Performance Evaluation of Tin Oxide Based Sensor for Monitoring Trace Levels of H_2 in Argon Cover Gas Plenum of FBTR

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Abstract. Tin oxide based thin film sensor was tested for low concentrations of hydrogen in argon cover gas over sodium expansion tank of Fast Breeder Test Reactor (FBTR). The sensor was tested for 10, 25, 50 and 100 ppm of H_2 in argon cover gas. The sensor exhibited its detection down to 10 ppm of hydrogen in cover gas during the temperature of operation of sodium at 453 K.

Key Words: hydrogen, gas sensor, tin oxide thin film, sodium, argon.

1. Introduction

Large volume of liquid sodium is being handled in primary and secondary coolant circuits in Fast Breeder Reactors (FBRs). In the steam generator section, sodium is separated from high pressure steam by a thin wall of ferritic steel [1, 2]. In the event of any sudden leak, high pressure steam comes in contact with liquid sodium resulting into sodium-water reaction. Such an eventuality needs to be detected at its inception in order to avert major reactor shutdown. The reactions lead to the formation of hydrogen, NaOH, Na_2O and NaH as a result of steam leak into sodium are shown in equations 1-4 [3].

$$\mathrm{Na(l) + H_2O \longrightarrow NaOH(s/l) + 1/2\,H_2(g)} \tag{1}$$

$$\mathrm{2Na(l) + NaOH(l) \longrightarrow NaH(s) + Na_2O(s)} \tag{2}$$

$$\mathrm{excess\ Na(l) + NaH(s) \longrightarrow [NaH]_{Na}} \tag{3}$$

$$\mathrm{excess\ Na(l) + 1/2\,H_2 \longrightarrow [NaH]_{Na}} \tag{4}$$

The dissolved hydrogen in sodium can be measured using in-sodium hydrogen meters by diffusion type hydrogen meters with a mass spectrometer and by electrochemical hydrogen meter [2, 4]. During the start-up and low power operation of the reactor, the temperature of sodium is about 473 K, at which the reactions 3 and 4 are kinetically hindered. Thus, the hydrogen formed by the reaction 1, will evolve in the argon cover gas over sodium. Thus, by monitoring hydrogen in argon cover gas will help the detection of steam leak into liquid sodium at its inception. Thermal conductivity detectors (TCD) are reported to be the most promising on-line monitor for hydrogen especially in inert streams [2, 5 & 6]. However, its lower detection limit is reported to be about 30 ppm only [6]. A sensor, which can sense below 30 ppm is preferable to identify the release of trace levels of H_2 in argon cover gas. Among various sensing materials, semi-conducting metal oxides like SnO_2, ZnO, etc. are promising materials for the detection of trace levels of hydrocarbons, hydrogen, carbon monoxide, etc [7, 8]. The working principle is the measurement of change in surface conductivity of the metal oxide at an elevated temperature during the interaction with the analyte, which is directly related to its concentration. A thin film based tin oxide sensor was developed, which can sense hydrogen below 70 ppm [9, 10]. This sensor was interfaced at the outlet of TCD in Fast Breeder Test Reactor.

This paper discusses the performance of SnO_2 in secondary sodium circuit of Fast Breeder Test Reactor (FBTR) towards hydrogen injections in the argon cover gas over sodium during shutdown condition of the reactor (sodium temperature : 453 K).

1.1 Hydrogen sensor system for argon

1.1.1 Thermal Conductivity Detector based system

The schematic representation of the integrated, TCD and tin oxide sensor in secondary sodium expansion tank (west) of FBTR is shown in Fig. 1. Thermal conductivity detector (TCD) based hydrogen detection system consists of a long, thin walled nickel tube, in the form of a coil, which is maintained at 773 K and positioned in the argon cover gas plenum as shown in Fig.1.

