20℃ at atmospheric pressure, which is 14 times larger than that of air, and its thermal conductivity is about seven times larger than that of air.

(6) The energy density per unit mass is large (light): heat that is evolved when burnt is 121 MJ/kg, which is 2.75 times larger than that of gasoline (44 MJ/kg).

(7) Hydrogen is more voluminous than gasoline: heat of combustion per unit volume is 8.6 J/m^3, which is 0.3 times that of gasoline (29.8 J/m^3).

(8) By generating electricity with fuel cells, it is possible to directly obtain electric energy without burning.

(9) Hydrogen has the smallest atomic radius (0.37Å) among the elements and can penetrate into material lattices with a high diffusion coefficient. This enables the storing of hydrogen in materials as energy and to extract it out when necessary.

(10) Hydrogen is a flammable gas and there is a risk of fire and explosion when the concentration in the air exceeds 4 vol. %. Furthermore, it easily ignites because the ignition energy is low.

(11) The density is as low as 1/14 of air and tends to collect at a high position in a closed space. However, it easily scatters in an open space because it has a very high diffusion speed and low viscosity.

industry such as the reduction of ores, the electronics industry such as the production of semiconductors, and the glass industry such as the production of optical fibers and glass[2,3]. In the future, hydrogen is also expected to be used for stationary fuel cells as distributed energy sources that utilize its energy conversion function and automobiles equipped with fuel cells. To expand the use of fuel-cell-powered vehicles (See Footnote 2) that use hydrogen as fuel, on-board hydrogen storage units that replace the gasoline tanks of gasoline-fueled vehicles are required. Furthermore, hydrogen supply stations corresponding to gasoline stations are required as an infrastructure. These needs require hydrogen technology that enables temporary storage as well as stable and safe supply of hydrogen as required at an appropriate speed.

It is apparent that the development of practical and economical hydrogen storage technology is indispensable for the propagation of hydrogen energy. This report, envisioning hydrogen fuel automobiles as a harbinger to the realization of a hydrogen energy system society, overviews recent trends in research and development of hydrogen storage technology from the viewpoint of materials, and proposes the direction we should proceed in the future.

Footnote 2:
In this report, fuel-cell-powered vehicles refer to only those that use pure hydrogen as fuel and do not include those of reforming type that reform gasoline or methanol using on-board reformers. However, the hybrid type that combines secondary batteries or capacitors as a supplementary electric source is included.

7.2 Characteristics required for hydrogen storage

Making full use of hydrogen as the fuel for fuel-cell-powered vehicles will solve the environmental problems in urban areas with heavy traffic, and, from the long-term point of view, we can expect that hydrogen will become the ultimate clean energy that starts with renewable energy, substituting the fossil fuels on which our present automobile society depends. However, it is true that there remain many technical problems and social/economic issues that must be solved for the propagation of hydrogen fuel-cell-powered vehicles. For the fuel-cell-powered vehicles to become popular, they must be as comfortable and economical as gasoline-powered vehicles. Figure 1 illustrates a conceptual diagram of a hydrogen fuel-cell-powered vehicle. Basically, a fuel-cell-powered vehicle consists of the fuel supply system, fuel cell unit, control system, and drive system. Whereas the basic performance of the fuel cell itself including output density must be improved for better performance of fuel-cell-powered vehicles, there are, at the same time, many problems to be solved relating to the storage of fuel.

The Fuel Cell Project Team, part of the vice ministers committee of the Ministry of Economy, Trade and Industry, the Ministry of Land, Infrastructure and Transport, and the Ministry of the Environment, has set a target of cruising distance for one fuel filling of a passenger car to 500 km or longer. They consider that a technology that enables the storage of 5 kg of hydrogen is necessary to achieve the target[4]. Since 5 kg of hydrogen occupies 56m^3 under the standard condition of 0℃ and at atmospheric pressure, it becomes necessary to develop a compact hydrogen storage system.

The following characteristics are required for hydrogen storage materials (See Footnote 3) :

(1) Stored hydrogen is effectively released without dead storage or dissipation (maximum amount of effective hydrogen storage) (See Footnote 4), and minimum energy is consumed in the storage-release cycles (high energy efficiency).

(2) Compact storage (maximum amount of effective hydrogen storage per unit volume of storage material).

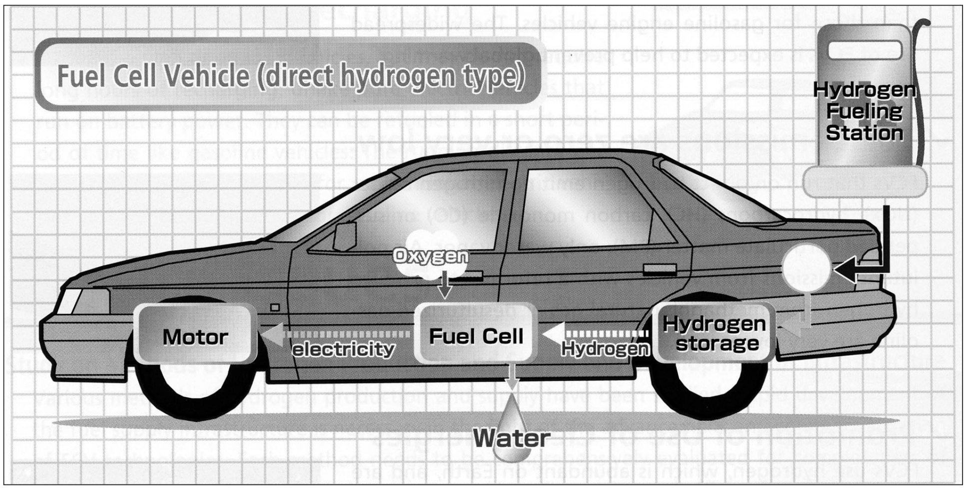
Footnote 3:

In this report, hydrogen storage materials refer to those that store hydrogen by themselves such as hydrogen storage alloys as well as those that are used for containers to store hydrogen such as hydrogen tanks in which hydrogen is to be filled.

