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Alternative Vehicles - Fire Scenarios within Confined Spaces - Road Tunnels

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Abstract

In the event of a fire involving alternative fuel vehicles in a confined space, such as a road tunnel, the risk of a hydrogen explosion presents a significant concern. Hydrogen is highly flammable and can ignite in the presence of an ignition source and oxygen. It's important for road tunnel operators to have robust fire safety protocols in place to minimize the risk of fire and to ensure an effective response in the event of an incident. This can include measures such as fire suppression systems, fire-resistant tunnel linings, and fireproof ventilation systems. Additionally, the proper use of hydrogen sensors can aid in the early detection of hydrogen gas in the event of a leak and help prevent the spread of fire. It is crucial that all road tunnel personnel are trained on the risks associated with alternative fuel vehicles and the procedures to be followed in the event of a fire, including the proper evacuation of the tunnel. Regular fire drills can also help to ensure that everyone is prepared in the event of an emergency. There are many commercially available hydrogen safety sensors. Because end-users have a broad range of sensor options for their specific applications, the final selection of an appropriate sensor technology can be complicated. Facility engineers and other end-users are expected to select the optimal sensor technology choice. However, some sensor technologies may not be a good fit for a given application. Informed decisions require an understanding of the general analytical performance specifications that can be expected by a given sensor technology. Although there are many commercial sensors, most can be classified into relatively few specific sensor types (e.g., electrochemical, metal oxide, catalytic bead, and others). Performance metrics of commercial sensors produced on a specific platform may vary between manufacturers, but to a significant degree a specific platform has characteristic analytical trends, advantages, and limitations. Knowledge of these trends facilitates the selection of the optimal technology for outdoor applications. An understanding of the various sensor options and their general analytical performance specifications would be invaluable in guiding the selection of the most appropriate technology for the designated application.

Acronyms

Abbreviation	Description
LPG	Liquefied Petroleum Gas
CNG	Compressed Natural Gas
BEV	Battery Electric Vehicles
FCEV	Fuel Cell Electric Vehicles
EV	Electric vehicle
ICEs	Internal combustion engines
FCEVs	Fuel cell electric vehicles
HGVs	Heavy Goods Vehicles
Al	Aluminum
LH_2	Liquid Hydrogen
CGH_2	Compressed hydrogen is the gaseous state
FCET	Fuel Cell Electric Trucks
PEM	Proton-Exchange Membrane fuel cells
SOCF	Solid Oxide Fuel Cell
BETs	Batter Electric Trucks
OEM	Original Equipment Manufacturer
LEL	Lower Explosive Limit
UEL	Upper Explosive Limit
NFPA	National Fire Protection Association
GC	Gas Chromatography
MS	Mass Spectrometry
CB	Catalytic Bead
CAT	Catalytic Combustion Sensor
TCD	Thermal Conductivity Detector
FETs	Field-Effect Transistors
DOE	Department of Energy
Pd	Palladium
SAW	Surface Acoustic Wave Sensor
QCMS	Quartz Crystal Microbalance Sensor
EC	Electrochemical Sensors
MOXS	Metal Oxide Sensors
PEM	Proton Exchange Membrane
CFD	Computational Fluid Dynamics
HRR	Heat Release Rate

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1. Introduction and scope

Due to the prospect of decreasing energy reserves and growing costs of the present energy resources, the age of increasing use of renewable energies has drastically approached. There are numerous vehicles which utilize alternative fuels, or fuels that differ from typical hydrocarbons such as gasoline and diesel, throughout the world. This shift is being driven by concerns over the environment impact of fusil fuel emissions, to reduce emissions from transport vehicles, as well as the desire to reduce dependence on foreign oil and increase energy security. Alternative energy carriers are expected to replace these traditional energy carriers. The number of vehicles powered with alternative energy carriers, include those running on the combustion of natural gas and propane as well as electrical drive vehicles utilizing batteries or hydrogen as energy storage, is expected to increase significantly in the next years.

Hydrogen alternative energy carrier gas is the principal subject of this thesis, hydrogen production, storage and conversion have reached a technological level at which its use as an energy carrier is of high interest. However, the storage of hydrogen is often considered a problem causing a bottleneck in the renewable energy economy based on hydrogen as an energy carrier [20]. Since hydrogen is the lightest elements and has very small molecules, it can escape from tanks and pipes more easily than conventional fuels [20]. The composition of the vehicle fleets that use tunnels will therefore change with unprecedented speed and magnitude towards alternative energy powered drive trains and vehicles. This might impact the safety in road tunnels.

Hydrogen risk increases in confined spaces like tunnels comparing to open roads. A deeper understanding of possible additional risks, especially in considering incidents in tunnel structures, is of greatest interest and is currently investigated in various research projects. Because the number of alternative fuels vehicles is expected to increase significantly, it is important to analyze the hazards and risks involved with these new technologies with respect to the regulations related to specific transport infrastructure, and it is necessary to understand the interactions between unexpected hydrogen presence and the risk mitigation systems in the confined infrastructures, such as bridges and tunnels.

Ventilation is one of the most important safety measures in tunnel systems, to discharge the contaminations from the fossil fuel driven vehicle exhausts then to keep the tunnel air quality at a required level in normal operations, and to extract toxic gases and smoke in case of tunnel fires thus to facilitate evacuation, rescue, and firefighting activities in fire emergencies.

Safety measures, emergency systems and corresponding regulations and standards are already available for existing traffic infrastructures, while hydrogen powered vehicles are joining gradually in the traffic. The understandings are hopefully used to improve current safety measures and to append additional new measures against hydrogen risks, in order to protect life and property especially when hydrogen vehicles are involved in traffic accidents in e.g., tunnels. Accordingly, the regulations, codes and standards for the traffic infrastructures should be updated to be suitable for both conventional and hydrogen vehicles.

For a process safety application, a hydrogen leak can be more dangerous, and its detection becomes more challenging than other gases. This report focuses on the best hydrogen sensors that could be used in order to decrease the hazards that are presented by hydrogen fuel cell electric vehicles. There are numerous research and analysis on hydrogen sensors and their response time, that are used in tunnel scenarios, to detect any leakage of hydrogen fuel and to lower the hazards.

Some of these available types of hydrogen sensors, each with different sensing principles and characteristics are:

Catalytic hydrogen sensors, they detect hydrogen by measuring the changes in the heat of reaction, they have high sensitivity and selectivity. These sensors typically have a response time of a few seconds to a few minutes, depending on the size of the sensor and the concentration of hydrogen. The response time can be improved by increasing the surface area of the catalyst or by optimizing the sensor design. These sensors typically have a point source detection capability, which means that they can detect the location of a hydrogen leak in close proximity to the sensor. However, their ability to detect the distribution of hydrogen concentration in each area is limited.

Metal-oxide hydrogen sensors, they use metal oxide films to detect hydrogen gas, when exposed to hydrogen, the metal oxide film undergoes a change in resistance, which is measured and used to detect the presence of hydrogen. These sensors typically have a response time of a few seconds to a few minutes, depending on the operating temperature and the concentration of hydrogen. The response time can be improved by increasing the operating temperature or by optimizing the sensor design. These sensors typically have a spatial resolution that is limited by the size of the sensing element. The size of the sensing element can range from a few millimeters to several centimeters.

Electrochemical hydrogen sensors, they use an electrochemical reaction to detect hydrogen gas, when exposed to hydrogen, the sensor produces an electrical signal, which is proportional to the concentration of hydrogen. These sensors typically have a response time of a few seconds to a few minutes, depending on the size of the sensor and the concentration of hydrogen. The response time can be improved by increasing the surface area of the electrode or by optimizing the sensor design. These sensors typically have a point source detection capability, like catalytic hydrogen sensors. However, some electrochemical sensors can be designed with an array of sensing elements to provide spatial resolution.

Optical hydrogen sensors use optical fibers coated with materials that change their optical properties in the presence of hydrogen, when hydrogen gas is present, the optical properties of the coating change, which can be detected by measuring changes in light intensity. These sensors typically have a response time of a few seconds to a few minutes, depending on the sensitivity of the optical fiber and the concentration of hydrogen. The response time can be improved by increasing the sensitivity of the optical fiber or by optimizing the sensor design. These sensors typically have a high spatial resolution, as they can detect the distribution of hydrogen concentration along the length of the optical fiber.

Thermal conductivity hydrogen sensors, they detect hydrogen by measuring changes in thermal conductivity when hydrogen gas is present, when exposed to hydrogen, the thermal conductivity of the sensing material changes, which is detected and used to determine the concentration of hydrogen. These sensors typically have a response time of a few seconds to a few minutes, depending on the size of the sensor and the concentration of hydrogen. The response time can be improved by increasing the thermal conductivity of the sensing material or by optimizing the sensor design. These sensors typically have a spatial resolution that is limited by the size of the sensing element. The size of the sensing element can range from a few millimeters to several centimeters.

It is important to note that the response time of a hydrogen sensor can depend on many factors, including the specific sensor design, the operating conditions, and the concentration of hydrogen. The response time can also be affected by factors such as humidity, temperature, and other interfering gases. Therefore, it is important to carefully select the appropriate hydrogen sensor for the specific application and to optimize the operating conditions to achieve the desired response time, sensitivity and required spatial resolution.

2. Alternative energy carriers

An energy carrier is either a substance or a phenomenon that can be used to produce mechanical work or heat or to operate chemical or physical processes. It is any system or substance that contains energy for conversion as usable energy later or somewhere else. This could be converted for use in, for example, an appliance or vehicle. Such carriers include springs, electrical batteries, capacitors, pressurized air dammed water, hydrogen, petroleum, coal, and natural gas. batteries,

In the context of vehicles, an energy carrier refers to the type of fuel or energy storage system used to power the vehicle. Traditional vehicles typically use fossil fuels such as gasoline or diesel as their energy carrier, while alternative vehicles use different types of energy carriers such as electricity, hydrogen, or biofuels. Several alternative vehicle and fuel options are under consideration to alleviate the triple threats of climate change, urban air pollution and foreign oil dependence caused by motor vehicles.

The type of energy carrier used by a vehicle can have significant implications for its environmental impact, as well as its performance and operating costs. As technology continues to develop and improve, new types of energy carriers may be introduced for vehicles, and the relative advantages and disadvantages of each will continue to evolve.

Traditional alternative energy carriers

Traditional energy carriers for vehicles typically refer to fossil fuels such as gasoline and diesel, which are derived from crude oil. These fuels have been widely used in the transportation sector for many years due to their high energy density, availability, and ease of use. There are two alternative fuel technologies that are already used with significant market share in certain countries.

1. Liquified petroleum gas

Liquefied petroleum gas (LPG or LP gas, also called Autogas) is non-renewable resource, it is a fuel gas, mostly composed of Propane and butane, that are odorless and colorless gases at room temperature [3]. The gas is produced in oil refineries. LPG is liquified under pressures between 5 to 10 Bar [3]. LPG is one of the most widely used and accepted separate alternative to the conventional petroleum-based transport fuels, gasoline, and diesel [3].

LPG is often used as an alternative to gasoline or diesel in vehicles because it produces fewer emissions and has a higher energy content than gasoline. Vehicles that run on LPG have a separate fuel system, which includes a storage tank, fuel lines, and a regulator to control the flow of gas. One of the benefits of using LPG in vehicles is that it is cheaper than gasoline or diesel in many countries. In addition, LPG-powered vehicles typically have a longer range than electric vehicles and produce fewer emissions than gasoline or diesel-powered vehicles.

Several countries today have well-developed Autogas markets. Global consumption of Autogas has been rising steadily in recent years, reaching 27.1 million tons in 2019. There are now over 27.8 million Autogas vehicles in use around the world [3]. Autogas is the third most popular automotive fuel in the world, with approximately 16 million of 600 million passenger cars powered using the fuel, representing less than 3% of the total market share.

Approximately half of all Autogas-fueled passenger vehicles are in the five largest markets (in descending order): Turkey, South Korea, Poland, Italy, and Australia [3].

Despite LPG being widely used as a fuel for cars, motorists in need of Autogas can sometimes face difficulties, especially in remote areas and in places where supply and demand are low. Therefore, they may need to plan their journeys around access to stations where LPG can reliably be obtained.

Propane Autogas vehicles emit 17% fewer greenhouse gases than gasoline fueled vehicles.

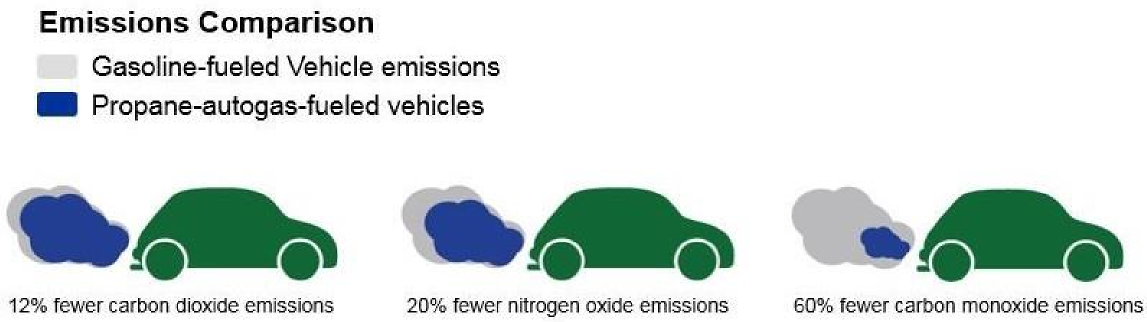

Figure 1 – Emissions Comparison between Propane Autogas fuel and Gasoline fuel

However, one of the disadvantages of using LPG is that it requires specialized equipment and infrastructure for refueling, which can be a barrier to adoption. In addition, the safety of LPG as a fuel can be a concern, as it is highly flammable and can pose a risk in the event of a leak or accident.

2. Compressed natural gas

Compressed natural gas (CNG) is a fuel gas mainly composed of methane (CH4). Methane is not as easily compressed as LPG [3]. Therefore, it is stored compressed in high pressure vessels, compressed to less than 1% of the volume it occupies at standard atmospheric pressure. It is stored and distributed in hard containers at a pressure of 20–25 megapascals (2,900–3,600 psi), usually in cylindrical or spherical shapes. This makes it easier and safer to transport and store, and it also takes up less space, making it more practical for use in vehicles.

CNG is used in traditional petrol/internal combustion engine vehicles that have been modified, or in vehicles specifically manufactured for CNG use: either alone (dedicated), with a segregated liquid fuel system to extend range (dual fuel), or in conjunction with another fuel (bi-fuel). It can be used in place of petrol (gasoline), diesel fuel, and liquefied petroleum gas (LPG). CNG combustion produces fewer undesirable gases than the fuels. In comparison to other fuels, natural gas poses less of a threat in the event of a spill, because it is lighter than air and disperses quickly when released.

The use of CNG is also limited to a few countries where the top three countries are China, Iran, and India. With about 28 million vehicles equipped with CNG it is in the same range as LPG. CNG is used in a variety of land-based motor vehicles, from two wheelers through to off-road [3]. In response to high fuel prices and environmental concerns, CNG has been used in auto rickshaws, pickup trucks, transit and school buses, and trains.

CNG is a clean-burning fuel, with lower emissions of pollutants such as carbon monoxide, nitrogen oxides, and particulate matter than gasoline or diesel. It also has lower greenhouse gas emissions than gasoline, making it a more environmentally friendly fuel option.

One potential drawback of CNG vehicles is that they have a shorter driving range than traditional vehicles. This is because the compressed gas takes up more space than liquid fuel, which limits the amount of fuel that can be stored in the vehicle. However, this issue can be mitigated by installing additional CNG tanks, which can extend the vehicle's range.

Overall, CNG vehicles are a practical and cost-effective alternative to traditional gasoline or diesel vehicles, particularly for fleets of vehicles that have centralized refueling stations. They are also becoming increasingly popular in the consumer market, as more and more people are looking for ways to reduce their environmental impact and save money on fuel costs.

3. Comparison between LPG and CNG

Both traditional alternative energy carriers (LPG and CNG) have been on the market for a long time. However, they have not demonstrated the potential to reach a significant share of vehicles compared to diesel or gasoline. They will remain a part of the local fleet composition where they already have a share of the market, but we do not expect that this will change over the next decade [3].

Energy content: CNG has a lower energy content per unit of volume than LPG, meaning that vehicles that run on CNG will have a shorter driving range than those that run on LPG. However, CNG is also less expensive than LPG on a per-gallon-equivalent basis.

Storage: CNG is stored in high-pressure cylinders that are designed to withstand the pressure of the compressed gas. LPG, on the other hand, is stored in liquid form in pressurized tanks. This means that LPG tanks can be smaller and lighter than CNG tanks, but they must be designed to handle the liquid form of the fuel.

Safety: Both CNG and LPG are flammable gases, so they require special handling and storage precautions to ensure safety. However, CNG is less dense than air and will disperse quickly if released, while LPG is heavier than air and can pool in low-lying areas, creating a potential explosion hazard.

Overall, the choice between CNG and LPG will depend on a variety of factors, including the availability and cost of the fuels, the driving range requirements of the vehicle, and the specific safety considerations of the application. In general, CNG is a more environmentally friendly option with lower fuel costs, while LPG has a longer driving range and may be more practical in certain applications.

Table 1 – Properties Comparison between CNG and LPG

Properties	CNG – Methane	LPG – Propane
Chemical Formula	CH_4	C_3H_8
Energy Content	9MJ/L	25MJ/L
Storage Pressure	20 – 25 MPa	2 MPa
Air: Gas Combustion Ratio	10:1	25:1
Opening Pressure	1.1 KPa	2.75 KPa
Density (vs Air)	0.5537:1	1.5219:1
Cylinder Weight	1	≈3x
State	Gas	Liquid or Gas

<u>Future alternative energy carriers</u>

To reach emission reduction targets, the mobility sector needs to reach the zero-emission state [3]. Alternative energy carriers that can potentially offer zero emission mobility are Battery Electric Vehicles (BEVs) where electric is stored in batteries, Fuel Cell Electric Vehicles (FCEVs) where the energy is chemically stored in hydrogen and then converted in a fuel cell to electricity and biofuel vehicles, or synthetic fuels (e.g., ammonia) [3].

These energy carriers differ in their efficiency, the vehicle autonomy, and the charging time of the vehicle [3]. This makes the different energy carriers a better or worse fit for different vehicle classes [3].

1. Battery electric vehicles

A battery electric vehicle (BEV) is a type of electric vehicle (EV) that exclusively uses chemical energy stored in rechargeable battery packs. BEVs use electric motors and motor controllers instead of internal combustion engines (ICEs) for propulsion. They derive all power from battery packs and thus have no internal combustion engine, fuel cell, or fuel tank. BEVs include bicycles, scooters, skateboards, railcars, watercraft, forklifts, buses, trucks, and cars.

Battery electric cars are becoming more and more attractive with the higher oil prices and the advancement of new battery technology (lithium-ion) that have higher power and energy density (i.e., greater possible acceleration and more range with fewer batteries), compared to older battery types such as lead-acid batteries. BEVs are zero emissions vehicles, as they do not generate any harmful tailpipe emissions or air pollution hazards caused by traditional gasoline-powered vehicles.

Battery electric vehicles are forecast to dominate in the car and urban transport sector due to battery energy content increases e.g., to cover longer distances and / or higher vehicle weights, and decreases in battery weight, cost, and charging. For heavy goods vehicles and long-distance buses, the additional battery weight cannibalizes the weight of the goods that can get transported and the long charging times decrease the commercial efficiency of the vehicle. With future improvements in battery technology this disadvantage may decrease, and battery powered electric vehicles could cover more transport applications.

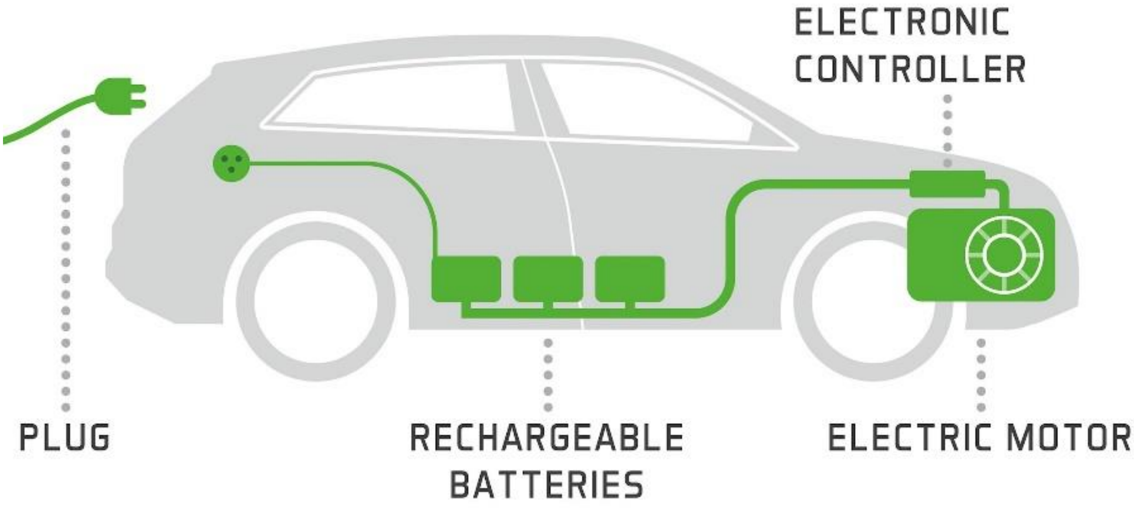

Figure 2 – BEV Battery Electric Vehicle Architecture

Many automakers are investing heavily in the development of BEVs, and governments around the world are offering incentives to encourage their adoption to reduce emissions and combat climate change.