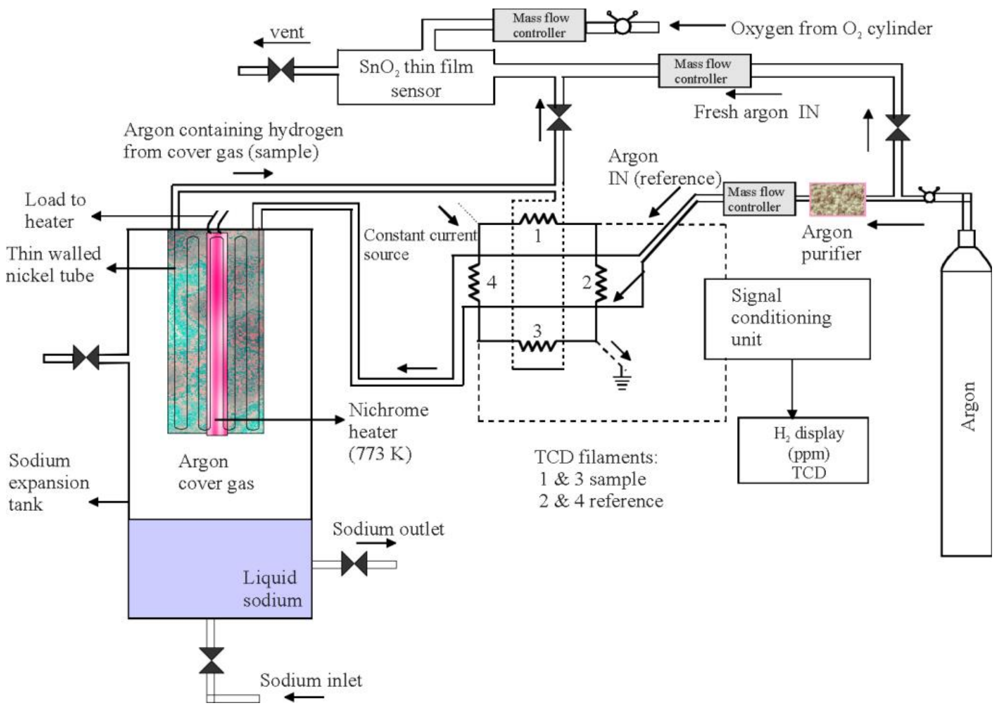

Fig. 1 Schematic arrangement of thermal conductivity detector (TCD) – cum – SnO_2 hydrogen sensor system for argon cover gas over sodium system

Using mass flow controllers, high purity argon (flow rate of 30 ml/min.) is continuously passed through reference arm of TCD filaments (filaments 2 & 4), which enters the nickel coil positioned in the argon cover gas. Hydrogen introduced / present in argon cover gas diffuses through the nickel tube (773 K), which is swept by the argon flowing through it. This argon containing hydrogen enters the sample arm of the TCD filaments (filaments 1 & 3) as seen from the Fig. 1. TCD produces an electrical signal due to difference in thermal conductivity between argon (reference) and argon containing hydrogen (sample). The net change in signal is directly proportional to concentration of hydrogen in cover gas.

1.1.2 Tin oxide based hydrogen sensor system

Tin oxide deposited as thin film on one side of an alumina substrate using pulsed laser deposition and platinum heater was screen printed on the other side. The sensor housing is about 8 ml with provisions for gas inlet and outlet. The detailed design, fabrication and operating principles are discussed elsewhere [9]. Using the platinum heater provided on the rear side of the substrate, sensor is maintained at 623 K. Due to compactness of the sensor geometry, it is difficult to incorporate temperature probe with the sensor for controlling the sensor temperature. The platinum heater itself is used as a probe to measure and control the sensor temperature. In-house developed electronic module was used to measure the temperature of the platinum heater and sensor output. Continuous logging of heater temperature and sensor signal was done by data acquisition system (Model 34970A, M/s Agilent Technologies, Malaysia) interfaced with a personal computer.

1.1.3 Integration of TCD and tin oxide sensors

Before the incorporation of SnO_2 sensor in the TCD outlet in FBTR, sensor was calibrated in the laboratory between the concentrations of 5 and 70 ppm of H_2.

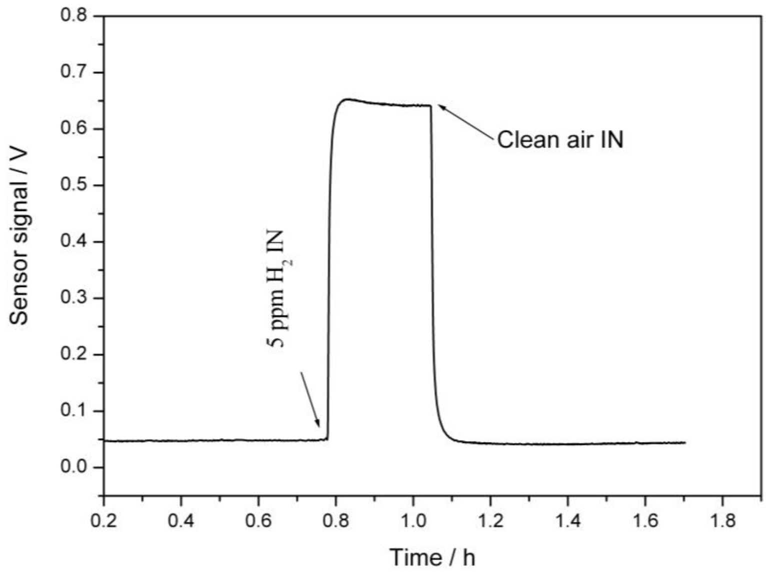

Fig. 2 Typical response characteristics of SnO_2 thin film towards 5 ppm of H_2 in air at a sensor temperature of 623 K

The typical response characteristic of the sensor towards 5 ppm of hydrogen at a sensor temperature of 623 K is shown in Fig. 2. The response time is around 140 sec to reach the stable signal in the presence of hydrogen and recovery time is around 260 sec. to establish baseline in the presence of clean air.

