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# BASICS OF HYDROGEN SAFETY FOR FIRST RESPONDERS

## Lecture. Introduction to FCH applications and hydrogen safety

# Content

- Main facts about hydrogen and fuel cells (FCH) technologies
- Overview of hydrogen production, storage, distribution and usage
- FC vehicles
- Hydrogen refuelling stations
- Stationary FC applications
- Overview of incidents and accidents involving hydrogen
- Hydrogen safety engineering

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# Objectives of the lecture

- Appreciate a novelty and a wealth of FCH technologies in modern society
- Understand a role of hydrogen as a new energy carrier
- Name the main routes of hydrogen production, transportation, delivery and use
- Recognise the difficulties of the public perception towards FCH technologies
- Define the main stream industrial hydrogen production methods
- Describe the working principle of a fuel cell (FC) and a FC stack
- Explain the operational principles and safety aspects of:
  - FC vehicles, including materials handling forklifts
  - Refuelling stations
  - Stationary FC, including back-up power and FC systems for combined heat and power (CHP)
  - Hydrogen distribution applications
- Give examples of incidents or accident that might occur on FCH applications
- Give insight into the hydrogen safety engineering framework

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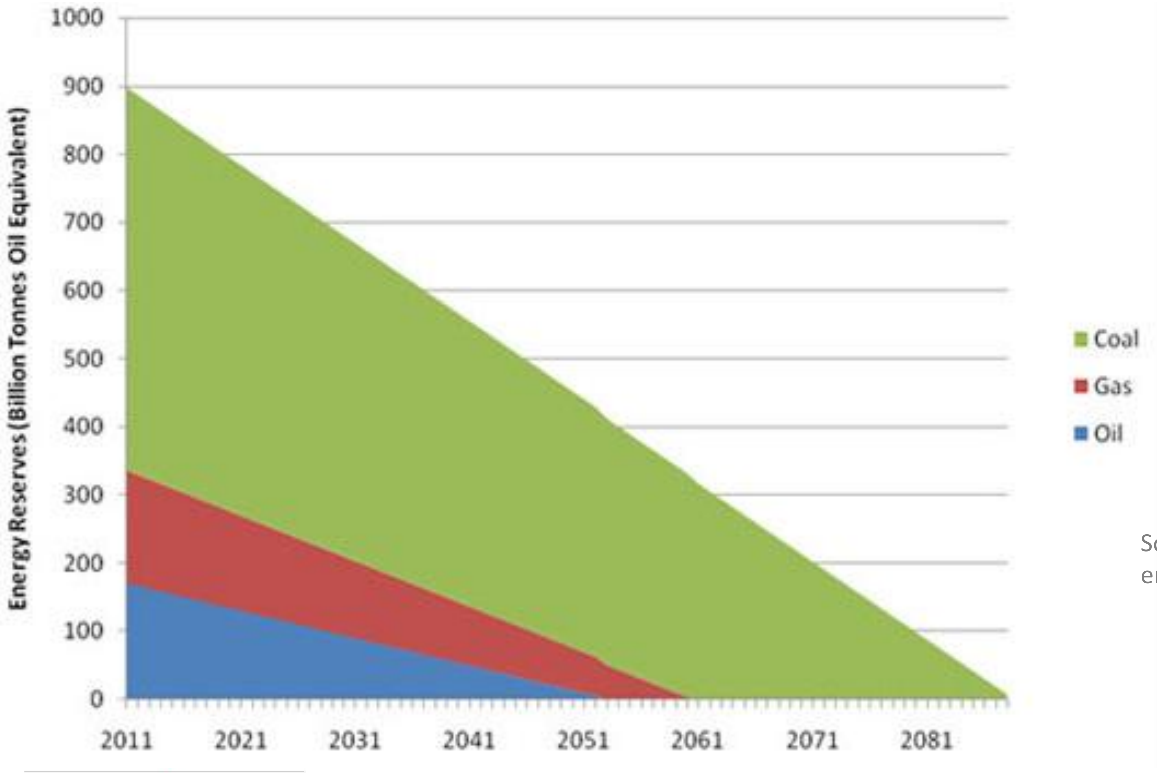
# Why hydrogen?

- **Fossil Fuel Reserves** are limited
- **Geopolitical fears:** fossil fuel depletion
- **Independence of energy supply**
- **Environment pollution:** green hydrogen (zero emission): renewable energy (wind, tide, solar, hydro) – hydrogen storage – fuel cells – vehicles, stationary and portable applications




Source: Ecotricity https://www.ecotricity.co.uk/our-green-energy/energy-independence/the-end-of-fossil-fuels)

# How hydrogen is used

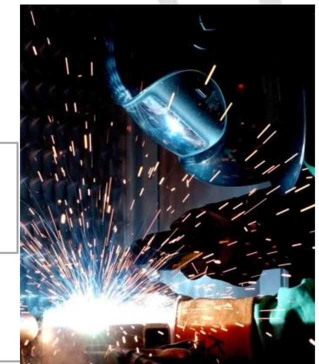
**Hydrogen has been used in industry safely for more than 100 years**

As a fuel in aerospace

In semiconductor industry

In pharmaceutical industry as a reducing agent

In chemical industry for the production of ammonia and methanol



$H_2$

For welding/cutting metals as a shielding gas

In metallurgy to reduce metal ores

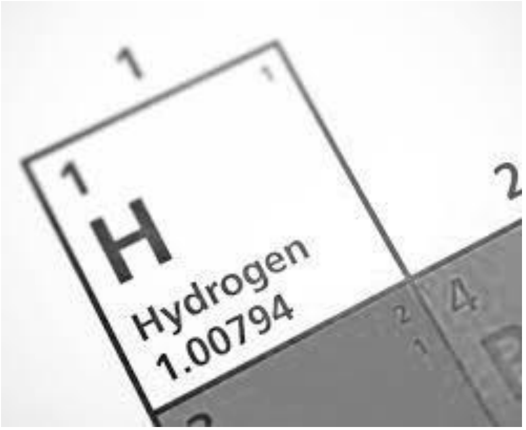
In food industry as a hydrogenating agent or food additive

In petrochemical and oil refining industries

Lifting gas for balloons and

For power generation as a

# What do we know about hydrogen? (1/2)




**HYDROGEN**

‘**Hydro**’ (water) + ‘**Genes**’ (generate) =

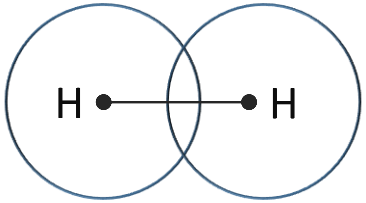
“Water forming”

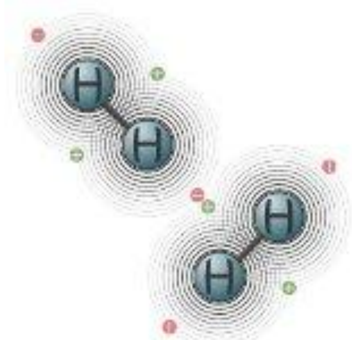
- Chemical symbol **H**; first element in the periodic table; atomic number 1.
- Hydrogen atom (1 proton and 1 electron)
- Hydrogen is the **lightest element** in the periodic table and in the universe.
- Hydrogen is the **most abundant** element in the **universe** (75% elemental mass).
- Hydrogen is the **third** (after oxygen and silicon) **most abundant** element **on Earth.**
- Hydrogen **can only be found in compounds** (e.g. water, hydrides, hydrocarbons and other organic compounds); it does not exist in a pure form.

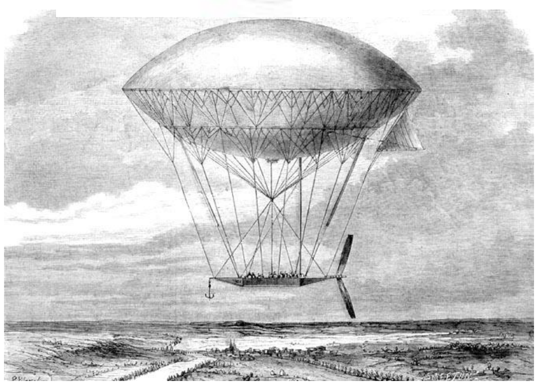
**hydrogen + oxygen → water + *energy***

$$H_{2(g)} + \frac{1}{2} O_{2(g)} \rightarrow H_2O + E$$

# What do we know about hydrogen? (2/2)





Giffard dirigible, built in France in 1852

- Hydrogen forms **diatomic molecules** with chemical formula $\mathbf{H_2}$ (at normal conditions)
- **Colourless, odourless and tasteless** gas (at normal conditions)
- The **lightest gas** (about 14 times lighter than air)
- $H_2$ **rises and disperses rapidly**[1]
- $H_2$ **reacts actively and easily** with other substances
- $H_2$ is a **flammable gas** and should be stored away from sources of heat, flames and sparks
- Experiments on hydrogen balloons[2]
- Hydrogen was used in industry for more than 100 years

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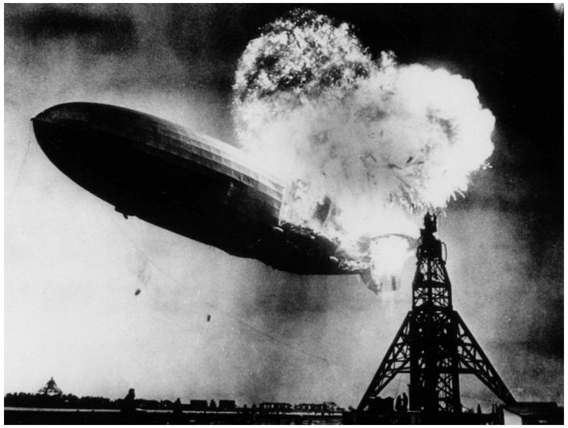
Sources: [1] - Introduction to Hydrogen for Code Officials, U.S. Department of Energy, Washington DC.
[2]- The Royal Institution

# Public perception of hydrogen



Hindenburg disaster, 6 May 1937


Fukushima nuclear disaster,
March 2011, Japan

Source: [1] - Nippon News Network

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## The Hindenburg disaster

- German passenger airship Hindenburg caught fire and was destroyed during its attempt to dock with its mooring mast at the Lakehurst Naval Air Station, New Jersey.
- 36 fatalities.

