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# Hydrogen Safety in Energy Infrastructure: A Review

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Posted Date: 15 September 2025

doi: 10.20944/preprints202509.1231.v1

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Remiero

# Hydrogen Safety in Energy Infrastructure: A Review

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# **Highlights:**

- Detailed overview of the effects on hydrogen permeation in metallic and polymer materials that influence the mechanical properties of materials
- More than ten standards are cited in addition to scientific studies, and important organizations, such as training materials for firefighters from HyResponder, TÜV SÜD, and EIGA
- Mentioned knowledge about hydrogen, hydrogen transport, compatibility materials with hydrogen, and hydrogen leakage
- Discussion of current hydrogen topics, including hydrogen blending in natural gas, hydrogen refueling stations, hydrogen fuel cells, hydrogen permeation in nuclear fusion reactors, and hydrogen-fueled gas turbines
- Safety measures are described to prevent hydrogen leakage, reduce pipeline lifetime, and mitigate the threat to human health
- Hydrogen applications in the Czech Republic and future challenges are provided

#### **Abstract**

For the transition to emission-free or low-emission energy, hydrogen is a promising energy carrier and fuel of the future with the possibility of long-term storage. Due to its specific properties, it poses certain safety risks; therefore, it is necessary to have a comprehensive understanding of hydrogen. This review article contains ten main chapters and provides, by synthesizing current findings primarily from standards and scientific studies (predominantly from 2023–2024), the theoretical basis for further research directed toward safe hydrogen infrastructure.

Keywords: hydrogen; permeability; hydrogen embrittlement; safety

#### 1. Introduction

Hydrogen, a promising fuel of the future, is a key energy carrier that contributes to energy decarbonization and self-sufficiency. Therefore, it is the optimal choice to meet the goals of the Green Deal, part of which is to achieve carbon neutrality by 2050 [1–3]. The great advantage of hydrogen is its high energy density and cleanliness (no CO<sub>2</sub> emissions are produced when it is burned [4]), so it is a suitable alternative to fossil fuels such as natural gas [5].

Despite these advantages, hydrogen has specific properties such as very low density, the tendency to diffuse into materials [6], and a wide range of flammability, which requires certain safety and technical measures for (expanding) hydrogen infrastructure [7]. The main challenges for the introduction of hydrogen into the current infrastructure are the change of mechanical properties of materials exposed to hydrogen [8] and hydrogen leakage [9]. For the safety of hydrogen technologies, risk assessment is essential [10,11].

Hydrogen can be used in various industrial sectors – in energy (for power generation, energy storage, and heating [11,12]), transport (fuel cells [13,14]), chemical and petrochemical industries (petroleum refining, ammonia production) food industry, metallurgy (steel production [11]), and others [15,16].

The expansion of hydrogen infrastructure (pipelines, refueling stations, combustion equipment) requires a comprehensive understanding of hydrogen behavior in a range of technical applications. This review article contains theoretical knowledge predominantly from standards, which are complemented by findings from scientific studies (predominantly from 2023–2024). The article mainly discusses the diffusion of hydrogen in materials and its associated problems (hydrogen embrittlement, hydrogen leakage) and safety measures. The article also discusses current hydrogen topics, such as hydrogen blending into existing natural gas pipelines, hydrogen refueling stations, hydrogen fuel cells, hydrogen permeation in nuclear fusion reactors, hydrogen-fueled gas turbines, and hydrogen leakages. These themes support the decarbonization of the energy sector.

By consolidating fragmented knowledge, this article provides a theoretical foundation for further progress in the field of safe implementation of sustainable hydrogen technologies in infrastructure for hydrogen production, storage, distribution, and combustion. The topic of hydrogen is very broad, and this review provides a summary of information on hydrogen, supported by relevant sources, providing support even for non-expert readers. While metals and polymers have been reviewed separately in the past, to our knowledge, this is among the first reviews to integrate both metals and polymers while also incorporating insights from relevant standards and providing practical recommendations. This work brings together the technical, material, and safety dimensions of hydrogen applications in one review.

# 2. Theoretical Foundation

#### 2.1. Physical and Chemical Properties of Hydrogen

Hydrogen is the lightest of all gases [4]; its density is only 0.081 kg/m³ at 1 bar and 25 °C [17], which is 14 times less than the density of air [18]. Thanks to this property, it has a high buoyancy [4], which causes the released hydrogen in the air to rapidly spread and rise upwards [18]. It reduces the risk of creating dangerous concentrations in open spaces that could cause an explosion [4].

The hydrogen is highly flammable (easily ignites) [19]. The minimum ignition energy (MIE) [20] to ignite a mixture of hydrogen and air is only 0.017 mJ [18], which means that, for example, an electrostatic discharge or a hot surface (> 585 °C [20]) is sufficient to ignite it [19,20]. Therefore, electrostatic protection (grounding) and the elimination of surface temperatures close to the self-ignition temperature of the hydrogen are necessary [20]. The mixture of hydrogen with air is explosive in the concentration range of 4–77 % obj. [19]. The self-ignition temperature of the mixture of hydrogen with air can occur at temperatures between 500 [21] and 560 °C [19]. Hydrogen also has the highest heating value (calorific value) of all fuels, approximately 120 MJ/kg [22].

The hydrogen exhibits, compared to other gases, an inverse Joule-Thomson effect, which means that when it expands (from a higher pressure to a lower one), its temperature increases [19,21]. The low ignition energy and increasing temperature of hydrogen during expansion are the reasons why auto-ignition of leaks and atmospheric vents is very likely [21].

Hydrogen burns in the air with a nearly unseen pale blue flame [21], partly due to its low emissivity (very little infrared radiation) [19]. Besides, it is odorless and tasteless, so it is hardly detectable by human senses and therefore poses a potential risk of personal injury [18]. The maximum velocity of flames spread in the air is up to 3 m/s [21].

For handling hydrogen, personal protective equipment is necessary due to the risk of hydrogen combustion (flame temperature, thermal radiation), and explosions (overpressure [23]) [24]. Liquid hydrogen, due to cryogenic temperatures, causes burns (e.g., by frostbite) and can cause solidification of atmospheric oxygen, which can lead to an explosion [25]. Hydrogen does not support respiration [21], and higher concentrations of hydrogen in a confined space cause asphyxiation [24].

