Carbon-hydride Energy Storage System

Hajime Emori
Toru Kawamura
Takao Ishikawa
Tetsuo Takamura

OVERVIEW: The carbon-hydride energy storage system stores hydrogen, which is difficult to handle, in the form of the stable liquid methylcyclohexane, thereby making it easy to transport and keep hydrogen in long-term storage as an energy medium. Since this makes it easy to convert energy into hydrogen for storage and reuse, it can contribute to the stable supply of renewable energy such as wind power, which fluctuates greatly. Expectations are high for this system as a means of improving Japan's energy self-sufficiency ratio by helping expand the use of renewable energy and accelerating the achievement of a low-carbon hydrogen society. Based on a 2011 contract with the National Institute of Polar Research, Hitachi, Ltd. has been working in the city of Nikaho in Akita Prefecture on the development of a practical version of this system while acquiring basic data that will, among other things, help improve the energy self-sufficiency ratio of Antarctica in the future.

INTRODUCTION

THE carbon-hydride energy storage system (CHES) makes it easy to store and transport large quantities of renewable energy such as wind and photovoltaic power, which fluctuates greatly. The electric power generated using renewable energy is converted into hydrogen, which is itself converted into methylcyclohexane (MCH), thereby transforming the energy medium of hydrogen into a form that is easy to handle. As a result, the excess amounts of wind power, photovoltaic power, and other forms of renewable energy where it is difficult to provide supply that matches demand can be stored for long periods of time, making it possible to achieve a stable energy supply.

This system, which makes it possible to store energy for a long period of time, can contribute to energy self-sufficiency in regions where the supply of renewable energy is a burden. For instance, the fuel currently used at Antarctica's Showa Station is transported by the Antarctica icebreaker Shirase, and it takes up approximately half of the vessel's cargo capacity. Since as energy demand increases in the future, fuel transportation will limit the amount of energy available, and so by obtaining renewable energy that is available in Antarctica itself such as wind and photovoltaic power, the station will need to achieve energy self-sufficiency. Antarctica faces the polar night without sun during winter, however, and the sun never goes down during the midnight sun period of summer. This is why Antarctica is an ideal candidate region for testing this system by acquiring large amounts of photovoltaic energy during summer for storage and reuse (re-generation) during winter.

As the case with Antarctica, expectations are high in a wide range of different scenarios for systems that can continuously supply stable renewable energy that enables self-sufficiency, including remote islands or international peace-keeping operations by Japan Ministry of Defense where energy supplies are unreliable, or disaster regions where externally supplied energy is not available due to isolation caused by the disaster.

This article provides an overview of the efforts of Hitachi with regards to CHES, and in particular describes the demonstration that was conducted in the city of Nikaho in Akita Prefecture based on a 2011 contract with the National Institute of Polar Research (an Inter-University Research Institute Corporation Research Organization of Information and Systems).

OVERVIEW OF CHES

The use of storage batteries is being considered as an efficient means of energy storage. However, when storage batteries are used to store energy, there are problems such as natural discharge over long periods of time, the volume necessary for large-scale storage, transport (weight) issues, cost, and other issues, all of which make storage batteries suitable for short-term electric power storage, but not suitable for long-term, large-scale energy storage and transport. In response to these issues, CHES uses a type of organic hydride called MCH as the energy storage medium.

Characteristics of MCH

"Organic hydride" is a general term for a hydrogenated aromatic compound that is obtained by adding hydrogen to an aromatic compound. Organic hydrides can use the reversible reactions hydrogenation and dehydrogenation with a catalyst to exchange hydrogen with an aromatic compound. The hydrogenation reaction is exothermic and the dehydrogenation reaction is endothermic, and these reactions can be used to create a cycle of storing and supplying hydrogen.