2. Fuel cell electric vehicles

Fuel cell electric vehicles (FCEVs) are powered by hydrogen (use hydrogen as energy carrier). They are more efficient than conventional internal combustion engine vehicles and produce no tailpipe emissions. Most fuel cell vehicles are classified as zero-emissions vehicles that emit only water and heat. As compared with internal combustion vehicles, hydrogen vehicles centralize pollutants at the site of the hydrogen production, where hydrogen is typically derived from reformed natural gas. FCEVs use a propulsion system like that of electric vehicles, where energy stored as hydrogen is converted to electricity by the fuel cell.

To cover peak energy demands from the drivetrain, fuel cell electric vehicles feature a small battery that buffers electric energy. The weight to energy relation of hydrogen as an energy carrier is much more favorable than with a battery as energy carrier [3]. As the battery has only to cover peak energy demands its size and weight does not increase with the distance.

This improves the vehicle weight to transport weight relation [3]. At the same time, the time to store energy in the vehicles is much shorter with hydrogen than it is with batteries. This makes fuel cell electric vehicles interesting for HGVs, long-distance buses as well as trains [3].

Fuel cells have been used in various kinds of vehicles including forklifts, especially in indoor applications where their clean emissions are important to air quality, and in space applications. The first commercially produced hydrogen fuel cell automobile, the Hyundai ix35 FCEV was introduced in 2013. Cells are being developed and tested in trucks, buses, boats, ships, motorcycles, and bicycles, among other kinds of vehicles.

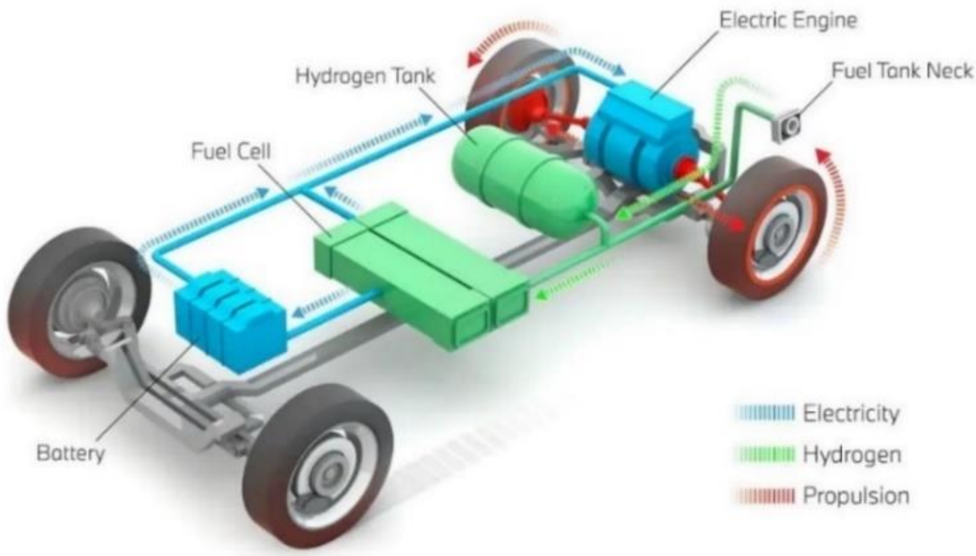

Figure 3 – FCEV Fuel Cell Electric Vehicle Architecture

One of the primary advantages of FCEVs is their long driving range. Hydrogen has a higher energy density than batteries, which means that FCEVs can travel further on a single tank of hydrogen than BEVs can travel on a single charge.

However, FCEVs also face several challenges. One of the primary challenges is the lack of infrastructure for producing, distributing, and storing hydrogen. The technology for producing hydrogen is still relatively expensive, and the infrastructure for delivering it to fueling stations is limited.

Despite these challenges, FCEVs have been gaining momentum in recent years, particularly in countries like Japan and South Korea where the government has been investing in hydrogen infrastructure. Several automakers, including Toyota and Hyundai, have released FCEVs to the market, and others are expected to follow suit in the coming years. With further advancements in technology and infrastructure, FCEVs have the potential to play a significant role in the transition to a more sustainable transportation system.

3. Synthetic fuels and Ammonia

Synthetic fuels and ammonia are both potential alternative energy carriers that are being explored as potential replacements for traditional fossil fuels.

Synthetic fuels, also known as carbon-neutral fuels, are created by capturing and reusing carbon dioxide emissions from industrial processes, such as power plants or cement factories. The captured carbon dioxide is combined with hydrogen, typically produced using renewable energy sources, to create a synthetic fuel that can be used as a replacement for traditional fossil fuels. Synthetic fuels have the potential to be used in existing engines and infrastructure, which could help to reduce the costs of transitioning away from fossil fuels.

Synthetic fuels are less efficient still, with the estimate being about 4 times worse than batteries. In other words, powering the current car fleet with synthetic fuels instead of batteries will require four times as much electricity generation, which seems completely impractical.

Ammonia is another potential alternative to fossil fuels. Ammonia is a compound that is made up of nitrogen and hydrogen, and it can be produced using renewable energy sources, such as wind or solar power. Ammonia has a high energy density, which means that it can store and transport large amounts of energy in a relatively small volume. It can also be used as a fuel for power generation, transportation, and heating. Ammonia can be burned in internal combustion engines with minor modifications, emitting only nitrogen and water vapor from the tailpipe. As the weight or the distance to cover by the vehicles increases, as is the case with aircrafts or ships.

One of the main challenges with synthetic fuels and ammonia is the lack of infrastructure to support their widespread adoption. The technology for producing these fuels is still in its early stages, and the costs of producing them are currently higher than traditional fossil fuels. However, as the costs of renewable energy sources continue to fall and the technology for producing synthetic fuels and ammonia improves, these alternative energy carriers could play a significant role in the transition to a more sustainable energy system.

3. Hydrogen storage technologies

The most abundant gas in the universe is hydrogen. Regardless of the reality that hydrogen is abundant throughout the universe, it is not found naturally as a free element Energies. Furthermore, it persists naturally in compounds with several other elements. Water is the most abundant compound on Earth that contains hydrogen. Methane is another hydrogen containing molecule. It can also be found in a variety of other compounds. Hydrogen, for example, may be present in almost all living creatures on the planet. Using hydrogen as an energy carrier is complicated because earthbound hydrogen can only be found in compounds with other elements. Before hydrogen can be used as an energy source, it must be separated from its raw material. Natural gas steam reforming and water electrolysis are two of the most common hydrogen generation methods currently in use.

Hydrogen has many favorable attributes, including an overall storage capacity, efficiency, renewability, cleanliness, massive distribution, high conversion, zero emissions, sources, versatility, and quick recovery, making it an excellent choice as an energy supply for heat and power, among many others. As a result, it is regarded as the most environmentally friendly and promising energy source of the twenty-first century. It is central to industrial applications, such as ammonia production, oil refining, and water–gas switch reactions.

As an energy carrier, hydrogen fuel can either be a compressed gas or a low-pressure cryogenic liquid. Storage of hydrogen as a gas typically requires high-pressure tanks (350–700 bar tank pressure). Storage of hydrogen as a liquid requires cryogenic temperatures because the boiling point of hydrogen at one atmosphere pressure is −252.8°C.

3.1 Properties of hydrogen

Hydrogen has several unique properties that make it useful in a variety of applications. It has a high energy content per unit mass, making it an attractive fuel source for vehicles and power plants. It is also a versatile reducing agent in chemical reactions and is used in the production of ammonia, methanol, and other chemicals. Additionally, hydrogen is a key component of water and organic compounds, which are essential for life.

Hydrogen is a colorless, odorless, tasteless, flammable gaseous substance that is the simplest member of the family of chemical elements. Hydrogen constitutes approximately 75% of the universe's mass. The hydrogen atom has a nucleus consisting of a proton bearing one unit of positive electrical charge; an electron, bearing one unit of negative electrical charge, is also associated with this nucleus.

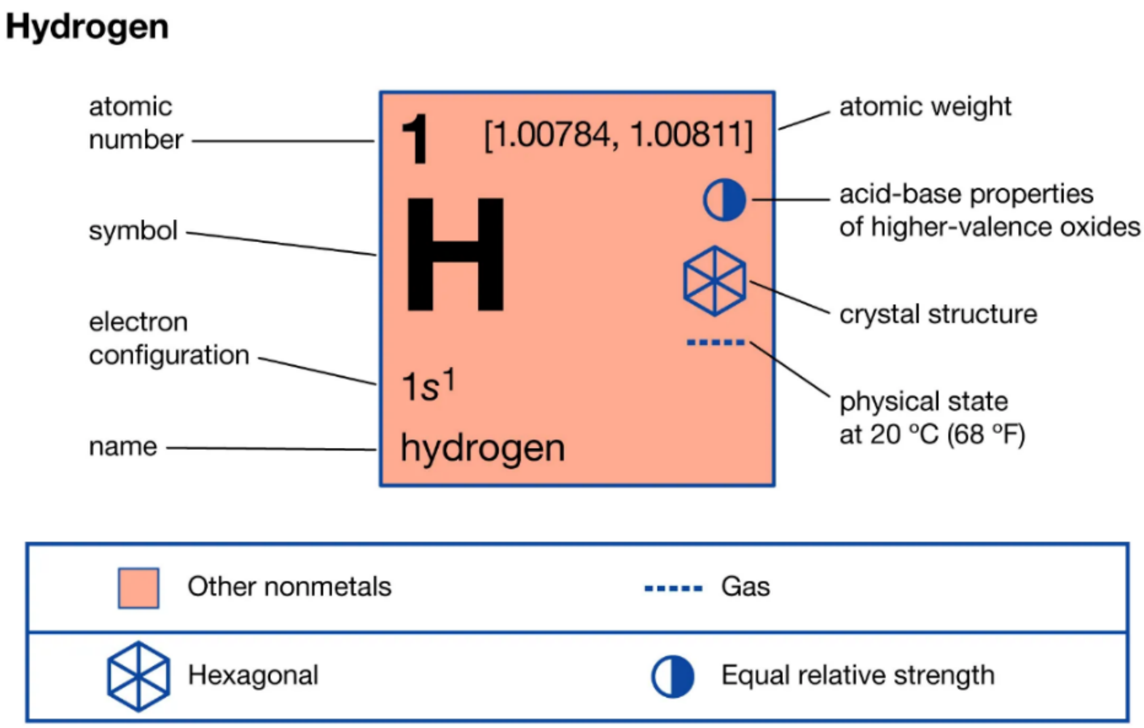

Figure 4 – Properties of Hydrogen

Hydrogen is the lightest gas (~1/14 as dense as air) and at standard temperature and pressure exists in the form of a hydrogen molecule with two atoms: H_2 [1]. Gaseous hydrogen can be stored in high pressure tanks to provide large amounts of energy; however, even more energy can be stored in low pressure cryogenic liquefied form [1]. Hydrogen has an expansion ratio of 1:848, which means that gaseous hydrogen at atmospheric conditions occupies 848 times more volume than liquid hydrogen. [1]

Table 2 – Physical and Chemical Properties of Hydrogen [1]

Property	Value
Molecular weight	2.0159
Gas Density	0.08988 g/L @ 0°C, 1 atm
Relative Vapor Density	0.07
Liquid Density	70.8 g/L @ -253 °C
Melting Point	-259.35 °C
Boiling Point	-252.8 °C
Auto-ignition Temperature	500 °C
Flammability Limits	4-75% (vol % in air)

3.2 Compressed hydrogen storage

Compressed hydrogen storage is the most established hydrogen storage technology; it involves the physical storage of compressed hydrogen gas in high-pressure vessels.

The advantages of compressed hydrogen storage include:

- Relatively low cost: Compressed hydrogen storage tanks are relatively simple and inexpensive to manufacture compared to other hydrogen storage technologies.
- Mature technology: Compressed hydrogen storage is a well-established technology and is widely used in industry and for transportation applications.
- High energy density: Compressed hydrogen gas has a high energy density per unit volume, making it suitable for applications where space is limited.
- Easy to transport: Compressed hydrogen gas can be transported using standard gas cylinders or specialized high-pressure trailers.

However, compressed hydrogen storage also has some limitations:

- Requires high-pressure storage tanks: Compressed hydrogen gas must be stored in high-pressure tanks that can withstand the high pressure, which adds weight and cost to the system.
- Limited storage capacity: The amount of hydrogen that can be stored in a compressed hydrogen tank is limited by the size and weight of the tank, which can make it challenging to store enough hydrogen for long-range transportation applications.
- Safety concerns: Compressed hydrogen gas is highly flammable and requires careful handling and storage to avoid safety hazards.

Despite these limitations, compressed hydrogen storage is a widely used and effective method of storing hydrogen for a variety of applications, including fuel cell vehicles and industrial processes.

Hydrogen storage vessels can be classified into four standard types based on the materials and technologies used to manufacture them. These classifications are commonly referred to as Type I, Type II, Type III, and Type IV.

Type I is an all-metal vessel (usually steel) and hence the heaviest, typically employed in industry for stationary use. Type I vessels store only about 1 wt% hydrogen at 200–300 bar. Type II is a metal liner hoop-wrapped composite cylinder, weighing less than Type I cylinder. However, both Types I and II vessels are unsuitable for vehicle applications due to their low hydrogen storage density, arising from their heavyweights, and also because of hydrogen embrittlement challenges.

Type III vessels comprise a fully wrapped composite cylinder with a metal liner that serves as the hydrogen permeation barrier [3]. The metal liner is made of aluminum (Al), which solves the problem of embrittlement, and it contributes >5% to the mechanical resistance. The composite overwrap (usually carbon fiber embedded in resin) acts fully as the load-bearing component. Type III vessels offer a 25%–75% mass gain over Types I and II vessels, making them more suitable for vehicle applications; however, they are more costly [3]. Type III vessels have also been shown to be reliable at pressures up to 450 bar but there are still challenges associated with pressure cycling tests at 700 bar [3].

Type IV vessels comprise a fully wrapped composite cylinder with a plastic liner (typically high-density polyethylene), which acts solely as the hydrogen permeation barrier. The composite overwrap serves as the load-bearing structure and is typically made up of carbon fiber or carbon/glass fiber composite in an epoxy matrix. Type IV vessels are the lightest of the pressure vessels, making them most suitable for vehicle applications, and they can endure high pressures up to 1,000 bar. However, they are too costly, due to the considerable cost contribution of the carbon fibers [3]. Cost projections show that the carbon fiber cost constitutes about 75% of the storage vessel cost, taking the high production volumes into consideration.

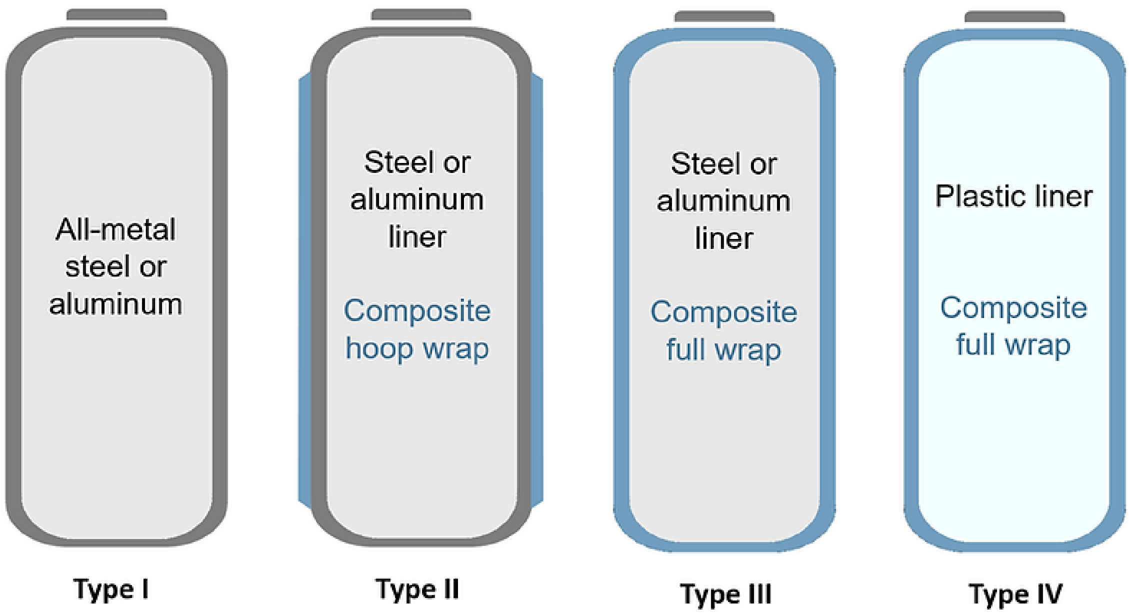

Figure 5 – Standard Types of Hydrogen Storage Vessels[18]

In general, Type IV storage vessels offer the best performance, but they are also the most expensive. Type I vessels are the most common and cost-effective, but they have lower storage capacity and are relatively heavy. Types II and III vessels offer a good balance between performance and cost, but their specific advantages and disadvantages depend on the application. It's important to consider the specific needs of each application when choosing a hydrogen storage vessel.

3.3 Cryogenic hydrogen storage

Besides compressed hydrogen storage, the physical storage of hydrogen can be in the form of a cryogenic liquid at atmospheric pressure. Cryogenic hydrogen storage has an advantage over compressed storage because it provides a more compact and safer storage option.

Storage of hydrogen as a liquid increases its volumetric density. The theoretical volumetric density of liquid hydrogen (LH_2) is 70 g L−1 at the boiling point of hydrogen (−253°C) and atmospheric pressure, whereas it is 24 g L−1 and 40 g L−1 for compressed hydrogen at 350 and 700 bar, respectively, at room temperature.

The key disadvantage associated with using liquefaction over-compression is the higher energy required by the liquefaction process. The critical temperature for hydrogen is –240°C; above this, it exists in a non-condensable state. Due to the low boiling point of hydrogen, cryogenic temperature is required to store hydrogen as a liquid. Therefore, cooling must be applied, it is an energy-intensive process that consumes 25%–40% of the energy content of hydrogen, compared with 10% energy loss for the compression of hydrogen. This decreases its efficiency. In comparison to the high-pressure storage vessels, cryogenic storage vessels operate around ambient pressures. The absence of high pressures decreases the risk associated with high pressure storage. The downside is that the tanks need to be thermally isolated, typically through vacuum insulation.

The cryogenic temperature required necessitates that LH_2 vessels be thermally insulated. Hence, cryogenic hydrogen vessels are usually vacuum insulated; they are double-walled vessels, with a vacuum providing thermal insulation between the inner and outer walls. This minimizes the loss of heat and improves the efficiency of the storage vessel. However, boil-off losses are unavoidable due to heat flow from the environment to the LH_2 and thermal conduction through other components. The boil-off rate is not only a function of thermal insulation, but also of the size and shape of the vessel; it can be up to 0.4% per day.

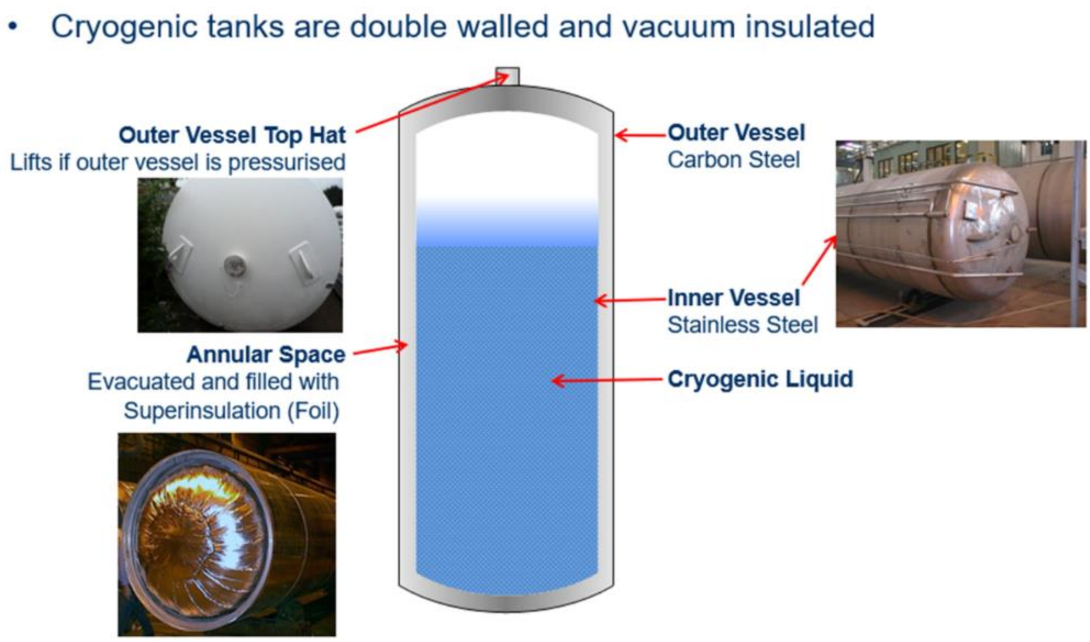

Figure 6 – Typical Cryogenic Tank Construction [17]

Cryogenic hydrogen storage offers several advantages over other storage methods. For example:

- High storage density: Hydrogen has a very low density in its gaseous state, but in its liquid state, it has a much higher density. This allows for a higher storage capacity in a smaller space.