Footnote 4:

WE-NET defines the "amount of effective hydrogen storage = amount of stored hydrogen at 10 atm. – amount of stored hydrogen at atmospheric pressure" with a release temperature of 60℃.

Figure 1: Conceptual diagram of a hydrogen fuel-cell-powered vehicle



Source: "FUEL CELL VEHICLE"– pamphlet of the Japan Hydrogen & Fuel Cell Demonstration Project

(3) Light weight (maximum amount of effective hydrogen storage per unit weight of storage material).
(4) Hydrogen is easily stored and released under normal environmental conditions (considering the compatibility with fuel cells, it is desirable that hydrogen be released at 100℃ or lower).
(5) Optimum cycle characteristic (storage capacity for effective hydrogen after 5,000 storage-release cycles must be 90% or more compared with the initial value).
(6) Low equipment costs and running costs.
(7) Safe and easy to handle.

At present, there is no technology that meets these requirements, and a method to practically load hydrogen fuel in a fuel-cell-powered vehicle has yet to be decided on. Automobile manufacturers are testing various types of hydrogen storage technology by developing hydrogen fuel-cell-powered vehicles that use hydrogen as pressurized gas[5,6,7] and liquid hydrogen[8].

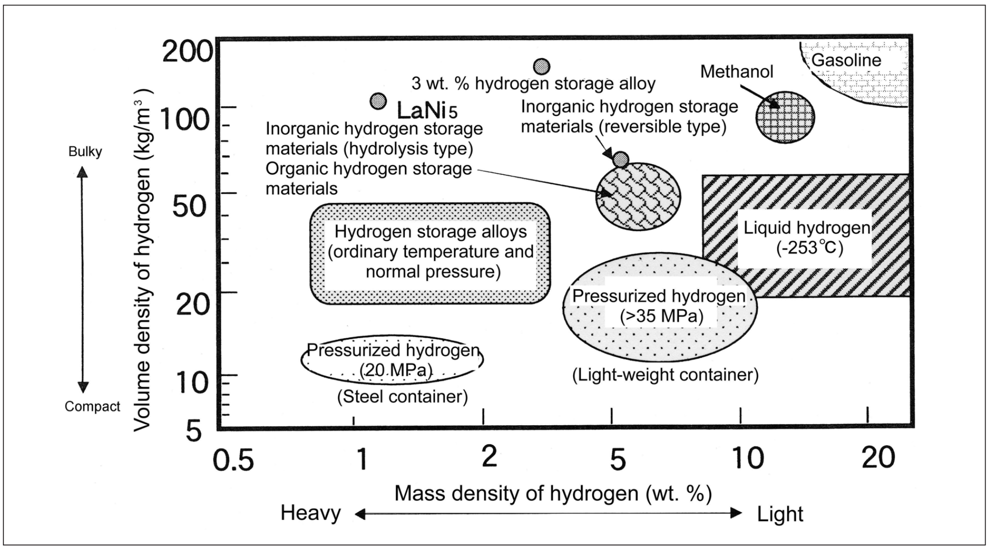
7.3 Various types of hydrogen storage materials

As the practical technology for hydrogen storage, pressurized gas type, liquid hydrogen type, and hydrogen storage alloys have been developed. Recently, research on chemical materials is being conducted as a new hydrogen storage technology including carbonic materials and hydrides of organic and complex compounds. Figure 2 shows the comparison of hydrogen densities of various types of hydrogen storage methods. In this chapter, the characteristics and problems of each hydrogen storage technology are explained.

7.3.1 Pressurized gas

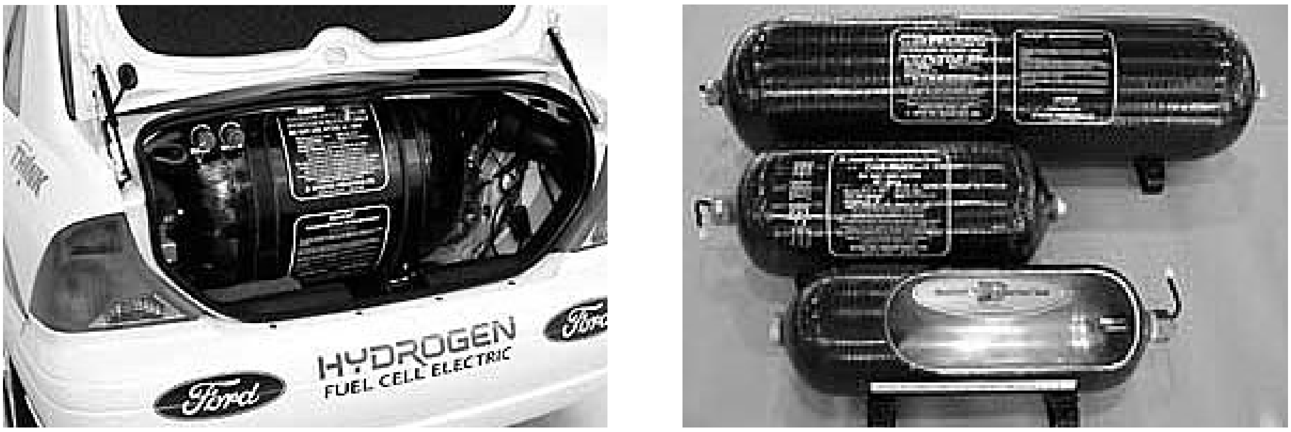
Hydrogen stored as pressurized gas is the most widely used method at present for its storage. Since the atomic radius of hydrogen is far smaller than those of metallic materials, hydrogen atoms can easily penetrate into materials. Generally speaking, metals embrittle when they absorb hydrogen (hydrogen brittleness); therefore, materials that do not suffer from hydrogen embrittlement must be selected for such containers. Normally, red colored pressure-resistant containers called hydrogen cylinders are used for the stationary storage of hydrogen. These cylinders are made of thick plates of mild steel, and hydrogen pressurized to about 150 to 200 atm (See Footnote 5). is filled within them[2]. However, such steel containers are too heavy for use in automobiles, and, as a result, lightweight pressure-resistant hydrogen tanks made of aluminum and strengthened with composite material of carbon-fiber-reinforced plastics have been developed[3]. Figure 3 illustrates examples of high-pressure gas

Figure 2: Comparison of hydrogen densities of various types of hydrogen storage methods



- Gasoline and methanol are converted by energy density.
- Both volume density of hydrogen and mass density of hydrogen are values including containers.
Source: Reference[18]

Figure 3: Examples of high-pressure gas tanks for automobiles



(a) 350-atm. Pressurized hydrogen tank placed in the trunk space of a passenger car.
Source:http://www.ford.com/en/ourVehicles/environmentalVehiles/hydrogenFuelCellElectricVehicles/ford-focus-fcv-hybrid.htm

(b) FRP containers for natural gas.
Source: http://www.nkk.co.jp/release/0111/1120-2.html

tanks for automobiles that have been developed.

