# A Review of Palladium-Based Fiber-Optic Sensors for Molecular Hydrogen Detection

Susana F. Silva, Luís Coelho, Orlando Frazão, José L. Santos, and F. Xavier Malcata

***Abstract*—Palladium-based fiber-optic sensors have been one of the most promising configurations for hydrogen sensing. In the latest decade, fiber-optic sensors have indeed earned a strong interest owing to their ability to monitor molecular hydrogen at specific spatial points—either as a sensing tip device or in large areas via multiple sensing regions distributed along the optical fiber.**

**This review focuses on the various types of optical fiber hydrogen sensors, containing specifically palladium as active element. Three distinct working principles are described, viz. interferometric-, intensity-, and fiber grating-based sensors; their characteristics and sensing performances are critically overviewed.**

***Index Terms*—Fiber grating, hydrogen detection, intensity, interferometry, optical fiber sensors.**

## I. Introduction

HYDROGEN is one of the cleanest energy sources: it can easily be obtained from water via electrolysis or photolysis (as happens with photosynthesis); and upon plain burning it turns into water, so it does not contribute to global warming via production of $CO_2$. Therefore, it has been used in many chemical processes in various fields, e.g., propellant in aerospace rockets, and fuel for fuel cells and explosion engines in automotive devices. However, liquid hydrogen is extremely volatile and flammable, and can even be explosive: at room temperature and pressure, hydrogen exhibits, in fact, a wide explosion range, from 4%(v/v) $H_2$ (i.e., lower explosive limit, LEL) up to 75%(v/v) (i.e., upper explosive limit, UEL), coupled with a low ignition energy (0.02 mJ) and a large flame propagation velocity. In addition, it diffuses very fast and easily, so it may eventually leak out of its container due to its reduced molecular size.

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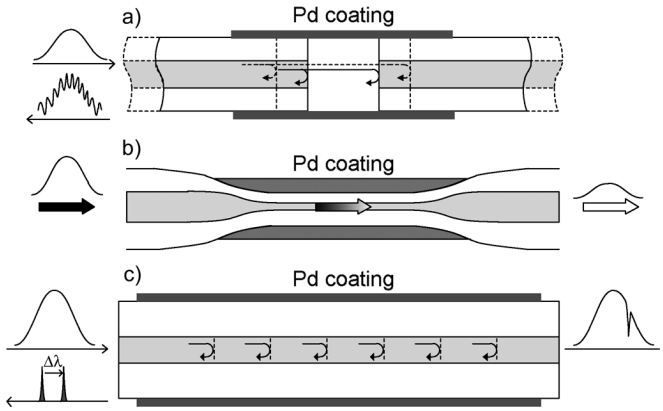


Fig. 1. Generic form of optical-based $H_2$-sensors, and underlying operating principles: (a) interferometric-based; (b) intensity-based; and (c) fiber grating-based sensors.

Therefore, control of $H_2$ concentration is of the utmost importance, which implies development of accurate and robust sensors—with sensitivity to $H_2$ as low as ppb levels.

To date, several hydrogen sensors have been described, based on distinct physicochemical principles: metal oxide semiconductor sensors [1], electrochemical sensors [2], thermoelectric sensors [3], surface acoustic wave sensors [4], and optical sensors [5], among others. The latter usually resort to optical fibers as a basis, and may in turn be classified according to their working principle: (a) interferometric-based; (b) intensity-based; or (c) fiber grating-based sensors. A schematic representation of these three types is available as Fig. 1.

Interferometric sensors were the first type of hydrogen sensors reported in the literature, yet intensity-based sensors have been the most common in terms of practical applications; in particular, evanescent wave absorption-based intensity sensors, relying on Pd-coated, etched or tapered optical fibers, have been the most usual configurations, owing to their good performance in terms of response time (usually below 1 min). On the other hand, fiber grating-based sensors that are wavelength-sensitive to $H_2$ concentration constitute an emerging sensing technology.

This review focuses only on the most promising $H_2$-sensors, i.e., those based on optical fiber devices containing Pd, and specifically aimed at $H_2$ detection below LEL; however, other types of $H_2$-sensors have been developed, e.g., for monitoring $H_2$ leaks in fuel cells in cars and aerospace applications, for measuring $H_2$ in harsh environments where concentrations are of the order of ppm, or for controlling $H_2$ under extreme temperatures ranging from $-100$ to 500 °C.

In the following sections, both the fundamental phenomena arising upon interaction of H and Pd, and the various types of

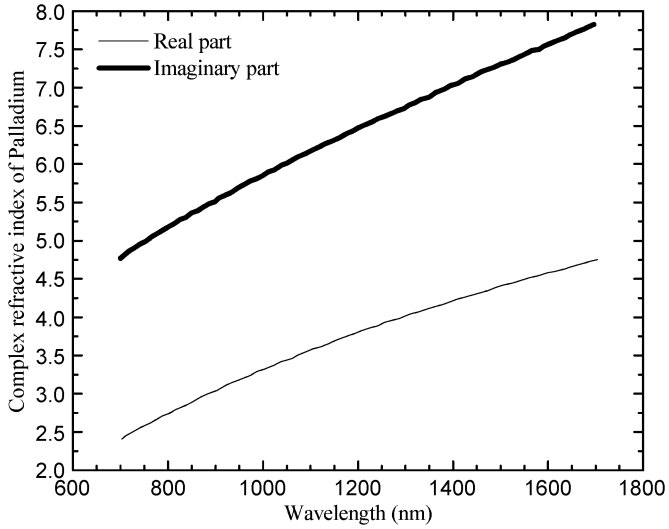


Fig. 2. Typical variation of the complex refractive index of palladium as a function of wavelength [10].

optical fiber sensors available are reviewed; the latter depart from general considerations to comprehensive focus on the three distinct configurations referred to above. A number of general conclusions and specific final remarks are presented in the last section.