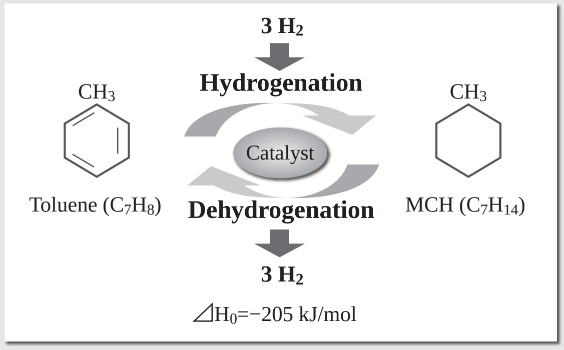
MCH is an organic hydride obtained from a toluene hydrogenation reaction, and both toluene and MCH are stable liquids at ordinary temperatures and pressures (see Fig. 1).

Both toluene and MCH are classified as Class IV petroleum in Category 1 hazardous materials under the Fire Service Act, and therefore offer a benefit whereby existing gasoline storage and transportation equipment and facilities can be used as they are.

The energy storage density offered by MCH is limited by the amount of energy in hydrogen that can be used in the dehydrogenation reaction, or approximately 1.58 kWh/L, which is roughly equivalent to eight times the energy density of a lithium-ion battery (see Fig. 2). Also, when it comes to storage, MCH is a liquid at normal temperatures and can be handled like gasoline, which means that it can be stored in large tanks just like petroleum products, and can be divided into smaller quantities for transport.

The transfer of hydrogen during MCH's hydrogenation and dehydrogenation reactions can be thought of as a means of storing hydrogen. Current mainstream methods of hydrogen storage include high-pressure hydrogen, liquid hydrogen, hydrogen storing alloys, and others, but hydrogen storage using organic hydrides is an extremely strong candidate as a storage method due to the aforementioned ease of handling and storage density benefits (see Fig. 3).

Organic hydrides include combinations such as benzene/cyclohexane, naphthalene/decalin, and others. Since the benzene in the benzene/cyclohexane combination is carcinogenic and requires careful handling, and the naphthalene in the naphthalene/decalin combination has a melting point of 80°C and is solid at normal temperatures, both of these combinations have problems in terms of practicality. The parts of the toluene/MCH combination are easy to handle and obtain, and are superior in terms of toxicity levels as well, making them an extremely practical type of organic hydride.



	MCH	Toluene	Class III light oil	Gasoline
Distillation temperature (°C)	100.4	110.6	175 or higher	17 to 220
Solidification point (°C)	−126	−95	−37.5	−40

MCH: methylcyclohexane

Fig. 1—MCH Hydrogenation and Dehydrogenation Reactions and Temperature Characteristics.
Toluene (C_7H_8) becomes MCH (C_7H_{14}) after a hydrogenation reaction (exothermic reaction) with three hydrogen molecules. MCH emits toluene and three hydrogen molecules after a dehydrogenation reaction (endothermic reaction). Both MCH and toluene are liquids at ordinary temperatures.

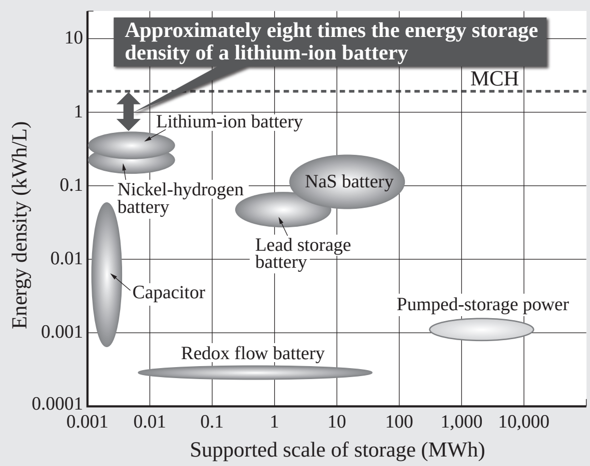


Fig. 2—Comparison of Energy Densities and Possible Scales of Storage Using Different Energy Storage Methods.
The energy density of MCH is approximately eight times that of a lithium-ion battery. The amount of MCH that can be stored depends on the volume of the storage tank, as with other petroleum products.

Principles and Issues of CHES

CHES is comprised of the following three subsystems (see Fig. 4).