Among the laws and regulations applicable to hydrogen gas (See Footnote 6), the "High Pressure Gas Safety Law" plays a central role with other governmental ordinances, ministerial ordinances, and notifications supplementing technical and safety criteria[9]. In the past, it was banned to carry pressurized hydrogen in vehicles, but the ban was canceled in April 2001. However, since the maximum pressure of hydrogen tanks is currently restricted to 350 atm (See Footnote 7) the present cruising distance of a hydrogen fuel-cell-powered vehicle is limited to 300–355 km[5,6]. In order to achieve a cruising distance comparable to gasoline-powered vehicles (500 km), it is desirable to increase the amount of hydrogen by raising the charging pressure, and the development of on-board super-high-pressure tanks resistant up to 700 atm. is now being studied[4]. As the energy loss during the pressurizing process increases with the increase in the charge pressure of hydrogen, it is also necessary to improve the efficiency of compressors.

Kokan Drum Co., one of the major drum manufacturers, is now selling containers for pressurized hydrogen gas up to 350 atm. (Figure 3 (a)). However, in view of the present circumstances in which vehicles that use higher-pressure hydrogen gas are being developed worldwide in order to increase the cruising distance of fuel-cell-powered vehicles, they have decided to develop a new system for loading pressurized hydrogen up to 700 atm. in vehicles and the corresponding filling system in cooperation with the Canadian company Dynetek Industries Ltd. They use containers made of aluminum lined with carbon FRP (See Footnote 8), which were originally used for natural-gas-powered vehicles (Figure 3 (b)). The

Footnote 5:

There are two kinds of pressure units: absolute pressure in which vacuum is 0, and gauge pressure in which the atmospheric pressure is 0. In this paper, pressures are expressed in gauge pressure. Furthermore, it is assumed that 0.1 MPa = 1 atm. for simplification. That is, 1.1 MPa = 1.0 MPaG = 10 atm.

Footnote 6:

Major laws related to hydrogen include the High Pressure Gas Safety Law, the Electric Utilities Industry Law (under the control of the Ministry of Economy, Trade and Industry), the Road Transportation Vehicle Law, the Road Traffic Law, the Building Standard Law (under the control of the Ministry of Land, Infrastructure and Transport), and the Fire Defense Law (under the control of the Ministry of Public Management, Home Affairs, Posts and Telecommunications).

Footnote 7:

Fiber reinforced plastic composite containers are interpreted as general-purpose composite containers based on the High Pressure Gas Safety Law, and the maximum pressure of the container is limited to 350 atm.

Footnote 8:
FRP = Fiber Reinforced Plastic

containers are being improved so that they can be used for pressurized hydrogen gas in order to develop a new system for hydrogen fuel-cell-powered vehicles[10]. As the development of such super-light-weight pressure-resistant vessels proceeds, deregulation of peripheral technologies is also being considered. At present, however, most of the infrastructure equipment devices related to hydrogen such as hydrogen compressors, electromagnetic valves, and high-pressure tanks are imported, and this may cause problems in promoting the improvement of the infrastructure for hydrogen[4]. It is important to possess these elemental technologies not only from a technical point of view but also from the viewpoint of ensuring the safety of hydrogen.

7.3.2 Liquid hydrogen

Hydrogen is liquefied at a cryogenic temperature of –253℃, and its volume is reduced to 1/800 of hydrogen gas under standard conditions, which is more compact than pressurized hydrogen gas. However, a problem of liquid hydrogen is that a large amount of energy is consumed to liquefy it at a cryogenic temperature, significantly lowering its total energy efficiency. It is also necessary to use special thermal insulated containers to prevent loss by evaporation called “boil-off.” Therefore, development of cryogenic materials and thermal insulation structure designs are indispensable for liquid hydrogen storage tanks.

For the cryogenic materials used for liquid hydrogen storage tanks, sufficient mechanical properties (tensile strength, fracture toughness, fatigue strength, etc.) in the temperature range from ordinary temperature to the liquid hydrogen temperature and resistance to low temperature embrittlement and hydrogen embrittlement are required. In WE-NET, stainless steels and aluminum alloys, which are time-proven materials for cryogenic structures, have been selected as the candidates and studies have been made. The results showed that while the base metals of selected materials had sufficient strength and toughness under the liquid hydrogen environment, welded zones were highly sensitive to low temperature embrittlement and hydrogen embrittlement requiring improvement in toughness. Studies on welding methods and welding materials aiming at the improvement of low temperature toughness showed that reduced-pressure electron beam welding (RPEB) was effective for stainless steels and friction stir welding (FSW) was effective for aluminum alloys for the improvement of low temperature brittleness[9]. It is expected in the future that detailed studies on the behavior of embrittlement under the hydrogen environment as well as studies on lightweight, high-strength titanium alloys that are assumed to be the materials for the thin-walled members of small- and middle-scale containers and for peripheral equipment will be promoted.

