

# Improved Nafion-based amperometric sensor for hydrogen in argon

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**Abstract** An improved polymer electrolyte membrane fuel cell-based amperometric hydrogen sensor has been developed. The sensor operates at room temperature, and the electrolyte used in the sensor is Nafion which is a proton-conducting solid polymer electrolyte. Platinum black is used as both anode and cathode. The sensor functions as a fuel cell,  $H_2/Pt//Nafion//Pt/O_2$ , and a mechanical barrier limits the supply of hydrogen to the sensing side electrode. The limiting current is found to be linearly related to the hydrogen concentration. The sensor can be used to measure hydrogen in argon in parts per million and percentage levels. The basic principle, details of assembly, and response behavior of the sensor are discussed.

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

## Introduction

Fuel cells are fast emerging as the technology driver of this century. Hydrogen is expected to replace conventional energy sources as a pollution-free source. It may not be an exaggeration if we consider the economy of twenty-first century as hydrogen economy. Recently, there is consider-

able development in automotive technology using fuel cell as power source, which aims at an efficient and pollution-free vehicle [1]. Hydrogen as fuel in futuristic automobiles using  $H_2/O_2$  fuel cell is, thus, a definite possibility, and there is need for hydrogen sensor to monitor the fuel leak. Because hydrogen forms an explosive mixture with air, safe usage of hydrogen is essential for its extended application. Gaseous hydrogen is used in power plants for removing friction heat in turbines. In nickel–hydrogen batteries used in satellites, hydrogen is stored at high pressure and has to be monitored for leak [2]. Hydrogen finds extensive application as a chemical in industries, as cryogenic-fuel in rockets, and as a lift-off gas in weather balloons, etc. Hydrogen is also an industrial by-product in chlor-alkali industry.

In fast breeder reactors, detection of steam generator leaks [3] is carried out by monitoring hydrogen in argon cover-gas. Normally, the hydrogen concentration in cover gas will be in parts per million (ppm) level, and any accidental sodium–water reaction would lead to sudden increase in hydrogen level. Hydrogen is required to be monitored during disposal of sodium used in fast breeder reactors such that there is no build-up of hydrogen that can form an explosive mixture on release to atmosphere. The hydrogen concentration during sodium cleaning by water vapor–carbon dioxide method will be in percentage level and has to be monitored and normally to be maintained below one percentage, which is the safe threshold level [4, 5]. Measurement of diffusible hydrogen in weld samples is part of certification of welding electrodes used in manual arc welding [6]. By measuring the amount of hydrogen evolved, kinetics of many reactions where hydrogen is released can be studied. Decontamination studies using acid formulations are typical examples involving hydrogen release [7–9]. Hydrogen sensors with good sensitivity,

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selectivity, response time, and long-term stability are required for all the above applications. Depending on the application, the sensor needs to be tuned to respond in ppm or percentage levels of concentration.

Quantitative measurement or even reliable detection of hydrogen has always been a technological challenge. A variety of sensors have been developed which include electrochemical, catalytic, semiconductor, and resistivity sensors. Electrochemical sensors include both potentiometric [10–12] and amperometric [13–18] devices. Although potentiometric sensors have a wide dynamic range, they 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 maintenance-free. Therefore, development of reliable sensors operable at low temperature 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 because it works at room temperature and on fuel-cell principle. Besides, this sensor can also operate in the absence of oxygen on the sensing side, whereas availability of oxygen is essential for pellister sensors. In applications like cover gas monitoring in fast breeder reactor circuits where no oxygen is available on the sensing side, the present proton-conducting solid electrolyte-based sensor becomes advantageous.

Either solid or liquid proton-conducting electrolytes can be used in electrochemical hydrogen sensors. Amperometric sensors using acid electrolyte are the commercial technology of today. But the life of these sensors is limited due to loss of electrolyte. Although solid electrolytes have an advantage against possibility of spillage when compared to liquid electrolytes, most of them (HUP, hydrated  $\text{WO}_3$ ) need humidification of sample gas. Proton-conducting polymer electrolyte-based sensors are evolving as a viable alternative to liquid electrolyte-based hydrogen sensors. Conducting solid polymer electrolytes include PVA/ $\text{H}_3\text{PO}_4$  blend, Nafion, acid-doped polybenzimidazole, etc.

Hydrogen sensor using PVA/ $\text{H}_3\text{PO}_4$  blend as electrolyte developed at our laboratory with palladium thin film as anode and platinum as cathode had been reported elsewhere

and tested for its performance [14]. Nafion has already been used in the development of hydrogen sensor by our laboratory and others [15, 16]. In the present work, we report the development of an amperometric hydrogen sensor that uses Nafion as solid polymer electrolyte, Pt as anode and cathode. The cell functions in fuel cell mode with hydrogen in argon on the sensing side and air on the counter electrode side. A membrane diffusion barrier on the sensing electrode side limits the supply of hydrogen to the sensing electrode so that the sensor functions as an amperometric device. The sensor is sensitive to ppm level of hydrogen in argon, has wide dynamic range, and has better response characteristics compared to the earlier reported sensors. The sensor is developed for monitoring hydrogen in argon cover gas of the fast breeder reactor circuits and other applications like hydrogen monitoring during sodium dissolution.

