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Multi-stage monitoring of hydrogen systems for improved maintenance approaches: an extensive review

Giulia Collina [a,*], Marta Bucelli [b], Nicola Paltrinieri [a]

[a] Department of Mechanical and Industrial Engineering, Norwegian University of Science and Technology, Trondheim, Norway
[b] SINTEF Energy Research AS, Trondheim, Norway

A R T I C L E I N F O

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A B S T R A C T

Hydrogen is considered a promising solution for global decarbonisation as an alternative to fossil fuels. However, it can interact with and brittle most metallic materials and is highly flammable. These properties call for a systematic investigation of physical and chemical hazards and for the definition of a comprehensive risk management and monitoring framework, including proper maintenance planning. This study aims at establishing a hydrogen monitoring scheme and it provides a descriptive, bibliometric, and interpretative review of the current state-of-the-art of suitable techniques to ensure the safe handling of hydrogen systems. The descriptive analysis outlines the technologies available to supervise the hydrogen-material interactions and detect hydrogen leaks and flames. The bibliometric analysis shows quantitative data to identify the most relevant research groups. The interpretative study discusses the findings and examines the possibility of combining the identified techniques with maintenance programs to prevent catastrophic events.

1. Introduction

Hydrogen is increasingly recognized as a leading element in global decarbonisation efforts [1]. As governments seek to meet ambitious climate goals in reducing greenhouse gas emissions, hydrogen emerges as a versatile and clean energy solution [2]. An additional boost to this impetus on the willingness to use hydrogen is the recent global energy crisis, which countries have received as a threat to their energy security [3]. Hydrogen has been employed for many years in refining, as a feedstock in the chemical industry, as a reducing agent in steel manufacturing, and in other applications. As reported in the last release on hydrogen by the International Energy Agency [3] many other sectors are now approaching the possibility of introducing hydrogen in their process as an alternative fuel e.g. enthusiasm for using hydrogen as a fuel to Fuel cell electric vehicles (FCEVs) for road transport is increasing. In addition, hydrogen is being investigated as a replacement for fossil fuels in the so-called hard-to-abate sectors, particularly in 100%-hydrogen direct reduced iron (DRI) and high-temperature heating.

Still, the maturity of hydrogen-related technologies varies significantly across the supply chain. Different hydrogen production processes have been investigated so far to reduce the final hydrogen price to the minimum. This is a fundamental step in guaranteeing a competitive advantage over fossil fuels and developing the hydrogen economy. The target is to find the most convenient combination of capital costs, operational expenses, maintenance costs, lifetime and sustainability [4]. Hydrogen presents peculiar characteristics, such as a low density (0.0899 kg/m^3) and low boiling point (20.39 K), which require specific transportation and storage solutions, including compression, cryogenic liquefaction, or cryo-compression [5], and impact the mentioned cost items.

In addition to the technological challenges, safety concerns are often associated with hydrogen properties. Safe handling has to be guaranteed, and methodologies to enhance hydrogen safety systems should grow in step with technological improvement along the entire value chain. Hydrogen can permeate and embrittle metallic materials due to its small size [6]; internal defects can be the site of hydrogen accumulation, which worsens mechanical properties and can potentially cause failure and loss of containment from hydrogen equipment. In this case, the substance combustion properties, such as the low minimum ignition energy (0.017 mJ), the wide flammability range (4–75% vol in air), and the scarce visibility of hydrogen flames, are other factors of concerns. Such a complex scenario highlights the intrinsic link between materials science and RAMS (reliability, availability, maintenance, and safety)

* Corresponding author.
E-mail address: giulia.collina@ntnu.no (G. Collina).

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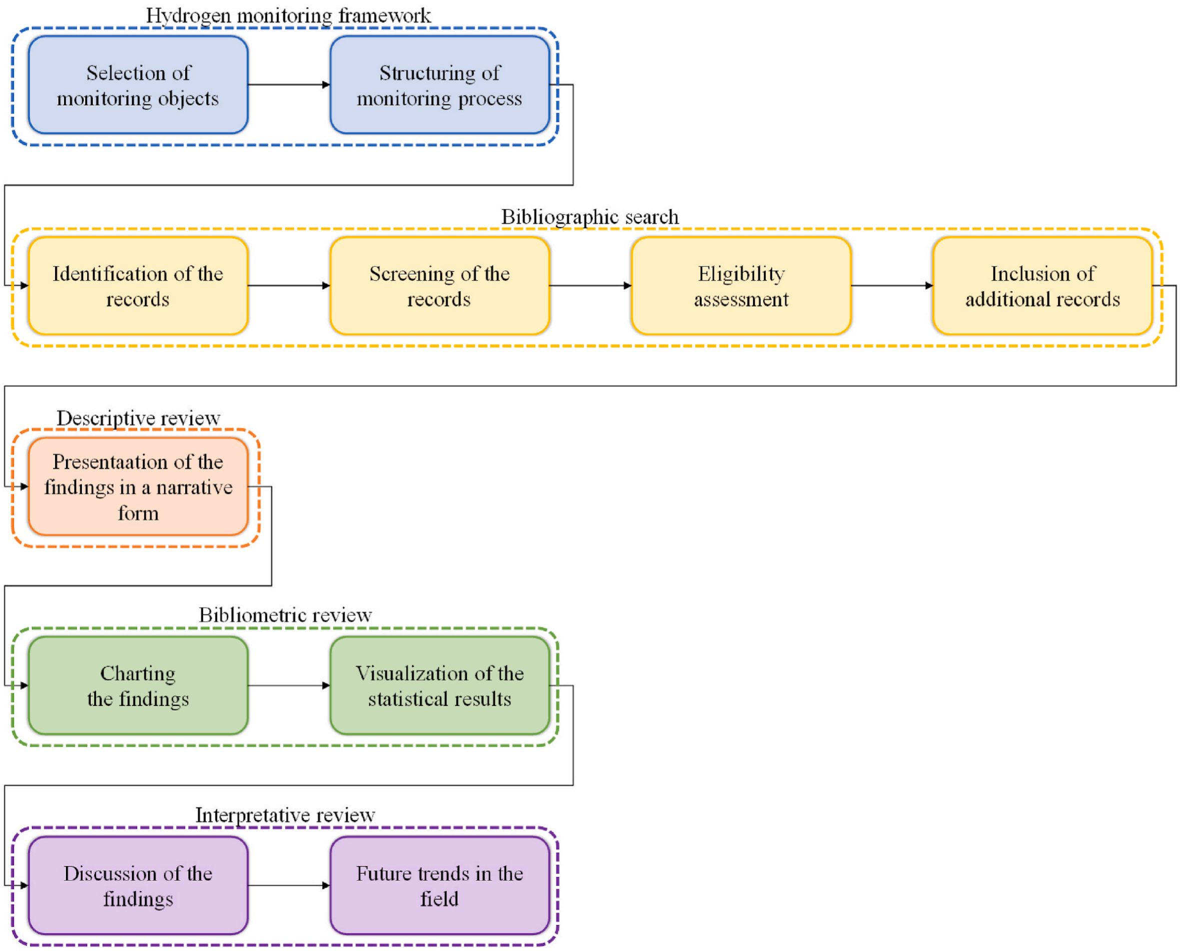


Fig. 1. Flow diagram of the methodology to conduct a descriptive-bibliometric-interpretative review.

engineering – two scientific domains which have been historically considered separated [7].

Relevant literature reflects specific focus on hydrogen embrittlement in different materials [8–10]. In addition, studies on hydrogen dispersion and explosion [11], hydrogen ignition [12], and, specifically, hydrogen jet fire [13] are also to consider when addressing hydrogen applications. Only recently the two scientific domains have been considered together, providing a more complete and interdisciplinary overview of the hydrogen safety field [6,14]. Approaches of general monitoring and maintenance practices could address such a heterogeneous range of criticalities [15]. In particular, monitoring reduces risk assessment uncertainties [16], and maintenance activities are crucial to mitigate such risk – the lack or improper management of the latter is also identified as a potential cause of accident scenarios [17].

This review paper aims to illustrate the state-of-the-art of hydrogen systems monitoring aimed at supporting maintenance activities by answering the following research questions.

- How to conduct comprehensive monitoring of hydrogen systems to address safety?
- What is the state-of-the-art of monitoring techniques for hydrogen systems?
- How can relevant information be used to improve maintenance operations as a proxy for safety improvement?

This work follows a hybrid approach, as explained in Section 2. The multidisciplinary necessity to understand hydrogen critical properties calls for a preliminary phase. Hence, Section 3 describes the hazards encountered in hydrogen applications and facilities to define a proper structure for the monitoring process; then, a framework addressing hydrogen monitoring for these emerging technologies is outlined to answer the first research question and define the boundaries of the review study. Section 4 gives details on the implementation of the research. Section 5, which presents the state of the art of the research field, and Section 6, which provides the quantitative results, meet the second research question. Section 7 comments on the findings and answers the third and last research question. Finally, the findings and insights from this study are summarised in Section 8.

2. Methodology

The methodology adopted in this study relies on a combined descriptive, bibliometric and interpretative review to perform a objective, transparent and reproducible analysis, overcoming bias and lack of completeness [18] of the state of the art of monitoring and maintenance approaches for hydrogen technologies. Fig. 1 shows the steps of the methodology.

First, a comprehensive hydrogen monitoring framework is established to address the first research question. During this phase, the safety aspects associated with hydrogen technologies are investigated to identify the monitoring objects. Subsequently, these findings, coupled with a careful consideration of the widely recognized representation of critical events in process safety, guide the structuring of the monitoring process. Based on that, the relevant records useful to answer the second research question are selected through bibliographic research. The information are gathered from the Web of Science Core Collection (WoS CC) database [19], a widely accepted tool for data extraction and scientific search. In this step, the four-phase diagram of the PRISMA

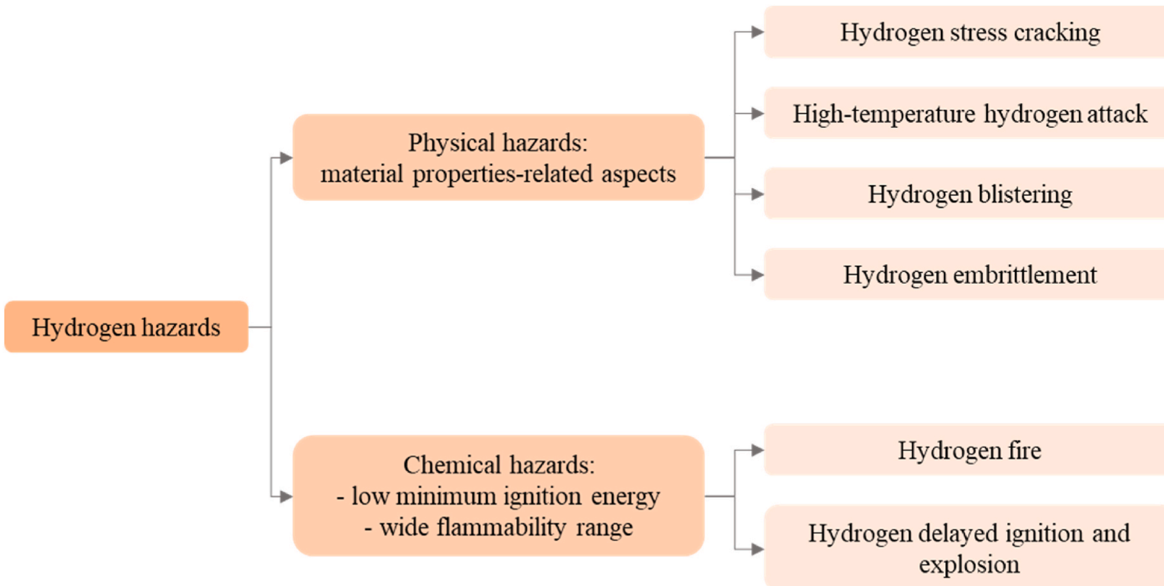


Fig. 2. Hydrogen-related hazards.

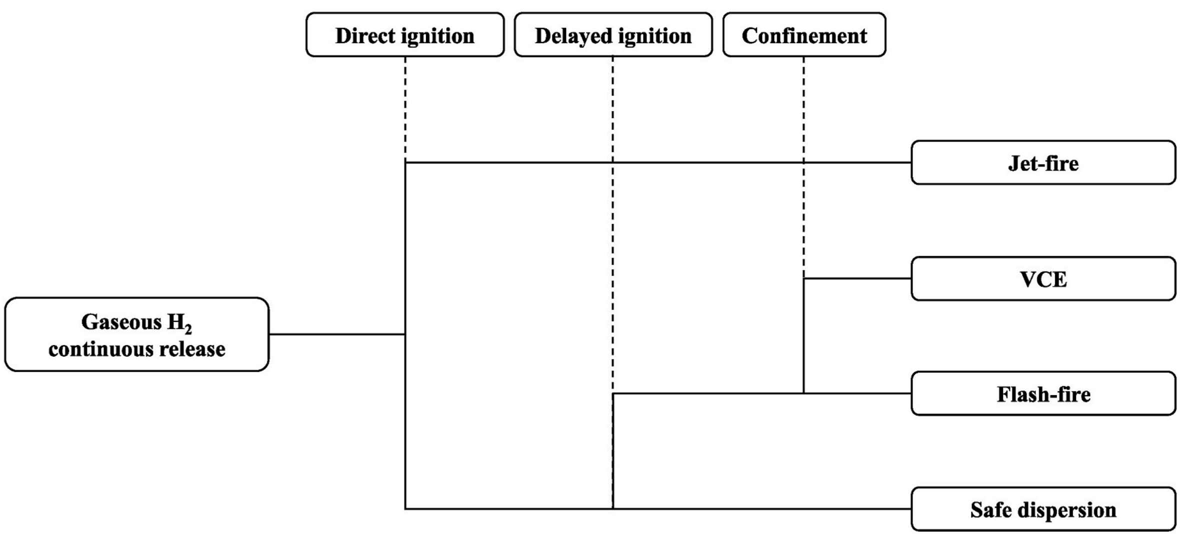


Fig. 3. Event tree of a continuous release of gaseous hydrogen.