Figure 3 shows the calibration plot of SnO_2 sensor. The plot was fitted to a first order polynomial with correlation coefficient of 0.999. After the calibration, sensor was positioned in the sample side vent of TCD in FBTR. The photograph of the installation of tin oxide sensor in secondary sodium expansion tank of FBTR is shown in fig. 4. Argon let out from the TCD is mixed with oxygen such that the overall oxygen concentration in the stream is 21% O_2.

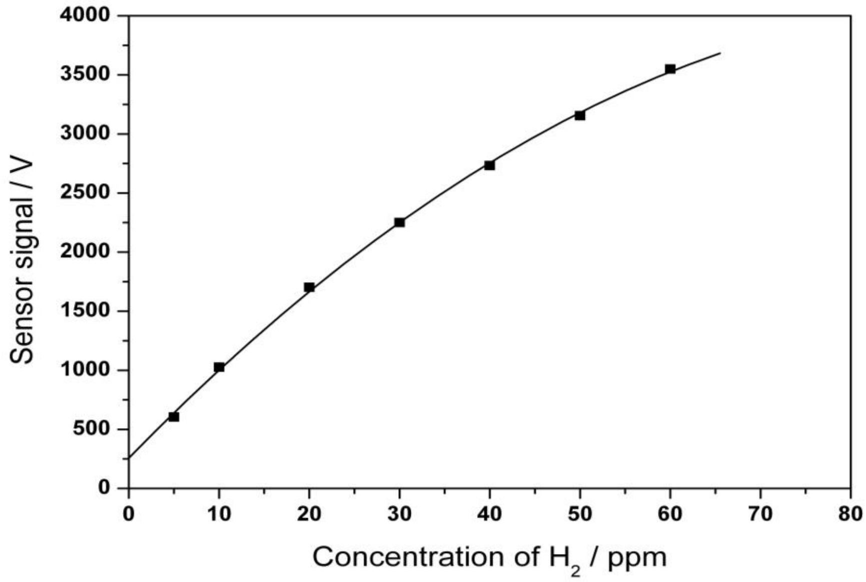

Fig. 3 Calibration plot of SnO_2 sensor towards hydrogen (sensor temperature: 623 K)

The baseline stability of the sensor was observed for a few days. After observing the stability, two sets of experimental campaigns were planned. In the first experiment, known volume of hydrogen (Concentrations: 25 & 50 ppm of H_2) was introduced in to the cover gas and the sensor response behavior was observed. After establishing stable signal in the presence of introduced hydrogen, fresh argon was let into the cover gas plenum to remove the hydrogen. In the second campaign, 10 and 100 ppm of H_2 were introduced. During the second campaign, sensor housed chamber alone was flushed using external argon by disconnecting argon containing hydrogen coming out from the TCD outlet as shown in Fig. 1.

Fig. 4 Photograph showing the installation of SnO_2 sensor at the TCD outlet in the secondary sodium circuit (west) of FBTR

2. Results and discussion

2.1 Characteristics of SnO_2 sensor

Figure 5 shows the typical baseline stability of SnO_2 sensor measured for about 100 h in the cover gas outlet of FBTR. The mean background voltage shown by the sensor is 0.087 V, which corresponds to less than 1 ppm of hydrogen in argon cover gas. The minimum detection (3σ) and quantification (10σ) limit shown by SnO_2 sensor towards H_2 are 1 ppm and 9 ppm respectively.