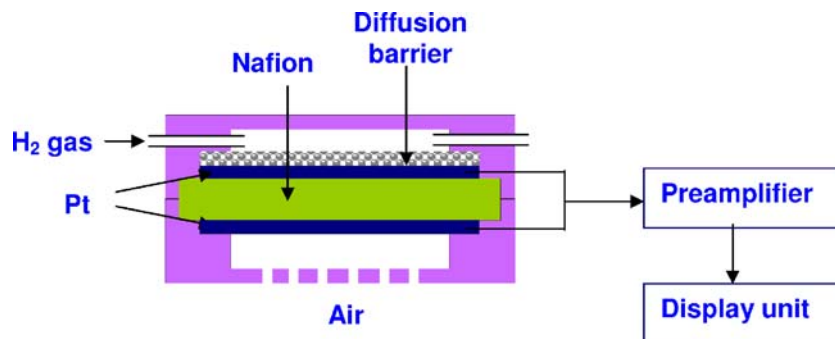
## Experimental

### Material preparation and sensor assembly

The sensor uses Nafion 117 as the proton-conducting solid polymer electrolyte. The electrolyte membrane is sandwiched between the platinum electrodes. The electrodes were deposited by decal transfer method [19]. A membrane diffusion barrier was positioned above the sensing electrode to limit the supply of hydrogen to the sensing electrode. The counter electrode is exposed to air. The assembly of the sensor was made using polycarbonate material. The schematic of the sensor is shown in Fig. 1.

The sensing and counter electrodes of the sensor were made of platinum black, and the electrochemical active area was found to be 20% of the surface area. A slurry of the catalyst was prepared by adding water to platinum black, mixed well, and sonicated for few minutes. To this mixture, isopropyl alcohol was added and sonicated until homogeneous ink-like paste was obtained. Before coating, a 25% of Teflon emulsion was added to the mixture. The slurry was coated directly on the polyamide sheet by screen-printing. The catalyst-coated sheet was sintered overnight at 110 °C

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



under vacuum. The catalyst was transferred to both sides of the Nafion 117 membrane by hot pressing at 120 °C at a pressure of 5 kg/cm<sup>2</sup> for 15 min. Platinum grids were used as current collectors on both the sides.

The sensing side with barrier 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-measuring device interfaced to a readout device. The assembly functions as an amperometric sensor, and the limiting current was found to be linearly related to the hydrogen concentration. Data processing is done by the readout device, which can store the calibration parameters and display the hydrogen concentration directly.

### Measurement

The experimental set-up for hydrogen measurement is shown in Fig. 2. Calibration of the sensor was carried out using commercially available calibration gas mixtures supplied by SGL, Mumbai. The required concentration of hydrogen in argon was prepared by blending commercially available calibrated Ar/H<sub>2</sub> mixture with argon using a gas-blending system consisting of two mass flow controllers of MKS, USA, connected to a mixing chamber (Fig. 2). Initially, commercial argon was passed (flow rate standard 200 cm<sup>3</sup> min<sup>-1</sup>) on the sensing side of the sensor till the baseline current was steady. The counter electrode side was exposed to atmospheric air all along. Thus, the sensor is a self-breathing device because no airflow is required at the counter electrode side. H<sub>2</sub>/Ar mixture of known concentration was let into the sensing side at the same flow rate as argon and retained till steady-state current was reached. Once the measurement was over, H<sub>2</sub>/Ar flow was stopped, and Argon flow resumed till the original baseline current was reached. The experiment was repeated for various concentrations of H<sub>2</sub> in argon, and the calibration curve was

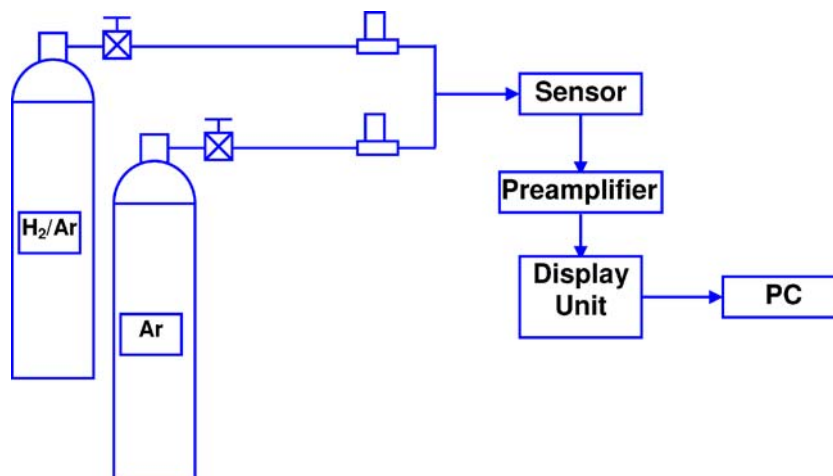
obtained by plotting steady-state current against concentration of hydrogen in argon. The hydrogen concentration of any sample gas can be estimated by knowing the steady-state current value and the calibration parameters of the sensor.