- Low pressure: Liquid hydrogen can be stored at low pressure, which reduces the risk of leaks and increases safety.

- Long-term storage: Cryogenic hydrogen storage is a viable option for long-term storage of large amounts of hydrogen, which makes it suitable for applications like fueling stations.

However, there are also some challenges associated with cryogenic hydrogen storage. For example:

- Energy consumption: Maintaining the extremely low temperatures required for cryogenic hydrogen storage requires a significant amount of energy.

- Cost: Cryogenic storage tanks are expensive to manufacture and maintain.

- Boil-off: Even with advanced insulation, some of the liquid hydrogen will boil off over time, resulting in the need for continuous replenishment.

Cryogenic hydrogen storage is commonly used in the space industry, as well as in industrial and research applications. It is also being explored as a potential option for large-scale energy storage and transportation.

4. Types of vehicles and their storage technologies

Hydrogen vehicle is a vehicle that uses hydrogen fuel for motive power. Hydrogen vehicles include hydrogen-fueled space rockets, as well as ships and aircraft. Power is generated by converting the chemical energy of hydrogen to mechanical energy, either by reacting hydrogen with oxygen in a fuel cell to power electric motors or, less commonly, by burning hydrogen in an internal combustion engine.

Automobiles, buses, forklifts, trains, canal boats, ships, airplanes, submarines, and rockets can run on hydrogen, in various form. NASA used hydrogen to launch Space Shuttles into space. A working toy model car runs on solar power, using a regenerative fuel cell to store energy in the form of hydrogen and oxygen gas.

When doubling the storage pressure from 35 to 70 MPa [350 to 700 bar], it results only in 1.68 times increased energy density on substance level due to the isothermal properties of hydrogen. On vehicle storage system level that increase is lower (~1.25) because of the higher tank material requirements and thus there is a higher specific weight compared to 35 MPa CGH_2 storage systems.

Trains: In trains there are fewer space restrictions. Therefore, compressed hydrogen vessels with 350 bar are used. They offer the best relation between costs and storage capacity [3]. This may change when the hydrogen vessels cannot be placed in the individual train wagons. When the vessels need to be located in the locomotive this may lead to the use of more expensive storage vessels with 700 bar pressures or future storage technologies like cryo or cryo compressed hydrogen vessels [3].

The use of hydrogen and, in particular, green hydrogen as a rail fuel offers a range of benefits, including supporting zero carbon goals as a clean energy source and offering more powerful and efficient energy output than with fossil fuels.

All hydrogen powered rail vehicles, whether large or small, are categorized as ‘hydrail,’ whether the fuel is used for the traction motors, auxiliary systems, or both. Hydrail vehicles currently tend to be hybrids, including renewable energy storage like batteries or super capacitors to supplement the hydrogen fuel, improving efficiency, and reducing the amount of hydrogen storage space required.

Hydrogen powered trains can achieve speeds of up to 140kmh and manage distances of up to 1000 km without refueling, which is ten times further than battery-powered electric trains. The refueling is also fast at less than 20 minutes.

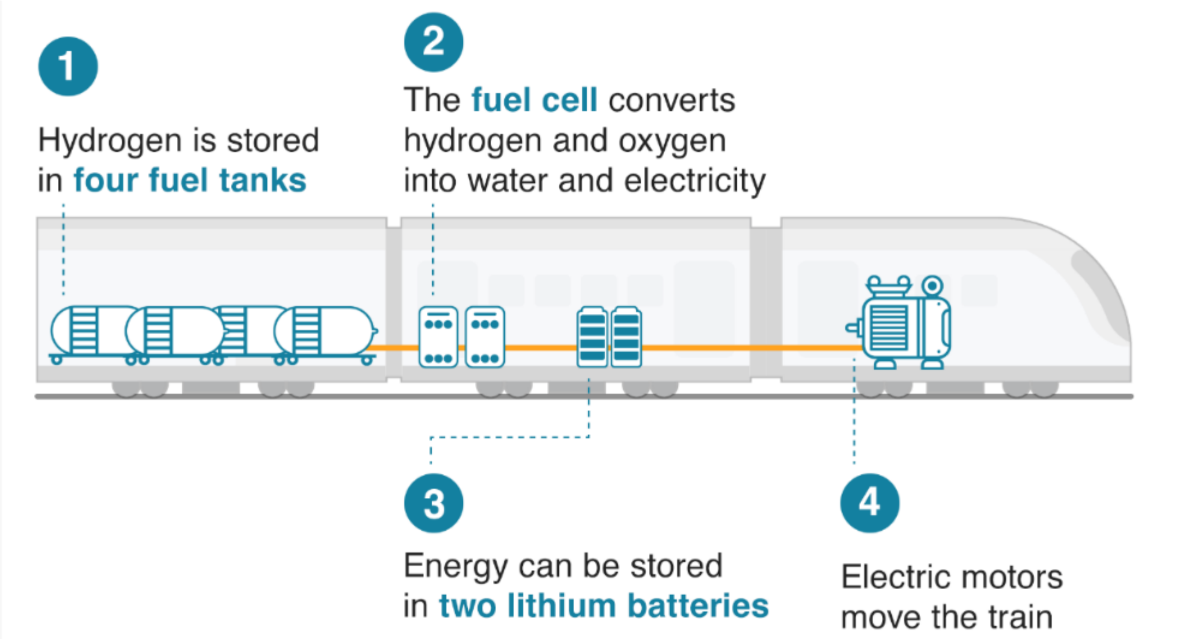

Figure 7 – How a zero-emission train works

Cars: Hydrogen FCEVs are electric vehicles and are very similar to standard EVs. They store energy in batteries and use that energy to run electric motors, like an EV. But instead of charging the batteries via cables and charging stations, hydrogen FCEVs fill tanks with highly pressurized hydrogen. The most important thing to note is that the only by-products of hydrogen cars are electricity and pure water.

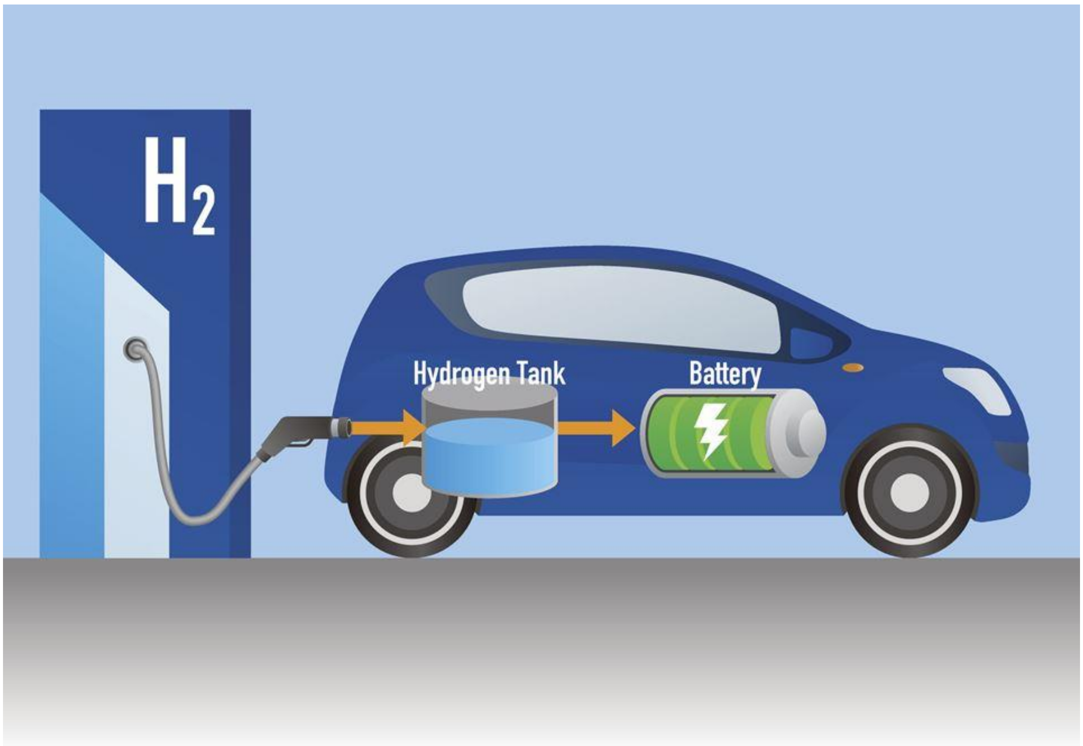

Figure 8 – Hydrogen Car

For cars hydrogen competes directly with battery electric vehicles. When hydrogen is used space is very restricted and only 700 Bar storages vessels are used [3]. Both hydrogen cars and EVs use electric motors to make them go, but the energy is stored in two different ways. For EV's the energy source is lithium-ion type batteries. But for hydrogen cars or vehicles, the energy source is hydrogen itself onboard. This allows for the flexibility of not having to stop and charge the battery, allowing for better or extended range capabilities. While EVs must be plugged in from anywhere between 4-8 hours, hydrogen cars can be filled up in a matter of minutes.

Buses: A fuel cell bus is a bus that uses a hydrogen fuel cell as its power source for electrically driven wheels, sometimes augmented in a hybrid fashion with batteries or a supercapacitor. The only emission from the bus is water. Several cities around the world have trailed and tested fuel cell buses, with over 5,600 buses in use worldwide, the majority of which are in China.

Buses are a good candidate for the incorporation of fuel cells into the commercial vehicle market. The difference between buses and automobiles are the power requirements, space availability, operating regimen, and refueling sites. Buses obviously require more power than automobiles and get more wear due to constant stops and starts. Despite this, the average fuel economy of a fuel cell bus is approximately 30-140% percent better than a diesel engine and natural gas buses. Buses can be refueled in a central facility, which makes refueling with hydrogen much easier. Large quantities of hydrogen can also be stored onboard easily because of the large area of a bus. Hydrogen is usually stored in a composite compressed gas cylinder located on the roof, there is enough space available for the use of 350 bar pressure vessels. This is a safe place to store the tank since hydrogen is lighter than air, and it is not near critical engine components.

Figure 9 – Hydrogen Bus

HGVs: Heavy good vehicles are like locomotives when it comes to the storage of hydrogen. Also here, the space available on the vehicle is reduced [3]. Additionally, the weight of the hydrogen storage competes with the weight of goods. Today HGVs use either 350 Bar or 700 Bar vessels [3].

The current generation of fuel cell electric trucks (FCET) is powered mainly by proton-exchange membrane fuel cells (PEM) using hydrogen as a fuel. In the longer term, solid oxide fuel cell (SOCF) technology that can convert other, denser fuels (like methanol) may also be an option; this is currently being researched.

Because of hydrogen's high mass energy density, FCETs are considered promising for long-haul transport. Its relatively low volume energy density, however, requires a greater internal tank volume (approx. 7 times for H_2 at 700 bar) for the same range as diesel. FCETs are currently being produced on a pilot scale, but several test concepts have been developed with ranges over 400 km, which is more than current BETs. According to the two companies, hydrogen fueled FCETs will be the preferred option for heavier loads and longer distances. Other OEMS, such as Renault, and MAN are also investing in hydrogen technology, while Scania is focusing more on BET.

The infrastructure for FCETs requires additional safety measures compared with conventional refueling infrastructure, but refueling time is equally short (under 10 minutes). Refueling stations can be supplied by trucks, pipelines (possibly retrofitted gas pipelines) or by on-site hydrogen production.

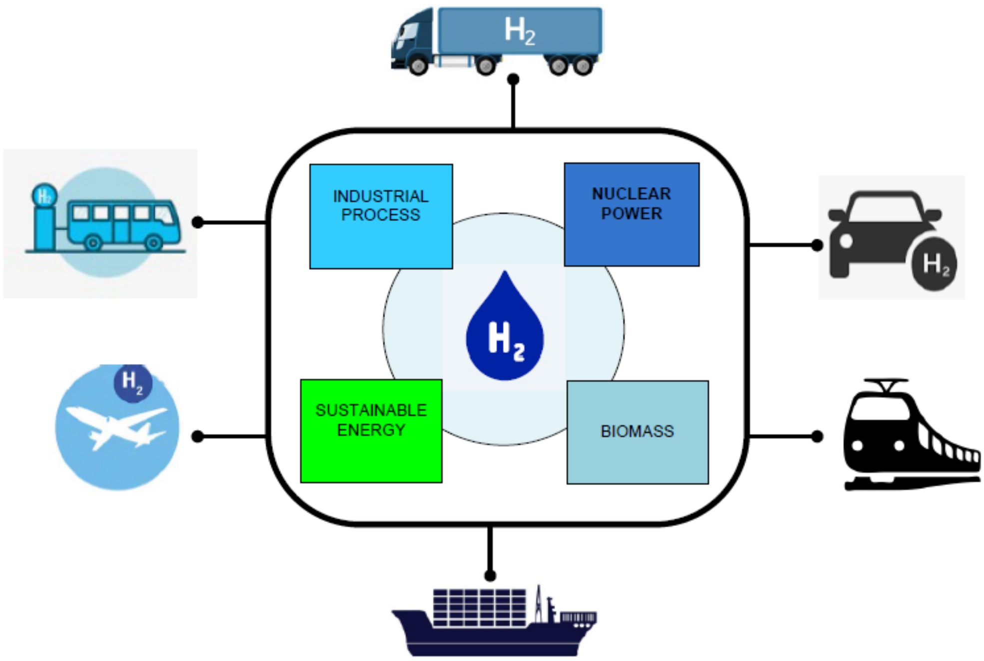

Figure 10 – Structure of Hydrogen Generation Sources at Various Transportation Sectors [5]

5. Sensor in Hydrogen Fuel Application

This chapter provides a general understanding of different hydrogen sensing technologies, their importance, applications, limitations, and provides an overview of the hydrogen measuring principles including traditional industrial methods and discusses their limitations.

5.1 Hydrogen Measuring Principles

The four key functional parameters to be satisfied by any hydrogen sensor to gain wide acceptance for use within the hydrogen infrastructure of production, storage, transportation, and utilization are:

Performance: sensors must have a broad operating range in air, nitrogen, and inert backgrounds (2–99% v/v) and good sensitivity well before the explosive limit (4% H_2) in air backgrounds to meet National Fire Protection Association (NFPA) safety guidelines. Continuous operation in gas streams containing hydrocarbons, sulfur compounds, and carbon monoxide is required for petrochemical applications. Fast response time to line out (<60 s) in high humidity is desired for diagnostic study and optimal operation of hydrogen transportation systems (vehicles, electrolyzers, battery rooms, fuel cells, storage containers, etc.).

Lifetime: sensors must have a usable lifetime consistent with the application for which it is intended. Sensors should also have a well-defined replacement, maintenance, and operational costs associated with them. Hydrogen analytical systems (gas chromatograph or mass spectrometer) for process monitoring and refinery applications are typically used for <10 years and require daily to weekly calibration. A low-cost in-line solid-state sensor with minimal annual calibration is more cost effective in the lifetime of a process. For transportation and automotive applications, the desired lifetime is greater than 10 years with minimal (annual) calibration. During this period, the hydrogen sensor must be operational without cleaning, frequent calibration, or replacements while exposed to harsh environmental conditions.

Reliability: sensors must indicate the presence of hydrogen specifically, and not provide false alarms. The sensors should have consistent reproducibility (e.g., ± 5% over 1 year at 2% v/v H_2 in air), long-term stability and minimal drift rates. Response must not drift outside acceptable limits over that lifetime without providing an alarm. The functionality of the sensors should be easily verifiable and there should be a low tolerance for false alarms. Material selectivity to hydrogen is necessary to the design of a hydrogen sensor to prevent false alarms. Sensors should be able to survive multiple excursions to hydrogen concentrations without damage. Hydrogen specificity in the sensor material is highly desired for sensor operation in contaminant backgrounds.

Cost: sensors and their controllers must justify their cost (purchase, installation, and maintenance) versus current technology by a factor of four or more to warrant purchase. In industrial process applications today, a unit cost of <$10,000 is highly desired for a sensor with minimal maintenance and installation costs for multiple-point installations. For automotive, fuel cell applications, a low-cost sensor package is needed with minimal maintenance costs, such as exchanging the sensor element (<$50). The cost alternative is better for most applications as long as performance, lifetime, and reliability are not compromised.

The US Department of Energy (DOE) is committed to the development of hydrogen as a clean and renewable alternative to carbon-based fuels. DOE and the National Renewable Energy Laboratory (NREL) have been working with standards and code development organizations (SDOs and CDOs) to develop relevant codes and standards to facilitate the implementation of the necessary hydrogen infrastructure. One critical aspect for the safe and efficient deployment of hydrogen is the ability of chemical sensors to meet the required performance specifications for the growing hydrogen infrastructure. Several crucial applications for hydrogen sensors have been recently identified by DOE, which include the Fuel Producer/Supplier Environment and the End-user Environment. Already, the use of hydrogen detectors is already required by NFPA 52. It is recognized that the availability of safety sensors will be critical for the successful utilization of hydrogen. Accordingly, DOE has published a list of target specifications for hydrogen safety sensors, which are summarized in the following table [4]:

Table 3 - DOE target Specifications for hydrogen safety sensor [4]

Parameter	Value
Measurement Range	0.1 to 10%
Operating Temperature	-30 to 80°C
Response Time	< 1 second
Accuracy	5% of full scale
Gas Environment	Ambient air, 10 to 98% RH
Lifetime	10 years
Interface	Resistance (e.g., hydrocarbons)

5.2 Hydrogen Associated Risks

Hydrogen is a highly flammable gas and will burn at concentrations as low as 4% in air. The lower explosive limit (LEL) and upper explosive limit (UEL) are the two most common terminologies used to indicate the flammable levels for many fuels including hydrogen. As indicated in Table 4, hydrogen is one of the least flammable materials at 4% but has a larger window (4–75% v/v H) of flammability in comparison to natural gas, gasoline, propane, ethane, methane, propylene, etc. The flammability limit of hydrogen is seven times wider than methane. It is, therefore, critical for a hydrogen gas sensor to have a wider measurement range (1–99% v/v H_2) for safety applications than most common fuels. Hydrogen is the lightest of elements and the smallest molecule; it, therefore, has the greatest tendency to leak. Thus, for a process safety application, a hydrogen leak can be more dangerous, and its detection becomes more challenging than other gases.

Hydrogen gas can diffuse through many materials, including metals, which can lead to the embrittlement and weakening of the material. Hydrogen must be stored at high pressures to achieve the energy density required for many applications, which can present a risk of rupture or leakage from the storage vessel.

Hydrogen gas is not toxic, but its combustion products, such as nitrogen oxides, can be harmful to human health and the environment. The widespread adoption of hydrogen as an energy carrier will require significant investment in infrastructure, including production, storage, and transportation, which can present challenges for safety and security.

It is essential to manage these risks through the development of appropriate safety standards, guidelines, and regulations, as well as the implementation of proper safety practices in the design, operation, and maintenance of hydrogen systems.

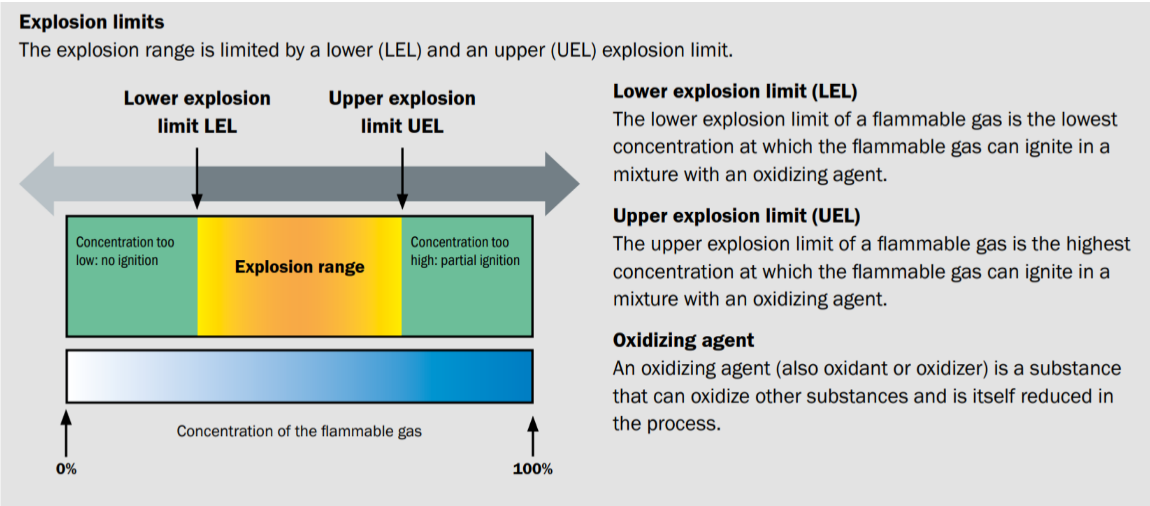

Figure 11 – Explosion Limits [3]

Table 4 – Explosive Limits for Common Constituents in Process Industries [6]

Fuel	LEL (%)	UEL (%)
Gasoline	1.4	7.6
Propane	2.1	10.1
Ethane	3	12.4
Hydrogen	4	75
Methane	5	15
Propylene	2	11.1

The fire triangle or combustion triangle is a simple model for understanding the necessary ingredients for most fires. The triangle illustrates the three elements a fire needs to ignite: heat, fuel, and an oxidizing agent (usually oxygen). A fire naturally occurs when the elements are present and combined in the right mixture. A fire can be prevented or extinguished by removing any one of the elements in the fire triangle. For example, covering a fire with a fire blanket blocks oxygen and can extinguish a fire. In large fires where firefighters are called in, decreasing the amount of oxygen is not usually an option because there is no effective way to make that happen in an extended area.

