# Diffusible Hydrogen Measurement in Steel Welds using an Electrochemical Hydrogen Sensor

**Girish Kumar Padhy[1], V. Ramasubbu[1], N. Murugesan[2], C. Remash[2] and S.K. Albert[*]**

[1]Material Technology Division, [2]Material Chemistry Division, Indira Gandhi Centre for Atomic Research, Kalpakkam-603102, Tamilnadu, India.

## ABSTRACT

Diffusible hydrogen ($H_D$) measurement in steel welding consumables having cellulose, rutile and basic coating has been carried out using a Proton Exchange Membrane Based Hydrogen Sensor (PEMHS). The sensor is an electrochemical fuel cell based device which uses Nafion@117 as proton exchange membrane electrolyte. This can detect hydrogen in an $Ar+H_2$ mixture with detectable limit of 1 ppm. Further, $H_D$ measurements have also been carried out on basic coated electrodes of modified 9Cr-1Mo steel, with very low levels of $H_D$ content. Results obtained have been compared with those obtained from $H_D$ measurement using mercury manometer as per standard ISO 3690. One to one correlation has been obtained between these two different methods of measurements. This sensor has shown good sensitivity, accuracy and precision hence is reliable for $H_D$ measurement. In addition to the above measurement, this method was used to study hydrogen evolution from the weldments as a function of time. The paper presents and discusses the principles of $H_D$ measurement using this sensor, its applications for $H_D$ measurements in weldment, the results obtained, its application to study the hydrogen evolution from weldment as a function of time and the possibility of using this sensor for measurement of hydrogen evolved from the weld specimens at high temperatures.

**Keywords:** Diffusible Hydrogen, Nafion Hydrogen Sensor, Hot Extraction, Hydrogen Diffusivity

## 1.0 INTRODUCTION

Hydrogen in the weldments of carbon and alloyed steels when accompanied with a crack susceptible microstructure and tensile residual stress in the weldment causes Hydrogen Assisted Cracking (HAC) in the weld metal and in the heat affected zone (HAZ). As these cracks are not acceptable in weldments, formation of these cracks should be prevented. For predicting the susceptibility of weldment to HAC, amount of diffusible hydrogen ($H_D$) content in steel weldment is used extensively (Yurioka and Suzuki, 1990). Though many sources such as shielding gas, oil/grease, hydrocarbons on the surface to be welded and moisture in the surrounding atmosphere may contribute to hydrogen in welds, the chief source is the chemically bonded water in the flux coated on the welding electrode (IIW Doc.II-805-85, 1985) which dissociate into hydrogen and oxygen atoms in the arc during welding. Very high temperature ($\sim1600°C$) of the molten metal causes dissolution of large amount of hydrogen atoms present in the arc atmosphere in the weld pool whereas oxygen atoms form oxides which become parts of the slag formed during welding. In general, solubility of hydrogen in ferritic steel is less than 2 ppm by weight at STP. However, the rapid cooling rate (80-150K/second) of the deposited metal during welding does not allow hydrogen to equilibrate with the deposited metal and results in supersaturation of hydrogen in the

deposited metal, which starts diffusing into the HAZ or out of the weld during solidification and subsequent cooling. During this diffusion, most of the hydrogen is retained at various defects called traps which are classified (Hirth, 1980) as reversible traps (e.g. grain boundaries, lath boundaries, dislocations etc.) and irreversible traps (e.g. vacancy, particle matrix, inclusions etc.) in the weld and in the HAZ. At room temperature, irreversible traps have higher binding energies and release of hydrogen from these traps is difficult. However, reversible traps, owing to their lower binding energies [(Iino, 1987), (Iino, 1998)] release hydrogen in subsequent times which is able to diffuse further. Hence, only a part of the total trapped hydrogen tends to diffuse at or near room temperature (25-45°C) which is referred as diffusible hydrogen ($H_D$). Cracking is caused by interaction of $H_D$ with defects, which are locations of stress concentration in the welds. Hence, $H_D$ content in the weld metal shall be controlled and estimation of hydrogen by a suitable technique is the first step in the efforts to avoid cracking. An understanding of the $H_D$ content is also useful to predict the minimum preheat temperature to be employed during welding of steels to avoid cracking [(Suzuki and Terasaki, 1986), (Ito and Bessyo, 1968)]. As one of the major sources of hydrogen is the welding consumables, they are classified based on the $H_D$ content in the weld metal produced by them.

Measurement of $H_D$ content from a weld is carried out by measuring hydrogen evolved from the weld at a fixed temperature for a given duration. Standards such as ISO, AWS, DIN, BIS and IS have recommended procedures for $H_D$ measurements which include mercury (ANSI/AWS A4.3-86, DIN 8572, ISO 3690, IS-11802-1986, JIS Z3118-1986) and gas chromatography (ANSI/ AWS A4.3-86, ISO 3690, JIS Z3118-1986, Ohtsubo et al., 1985, Quintana and Dennecker, 1986) methods. A good agreement between the results has been reported with measurements carried out using mercury and gas chromatography methods (De Abreu et al., 1995). However, these methods are not free from drawbacks. Limitations in using the mercury method are the health and safety issues associated in the handling of mercury, the long durations of hydrogen collection (72 hours or longer after welding (Ravi and Honavar, 1987)), non-applicability of this method at higher temperature for hydrogen collection which would reduce the time of hydrogen collection. Also, this method provides no scope for studies such as the evolution of hydrogen from the weld as a function of time from a single specimen, the evolution of hydrogen at higher temperatures etc. For welding consumable manufacturers the test duration of 72 hours is quite long; but time cannot be shortened with this method as the measurement cannot be carried out at high temperatures. Gas chromatography method permits heating of samples up to a maximum of 400°C reducing the test duration to 20-30 minutes. However, the equipment is costly. Another method, involved in collection of $H_D$ over glycerin (JIS Z3113-1975) is in limited use [(Quintana, 1984), (Siewert, 1986)] because it lacked accuracy and furnished lower $H_D$ contents than those obtained using gas chromatography and mercury methods (Kotecki and La Fave, 1985). The lower $H_D$ contents obtained using the collection of hydrogen over glycerin is attributed to the fact that hydrogen is partially soluble in glycerin. Many other techniques such as determination of HD content using mass spectrometer [(Noble, 1985), (Pressouyre et al., 1988)], low frequency impedance based non contact diffusible hydrogen sensor (Lasseigne, 2008), and computer aided determination of diffusible hydrogen (Karkhin and Levchenko, 2007) are also reported.