(1) Hydrogen generation subsystem

This subsystem generates hydrogen by using the electric power derived from renewable energies such

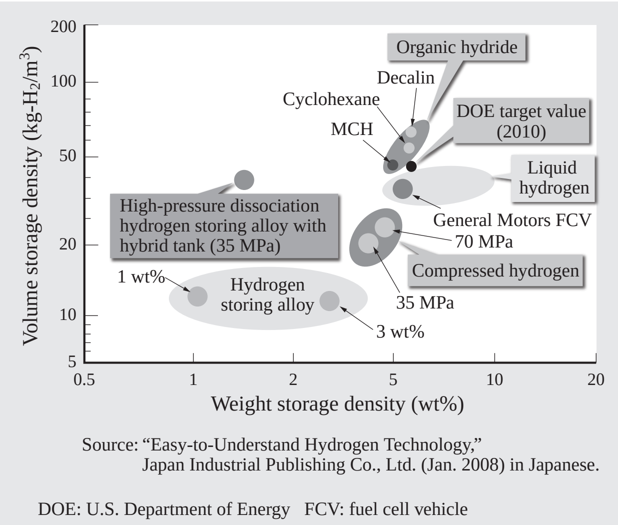


Fig. 3—Comparison of Storage Efficiencies Using Different Hydrogen Storage Methods.
This figure compares the storage efficiency of various hydrogen storage methods. Organic hydride is also an effective method from the perspective of hydrogen storage density.

as wind or photovoltaic power, excess power, or other sources of energy to electrolyze water using a water electrolyzer.

General water electrolyzers are designed for rated operation, and do not respond well to large fluctuations in input. For this reason, it is difficult to efficiently generate hydrogen from renewable energy due to the way it fluctuates.

A water electrolyzer must be developed that can respond to fluctuations in electric power input, so that generated renewable energy can be efficiently recovered, stored, and reused.

(2) Storage subsystem

The hydrogen generated by the hydrogen generation subsystem and the toluene stored in a tank are sent to the hydrogenation device in order to generate MCH through the hydrogenation reaction. The generated MCH is then stored in another tank.

The reactor used for the hydrogenation reaction was large, and there were issues related to reducing the size of the reactor for use in decentralized power supply systems and other situations. In addition, it is necessary to control the amount of toluene supplied based on the amount of hydrogen supplied by the hydrogen generation subsystem.

(3) Re-generation subsystem

The MCH stored in the MCH tank is sent to the dehydrogenator, and a dehydrogenation reaction is used to separate it into hydrogen and toluene. The reaction heat required for this dehydrogenation reaction is supplied using the exhaust heat of a hydrogen combined engine generator.

The separated hydrogen is used in the hydrogen combined diesel engine generator or hydrogen combined gas engine generator to generate electric power and heat, which is then supplied to the consumer. The separated toluene is stored in a tank, and then reused to produce MCH.

Engine control technology is indispensable here in order to optimize the combustion of the hydrogen mixing engine.