## The Fukushima Daiichi nuclear disaster

- Hydrogen-air explosions [1] occurred in Units 1,3,4 of power plant from 12 to 15 March 2011.
- In Reactors 1, 2 and 3, overheating caused a reaction between the water and the zircaloy generating up to 1,000 kg of hydrogen gas.
- No casualties officially reported.

## Challenger Disaster

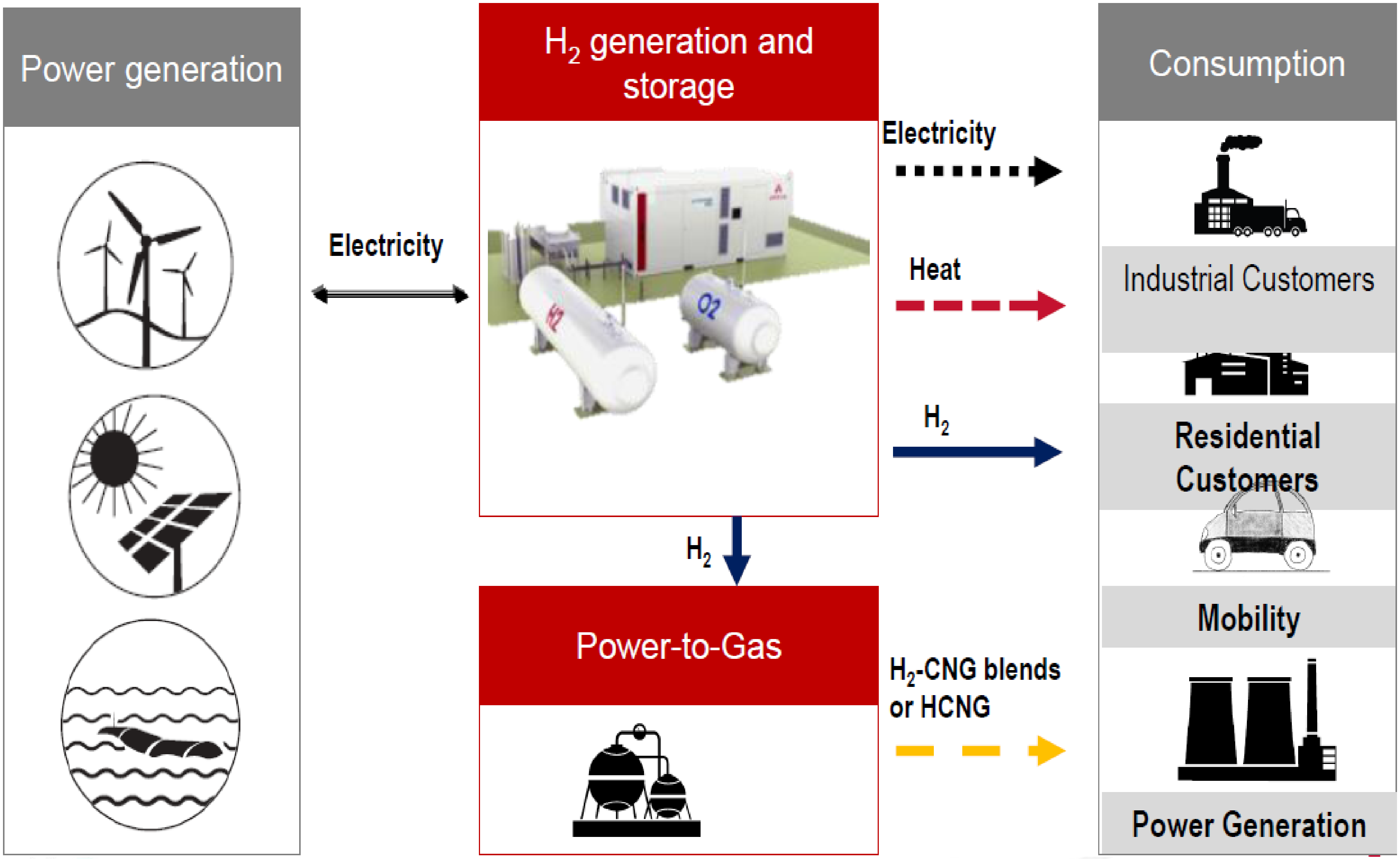
- 73 seconds into its flight.
- 7 crew members
- a failure in the O-rings sealing

a joint on the right solid rocket booster, which allowed pressurized hot gases and eventually flame to "blow by" the O-ring and make contact with the adjacent external tank, causing structural failure.


Challenger Space Shuttle, January 1986, USA

# New FCH technologies

## Hydrogen as an energy carrier

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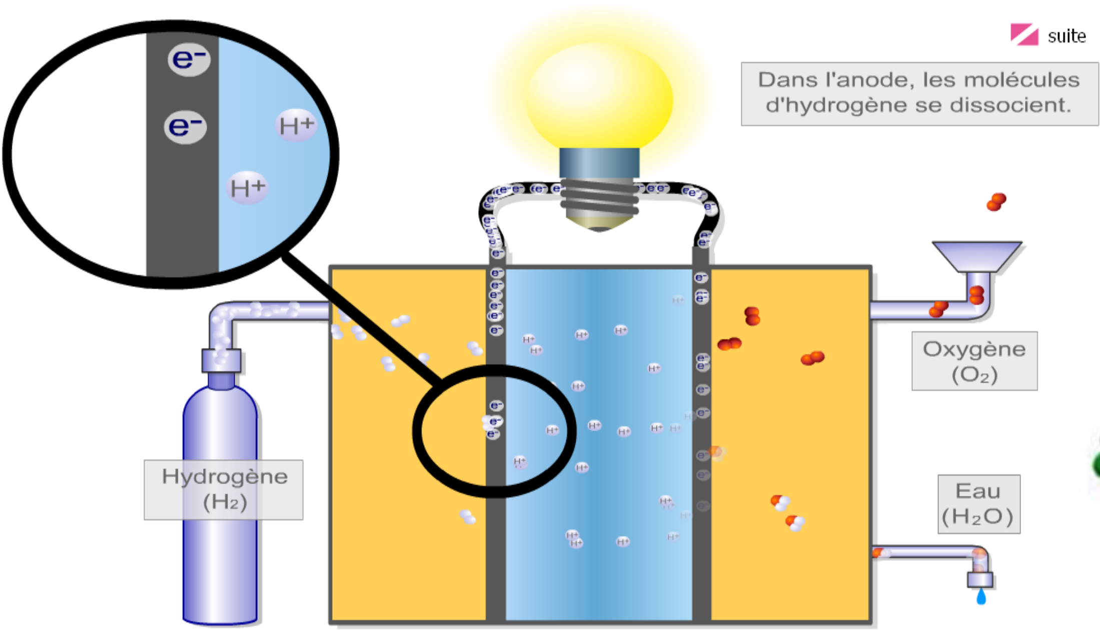
Source: Franck Verbecke, H2FC Technical School , 2014

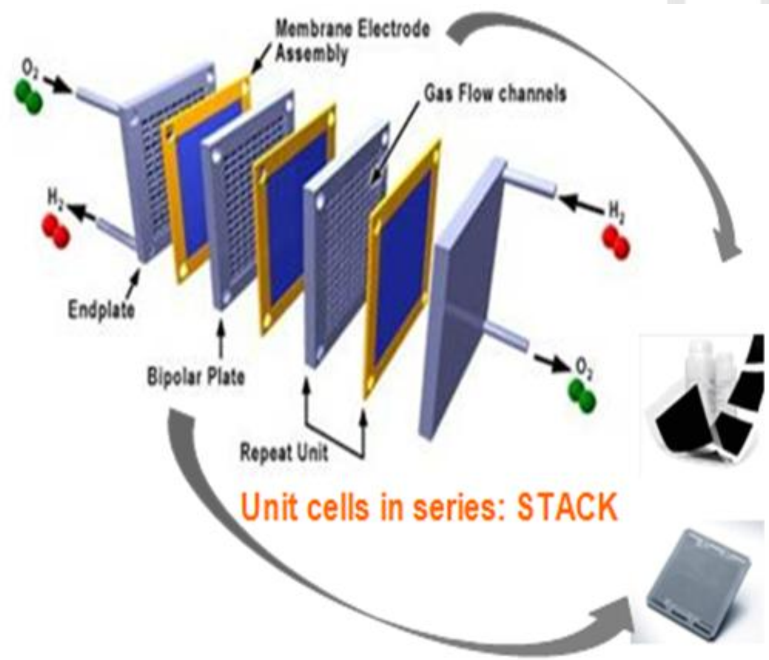
# What is a Fuel Cell (FC)?

[How fuel cell works? (California FC Partnership)]




- A process reverse to the electrolysis of water: $2H_2 + O_2 \rightarrow 2H_2O$
- FC generates electricity but does not store it. It is stored in batteries of FCH vehicles.

