A pH Sensor Based on a Stainless Steel Electrode Electrodeposited With Iridium Oxide

Carmen C. Mayorga Martinez, Rossana E. Madrid, and Carmelo J. Felice

***Abstract*—A simple procedure to make an iridium oxide (IrO_2) electrodeposited pH sensor, that can be used in a chemical, biomedical, or materials laboratory, is presented here. Some exercises, based on this sensor, that can be used to teach important concepts in the field of biomedical, biochemical, tissue, or materials engineering, are also presented. This novel procedure is based on the electrodeposition of IrO_2 on a stainless steel electrode, which uses a similar mechanism to an ion selective electrode (ISE) and senses changes in pH. The simplicity and cost effectiveness of this method facilitates the teaching of the concept of half-cell potential and the basics of sensors. This novel sensor has also been shown to outperform the classical glass pH-sensor. In this new methodology, students learn to build the electrode, to calibrate it, and to measure its sensitivity, repeatability, and time-response.**

***Index Terms*—Electrodeposition of IrO_2 film (EIROF), Nerst equation, oxide reduction process, transducer evaluation.**

I. Introduction

TISSUE, chemical, electrical biochemical, biomedical, and materials engineering are fields where the pH is employed to control many processes. Hence, it is very important to be able to measure pH accurately and reliably. The well-known pH glass electrodes are usually used for this purpose [1], [2].

Nevertheless, the use of these conventional glass electrodes to determine pH has several disadvantages: they are easily breakable, expensive, tricky to build, highly sensitive to alkaline and fluoridric acid solutions [3], and show high output impedance and delayed response.

A novel pH sensor is described here, based on the electrodeposition of IrO_2 film (EIROF) on a stainless steel substrate by applying a combination of potentiodynamic cycling followed by potential pulsing [4], [5]. Thus, the sensor obtained overcomes the previously mentioned difficulties associated with the glass electrode. Although electrodeposition of noble metals, such as iridium, platinum, gold, or titanium, has been reported, this tends not to have been on stainless steel. However, this material can be useful and cost-effective.

Manuscript received June 26, 2007; revised January 11, 2008. Current version published February 4, 2009. This work was supported by grants from the Agencia Nacional de Promoción Científica y Tecnológica, the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), the Consejo de Investigaciones de la Universidad Nacional de Tucumán (CIUNT), and by the Instituto Superior de Investigaciones Biológicas (INSIBIO).

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Digital Object Identifier 10.1109/TE.2008.921451

A number of metallic oxides of high conductivity including SbO_3, PbO, PtO_2, RuO_2, OsO_2, TaO_2, RhO_2, TiO_2, SnO_2, and IrO_2, have been used to build pH electrodes. RuO_2 and IrO_2 are the most promising because of their specificity and high sensitivity. In addition, IrO_2 shows great stability for a wide range of pH, even at high temperatures (up to 250 °C) and high pressure [3].

The half-cell potential generated in the interface between the electrodeposited IrO_2 and the electrolyte depends on H^+ concentration and follows the Nernst equation. This equation applies to electrochemical systems and is an important concept in the field of electrochemistry [3]–[12].

Multiple applications for IrO_2 pH sensors have been reported, mainly for pH sensing in microsystems, including microenvironmental studies [6], microfluid-based microsystems for cell culture [7], measurement of extracellular myocardial acidosis [8], spatiotemporal pH dynamics following insertion of neural microelectrode arrays [9], and differential pH measurements of metabolic cellular activity in nanolitre culture volumes using microfabricated IrO_2 electrodes [10].

Preparation of the pH sensor and the testing of its static and dynamic properties, such as calibration, repeatability, sensitivity, and time-response constitute an interesting and relevant subject for practical work in a chemical, transducer and microsystems laboratory. This exercise can also demonstrate that this sensor can be used to measure pH in the same manner as a conventional glass electrode, thanks to its repeatability and precision.

II. Materials

The electrodeposition solution contains hydrated iridium tetrachloride $IrCl_4$ 99.9% (Aldrich), dihydrated oxalic acid 99.5% (Fluka), and anhydrous potassium carbonate K_2CO_3 99.0% (Fluka). For the calibration curve, the titration buffer contains 0.1 N citric acid, 0.1 N phosphoric acid, and 0.33 N orthoboric acid. This solution has a pH of 2.14 and can be acidified with 1 N hydrochlorate acid (HCl) (Ciccarelli) or can be alkalinized using 1 N sodium hydroxide (NaOH). All the solutions should be prepared with distilled water (5 μS).

