Journal of Applied Electrochemistry **29**: 971–977, 1999.

Nonisothermal electrochemical cell for monitoring hydrogen or oxygen in high temperature water

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Received 16 June 1998; accepted in revised form 5 January 1999

Key words: electrochemical sensor, high temperature water, hydrogen, oxygen

Abstract

A nonisothermal, solid state electrochemical sensor for monitoring hydrogen or oxygen dissolved in high temperature (to about 500 K) water is described. Nafion® in the form of tube was used as the electrolyte. The reference electrode at ambient temperature and pressure was a saturated aqueous solution of Fe^{2+} and Fe^{3+} sulphates. Sensor voltage measurements with dissolved hydrogen showed good reproducibility and long term stability. A regression equation for the hydrogen concentration related to cell voltage and water temperature was derived. Sensor voltage measurements with dissolved oxygen showed relatively poor reproducibility and long term stability. This is attributed to the greater complexity of electrode reactions involving oxygen and water.

1. Introduction

Determination of the concentration of hydrogen and/or oxygen in water at high temperature is a significant technical problem. Commercial instruments for the determination of hydrogen and oxygen operate at ambient temperature and hence necessitate sample cooling and analysis at a location remote from the sampling point with concomitant time delays. Recently, the use of palladium as a differential electrical-resistance sensor for hydrogen in water has been proposed [1]. The sensor has also been used for determination of Henry's law constant in water at high temperature [2]. In this paper, the development of a nonisothermal electrochemical cell, for monitoring hydrogen or oxygen in water at high temperature, is described. The cell utilizes Nafion® in the form of a tube which enabled the reference electrode to be located remote from the sensing electrode. Electrochemical cells involving the use of Nafion® have been described [3, 4].

2. Theory

The nonisothermal electrochemical cell may be represented schematically as

$$\begin{array}{ccccc} H_2O, H_2(\text{or } O_2)_{(aq)}, Pt \mid & \text{Nafion}^{\circledR}\ H & \mid Fe^{2+}, Fe^{3+}_{(aq)}, Pt \\ T_I, p_I & I & II & T_{II}, p_{II} \end{array} \qquad ①$$

where H_2O, H_2 (or $O_2)_{(aq)}$ represents the aqueous solution of hydrogen (or oxygen) in water at the temperature T_I, total pressure p_I. Fe^{2+}, $Fe^{3+}_{(aq)}$ represents the reference electrode comprising a saturated aqueous solution of Fe^{2+} and Fe^{3+} sulphates at the fixed temperature T_{II} (~30 °C), total pressure p_{II} (~101.3 kPa). Nafion® H is a perfluorinated ionomer in the hydrogen form conductive to H^+ ions. Pt represents platinum metal.

The electromotive force (e.m.f) of the cell ① $E_{①}$ is given by

$$E_{①} = -\frac{1}{F}(\eta_{e\text{-}II} - \eta_{e\text{-}I}) \qquad (1)$$

where η_{e^-} is the electrochemical potential of electrons at electrodes I and II and F is the Faraday constant. The equilibria at the interfaces I and II are postulated to be

$$\text{Interface I} \qquad H^+_{(Naf.)} + e^-_{I(Pt)} \rightleftharpoons \tfrac{1}{2}H_{2(aq)} \qquad (2)$$

or

$$O_{2(aq)} + z\,H^{+}_{(Naf.)} + z\,e^{-}_{I(Pt)} \rightleftharpoons \text{ product} \tag{3}$$

$$\text{Interface II} \qquad Fe^{3+} + e^{-}_{II} \rightleftharpoons Fe^{2+} \tag{4}$$

where z is the number of electrons associated with reaction at the oxygen electrode. The oxygen electrode reaction in the presence of water is complex [5] with the possibility of parallel reactions, the relative dominance of which may change with temperature. Hence, z may change with temperature.

For Equation 2, the condition of equilibrium is

$$\eta_{H^+} + \eta_{e\text{-}I} = \frac{1}{2}\eta_{H_2} = \frac{1}{2}\mu_{H_2}(T_I) \tag{5}$$

where $\mu_{H_2}(T_I)$ is the chemical potential of hydrogen at the sensing electrode. Assuming the Nafion® is conductive only to H^+ ions, at open circuit:

$$d\eta_{H^+} = -\bar{\bar{s}}_{H^+}dT \tag{6}$$

where $\bar{\bar{s}}_{H^+}$ is the transported entropy of hydrogen ion [6].

