Mission Innovation
Clean Hydrogen Mission

Hydrogen Detection Technologies for Hydrogen Safety

Applications and Technologies

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METI
Ministry of Economy, Trade and Industry

CLEAN HYDROGEN MISSION

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Executive Summary

1 Characteristics of Hydrogen

(1) Characteristics of Hydrogen

Because gaseous hydrogen consists of a very small molecule, small leaks are common. In properly designed systems these very small leaks do not present a problem as the tiny amount of hydrogen released will not be enough to cause a flammable mixture in air. Small gaseous hydrogen leaks are difficult to detect by human senses since hydrogen is colorless, odorless, and tasteless.

Leaking hydrogen will rise and diffuse quickly in air because its low density results in high buoyancy (14 times less dense than air). Only when hydrogen gas can accumulate over time in a confined area will a risk of a flammable mixture or asphyxiation arise.

Hydrogen burns with a pale blue flame that is nearly invisible in daylight. The flame may appear yellow if there are impurities in the air like dust or sodium.

For these reasons, hydrogen detection technology is key for safe handling of hydrogen.

(2) Hydrogen as an Energy Carrier (Hydrogen Carrier)

For large-scale transportation of hydrogen, compressed hydrogen (CH2), liquid hydrogen (LH2), liquid organic hydrogen carrier (LOHC) or ammonia may be used. For each form and mode of transport, hydrogen should be properly stored and handled, and appropriate hydrogen detection devices should be installed within the transport and distribution systems.

The choice of hydrogen carrier also depends on the overall energy efficiency. Hydrogenleakage should be minimized, which can be facilitated by implementing proper detection system over the supply chain.

(3) International Trade of Hydrogen

The world energy trade is expected to shift from an oil-dominant portfolio in 2020 to a non-fossil-energy dominant portfolio by 2050, when hydrogen and ammonia trade will have about 20% combined share in trade value. It is expected that by 2050 there will be more than 40 different trade routes for hydrogen with a capacity of more than one million tons per annum, and the largest carrying more than 20 million tons per annum.

(4) International Cooperation on Hydrogen Safety

Mission Innovation's Clean Hydrogen Mission (CHM) has the goal to increase the cost-competitiveness of clean hydrogen by reducing end-to-end costs to a tipping point of 2 USD/kg by 2030. Hydrogen safety is a major focus for CHM activities.

The International Partnership for Hydrogen and Fuel Cells in the Economy (IPHE) has Regulations, Codes, Standards, & Safety (RCSS) Working Group, issued the "Compendium of Regulatory Areas for Action in Hydrogen Infrastructure and Mobility/Transportation Technologies" in September 2021. According to the report, for hydrogen infrastructure, safety requirements and process are critical for all application areas.

For mobility/transportation, especially for maritime applications, safety guidelines for vessels appear to be nonexistent in many national regulations, so guideline development is critical for these applications.

Research and innovation is needed for improved and adapted detection technologies since new production technologies and applications are developed.

2 Hydrogen Applications and Detection Technology

(1) Fuel Cell Electric Vehicles (FCEVs)

Today, there are several types of FCEVs on the road, and these FCEVs are equipped with hydrogen leak detection sensors. Toyota's MIRAI has three leak detection sensors; one at the forward compartment (near fuel cell stack), and two at the hydrogen tanks. MIRAI's detection sensor is a contact combustion type, which detects the temperature rise (change in resistance) of noble metal coils arising from the catalyzed oxidation of hydrogen that contacts the surface of the sensor.

(2) Off-Road Vehicles

Possible hydrogen applications for off-road vehicles include mining (open pit mining), construction, utility, and agriculture vehicles / equipment. In terms of hydrogen safety, the most challenging application is mining because of the wide range of environmental conditions, need for dust-resilience, large storage volume and need for fast hydrogen refueling.

(3) Hydrogen Refueling Stations (HRS)

Since hydrogen refueling stations (HRS) are usually built within cities, mitigation of risk is essential to protect FCVs, the surrounding environment, and nearby pospulation from possible hazards. The combination of safety devices and safety systems for HRS will vary depending on jurisdictions and regions.

Hydrogen leak detection sensors and flame detection sensors are essential and are installed in several locations within the HRS (production facility, compressors, storage tanks and dispensers a d others).

(4) Maritime (Hydrogen Carrier Ships)

Hydrogen is expected to be widely traded internationally as a commodity. One of the major modes of international transport of hydrogen is by shipping in the form of LH2. LH2 carrier ships should be equipped with hydrogen detection system.

The International Maritime Organization (IMO) has been amending its International Code of Safety for Ships using Gases or other Low-flashpoint Fuels (IGF) code, which requiressafety equipment and systems to detect flames, protect emergency shutdown areas, shut off fuel flow in case of emergency and enforce air flow for tank connection space.

(5) Aerospace

Major aircraft developers have announced concepts for zero-carbon aircrafts, which use hydrogen as a fuel. In many cases, LH2 can be the main form of onborard storage.

Aircraft applications require safe handling of LH2 at a significantly more stringent level than that required for other applications.

3 Hydrogen Detection Technology

(1) Conventional Hydrogen Detection Technologies

There are numerous conventional, commercially-available technologies for detecting combustible gases such as hydrogen. These include high temperature semiconductor sensor (e.g., metal oxide sensors), catalytic combustion sensors. and heat conduction sensor such as the thermoconductivity sensor).

In addition, hydrogen can be readily detected by electrochemical sensors and by sensor platforms that utilize palladium thin films, in which the adsorption of hydrogen changes the electrical and optical properties of the thin-film. Each conventional hydrogen detection technology has optimum operation conditions and performance specifications of H2 concentration range, measurement response time, and robustness from chemical interferences.

(2) Other Hydrogen Detection Technologies

Other than conventional technologies, there are several emerging technologies for the detection of hydrogen releases, including fiber optic sensors, ultrasonic detection, and Schlieren imaging. Each of these technologies has advantages and disadvantages for use and application.

1 Characteristics of Hydrogen

1-1 Characteristics of Hydrogen

Hydrogen is the most common element in the universe. Properly speaking, hydrogen is the lightest element in the periodic table, although it is hardly be found in elemental form as an isolated atom. Instead it exists mostly in compound form, such as diatomic hydrogen (H2), water (H_2O) or hydrocarbons. The term “hydrogen” typically refers to diatomic hydrogen while the term hydrogen atom is used to refer to the element; this convention is used in this report.

Hydrogen has been used in a variety of industries for over 50 years as a feedstock. These include;

- Petroleum refining
- Food processing (hydrogenation of unsaturated fatty acids in vegetable oil)
- Fertilizer production
- Plastics production
- Glass purification
- Semiconductor manufacturing
- Aerospace applications
- Welding, annealing and heat-treating metals
- Pharmaceuticals
- Coolant in power plant generators

Table 1 shows major characteristics of hydrogen. Hydrogen, which is a gaseous at ambient temperature, is odorless, colorless, non-toxic, although it is flammable and explosive over a wide range of concentrations and has a low ignition energy.

- There are differences in the properties of hydrogen and methane[1] which significantly affect their respective safety properties, including the following: The flammability range (FR) of hydrogen is much wider than methane’s FR, ranging from approximately 4 to 74 vol% for hydrogen and 5 to 15 vol% for methane.
- The specific gravity of hydrogen is much lower than air (0.0696), so pure hydrogen released with low momentum rises about 6 times faster than methane. Hydrogen’s dilution in air is also faster than that of methane. The specific gravity of methane is 0.554.
- The required ignition energy for hydrogen is much lower than that of methane.

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[1] Methane is the main hydrocarbon constituent of natural gas and as such is used as a test gas for evaluating technologies for use with natural gas, including detectors.

Because gaseous hydrogen consists of a very small molecule, small leaks are common. In properly designed systems these very small leaks do not present a problem as the tiny amount of hydrogen released will not be enough to cause a flammable mixture in air. Small gaseous hydrogen leaks are difficult to detect by human senses since hydrogen is colorless, odorless, and tasteless. Leaking hydrogen will rise and diffuse quickly in air because its low density results in high buoyancy (14 times less dense than air). Only when hydrogen gas can accumulate over time in a confined area will a risk of a flammable mixture or asphyxiation arise.

