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## An improved polymer electrolyte-based amperometric hydrogen sensor

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**Abstract** An improved polymer electrolyte membrane (PEM) fuel cell-based amperometric hydrogen sensor that operates at room temperature has been developed. The electrolyte used in the sensor is a PVA/H<sub>3</sub>PO<sub>4</sub> blend, which is a proton-conducting solid polymer electrolyte. A thin film of palladium is used as the anode and platinum supported on carbon as the cathode. The sensor functions as a fuel cell, H<sub>2</sub>/Pd//PVA-H<sub>3</sub>PO<sub>4</sub>//Pt/O<sub>2</sub>, and the short-circuit current is found to be linearly related to the hydrogen concentration. The basic principle, details of assembly, response behaviour of the sensor and its application are discussed.

**Keywords** Polymer electrolyte · Amperometric method · Hydrogen sensor · Diffusion barrier · Fuel cell

### Introduction

Hydrogen finds extensive application as a chemical in industries, as a cryogenic fuel in rockets, and as a lift-off gas in weather balloons, etc. Hydrogen is an industrial by-product in the chlor-alkali industry. In power plants, gaseous hydrogen is used for removing friction heat in turbines. In recent years, there has been considerable development in automotive technology using fuel cells as a power source, which aims at efficient and less polluting vehicles [1]. Hydrogen as a fuel in futuristic automobiles using a H<sub>2</sub>/O<sub>2</sub> fuel cell is a definite possibility, but there is a need for a hydrogen sensor to monitor any fuel leak.

In nickel-hydrogen batteries used in satellites, hydrogen is stored at high pressure and has to be monitored for leaks [2].

In fast reactors, hydrogen monitoring in the cover gas is essential to detect steam generator leaks [3]. Measurement of diffusible hydrogen in weld samples is part of the certification of welding electrodes used in manual arc welding [4]. By measuring the amount of hydrogen evolved, the kinetics of many reactions where hydrogen is released can be studied. Decontamination studies using acid formulations are typical examples involving hydrogen release [5]. The many applications of hydrogen sensors necessitate extensive R&D in the development of a hydrogen sensor with good sensitivity, selectivity, response time and long-term stability.

Detection and measurement of hydrogen has always been a technological challenge. A variety of sensors has been developed, including electrochemical, catalytic, semiconductor and resistivity sensors. Electrochemical sensors include both potentiometric [6, 7] and amperometric [8, 9] devices. Potentiometric sensors have a wide dynamic range but lack accuracy at higher concentrations because of their logarithmic response. Amperometric sensors are linear in their response and are more accurate. An ideal sensor should be cost effective and relatively low in maintenance. Therefore, reliable sensor operation at low temperature and low humidity is one of the goals for continuing research in this area. Energy consumption is more for catalytic sensors which work at higher temperatures. The electrochemical sensor reported here does not require power to operate since it works at room temperature on the fuel-cell principle. Besides, this sensor can also operate in the absence of oxygen on the sensing side, whereas the availability of oxygen is essential for pellister sensors. In applications like cover gas monitoring in fast reactors, where there is no oxygen on the sensing side, the present sensor based on a proton-conducting solid electrolyte becomes advantageous.

Electrochemical hydrogen sensors may use both solid and liquid proton-conducting electrolytes. Solid electrolytes have an advantage against the possibility of

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spillage when compared to liquid electrolytes, but most of them (HUP, hydrated  $\text{WO}_3$ ) need humidification of the sample gas. Conducting solid polymer electrolytes include a PVA/ $\text{H}_3\text{PO}_4$  blend, Nafion, acid-doped polybenzimidazole, etc.

PVA/ $\text{H}_3\text{PO}_4$  has already been used in the development of a potentiometric hydrogen sensor [10] with Pd electrodes on both sides. We have previously developed an amperometric sensor that uses a PVA/ $\text{H}_3\text{PO}_4$  blend as electrolyte and Pd thin films as electrodes and tested its performance [11]. In this work, we report the development of an improved amperometric hydrogen sensor that uses a PVA/ $\text{H}_3\text{PO}_4$  blend as a solid polymer electrolyte, palladium as the anode and platinum as the cathode. The combination of high lattice hydrogen solubility and high values of the hydrogen diffusion coefficient and retention of metallic elasticity makes palladium the best choice for the sensor anode at low hydrogen partial pressures. Platinum is used as cathode owing to its lower activation energy for reduction of oxygen than palladium. The cell functions in fuel cell mode with hydrogen in argon on the sensing side and air on the counter electrode side. The sensor is sensitive at the parts per million (ppm) level of hydrogen in argon. The sensor was developed for monitoring hydrogen in argon cover gas in the fast reactor at IGCAR, Kalpakkam, India.