For Equation 4 the condition of equilibrium is

$$\eta_{Fe^{3+}} + \eta_{e\text{-}II} = \eta_{Fe^{2+}} \tag{7}$$

Hence for cell ① with hydrogen at the sensing electrode I, the e.m.f. E_H is given by

$$E_H = \frac{1}{2F}\mu_{H_2}(T_I) + \frac{1}{F}\int \bar{\bar{s}}_{H^+}dT + E_{Fe^{3+}/Fe^{2+}} \equiv E_{II} - E_I \tag{8}$$

where $E_{Fe^{3+}/Fe^{2+}}$ is the potential at the reference electrode In principle, for the cell ① a contribution to the cell voltage due to the pressure gradient will also arise. However, according to Macdonald [7] this contribution is negligible for pressure differentials associated with aqueous systems.

Hydrogen in water obeys Henry's law [8], hence:

$$\mu_{H_2}(T_I) = \mu^{\square}_{H_2}(T_I) + RT_I \ \ln m_{H_2} \tag{9}$$

where $\mu^{\square}_{H_2}(T_I)$ is the chemical potential of hydrogen in the aqueous solution at temperature T_I and unit molality, m. Hence, Equation 8 becomes

$$E_H = E^{\circ}_{H}(T_I) + \frac{RT_I}{2F}\ln m_{H_2} + \frac{1}{F}\int \bar{\bar{s}}_{H^+}dT \tag{10}$$

where $E^{\circ}_{H}(T_I) \equiv (1/2F)\mu^{\square}_{H_2}(T_I) + E_{Fe^{3+}/Fe^{2+}}$ is a constant at a fixed temperature T_I. The dependency of the cell e.m.f. with respect to temperature T_I may be shown to be as follows:

$$\frac{\partial E_H}{\partial T_I} = -\frac{\partial E_I}{\partial T_I} = \frac{1}{2F}\left[R\ln\ m_{H_2} - s^{\square}_{H_2}(T_I) + 2\bar{\bar{s}}_{H^+}\right] \tag{11}$$

where $s^{\square}_{H_2}(T_I)$ is the molar entropy of hydrogen in the ideal aqueous solution at unit molality, temperature T_I. Hence measurements of E_H as a function of T_I, m_{H_2} enable determination of $\bar{\bar{s}}_{H^+}$. Similar analysis for the cell ① with oxygen at the sensing electrode, with the supposition that equilibrium behaviour H_2O, O_2 and H_2 is established at the sensing electrode gives for the temperature dependency of the cell voltage E_O:

$$\frac{\partial E_O}{\partial T_I} = \frac{1}{4F}\left[-R\ \ln m_{O_2} + s^{\square}_{O_2}(T_I) - 2\,s^{\circ}_{H_2O}(T_I) + 4\bar{\bar{s}}_{H^+}\right] \tag{12}$$

In Equation 12, m_{O_2} is the concentration (molarity) of oxygen in the water solution, $s^{\square}_{O_2}(T_I)$ and $s^{\circ}_{H_2O}(T_I)$ are the molar entropy of oxygen in the ideal aqueous solution at unit molarity and the molar entropy of pure water respectively, both at the temperature T_I.

3. Experimental details

A cross section drawing of the sensor is shown in Figure 1. Platinum metal was deposited in the Nafion® at the sensing electrode by a chemical deposition process [9]. The sensing electrode was inserted in an autoclave through which water, presaturated with hydrogen or oxygen, was circulated. A flow diagram is shown in Figure 2. Details of construction and assembly are described elsewhere [10]. The following measurements were made:

(i) Powder X ray diffraction measurements of solid phases and voltage stability of the Fe^{3+}/Fe^{2+} reference electrode system. Voltage measurements were made utilizing a calomel electrode, incorporating a Nafion® membrane salt bridge.
(ii) Sensor calibrations with humidified H_2/N_2 or O_2/N_2 gas mixtures at ambient temperature.
(iii) Voltage measurements in high temperature aqueous solutions of hydrogen or oxygen. Temperature range $25\,°C \leq t_I \leq \sim 230\ °C$. Pressure $p_I \sim 4$ MPa. Measurements were made at fixed T_I, variable $H_{2(aq)}$ or $O_{2(aq)}$ concentration in random sequence.