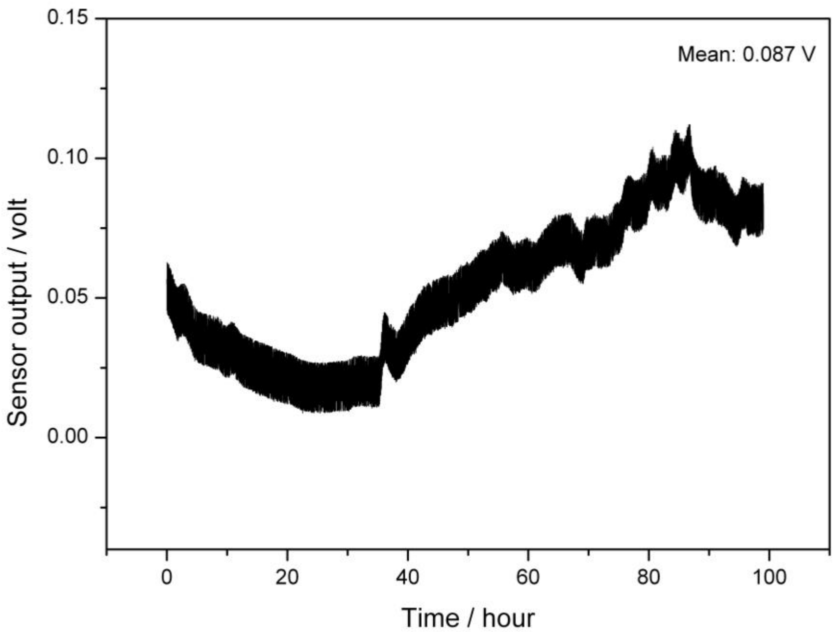

Fig. 5 SnO_2 sensor output installed in FBTR as a function of time

2.2 Performance of SnO_2 sensor for hydrogen injections in FBTR

Figure 6 shows the response behavior of SnO_2 sensor towards 25 ppm of hydrogen. The sensor exhibited response towards H_2 after seventh minute of the hydrogen introduction. There was a gradual increase in voltage exhibited by the sensor in the presence of hydrogen, which stabilized after 35 minutes of hydrogen injection. This duration is a composite of travel of hydrogen from the injection point to argon cover gas plenum, mixing and diffusion through nickel coil assembly. After establishing stable signal in the presence of introduced hydrogen, clean argon was introduced into the argon cover gas. The flushing of hydrogen in cover gas was carried out for about three hours using argon. Sensor showed a background value of 1.12 V, which corresponded to 11 ppm of H_2. It takes more than 24 h to remove completely the introduced hydrogen in argon cover gas. After establishing stable background baseline second campaign of experiments were carried out.

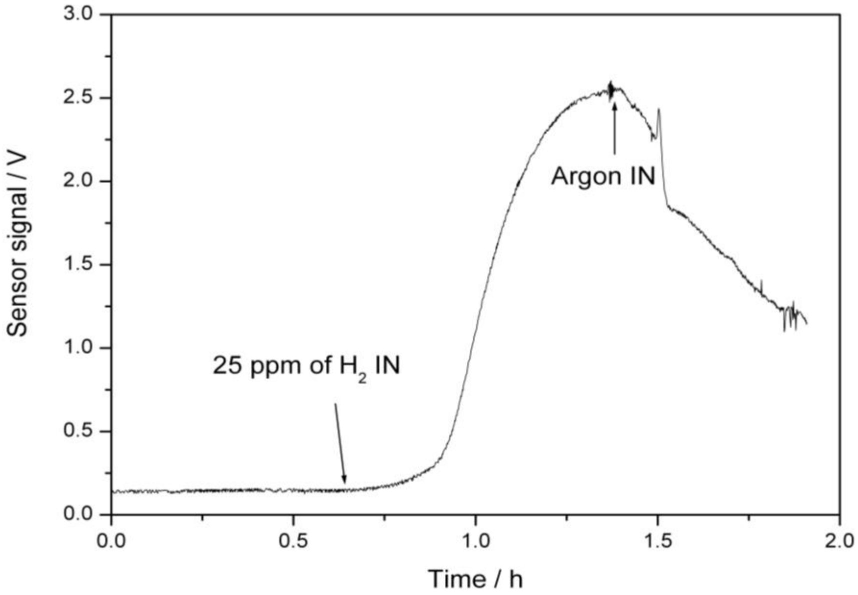

Fig. 6 Response shown by SnO_2 sensor during the introduction of 25 ppm of H_2 in argon cover gas of sodium expansion tank of FBTR

Figure 7 shows the response behavior of SnO_2 sensor towards 10 ppm of H_2 in argon cover gas. It took about 35 minutes from the time of injection of hydrogen to attain a stable sensor output. To check the retrace behavior of the sensor, pure argon was introduced (flow rate 30 ml/min) directly into the sensor chamber by bypassing hydrogen containing argon line from TCD. It took about 20 min. to attain 90% recovery (Fig. 7), which corresponded to a baseline voltage of 0.2 V (less than 1 ppm of H_2 in the sensor chamber).

3. Conclusions

The present experimental studies and the results demonstrate the usefulness of tin oxide based sensor for monitoring low levels of hydrogen in argon cover gas over sodium system when sodium temperature is maintained at 453 K (shutdown conditions) in FBTR. The start of the sensor response is found to be about 7 minutes in all the hydrogen injection experiments. The sensor responded to down to 10 ppm level of hydrogen in argon. The present investigations show when the tin oxide based sensor is used in conjunction with the TCD, the lower detection limit for hydrogen in argon cover gas over sodium system in FBTR can be about 10 ppm.

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