Statement [20], which is representative of the systematic approach, is used. After identifying records through significant queries, they are screened based on title, keywords, and abstract. Then, reading the full texts allows the eligibility assessment. In addition, further studies are included through backward searches.

As a third step, the information collected are comprehensively analysed and presented descriptively, according to the structure of the monitoring process defined in the first step.

Then, the selected bibliographic materials are used as input for VOS viewer [20], a software tool designed to perform bibliometric analysis by providing keywords, co-occurrence maps, and co-authorship networks.

Finally, an interpretative analysis of the bibliometric results and the descriptive review is conducted to understand the current and future trends in the monitoring techniques for hydrogen systems. The insights emerging from this phase are responsible for answering to the third research question.

3. Hydrogen monitoring framework

3.1. Selection of monitoring objects

Over the last ten years, many researchers have focused on reviewing hydrogen safety aspects along the entire value chain. Najjar [21] reviewed hydrogen safety during production, transmission and use, highlighting the general hydrogen hazards and the necessity of reliable and economical sensors for leak detection. Moradi and Growth [22] discussed the state of the art in safety and reliability analysis for hydrogen storage and delivery. Ustolin [14] offered a systematic review of the loss of integrity of hydrogen services, pointing out the causes and the consequences of critical events. Abohamzeh [6] also reviewed safety challenges related to hydrogen, focusing on hydrogen storage, transmission, and application processes, focusing on CFD tools as a suitable method for predicting hazardous scenarios in hydrogen applications. Yang et al. [23] summarised several key issues regarding the safe utilization of hydrogen energy, including incident investigation, which observed that failures of pipes/valves/filters in the hydrogen system are

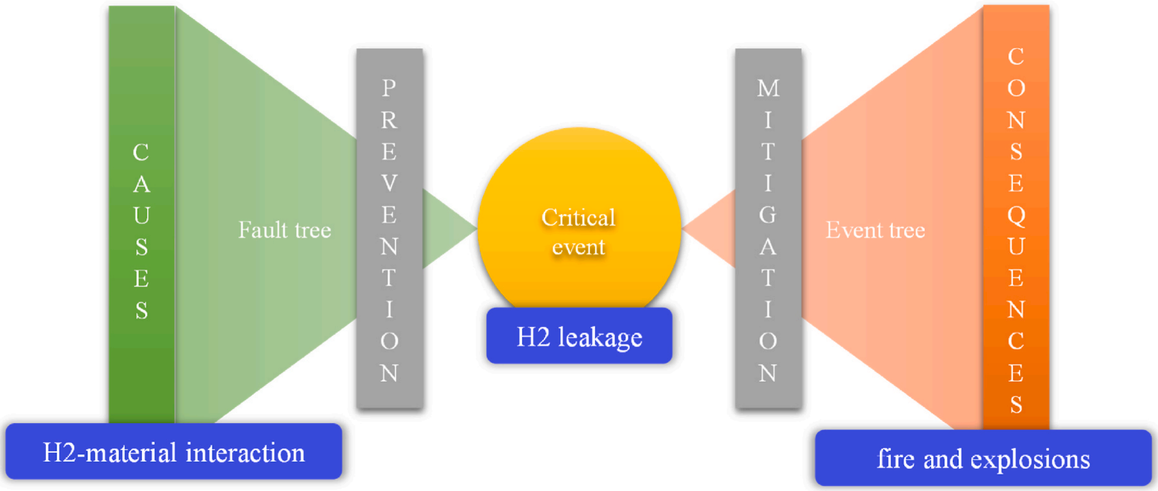


Fig. 4. Bowtie general approach.

notably the most common cause of hydrogen-related incident and therefore fault diagnosis and regular leak detection are very important. Finally, Guo et al. [5] revised safety during hydrogen production, transmission and use and analysed several typical hydrogen accident cases. Fig. 2 outlines what has emerged from the main review studies on hydrogen safety. The following two paragraphs provide more details about these aspects.

3.1.1. Hydrogen-material interactions

In this section, the attention is on the Hydrogen-induced Damages (HDs) to metals. This term refers to a wide range of deterioration effects resulting from three concurring factors: the environment (hydrogen amount, form and process), the material, and the field type (load and stress field, electrochemical driving force, fatigue) [24]. These mechanisms usually reduce mechanical properties of a component, such as tensile strength, fracture toughness, elongation to failure, fatigue life, and crack propagation rate [25], and eventual failures. Despite the variability in the classification of hydrogen damage mechanisms, the work presented in this study refers to: hydrogen embrittlement (HE), high-temperature hydrogen attack (HTHA), hydrogen blistering, hydrogen-induced cracking (HIC), and hydrogen stress cracking (HSC) [24]. Many hydrogen-induced industrial failures have occurred over the years, as outlined in the analysis of pertinent databases [26]. Hydrogen embrittlement and high-temperature hydrogen attack are the damage mechanism responsible for most of the failures reported. Hydrogen embrittlement refers to the degradation process resulting in the reduction of the strength and ductility of a material due to the entry of atomic hydrogen into the metal lattice [27]. High-temperature hydrogen attack occurs when a metal is exposed to temperatures higher than 200 °C, which facilitates hydrogen absorption and mobilisation inside the structure [25]. In the microstructural defects, the diffused atomic hydrogen recombines to form hydrogen molecules, which react with the material's carbon forming gaseous methane. The effects are the reduction of the strength of the material and the eventual methane pressure build-up, which may generate cracks.

3.1.2. Hydrogen releases

The release of hydrogen could result in various physical consequences and associated hazards [28]. The Hydrogen Incident and Accident Database (HIAD 2.1) developed by the Joint Research Centre of the European Commission classifies the relevant physical effects of hydrogen events as hydrogen release and ignition or unignited hydrogen release, and the nature of consequences as explosion, fire, leak no ignition, false alarm and near miss [29]. Fig. 3 shows, as a reference, the event tree for continuous releases of gaseous hydrogen. These include unignited releases in cases of safe dispersion, jet fires resulting from the direct ignition of a hydrogen jet characterized by intense thermal effects, flash fires arising from the deflagration of accumulated hydrogen gas primarily driven by thermal effects, and vapour cloud explosions caused by the deflagration or detonation of accumulated hydrogen gas dominated by overpressure effects.

When the event tree tool is used in a quantitative approach, it is evident that to calculate the probability of the final event the probability of the initial event must be considered, as well as the probability of direct ignition, delayed ignition, and confinement.

3.2. Structuring of monitoring process

The bowtie method is an established tool widely used in the safety field for decades, especially in the high-hazard industries, such as oil and gas, aviation and mining, to represent a critical event [30]. A bowtie is centred on an event, which is generally defined as a Loss of Containment (LOC) or a Loss of Physical Integrity (LPI). As in the most common version [31], the left side of the bowtie, called fault tree, identifies the possible causes of a critical event through Boolean logic, showing the different paths of failures potentially leading to the critical event. The right side of the bowtie, namely event tree, identifies the possible consequences of a critical event [31] considering a dichotomous barrier (i.e., success/failure, true/false, or yes/no) of accident escalation factor (e.g., ignition, explosion, dispersion) [32].

An additional essential element in the bowtie approach is the application of barriers in the diagram. Barriers are positioned on both sides of the critical event: those on the left aim to eliminate or prevent the critical event, while those on the right focus on recovering from or mitigating its effects [30]. Therefore, barriers located on the left side of the bow tie are named "preventive" while those on the right side are defined "mitigating”.

Fig. 4 shows the standard shape of a bowtie diagram and emphasises the peculiarities of hydrogen described in the previous paragraphs. Considering the peculiarities of hydrogen and the main elements characterizing the bowtie approach (causes, critical event, and consequences), three monitoring stages define the hydrogen monitoring framework and set the boundaries for thisreview study.

1. Stage 1. Material degradation monitoring, a preventive action to surveil hydrogen carrying equipment and any deterioration of their mechanical performances;
2. Stage 2. Hydrogen leak detection, a mitigating step aimed at ensuring early detection of released hydrogen before reaching a concentration within the flammability range; and

Table 1
Queries selected for the SR.

Monitoring stage	Type	Option selected
1st stage	Queries	(("hydrogen* damage*") OR ("h2 damage*") OR ("hydrogen* embrittlement*") OR ("high temperature hydrogen* attack*") OR ("hydrogen* degradation*") OR ("hydrogen metal* interaction*") OR ("hydrogen material* interaction*")) AND ("maintenance*" OR "inspection*" OR "monitor*" OR "detection*") AND ("method*" OR "technique*" OR "procedure*")
	Analysis field	Topic (title, abstract, keywords)
	Document type	Article, Proceeding paper, Review
	Language	English
	Excluded Research areas	Transportation Research Experimental Medicine Marine Freshwater Biology Geochemistry Geophysics Biotechnology applied Microbiology Biophysics Radiology Nuclear Medicine Medical imaging Imaging science Photographic technology Construction Building technology Nuclear science technology Science technology other topics
2nd stage	Queries	("hydrogen sensor*" OR "hydrogen detect*" OR "H2 sensor*" OR "H2 detect*") AND ("safety" OR "leak")
	Analysis field	Topic (title, abstract, keywords)
	Document type	Article, Proceeding paper, Review
	Language	English
	Excluded Research areas	Biotechnology applied Microbiology Food science technology Mathematics Infectious Diseases Mathematical methods in Social sciences Mining Mineral processing Neurosciences Neurology Oceanography Pharmacology Pharmacy Polymer science Public environmental occupational Health Thermodynamics Transportation
3rd stage	Queries	("Flame* detect*" OR "fire detect*" OR "fire sensor*" OR "flame* sensor") AND ("hydrogen" OR H2)
	Analysis field	Topic (title, abstract, keywords)
	Document type	Article, Proceeding paper, Review
	Language	English
	Excluded Research areas	Mining Mineral processing Agricolture Food science technology Mining Mineral processing Entomology Mycology Nutrition Dietetics Oceonography Biochemistry Molecular Biology Environmental sciences Ecology Forestry

3. Stage 3. Hydrogen flame detection, another mitigation action only responsible for reacting as quickly as possible in the event of immediate ignition of a hydrogen leak.

4. Bibliographic search

The research was completed on January 25, 2024 and revised on December 15, 2024. Table 1 reports the queries submitted to the WoS CC database based on the three monitoring phases.

The first one covers the techniques to monitor the hydrogen-material interaction, the second one investigates the state of the art of the sensors to detect hydrogen leakages, and the third one considers the hydrogen flame detection. The quotation mark allows searching for an exact word or phrase, whereas the asterisk can be used to look also for similar words. Only the title, abstract, and keywords ("Topic" in WoS CC) were selected in the analysis field, and several filters, available in Table 1, were applied to narrow the articles down.

Table 2
Studies included in the literature review.

Monitoring stage	Phase	Records included	Records excluded	Reasons for inclusion or exclusion
1st stage	Identification	220		
	Filtering	182	38	Filters in Table 1
	Screening by title and abstract	52	130	Unrelated to hydrogen Study on material performance Post mortem analysis Unrelated to inspection
	Eligibility	38	14	Unrelated to hydrogen Study on material performance
2nd stage	Identification	374		
	Filtering	347	27	Filters in Table 1
	Screening by title and abstract	232	115	Nuclear application Food application
	Eligibility	184	48	Aerospace application Production Not available
	Additional inclusion	2		Snowballing
	Total number of studies	186		
3rd stage	Identification	76		
	Filtering	56	20	Filters in Table 1
	Screening by title and abstract	5	51	Detection of hydrogen as combustion product Studies on hydrogen flame Flame detector cited for other experiments
	Eligibility	4	1	Detection of hydrogen as combustion product
	Additional inclusion	2		Grey literature (company report)
		6		

Table 2 shows the process of the PRISMA Statement. Part of the additional inclusion resulted from the hydrogen monitoring framework phase.

5. Descriptive review

5.1. Material degradation monitoring

The effective identification of the degradation of materials ensures the safe operability of the equipment, as explained in the previous sections. Over the years, the evaluation of hydrogen damage in steel has been carried out by destructive tests, such as metallographic analysis, tensile test, bending test and impact test [33], to assess the mechanical properties of materials. However, these tests are not helpful in getting online information on equipment damage. On the other hand, the investigation of Non-Destructive Testing (NDT) to evaluate hydrogen

Table 3
Classification of relevant studies included in the 1st stage of monitoring. Note that not all of them gave relevant information.