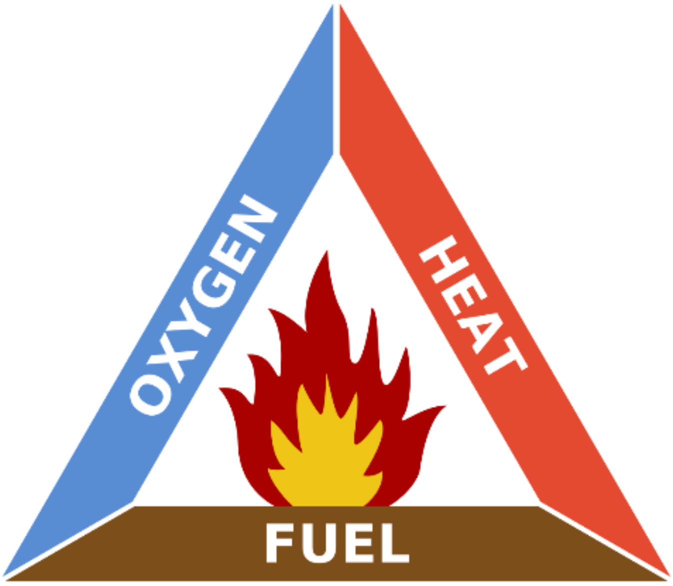

Figure 12 - Explosion Triangle [3]

As people travel in road tunnels and they require oxygen for breathing it is not possible to reduce or eliminate oxygen. In the same way it is not possible to eliminate the combustible substance or fuel as this is the alternative energy source (hydrogen) the vehicles use. The only ingredient we might eliminate is the ignition source.

It is common practice to use gas sensors to measure the concentration of explosive gases to help to avoid explosions by eliminating ignition sources. The gas sensors measure the gas concentration as % of the lower explosion level [3]. If the combustible gas concentration is far away from the LEL there is no risk for an explosion. When the gas sensor detects that the combustible gas concentration gets closer to the LEL e.g., 50% of the LEL a control system eliminates potential ignition sources [3]. The control system can for instance shut the electrical power in the area around the gas sensor off [3].

This can be a viable way to eliminate the risk of explosion in road tunnels as well. In case hydrogen accumulates in a tunnel section, hydrogen sensors can detect the distance to the LEL and in case the concentration approximates a certain LEL threshold the tunnel control system can switch off the power in the close vicinity of the gas sensor.

Hydrogen minimum ignition energy (MIE) is an order of magnitude lower than the other fuel types. This introduces the possibility of ignition even from weak electrostatic discharged [1]. Figure 13 illustrates the MIE of different fuels as a function of concentration in air by volume. As shown in the figure, between approximately 10% and 60% volumetric concentration, hydrogen has a lower ignition energy than methane and gasoline over a much wider range of concentration [1]. However, for hazard evaluation the MIE of lean mixtures is more relevant, and hydrogen does not differ from other fuels. At the LFL concentrations for each of the fuels, the ignition energies are much more similar between fuels.[1]

However, it should be noted that these characteristics have led to robust system safety requirements to reduce the likelihood of hydrogen release after an accident.[1]

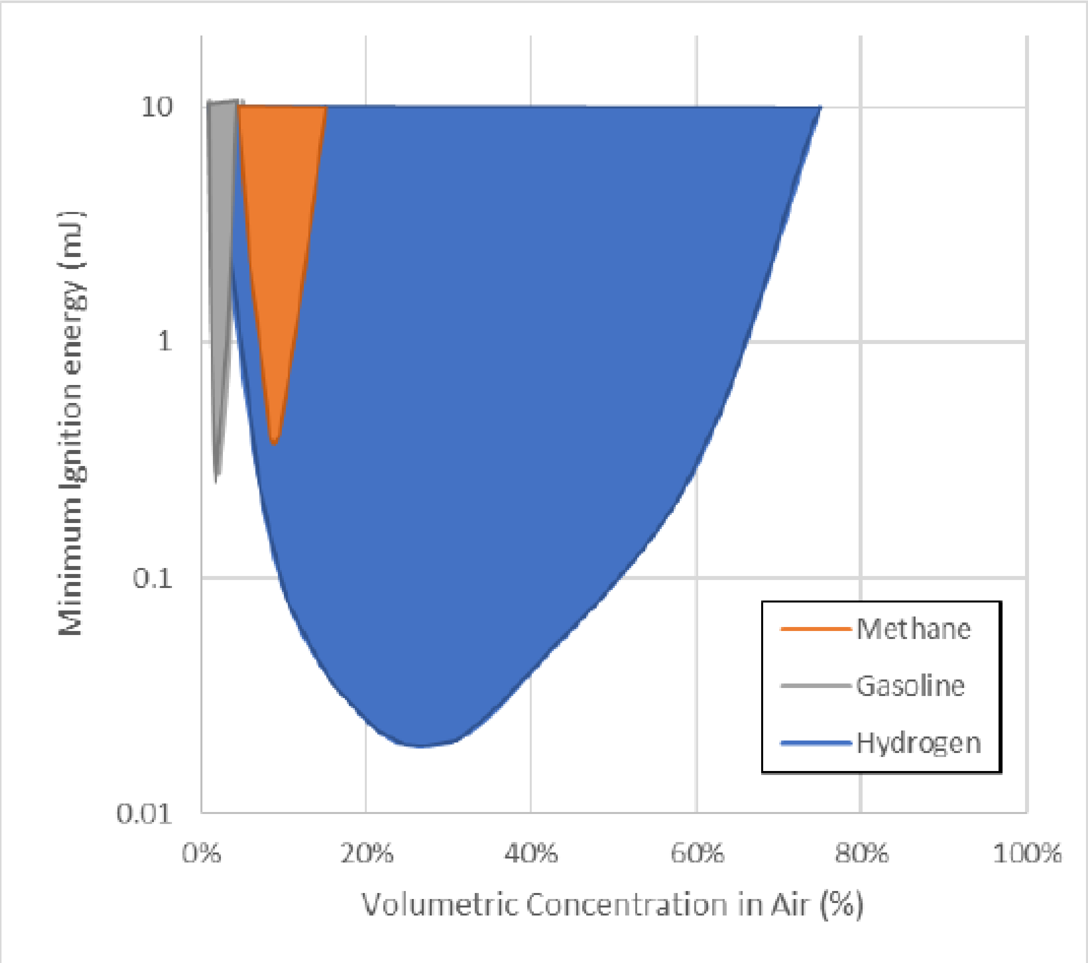

Figure 13 - Minimum Ignition Energy for Different Fuels vs. Concentration [1]

Key risks associated with hydrogen

There are a variety of risks associated with the use and storage of hydrogen to be aware of. Many of these can be more easily mitigated when on land but pose an even greater threat when in confined spaces.

Fire: When used as fuel, hydrogen is highly flammable. This is perhaps the most well-known risk associated with hydrogen and other gases such as propane, acetylene, and butane. However, hydrogen fires are markedly different compared with other fuel-based fires. When heavier fuels such as petrol or diesel leak, they pool close to the ground. But as one of the lightest elements on earth, hydrogen quickly disperses upwards instead. The risks associated with this are exacerbated further by hydrogen's heightened reactivity, it ignites and burns much more easily than other fuels. On top of this, hydrogen flames are invisible making it difficult to pinpoint where the fire is located.

Asphyxiation: In its usual state hydrogen is non-toxic – but in confined indoor environments it can build up and displace oxygen, leading to asphyxiation. Hydrogen is usually kept in confined spaces such as battery storage rooms which could quickly be filled with the odorless gas, making the need for a highly sensitive and reliable detection system paramount to ensure crew safety. Some providers attempt to mitigate the risk of asphyxiation from hydrogen and other gases such as Methane and Propane by adding odorants, artificial smells designed to alert those close by to a leak. But this can't be relied on as a safety measure – as hydrogen disperses rapidly the odorant usually doesn't travel with it, leaving crew open to its deadly effects long before a leak is detected.

Detectability: A secondary risk is its undetectability. Hydrogen is odorless, colorless, and tasteless, so leaks are almost impossible to detect using human senses alone. This can cause valuable time to be lost between an initial leak and the build-up to a potential incident, highlighting the need for reliable, efficient sensor technology (covered in greater detail below).

Injury: A less common but notable risk of hydrogen is frostbite. As hydrogen is usually stored and transported in a liquified state in compressed hydrogen tanks, it is extremely cold. If hydrogen in this state escapes and comes into contact with the skin, it can cause severe frostbite and even loss of extremities. In high concentrations, hydrogen gas can be toxic to humans and animals, causing symptoms such as headaches, dizziness, nausea, and even death.

Structural damage: Hydrogen gas can cause structural damage to tunnel linings and support structures, particularly if it is allowed to build up over time.

To mitigate the ignition hazards of hydrogen, sensors are placed in indoor and enclosed locations where hydrogen has the potential to be trapped and accumulate flammable concentrations. These sensors can be programmed to alert when the hydrogen reaches some fraction of the LFL. Because hydrogen is lighter than air, sensors should be placed above potential release points but below ceiling height to avoid elevated temperatures. Consideration should be given to understand the effect of ventilation systems and how air flow might be altered. Most of the hydrogen fuel system will be at a pressure that will result in momentum driven jets of hydrogen. In outdoor locations, hydrogen releases rise away from ignition sources because it is more buoyant than air. This means that hydrogen leaks can dissipate readily, potentially avoiding a concentrated, explosive atmosphere.

5.2.1 Past Incidents

The Hindenburg Disaster: The Hindenburg disaster at Lakehurst, New Jersey on May 6, 1937, brought an end to the age of the rigid airship [8]. The disaster killed 35 persons on the airship, and one member of the ground crew, but miraculously 62 of the 97 passengers and crew survived [8]. Almost 80 years of research and scientific tests support the same conclusion reached by the original German and American accident investigations in 1937: It seems clear that the Hindenburg disaster was caused by an electrostatic discharge (i.e., a spark) that ignited leaking hydrogen [8]. The spark was most likely caused by a difference in electric potential between the airship and the surrounding air: The airship was approximately 60 meters (about 200 feet) above the airfield in an electrically charged atmosphere, but the ship's metal framework was grounded by its landing line; the difference in electric potential likely caused a spark to jump from the ship's fabric covering (which had the ability to hold a charge) to the ship's framework (which was grounded through the landing line) [8]. A somewhat less likely but still plausible theory attributes the spark to coronal discharge, more commonly known as St. Elmo's Fire. The cause of the hydrogen leak is more of a mystery, but we know the ship experienced a significant leakage of hydrogen before the disaster [8].

Figure 14 - The Hindenburg Disaster[8]

<u>Phillips Disaster 1989:</u> on October 23rd, 1989, an earth-shattering explosion at the Phillips Petroleum Company's plastics plant in Pasadena, Texas. The explosion occurred in a polyethylene reactor at the facility and caused a massive fire that burned for several days. The explosion was reportedly heard from several miles away, and the resulting fire could be seen from even further away. The incident resulted in 23 deaths and injured more than 130 others, as well as extensive damage to the facility and the surrounding area [9]. The cause of the explosion was later determined to be a faulty valve that allowed flammable gas to escape from the reactor. The Phillips 66 Houston Chemical Complex explosion was one of the deadliest industrial accidents in United States history and led to increased scrutiny of safety procedures in the chemical industry [9]. The accident resulted from a release of extremely flammable process gases that occurred during regular maintenance operations on one of the plant's polyethylene reactors. More than 85,000 lb (39 t) of highly flammable gases were released through an open valve almost instantaneously [9].

Figure 15 - October 23, 1989. Fire and smoke at Phillips Petroleum's Pasadena, Texas plastics plant, following explosion that would kill 23 workers and injure more than 130 others. Homes were damaged within an 8-mile radius of the blast. (AP Photo/Ed Kolenovsky) [10]

5.3 Hydrogen Fuel Cells and Automobiles

Hydrogen is used as a fuel in proton exchange membrane fuel cells. Hydrogen concentrations of 60–100% are used as feed gas to fuel cells. The hydrogen is converted to water and electrons through a proton exchange mechanism in the polymer membrane. Hydrogen powered fuel cells are used to drive automotives and can be used as backup for generators and small power plants [6]. Hydrogen is a cleaner fuel for fuel cells compared to natural gas since it has lower emissions. Hydrogen, when used as a fuel source in an automobile or in a generator room must be accurately monitored to prevent the risks of explosion [6].

Accurate monitoring of hydrogen in fuel cell stacks are required for proton exchange membrane (PEM) fuel cells. Hydrogen is used as a feed in a fuel cell (Figure 16) in the anode side, and air is fed into the cathode side [6]. A catalyst causes the hydrogen to split into protons and electrons. The PEM membrane allows the protons to pass through the cathode. The electrons travel along the circuit to the cathode to cause an electric current. Hydrogen detection is required in the fuel cell anode loop (~60–100% H_2 in nitrogen background). There is a high concentration of water vapor at the cathode side as the electrons and protons combine with oxygen to form water [6]. The hydrogen sensor installed in the anode loop of the fuel cell should not have a response time delay or lower sensitivity in the presence of water vapor (H_2O) [6]. The emissions from fuel oxidant outlet of a fuel cell must be monitored for hydrogen concentrations to prevent possible explosions since the concentration of hydrogen is in the range 0–4% H_2 in an oxygen-reduced background [6]. Hydrogen leak detection is also required in the fuel cell ventilation areas. An accurate leak detector should be able to detect 0–4% H_2

in air backgrounds without any cross-sensitivity to common gases in exhausts such as methane (CH_4), carbon dioxide (CO_2), carbon monoxide (CO), and nitrous oxides (NO, NO_2) [6].

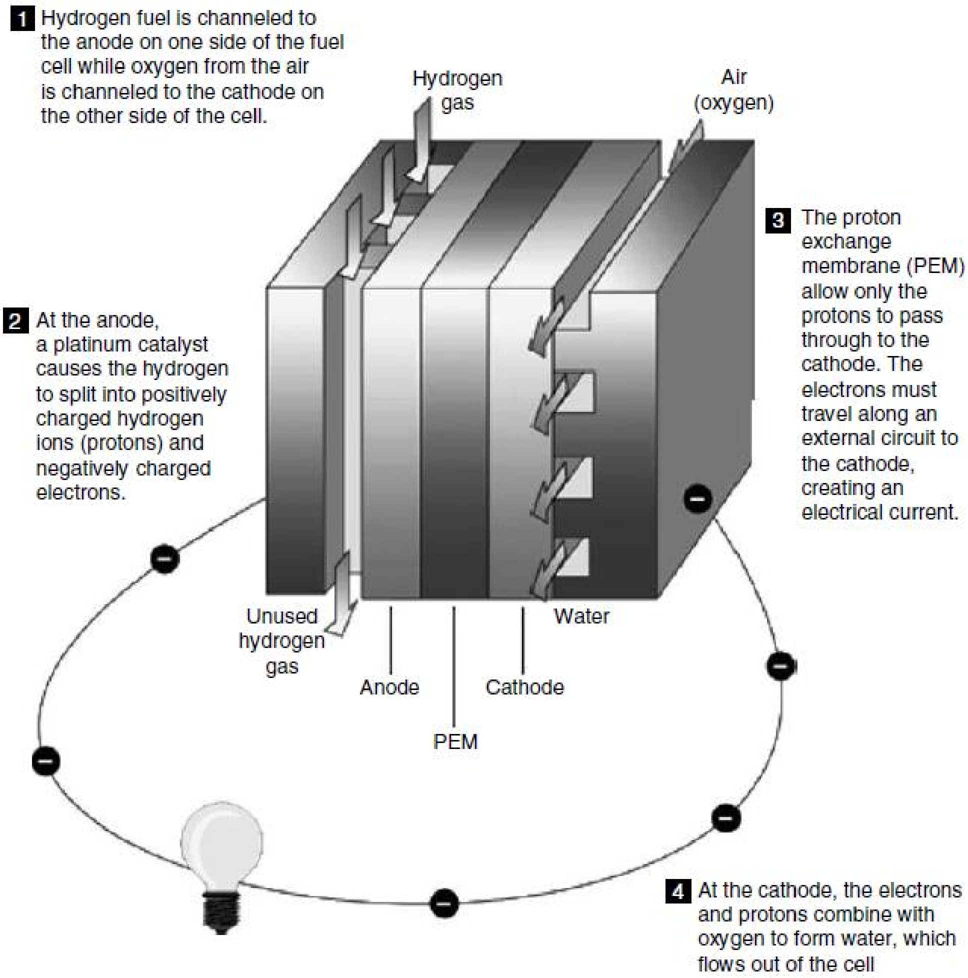

Figure 16 - A typical PEM hydrogen fuel cell [6]

The major requirement for a reliable hydrogen sensor operation in the fuel cell environment is in 100% condensing humidity. Most of the fuel cells have abundant humidity and the sensor needs to operate continuously in humid environments. In some cases, the hydrogen sensor can also be operated at very low temperatures (as low as −40°C) [6]. The fuel cells regularly have a cold start, when operated from a very low ambient temperature; the sensor needs to attain ambient temperature quickly (<30 s) and continue operation well below ambient temperature before the fuel cell itself reaches the ambient temperature [6].

Figure 17 shows the hydrogen sensor locations in a fuel cell vehicle. In a hydrogen powered vehicle, gas mileage is important, therefore, the "unused hydrogen" is recirculated. Hydrogen area monitors are needed in garages/tunnels to ensure that there is no leak from a hydrogen-powered vehicle [6]. The passenger compartment should be monitored for hydrogen leaks to ensure the safety of passengers. The hydrogen is generally stored in the compartment and the ambient hydrogen has to be monitored in the fuel storage area and high-pressure leaks. Accurate hydrogen monitoring is also required in fuel cell ventilation systems, oxidant outlets, and fuel cell anode loop as described in Figure 17. In a fuel cell loop, a fast responsive sensor is necessary to monitor the recirculated hydrogen during start up and shut down and to control electrical load appropriately to avoid catalyst degradation [6].

Most solid-state sensors are heated to well above 100°C and can operate in the “cold start” condition in a fuel cell. Another important performance parameter for a hydrogen sensor in a fuel cell is its resistance to water entry. Most fuel cells have excess of liquids including water during operation [6]. It is highly possible that water will splash or penetrate the hydrogen sensor mounted in the ventilation or outlet of a fuel cell. Hydrophobic membranes are generally used in hydrogen sensors to prevent water entry into the sensors. Recent developments in solid-state hydrogen sensors and molecular-level inorganic coating technologies enable sensor operations without interference from condensing water and high relative humidity. Hydrogen sensors for fuel cell applications also need to operate in a wide operating temperature range (−40 to +100°C) and should have fast response times [6].

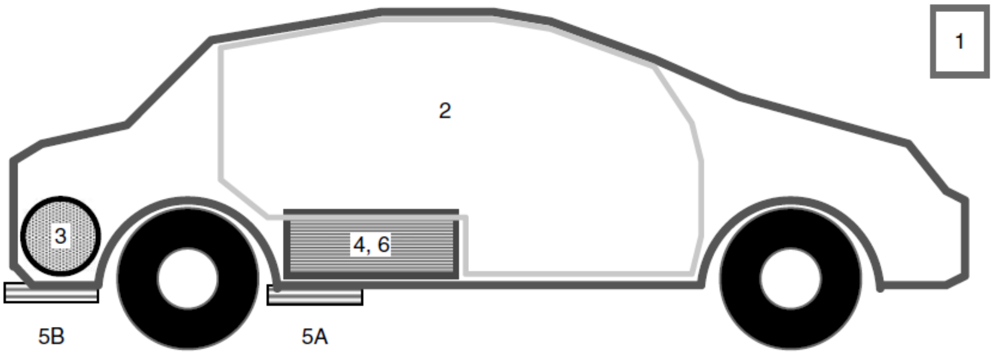

Figure 17 - Hydrogen sensor location in fuel cell vehicle [6]

1| Garage/Tunnel ambient (safety)
2| Passenger compartment (safety)
3| Full storage area and high-pressure piping (leaks)
4| Fuel cell system area (leaks into ventilation air)
5A| Fuel cell oxidant outlet (emissions)
5B| Vehicle exhaust (emissions)
6| Fuel cell anode loop (control)

5.4 Hydrogen Sensing

General performance parameters for the various sensor types are discussed below. The focus is on sensor technology. The actual performance between commercial devices can show significance variability. In some cases, devices with very similar design parameters have dramatically different behavior [4]. Figure 18 is an extreme example of the potential variability between devices fabricated with ostensibly identical design parameters but manufactured by different vendors [4]. In each case the sensor was powered up and allowed to stabilize for a period in accordance with manufacturer recommendations. Sensor control circuitry and operation was also in accordance to manufacture recommendations. After warm-up, the sensor was then subjected to three series of 10-minute exposures comprised of 0.0, 0.2, 1.0, and 2.0% hydrogen at a constant flow rate of 500 sccm [4]. The device on the left exhibits excellent repeatability and had a signal that was highly correlated to concentration. A second sensor was subjected to the same protocol, and the results are shown in the right trace of Figure 18. The trace on the right tended to show less repeatability and was prone to saturation. Although this device responded with high sensitivity to the low concentration of hydrogen, it would be impossible to correlate the signal with hydrogen concentration [4]. These results clearly show that performance can vary dramatically between commercial devices and emphasize the need for performance validation prior to selection of a technology for a particular application [4]. Nevertheless, general performance trends can be defined by the sensor platform since these are defined primarily by the chemical interaction of the analyte and environment with the platform [4].

