



AN ELECTROCHEMICAL SENSOR FOR MONITORING OXYGEN OR HYDROGEN IN WATER

LEITAI YANG* , D.R. MORRIS, D.H. LISTER
Department of Chemical Engineering,
University of New Brunswick,
Fredericton, Canada

Abstract

Preliminary studies have been done on a simple electrochemical sensor which shows promise as a cheap, robust instrument for measuring dissolved oxygen or hydrogen in water. The sensor is based upon the solid-state electrolyte "Nafion" (trade name of perfluorinated sulphonic acid, manufactured by DuPont Inc.).

The Nafion was dissolved in a mixture of aliphatic alcohols, made into a slurry with platinum black, and applied to a ~1 cm-square electrode made of stainless steel gauze. The potential of the electrode was measured relative to a standard calomel electrode (SCE) in acid solutions at room temperature through which mixtures of oxygen and nitrogen or hydrogen and nitrogen were bubbled. The sensor was responsive to the equilibrating gas with good reproducibility. A similar sensor without the Nafion was not at all sensitive to changes in oxygen concentration. The voltage response of the sensor showed non-Nernstian behaviour, which suggests that the electrochemical reactions at the electrode surface are complex. Further testing of the sensor is required to verify its sensitivity and responsiveness in typical reactor coolant chemistries and to demonstrate its durability over a range of temperatures.

* Present Address: Centre for Nuclear Energy Research
University of New Brunswick,
Fredericton, Canada

2. Introduction

An important aspect of corrosion control in nuclear reactors is the reduction of dissolved oxygen in coolant systems. In the primary coolant of PWRs and CANDUs, this entails adding hydrogen to promote the radiolytic back-reactions that occur in the core. A similar philosophy is behind the addition of hydrogen to BWR feedwater in the application of Hydrogen Water Chemistry. In secondary coolants, too, control of dissolved oxygen is important to minimize damage to steam generator components.

Effective control of dissolved gases depends upon efficient monitoring techniques. Traditional methods of hydrogen and oxygen measurement involve sampling the coolant and extracting the gases for analysis on a "gas rack" system. Over the last ten years or so, electrochemical instruments have been used more and more - usually with extracted samples. These instruments are expensive and somewhat difficult to operate and maintain. There is clearly a need for a cheap, compact and robust instrument that can measure dissolved oxygen or hydrogen in water.

Solid-state electrolytes are promising materials to form the basis of such instruments. At the University of New Brunswick, studies have been carried out on a sensor consisting of the solid-state electrolyte Nafion, mixed with platinum black and supported on a stainless steel gauze.

3. Experimental

A diagram of the sensor is shown in Fig. 1. It comprises a stainless steel gauze ~1 cm square to which a slurry of platinum black in Nafion solution has been applied. Nafion is a copolymer proton conductor [1] and an excellent catalyst [2]. It is insoluble in water, resistant to oxidizing and reducing environments and can withstand temperatures up to 200°C or so. The

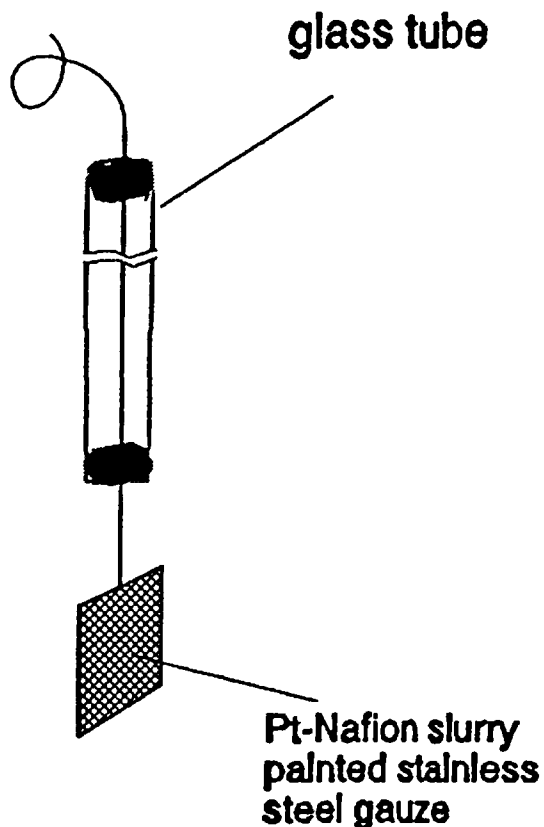
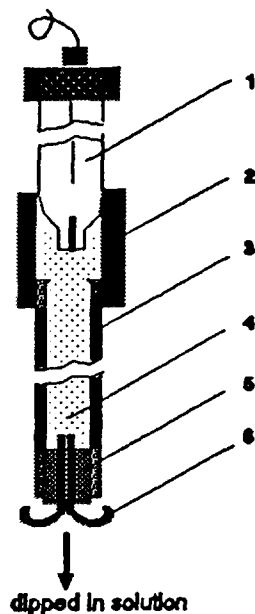


