Development of Hydrogen Production Technology Initiative to Create Decarbonized World

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Against the backdrop of accelerating energy transition across the world, it is urgent need to achieve carbon neutrality in Gas Turbine Combined Cycle (GTCC) and steam power generation systems, which are the main products of Mitsubishi Heavy Industries, Ltd. (MHI). Decarbonization of these thermal power generation systems necessitates developing not only decarbonization technologies for power generation facilities but also hydrogen production technologies, which will be an alternative fuel.

MHI is developing both power generation facilities and hydrogen production systems. Focusing on hydrogen production technologies, which were reported in the past in relation to the Hydrogen Park TAKASAGO and the Carbon Neutral Park NAGASAKI(1)(2), this report presents their technological characteristics and progress in the development.

1. Introduction

Solving global warming problems is critical to humanity. In October 2020, along with the growing momentum of international climate action such as the Conference of Parties (COP) on climate change, the Japanese government declared its intention of achieving “carbon neutrality” by reducing greenhouse gas emissions to net zero by 2050. The term “net zero” means that the total amount of greenhouse gases including carbon dioxide (CO_2) becomes practically zero, when calculating the amount of “(artificial) emissions” minus the amount of “(artificial) absorption” through means such as afforestation and forest management. To achieve such carbon neutrality, it is indispensable to substantially expand the use of renewable energy. Simultaneously, it is also important to maintain economic efficiency and stable energy supply. MHI aims to achieve a carbon-neutral society in a realistic and speedy way, while minimizing social costs by promoting energy transition of existing thermal energy facilities, e.g. power stations, chemical plants, and so on.

Renewable energy greatly contributes to the achievement of a carbon neutral society. However, because weather is easy to change, the output from sources such as solar and wind is quite variable, making it difficult to respond to the demand that significantly changes every minute. The expansion of the use therefore requires the introduction of energy storage technology. In general, lithium batteries are advantageous for storing energy for a short period of time, but for a relatively long period of time, such as days or weeks, it is advantageous to convert it into chemical energy such as hydrogen, which can be stored and transported.

Since the 1980s, MHI has been engaged in developing products based on the chemical energy conversion technology such as Solid Oxide Fuel Cell (SOFC), Polymer Electrolyte Fuel Cell (PEFC), hydrogen production by water electrolysis using a Proton Exchange Membrane (PEM), and production of carbon nanotubes using a fluidized bed reactor. With regard to the hydrogen value chain (**Figure 1**), MHI has taken part in World Energy NETwork (WE-NET) (3)(4) and accumulated

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technologies are now attracting attention again. Zooming out to the world, we can see each region requiring different types of technologies etc., depending on the regional characteristics. Therefore, we reconsidered what types of hydrogen production technologies would be in demand worldwide and conducted in-house stocktaking of the knowledge before resuming work on their development. This report presents our progress in technological development for producing hydrogen and synthetic fuel, both of which are indispensable for achieving a decarbonized society.

Figure 1 Schematic representation of WE-NET(5)

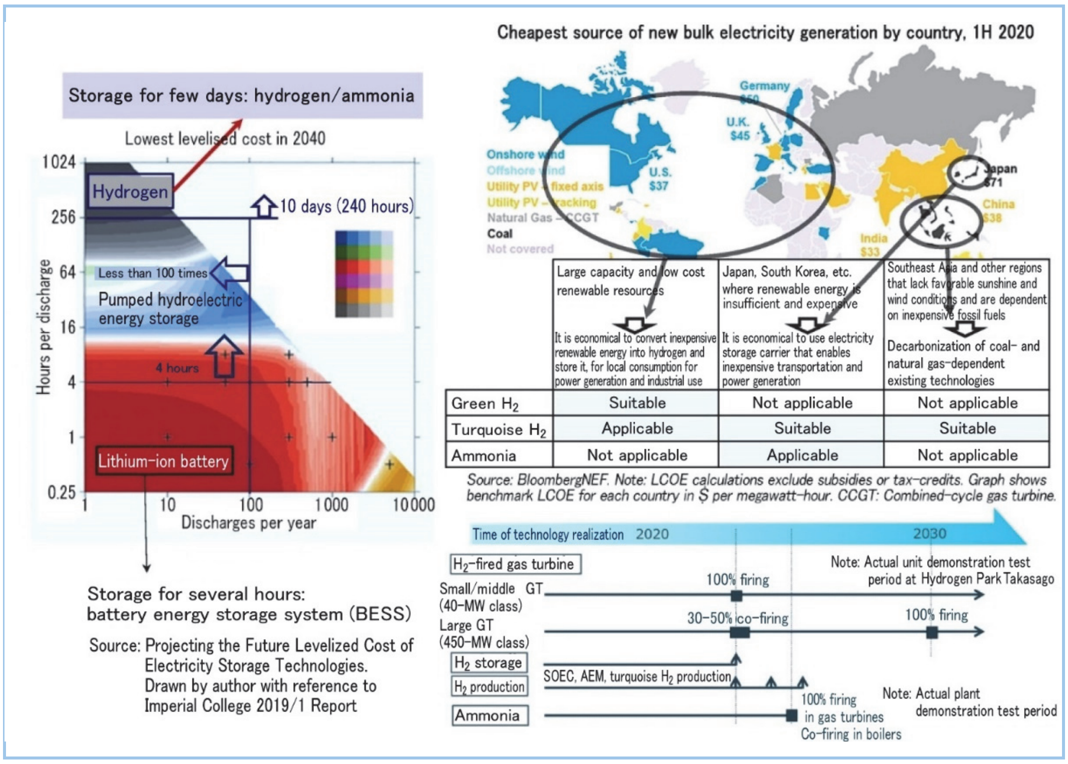
2. Summary of MHI’s hydrogen production technology

Having declared “MISSION NET ZERO”, MHI Group intends to achieve carbon neutrality Net Zero CO_2 emissions from the group’s production activities and the entire value chain by 2040 concerning. MHI Group also aims to offer products and technologies that can make it viable for customers to achieve carbon neutrality by 2050. Our major undertakings include the energy transition for low-carbonization and decarbonization of businesses/products, and the expansion of carbon capture utilization and storage (CCUS) including CO_2 capture and contribute to creating a carbon neutral society.

