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Evaluation of a high sensitivity PbO_2 pH-sensor

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Abstract

In this paper, a new high sensitivity potentiometric pH-electrode with a response in the acid region is proposed. It consists of a PbO_2–paraffin matrix deposited on graphite. Its simple construction and studies of some variables at 0.5 mol L^{-1} ionic strength are reported. A direct relationship between the electric potential difference and the solution pH was observed for pH values ranging from 1.2 to 7.5. A slope greater than 100 mV/decade and a conditional electric potential of about 1250 mV were obtained. The results presented a high correlation with those from a conventional glass pH-electrode in complex matrix samples.

Keywords: pH-sensor; PbO_2–paraffin membrane; High sensitivity pH-electrode

1. Introduction

The first uses of the glass pH-electrode as an ion-selective electrode (ISE) date from the beginning of the 20th century [1]. Since then this kind of electrode has undoubtedly become the most used ISE, although other electrodes formed, say, by an interface of metal and metal oxides or oxides immobilized in some kind of matrix have been reported [1–3]. However, the absolute value of the slope of the analytical curves for those electrodes has usually been observed to be equal or below the pH-glass response (59.16 mV/decade at 25 °C) although exceptions to this behavior have also been found.

For example, among various ceramic and bronze sensors tested in Ref. [4], only Na–tungsten bronze sensor showed a 76.3 mV/decade response in a pH range from 4 to 9. Supernerstian polyaniline pH sensors were also studied, but restricted to a very narrow pH linear range [5,6]. More recently, an IrOx sensor with 73.7 mV/decade in an analytical range of pH from 1.5 to 11.5 has been found [7].

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The response of PbO_2 to solution pH was studied by Cassiano and Capelato [8]. The oxide deposited electrolytically on a graphite electrode was observed to form a rigid film. The response of the composite electrode, used as a pH-sensor in acid-base titrations, was based on the half-reaction:

$$PbO_2(s) + 4H^+(aq) + 2e \rightleftharpoons Pb^{2+}(aq) + H_2O \qquad (1)$$

to which corresponds Eq. (2):

$$E = E^{\circ\prime} - 2S\beta_1 pH - \frac{S}{2}\beta_2 \log[Pb^{2+}] \qquad (2)$$

where $E^{\circ\prime}$ is the conditional potential, S, the slope ($2.303RT/F$), and β_1 and β_2 are electrode efficiency parameters known as electromotive factors [8].

Although $2S \sim 118.3$ mV/decade, the value for the slope $2S\beta_1$ in Eq. (2) was determined experimentally to be in the range between 52 and 56 mV/decade, indicating that the value of the electromotive factor β_1 was less than one half. The electrode presented a wide pH response range, from 2 to 13. The response of the sensor to Pb^{2+} ions in acid media was also studied. The slope for this ion varied between 25.3

and 27.6 mV/decade (or, equivalently, β_2 varied from 0.86 to 0.94), with little dependency on the pH of solution.

The analytical response of PbO_2 in poly(vinyl chloride) (PVC) was also studied for acid-base titration [9]. A dependency of the pH-slope with the matrix composition was observed. For composition varying between 25 and 75% PbO_2, the corresponding slope ranged from −44 to −56.0 mV/decade. A similar study was carried out with a PbO_2–epoxi-graphite electrode [10]. The best slope, −58.7 mV/decade, was obtained for a 40% (w/w) PbO_2 electrode.

Another example of pH-electrode reported in the literature includes the lead oxide film on aluminum electrode [11]. The pH response was studied for modified electrodes with thin films of α-PbO_2 and β-PbO_2. It was shown that the potentiometric responses were similar for both phases, and their slopes were very close to 59.16 mV/decade.

In the present work, the influence of some parameters on the slope of the composite PbO_2–paraffin electrode is discussed. The principal feature of the electrode was the high β_1 factor obtained ($\beta_1 = 0.95$), corresponding to a slope of about −112 mV/decade.

2. Experimental

All solutions were prepared with deionized water and analytical grade reagents. The solutions ionic strength was adjusted with $NaNO_3$ to 0.5 mol L^{-1}.

An 8.0 mmol L^{-1} buffer solution with pH 7.5 was prepared dissolving 0.5678 g of Na_2HPO_4 and 20.3988 g of $NaNO_3$ in water. The pH was adjusted by adding NaOH to the solution (a pHmeter Digimed model DM21 was used for the pH determinations) and the total volume was completed to 500 mL. An Ag/AgCl single junction reference electrode with KCl 3.0 mol/L (Digimed) was used.

A volume of 500 mL of a 60 mmol L^{-1} sulfuric acid solution was prepared by dissolving in water 3.0 mL of concentrated H_2SO_4 and 13.5992 g of $NaNO_3$.