A glass tripolar cell is employed for the electrodeposition (Fig. 1). A stainless steel concave counter-electrode, 85 mm in diameter, and an Ag/AgCl reference electrode are used. The working electrodes are stainless steel AISI 316 L cylinders electrodeposited with IrO_2, mounted in acrylic, leaving a circular exposed area of 1.27 cm^2 (Fig. 2). The same cell is used for the electrochemical measurements of pH, but without the counter-electrode (bipolar cell) (Fig. 1).

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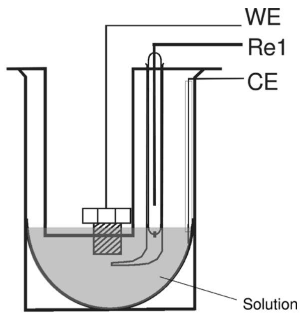

Fig. 1. Electrodeposition cell. (WE: Working electrode; Re1: Ag/AgCl reference electrode; CE: counter electrode.)

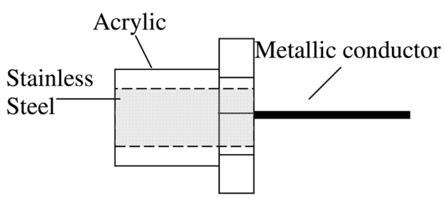

Fig. 2. Working electrode.

The measurements are carried out with the Solartron system 12508 W, which includes a frequency response analyzer 1250 and an electrochemical interface 1287. The data visualization and processing are carried out with the Solartron's commercial system Software CorrView. An Altronix pH-meter, that uses a conventional pH glass electrode which has been previously calibrated with standard buffers of pH 4, 7 and 10 (Anedra), is used to calibrate the IrO_2 pH sensor.

For the evaluation of the repeatability (ri) of the electrodes, the one-way-Anova statistical test, using software GraphPad Prism version 3.00, with a confidence interval of 0.95 is used. The following equation is applied:

$$r_i = [E/(E+D)] \tag{1}$$

where E is the variance between electrodes and D is the variance within the measurements of the same electrode.

III. Exercises

A. The pH Sensor Fabrication

Polishing of the Electrodes: Each electrode is polished as shown in Table I, using sandpapers of different roughness, diamond paste, and alumina dust to obtain a polished surface.

Electrodeposition Solution Preparation: The electrodeposition solution is prepared by dissolving 4 mM $IrCl_4$ in 40 mM oxalic acid, followed by the slow addition of 340 mM K_2CO_3 to a final pH of 10.3 [4]. The K_2CO_3 prevents passivation (spontaneous oxide formation) of the surface of the stainless steel electrode [13]. The solution is magnetically stirred until all the compounds are dissolved. The solution is allowed to sit quiescently at room temperature in the dark for eight days. The solution turns blue and it is ready to be stored at 4 °C for two or three weeks prior to use [7].

TABLE I
POLISHING PROTOCOL (*THE SIZE OF THE GRAIN MATCHES THE EUROPEAN STANDARDS FEPA STANDARD 43-GB-1984 (R1993) [15])

Steps	Abrasive	Grain size (μm) FEPA*
1	Sandpaper 120 BUEHLER®	127
2	Sandpaper 240 BUEHLER®	58.5
3	Sandpaper 400 BUEHLER®	35
4	Sandpaper 600 BUEHLER®	15.3
5	Diamond paste Prazis® and polishing cloth No. 40-7068	6
6	Diamond paste Prazis® and polishing cloth No. 40-7068	3
7	Alumina powder Prazis® and polishing cloth No. 40-7218	1

Electrodeposition: A stainless steel electrode is electrodeposited with an IrO_2 film, which is the pH sensing material. A potentiodynamic known protocol is employed [4], which consists of the combination of potential cycling with a triangular wave (50 cycles between 0.0 – 0.55 V versus the Ag/AgCl reference electrode at a 50 mV/s sweep rate) followed immediately by rectangular potential pulsing (same potential limits for up to 3000 pulses of 0.5 s each). The electrodeposition takes place in a water bath at 30°C. Following this procedure, the electrodes are kept submerged for 45 min and, thereafter, stored in the dark at room temperature.

B. Analytical Evaluation of the pH Sensor

The first practical lesson in a sensor laboratory consists of the evaluation of the static and dynamic characteristics of a sensor. Among the static characteristics are precision, sensitivity, and repeatability. For this exercise, calibration of the sensor with respect to a standard is needed. In the present case, the pH standard (or reference) measurements are those obtained with a conventional glass electrode, which was first calibrated against standard buffer solutions. The slope of the calibration curve obtained corresponds to the "sensitivity." Precision and repeatability are evaluated by making repeated measurements with the same electrode and calculating the error. Dynamic characteristics evaluate the sensor response to time variant signals.