Hydrogen burns with a pale blue flame that is nearly invisible in daylight. (Figure 1) The flame may appear yellow if there are impurities in the air like dust or sodium. For these reasons, hydrogen detection technology is essential for the safe handling of hydrogen.

Table 1 Characteristics of Hydrogen and Other Energies

	Hydrogen (Gas)	Methane (Gas)	Gasoline (Liquid)	Propane (Liquid)
Lower heating value (kWh/kg)	33.3	13.6	12.0	12.9
Specific gravity (Air = 1)	0.070	0.559	-	-
Minimum Ignition Energy (MIE) [mJ]	0.017	0.22	0.8	0.25
Autoignition temperature in air (°C)	585	540	257	450
Flammability limit in air (%)	4.1–74	5.3–15	1.4–7.6	2.2–9.5

Source: Various source

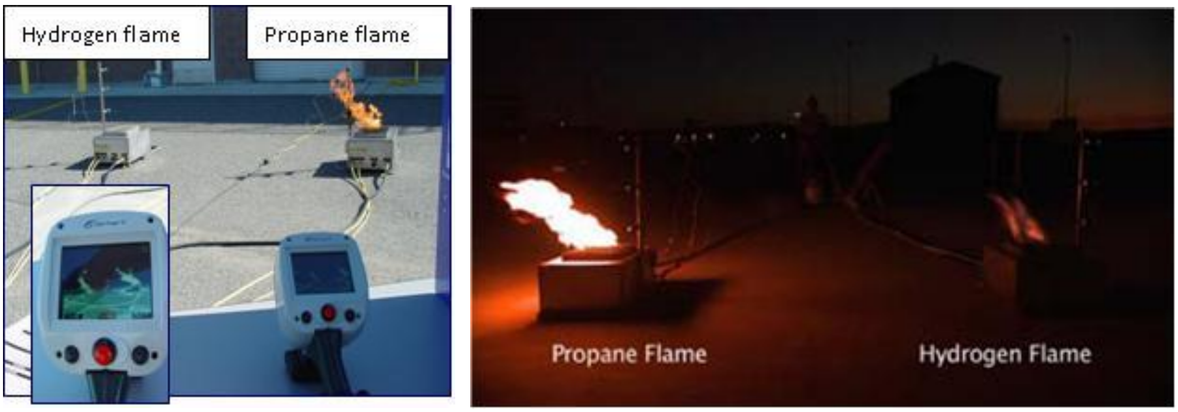

Figure 1 Hydrogen Flame and Propane Flame in Daylight and at Night

Source: Hydrogen Tools (US DOE)

1-2 Hydrogen as an Energy Carrier (Hydrogen Carrier)

Today, hydrogen is emerging as a new energy carrier for wide variety of applications, including hard-to-decarbonize sectors. The use of hydrogen as an energy carrier is expected to become mainstream in many countries that plan to use renewable energy sources in their energy systems.

For this purpose, hydrogen can be produced renewably (e.g., electrolysis of water powered by renewable electricity), and then transported and distributed to end-users in various forms and via various transport modes (Figure 2). Transport forms ("hydrogen carriers") can include compressed hydrogen gas (GH2), liquid hydrogen (LH2), liquid organic hydrogen carrier (LOHC)[2] or ammonia. The main modes for large-scale hydrogen transportare envisioned to include LH2, LOHC or ammonia[3].

Currently, hydrogen can be transported by truck, ship, or pipeline. In the future, hydrogen could also be transported by trains and airplanes. For all transport forms and modes, hydrogen should be properly stored and handled, and hydrogen detection devices should be installed throughout thetransport and distribution systems.

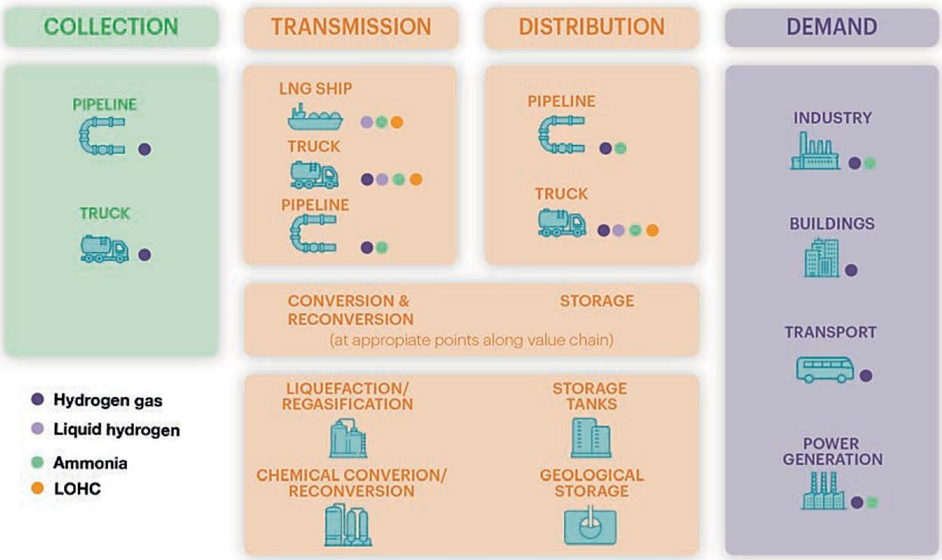

Figure 2 Hydrogen Carrier: Transmission, Distribution and Storage of Hydrogen Value Chains

Source: IEA "The Future of Hydrogen" (June 2019)

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2 There are several types of LOHC. Major one is Toluene / Methylcyclohexane (MCH) system, whose chemical reaction is as follows:

$C_6H_5CH_3 + 3H_2 = C_6H_{11}CH_3$

Other than this, dibenzyl-toluene (H0-DBT) / octadecahydro-dibenzyltoluene (H18-DBT) system is also proposed.

$H0\text{-}DBT + 9H_2 = H18\text{-}DBT$

3 Sometimes hydrogen carriers include synthetic chemicals such as methane.

Table 2 indicates Properties of major hydrogen carriers (LH2, LOHC and ammonia). LH2 has many of the same hazards as those associated with compressed hydrogen. However, LH2 will pose additional hazards associated with a cryogenic liquid, including risks associated with physical contact of cold liquid or gas releases.The temperature of LH2 is -253 °C (20 K) or below, which is lower than oxygen’s boiling point of -183 °C (90 K) and melting point of -219 °C (54 K). Therefore, a large spill of LH2 may cause the formation of liquid or icy oxygen, which may create an explosive environment due to enriched oxygen. LH2 systems require hydrogen detection devices, similar to GH2 systems, in addition to devices suitable for low-temperature use. Table 3 explains some of LH2’s Cryogenic Hazards.

Table 2　Properties of Hydrogen Carriers

		LH2	LOHC (Toluene/ MCH)	Ammonia
Process and technology maturity*	Conversion	Small scale: High Large scale: Low	Medium	High
	Tank storage	High	High	High
	Transport	Ship: Low Pipeline: High Truck: High	Ship: High Pipeline: High Truck: High	Ship: High Pipeline: High Truck: High
	Reconversion	High	Medium	Medium
	Supply chain integration	Medium/high	Medium	High
Hazards**		Flammable; no smell or flame visibility	Toluene: flammable; moderate toxicity (Other LOHCs can be safer)	Flammable; acute toxicity; precursor to air pollution; corrosive
Conversion and reconversion energy required***		Current: 25 - 35% Potential: 18%	Current: 35 - 40% Potential: 25%	Conversion: 7 - 18% Reconversion: < 20%
Technology improvements and scale-up needs		Production plant efficiency; boil-off management	Utilisation of conversion heat; reconversion efficiency	Integration with flexible electrolysers; improved conversion efficiency; H2 purification
Selected organisations developing supply chain		HySTRA; CSIRO; Fortescue Metals Group; Air Liquide	AHEAD; Chiyoda; Hydrogenious; Framatome; Clariant	Green Ammonia consortium; IHI Corporation; US DOE

*　High = proven and commercial; Medium = prototype demonstrated; Low = validated or under development; Small scale = < 5 tonnes per day; Large scale = > 100 tonnes per day.