- **A FC stack** used to power a car (provides a motor with electricity)

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# How hydrogen is produced

- Hydrogen **must be produced from compounds** that contain it (*e.g.* from water, methane, ammonia, ethanol, etc.)
- **Two main technologies** available in the market for industrial production of hydrogen: **electrolysis of water** and **steam reforming** technologies

**Hydrogen production**

**Water electrolysis**

**PEM electrolysis**

PEM electrolyser

**Alkaline electrolysis**

Alkaline electrolyser IHT type S-556, 760 $Nm^3/h$ and 30 bars

**Steam reforming**

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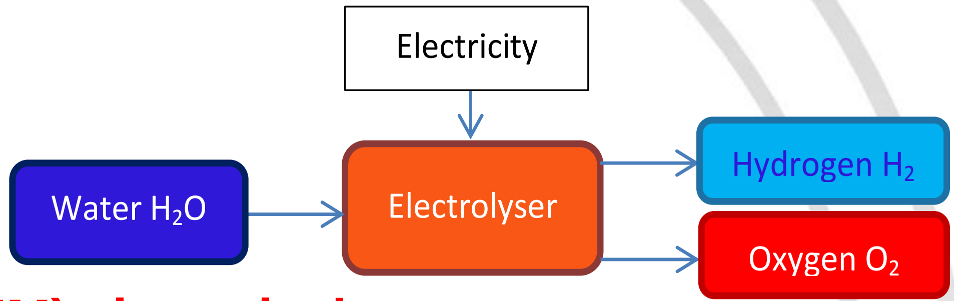
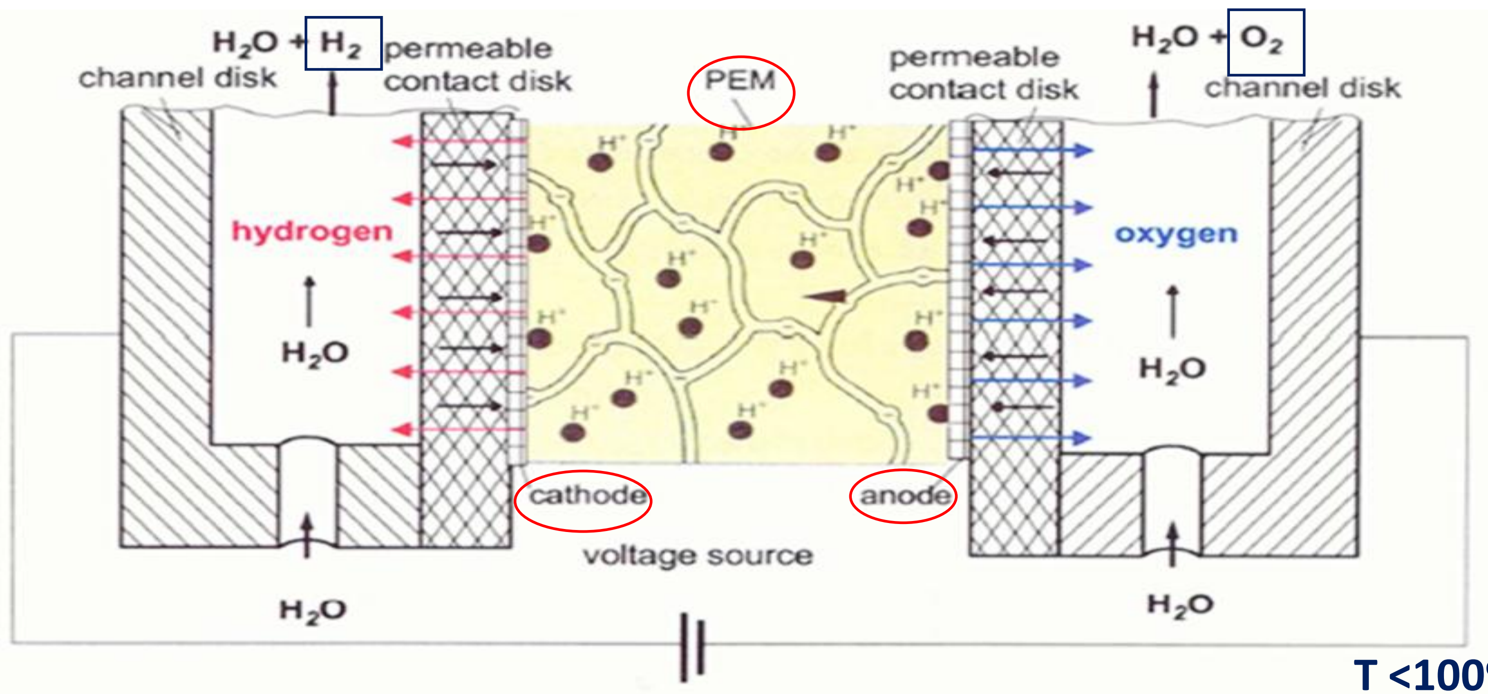
# Water electrolysis (1/2)

Electrical energy converted to chemical energy (as opposed to fuel cell).




## Proton Exchange Membrane (PEM) electrolysis process




T <100°C

cathode:

$4\ H^+ + 4\ e^- \Rightarrow 4\ H_{abs}$

$4\ H_{abs} \Rightarrow 2\ H_2$

anode:

$2\ H_2O \Rightarrow 2\ O_{abs} + 4\ H^+ + 4\ e^-$

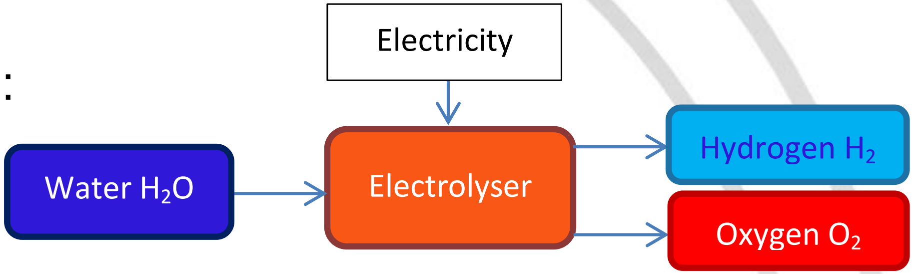
$2\ O_{abs} \Rightarrow O_2$

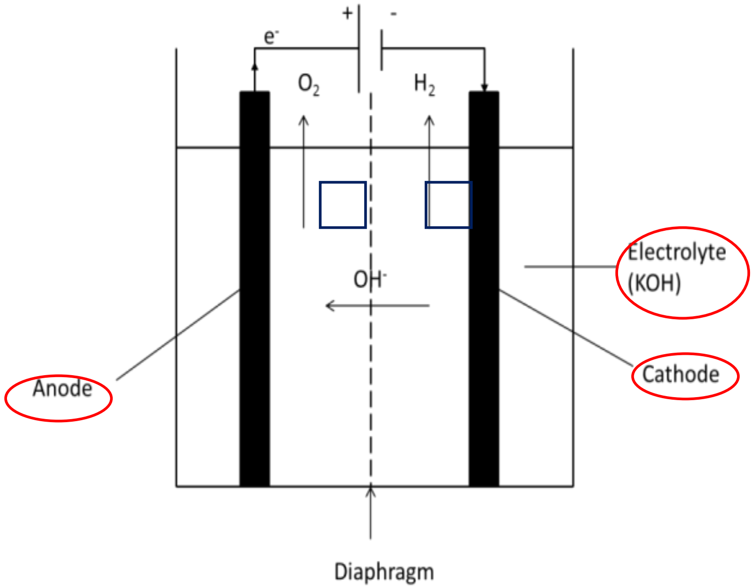
# Water electrolysis (2/2)

The same principle:

Animation: [how electrolysis works](#)

**Alkaline electrolysis process**




- A well-matured technology in industry for hydrogen production
- Two electrodes (**cathode** and **anode**) immersed into **aqueous solution of alkaline electrolyte**, potassium hydroxide **KOH**
- Operating conditions: pressure 1-30 bar; temperature 80-160 ºC
- Commercial electrolysers usually consist of a number of electrolytic cells arranged in a cell stack.

**At the anode (positive electrode):**

$$2\ OH^- \rightarrow \tfrac{1}{2}\ O_2 + H_2O + 2\ e^-$$

**At the cathode (negative electrode):**

$$2\ H_2O + 2\ e^- \rightarrow H_2 + 2\ OH^-$$

**Total reaction:** $H_2O \rightarrow H_2 + \tfrac{1}{2}\ O_2$

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# Comments on electrolysis

- Electrolysers produce very pure hydrogen (could be at pressure more than 1 bar)
- Produced hydrogen can be either utilized immediately or stored for a later use
- Electrolysers capacities range from less than 45 kg/h to more than 1,798 kg/h [1].
- No carbon dioxide ($CO_2$) emissions as opposed to reformers
- Safety concerns:

- **ATEX atmospheres** (i.e. formation of $H_2$-$O_2$ explosive mixtures ) due to a membrane degradation/rupture or due to a failure of water transfer line;
- **fires** either due to hydrogen leaks and/or overheating of high current electrical components;
- a leakage of corrosive electrolyte (for alkaline electrolysis);
- short circuits due to the electrolyte leaks;
- hydrogen leaks within high pressure electrolysers may lead to possible deflagrations

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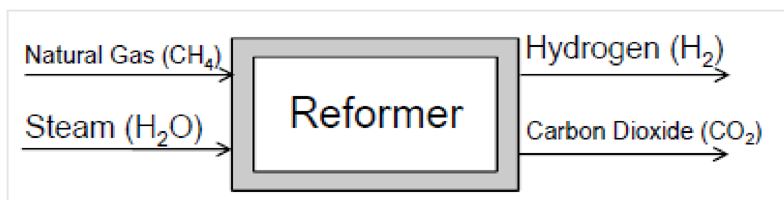
Source: HyFacts (2013). Chapter PD: Safety of applications, including coverage by standards: production and distribution.