Inspection techniques	Hydrogen Damages			
	Hydrogen Embrittlement	High-Temperature Hydrogen Attack	Hydrogen-induced Cracking	Other
Ultrasonic testing	[33,36]	[36–41]	[42]	[35, 43]
Acoustic emission technique	[44]	[45,46]	[47]	[35, 48]
Electromagnetic	[49–51]	[49,51]	[49,51]	[52]
Other				[51, 53–55]

damages has raised attention among researchers because of the hydrogen ability to change the transmission properties of the permeated material [34] and the possibility of having portable equipment which enables online monitoring. NDT techniques analyse the response signal generated from the interaction of the material properties and state with some form of energy applied to specific areas or the entire component [35]. The material properties that are affected and therefore evaluated are geometric, mechanical, electrical, magnetic, acoustic, chemical, and thermal. In the specific case of hydrogen, its permeation leads to changes in ultrasonic, acoustic emission, eddy current, and other NDT signals [33]. Table 3 summarises and categorizes the studies included in this step of the literature review.

5.1.1. Ultrasonic techniques

Ultrasonic testing (UT) is one of the dominating techniques for hydrogen damage detection [43,56]. This technology is based on generating sound waves of frequency higher than the limit of human hearing, commonly between 0.5 and 25 MHz [35]. As the ultrasonic wave propagates through the material, the velocity of the wave, the attenuation, and the energy loss can be assessed to determine if any cracks or defects are present [52]. Taktsubo and Yamamoto [57] developed a method to detect bubbles and microcracks to evaluate the effect of hydrogen attack quantitatively. The results showed how using the pore response function can help assess the mean sizes and area fractions of the microcracks generated by the hydrogen attack. Krüger et al. [43] tested the ultrasonic spectral analysis on steel samples to detect minute cracks caused by hydrogen by comparing it with the metallographic analysis. The results confirmed the potentiality of this technique to detect hydrogen minute cracks, even if the localisation of the defect was not possible. Gajdacsi et al. [38] proposed a monitoring setup and signal processing technique to solve one of the drawbacks of ultrasonic analysis in detecting high-temperature hydrogen attack degradation. The methane voids change the ultrasonic properties of a degraded material, but the results are operator-dependent, and the testing reliability is subjective [37]. Le Nevé et al. [39] compared the effectiveness of various ultrasonic testing techniques in identifying high-temperature hydrogen attack. Phased Array (PA), Time-of-Flight Diffraction (TOFD), and the Total Focusing Method (TFM) were examined as different transducers which is responsible for converting the reflected signal into an electrical signal. Only TFM and TOFD 7.5 MHz allow the detection of early damages (defect size equal to 10 μm). Also in this study, the authors stressed the necessity of skilled technicians having a good understanding of the ultrasonic response in case of HTHA damage. The same result was found in a comparison of different techniques to detect hydrogen-induced cracking on carbon steels [42]. Total Focus Method is the most effective, enabling the detection of blisters and cracking 200 μm of size at 7.5 MHz; the Time-of-Flight Diffraction (TOFD) also has the potential to detect HIC affected zones, while the advanced ultrasonic backscatter technique has good performance only as an additional tool for the assessment of HIC (hydrogen-induced cracking) at specific already detected area.

In addition, Prueter et al. [40] highlighted the possibility of HTHA detection through Time-of-Flight Diffraction. On the other hand, according to Mc Govern et al. [41] the traditional ultrasonic testing can only detect HTHA when the cracks are already large enough that the danger of imminent failure is present. In fact, the lengths of the microstructural changes caused by HTHA damage are smaller than the wavelengths of the traditional technique. Therefore, the authors tested the capabilities of a non-linear ultrasonic approach on detecting HTHA in carbon steel pressure vessels, showing strong potential. Wu et al. [36] studied the changes in the wave behaviour on a 2.25Cr1Mo0.25V steel after the exposure to hydrogen. The signal emitted by the ultrasonic wave passed through the specimen, reflected back and received after a period of time. The results showed a variation of the period and the energy of the wave, and the decreasing of the peak of the echo, confirming the potential of this detection technique. Ye et al. [33] carried out another study on the same material also adopting an high-frequency longitudinal probe to analyse the ultrasonic echo signals and time frequency-domain feature of the specimens with different hydrogen contents. Again, the results demonstrate a relationship between the HE in the steel and the ultrasonic characterisation parameters and the possibility to emply this methodology to ensure the structural integrity of high-strength steels.

5.1.2. Acoustic emission techniques

Acoustic emission technique (AET) is based on the detection of sound waves generated by material subjected to an external stimulus (e.g., temperature, change in pressure, loads). The sources of the sound waves are local internal damages or micro-failure [35]. A sensor is responsible for converting the sound waves to electrical signals. The acoustic emission signal is characterised by the maximum amplitude (dB), the duration (μs), the rise time (μs), and the number of times where the amplitude exceeds the value of the threshold [48]. The main difference with other techniques is the possibility to detect only active defects, since it deals with a changes in a material.

Hlongwa et al. [45] indicated AET as one of the promising solution for real-time monitoring of equipment in contact with hydrogen, since its simplicity. Allevato [46] showed the AE signals from a high-temperature hydrogen attack damage on a catalytic reformer. The detected damages were also confirmed by ultrasonic scans, proving that AET is a powerful tool to screen components subjected to HTHA, even if it just allows to detect defects, requiring a follow-up inspection with other techniques to fully assess the damage and the possibility of continuing the service. Hydrogen embrittlement damage is also detectable trough AET: the initial embrittlement phase in a low-alloy high strength steel is characterised by low-amplitude signals (35–55 dB), while the rapid crack growth is marked with high-amplitude signals (60–100 dB) [44]. Another study carried out on high-strength steel proposes different range of amplitude signals: below 30 dB is associated with cracks initiation, 30–40 dB is related to cracks propagation and above 55 dB to steel failure [58]. Additionally, Djeddi et al. [48] performed experiments on high-strength steels exposed to corrosive atmosphere: the authors found out that the stress corrosion cracking process was associated with hydrogen absorption, and the difference in the AE signals corresponds to various degradation states. This study makes clear the increasing of amplitudes with the damage progess, despite not providing any defined ranges. Hydrogen assisted cracking in Ni-alloy 625+ was analysed through different techniques, including AET [47] during a slow strain rate test: in this specific case, the cumulative events did not show a spike during crack initiation and brittle failure.

5.1.3. Electromagnetism testing

This approach aims at establishing a magnetic field in the object under monitoring and detecting any defects based on the deviation of the generated magnetic field. Several types of electromagnetism tests

Table 4
Monitoring techniques to detect hydrogen degradation mechanisms according to the American Petroleum Institute [60].

Type of inspection	Hydrogen Damages	Notes
Visual testing (VT)	High-temperature hydrogen attack	Detection of damage underneath cladding or weld and only superficial cracks
Liquid penetrant testing (PT)	Hydrogen embrittlement	Detection of surface cracking
	High-temperature hydrogen attack	Detection of damage underneath cladding or weld
Magnetic particle testing (MT)	Hydrogen embrittlement	Detection of surface cracking
Phased array ultrasonic testing (PAUT)	Hydrogen embrittlement	Detect and size cracks
	High-temperature hydrogen attack	Detect surface and internal damages
Field metallographic replication (FMR)	High-temperature hydrogen attack	Detection of microvoids, microfissures and decarburisation. Only for examination of areas known to be damaged
Wet fluorescent magnetic particle (WFPT)	Hydrogen embrittlement	Detection of surface cracking
Shear wave ultrasonic testing (SWUT)	Hydrogen embrittlement	Detect and size cracks
Automated ultrasonic backsetter testing (AUBT)	High-temperature hydrogen attack	Detect microvoids, microfissures, not reliable
Angle beam spectral analysis (ABSA)	High-temperature hydrogen attack	Detect microvoids, microfissures, not reliable
Time of flight diffraction (TOFD)	High-temperature hydrogen attack	Detect surface and internal damages

Table 5
Technical performance requirements for hydogen sensors.

Parameter	Department of Energy for fuel cells [66]	Requirements by automobile manufacturers [65]	ISO 26142:2010 [69]
Measurement range	0.1 %–10 %	Up to 4 %, survivability at 100%	Up to 4 %, survivability at 100%
Detection limit		<0.1 %	<0.01 %
Operating temperature	−30 °C to 80 °C	−40 °C to 85 °C	−20 °C to 50 °C
Operating pressure		62–107 kPa	80–110 kPa
Response time	<1 s	<1 s	<30 s
Recovery time		<1 s	<60 s
Accuracy	5% of full scale	±5 % of reading	±25 % or 50 % depending on hydrogen concentration
Gas environment	Ambient air, 10 %–98 %	0–95 % relative humidity	20–80 % relative humidity
Power consumption		<1 W	
Lifetime	10 years	6000 h	
Interference	Resistance (e.g. hydrocarbons)		

are available.

Eddy Currents testing (EC) relies on the interaction of two magnetic fields. When the primary magnetic field, generated by a coil connected to an alternating current, gets in contact with a conductive material, a secondary field and a eddy/Foucalt currents are generated. In case of defects in the material, the induced electric field undergoes a deviation detected by monitoring the current and/or voltage [59]. Despite this technique has been successfully for several applications [35], Bellemare et al. [49] evaluated the feasibility of its usage to detect the presence of hydrogen in high-strength steels obtaining no significant results. The electric and magnetic properties of the material remained the same even with hydrogen concentration up to 1400 ppm. Khwaja and Paul [52] reviewed the main inspection techniques available, but they did not include eddy current in summarising the ones suitable for hydrogen damage. On the other hand, the experiments performed by Zhou et al. [50] on carbon alloy steels showed the potentiality of EC on characterising the hydrogen-induced performance degradation state of the material, since the increasing of the output signal amplitude corresponds to the increasing of the hydrogen embrittlement index.

Magnetic flux leakage (MFL) is based on the occurrence of a magnetic flux leakage in correspondence of a defect after a material with high magnetic permeability is exposed to a magnetic field. Khwaja and Paul [52] indicated this technology as suitable for detecting corrosion in hydrogen transportation pipeline. Magnetic inspection is also mentioned to be suitable to detect hydrogen-based failure by Shehata and El-Shamy [51].

5.1.4. Other relevant contribution

Reviewing the techniques appropriate for hydrogen-based failure in oil and gas pipelines, Shehata and El-Shamy [51] mentioned liquid die technique and continuous hydrogen flux monitoring in addition to others already described above.

In addition, going back a little in time, Gibbons et al. [53] tested the neutron tomography for the detection of low concentrations of hydrogen in aircraft components, very susceptible to hydrogen embrittlement. According to their results, neutron tomography is able to detect hydrogen in titanium engine blades with concentration around 500 ppm, or 200 ppm after an upgrading of the technology is implemented [54]. Another less recent study investigated the possibility of obtaining information about hydrogen damages in steels studying the effects of light [55].

5.1.5. Standards

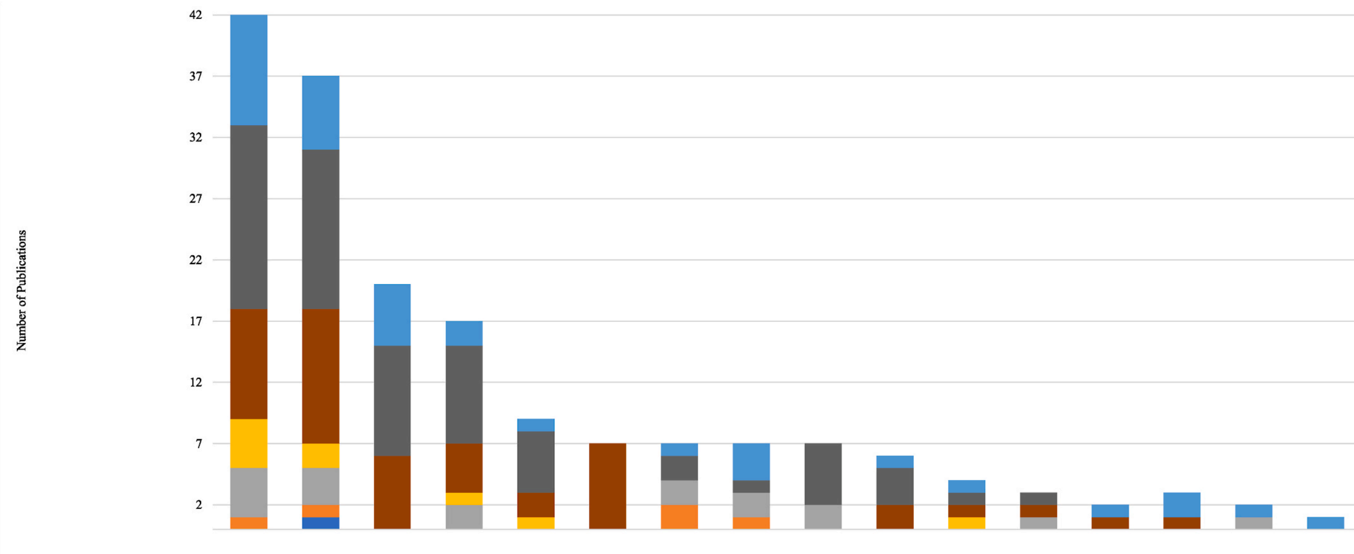
In addition, the American Petroleum Institute published a recommended practice to provide useful information about damage mechanisms for oil refineries, extendible to other industrial sectors [60]. For each damage mechanism, guidance for detecting and monitoring is provided. This document covers a remarkable number of material degradation processes, including hydrogen embrittlement and high-temperature hydrogen attack. Table 4 collects the damages detectable for each type of technique mentioned in the API RP 571 [60].