#### 2.2. Hydrogen Production

#### 2.2.1. Production Methods

Gaseous hydrogen can be produced from fossil sources by reforming fossil fuels (natural gas, methanol [26]) or other hydrocarbons [27]. Among the common methods is natural gas reforming, specifically steam methane reforming (SMR) [28]. This method produces grey hydrogen, and in the case of CO<sub>2</sub> capture from the flue gas (e.g., by carbon capture and storage – CCS or carbon capture and utilization –CCU [29]), blue hydrogen can be produced [30,31]. Another method can be coal gasification, which produces brown hydrogen [29,32]. Green hydrogen can be produced from renewable sources via an electrolyzer (renewable fuels of non-biological origin – RFNBO [33], power to gas – P2G [34]), and pink hydrogen can be produced from nuclear energy [35]. There is also turquoise hydrogen, which is produced by the pyrolysis of methane and, in conjunction with renewable sources, is CO<sub>2</sub> neutral [36]. Biological methods [27] have a potential for sustainable hydrogen production, for example, via water biophotolysis using microalgae [37] or via biological fermentation [38].

#### 2.2.2. Electrolyzers

For hydrogen production, water electrolyzers are commonly used, which use electricity to electrochemically split water into hydrogen and oxygen [39]. In an electrolyzer, two electrodes (anode and cathode) are immersed in or in contact with the electrolyte, depending on the type of electrolyzer [39,40]. Generally, water oxidation occurs at the anode, releasing oxygen and producing ions, depending on the type of electrolyzer [39]. At the cathode, the reduction of these ions occurs, which produces molecular hydrogen [39]. Common electrolyzers include alkaline (AEL), Proton Exchange Membrane, or Polymer-electrolyte membrane (PEM), Anion Exchange Membrane (AEM), and Solid Oxide Electrolyzer cell (SOEC) [40,41].

The advantage of AEM electrolyzers is that the catalysts are made of non-noble materials [42]. Whereas PEM electrolyzers have electrolyzers made of expensive noble metals (platinum or iridium) [43]. However, the advantage of PEM electrolyzers is their suitability in combination with variable renewable energy sources (solar and wind energy) [44]. A "fast hydrogen electrolyzer" developed by researchers from the Czech Republic is moving toward practical application [45]. In combination with renewable sources, it will provide grid stabilization [45]. Respectively, electrolyzers can use surplus electricity from renewable sources, which leads to grid stabilization [46]. Electrolyzers SOEC are a promising technology, but require high temperatures of 500–1000 °C for their operation [47]. In coupling the SOEC electrolyzer with the nuclear power plant, the electrical energy and thermal energy from the process steam of the nuclear reactors are used to operate the electrolyzer, thus ensuring the high efficiency of the electrolyzer [47,48].

#### 2.3. Hydrogen Storage and Distribution

Hydrogen can be stored in gaseous (compressed), liquefied, or solid form (in solid materials) [27,49]. Gaseous hydrogen can be stored in pressure cylinders/tanks (20–100 MPa) [4]. Liquid hydrogen (LH<sub>2</sub>) is stored at cryogenic temperatures (–253 °C) [49] and ordinarily saturated vapor pressure of 4 bar [19]. Hydrogen can also be stored in metal hydrides or nanostructured materials (Metal-organic frameworks – MOFs, carbon materials) [50]. Hydrogen can also be stored underground in salt caverns [51].

Hydrogen can be distributed by gaseous hydrogen suppliers (e.g., in high-pressure cylinders, tube trailers, or bundles), liquid hydrogen suppliers (e.g., in tanker trucks), or through pipeline distribution systems for gaseous hydrogen [27]. Hydrogen can also be transported in the form of ammonia or liquid organic hydrogen carriers (LOHC) [52,53]. For long-distance hydrogen transport, pipelines are the most economically effective [54].

# 3. Hydrogen Transport

#### 3.1. Hydrogen Transport Mechanism in Metal Materials

Hydrogen atoms are very small and can easily be absorbed into various materials [6,55]. Hydrogen transport within a material is described by three main quantities – solubility, diffusivity, and permeability [56]. According to Sievert's law, higher hydrogen partial pressure increases the hydrogen concentration (or the hydrogen solubility) in the metal [6,57]. Generally, temperature increases lead to higher hydrogen mobility of dissolved hydrogen [57] and higher hydrogen solubility [58].

Hydrogen diffusivity in metals includes interstitial diffusion and quantum mechanical tunnel diffusion [6,59]. Hydrogen atoms move through interstitial sites – octahedral or tetrahedral, depending on the type of crystal structures (FCC, HCP, BCC) [6]. Higher hydrogen mobility is in metals with a bcc crystal lattice [6,59]. Permeability of hydrogen is the process of hydrogen transport, by which the hydrogen permeates through materials [60]. The mentioned main hydrogen transport quantities are interconnected by this equation [56].

$$P = SD \tag{1}$$

where P is the permeability coefficient, cm<sup>3</sup>·cm/(cm<sup>2</sup>·s·MPa); S is the solubility coefficient, cm<sup>3</sup>/(cm<sup>3</sup>·MPa) and D is the diffusion coefficient, cm<sup>2</sup>/s [56].

These mentioned quantities are dependent on experimental conditions (e.g., temperature and pressure) and material type and can be expressed by Arrhenius law [56]:

$$S = S_0 \times \exp\left(-\frac{\Delta H_s}{RT}\right) \tag{2}$$

$$D = D_0 \times \exp\left(-\frac{E_d}{RT}\right) \tag{3}$$

$$P = P_0 \times \exp\left(-\frac{E_p}{RT}\right) \tag{4}$$

Fick's first law applies to steady-state conditions and states that the diffusive flux (J) of hydrogen through a material is proportional to the hydrogen concentration gradient [61].

$$J = -D\frac{\partial c}{\partial x} \tag{5}$$

The second Fick's law applies to unsteady-state conditions and expresses the change in concentration gradient over time during diffusion [61].

$$\frac{\partial}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \tag{6}$$

Apart from the processes that occur inside materials, we distinguish other processes occurring outside the material. The overall hydrogen transport is as follows: The hydrogen molecule is adsorbed on the surface of the steel, and in the case of chemical adsorption (chemisorption), the H<sub>2</sub> molecule dissociates into hydrogen atoms, which subsequently diffuse into the subsurface layer of the steel, where they become absorbed hydrogen atoms, which subsequently diffuse into the interior of the steel [50,62]. On the opposite side of the material, hydrogen atoms can recombine to form H<sub>2</sub> hydrogen molecules and subsequently desorb from the surface, see Figure 1 [63].