Figure 2 gives the background of hydrogen and ammonia utilization. As mentioned earlier, the introduction necessity of energy storage technologies and the strengths of each technology are as follows. Lithium batteries are advantageous for short-time storage, while conversion to chemical energy such as hydrogen is advantageous necessary for storing energy for a relatively long period of time such as days and weeks. The right side of Figure 2 shows the regional characteristics of renewable energy resource. It is expected that the use of renewable energy will become more common across many regions of the world and that hydrogen products produced through water electrolysis by using surplus renewable electricity will become widely used. On the other hand, in regions that are not rich in renewable resources such as Japan and South Korea, the application of ammonia with a high transportation efficiency will take precedence. There are also high expectations for turquoise hydrogen, which can be produced using existing natural gas infrastructure. Specifically, the production process is the pyrolysis of natural gas and is characterized by the by-product of solid carbon. As versatile as it may be, the term decarbonization can pertain to different technologies depending on the needs of each region, whose verification and social implementation are a matter of urgency.

Inexpensive hydrogen is needed to cut the social costs incurred by growing out of fossil fuels. As almost all of the cost of electrolytic hydrogen production is attributed to electricity, high-efficiency energy conversion technology is required. Moreover, many of the hydrogen applications involve pressures as high as several MPa. The power used for hydrogen compression considerably decreases the overall system efficiency. Because generally energy consumption can be reduced for liquid pressurization than gas compression, it is desirable to have the equipment that can electrolyze high-pressure water or steam.

In order to first focus on the utilization of hydrogen for power generation, MHI’s Energy Systems Domain is working on the development of three types of hydrogen production technologies: (1) Solid Oxide Electrolysis Cells (SOEC), (2) Anion Exchange Membrane (AEM) water electrolysis, and (3) production of turquoise hydrogen by methane pyrolysis which can achieve high pressure, high-efficiency and large-capacity. Synthetic fuel production technologies in which these electrolyzers are employed are also in development. The lower right of Figure 2 shows the technological development road map for decarbonized power generation. These core technologies are being tested comprehensively for long-term demonstration at the Hydrogen Park TAKASAGO on the premises of MHI's Takasago District. On the other hand, the Carbon Neutral Park NAGASAKI located at MHI's Nagasaki District is responsible for the development of core technologies.



Source: Projecting the Future Levelized Cost of Electricity Storage Technologies. Drawn by author with reference to Imperial College 2019/1 Report

	Large capacity and low cost renewable resources It is economical to convert inexpensive renewable energy into hydrogen and store it, for local consumption for power generation and industrial use	Japan, South Korea, etc. where renewable energy is insufficient and expensive It is economical to use electricity storage carrier that enables inexpensive transportation and power generation	Southeast Asia and other regions that lack favorable sunshine and wind conditions and are dependent on inexpensive fossil fuels Decarbonization of coal- and natural gas-dependent existing technologies
Green H$_2$	Suitable	Not applicable	Not applicable
Turquoise H$_2$	Applicable	Suitable	Suitable
Ammonia	Not applicable	Applicable	Not applicable

Source: BloombergNEF. Note: LCOE calculations exclude subsidies or tax-credits. Graph shows benchmark LCOE for each country in $ per megawatt-hour. CCGT: Combined-cycle gas turbine.

Figure 2 Background for hydrogen and ammonia utilization and technological development road map for decarbonization

3. Current status of SOEC development

Figure 3 is the operating principle of SOEC, namely that steam is electrolyzed to produce hydrogen. The tubular cell stack, most important component of our SOEC system is MHI original technology. In this component, cells are formed on the surface of a ceramic substrate tube, which is a structural member. While electrolysis occurs in each cell (which consists of layers of hydrogen electrode (anode), electrolyte and oxygen electrode (cathode)), an electron-conductive ceramic interconnector is positioned between the cells to connect them in series. Several hundred of such cell stacks are then bundled together to form a cartridge. Once cartridges are placed in a pressure vessel, it is called a module. The SOEC system is comprised of this module and auxiliary equipment such as the boiler, turbine expander and rectifier (**Figure 4**).

Our SOFC technologies can be employed in the SOEC system. Characterized by its advantage of high efficiency, MHI's SOEC system is also capable of operating at high pressures, which is not possible with those systems of our competitors, and is therefore considered suitable for the application to large hydrogen production plants. **Figure 5** shows our plan for SOEC system development. In addition to developing and mass-producing SOFCs, MHI has a proven record of manufacturing and selling system of 200-kW class SOFCs, in which numerous cells are bundled up. The development of a large SOEC plant is aimed for by combining such expertise with our other technologies for handling high-temperature and high-pressure steam and gas, which were developed through engagement in steam power generation.