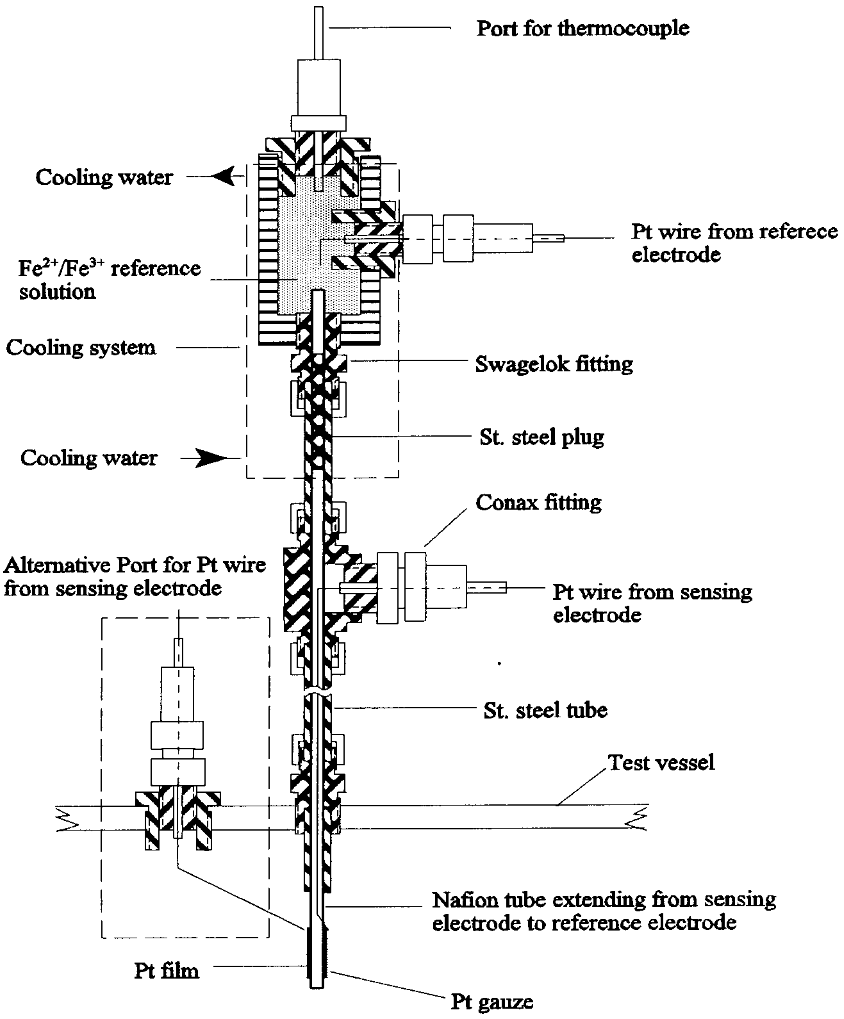

Fig. 1. Sectional drawing of nonisothermal sensor.

4. Results and discussion

4.1. *Stability of reference electrode*

X-ray diffraction analysis of the solid phases in the saturated Fe^{3+}/Fe^{2+} aqueous solution identified the following crystals:

$Fe^{2+}(Fe^{3+})_2(SO_4^{2-})_4.14\,H_2O$
$Fe^{2+}(SO_4^{2-}).H_2O$
$H^+Fe^{3+}(SO_4^{2-})_2.4\,H_2O$

Hence, the four component, four phase system is invariant at fixed temperature (T_{II}) and fixed pressure (p_{II}).

Voltage measurement relative to the calomel electrode over a 30 h period at $T_{\mathrm{II}} \sim 25\,^{\circ}\mathrm{C}$, $p_{\mathrm{II}} \sim 101.3$ kPa gave E_{II} (SCE) = +0.4733 ± 0.0006 V. This voltage was not influenced by the pressure of hydrogen at the sensing electrode I. The standard potential of the calomel electrode is E°_{cal} (SHE) = +0.268 V [11] hence E_{II} (SHE) = +0.741 V. The standard potential of the Fe^{3+}/Fe^{2+} electrode reaction is reported as $E^{\circ}_{\mathrm{Fe^{3+}/Fe^{2+}}}$(SHE) = +0.771 V [11].