$H_D$ measurement can also be carried out using chemical sensors available for detection and measurement of hydrogen in gas mixtures. These sensors include pellistor sensors [(Krawczyk, 2003), (http://www.e2v.com)], semiconductor sensors (Lin et al., 2003), thermal conductivity based devices, electrochemical sensors etc. Pellistor sensors require atmospheres containing oxygen/air in explosive range hence are not suitable for $H_D$ measurement. Semiconductor sensors are based on conductivity changes caused by the chemisorbed oxygen due to hydrogen exposure. Hence oxygen is required along with hydrogen. Thermal conductivity based devices are bulky and not suitable for field applications. Electrochemical sensors for hydrogen measurement include both potentiometric [(Miura, 1983), (Miura and Yamazoe 1988)] and amperometric [(Miura, 1984), (Miura, 1989)]. Potentiometric sensors are suitable at low concentrations but are nonlinear in response. Amperometric sensors are linear in response and use of an amperometric sensor, $H_2/Pt//PVA//Pt/O2$, (comprising of a proton-conducting polymer, Polyvinyl Alcohol (PVA) as its electrolyte) for $H_D$ measurement has been reported [(Albert et al., 1997), (Albert, Ph.D Thesis, 1996)]. The results obtained from the sensor agreed well

with that of the standard Gas Chromatography method. However, it was seen that the PVA membrane suffers from poor long term stability. A modest comparison of all the available solid and liquid electrolytes showed that Nafion is the best available polymer membrane because of its high longevity (>60,000 hours), high chemical stability and high ionic conductivity to opt for PEM fuel cell applications [(Smitha et al., 2005), (Neburchilov et al., 2005), (Viswanathan and Helen, 2007)]. Nafion based electrochemical cells, $H_2/Pt//$Nafion//$Pt/O2$, has been used for measurement of hydrogen in Argon [(Sakthivel and Weppner, 2006), (Velayutham et al., 2004), (Ramesh et al., 2008)]. The present study is involved in the application of this Nafion based electrochemical sensor for HD measurement in welding consumables.

## 2.0 EXPERIMENTAL

### 2.1 Materials used in the study

#### 2.1.1 Test specimen

For $H_D$ measurement, the specimen was prepared as per standard ISO 3690. A triplicate set of specimen assembly comprising of a specimen of dimension 30 mm x 15 mm x 10 mm, a run-on and a run-off piece each of dimension 44 mm x 15 mm x 10 mm were prepared from mild steel and modified 9Cr-1Mo steel. The chemical composition of steels used is given in **Table 1**. The surfaces of the triplicate set were finished at right angles to ensure good contact between the adjacent pieces. The sample was weighed to the nearest 0.01g prior to welding. The specimen assembly was clamped in a copper fixture. The dimensions of the fixture was such that during welding, the heat is conducted away immediately from the test

Table 1: Chemical compositions in of mild steel and modified 9Cr-1Mo in Wt%

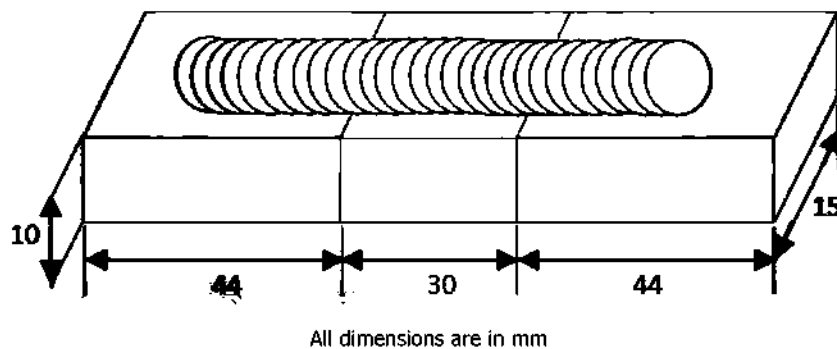| Elements | Mild steel | Modified 9Cr-1Mo |
|---|---|---|
| C | 0.205 | 0.114 |
| Cr | - | 8.838 |
| Mo | - | 0.860 |
| Mn | 0.551 | 0.403 |
| Si | 0.061 | 0.309 |
| P | 0.039 | 0.014 |
| Sr | 0.047 | |
| Nb | - | 0.080 |
| V | - | 0.027 |
| Cu | 0.321 | |
| Fe | Balance | Balance |



All dimensions are in mm

**Fig. 1 : Schematic of the Specimen assembly**

assembly to the fixture. Beads were deposited with welding electrodes with different hydrogen levels on the specimen assembly by manual metal arc welding (MMAW) process. A schematic diagram of the specimen assembly is shown in **Fig. 1.**

#### 2.1.2 Hydrogen Collection Chamber

A hydrogen collection chamber (Lundin et al., 1986) was used to collect $H_D$ from the weld specimen. The chamber is made of stainless steel and has an inlet and an outlet connected to needle

valves. The chamber can be opened or closed using a plug and the leak tightness of the plug is ensured with the help of an O-ring. The chamber was subjected to helium leak testing and it was found that the leak rate is less than $10^{-9}$ sccm. **Fig. 2** shows the schematic of the chamber along with plug. The volume of the chamber is measured by filling it with distilled water and draining the water completely into a measuring jar.

#### 2.1.3 Gas sampling valve
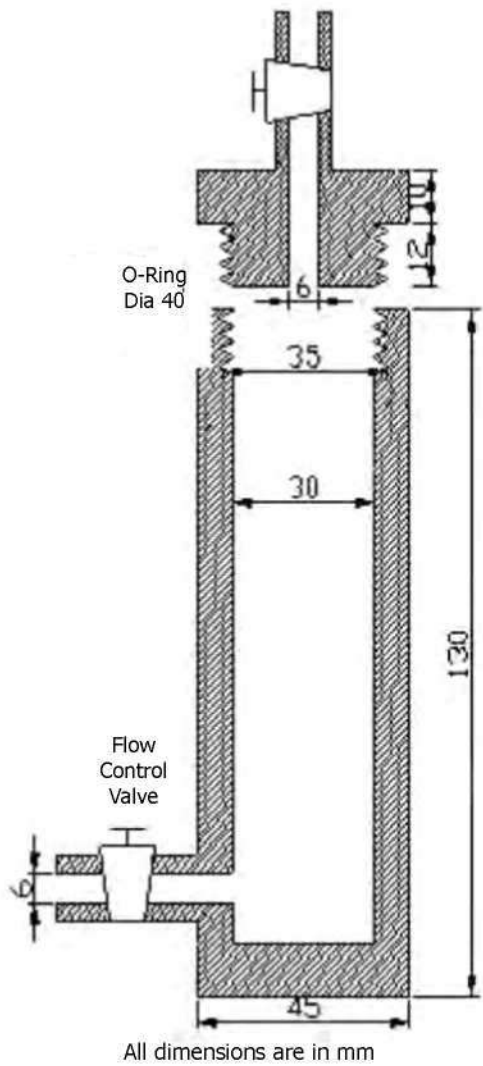
An 8-port gas sampling valve with a

Fig. 2 : Schematic diagram of Hydrogen Collection Chamber
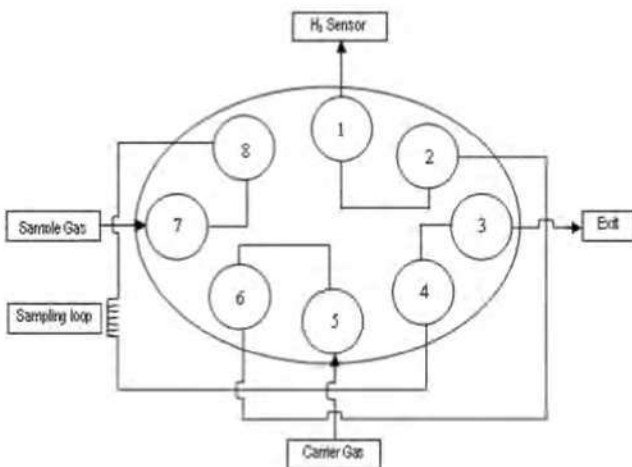
All dimensions are in mm