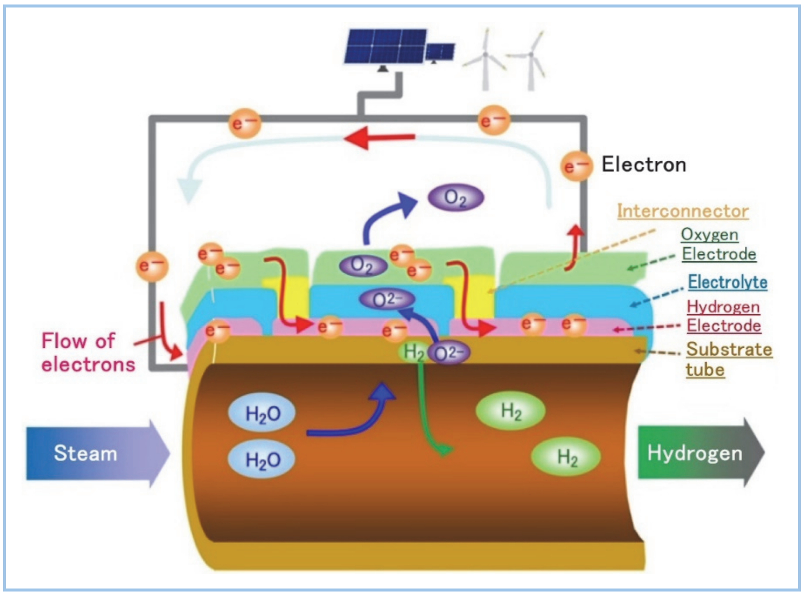


Figure 3　Operating principle of SOEC

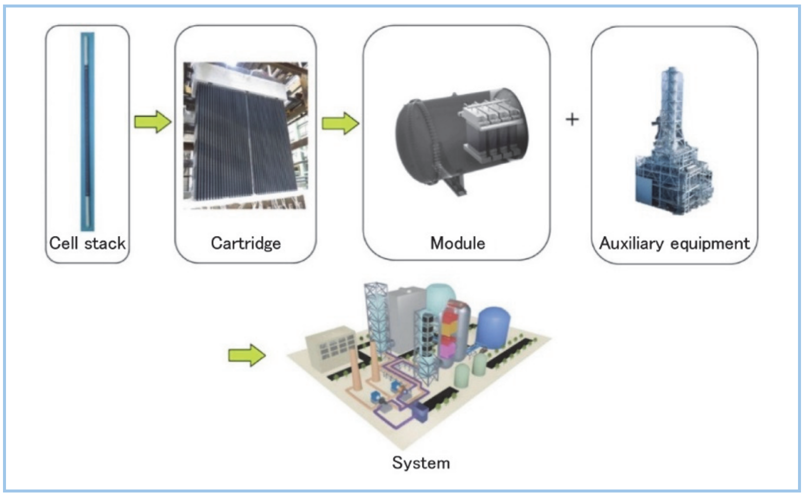


Figure 4　SOEC system components

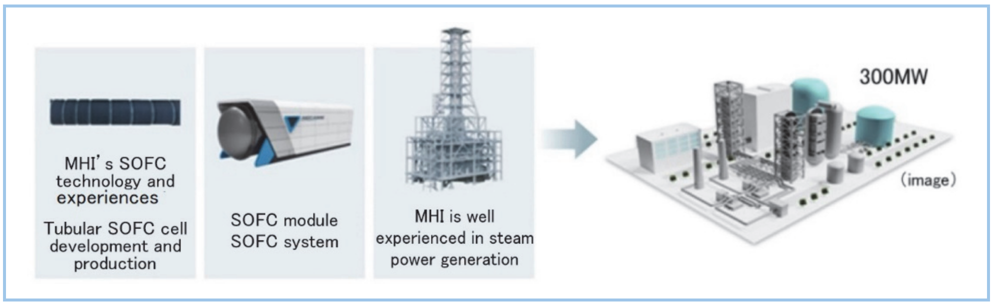
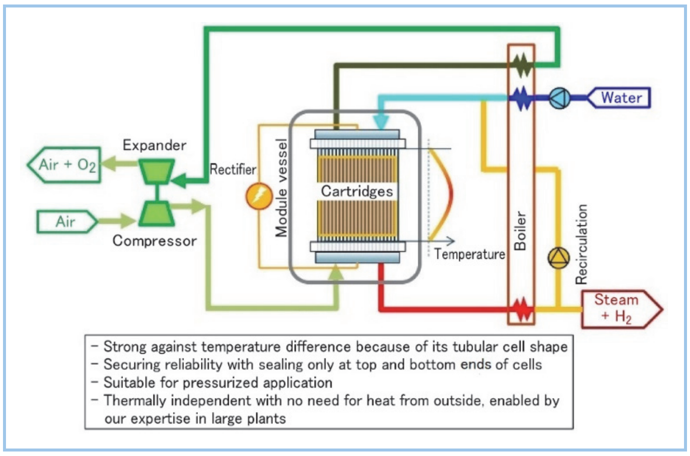


Figure 5　SOEC development plan

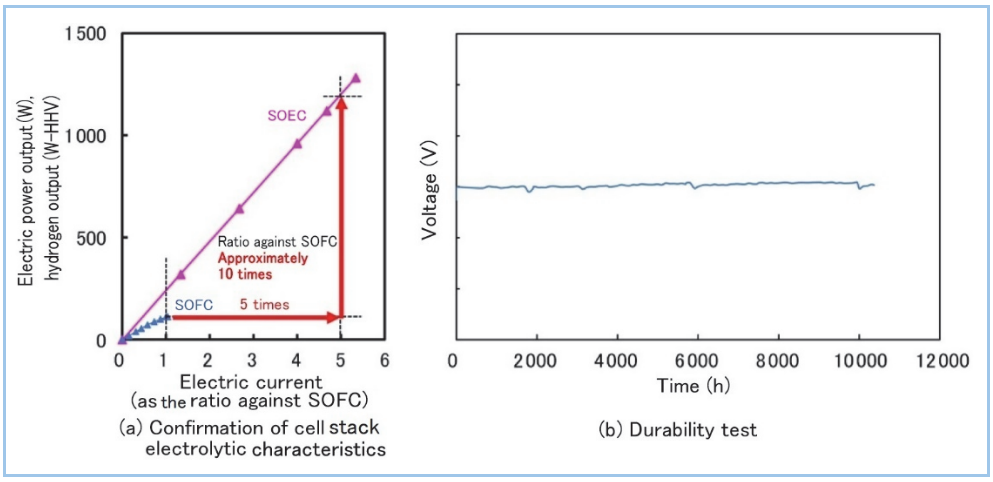
Figure 6 is an example of large SOEC system configuration. It is characterized by "thermally independent", which is to say that hydrogen can be produced by just supplying water and electricity because when electricity is applied to the cell stack, the Joule heat produced by electrolysis is used to generate steam. As the auxiliary equipment such as the boiler, compressor and expander are configured similarly to steam power plants, it is considered that there are economies of scale with larger sizes and higher pressures. As mentioned earlier, the use of high-pressure hydrogen is preferred. Therefore, a high-pressure SOEC system with an operating pressure of 3 to 5MPa is in development. With regard to hydrogen production efficiency, we aim at an overall efficiency of as high as 90% (on a higher heating value) for several-hundred-MW class plants (ca 100,000 Nm^3/h of hydrogen).



- Strong against temperature difference because of its tubular cell shape
- Securing reliability with sealing only at top and bottom ends of cells
- Suitable for pressurized application
- Thermally independent with no need for heat from outside, enabled by our expertise in large plants

Figure 6 Example of large SOEC system configuration

An electrolytic hydrogen production test was conducted. In this test, an SOFC cell stack, which is the current model in use, was operated as an SOEC. As shown in **Figure 7**(a), the results have confirmed that about 5 times more electric current can flow in comparison with the operation as an SOFC. The output of hydrogen (on an HHV basis) exceeds 1kW/stack, indicating that the heating value of hydrogen produced is about 10 times higher than the normal power generation output from the SOFC operation using the same cell stack (ca 100W/stack). A durability test is also underway using the same type of cell stack. As shown in Figure 7(b), it has been run for a total electrolysis time of >10,000 hours with the same amount of electric current as the SOFC operation. As the test is continuing without significant degradation, it is expected that the operating life will reach several tens of thousands of hours. Moreover, another cell stack durability test has been started under larger amounts of electric current condition.