# Overview of steam reforming of natural gas

- The **most common way** for hydrogen production
- Endothermic (*i.e.* requires high temperatures) conversion of methane and steam into hydrogen and carbon dioxide $CO_2$
- **Two-stage [process](process) that emits $CO_2$**
- A reformer can be operated on 24/7 basis at a constant load
- The efficiency of the reformer rarely exceeds 80%
- Produced **hydrogen is not pure** (contaminated with $CO/CO_2$) and is at atmospheric pressure.
- To improve sustainability of the process $CO_2$ capture and sequestration are required




T=350-850ºC (heat)
Catalyst (Ni), p=25 bar

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$$

(natural gas) (steam) (syn-gas)

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# Other hydrogen production methods (1/2)

**From water:**

- Nuclear methods (radiolysis; thermolysis)
- Photo-electrolysis (photovoltaic systems coupled with electrolysers)
- Thermo-chemical cycle
- Ferro-silicon method (water, sodium hydroxide and ferrosilicon)
- Photo-biological water splitting (two steps: photosynthesis and H production catalysed by hydrogenases)
- Photo-chemical water splitting
- Biological routes (fermentation; enzymatic; microbiological; and bio-catalytic)

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# Other hydrogen production methods (2/2)

## From fossil fuels:

- Partial oxidation of oil
- Coal gasification
- Plasma reforming (light hydrocarbons heated by plasma to 1600°C and produce hydrogen and carbon, no $CO_2$ emissions)
- Dry reforming (natural gas reformed in the stream $CO_2$)

## From complex metal hydrides [1]:

$NaBH_4 + 4H_2O \rightarrow NaOH + HBO_3 + 5H_2$ (36 wt. %)

Sodium borohydride

$LiBH_4 + 4H_2O \rightarrow LiOH + HBO_3 + 5H_2$ (46 wt. %)

Lithium borohydride

Used for hydrogen production and storage

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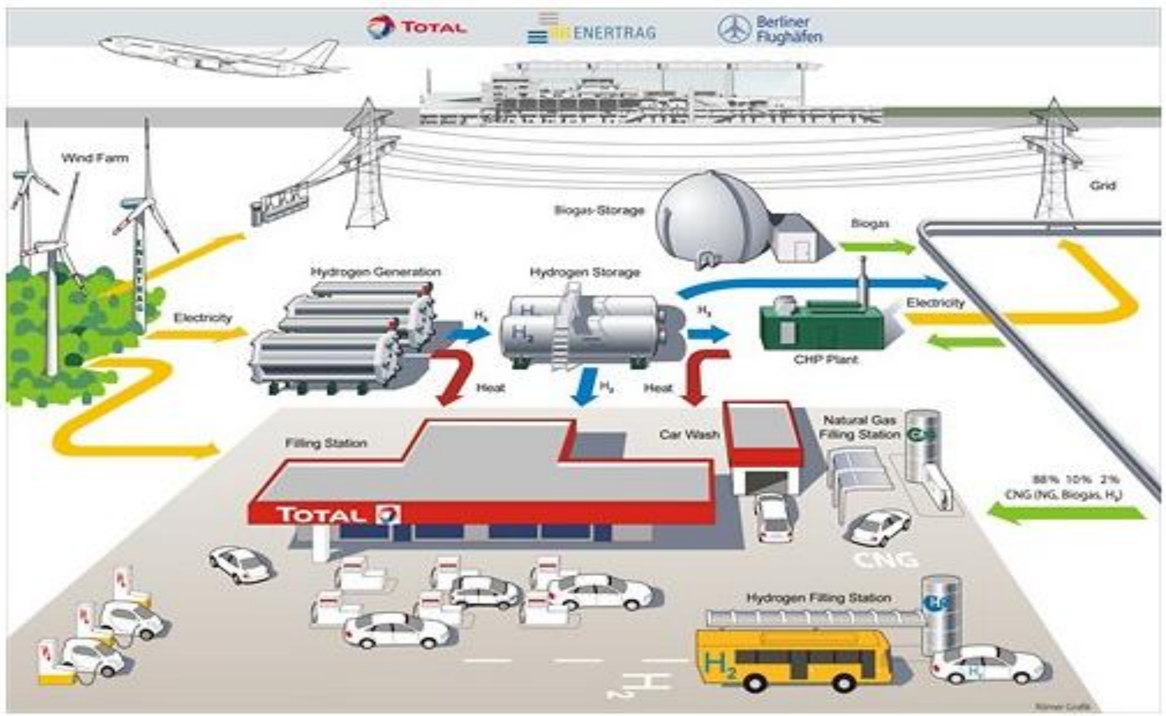
Source: [1] Züttel, A (2003) Materials for hydrogen storage. Materialstoday, Vol. 6, Issue 9, pp. 24-33

# Renewable routes to hydrogen

- Renewable electricity sources: solar panels; wind turbines; tidal energy; hydroelectric energy etc. Currently in place for power-to-gas schemes.
- Production of hydrogen from biomass, methanol, ethanol or landfill gas.
- Biomass conversion (no commercial plants yet).
- Gasification and pyrolysis are the most promising technologies for commercial production of hydrogen from biomass.




Integrated renewables and hydrogen are a reality in Germany. Image: Römer Grafik, from TOTAL Germany website

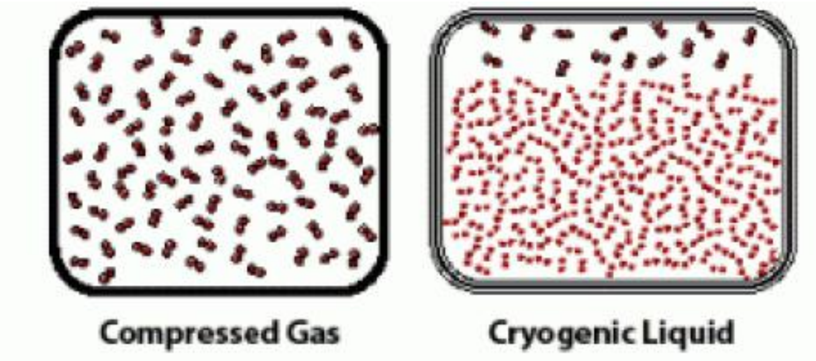
# How hydrogen is stored (1/2)

Hydrogen can be stored as a gas, as a cryogenic liquid or as a cryo-compressed gas

**In tanks:**

**High pressure**
**p=20, 35, 70 MPa**

**Low temperature T**
**<20 K (-253ºC)**





Note: pressure, p.
Units: MPa or Pa, bar.
1MPa =10 bar; 1MPa = $10^6$ Pa

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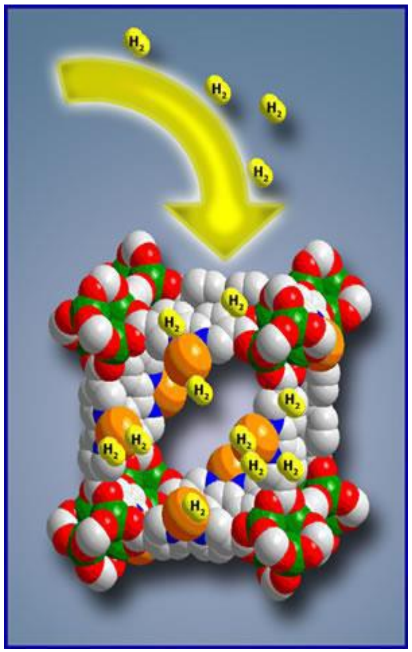
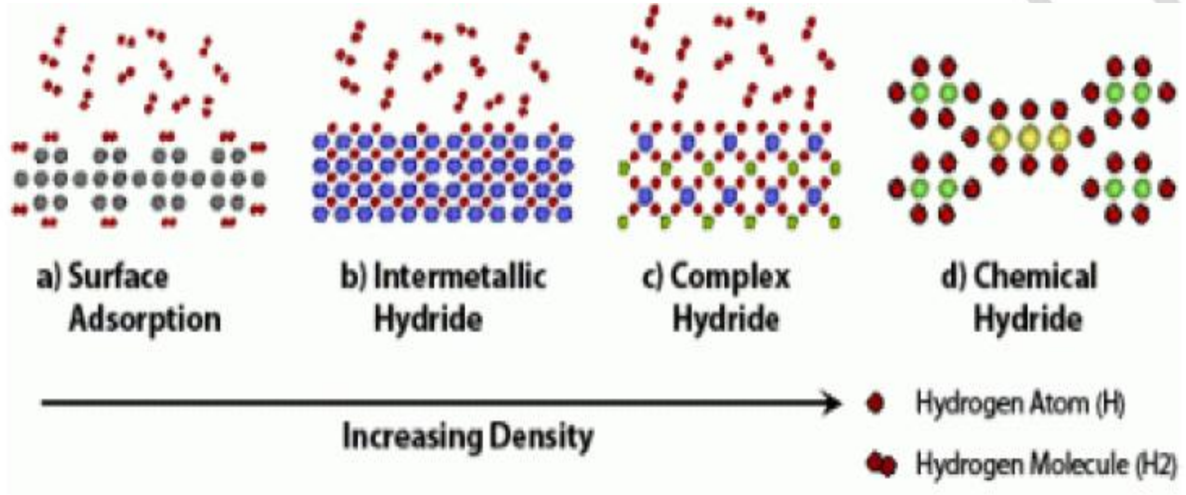
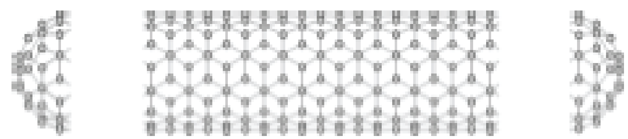
# How hydrogen is stored (2/2)

## In solid materials:





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Source: Tim Mays, H2FC Technical School , 2014

# How hydrogen is distributed: trucks and trailers

## Hydrogen transport by road

Gaseous trucks


Two types of compressed $GH_2$ trailers operated by Air Liquide in Europe: tube trailers carrying between 2,000 to 3,000 $Nm^3$ of $H_2$ and Type II composite cylinder trailers carrying 6,200 $Nm^3$ of $H_2$ (540 kg)