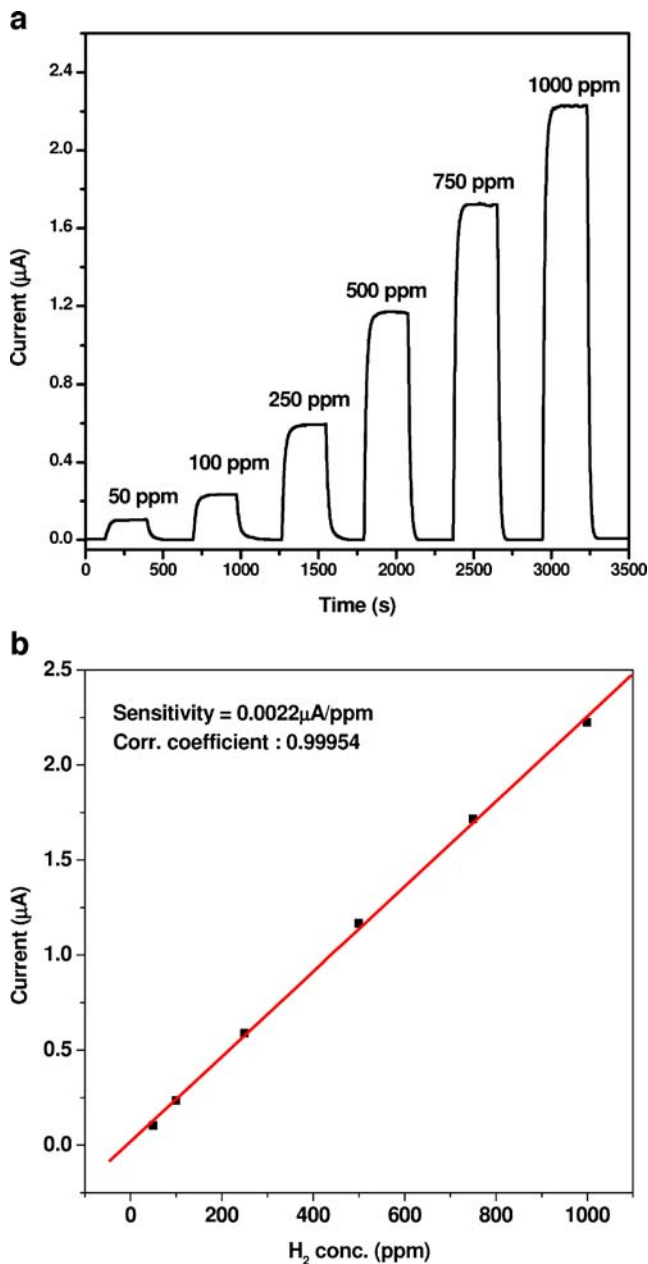
The sensor is provided with a direct readout unit such that the sensor becomes user-friendly and suitable for field applications. The readout unit collects the digital output from the current-measuring unit of the sensor continuously. The sensor with direct readout unit is calibrated by the same procedure as sensor is calibrated. Because the sensor response is fast, the steady-state current is attained in less than a minute. The steady-state current value obtained after a set time (a minute) for any given concentration of hydrogen is monitored at regular short intervals, averaged, and stored in the direct readout device. The stored steady-state current signals for different concentrations of hydrogen are fitted to a first-order fit using least square fitting program embedded in the readout device, and the fit parameters are also stored in the device. Any unknown concentration can be directly read in the readout device by passing the gas containing hydrogen through the sensor. The readout device calculates and displays the actual concentration of hydrogen by using the fit parameters already saved. The whole calibration exercise can be carried out in less than 10 min. The readout device gives an analogue voltage output and digital output for data logging.

### Results and discussion

The sensor response to various concentrations of hydrogen in argon was studied. The response behavior in ppm range of H<sub>2</sub> in Ar is shown in Fig. 3a. Figure 3b is the calibration plot for 50–1,000 ppm of H<sub>2</sub> in Ar. It is evident from the response curve that the sensor responds rapidly to H<sub>2</sub> in Ar in ppm range of concentration. Throughout the study, the