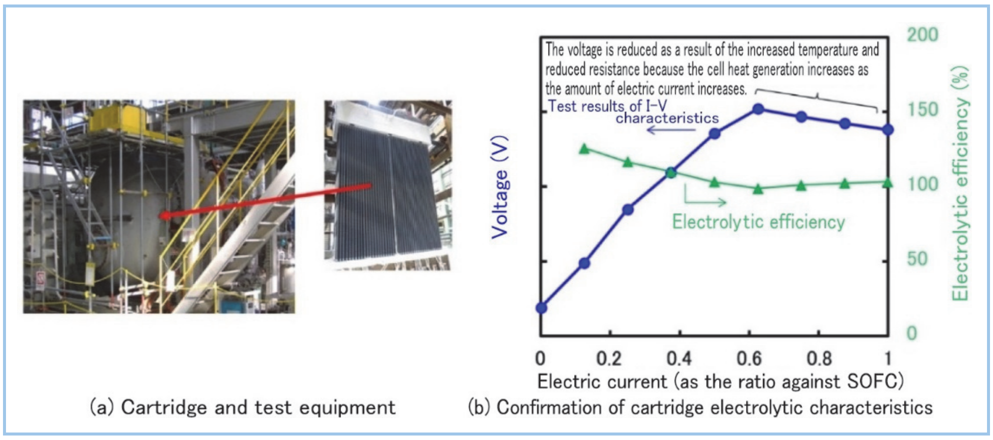


(a) Confirmation of cell stack electrolytic characteristics

(b) Durability test

Figure 7 Cell stack test

Figure 8 shows the results of the electrolysis test using a cartridge bundled several hundred cell stacks. Hydrogen production of 0.1MW (HHV) and 30Nm^3/h was achieved, with the amount of electric current being the same as the SOFC operation. When defined as the HHV of produced hydrogen divided by the amount of power applied for electrolysis, the obtained electrolytic efficiency exceeded 100% because of the absorption of Joule heat or heat from the feed steam and air. In order to increase the amount of electric current in the cartridge test as well, the core technologies required to increase the amount of electric current and the level of voltage in the components, and the amounts of feed steam/gas are in development.



(a) Cartridge and test equipment (b) Confirmation of cartridge electrolytic characteristics

Figure 8 Cartridge test results

A 0.4-MW class module, which is built using four cartridges of this 0.1MW cartridge, will be operated at the Hydrogen Park TAKASAGO for a demonstration test. As of December 2023, the installation of this test module is underway. Hydrogen production will be started in 2024.

As shown in **Figure 9**, the plan is to conduct a system demonstration.

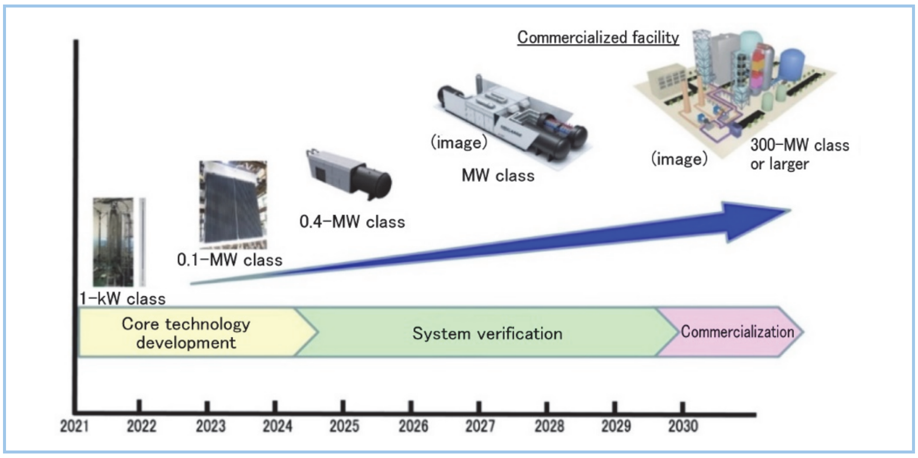


Figure 9 Road map for SOEC development

4. Current status in development of AEM water electrolysis

The development of electrolysis technology using a solid polymer electrolyte membrane is concentrated on PEM water electrolysis using a hydrogen ion permeable membrane. On one hand, it can operate at a higher current density and can also be downsized than alkaline electrolysis, which has been utilized for social implementation in many caustic soda production systems. On the other hand, as PEM containing many hydrogen ions is under strongly acidic environment, it requires the use of expensive noble metals or titanium-based materials as catalysts or for the parts in liquid contact. Purity control through metal ion removal is also necessary to prevent performance decline due to impurities in the water supply. However, AEM water electrolysis, which is referred to as next-generation water electrolysis, can operate at a high current density as PEM water electrolysis with the electrolytic cell being able to be downsized. Moreover, since the alkaline environment containing many hydroxide ions, costs are expected to be reduced with the use of inexpensive materials such as stainless steel.

At present, MHI is tackling multiple projects for understanding the initial characteristics and durability of a small element cell with an electrode area of several tens of cm^2, prototyping and evaluating a large cell stack of several hundreds of cm^2, determining an appropriate manufacturing method for stack materials and assembly, and optimizing the system configuration and operating conditions using a kW class test facility as shown in **Figures 10** and **11**.

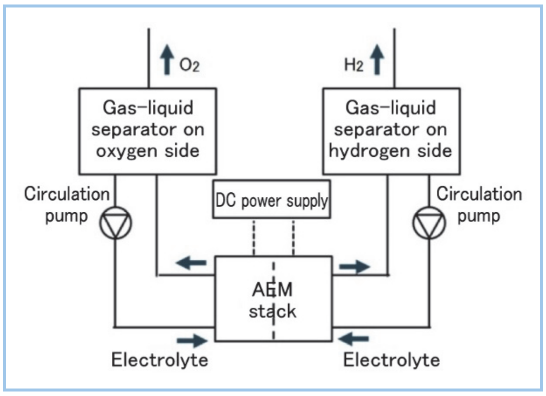


Figure 10 AEM water electrolysis system diagram

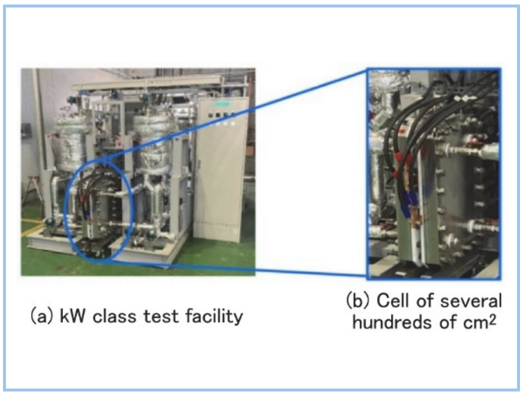


Figure 11 kW class test facility

Figure 12 shows the results of prototyping and evaluating a small element cell and a large cell stack. Even the large cell stack exhibited the same current-voltage characteristics as the small element cell. This result increase in the current density can be expected in comparison with alkaline water electrolysis in general.