## Experimental

### Materials preparation and sensor assembly

The sensor uses a film of PVA/ $\text{H}_3\text{PO}_4$  blend as the proton-conducting solid polymer electrolyte. The blend was prepared by casting on a Teflon sheet. The details of the preparation technique

are given elsewhere [12]. The electrolyte film was then fixed to a supporting ring and coated with palladium as the anode on the sensing side and platinum as the cathode on the counter electrode side. The diameter of the electrodes was 38 mm. The assembly of the sensor was made using polycarbonate material. A schematic diagram of the sensor is shown in Fig. 1.

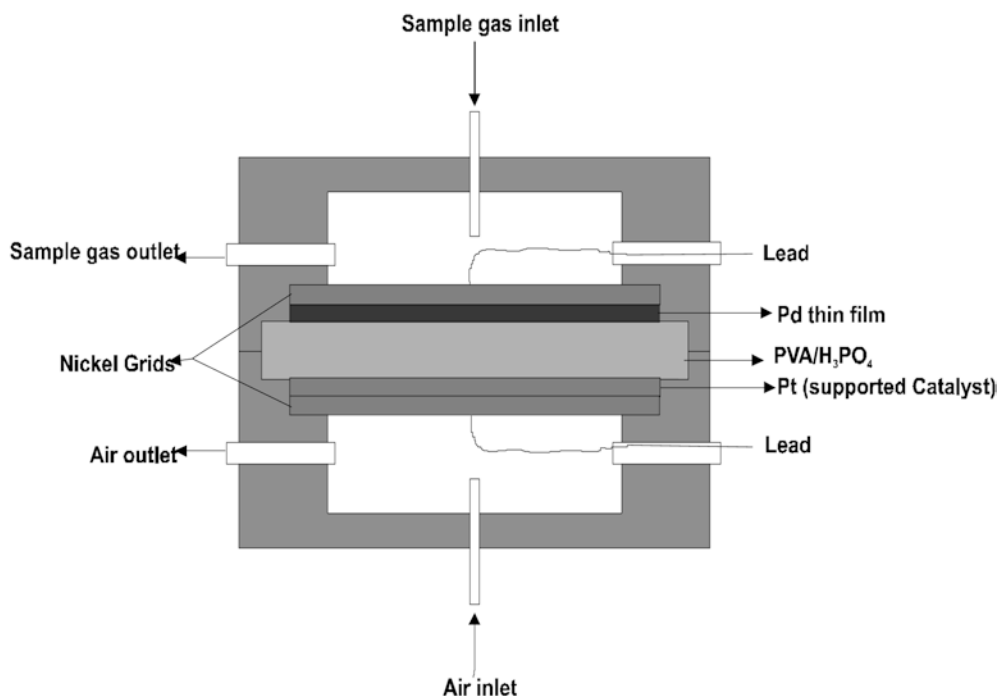
The palladium anode was deposited by vacuum vapour deposition at a vacuum level of  $10^{-6}$  Torr using a high-vacuum coating unit (model HHVF6, Hind High Vacuum, Bangalore). The coating was carried at a deposition rate of  $8 \text{ \AA s}^{-1}$ . The thickness of the anode film in the sensor was of the order of 1000  $\text{\AA}$ . The electrochemical active area was measured by cyclic voltammetry and was found to be 2.5% of the surface area of the palladium catalyst. The cast electrolyte thickness was about 2 mm. The cathode on the counter electrode side of the sensor was platinum supported on carbon and the active area was 20% of the surface area. A slurry of the catalyst was prepared by adding water to platinum on carbon, mixing well and sonicating for a few minutes. To this mixture, isopropyl alcohol was added and sonicated until a homogeneous ink-like paste was obtained. Before coating, a 20–25% Teflon emulsion was added to the mixture. The slurry was coated directly on the membrane by screen-printing. The electrode was sintered at  $100^\circ\text{C}$  under vacuum. Two gold-coated nickel grids were used as current collectors on both the sides.