Since liquid hydrogen provides higher storage density than pressurized hydrogen gas, it is presently used for the fuel of space rockets. However, because measures must be taken to prevent high energy consumption during the storage at cryogenic temperature and boil-off gas, liquid hydrogen is considered to be suitable for storage and transportation in large quantities, such as liquid hydrogen tankers and liquid hydrogen trailers, where specific surface areas are small enough to obtain high thermal insulation performance. Liquid hydrogen storage is planned to be demonstrated by some of the hydrogen supply stations that are planned to be built in the metropolitan area[11]. Also, GM announced that they are going to carry out commercial testing of fuel-cell-powered delivery vehicles loaded with liquid hydrogen in Tokyo from 2003[8].

7.3.3 Hydrogen storage alloys

Some metals tend to react with hydrogen, thereby generating metal hydrides. When hydrogen contacts the surface of metals, the hydrogen molecules are adsorbed on the surface and decomposed to atomic hydrogen. The hydrogen atoms penetrate into the gaps of the lattice of metal atoms and quickly diffuse to form metal hydrides being trapped as interstitials. By combining a metal (A) that tends to form hydride and a metal (B) that scarcely forms hydride, a hydrogen storage alloy that absorbs and desorbs hydrogen can be produced. Hydrogen storage

Table 1: Typical hydrogen storage alloys and the properties of their hydrides

Alloy Type	Alloy	Hydride	Amount of absorbed hydrogen wt. %	Hydrogen desorption pressure (MPa*) and temperature (℃)
AB_5	$LaNi_5$	$LaNi_5H_{6.0}$	1.4	0.4(50)
	$LaNi_{4.6}Al_{0.4}$	$LaNi_{4.6}Al_{0.4}H_{5.5}$	1.3	0.2(80)
	$MmNi_5$	$MmNi_5H_{6.3}$	1.4	3.4(50)
	$MmNi_{4.5}Mn_{0.5}$	$MmNi_{4.5}Mn_{0.5}H_{6.6}$	1.5	0.4(50)
	$MmNi_{4.5}Al_{0.5}$	$MmNi_{4.5}Al_{0.5}H_{4.9}$	1.2	0.5(50)
	$MmNi_{2.5}Co_{2.5}$	$MmNi_{2.5}Co_{2.5}H_{5.2}$	1.2	0.6(50)
	$MmNi_{4.5}Cr_{0.5}$	$MmNi_{4.5}Cr_{0.5}H_{6.3}$	1.4	1.4(50)
	$Mm_{0.5}Ca_{0.5}Ni_5$	$Mm_{0.5}Ca_{0.5}Ni_5H_{5.0}$	1.3	1.9(50)
	$CaNi_5$	$CaNi_5H_{4.0}$	1.2	0.04(30)
AB_2	$TiMn_{1.5}$	$TiMn_{1.5}H_{2.47}$	1.8	0.7(20)
	$TiCr_{1.8}$	$TiCr_{1.8}H_{3.6}$	2.4	0.2~5(-78)
	$ZrMn_2$	$ZrMn_2H_{3.46}$	1.7	0.1(210)
	ZrV_2	$ZrV_2H_{4.8}$	2.0	10^{-9}(50)
AB	TiFe	$TiFeH_{1.95}$	1.8	1.0(50)
	$TiFe_{0.8}Mn_{0.2}$	$TiFe_{0.8}Mn_{0.2}H_{1.95}$	1.9	0.9(80)
A_2B	Mg_2Ni	$Mg_2NiH_{4.0}$	3.6	0.1(253)

* In this table, pressures are expressed in absolute pressure.

Source: Authors' compilation based on reference [2]

alloys are classified into AB_5 type alloy, AB_2 type alloy, etc., according to the atomic ratio between A and B. Elements for the A site consists of metals of 2A – 5A groups such as Mg, Ti, Zr, V, and rare earth metals; and elements for the B site consist of metals of 6A – 8 groups such as Fe and Ni. When hydrogen is fixed in the alloy as hydride, its volume is normally compacted to about 1/1000 of the volume under ordinary temperature and normal pressure. However, the problem is that the mass density is almost the same as that of the steel container, making the hydrogen tank heavy. Table 1 shows typical hydrogen storage alloys and the properties of their hydrides.

The forerunner of practical hydrogen storage alloys was the electrode material (AB_5 Type) for nickel-hydrogen secondary batteries. In the early stage of the development of hydrogen storage alloys, WE-NET set the target of the amount of effective hydrogen storage at 3 wt. %. However, the target was changed to 5.5 wt. % by strongly considering application to the tanks for hydrogen-powered vehicles[12]. At present, the values of almost all alloys shown in Table 1 are as low as 1 to 2 wt. %, and only hopeful alloys that may realize weight saving are Mg-based alloys. In the Hydrogen Project at Munich Airport, multiple methods of supplying and storing hydrogen are used for the system, and a hydrogen storage alloy of Fe-Ti system (5℃ for absorption and 77℃ for desorption) that can store 2,000 Nm³ at 30 atm. was used for the hydrogen storage in the hydrogen station[13].

Since the hydrogenation and dehydrogenation of hydrogen storage alloys are chemical reactions, evolution and absorption of heat are involved. Absorption of hydrogen is an exothermic reaction, and desorption of hydrogen is an endothermic reaction. If the temperature of alloys changes to a large extent during the reaction, the hydrogenation and dehydrogenation are disturbed due to fluctuation of the chemical equilibrium. For this reason, materials with high heat conductivity and favorable structure design that enable quick transfer of reaction heat must be adopted for the containers of hydrogen storage alloys. Furthermore, the cycles of absorption and desorption of hydrogen cause repeated expansion and shrinkage of the volume of the hydrogen storage alloys, so that cracking of alloys proceeds and results in the generation of fine powders. To prevent these fine powders from aggregating nonuniformly in the container, thereby leading to the distortion of the container, it is required to control the packing density or separate the inside of the container with partitions. It is also necessary to take measures to avoid poisoning with impurity gases. From the viewpoint of weight saving, further technological breakthrough must be made for hydrogen storage alloys. Relating to the handling of reaction heat and decrepitation, measures must be taken for both alloys and the structure of containers.