Additionally, the American Petroleum Institute developed a specific document for steels for hydrogen service at elevated temperatures, providing detailed information about high-temperature hydrogen attack [61]. According to API RP 941, ultrasonic testing is the most effective method to detect HTHA damage, but two or more methods are recommended to overcome the limitations of any single method.

5.2. Hydrogen leak detection

The detection and concentration measurement of hydrogen is crucial because of the safety-critical hydrogen properties described above. Over the years, a massive amount of studies on hydrogen sensors have been published in the relevant literature. Hydrogen sensing is essential in disparate fields: a few examples of sectors in which monitoring its concentration is important are chemical and petrochemical processes and metallurgical processes, such as aluminium production, semiconductor manufacturing, or the lighting industry [62]. For this reason, adding "safety" or "leak" as queries was essential to restrict the focus of this section to hydrogen sensors suitable for safety monitoring of the emerging hydrogen-based industry and infrastructure. In fact, the number of identified studies has dropped from more than 3500 to about 300 papers.

Before describing the main existing sensing technologies and the research trend, a brief overview of the key parameters for hydrogen detectors in safety applications is provided. For the first time,



	sensitivity	response time	selectivity	detection limit	recovery time	poisoning	power consumption	cost	stability	humidity resistance	temperature range	dimension	detection range	lifetime	ease of operation	safety
Optical	9	6	5	2	1	0	1	3	0	1	1	0	1	2	1	1
Resistance-based	15	13	9	8	5	0	2	1	5	3	1	1	0	0	0	0
Pd NPs-based	9	11	6	4	2	7	0	0	0	2	1	1	1	1	0	0
Metal-oxide semiconductor (MOS)	4	2	0	1	1	0	0	0	0	0	1	0	0	0	0	0
Electrochemical	4	3	0	2	0	0	2	2	2	0	0	1	0	0	1	0
Catalytic	1	1	0	0	0	0	2	1	0	0	0	0	0	0	0	0
Acoustic	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0

Fig. 5. Key parameters targeted by each publication selected from the database WoS CC, categorised based on the typology of the proposed sensor.

researchers at the Joint Research Council (JRC), Institute for Energy, in Netherlands, proposed a test protocol to test sensor performance specifically for automotive applications [63,64]. Later on, a comparison of commercially available sensors has been done to guide further research [65]. In parallel, other researchers from the National Renewable Energy Laboratory (NREL) reported a list of target specifications in accordance with the U.S. Department of Energy (DOE) and summarised the general performance specifications of the most common sensor technologies [66]. Both research groups highlighted the same key parameters: the measuring range, focusing, in particular, on the lower detection limit, the sensitivity, the accuracy, the response time, the recovery time, the resistance to environmental conditions, the power consumption, the lifetime and the interference [64–66]. Considering the specific application they are referring to in their study, Boon-Brett et al. [63] underlined the cross-sensitivity to carbon monoxide, as indicated by the automotive manufacturers. Subsequently, joint works by the two groups focused on the cross-sensitivity resistance towards CO, CO_2 and CH_4 [67] and towards SO_2, H_2S, NO_2, and HMDS [68], as they found to be the most common poison for hydrogen sensors. In parallel, ISO 26142:2010 [69] was developed for hydrogen sensors in stationary applications.

Table 5 summarises the technical requirements proposed by the Department of Energy, the results of a survey distributed by the Joint Research Centre to some car manufacturers to collect information about their needs, and the condition ranges in which hydrogen sensors should be tested according to the ISO 26142:2010: Hydrogen detection apparatus – stationary applications.

Disparate types of sensor technologies are available and studied in the literature: the most common are catalytic sensors, thermal conductivity sensors, electrochemical sensors, optical sensors, Pd-based sensors, resistance-based sensors, such as semiconductive metal-oxide sensors (MOx), acoustic sensors, and combined technology. Fig. 5 shows the key parameters targeted by different types of sensors, counting the studies included in the literature review that propose a technological improvement. For bibliographical references, Table 6 is available.

5.2.1. *Catalytic*

Catalytic sensors rely on the heat released by the hydrogen reaction with oxygen on the catalytic sensor surface; these sensors are available in two different versions. Pellistor type include two coils embedded in ceramic beads mounted in a Wheatstone bridge circuit. Electrical current passes through the coils causing them to reach high temperatures, suitable for the activation of the catalyst placed in one bead: the exothermic reaction between hydrogen chemisorbed on the catalyst surface and the oxygen adsorbed raise the temperature of the activated bead, changing the electrical resistance of the coil. In this way, the sensor signal is generated. The second bead serves only as compensation: there is not an active part and, in case of any other imbalance due to external factors, both the beads are influenced. Thermoelectric type also relies on the generation of an electrical signal as consequence of the catalysed exothermic reaction. The Seebeck effect consists of the detection of a voltage difference, as in equation (1), between two points of a conductor material when there is a temperature difference.

$$U = \alpha \bullet \Delta T \approx \alpha \bullet \left[k\, exp\left(-\frac{E_a}{RT}\right)\right] \bullet \Delta H \tag{1}$$

where α is the Seebeck coefficient, ΔT is the temperature difference generated from the combustion, $\left[const \bullet exp\left(-\frac{E_a}{RT}\right)\right]$ represents the reaction rate of combustion (E_a is the activation energy of the combustion reaction, R is the universal gas constant and ΔH is the heat of hydrogen combustion). The research for these sensors is mainly on lowering the power consumption to heat up the coils. A micro thermoelectric hydrogen sensor has been developed to meet the requirements for hydrogen refueling stations [71]. A more recent study focuses on the realising of a self-powered silicon-based thermoelectric sensor which not requires high temperature to be activated [72].

5.2.2. *Electrochemical*

Hydrogen in contact with sensing electrode raises electrochemical reactions which change charging transport or electrical properties. An extensive review on electrochemical hydrogen sensors has recently been

Table 6
Relevant studies selected from the database WoS CC categorised based on the key parameters targeted and the typology of the proposed sensor.

Typology	Key performance parameters															
	Response time	Recovery time	Low detection limit	Detection range	Sensitivity	Selectivity	Temperature range	Humidity resistance	Lifetime	Power consumption	Poisoning	Easy operability	Dimension	Cost	Stability	Safety
Acoustic	[70]															
Catalytic	[71]				[72]					[71,72]				[72]		
Electrochemical	[73–75]		[76,77]		[74–78]					[73,76]		[73]	[73]	[77, 79]	[77,79]	
Metal-oxide semiconductor (MOS)	[80,81]	[81]	[81]		[80–83]		[84]									
Optical	[85–87]		[88,89]		[86,90–94]	[88]			[95]	[96]		[85]		[85, 96]		[91]
Optical-fiber	[97,98]	[97]		[99]	[98,100–102]	[99,103,104]	[105]	[103],	[101]				[106]			
Pd-based	[106–115]	[111,112]	[107,112, 113,116]	[150]	[108,110, 111,115, 117–121]	[106,110,117, 119,121,122]	[123]	[124,125]	[125]		[109,110, 114,126]		[106]			
Resistance-based	[127–139]	[129,133, 136, 138–140]	[132,135, 137,138, 141–143]		[130,132, 136–139, 143–148]	[129,135,139, 143,145, 149–151]	[152]	[146,153]		[154,155]		[155]		[140]	[134,143, 147,149, 156]	
Other	[157–160]	[158,159]	[159,161]	[162]	[160,163, 164]	[158,163,164]					[165]		[160]		[166]	

proposed by Gorbova et al. [167]. Two main operating principles exist: amperometric and potentiometric sensors. An electrochemical cell containing a proton conducting as an electrolyte and two electrodes is the main part of the amperometric sensor. In the traditional version, the electrode receiving electrons from oxidised hydrogen is the working or sensing one, while the one reducing oxygen is the counter electrode. The flow of electrons from the sensing to the counter electrode generates an electric current. Most of the time, amperometric sensors also contain a reference electrode and a potentiostat to maintain the constant voltage. Another key component of the sensor to quantify the detected hydrogen is the diffusion barrier covering the sensing electrode, selecting the gas passage. Combining Farady's law and Fick's law, equation (2) correlates the measured current with the hydrogen concentration [168]:

$$i = 2qAD_{H2} \bullet \frac{\partial P_{H2}}{\partial x} \tag{2}$$

where i is the current in Coulombs/s, q is the electric charge of an electron (1.6×10^{-19} Coulombs), A is the area of the diffusion barrier in m^2, D_{H2} is the diffusion coefficient in m^2/s, P_{H2} is the hydrogen concentration in mol/m^3, and x is the thickness of the barrier in m.

A similar structure characterises the potentiometric sensors: two electrodes are embedded in an electrolyte. However, the measuring system is different since this type operates at zero current and relies on the potential difference between the sensing electrode and the other one once the electrochemical reaction occurring on the sensing electrode reaches the thermodynamic equilibrium. The evaluation of hydrogen concentration based on the potential difference is given by the Nernst equation, as in (3).

$$E = E^0 + \left[\frac{R\ T}{z\ F}\right] \bullet ln\left(\frac{a}{a_0}\right) \tag{3}$$

where E is the electrode potential, E^0 is the standard electrode potential, R is the universal gas constant, T is the absolute temperature, F is the Faraday constant, z is the number of electrons taking part in the reaction, a is the chemical activity of the analytes (proportional to hydrogen concentration), a_0 = is the activity of the reference.

Among the most dated studies on these sensors, Martin et al. [169] proposed a potentiometric sensor as a leak detector in the passenger cabin of a PEM fuel cell-powered vehicle: an active tin-doped indium oxide (ITO) as a sensing electrode and a silver reference electrode are attached to yttria-stabilised zirconia (YSZ) electrolyte showing fast response time and good selectivity versus H_2O and CH_4. In the alternative, Martin et al. [49] developed the same sensor using Platinum as the reference electrode for the same use, analysing the effect of the ITO thickness and looking for the optimal to reach high sensitivity and short response time. A few years later, Sekhar et al. [73] added to that sensor an integrated Pt heater to achieve precise operating temperature and decrease the power consumption. Another direction of research for this type of sensor is the development of Pt-free sensors because of the high cost and the use of solid electrolytes to stabilise the sensor response. Fauzi et al. [79] developed a potentiometric sensor using tungsten trioxide and reduced graphene oxide as the sensing electrode (WO3-rGO) and graphene oxide as a solid electrolyte. Gao et al. [77] suggested a sandwich device based on solid polymer electrolyte and titanium foam electrodes to enhance sensitivity and stability and to decrease cost and the low detection limit.

5.2.3. Resistance based

Hydrogen, as a reducing gas, changes the electrical properties of semiconducting metal-oxides. A metal-oxide film is usually applied to an insulating substrate and is heated up to 500 °C to facilitate the reaction with hydrogen and to remove the water formed from the reaction [62]. The change in the measured resistance is linear with the hydrogen concentration as in (4).

$$R(c) = a \bullet b \bullet c \tag{4}$$

where a and b are sensor-specific parameters and c is the hydrogen concentration. The performance of many materials has been investigated over the years, such as SnO_2 [142], ZnO [150], WO_3, Ga_2O_3, TiO_2, FeO, Fe_2O_3, MoO_3, WO_3 and In_2O_3 [170]. Testing different materials helped improve general performance, but recently, TiO_2-based sensors attracted attention due to their possibility of working at room temperature when modified with metal particles on their surface [137]. Zhou et al. proposed a hydrogen sensor based on (004) oriented anatase TiO2 thin films to ensure a room-temperature sensor with remarkable sensitivity, a shortened response time at the low H2 concentration detecting limit, and a short recovery time [138]. Hübert et al. [62] highlighted the interference from humidity as a disadvantage of this class of sensors; hence, Li et al. [146] developed a sandwich-structured $PtSn_x$-rGO-SnO_2, where the $PtSn_x$ modification reduces the optimal operating temperature of the sensors and improves their moisture resistance. At the same time, Tan et al. [153] inserted a Teflone membrane with high hydrophobicity to enhance the anti-humidity performance of SnO_2-based sensors.

In alternative to the metal-oxide layer, materials such as MoS_2 have been investigated as potential candidates for hydrogen sensing device applications [132,144,145,149]. Wadhwa et al. [136] proposed a Pt nanoparticles-sensitised MoS_2 sensor capable of detecting even 0.5 ppm hydrogen concentration without the necessity to be heated up and guaranteeing high selectivity over other gases and high sensitivity.

5.2.4. Work function based

Metal-oxide semiconductor (MOS) sensors have a triple-layer structure: a metal layer (M), an insulator layer, which usually is an oxide (O), and a semiconductor layer (S). This class of sensors relies on the change of the work function of the metal layer when hydrogen diffuses through the metal and adsorbs at the interface between the metal and the oxide layers. Three types of detection mechanisms are included: the metal-(insulator)-semiconductor Schottky diode (MS/MIS), the metal-oxide-semiconductor field effect transistors (MOSFET), and the metal-oxide-semiconductor capacitors. The Schottky-type sensors exploit the adjustments of the Fermi level when a metal is brought in contact with a semiconductor, even if there is a thin insulating layer. The alignment is by an amount equal to the difference between the two work functions of the materials, known as Schottky barrier height. Hydrogen atoms, after reaching the metal-semiconductor interface, are polarised and form a dipolar layer, which varies the metal work function and, consequently, the Schottky barrier height, causing a shift in the current-voltage characteristics at constant bias current, constituting the sensor response to the gas concentration. The choice of metal typically comes down to either palladium or platinum, while for the semiconductors various materials are proposed, such as GaN, SiC, InP [171].