Fig. 3 : Valve in Mode 1 for sampling the diffusible hydrogen gas

sampling loop of known volume was used for sampling the gas from the hydrogen collection chamber for analysis. The sampling valve operates in two modes as shown in **Fig. 3**. Mode 1 is the sampling mode and Mode 2 is injection mode. In mode 1, as shown in **Fig. 3**, the inlet of the sampling loop is connected to the specimen chamber (sample gas) through port 7 and port 8 and the outlet is open to atmosphere through port 4 and port 3. In this mode only the carrier gas which enters through port 5, is passed onto the detector/sensor through port 2 and port 1. In Mode 2, as shown in **Fig. 4**, the inlet of the sampling loop is connected to the carrier gas line through ports 5 and port 4 and outlet to the detector/sensor through port 8 and port 1. In this process, the sample gas collected in the loop while operating in Mode 1 is carried away to the sensor by the carrier gas. While operating in this mode specimen chamber is kept closed so that gas inside the specimen chamber is conserved.

For analysis of the gas, initially the valve was operated at mode 1. The gas from the specimen chamber, which was filled at a higher pressure than the ambient pressure, was used to flush the sampling loop while the carrier gas was flowing into the sensor. At the end of flushing, the valve was switched over to mode 2 operation and the carrier gas flowed through the sampling loop to the sensor carrying the gas trapped in the loop along with it. The sensor gives a signal corresponding to concentration of hydrogen in the gas mixture.

### 2.1.4 Hydrogen Sensor

The hydrogen sensor used is an electro-chemical cell which has Nafion, a proton conducting polymer, as its electrolyte. The polymer is cast as a film, coated with platinum black on the sensing and counter electrode side. The sensing side of the coated polymer is exposed to the hydrogen argon gas mixture while the counter side is exposed to air. Thus the sensor consists of hydrogen exposed inner platinum film and air exposed outer platinum film with the conducting polymer Nafion, sandwiched between them acts as a fuel cell. A mechanical barrier limits the supply of hydrogen at the sensing electrode. A schematic representation of the sensor with conducting leads is shown in **Fig. 5.** Hydrogen present in the Ar-$H_2$ mixture gets chemisorbed at the sensing electrode and loses its electron to form $H^+$ which permeates through the polymer to reach the counter electrode where it encounters oxide ion ($O^{2-}$, which is produced by taking up the electrons lost by hydrogen and oxygen from the ambient) to form $H_2O$. The reactions taking place at the anode and at the cathode of the
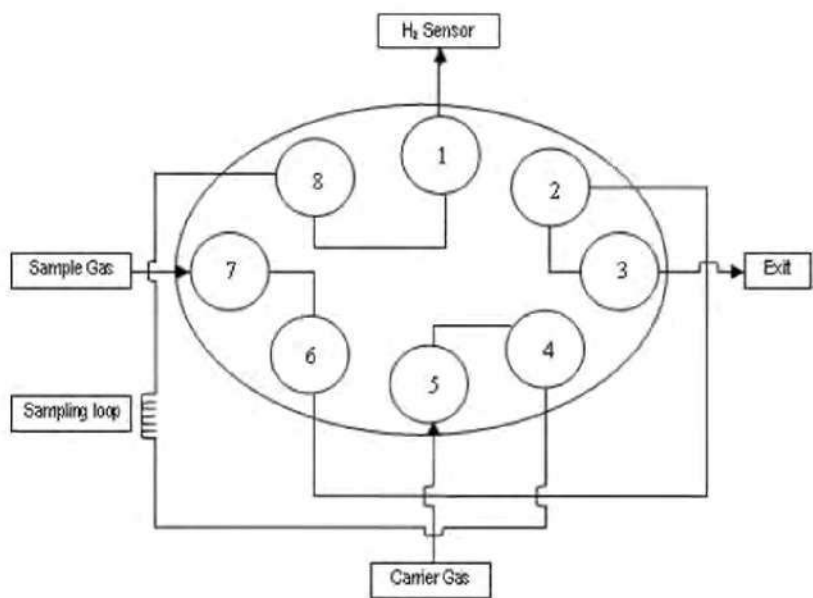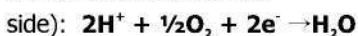
**Fig. 4 : Valve in Mode 2 for injection of sampled gas onto the sensor**

above electro-chemical cell are as follows:

At the anode
(Sensing side): $H_2 \rightarrow 2H^+ + 2e^-$

At the cathode (Couneter
side): $2H^+ + \frac{1}{2}O_2 + 2e^- \rightarrow H_2O$

During the conduction of hydrogen ion through the polymer membrane, a short circuit current is produced and a peak corresponding to the short circuit current was observed in the data acquisition system which in turn is used to measure the concentration of

hydrogen in the hydrogen collection chamber.

## 2.2 Diffusible Hydrogen Measurement

### 2.2.1 Preparation of specimen for the HD measurement

Five different classes of electrodes which are known to have different levels of $H_D$ content were used for $H_D$ measurement using the sensor. Prior to welding, the specimen was degassed by holding it at 650°C for 1 hour and the welding electrodes were baked as per the requirement given in **Table 2**. Weld specimens were prepared by depositing
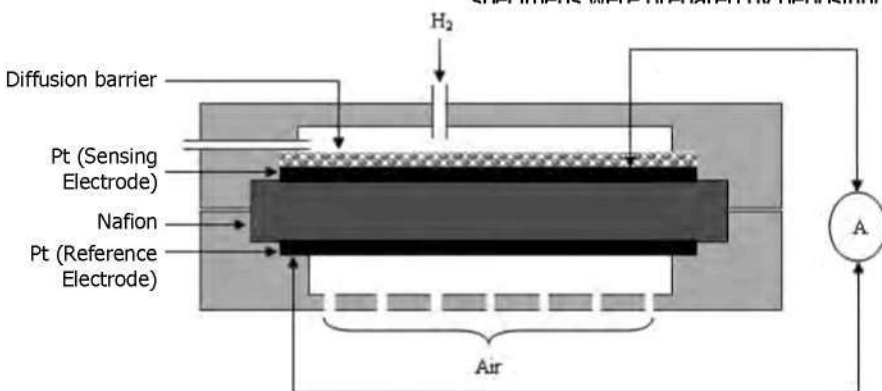