7.3.4 Carbonic materials

Recently, new carbonic materials with nano-structures such as carbon nano-tubes and graphite nano-fibers have been discovered, and it has been reported that these materials have quite excellent mechanical, electrical, and chemical properties. Their characteristics of hydrogen absorption and adsorption have also attracted much attention, and intensive research has been conducted everywhere. Among the reports on the characteristics of hydrogen absorption and adsorption of these carbonic materials, some assert that they are far superior to hydrogen storage alloys in the amount of stored hydrogen[14,15], while some others report that they scarcely occlude hydrogen[16]. Relating to these materials, no neutral research organization has verified the reproducibility of hydrogen occlusion. This has occurred because both stable production processes and measuring methods for the amount of hydrogen stored in small amounts of materials have not been established. What we should do at the moment is to improve the production and measuring technologies as well as to theoretically elucidate the mechanism of hydrogen absorption and adsorption by studying the interaction between hydrogen atoms and carbon atoms.

On the other hand, it has been reported that more than 7 wt. % of hydrogen can be stored in a nano-structure developed by pulverizing graphite with a lamellar structure in hydrogen atmosphere[17]. In this case, carbon and hydrogen combine in two ways. Hydrogen that has strongly combined with carbon is released at as high as 630℃, making it unfavorable for hydrogen storage; while hydrogen that has weakly combined with carbon is released at 300℃ and the amount of stored hydrogen is 6 wt. %. Research on catalysts and other methods to lower this release temperature down to 100℃ or lower is now being conducted.

It is generally said that since the bulk density of carbonic materials is low, they are not suitable for the compact storage of hydrogen. But they appear to become competitive as hydrogen storage materials if a mass density of hydrogen close to 10 wt. % is attained. In order to develop and produce innovative hydrogen storage materials, it is necessary to design the material structure at the atomic level and to control the bonding of hydrogen and the atoms of the storage material at the electron level. Thus, nano-technology plays an important role in the creation of new materials.

7.3.5 Organic hydride compounds (Organic chemical hydrides)

As for organic compound hydrogen storage materials, technologies that use the hydrogenation and dehydrogenation reactions of organic compounds such as the cyclohexane-benzene system, the methylcyclohexane-toluene system, and the decalin-naphthalene system are attracting attention. The amounts of stored hydrogen in these materials are as high as 7.1, 6.2, and 7.3 wt. % by weight and 55, 48, and 65 kg/m^3 by volume, respectively. Since these materials are liquids at room temperature except for naphthalene, they can be handled at ordinary temperature and normal pressure without requiring special conditions such as high pressure or low temperature, thus permitting easy transportation and filling operation[18]. However, benzene, toluene, naphthalene and other residues remain after the dehydrogenation and they must be recovered and reclaimed by hydrogenating again.

Since organic compound hydrogen storage materials generally require temperatures as high as 250 – 400℃ and the amount of heat absorbed in the dehydrogenation reaction is twice that of hydrogen storage alloys, much energy is required for the release of hydrogen. Furthermore, an additional process for separating hydrogen and the vapor of organic materials in the dehydrogenation reaction must be provide. At present, basic research such as the search for supported catalysts that promote the hydrogenation and dehydrogenation at lower temperatures and optimization of reaction conditions are being conducted.

To use organic compound hydrogen storage materials for automobiles, a distribution system for cartridge type tanks that can be changed as a whole must be established, and reactors and purifiers for taking out hydrogen must be prepared in addition to the containers of the hydrogen storage material itself. Therefore, it is difficult to simply compare advantages and disadvantages of organic compound hydrogen storage materials used for automobiles with other hydrogen storage materials. At the start, it seems that the economical rationality and practicality of the technology in the hydrogen supply infrastructure is evaluated.

7.3.6 Complex compound hydrides

Inorganic hydrides, called alanates, comprising of aluminum hydrides are now attracting attention as hydrogen storage materials[19]. When titanium salts are added to $NaAlH_4$, hydrogen is reversibly occluded and released at around one hundred and tens degrees centigrade. The hydrogenation process proceeds in two stages: hydrogen is occluded up to 3.7 wt. % in the first stage, and up to 5.5 wt. % in total, with the volume density of hydrogen at 43.2 and 70.6 kg/m^3 respectively, which are comparable to or higher than those of hydrogen storage alloys (20 – 50 kg/m^3). Since alanates can be packed in the container after compression molding as hydride, a high filling ratio can be obtained compared with hydrogen storage alloys, which must be filled in the container before hydrogenation while taking the volume expansion by hydrogenation into account. In any event, since the present reaction temperature and reaction rate are not sufficient for practical use, further development is required[18].

In addition to $NaAlH_4$, there are Na_3AlH_6, Na_2LiAlH_6, and Li_3AlH_6, and the theoretical amounts of hydrogen occlusion are 3.0, 3.5, 5.2 wt. %, respectively. However, actual amounts of hydrogen occlusion greatly vary depending on the experimental conditions, and further basic research including the reversibility, reaction rate and reaction temperature must be conducted to assess the applicability of these materials for hydrogen storage materials[12,18].

Boron hydrides (borohydrides) of light metals such as $NaBH_4$ have also been proposed as hydrogen storage materials. These materials react with water to generate hydrogen and, in the case of $NaBH_4$, the hydrogen content in the reactants including water is as high as 10.8 wt. %. In the hydrogen storage system using borohydrides, hydrogen is generated by the hydrolysis of hydrogen storage materials with water under the presence of catalysts, and it is a characteristic of this system that sufficient hydrogen supply speed is obtained at ordinary temperature and normal pressure[20]. It does require a system to recover the $NaBO_2$ that is generated in the hydrolysis reaction and reclaim hydrides for recycling. Since about one third of the combustion energy of hydrogen is theoretically consumed for the process to reclaim hydrides by reducing the $NaBO_2$ generated in the reaction with water, energy efficiency may be a problem in this technology[18].