The film on the sensing side was exposed to the gas containing hydrogen. The electrode on the other side was exposed to air. The two electrodes were short-circuited and the short-circuit current was measured using a sensitive current integrator (EG&G, Ortec model 439) interfaced to a computer and related to the concentration of hydrogen on the sensing side.

### Measurement

A block diagram of the experimental set-up for hydrogen measurement is shown in Fig. 2. Commercially available calibration gas mixtures (SGL, Mumbai) were used for calibration of the sensor. The required concentration of hydrogen in argon was prepared by blending a commercially available calibrated  $\text{Ar}/\text{H}_2$  mixture with argon, using a gas blending system consisting of two mass-flow controllers (MKS, USA) connected to a mixing chamber (Fig. 2). Initially, commercial argon was passed (flow rate

**Fig. 1** Schematic diagram of the polymer electrolyte-based amperometric hydrogen sensor



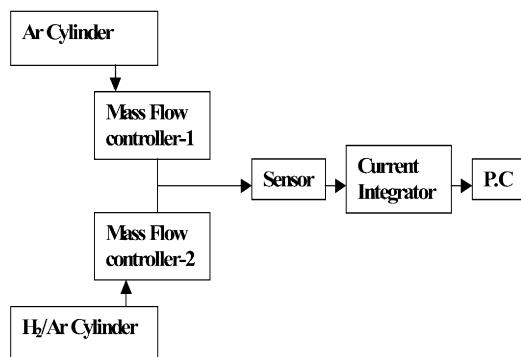


Fig. 2 Schematic representation of the sensor set-up

200 standard  $\text{cm}^3 \text{min}^{-1}$ ) on the sensing side of the sensor until the baseline current was steady. Airflow was maintained at the counter electrode side continuously. A  $\text{H}_2/\text{Ar}$  mixture of known concentration was let into the sensing side at the same flow rate as argon and retained until a steady-state current was reached. Once the measurement was over, the  $\text{H}_2/\text{Ar}$  flow was stopped and Ar flow resumed until the original baseline current was reached. The experiment was repeated for various concentrations of  $\text{H}_2$  in Ar and the calibration curve was obtained by plotting the steady-state current against the concentration of hydrogen in argon.

Since the current integrator was interfaced to a computer, it was possible to observe online the response of the sensor to varying concentrations of hydrogen in argon. The response of the sensor was also observed over a period of time so as to assess its long-term stability.

The sensor was found to operate satisfactorily up to  $70^\circ\text{C}$ . Softening of the polymer was observed at higher temperatures since the glass transition temperature for the polymer is  $72^\circ\text{C}$ .

## Results and discussion

The response of the sensor when exposed to concentrations of  $\text{H}_2$  in the range 10–40 ppm is illustrated in Fig. 3. It is clear from the results that the sensor responds quickly to changes in concentration. The 90% response time of the sensor is less than a minute, as is evident from Fig. 11 where measurement was carried out without a mixing chamber. The sensor is being developed for cover gas monitoring in a fast breeder reactor and hence the range of calibration is limited to lower concentrations.

The plot of limiting current versus concentration of hydrogen is shown in Fig. 4. Figure 5 gives the response of the sensor as a function of time when different amounts of hydrogen were introduced into the sensor. Figure 6 is the calibration graph of the sensor for various amounts of hydrogen introduced. The sensing mechanism in the present sensor can be considered to be similar to that reported in the case of an amperometric sensor using antimonite acid as the solid electrolyte and platinum as the electrode [13].

The electrochemical processes occurring at the electrodes are:



and

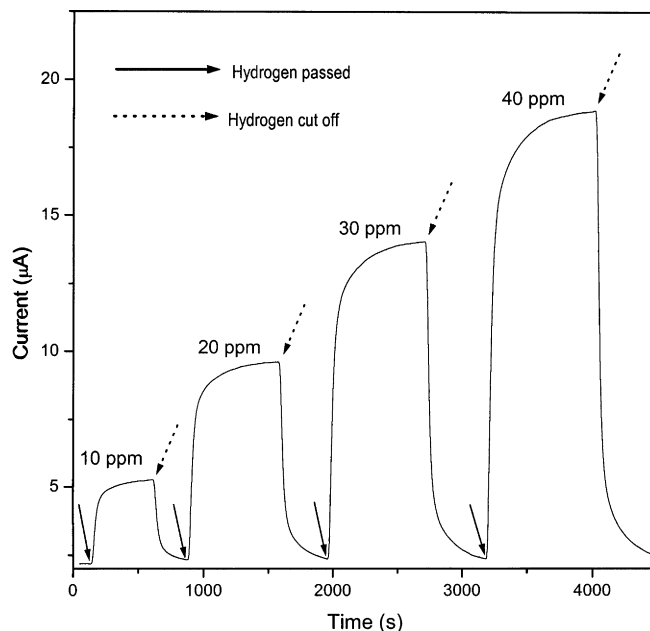


Fig. 3 Response of the sensor for various concentrations of hydrogen in argon

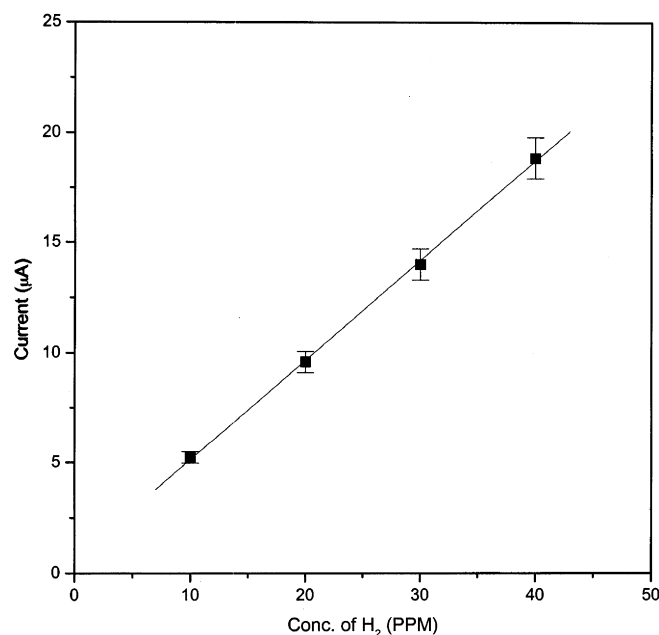


Fig. 4 Calibration plot of the sensor



The electrochemical reactions at the electrodes are schematically indicated in Fig. 7. The anodic overpotential is the diffusion overpotential and hence the oxidation reaction is a diffusion-limited process, as shown in Fig. 8. This has been experimentally confirmed [14].