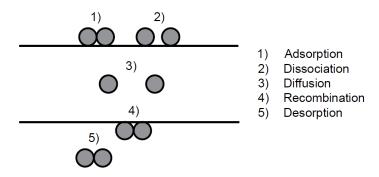


Figure 1. Hydrogen transport mechanisms through metal (Redrawn) [63].

Table 1 shows the values of the diffusion coefficients of hydrogen or deuterium for different metal materials. The diffusion coefficients, which are functions of the gas constant and temperature, are for comparison converted to values where R is 8.314 J·K<sup>-1</sup>·mol<sup>-1</sup> and T is 20 °C. For comparison, it is necessary to distinguish the type of diffusion coefficient and gas (hydrogen or deuterium). For clarity, the authors of this study plan to publish the original database of diffusion, solubility, and permeability coefficients for various types of materials, numbering more than 50.

**Table 1.** Diffusion coefficients of different metal materials.

Material	Gas	Diffusion coefficient [m²/s]	Permeability coefficient [mol m <sup>-1</sup> s <sup>-1</sup> Pa <sup>-0.5</sup> ]	Туре
X52 high-strength, low-alloy steel [64]	Hydrogen	~1.20–1.70 × 10 <sup>-9</sup> (for layers of different hardness)		Effective
Cantor HEA – CoCrFeMnNi [65]	Hydrogen	1.81 × 10 <sup>-11</sup>		Effective
316L stainless steel [65]	Hydrogen	1.31 × 10 <sup>-11</sup>		Effective
316L stainless steel [67]	Hydrogen	$f(R,T) = 1.89 \times 10^{-12}$	$f(R,T) = 2.78 \times 10^{-21}$	Lattice
Eurofer 97 – 9CrWVTa [68]	Hydrogen	$f(R,T) = 4.86 \times 10^{-7}$	$f(R,T) = 2.23 \times 10^{-11}$	Lattice
Martensitic steel – CLAM [69]	Deuterium	$f(R,T) = 2.02 \times 10^{-11}$	$f(R,T) = 2.47 \times 10^{-16}$	Lattice
Martensitic steel – CLF-1 [69]	Deuterium	$f(R,T) = 9.94 \times 10^{-11}$	$f(R,T) = 2.65 \times 10^{-16}$	Lattice
9Cr–1MoVNbN high- strength [66]	Hydrogen	$f(T) = 4.08 \times 10^{-11}$		Apparent

A comparison of effective diffusion coefficients shows that 316L stainless steel has the lowest diffusion coefficient value. X52 high-strength, low-alloy steel is more suitable for lower pressures. Eurofer 97 – 9CrWVTa compared to 316L stainless steel, has very high permeability. Martensitic steels – CLAM and CLF-1 have similar values, and it should be noted that they were tested with deuterium, not hydrogen.

### 3.2. Hydrogen Transport Mechanism in Polymer Materials (PE)

In amorphous polyethylene (PE) material, as well as in metallic materials, the solubility of hydrogen increases with increasing temperature [56]. But not based on Sieverts' law, as in metallic materials, but based on "reverse solubility", where the increase in temperature increases the free volume inside the polymer [56].

Hydrogen transport (hydrogen permeation) in PE materials occurs based on the principle of "dissolution-diffusion" [56]. Hydrogen molecules are not dissociated into atomic hydrogen on the surface of PE as they are in metallic materials [55]. Hydrogen molecules at first are dissolved in the polymer, subsequently, they diffuse in the polymer, and finally, they are desorbed from the surface on the opposite side [70], see Figure 2.

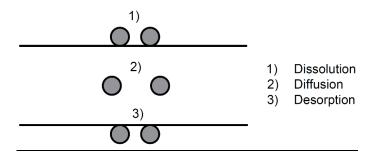


Figure 2. Hydrogen transport mechanisms through polymer (Redrawn) [56].

Zheng et al. [56] found that hydrogen diffusion in PE occurs according to the "hopping" mechanism, where hydrogen molecules vibrate in the pores of the free volume and subsequently rapidly jump into adjacent pores, which gradually moves them away from their original position until they finally permeate the material.

#### 3.3. Hydrogen Sources in Metal and Polymer

There are three sources of hydrogen, which are contained in metals [71,72]. The first source of hydrogen in steel is hydrogen that occurred during steel production (e.g. pickling, smelting, welding, electrochemical processes, such as electroplating, cathodic protection, and corrosion [71,73,74]) (it is called "internal hydrogen" if it occurs in the steel before its use) [71]. The second source of hydrogen in steel is hydrogen originating from the operating environment, containing hydrogen gas, of which the hydrogen atoms are absorbed into the steel [71]. The third source is hydrogen contained in the liquid phase [71]. In the case that the corrosion potential is lower than the hydrogen evolution line, hydrogen atoms are formed on the steel surface, which are adsorbed to the surface and subsequently permeate into the internal structure of the steel [71].

In polymer pipelines, hydrogen is contained only in the gas phase. Due to the amorphous or semi-crystalline structure of polymers, which do not contain the crystal lattice typical for metals, internal hydrogen is not considered during production. Also, corrosion does not take place in these materials, and therefore, hydrogen from the liquid phase is not a source.

#### 3.4. Hydrogen Traps and Types of Hydrogen

Hydrogen atoms in metals (steels) gather in hydrogen traps respectively in microstructural defects such as dislocations (crystal lattice defects), grain boundary layers, precipitates (e.g. carbonitrides [75]), non-metallic inclusions [75] (oxides, sulfides or silicates [75,76]), vacancies or interstitial sites [75,77], see Figure 3.

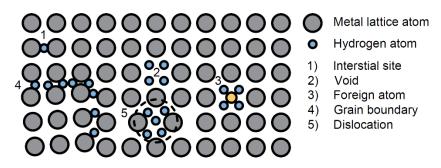


Figure 3. Hydrogen traps in the metal structure (Redrawn) [59,78].

In steel, hydrogen can occur in two forms, such as mobile and immobile [77]. Mobile hydrogen is kept in reversible (shallow) traps and can move freely; respectively, hydrogen is kept temporarily [77], e.g., in dislocations or in interstitial sites [75]. Immobile hydrogen is trapped in irreversible (deep [73]) traps, respectively, hydrogen is kept permanently [75], for example, in vacancies, precipitates,

and inclusions [77]. The critical binding energy between the trap and hydrogen is 60 kJ/mol, which determines whether the trap is reversible (low binding energy) or irreversible (high binding energy) [77].