**　Toxicity criteria based on inhalation.

***　Given as a percentage of lower heating value of hydrogen; values are for hydrogen that could be used in fuel cells; lower-purity hydrogen would require less energy.

Source: IEA “The Future of Hydrogen” (June 2019)

Table 3 LH2 Cryogenic Hazards

Material embrittlement	- Cryogenic temperatures on materials can reduce strength of structures up to irreversible failures.
Solidification of air components	- In case of LH2 or cold H2 releases, it could be possible that solid particles (water and CO 2 freezing) and/or LH2 droplets and air condensate droplets (friction and break up) may ignite.
Extreme cold hazard	- Cryogenic liquids and their associated cold vapours can produce effects on the skin similar to a thermal burn. - Brief exposures can damage delicate tissues such as the eyes Prolonged exposure of the skin or contact with cold surfaces can cause frostbite. - Unprotected skin can stick to metal that is cooled by cryogenic liquids The skin can then tear when pulled away Prolonged breathing of extremely cold air may damage the lungs.
Asphyxiation hazard	- The gas produced by evaporation of cryogenic liquids can accumulate in a confined space Even if the gas is non toxic, asphyxiation and death can occur Oxygen deficiency is a serious hazard in enclosed or confined spaces.

Source: European Hydrogen Train the Trainer Programme for Responders “Liquefied hydrogen (LH2)”

LOHC (Toluene/ MCH) has similar characteristics like gasoline, such as gasoline-like hazards (flammability, toxicity). Detection devices similar to those used for other liquid fuels can be used for detection of LOHCs, which including photoionization detectors for hydrocarbon detection, gas chromatographs, and infrared methodologies. Also vapors of liquid fuels will respond on high-temperatrue catalytic sensors..

Ammonia is a flammable liquid with acute toxicity. Ammonia is colorless gas, but has a very pungent odor, so that leakage can be easily detected by human olfaction or electronic methods of detection. Ammonia detection devices are well-developed and widely used in the ammonia industry. Ammonia is an internationally traded commodity with mature handling procedures.

In addition to the need for mitigating hazards, the choice of hydrogen carrier also depends on the overall energy efficiency (Figure 3) and the need to maximize product delivery efficiency from the point of production to end-use. The leakage of hydrogen carriers at each step may affect the overall efficiency, so leakage should be minimized through the implementation of aproper detection system for quantifying hydrogen releases over the supply chain.

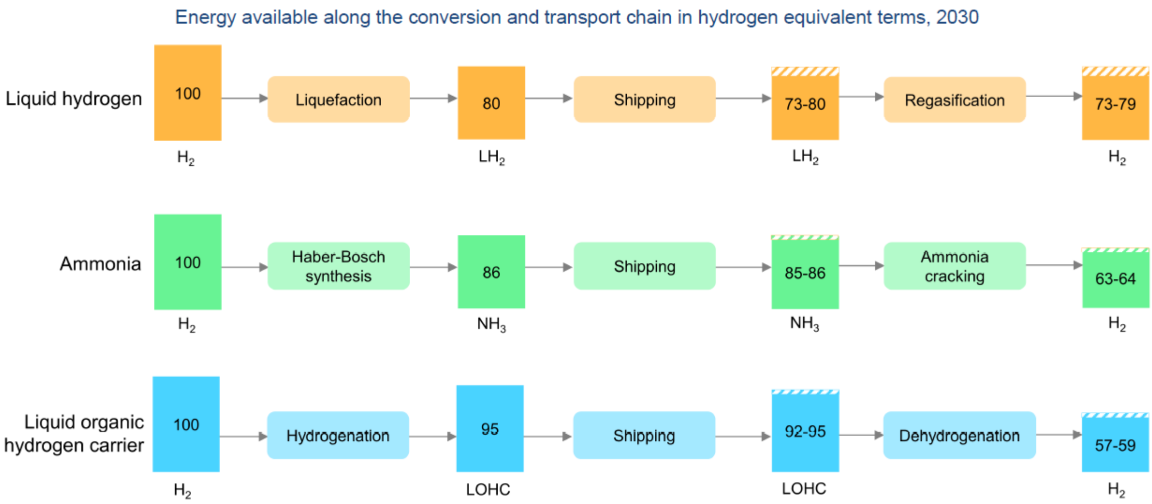


Figure 3 Overall Energy Efficiency of Hydrogen Carriers (LH2, Ammonia and LOHC)

Source: IEA "Global Hydrogen Review 2022" (October 2022)

1-3 International Trade of Hydrogen

In the future, hydrogen is expected to be traded in large volumes worldwide. According to the International Renewable Energy Agency (IRENA), the world energy trade is expected to shift from an oil-dominant portfolio in 2020 to a non-fossil-energy dominant portfolio by 2050, when hydrogen and ammonia trade will have about 20% combined share in trade value (Figure 4).

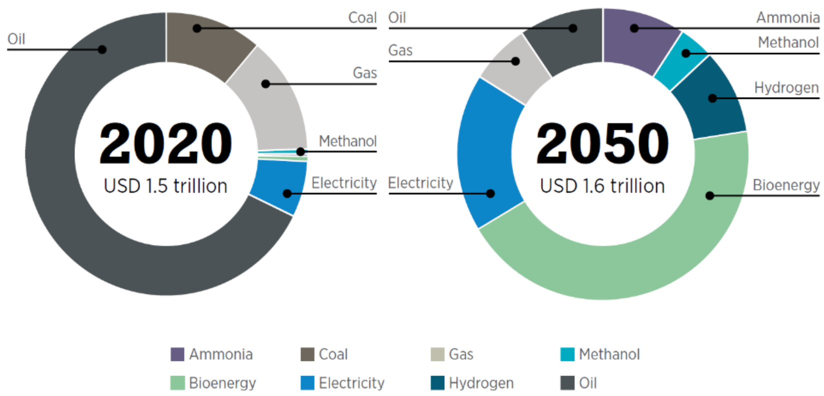


Figure 4 Shifts in the Value of Trade in Energy Commodities, 2020 to 2050

Source: IRENA "Geopolitics of the Energy Transformation - The Hydrogen Factor" (Jan 2022)

It is projected that by 2050, there will be more than 40 different trade routes for hydrogen, each with a capacity of more than one million tons per annum, with the largest reaching more than 20 million tons per annum (Figure 5). Europe is projected to rely primarily on pipeline supply, while Asia may rely on shipping.

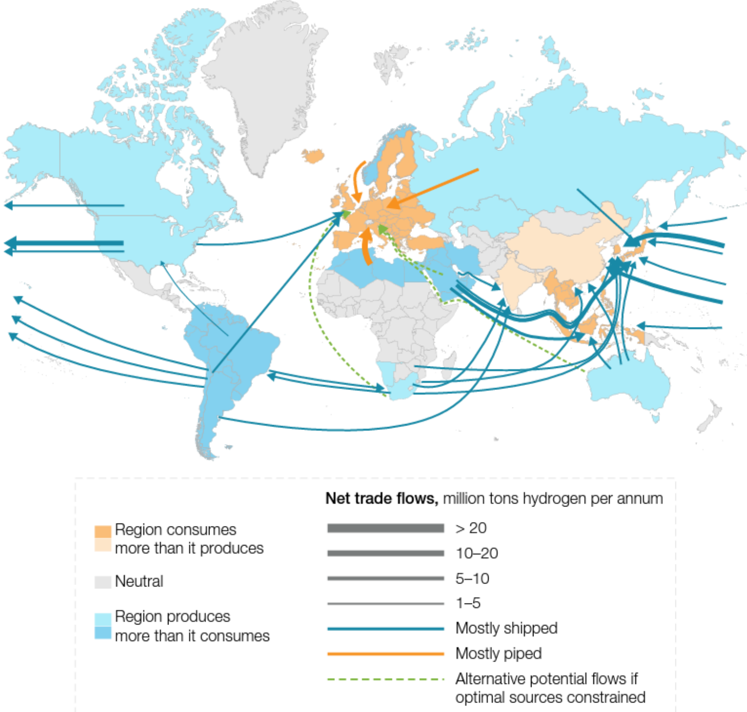


Figure 5　Expected Hydrogen Trade in 2050

Source: Hydrogen Council "Global Hydrogen Flows: Hydrogen trade as a key enabler for efficient decarbonization"(October, 2022)

Hydrogen can be shipped as LH2, LOHC or Ammonia. For shipping, the vessels and storage tanks should be equipped with proper leak detection devices appropriate for each form for safe operation. This is also true for loading terminals and receiving terminals (e.g. loading system and storage tanks). An example of a LH2 receiving terminal is shown in Figure 6.

