Concept of Energy Carrier, Candidate Materials, and Reactions

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Abstract The importance of the energy carrier for the utilization of renewable energy has been recognized in recent years because hydrogen is considered a clean and efficient energy source for the near future. Long-term and stable storage of hydrogen should complete its supply chain in the form of energy carriers. Candidate substances for these carriers are liquid hydrogen, organic chemical hydride, and ammonia. For transportation between continents, storage of hydrogen or hydride in stable liquid form is required. Properties, production, transportation, and utilization of candidate materials for energy carriers are summarized.

Keywords Energy carrier • Hydrogen • Ammonia • Fuel cell • Renewable energy

1 Introduction

The ultimate solution to the energy problem is to establish a long-term vision of the energy resource using renewable energy. In this section, solar energy is taken as an example of a highly attractive renewable source. Generally, candidate production sites of electrical and thermal energies from abundant solar radiation and heat are remote from their consumption sites. The amounts of these energies cannot be controlled and change significantly over time and seasons, irrespective of demands. It is very difficult to solve this major obstacle of spatiotemporal differences between renewable energy supply and electricity demand.

Fuel cell power systems have been recently commercialized in several applications such as household cogeneration units and stationary power sources. In particular, vehicle power sources have been attracting attention as clean and efficient generation systems of the near future. In this situation, effective production, supply chain, and efficient utilization of hydrogen are desired to be developed for the construction of a future energy demand and supply framework. Hydrogen is currently produced by conversion of fossil fuels with well-developed catalytic

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reaction technologies, but it is reasonable to transition in the future to energy conversion technologies based on hydrogen produced from renewable sources.

To promote the hydrogen supply based on renewable sources, energy storage media (energy carriers) or hydrogen carriers and their handling systems must be designed and developed. The hydrogen carrier, containing large amounts of hydrogen in molecules, can be transported over long distances and stably stored as liquid. Hydrogen must be easily extracted at consumption sites from the energy carrier. Another possibility is to consume the energy carrier directly as fuel for combustors or fuel cells. In particular, production of energy carriers should be accomplished with utilization of renewable energy as solar heat and power. Battery systems have been developed for energy storage, but their energy density and stability are insufficient compared with the aforementioned energy carrier.

Figure 1 shows a schematic of the flow of materials and energy conversion based on hydrogen. Hydrogen has been produced from fossil fuels by a steam-reforming reaction and coal gasification. The primary energy resource for hydrogen production will shift to renewable energy. Part of the produced hydrogen is converted into energy carrier compounds such as liquid hydrogen, methane, organic chemical hydride, and ammonia for transportation to remote sites with heavy energy demands. The final stage is energy conversion with combustion and fuel cells. There are other possible energy resources, energy carriers, and utilization methods that are not included in the scheme.

Carbon monoxide hydrogenation to hydrocarbon compounds with Fischer–Tropsch (FT) synthesis or the gas-to-liquids (GTL) process has been investigated and partially commercialized as conversion and utilization of fossil fuel during the long history of their development. In the future, however, this technology should be investigated as a possible utilization of renewable energy as energy carrier