Container with 4 composite tanks developed by Lincoln Composites.
Source: Lincoln Composites

- Single cylinder bottles, multi-cylinder bundles or long cylindrical tubes are installed on trailers.
- Storage pressures range from 200 to 300 bar
- Amount of hydrogen: from 180 to 540 kg

Cryogenic liquid trucks

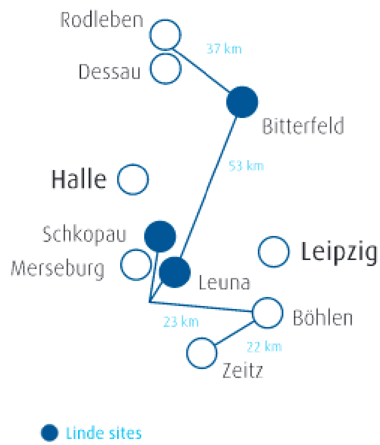
Road tanker operated by Air Liquide for conveying $LH_2$ to user.
Source: Air Liquide Image Bank

# How hydrogen is distributed: pipelines

## Hydrogen transport via pipelines

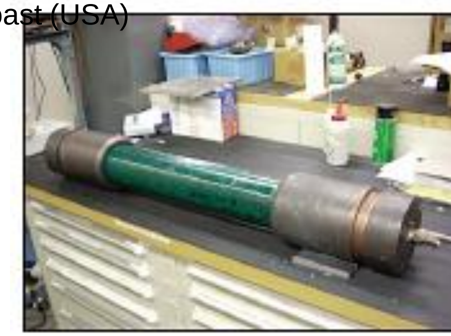
Commercial hydrogen pipelines


Air Liquide hydrogen pipelines in Benelux, France and Germany (Ruhr area); 240 km




Linde hydrogen pipelines in Germany, 100 km

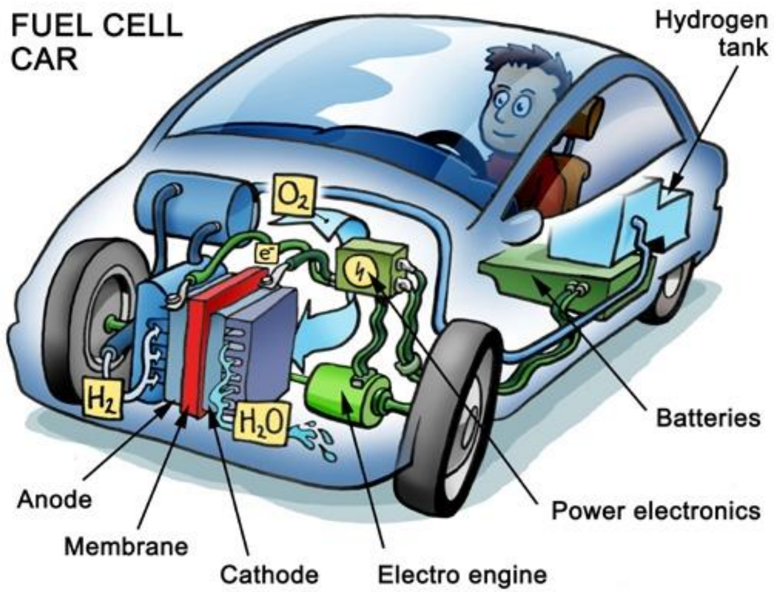

Air Liquide hydrogen pipelines in the Gulf Coast (USA)



Fiber-reinforced polymeric composite pipeline

- The hydrogen network is estimated at around 1,600 km in Europe and 1,100 km in North America
- Major players: Air Liquide, Air Products, Linde and Praxair companies
- Locations: North of Europe (The Netherlands, Northern France and Belgium); Germany (Ruhr and Leipzig areas), and UK (Teesside)
- Operating pressures: between 4-7 MPa; diameter of pipelines: 10 to 300 mm
- Current pipelines are made of steels
- Research for new pipeline materials: polymeric and fiber-reinforced polymers

# FC vehicles

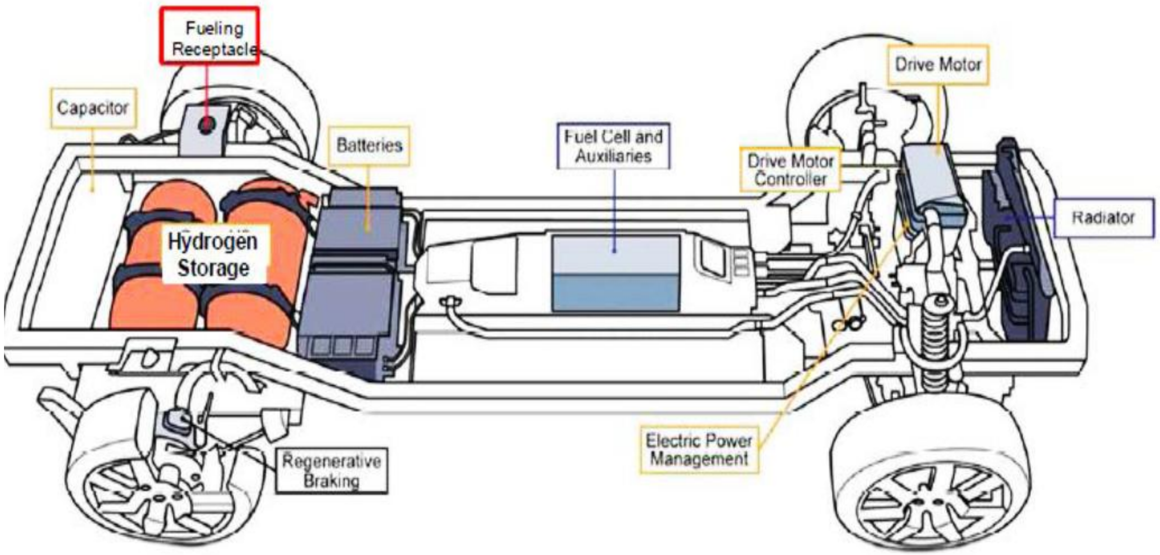




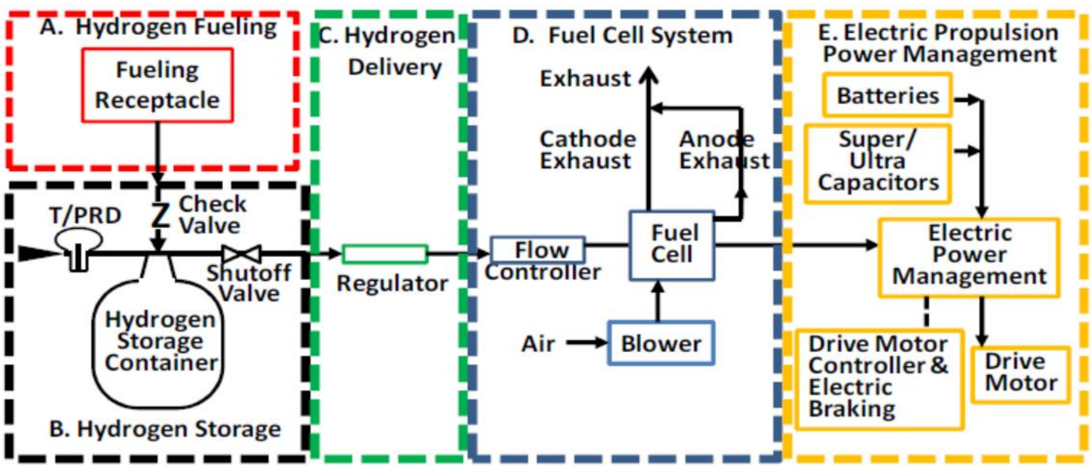


Source: Intelligent Energy

# FC vehicle: key elements




(A) Hydrogen fuelling system
(B) Hydrogen storage system
(C) Hydrogen fuel delivery system
(D) Fuel cell system
(E) Electric propulsion and power management system

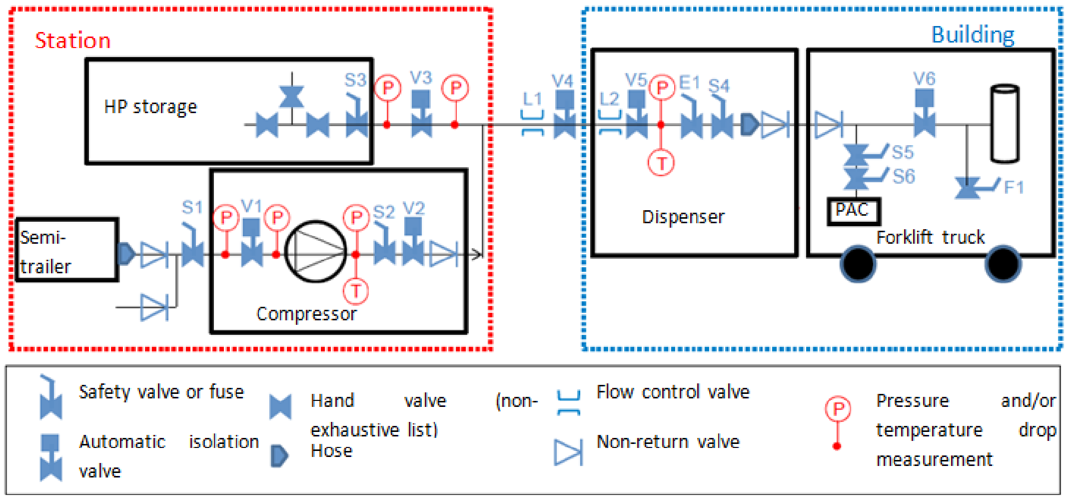



Videos:
How does FC car work?
What is it like to drive an FC car?