## II. Concept of Palladium-Based Hydrogen Sensing

When Pd is exposed to molecular hydrogen, $\mathrm{H_2}$ is dissociated into atomic hydrogen—i.e., $\mathrm{H_2}$ becomes 2H, on the Pd surface; this phenomenon is characterized by a high dissociation rate [6]. Because hydrogen atoms diffuse easily through a Pd film, the metal is rapidly converted into palladium-hydride $(\mathrm{PdH}_x, 0 \leq x \leq 1)$; note that hydrogen does not undergo molecular bonding to Pd, instead it remains in close proximity and is even held inside the lattice by van-de-Waals forces acting on the H atom and accounted for by several Pd atoms in its vicinity. The composition of $\mathrm{PdH}_x$ depends reversibly on the partial pressure of hydrogen gas, and can be related to a crystallographic phase transition represented by "pressure-composition isotherms" [7]. Therefore, hydration of palladium leads to crystallographic changes associated with an increment in lattice parameters. The Pd film consequently expands, and the volume density of free electrons consequently decreases—which cause reduction of both the real and imaginary parts of the Pd complex refractive index [8]. Bévenot *et al.* [9] proposed a simple empirical equation to describe this effect, in which the complex permittivity of the $\mathrm{PdH}_x$ film, $\varepsilon_{PdHx}$, is expressed as

$$\varepsilon_{PdHx} = h \times \varepsilon_{Pd} \tag{1}$$

where $\varepsilon_{Pd}$ is the complex permittivity of the hydrogen-free Pd film, and $h$ is a nonlinear function that decreases with $\mathrm{H_2}$ concentration and takes values below unity; the typical variation of the complex refractive index of palladium is illustrated in Fig. 2 [10].

Usually, a Pd-based optical device is an optical fiber structure previously coated with a Pd film, ranging in thickness from a few nm to tens of $\mu\mathrm{m}$. When the device is exposed to $\mathrm{H_2}$, the expansion of the Pd film induces mechanical stress in the optical fiber, so two responses may occur: (i) changes of the real part of the Pd-complex refractive index—which produce an effective phase alteration of the guided light, according to the elasto-optic effect that can be detected using interferometric techniques or (ii) changes of the imaginary part of the Pd-complex refractive index—which cause alterations in absorption of the guided light that can be detected via monitoring the intensity of the optical signal.

Several optical fiber configurations will be described and discussed below encompassing specifically $\mathrm{H_2}$ detection, which rely on either (or both) of these sensing concepts.

## III. Topologies of Palladium-Based Optical Fiber Sensors

As described above, three sensing modes have been taken advantage of in designing Pd-based optical sensors: effects monitored by using interferometry or intensity, and Pd-sensitive fiber gratings. Pd-based interferometric optical fiber sensors rely on the assumption that, upon exposure to $\mathrm{H_2}$, the associated change in physical dimensions of the Pd moiety induces mechanical stress into the optical fiber device, thus changing the effective optical path length.

However, intensity-based sensors based on evanescent wave absorption have to date been the most common ones in practical use. Their sensing mechanism lies upon the evanescent field interaction between the surface of an etched or tapered optical fiber and the Pd film previously coated onto the device—thus leading to intensity variations of the transmitted optical signal, when exposed to $\mathrm{H_2}$. Another related example is reflectivity-based intensity sensors, where the fiber tip is coated with Pd; once again, the degree of change in absorption of the guided light will be detected via monitoring the intensity of the reflected (rather than transmitted) optical signal.

Finally, fiber gratings are periodic structures aimed at refractive index modulation in the core of an optical fiber, and characterized by a constant modulation period. The sensing mechanism of Pd-coated optical devices is based on mechanical stress induced by adsorption of $\mathrm{H_2}$ onto the Pd coating—which shifts the Bragg wavelength, depending on the prevailing $\mathrm{H_2}$ concentration. On the other hand, the sensing mechanism of Pd-coated, long-period grating devices is mainly based on coupling between the cladding modes and the evanescent waves. Therefore, Pd-coated fiber Bragg gratings rely on mechanical expansion of the Pd coating, whereas Pd-coated long-period gratings rely on change of the imaginary part of the Pd complex refractive index instead.

### A. Interferometric-Based Optical Fiber Sensors

Butler [11] presented the first optical fiber sensor designed specifically for $\mathrm{H_2}$ assay. The sensing element was a 3 cm-long single-mode fiber, on the surface of which a 10 $\mu\mathrm{m}$-thick Pd layer was deposited: a 100 Å-thick titanium layer had also been deposited between the Pd layer and the surface of the optical fiber to enhance adhesion. This sensing fiber was one of the arms of a Mach–Zehnder interferometer: when the coated fiber was

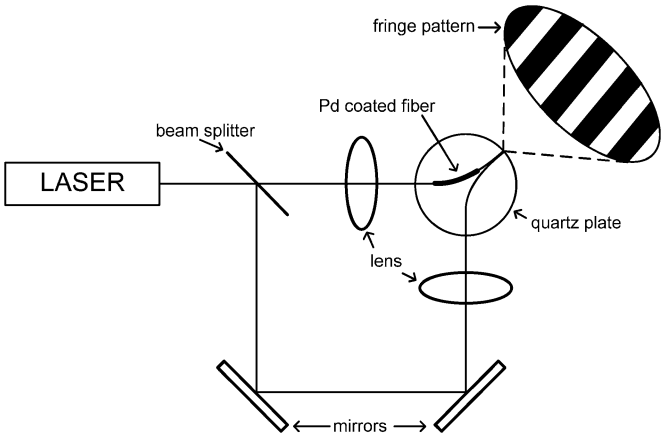


Fig. 3. Schematic of fiber-optic hydrogen sensor based on the Mach–Zehnder interferometer [11].