# 4. Compatibility of Gas Pipeline Materials with Hydrogen

Generally, in the Czech Republic (EU), outdoor gas pipelines are made from steel or polymer PE. The internal piping is made of steel, copper, PEX-AL-PEX multilayer pipe, or flexible corrugated stainless steel. This review article is focused on steels and polymers (PE).

The compatibility of materials with hydrogen depends on operating conditions, such as pressure, temperature, flow rate, kinetic energy of the hydrogen particles, and device geometry [60].

Generally, the compatibility of hydrogen in interaction with metals is affected by corrosion, hydrogen embrittlement (HE – subset is HIC), low-temperature embrittlement ("cold embrittlement"), and intense reactions, e.g., ignition [55,79]. At high temperatures, corrosive hydrides can be formed, creating gas bubbles (the so-called blisters) inside the metal lattice [55]. Pure hydrogen exhibits unique corrosive mechanisms, and in combination with impurities, the risk of corrosion is several times higher [21].

Hydrogen in interaction with polymers can cause blistering, swelling, and polymer damage, leading to an increased hydrogen permeation rate through the polymer [55]. The hydrogen permeation rate must be regulated in order not to exceed the lower flammability limit of hydrogen (LFL), especially for containers of type IV with polymer liner [49,80] (for other containers of type I, II, and III, the permeation rate is negligible) [55].

#### 4.1. Hydrogen Embrittlement

One of the most important criteria regarding the safe operation of hydrogen pipelines is resistance to stress corrosion cracking (SCC, external corrosion) and hydrogen gas embrittlement (HGE, internal corrosion) [21]. The cause of SCC is improper coatings and cathodic protection, and adverse soil conditions [21]. The danger of their occurrence increases at high temperatures and pressures and decreases with low stress [21].

Compressed hydrogen and some gases containing hydrogen cause embrittlement of steels (can cause the rupture of metals) [81]. For mixtures of gases containing hydrogen, the risk of HE occurs if the partial pressure of the gas is higher than 5 MPa (50 bar) (for a metal cylinder) [79]. HE occurs when hydrogen atoms permeate the microstructure of the metal and accumulate at energetically more active sites (defects) [82]. HE is the phenomenon of stress-cracking formation [79]. HE reduces mechanical properties (tensile strength and ductility) and increases the rate of fatigue crack growth [83]. The intensity of HE is influenced by several factors mentioned in Chapter 5. In addition to the mentioned factors purity/quality of hydrogen is also important [21].

The risks of HE can be minimized by reducing global or local stresses in the material and careful selection of materials [21]. Stress reduction is usually achieved by smaller distances between pipe supports, thicker pipe walls, and thermal relief of residual stresses when welding [21], this could mean preheating the welded surfaces.

The proposed mechanisms of HE are Hydrogen enhanced localized plasticity (HELP), Hydrogen enhanced decohesion (HEDE), Adsorption induced dislocation emission (AIDE), and hydrogenenhanced strain-induced vacancy (HESIV) [82,84,85]. The exact mechanism of HE still remains uncertain [3,82].

The suitable choice of materials for pipelines, storage vessels, and accessories (filling connections, fittings, etc.) is essential for the safe operation of hydrogen systems [55].

#### 4.2. Metal Pipeline – Recommendation

Metal pipeline systems transporting pure hydrogen or hydrogen mixtures have a temperature and pressure range of -40 °C to 175 °C and 1 MPa to 21 MPa [21]. High-pressure hydrogen is usually



considered at pressures equal to or higher than ~21 MPa [83]. For stainless steels, the partial pressure of hydrogen is above 0.2 MPa [21].

In high-pressure hydrogen operation, many engineering alloys can be susceptible to HE [83]. Carbon and low alloy steels are susceptible to fatigue crack growth at high temperatures or low gas pressure [83,86]. The risk of HE can be reduced by using corrosion-resistant steel [79]. API 5L X52 microalloyed pipeline has been used for hydrogen gas transport since the 1990s (with pressure > 7 MPa) [21].

Recommended for high-pressure operation are series 300 austenitic stainless steels, thanks to their high toughness [21]. Austenite type 316/316L is preferred for hydrogen gas thanks to its higher austenite stability and less susceptibility to HE [21,83]. It is recommended to use seamless welded pipelines with heat treatment (annealed) for the elimination of defects caused by welding (to prevent the spread of cracks as a result of HE) [83]. Connections by soft soldering are not allowed [83].

For operation with gaseous and liquid hydrogen, the single-wall pipeline is used unless thermal insulation is required [83]. For operation with liquid hydrogen, a pipeline with vacuum insulation is recommended [83]. Hydrogen pipelines are cleaned by various cleaning methods to achieve the desired surface cleanliness, for example, usually by various types of cleaning pigs (cleaning elements) that are forced through the hydrogen pipeline by a pressurized system [21].

Hydrogen pipeline systems and hydrogen storage systems (storage vessels [49]) must be equipped with pressure relief devices (PRD) in case the maximum permissible working pressure of the system is exceeded [83]. Another important component is the thermally activated overpressure relief device (thermal pressure relief device – TPRD) [25].

The speed of sound in hydrogen is around four times higher than most combustible gases [21]. Therefore, in piping systems, erosion and abrasion can occur at components such as control and relief valves where hydrogen can locally reach sonic or nearly sonic velocities [21]. Also, bends for turning can be a problematic area. Due to the high sonic velocity, problems may occur at differential pressure [21].

# 5. Factors Affecting Permeation (Diffusion) of Hydrogen and HE

Hydrogen permeation or diffusion in metal and polymer materials depends on several factors:

Temperature and pressure: Xu et al. [87] found that with increasing temperature in X52 steel, there is increased hydrogen permeation, leading to an increase in hydrogen content, which increases the risk of HE. In general, with increasing pressure, the susceptibility to HE increases in steel [87]. Zheng et al. [56] found that in amorphous PE pipelines, in accordance with Arrhenius law, the hydrogen diffusion, solubility, and permeability coefficients increase with temperature, while the effect of pressure is negligible on hydrogen permeability in PE pipelines. To reduce the effect of temperature on hydrogen permeation, it is recommended to bury the pipeline deeper in the ground or use an insulating layer [56].