**Fig. 5 : Schematic of Hydrogen Sensor**

beads of the above mentioned electrodes on mild steel specimen and bead of the low hydrogen electrode, P91M (with a composition modified from that of E9015-B9), on modified 9Cr-1Mo specimen. **Table 2** give the electrode details and welding parameters employed for preparation of specimens for $H_D$ measurement. The specimen assembly for $H_D$ measurement was removed from the copper fixture immediately after welding, quenched in ice cold water followed by liquid nitrogen. The test specimen was separated from the run-on and run-off pieces within 4-6 seconds. Any flux remaining on the weld specimen was removed within 20 seconds and was stored in liquid nitrogen until its transfer into the hydrogen collection chamber for collection of $H_D$.

### 2.2.2 Collection and measurement of diffusible hydrogen using the sensor

For the collection of $H_D$ evolved from the weld specimen, it was cleaned with acetone to remove the ice/moisture, gently warmed to remove excess acetone and was transferred into the collection chamber within one minute. The chamber along with the specimen was flushed and pressurized with argon gas to a known pressure higher than the ambient. After pressurizing, the weld specimen was held in the chamber for 72 hrs for collection of $H_D$ as a mixture of hydrogen in argon (Ar-$H_2$ gas mixture). Volume of $H_D$ in the Ar-$H_2$ gas mixture is measured by the sensor as described below.

Prior to the measurement of Volume of $H_D$ in the chamber, sensor was calibrated with different known concentrations of hydrogen in the Ar-$H_2$ gas mixture of by injecting a fixed volume (this volume is

39

### Table 2: Baking and Welding parameters of different electrodes

| Electrodes | Baking conditions | Welding current (Amp) | Voltage (Volt) |
|---|---|---|---|
| E6010 | Not Baked | 110 | 25 |
| E6013 | 125°C/1h | 110 | 27 |
| E7016 | 250°C/2h | 110 | 28 |
| E7018-1 | 250°C/2h | 110 | 27 |
| P91M | 300°C/2h | 90 | 28 |

equal to the volume of the sampling loop of the valve shown in **Figs. 3 and 4**) of the gas mixture onto the sensor with the help of the 8-port valve. Concentrations of hydrogen in the gas mixture were varied by standard mass flow controllers. Signal/response of the sensor corresponding to each concentration of hydrogen in the Ar-$H_2$ gas mixture was recorded as a peak height of the peak is proportional to the concentration of hydrogen in the gas mixture. After calibration, the inlet of sampling loop of the 8-port valve was connected to the chamber, the sampling loop is flushed and filled with the gas in the chamber. Subsequently, by choosing the injection mode of the eight port valve, the gas mixture in the sampling loop was injected into the sensor. A response corresponding to the concentration of hydrogen in the chamber is recorded in the data acquisition system and compared with the calibration to obtain the concentration of $H_D$ collected in the chamber. As the specimen chamber is at a higher pressure than the ambient, it was possible to repeat the measurement at least thrice using the gas mixture available in the chamber. After measuring $H_D$ concentration, the weld specimen was taken out of the chamber, cleaned, dried and weighed. From the volume of the chamber, hydrogen

concentration in the gas mixture, pressure of the gas inside the chamber, weight of the deposited metal, volume of $H_D$ content was estimated and was reported in ml/100g of the deposited metal. For each set of specimens, five separate measurements were carried out and the average values were reported.

### 2.2.3 Measurement of diffusible hydrogen with respect to time

In addition to the standard 72 hour measurement, $H_D$ measurement from weld specimen was also carried out at different time intervals using the sensor. For feasibility of the measurements, they were carried out at long time intervals after 72h. Apart from the difference in the time duration of collection of $H_D$, the procedures of specimen preparation and $H_D$ measurement were the same as discussed in sections 2.2.1 and 2.2.2. In this study, $H_D$ was collected from a single weld specimen for time intervals of 0-24, 24-48, 48-72, 72-120, 120-192, 192-264 h and was measured using the sensor. After measuring the concentration of hydrogen evolved for a certain time interval, the chamber containing the same specimen was flushed and pressurized again with argon to a known pressure and the measurement was repeated for the next interval until no

further sizable hydrogen concentration in the Ar-$H_2$ mixture was obtained for a subsequent time interval after 264 h of $H_D$ measurement.

### 2.2.4 Measurement of diffusible hydrogen at high temperature.

For collection of $H_D$ at high temperature, a new chamber was designed (**Fig. 6**) which has heating arrangements inside it. Weld specimen was prepared as per the standard procedure already described and for $H_D$ measurement it was transferred into heater inside the chamber. The chamber along with the weld specimen is flushed and pressurized with argon; then the specimen is heated to 400°C for 0.5h and hydrogen diffused out from the specimen is collected inside the chamber. It is cooled down to room temperature and the concentration of hydrogen is measured with the sensor.

### 2.2.5 Measurement of diffusible hydrogen by the mercury method

Since the sensor method is a new technique, all the $H_D$ measurements carried out using this method were compared with similar measurements using mercury method following standard ISO 3690 procedure. The quenched and cleaned specimen was transferred into the Y- tube filled with mercury. The Y- tube was evacuated and the specimen inside was allowed for hydrogen evolution for 72 hours. Hydrogen evolved was collected in the burette of the Y-tube. This volume is subsequently converted to the volume at STP and knowing the mass of the specimen, $H_D$ content was normalized by the following relationship:

$$H_D = \left(\frac{273}{273+T}\right)\left(\frac{P-H}{760}\right)\left(\frac{100}{L_2-L_1}\right)$$