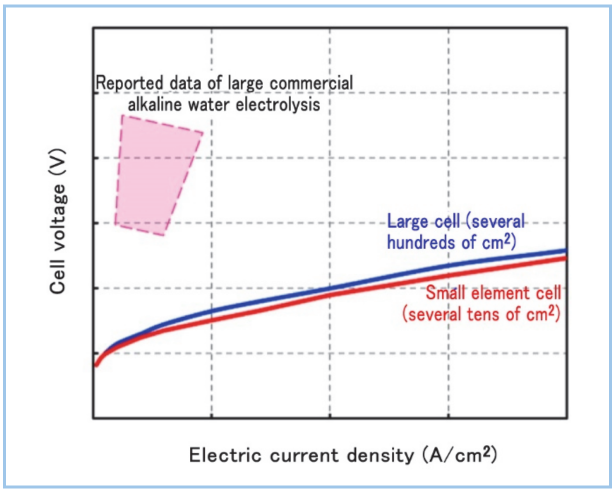


Figure 12 Evaluating results of small element cell and prototyping large cell stack

Designing an AEM water electrolyzer necessitates wide-ranging technological developments in terms of performance of internal components, inner fluid leakage prevention, electrolysis surface pressure, flow rate control, and flow distribution into the layers. Making utilization of our technologies acquired through developing various types of energy equipment, we can proceed with development by combining numerical analysis and element testing. For example, the Finite Element Method (FEM) analysis and the surface pressure test are conducted to properly determine the structure. Some examples are shown in **Figures 13** and **14**.

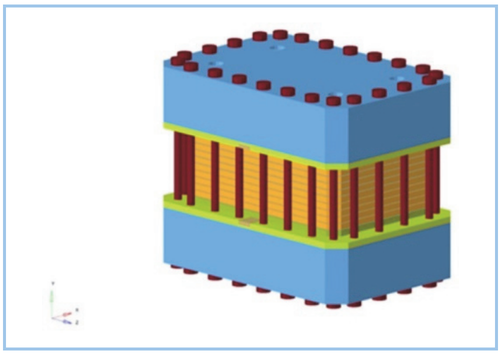


Figure 13 FEM analysis model

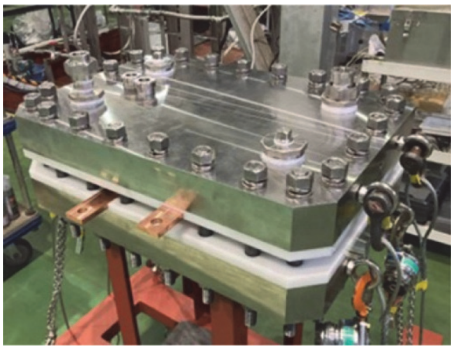


Figure 14 Surface pressure test

Looking forward, we will continue to work on the development of large full-size stacks based on the test results of the kW class unit and the outcomes/knowhow obtained through the aforementioned projects, as shown in **Figure 15**. Our plan is to conduct a demonstration test using a several-MW class unit at the Hydrogen Park TAKSAGO, before applying the technology to a commercialized facility.

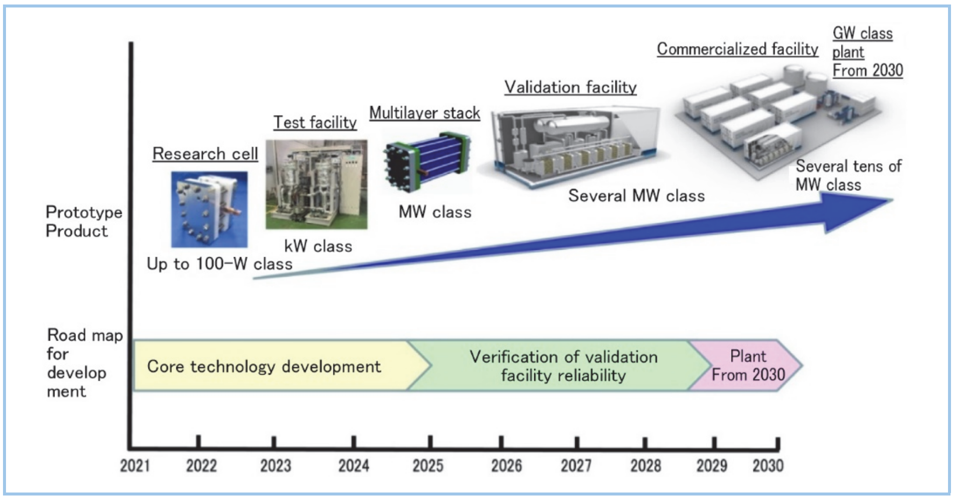


Figure 15　Road map for AEM water electrolysis

5. Current status in development of turquoise hydrogen (methane pyrolysis)

Turquoise hydrogen production by methane pyrolysis is a technology of decomposing natural gas into solid carbon and hydrogen at high temperatures. Conventionally, this method has been used to produce industrial carbon materials such as carbon black. Placing the focus on the co-produced hydrogen, MHI identified the reaction mechanism to produce hydrogen efficiently.

Figure 16 illustrates the turquoise hydrogen production technology. Natural gas infrastructure has already been established. A turquoise hydrogen production plant will be installed between the natural gas infrastructure supply line and the consumer, or upstream of the consumer's consumption equipment, and the gas turbine will achieve decarbonization. Taking a natural gas-fired power plant (GTCC) as an example, upgrading to hydrogen firing can be done if the gas turbine's combustor is adapted to take hydrogen. Moreover, the by-product carbon is solid, which makes it easier to fix or store than gaseous CO_2 at normal temperatures and pressures. Combined with such turquoise hydrogen, existing thermal power plants can achieve substantially reduced carbonization and eventually decarbonization (that is, power generation with no CO_2 emissions).