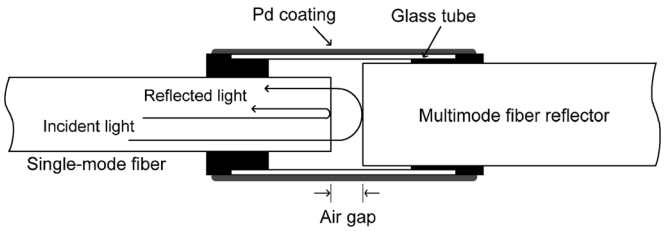


Fig. 4. Schematic of fiber-optic hydrogen sensor based on the Fabry–Perot interferometer [14].

exposed to $H_2$, the Pd film expanded, and the induced mechanical stress caused its effective optical path length to change. This experimental configuration is depicted in Fig. 3.

This sensor was able to detect a minimum of 0.6%(v/v) $H_2$ in a nitrogen atmosphere, with a response period below 3 min at room temperature. Subsequent improvements of this technique [12] encompassed a 28 cm-long single-mode fiber coated with a 100 Å-thick Ti layer, followed by a 1 $\mu$m-thick Pd layer. This thinner sensing head permitted the sensitivity of $H_2$ in $N_2$ to be as low as 2 ppb (with an upper limit of 2%(v/v)), and to exhibit a response time of only ca. 30 s.

Farahi *et al.* [13] proposed an optical fiber sensor for measurement of $H_2$ partial pressures in a gaseous environment, in which the primary sensing element was a 0.06 m-long, 0.5 mm-diameter Pd wire attached to a single-mode fiber using a quick-setting epoxy resin. Said sensing fiber was the arm of an (all-fiber) Michelson interferometer. This sensor would detect variation in $H_2$ pressure in a nitrogen atmosphere, covering the range from 0.54 to 100 Pa—with response times not above 8 min, at room temperature.

Zeakes *et al.* [14] inserted a single-mode fiber in a glass alignment tube opposite to a large diameter multimode fiber reflector, so as to form a low-finesse Fabry–Perot sensing cavity characterized by a 50 $\mu$m-air gap; such a device was then coated with a 2 $\mu$m-thick Pd film, which served as active sensing element. When the device was exposed to $H_2$, the expansion of the Pd film induced variations in the cavity length, and consequently changed the effective optical path length. This sensing head is shown in Fig. 4. The response time of this sensor to 0.5%(v/v) $H_2$ in $N_2$ was less than 5 s, and it presented a maximum sensitivity of 35 ppm.

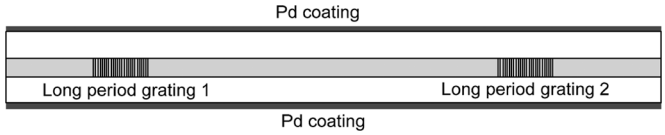


Fig. 5. Schematic of fiber-optic hydrogen sensor based on two fiber-optic long-period gratings [17].

Therefore, Pd-based interferometric fiber-optic sensors proved effective in $H_2$ detection—with short time responses and good sensitivity to low concentrations; however, the complexity of the devices based thereon made them relatively unattractive for $H_2$ detection in routine practice. This is why the pursuit of this type of approach for $H_2$-sensing was revisited only more than a decade later—as reported by Maciak *et al.* [15], regarding a fiber-optic Fabry–Perot interferometer relying on the fiber tip concept. The sensing head was based on a layered structure deposited on the tip of a multimode fiber core, rather than along the outer surface of a single-mode fiber—as previous researchers did. The first fiber tip mirror was the boundary between the fiber and a $TiO_2$ (or $NiO_x$) layer; this interface exhibited indeed a very high dielectric contrast. The 10 nm-layer of Pd deposited on the top of it acted simultaneously as a catalyst—thus ensuring the dissociation of molecular hydrogen; and the second mirror was a multimode fiber, with modulated sensor properties. The active sensing layer of the transition metal (Ti or Ni) oxide was deposited onto the tip of the multimode fiber, and was characterized by 62.5 $\mu$m- and 125 $\mu$m-diameters for the core and the cladding, respectively; the film thickness of $TiO_2$ and $NiO_x$ was ca. 145 and 155 nm, respectively. Both $Pd/TiO_2$ and $Pd/NiO_x$ fiber-optic tip sensors were then tested with various concentrations of $H_2$—ranging from 0.5 to 3%(v/v) in synthetic air. The first sensing tip underwent a significant increase in optical power at 2%(v/v) $H_2$; at this concentration, the response time was ca. 4 min, and another ca. 1 min was required for signal regeneration. However, the second sensing tip produced better results: a significant increase in the optical signal was recorded for 3%(v/v) $H_2$ in air, the response time was just ca. 30 s and signal regeneration required less than 40 s.

In the same year, Ianuzzi *et al.* [16] developed a Fabry–Perot sensor based on a 150 nm-thick Pd-coated cantilever, carved out of the cleaved edge of a single-mode fiber; upon expansion of the Pd film in the presence of $H_2$, the cantilever suffered displacement that produce a change in the effective optical path length owing to the air cavity variation. The optical signal exhibited a significant change by 240 s, when submitted to 5%(v/v) $H_2$ in Ar.

Kim *et al.* [17] proposed, on the following year, a hydrogen sensor based on Mach–Zehnder fiber-optics, which was formed by two identical Pd-coated long-period gratings; each had a 500 $\mu$m-period, and was characterized by a length of 20 mm and a center-to-center distance of 50 mm. A 50 nm-thick Pd film was uniformly deposited over the cladding of a single-mode fiber; the total Pd-coated sensing length was 70 mm. This sensing head is shown in Fig. 5.