Figure 6　Example of LH2 Receiving Terminal

Source: HySTRA

1-4 International Cooperation on Hydrogen Safety

1-4-1 Mission Innovation: Clean Hydrogen Mission

Mission Innovation (MI) is a global initiative catalysing a decade of action and investment in research, development and demonstration to make clean energy affordable, attractive and accessible for all. It originally initiated in 2015, with the target to double its governmental and/or state-directed clean energy research and development investment over five years. After the achievement of this target, MI initiated its second phase “Mission Innovation 2.0 (MI2.0)” to support faster, cleaner, affordable energy transitions, increasing global confidence to set, or strengthen, ambitious climate and energy goals.

Currently MI2.0 has eight missions, one of which is Clean Hydrogen Mission (CHM)[4]. CHM has the goal to increase the cost-competitiveness of clean hydrogen by reducing end-to-end costs to a tipping point of 2 USD/kg by 2030. The Mission released “Action Plan 2022-2024” in September 2022, which describes actions toward the mission goal.

Currently, CHM has three pillars (Figure 7), and hydrogen safety is a major discussion topic for the “end-use application working group” in Pillar 1 (Research and Innovation), and for the “Codes and Standards Working Group” in Pillar 3 (Enabling Environment).

CHM supports Hydrogen Fuel Cell Off-Road Equipment and Vehicles Working Group. The overall goals of the group are: 1) Accelerate commercialization, 2) Facilitate collaboration and cooperation, 3) Develop capital equipment and fuel costs comparable to incumbent technologies, 4) Demonstrate in real world operating conditions.

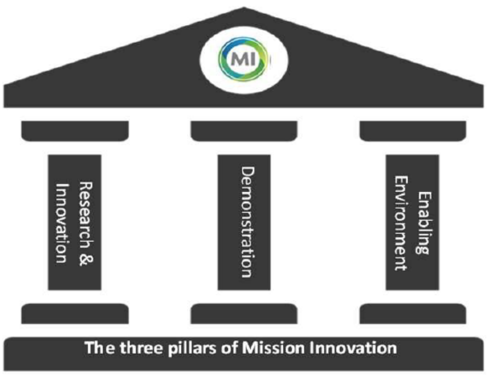


Figure 7 Clean Hydrogen Mission’s 3 Pillars

Source: Mission Innovation: The Clean Hydrogen “Mission Action Plan 2022-2024” (September 2022)

[4] Co-leads: Australia, Chile, European Union, United Kingdom and United States

1-4-2 IPHE Regulations, Codes, Standards, & Safety Working Group

The International Partnership for Hydrogen and Fuel Cells in the Economy (IPHE) was established in 2003 as an international inter-governmental partnership with 21 countries and the European Commission. The IPHE Regulations, Codes, Standards, & Safety (RCSS) Working Group aims to share information, lessons learned and best practices with a focus on hydrogen safety, as well as the harmonization of codes and standards developed by relevant industry code and standards development organizations.

The RCSS WG issued "Compendium of Regulatory Areas for Action in Hydrogen Infrastructure and Mobility/Transportation Technologies" in September 2021, which is a survey-based compendium to determine the regulatory gaps in critical areas for hydrogen and fuel cell deployment, to facilitate and accelerate the transition to clean and efficient energy and mobility systems. The report consists of several heatmaps of critical areas (Table 4).

Table 4 Heatmap of Critical Areas as Identified by the IPHE RCSSWG

(red is considered most critical, orange is moderately critical, and yellow is less critical)

Hydrogen Infrastructure						Hydrogen for Mobility/Transportation		
Hydrogen injection at transmission level	Hydrogen injection at distribution level	Methanation and injection of Methane (SNG) via methanation from hydrogen at transmission / distribution level	H2 refilling station (HRS)		Maritime Infra	Mobility infra (tunnel, bridge, underground parking...)	Heavy Duty vehicles	H2 and H2-based fuel vessels
Legal framework: permissions and restrictions (and Ownership constraints (unbundling))	Legal framework: permissions and restrictions (and Ownership constraints (unbundling))	Legal framework: permissions and restrictions (and Ownership constraints (unbundling))	Land use plan (zone prohibition)		Off-shore refueling	Restrictions & Incentives	Type approval & Individual vehicle registration - Process	Legal framework: permissions and restrictions (and Ownership constraints (unbundling))
Permission to connect/ inject	Permission to connect/ inject	Permission to connect/inject	(LH2) Permitting requirements/ process	(GH2) Permitting requirements/ process	On-shore refueling		Restrictions & Incentives	Safety requirements (compliance with safety regulation/ risk control expectations)
Safety requirements and process (safety distances internal / external)	Safety requirements and process (safety distances internal / external)	Safety requirements (compliance with safety regulation / risk control expectations)	(LH2) Safety requirements and process (safety distances internal/ external)	(GH2) Safety requirements and process (safety distances internal/ external)			Service and maintenance	H2 on-board storage
Gas quality requirements	Gas quality requirements	H2/ SNG quality requirements	H2 quality requirements					
			Quality measurement requirements					

Source: IPHE RCSS WG "Compendium of Regulatory Areas for Action in Hydrogen Infrastructure and Mobility/Transportation Technologies" (September 2021)

According to the report, safety (including maintenance requirements, approvals, and inspections) is a priority, and safety improvements should be incorporated into efforts to address the other gaps identified. For hydrogen infrastructure, safety requirements and processes (e.g. safety distances, leak detection) are critical for all application areas (hydrogen injection into pipelines, methanation and injection into pipelines, hydrogen refueling stations, and maritime infrastructure). For mobility/transportation, especially for maritime applications, safety guidelines for vessels appear to be nonexistent in many national regulations, so that guideline development is critical for these applications.

1-4-3 The Center for Hydrogen Safety

Communication of hydrogen-specific safety guidance will be critical to the success of hydrogen as a part of the global energy transition. While hydrogen has been used safely in industrial applications for nearly a century, expanding its use as a fuel involves a wider and more diverse group of stakeholders. Establishing and communicating best practices from a trusted, independent safety resource is a valuable part of the hydrogen ecosystem.

Founded in 2018, the Center for Hydrogen Safety (CHS) is an international, non-profit, corporate membership organization promoting the safe operation, handling, and use of hydrogen and hydrogen systems across all installations and applications. CHS has more than 100 global member organizations and 14 strategic partners and utilizes best practices, lessons learned, education resources, conferences, webinars, workshops, and working groups to develop and share hydrogen safety knowledge.

CHS has active working groups on hydrogen blending with natural gas (including the development of best practices for leak detection in this application), equipment and components failure rates, workforce development, and safety culture. The Center has more than 20 eLearning and education resources and anticipates the release of its first multi-lingual course, which will include translation to Japanese, French, and Spanish. CHS also follows recent incidents closely to identify learnings and keep its membership informed.

2 Hydrogen Applications and Detection Technology

2-1 Fuel Cell Electric Vehicles (FCEVs)

Fuel Cell Electric Vehicles (FCEV), or simply Fuel Cell Vehicles (FCVs), are one of the most common hydrogen application in cities. Today, there are several types of FCEVs are on the road, and these FCEVs are equipped with hydrogen leak detection sensors. One commercial vehicle is the light duty (LD) FCEV, which corresponds to passenger cars and industrial trucks such as lift trucks; typically these have on-board hydrogen storage of less than 10 kg (usually as GH2).

