Chapter 51
A Research Study and Development of a Hydrogen Sensor for Fuel Cells

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Abstract The design and development of a new sensor prototype for hydrogen concentration detection in the fuel cells stream is reported. The sensor's operation principle is based on the effects induced to high thermal conductivity of hydrogen, monitored by means of a PID (proportional-integral-derivative) control. The sensor is also implemented with a semiconducting layer which provides an additional output response. The sensor shows good linearity in the 0–100% range and it is suited to detect hydrogen in the stream of fuel cells with fast response.

51.1 Introduction

In the near future hydrogen will gain greater importance as a clean fuel in fuel cells for automotive, maritime and space system power applications. Inexpensive hydrogen sensors are then crucial for the future hydrogen economy. Hydrogen sensors may be used in a fuel cell to monitor possible hydrogen leak and hydrogen concentration in the fuel stream [1, 2]. Hydrogen concentration may be used as an indicator of the fuel cell performance and operating efficiency. For example, an excessive amount of hydrogen in the fuel stream exhausted from the fuel cell may

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indicate poor operating efficiency. Hydrogen which is not consumed in the stack may be recycled to the main hydrogen stream. However, an undesirable amount of nitrogen is often present in the unused hydrogen exiting the fuel cell. Before reintroducing the unused hydrogen into the main hydrogen supply, a portion of the hydrogen/nitrogen mixture is exhausted into the atmosphere. Instead of simply periodically purging the anode exhaust stream, the anode exhaust could be purged as a result of a measured hydrogen concentration falling below a threshold value.

The main requirements for a hydrogen concentration sensor for fuel cells are: hydrogen detection in an inert atmosphere (nitrogen) up to 100% H_2 without saturation effects, fast response, and insensitivity to humidity and CO concentrations. To accomplish these stringent requirements, the design and development of a sensor prototype for hydrogen detection was undertaken. The operation principle of the sensor was based on the peculiar thermal properties of hydrogen that allow to distinguish it from other gases present in the environment, due to its highest cooling effect. In an up-dated configuration, the sensor was implemented with an additional semiconducting layer with the aim of providing an additional output response.

51.2 Experimental

The prototype of hydrogen gas sensor under study consists of a planar Pt heater deposited by high vacuum sputtering on a ceramic substrate. Pt contacts are 250 μm wide and the gap between the contacts is 150 μm wide. Thickness of the Pt contacts is about 5 μm and the measured resistance at 25°C is around 3 Ω. The planar Pt heater is able to maintain constant the temperature within 0.1°C at operating temperature in the range 50–500°C. On the backside of the sensor, a TiO_2-based semiconducting layer was deposited on Pt interdigitated contacts.

The devices are powered by a DC power supply (Agilent E3632A) and controlled by a software interface ad hoc realized on IEEE 488 protocol.

51.3 Results and Discussion

In a previous report, we discussed on the possibility of using transient thermal effects during gas detection for monitoring hydrogen in H_2/N_2 mixtures [3]. This was accomplished by developing a simple device, consisting in a platinum heater on a ceramic substrate, under a home-made PID control.

The sensor detection mechanism relies on the transient variation of temperature under different hydrogen concentrations. Indeed, as hydrogen posses the highest thermal conductivity of all known gases, 0.172 W/m K at 20°C, one order of magnitude higher than value for nitrogen (0.0234 W/m K) at the same temperature, a gas stream containing H_2 has a higher capability to cool the sensor surface

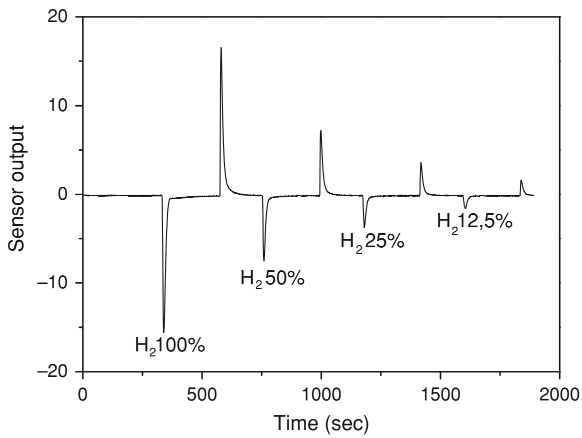

Fig. 51.1 Sensor output to different concentrations of H_2 in N_2. Working temperature = 150°C

than pure N_2. The transient thermal effect associated can be easily monitored through the PID control, by means of the variation of power (sensor response) supplied to the heater (Fig. 51.1).