4.2. *Sensor calibration with gas mixtures*

Sensor calibration with H_2/N_2 or O_2/N_2 gas mixtures were identical to published results [3]. Calibrations conformed to the Nernst equation for the isothermal cell ① corresponding to equilibria Equations 2 or 3. For Equation 3 $z \sim 1.0$ at ambient temperature.

4.3. *Measurements with high temperature aqueous solutions of hydrogen*

The results of experiments with a nonisothermal sensor (Pd-6) utilizing aqueous solutions of hydrogen gas with

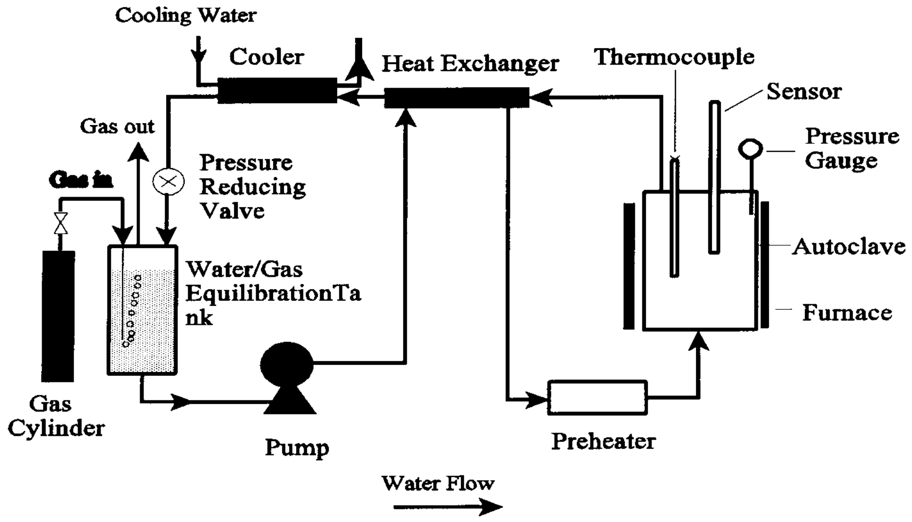

Fig. 2. Flow diagram of test loop for sensor.

the sensor electrode 298 K $\leq T_I \leq$ 469 K, p_I = 3.4 MPa are presented in Figure 3. The sensor voltage at a given temperature is a linear function of the logarithm of the hydrogen concentration. The linear slope is not a function of the temperature at the sensing electrode. Cross plots at a particular concentration of hydrogen in the water for three sensors are shown in Figure 4. The sensor voltage falls substantially, from about 0.6 V at T_I = 300 K to $\sim$0.0 V at T_I = 510 K. The three sensors showed some variation in response for reasons unknown.

For the sensor Pd-6, curve fitting with a fifth order polynomial with C_{H_2} = 0.0359 cm^3 (STP) H_2 kg^{-1} H_2O in T_I gives

$$E_H = \sum_i A_i T_I^i \tag{13}$$

with $A_0 = -0.5740$, $A_1 = -6.114 \times 10^{-2}$, $A_2 = 7.272 \times 10^{-4}$, $A_3 = -3.070 \times 10^{-6}$, $A_4 = 5.656 \times 10^{-9}$ and $A_5 = -3.884 \times 10^{-12}$.

Differentiation of Equation 13 gives $\partial E_I/\partial T_I = -\partial E_H/\partial T_I \geq 0.078$ mV K^{-1} at T_I = 298 K. Over the temperature interval 298 to 323 K, $\Delta E_I/\Delta T_I$ = 1.12 mV K^{-1}. The temperature coefficient of the standard hydrogen electrode is 0.86 mV K^{-1} [11] at 298 K.