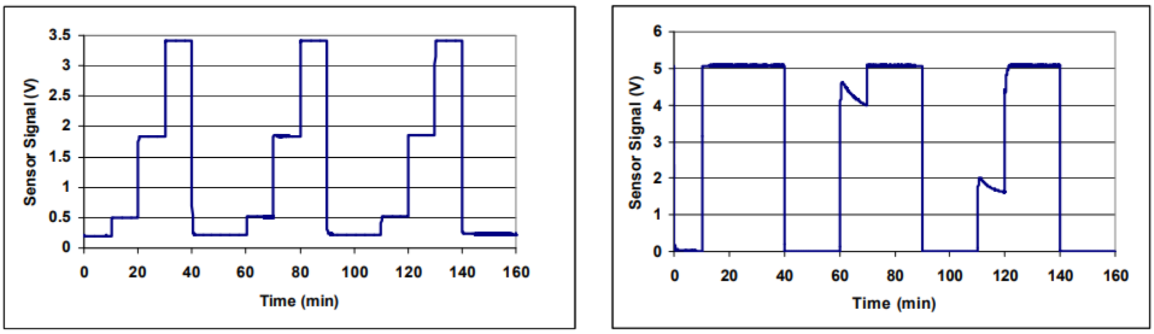

Figure 18 - Sensor response to three series of 10-minute exposures comprised of 0.0, 0.2, 1.0, and 2.0% hydrogen. The response curves for two different commercial devices are shown. The basic design features between the two devices were nearly identical, although they were provided by different manufacturers [4]

1. Catalytic combustion sensors

Catalytic combustion sensors have been improved and are now more widely used throughout various industrial sectors as reliable sensors.

- Accuracy and reproducibility are excellent
- Low power consumption allows devices to be more compact
- Hardly affected by ambient temperature and humidity
- The output curve (to just short of the explosion threshold) is almost a straight line

A catalytic combustion sensor (CAT) that evaluates the heat of hydrogen combustion. The sensor consists of a detector cell and a reference cell. The detector cell basically is a platinum wire coil to which the carrier is attached, and it is coated with an oxidization catalyst such as alumina. When the powered sensor is exposed to combustible gas, the gas will burn [14]. The reference cell is essentially an identical platinum coil, that has been treated to prevent combustible gas from igniting upon contact [14]. Since both cells become extremely hot during use which could ignite the combustible gas, they are enclosed in an explosion-proofed protective sintered metal and stainless steel 200-mesh netting to prevent sparking [14].

The sensitivity of a contact combustion type sensor shows almost equal sensitivity to all concentrations below the LEL (lower explosion limit) threshold of virtually all combustible gases (or mixed concentrations thereof) [14]. Therefore, almost all combustible gases can be measured with any measuring device that can be calibrated with a scale having the LEL as 100% [14].

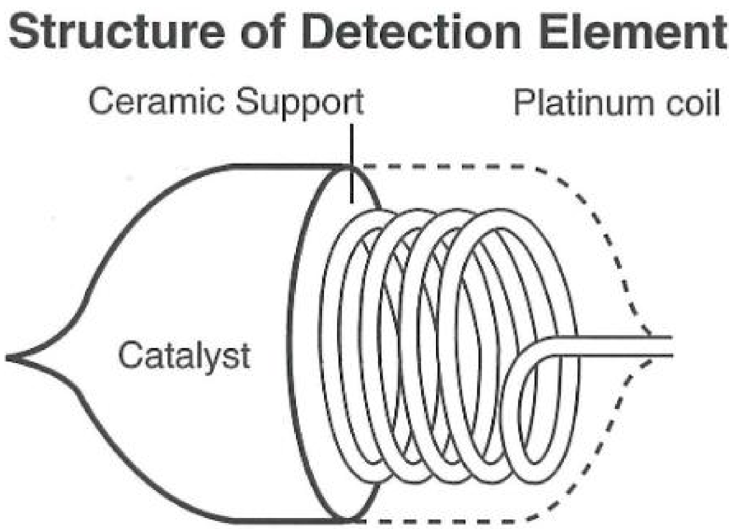

Figure 19 – Catalytic Combustion Sensor [14]

2. Thermal conductivity sensors

Thermal conductivity detector (TCD) is also known as Katharometers. Thermal conductivity is the most widely applied measuring principle for the determination of hydrogen [6]. The measuring principle is based on the differences in thermal conductivity of the gases to be measured. A thermal conductivity detector (TCD) measures the concentration of a gas in a binary gas mixture by measuring the thermal conductivity of the sample gas and comparing it to the thermal conductivity of a selected reference gas (Figure 20). Two or four ultrastable, precision glass-coated thermistors are used, one (or two) in contact with the sample gas and the other (or two) in contact with the reference gas (such as chlorine in a sealed chamber). The thermistors are mounted so that they are in close proximity to the walls of the gas chambers. The entire cell is temperature-controlled, and the thermistors are heated to an elevated temperature in a constant current Wheatstone bridge. The thermistors lose heat to the walls of the gas chambers at a rate that is proportional to the thermal conductivity of the gas surrounding them. Thus, each thermistor will reach a different equilibrium temperature [6]. The temperature difference between the two (or four) thermistors is detected in the Wheatstone bridge, and the resulting bridge voltage is amplified and converted to a linear 4–20 mA output proportional to the concentration of hydrogen in the binary gas mixture. The TCD will detect any gas or vapor that has a thermal conductivity that differs significantly from the high thermal conductivity of helium [6]. The general accepted lower detection limit for the TCD is 50 ppm v/v [6].

TC sensors are stable devices, and since they do not chemically interact with the analyte (heat transfer is a physical process), are less prone to contamination. They tend to be non-selective, but with proprietary coatings, vendors have reported improved selectivity. They are affected by environmental parameters including temperature, pressure, and humidity. As with many technologies, the environmental effects can be compensated, but this requires independent measurement of ambient conditions. The TC device is amenable to MEMS technology, which not only lowers the power requirements to much less than a milliwatt (useful for battery operation), but miniaturization also results in rapid response times.

Response times of significantly less than 1 second have been reported. Unlike almost every other sensor platform, the TC sensor does not require oxygen for operation, which makes it amenable for use in process streams or for those applications which use a nitrogen purge.

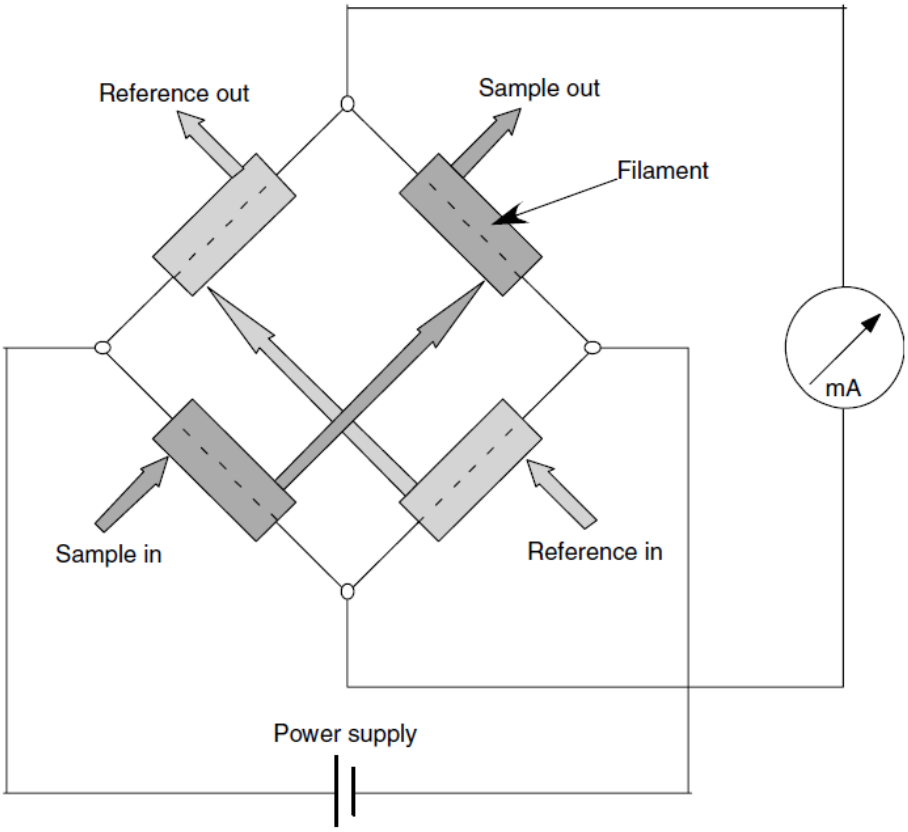

Figure 20 – Schematic drawing of TCD [6]

3. Gas Chromatography

Gas chromatography is the second most applied measuring principle for hydrogen detection [6]. The disadvantages of GC are long response times (minutes) due to the chromatography, time-intensive sample preparation, consumable (carrier and calibration gases), and labor-intensive handling procedures. An advantage, however, is the ability to measure other gases such as nitrogen, oxygen, and carbon dioxide in the presence of hydrogen. But this adds time to the total analysis [6]. The use of a dedicated hydrogen sensor avoids these issues and costs. It is true that the GC and mass spectrometer can identify and quantify other species in the sample stream, but if the need is to control the process hydrogen content a sensor system can do the task at the lowest cost, in the shortest time frame, and at the highest precision [6].

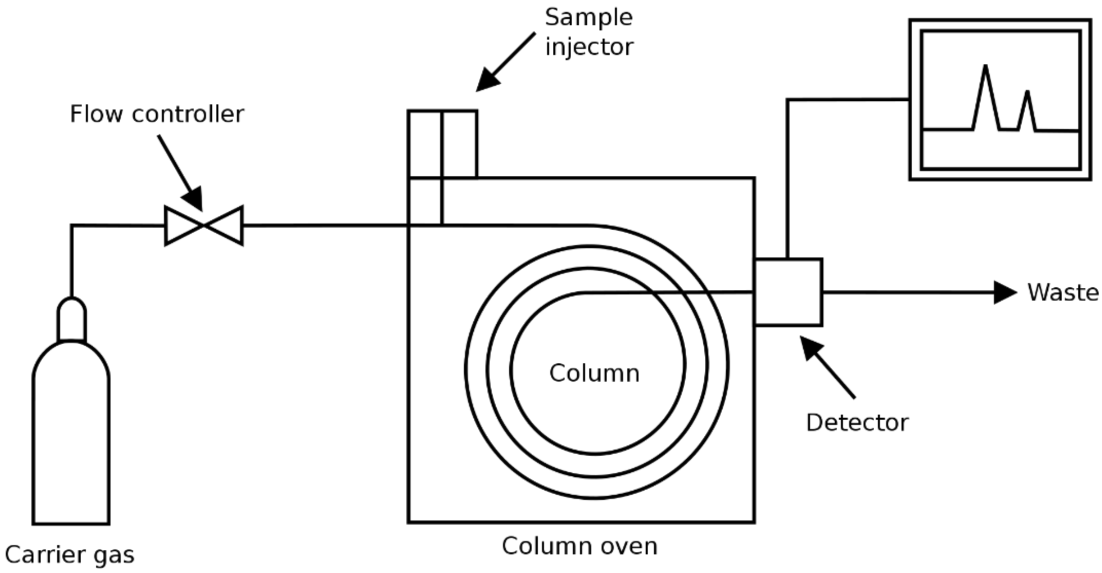

Figure 21 – Diagram of Gas Chromatograph

4. Mass Spectrometry

Mass spectrometry is another widely used technology for hydrogen sensing in the industry. Process mass spectrometers such as gas chromatographs must be safety certified to operate in the plant environment. Mass spectrometers require special air-conditioned shelters, safety monitors, many calibration gases (e.g., fragmentation gases), and routine (weekly) maintenance by a skilled operator [6].

The mass spectrometer can be configured to identify a host of species in a sample stream as long as there is no overlap in signal. Similar to GC, the mass spectrometer requires extensive sample systems and continuous bypass flow of sample gases that add to the complexity and cost to perform [6].

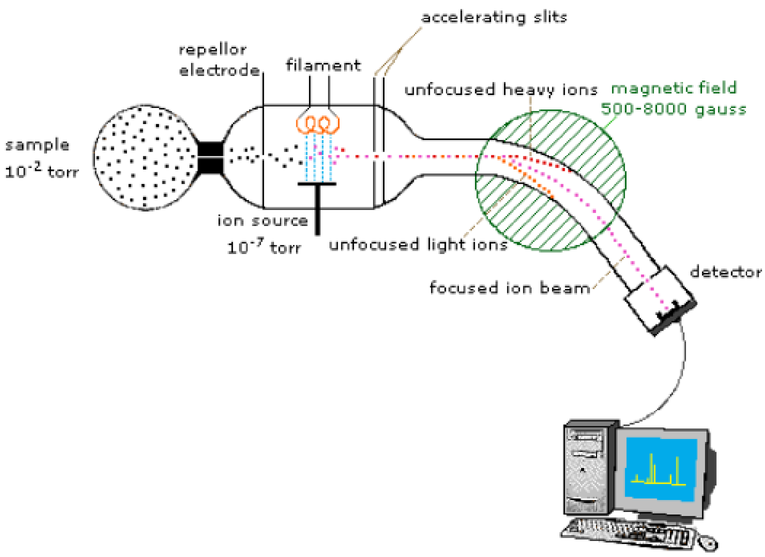

Figure 22 - Mass Spectrometry Sensor Detection [16]

5. Hydrogen Palladium Sensors

Pd-film and Pd-alloy films (Pd), because of the unique and highly selective permeability of hydrogen into palladium (Pd), Pd-film technology has been applied to several classes and types of hydrogen sensors [4]. One basic technology that appears promising is the Pd- and Pd-alloy resistor films, whose conduction (or resistance) varies with hydrogen concentration. The film resistance changes with adsorption of hydrogen and this resistance can be monitored directly as in a chemi-resistor. Such devices have the advantage of a very simple transduction signal [4]. Alternatively, thin Pd films have been incorporated into field effect transistor devices wherein the gate is Pd, and the transistor performance is controlled by the changes in the gate resistivity (Figure 23) [4].

Pd-films can be applied to other sensor classes (e.g., mechanical devices such as the surface acoustic wave sensor--SAW or quartz crystal microbalance sensor--QCM) to achieve hydrogen selectivity; for example, as a coating on a SAW or a QCM device [4]. When used in this manner, adsorption of hydrogen changes the mass of the Pd-film, and this mass change affects the resonant frequency of the mechanical sensor [4]. Small changes in frequency can be accurately measured, which makes for an excellent lower detection limit and range of these devices [4]. The change in frequency and performance of the mechanical structure can be used to measure hydrogen. Commercialization of the hydrogen SAW and QCM devices has however been limited [4].

In general, Pd-film devices suffer from poor performance under anaerobic conditions, partly because of a phase change and because the oxygen in the air is needed to enhance reversibility of the hydrogen in Pd effect. Pd-films are also susceptible to chemical poisoning, especially by sulfide [4]. However, several vendors have alleviated much of the deleterious effects of sulfur and other potential poisons by the incorporation of a protective, hydrogen-permeable but sulfur impermeable coating over the Pd [4]. The long-term stability of the coating is not fully characterized in many real-world environments, but promising performance has been reported by some vendors. The devices tend to show slow response time relative to other sensors, particularly thermal conductivity devices and some of the new thin film sensor platforms. Permeation into palladium films can be significantly slowed down at low temperature [4].

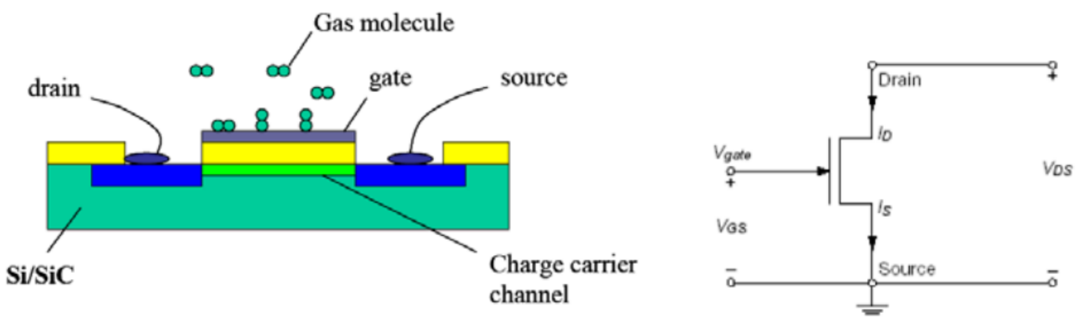

Figure 23 - Schematic illustration of a ChemFET sensor that uses a palladium film at the gate. Adsorption of hydrogen changes the potential at the gate and thereby increases the conductivity between the source and drain [4]

6. Metal Oxide Sensors

Metal oxide sensors are fabricated with a wide band gap semiconductor material such as tin oxide or other metal oxide as the active element of the sensor. The material is usually embedded in a porous ceramic matrix traditionally configured as a bead formed around an internal heater coil [4]. Operation at elevated temperatures (ca. 400 °C or greater) is required to obtain a stable measurable conductivity (or resistance). Gaseous analytes, such as hydrogen diffuse into the porous structure and react with the sensor to decrease the surface concentration of oxygen. This then lowers the surface potential between grains, thereby decreasing resistance. In addition to the embedded heater, a probe wire is also embedded and is used to measure device resistance (the ground point of the embedded heater often serves as the second probe point for resistance measurements) [4]. The MOX sensor is a small readily produced device [4]. The device readily has sufficient sensitivity for hydrogen safety application. As a high temperature device, the MOX sensor is not dramatically affected by temperature variations. However, the MOX sensor is not considered a selective device and may react with other compounds which might be present, including moisture [4]. Moisture variations may also affect the MOX calibration curve. The response of the classic MOX was not linear and tended to follow a power law relationship with concentration. Another major disadvantage of the classic MOX sensor was a long response and even longer recovery time [4]. The performance of a MOX sensor can be permanently degraded when exposed to certain silicon compounds (which can include common sealants). Generally, these devices require oxygen for stable responses and have not been widely applied to process streams or very high concentrations of hydrogen, thus these devices cannot be readily deployed in a nitrogen purged environment [4].

However, recent advances in MOX technology have been made, particularly in the development of miniaturized thin film designs. The film geometry not only requires significantly less power for operation, improved analytical performance has been observed in linearity as well as response time [4]. Figure 24 shows the response of a commercial MOX hydrogen sensor from 2004 compared to a more recently developed device manufactured in a thin film configuration. The robustness of these thin-film designs to environmental parameters (pressure and RH) and selectivity needs to be further investigated [4].

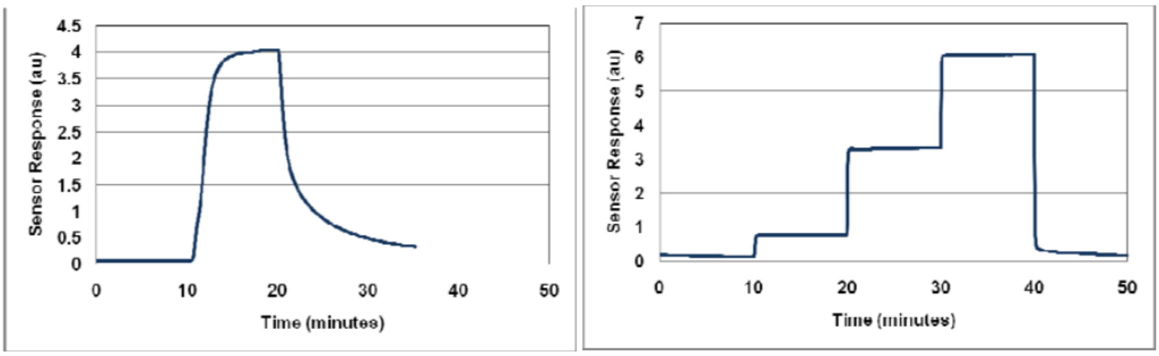

Figure 24 - Response of a classic MOX sensor (bead structure, circa 2004) to 2% hydrogen (left) compared to the response of a thin-film MOX sensor to 0.2, 1, and 2% hydrogen (2009) [4]

7. Electrochemical Sensors (EC)

Amperometric and Potentiometric sensors are two main electrochemical sensor platforms. Amperometric hydrogen sensors are more common commercially. Amperometric sensors operate by electrochemically reacting with the gas of interest and producing an electrical signal proportional to the gas concentration. In amperometry, the target molecule will undergo a change in oxidation state, which involves transfer of electrons between the molecule and the electrode. Hydrogen gas (H_2) is oxidized to hydrogen ions ($H+$), a process that involves the loss of 2 electrons per hydrogen molecule to the electrode [4]. A typical electrochemical sensor consists of a sensing electrode (or working electrode), and a counter electrode separated by a thin layer of electrolyte. Gas that comes in contact with the sensor first passes through a small capillary-type opening and then diffuses through a hydrophobic barrier, and eventually reaches the electrode surface. This approach is adopted to allow the proper amount of gas to react at the sensing electrode to produce a sufficient electrical signal for measurement while preventing the electrolyte from leaking out of the sensor [4]. The gas that diffuses through the barrier then reacts at the surface of the sensing electrode involving either an oxidation or reduction mechanism [4]. These reactions are catalyzed by the electrode materials specifically developed for the gas of interest. With a resistor (or more sophisticated circuit) connected across the electrodes, a current proportional to the gas concentration flows between the anode and the cathode. Amperometric gas sensors are typically controlled by an electronic circuit known as a potentiostat, which not only controls the electrochemical conditions (e.g., bias) of the sensor but also provides a ready means to measure the current. The current can be measured to determine the gas concentration. Because a current is generated in the process, the electrochemical sensor is often described as an amperometric gas sensor or a micro fuel cell [4].