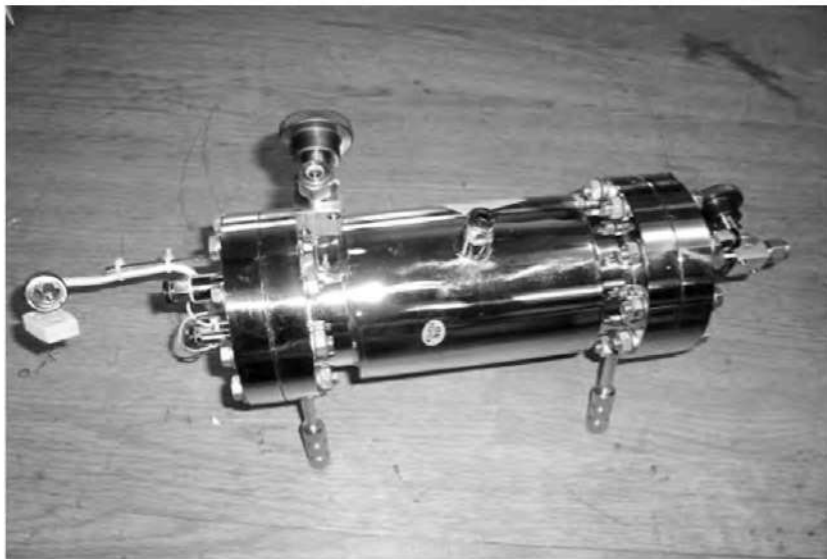$(V_2 - V_1)$ ml / 100g of weld deposit ..(1)
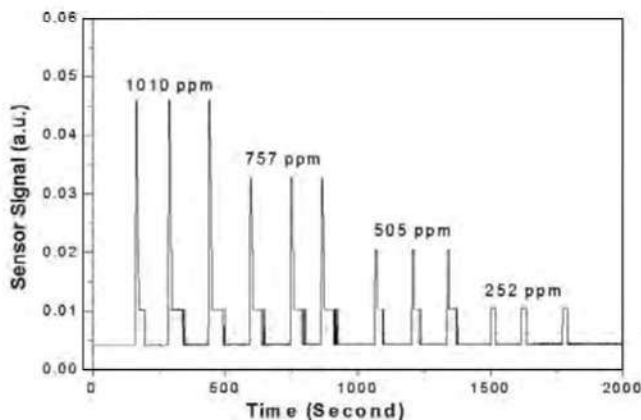
Fig. 6 : Hydrogen collection chamber



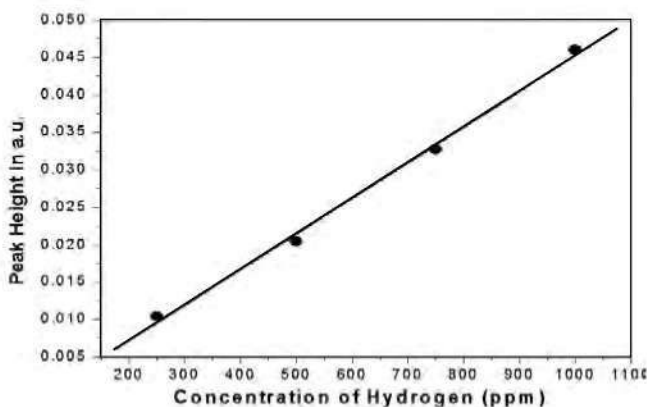Fig. 7 : Response of the hydrogen sensor against the concentration of hydrogen



Fig. 8 Calibration curve for hydrogen sensor obtained using standard Ar-H 2 mixtures

Where,

$H_D$ = Diffusible hydrogen at STP (ml/100g)

T = the room temperature (K)

P = the barometric pressure (mm)

H = $(L_2 - L_1)$, the head of mercury (mm)

$L_1$ = Height of mercury level in the graduated limb after 72 hours (mm)

$L_2$ = Height of mercury level in the non-graduated limb after 72 hours (mm)

$V_1$ = left over gas in the graduated capillary of the closed limb before evacuation (ml)

$V_2$ = the volume of hydrogen collected in the graduated limb after 72 hrs (ml)

## 3.0 RESULTS AND DISCUSSION

### 3.1 Diffusible Hydrogen content

A typical response of the sensor for different concentrations of hydrogen in the Ar-H$_2$ mixture is shown in **Fig. 7**. **Fig. 8** shows the calibration of the sensor which presents variation in peak heights with concentrations of hydrogen. The trend indicates a linear relationship of peak height with the concentration of hydrogen. Sensor was calibrated prior to each set of measurements.

Results of the $H_D$ measurements for welding electrodes carried out using the Nafion sensor and mercury method are shown in **Fig. 9**. A good agreement for the results obtained both from the sensor and the mercury method for a wide range of electrodes and levels $H_D$ contents is obvious. In fact standard deviation is less for measurements made using the sensor than those made by mercury method. Further, in **Fig. 10**,

41

a plot of $H_D$ contents obtained using sensor method against $H_D$ contents obtained using mercury method for similar test sets was seen linearly related with $R^2 = 0.9999$. A mathematical correlation of $H_D$ contents obtained for different test sets using both these methods show one to one correspondence between these two methods as given below :

$$H_{Sensor\ Method} = 0.99 H_{Mercury\ Method} - 0.05 \quad ...(2)$$

Hence, the results prove that the Nafion based hydrogen sensor can be used for $H_D$ measurements in the weld joints

### 3.2 Accuracy of the Sensor Method by t-Test

Following the recommendation of ISO 3690, t-Test has been carried out to check the accuracy of the hot extraction method as compared to mercury method. In this test, the means of $H_D$ contents of each electrode measured by the mercury method (primary method) and the mensor method (alternate method) are compared statistically by two-sided t-Test. The observed t value ($t_{estimated}$) is estimated from equation (3). The $t_{estimated}$ for each electrode was compared with the $t_{statistical}$ obtained from the t-table of statistics for the number of degrees of freedom, $\nu = 9$ (Where, $\nu = nP + nR - 2$) at 95% confidence level (i.e., the level of significance, $\nu = \pm 0.025$ for two-sided t-test) for each electrode. The details are given in **Table 3**

$$t_{estimated} = \frac{(x_R - x_P)}{\sqrt{\dfrac{S^2_R}{n_R} + \dfrac{S^2_P}{n_P}}} \quad ...... (3)$$

Where,

$t_{estimated}$ = the probability of difference in means not due to chance

$x_R$ = Mean of the sensor method (Alternate)

$x_P$ = Mean of the primary method (Mercury)

$s_R$ = Standard deviation of the rapid method (Hot extraction-PEMHS)

$s_P$ = Standard deviation of the primary method (Mercury)

$n_R$ = Sample size in the rapid method (Hot Extraction-PEMHS)

$n_P$ = Sample size in the primary method (Mercury)



Fig. 9 : Comparison of Mercury method and Sensor method
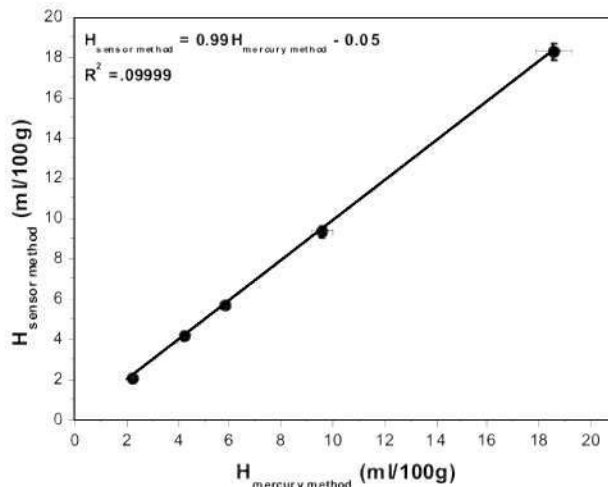