From Equations 11 and 13, $\bar{s}_{H^+}$ may be determined. Results of calculation are presented in Figure 5 at the

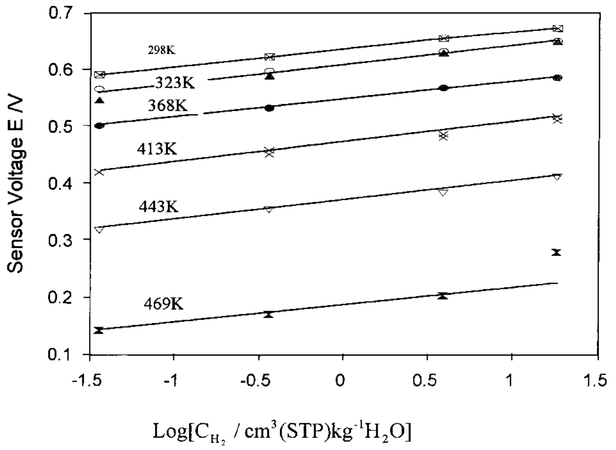

Fig. 3. Typical responses of nonisothermal sensor to dissolved hydrogen concentration in water sensor: Pd 6, pressure: 3.4 MPa, date: 1 Feb. to 6 March 1996. Temperature T_I of sensing electrode is indicated.

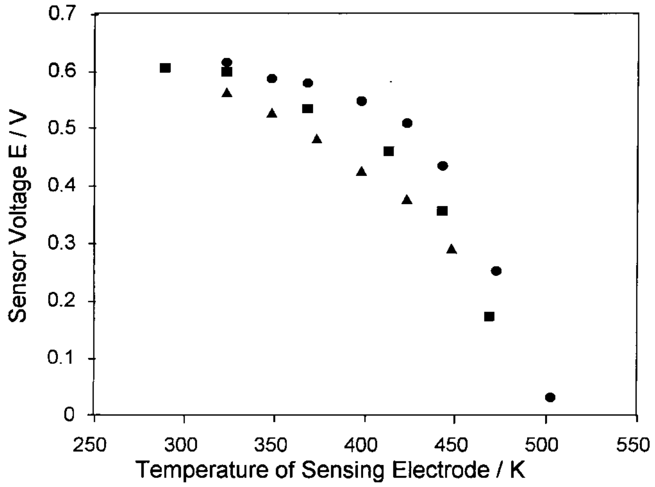

Fig. 4. Dependency of voltage of hydrogen sensor on temperature of sensing electrode. Hydrogen concentration: 0.37 cm^3 (STP) H_2 kg^{-1} H_2O. Pressure 3.4 MPa. Key: (▲) Pd-5; (■) Pd-6; (●) Pd-7.

hydrogen concentration $C_{H_2} = 0.0359$ cm^3(STP) H_2 kg^{-1} H_2O, $m_{H_2} = 1.603 \times 10^{-6}$ mol H_2 kg^{-1} H_2O. Entropy data for the ideal solution of hydrogen in water at unit molality were taken from Barner and Scheuerman [12]. The transported entropy is essentially independent of temperature to T_I ~350 K.

From equation 11:

$$\frac{\partial E_H}{\partial T_I} = \frac{1}{2F}\left[R \ln m_{H_2} - s^{\square}_{H_2}(T_I)\right] + \frac{\bar{\bar{s}}_{H^+}}{F} \equiv \frac{\partial E_t}{\partial T_I} + \frac{\partial E_{th}}{\partial T_I} \tag{14}$$

where E_t is the contribution to the cell voltage E_H arising from the electrochemical reaction and E_{th} is the contribution arising from thermal diffusion. The contributions of the two terms of Equation 14 are shown in Figure 6. There was no evidence of long-term time dependent effects upon the cell voltage. Good reproducibility of the sensor voltage (e.g., at $T_I = 413$ K, Figure 3) was achieved following measurements at higher temperature. The large contribution of the thermal diffusion potential to the sensor voltage (Figure 6) may be expected to cause such time dependent effect. However, C_{H_2}, T_I and T_{II} are maintained constant in an experiment and any transported H^+ ion must be reacted or created at the reference electrode. It is concluded that this reaction is extremely rapid such as not to interfere with the stability of the reference electrode.

