Available online at ScienceDirect

ScienceDirect

J. Mater. Sci. Technol., 2014, 30(11), 1160–1165

JMST

www.JMST.org

# Performance of Amperometric and Potentiometric Hydrogen Sensors

*Yuejun Ouyang*[1,2], *Xiaojian Wang*[1], *Gang Yu*[1]*, *Zhengwei Song*[1], *Xueyuan Zhang*[1]*

1) State Key Laboratory of Chemo/Biosensing and Chemometrics, College of Chemistry and Chemical Engineering, Hunan University, Changsha 410082, China

2) Materials Science and Engineering Laboratory, Huaihua University, Huaihua 418000, PR China

[Manuscript received February 24, 2013, in revised form April 24, 2013, Available online 24 July 2014]

The principle, design, construction and performance of the amperometric and potentiometric sensors for measuring the permeation rate of hydrogen through the wall of metal equipment were investigated in order to develop a new type of hydrogen sensor with high accuracy. The transient curves of hydrogen permeation under a given charging condition were employed to evaluate the performance of two types of hydrogen sensors. The relative deviation of the hydrogen concentration detected with two types of sensors under the same condition varied from 3.0% to 13%. The accuracy, response time, reproducibility, and installation were discussed and compared. Response time of the potentiometric sensor (E-sensor) was shorter than that of the amperometric sensor (I-sensor). Both types of sensors exhibited good reproducibility. Development of I-sensor composed of a kind of proton conductor adhesives or non-fluid electrolytes which contain two functions of high electrical conductivity and a strong adhesion will be a promising prospect in order to measure hydrogen permeation at high temperature.

**KEY WORDS: Hydrogen sensor; Hydrogen diffusion; Hydrogen embrittlement; Nickel**

## 1. Introduction

One of the most important safety concerns in the oil and gas industry is so-called $H_2S$ corrosion. Hydrogen is generated during the corrosion of metal container exposed to acidic process streams or during the pretreatment process such as picking and plating process, etc[1–3]. In the presence of $H_2S$, hydrogen generated by corrosion reactions could be easily absorbed and severely permeated into the metal leading to hydrogen damage. Since the important role of hydrogen in the catastrophic failure of metal has been recognized, it is necessary to develop on-line hydrogen permeation probes used in the industry in order to prevent premature component failures or to monitor the efficacy of anticorrosive measures[4].

Industrial hydrogen sensors are usually grouped into pressure or vacuum type[5–9] and electrochemical type[10–13] according to the measurement principle. Among all the permeation sensors, electrochemical sensors have received increasing attentions in recent years due to their peculiar merits such as fast response, high sensitivity, strong output signal, and low costs, etc[14,15]. Amperometric sensors (I-sensors) and potentiometric sensors (E-sensors) are thought as two main types of electrochemical sensor. E-sensors have a wide dynamic range but lack of accuracy due to their logarithmic response[16–18]. I-sensors have faster response and more accurate measurement. The alkaline solution was used[19,20] as electrolyte in I-sensor constructed from anodic chamber of Devanathan and Stachurski (DS) cell. Cheng et al.[21] developed an intelligent electrochemical sensor for in-situ inspection of the hydrogen induced cracking susceptibility in boiler pipe systems during the picking process, which was a button type of sensor based on a modified DS cell. Ouyang et al.[22] further improved the button sensor of two electrodes into a sealed three electrodes sensor, which were composed of palladium alloy as both of anode and cathode, a nickel wire as reference electrode, 0.2 mol $dm^{-3}$ KOH as electrolyte. A potentiostat was used to exert a constant potential to oxidize hydrogen atom diffused to the Pd alloy membrane of the sensor, which was successfully applied to monitor hydrogen due to the corrosion in propane storage tank. E-sensors are based on the measurement of the potential difference between two electrodes in an electrochemical cell. Solid-state electrolyte was commonly used in E-sensors in order to prevent electrolyte leakage[23–25].

---

* Corresponding authors. Prof., Ph.D.; Tel.: +86 731 88822275; Fax: +86 731 88713642; E-mail addresses: yuganghnu@163.com (G. Yu), uwoxyzhang@gmail.com (X. Zhang).

http://dx.doi.org/10.1016/j.jmst.2014.07.001

Lundsgaard[26] first developed an E-sensor utilizing $HUO_2$-$PO_4 \cdot 4H_2O$ (HUP) as electrolyte and Pd/HUP or Pt/HUP mixture powders as electrodes. Subsequently, Lyon and Fray[27] reported a solid state hydrogen sensor using HUP electrolyte and $H_xWO_3$ reference material. This sensor was used to detect hydrogen in inert gases and in steel. Gnanasekaran et al.[28] described a sensor using $CaCl_2$−$CaH_2$ as electrolyte and Li−LiH as reference mixture to detect hydrogen in liquid sodium. Recently, Ando and Yamakawa[29] developed a ceramic E-sensor with solid electrolyte (5 mol% $Yb_2O_3$−$SrCeO_3$) to detect hydrogen permeated through steel structure at elevated temperatures, but his research was only limited in the laboratory. The application of electrochemical hydrogen sensor at high temperature in industry has not been reported so far. The comparison in the response time and accuracy between two types of electrochemical sensors has not been carried out till now.