Thickness and strength: Zheng et al. [73]. found that the higher the thickness of the material, the higher the apparent diffusion, and hence, the penetration time is higher through the material. Li et al. [88] found that the higher thickness of API X90 increases fracture toughness, leading to a greater risk of HE. High-strength steels (X52, X65, X70, X80, X100) compared to low-strength steels (X42, X46) have a greater susceptibility to hydrogen absorption and HE [3,89]. Peng et al. [90] found that steel X80 contains a higher density of hydrogen traps than X65 steel with lower strength, which can potentially lead to an increased susceptibility of X80 steel to hydrogen-induced cracking (HIC) (a subset of HE). To reduce the risk of HE, it is recommended to use high-purity steels (without non-metallic inclusions that decrease toughness) [21].

Microstructure: The hydrogen diffusion in metals is affected, in addition to the interatomic interaction between metal and hydrogen, also by the material microstructure (atomic configurations) [82]. The presence of hydrogen traps (Chapter 3.4.) slows down hydrogen transport [91]. Cheng et al. [92] found that the effective diffusivity decreases with higher binding energy of hydrogen traps and with higher density of trapping sites, but increases with higher hydrogen content. Cheng et al. [93]

found that steel with the highest content of precipitates of semi-coherent vanadium carbides (V8C7) increased the resistance of steel to hydrogen-induced cracking (HIC). The small size of V8C7 reduced the hydrogen diffusion coefficient [93]. Thomas et al. [77] found that increasing the grain size in X70 steel leads to reduced hydrogen traps and hence higher diffusion. In addition to that, they found that the path for hydrogen diffusion is the easiest through cementites. To reduce the risk of HE of alloys, it is recommended to use uniform fine-grained microstructures [21].

Generally, polymer pipeline materials (PE) are more susceptible to permeation and leakage of hydrogen than metal (steel) [56]. The hydrogen permeation (permeability) of non-metallic materials is significant [60]. Zheng et al. [56] found that higher crystallinity (lower amorphousness) in PE reduces hydrogen permeability.

Chemical composition: Zhao et al. [94] found that the addition of a chemical inhibitor, carbon monoxide (CO), to X80 steel reduces hydrogen permeation, thereby reducing the susceptibility to HE, especially in the welds, which are the most sensitive area to HE. The importance of the welds was confirmed in a study by Wang et al. [95]. Nyrkova et al. [96] found that the addition of alloying elements and microalloying elements such as Mn, Nb, Ti, and V to steel increases its strength but also reduces its plasticity, which is due to anisotropic microstructure. This phenomenon increases the susceptibility of steels to HE. The addition of elements such as Nb, Ti, and V creates nanoscale carbides in the steel that act as both irreversible and reversible hydrogen traps, thereby reducing hydrogen diffusion and the risk of HIC [93,97]. Wu et al. [82] found that Ni adding limits hydrogen diffusion in alloys. Omura et al. [98] found that Ti, Mn, and Cr reduce fracture elongation of alloy, which means they increase the susceptibility of alloy to HE. Padhy et. al [66] confirmed that steels with increased alloying elements have a higher susceptibility to hydrogen-assisted cracking (HAC). Lee et al. [65] found that SS 316L and HEA (CoCrFeMnNi high-entropy alloy), in comparison to SS 304, do not undergo martensitic transformation during hydrogen permeation due to their more stable austenitic structure. It was found that heat treatment reduces the density of hydrogen traps and can heal cracks in steel [99,100].

Surface treatments (coatings): Moshref-Javadi et al. [101] found that thermally sprayed coatings (TSC) on AISI 316L stainless steel contain ferritic phases in the microstructure of the coating and a dense dendritic structure, due to which hydrogen rapidly permeates through the material. Vargas et al. [102] found that TSC can reduce HE, but its efficiency depends on several factors. For example, coatings containing nickel and chrome provide more effective protection against HE. Shi et al. [103] found that multi-layered graphene (MLG) coatings reduce hydrogen permeation and increase resistance to HE. Wetegrove et. al [104] in their review article, other barrier coatings, such as Al<sub>2</sub>O<sub>3</sub>, TiAIN, and TiC, were described. Cai et al. [105] prepared composite hydrogen barrier coatings with sandwich structures.

**Cathodic protection:** Cathodic protection is used to protect the metal from corrosion. Nyrkova et al. [96] mentioned that higher polarization current density and more negative cathodic polarization potential (-0.95 V) increase hydrogen absorption into the steel, which leads to a higher susceptibility to HE. Yin et al. [106] determined the limiting cathodic polarization potential (-0.992 V) at which 10Ni5CrMo steel in seawater is susceptible to HE.

**Mechanical stress and plastic deformation**: Cold-deformed steel increases the density of hydrogen traps (dislocations) [71,107], and thus higher diffusible hydrogen concentration, which increases the risk of HE [107]. Shang et al. [108] found that severe plastic deformation generates dislocation traps with increased binding energy of hydrogen traps, which leads to higher hydrogen concentration in X80 steel. Yin et al. [109] found that when tensile stress in metallic materials occurs in the elastic strain phase, hydrogen diffusion increases, and HE susceptibility increases.

Environmental factors: The presence of CO<sub>2</sub> or H<sub>2</sub>S causes an increase in the concentration of atomic hydrogen on the surface of the steel; corrosion of the steel occurs in the presence of H<sub>2</sub>S, and there is increased hydrogen permeation, thereby increasing the risk of HE [110,111]. Du et al. [112] found that the lower the pH (more acidic environment), the higher the hydrogen diffusion coefficient and the concentration of diffusible hydrogen, which increases the risk of HE. Sun et al. [74] found

that SRB (sulfate-reducing bacteria) (producing e.g., H<sub>2</sub>S) in the marine environment increases the hydrogen concentration in X70 steel. Another chemical inhibitor besides CO is La<sup>3+</sup> cations in the corrosion products, which can reduce the adsorption of hydrogen on the subsurface, thus reducing the risk of HE [110].

Besides the already mentioned materials (steels, polymers), hydrogen transport is also studied in materials suitable for the separation of pure hydrogen, such as perovskite membranes [113,114].

# 6. Hydrogen Current Topics

#### 6.1. Hydrogen Blending in Natural Gas

For high-capacity transport, the gas pipelines are key [85]. Existing gas pipeline infrastructure could be used to transport hydrogen or mixtures of hydrogen and natural gas, such as hydrogen-blended natural gas (HBNG) [28,85,115] and hydrogen-enriched compressed natural gas (HCNG) [116]. The use of existing gas pipelines would eliminate the financial and time requirements for the construction of new pipelines. There are, however, required costs for hydrogen technology separation from natural gas at the point of use [54].