7.4 Status of the development of hydrogen storage technology for fuel-cell-powered vehicles

7.4.1 Loading fuel-cell-powered vehicles with hydrogen

On December 2, 2002, Toyota Motor Corp. and Honda Motor Co. put fuel-cell-powered passenger cars onto the market for the first time in the world[5,6]. Both of them use pure hydrogen as the fuel (direct hydrogen supply type) that is stored in pressurized hydrogen tanks with a maximum filling pressure of 350 atm. Although the accelerating performance and quietness of these automobiles were highly appreciated, their cruising distances of 300 km and 355 km, respectively, are shorter than those of gasoline-powered passenger cars. It cannot be denied that the development of hydrogen storage technology for fuel lags behind the development of technology for power units. It goes without saying that not only the costs but also the development of hydrogen storage technology is the key to the deployment of fuel-cell-powered vehicles.

NEDO’s WE-NET project is known as a representative project for hydrogen energy development. In the first stage of the project (from fiscal 1993 to 1998), a magnificent picture was drawn in which a worldwide clean energy network was to be established by producing hydrogen making use of renewable energy such as hydraulic power, sunlight, and wind power, and using the hydrogen as the medium for the transportation and storage of secondary energy. Under this concept, research and development of hydrogen storage technologies was made as the tasks of WE-NET including the development of structural materials that can be used under liquid hydrogen conditions and hydrogen storage alloys for the distributed transportation and storage of hydrogen. In the second stage that started in fiscal 1999, however, WE-NET shifted the priority to the development of technologies for small-scale distributed applications, and the development of fuel cells has been incorporated into the WE-NET project from 2001.

In Japan, hydrogen storage alloys were the initial targets of development as the fuel loading method for hydrogen-powered vehicles, because regulations controlled the loading of vehicles with high-pressure gas such as hydrogen. In the second stage of the WE-NET project, research and development of peripheral technologies related to hydrogen-powered vehicles and hydrogen storage alloys for vehicles and hydrogen supply stations have been developed. Although the initial target of hydrogen storage alloy with a capacity of 3 wt. % has been almost achieved[18], the amount of hydrogen stored by this alloy is only 3 kg per 100 kg of the alloy, which provides a cruising distance of only about 300 km, not enough for practical use. In 2001, the Ministry of Economy, Trade and Industry set targets for the volume and weight of fuel loading systems to a level comparable to the fuel tanks of conventional gasoline-powered vehicles in the technological development strategy for the application of fuel cells and hydrogen energy. In accordance with this strategy, the WE-NET project changed the development goal for the amount of hydrogen storage of hydrogen storage materials to 5.5 wt. % in fiscal 2002[12]. At present, no promising material to achieve this goal has yet been found.

Since the ban on loading hydrogen gas tanks in vehicles was withdrawn in April 2001, the direction of development of fuel storage methods for fuel-cell-powered vehicles has been changed from hydrogen storage alloys to pressurized hydrogen gas, which has made the practical use of fuel-cell-powered vehicles more realistic. The present hydrogen gas tanks used are made of composite materials strengthened with fiber reinforced plastics and the maximum pressure is limited by regulation to 350 atm., but it is expected that lighter high-pressure containers will be realized in the near future.

7.4.2 Demonstration of hydrogen supply stations

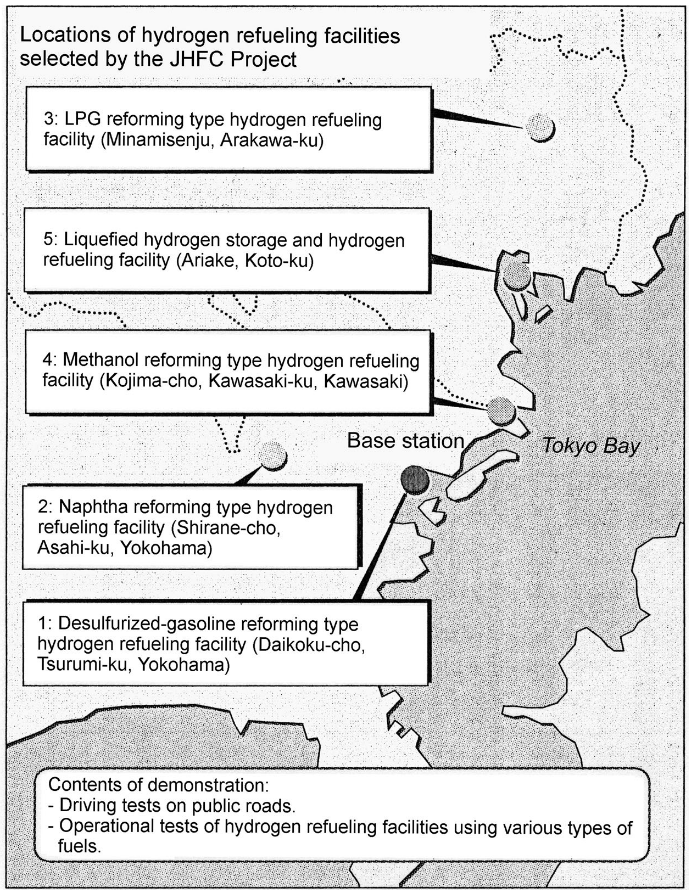
The Fuel Cell Commercialization Strategy Study Group has set a goal for the number of fuel-cell-powered vehicles in 2020 at five million, which corresponds to one-tenth of the present total number of automobiles, and the number of hydrogen supply stations required at such time is estimated at 3,300[21]. Relating to the hydrogen supply station as one of the hydrogen application technologies, WE-NET has set up three domestic stations in fiscal 2002. Plans are to conduct tests and research required for commercialization using these stations, to prepare technical guidelines for safety and design, and to establish standard specifications for future hydrogen supply stations. The stations in Osaka and Takamatsu adopt both the hydrogen storage alloy method and the pressurized hydrogen gas method, while the station in Yokohama adopts the pressurized hydrogen gas method. Apart from these hydrogen stations, Toho Gas Co. has built a pressurized gas type hydrogen supply station in Tokai City, and is conducting technical studies and demonstrations on safety.