Fig. 10 : Relationship between mercury and sensor methods

$t_{statistical} = t_{\pm 0.025,\ 9}$ (at 95% confidence level in two sided test)

From the **Table 3**, it is obvious that $t_{estimated}$ for all the set of measurements, except one, fall within the interval of $t_{statistical} = \pm 2.262$ (Obtained from statistical t-table (Beckwith et al., 2006). The lone deviation observed is for the E9015-B3 electrode deposited on mild steel base metal; it may be noted that composition of the base metal (mild steel) and weld metal (9Cr-1Mo steel) are vastly different and this could be the
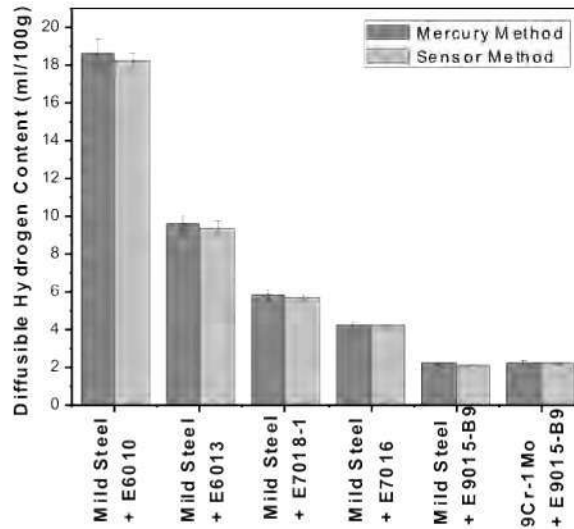
reason for large value of $t_{estimated}$. Results prove that probability that good correlation obtained for $H_D$ content measured by the sensor method and the mercury method for different electrode is by chance is less that 5%. In other words, with more than 95% confidence level, it can be said that the results obtained for $H_D$ measurement using sensor method is as accurate and as reliable as the results obtained from the standard mercury method. The differences in means are only due to random errors and not due to any systematic errors. Hence, sensor method can be used to measure $H_D$ measurement as an alternative to the standard mercury method. This method is environment friendly and possibly emerges as a rapid method for $H_D$ measurement. Once developed into a commercial product, it is expected to be much cheaper than the Gas Chromatography method, another rapid method currently available for $H_D$ measurement.

### 3.3 Hydrogen evolution as function of time

As per one of the applications mentioned above, the new sensor method was successfully employed to study evolution of hydrogen as a function of time. In this study, hydrogen concentration in the chamber was measured for different time intervals from weldment of modified 9Cr-1Mo electrode (modified E9015-B9) on mild steel base metal up to 264 hours. This class of electrode was chosen because it is an alloy steel electrode and in the as welded condition, the microstructure of the weld metal is fully martensitic and diffusion coefficient for hydrogen in this class of steel at ambient temperature is two orders magnitude lower than that in mild steel (Albert et al., 2003). It was observed that evolution of hydrogen continued even after 264 hours. $H_D$ contents measured at various intervals for modified E9015-B9 deposited on mild steel is shown in **Fig. 11**. The exponentially decreasing pattern of diffusible hydrogen content with respect to succeeding time intervals was not observed from this data because the time intervals of measurement were not equal. Hence, the data in **Fig. 11** has been normalized by estimating the rate of evolution of hydrogen per hour within the time intervals of $H_D$ collection and plotted against time in **Fig. 12** which shows rate of hydrogen evolution decreases exponentially with time. Also, in **Fig. 13**, the cumulative total of $H_D$ contents collected after different time periods clarifies that hydrogen evolution is maximum within the first 24 hours then it decreases exponentially with time. However, it should be noted that total $H_D$ measured after 72 h (1.85 ml/100 g) is lower than $H_D$ obtained for the single measurement carried out after 72 h (2.1 ml/100 g). This could be because, the first 72 h measurement was divided into three 24h measure-ments and were carried out using a single sample and in between two successive measurements, few hours are lost for measurement (gas from the specimen chamber is sampled at least thrice for each measurement), flushing the chamber and refilling with Ar gas. Hence, gas evolved during these periods is not collected. However, the results are sufficient to demonstrate that rate of hydrogen evolution decreases with time and hydrogen evolution continues much beyond 72 h.

**Table 3: Comparison of means of HD obtained from both the methods by t-test**

| Base Metal + Electrodes | Average $H_D$ content (ml/100g) | | Standard Deviation of $H_D$ content (ml/100g) | | t-Value | |
|---|---|---|---|---|---|---|
| | Sensor Method | Mercury Method | Sensor Method | Mercury Method | $t_{estimated}$ | $t_{statistical}$ (From Table) |
| Mild Steel +E6010 | 18.28 | 18.58 | 0.412 | 0.871 | -0.7444 | |
| Mild Steel +E6013 | 9.37 | 9.56 | 0.338 | 0.438 | -0.8352 | |
| Mild Steel + E7018-1 | 5.68 | 5.81 | 0.214 | 0.248 | -0.9488 | $(t_{statistical}$ $= t_{\pm 0.025,9})$ $\pm 2.262$ |
| Mild Steel + E7016 | 4.19 | 4.26 | 0.102 | 0.124 | -0.9449 | |
| Mild Steel + E9015-B9 | 2.11 | 2.19 | 0.0311 | 0.0588 | -2.8317 | |
| 9Cr-1Mo + E9015-B9 | 2.19 | 2.26 | 0.0711 | 0.117 | -1.1950 | |

## 3.4 Diffusible hydrogen measurement by the sensor at high temperatures

Measurement of diffusible hydrogen was carried out at 400°C from the weldment prepared by depositing P91M welding electrodes on mild steel. Hydrogen from weld metal was collected in the chamber mentioned in section 2.2.4 and its concentration was measured with the sensor. The results of this measurement are given in **Table 4**. These results are found to be in good agreement with the results obtained by the standard mercury method and with the results obtained with the sensor method at room temperature. Measurement of diffusible hydrogen in welding electrodes with various levels of hydrogen using the high temperature method is in progress.

## 4.0 CONCLUSIONS

1. The Nafion based hydrogen sensor has been successfully employed for measuring diffusible hydrogen content in the welding consumables.

2. Measurements were carried out for five different classes of welding consumables with diffusible hydrogen content in the range of 2-18 ml/100g of weld metal using the sensor and the standard mercury method. Results obtained correlate well with those obtained by mercury method.