When Pd was exposed to $H_2$, a change in the boundary condition was induced between the cladding surface and the Pd layer,

TABLE I
INTERFEROMETRIC-BASED OPTICAL FIBER SENSORS

| Author, Ref | Concentration range | Sensing head | Time response |
|---|---|---|---|
| Butler, [11], [12] | 0.6%/(2ppb – 2%) | 100 Å Ti, 10 μm Pd, 30 mm/28 cm long SMF | < 3 min/< 30 s |
| Fahari, [13] | 0.54 – 100 Pa | Palladium wire with 0.06 m length and 0.5 mm ϕ + SMF | < 8 min |
| Zeakes, [14] | 0.5% 33 ppm sensitivity | SMF and MMF Fabry-Perot cavity 2 μm Pd, 50 μm cavity length | < 5 s |
| Maciak, [15] | 0.5 – 3% | MMF Fabry-Perot tip with 145 nm $TiO_2$ and 10 nm Pd | 4 min (2%) |
| | | MMF Fabry-Perot tip with 155 nm $NiO_x$ and 10 nm Pd | 30 s (3%) |
| Iannuzzi, [16] | 5% | Cantilever on cleaved edge of SMF 150 nm Pd | 240 s |
| Kim, [17] | 4% | LPG Mach-Zehnder interferometer coated with 50 nm Pd | 8 min |
| Ma, [18] | 1% | SMF-30 μm-long MMF fiber tip | -- |

as well as in the effective index difference between the core and the cladding modes; as a consequence, the effective optical path length of the interferometer varied. When submitted in particular to 4%(v/v) $H_2$ in $N_2$, the interference peak shifted 2.3 nm within an 8 min time, followed by signal saturation.

More recently, Ma *et al.* [18] described a Fabry–Perot device based on a fiber tip heterostructure. The sensing head was in this case a single-mode fiber spliced to a 30 $\mu$m-long multimode fiber section; a resonator layout was implemented at the tip, including vibration arms and a chromium/gold-coated center reflector. A submicrometer layer of Pt was then coated on the vibration arms of the resonator, with the purpose of serving as catalytic heater upon $H_2$ exposure: the heat generated locally raised the resonator temperature, thus leading to an acoustic resonance frequency shift. When the sensing tip was exposed to 1%(v/v) $H_2$, the resonance frequency at 1.7 MHz shifted 1.17 kHz; the associated sensitivity was estimated to be better than 0.1%(v/v).

An overview of the various types of interferometric-based optical fiber sensors for hydrogen detection is presented in Table I.

### B. Intensity-Based Optical Fiber Sensors

The first hydrogen optical fiber sensor based on the intensity concept used a fiber tip, and was originally reported by Butler [19]; the sensing device was a 10 nm-thick Pd film, deposited at the cleaved end of a multimode fiber, with core and cladding diameters of 50 and 125 $\mu$m, respectively. The sensing head is presented in Fig. 6. The Pd-film acted has a micromirror when exposed to $H_2$, thus causing a reflectivity variation of this film. The sensor showed a rapid decrease in reflectivity (ca. 22%) when exposed to 2%(v/v) $H_2$ in $N_2$, at room temperature; however, the response time was estimated to be longer than 150 min. The same author [20] presented a more detailed study on the micromirror optical fiber sensor, in attempts to elucidate the nature of the response of this type of device.

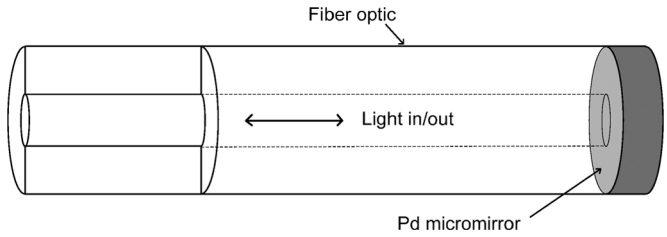


Fig. 6. Schematic of fiber-optic hydrogen sensor based on micromirror [19].

Due to its intrinsic simplicity, Bévenot *et al.* [9] used an identical apparatus but pursued the goal of improving its performance to a significant degree; note that the micromirror sensor had previously been operated only at room temperature, and no reliable information on the response time was provided. Hence, a 13 nm-thick Pd layer was deposited on the cleaved end of a multimode fiber, with a 400 $\mu$m-core diameter and possessing a hard polymer cladding. The micromirror sensor was tested using a high power laser diode as light source that caused optical heating of the Pd layer; this allowed the sensor to operate in a wide range of temperatures, between −196 °C and 23 °C. When the optical sensor was exposed to 4%(v/v) $H_2$ in $N_2$, the reflectivity detection responses spanned 1–17%, depending on the actual temperature—and with response times shorter than 5 s.

Tabib–Azar *et al.* [21] proposed the first evanescent wave absorption-based hydrogen optical fiber sensor; its sensing head was a multimode fiber possessing an etched core region, with an active length of 1.5 cm and coated with a 10 nm-thick Pd film. The structure detail is shown in Fig. 7. This sensor was able to detect low concentrations of $H_2$ in $N_2$, at room temperature; for 0.2 and 0.6%(v/v) $H_2$, response times of 20 and 30 s, respectively, were attained.

A similar physical concept, but resorting instead to a Pd-supported tungsten oxide ($WO_3$) layer as sensing cladding media, was described by Sekimoto *et al.* [22]. These authors adopted two different approaches for fiber fabrication: one used a dip-

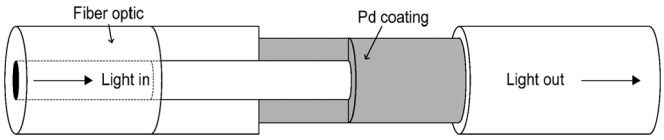


Fig. 7. Schematic of fiber-optic hydrogen sensor based on evanescent field [21].

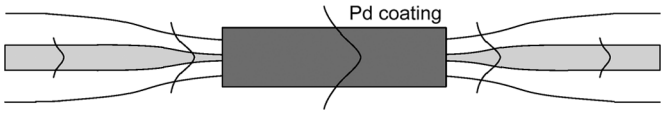


Fig. 8. Schematic of fiber-optic hydrogen sensor based on Pd-coated tapered single-mode fiber [26].

coated, ca. 3 $\mu$m $-$ $Pd/WO_3$ film containing silicone resin; and the other took advantage of the sol-gel process to form a ca. 1 $\mu$m-thick film of $Pt/WO_3$ cladding; both were characterized by a 7.5 cm-sensing length. In the presence of $H_2$, strong evanescent-wave absorption was observed as a result of formation of tungsten bronze. Both types of sensors were submitted to plain $H_2$ atmosphere: the $Pd/WO_3$-based multimode fiber sensor exhibited a response time of ca. 1 h; the result was greatly improved in the case of the $Pt/WO_3$-based sensor, for which a response time of a mere 7 min was recorded. Okazaki *et al.* [23] used the latter sensor, with a 15 cm-sensing length; it could operate also within a wide temperature range ($-30$ °C to 45 °C) with response times above 250 s, for 1%(v/v) $H_2$ in $N_2$.