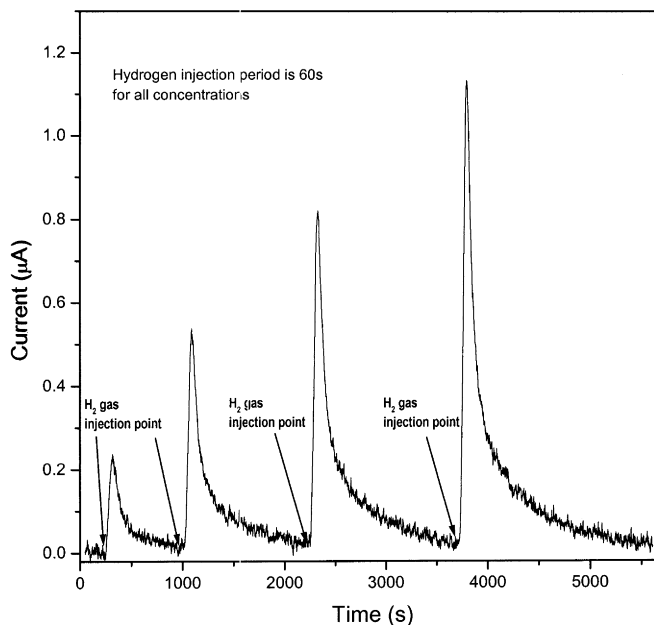


Fig. 5 Sensor response in hydrogen injection mode

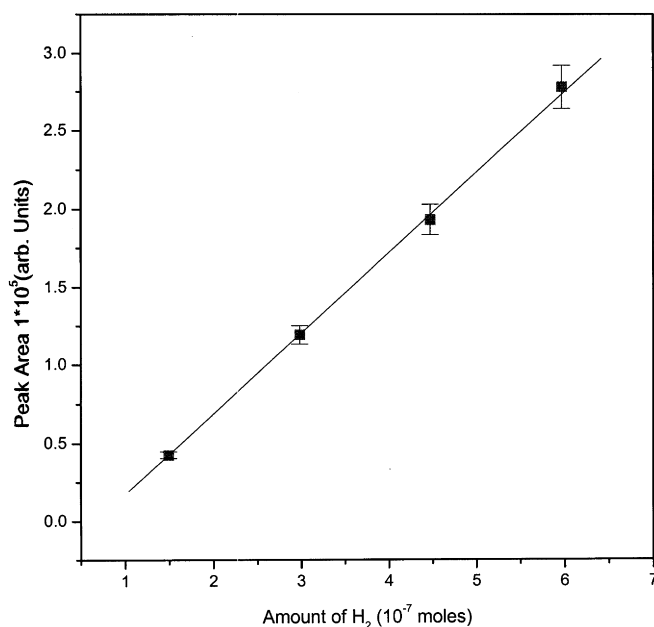


Fig. 6 Calibration of the sensor for various amounts of hydrogen

During our earlier investigation of the mechanism of the polymer sensor [11], it was observed that palladium is not a suitable material for the cathode side of the sensor. The overpotential for oxygen reduction at the Pd cathode was observed to be high and there was also a switch-over from an activation-controlled electrode process to a diffusion-controlled electrode process (possibly due to the high solubility of hydrogen in palladium). Besides, there is a decrease in catalytic activity of the Pd cathode owing to oxide formation on the air side. Hence, in the present sensor, Pt was chosen as the

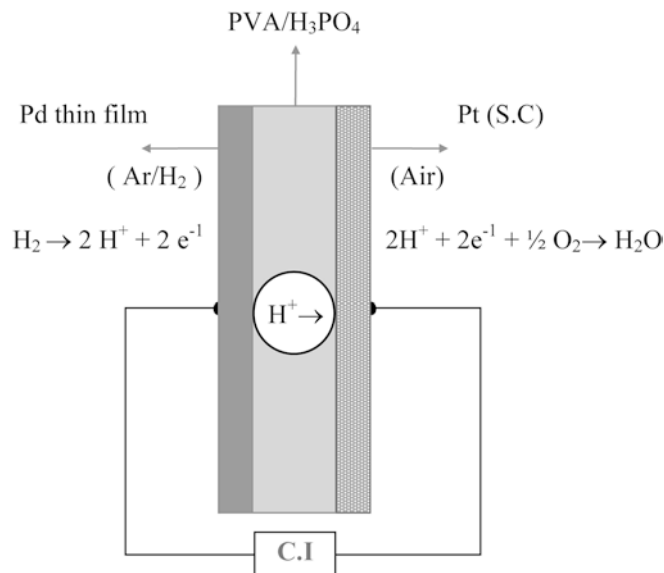


Fig. 7 Reactions occurring at the sensor electrodes

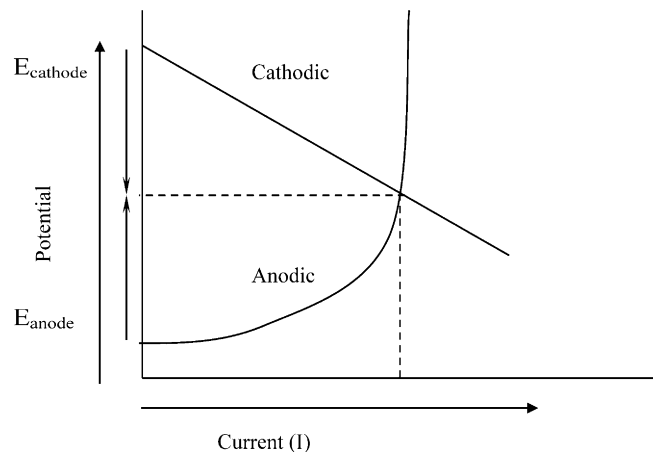


Fig. 8 Polarization curves of the sensor

cathode material because of the lower overpotential for oxygen reduction and lower solubility for hydrogen. The anode was retained as a Pd film since the high solubility, sticking coefficient and diffusion coefficient for hydrogen in Pd are advantageous for sensing low concentrations of hydrogen in argon. The low overpotential for hydrogen oxidation on a Pd film anode was also found to be advantageous from the point of view of sensor applications.