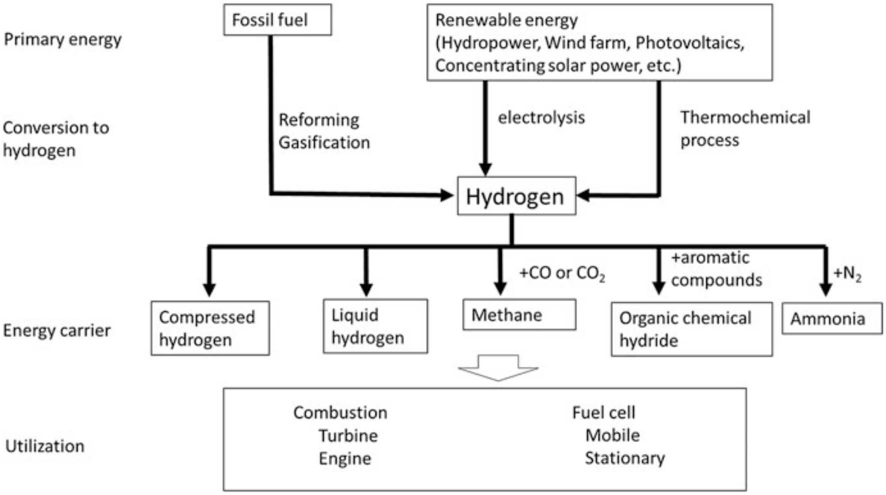


Fig. 1 Production of hydrogen and conversion to energy carriers

production. Various types of energy carrier candidate substances including methanol and methane are expected to find their respective application fields. A direct synthetic route developed recently for dimethyl ether (DME) makes it a candidate for energy carrier. A series of these hydrocarbons and oxygenated compounds are synthesized from $CO+H_2$ synthetic gas or CO_2+H_2 by vapor-phase catalytic processes. Although fabrication of such compounds is currently considered an effective use of fossil fuels, they can be reconsidered as energy storage substances because of their energy density and chemical stability during storage and ease of hydrogen production. However, consumption of this fuel is accompanied by emission of CO_2. Therefore, carbon-free or carbon-neutral technologies without CO_2 emission are the ultimate targets. For such a purpose, liquid hydrogen, organic chemical hydride, and ammonia are beginning to be studied as major candidates for a national project in Japan. Effective synthetic and utilization technologies for such energy carriers were selected as one theme of the Strategic Innovation Promotion Program (SIP) that commenced in 2014 [1].

2 Hydrogen Production

A variety of renewable energies have been considered as possible future resources. Hydrogen production from solar energy is considered the first stage in the design of energy carrier systems. For realizing this system, international development and cooperation with countries in the Sunbelt areas of the world are indispensable. Electrical and thermal energies from sunlight are used for the production of hydrogen and hydrogen carriers. The principal candidate carriers selected in the research program are liquid hydrogen, organic chemical hydride, and ammonia. These energy carriers are transported as liquid by marine transportation to consumption locations such as Japan. Effective conversion of carriers into electrical energy or hydrogen extraction is another important topic. Energy carriers transported to Japan are used in conversion systems such as fuel cells, combustors, and hydrogen-fueled devices.

For the conversion of solar light, photovoltaic cells are commonly used, but the collection of solar heat is attracting attention as concentrated solar power (CSP) [2]. CSP systems have been developed in areas with abundant flat space and sufficient sunlight to produce heat and electricity, through a combination of numerous mirrors and steam turbines. This technology has recently attracted attention for hydrogen production, using abundant electricity and heat. In tower-type power generation by CSP, angles of a number of plane mirrors are computer controlled via heliostats to track sun motion and concentrate sunlight at a collector atop a tower. Thermal energy is transferred to a heating medium and accumulated. The second typical CSP system is a combination of elliptic mirror (parabolic trough) and heating tubes located at the focus. A flowing medium in the pipe is heated by focused sunlight. Other CSP methods have been proposed and developed (Fig. 2). Electricity is generated by a steam turbine from provided heat. Unfortunately, few

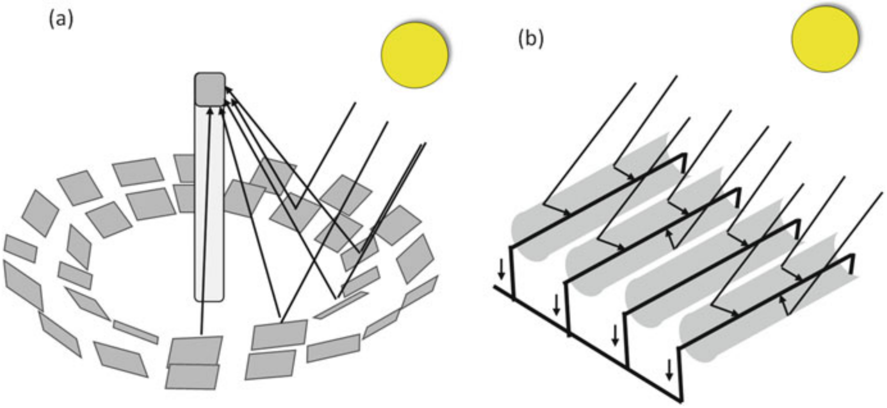


Fig. 2 Types of concentrated solar power systems [2]. (**a**) Power tower, (**b**) parabolic trough

areas have sufficient solar heat for this purpose in Japan. There is no large-scale proof-of-concept example in the country, but investigation continues in European countries such as Spain, in the United States, and in other countries. Overseas resources are also attracting attention regarding the use of wind energy.