Hydrogen, compared to natural gas and gasoline, has more than twice the calorific value [117]. But a wider range of ignition than natural gas, therefore, mixtures of hydrogen and natural gas show an increased risk of explosions during leakage [117,118]. Pure hydrogen and mixtures of natural gas with hydrogen have different degrading effects on fracture toughness, depending on the type of steel and pressure [119].

Wang et al. [50] set the critical safety hydrogen blending ratio with natural gas for X80 steel gas pipelines at 10 %, which ensures operation of up to 10 % without significant risk of HE. For polymer materials, a hydrogen content of up to 20 % does not pose a risk of hydrogen losses due to its permeation [120]. Peng et al. [1] found that under typical pipeline conditions, gravitational stratification (separation of hydrogen from methane) of the mixture  $H_2/CH_4$  in a vertical pipeline is negligible and thus does not affect the risk of HE. Zhu et al. [121] found that stratification of  $H_2/CH_4$  occurs only temporarily during leakage from a buried pipeline. Klopffer et al. [122] found that hydrogen permeability is higher than methane permeability (a component of natural gas) in polymer pipelines.

Another approach that may be safer is pipe-in-pipe, where pure hydrogen is in the inner pipeline and natural gas is in the outer pipeline [123]. Inner pipeline can be made of promising fiber-reinforced polymer material [124]. Alternatively, an existing outer pipeline could be used where only air would be present, and the inner pipe would be with appropriate material for hydrogen. The advantage is that excavation work is eliminated. The disadvantage is the reduction of the diameter of the pipeline and the reduction of the volumetric flow rate of distributed gas. To maintain the same amount of distributed gas, an increase in pressure is necessary.

Heating using a mixture of hydrogen and natural gas with 20–30 % hydrogen is possible in existing condensing boilers for natural gas [125] and gas appliances (e.g., stoves [126]).

#### 6.2. Hydrogen Refueling Stations

Hydrogen refueling stations (HRS) are a key infrastructure for refueling hydrogen in fuel cell vehicles (FCV), which are complementary to battery electric vehicles [127]. Hydrogen is either transported (off-site production) to HRS or is produced on-site (on-site production, e.g., small-scale hydrogen production [128]) that has a certain capacity for hydrogen (kg/day) [129].

We distinguish between gaseous hydrogen refueling stations (GHRS) and liquid hydrogen refueling stations (LHRS) [130]. GHRS includes compressors, high-pressure or mid-pressure buffer storage vessels for gaseous hydrogen, pre-cooling devices, hydrogen dispensers, and a high-pressure connector for refueling gaseous hydrogen [130]. LHRS, compared to GHRS, contains, before the buffer storage vessels, a liquid pump instead of a compressor and still an exchanger (vaporizer) [130].

The dispensing pressure is according to the type of dispenser; for passenger vehicles with fuel cells, it is 700 bar (70 MPa), and the maximum flow rate when refueling passenger vehicles is 60 g/s [130]. Other parameters for refueling vehicles with gaseous hydrogen are set by SAE J2601, such as fuel delivery temperatures (-40°C, -30°C, and -20°C) [131]. The quality of gaseous hydrogen is determined by ISO 19880-8 and ISO 14687 [27,132]. The general requirements for hydrogen fuelling stations for gaseous hydrogen, including leak testing of the hydrogen fuelling system, are based on ISO 19880-1 [10].

The fuel dispenser assembly consists of a breakaway, fuel hose, and fueling nozzle [133], which can contain communication hardware and software specified by the current standard SAE J2799 [134]. The safety of hydrogen refueling stations includes leak detection, ventilation, TPRD, fire protection systems (e.g. water mist system [135]), pressure safety valve (PSV), monitoring of temperature and pressure of hydrogen during filling, measurement of the amount of delivered fuel to the vehicle [133], push-button emergency switches, use of protective personal covers [10], etc. [130,136]. Furthermore, fuel filtration to ensure fuel quality using filters in dispensers for capturing PM larger than 5 µm with a filtration efficiency of 99 % [10,133]. Safety distances are specified by standards ISO 19880-1 [133] and ČSN 73 6060 [137]. It is recommended to use a tube-in-tube evaporator, one reason being that it does not create O<sub>2</sub>-enriched zones [130]. Composite storage vessels require more strict safety measures than metallic ones [10]. Other requirements are set out in the technical rules for filling stations of compressed hydrogen TPG 304 03 [138].

#### 6.3. Hydrogen Fuel Cells

Hydrogen fuel cells are electrochemical technologies enabling the conversion of the chemical energy of hydrogen into electrical energy in the presence of oxygen [139]. Fuel cells consist of two electrodes (anode and cathode) with an electrolyte in between [139]. The molecular hydrogen supplied to the anode (negative electrode) is electrochemically split at the catalyst into protons (positively charged hydrogen ions) and electrons [139]. Oxygen supplied to the cathode (positive electrode) reacts with protons and electrons to produce water. Another byproduct is heat [139].

Among the common fuel cells are proton exchange membrane fuel cells (PEMFC), solid oxide fuel cells (SOFC), alkaline fuel cells (AFC), phosphoric acid fuel cells (PAFC), and molten carbonate fuel cells (MCFC) [140]. Proton exchange membrane fuel cells (PEMFC) are suitable for small decentralized systems (vehicles [141]) thanks to their operation at lower temperatures (60–80 °C [141]) [142,143].

Hydrogen fuel cells are used in transport vehicles. Fuel cell electric vehicles (FCEV) generate electricity to power the electric motor through the fuel cell, and the excess energy is stored in a small lithium-ion battery for optimizing vehicle operation (acceleration, regenerative braking system, regenerative suspension module) [144,145]. In comparison with battery electric vehicles (BEV), FCEVs have a longer range and faster refueling [146]. FCEVs are currently offered, for example, by Hyundai, Toyota, Honda, and BMW. Hydrogen can also be used in cars with hydrogen direct injection (H<sub>2</sub>DI) internal combustion engines [147].

Hydrogen fuel cells can also be used in cogeneration or micro-cogeneration systems for combined heat and electricity [148]. Micro-cogeneration (Micro-CHP) with an output of less than 50 kWel can be used, for example, in households [148]. Their advantage is a high efficiency of > 80 %, thanks to the use of waste heat, for example, for hot water heating [148]. Elkhatib et al. [149] dealt with the production of green hydrogen for microcogeneration with the use of a PEMFC fuel cell. The supplementary heat source was a condensing boiler. Shboul et al. [150] optimized by numerical modeling of photovoltaic-fuel cell system. The electrolyzer, in combination with photovoltaic panels, can produce green hydrogen, which can subsequently be stored in a hydrogen storage tank, and at the time when electricity is necessary and photovoltaics do not produce electricity, the stored hydrogen can be used to generate electricity through a fuel cell. The system can be further supplemented with lithium batteries [151]. Bhogilla et al. [152] found that the efficiency of a cogeneration system using a PEMFS can be increased through metal hydride hydrogen storage

(MHHS), during which waste heat is generated by the hydrogen absorption and can be utilized for a variable absorption refrigeration system (VARS).