As the H_2 concentration in the mixture varies there is a variation in temperature which results in a change of the Pt heater resistance. The developed sensor was sensitive to H_2 gas over a wide range of concentration: the lowest concentration tested being ~2% H_2 in nitrogen. No saturation of the signal was observed up to 100% H_2 flow. In the continuous operation mode with varying H_2 concentration, a clear and sharp response was recorded with no memory effects during ramping up and down cycles of H_2 concentration in nitrogen mixture, and with no humidity interference [3].

The above sensor was further implemented with a semiconducting layer with the aim to provide an additional response channel and allow to investigate the hydrogen sensing mechanism. A thick TiO_2-based semiconducting film was then deposited on the interdigitated platinum contact on the backside of the ceramic substrate, so that the variation of the semiconducting film resistance could be monitored in real time. Figure 51.2a reports the resistance of the semiconducting film in air in the range of temperature investigated.

Figure 51.2b shows the simultaneous measurements of the TiO_2-based film resistance and power supplied to the heater of the same device, during successive H_2 pulses of different concentration in nitrogen. The resistance of the semiconducting film increases as a result of the presence of hydrogen in the mixture, while the power supplied to the heater decreases when the sensor is exposed to H_2, and increases in pure N_2.

In inert atmosphere, the interaction between the TiO_2 sensing layer and hydrogen occurs via chemisorption of the dissociated hydrogen on the metal oxide surface. As TiO_2 is a n-type semiconducting metal oxide, a decrease of resistance should be observed [4]. The increase of resistance after hydrogen addition, along with the sharp response, suggests instead that the resistance variations originate from the cooling effect of hydrogen in agreement with a report by Fawcett et al. on

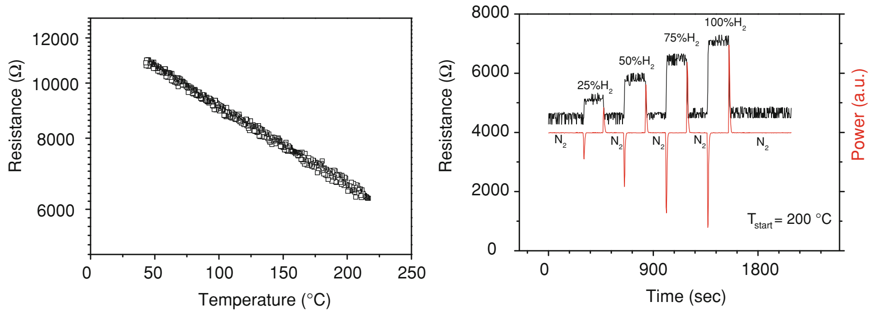

Fig. 51.2 **a** Resistance versus temperature in air of the TiO_2-based semiconducting film; **b** Simultaneous measurement of the TiO_2-based film resistance and power supplied to the heater during successive H_2 pulses

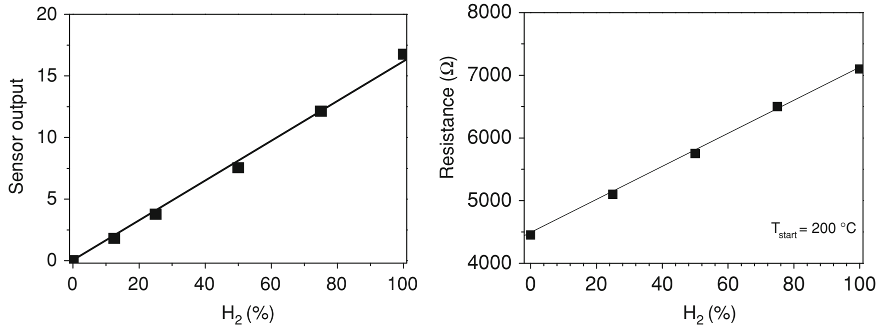

Fig. 51.3 **a** Sensor output versus different concentrations of hydrogen in N_2. Working temperature = 150°C; **b** Resistance of the TiO_2-based semiconducting film versus the hydrogen concentration in N_2

a SiC-based resistive sensor. On the basis of the increase of resistance observed during hydrogen pulses and the associated temperature variations, they provide evidence that the hydrogen sensing mechanism on the SiC sensor is most likely driven by thermal effects [5].

It can be noted that both the output response and resistance of the TiO_2-based semiconducting film (Fig. 51.3a–b), show a linear relationships with H_2 concentration in the H_2/N_2 mixture.

51.4 Conclusion

The design and development of a new sensor prototype for hydrogen detection has been reported. The sensor developed shows good linearity in the 0–100% H_2 concentration range. The sensor capability to detect high hydrogen concentration with sufficient sensitivity and fast response, makes this device well suited for applications in fuel cells.

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