Thermochemical water splitting and water electrolysis have been considered hydrogen manufacturing processes using renewable energy. Thermochemical processes constructed with sulfur and iodine compounds have been studied in the energy carrier project (Fig. 3). These processes were developed earlier for utilization of heat from nuclear reactors, including gas-cooled fast reactors. Suitable processes have begun to be pursued for high-temperature thermal energy from renewable sources. The iodine–sulfur (IS) process is composed of multiple processes through conversion of iodine (I) and sulfur (S) compounds. This produces hydrogen (H_2) and oxygen (O_2) by splitting water in multistage reactions, with inputs of water (H_2O) and high-temperature heat during the process [3].

Bunsen reaction, exothermic

$$I_2 + SO_2 + 2H_2O \rightarrow 2HI + H_2SO_4 \tag{1}$$

Decomposition of hydrogen iodide, weakly endothermic

$$2HI \rightarrow H_2 + I_2 \tag{2}$$

Decomposition of sulfuric acid, endothermic

$$H_2SO_4 \rightarrow H_2O + SO_2 + 0.5\,O_2 \tag{3}$$

Hydrogen production by the electrolysis of water is another candidate process for hydrogen production from renewable energies. Electrolysis of concentrated aqueous alkaline solution is widely done, using low-carbon steel or nickel as

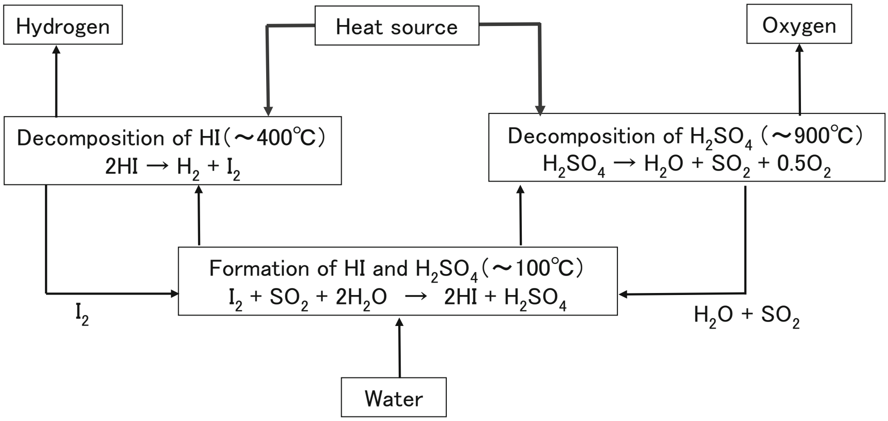


Fig. 3 Outline of thermochemical IS process [3]

electrodes [4]. The metal electrodes are immersed in concentrated KOH solution in the electrolysis batch, in which a porous diaphragm is located to avoid mixing formed hydrogen and oxygen at cathode and anode sides, respectively. As gaseous bubbles are vigorously generated with enhanced electrolysis current, gas diffusion resistance becomes dominant.

Anodic reaction

$$2\,\mathrm{OH}^- \rightarrow \mathrm{H_2O} + 1/2\mathrm{O_2} + 2\,\mathrm{e}^- \tag{4}$$

Cathodic reaction

$$2\,\mathrm{H_2O} + 2\,\mathrm{e}^- \rightarrow \mathrm{H_2} + 2\,\mathrm{OH}^- \tag{5}$$

Water electrolysis using a proton-exchange membrane has been developed in accordance with commercialization of proton-exchange membrane fuel cells (PEMFCs). Polymer electrolyte fuel cells (PEFCs) are popular. In this section, however, the term PEMFCs is used to distinguish them from anion-exchange membrane fuel cells (AEMFCs). Water electrolysis using PEM has been commercialized for practical use. Small hydrogen production devices, e.g., for gas chromatography, are popular, and larger systems are in operation. Iridium-based alloy electrodes are attached on the PEM because of rapid degradation of the Pt-based electrodes. The produced hydrogen and oxygen, being separated by the PEM film, are less mixed with each other than in the conventional electrolysis method. Highly concentrated hydrogen of $>99.999\,\%$ purity can be produced without further purification.

Anodic reaction

$$H_2O \rightarrow 2\,H^+ + 1/2O_2 + 2\,e^- \tag{6}$$

Cathodic reaction

$$2\,H^+ + 2\,e^- \rightarrow H_2 \tag{7}$$

Pressurized hydrogen is also produced electrochemically by this method. The PEM should be reinforced by a metallic mesh to tolerate the strong differential pressure that develops between the hydrogen and oxygen chambers. The Nernst potential corresponding to the pressure difference is supplied to the electrodes, which is equivalent to the electrochemical potential estimated from that difference.