Figure 1 Sensor Electrode for Monitoring Oxygen or Hydrogen in Water.

Nafion solution (which was supplied by Aldrich Chemicals) contains 5%wt of Nafion in the H^+ form, mixed with lower aliphatic alcohols and 10% water. The platinum black was a fuel-cell grade supplied by Johnson Matthey Ltd. (99.9%, surface area $>20 \text{ m}^2/\text{g}$). After the evaporation of the alcohols and water, the platinum black was bonded onto the gauze with a thin film of Nafion.

The electrode potential of the sensor was measured with an electrometer (Keithley 610C) against a calomel reference electrode which was in contact with the test water through a bridge as shown in Fig. 2. The oxygen and hydrogen concentrations in the water were controlled by bubbling a H_2-N_2 or O_2-N_2 gas mixture of known composition at a constant temperature. A stirrer was installed in the air-tight electrochemical cell. In order to have a conducting medium between the sensor electrode and the reference electrode,



- | | |
|----------------------|------------------|
| 1. Calomel electrode | 4. KCl solution |
| 2. Seal | 5. Epoxy seal |
| 3. Glass tube | 6. Nafion strips |

Figure 2 Nafion Membrane Salt Bridge

the water was slightly acidified by adding a drop of concentrated acid (nitric, acetic or sulphuric).

4. Results and Discussions

The results of a typical experiment with water that was acidified with acetic acid (pH = 1.3) are shown in Fig. 3. The response of the sensor to the change of oxygen concentration was satisfactory for oxygen concentrations >1.4 mg/kg (the corresponding partial pressures were >0.049 atm). The stability of the sensor potential at constant oxygen concentration for partial pressures >0.049 atm is excellent in comparison with those reported in the literature for a bare metal platinum electrode [3]. When such a bare metal electrode was tested in the same solution as the sensor, its potential was unstable and hardly responded to the change of oxygen concentration. This may be an indication that the catalytic ability of platinum was greatly