Likewise, Sumida *et al.* [24] characterized a device possessing an optical time-domain reflectometer. When their sensor was exposed to 1%(v/v) $H_2$ in $N_2$ at room temperature, it displayed a response time of ca. 5 min for a 5 dB-increase in the propagation loss. This technique indicated that the $Pt/WO_3$-based multimode fiber sensor had the potential to detect the location of $H_2$ leakage points along the path of an optical fiber. Recently, Watanabe *et al.* [25] used electron beam deposition as fabrication technique—in view of its versatility in adjusting the deposition parameters. The sensing device thus developed was a 15 cm-length multimode fiber with a two-layered thin film, composed by 50 nm-thick $WO_3$ and 5 nm-thick Pt layers. When the sensor was exposed to plain $H_2$, the response time observed was 3 s, and the recovery time was ca. 1 min—hence showing a better performance than previous sensors.

Villatoro *et al.* [26] described an optical fiber hydrogen sensor based on the absorption change of the evanescent field in a Pd-coated tapered single-mode fiber; the taper was 25 $\mu$m in diameter, 15 mm in interaction length and 12 nm in thickness of Pd coating. The sensing head is shown in Fig. 8. Such a sensor could detect $H_2$ in $N_2$, in the range 1.8%–10%(v/v), with an overall response time below 100 s at room temperature—and required ca. 75 s for signal regeneration. The same authors [27] presented later results pertaining to three symmetric sensors—with the same interaction length and film thickness, but different taper diameters, viz. 20, 25, and 30 $\mu$m. For 10%(v/v) $H_2$ in $N_2$, signal changes as high as 60% were found for the narrowest device.

A different intensity-based sensor was proposed by Bévenot *et al.* [28]—which relied on optical fiber surface plasmon resonance; the sensing head was a 12 nm-thick Pd layer deposited on the 15 mm-long, multimode fiber core. This device allowed detection of $H_2$ in $N_2$ within the range 0–100%(v/v), at room temperature; and the response time varied between 3 s for pure $H_2$ and 300 s for the lowest concentration tested, viz. 0.8%(v/v). Such a wide range could be rationalized by the two different crystallographic phases of the $Pd - H_2$ system; moreover, the response was strongly dependent on length of the sensing area.

Barmenkov *et al.* [29] used a distinct technique, based on an Er-doped fiber laser with a Pd-coated tapered multimode fiber within the laser cavity. The fiber taper, with an interaction length of 8 mm and a diameter of 25 $\mu$m, was coated with a 10 nm-thick Pd film that acted as $H_2$-sensing element. When exposed to an $H_2$ atmosphere, its attenuation decreased, thus changing the cavity losses and modifying the laser transient. The sensor presented an $H_2$ sensing range of 0–10%(v/v) at room temperature; when exposed to 4%(v/v) $H_2$, the response time was ca. 90 s and the recovery time was ca. 450 s.

In 2004, Zalvidea *et al.* [30] recalled the previous work by Villatoro *et al.* [26], [27] as starting point—but added a fiber grating in parallel to the Pd-coated, tapered single-mode fiber. The taper had a diameter of 25 $\mu$m, an interaction length of 8 mm and a Pd-coating of 8 nm in thickness. The operation of this device was again based on interaction between the evanescent field along the taper and the Pd coating; however, the $H_2$ concentration was in this case detected through changes in intensity of light reflected by the fiber Bragg grating. The sensor was reliable within the 0–9%(v/v) $H_2$ concentration range, at room temperature; upon exposure to 4%(v/v) $H_2$ in $N_2$, the response time was ca. 50 s and ca. 40 s was needed for signal regeneration.

A few years later, Villatoro *et al.* [31] pursued this line of thought and produced a Pd-coated taper in a multimode fiber; tapers with waist diameters of 30 and 60 $\mu$m, a length of 10 mm and a coating thickness of 14 nm for the Pd film were indeed employed. Such sensors were able to detect $H_2$ within 0.3%–3.5%(v/v), at room temperature; the response time required for each sensing device was ca. 30 s for 2%(v/v) $H_2$ in $N_2$. Those authors further improved this technique [32] by developing a multimode fiber nano-taper, coated with a 4 nm-thick Pd film; the taper was 1300 nm in diameter and 4 mm in length, and the Pd-coated zone (or interaction length) was 2 mm. The response time was now ca. 10 s, for 3.9%(v/v) $H_2$ in $N_2$.

In the same line of research, Zalvidea *et al.* [33] presented data on the temperature effects upon the response of a Pd-coated tapered single-mode fiber device, the transmission signal of the sensor, when exposed to 4%(v/v) $H_2$ in $N_2$, increased from less than 1% at 80 °C, to 800% at $-30$ °C, and the response time increased significantly, from ca. 10 s at 80 °C up to 1000 s at $-30$ °C.

More recently, Kim *et al.* [34] developed a simple technique based on a side-polished single-mode fiber, coated with a Pd thin film and embedded in a quartz fiber-holding circular groove—as shown in Fig. 9. The sensing device consisted of a 40 nm-thick Pd film; when exposed to 4%(v/v) $H_2$ in $N_2$, it

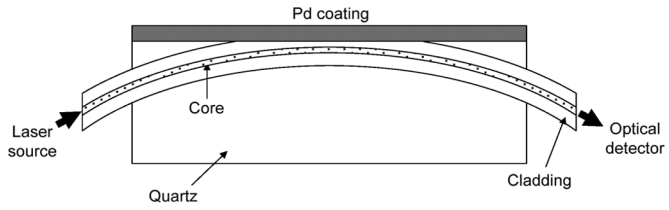


Fig. 9. Schematic of fiber-optic hydrogen sensor based on Pd-coated side-polished fiber [34].

yielded a response time of ca. 100 s, and required 150 s for signal regeneration.