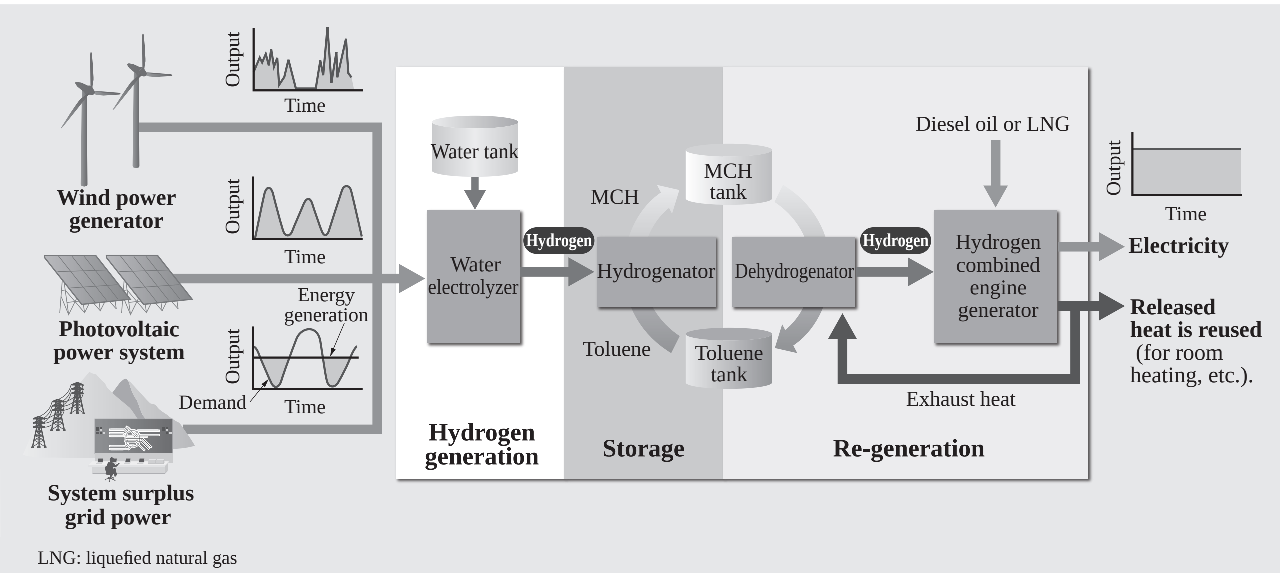


Fig. 4—Configuration of Carbon-hydride Energy Storage System (CHES).
The CHES is comprised of three subsystems: hydrogen generation, storage, and re-generation.

The efficiency of diesel engine generators used in power generation is generally around 40%, with most of the loss due to exhaust heat, and this is the number one cause of reduced energy efficiency in this system. Therefore, the effective utilization of exhaust heat is an issue that must be addressed in order to improve energy efficiency.

Development of CHES

Hitachi has been researching systems using organic hydrides for a long time. The issues described above have already been resolved, and a 40-kW-class demonstration plant has already been built in the city of Hitachi in Ibaraki Prefecture in order to work towards practical application of the system. This plant has implemented high-efficiency water electrolyzers, small and highly efficient hydrogenators, dehydrogenators, and other equipment (see Fig. 5).

This demonstration plant has hydrogen combined diesel engine generators that mix hydrogen in the diesel generator during combustion, which has been verified to reduce diesel oil consumption by approximately 30%. The plant where these facilities are installed is implementing on-site microgrid demonstrations such as wind power generation facilities, photovoltaic power facilities, power cogeneration facilities, large-scale lead storage batteries, and other experiments. There are plans to collaborate with these facilities as well.

(1) High-efficiency water electrolyzer

In order to resolve the hydrogen generation subsystem issue of responding to fluctuations in electric power input due to the use of renewable energy, a specially developed electrode material was adopted for use in the water electrolyzer that offers excellent corrosion resistance and responsiveness. Furthermore, by partitioning the electrolyzer into a large number of cells and controlling the number of operating cells in realtime based on the amount of electric power input , each electrolyzer cell can be run under the most efficient conditions possible, thereby achieving a high level of electrolysis efficiency that corresponds to fluctuations in input (see Fig. 6).

(2) Compact high-efficiency hydrogenator/dehydrogenator

The hydrogenator/dehydrogenator used in the storage subsystem and re-generation subsystem has optimized physical properties in the catalytic surface, and catalytic material was developed that is suited to both hydrogenation and dehydrogenation reactions based on temperature and pressure conditions (see Fig. 7).

Fig. 5—40-kW Class Cycling Renewable Energy Demonstration Plant.
A 40-kW-class demonstration plant was built in the city of Hitachi in Ibaraki Prefecture, and is being used to develop practical applications of CHES.