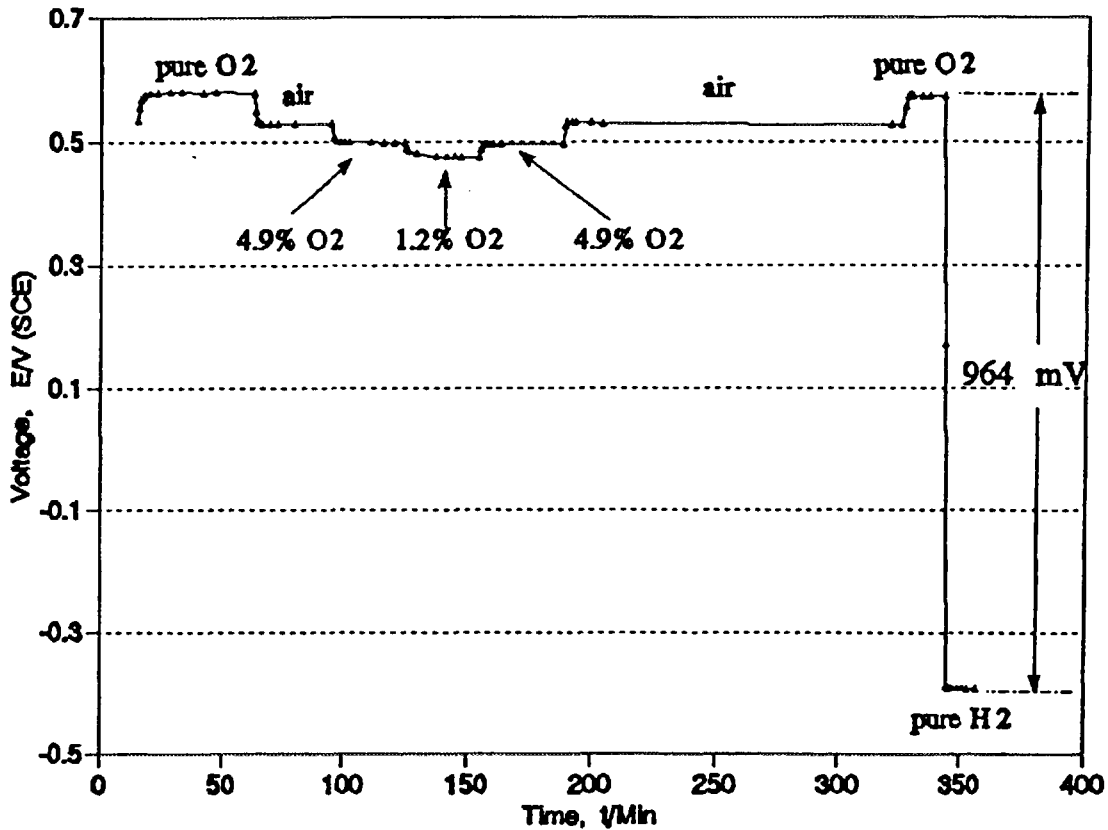


Figure 3 Sensor Response to Oxygen and Hydrogen in Acidified Water

enhanced by the addition of Nafion. Fig. 3 also shows that the open circuit potential of the sensor for pure oxygen (partial pressure = 1 atm) is 964 mV against that of pure hydrogen. This agrees well with the reported results [3].

The potential of an electrochemical sensor, E , is related to the concentration or pressure P of the active species, and is frequently represented in terms of the Nernst equation, of the form:

$$E = E^{\circ} + \frac{2.3RT}{zF} \log P \quad (1)$$

where E° is a constant, z is the number of electrons involved in the electrochemical reaction and R , T , and F , have their usual meaning.

The results of the experiments with oxygen/nitrogen gas mixtures shown in Fig. 3 are presented in terms of Equation (1) in Fig. 4. It is seen that the voltage is a curvilinear function of $\log P$, which suggests that the electrochemical reaction at the sensor is complex. For oxygen partial pressures >0.049 , the slope in Fig. 4 is 60 mV/decade which indicates, according to Equation 1, that the number of electrons involved in the electrochemical reaction is unity.