In the same year, Luna-Moreno *et al.* [35], [36] developed a heterostructure based on a 5 mm-length single-mode fiber, coated with a 10 nm-thick Pd-Au film and sandwiched between two multimode fibers. The evanescent field on the fiber cladding was strong—due to core diameter mismatch of the interaction with the Pd-Au sensing layer, when exposed to $H_2$. The Pd-Au layer was independently deposited onto one side, two sides at 180°, or three sides at 120° of the single-mode fiber section. The three configurations led to essentially similar behaviors; when exposed to 4%(v/v) $H_2$ in $N_2$, the response time was ca. 15 s and the recovery time was ca. 200 s. This type of sensor had a dynamic $H_2$ concentration range of 0%–5%(v/v), and could detect $H_2$ at levels as low as 0.2%(v/v). Meanwhile, Monzón-Hernández *et al.* [37] reported an almost identical hetero-structure; however, thin layers of 1.4 nm-thick Pd and 0.6 nm-thick Au were alternately deposited onto the fiber section—which greatly improved sensor performance. In fact, the response time of the improved sensor was ca. 6 s, for 4%(v/v) $H_2$ in $N_2$, and the recovery time was ca. 13 s—with a sensitivity of 0.8%(v/v).

In another perspective, Slaman *et al.* [38] entailed the development of optical fiber tip sensors—using a multimode fiber tip, coated with Pd-capped chemo-chromic hydride; the device used a 30 nm-thick Pd layer to catalyze $H_2$ adsorption, via a 50 nm-thick $Mg_{70}Ti_{30}$ switchable mirror; and both films were deposited on the tip of fibers, characterized by 200 and 15 $\mu$m of core and cladding diameters, respectively. Due to change in the optical properties of the Mg-based alloy arising from $H_2$ adsorption, a drop by a factor of 10 in reflectivity was obtained for $H_2$ levels below 1%(v/v); the sensor featured response times below 20 s, for 1, 0.7 and 0.4%(v/v) $H_2$ in either $O_2$ or Ar.

Recently, Schroeder *et al.* [39] reported a Pd-coated fiber Bragg grating impressed in the central part of a side-polished single-mode fiber, its construction and operation details will be discussed in the next subsection. Small *et al.* [40] proposed in the same year a hydrogen getter-doped polymer film, mounted on the end of a multimode fiber; chemical-to-optical transduction was achieved by detecting the intensity of a 670 nm-laser light, transmitted through the device. The polymer film was doped with a mixture of 1.4-bis-(phenylethynyl)-benzene and carbon-supported Pd catalyst, which had the ability to capture $H_2$ permanently. When exposed to 5%(v/v) $H_2$ in Ar at room temperature, the sensing head exhibited sensitivities between 6 and 13 h.

An overview of several of the intensity-based fiber-optic sensors described previously is given in Table II.

### C. Grating-Based Optical Fiber Sensors

The first fiber grating-based hydrogen sensor was reported by Sutapun *et al.* [41]; its sensing head was an etched 2–3 cm-long fiber Bragg grating, coated with a 560 nm-thick Pd film—which is shown in Fig. 10. A linear sensitivity of $1.95 \times 10^{-2}$ nm/% (v/v) $H_2$ was observed, within the range 0.3%–1.8%(v/v) $H_2$ in $N_2$. A unique feature of this sensing device was that it could be multiplexed on a single optical fiber, using fiber Bragg gratings with distinct Bragg wavelengths.

Zalvidea *et al.* [30] used a fiber Bragg grating in parallel with a Pd-coated tapered single-mode fiber—but in this case said grating was used only to obtain light intensity changes as reflected by the device, instead of monitoring light in transmission.

A few years later, Buric *et al.* [42] proposed a fiber Bragg grating coated with a 350 nm-thick Pd film. This sensor produced a 0.37 nm-wavelength shift when exposed to 10%(v/v) $H_2$, with a response time of 30 s at room temperature. Infrared power laser light was used to induce heating in the Pd coating, which dramatically improved its sensitivity to, and response time at low $H_2$ concentrations.

Schroeder *et al.* [39] followed on the work developed by Kim *et al.* [34], in that a 1.5 mm-long fiber Bragg grating was added to the central part of a side-polished single-mode fiber, and coated with a 50 nm-thick Pd film; a second 2 mm-long fiber Bragg grating was written at a distance of 8 mm from the center, for temperature compensation. The working principle was evanescent field interaction, between the exposed fiber Bragg grating and the Pd film. This sensor was monitored by spectral shift of the Bragg wavelength, caused by the decreasing complex refractive index of the Pd-film upon adsorption of $H_2$. A response time of ca. 30 s was achieved, for 4%(v/v) $H_2$ in Ar at room temperature, with a corresponding sensitivity of 33 pm/%(v/v) $H_2$.

In 2006, Trouillet *et al.* [43] described the first long-period grating-based hydrogen sensor—which departed from a long-period grating coated with a 50 nm-thick Pd film on one side of the fiber, through a 3 cm-length mask centered on the structure. The device is shown in Fig. 11. This structure was compared with a similar one comprising a fiber Bragg grating instead: in the presence of 4%(v/v) $H_2$ in $N_2$, the latter exhibited a wavelength shift of ca. 14 pm, whereas $-5$ and $-7$ nm were obtained for the two wavelength resonance peaks, at room temperature, for the long-period grating. Saturated, reversible and reproducible responses were observed by 2 min in either case; however, sensitivity was enhanced by more than 500-fold when the new device was employed.

As already reported in interferometric-based optical fiber sensors, Kim *et al.* [17] used a long-period grating-based Mach–Zehnder interferometer—in which a 2.3 nm-shift of the interference peak was observed within 8 min, followed by signal saturation in the presence of 4%(v/v) $H_2$ in $N_2$.