In recent years, solid oxide fuel cell (SOFC) systems have been commercialized using the yttria-stabilized zirconia (YSZ) solid electrolyte. The operational temperature of the household cogeneration system is set to ~750 °C. Electrolysis cells with reverse operation of SOFCs have also been actively investigated. Solid oxide electrochemical cell (SOEC) systems are superior to other electrolysis processes in their greater reversibility near the open circuit. The high operational temperature of SOEC also reduces the theoretical decomposition voltage E°; since E° originates from the free energy, ΔG°, from the water decomposition reaction of $H_2O \rightarrow H_2 + 1/2\ O_2$, is $\Delta G^\circ = nFE^\circ$. Thus, E° decreases with increasing electrolysis temperature. A large margin of the endothermic region is thus created in the I–V characteristics of SOEC. Therefore, a combination of SOEC with heat storage material is considered an effective regenerative cell.

3 Hydrogen Storage and Carrier

Among the variety of energy storage technologies, some with different concepts are competing. For storage of electricity, secondary batteries are considered important for transportation, stationary systems, and portable applications. The application area of hydrogen carriers partially overlaps with that of batteries. A high-pressure hydrogen container is put to practical use in fuel cell electric vehicles (FCEVs) and batteries and in capacitors for electric vehicles. Metal hydrides are also developed for hydrogen storage and hybrid tanks of such containers. A series of secondary batteries has been used as portable devices for electricity storage. The most suitable device or energy storage system is chosen from a variety of methods to achieve convenience and suitability. Selection and differentiation between energy carrier storages are possible for a typical usage, but there are several competing energy storage methods, including energy carriers, in many application fields. Therefore, introduction of an energy carrier system should be carefully considered based on introduction period, location, application, and cost. Some candidate materials for hydrogen carriers are compared in Fig. 4 for their gravimetric and volumetric

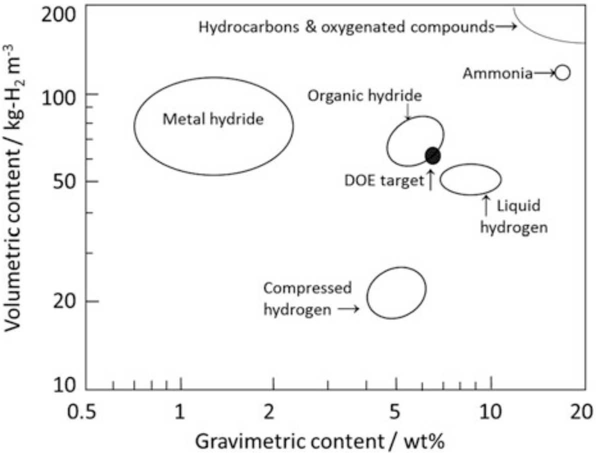


Fig. 4 Volumetric and gravimetric hydrogen contents of various compounds. x and y axes have logarithmic scales

contents of hydrogen. Either volumetric or gravimetric content is high for hydrocarbons and their oxygenated compounds, such as methanol, ethanol, and dimethyl ether. However, these compounds have been developed for effective utilization of fossil fuels. These fuels are accompanied by the formation of carbon dioxide with hydrogen production. Ammonia, organic chemical hydride, and liquid hydrogen demonstrate acceptable hydrogen contents compared with US Department of Energy (DOE) targets. Metal hydrides and compressed hydrogen are inferior because of their gravimetric and volumetric contents, respectively.

Some example compounds for hydrogen are described in Table 1 along with liquid and pressurized hydrogen. Hydrocarbons and oxygenated compounds produce a large amount of hydrogen via the reforming reactions. Steam reforming of higher hydrocarbons generates a greater volumetric production amount per unit volume of liquid. These processes are adopted in petroleum refining industries.

In the production of methanol and DME, solid catalysts are important in their synthesis at high pressures. Hydrogen production from these compounds involves steam reforming of methanol and dimethyl ether over solid catalysts. For reforming of DME, water is mixed with it to produce substantial amounts of hydrogen. DME is attractive as a carrier owing to its lower reforming temperature relative to hydrocarbons [5]. This catalysis series has been developed as clean fuel conversion processes using synthetic gas derived from fossil fuels. Hydrocarbon and methane fuels are produced by FT synthesis and methanation reaction, respectively. Fuels from FT synthesis or the GTL process can be directly used in currently available oil infrastructure.