3. Statistical analysis of the results, as recommended by ISO 3690 confirms that confidence level on the accuracy of the measurement of diffusible hydrogen using the sensor is better than 95%. Hence, this method can be used as an alternate method for diffusible hydrogen measurement from the welding consumables.
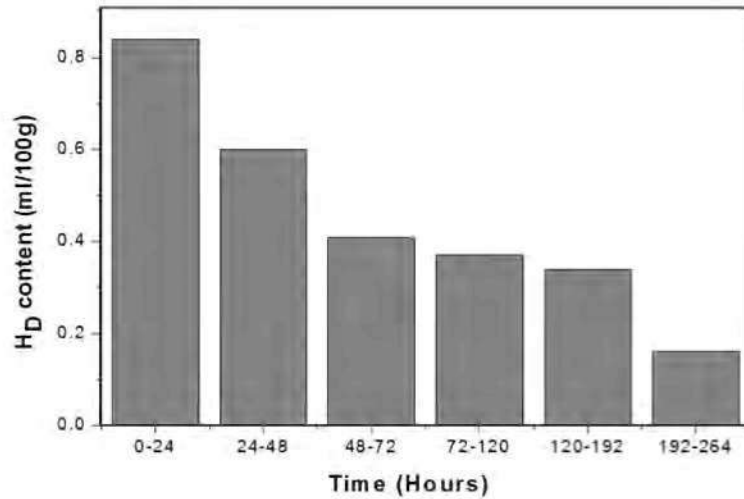


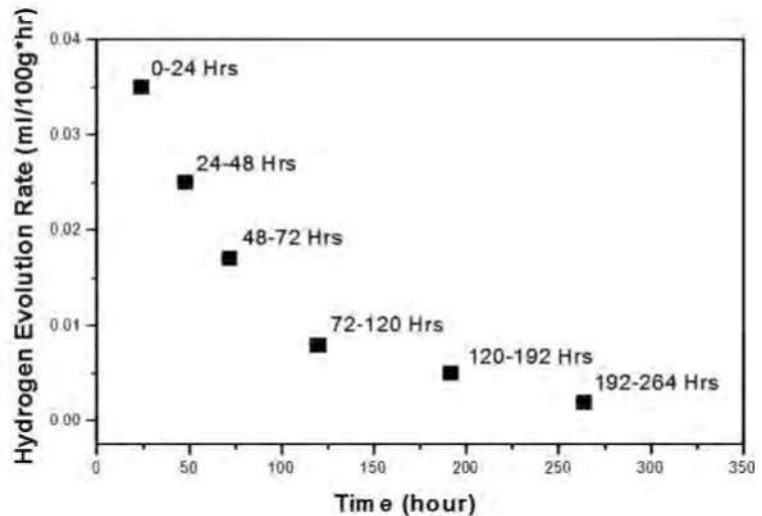Fig. 11 : Diffusible hydrogen measured at different intervals



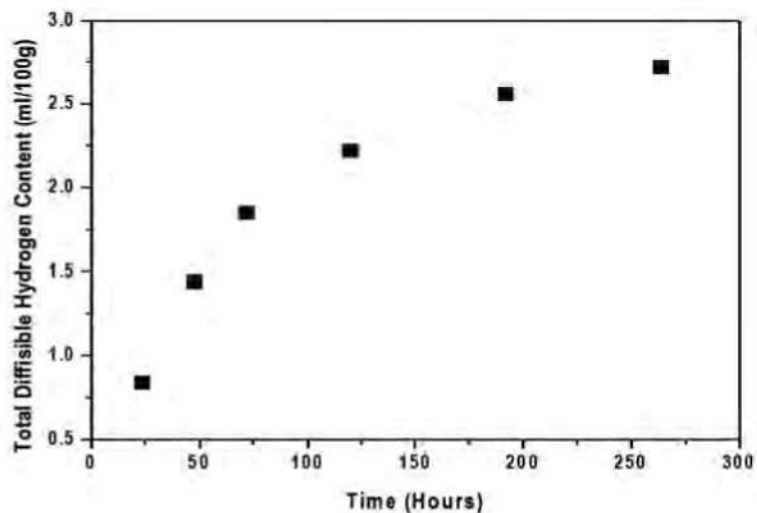Fig. 12 : Rate of hydrogen evolution with time



Fig. 13 : Cumulative diffusible hydrogen Content

44

4. One of the possible application of the new method, hydrogen evolution from the weld as a function of time was also demonstrated by conducting measurement on a weld of modified 9Cr-1Mo steel electrode deposited on mild steel. It is shown that rate of hydrogen evolution decreases exponentially with time and it continues much beyond 72 h, the standard time of diffusible hydrogen measurement at ambient temperatures.

5. A new method for measurement of diffusible hydrogen at high temperature using the sensor with considerable reduction of the collection time of hydrogen from the weld is demonstrated.

**Table 4 : Diffusible Hydrogen Measurements by Hot Extraction**

| Base Metal + Electrodes | $H_D$ measured by sensor method at 400°C (ml/100g) | $H_D$ measured by sensor method at room temperature (ml/100g) | $H_D$ measured by Mercury method (ml/100g) |
|---|---|---|---|
| **Mild Steel + P91M (Baked)** | 2.43 | 2.14 | 2.18 |
| | 2.51 | 2.14 | 2.23 |
| | 2.39 | 2.10 | 2.24 |
| Average | 2.44 | 2.13 | 2.22 |

## REFERENCES

Albert, S. K., Ramasubbu, V., Parvathavarthini, N. and Gill, T.P.S. (2003); Influence of alloying on Hydrogen assisted cracking and diffusible hydrogen content in Cr-Mo steel welds, Sₐdhanₐ 28(3-4), pp. 383-393.

Albert, S. K., Ramesh, C., Murugesan, N., Gill, T. P. S., Periaswami, G. and Kulkarni, S. D. (1997); A New Method to Measure Diffusible Hydrogen Content in Steel Weldments Using a Polymer Electrolyte Based Hydrogen Sensor, Weld. J., 76(7), pp. 251s-255s.

Albert, S. K., Studies on some aspects of weldability of Cr-Mo Steels, Ph.D Thesis, IIT-Bombay.

ANSI/AWS A4.3 - 93: Standard methods for determination of the diffusible hydrogen content of martensitic, bainitic and ferritic steel weld metal produced by arc welding, American Welding Society, Miami, Florida (1986).

Beckwith, T. G., Maragoni, R.D., Lienhard, J. H., (2006); Mechanical Measurements, Fifth Edition, Pearson Education.

De Abreu, L. C., Modenesi, P. J. and Villani-Marques, P. (1995); Comparative study of methods for determining the diffusible hydrogen content in welds Welding International, 9(1), pp. 26-31.

DIN 8572 Part 1: Determination of diffusible hydrogen in weld metal, Deutsches Institut fur Normurg e.V., Berlin (1981).