**Fig. 2** Block diagram of the experimental setup



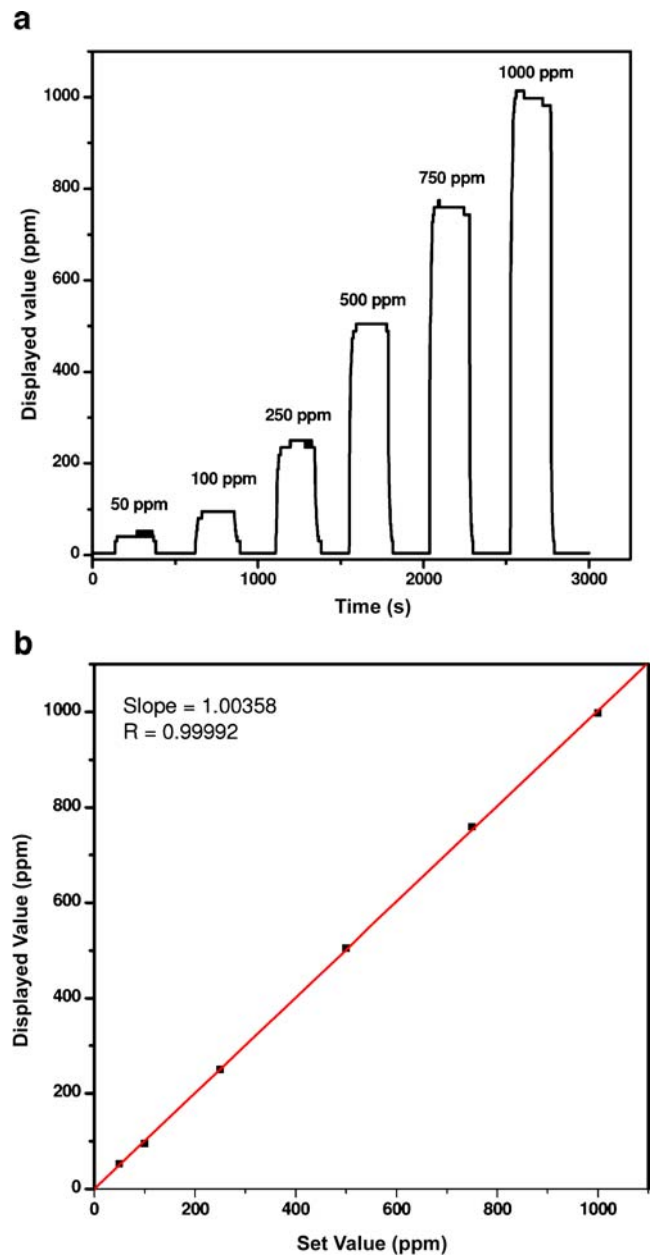


**Fig. 3** **a** Response of the sensor for various concentrations of hydrogen in Ar in ppm range. **b** Calibration plot of the sensor for hydrogen in argon in ppm range

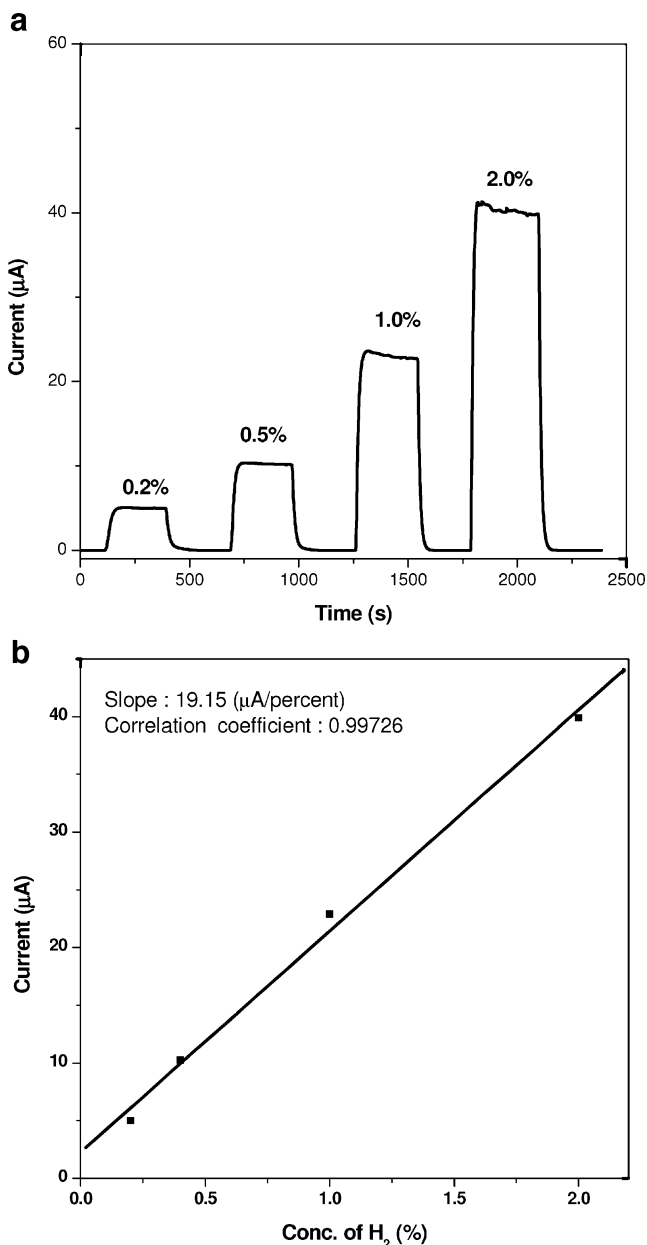
sensor was in self-breathing mode and no airflow was maintained at the counter electrode side. The air diffusing to the counter electrode side through the pores provided in the sensor body at the counter electrode side was sufficient to supply the required oxygen for the cathode reaction.