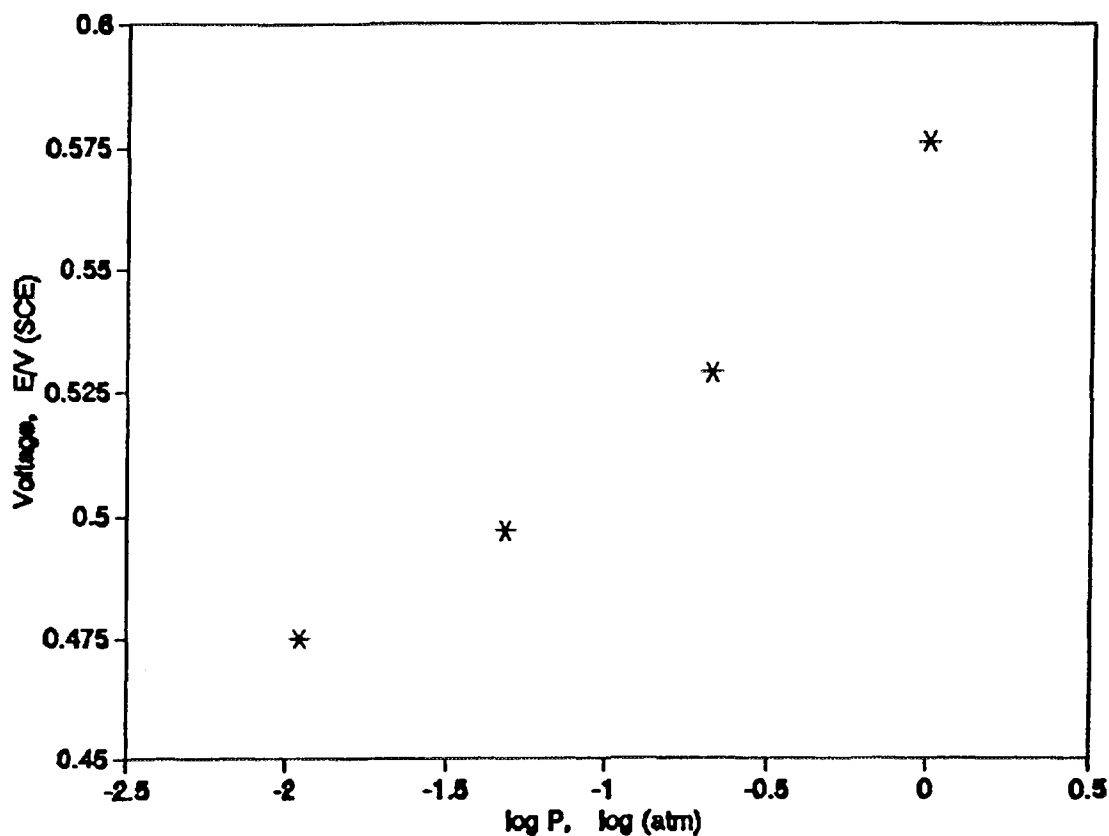


Figure 4 Response of Sensor Potential to Oxygen Pressure

Table I summarizes the relationships between the sensor potential and the logarithm of the partial pressure of oxygen (for the higher values 0.049 to 1 atm) which was equilibrated in water acidified with different acids. All results indicate that the

Table I SENSOR RESPONSES TO PARTIAL PRESSURE OF OXYGEN BUBBLING IN WATER

Acid added and pH	Slope (V/decade)	Regression coefficient	z
H ₂ SO ₄ pH=1.7	0.0573	0.998	1.04
HAC pH=1.3	0.0619	0.993	0.961
HNO ₃ pH=2.6	0.0566	0.995	1.05

Temperature: 27°C. Oxygen pressure range: 0.049 to 1 atm.

slopes of the Nernstian plots correspond to a single-electron transfer reaction ($z=1.017\pm 0.049$).

Other observations are summarized as follows:

- For all the solutions tested (i.e., for pH < 3.5), sensor potential was independent of pH. This may be due to the fact that the concentration of H⁺ in Nafion is 1.6 M, which is significantly higher than that of the test water. Neutral or alkaline coolants might have to be acidified to give steady results.
- The sensor would not respond to the changes of oxygen partial pressure if the concentration of chloride ion was >70 mg/kg. Such non-responsiveness is due to chloride poisoning of the reactions at the Pt-Nafion electrode, as reported by Paffett et al [4]. This should pose no problems at the low chloride levels experienced in reactor systems.
- It was necessary to maintain a high speed of agitation of the solutions. At low speeds, the electrode potential was not

stable and the responses to changes of oxygen concentration were slow. This behaviour is attributed to mass transfer effects at the electrode/water interface.

5. Summary and Conclusions

The simplicity of the sensor makes it an ideal instrument for routine use, while its cheapness means that it can be replaced frequently if necessary. The tests so far have given promising results, though issues still to be resolved include:

- determining the response at low oxygen and hydrogen concentrations;
- resolving difficulties with interference from hydrogen contamination during oxygen measurement and vice versa (note that such difficulties are common in electrochemical measurements of REDOX conditions);
- characterizing the effects of temperature, high pH and ionic strength; for maximum usefulness, the sensor should work in primary coolant streams (>260°C) with lithium hydroxide to pH ~10.3 (CANDU systems) and high boron and lithium concentrations (PWR systems).

ACKNOWLEDGEMENT

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