Toyota’s MIRAI has three leak detection sensors; one at the forward compartment (near the fuel cell stack) and two at the hydrogen tanks (Figure 8). According to Toyota, “if a hydrogen leak of a certain concentration or higher is detected, a warning lamp appears on the meter and it shuts off the valve of hydrogen tanks,” and “all three hydrogen tanks and the fuel cell unit are located outside the cabin space. The vehicle structure ensures that, even in the unlikely event that a hydrogen leak occurs, leaked hydrogen easily escapes to the outside for quick dissipation.”

MIRAI’s detection sensor is a catalitic combustion type, which when exposed to hydrogen causes the device temperature to rise. The temperature rise is measured as a change in resistance of an embedded noble metal coil. Mechanistically, the oxidation of hydrogen occurs when it comes in contact with the surface of a catalyst (Figure 9).

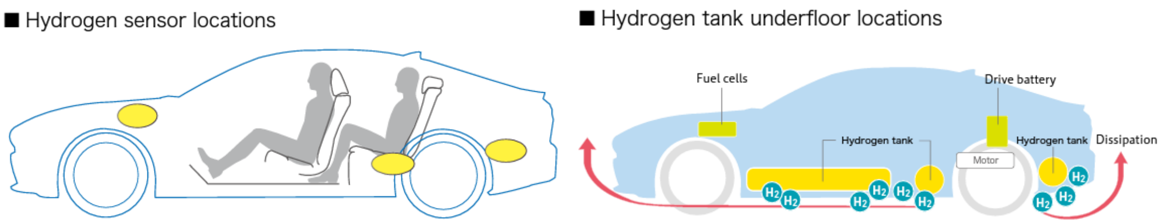


Figure 8 Toyota MIRAI’s Hydrogen Leak Sensors

Source: Toyota “New MIRAI Press Information 2020”

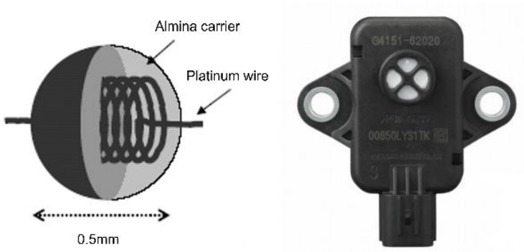


Figure 9 MIRAI’s Hydrogen Leak Sensor – Detection Mechanism

Source: New Cosmos Electric

2-2 Off-Road Vehicles

Possible hydrogen application on off-road vehicles include mining, construction, utility and agriculture vehicles / equipment (Figure 10, Figure 11).

This application is also classified as heavy duty vehicles, which refers to size of the vehicle and its fueling requirements (hydrogen on-board storage is often 10 times that amound for light duty vehicles). The detection requirements for off-road vehicles are similar to the requirements of light-duty vehicles, but must withstand harsher environmental conditions. The largest vehicles in this segment would be condiered ultra heavy duty with upto 1,000 kg of H_2 on board.

Figure 10 Examples of Off-Road Vehicles – Mining, Construction and Utility equipment

Source: Komatsu “Decarbonization Approaches Construction Equipment” (September 2021)
(Mission Innovation Hydrogen Fuel Cell Off-Road Equipment and Vehicles Virtual Workshop)

Figure 11 Examples of Off-Road Vehicles – Agriculture

Source: [Upper] John Deere (September 2021)
[Lower] CNHi “Technology Challenges for Hydrogen Fuel Cells in Agricultural Applications” (September 2021)
(Mission Innovation Hydrogen Fuel Cell Off-Road Equipment and Vehicles Virtual Workshop)

In terms of hydrogen safety, the most challenging application is mining, because of the wide range of environmental conditions, need for dust-resilience, large storage volumes and need for fast hydrogen refueling (Table 5).

Currently in South Africa, Anglo American, ENGIE, Plug Power, and Ballard Power Systems have been collaborating to operate a hydrogen-powered mining haul truck “nuGen” in Anglo American’s Mogalakwena Platinum mine (Figure 12). With a payload of 290 tons, the truck is currently the world’s largest heavy-duty hydrogen vehicle. At the moment, the consortium has not yet publicly disclosed the details of the truck system or the hydrogen detection system installed. However, due to the severe and harsh operation condition for such trucks, the adoption of hydrogen detection technology is considered necessary.

Table 5 Challenges Associated with Adoption of Hydrogen for Mining (by Komatsu)

Application
・ Wide range of environmental conditions ranging from Artic/Northern Latitudes (40°C), desert (>50°C), rainforest (>90%RH), to high altitude (>4000m)
・ Most severe uphill hauls of several kms at 10% grade
・ Many profiles exist at each operation and vary over time as the mine develops
・ General expectation of mine operators zero emission equipment should have similar performance to current (ICE)
Onboard Systems
・ Safety is of prime importance
・ Space claim of FC and battery
・ Hydrogen tanks physical size and capacity
・ Dust resilience
・ Availability, reliability, and maintainability/serviceability
Infrastructure
・ Safety is of prime importance
・ Generally, no experience with H2 or cryogenics
・ Fast fueling is a must, H2 requirements will be ~800 1200 kg/day/truck.
Commercials
・ TCO must be competitive!

Source: Komatsu “Decarbonization Approaches Construction Equipment” (September 2021)
(Mission Innovation Hydrogen Fuel Cell Off-Road Equipment and Vehicles Virtual Workshop)

Figure 12 Hydrogen-Powered Mining Haul Truck “nuGen”

Source: Anglo American

2-3 Hydrogen Refueling Stations (HRS)

Hydrogen refueling stations (HRS) are becoming more familiar to the public with the increasing number of FCVs on the road. Since many HRS are built within cities, the mitigation of risk of hydrogen hazards is indispensable to protect FCVs, the surrounding areas, and people (Table 6).

Table 6 L List of Possible Hazards of HRS

Failure mode	Source of failure	Effect	Severity (1-10)	Probability of Occurrence (1-10)
Fire and explosion	Ignition in the vicinity of H2 and O2 mixture	Equipment damage and possible injuries	10	2
Hydrogen leak in piping	Mechanical failure / improper joints and fittings	Potential fire and explosion	7	3
Hydrogen leak in electrolyser	Overpressure causing rupture of membrane	Potential fire and explosion	8	3
Hydrogen leak in storage tank	Mechanical failure / improper joints and fittings	Potential fire and explosion	8	3
Compressor failure	Equipment failure, worn out seals	Potential H2 leaks	5	6
Hose pressure rating verification error	Human error	Overpressure in vehicle tank, potential H2 leaks	6	3
Leak at breakaway fitting	Equipment failure at dispenser	Potential fire	7	2
Improper fill speed at fuel dispenser	Failure to follow standard operating procedures, deficiency in procedures, software failure	Overheating on receiving fuel tank	5	4
Incorrect check valve installation	Human error, inadequate inspections	Property damage	7	2
Vehicle crashing into refuelling system	External factor	Property damage and injuries	7	2

Source: Ján Vereš et al. “Safety Aspects of Hydrogen Fuelling Stations”
Chemical Engineering Transactions, Vol. 91, 2022

The combination of safety devices and safety systems for HRS is different depending on jurisdictions and regions. For example, Japanese HRS are equipped with several safety devices and systems, some of which are specialized for Japanese deployment requirements (e.g. seismometers and water sprinklers).

Especially for hydrogen detection, gas leak detection sensors and flame detection sensors are indispensable for facility safety and are installed in several places at HRS (production facility, compressors, storage tanks and dispensers). The use of hydrogen leak detection systems are mandated in most jurisdictions.

Figure 14 shows the details of a dispenser system. Other than a gas leak detection sensor and flame detection sensor, there also are temperature and pressure sensors, and an ambient temperature sensors installed.