#### 6.4. Hydrogen Permeation in Nuclear Fusion Reactors

In nuclear fusion reactors, nuclear fusion occurs, from which an emission-free source of energy can be obtained. A deuterium-tritium (D-T) nuclear fusion reactor (or a fission high-temperature gascooled reactor HTGR [153]) must be resistant to operating conditions, such as increased temperature, corrosive environments, mechanical loads, and neutron exposure [154]. Plasma exposure causes surface changes – surface roughness and microstructure changes [155]. For nuclear fusion reactors, reduced-activation ferritic-martensitic (RAFM) steels, such as Eurofer [156], CLAM, and CLF are used [157]. Hydrogen isotopes (deuterium, tritium) permeate the fusion reactor; therefore, tritium permeation barriers (TPB) are essential [158,159].

Serra et al. [160] found that at low temperatures (up to 523 K), significant deuterium trapping occurs in the microstructure of F82H and Batman. Esteban et al. [161] found that the permeability constant for martensitic steels (OPTIFER-IVb) is higher than that for austenitic steels. Esteban et al. [162] found that the layer of MnCr<sub>2</sub>O<sub>4</sub> is an effective barrier for deuterium transport in Incoloy 800. Aiello et al. [163] found that deuterium permeation is higher for the Eurofer 97 steel than for AISI 316L steel. Wang et al. [69] and Zhou et al. [157] found, that the hydrogen diffusion coefficient for CLAM steel is higher than for CLF-1. A thin Palladium membrane was applied to the steels to reduce the effect of anodic polarization on hydrogen diffusion [157,164]. Katayama et al. [153] found that the hydrogen/tritium permeability in the Zr pipe is higher than in Al<sub>2</sub>O<sub>3</sub> (HTGR). In other studies, it has been found that the tritium permeation of SiC is less than that of SS316 steels [165,166]. Houben et al. [158] investigated deuterium permeation through Eurofer97 and 316L(N) and found that oxidation, surface roughening, or technical surface have little effect on reducing deuterium permeation flux; respectively, the affected surface roughness by plasma exposure does not affect hydrogen permeation. And tritium permeation barriers (TPB) are essential. Houben et al. [155] demonstrated that tungsten oxide contamination on 316L(N)-IG samples reduces permeation flux.

#### 6.5. Hydrogen-Fueled Gas Turbines

The combustion turbine converts the chemical energy of the fuel into mechanical energy by rotating the rotor shaft. This mechanical energy is subsequently converted into electrical energy via a generator. The gas turbines can be operated in a mixture of natural gas and hydrogen or only with pure hydrogen (Siemens Energy SGT-400), which supports decarbonization [167]. Amrouche et al. [168] found that the use of hydrogen fuel in the MS5002C turbine leads to a reduced carbon footprint but slightly increased NOx emissions in comparison to natural gas. Optimal excess air increases gas turbine efficiency. Emissions of NOx can be reduced by injection of a reducing agent and the use of selective catalytic reduction (SCR) systems [169]. Due to the properties of hydrogen, suitable blade materials [170,171] and suitable cooling technologies must be chosen [172]. For example, high-temperature resistant ceramic matrix composites (CMCs) are currently being investigated for thermally stressed parts of a turbine, such as blades and combustion chambers [173].

# 7. Hydrogen Leakage

Hydrogen leakage is defined as the loss of hydrogen (in the gas or liquid phase) under specific test conditions expressed as a change in concentration or leak rate [174].

A leak of gaseous hydrogen from a leak source, such as pipe joints, creates a stream or cloud of gas depending on the pressure at the leak point [19]. Hydrogen has a lower density than air; therefore, it rises and dissipates rapidly in the surrounding environment [19]. With decreasing hydrogen concentration, the density of the mixture approaches the density of air, which causes it to move together with the air [19]. Leakage of hydrogen can lead to fires or explosions if an external ignition

source is present [175]. The high-pressure leaking hydrogen, in the case of its ignition, creates a loud beam of invisible flame, which is very dangerous [19].

The spread of hydrogen is affected by the relative density of the gas [19], pressure, flow rate, leak location, geometry of the leak source, ventilation, and atmospheric conditions (degree of turbulent mixing [19]) inside and outside the leak source [175,176].

High concentrations of escaped hydrogen can accumulate under ceilings and in areas that are poorly ventilated (e.g., in dormers and roof ridges) [19]. For limiting hazardous concentrations (for rapid dissipation of escaped hydrogen), natural or forced ventilation (in the case of indoor space) is necessary [10].

Wang et al. [177] determined the critical ventilation flow rate to reduce the risk of explosion in containers for hydrogen production. Sun et al. [117] investigated the leakage of a mixture of hydrogen with natural gas (CH<sub>4</sub>) from an indoor pipeline. Yang et al. [175] confirmed the importance of ventilation in confined spaces to limit hazardous concentrations.

Leakages of hydrogen are critical in systems with high pressure and temperature; therefore, additional safety measures (rectifying covers, and steam (air) nozzles for humidification of the gas) should be considered [19]. The safety rules include placing the hydrogen system in an outdoor environment (not indoors), decreasing the diameter of the hydrogen supply pipeline, and operating pressure of the hydrogen [178].

Risk assessment of leakages (from pipelines or storage vessels) and hydrogen explosions is possible using simulation software: Chen et al. [179] found using the simulation software ALOHA that pipe pressure, wind speed, terrain roughness, and gap size affect the accident consequences. Liang et al. [180] used the simulation software FLACS for the leakage accidents of hydrogen storage in hydrogen refueling stations (HRSs). The safety distances of hydrogen refueling stations are established. Wang et al. [181] simulated leakages of pipeline HBNG in the utility tunnels using the software Fluent.