Hirth, J. P. (1980); Effects of hydrogen on the properties of iron and steel, Metall. Trans. A, 11(6), pp.861-890.

http://www.e2v.com/assets/media/files/sensors_datasheets/Pellistors/pellistor_an1.pdf (Web Source: Pellistor Sensor Technology and Applications)

Iino, M. (1987); Evaluation of hydrogen trap binding enthalpy I, Metall. Trans. A, 18A (9), pp.1559-1564.

Iino, M. (1998); Evaluation of hydrogen trap binding enthalpy II, Metall. Trans. A, 29A (9), pp. 1017-1021.

IIW Doc.II-805-85 (1985); The measurement of weld hydrogen levels, Welding in the World, 1985, 23 (3/4), pp. 50-62.

ISO 3690: Determination of hydrogen content in arc weld metal, II-E-586-10.

IS-11802-1986: Methods of determination of diffusible hydrogen content of deposited weld metal from covered electrodes for welding mild and low alloy steels, Bureau of Indian standards, New Delhi.

Ito, Y. and Bessyo, K. (1968); Cracking parameter of high strength steels related to Heat-Affected-Zone cracking, IIW Doc.IX-576-68.

JIS Z3118-1986: Method of measurement of hydrogen evolved from steel, Japanese Standards Association, 1986.

JIS Z3113-1975: Method for measurement of hydrogen evolved from deposited metal.

Karkhin, V. A. and Levchenko, A. M. (2007); Computer-aided determination of diffusible hydrogen in deposited weld metal, IIW-Doc. II-1634-07 (II-A-182-07).

Kotecki, D. J. and La Fave, R. A. (1985); AWS A5 Committee studies of weld metal diffusible hydrogen, Weld. J., 64 (3): 31-37.

Krawczyk, M. and Namiesnik, J. (2003); Application of a catalytic combustion sensor (Pellistor) for the monitoring of the explosiveness of a hydrogen-air mixture in the upper explosive limit range, Journal of Automated Methods & Management in Chemistry, 2003, 25(5), pp. 115-122.

Lasseigne, A., McColskey, D., Koenig, K., Jackson, J., Olson, D. and Mishra, B. (2008); Advanced Non-Contact Diffusible Hydrogen Sensors for Steel Weldments, Trends in Welding Research, Proc. 8th Inter.l Conf. 2-6 June, Pine Mountain, Georgia, USA, pp.424-429.

Lin K. W., Chen H. I., Lu C. T., Tsai Y. Y., Chuang H. M., Chen C. Y. and Liu W. C. (2003); A hydrogen sensing Pd/InGaP metal-semiconductor (MS) Schottky diode hydrogen sensor, Semicond. Sci. Technol., 18 (7), pp. 615-619

Lundin, C. D., Milton, R., Henning, J. A. and Richy, R. A., (1986), Advances in Welding Science and Technology, ASM International, Materials Park, Ohio: 585-596

Miura, N., and Yamazoe, N. (1988) Development of a solid-state gas sensor using proton conductor operative at room temperature, Chemical Sensor Technology, 1(2), Kodansha, Tokyo/Elsevier, Amsterdam, pp 123-139

Miura, N., Harada, T. and Yamazoe, N. (1989); Sensing characteristics and working mechanism of four-probe type solid-state hydrogen sensor using proton conductor, J. Electrochem. Soc., 136, pp. 1215-1219.

Miura, N., Kato, H., Ozawa, Y., Yamazoe, N. and Seiyama, T. (1984); Amperometric Gas Sensor Using Solid State Proton Conductor Sensitive To Hydrogen In Air At Room Temperature, Chem. Lett., 17(2), pp. 1905-1908

Miura, N., Kato, H., Yamazoe, N., and Seiyama, T. (1983); An improved type of proton conductor sensor sensitive to H2 and CO at room temperature Chem. Lett., 12(10), pp. 1573-1576

Neburchilov, V., Martin, J., Wang, H. and Zhang, J. (2007); A review of polymer electrolyte membranes for direct methanol fuel cells, Journal of Power Sources, 2007, 169(3); pp. 221-238.

Noble, D. N. (1985); HAZ Hydrogen Measurement during Weld Cladding, Met. Const., 17(11), pp. 754-757.

Ohtsubo, T., Goto, S. and Amano, M. (1985); Development of Apparatus for Determination of Diffusible Hydrogen in Steel, Transactions ISIJ, 25(1), pp.21-29.

Pressouyre, G. M., Lemoine, L., Dubois, D. J. M., Leblonde, J. Saillard, P. R. and Faure, F.M. (1988); In situ measurement of hydrogen in weld heat affected zones through Mass Spectrometry and computer analysis (Ref.6), pp. 219-237.

Quintana, M. A. and Dannecker, J. R. (1986); Diffusible Hydrogen Testing by Gas Chromatography, Hydrogen Embrittlement: Prevention and control and Control, L. Raymond, ASTM STP 962, American Society for Testing of Materials, Philadelphia, pp. 247- 286.

Quintana, M. A. (1984); A critical Evaluation of glycerin test, Weld. J., 73(5), pp. 141s-149s.

Ramesh, C., Murugesan, N., Krishnaiah, M.V., Ganesan, V. and Periaswami, G. (2008); Improved Nafion-based amperometric sensor for hydrogen in argon, Journal of Solid State Electrochemistry, 12(9), pp. 1109-1116.

Ravi, R. and Honavar, D. S. (1987); Hydrogen in steel weldments - A review, Procs of Nat. Weld.Sem., 26-28 November, Bangalore, India.

Sakthivel, M. and Weppner, W. (2006); Development of a hydrogen sensor based on solid polymer electrolyte membranes, Sensors and Actuators B, 113, pp. 998-1004.

Siewert, T. A. (1986); Testing of Welding Electrodes for Diffusible Hydrogen and Coating Moisture, Hydrogen Embrittlement: Prevention and control and Control, ASTM STP 962, American Society for Testing of Materials, Philadelphia, pp. 238- 246

Smitha, B., Sridhar, S. and Khan, A. A. (2005); Solid polymer electrolyte membranes for fuel cell applications-A review, Journal of Membrane Science, 2005, 259 (1-2); pp. 10-26.

Suzuki, H. and Terasaki, T. (1986); Estimating critical stress and preheat temperature to avoid cold cracking, IIW Doc. IX-1417-86.

Velayutham, G., Ramesh, C., Murugesan, N., Manivannan, V., Dhathathreyan K. S. and Periaswami G. (2004); Nafion based amperometric hydrogen sensor, Ionics, 10(1/2), pp. 63-67.

Viswanathan, B. and Helen, M. (2007); Is nafion, the only choice?, Bulletin of the Catalysis Society of India, 6, pp. 50-66.

Yurioka, N. and Suzuki, H. (1990); Hydrogen assisted cracking in C-Mn and low alloy steel weldments, Int. Mat. Rev., 35(4), pp. 217-249.