As shown in Fig. 9, the anodic overpotential is linearly dependent on  $\log(1-i/i_L)$ , where  $i$  is the anodic current at any given value of overpotential and  $i_L$  is the steady-state short-circuit current. The amount of  $H^+$  produced by the anodic reaction is proportional to the partial pressure of  $H_2$  on the sensing side. So the short-circuit current can be expected to vary linearly with the hydrogen partial pressure, as observed in this study.

From the electrode reactions it is evident that oxygen or any chemical species that is catalytically reduced by

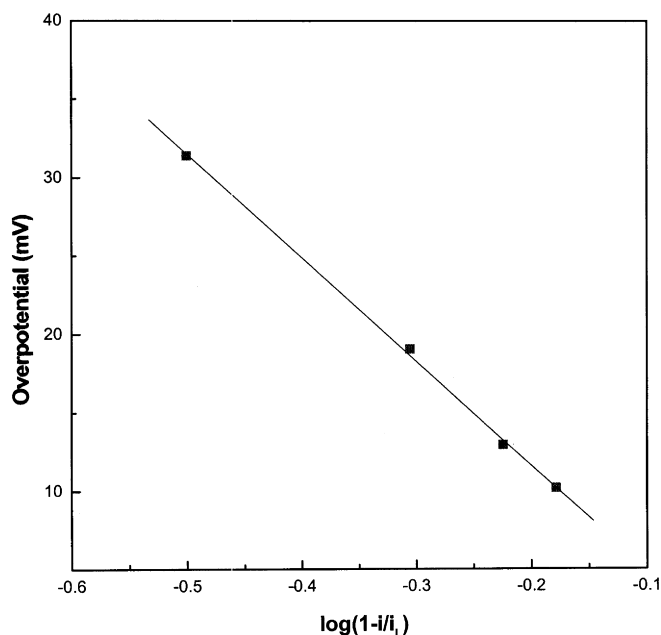


Fig. 9 Anodic overpotential showing diffusion-limited current

the hydrogen on the sensing side can interfere with the measurement. When oxygen is present on the sensing side, the short-circuit current is reduced owing to the occurrence of both reactions (1) and (2) on the sensing side, thus reducing the current flowing through the external circuit as observed in the present study.

The long-term stability of the sensor was monitored and is shown in Fig. 10. No variation with respect to response time was observed. However, a marginal decrease in the limiting current values was found. From the sensor mechanism it is evident that the electrolyte conductivity plays a role in the magnitude of the response of

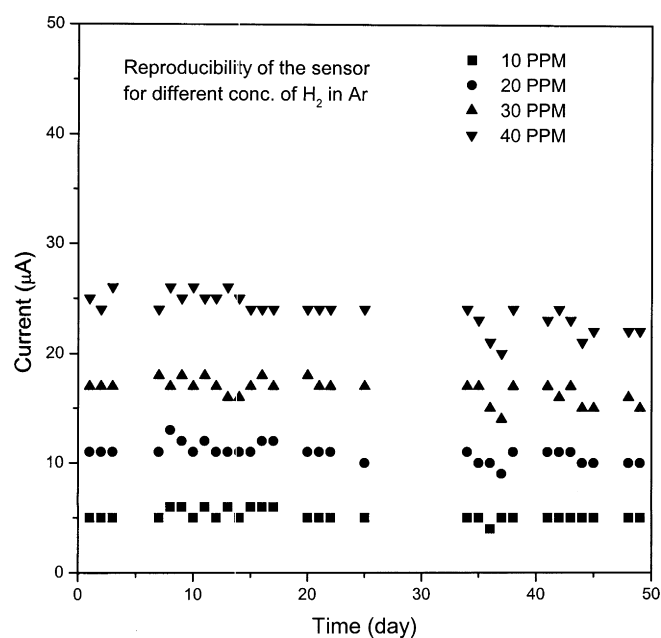


Fig. 10 Long-term performance of the sensor

the sensor. However, there was no drastic variation in conductivity during the measurement period to affect the sensor response. This may be due to the palladium film coating, which serves as an impervious barrier for moisture on the sensing side. Moisture is removed from the electrolyte to a great extent since the anode film deposition is carried out at high vacuum. During the experiment, no moistening of the sensing gas was done.