Hydrogen can be easily detected by electrochemical sensors, especially amperometric devices, which are readily available from numerous vendors. Amperometric gas sensors are physically small, have good sensitivity and typically have a broad linear range. The sensors are stable with lifetimes of up to 2 years being routine, although this is considerably less than the DOE target. Limitations include limited selectivity (e.g., CO may affect the sensor), a restricted temperature range due to a liquid electrolyte, and a dependence on barometric pressure. Alternatively, humidity fluctuations have nearly negligible effect on the devices. To some extent, the temperature and pressure dependencies can be compensated via electronics or microprocessor-controlled corrections. Many amperometric gas sensors require oxygen for long-term stability, and thus should not be used in nitrogen or other inert atmosphere without prior validation for a specific model. Prices currently range from $10 – $100, dependent to a large part on quantity and severity of application. With conventional designs, the price is expected to remain at around $10 – $100 [4].

8. Optical Hydrogen Sensors

Optical hydrogen sensors are devices that use light to detect the presence of hydrogen gas in a particular environment. These sensors are useful in a wide range of applications, including industrial and medical settings. The basic principle behind optical hydrogen sensors is that hydrogen gas absorbs certain wavelengths of light, which can be detected and measured using specialized equipment. The sensor typically consists of a light source that emits a beam of light, a hydrogen-sensitive material, and a detector that measures the amount of light absorbed by the hydrogen gas.

One common type of optical hydrogen sensor is the fiber optic sensor. This sensor uses a fiber optic cable to transmit light from a source to a detector, with a hydrogen-sensitive material coated on the surface of the fiber. When hydrogen gas is present, it absorbs certain wavelengths of light passing through the fiber, causing a reduction in the amount of light reaching the detector. The detector can then measure the amount of light absorbed by the hydrogen gas and provide an indication of its concentration.

Optical hydrogen sensors are particularly useful in vehicles operating in confined spaces because they offer a high degree of sensitivity and can detect even low concentrations of hydrogen gas. Additionally, they are non-intrusive, meaning that they do not require direct contact with the gas being measured, which reduces the risk of exposure to hazardous materials. Additionally, optical hydrogen sensors are resistant to electromagnetic interference and can operate in harsh environments. Overall, optical hydrogen sensors are an important tool in many industries and applications, providing accurate and reliable detection of hydrogen gas for a wide range of purposes.

5.5 Market Hydrogen Sensors

Hydrogen sensors are used to detect hydrogen wherever it is produced, stored, distributed, or used. There is a rapidly growing number of hydrogen sensors available on the commercial market. Different types of sensors exist, and the most commonly available hydrogen sensors include catalytic, electrochemical, metal oxide semiconductors and thermal conductivity sensors. Each type of hydrogen sensor has its own advantages and disadvantages in terms of performance.

The hydrogen gas sensor market is segmented based on technology, end-user industry, and geography. The market is categorized based on end-user industry which includes automotive, oil and gas, healthcare, aerospace and defense, and others. Further, the market is analyzed based on five regions, namely, North America, Europe, Asia-Pacific, Middle East and Africa, and South America.

The market is set to grow exponentially in the future:

Short Term (2022 - 2025): Growing power generation and automotive industry will positively impact hydrogen sensor market growth [7].

Medium Term (2025 - 2028): Germany and the U.S are projected to witness comparatively high demand for hydrogen sensors due to increased awareness of green hydrogen as a newer source of energy for vehicles [7].

Long Term (2028 - 2032): Hydrogen sensor, when integrated into IoT-enabled detection devices, provide exact real-time information on the presence of hydrogen, prevent equipment malfunction, and avoid preventable accidents [7].

Over the 2017-2021 period, the global market for hydrogen sensors registered a CAGR of 1.5%. A market research and competitive intelligence provider, predicts that the market will exhibit growth at 6.7% CAGR between 2022 and 2032[7].

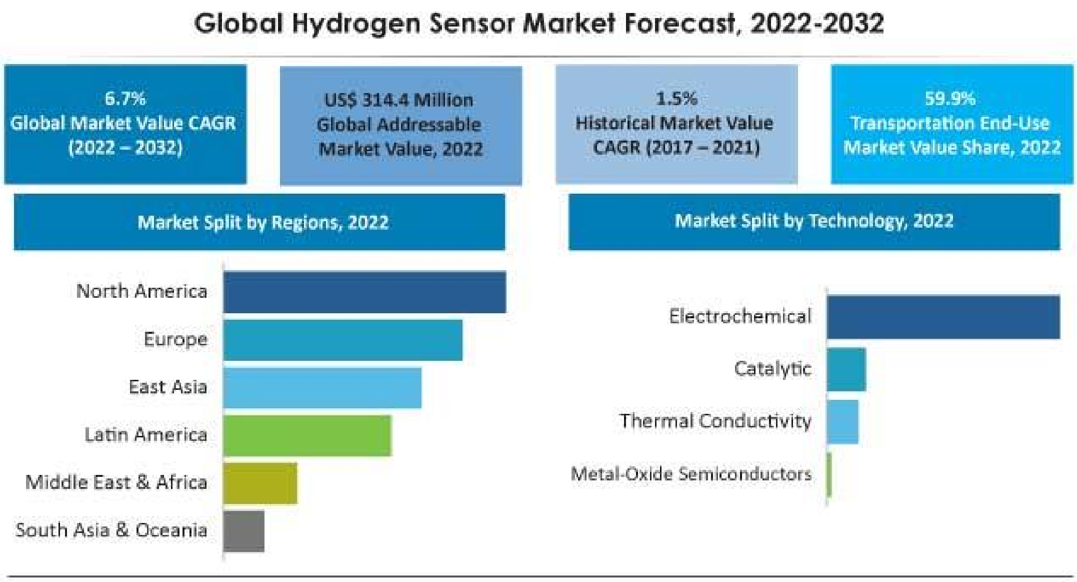

Figure 25 - Global Hydrogen Sensor Market Forecast, 2022-2032 [7]

Table 5 summarizes the commercially available hydrogen sensor products for leak detection and process monitoring. Hydrogen sensors are available with different packaging configurations depending on the application requirement [6]. Palladium-based resistors are the most hydrogen specific and should be used where a false alarm cannot be tolerated during hydrogen detection [6]. The most commercially successful low-cost technology is CB, semiconductor metal oxide, and electrochemical sensors. Nanotube-based technologies are still under development by research laboratories for leak detection [6].

Process hydrogen sensing technologies include GC, MS, thermal conductivity, and emerging solid-state technologies. Process gas chromatographs and mass spectrometers have high unit costs but are still most widely used in the industry. These instruments have to be enclosed in a closed room and have to be monitored continuously [6]. Process hardened in-line solid-state sensors will eventually replace costly single-point analyzers. Networked point-of-use sensors for remote monitoring of hydrogen in process streams offer several advantages including rapid deployment - low cost to install; inline operation - low cost of ownership; and operate with limited sample conditioning - no lab space/analyst required [6].

Table 5 - commercially available hydrogen sensor products for leak detection and process monitoring [6]

Type	Vendor	Range Leak Detection	Approximate Cost
Pd – Ni Alloy	H_2 scan Corporation	0.5 – 100%	$500 – $3,000
Pd – Ag Alloy	Makel Engineering	1000 ppm to 100%	$500 – $3,000
Catalytic Bead	RKI Instruments	0 – 5%	$500 – $4,000
Semiconducting oxides	RKI Instruments	0 - 2,000 ppm	$100 – $500
Electrochemical	Draeger Safety Inc.	100 – 1,000 ppm	$300 – $1,200
Electrochemical	Toxaler Inc.	0 – 1,000 ppm	$300 – $1,200
Nanotube	NanoMaterials Research	10 – 1,000 ppm	$100 – $500
Binary gas analyzer	Applied Analystics, Gow-mac	0 – 100%	<$25
Gas chromatography	ABB, Siemens, Thermo-Fisher	0 – 100%	<$25
Process mass spectrometer	Extrel, ThermoFisher, Amtek	0 – 100%	<$25

As the demand for hydrogen sensors grows, the accurate hydrogen detection is critical in several industries for everyday safety and process improvement [6]. The user should carefully consider the application and environmental parameters before selecting an optimum hydrogen sensor. Real-time, in-line hydrogen sensors are in immediate need for the process industry as replacements to analytical techniques such as GC. Hydrogen specificity is a must for almost any applications to prevent false alarms [6].

Hydrogen sensors will be ubiquitous in the next 5–10 years due to the advent of hydrogen economy and related infrastructure. The palladium-based hydrogen-specific sensors are the most extensively researched and hold the most promise for the industry [6]. Hydrogen sensors will find applications in petrochemical plants, petroleum refineries, hydrogen production facilities, chlorine plants, nuclear power plants, fuel cells, IC engines, power transformer monitoring, medical diagnostics, leak detection, and other applications [6].

6. Tunnel Fire safety

Tunnel safety refers to measures taken to ensure the safety of travelers and workers in tunnels, particularly during construction and operation. These measures may include:

- Fire safety systems such as fire suppression systems, smoke ventilation, and fireproof walls and doors
- Structural integrity and stability, including regular inspections and maintenance
- Emergency communication systems, such as alarms and PA systems
- Emergency lighting, signages and escape routes
- Traffic management systems to control the flow of vehicles and minimize the risk of collision
- Worker's safety, including protective gear and training
- Air quality control to prevent exposure to toxic gases
- Surveillance and security systems to monitor the tunnel and respond to incidents

It is important to maintain high safety standards in tunnels to minimize the risk of accidents, fire, and other emergencies.

Tunnels are an increasingly important part of the traffic infrastructure especially in territorially uneven mountain areas. They create challenges for prevention and management of incidents/accidents, fire and explosion protection and security against attacks or sabotage. The use of alternative fuels, including compressed gaseous hydrogen (CGH_2) and cryogenic liquid hydrogen (LH_2), in tunnels and similar confined spaces creates new challenges to provision of life safety, property and environment protection at acceptable level of risk.

6.1 Tunnel characteristics and Operation

A tunnel is a subterranean passage typically used for transportation or utility purposes. The characteristics of a tunnel can include:

Geometry:

- Length: the distance between the entrance and exit points of the tunnel.
- Cross-section: the shape and dimensions of the tunnel's interior.
- Profile: the vertical alignment of the tunnel, including the gradient and vertical curves.

Construction materials:

- This addresses the resistance of the tunnel walls and lining materials to fire gases and radiation fluxes. Resistance of concrete to spalling has been of particular interest in recent years, and a number of developments in respect to improved performance have been reported, e.g., addition of fibers into the concrete mix. The structural integrity of tunnel construction is usually designed for and tested in terms of exposure to a specified time- temperature curve, representing the exposure conditions to be expected for the design scenario. The construction may also consider the resistance to the effects of explosion.[2]

Ventilation:

- The provision of fresh air to the tunnel, Maintaining a safe and healthy environment within the tunnel.

Lighting and signage:

- The type and intensity of lighting provided inside the tunnel and clear signage for safe travel.

Fire safety:

- The provision of fire suppression systems, emergency escape routes, and other measures to ensure the safety of those using the tunnel in the event of a fire.

Monitoring:

- Continuously monitoring tunnel conditions and traffic flow.

Egress and tunnel user behavior:

- The safe evacuation of tunnel users in the event of an emergency has received much attention in recent years, prompted in part by the series of catastrophic fires in a number of alpine road tunnels in Europe.[2]

Detection and surveillance

- In normal operation, detection of vehicle emissions, e.g., CO, may be incorporated in the tunnel design. Additional ventilation can then be provided to alleviate conditions inside the tunnel [2]. Heat detection is used principally to detect a fire event. Video surveillance, including in the infrared, may be used to detect the presence of smoke, and coupled with appropriate image processing technology may be able to automatically detect the onset of a fire.[2]

Other emergency facilities are all important like emergency telephone, pushbutton type information equipment, emergency alarm equipment, escape passage, guide board, radio broadcasting equipment, loudspeaker, observation system…

In the background of hydrogen applications in the HyTunnel-CS, an immediate attention should be paid to the ventilation amongst the listed above, in that, both in normal and emergency modes, any accidentally released hydrogen distribution in tunnels is determined by the tunnel ventilation systems and influenced by the traffic and environmental conditions. Secondly, installations of hydrogen detection and water suppression system are also of significant importance, due to the diagnostic function of a hydrogen induced accident at an earlier stage and the interaction between water component and hydrogen combustion at a later stage of accident evolution, respectively.

6.2 Real Tunnel Fires Incidents

6.2.1 Mont Blanc Tunnel Fire

On 24 March 1999, a transport truck caught fire while driving through the Mont Blanc Tunnel between France and Italy. When it stopped halfway through the tunnel, it violently combusted [11]. Other vehicles traveling through the tunnel quickly became trapped and they also caught fire as firefighters were unable to reach the transport truck. 39 people were killed. In the aftermath, major changes were made to the tunnel to improve its safety [11]. The fire was caused by a truck carrying a load of magnesium, which caught fire and exploded. The explosion caused a massive fire that spread throughout the tunnel. The incident highlighted the risks associated with transporting hazardous materials through road tunnels [11].

6.2.2 Baku Metro Fire

The 1995 Baku Metro fire broke out in the subway system of Baku, Azerbaijan's capital, on 28 October 1995, between the stations Ulduz and Nariman Narimanov. The fire killed 337 passengers (including 28 children) and three rescue workers, totaling 289, while 270 people were injured [12]. The fire was deemed to have been caused by electrical malfunction, but the possibility of deliberate sabotage was not excluded. Although a number of people who evacuated the train survived, the fire remains the world's deadliest subway disaster.[3] One person, Chingiz Babayev, was posthumously awarded the title of the National Hero of Azerbaijan for saving passengers' lives [12].

The fire, caused by an electrical fault (one of the leading causes of fires), occurred during the Saturday evening rush hour at about 6:00 p.m. The affected train, consisting of five fully loaded cars, had just left Ulduz station for Nariman Narimanov [12]. The passengers in car number 5 smelled smoke. Later, passengers in car 4 observed white smoke, which soon turned black and caused irritation. The putative electrical malfunction (a sparkover or electric arc in electrical equipment in the rear of the fourth car) stopped the train about 200 meters from Ulduz station [12]. When the train stopped, the tunnel became filled with smoke. The driver reported the incident and demanded that the power be cut. However, lethal emissions of carbon monoxide from the burning synthetic materials in the cars quickly affected the passengers. Because of difficulties opening the doors in one of the cars, the passengers were forced to evacuate through another car. Some 15 minutes after the fire started, the ventilation system was switched to exhaust mode and much of the smoke was drawn in the direction of evacuation. Several people were electrocuted while trying to grasp cables in order to escape the blazing train [12]

.

The majority of those killed (including 28 children) were found inside the train, most of them either crushed or trampled to death. Forty bodies were found inside the tunnel [12]. Survivors recalled sparks flying from high-voltage cables just after the train left the Ulduz station. One of the passengers, Tabil Huseynov, 45, described the situation as follows: "As soon as the train entered the tunnel, I saw a flash. Then the flames enveloped the train car, there was a sound of breaking glass, and the lights went out. People started breaking windows to get out. We were starting to suffocate" [12].

The estimated number of victims varied after the fire. Morgue officials reportedly counted at least 303 bodies, while the independent Azerbaijani news agency Turan quoted medical officials as saying the number of people killed was 337 [12]. A two-day mourning period was declared. Foreign aid was sent, particularly by the Swedish Rescue Services Agency. Lukoil rendered $9,000 in financial aid to the families of victims [12].

The government inquiry commission concluded that the fire was caused by an electrical fault. The fire started in the traction motor of one railway car. No explosives were found. The commission's chairman, Deputy Prime Minister Abbas Abbasov mentioned the "outdated Soviet" equipment [12]. However, two mysterious large holes in the side of one of the wrecked carriages were reportedly found and Azeri national television quoted experts who said the holes indicated the use of an explosive device. President Heydar Aliyev told a United States official that, while preliminary information indicated a technical fault, the fire was "possibly an organized act of sabotage". The Supreme Court of Azerbaijan convicted two persons for criminal negligence. The metro operator was sentenced to 15 years in prison and the station traffic-controller to 10 years [12].

6.3 Protection Systems

6.3.1 Tunnel ventilation

Tunnel ventilation is a very important design element in the construction of tunnels. Ventilation is necessary to maintain a pleasant and safe driving environment by discharging pollutants, such as carbon monoxide, emitted by automobiles from the tunnel. In addition, in cases of emergencies in tunnels, such as fires, the ventilation plays a role in smoke control, saving lives, and restoring the tunnel to normal functioning. Hence, an appropriate ventilation system is necessary when planning and constructing tunnels.

Tunnel ventilation is the process of supplying and removing air from within a tunnel to maintain acceptable air quality for the users and workers within it. This is typically done through a combination of natural and forced ventilation, using fans, ducts, and ventilation shafts to circulate fresh air and remove contaminated air. The main objectives of tunnel ventilation are to provide a safe, healthy, and comfortable environment, to remove harmful emissions and fumes, and to maintain visibility. Tunnel ventilation design and operation must consider various factors such as the type of tunnel, traffic volume, emissions, fire risk, and other environmental conditions.

Additional emergency ventilation is necessary, when tunnel is long enough, to mitigate the effects of the heat and smoke in case of fire events, and to assist in the egress of tunnel users and then to assist firefighting and emergency operations.

In view of hydrogen safety, tunnel ventilation is concerned owing to the following two reasons:

1. In the dispersion stage of hydrogen after unintentional release in a tunnel, the ventilation function strongly influences the hydrogen distribution, stratification, and mixing with air in the tunnel. Meanwhile the tunnel geometry and adjacent vehicle dimensions and positions play also important roles to form the gas flow field initially driven by the ventilation.

2. In the hydrogen combustion stage, after an unwanted ignition of hydrogen release from e.g., a hydrogen powered vehicle, the ventilation changes from normal operation to emergency mode, which influences much on the propagation of hydrogen flames and combustion regime evolutions. As thermal and pressure hazards, the combustion heat even explosion pressure shock waves endanger other hydrogen vehicles in the tunnel and the tunnel structure itself.

Many concerns are focused on the thermal and smoke distributions with emergency ventilation modes specifically for fire accident scenarios in tunnels. The situations are directly relevant to hydrogen dispersion. Hydrogen behaves to some extent like the smoke from a fire due to the buoyancy effect caused by the lighter density of hydrogen or smoke than air.

The exact ventilation performance is determined by the vented flow field in the tunnel and ventilation ducts. Given a tunnel geometry, ventilation device and a hydrogen release, at least a CFD study or even laboratory experiments are required to make meaningful judgement about what is a proper ventilation for a tunnel.

Existing tunnel ventilation systems are categorized basically into three types: natural ventilation, longitudinal ventilation, transverse ventilation. Other variants are also in application such as, semi-transverse ventilation or longitudinal ventilation with Saccardo nozzle. These are reviewed in following sub-sections.

6.3.1.1 Types of Tunnel Ventilation

6.3.1.1.1 Natural ventilation

When from one portal to next portal of the tunnel, there is a provision of drift, it forms a fair ventilation during the operations involving enlarging. This is when the tunnel length is short. In the case of long tunnels, such natural ventilation will be inadequate, and we must design separate mechanical ventilation system.