Calibration Curve: The open circuit potential of the IrO_2 electrode is measured as a function of the pH of the test solution (within a pH range from two to twelve) using a Ag/AgCl reference electrode. The open circuit potential is registered once the variations are stable and below 0.05 V for 30 s. The sensor is calibrated with respect to the conventional pH glass electrode. The different pH solutions were obtained using this electrode. The calibration curve obtained is showed in Fig. 3 along with its linear regression.

Measuring a Sample Solution: The sample is obtained by adding an unknown volume of HCl to 200 ml of distilled water. The open circuit potential is measured and the corresponding pH is calculated by means of the calibration curve. In one particular solution, the obtained value for the IrO_2 electrode was 3.8, while the pH measured with the glass electrode was 3.69, giving a difference of 0.11.

TABLE II
VOLUMES OF 1 N NAOH ADDED TO THE UNIVERSAL HOMEMADE BUFFER AND THE CORRESPONDING pH OBTAINED

ml of 1N NaOH added	0.00	7.70	5.80	6.80	7.00	4.40	3.00	5.00	4.20	5.10	32.7
Resulting pH	2.14	3.01	4.00	5.00	6.01	7.02	8.13	9.00	10.00	11.02	11.72

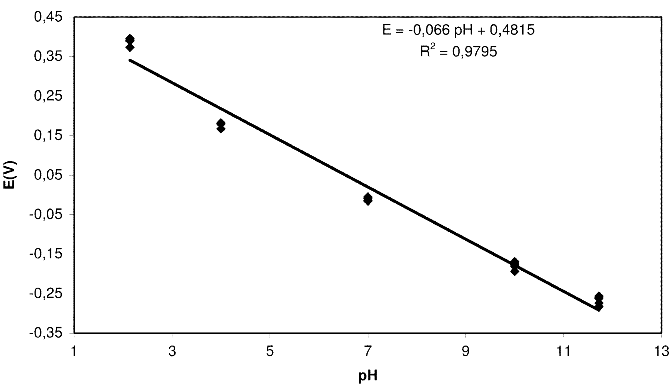

Fig. 3. Calibration curve: open circuit potential E versus pH.

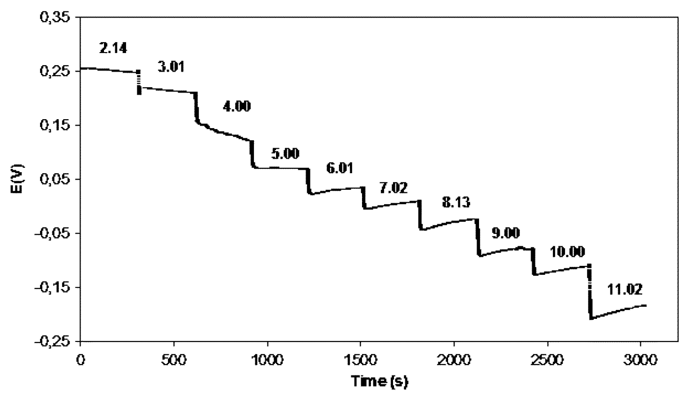

Fig. 5. Dynamic response of the IrO_2 pH sensor. Potential-time response curve.

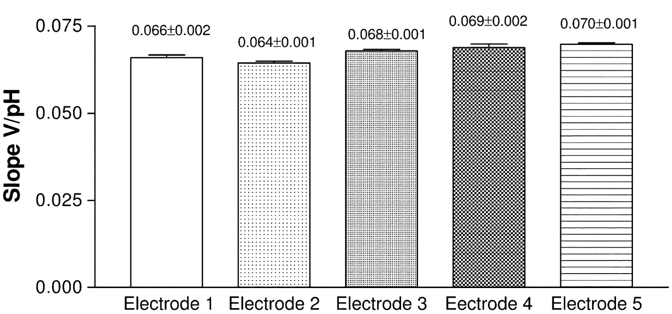

Fig. 4. Evaluation of the slopes of the calibration curves of five electrodes with five repetitions per electrode.