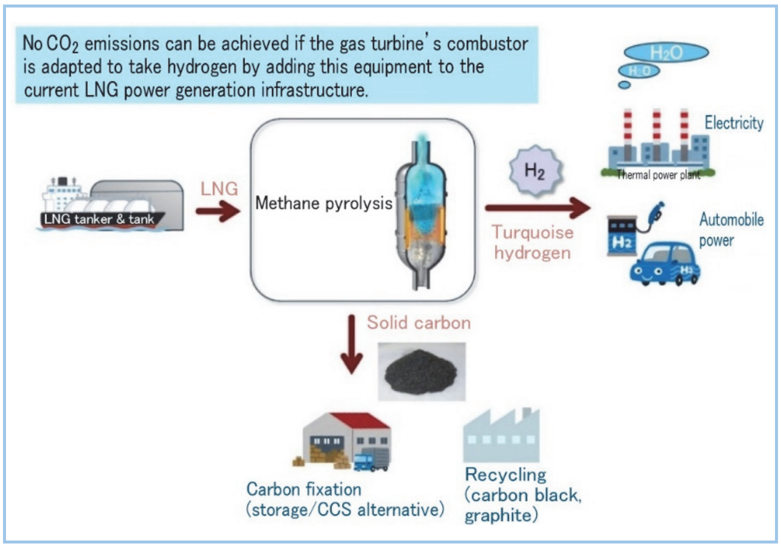
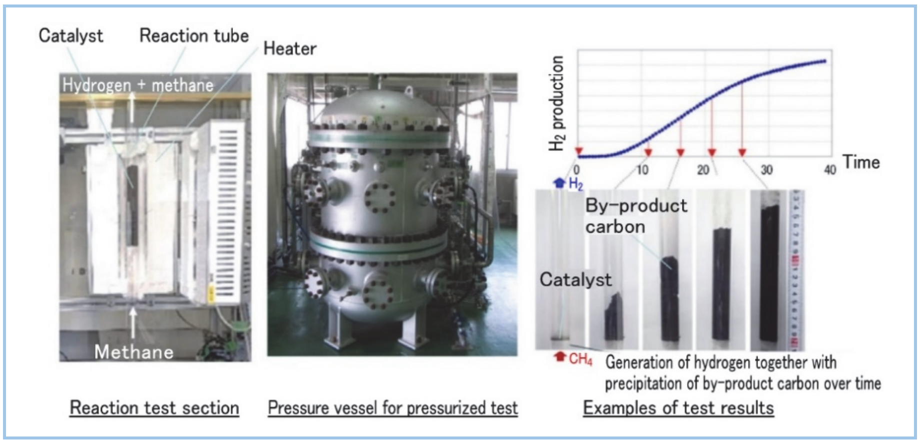

No CO_2 emissions can be achieved if the gas turbine's combustor is adapted to take hydrogen by adding this equipment to the current LNG power generation infrastructure.

Figure 16　Overview of turquoise hydrogen production technology

Having selected a fluidized bed as the reactor for methane pyrolysis, we are conducting an examination into how the reaction progresses and the screening for appropriate conditions using element test equipment. Shown in **Figure 17** are the batch-type fluidized bed test equipment and the typical test results. In this equipment, a catalyst is placed in the reaction tube. While allowing methane to pass through, the reaction tube is heated by the heater to let methane pyrolysis occur. As methane is thermally decomposed, the by-product carbon accumulates in the reaction tube.



Reaction test section Pressure vessel for pressurized test Examples of test results

Figure 17 Batch-type fluidized bed test equipment and test results

Figure 18 shows the continuous pressurized fluidized bed test equipment. In addition to a fluidized bed reactor and heaters installed in the pressure vessel, the equipment also has a catalyst feeder and a by-product carbon removal system. Thus, the methane pyrolysis reaction test can be conducted continuously. Typical test results are given in **Figure 19**. Catalyst feeding and by-product carbon removal are carried out constantly under pressurized high-temperature conditions. Maintaining a constant height of the fluidized bed, the equipment is continuously operating for more than 40 hours in steady-state conditions. It has been confirmed that the conversion rate of methane (the amount of hydrogen produced) is almost the same as the estimated value based on the reaction characteristics from the batch-type unit test.

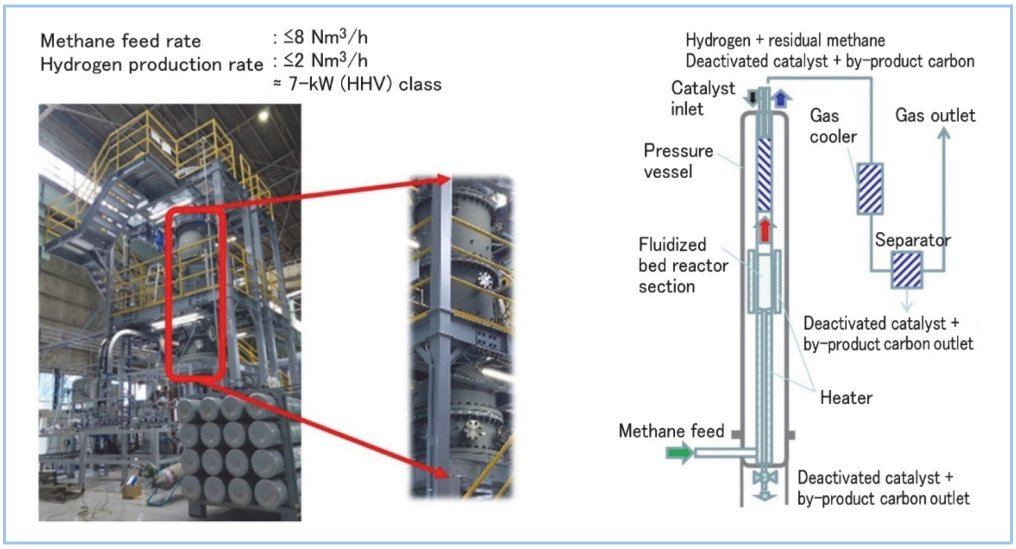


Figure 18 Continuous pressurized fluidized bed test equipment

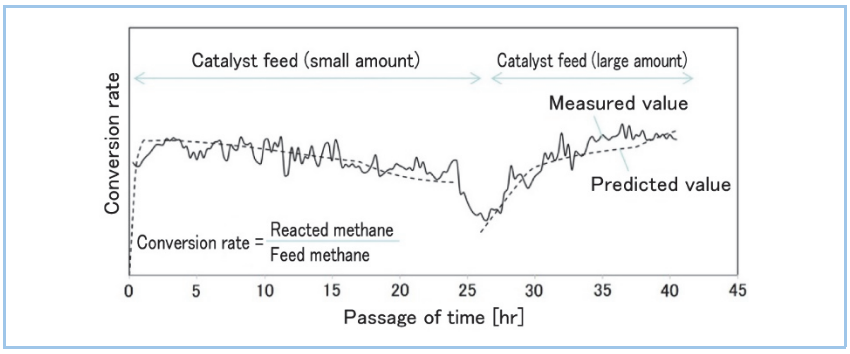


Figure 19 Methane pyrolysis test results using pressurized fluidized bed

Figure 20 shows the road map for development. Now while the reactor test through the aforementioned batch-type and continuous reactor tests is in progress to investigate the characteristics, another demonstration test unit is being designed, which will be used to verify the whole process of the hydrogen production facility. It will be operated at the Hydrogen Park TAKASAGO in 2026.