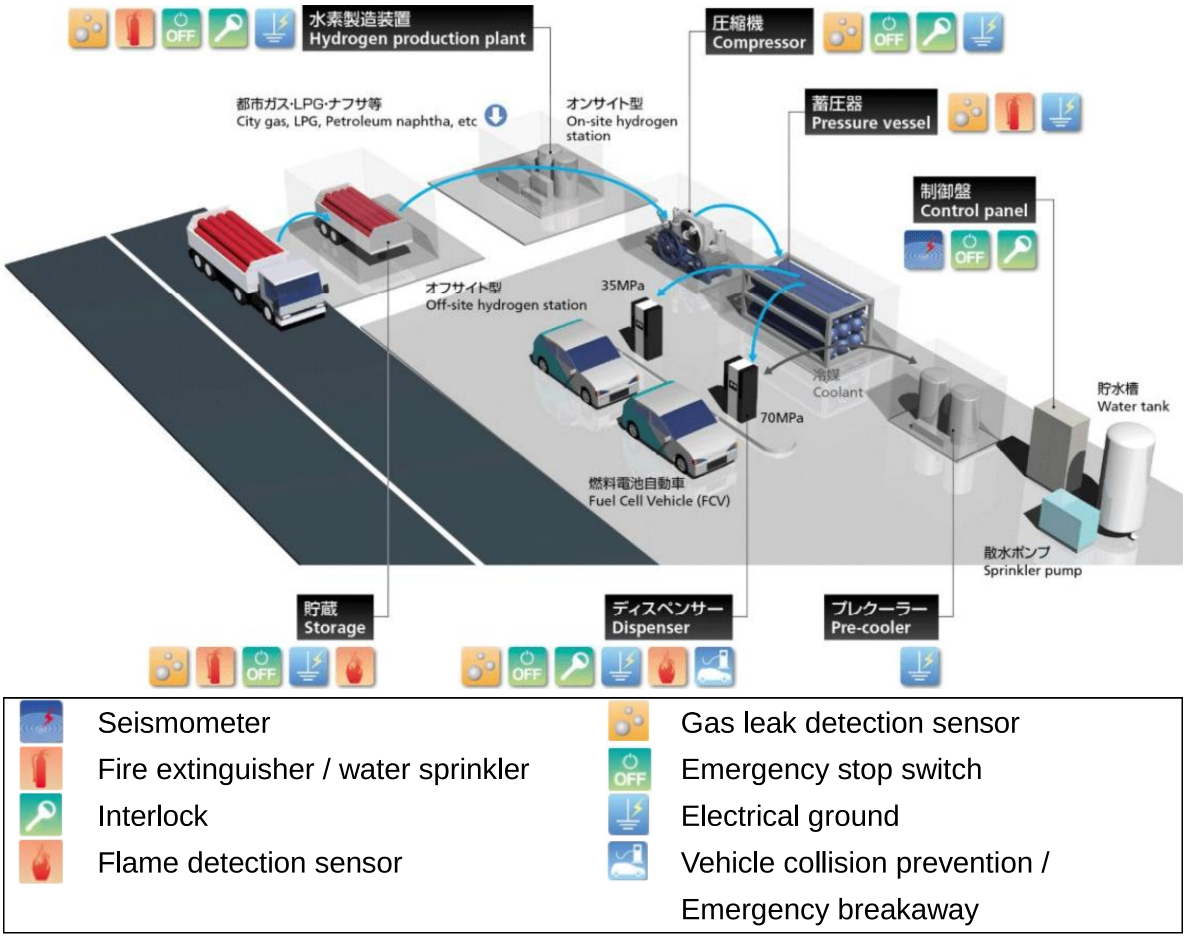


Figure 13 Safety Devices and Systems for HRS (Japan)

Source: The Association of Hydrogen Supply and Utilization Technology (HySUT)

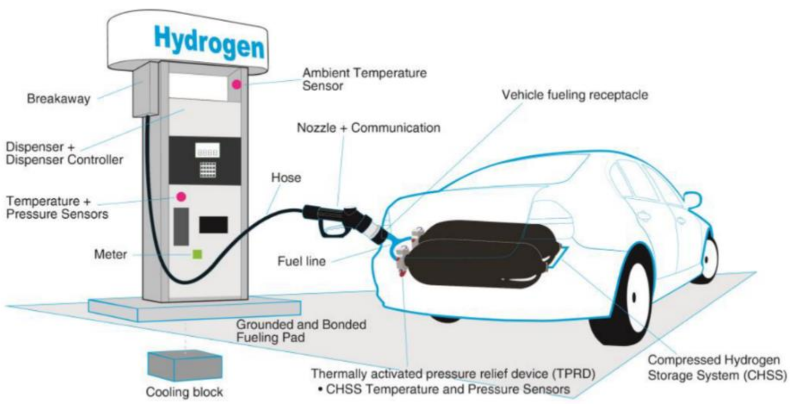


Figure 14 Hydrogen Fueling Diagram Illustrating Key Components of a Hydrogen Dispenser

Source: ISO 19880-1:2020

2-4 Maritime (Hydrogen Carrier ships)

Hydrogen is expected to be widely traded internationally as a commodity. One major international transport means for hydrogen is by shipping in the form of LH2. Already, ships and infrastructure are being developed and demonstrated for large scale transport of LH2 from remote production sites to end-use locations.

Kawasaki Heavy Industries has developed the world's first LH2 carrier “Suiso Frontier” with a hydrogen tank of 1250 kL (about 75 tonnes) of LH2 (Figure 15). The ship made the first round trip between Kobe, Japan and Hasting, Australia in December 2021-February 2022. LH2 was loaded in Hasting and unloaded in Kobe as a proof-of-concept of the LH2 supply chain. Ships carrying LH2 should be equipped with hydrogen detection system according with Interrim recommendation for carriage of liquefied hydrogen in bulk by International Maritime Organization. At this moment, there is no known detailed guidance that has been published on hydrogen detection systems for maritime applications.

The International Maritime Organization (IMO) has been amending its International Code of Safety for Ships using Gases or other Low-flashpoint Fuels (IGF) code, based on LNG, to include LH2 as a fuel. The draft Interim guidelines are expected to be finalized in 2023. The current IGF code requires equipment to detect flames, protect emergency shutdown areas, shut off the fuel flow in case or emergency and enforce air flow for tank connection spaces. Therefore, hydrogen detection devices are necessary to meet these needs.

Currently hydrogen carrier ships are powered by conventional fuels, but in the future, they are expected to be powered by hydrogen (possibly by LH2), so safety measures for both carried (stored) LH2 and fuel LH2 are required.

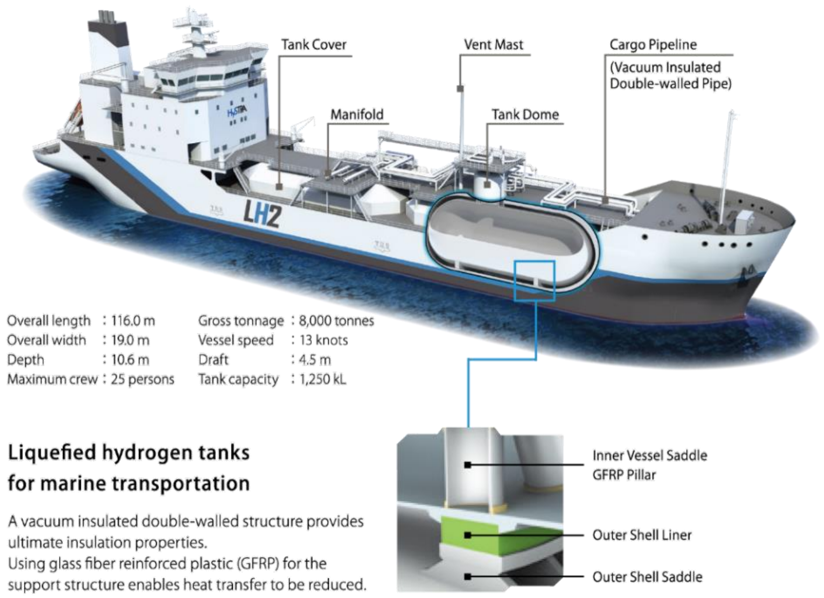


Figure 15 Liquefied Hydrogen Carrier “Suiso Frontier”

Source: HySTRA

2-5 Aerospace

Hydrogen has been widely used for the aerospace industry, especially for rockets. Recently, major aircraft industries have announced the concepts for carbon-free fuel for aircrafts, which use hydrogen as a fuel (Figure 16).