Source: GTR, Proposal for a global technical regulation (gtr) on hydrogen fuelled vehicles, 2013

# Hydrogen refuelling stations (1/2)

**Operating principle:**




## Main components:

- Storage
- Compressor
- Dispenser

Semi-trailer: hydrogen stored at p=200 bar.

HP storage: p=450 bar (forklift/bus) or 700 bar (car)

**Average refuelling times:**

Forklift: 3 min

Car: 3 min

Bus: 20 min

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# Hydrogen refuelling stations (2/2)

- 200 stations around the globe (2015)
- Tested in the last 10 years
- Hydrogen either delivered to the station or produced on-site.
- Map of hydrogen refuelling stations is available at: http://www.netinform.net/h2/H2Stations/Default.aspx
- How does it operate?
- SAE TIR J2601 (fuelling protocols)
- **What can go wrong?**

Let's watch the videos: fire at propane refuelling station in S.Korea; other type of accident.

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# Stationary FC applications


FC backup power coupled to the IP energy data center

Back-up power systems (e.g. telecoms market)


FC for residential micro-combined heat and power (CHP) systems

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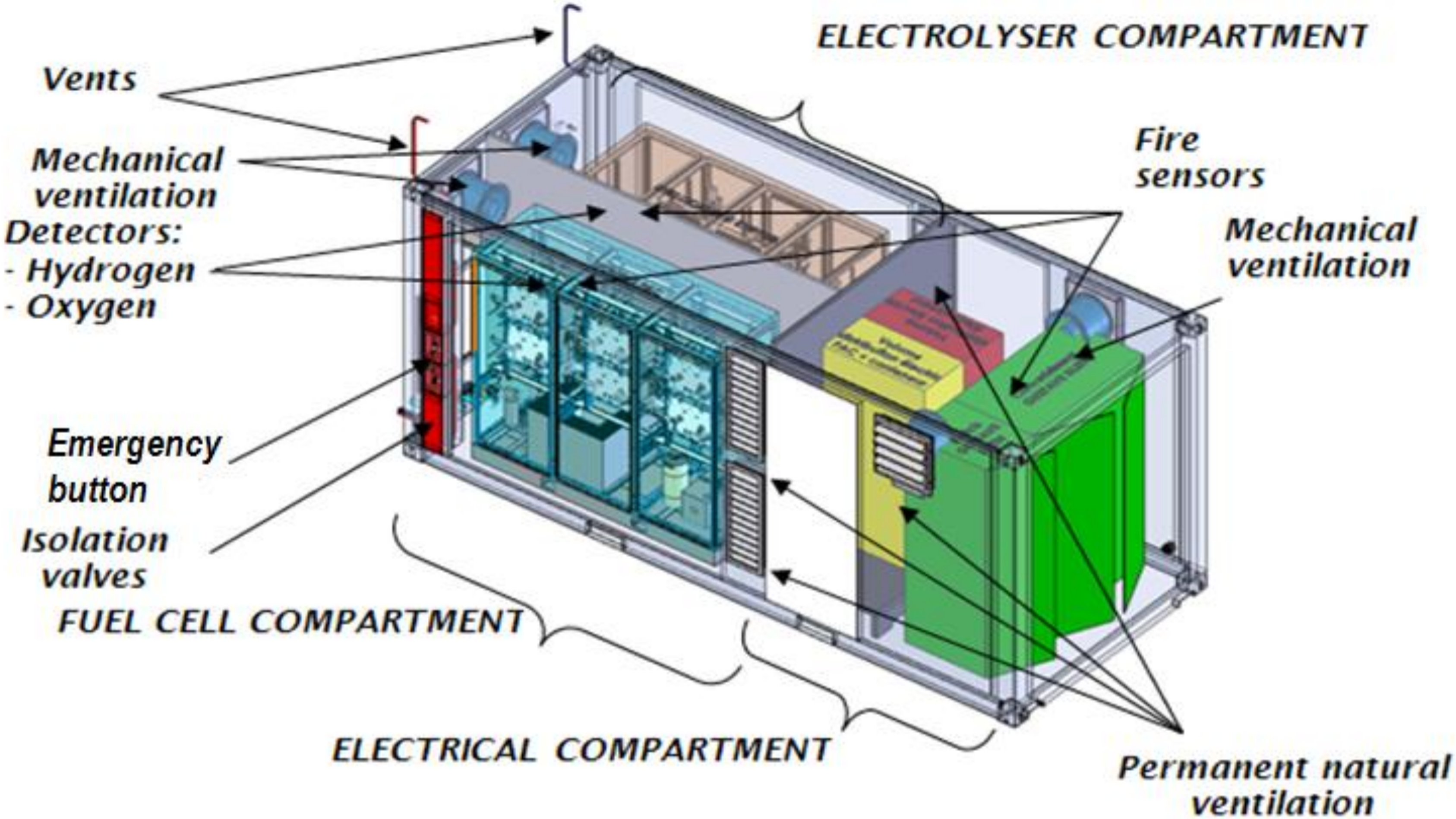
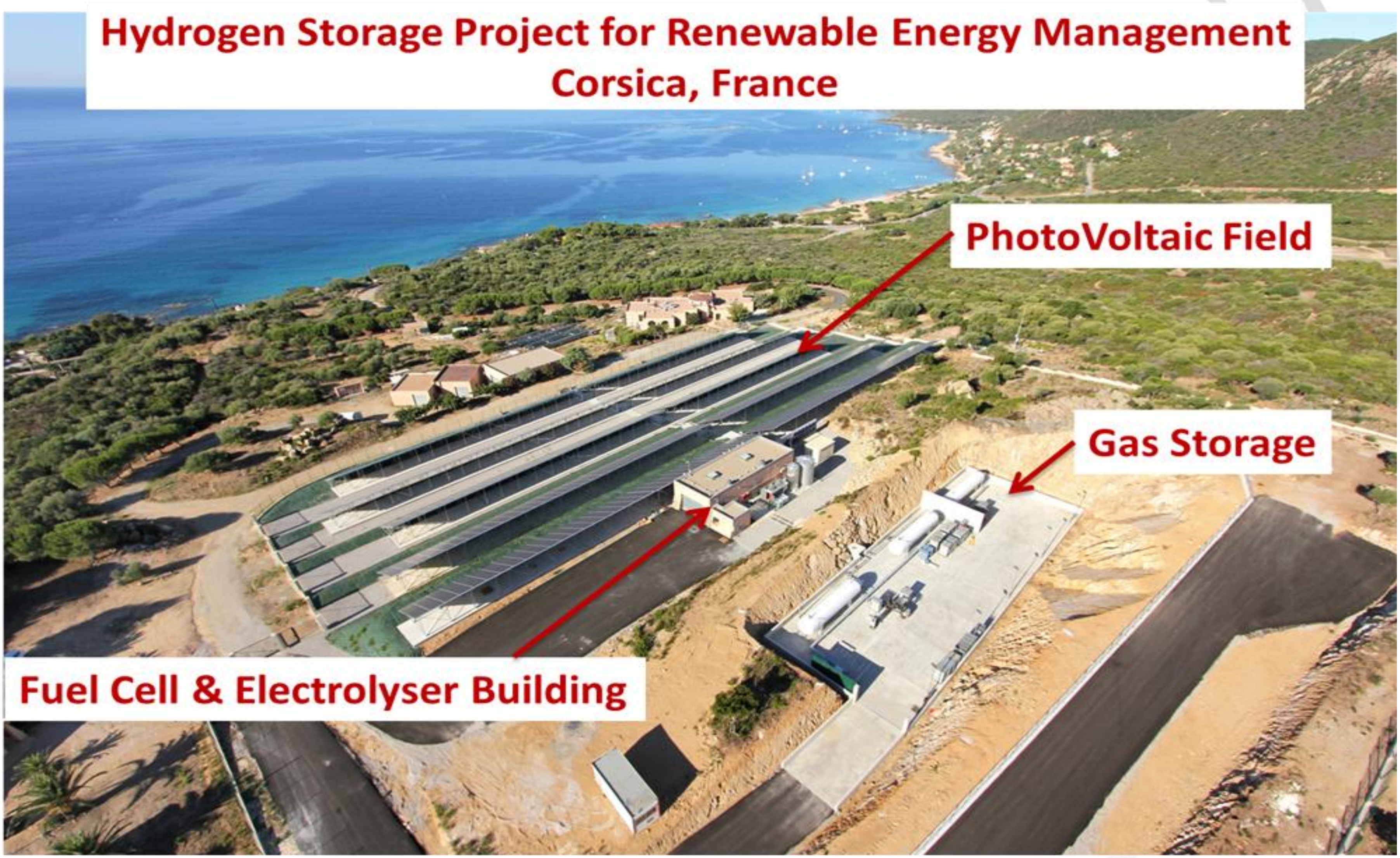
# Hydrogen-based energy storage systems

## Compartments of the Greenenergy Box™



# MYRTE platform



# Hydrogen incidents and accidents: information

Databases of incidents and accidents:

- Hydrogen lessons learnt from incidents to near-misses: http://h2tools.org/lessons/
- Hydrogen Incidents and Accidents Database HIAD database: https://odin.jrc.ec.europa.eu/engineering-databases.jsp
- Incidents on hydrogen releases and their ignition is analysed by Astbury, GR and Hawksworth, SJ (2007)
- Hydrogen tools app

H2 Safety best practices is useful: http://h2bestpractices.org/

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# Incidents and accidents: hydrogen production

- 400 bar electrolyser (Japan):
- Titanium electrolyser before and after the accident

Explosion at the Silver Eagle Refinery, Woods Cross, Utah (US)

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# Incidents and accidents: refuelling stations

- Hydrogen gas release at **Emeryvile fuelling station**: PRD failed; 300 kg of hydrogen released and subsequently ignited. The gas ignited at the exit of the vent pipe and burned for 2.5 hours until technicians were permitted by the local fire department to enter the station and stop the flow of gas. During this incident the fire department evacuated nearby businesses and schools, closed adjacent streets.
- Root-causes:
  - the use of incompatible materials in the manufacturing of the PRD,
  - improper assembly resulting in over-torqueing of the inner assembly,
  - over-hardening of the inner assembly materials by the valve manufacturer.