The MOSFET sensors traditionally consist of a metal (gate) with catalytic properties towards the target gas, SiO2 as an insulator and Si as a semiconductor. Two regions of the semiconductor are ion-implemented, forming a source and a drain, which are connected through a current flow generated by the application of a positive bias to the gate. In this case, hydrogen atoms diffuse through the gate to the metal-insulator interface, forming a dipole layer that changes the metal work function and results in a voltage change in the sensor signal.

The metal-oxide semiconductor capacitor sensors include a thicker insulating layer than the previous ones to prevent current conduction and facilitate the build-up of charge on both sides. The absorption of hydrogen at the metal-oxide interface causes a capacitance shift proportional to the hydrogen concentration. As for the transistor, the most common semiconductor used for this type of sensor is silicon, and the metal is palladium; examples are Pd/SiO2/Si, Pd/TiO2/Si and Ni/SiO2/Si [171].

For the sake of clarity, the three working principles are not differentiated in this study, and the studies are categorised as metal-oxide semiconductors (MOS) to highlight the main performance parameters on which research is focusing to improve [80–82,84]. The small amount of studies included in this category leads to their exclusion from safety applications; for further investigation, reading of the extensive overview of work function-based sensors is suggested [171].

5.2.5. Optical

Some materials change their optical properties after absorbing hydrogen. The deposition of such materials on optical fiber results in a change of the optical signal, which can be the intensity, the phase, the wavelength, and the polarisation. Two factors are critical for optical sensors: the measurement techniques and the sensing materials. Recently, Bannenberg et al. [172] provided reflections on how the sensors performance are related to the choice of the material, focusing on metals. Palladium is the most common [62], but the synergy with other materials has been investigated. For instance, Liu and Li [100] reported an optical fibre hydrogen sensor with two pieces of Pd/Y alloy thin film to improve the sensitivity. Based on the measurement techniques, five types of sensors are identified: micromirror, interferometric, evanescent field, surface plasmon resonance (SPR), and Fibre Bragg Gratings (FBGs), [173]. Micromirror sensors consist of an optical fibre coated with a thin film of selected material (usually Pd), which acts as a chemical transducer through changes in its reflectivity on exposure to hydrogen [174]. A proper sensing material film expands on exposure to hydrogen, and the induced mechanical stress causes a phase change in the fibre light beam, detectable through an interferometer. Wang et al. [175] reported a Pd-based Fabry-Perot interferometry hydrogen sensor.

A sensing layer coating an optical fibre in contact with hydrogen changes the refractive index and attenuates the evanescent field, a peculiar electromagnetic field formed at the core of the optical fibre. This phenomenon can be detected as an alteration of transmittance correlated to the gas concentration and is exploited in the evanescent field hydrogen sensors [173].

A similar structure characterises the surface plasmon resonance sensors, having an unclad fibre core coated with gold, silver, or palladium as sensing material generating the SPR effect, electromagnetic waves that are sensitive to changes in the structure of the metal surface. Again, hydrogen varies the sensing material refracting index depending on its concentration; hence, the SPR spectrum of the sensor changes the resonant wavelength or the resonant angle of incident light wave or the intensity of the reflected light [176].

Gratings coated with sensitive material (Bragg gratings) generate heat or expansion by reacting with hydrogen, causing a variation in the wavelength of the optical fibre in which they are included [173]. The detection of this variation is the working principle of the FBG sensors. Recently, the combined use of platinum and WO_3 has been very attractive in increasing the sensitivity of these sensors [102,177,178], addressing the disadvantage highlighted by Wang et al. [173], who classified them last in the sensitivity ranking of optical sensors (interference > SPR > evanescent-field > micromirror > FBG).

5.2.6. Palladium nanoparticles-based

Researchers have investigated and are still investigating palladium due to its sensitivity to hydrogen, considering its very high hydrogen absorption capacity. Recently, Pd nanoparticles (NPs) have attracted a lot of interest: the increased surface-to-volume ratio leads to a higher effective surface available for interaction between Pd and hydrogen molecules, improving sensor performance. When hydrogen comes in contact with Pd-based materials, the optical or electrical properties are structurally affected. For this reason, the literature offers studies on Pd NPs-based, either electrical or optical sensors [179]. Le et al. [120] proposed a superfast PdAualloy@ZnO core–shell nanoparticles (CSNPs) sensor. Wu et al. [127] developed an ultrafast Pd-decorated sodium titanate nanoribbons to outperform the state-of-the-art of electrical sensors even at room temperature. Darmadi et al. [126] applied the characteristics of poly-methyl methacrylate (PMMA) to develop a sensor

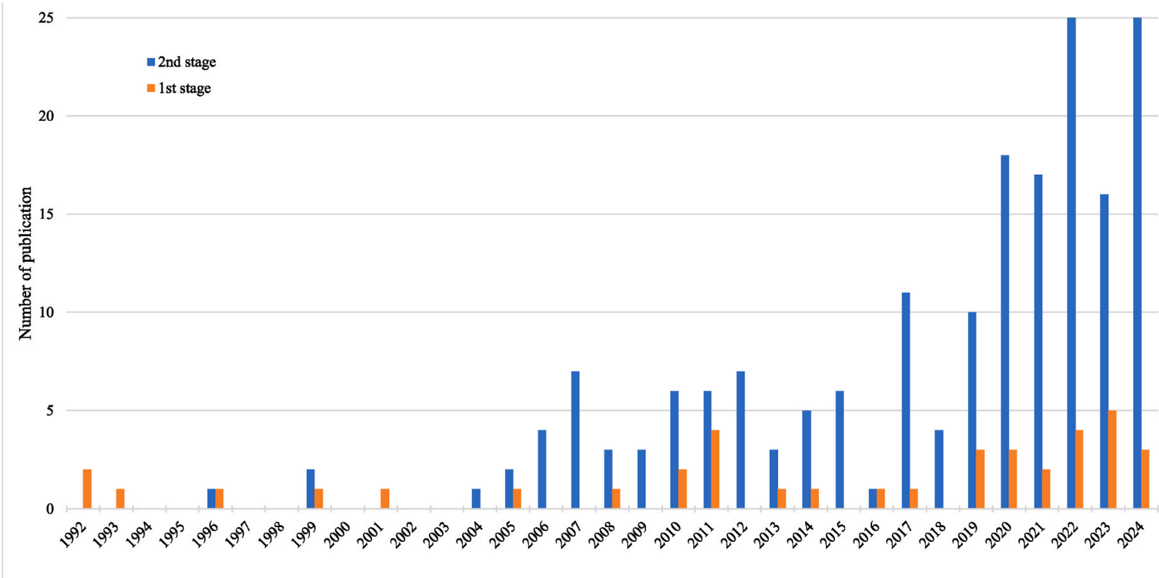


Fig. 6. Publication year of the papers selected from the database WoS CC.

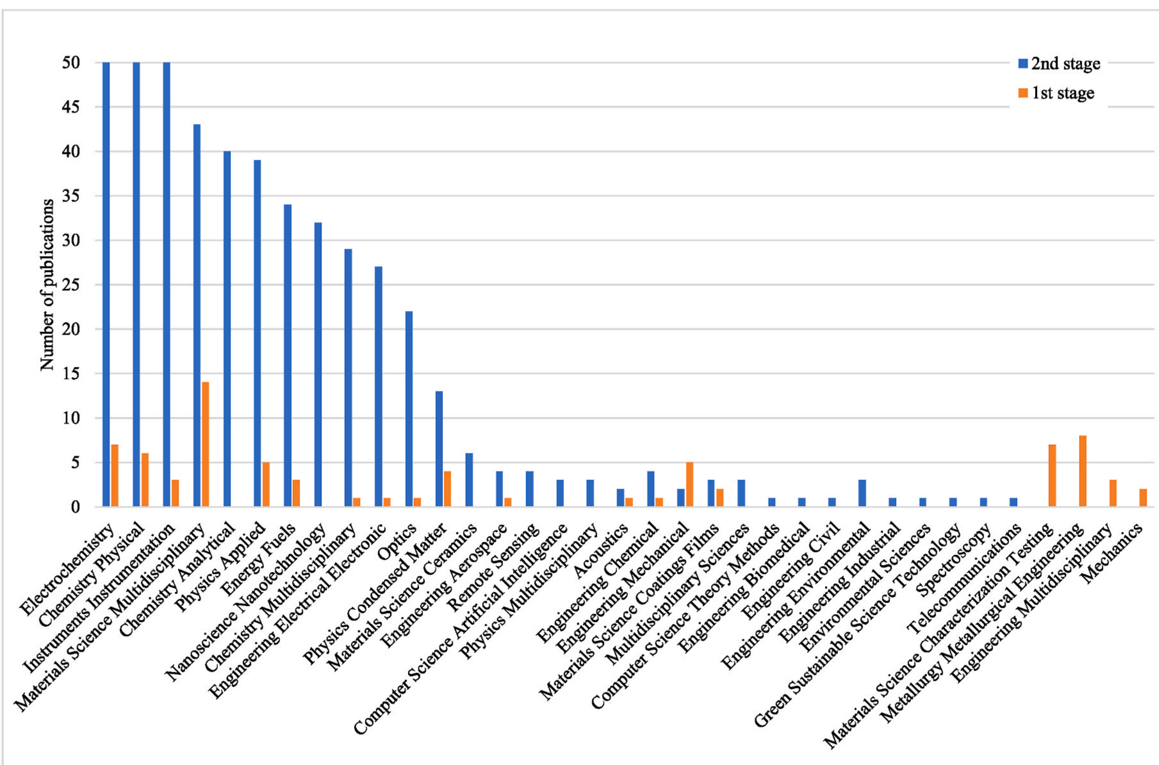


Fig. 7. Records from WoS CC filtered by topical area.

resistant to CO poisoning. Few years later, Östergren et al. [108] fixed the small response time due to the slow H2 diffusion caused by the PMMA covering, using amorphous fluorinated polymer poly(4, 5-difluoro2,2-bis(trifluoromethyl)-1,3-dioxole-*co*-tetrafluoroethylene) (Teflon AF) to embed Pd NPs. In addition, Nugroho et al. [110] embedded AuPd alloy nanodisks in PTFE (polytetrafluoroethylene) and PMMA to increase the resistance to gas interference and to decrease the response time.

5.2.7. Acoustic

Hydrogen interaction with a piezoelectric material changes the properties of the acoustic waves. This principle is the basis for the surface acoustic wave sensors (SAW), which consist of a piezoelectric substrate with two sets of interdigital transducers responsible for generating the acoustic wave from an applied electrical input and for converting the wave back into an electrical output. The acoustic wave passes through a sensing material, and the changes are detected by the output signal. Recently, Cui et al. [180] published a detailed review of this class of sensors, underlining the crucial role of the sensing material:

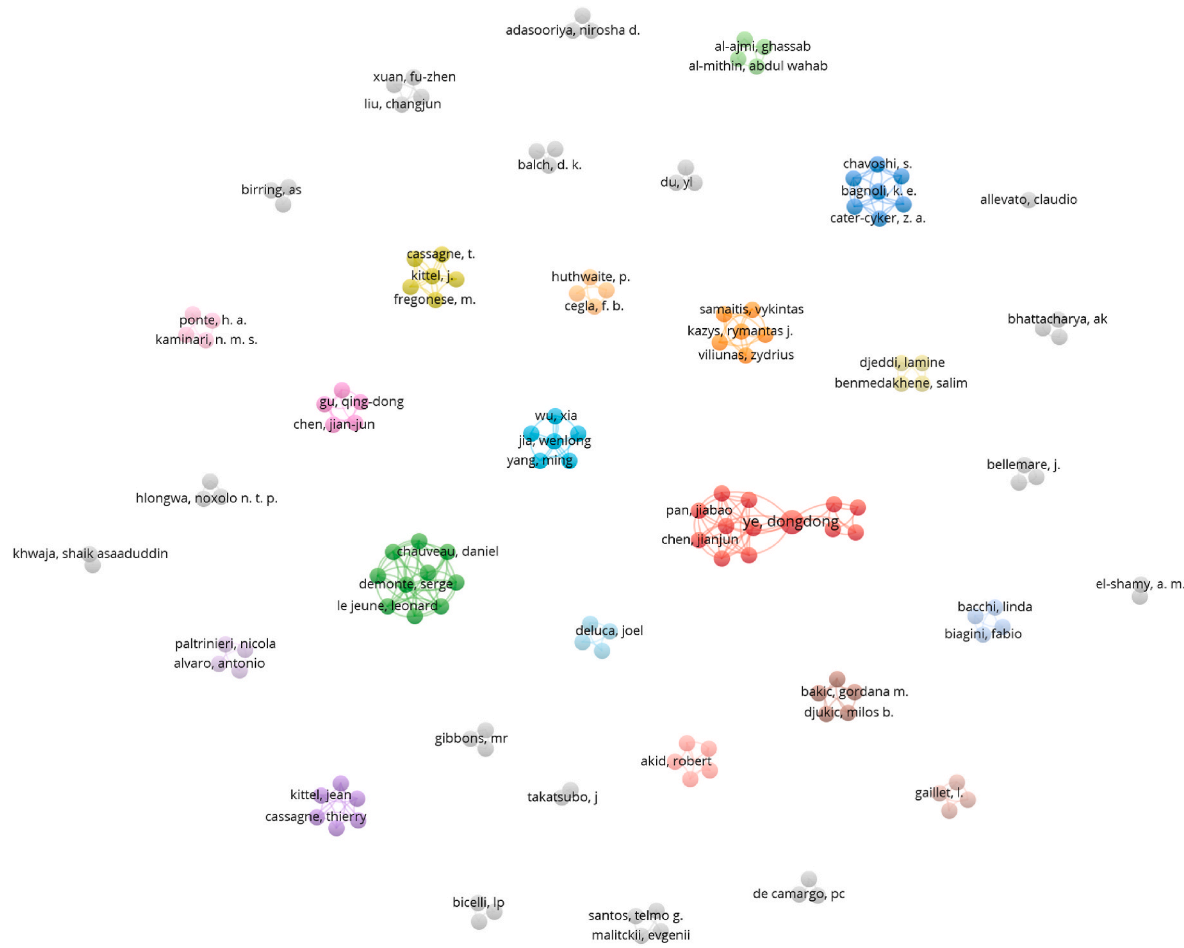


Fig. 8. Co-authorship network map for 1st monitoring stage weighted on the number of publications.