The sensor voltage E_H is a function of the hydrogen concentration C_{H_2} and the temperature at the sensing electrode T_I:

$$E_H = f(C_{H_2}, T_I)$$

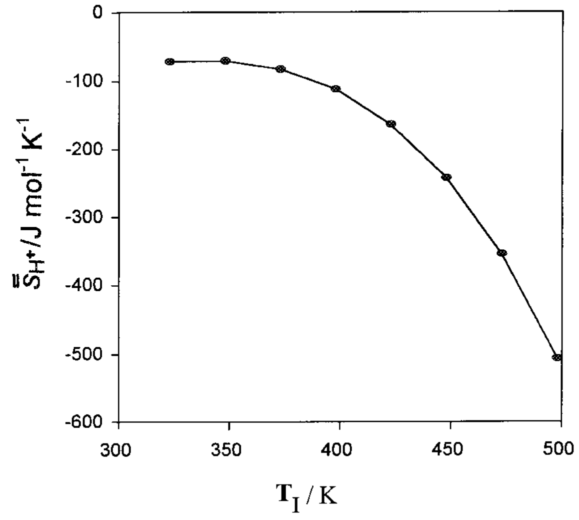

Fig. 5. Transported entropy for nonisothermal cell involving hydrogen.

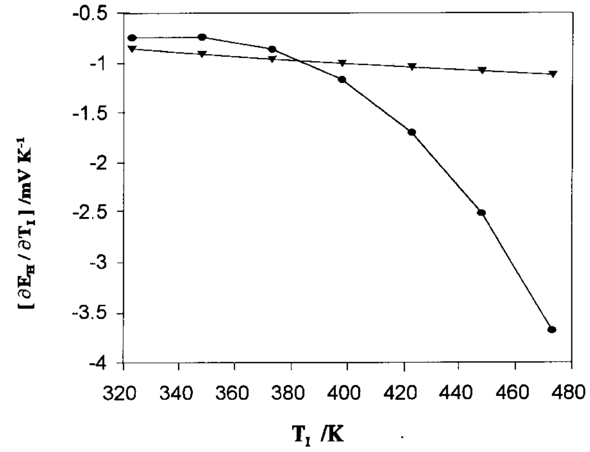

Fig. 6. Contributions of electrochemical reaction and thermal diffusion to temperature dependency of sensor voltage involving hydrogen. Key: (●) $\partial E_{th}/\partial T_I$; (▼) $\partial E_t/\partial T_I$.

Hence,

$$E_H - E_{H_0} = \int \left(\frac{\partial E_H}{\partial C_{H_2}}\right)_{T_I} dC_{H_2} + \int \left(\frac{\partial E_H}{\partial T_I}\right)_{C_{H_2}} dT_I \tag{15}$$

From Figure 3:

$$\left(\frac{\partial E_H}{\partial C_{H_2}}\right)_{T_I} = \left(\frac{\partial E_H}{\partial \log C_{H_2}} \cdot \frac{\partial \log C_{H_2}}{\partial C_{H_2}}\right)_{T_I} = (0.033\,26 \pm 0.002\,06)\frac{\partial \log C_{H_2}}{\partial C_{H_2}} \tag{16}$$

Hence, Equation 15 with Equations 13 and 16 gives

$$\log C_{H_2} = \frac{1}{3.326 \pm 0.2056}(100\,E_H + 6.114\,T_I - 7.272 \times 10^2\,T_I^2 + 3.070 \times 10^{-4}\,T_I^3 - 5.657 \times 10^7\,T_I^4 + 3.884 \times 10^{-10}\,T_I^5 - 1.464) \tag{17}$$

Hence, with Equation 17, from the measured voltage E_H and temperature T_I, the hydrogen concentration may be calculated. For example, with $T_I = 400$ K, $E_H = 0.48$ V, $C_{H_2} = 6.91 \pm 0.84$ cm^3 (STP) H_2 kg^{-1} H_2O.

4.4. *Measurements with high temperature aqueous solutions of oxygen*

Figure 7 is a typical response curve of a sensor to dissolved oxygen concentration in the range of 0.35~34.57 cm^3 (STP) O_2 kg^{-1} H_2O. It can be seen that the sensor voltage decreases as dissolved oxygen concentration increases at a given temperature of the

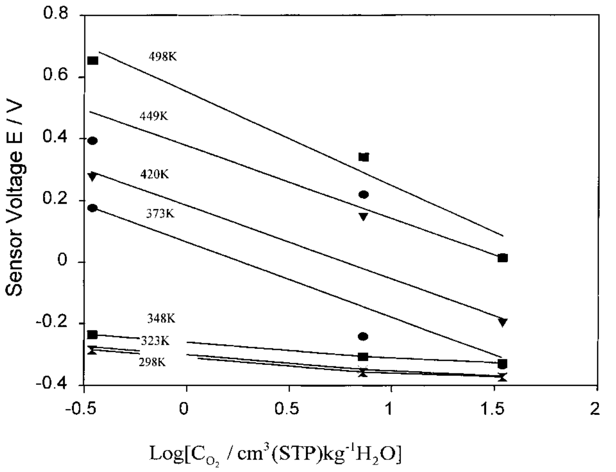

Fig. 7. Typical responses of nonisothermal sensor to dissolved oxygen concentration in water. Sensor Pd 11, pressure: 4.08 MPa, temperature T_I of sensing electrode is indicated.