Furthermore, in the Japan Hydrogen & Fuel Cell Demonstration Project (See Footnote 9) that started in 2002, a large-scale demonstration of fuel-cell-powered vehicles is scheduled for the first time in the country, in which industry, academia

Footnote 9:

Japan Hydrogen & Fuel Cell Demonstration Project (JHFC Project). A project aided by the Ministry of Economy, Trade and Industry, consisting of the “demonstration study on fuel-cell-powered vehicles” and the “demonstration study on hydrogen supply facilities for fuel-cell-powered vehicles.” The project continues from fiscal 2002 to 2004.

Figure 4: Hydrogen refueling facilities to be built by the Japan Hydrogen & Fuel Cell Demonstration Project



Source: Reference[22]

and the government systematically cooperate in the study of loading methods for hydrogen and will share the basic data on performance and safety. At the same time, plans are underway to build five hydrogen supply facilities in fiscal 2002 in the metropolitan area, which will adopt multiple types of hydrogen including liquid hydrogen and pressurized hydrogen. Figure 4 shows the locations of the five hydrogen supply stations selected by the project and the hydrogen supply methods[22]. It is scheduled through a three-year demonstration to elucidate technical issues for practical use, and to collect and analyze data relating to environmental characteristics, total energy efficiency, fuel characteristics, safety, and durability[11]. In this project, not only domestic car manufacturers (Toyota, Nissan and Honda) but also overseas car manufacturers (GM and Daimler-Chrysler) are participating, and it is expected that the development of fuel-cell-powered vehicles will be further promoted through international cooperation and competition.

7.4.3 Safety measures for hydrogen

When using hydrogen as fuel, it is a major premise to secure safety. The WE-NET project has set up the dedicated sub-task of "investigation and studies on safety measures," and has been making efforts to establish criteria for safety design and methods to assess safety[9]. Potential accidents in hydrogen supply stations have been researched and, particularly for hydrogen storage, continuous hydrogen release from hydrogen tanks was selected as a representative event. Experiments that are being made include: run-off, evaporation, and diffusion of liquid hydrogen; explosion of hydrogen; and the relationship between the form of hydrogen leakage and ignition conditions when leakage of pressurized hydrogen occurs. Simulation models are also being established through verification analyses of the results of experiments. In the Basic Technology Development for the Safe Use of Hydrogen Project that starts in fiscal 2003, fundamentals on safety and infrastructure will be improved. As data on safety are collected, the present regulations will be reviewed by the related public institutions, and positive efforts must be made to publicly publish these test data. In order to address public concerns over the safety of hydrogen and to obtain the understanding and cooperation of the general public, it is desirable that the results of WE-NET and the Japan Hydrogen & Fuel Cell Demonstration Project be widely published as a part of the public relations activities and shared by many people.

7.5 Overseas situation

7.5.1 The U.S.

Development of hydrogen energy technology in the U.S. got into full swing when the Hydrogen Program of DOE was established (See Footnote 10) in 1992. The development has been mainly carried out as part of PNGV (Partnership for a New Generation of Vehicles), which is a development project of the federal government for the next-generation automobiles started in 1993, as well as part of CaFCP (California Fuel Cell Partnership) by the state of California. Particularly, the international character of CaFCP is worthy of attention. Among the participants are Daimler-Chrysler, Ford, Nissan, Honda, Volkswagen, and Korean Hyundai; GM and Toyota also joined in October 2000.

In January 2002, the U.S. government announced that under the DOE leadership PNGV would be dissolved and Freedom CAR (Freedom Cooperative Automotive Research Partnership) would be created. This project aims at the development of high-risk technologies, in partnership of the U.S. government and the Big Three, particularly the development of elemental technologies with emphasis on technologies related to hydrogen fuel-cell-powered vehicles[4]. In January 2003, President Bush announced the Freedom Fuel Plan in his State of the Union Address, promising to promote the necessary technical development and to improve the social infrastructure in order to promote commercialization of fuel-cell-powered vehicles.

In the Hydrogen Research Program sponsored by DOE, the focus is placed on the technologies for the transportation and storage of hydrogen in addition to the technologies for the production and application of hydrogen. With application to automobiles in mind, research on pressurized-gas tanks, liquid-hydrogen tanks, chemical storage, metal hydrides, and occlusion by carbonic materials are being conducted intensively with a goal of 6.5 wt. % for the amount of stored hydrogen[23]. DOE is now planning to integrate all of the projects related to hydrogen that are now carried out by the energy efficiency and renewable energy department, fossil energy department, and nuclear energy department into the Integrated Hydrogen Program of DOE. DOE also published The National Hydrogen Energy Roadmap in November 2002, proposing a road to realize the Hydrogen Economy Society by introducing fuel-cell-powered vehicles and distributed electric source systems[24]. In this roadmap, hydrogen is perceived from not only the viewpoint of clean energy but also from the viewpoint of energy security. Hydrogen storage is recognized as the key technology for the realization of the Hydrogen Economy Society, and the necessity for the cooperation of industry and government in the reduction of costs, improvement of characteristics and development of advanced technologies is stressed because the present hydrogen storage technology is not adequate for both suppliers and end users. It also points out that efforts should be concentrated on the development of conventional commercial technologies including pressurized hydrogen gas and liquid hydrogen and on the search for new storage technologies that are more difficult to realize including advanced materials (such as light metal hydrides and carbon nanotubes).

7.5.2 Europe

In Europe, many countries have announced their intentions to carry out demonstration programs for fuel-cell-powered buses with the support of the European Commission. In the ECTOS (Ecological City Transport System)[25] project of Iceland and the CUTE (Clean Urban Transport for Europe)[26] project consisting of seven countries including Germany and the United Kingdom, 30 fuel-cell-powered buses using

Footnote 10:
U.S. Department of Energy

pressurized hydrogen (manufactured by DaimlerChrysler) are scheduled to be introduced into 10 cities (See Footnote 11) for fleet tests from 2003[4]. Particularly, ECTOS is worthy of attention as a model case of the challenge to a hydrogen energy society. It is a project that pursues complete transformation of Iceland into a hydrogen society (See Footnote 12). Since Iceland is blessed with renewable energy resources such as hydraulic power and geothermal power, the project plans to produce hydrogen by making use of these resources and to convert the country to a hydrogen society by completely eliminating the use of fossil fuels within 20 to 30 years. To start with, it is planned that the infrastructure for hydrogen stations in the capital city of Reykjavik is to be established and three hydrogen fuel-cell-powered buses are to used for daily urban transportation. Then, the use of hydrogen energy is to be expanded to private cars and boats in the fishing industry, which is Iceland's main industry. It is also in their view to export hydrogen made from their renewable energy to other European countries.

