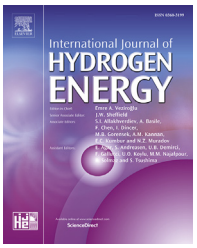
INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2018) 1–7

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he



Development of a hydrogen dual sensor for fuel cell applications

*Salvatore Gianluca Leonardi, Anna Bonavita, Nicola Donato, Giovanni Neri**

Department of Engineering, University of Messina, Contrada Di Dio, I-98166, Messina, Italy

ARTICLE INFO

Article history:
Received 10 November 2017
Received in revised form
2 February 2018
Accepted 3 February 2018
Available online xxx

Keywords:
Hydrogen
Sensor
Fuel cell

ABSTRACT

The development and application of a hydrogen dual sensor (HDS) for the application in the fuel cell (FC) field, is reported. The dual sensing device is based on a ceramic platform head with a semiconducting metal oxide layer (MOx) printed on Pt interdigitated contacts on one side and a Pt serpentine resistance on the back side. MOx layer acts as a conductometric (resistive) gas sensor, allowing to detect low H_2 concentrations in air with high sensitivity and fast response, making it suitable as a leak hydrogen sensor. The proposed Co-doped SnO_2 layer shows high sensitivity to hydrogen ($R_0/R = 90$, for 2000 ppm of H_2) at 250 °C in air, and with fast response (<3 s). Pt resistance serves as a thermal conductivity sensor, and can used to monitor the whole range of hydrogen concentration (0–100%) in the fuel cell feed line with short response-recovery times, lower than 13 s and 14 s, respectively. The effect of the main functional parameters on the sensor response have been evaluated by bench tests. The results demonstrate that the dual sensor, in spite of its simplicity and cheapness, is promising for application in safety and efficiency control systems for FC power source.

Introduction

The increasing attention on use of technologies and materials with low environmental impact and the consequent interest toward fuels differing from the fossil ones, mainly responsible of the global warming, has attracted much interest toward the use of hydrogen as a fuel [1]. The perspective of using hydrogen as clean combustible in alternative to conventional fossil fuels in energetic devices as fuel cells arises from the fact that H_2 does not produces greenhouse gases. Indeed, when hydrogen is the source fuel used, with O_2 or air as oxidant, the only byproduct is water.

However, some drawbacks can limit the use of hydrogen in fuel cell application. High efficient fuel cell use pure hydrogen but, during the normal functioning of the FC, nitrogen spill-over can across the electrolyte membrane, thus diluting the hydrogen concentration in the anode compartment, which results in the main cause of inefficiency in such energetic devices. Therefore, it is necessary to guarantee into the FC system the supply of hydrogen concentration as high as possible (near to 100%) [2]. Another serious limitation of hydrogen is its explosive character. Then, for both safety and technical reasons, monitoring hydrogen in fuel cell application is of outmost importance in perspective. Researchers have been then engaged from long time to develop H_2 sensors,

* *Corresponding author.*
E-mail address: gneri@unime.it (G. Neri).

https://doi.org/10.1016/j.ijhydene.2018.02.019

having the requested performances for both applications [3,4]. Hydrogen leak sensors are devices that will immediately activate an alert in the event of a hydrogen leak. Hydrogen has very good combustible characteristics: a low minimum energy ignition energy (0.017 mJ), a wide flammable range (4–75% vol.) and an ignition temperature of 560 °C. The overmentioned characteristics, coupled with the hydrogen high burning velocity and detonation sensitivity, high permeability, odorless characteristic make stringent the necessity to introduce reliable hydrogen leak sensors in fuel cell. H_2 leak sensors should display high selectivity and sensitivity to low hydrogen concentrations in the ambient atmosphere. The limit of detection normally fixed corresponds to the 50% of the Low Explosively Limit (LEL) of the gas target (4% for H_2 in air) [5,6].

Monitoring hydrogen in the range of high concentrations is instead of primary importance in order to optimize the energetic efficiency of the fuel cell. Sensors for hydrogen concentration measurements in the feed have to be sensitive to high concentrations of H_2, up to 100%, and not affected by saturation effects. These sensors, coupled with a system of control and automatic bypass of the feed became so indispensable in order to suddenly enrich with H_2 the fuel feed and maintain efficiency as high as possible for long time [2].