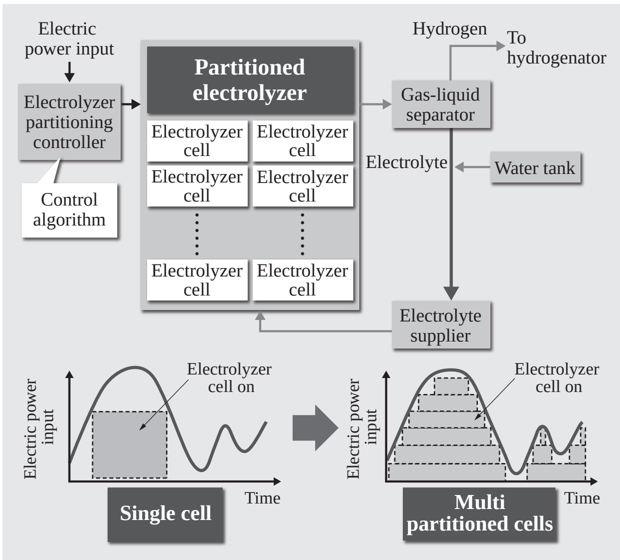


Fig. 6—Water Electrolyzer Features.
The electrolyzer cell is split into many segments in order to follow the fluctuations in electric power input and constantly operate at the ideal voltage, thereby achieving high-efficiency electrolysis.

The reactor's heat transfer path was optimized, and a compact, high-efficiency heat exchange reactor was developed that can be attached to the engine's exhaust pipe for use with the engine's high-temperature exhaust gas. This reactor's hydrogenation reaction occurs at approximately 200°C, and its dehydrogenation reaction occurs at approximately 350°C, both of which are within the range stipulated by the regulations of the High Pressure Gas Safety Act (less than 0.2 MPa). The implementation of this compact high-efficiency reactor means that the system does not suffer from

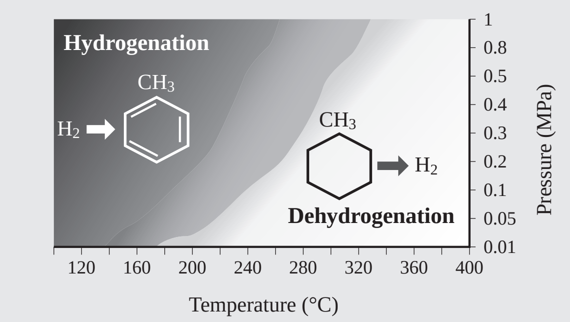


Fig. 7—Characteristics of Catalyst for Hydrogenator/Dehydrogenator.
Hydrogenation and dehydrogenation are switched between based on temperature and pressure conditions. This can be used within the range stipulated by the regulations of the High Pressure Gas Safety Act (under 0.2 MPa).

restrictions in installation locations, and is practical in that it can be adopted for use as a dispersed power source and in other such situations.

Furthermore, by recovering and reusing the heat of the high-temperature exhaust gas, the efficiency of the engine generator was improved by an equivalent of 5%.

CHES Issues and Solutions

The issue facing this system is energy efficiency. With the current system, the ratio of electric power output to input is approximately 30%. Multiple processes must be performed between input and output, and loss accumulates with each one.

Of these processes, the heat lost as exhaust heat at the diesel engine generator is the biggest factor, and the re-generation and reuse of this heat is the key to improving efficiency. Even in the current system, some of the exhaust heat is recovered for the dehydrogenator's endothermic reaction, and the efficiency of the diesel engine generator is improved by approximately 5%, but the remaining exhaust heat must be utilized in order to improve energy efficiency further.

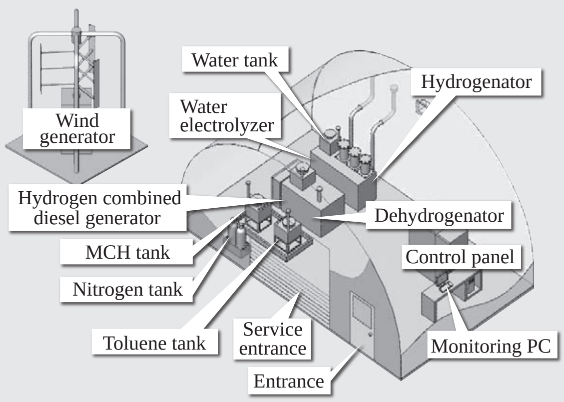
The goal is to recover more than 60% of input energy in the future, including the engine's exhaust heat supply, heat and power supply due to cogeneration, and so on.