Wei *et al.* [44] presented a long-period grating coated with a 70 nm-thick Pd film—which exhibited an enhanced performance: when the sensor was exposed to 4%(v/v) $H_2$ in He, the response time did not go above 70 s, at both 30 and 100 °C, with corresponding wavelength shifts of ca. $-4$ and $-0.7$ nm.

TABLE II
INTENSITY-BASED OPTICAL FIBER SENSORS

| Author, Ref | Concentration range | Sensing head | Time response |
|---|---|---|---|
| Butler, [19], [20] | 4% | 10 nm Pd-coated MMF tip | 150 min |
| Bévenot, [9] | 1 – 17% | 13 nm Pd-coated MMF tip | < 5 s |
| Tabib-Azar, [21] | 0.2 – 0.6% | 10 nm Pd<br>15 mm long etched MMF | 30 to 20 s |
| Sekimoto, [22] | 100% | Pd/$WO_3$ with silicone resin (>3 μm)<br>Pd/WO3 sol-gel process (1 μm)<br>MMF (100 μm) | 1 h<br>7 min |
| Okazaki, [23] | 1% | Pt/$WO_3$ sol-gel process<br>15 cm long MMF (200 μm) | 250 s |
| Sumida, [24] | 1% | Pt/$WO_3$ sol-gel process<br>15 cm long MMF (100 μm) | 5 min |
| Watanabe, [25] | 100% | Pt/$WO_3$ sol-gel process<br>15 cm long MMF (100 μm) | 3 s |
| Villatoro, [26], [27] | 1.8 – 10% | Tapered SMF<br>15 mm length, 25 μm ϕ, 12 nm Pd | < 100 s |
| Bévenot, [28] | 0.8 – 100% | SPR<br>MMF core coated with 12 nm Pd | 300 to 3 s |
| Barmenkov, [29] | 0 – 10%<br>0.1% resolution | Tapered SMF<br>8 mm length, 25 μm ϕ, 10 nm Pd | 90 s (4% $H_2$) |
| Zalvidea, [30] | 0 – 9% | Tapered SMF + FBG<br>8 mm length, 25 μm ϕ, 8 nm Pd | 50 s (4% $H_2$) |
| Villatoro, [31], [32] | 0.3 – 3.5% | Tapered MMF<br>30 and 60 μm ϕ, 10 mm length<br>14 nm Pd | 30 s (2%) |
| Zalvidea, [33] | 4% | Tapered SMF<br>8 mm length, 25 μm ϕ, 8 nm Pd | 10 s (80 ºC)<br>up to 1000 s (−30 ºC) |
| Kim, [34] | 4% | Side-polished SMF<br>40 nm Pd | 100 s |
| Luna-Moreno, [35], [36] | 0.2 – 5% | Hetero-structure MMF/SMF/MMF<br>10 nm Pd-Au | 15 s (4%) |
| Monzon-Hernandez, [37] | 0.8 – 4% | Hetero-structure MMF/SMF/MMF<br>Pd (1.4 nm) and Au (0.6 nm) alternately | 6 s (4%) |
| Slaman, [38] | 0.4 – 1% | MMF tip, with 30 nm $Mg_{70}Ti_{30}$ and 50 nm Pd | < 20 s (0.4 to 1%) |
| Schroeder, [39] | 0.1 – 4% | FBG (15 mm length) side-polished<br>50 nm Pd | 2 min (<1%)<br>30 s (4%) |
| Small, [40] | 5% | Hydrogen getter-doped polymer film at the MMF tip | 6 to 13 h |

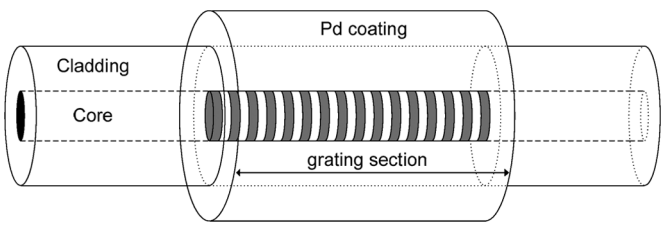


Fig. 10. Schematic of fiber-optic hydrogen sensor based on Pd-coated fiber Bragg grating [41].

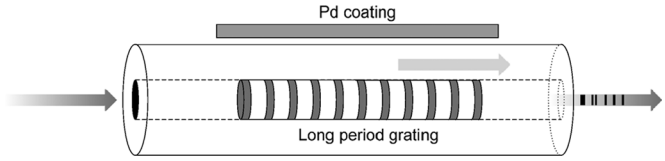


Fig. 11. Schematic of fiber-optic hydrogen sensor based on Pd-coated long-period grating [43].

More recently, Tang *et al.* [45] developed an $H_2$ sensor based on a long-period grating coated with a proton-conducting perovskite oxide thin film—designed for high-temperature, *in situ* measurement of bulk hydrogen in fossil- and biomass-derived syngas. In this case, the long period grating was coated with a 500 nm-thick perovskite oxide film. The sensing mechanism

TABLE III
GRATING-BASED OPTICAL FIBER SENSORS

| Author, Ref | Concentration range | Sensing head | Time response |
|---|---|---|---|
| Sutapun, [41] | 0.3 – 1.8% | 560 nm Pd<br>20 mm-long etched FBG | -- |
| Zalvidea, [30] | 0 – 9% | Tapered SMF + FBG<br>8 mm length, 25 μm ϕ, 8 nm Pd | 50 s (4% $H_2$) |
| Buric, [42] | 0.5% | FBG coated 350 nm Pd | < 10 s |
| Schroeder, [39] | 0.1 – 4% | FBG (15 mm length) side-polished<br>50 nm Pd | 2 min (<1%)<br>30 s (4%) |
| Trouillet, [43] | 4% | FBG and LPG<br>50 nm Pd | 2 min |
| Kim, [17] | 4% | LPG Mach-Zehnder interferometer<br>coated 50 nm Pd | 8 min |
| Wei, [44] | 0 – 16% | 70 nm Pd coated LPG | < 70 s (4%) |
| Tang, [45] | 0 – 80% | SCZY (500 nm) coated LPG | -- |

was based on monitoring of the resonant wavelength, which was a function of the refractive index of said film. All tests were performed at 500 °C, under atmospheric pressure; and the aforementioned sensor was exposed to $H_2$ concentrations ranging from 0 to 80%(v/v), thus showing a maximum wavelength variation of 14 nm.