Ammonia and organic chemical hydride are expected to be compatible with various applications for storage as an energy carrier material. However, efficiencies of the various applications are not clearly understood. These applications include long-distance transportation without degradation. For their acceptance as new energy storage media, life-cycle assessment (LCA) is necessary for choosing

Table 1 Candidate compounds and properties for energy carrier

Energy carrier	Density of hydrogen (kg-H_2/m^3-liq.)		Boiling point (°C)	Reaction enthalpy, ΔH_r° (kJ/mol-H_2)
	In molecule	Formed hydrogen		
Ammonia, NH_3	120	–	−33.3	–
$2NH_3 \rightarrow N_2 + 3H_2$	–	120	–	31
Methylcyclohexane, C_7H_{14}	110.0	–	101	–
$C_7H_{14} \rightarrow C_7H_8 + 3H_2$	–	47	–	68
Methane, CH_4	106		−162	–
$CH_4 + H_2O \rightarrow CO_2 + 3H_2$		212	–	69
Methanol, CH_3OH	99		64.7	–
$CH_3OH + H_2O \rightarrow CO_2 + 3H_2$		148	–	16
Dimethyl ether (DME), CH_3OCH_3	96	–	−24.8	–
$(CH_3)_2O + 3H_2O \rightarrow 2CO_2 + 6H_2$	–	192	–	20
Liquid hydrogen	71		−252	
Compressed hydrogen (70 MPa)	39 (kg/m^3-gas)		–	

from various candidate materials, with consideration of new manufacturing methods, conversion to electricity, energy interconversion, and chemical properties.

Candidate compounds for energy carriers in Table 1 are ammonia, methylcyclohexane, methane, methanol, and dimethyl ether, as well as liquid hydrogen. Among these, ammonia, methylcyclohexane, and liquid hydrogen are not accompanied by the formation of carbon dioxide in hydrogen recovery processes. It is reported, for example, that methylcyclohexane and ammonia are proven as chemical substances of the energy carrier candidates. Characteristic properties of each energy carrier material should be clarified for selection of the most suitable system, from utilization of a renewable source to conversion into consumer energy. Examples of such properties are hydrogen production reaction, energy carrier production, stability during storage and transportation, safety, and conversion into electricity and combustion energy. The boiling point of a carrier compound is important for liquefaction and transportation, because transportation in liquid form over long distances can be effective.

For hydrogen extraction from an energy carrier, catalytic reactions at elevated temperatures are required. For effective energy utilization, fuel cells with various operational temperatures are receiving attention. Typical temperature ranges of catalytic hydrogen production from hydrocarbons and energy carrier materials, hydrogen production by electrolysis, and driving temperature ranges of the fuel

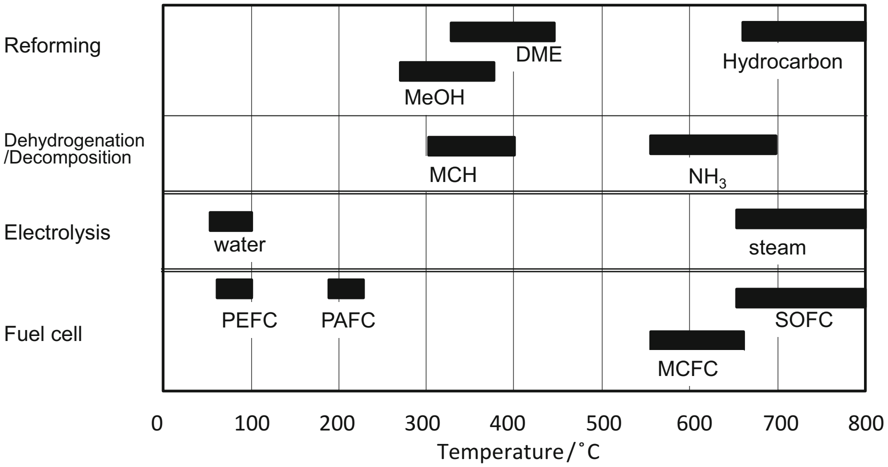
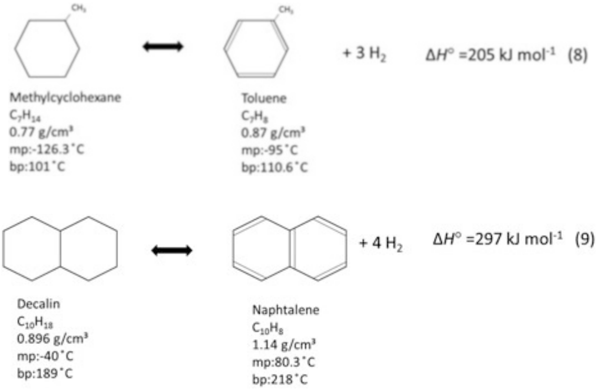