For these scopes, there are many hydrogen sensor typologies known, the most common are: catalytic, thermal conductivity, electrochemical, conductometric (resistive), mechanical, optical, acoustic [7–9]. In this work, a simple hydrogen dual sensor (HDS), combining a resistive and a thermal conductivity sensor on a ceramic platform is proposed. HDS sensor head has a double face (Fig. 1). A MOx layer is printed on a pair of Pt interdigitated contacts on one side. The MOx sensing layer is made of a porous ZnO or SnO_2-based material, where hydrogen is easily adsorbed and can react with adsorbed oxygen on the surface [10–12]. Surface processes change the electrical resistance of the MOx semiconducting layer, in a proportional way to hydrogen concentration, so allowing its monitoring in air. On the opposite side of the ceramic head, a serpentine platinum resistance is printed. When the hydrogen flow contacts the platinum serpentine, the resistance changes as a consequence of the temperature variation induced by the high thermal conductivity of hydrogen, compared to other gases. Through the resistance measurement, high hydrogen content in simple mixtures can be monitored in a simply way. The fabrication, characterization and testing in the monitoring of hydrogen in a very large hydrogen concentration range will be described in the following paragraphs.

Experimental

Sensors fabrication

The detailed configuration of the HDS sensor is depicted in Fig. 1. The probe consists of an alumina substrate (3 mm × 6 mm), where a pair of Pt interdigitated contacts are printed on the right side (Fig. 1a) and on the back side a Pt serpentine resistance (Fig. 1b). The serpentine is biased and measured by means of the four wires remote voltage sensing of 3632 A power supply, removing the shorting bars placed between the output and sense terminals connections. Both biasing and sensing connections are placed at the two contacts of the Pt serpentine wires, allowing to remove the cable electrical resistance placed from the power supply connections to the Pt electrical contacts.

Fig. 1c shows the MOx semiconductor layer, printed by screen printing, on the Pt interdigitated contacts side. ZnO and a Co-doped SnO_2 have been used here. Details on the preparation of these materials can be found in previous papers [4,13]. A picture of one such fabricated sensor mounted on the sensor holder is shown in Fig. 1d.

Sensing tests

Sensing tests were carried out introducing the HDS sensor in a suitable stainless steel chamber where they were exposed to hydrogen in controlled atmosphere. Hydrogen coming from certified cylinders can be further diluted in nitrogen or air at given concentrations by means of mass flow controllers. The measurements were carried out under a constant air stream of 100 sccm, controlling the working temperature changing the current passing thought by means of a power supply instrument Agilent E3632A. A multimeter data acquisition unit Agilent 34970 A was used for acquiring the signal coming from the HDS sensor.

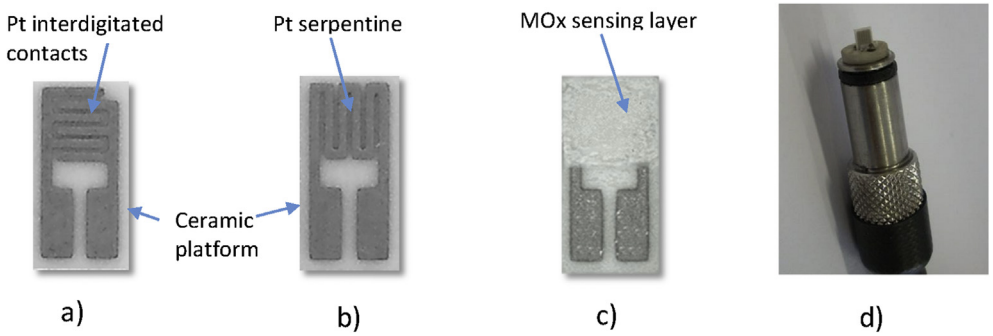


Fig. 1 – Pictures showing the HDS sensor configuration. a) Right side of ceramic substrate with the Pt interdigitated contacts; b) Back side with Pt serpentine; c) MOx sensing layer printed on Pt interdigitated contacts; d) Picture of the HDS sensor mounted on the sensor holder.

Please cite this article in press as: Leonardi SG, et al., Development of a hydrogen dual sensor for fuel cell applications, International Journal of Hydrogen Energy (2018), https://doi.org/10.1016/j.ijhydene.2018.02.019