The readout device displays the concentrations as first-order fit of the limiting current to the hydrogen concentration. The calibration was carried out as explained earlier, and the calibration parameters were stored in the readout device. Figure 4a is the recorded display value for various concentrations of hydrogen in argon. Figure 4b is the

correlation of the display values to actual concentrations. Sensor responds sharply for the concentrations of hydrogen from 50 to 1,000 ppm, and Fig. 7a shows the comparison of response time in signal mode as well as direct display mode. In both the modes, response time is well below a minute and varies from 50 to 20 s which is comparable with commercial sensors available in the market. However, the higher response time (120 s) for 50 ppm in the direct display mode is due to the low resolution of the analogue output device, and actually, the sensor is sharp in response. It is evident from signal response curve of the sensor that



**Fig. 4** **a** Recorded display values of the sensor for various concentrations of hydrogen in Ar in ppm range. **b** Correlation of the sensor between set value and displayed value of the concentration



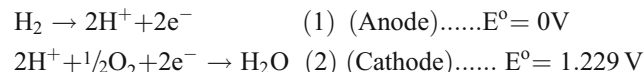
**Fig. 5** **a** Response of the sensor for hydrogen in argon in percentage level. **b** Calibration plot of the sensor for hydrogen in Argon in ppm range

the response time is only 60 s for that corresponding concentration.

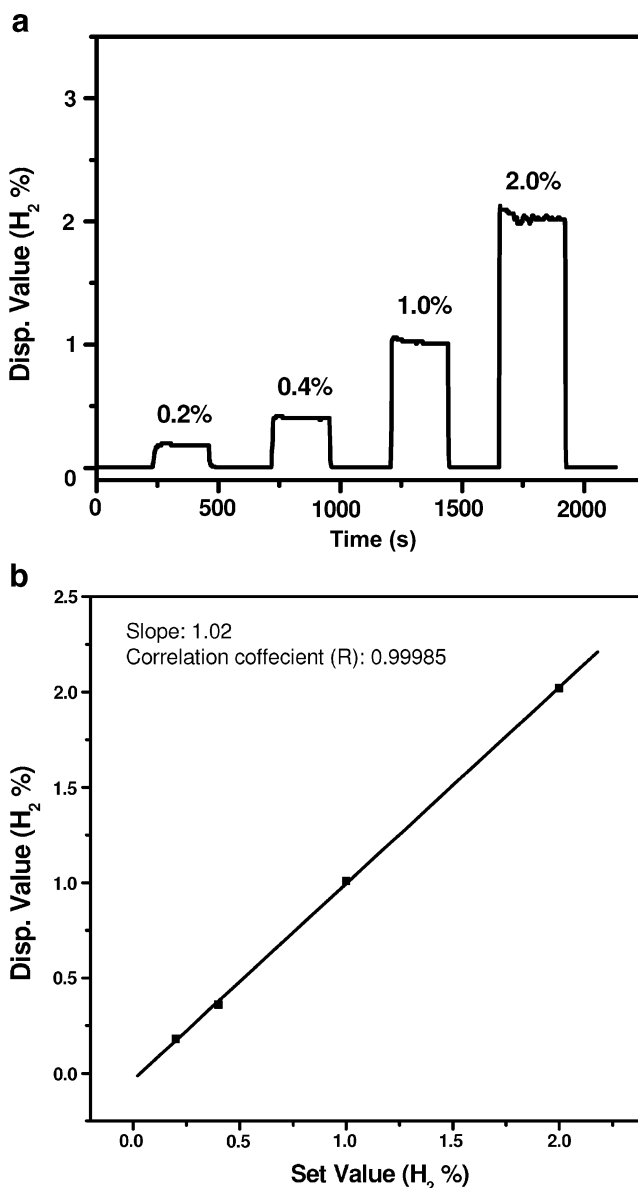
Figure 5a and b shows the response curves and the calibration plot of the sensor for  $\text{H}_2$  in Ar in the concentration range 0.2 to 2%. The sensor responds sharply to any change in concentration in percentage range also. However, beyond 2%, sensor behavior changes nonlinearly. Figure 6a shows the displayed concentration values when various concentrations of hydrogen in argon in percentage level are introduced into the sensor. Figure 6b shows the correlation between the displayed values and actual concentrations. Figure 7b is the comparison of response

time in both the modes of the sensor, namely, current mode and direct display mode, and the response time of the sensor is much sharper in percentage level than ppm range and varies from 20 to 5 s.

