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Recent advancements in optical fiber hydrogen sensors

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ABSTRACT

A review for optical fiber hydrogen sensors based on palladium (Pd) and tungsten oxide (WO_3) thin films is presented, with specific focus on the measurement methods, probe structures, and sensing properties of different sensors. Firstly, the theoretical models behind the optical fiber hydrogen sensors, as well as their practical limitations, are addressed. Secondly, four mainstream measurement methods, including intensity, fiber Bragg grating (FBG), interferometer, surface plasmon resonance (SPR), which have been proposed to sense the physicochemical properties variations of sensitive thin films when exposed to hydrogen, are reviewed. Then, the advantages and disadvantages of all the above measurement methods are also discussed and compared. Finally, the existing problems and future prospects of optical fiber hydrogen sensors are pointed out.

Contents

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1. Introduction

As a new energy of high efficiency, non-pollution, sustainability, and abundant availability, hydrogen plays an important role in solving the energy crisis at present [1]. Meanwhile, hydrogen is also the characteristic gas for fault diagnosis of power transformers [2]. Recently, hydrogen has been widely used in aerospace engineering, petroleum explorations, metallurgical refineries, cryogenic cooling, chemical processing, automobiles, and many other fields [3,4]. However, hydrogen is also a highly flammable and explosive gas due to its high diffusion coefficient (0.16 cm^2/s in air), low ignition energy (0.018 mJ), high combustion heat (285.8 kJ/mol), and wide explosion concentration range (4%–75%). Therefore, it is potentially dangerous in the utilization, storing, or transportation of hydrogen [5].

To mitigate the risks of explosion or assess health statuses of transformers, it is needed to realize the high-sensitive, high-precision, rapid, robust, real-time, on-line, and long-distance monitoring of hydrogen concentration [6]. Therefore, many researches on developing high-performance hydrogen sensors have been stimulated in recent years [7], among which the optical fiber hydrogen sensors have become research hotpot due to their outstanding advantages, such as intrinsic safety, corrosion resistance, suitable for remote sensing, and immune to electromagnetic interference. Besides, the optical fiber hydrogen sensors are also applicable to the hazardous or foul environments since their sensing mediums are optical signal and there is no risk of spark or ignition in the sensing regions.

The typical probe structure of an optical fiber hydrogen sensor is relied on sensitive thin film coating on surface of optical fiber [8,9]. When surrounding hydrogen concentration is changed, the physicochemical characteristics of sensitive thin film will change according to certain relationship, and then induce the variations of optical signal that transmitted in the optical fiber, in terms of intensity, wavelength, and/or phase. As a result, the hydrogen concentration can be deduced by monitoring the variations of optical signals. Based on this sensing mechanism, a number of measurement methods of optical fiber hydrogen sensor have been proposed and demonstrated, including absorption intensity [10], fiber gratings [11], interferometers [12], and surface plasmon resonance (SPR) [13].

In this paper, an overview of optical fiber hydrogen sensors over recent years is introduced in detail, wherever available, to give some inspirations for further researches on other measurement methods of optical fiber hydrogen sensors. The rest of this paper is organized as follows: In Section 2, the method principles of optical fiber hydrogen sensors are analyzed and discussed. In Section 3, various measurement methods of optical fiber hydrogen sensors, along with their structures, sensing properties, advantages and disadvantages are presented. In Section 4, the existing problems and future research directions of optical fiber hydrogen sensors are put forward. Finally in Section 6, we draw a brief conclusion and prospect.

2. Measurement principle

The main developing trends of optical fiber hydrogen sensors are based on two kinds of sensitive thin films, i.e. palladium (Pd)-based thin films and tungsten oxide (WO_3)-based thin films, coating onto the tip or along the length of an optical fiber.

2.1. Pd-based sensitive thin films

As a hydrogen reactant, Pd has particular appeal to hydrogen. When hydrogen appears near the Pd film, the molecular hydrogen (H_2) will be dissociated into atomic hydrogen (H), which is characterized by a high dissociation rate. Then the hydrogen atoms will diffuse through the Pd film easily, and finally the Pd film will rapidly convert into a reversible palladium hydride PdH_k, where k represents the atomic ratio of H to Pd. The hydration of Pd can also be related to a crystallographic phase transition represented by α and β, which can be described as:

$$(\alpha)\mathrm{Pd}+\frac{k}{2}\mathrm{H}_2 \leftrightarrow (\beta)\mathrm{PdH}_k \tag{1}$$

From a physical standpoint, the crystallographic change of Pd leads to an increment in lattice parameter. Consequently, the volume of Pd film expands (up to 900 times) associated with a reduction in dielectric constant of Pd film. Besides, the larger the concentration of surrounding hydrogen is, the lower the dielectric constant of Pd film is. The relationship between hydrogen concentration c and the dielectric constant ε of Pd film can be expressed by the following equation:

$$\varepsilon_{\mathrm{Pd}}(c) = h(c) \times \varepsilon_{\mathrm{Pd}}(0) \tag{2}$$

where $\varepsilon_{\mathrm{Pd}}(c)$ is the dielectric constant of Pd film for concentration c of hydrogen; $\varepsilon_{\mathrm{Pd}}(0)$ is the dielectric constant of Pd film in the absence of hydrogen, which equals to 3.24; $h(c)$ is a nonlinear function. In Ref. [14], it is demonstrated that the values of $h(c)$ are 1.0 and 0.8 for hydrogen concentration of 0% and 4%, respectively [14]. The results also show that the dielectric constant of Pd film will decrease with the increase of hydrogen concentration.

By coating Pd film onto fiber surface, the variation of hydrogen concentration can alter the volume and dielectric constant of Pd, which will then induce the change of optical signals in terms of intensity, wavelength, and/or phase according to different sensor configurations. These changes can be monitored to deduce the variations of hydrogen concentration [15].