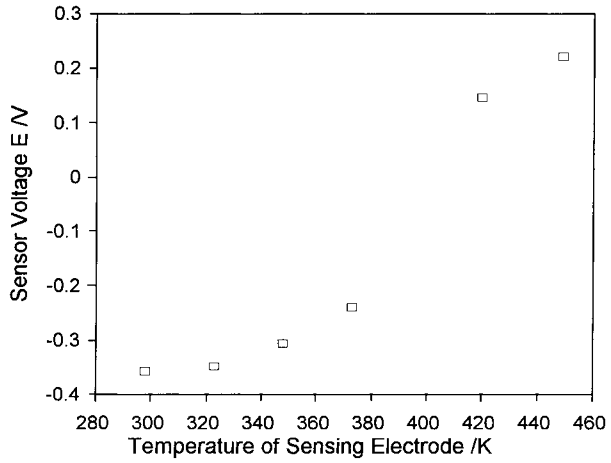

Fig. 8. Dependency of voltage of oxygen sensor on temperature of sensing electrode. Sensor: Pd 11, pressure: 4.08 MPa, oxygen concentration: 7.23 cm^3 (STP) O_2 kg^{-1} H_2O.

sensing electrode (T_I). The sensor voltage increases at a given C_{O_2} value as the temperature of the sensing electrode increases. This behaviour is the opposite to the effects observed with hydrogen (see Figure 3). It is noted that the sensor voltage is a linear function of log C_{O_2} (slope of 46.977 ± 1.037 mV decade^{-1}) in low temperature range (to about 348 K) but shows an irregular relationship at high temperature. This may be due to the complicated electrode reaction of oxygen in water at high temperature. Tarasevich et al. [5], in a review article, concluded that the mechanisms of the oxygen electrode remain mostly a matter of speculation. There is evidently a dearth of experimental work at high temperatures in the aqueous/oxygen system since these authors recommend such studies.

The temperature dependency of the sensor voltage is shown in Figure 8. The oxygen concentration is 0.35 cm^3 (STP) O_2 kg^{-1} H_2O. The sensor voltage increases as the temperature of the sensing electrode increases.

In principle the data may be analysed by procedures similar to those used for the hydrogen sensor. However the scatter of data are such that such an analysis is not justified.

5. Conclusions

(i) A nonisothermal electrochemical cell has been developed for monitoring hydrogen or oxygen in high temperature (~230 °C) water. The sensing electrode is platinum deposited on an ionic conducting polymer, Nafion®, in the form of a tube. The reference electrode is a saturated aqueous solution of Fe^{2+} and Fe^{3+} sulphates, operated at ambient.

(ii) The saturated aqueous solution of $FeSO_4.7H_2O$ and $Fe_2(SO_4)_3.5H_2O$ mixture with molar ratio 2:1 was used as the reference electrode. The composition of this mixture was determined by X-ray diffraction, indicating the presence of four phases (three solid phases, one liquid phase). The voltage stability of the system was verified relative to a calomel electrode. Hence the system is invariant at fixed temperature and pressure. The result showed that the saturated solution was stable at fixed temperature and pressure, hence it was suitable as a reference electrode.

(iii) The sensor responded to dissolved hydrogen in water and showed a good repeatability. The sensor voltages were linearly related to logarithm of dissolved hydrogen concentration with slopes of 30.0~38.3 mV decade^{-1} C_{H_2} in the temperature range of 25~230 °C. The sensor had negative temperature coefficient of voltage in the temperature range of 25~230 °C.

(iv) The sensor responded to dissolved oxygen in water. The sensor had a positive temperature coefficient of voltage in range of 25~230 °C. The slope of the sensor voltage vs the logarithm of dissolved oxygen concentration was a function of temperature.

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