Hydrogen permeation curves in a pure iron membrane were measured with two types of sensors in order to compare their general performance specifications. Their response and accuracy were analyzed in detail in order to develop a hydrogen sensor with high-precision.

## 2. Principle, Design and Structure of Electrochemical Hydrogen Sensors

### 2.1. Principle and design of I-sensor

Devanathan and Stachurski (DS) proposed an electrochemically sensitive system with instantaneous recorder of hydrogen permeation rate in an electrolytic process through a metallic foil, sheet or membrane. The specimen of a metal membrane is clamped to two separate cells. Its structural model is shown in Fig. 1[30].

One side of the membrane acts as the cathode and the other as the anode. In Fig. 1, the left cell (input side) contains a solution with high concentration of hydrogen ions like $H_2SO_4$ solution, while in the right side cell (exit side), it is necessary to have a basic solution (usually KOH) in order to avoid corrosion on the steel surface which affects hydrogen permeation detection. Previous results have indicated that it is necessary to cover the membrane with palladium or nickel to avoid corrosion and to provide catalysis for a complete oxidation of diffused hydrogen atoms[31−34]. The mechanism of I-sensor could be expressed as follows:

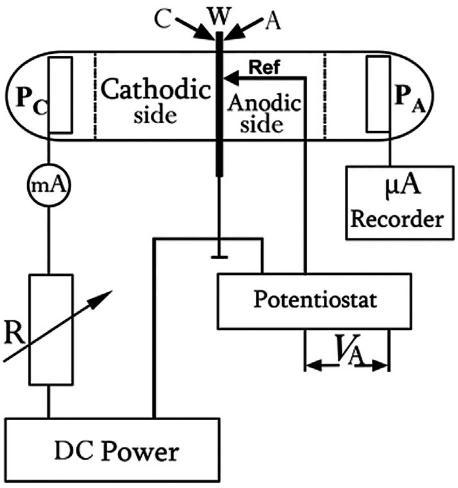

**Fig. 1** Schematic structural model of Devanathan−Stachurski double cell. C: cathodic side of working electrode; A: anodic side of working electrode; $P_A$, $P_C$: auxiliary electrode; r: reference electrode; W: working electrode; R: variable resistor.

$$\text{Anodic reaction: } H + OH^- \rightarrow H_2O + e^-$$

$$\text{Cathodic reaction: } H_2O + e^- \rightarrow OH^- + H$$

$$\text{Cell reaction: } H \rightarrow 1/2H_2$$

Hydrogen atoms penetrate through cathodic Ni or Pd foil in sensor and are recombined to $H_2$ on the external surface of sensor and to escape to the atmosphere finally.

The distribution of hydrogen in steel profiles could be calculated by Fick's first diffusion law according to the permeation rate of hydrogen from the internal surface in the reactor steel wall to the nickel electroplated interface in the sensor.

In the steady state, the H concentration at inner wall of metal membrane, *i.e*, entrance side, $c_0$ (mol cm$^{-3}$), could be calculated from the following equation:

$$c_0 = \frac{i_\infty L}{FD} \tag{1}$$

where $i_\infty$ (A cm$^{-2}$) is the permeation current density at the steady state; $L$ (cm) is the specimen thickness; $F$ is the Faraday constant (96500 A s); $D$ (cm$^2$ s$^{-1}$) is the hydrogen diffusion coefficient in the metal specimen, calculation with $6.6 \times 10^{-5}$ cm$^2$ s$^{-1}$ for iron membrane at 298 K[35].

### 2.2. Principle and design of E-sensor

The E-sensor could be described in terms of the following galvanic cell:

$$(-)\text{Ni(H)}|0.2 \text{ mol dm}^{-3} \text{ KOH}|\text{NiO}_2\text{(s)}(+)$$

$$\text{Anode reaction: } 2H + 2OH^- = 2H_2O + 2e^-$$

$$\text{Cathode reaction: } NiO_2(s) + 2H_2O + 2e^- = Ni(OH)_2(s) + 2OH^-$$

The overall cell reaction may be represented as: $NiO_2$ (s) + 2H = $Ni(OH)_2$ (s).

The electromotive force generated when the cell anode is exposed to hydrogen atoms, may be represented by the Nernst's equation:

$$E_\infty = E^\ominus - \frac{RT}{zF}\ln\frac{a_{Ni(OH)_2}}{a_{NiO_2}a_H^2} \tag{2}$$

The concentration of hydrogen in the metal could represent the activity when the concentration of hydrogen is very low, then