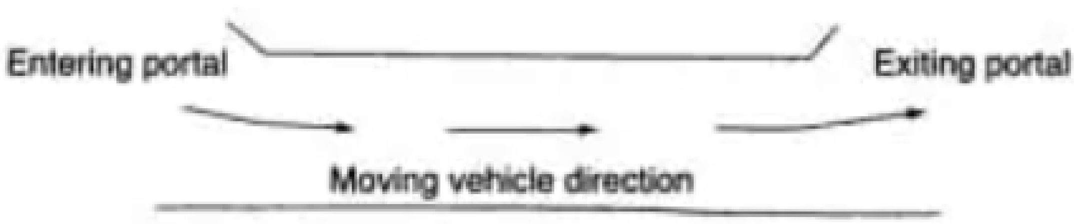

Figure 26 - Natural Ventilation Configuration in Tunnels [2]

Portal to portal case air enters the tunnel from one portal and exits from the other. The pollution of vehicle emissions is accumulated gradually by the convection air flow from upstream to downstream. If the vehicle emissions are evenly distributed along the tunnel length and the air flow in the tunnel is uniform, both the emission concentration and the air temperature linearly increase along the length of the tunnel, resulting in a most pollutant level of air quality at the exit portal. It is indicated by the solid lines in Figure 27 [2]. that a sudden change in wind direction or the wind velocity can affect adversely the natural ventilation effects along with the vehicle generated piston effect. Such a situation brings a lower air venting velocity and thus elevated contamination of air in the tunnel, as presented by the dashed lines in Figure 27 [2].

Several factors influence natural ventilation effect by means of influencing the air flow velocity, e.g., the ambient air temperature difference, wind direction and velocity, the structural configuration of the tunnel portals or shafts, etc. Depending on the local traffic density, the maximum allowed length of tunnel is up to 1000 m, where only natural ventilation suffices, and no extra mechanical ventilation is equipped.[2]

It is obvious that natural ventilation is not reliable for a relatively long tunnel, because it is insufficient to supply fresh air for tunnel users and to protect them from hazardous conditions e.g., in case of accidental release of chemical poisons or even in a big fire with heavy smoke [2]. Therefore, active ventilation driven by extra power is required, at least in emergency cases, or when the contaminated air by vehicle emissions is too bad to be respired in the tunnel.[2]

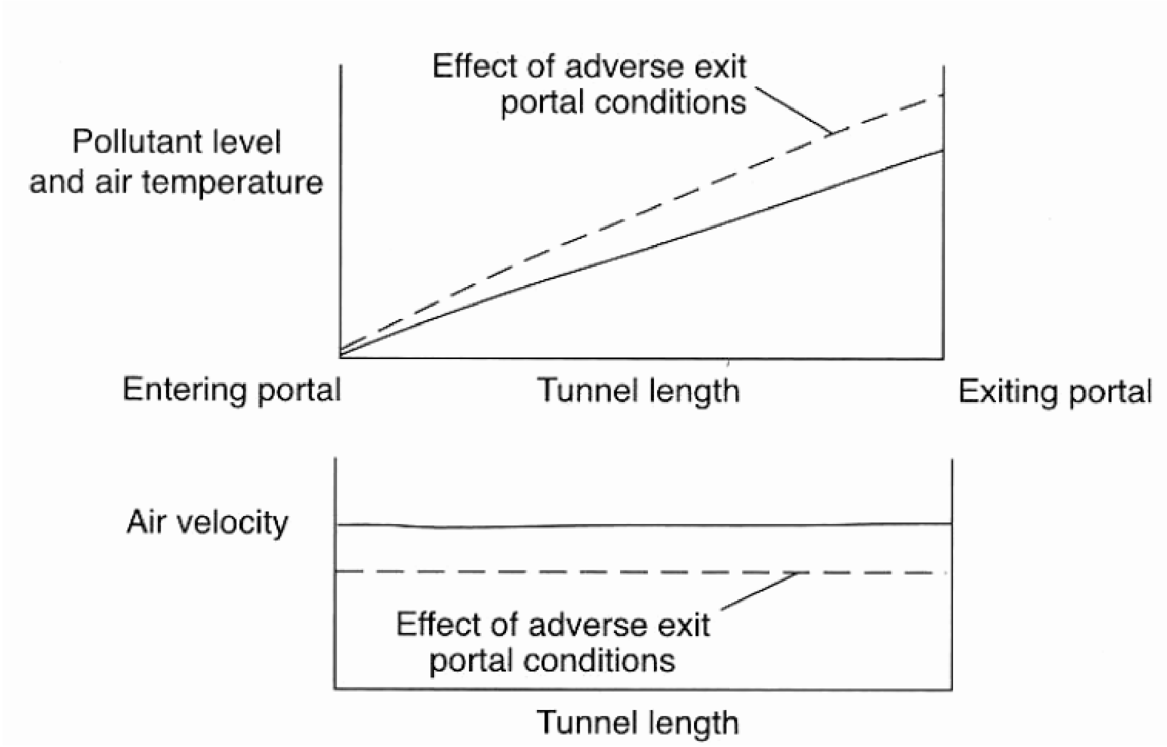

Figure 27 - Airflow Characteristics in Natural Ventilation System in Tunnels [2]

6.3.1.1.2 Longitudinal ventilation

It is similar to natural ventilation with the addition of mechanical fans normally located in the tunnel. The airflow is longitudinal through the tunnel and essentially moves the pollutants and/or heated gases along with the incoming fresh air and provides fresh air at the beginning of the tunnel or tunnel section and discharges heated or polluted air at the tunnel portal or at the end of the tunnel section [15]. Active ventilation system for tunnels employs mechanical devices like electric fans, exhaust, and blowers, which removes the exhaust gasses from the tunnel [15].

The maximum tunnel length that can be ventilated by longitudinal ventilation is limited by the maximum allowable pollution and visibility in the tunnel tube. Depending on the amount and type of vehicles, the maximum tunnel length that it is possible to ventilate with longitudinal ventilation is 3 - 6 km.

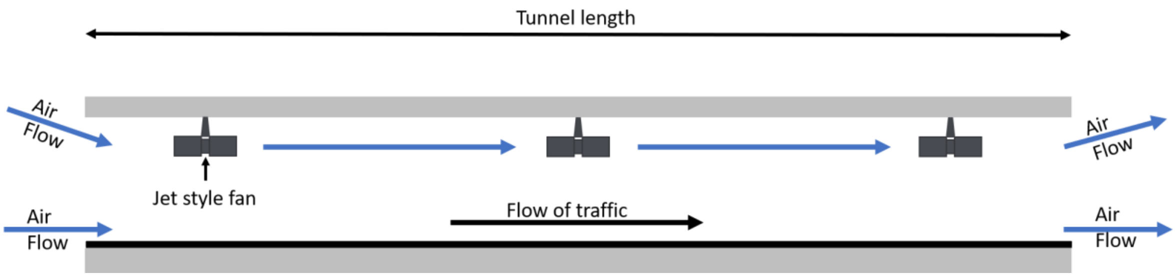

Figure 28 - longitudinal ventilation system using jet fans in tunnels [15]

Another less common type of longitudinal ventilation system uses a configuration known as a Saccardo nozzle to provide unidirectional longitudinal ventilation [15]. This is used where headroom in the tunnel is limited, such as in a retrofit for an existing unventilated tunnel [15].

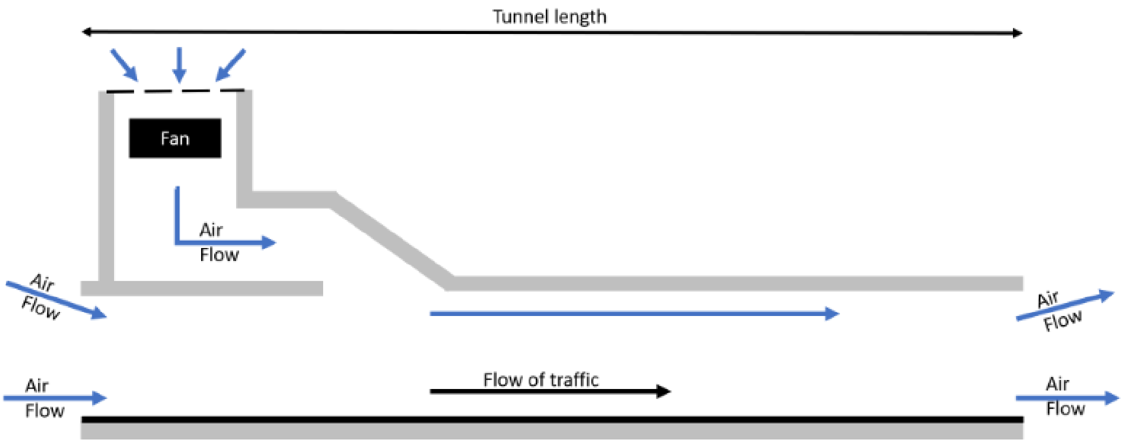

Figure 29 - Saccade nozzle longitudinal ventilation system used in tunnels [15]

6.3.1.1.3 Transverse and semi transverse Ventilation

The uniform distribution and collection of air throughout the length of a tunnel will provide a consistent level of temperature and pollutants throughout the tunnel. The transverse ventilation system can be configured as fully transverse or semi-transverse.

Transversal ventilation uses separate air ducts to introduce inside the tunnel set flow rates of fresh air and extract the flue air from the tunnel. The system grants the greatest safety and efficiency to the tunnel users but is also the most expensive solution due to the high civil work costs involved (large ventilation rooms and large cross-sections to allow ducting). Normally used for long bi-directional tunnels with high traffic levels and high percentage of heavy good vehicles transit.

With a transverse ventilation system, fresh air is normally delivered transversely along one side of the tunnel with corresponding extraction points for contaminated air along the other. Airflow is transversely across the tunnel cross-section. Both fresh air supply and exhaust air removal is by means of plenums running longitudinally along the tunnel. These can be formed in the space below the road surface or above a false ceiling to the roadway. The ventilation system makes use of mechanical fans, but these are located in ventilation facilities external the tunnel.

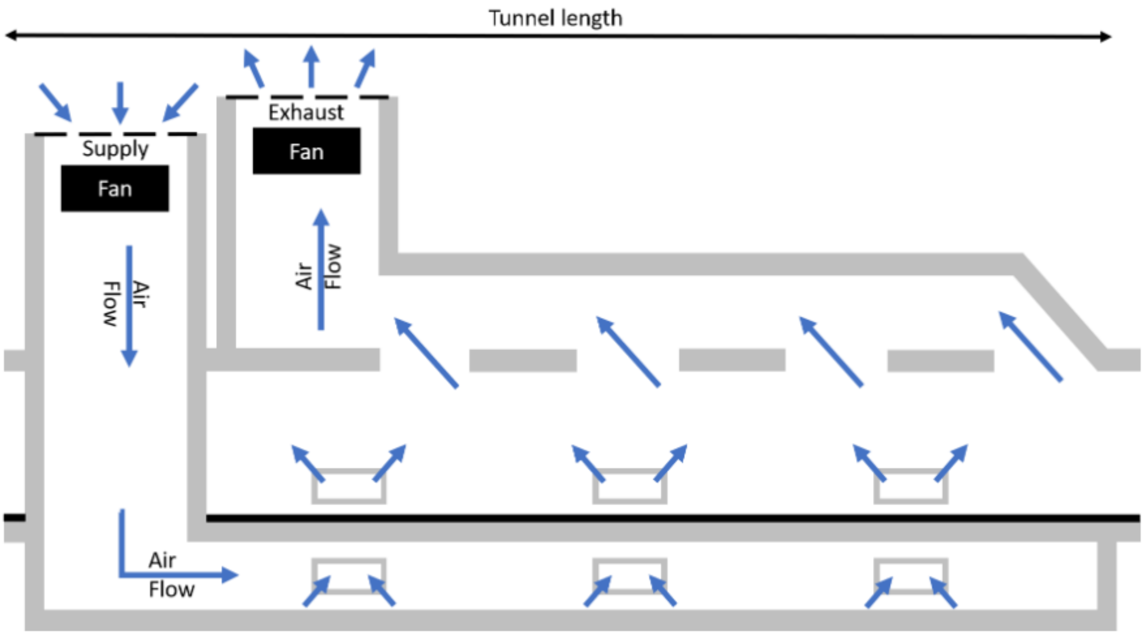

Figure 30 - Transverse Ventilation System Used in Tunnels [15]

With a semi transverse ventilation system, Fresh air is normally introduced transversely throughout the tunnel length with contaminated air being exhausted longitudinally through the portals. An adjoining space known as a plenum is used to facilitate air supply, which is incorporated above or below the tunnel with ducts and air distribution units that allow for even distribution of air throughout the tunnel [15].

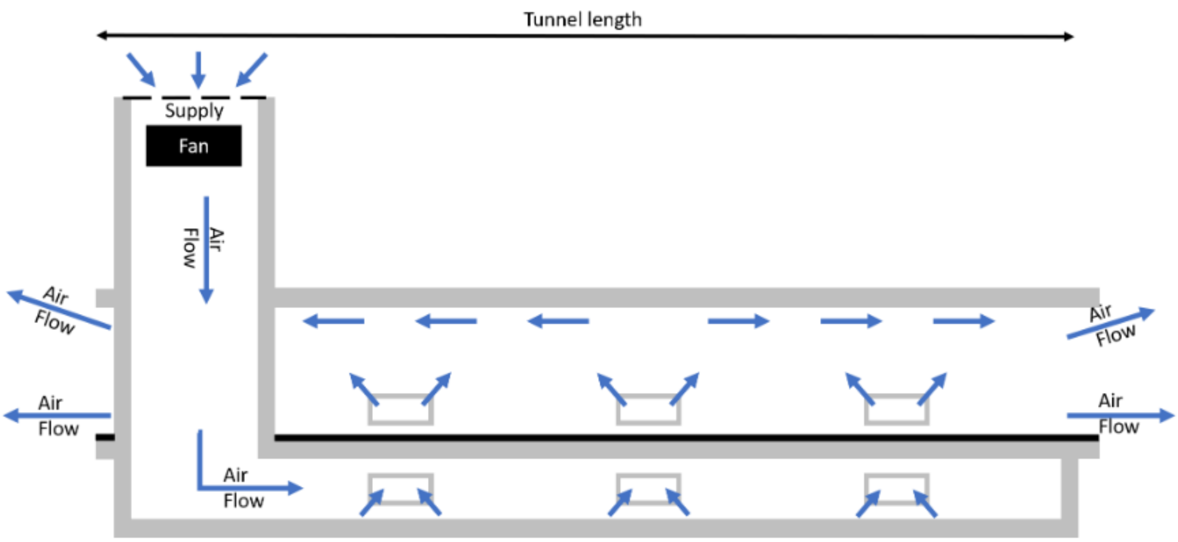

Figure 31 - semi-transverse Ventilation System Used in Tunnels [15]

6.3.2 Water Mist System

Catastrophic fires in tunnels have resulted in loss of life, large property losses and relatively long business interruption periods. In the wake of such fires, authorities tend to focus their efforts almost exclusively on addressing fire safety issues. Property conservation and business continuity aspects are generally not considered. From a risk management standpoint (including risk financing/transfer) this situation is not sustainable. Fire protection solutions should be included as part of the overall design of a transportation tunnel.

Several tunnel fire detection and fighting systems are currently available in the market, each with its own pros and cons. Although no single system is perfect, the water mist system is one of the top-performing conventional tunnel fire suppression systems available. The problem is that such system is expensive. More affordable equipment with similar performance would be a breakthrough in the field of tunnel safety.

A water mist system is a conventional fire suppression system that uses water droplets to extinguish or control a fire. This system has been proven to be effective in suppressing fires in various applications, including tunnels, due to its ability to cool and smother a fire.

In a water mist system, water is pressurized and released through specially designed nozzles to create a fine mist or spray of water droplets. The mist effectively cools the fire and reduces the oxygen level in the surrounding area, which helps to extinguish the fire. Additionally, the water mist system can create a barrier between the fire and the surrounding materials, preventing the spread of flames. Water mist systems are considered to be more effective than traditional sprinkler systems because they use less water, reducing water damage to the structure and surrounding areas. They are also more efficient in suppressing fires in enclosed spaces such as tunnels, where a high concentration of water droplets can be created quickly, and where there is limited ventilation.

Overall, the water mist system is considered to be a top-performing conventional tunnel fire suppression system and is often the preferred choice for tunnels and other enclosed spaces where fires can pose a significant risk.

6.4 Tunnel Regulations codes and Standards

Both the NFPA 502 by the US National Fire Protection Association (NFPA, 2008) and the PIARC by the World Road Association (PIARC, 2008) are widely cited codes. Tunnel regulations, codes, and standards vary depending on the country and region. In this paragraph we will mention some of these regulations.[2]

<u>Allowed maximum length of tunnel with only natural ventilation</u>: The maximum length of tunnel that requires no mechanical ventilation varies from 200 m to 800 m, depending on different countries, traffic densities, tunnel gradients, urban or rural locations etc. The new EU Directive (European Union, 2004) prescribes that 'mechanical ventilation system shall be installed in all tunnels longer than 1000 m with a traffic volume higher than 2000 vehicles per lane'. It is hereby proposed that any tunnel longer than 400 m should be equipped mechanical ventilation, otherwise, natural ventilation is thought adequate. [2]

<u>Restrictions on mechanical longitudinal ventilation:</u> Mechanical longitudinal ventilation is either discouraged or forbidden in two-way or congested tunnels, and risk analysis are required

in these cases if a design with only longitudinal ventilation is accepted. Transverse or semi-transverse ventilation is, however, the preferred option for two-way or congested tunnels, usually with a high traffic volume. For one-way tunnels in countryside, longitudinal ventilation is generally accepted in tunnels of any length. In this case, other engineering limitations may dominate the tunnel design. For an instance, the air quality levels should remain acceptable at the exit portal, unless intermediate shafts are constructed for ventilation [2].

Restrictions on ventilation air flow velocity: There is generally a maximum allowed ventilation air flow velocity within a tunnel, which should be no less than the minimum critical velocity, meanwhile, not exceed certain limits to protect human activities in emergency. The upper limit about the velocity is quoted in a range of 7 to 11 m/s in respect to means of evacuation. The lower limit is suggested as 3 or 3.5 m/s with an aim to maintain smoke stratification as long as needed in emergency cases [2].

Restrictions on dimensions and distances of tunnel cross-sections: Two geometry forms of cross sections are often chosen for the traffic space in tunnels, rectangular profile ("box") and arch profile ("horseshoe"). Stipulations about minimum clearance distances, bore widths, provisions about sidewalk passage, etc. are included in regulations [2]. Regarding the rail traffic system, a general scope directive on rail safety can refer to the Directive (EU) 2016/798 of the European Parliament and of the Council of 11 May 2016 (European Union, 2016). The rail tunnel safety regulation can refer to the Commission Regulation (EU) No 1303/2014 of 18 November 2014 concerning the technical specification for interoperability relating to 'safety in railway tunnels' of the rail system of the European Union (European Union, 2014) [2].

Road surface construction: Road surfaces are typically either exposed concrete or have an asphalt or bituminous covering. However, regulations may not allow asphalt or bituminous coverings, e.g., in Spain, as it is considered that they may contribute to fire spread, or they may be degraded [2].

Road drainage: Drainage of water, fuel or other spills is included in the tunnel design by including a transverse gradient (i.e., downwards towards the side of the tunnel bore). Typical values between 0.5 % and 2.5 % may be specified. Provision for prevention of the spreading of hazardous spills is generally required where hazardous cargoes are allowed to use the tunnel. This may be in the form of gutters or other measures, and there is likely to be a requirement for liquid sumps [2].

Maximum tunnel gradients: The maximum tunnel gradient is generally specified in national guidelines and may vary depending on traffic density and means of ventilation. Typical maximum gradients are 5 % to 6 % [2].

7. Fire Scenarios within Confined Spaces

7.1 Fire experiments of carrier loaded FCEV in full-scale model tunnel

A series of fire experiments and numerical simulations of a carrier loaded with hydrogen FCEVs in a full-scale tunnel were conducted to calculate heat release and smoke generation rates by Seike et al. [1]. As shown in Figure 32, the experimental tunnel is 80 m long, 12.4 m wide, and 7.36 m wide with a horseshoe cross-section [1]. The total HRR of the carrier loaded with hydrogen FCEVs was determined from the experimentally obtained temperature variation near the fire [1].

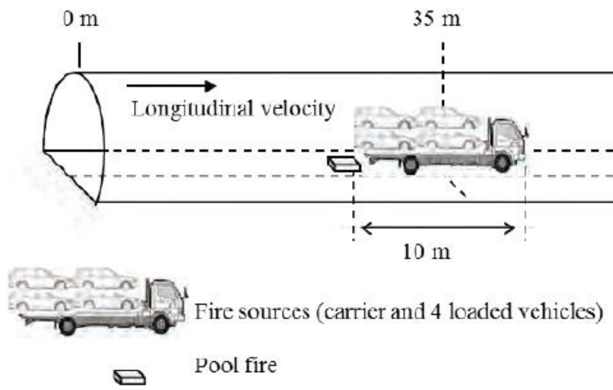

Figure 32 - Experimental Tunnel Configuration and Carrier [1]

The total HRR was also estimated through numerical simulation. The individual HRR of each part of the car was calculated and summed to determine the total HRR. The different parts of concern were the carried vehicles without fuel, the hydrogen fuel which was approximately 17.6 m3 of low-pressure hydrogen and another case of 43.6 m^3 of high-pressure hydrogen, the rear wheels, the driver's seat in the carrier vehicle, and a 1 m^2 gasoline pool fire [1]. The methodology of estimating the HRR of each part and superimposing them to obtain the total HRR was then compared to the experimental results. As shown in Figure 33, for a vehicle containing 43.6 m3 of compressed hydrogen, the numerical method and experimental results are in fairly good agreement [1].