Fig. 5 Operational temperature ranges of hydrogen production and fuel cell systems. *DME* dimethyl ether, *MCH* methylcyclohexane, *PEFC* polymer electrolyte fuel cell, *PAFC* phosphoric acid fuel cell, *MCFC* molten carbonate fuel cell, *SOFC* solid oxide fuel cell

cells are summarized in Fig. 5. For hydrogen production, heat supply in each temperature range is necessary to compensate endothermic heat of the reforming or dehydrogenation reaction and to advance hydrogen production at an energy-consuming site. The source of this heat supply determines the effectiveness of the overall energy carrier system. Further investigation is required for most energy carrier systems to optimize efficiency. For example, endothermic heat in a reformer or cracker is chemically recovered by Joule's heat and thermodynamically emitted heat from a generator with a high-temperature fuel cell, if the temperature range is compatible. A combination of reactors constitutes a system of high efficiency, because combustion and fuel cell generation are exothermic reactions.

Several candidate materials of energy carriers, such as ammonia (NH_3), DME, methanol, and methylcyclohexane, can be considered for their ease in liquefaction, such that large amounts of hydrogen are stored in liquid form. Liquefaction of hydrogen accompanies its high purity because of a low melting point. High-purity hydrogen is attractive as a carrier and for its direct connection to the supply chain. Hydrogen is cooled and liquefied by Joule–Thomson expansion. Hydrogen liquefaction requires substantial energy for cooling. In addition, part of the liquid hydrogen vaporizes to be lost by boil-off, because of the extremely low boiling temperature during transportation. It is crucial to technically minimize this boil-off during long-distance transport. Although the high purity is desirable, the density of liquid hydrogen is generally less than other liquids.

Organic chemical hydrides have been proposed as future energy carriers and have been actively investigated. Because the hydrogenation and dehydrogenation processes use hydrocarbon-based technology, these hydrides are superior for direct use of existing infrastructure in oil storage and transportation. The process initiates catalytic production of cycloparaffin by hydrogenation of an aromatic compound at energy-abundant sites. The cycloparaffin oil is then converted by dehydrogenation for extraction of hydrogen. The energy carrier cycle is withstood either using energy and sources of fossil fuels or solar energy. The key technology for the process is catalytic dehydrogenation of cycloparaffin to obtain hydrogen. Methylcyclohexane and decalin have been recently considered candidates for energy carrier compounds and are called organic chemical hydrides.



The Chiyoda Corporation proposed to store methylcyclohexane as organic chemical hydride via toluene hydrogenation [6]. Discovery of a new active catalyst for dehydrogenation advanced organic hydride systems for practical use. A toluene hydrogenation catalyst and reactor have already been developed. As for dehydrogenation, a catalyst with sufficient durability was first developed for implementation. At a hydrogen-consuming site, the heat source to compensate endothermic dehydrogenation is an important factor for realization. Because of the similarity of the physicochemical properties to gasoline or oil, the organic chemical hydride can be adapted to the oil-based infrastructure in operation. This situation is extremely advantageous, since toluene and methylcyclohexane are stored in tanks and stand in for oil. One of the proposed application models is composed of a dehydrogenation reactor for supply to the hydrogen dispenser after on-site purification at the hydrogen stations.

4 Effective Utilization of Energy Carrier

Utilization technology of the energy carrier as fuel must be examined based on efficiency and environmental adaptability. Fuel cells are establishing a position as a stationary generation system of high efficiency. More than 100,000 units of the household fuel cell system with city gas or LPG-reforming reactor were installed by the end of 2014 in Japan, under the brand name “Ene-Farm.” Furthermore, it is most

Table 2 Specification of hydrogen for FCV (ISO14687-2)