An overview of the several types of fiber grating-based optical fiber sensors for hydrogen detection is provided in Table III.

### D. Comparison Between Optical Sensors

A few works have compared different Pd-coated sensing devices; e.g., differences in performance between a bulk Pd-film, a Pd-coated fiber Bragg grating and a long length single-mode fiber for testing nuclear waste repositories was reported by Aleixandre *et al.* [46]; the fiber Bragg grating device exhibited the best sensing performance. Three distinct structures, viz. a semicircular cross-section Pd-tube with two fiber Bragg gratings, an optical fiber Fabry–Perot interferometer and a Pd-coated long-period grating were also studied by Maier *et al.* [47], [48]—with the latter leading to the best sensing response.

Finally, it is instructive to overview all sensors described to date in the literature—as pooled together in Fig. 12, aiming at comparison of the two most meaningful performance indicators, viz. solute sensitivity and response time. On inspection of this figure, it is apparent that sensors based on fiber-grating systematically exhibit poorer sensitivities to $H_2$ concentration than the other two types—but reasonable response times. Conversely, interferometric based-sensors have intermediate sensitivities and intermediate response times; whereas intensity-based sensors span the whole range of sensitivities and response times. The best performance is thus found in the lower left corner of this graph—which is occupied chiefly by intensity-based sensors.

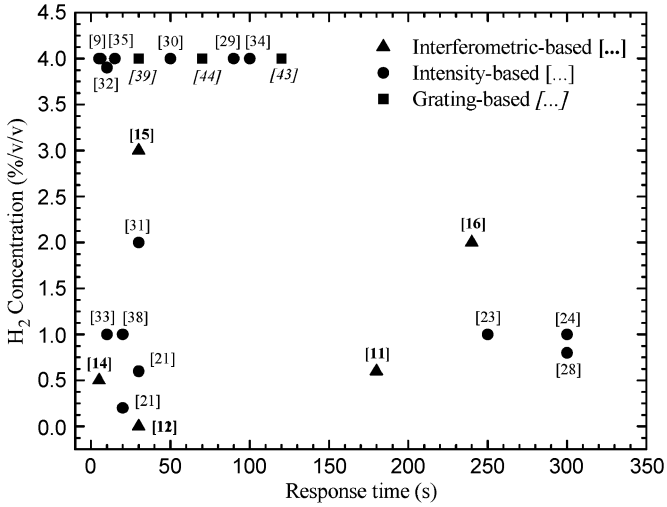


Fig. 12. Representation of sensitivity versus response time of the various types of Pd-based, fiber-optic hydrogen sensors.

## IV. GENERAL CONCLUSIONS AND FINAL REMARKS

Over the latest 30 years, a variety of configurations for hydrogen sensing have been attempted and successfully demonstrated. Many devices developed in that period have found a place in the market, due to the need of monitoring hydrogen-based systems namely with regard to the inherent explosion risk. The need for local detection of hydrogen in hazardous atmospheres and/or at high temperatures has consistently led to choice of optical fiber sensors, in fact, when compared with conventional sensors, optical fiber-based hydrogen ones possess as main advantage their being risk-free in potentially explosive environments. They also enable remote sensing and multipoint measurement, and are immune to electromagnetic interferences. So far, Pd has been the most common transducer used with the optical fiber, due to its high sensitivity to, and selectivity for molecular hydrogen.

Many complementary efforts have accordingly been made to develop Pd-based optical fiber sensors for hydrogen sensing. As shown in this review, the different types of Pd-based optical fiber sensors can be divided into three main groups: interferometric-based, intensity-based and fiber grating-based fiber-optic sensors. Intensity-based devices have in general shown better time responses. Several sensing structures were developed, ranging

from fiber tip to in-line fiber devices, either for single-point or multipoint hydrogen monitoring. In particular, multimode fiber-based configurations have proven attractive sensing devices, owing to their good performance and simplicity, associated with a low-cost fabrication. Tapered/etched fiber structures tend to be more fragile due to their reduced sensing area whereas fiber tip-based sensors are noteworthy for their long-term stability. Nevertheless, intensity-based sensors for hydrogen detection have shown an overall excellent repeatability of results.

On the other hand, interferometric-based sensors are potentially more sensitive—fiber Fabry-Perot devices have indeed shown short time responses, with the possibility of use as single-point sensors because of their small dimensions. However, these sensors are more complex structures—and often require thermal isolation and high stability to ensure good a performance. Fiber grating-based sensors are robust structures and easily reproducible, and further exhibit the unique advantage that they can be multiplexed. In particular, FBGs usually require etching to enhance sensitivity, which in turn reduces mechanical strength. Conversely, LPGs present high stability for hydrogen detection.

Meanwhile, other fiber-optic-based sensors have been developed, either using different metals or alloys as transducers, or resorting to distinct deposition techniques (viz. sol-gel process), and regarding the type of sensing head used; some have met with reasonable to good performance. Pd alloys using Ti and Au were indeed developed to reduce response time, and increase the stability and durability of the hydrogen sensor. Transition metal oxides such as $TiO_2$, $NiO_x$, and $WO_3$ were used to provide good repeatability to cyclic hydrogen changes and enhance stability of the sensor. Optical fiber sensors using novel materials, such as Perovskite-Type oxide thin films, have meanwhile undergone investigation toward detection of hydrogen in high-temperature environments.

Regardless of the technology used, one notices that the recovery time is still quite long (many seconds, and in some cases, minutes or hours); hence, further research investment is required to address this issue, to eventually be able to design and implement better configurations for hydrogen sensing.

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