To assess the performance of the sensor in comparison to a commercially available hydrogen sensor, the response of the present sensor and a commercially procured sensor (NUCON model 500) to hydrogen in argon was studied in sequence with the automated system as described earlier. Figure 11 gives a comparison of the normalized response of the present sensor to the commercial sensor. The response behaviour and sensitivity are comparable at the low range of hydrogen concentrations.

Compared to earlier sensor [11], the present sensor is more compact, lightweight, and less susceptible to electromagnetic interference. The improved design with the current collector and the changing of the cathode from a palladium film to a platinum thick film is responsible for the improved performance. The present sensor is developed with objective of measurement of  $H_2/Ar$  at the ppm level (Cover gas monitoring and other applications [14, 15, 16]). Miura's sensor [7, 8, 9] is sensitive at a percentage level in air, whereas the reported sensor is sensitive at the ppm level in argon. The improved sensitivity of the reported sensor is achieved by the incorporation of certain features as listed below.

The reported sensor has a larger geometrical and active area since a polymer electrolyte membrane and not a pellet is used as the electrolyte. This ensured a larger signal and hence better sensitivity at very low concentrations. The reported sensor is tested with gas

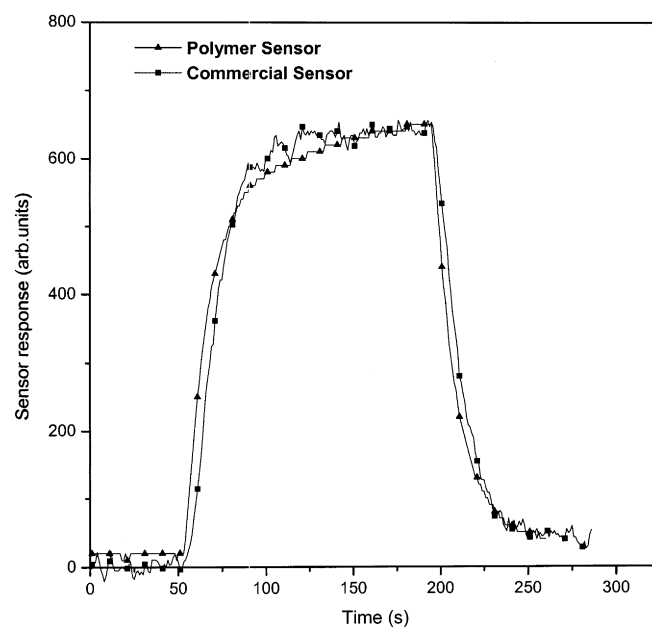


Fig. 11 Performance comparison of sensors at 7 ppm hydrogen in argon

without any moistening, which makes it applicable in fast reactors where water is not admissible in the reactor building as a safety precaution against a sodium fire due to water-sodium reaction (sodium is used as coolant in the reactor). The background noise level is also low, which leads to a low detection limit (ppm level). The design of the sensor is optimized with a low dead volume, an effective current collection and light weight, in spite of the large surface area.

The type of electrodes used and even the method of obtaining the electrical contact in the reported sensor are carried out with the objective of achieving a low detection limit for hydrogen. The sensing side electrode is a thin film of palladium deposited by physical vapour deposition on the proton-conducting membrane. Pd has a high sticking coefficient at low hydrogen concentrations and this helps in improving the detection limit and sensitivity. The cathode is a Pt-supported catalyst, which provides a larger electrochemical surface area compared to Pt black. As it is not available commercially, we have developed a procedure for casting the polymer electrolyte membrane as a supported membrane to give sufficient mechanical strength.

#### Applications of the sensor

The sensor was developed to monitor hydrogen in argon cover gas in the fast reactor at our centre. A new method for the measurement of diffusible hydrogen in weld samples has been developed [14] and the present sensor replaces the earlier version [11]. The sensor finds application in the new method for on-line corrosion measurement in acid medium [15, 16]. We have also applied the sensor to measure the hydrogen content in metals and alloys by on-line measurement of hydrogen released during heating the sample.

#### Conclusion

A polymer electrolyte fuel cell-based amperometric hydrogen sensor using a Pd anode and a Pt cathode has

been developed and its response to hydrogen studied at the ppm level. The sensor is operable at room temperature and can monitor hydrogen in an inert atmosphere. The sensor response is comparable to a commercial sensor. The sensor finds application in variety of technologically relevant areas.

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