These problems could have been avoided by adequate quality assurance/quality control procedures during the design and safety reviews.

- Two explosions near Rochester airport (US) at a refuelling station
- Ignition caused by static electricity (not hydrogen!)

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# Main terminology (1/2)

- **Accident:** an unforeseen and unplanned event or circumstance.
- **Hazard**: chemical or physical condition that has the potential for causing damage to people, property and the environment.
- **Consequences:** expected effects from the realisation of the hazard and severity, usually measured in terms of life safety exposure, property damage and environmental impact.
- **Risk:** combination of the probability of an event and its consequence.
- **Deterministic study:** methodology, based on physical relationships derived from scientific theories and empirical results that, for a given set of initial conditions, will always produce the same outcome.
- **Probabilistic study:** systematic development of numerical estimates of the expected frequency and/or consequence of potential accidents.

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# Main terminology (2/2)

- **Trial safety design:** package of hydrogen safety measures which in the context of the system and/or infrastructure *may* meet the specified safety objectives.
- **Acceptance criteria:** term of reference against which the performance of a design is assessed.
- **Scenario:** set of circumstances, chosen as an example, that defines the development of accident.
- **Hazard distance,** as per draft ISO TC197 definition, is a distance from the (source of) hazard to a determined (by physical or numerical modeling, or by a regulation) physical effect value (normally, thermal or pressure) that may lead to a harm condition (ranging from "no harm" to "max harm") to people, equipment or environment. (will be used in later lectures).

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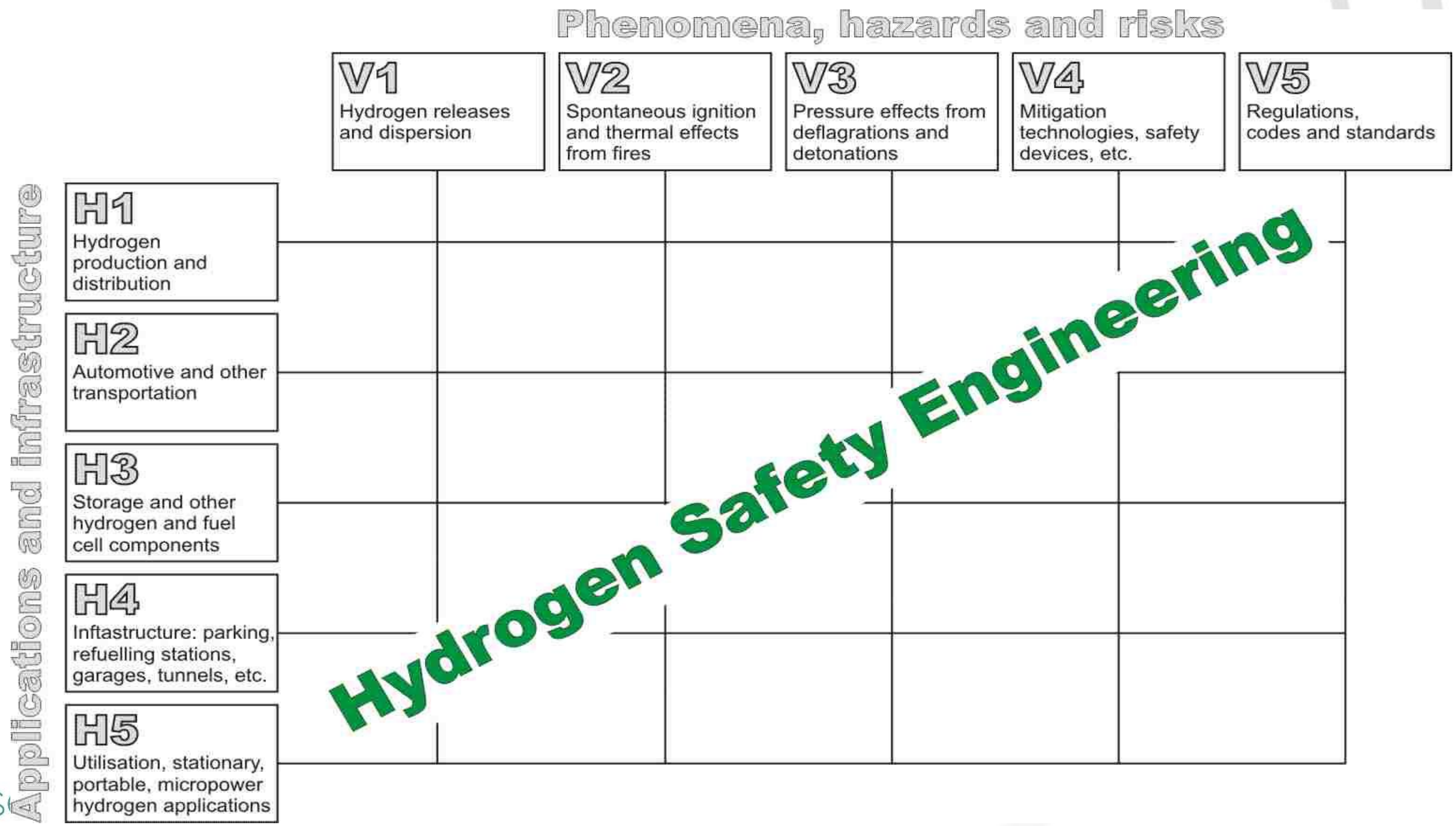
# Hydrogen safety engineering (1/3)

- Hydrogen safety engineering (HSE) is defined as an application of scientific and engineering principles to the protection of life, property and environment from adverse effects of incidents/accidents involving hydrogen (Molkov and Saffers, 2012).
- HSE comprises a design framework and technical sub-systems.

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# Hydrogen safety engineering (2/3)

- The viability and public acceptance of the hydrogen and fuel cell systems depend on their robust safety engineering design, education and training of the workforce (*P* up to 1000 bar and *T* down to -253ºC). This can be provided only through **building up and maturity of the hydrogen safety engineering (HSE) profession**.

- Design for hydrogen safety should be treated as an **engineering responsibility rather than as a matter for detailed regulatory control**; designers should develop a greater understanding of hydrogen safety.

- **Hydrogen safety engineering (HSE)** is the application of **scientific and engineering principles** to the protection of life, property and environment from adverse effects of accidents involving hydrogen.

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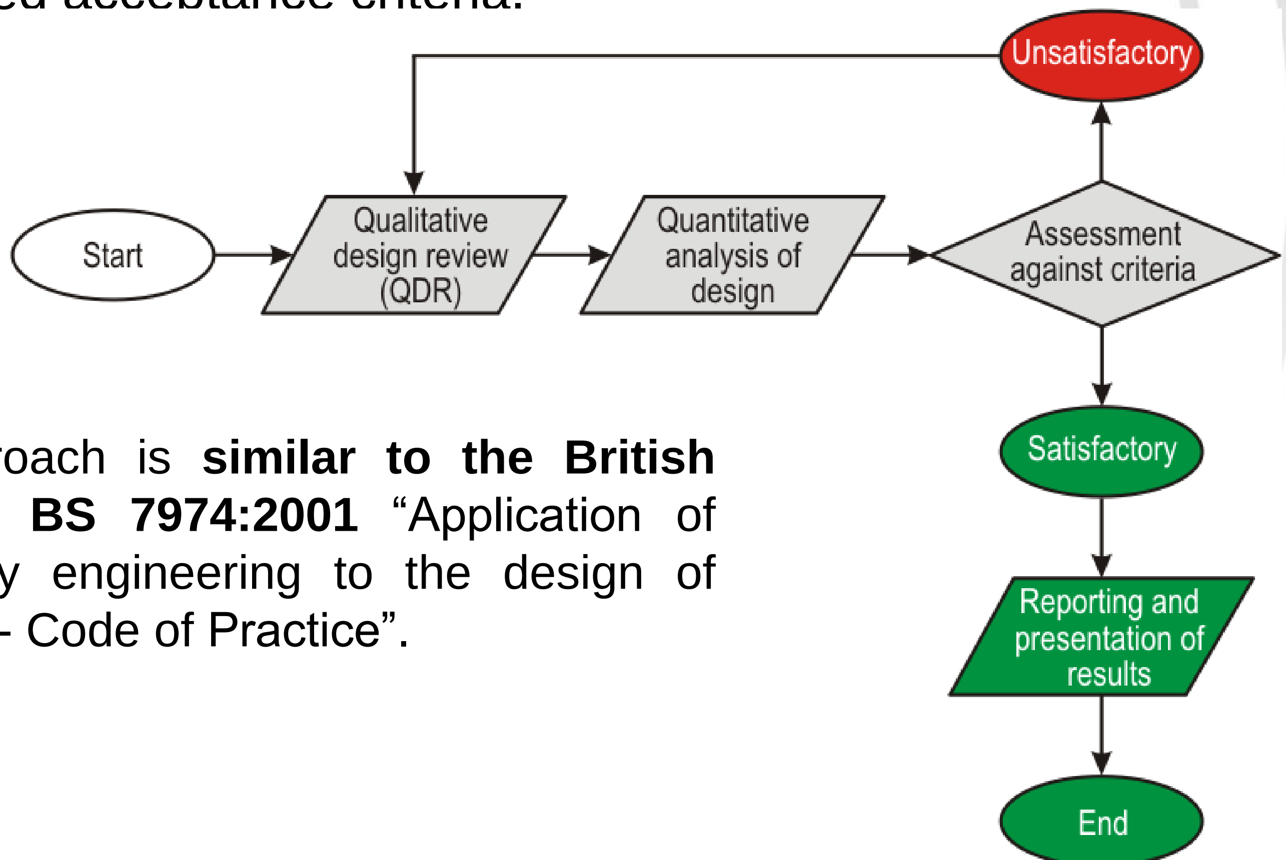
# Hydrogen safety engineering (3/3)

- The HSE process includes three main steps: 1) a qualitative design review; 2) a quantitative safety analysis of selected scenarios and trial designs; 3) the performance of a hydrogen and/or fuel cell system under the trial safety designs is assessed against predefined acceptance criteria.