DEMONSTRATION IN NIKAHO

Objectives, Test Equipment Configuration, and Test Details

In the future, it is expected that large amounts of renewable energy will be generated in Antarctica at Showa Station, for the station's own use. Based on a contract with the National Institute of Polar Research, Hitachi conducted a demonstration at Nikaho Heights in the city of Nikaho in Akita Prefecture between November 2011 and March 2012 in order to gather basic data that can be used to improve the energy self-sufficiency ratio of Showa Station in the future (see Fig. 8).

The test equipment's engine generator capacity is envisioned with wind generator capacity utilization at between approximately 10% and 15%, and a 3-kW generator was adopted based on the wind generator's rating of 20 kW. Based on a balance between electric power input and the scale of equipment, the water electrolyzer cell tank was split into 16 segments.



Configuration of demonstration testing equipment at Nikaho Heights

Exterior view of building

Exterior view of system

Equipment	Specifications
Wind power generator	20 kW
Water electrolyzer	16-segment electrolyzer cell (volume: 3 L)
Toluene tank	90 L
MCH tank	90 L
Diesel engine generator	3 kW
Hydrogenator	1.28 L
Dehydrogenator	1.28 L

Fig. 8—Demonstration in Nikaho, Akita Prefecture.
The system was connected to a previously installed wind generator owned by the National Institute of Polar Research (an Inter-University Research Institute Corporation Research Organization of Information and Systems) to collect test data.

TABLE 1. Results of Demonstration Testing at Nikaho Heights
Other than the toluene recovery rate, each value is slightly lower at Nikaho Heights.

Performance item	Performance indicator	Test results at factory	Test results at Nikaho Heights
Electrolysis efficiency	Hydrogen production efficiency (%)	65%	61.4%
MCH production rate	MCH production rate (%)	99%	94%
Diesel oil saving	Diesel oil saving rate (%)	23%	22%
H_2 re-generation efficiency (dehydrogenation efficiency)	Dehydrogenation efficiency (%)	85%	82%
Toluene recycle rate	Toluene recycle rate (%)	95%	99.6%
—	Outside air temperature (°C)	Between 14 and 23°C	Between −3 and 2°C

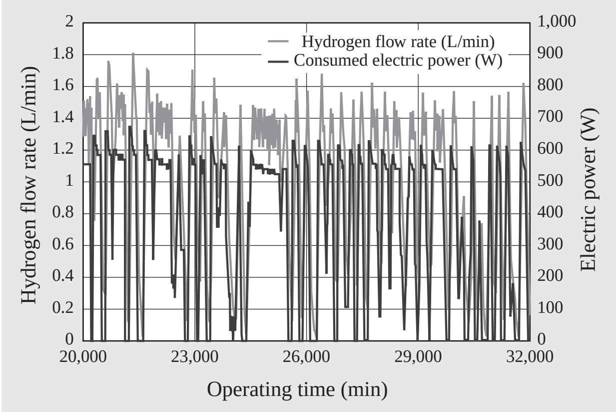


Fig. 9—Water Electrolyzer Responsiveness.
There is a time lag of approximately 10 seconds after fluctuations in electric power, and it was verified that based on a consideration of the buffer caused by pipes and other factors, that this is a good level of responsiveness.

The wind conditions of Nikaho Heights are similar to those of Showa Station because it also has a cold climate, and therefore the results of analyzing CHES characteristics and problems distilled here will be vital information for application to the development of a practical system for use in Antarctica in the future.

Specifically, before the system was sent to Nikaho Heights, factory testing was performed to collect data on 16 items, including the electric power input to the electrolyzer, temperature, density, amount of hydrogen generated, and so on, and the results were compared with the same data acquired on Nikaho Heights in order to analyze characteristics particular to use in a cold climate while distilling issues.

Solutions to these issues will be implemented as the system is prepared for future practical application in Antarctica.

Test Results and Considerations

As a result of testing, diesel oil was reduced by approximately 22%. In addition, the rate of toluene recovery was shown to be more beneficial for vapor-liquid separation as the temperature dropped, with the result that efficiency in this area was higher at Nikaho Heights. On the other hand, electrolysis efficiency, MCH generation rate, and regeneration efficiency were all slightly lower at Nikaho Heights (see Table 1).