Repeatability Evaluation of the pH Sensor: Five electrodes are used and five calibration curves are made for each. The values of the slopes of each electrode are analyzed (Fig. 4) to evaluate the IrO_2 electrode response repeatability. Iridium oxide pH sensors have a repeatability of $r_i = 0.84$ (1). The very low error obtained for measurements of the same electrode shows how precise the pH measurements can be using these sensors.

Dynamic Response of the pH Sensor: The open circuit potential of the IrO_2 electrode is measured in 200 ml of titration buffer until a variation of < 0.05 V over 30 s occurs. Known volumes of 1 N NaOH are added according to Table II, and the corresponding potentials are registered. Fig. 5 shows the dynamic response of the pH sensor.

IV. DISCUSSION

When a pH sensor is evaluated, a conventional glass electrode is used, which is normally acquired commercially rather than fabricated by the students. The exercises presented here offer the possibility of making the same evaluation by means of a novel, robust and precise pH sensor, easily fabricated by students in the laboratory.

The IrO_2 pH sensor shows an excellent correlation against results obtained with the conventional glass electrode, which suggests its potential applicability for pH measurements. This high correlation (0.99) is significant, and suggests that this sensor is worth serious consideration. It would be interesting to study the degree to which this sensor could behave in the same way as a conventional pH glass sensor.

The sensor has a good repeatability ($r_i = 0.84$) because a $r_i > 0.7$ is considered as repeatable. The sensor also has a fast time response, reaching 90% of the established value in less than 10 s. The dynamic behavior of the sensor corresponds to the response of a first-order system.

Another important concept used in biomedical, chemical or materials engineering is the "half-cell potential," which is the potential generated in the interface between the electrodeposited IrO_2 electrode and the electrolyte. This potential depends on the H^+ concentration and follows the Nernst equation [3]–[12].

In the pH IrO_2 electrode, the oxidation-reduction reaction taking place on the surface of the electrode in contact with the solution is described by

$$2\,\mathrm{IrO(OH)} + 2\,\mathrm{H}^+ + 2\,\mathrm{e}^- \longleftrightarrow \mathrm{Ir_2O(OH)_2} + \mathrm{H_2O}.$$

The half-cell potential is obtained by applying Nernst equation, as follows:

$$E = E^\circ + \frac{2.303RT}{nF}\log\frac{[IrOOH]^2[H^+]^2}{[IrO(OH)_2]}. \quad (2)$$

Where

$E^\circ =$ standard redox potential at $\mathrm{pH} = 7.0$
$E =$ measured potential
$R =$ gas constant: 8.31 J/° mol
$T =$ absolute temperature in ° K (298° K)

$F =$ Faraday constant: 23 062 cal/V or 96 406 J/V.
Rearranging (2)

$$E = E^{\circ} + \frac{2.303RT}{nF}\log\frac{[IrOOH]^2}{[IrO(OH)_2]} + \frac{2.303RT}{nF}\log[H^+]^2 \quad (3)$$

$$E = E^{\circ\prime} - \frac{2.303RT}{F}\text{pH} \quad (4)$$

where $E^{0\prime}$ is

$$E^{0\prime} = E^{\circ} + \frac{2.303RT}{nF}\log\frac{[IrOOH]^2}{[IrO(OH)_2]}. \quad (5)$$

Replacing the constant values in (4) the equation can be written as

$$E = E^{\circ\prime} - 0.059\text{pH}.$$

A slope of -0.059 implies a Nernstian behaviour. This sensor presents a super-Nernstian response because the slope calculated from the calibration curve is -0.066 V/pH (Fig. 3), which is already reported [3]–[6].

V. Conclusion

The exercises presented in this paper enable students to learn basic concepts in the area of sensors, such as calibration, repeatability, precision and dynamic behavior, by evaluating a simple but novel pH sensor. The calibration curve offers one way to teach these important concepts, but an alternative method is for students to validate Nernst equation, by quantifying the slope of the calibration curves obtained for these pH electrodes.

The high precision and repeatability of these sensors show that they can be used to design measurement systems, where conventional pH glass electrodes are difficult to implement, such as with micro or nanosystems, or bioMEMS (Bio electro mechanical systems). The open circuit measurements described are made with a potentiostat, but these measurements could also be made with an instrumentation amplifier and a multimeter, which could kindle students' interest in design.

These sensors and the working cells are easily fabricated by students in a laboratory setting. Their performance and toughness enable them to be used in a student laboratory, thus overcoming the known disadvantages of the conventional pH glass electrode.

Acknowledgment

The authors would like to thank Dr. C. M. Whitacre and Dr. M. Valentinuzzi for their critical reading and for their translation assistance in the final preparation of the manuscript.

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