Pd, Pd-based, Pt–Al_2O_3, and Pt-based Indium oxide are only a few examples. However, another critical part is the sensing device: Abe et al. proposed a digital quadrature detector, for instance Ref. [70]. to increase the response time.

For the sake of completeness, even if not present in the considered studies, ultrasonic gas leak detectors have to be mentioned as non-traditional devices. All the above-mentioned devices are concentration-based and rely on their contact with hydrogen. For this reason, Fecarotta and Janowski [181] stressed the necessity of a new concept of hydrogen sensors capable of responding to the high-frequency ultrasound emitted by all high-pressure gas leaks. In this way, hydrogen does not have to reach the sensor, and this is an important advantage for outdoor applications, where more time is required to accumulate hydrogen in enough amount to receive the signal.

5.3. *Hydrogen flame detection*

The detection of hydrogen flames is the final stage of monitoring, and it is considered a tool to take action as quickly as possible. Compared to other fuels, the low ignition energy of hydrogen increases the possibility of ignition. The increasing likelihood of having jet fires, flash fires, or fireballs [182] rises concerns because of their direct or indirect impact on humans, the environment, structures, and properties [6]. Also, hydrogen flames are remarkably weaker than those from other comparable fuels, and they are only visible at reduced light levels in most cases [183]. In addition, smoke and soot are almost absent when hydrogen fires burn, which is positive in terms of environmental impact but makes detection more difficult. For these reasons, hydrogen detections can not count on visual surveillance or optical techniques to spot smoke particles, which are the two less expensive devices used for hydrocarbons [184].

Thermal heat detectors rely on the heat radiation emitted by the hydrogen flame; a proper sensing material is selected to react to changes in temperature. For instance, in a fusible element heat detector, a fusible element melts and creates a short on the sensing circuit, generating a signal. Distributed optical fibre is an innovative and effective technology and relies on measuring heat distribution along the optical fibre cable using the fibre itself as a sensor. The Raman effect is used to detect heat: when an optical pulse travels through the fibre, some of it scatters and returns to the transmitting end, where the data is processed. The intensity of Raman scattering indicates the temperature along the cable [185]. Brillouin backscatter is also used for temperature detection as an effective alternative to Raman scattering [185]. Bimetallic sensing is another static heat detection method and relies on the different expansion rates of metal strips [184]. The drawback of these sensors is related to the low radiant heat emitted by a hydrogen flame compared to hydrocarbon fires, which makes their location a big challenge.

Light detectors are the most valid solutions for hydrogen applications, even if they are more complex and expensive. Based on the chemical composition of the burning material, the frequency spectrum of a flame will be in the visible, ultraviolet (UV), or infrared (IR) region. Arens et al. [186] clarified the intensity of the hydrogen flame spectrum and discussed how errors in literature were made because of wrong calibration. Hydrogen produces a very strong ultraviolet signal [187]. Oktavianto et al. [188] realises a single-chip smart UV sensor that, besides detecting the presence of the hydrogen flame, generates information about the flame related to its location, size, moving speed, moving

Table 7
Top five publications on the 1st stage of monitoring by number of citations.

Author	Country	Affiliation	No. of citations	Year
Djukic M.B. Bakic G.M. Zarvcic V.S. Sedmak A. Rajicic B.	Serbia	University of Belgrade	121	2016
Ramadan S.	France	Institut National des sciences Appliquees de Lyon	97	2008
Gaillet L.		Laboratoire Central des Ponts et Chaussees (LCPC)		
Tessier C.		Laboratoire Central des Ponts et Chaussees (LCPC)		
Idrissi H.		Institut National des sciences Appliquees de Lyon		
Wu X.	China	Southwest Petroleum University	54	2022
Zhang H.		Southwest Petroleum University		
Yang M.		PipeChina group Western pipeline co.		
Jia W.		Southwest Petroleum University		
Qiu Y.		Shandong Haiyun Asphalt co.		
Lan L.		Southwest Petroleum University		
Smanio V.	France	Total SA	29	2011
Kittel J.		IFP Energies Nouvelles		
Fregonese M.		Université de Lyon, INSA-Lyon		
Cassagne T.		Total SA		
Normand B.		Université de Lyon, INSA-Lyon		
Ropital F.		IFP Energies Nouvelles		
Martelo D.	UK	University of Manchester	22	2019
Sampath D.	UK	University of Manchester		
Monici A.	Italy	ETS Sistemi Industriali Srl		
Morana R.	UK	BP exploration operating Company limited		
Akid R.	UK	University of Manchester		

direction, and spreading status without a computer system. However, since UV detectors can generate false alarms, a combination of ultraviolet (0.18–0.26 μm range) and infrared technologies (2.5–3.0 μm range) have been developed (UVIR sensors). Multi-spectrum Infrared (MIR) flame detectors using a combination of IR sensor filters and software analysis to detect flames while minimising false alarms, have also been developed [189].

6. Bibliometric review

The quantitative analysis of the state-of-the-art monitoring stages is presented in this section through co-authorship patterns, collaboration network maps between different authors, citation networks, and recurring keywords. The selection of the queries and the inclusion and exclusion criteria resulted in a total of 38 studies for the monitoring of hydrogen-material interaction, 186 papers for leak detection and 6 publications for flame detection. Considering the very limited number of results, the third stage of monitoring was excluded from this analysis.

Fig. 6 shows the time distribution related to the two research topics, clarifying that no restrictions on the publication year were adopted. It is evident, especially for the second stage of monitoring, how the interest in this topic has greatly increased in the last years.

This trend reflects the growth rate of scientific publications [190], and, even more interesting, it follows the publication years trend of the general attention hydrogen projects [191]: a fluctuation between 2007 and 2012, an increase until 2017, and the explosion in the last years.

Fig. 7 shows the distribution by topical area, including only the categories defined by WoS CC; each publication belongs to more than one topical area. Some topical areas are in common between the two stages, particularly Materials Science Multidisciplinary, Chemistry Physical and Electrochemistry.

Maps of co-authorships provide information about various research groups and their connections. Fig. 8 shows the co-authorship network map for the first monitoring stage, weighted by the number of publications. The node size is dependent on the number of publications, and it clearly shows that only one author has two publications [33,50]. Dongdong Ye from Anhui Polytechnic University is the connection between researchers from China Jiliang University, Ningbo Special Equipment Inspection and Research Institute, Wuhu Institute of Technology, East China University of Science and Technology, and Nanjing University of Aeronautics and Astronautics. However, he does not compare in Table 7, which shows the top five papers, including the authors and their respective affiliations, and the year of publication, being a relevant parameter when comparing papers based on the number of citations. In this table, there is no distinction in the number of documents for each author because all of them are included in this literature review with one publication.

Fig. 9 shows the co-authorship network map for the second monitoring stage, weighted by the number of publications. Considering the number of studies included, the filter of at least two publications and ten citations was applied to print this picture. Table 8 shows the first ten authors with the highest number of publications in the field, specifying their number of documents and citations, as well as their country and affiliation. Not ranking the studies based on the number of citations cuts out Thomas Hübert, the author of the first relevant review on hydrogen sensors.

The red cluster in Fig. 9 represents the joint synergic research studies of two institutions: the Joint Research Centre, representing the European Union, and the National Renewable Energy Laboratory, a federally funded research and development centre sponsored by the Department of Energy of the US. As already mentioned in Section 5.2, they separately focused their attention on identifying the key parameters and providing guidelines for automotive applications. Later on, from 2014, they combined their efforts to investigate and give guidelines on sensor selectivity.

The other big cluster in Fig. 9 is made of Iwan Darmadi and Ferry Anggoro Ardy Nugroho, respectively, from Chalmers University of Technology and Vrije Universiteit Amsterdam, coupling their efforts on developing plasmonic optical sensors using nanomaterials. The presence of several small clusters is consistent with the existence of a variety of classes of hydrogen leak detectors, as highlighted in the previous sections.

Figs. 10 and 11 show the co-citations network maps respectively for the material degradation monitoring and for hydrogen leak detection. A limit of five citations was decided to print the first picture, and a limit of ten citations to collect the second one. Of greater interest is Fig. 12 which shows the very scarce connection between the two stages of monitoring.

Finally, the co-occurrence network map was generated for the keywords with a minimum of five occurrences in the considered papers. Fig. 13 shows the map of the most co-occurrent keywords present in the studies considered in the SR as relevant for the first monitoring stage: "hydrogen embrittlement", "high-temperature hydrogen attack", "stress corrosion cracking", "hydrogen damage", "failure", "assisted cracking", "hydrogen permeation", "fatigue crack growth rate" are related to material damages. Additionally, "acoustic emission", "non-destructive testing", "inspection", and "ultrasonic" are related to monitoring techniques. On the other hand, Fig. 14 shows the map of the most co-occurrent keywords present in the records considered in the SR as relevant for the second monitoring stage: "h2 sensor", "hydrogen detection", "hydrogen safety", and "leak" are certainly among the most frequently mentioned. Then, "fast response", "sensitivity", "selectivity", "temperature", "size", "selectivity", "performance", and "sensing performance" are related to the performance parameters of the sensors. A few keywords are related to different classes of sensors, such as "fiber optic",

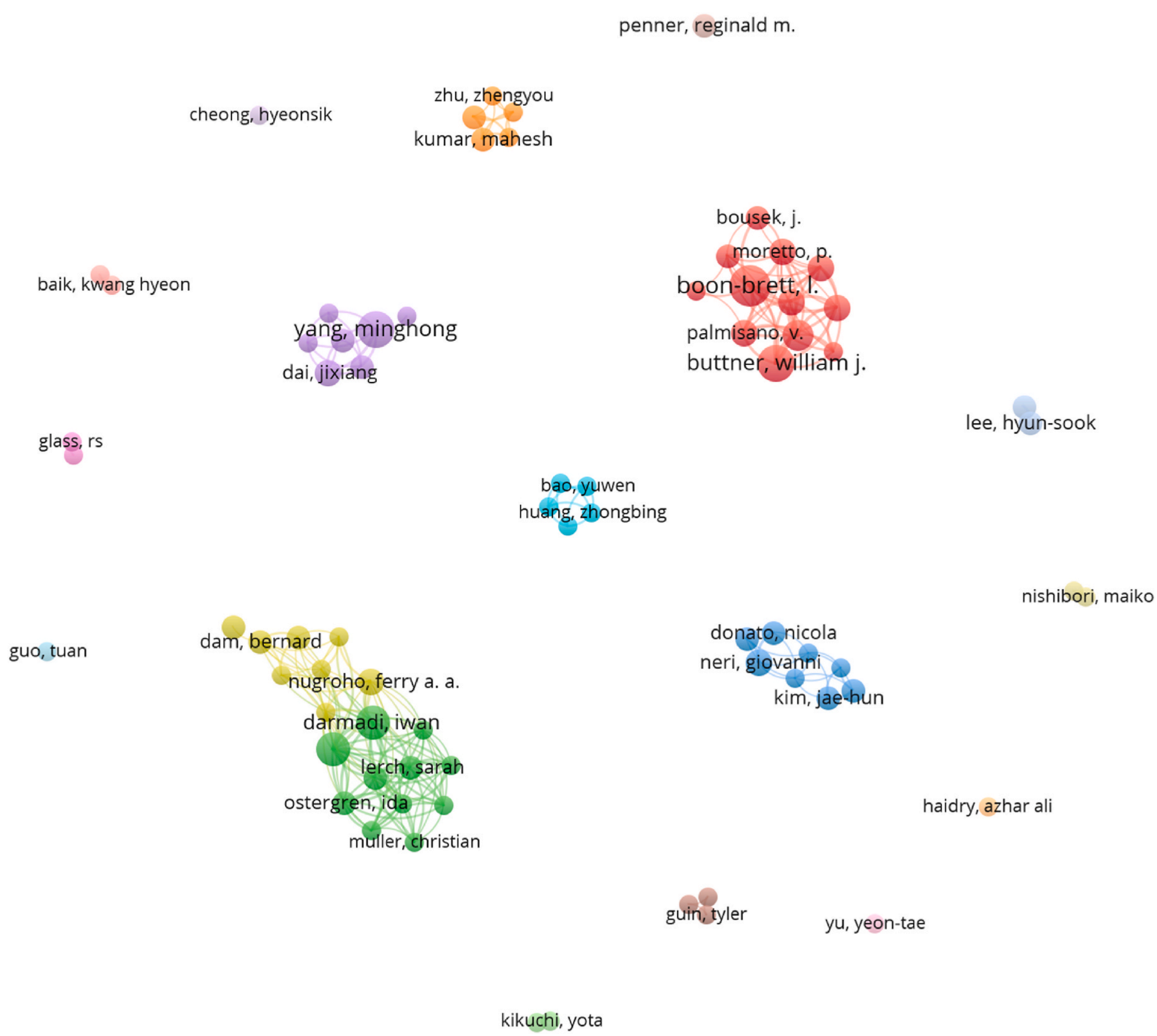


Fig. 9. Co-authorship network map for 2nd monitoring stage weighted on the number of publications.