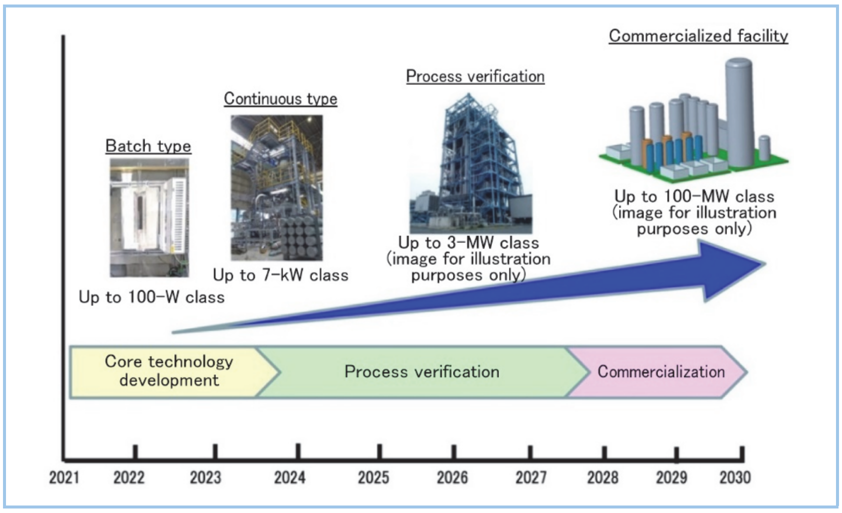


Figure 20 Road map for turquoise hydrogen development

6. Current status in development of synthetic fuel production technology

The previous chapters gave an overview of MHI's hydrogen production technology. This chapter focuses on examples of how to use such hydrogen and presents MHI's progress in the development of manufacturing liquid synthetic fuel (synthetic fuel) as carbon-neutral fuel (CN fuel) production.

(1) Position of CN fuel

The power generation sector is currently responsible for a large part of the world's carbon dioxide emissions, followed by the sectors of transportation, industry and civil sector (**Figure 21**). To achieve worldwide carbon neutrality, the key lies in each field's capability of executing effective initiatives. In the field of power generation, for example, MHI is working on the development of hydrogen or ammonia-fired gas turbine(6) and ammonia-cofiring technology for coal-fired power generation boilers(7), thus steadily moving forward to achieve the target of 50% reduction in CO_2 emissions by 2040(8).

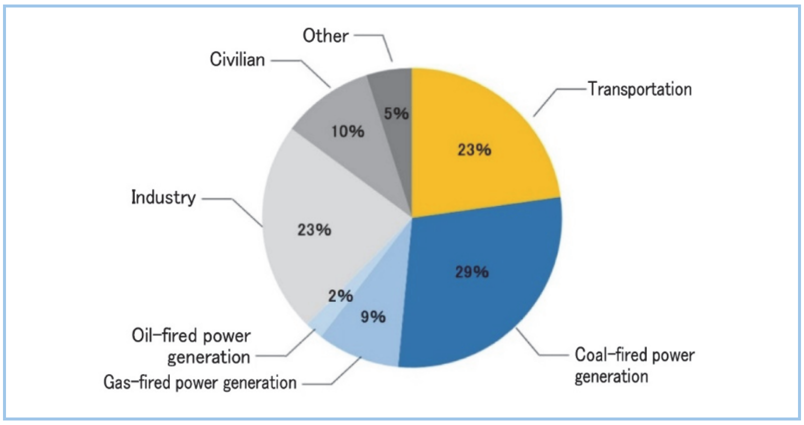


Figure 21 Global CO_2 emissions by sector (source: IEA WEO 2023)

Regarding the transportation sector, the trend is shifting to Electric Vehicles (EVs) and Fuel Cell Vehicles (FCVs). However, CN fuels, whose use involves no increase in CO_2 emissions, are also one of the promising options to choose. As it is especially difficult for medium and large aircraft to be turned into an EV or FCV, demand for Sustainable Aviation Fuel (SAF) is expected to expand rapidly. **Figure 22** systematizes the production processes of CN fuels including SAF.

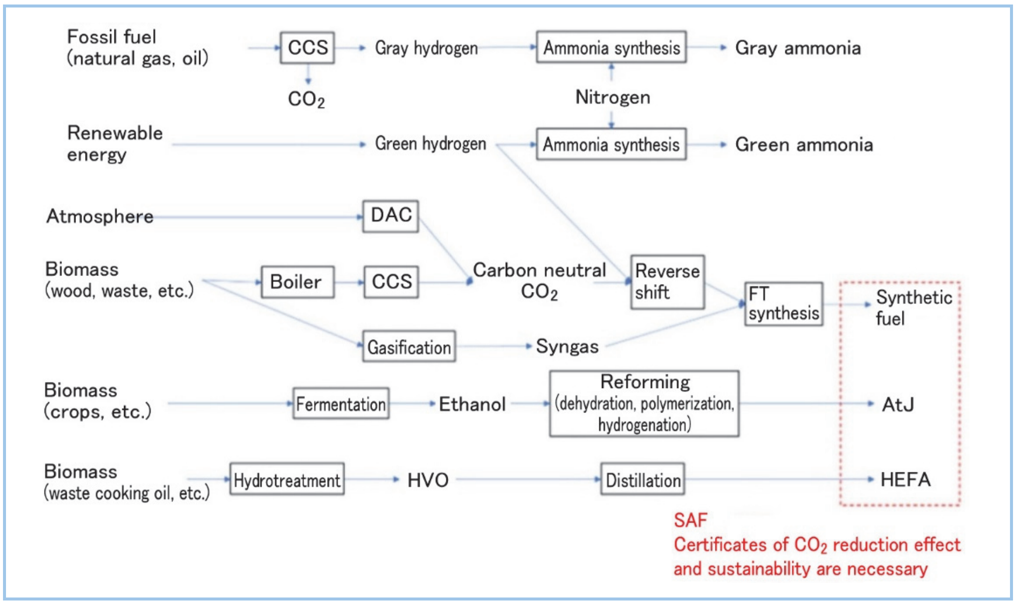


Figure 22 Systematized production processes of CN fuels

(i) CN fuel production technology using blue or green hydrogen

CN fuels include green hydrogen, which is produced using renewable energy, and blue hydrogen, which is the product of fossil fuel reforming with CO_2 removal via the Carbon Dioxide Capture and Storage (CCS) system. However, considering hydrogen's transportability, safety, energy density and other factors, it is preferable to have a liquid CN fuel. Therefore, it becomes versatile, if green or blue hydrogen is either converted into ammonia, which is liquid at 0.86MPa and at a normal temperature (20°C) like LPG, or is used to produce a synthetic fuel by combining with CO_2. In the case of ammonia, it is classified as green or blue, depending on which type of hydrogen is used for production.