Hydrogen purity		99.97 %
Impurity	Total hydrocarbons	2 ppm
	Moisture	5 ppm
	Oxygen	5 ppm
	N_2, Ar	100 ppm
	He	300 ppm
	CO_2	2 ppm
	CO	0.2 ppm
	Sulfur compounds	0.004 ppm
	Formaldehyde	0.01 ppm
	Formic acid	0.2 ppm
	Ammonia	0.1 ppm
	Total halogen compounds	0.05 ppm
	Particle	1 mg/kg

desirable for the energy carrier supply chain to be connected to the hydrogen supply network as a hydrogen station to FCEVs. Hydrogen stations are expected to be readily installed, because FCEVs were commercialized in 2014. Therefore, for realization of the energy carrier, the means of connecting this hydrogen supply network is important. However, production sites with abundant renewable energy are generally remote from consumption sites with strong hydrogen demand. High-purity hydrogen should be stored at hydrogen stations at high pressure to supply FCEVs, to be dispensed at up to 70 MPa. Other gas ingredients and impurity density are strictly limited [7]. High-purity hydrogen can be produced by cryogenic separation or pressure swing adsorption (PSA). The impurity levels summarized in Table 2 are considered acceptable for the introductory commercialization period of FCEVs. These levels may include some safety margins.

Hydrogen separation by means of PSA attains high purity, to 99.99 %. However, it is necessary to use purified hydrogen for cleanup of adsorbate, which is contaminated by impure gases. Thus, production efficiency of a practical PSA unit is reduced to ~70 % of high-purity hydrogen which is consumed for purging adsorbed impurities on adsorbent materials for reproduction.

Progress in effective separation technology is expected by the development of membranes with hydrogen permselectivity. Alloy membranes of Pd-Cu or Pd-Ag have been used, which are mechanically reinforced by mounting on porous metallic or ceramic supports. To ensure mechanical strength and a pinhole-free membrane, the thickness of the alloy membrane is determined, but the permeation rate is often insufficient. It is also difficult to fabricate a pinhole-free membrane, but permeation selectivity is weakened by a small number of membrane defects. Hydrogen separation with tubular porous ceramics is another possible membrane separation process because of its high permeation rate. Improvement of permeation selectivity is essential to realization of this separation method. Stability and reliability of the porous filter film should be attained, because weakening of the permeation rate and selectivity of the film are often caused by impurities such as moisture.

The supply chain and effective use of hydrogen should be developed. However, combustion of energy carriers with gas turbines or other types of heat engines, boilers, and furnaces is considered conventionally. A hydrogen engine and the hydrogen combustion gas turbine are also considered.

5 Ammonia as an Energy Carrier

For the development of carbon-free energy systems, ammonia is considered a promising candidate as an energy carrier. The amount of synthetic ammonia exceeds 150 million tons per annum by the Haber–Bosch process. Large quantities of ammonia are consumed as agricultural fertilizer and as a base chemical for various derivative compounds. Haber–Bosch has been a well-established technology for ammonia synthesis from its invention in 1906, for which doubly promoted iron has been used as a catalyst. Since the reactor is compact to function under elevated temperature and pressure, the Haber–Bosch method remains superior to other catalytic systems.

A Ru-based ammonia synthesis catalyst, first discovered by Aika and Ozaki in 1992, is known to be more active than Fe-based catalysts. Recently, active Ru-loaded electrode $[Ca_{24}Al_{28}O_{64}]^{4+}(e^{-})_4$ catalysts were reported to be more active than other ammonia synthesis catalysts [8, 9]. Ammonia has not been synthesized or used as an energy carrier or fuel thus far. An international conference on ammonia fuel is held every year in the United States [10], and ammonia is gradually attracting more attention as an energy carrier or fuel. Clearly, the catalysts are keys in the production and utilization of ammonia fuel.

Direct combustion of ammonia in internal combustion engines has been studied. An early-stage example is an ammonia-fueled engine for a bus, tested in Belgium in 1940. Recently, an Italian automobile company, Marangoni Corporation [10], succeeded in driving a sports car with hybrid LPG/ammonia fuel equipped with an engine made by Toyota [11]. National Institute of Advanced Industrial Science and Technology (AIST) in Japan operated a 20-kW gas turbine with fuel mixture kerosene and ammonia in 2014. As shown by these examples, direct combustion of ammonia by engines is feasible. Further investigation is necessary for other internal combustion engines burning pure ammonia fuel.

One problem of ammonia combustion systems is NO_x formation. Thermal NO_x emitted at high temperature is problematic in hydrocarbon combustion, but fuel NO_x mainly contributes to ammonia combustion in the ignition stage. Fuel NO_x decreases with temperature toward the equilibrium concentration, until the thermal NO_x emission becomes dominant. Furthermore, ammonia is less flammable relative to hydrocarbons. The stable combustion range of air/fuel ratio is narrow, and combustion is slow. Therefore, the combustion mechanism and characteristics are worth studying [12].