Like rockets, hydrogen-based aircraftsuse LH2 for fuel, because of its compactness compared to compressed hydrogen. These aircrafts require stricter handling of LH2 than road and maritime applications, because they rely on LH2 for propulsion in the air. Like FCEVs (MIRAI), the hydrogen storage system is separated from the passenger compartment, but any leakage of hydrogen may strongly damage the operation of the aircraft. At the moment, there is no known detailed guidance that has been published for hydrogen detection system for hydrogen-based aircrafts.

Turbofan

Two hybrid-hydrogen turbofan engines provide thrust. The liquid hydrogen storage and distribution system is located behind the rear pressure bulkhead.

Turboprop

Two hybrid-hydrogen turboprop engines, which drive eight-bladed propellers, provide thrust. The liquid hydrogen storage and distribution system is located behind the rear pressure bulkhead.

Blended-Wing Body (BWB)

The exceptionally wide interior opens up multiple options for hydrogen storage and distribution. Here, the liquid hydrogen storage tanks are stored underneath the wings. Two hybrid-hydrogen turbofan engines provide thrust.

Figure 16 Example of Hydrogen-based Aircrafts: Airbus’s ZEROe concept

Source: AirBus “ZEROe”

3 Hydrogen Detection Technology

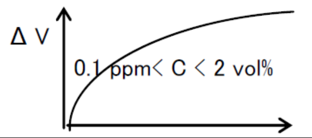
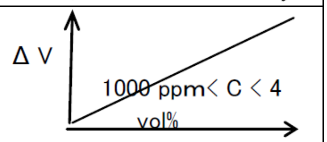
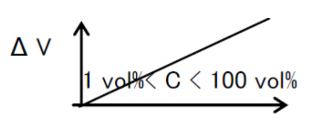
3-1 Conventional Hydrogen Detection Technologies

As mentioned before, hydrogen is an odorless and invisible gas, and thus requires hydrogen detection technologies for leak detection. .

Three conventional technologies for detecting combustible gas including hydrogen are summarized in Table 7. As discussed above, there are other hydrogen detection technologies. Hydrogen can be readily detected by electrochemical sensors and by sensor platforms that utilize palladium thin films, in which the adsorption of hydrogen changes the electrical and optical properties of the thin-film. Each conventional hydrogen detection technology has optimum operation conditions and performance specifications of hydrogen concentration range, measurement response time, and robustness from chemical interferences.

Most of the common detection methodologies have been optimized for hydrogen detection near its lower flammable limit of 4 vol%. As shown in Figure 17,¥conventional hydrogen detection technology based on thermoelectric responses has optimum operation conditions, in term of hydrogen concentration. This results is a generalized summary, and performance metrics vary widly with sensor model and manufacturer.

Table 7 Conventional Hydrogen Detection Technologies – General Characteristics

Type	Principle	Characteristics	Concentration and detection voltage
Hot-wire semiconductor sensor	- Detection of the change of electron conductivity due to the oxidation of H2	- High resolution / high selectivity - Response (90%): ~20 sec	
Catalytic combustion sensor	- Detection of temperature change of catalysts (Pd, Pt/Al_2O_3)	- Low selectivity for hydrogen - Response (90%): 5-10 sec	
Heat conduction sensor	- Detection of the change of gas thermal conductivity due to the mixture	- Low resolution / high selectivity - Response (90%): 5-10 sec	

Source: H. KITAGUCHI, "The present situation and some subjects of the hydrogen gas sensor", HESS (Hydrogen Energy Systems Society of Japan) vol 30, No.2 (2005) (in Japanese)
https://www.hess.jp/Search/data/30-02-035.pdf

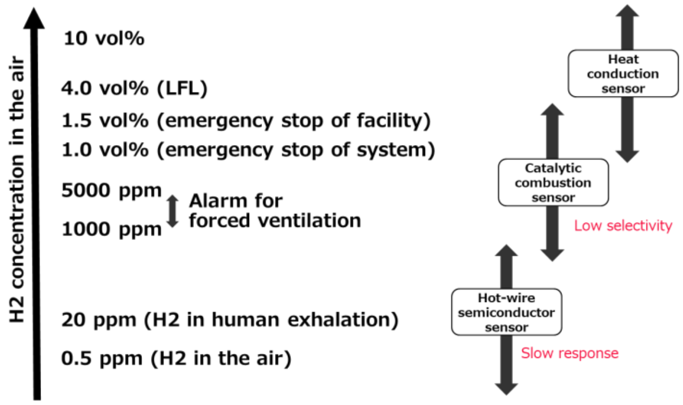


Figure 17 Conventional Hydrogen Detection Technologies – Range of Hydrogen Concentration

Source: AIST, "Thermoelectric hydrogen gas sensor", Synthesiology, Vol.4, No.2 (2011) in Japanese
https://www.aist.go.jp/pdf/aist_j/synthesiology/vol04_02/vol04_02_p92_p99.pdf

3-2 New Hydrogen Detection Technologies

3-2-1 Fiber Optic Sensor

The Idea of using fiber optic for hydrogen sensor has several advantages, e.g. no-risk for explosion, high durability, high corrosion-resistance, wider coverage of sensing points, compactness and lightness of devices.

The basic mechanism for fiber optic sensors is to detect the change of interference of lights, caused by physical or chemical change on the surface of the fiber. Sensing elements can be at a discrete point on the fiber (e.g. the tip) or distributed along the length of the fiber at closely spaced discrete location. The sensing elements can respond chemically to hydrogen or to a physical response associated with a leak (e.g., acoustic signal, stresses). One approach is using Fiber Bragg Grating (FBG) technique that incorporates Pd or Pd alloy thin film on the fiber surface that will swell with hydrogen is gas adsorbed, resulting in the change of wavelength shift of FBG (Figure 18). In addition to remote monitoring potential, a fiber optic sensor with distributed sensing elements can be possibly used for hydrogen pipeline monitoring.

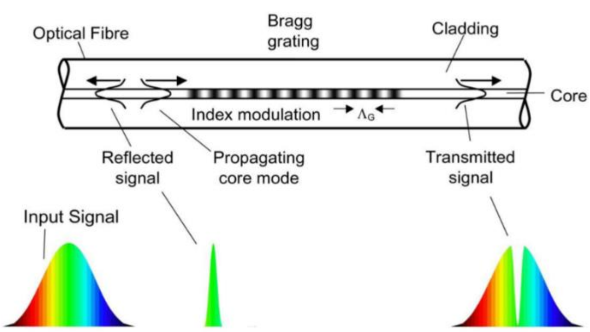


Figure 18 Schematic Diagram of an FBG Hydrogen Sensor

Source: Stephen J. Mihailov "Fiber Bragg Grating Sensors for Harsh Environments" Sensors 2012, 12(2), 1898-1918

3-2-2 Ultrasonic

Ultrasonic leak detectors are designed to respond to the acoustic signal that is generate as a pressureized gas passes through an orifice (e.g., a leak). These devices are optimized to measure the ultrasonic signatures of leaks. Performance is optimized by developing methodologies to distinguish from operational and background acoustic signals; this is usually based upon duration and intensity of the measured acoustic signal (e.g., leaks tend to be louder and of longer duration than most operational signatures). This method quickly detects leaks as they are occurring. Commercial systems have been developed but their use in hydrogen facilities has been limited. A current research focus area is to utilize multiple ultrasonic leak detection systems to identify the source of the leak.

Another acostic sensor concept, which is much less developed is based upon the speed of sound through a low density medium. The sound velocity of hydrogen is about four times faster than that of the air, so that increased hydrogen concentration in the air may change the sound velocity, which can be detected by ultrasonic sensors (Figure 19). Such ultrasonic methodology has been used for the measurement of distance between objects but has had limited development for gas detection. Like optical fibers, ultrasonic sensor technology has no-risk for explosion, high durability, and high corrosion-resistance.