In Germany, the "Hydrogen Project at Munich Airport" started in 1995, in which buses and small-size cars are replaced with hydrogen-powered vehicles. At present, three buses that use pressurized hydrogen and passenger cars that use liquid hydrogen are in service within the Munich international airport[27]. In this project, not only the production and storage of hydrogen for a fleet of vehicles but also completely automated hydrogen charging is demonstrated along with the verification of its safety.

Meanwhile, in private projects, DaimlerChrysler has been continuing its development of fuel-cell-powered vehicles since 1990. The fuel-cell-powered bus NEBUS, which started running on public roads for the first time in 1997, adopted a hydrogen tank system with a cruising distance of 250 km. NECAR4, a fuel-cell-powered vehicle developed in 1999, adopted a liquid hydrogen system with its cruising distance reaching 450 km. Although having developed NECAR5, which produces hydrogen through an on-board reformer using methanol as the fuel, DaimlerChrysler intends to use pressurized hydrogen tanks for the buses and passenger cars that are sold in a limited number from the end of 2002 to the beginning of 2003[28].

7.5.3 International standardization

In the view of the above-mentioned international activities, the trends in international standardization must be watched. Since automobiles are cross-border international merchandise, it is expected that international regulations and standards including standard pressures will be established for hydrogen fuel-cell-powered vehicles in the future. In addition, relating to such peripheral technologies as dispensers and hydrogen supplying connectors, countries that are ahead in the development of these technologies are trying to establish their own de facto standards as international standards. As for fuel cells, the U.S. and European countries are energetically deliberating at the tables of ISO (See Footnote 13) and IEC (See Footnote 14),[4]. In order to strongly express own opinion, Japan must engage in technical discussions based on practical information (data) at the table of debate. Therefore,

Footnote 11:

Hydrogen fuel-cell-powered buses are scheduled to be introduced for public transportation in the following 10 cities: ECTOS: Iceland (Reykjavik); CUTE: Netherlands (Amsterdam), Spain (Madrid and Barcelona), Germany (Hamburg and Stuttgart), the United Kingdom (London), Luxembourg, Portuguese (Porto), and Sweden (Stockholm).

Footnote 12:

The Icelandic New Energy Co., established for carrying out ECTOS, states on its website as follows:The mission of Icelandic New Energy is to "investigate the potential for eventually replacing the use of fossil fuels in Iceland with hydrogen and create the world's first hydrogen economy."

Footnote 13:

International Organization for Standardization

Footnote 14:

International Electrotechnical Commission positive utilization of the fruits of such projects as WE-NET and the Japan Hydrogen and Fuel Cell Demonstration Project is desired. It is also necessary for the related institutions to cooperate in the development and standardization of regulations and systems.

7.6 Conclusion

In the early stage of technical demonstration of hydrogen fuel-cell-powered vehicles, hydrogen storage started with the high-pressure tank system that had been used for natural-gas-powered vehicles. Since large vehicles such as buses have enough space to carry many hydrogen tanks on the roof and under the floor, there is no severe restriction for weight and space. For passenger cars that have only limited space, however, the storage of hydrogen by present pressurized-hydrogen tanks of 350 atm. is insufficient. On the other hand, hydrogen storage alloys are compact but heavy, and liquid hydrogen is compact and light but requires complicated handling and consumes energy in the process of liquefying. Thus, each method has its advantages and disadvantages and there remain many technical problems to be solved.There are many issues to be tackled for the development of on-board hydrogen storage and the final solution has not been given, leaving large room for further research and development of innovative materials.

It is an urgent necessity to develop hydrogen storage materials having higher performance now that hydrogen fuel-cell-powered vehicles have become a reality. As in the case of fuel-cell-powered vehicles, it is desirable that hydrogen storage materials are developed through cooperation and competition. While material development has been carried out separately by each field up to now, it is hoped that from here forward the common target of achieving a hydrogen energy society and the time schedule to realize it are shared worldwide and the development promoted through cooperation and competition. In the development of hydrogen energy, governments must play an important role to coordinate multiple projects related to hydrogen energy and bring forth the overall effects. It is expected that light, compact hydrogen storage materials with excellent storage characteristics will be developed to build up the basis for the wide use of the ultimate clean vehicles.

The automobile industry is an integrated industry that has a great propagation effect on supporting industries and has large-scale production and economic effects in the global market. The fuel-cell-powered vehicle belongs to one of the fields in which Japan has competitive technological capability that can lead the world. It holds great significance for Japan to lead the world in the development of fuel-cell-powered vehicles not only with the international contribution Japan makes as a forerunner of global environmental conservation activities but also for the maintenance and development of Japan's industrial competitiveness.

To realize a hydrogen energy society, the final picture of ultimate clean energy systems that start with renewable energy must be drawn as a long-term vision. On the other hand, it is also indispensable for the social acceptance and propagation of hydrogen energy to draw up intermediate strategic scenarios. Through realistic promotional measures including effective utilization of fossil energy and educational campaigns, creation of an atmosphere of public acceptance, establishment of regulations and systems, and standardization should be promoted.

Acknowledgements

The authors wish to express their profound gratitude to the following people for their valuable advice and information: Honorary Professor Takuya Homma of Tsukuba University, executive director of the Fuel Cell Development Information Center; Professor Yasukazu Saito, Department of Industrial Chemistry, Faculty of Engineering, Tokyo University of Science; Mr. Kazukiyo Okano, director of the Hydrogen Energy Systems Society of Japan; and Mr. Shoji Tange, general manager of FCEV Center, Japan Electric Vehicle Association.

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(Original Japanese version: published in February 2003)