Synthetic fuel is the generic term for fuels synthesized from hydrogen and CO_2. SAF, in particular, can serve as an alternative to jet fuel (kerosene) in terms of properties and can be blended at the predetermined blending ratio for use in existing aircraft engines. However, the prerequisite for carbon-neutral synthetic fuel is the carbon neutrality of raw materials H_2 and CO_2. Being carbon neutral, CO_2 is considered to be taken either from the air by Direct Air Capture (DAC) or the exhaust gas from biomass combustion. At present, the use of biomass combustion exhaust gas with a higher CO_2 concentration is advantageous from the viewpoint of capture efficiency (i.e., the required energy per unit of captured CO_2).

(ii) CN fuel production technology using biomass

Another method of producing a synthetic fuel is the biomass gasification and Fischer-Tropsch (FT) synthesis method in which syngas generated by gasification of feedstock such as wood biomass and waste is used to directly produce a synthetic fuel by the FT method. MHI has also been developing this technology(9).

The CN fuels produced from other types of biomasses such as grains and waste cooking oil are bio fuels such as ethanol and Hydrotreated Vegetable Oil (HVO). When these two types of bio fuels are prepared (e.g., by reforming), they are turned into SAFs, respectively called Alcohol to Jet (ATJ), with the technology to produce fuel from alcohol, and Hydroprocessed Esters and Fatty Acids (HEFA), with the technology to produce fuel from waste cooking oil, vegetable oil and such.

(2) Synthetic fuel production using electrolysis hydrogen

Chemical conversion by the reverse shift reaction between hydrogen (produced by electrolysis using renewable energy) and CO_2 (captured from an exhaust gas of biomass combustion) produces a syngas containing H_2 and CO as main components. The syngas is then subjected to FT synthesis, thus enabling the production of carbon neutral SAF or synthetic fuel (**Figure 23**).

The reverse shift reaction is a reaction in which CO and steam are produced from CO_2 and hydrogen, as shown by equation 1. This is the backward reaction of the so-called shift reaction, in which CO is converted into CO_2 for syngas decarboxylation.

$CO_2 + H_2 \rightarrow CO + H_2O$ (Equation 1)

From a chemical equilibrium point of view, high temperatures favor the reverse shift reaction (conversely, low temperatures are advantageous for the shift reaction), thus requiring a high temperature of 600°C or above. The catalysts, which are in use industrially, are mainly for low-temperature applications in the shift reaction. Problems such as durability arise in the case of their use at high temperatures, thus, the development of new catalysts is in progress.

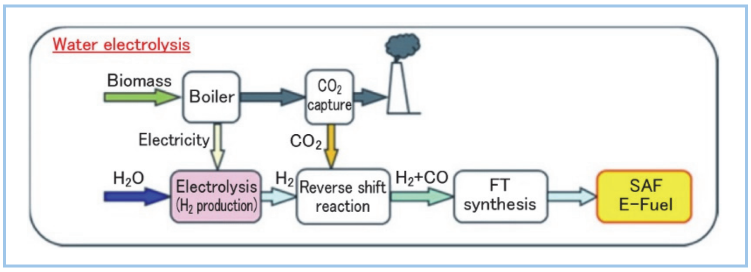
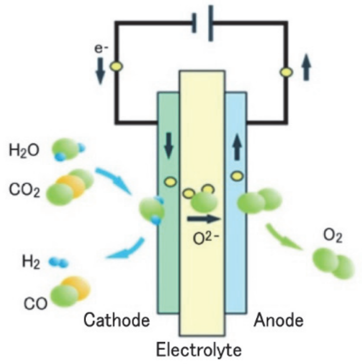


Figure 23 Schematic flow diagram of SAF production using electrolysis hydrogen

In addition to the reverse shift reaction, other innovative processes have been developed in recent years, including electrolysis of CO_2 in which CO_2 is electrochemically reduced to CO, and co-electrolysis of water and CO_2 electrolysis simultaneously. **Figure 24** illustrates the principle of co-electrolysis of steam and CO_2 using SOEC. As in the case of steam electrolysis, electrolysis of CO_2 involves oxygen ions passing through the electrolytic membrane together with simultaneous reduction of CO_2 to CO. Adjusting the operating conditions such as gas properties at the SOEC inlet makes it possible to produce source gas suitable for FT synthesis. The test using MHI's current SOEC cell model in use has confirmed already the capability of co-electrolysis.



Cathode: $CO_2 + 2e^- \rightarrow CO + O^{2-}$
$H_2O + 2e^- \rightarrow H_2 + O^{2-}$
Anode: $O^{2-} \rightarrow 1/2\ O_2 + 2e^-$
Side reaction: $CO + H_2O \rightarrow CO_2 + H_2$
$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$

Figure 24 Principle of steam/CO_2 co-electrolysis using SOEC

Figure 25 is a schematic flow diagram of SAF production by co-electrolysis of steam and CO_2. Therein, the co-electrolyzer replaces the electrolyzer (hydrogen production) and the reactor for the reverse shift reaction shown in the flow diagram of Figure 23. The system configuration is thus simplified. The FT synthesis yield is also expected to be improved.

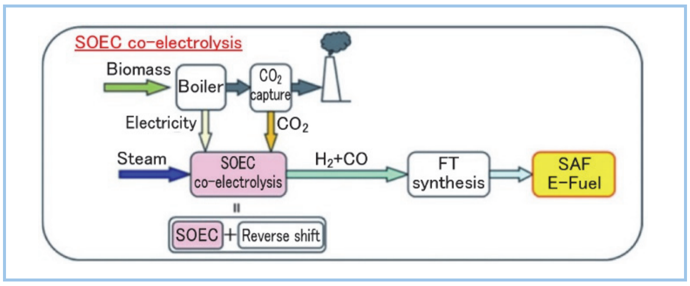


Figure 25 Schematic flow diagram of SAF production by co-electrolysis of steam and CO_2

7. Conclusion

Focusing on utilization of hydrogen for power generation, this report summarizes the development of three types of hydrogen production technologies (i.e., high pressure, high efficiency and large capacity SOEC, AEM water electrolysis, and methane pyrolysis) and our technological progress in the development of synthetic fuel production using hydrogen.

Making use of the technologies for energy transition in this report, we aim to fulfil MHI Group's declaration of "MISSION NET ZERO" for 2040 and thus also commit ourselves to contribute to the realize of a carbon-neutral society.

"Hydrogen Is Not the Future, This Is Real."

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