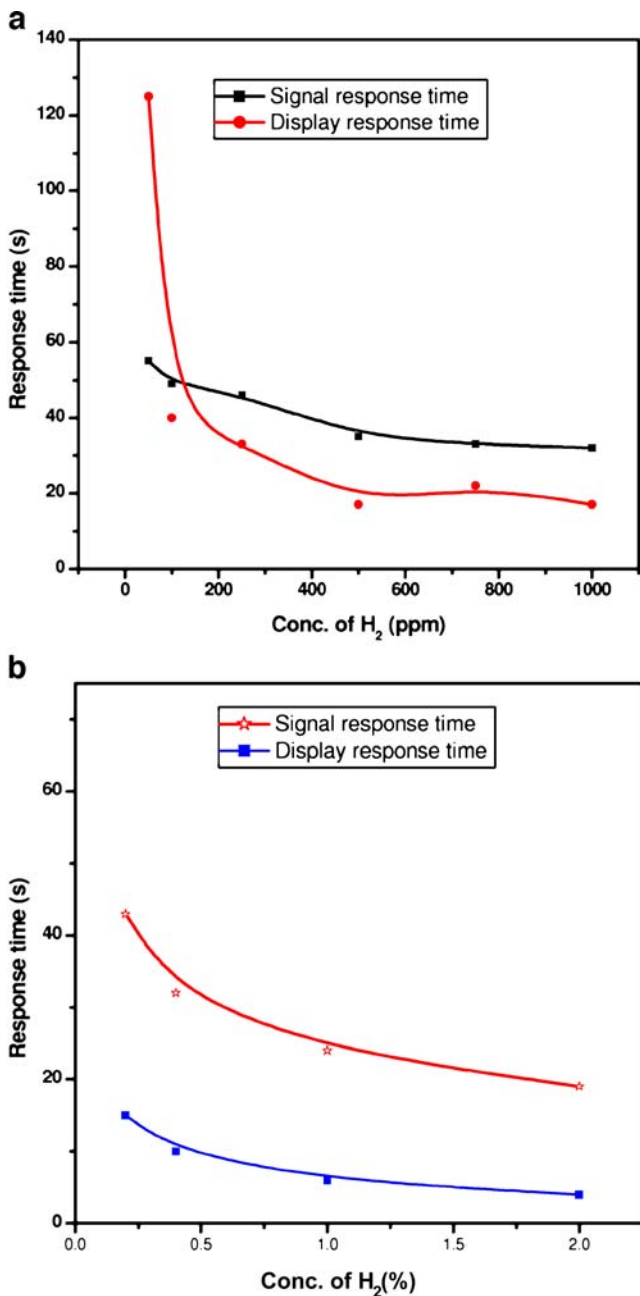
The electrochemical processes occurring at the electrodes are shown as given below.



The sensor cell  $\text{H}_2$  (in Argon), Pt/Nafion/Pt, air, is a self-driven fuel cell device and operates without application of external voltage. The standard reduction potential for anode and cathode reactions is indicated above. The sensing

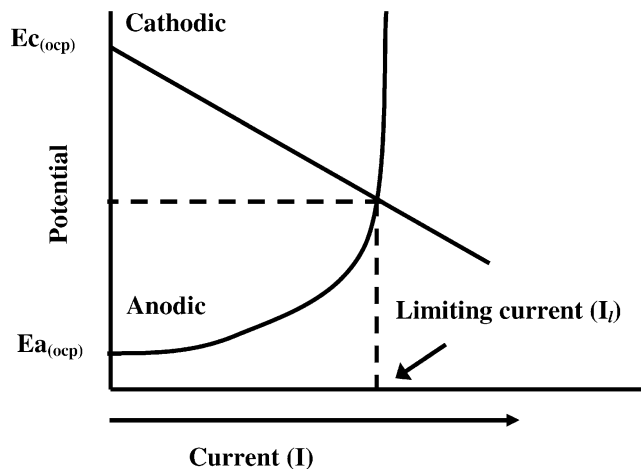


**Fig. 6** **a** Response of the sensor for hydrogen in argon in percentage range with display unit. **b** Correlation of the sensor between set value and displayed value in percentage level



**Fig. 7** **a** Comparison of response time for original signal and display unit of the sensor in ppm range. **b** Comparison of response time for original signal and display unit of the sensor in percentage range

electrode is a non-polarizable electrode, and hence, the rate of redox process at the sensing electrode is significantly altered by even minimal polarizing potential. The counter electrode has high standard reduction potential and hence gives the required polarizing potential to the sensing electrode. No external voltage was required to be applied for the range of measurement in the sensor. The anodic and cathodic polarization curves are shown in Fig. 8. Although the sensor operated satisfactorily in the amperometric mode, the sensor did not develop stable potential in open