When the effectiveness of ammonia as an energy carrier is accepted, it will receive attention for supplying fuel cell generators with higher efficiency. Direct

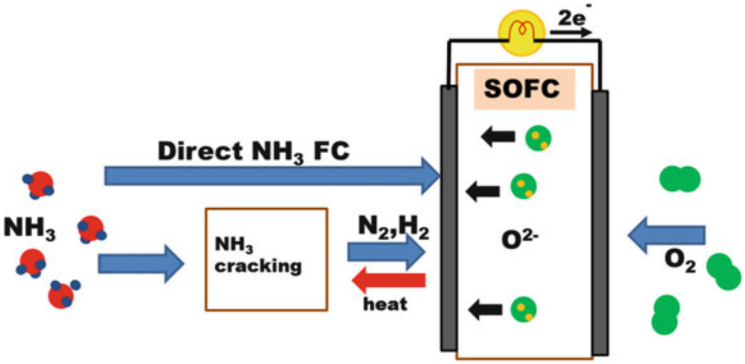


Fig. 6 Solid oxide fuel cell based on internal decomposition of ammonia

supply of ammonia to a fuel cell leads to a simplified system with high-efficiency generation. From the standpoint of compatibility with ammonia fuel, the anion-exchange membrane type of fuel cell, which possesses conductive OH^- ions and a SOFC with conductive O^{2-} ions, is a candidate type [12].

Operational SOFC temperatures are 700–900 °C, and NH_3 decomposition with endothermic heat readily proceeds in a catalytic reactor operated at such high temperatures in the fuel cell chamber with the aid of effective transfer of exothermic heat from the SOFC. A supported Ru catalyst is known to be most active for this decomposition. However, a noble metal catalyst is unnecessary. This is because the supported Ni catalysts demonstrate sufficiently high conversion, owing to the high temperature even with indirect internal decomposition operation (Fig. 6).

As a result of screening of various inexpensive base metal catalysts, supported nickel catalysts showed sufficient activity for decomposition of ammonia in the operational SOFC temperature range. The activity of a Ni/Al_2O_3 system was high because of the large surface area of the support [13, 14].

The high operational temperature and activity of Ni–YSZ cermet enables direct supply of ammonia to the electrode (Fig. 6), which simplified the system. It is also possible to introduce ammonia to the SOFC stack in the direct internal decomposition operation. For direct introduction of ammonia, the following electrochemical process can be expected.

Anodic reaction

$$2\,NH_3 + 3\,O^{2-} \rightarrow N_2 + 3\,H_2O + 6\,e^- \tag{10}$$

Cathodic reaction

$$3/2\,O_2 + 6\,e^- \rightarrow 3\,O^{2-} \tag{11}$$

A possible alternative process is combination of thermal catalytic decomposition and electrochemical oxidation of hydrogen.

Thermal catalytic reaction

$$2\,NH_3 \rightarrow N_2 + 3\,H_2 \quad (12)$$

Anodic reaction

$$H_2 + O^{2-} \rightarrow H_2O + 2\,e^- \quad (13)$$

Cathodic reaction

$$1/2\,O_2 + 2\,e^- \rightarrow O^{2-} \quad (14)$$

The reaction process is estimated from the open-circuit voltage of the aforementioned reactions (Reactions 10 and 11 or Reactions 13 and 14). Actually, ammonia is decomposed catalytically into hydrogen and nitrogen on the electrode surface and subsequently converted by electrochemical oxidation of hydrogen processes. Exothermic heat from the fuel cell unit (electrochemical oxidation) is effectively used, resulting in high efficiency.

A hydrocarbon-based polymer with the quaternary ammonium ion incorporated in the chain is the low-temperature anion-exchange membrane (AEM). A fuel cell with AEM electrolyte has been investigated as an OH^- ion conductive device. Because the operational temperature of AEMFCs is ~50 °C, hydrogen is supplied from an external ammonia decomposition reactor. Ammonia is less harmful to this membrane than a proton-exchange membrane type, and residual ammonia is permitted to some extent. However, because an atomic nitrogen adsorption formed by dissociation of ammonia becomes a catalyst poison for the Pt electrode, concentrated ammonia cannot be introduced directly.

6 Conclusions

Production, transportation, and effective utilization of energy carrier materials are important technologies in the realization of future energy networks using renewable energy. Materials development in conjunction with system design and evaluation is critical in the realization of energy carrier systems using renewable energy.

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