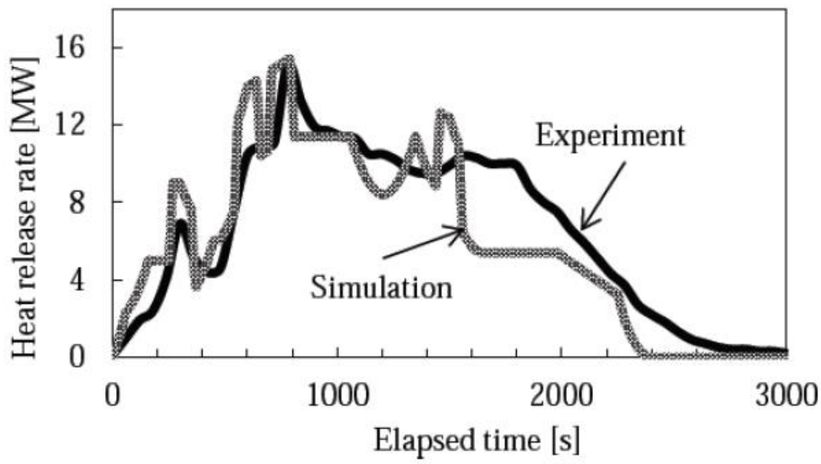

Figure 33 - Comparison of Experimental & Simulated HRR for High Pressure Case [1]

This methodology was extended to predict the HRR of a carrier loaded with eight hydrogen FCEVs. It was determined that, when compared to a large bus fire, the HRR was larger after 10 minutes and the maximum HRR was 1.5 times greater [1].

7.2 Releases from Hydrogen Fuel-cell Vehicles in Tunnels

In order to validate the dispersion/deflagration modeling, a set of experiments were performed at the SRI Corral Hollow Experiment Site (see Figure 34) by Houf et al. [1]. A set of scaled tunnel tests were performed to approximate the full-scale dimensions of the tunnel from the modeling effort [13]. The hydrogen mass, release rate, initial tank pressure, and TPRD release diameter were scaled to approximate the modeling parameters. Figure 34 shows a comparison of the peak overpressures from the experiments with the results from the model simulations. The peak overpressure from the experiments is in good agreement with the modeling results [13].

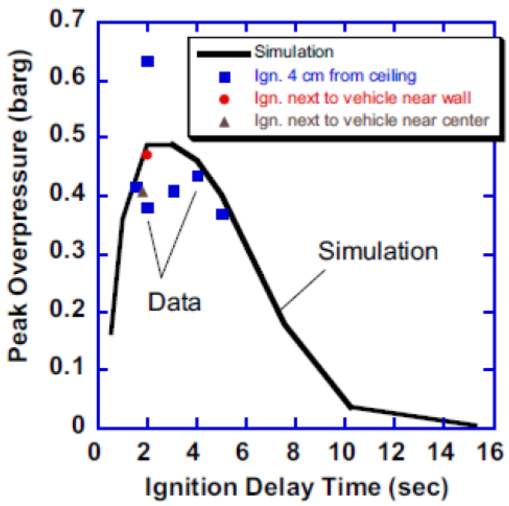

Figure 34 - Comparison of Experimental and Modeling Results [13]

Figure 35 shows a comparison of the hydrogen concentration at discrete locations within the tunnel as a function of time. As shown, the predicted and measured values are generally in good agreement [1]. While the simulation does approximate the overpressure there are some points in the data that might be considered outliers [13].

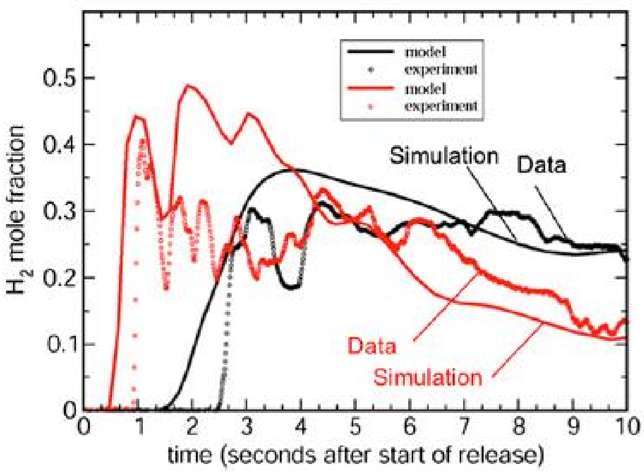

Figure 35 - Comparison of Time-dependent Hydrogen Concentration Values [13]

7.3 Risk Analysis

Once hydrogen is leaked, it will immediately ignite and form a jet flame. If the jet encounters an obstacle or a lump in a confine space, it will form a cloud of combustible gas (volume fraction between 4% and 74.6%), which will explode when it encounters fire and over pressure, with a high potential to cause injury or death. Therefore, it is urgent to explore the potential risk of fire in hydrogen fuel cell vehicles and to clarify the evolution of hydrogen leakage and explosion accidents [19].

The risk analysis for a hydrogen leakage fire incident scenario in a road tunnel:

- Hazard Identification: The primary hazard in this scenario is a fire caused by a hydrogen leak. The potential consequences include property damage, injury or loss of life, and disruption of traffic and commerce.

- Risk Assessment: The likelihood and severity of the consequences depend on several factors, including the size and location of the hydrogen leak, the duration of the leak, the ignition source, and the response time of emergency services. The risk can be classified as high due to the potential for a catastrophic incident.

The following tables can help us to rate the severity of the risk. The fifth level is the worst consequence, and the first level is the lightest [19]. The consequence levels and their judgment criteria are shown in Table 6 [19]. The probability that the risk may occur is divided into four levels. The fourth level is judged to be a frequent risk, and the first level is the risk that cannot occur. The probability level of risk occurrence is shown in Table 7 [19]. As shown in Table 8, there are three levels of risk values: low risk, medium risk, and high risk. Risk values are 1–6 for low risk, 5–12 for medium risk, and 13–20 for high risk. [19]

Table 6 - Risk consequence level and judgment criteria [19]

Level	Judging criteria
5	Fire or explosion, death of persons
4	Fire or explosion, injuries to personnel
3	Fire, property damage
2	Fire, damage to vehicle integrity
1	Vehicle integrity is compromised

Table 7 - Risk Occurrence Probability Level [19]

Level	Judging criteria
4	Occurs frequently
3	Without protection, it will happen
2	Can be detected and controlled in time, occasionally occuring
1	Highly unlikely to happen

Table 8 - Value-at-Risk Levels [19]

Risk value	Risk level
13–20	High risk
5–12	Medium risk
1–6	Low risk

- Risk Mitigation: Several risk reduction measures can be implemented to reduce the likelihood and severity of the consequences, including:

- Implementing hydrogen sensor systems with fast response times and high spatial resolution to detect and localize hydrogen leaks as quickly as possible.

- Providing adequate ventilation to disperse any leaked hydrogen gas.

- Ensuring adequate fire suppression systems are in place, such as automatic fire extinguishers and water mist systems.

- Establishing emergency response plans and procedures, including evacuation plans and coordination with local fire departments and other emergency services.

- Conducting regular training and drills to ensure effective implementation of emergency response plans.

- Risk Monitoring and Management: Regular monitoring and review of the risk mitigation measures can help identify any areas for improvement and ensure their ongoing effectiveness. This includes regular testing and maintenance of the hydrogen sensor systems and other risk reduction measures.

By conducting a thorough risk analysis, implementing effective risk reduction measures, and regularly monitoring and managing the risk, the potential consequences of a hydrogen leakage fire incident in a road tunnel can be minimized, and the safe deployment of hydrogen fuel as an alternative energy carrier can be ensured.

In the event of a fire incident, the response time and spatial resolution of a hydrogen sensor system can be affected by several factors, including the intensity and duration of the fire, the location of the sensor system, and the environmental conditions in the tunnel.

There are several factors that can affect the effectiveness of the hydrogen sensor system in tunnel scenarios. The first factor is the location of the sensor system. If the sensor system is located too far away from the point of release, it may not be able to detect the hydrogen gas in time to prevent an explosion or other hazards.

The second factor is the environmental conditions in the tunnel. If there is poor ventilation in the tunnel . The influence of ambient wind on hydrogen leakage is very large, and the effect is more obvious with the increase of wind speed [19]. Under the influence of ambient winds, the air clouds will shift in the direction of the wind. In addition, the diffusion rate of combustible clouds increases, resulting in the concentration decreasing below the combustible concentration of hydrogen at a faster rate, and the distribution range is significantly reduced. [19]

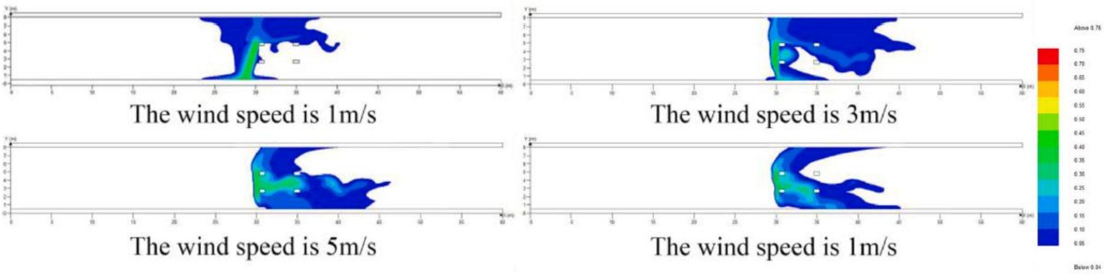

Figure 36 - Variation of hydrogen leaking combustible cloud in different wind speeds in the tunnel [19]

High temperatures can affect the sensitivity of the hydrogen sensor, causing it to produce inaccurate readings. This is particularly relevant in the case of a fire incident, where the temperature can rapidly increase to very high levels. If a fire occurs in the road tunnel, the high temperatures and flames can affect the hydrogen sensor system in several ways. First, the high temperatures can damage the sensors and other components of the system, potentially rendering it ineffective or causing false alarms. Second, the heat generated by the fire can cause thermal gradients in the tunnel, which can affect the dispersion of hydrogen gas and make it more difficult for the sensor system to accurately locate the source of any leaks.

Other effects regarding the high levels of humidity can also affect the performance of the hydrogen sensor, causing it to produce false alarms or fail to detect hydrogen. In the case of a fire incident, humidity levels can increase due to the presence of water or other firefighting agents.

The presence of smoke can interfere with the performance of the hydrogen sensor, making it difficult to accurately detect hydrogen levels. This can be particularly problematic in the case of a fire incident, where smoke levels can be very high.

The hydrogen sensor can be physically damaged during a fire incident, particularly if it is exposed to high temperatures or direct flames. This can cause the sensor to fail or produce inaccurate readings.

As a result of these factors, the hydrogen sensor may not be able to provide accurate and timely warnings in the event of a hydrogen release, increasing the risk of a potential explosion or other safety hazards. Overall, this scenario highlights the importance of carefully considering the location, environmental conditions, and response protocols when deploying a hydrogen sensor system in a road tunnel. It is important to regularly test, maintain the sensor system and regularly calibrated to ensure its accuracy and reliability. In the case of a fire incident, the sensor may become out of calibration due to exposure to high temperatures or other environmental factors. It also highlights the importance of carefully selecting and deploying a hydrogen sensor system with appropriate time and spatial resolution in road tunnels. Appropriate measures should be taken to minimize the impact of these factors and ensure the hydrogen sensor provides accurate readings to help manage the risk of hydrogen release during a fire incident. To mitigate the risks associated with a fire incident, it is important to ensure that the hydrogen sensor system is designed and installed to withstand high temperatures and other environmental conditions that may be present in the tunnel during a fire.

To improve the risk analysis for a hydrogen leakage fire incident scenario in a road tunnel, the following steps can be taken:

Refine the hazard identification: Conduct a detailed analysis of the specific properties and behavior of hydrogen gas in the context of road tunnels to better identify and characterize the hazards associated with a potential hydrogen leak and fire incident.

Collect and analyze more comprehensive data: Collect and analyze more comprehensive and up-to-date data on the specific road tunnel, its surrounding environment, and the potential sources of ignition that could trigger a hydrogen fire, as well as the properties of hydrogen gas itself.

Improve modeling and simulation tools: Develop more sophisticated modeling and simulation tools that can better predict the potential outcomes of different hydrogen-related scenarios in road tunnels, including the potential spread of hydrogen gas, the ignition source, and the extent and severity of the resulting fire.

Enhance sensor technology: Explore and adopt the latest advancements in hydrogen sensor technology, such as advanced sensors with improved sensitivity, selectivity, and spatial resolution, as well as real-time monitoring and data analysis capabilities.

Conduct more comprehensive testing and certification: Conduct more rigorous and comprehensive testing and certification of hydrogen sensor systems and other risk reduction measures, including simulated testing and real-world testing under a range of different conditions.

Involve stakeholders: Involve stakeholders such as government agencies, emergency services, industry associations, and the public in the risk analysis and risk management process and incorporate their feedback and input to help identify potential gaps and areas for improvement.

By continuously improving these areas, the risk analysis for a hydrogen leakage fire incident scenario in a road tunnel can be enhanced, and the safety and effectiveness of risk reduction measures can be optimized

8. FBK SnO_2 Gas Sensor Test

Fondazione Bruno Kessler (FBK) is a research institute based in Trento (Italy) that promotes excellence in fundamental and applied research.

An SnO_2 gas sensor is a type of gas sensor that uses a sensing element made of tin dioxide (SnO_2) to detect the presence of certain gases in the air. SnO_2 gas sensors are commonly used to detect gases such as carbon monoxide (CO), nitrogen dioxide (NO_2), hydrogen (H_2), and methane (CH_4). The sensing mechanism of an SnO_2 gas sensor is based on the changes in the electrical conductivity of the SnO_2 sensing element when it comes into contact with the target gas. When the target gas adsorbs onto the surface of the SnO_2 sensing element, it causes a change in the electrical properties of the material. This change is then detected and measured by the sensor electronics, which can determine the concentration of the target gas.

SnO_2 gas sensors are commonly used in industrial settings for monitoring air quality and detecting gas leaks. They are also used in automotive applications for monitoring exhaust gases and in home safety systems for detecting the presence of carbon monoxide. SnO_2 is a common material used in hydrogen sensors, particularly in metal-oxide semiconductor (MOS) hydrogen sensors. SnO_2 is a n-type semiconductor, which means that it has excess electrons that can be excited by the presence of hydrogen gas. In a typical SnO_2 hydrogen sensor, a thin film of SnO_2 is deposited onto a substrate, such as a silicon wafer or a ceramic substrate. The SnO_2 film is then doped with additional elements, such as palladium or platinum, to enhance its sensitivity to hydrogen gas. When exposed to hydrogen gas, the SnO_2 film undergoes an oxidation reaction that causes a change in resistance, which is measured and used to detect the presence of hydrogen and determine the concentration of hydrogen gas. This change in resistance occurs because the hydrogen gas interacts with the SnO_2 surface, causing a decrease in the number of excess electrons and an increase in the resistance of the film.

SnO_2 hydrogen sensors have several advantages, including low cost, ease of fabrication, and high sensitivity. They can detect hydrogen concentrations in the range of parts per million (ppm) to percent levels, depending on the operating conditions and the specific sensor design. In addition, SnO_2 sensors have a fast response time, typically in the range of a few seconds, which makes them suitable for real-time monitoring applications.

However, SnO_2 sensors can also suffer from some drawbacks when detecting hydrogen gas. One major issue is their selectivity, as they can also respond to other reducing gases such as carbon monoxide (CO) and methane (CH4), which can cause interference and false readings. To address this issue, SnO_2 sensors can be designed with additional features such as a filter or a catalytic coating that increases their selectivity to hydrogen gas.

8.1 Results of testing SnO_2 gas sensor

We tested an SnO_2 gas sensor developed at FBK company in Trento. Below we can find the calibration curves related to SnO_2 gas sensors, vs. different H_2 concentrations.

Specifically, M1-M4 acronym represent the same SnO_2 gas sensor, but activated at four different activation temperatures:

- M1: SnO_2 activated at 380C
- M2: SnO_2 activated at 355C
- M3: SnO_2 activated at 330C
- M4: SnO_2 activated at 300C

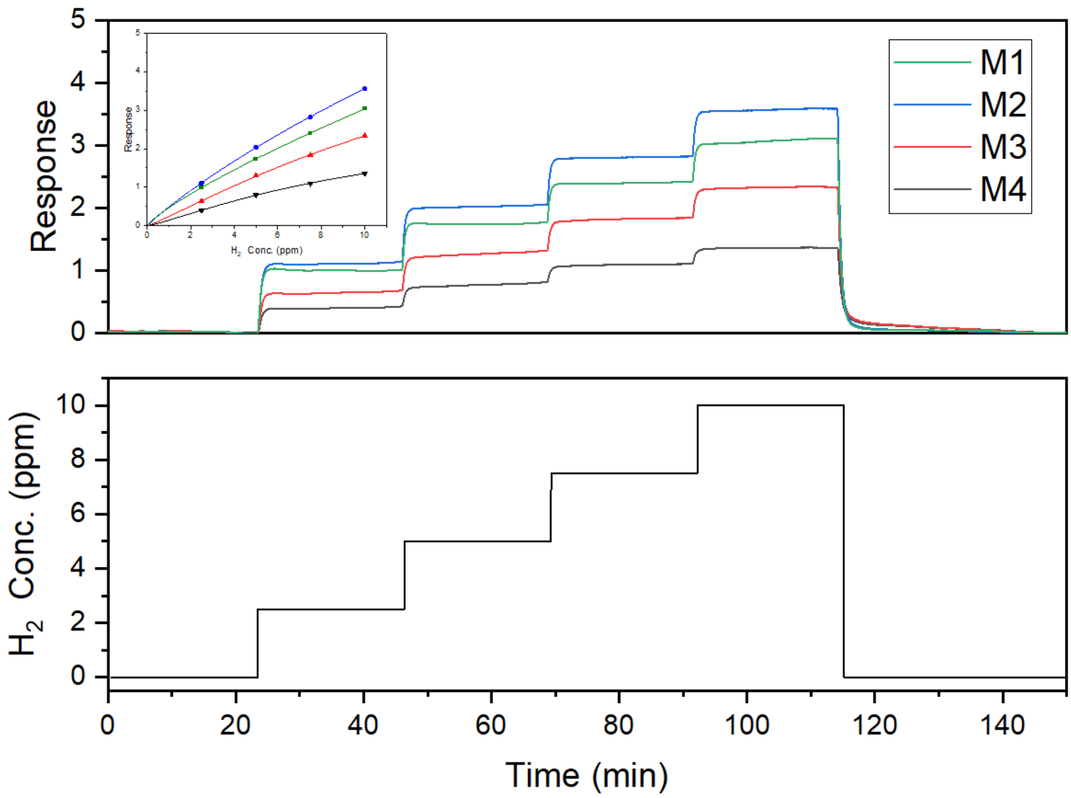

Figure 37 - Dynamic response of SnO_2 sensor, activated at different temperature, vs. different H_2 concentrations

The figure above represents the dynamic response of the sensor, activated at different temperature, vs. different H_2 concentrations. The inset is the calibration curve (responses vs. H_2 concentrations graph).

Overall, SnO_2 gas sensors can be an effective and reliable option for detecting hydrogen gas in various industrial, automotive, and safety applications. However, their performance and suitability for a particular application depend on various factors such as the target gas concentration, environmental conditions, and the presence of interfering gases.

9. Conclusion

Alternative vehicles, such as electric vehicles and hydrogen fuel cell vehicles, pose unique challenges in terms of fire safety compared to conventional gasoline and diesel-powered vehicles. This is due to their different fuel sources and operating mechanisms, which can increase the risk of fire and present challenges in terms of fire suppression. Hydrogen fuel cells can ignite and cause explosions when exposed to heat or flames. These risks can be exacerbated in confined spaces like road tunnels, where fire and smoke can spread quickly, potentially causing serious damage and loss of life. In addition, the current fire safety regulations and procedures for road tunnels may not be adequate for addressing the specific risks posed by alternative vehicles. This is because the regulations were developed primarily for conventional gasoline and diesel-powered vehicles, which operate differently and have different fire risks.

Through this research study, we can conclude that the number of available sensor technologies is quite large, and the number of vendors marketing commercial sensors increases every year. Although new platforms are being developed and commercialized, most mature hydrogen sensor technology can be categorized into a relatively small number of platforms. Each of the technologies discussed in this thesis is a good sensor platform with significant positive performance metrics. Many are commercially successful. However, none is ideally suited for every application. One must, therefore, strive to choose the most appropriate technology that will best meet the application requirements. Although specific performance may vary between vendors.

The require property of a sensor is to sense fast and accurately and should be highly selective and sensitive, and there should not be any fault signals from the other gases. These sensors required to be low-cost compact, small and should have a fast response. So, the important topic for the future is how to improve the sensitivity, selectivity, reliability and reducing response time of these sensors.

In conclusion, the research on alternative vehicles and fire scenarios within confined spaces highlights the need for continued attention and investment in fire safety measures for these vehicles, particularly as they become more prevalent on our roads and highways. By developing specialized fire safety strategies and equipment, this could include measures such as improved ventilation systems, specialized fire suppression equipment, and enhanced training for emergency responders, we can better protect drivers, passengers, and emergency responders from the risks posed by alternative vehicles in the event of a fire.

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