#### 7.1. Methods of Verifying Tightness and Detection of Hydrogen Leakage

The pipeline system must be tested for leakage before commissioning and after maintenance [83]. Pipelines (or cylinders [182]) are usually tested hydrostatically or pneumatically [83,183]. Pneumatic tests for leak detection use mixtures containing at least 10 % helium, or 5–10 % hydrogen in an inert gas [83]. The leak tightness for cylinders is according to the standard DIN EN 12245 (or ISO 11119-3), where the pressure in the liner is gradually increased until it reaches the defined pressure of liner resistance [182].

For fuelling assembly test methods of leakages, namely bubble testing or pressure decay testing (pneumatic method) are used [10].

Local leak measurements of smaller systems using detectors are performed using the detector probe (sniffing) method [174,184] or ultrasonic gas detection [10]. For leak testing, gases such as dry hydrogen, dry helium, nitrogen-based mixtures containing hydrogen (>10 %) or helium are used [185]. For example, leak testing for high-pressure hydrogen applications is performed with helium up to 180 bar [186]. Pipeline surveys using a detector should be carried out regularly, once to four times a year, based on the area's population density and in accordance with national regulations [21]. Attention should be given to, for example, valve stems and compression fittings [21].

Sensors should be installed at hydrogen accumulation locations in the case of a leak [83]. They are installed at the height of the hydrogen system or above it [83]. The triggering of detector alarms in the case of a hydrogen leak and shutdown of the system should be set to the desired hydrogen concentrations [83]. In indoor spaces, sensors should be installed above locations of hydrogen leakages, or near the ceiling, exhaust ducts, and extraction fans [19].

Sensors need to be calibrated with a suitable calibration gas at regular intervals [19,174], for example, according to ISO 15848-1 [174] for industrial valves.

# 8. Hydrogen Applications in the Czech Republic

According to the Hydrogen Strategy of the Czech Republic 2024, increased production of low-emission/emission-free green hydrogen is planned in the future, which will lead to a greater expansion of electrolyzers for larger industrial systems [187,188] and an increased number of hydrogen refueling stations [33]. The expected lower price of hydrogen in the future will lead to a greater deployment of hydrogen.

Currently, hydrogen in the Czech Republic is mainly used in the chemical sector, with growing applications in transportation and planned future use in power generation and heating.

Some specific future applications include:

The deployment of several Solaris hydrogen buses [189].

In Prague, the ORLEN Group plans to establish several hydrogen refueling stations across the country by 2030 [190].

# 9. Future Challenges

Harmonization and the creation of up-to-date standards are important steps toward the safe implementation of hydrogen technology in practice. Also, the synthesis of information from the up-to-date standards and regulations is necessary.

Metal and plastic (PE) pipes are sufficiently experimentally tested in terms of permeation, but there is a lack of testing of other materials that are commonly used in indoor installations, such as PEX-AL-PEX multilayer pipes. Their research is needed to expand the hydrogen infrastructure. Furthermore, research on new materials such as high-entropy alloys [65] and fiber-reinforced polymer materials is lacking [124].

#### 10. Conclusions

The review article provides a overview of hydrogen safety in energy infrastructure. Based on the standards and research articles, it shows that with a thorough understanding of hydrogen permeation through metal and polymer materials, hydrogen embrittlement in metal materials, and leak detection, safe and efficient integration of hydrogen technologies into existing and future energy systems can be achieved.

The main conclusions are as follows:

Conduct experimental research on internal piping made from PEX-AL-PEX multilayer pipe.

Evaluate next-generation materials, such as high-entropy alloys and ceramic matrix composites, under real operational conditions.

Develop and validate risk-mitigation methods, such as cost-effective pipe-in-pipe design solutions.

**Author Contributions: Eva Gregorovičová:** Conceptualization, Formal analysis, Funding acquisition, Investigation, Validation, Visualization, Writing – original draft, Writing – review & editing. **Jiří Pospíšil:** Funding acquisition, Project administration, Supervision, Writing – review & editing.

**Acknowledgements** This research was funded by projects of the Technology Agency of the Czech Republic: TN02000007 National Hydrogen Mobility Center.

**Conflicts of Interest:** The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

# **Acronyms**

AEL Alkaline Electrolysis

AEM Anion Exchange Membrane

AFC Alkaline Fuel Cell

AIDE Adsorption Induced Dislocation Emission

AISI American Iron and Steel Institute

BCC Body Centred Cubic
BEV Battery Electric Vehicle
CCS Carbon Capture and Storage
CCU Carbon Capture and Utilisation
CLAM China Low Activation Martensitic
CLF China Low-activation Ferrite
CMC Ceramic Matrix Composite

D-T Deuterium-Tritium
FCC Face Centred Cubic
FCEV Fuel Cell Electric Vehicle

FCV Fuel Cell Vehicle

GHRS Gaseous Hydrogen Refueling Station

H2DI Hydrogen Direct InjectionHAC Hydrogen-Assisted CrackingHBNG Hydrogen-Blended Natural Gas

HCNG Hydrogen Enriched-Compressed Natural Gas

HCP Hexagonal Close-Packed HE Hydrogen Embrittlement HEA High-Entropy Alloy

HEDE Hydrogen Enhanced Decohesion

HELP Hydrogen Enhanced Localized Plasticity
HESIV Hydrogen-Enhanced Strain-Induced Vacancy

HGE Hydrogen Gas Embrittlement
HIC Hydrogen-Induced Cracking
HRS Hydrogen Refueling Station
CHP Combined Heat and Power
LFL Lower Flammability Limit

LH2 Liquid Hydrogen

LHRS Liquid Hydrogen Refueling Station LOHC Liquid Organic Hydrogen Carrier

MCFC Molten Carbonate Fuel Cell

MHHS Metal Hydride Hydrogen Storage
MIE The Minimum Ignition Energy

MLG Multi-Layer Graphene MOF Metal-Organic Framework

P2G Power to Gas

PAFC Phosphoric Acid Fuel Cell

PE Polyethylene

PEM Polymer-Electrolyte Membrane
PEMFC Proton Exchange Membrane Fuel Cell

PRD Pressure Relief Devices PSV Pressure Safety Valve

RAFM Reduced-Activation Ferritic-Martensitic RFNBO Renewable Fuels of Non-Biological Origin

SCC Stress Corrosion Cracking SCR Selective Catalytic Reduction SMR Steam Methane Reforming

SOEC Solid Oxide Electrolyzer Cell

SOFC Solid Oxide Fuel Cell
SRB Sulfate-Reducing Bacteria

SS Stainless Steel

TPB Tritium Permeation Barrier
TPRD Thermal Pressure Relief Device

TSC Thermal Spray Coating

VARS Variable Absorption Refrigeration System

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