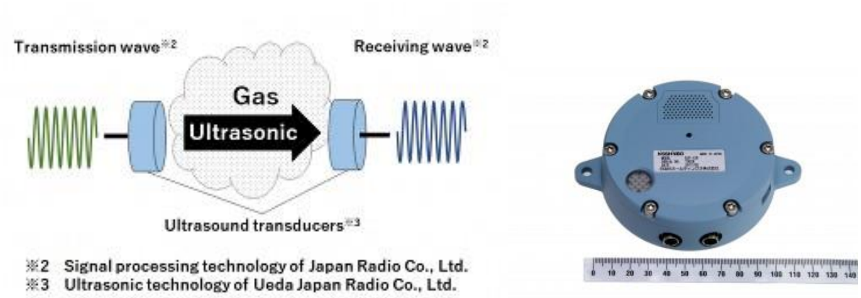


Figure 19 Schematic Diagram and Prototype Model of an Ultrasonic Hydrogen Sensor

Source: Nisshinbo News “Notice regarding Ultrasonic Hydrogen Gas Sensor” (November 7, 2017)

3-2-3 Schlieren Imaging

Schlieren Imaging is a visualization technique using Schlieren photography, which monitors the difference of gas density in transparent media (Figure 20). The image is real-time, but two-dimensional (2D). This technique is widely used for the analysis of hydrogen jets or flames (or a mixture of hydrogen and other gases) (Figure 21).

Schlieren Imaging gives users detailed information of hydrogen behavior and is widely used especially at laboratories. This technique has traditionally been used for the development of devices and system, and not for the monitoring of hydrogen in commercial facilities.

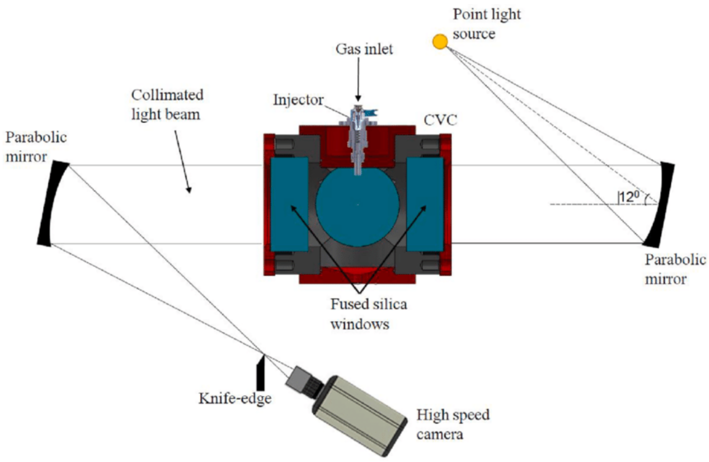


Figure 20　Schematic Diagram of Schlieren Imaging Experimental Setup

Source: Nisshinbo News "Notice regarding Ultrasonic Hydrogen Gas Sensor" (November 7, 2017)

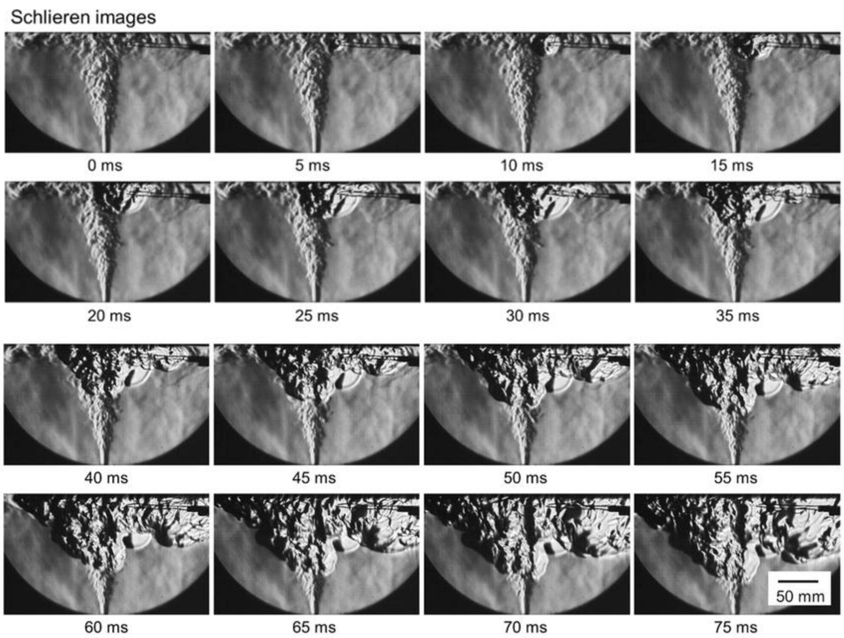


Figure 21　Image Sequences of a Methane/Hydrogen Mixture Impinging Flame

Source: Q. Wang et al. "An Optimization and Parametric Study of a Schlieren Motion Estimation Method" Flow, Turbulence and Combustion volume 107, pages609–630 (2021)

3-2-4　Memory-based Sensor

One of new approaches for light and small hydrogen sensor with low power consumtion is to apply semiconductor technology for hydrogen detection. Resistive Random Access Memory (ReRAM or RRAM) is a non-volatilerandom-access memory whose the resistance is changed by redox reaction. Using this princicple, hydrogen, as a reducing agent, can be detected by the change of rerstance, in accordance with hydrogen concetration. One of such working mechanisims is shown in Figure 22.

A Japanese company, Nuvoton Technology, is developing ReRAM-based hydrogen sensor using NEDO fund. One of prototype model consumes only 0.01 mW with hydrogen detection range of 0.1 - 4%.

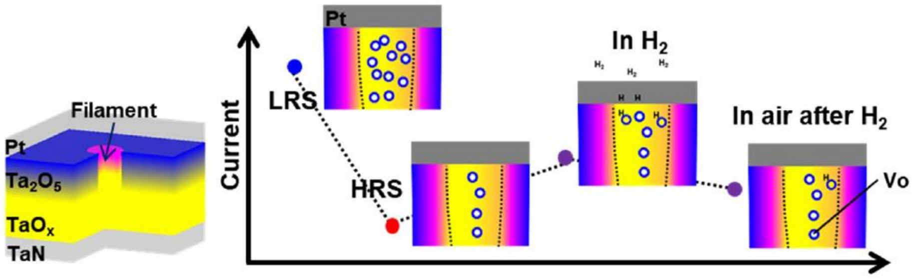


Figure 22 Image Sequences of a Methane/Hydrogen Mixture Impinging Flame

Source: Z. Wei et al., "From Memory to Sensor: ultra-Low Power and High Selectivity Hydrogen Sensor Based on ReRAM Technology," 2018 IEEE Symposium on VLSI Technology, Honolulu, HI, USA, 2018, pp. 63-64

4 Resources

Mission Innovation
http://mission-innovation.net/

Mission Innovation – Clean Hydrogen Mission
https://explore.mission-innovation.net/mission/clean-hydrogen/

International Partnership for Hydrogen and Fuel Cells in the Economy (IPHE)
https://www.iphe.net/

IA HySafe
https://hysafe.info/

Center for Hydrogen Safety
CHS | Center for Hydrogen Safety (aiche.org)

DOE H2 Tools
https://h2tools.org/

DOE Hydrogen Safety Panel
https://h2tools.org/hsp

European Hydrogen Safety Panel
https://www.clean-hydrogen.europa.eu/get-involved/european-hydrogen-safety-panel-0_en

Mission Innovation Hydrogen Fuel Cell Off-Road Equipment and Vehicles Virtual Workshop
https://www.energy.gov/eere/fuelcells/mission-innovation-hydrogen-fuel-cell-road-equipment-and-vehicles-virtual-workshop

CO_2-free Hydrogen Energy Supply-chain Technology Research Association (HySTRA)
https://www.hystra.or.jp/en/

Advanced Hydrogen Energy Chain Association for Technology Development (AHEAD)
https://www.ahead.or.jp/en/

Clean Fuel Ammonia Association
https://greenammonia.org/en/

Missionn Innovation
Clean Hydrogen Mission

Hydrogen Detection Technologies
for Hydrogen Safety
Current status of Technology

March 2023

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