The approach is **similar to the British standard BS 7974:2001** “Application of fire safety engineering to the design of buildings - Code of Practice”.

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# Main stages of HSE process

- **Qualitative design review (QDR).** A QDR team (see later) carries out: review of design; definition of safety objectives; analysis of hazards and consequences; establishment of ***trial safety designs***; definition of ***acceptance criteria***, ***scenarios*** to study. Key information is compiled to evaluate trial design in the quantitative analysis.
- **Quantitative analysis.** Engineering methods and tools are used to ***evaluate the trial safety designs*** identified in QDR following scenario(s). Quantitative analysis can be time-based analysis using appropriate sub-system guidelines to give numerical values of the impact of accident on people, property and environment.
- **Assessment against acceptance criteria.** The output of the quantitative analysis is ***compared against the acceptance criteria*** identified in QDR. If the safety performance of a hydrogen system does not match acceptance criteria, the design is unsatisfactory and the objectives are not fulfilled it is necessary to restart a new study from QDR stage.

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# Technical sub-systems and guides

To simplify the evaluation of hydrogen safety design, the process is broken down into Technical Sub-Systems (TSS):

- TSS1: Initiation of release and dispersion.
- TSS2: Ignitions.
- TSS3: Deflagrations, detonations, blast waves.
- TSS4: Fires.
- TSS5: Impact on people, structures and environment.
- TSS6: Mitigation techniques.
- TSS7: Emergency service intervention.
- Plus “*Guide to* design framework and hydrogen safety engineering procedures”.
- Plus “*Guide on* probabilistic hydrogen risk assessment”.

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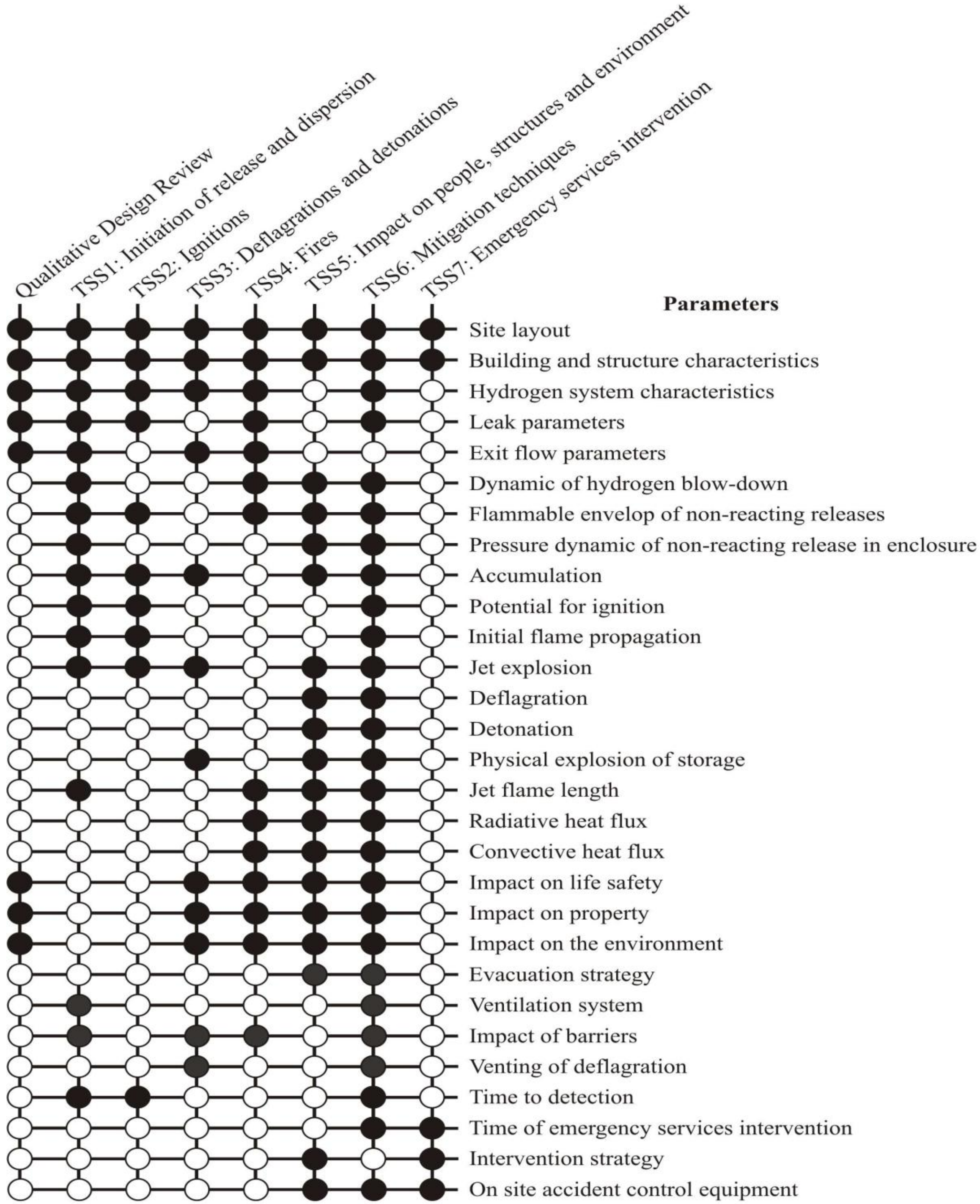
# Example of TSS interaction




Source: Saffers, J-B and Molkov, V (2014). Hydrogen safety engineering framework and elementary safety design tools. International Journal of Hydrogen Energy. Vol. 39, pp. 6268-6285.

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# HSE: reporting

**The report on HSE could contain the following:**

- Objectives of the study;
- Full description of the HFC system/infrastructure;
- Results of the QDR;
- Quantitative analysis:
  - 1) Assumptions;
  - 2) Engineering judgments;
  - 3) Calculation procedures;
  - 4) Validation of methodologies;
  - 5) Sensitivity analysis;
- Assessment of analysis results against criteria;
- Conclusions:
  - 1) Hydrogen safety strategy;
  - 2) Management requirements;
  - 3) Any limitations on use;
- References, e.g. drawings, design documentation, technical literature, etc.

# Hydrogen safety engineering: benefits

- Provides an engineer with a disciplined approach to hydrogen safety design.
- Allows safety levels for alternative designs to be compared.
- Provides a basis for selection of the most appropriate hydrogen safety systems.
- Provides opportunities for innovative design, including new engineering tools (not yet in RCS).
- Provides information on the management of hydrogen safety.

Source: Molkov, V (2012). Fundamentals of hydrogen safety engineering, Part I and Part II. Available from: www.bookboon.com, free download e-book.

# References


- Molkov, V (2012). Fundamentals of hydrogen safety engineering, Part I and Part II. Available from: www.bookboon.com, free download e-book.
- Rigas, F and Amyotte, P (2013). Hydrogen safety. Boca Raton: CRC press. Taylor and Francis Group.
- Bain, A and Van Vorst, WD (1999). The Hindenburg tragedy revisited: the fatal flaw found, International Journal of Hydrogen Energy. Vol. 24, pp. 399–403.
- The Fuel Cell Industry Review (2012). Available from: http://www.fuelcelltoday.com/media/1713685/fct_review_2012.pdf [accessed on 29.04.14].
- Sorensen, B. Hydrogen and Fuel Cells (2005). Emerging technologies and applications, Elsevier.
- FCTO, Fuel Cell Technologies Office (2014). Available from: http://energy.gov/eere/fuelcells/fuel-cell-technologies-office [accessed on 01.05.14].
- GTR, Proposal for a global technical regulation (gtr) on hydrogen fuelled vehicles, 2013. ECE/TRANS/WP.29/GRSP/2013/41. United Nations. Economic Commission for Europe. Inland Transport Committee. World Forum for Harmonization of Vehicle Regulations, 160th Session, Geneva, 25-28 June 2013.
- US DoE, US Department of Energy (2008). Hydrogen safety training for first responders. Available from: http://hydrogen.pnl.gov/FirstResponders/ [accessed on 13.05.14].
- CEP, Clean Energy Partnership, 2014. Available from: http://www.cleanenergypartnership.de/tech/site.php?l=en [accessed on 01.05.14].
- California Fuel Cells Partnership, 2014. Available from: http://cafcp.org/ [accessed on 01.05.14].
- Adams, P (2004). Identification of the optimum on-board storage pressure for gaseous hydrogen city buses. European Integrated Hydrogen project – Phase 2 (EIHP2), March 2004.
- Millet, P, Ranjbari, A, de Guglielmo, F, Grigoriev, SA and Etiévant, C (2011). Cell failure mechanism in PEM water electrolyzers. Proceedings of the Fourth International Conference on Hydrogen Safety, paper ID 254, 12-14 September 2011, San Francisco, USA.
- Saffers, J-B and Molkov, V (2014). Hydrogen safety engineering framework and elementary design safety tools. International Journal of Hydrogen Energy, 39 (11). pp. 6268-6285.
- BRHS, Biennial Report on Hydrogen Safety (2009). The European network of excellence "Safety of hydrogen as an energy carrier" (NoE HySafe). Available from: www.hysafe.org [accessed on 13.05.14].