When the water electrolyzer's electric power input is compared with the flow rate of generated hydrogen, it was found that there is a time lag of around 10 seconds after the wind generator's input fluctuations, showing that when compared to rated operation during testing within the plant, electrolysis efficiency did not drop drastically with respect to fluctuations in electric power at Nikaho Heights. This delay is thought to be caused by the buffer effect in pipes and other equipment, and the effects of splitting the electrolyzer cell into many segments were verified (see Fig. 9).

It is conjectured that the reductions in electrolysis efficiency, MCH generation rate, and regeneration efficiency were caused by the reductions in catalyst efficiency in the electrolyzer cells and reactor due to the low-temperature environment. Therefore, countermeasures are being considered so that when the system is put to practical use in the future, heat can be retained while heat radiation is inhibited so that the temperature environment of each reaction process is improved based on the ambient temperature, and efficiency can be otherwise improved for each process.

CONCLUSIONS

This article provided an overview of the CHES efforts of Hitachi, and described the demonstration Hitachi conducted in Nikaho, Akita based on a 2011 contract with the National Institute of Polar Research.

Since CHES makes it possible to store the renewable energy generated in Antarctica for long periods of time, and since reuse makes it possible to reduce fuel consumption, it is seen as a way to contribute to resolving Antarctica's energy problems. Also, since it reduces consumption of fossil fuel, it also contributes to a reduction in carbon dioxide (CO_2) without modification.

According to the "Energy White Paper 2011," Japan's energy self-sufficiency ratio is 7%, or 19% if nuclear energy is added. Even when the results of resource development led by Japan is added, the autonomous energy ratio is still as low as 38%, and this shows incontrovertibly that Japan's energy foundation is fragile.

It is imperative that Japan improve its energy self-sufficiency ratio from an energy security perspective, and to this end, expectations are high regarding the prospects of improving the usage ratio of renewable energy. This system offers an easy way to store, transport, and otherwise handle the power generated through renewable energy, which fluctuates greatly. As such, it is a technology that can also contribute to improving Japan's energy self-sufficiency ratio.

For this technology to contribute to improving the energy self-sufficiency ratio, however, the use of the hydrogen energy provided through CHES must expand, diversify, and spread correspondingly. For this to happen, hydrogen must be adopted as fuel for the hydrogen mixed combustion used in thermal power generation, fuel cells, burners, boilers, absorption refrigerators, and other purposes, while a wide range of technologies using hydrogen must be developed, spread, and expanded, including hydrogen engines.

Although the "hydrogen society" has been proposed for a long time, it is unfortunately true that realization of this goal still eludes Japan. Reasons for this include the fact that hydrogen is difficult to handle, and that hydrogen usage technology has not progressed. Hitachi will continue researching and developing this system in the hope that the spread of this technology will help make hydrogen easy to handle, that the growth of hydrogen energy usage technology will gain momentum, and that this will help open the door to a low-carbon hydrogen society.

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ABOUT THE AUTHORS

Hajime Emori

Joined Hitachi, Ltd. in 1982, and now works at the Planning & Engineering Department, Defense Systems Company. He is currently engaged in the commercialization of security systems in the fields of energy and essential facilities.

Toru Kawamura

Joined Hitachi, Ltd. in 1991, and now works at the Electrical Systems Planning Department, Electronics & System Integration Division, Defense Systems Company. He is currently engaged in the design of security systems in the fields of energy and essential facilities.

Takao Ishikawa

Joined Hitachi, Ltd. in 1992, and now works at 221 Unit of the Energy Conversion Electronics Research Department, Central Research Laboratory. He is currently engaged in the development of hydrogen energy and other new energy fields.

Tetsuo Takamura

Joined Hitachi Engineering & Services Co., Ltd. (currently Hitachi Power Solutions Co., Ltd.) in 1976, and now works at the Energy Network Systems Division, Energy System Integration Center, Onuma Works. He is currently engaged in the business of carbon-hydride energy storage (CHES) systems. Mr. Takamura is a member of the Japan Society of Refrigerating and Air Conditioning Engineers (JSRAE).