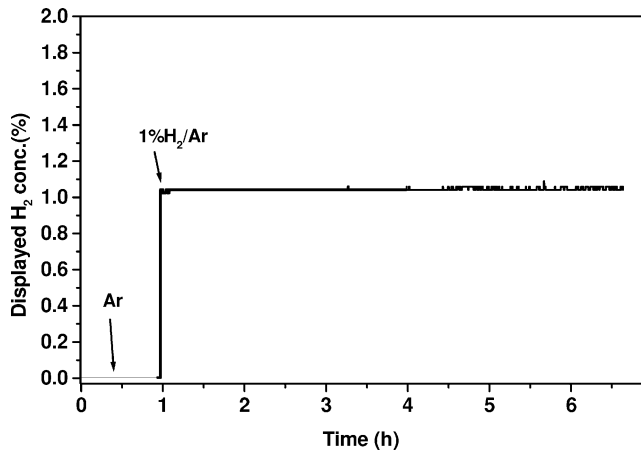


**Fig. 8** Anodic and cathodic polarization curves of the sensor

circuit condition. Amperometric measurement is a steady-state measurement of current in limiting current regime and hence ensures minimal concentration of hydrogen at sensing electrode at steady-state condition. Hence, molecular crossover of hydrogen does not happen in amperometric mode. Under open circuit condition, there is no removal of hydrogen at the sensing electrode due to oxidation, and hence, molecular crossover of H<sub>2</sub> to the cathode side can occur leading to unstable potential.

The stability of the sensor was monitored for a period of 3 weeks and found to be stable within ±10% of the concentration value. The response of the sensor for 1% of hydrogen in argon for a period of 3 weeks is shown in Fig. 9. However, the sensor showed excellent short-term stability as is evident from Fig. 10. The temperature dependence of the sensor response was also studied and was found to be marginally affected by temperature changes, and Fig. 11 shows the change in sensor with temperature.

The barrier material used in the sensor was polypropylene. When the rate of oxidation of hydrogen at the sensing



**Fig. 9** Stability of the sensor signal for 1% of hydrogen in argon



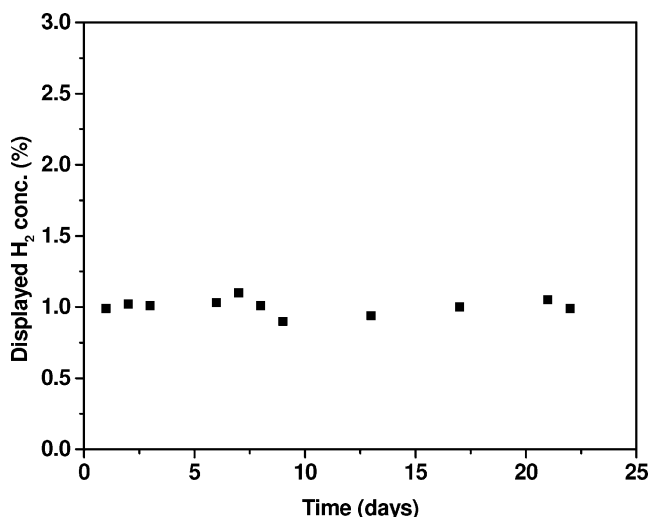


Fig. 10 Reproducibility of the sensor signal for 1% of hydrogen in argon

electrode is higher than the rate of supply of hydrogen to the electrode, the electrochemical process becomes diffusion controlled. It may be noted that hydrogen oxidation at the sensing electrode is a kinetically fast process, and hence, the diffusion of hydrogen to the electrode becomes the slowest and rate-determining step. The high conductivity of the electrolyte, Nafion, ensures that the resistive overpotential is minimal, and hence, moderate changes in electrolyte conductivity cannot influence the magnitude of limiting current. If the magnitude of limiting current is also maintained low by regulating the supply of hydrogen to anode by optimizing the barrier, the influence of variation in the electrolyte conductivity on limiting current value will be further reduced. The current measurement device has to be improved such that the detection limit is not compromised while reducing the hydrogen flux at the sensing