Table 8
Top ten authors by number of published papers and number of citations.

Author	Country	Affiliation	No. Of documents	No. Of citations
Boon-Brett L.	The Netherlands	Joint Research centre	10	1659
Buttner W.	USA	National Renewable energy Laboratory	7	515
Yang M.	China	Wuhan University of technology	7	228
Darmadi I.	Sweden	Chalmers University of technology	7	551
Langhammer C.	Sweden	Chalmers University of technology	7	551
Rivkin C.	USA	National Renewable energy Laboratory	6	499
Moretto P.	The Netherlands	Joint Research centre	6	303
Neri G.	Italy	University of Messina	5	144
Javahiraly N.	France	Université de Strasbourg	5	140
Burgess R.	USA	National Renewable energy Laboratory	5	91

“fiber bragg grating". Moreover, some keywords are specific to the sensing materials: "palladium", "graphene oxide", SnO_2'', "TiO_2'', "oxide", "palladium nanoparticles", "thin-film", "nanowire".

7. Interpretative review

The combined analysis of the hydrogen properties and the bow tie diagram identified three monitoring stages to better manage the safety and operability of hydrogen systems.

Preventing the critical event by inspecting the material conditions after the exposure to hydrogen and eventually maintaining the equipment is defined as the first monitoring stage in this study. The 38 studies included in the review clearly show that there is no optimal technique to detect hydrogen-induced damage. Ultrasonic, electromagnetism and acoustic emission testing resulted in the most mentioned techniques in the literature. Each of them presents some limitations.

- electromagnetism testing is efficient only with specific materials;
- acoustic emission techniques are effective in screening the active defects but usually require additional techniques to assess the damage thoroughly, and it is not even mentioned in the recommended practice by the American Petroleum Institute.
- the ultrasonic technique is suggested to detect high-temperature hydrogen attack, especially in the Time-of-Flight Diffraction version, and hydrogen embrittlement through the analysis of the changes of the ultrasonic wave. The disadvantage is the need for highly qualified personnel to avoid problems with wrong interpretation of inspection results.

The slight increase in publications in recent years is a promising result to expect that new inspection technologies will be proposed or that existing ones will be improved. Hence, La Nevé et al. [39] declared that Total and other French partners are investing in finding an effective way to detect and identify HTHA degradations early and guarantee the integrity of its industrial assets. Similarly, Shehata and El-Shamy [50] emphasised the importance of developing more accurate monitoring and inspection techniques to detect hydrogen-induced cracking. This encouragement for further investigation will hopefully also lead to an increase in collaboration between research groups, which is currently lacking, as evident from the results of the bibliometric analysis.

It is essential to underline that this study focuses on showing the efforts made by researchers to develop suitable technologies to detect possible failure caused by hydrogen damage early. However, the commercially available non-destructive testing (NDT) tools are primarily designed to detect general material defects, such as cracks, rather than explicitly tailored for hydrogen-related damages. Lately, hydrogen embrittlement has received the most attention due to the desire to retrofit existing pipelines for hydrogen transport. Indeed, among the studies under analysis, the most recent publications focus on detecting hydrogen embrittlement. For instance, Abiru et al. [192] stressed the possibility of using their developed testing in automated systems to ensure accurate and continuous pipeline integrity monitoring. A remarkable number of studies were found for the second monitoring stage, even after filtering only the studies addressing hydrogen safety.

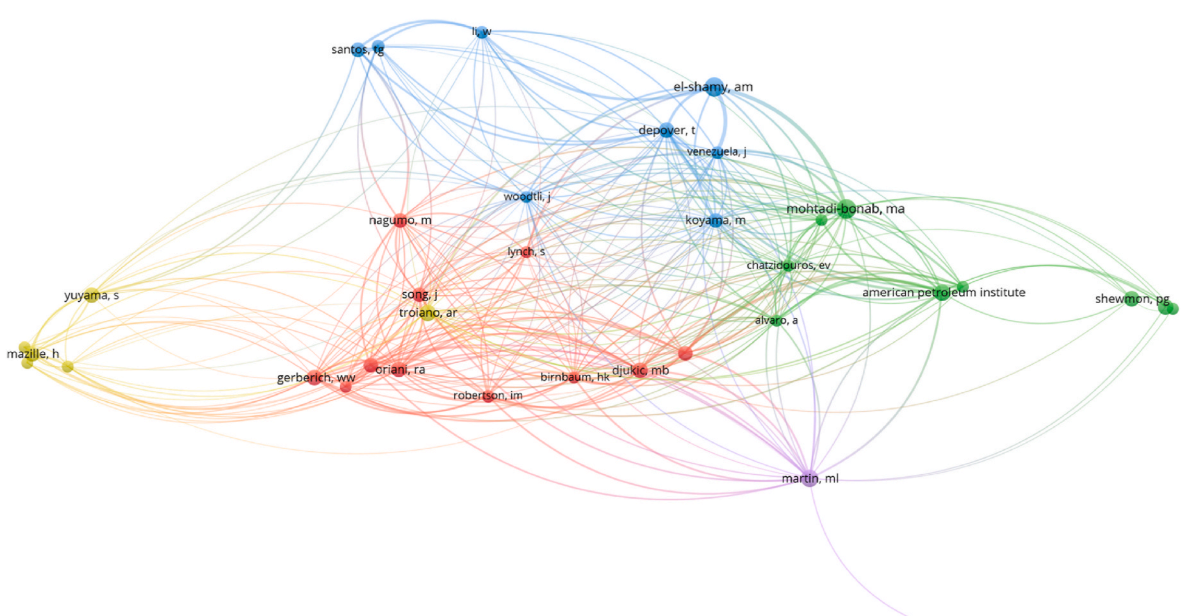


Fig. 10. Co-citations network map for 1st monitoring stage weighted on the number of citations.

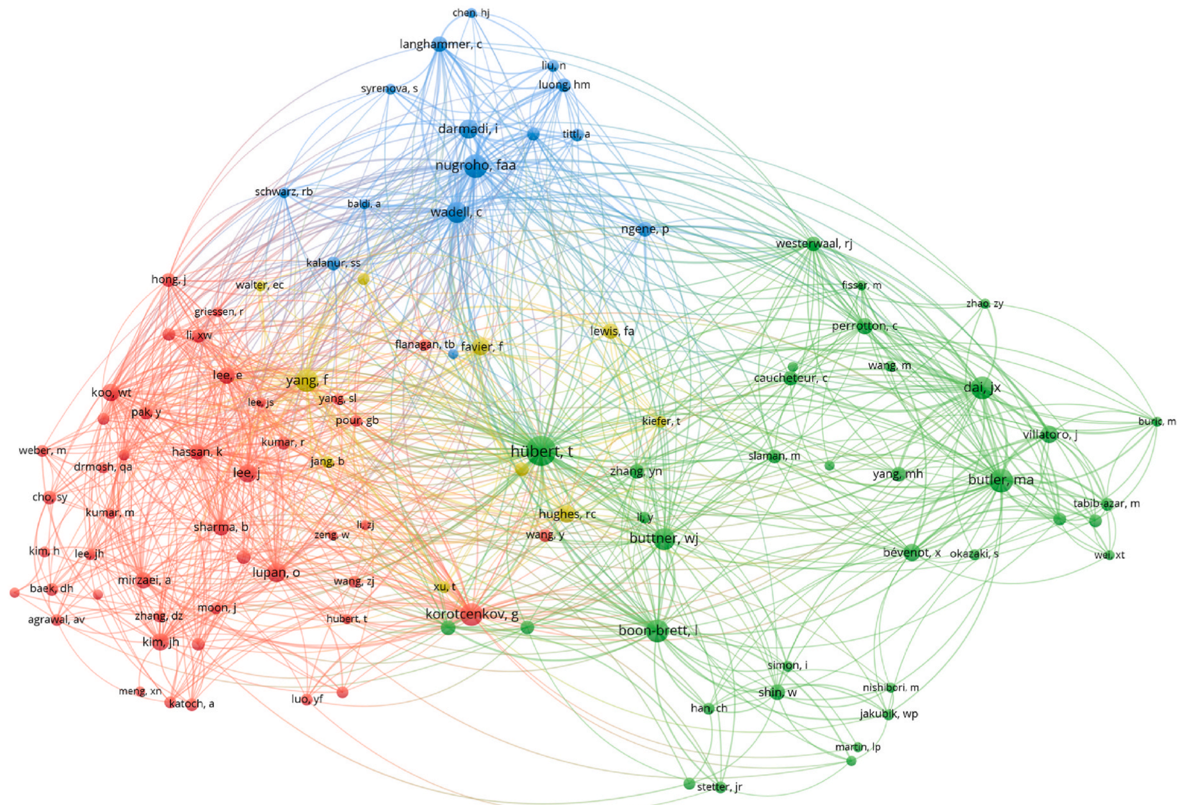


Fig. 11. Co-citations network map for 2nd monitoring stage weighted on the number of citations.

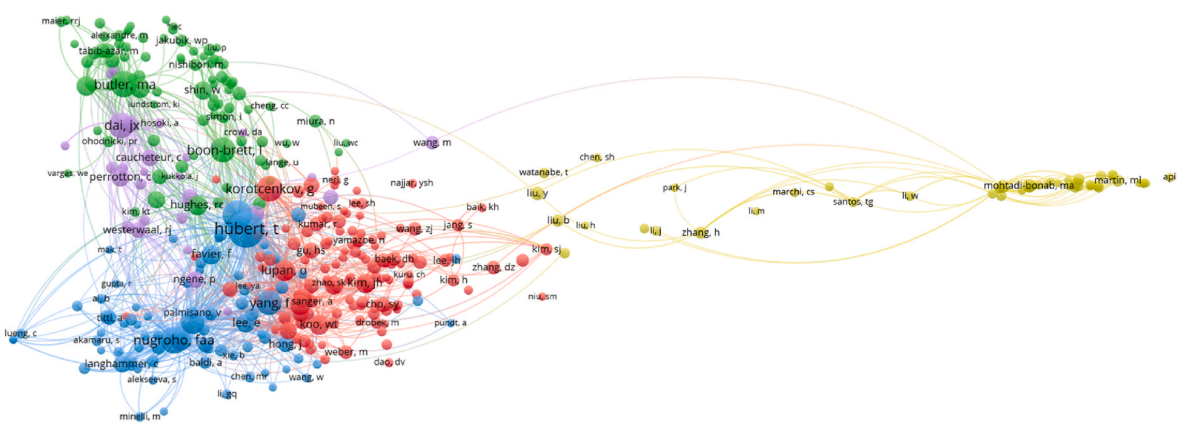


Fig. 12. Co-citations network map weighted on the number of citations. Both degradation monitoring and hydrogen leak detection results are considered in this case.

The increasing number of publications in this field traces the penetration of hydrogen in several sectors and the research attention on safety issues. Among the selected publications, the ones providing technological improvements were organised based on the type of sensor and the improvement sought. The addressed parameters are consistent with the ones considered relevant by the Department of Energy for fuel cells [66], the pioneering study carried out by Boon Brett et al. [65] about the requirements for automobile manufacturers and the ISO 26142:2010 [69]. The feature receiving the most attention is sensitivity, the calculation of which depends on the type of sensor and response time. The detection range and limit were considered separately to enhance the fact that detecting very low concentrations is more important for hydrogen safety applications. Catalytic and electrochemical sensors are very common as hydrogen detection systems. Still, in this study, only a few publications were linked to these types of sensors because they require high temperatures to work, introducing another critical safety issue. Indeed, for these sensors, the main improvement that researchers are aiming for is decreasing the power consumption and the operating temperature [193]. Nasir et al. [91] highlighted this issue by proposing a highly sensitive and extremely safe optical hydrogen detector, emphasising that it is safer than conventional electrical detectors, presenting an explosive hazard. The bibliometric analysis of the second monitoring stage through the co-authorship network map shows independent and unconnected clusters. The bigger ones correspond to the collaboration between the JRC and NREL, providing guidelines for hydrogen safety sensors, and the cooperation between different departments of Chalmers University of Technology and other universities, such as Delft University of Technology, to develop improved optical Pd-based sensors. On the other hand, the co-citation map shows the awareness of researchers of the existence of many classes of sensors and the guidelines from the JRC