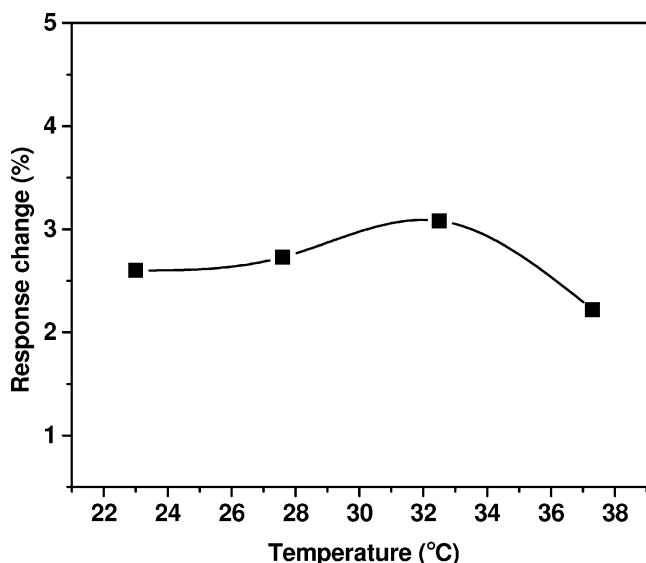


Fig. 11 Deviation of the sensor signal as function of temperature

electrode. In the reported sensor, we could achieve a theoretical detection limit of 2 ppm, and we have practically measured down to 5 ppm. Unlike presently available commercial sensors, the present sensor has measurement range from ppm to percentage level and is linear in ppm and percentage range. Although the counter electrode reaction is a kinetically slow and activation-controlled process, high concentration of electro-active species at the cathode (H<sup>+</sup>, O<sub>2</sub>, and moisture) ensures that the rate of the electrochemical reaction at the cathode is much higher than the rate of diffusion of hydrogen through the diffusion membrane at the sensing electrode side. Thus, the sensor functions as a limiting current device and hence as an amperometric sensor.

The volume between the membrane barrier and the anode is minimized in our design so that the electrochemical activity of the electrode is sufficient to cater to the flux of hydrogen diffusing through the membrane and steady state is attained fast. This ensures minimal response time for the sensor. The thickness of the barrier membrane is 0.2 mm. Because the electrode is in close proximity to the thin membrane, the steady-state limiting current at a given concentration can be derived as follows.

- Diffusion rate of hydrogen through the membrane= Rate of oxidation of hydrogen per unit areas at sensing electrode
- Diffusion rate of hydrogen (H<sub>2</sub>) through the membrane=  $DC/t$
- Rate of oxidation of hydrogen (H<sub>2</sub>) at sensing electrode per unit area= $I/2AF$

$$DC/t=I/2AF$$

$$I=2DCAF/t$$

where  $I$  is the limiting current,  $D$  is the diffusion coefficient for hydrogen through the polypropylene barrier membrane,  $C$  is the hydrogen concentration in argon,  $t$  is the thickness of the barrier membrane,  $A$  is the geometrical area of the electrode, and  $F$  is Faraday constant. The diffusion through the membrane is via the fine pores in the membrane. At steady-state limiting current situation, it can be safely considered that the hydrogen concentration in the vicinity of the sensing electrode is zero.

It is evident from the above analysis that the limiting current can be optimized to the desired range using barrier material of optimal thickness and diffusion coefficient. As explained earlier, the limiting current is to be regulated to the desired range such that the sensor sensitivity is attained with minimal sensitivity to conductivity changes in the electrolyte. It is advisable to have as low a limiting current as possible, but is constrained by the signal-to-noise ratio of the current-measuring device. The present sensor has a sensitivity of 0.56 μA/ppm hydrogen in argon, and attempts

are being made to improve the current measurement technique such that the detection limit is retained with much less value of limiting current.

Large electrochemical activity at the sensing and counter electrodes ensures large excess reserve activity at the electrodes. This ensures that the rate limiting current is reached with minimum delay and ensures that the sensor response time is minimal. Response time decreases with increasing concentration and shows a plateau region at higher concentration.

We had reported hydrogen sensors based on PVA-H<sub>3</sub>PO<sub>4</sub> and Nafion for monitoring hydrogen in argon [16, 17]. Both these sensors are applicable only in ppm range of concentrations and are constrained by the absence of a physical diffusion barrier. In the absence of a diffusion barrier, the oxidation rate of hydrogen at the sensing electrode is unable to exceed the rate of availability at higher concentrations. Hence, the measured current is no more a diffusion-controlled process. Thus, the sensor gets limited to ppm level in its application range. The present sensor is functional in both ppm and percentage levels of hydrogen concentration. The response and retrace time in the present sensor is much better at both ppm and percentage levels due to the mechanical barrier provided. The direct readout device incorporated in the present sensor makes the sensor user-friendly and suitable for field applications.

The long-term stability of the sensor was monitored for a month, and the deviation was observed to be within 10%. The response of the sensor was monitored at altered temperatures from the ambient ( $\pm 5$  °C), and the variation in response was found to be within 5% which is shown in Fig. 11.

### Applications of the sensor

The sensor has been used to monitor hydrogen release during studies of sodium cleaning and decontamination of fast breeder reactor components. The sensor finds application for monitoring hydrogen in argon cover gas in the fast breeder reactor at our center. A new method for the measurement of diffusible hydrogen in weld samples has been developed [20], and the present sensor replaces the earlier version [6]. The sensor finds application in the new method for online corrosion measurement in acid medium [7–9]. We have also applied the sensor to measure the hydrogen content in refractory metals and alloys.

### Conclusion

A polymer electrolyte fuel cell-based amperometric hydrogen sensor using Pt electrodes has been developed and its response to hydrogen studied in ppm and percentage level. The sensor is operable at room temperature and can monitor hydrogen in 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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