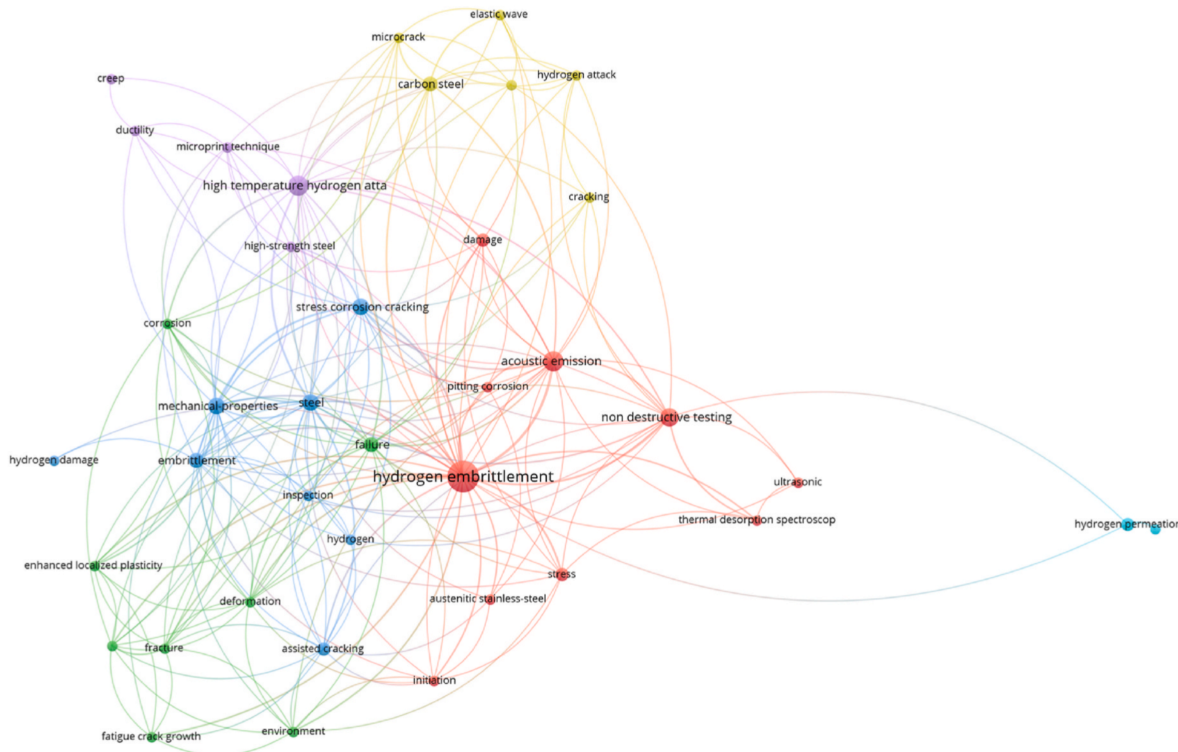


Fig. 13. Co-occurrence map for 1st monitoring stage for the keywords.

and NREL.

The advancing sensing technologies highlighted in this study are followed by several proposals from sensor manufacturers. In 2015, the Federal Institute for Materials Research and Testing (BAM) provided the H2sense database, a list of different manufacturers showing the type and some characteristics [194]. More recently, Qanbar and Hong [195] showed that most commercially available hydrogen sensors in the market are either electrochemical, catalytic or resistance-based, providing a list of seven manufacturers. The increasing research efforts on other types of sensing technologies that this study emphasised will certainly penetrate the market. It is also essential to mention that selecting an appropriate hydrogen sensor for a specific application depends on the particular needs. Still, the safety-critical hydrogen properties make the response time and the low detection limit the two most important parameters to consider in the selection. In addition, it is worth emphasising that the market for outdoor applications, such as monitoring the refueling stations, is monopolised by ultrasonic sensors that do not need to come into contact with hydrogen concentrations.

Very few publications were found about the last stage of monitoring. Conventional fire detectors rely on the detection of other combustion products. Many studies, in fact, were excluded from the SR because hydrogen is only mentioned as a combustion product. Considering the hydrogen characteristics, UVIR and MIR flame detectors are preferable and commercially available. The exclusion of this stage from the bibliometric analysis was due to the limited amount of information that could have been obtained.

Conversely, the combined quantitative analysis of the first and second stages provided a valuable result. The co-citations network map in Fig. 12 confirmed what was stated in the introduction about the lack of an extensive review that considers the available tools for monitoring the emerging hydrogen-based industry. Furthermore, no study mentions how to use data collected from the monitoring stages in a visionary way. It is clear that the first monitoring stage serves to track the fitness of the component for hydrogen service and, eventually, take action with maintenance activities if required, following the preventive, condition-based maintenance approach. In parallel, hydrogen leak detectors allow for the fastest possible intervention but do not prevent the cause. Once the leak is detected, the component should be checked and possibly repaired or replaced. This attitude complies with the corrective maintenance approach, which is the least advisable when dealing hazardous substances [196]. Nevertheless, maintenance activity aims at guaranteeing quality, safety, and productivity. For this reason, the industry is shifting to a predictive maintenance approach [197], especially the data-driven version, which relies on statistics, pattern recognition, artificial intelligence, or machine learning algorithms. Recently, some studies [7,198,199] highlighted the benefits and the limitations of using the Risk-Based Inspection and Maintenance program for hydrogen technologies. Once established that risk is the combination of probability of failure and consequence of failure, prioritising these activities on higher-risk components is an already well-established methodology for the chemical and petrochemical sectors. Still, it requires adaptation to be applied to hydrogen systems, as comprehensively explained by Campari et al. [200]. Cooperation between safety and materials experts has been recently suggested and is ongoing to avoid inaccurate calculations of the probability of failure of hydrogen components.

Complying with the need to update and have this methodology ready as soon as possible and following the trend of the overall maintenance field, a data-driven approach should be investigated. In this scenario, data from the three monitoring stages should be collected and shared among industries, feeding the component reliability database proposed by Growth et al. [201] and enhancing the RBM approach. Collecting data from the results of the non-destructive tests is valuable in increasing information on material degradations; gathering and sharing information on hydrogen leakages helps in conducting statistical analysis and directly updating the probability of failure of a component. However, keeping combined data from flame detection and leak detection is also valuable in updating the probability of ignition, which is an input parameter for the overall risk assessment.

8. Conclusion

This study reviewed the critical issues of hydrogen safety,

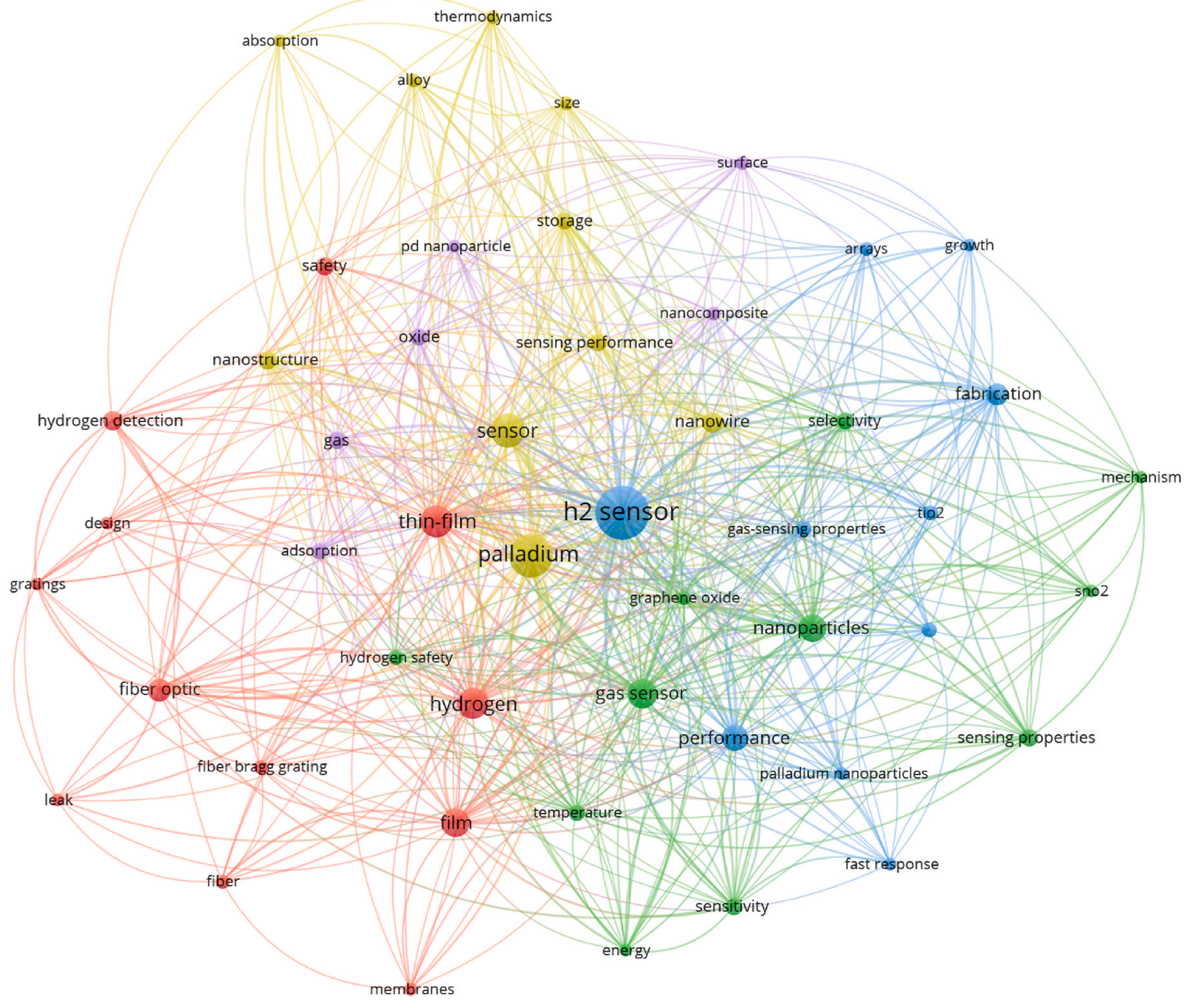


Fig. 14. Co-occurrence map for 2nd monitoring stage for the keywords.

emphasising the necessity for a robust monitoring framework to ensure the safe and efficient integration of hydrogen technologies across various sectors. This analysis, combined with the standard risk management approach, identified three critical monitoring stages: preventive material inspection, real-time hydrogen leak detection, and combustion monitoring. Each stage was reviewed, and appropriate queries were selected to collect data from the Web of Science Core Collection (WoS CC) database. The results showed the unique challenges and opportunities for each monitoring phase, underscoring the need for continuous technological improvement. The degradation monitoring highlighted the current limitations in existing techniques, such as ultrasonic, electromagnetic, and acoustic emission testing: each one has some limitations that require further research and innovation. The slight increase in recent publications suggested a growing interest and investment in improving these technologies. The promise of collaborative efforts among some researchers indicated a promising trend towards developing more accurate and efficient tools for detecting hydrogen-induced damage. The second monitoring stage is crucial to prevent the potential ignition of hydrogen leaks and further harm. The review identified various sensor technologies without indicating the best solution because each has drawbacks. The bibliometric analysis revealed a fragmented research landscape, but the performance parameters to be improved are shared, and all research groups strive for the same improvements. The investigation of the flame detection stage showed that it is underexplored even though conventional fire detectors are inadequate for the unique properties of hydrogen combustion.

The statistical analysis showed an evident absence of collaboration between the research groups studying the techniques for material degradation monitoring and the leak detection tools, proving that there is still no overall monitoring program specific to hydrogen services. In line with the objective of this study, the results highlighted the imperative for a holistic and interdisciplinary approach to hydrogen safety. The potential use of information from the analysed monitoring techniques for planning maintenance activities, which is essential to ensure a certain level of system safety, was also discussed. Integrating data from monitoring stages into a preventive maintenance framework offers an ambitious approach to enhancing hydrogen safety. Moreover, this concept and the application of a risk-based methodology could represent the breakthrough in overcoming concerns about the shift to the hydrogen industry.

CRediT authorship contribution statement

Giulia Collina: Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Marta Bucelli:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization. **Nicola Paltrinieri:** Writing – review & editing, Supervision, Project administration, Methodology, Funding acquisition.

Declaration of competing 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.

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List of acronyms

AET	Acoustic emission technique
ABSA	Angle beam spectral analysis
AUBT	Automated ultrasonic backsetter testing
CFD	Computational fluid dynamics
DRI	Direct reduced iron
EC	Eddy current
FBG	Fibre bragg gratings
FMR	Field metallographic replication
FCEVs	Fuel cell electric vehicles
HTHA	High-temperature hydrogen attack
H2	Hydrogen
HE	Hydrogen embrittlement
HSC	Hydrogen stress cracking
HIC	Hydrogen-induced cracking
HDs	Hydrogen-induced damages
IR	Infrared
PT	Liquid penetrant testing
LOC	Loss of containment
LPI	Loss of physical integrity
MFL	Magnetic flux leakage
MT	Magnetic particle testing
MOx	Metal-oxide
MOS	Metal-oxide semiconductor
MOSFET	Metal-oxide semiconductor field effect transistors
MIR	Multi-spectrum infrared
NDT	Non-destructive testing
PA	Phased array
PAUT	Phased array ultrasonic testing
PMMA	Poly-methyl methacrylate
PTFE	Polytetrafluoroethylene
PEM	Proton exchange membrane
RAMS	Reliability, availability, maintenance and safety
SWUT	Shear wave ultrasonic testing
SAW	Surface acoustic wave
SPR	Surface plasmon resonance
TOFD	Times of flight diffraction
ITO	Tin-doped indium oxide
TFM	Total focusing method
UT	Ultrasonic testing
UV	Ultraviolet
VT	Visual testing
WFPT	Wet fluorescent magnetic particle
YSZ	Yttria-stabilised zirconia

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