Paraffin–PbO_2 membranes were prepared by dispersion of a convenient amount of PbO_2 (Carlo Erba) and paraffin (Polifarma) to obtain 5.00 g of composite in a beaker on a hot plate. The membranes were spread on different support materials such as graphite (2-mm diameter rod, Rayovac Corporation), gold (3-mm diameter rod, Aldrich), tungsten (4-mm diameter rod, Aldrich), antimony (4-mm diameter rod, Aldrich) and copper (6.35-mm diameter rod, Aldrich) by dipping the support material into the melted composite at a temperature near paraffin melting point. The paraffin was kept in the melting state only for a few seconds. Membranes with almost uniform thickness (0.2–1 mm) and surface area approximately 1.5 mm^2 were obtained. Teflon tape was used for isolation of the support material rods. The schematic representation of the sensors is shown in Fig. 1.

Aliquots of the 60 mmol L^{-1} sulfuric acid solution were added in a 50-mL potentiometric cell with 25 mL of 8.0 mmol L^{-1} buffer solution and the combined pH-glass electrode coupled to a pH-meter, calibrated with 4.00 and 6.86 pH reference solutions, was used for pH measurements.

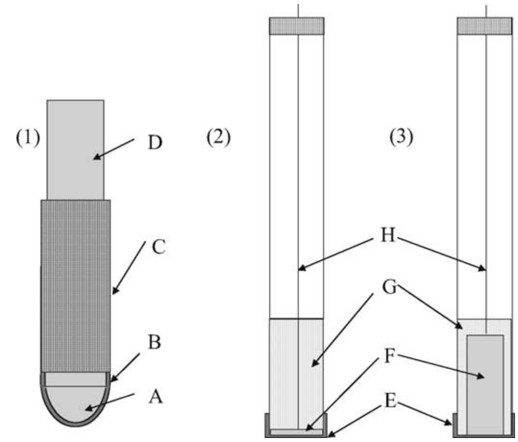

Fig. 1. Schematic representation of PbO_2-parafin pH-sensor in different supports. (1) Copper wire and grafite support: (A) support, (B) paraffin membrane, (C) Teflon tape, (D) electric contact region. (2) Copper plate: (E) paraffin membrane, (F) support, (G) epoxi resin, (H) electric contact wire. (3) Other support materials.

For electromotive force measurements the proposed electrode and an Ag/AgCl electrode used as reference were coupled to a second pHmeter. The magnetic agitation was kept constant.

A known volume of electrolytic solution was added, in each compartment, and Ag/AgCl reference electrodes were immersed in the solutions.

3. Results and discussion

The effect of membranes composition on the response of the electrode was studied from 35 to 90% (w/w) of PbO_2 on a graphite support. Three to five electrodes were tested for each composition. No response was observed below 65% (w/w). For membranes with composition between 65 and 85% (w/w) it was observed that the slopes and the conditional potentials were similar (Fig. 2), with a high reproducibility of the analytical curves. On the other hand, the potentiometric response for the 90% (w/w) of PbO_2 electrode was unstable.

In the optimal composition region (65–85%), the slope varied from −109.0 to −112.6 mV/decade and the conditional potential ranged from 1253 to 1276 mV. The linear pH range for the analytical curves was 1.2–7.5. The electrodes presented fast response time to the solution pH (a few seconds).

The Pb^{2+} response forecast in Eq. (2) was verified at pH 4.2, resulting in a slope of 25.5 mV/decade.

The potentiometric response associated with the half-reaction of reduction of PbO_2 Eq. (1) is shown in Eq. (3) for the 75% (w/w) PbO_2 membrane.

$$E = 1276 - 112.6\text{pH} - 25.5 \log[Pb^{2+}] \quad (3)$$

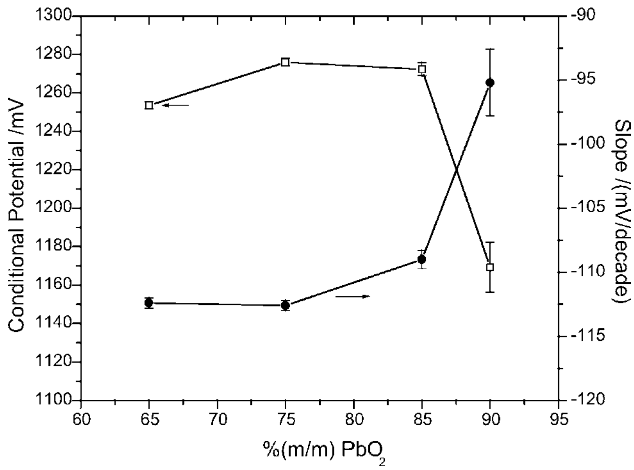

Fig. 2. Effect of matrix composition on the electrode response. (□) conditional potential; (●) slope. Support: graphite.

This equation expresses the high sensitivity of this electrode with respect to pH as well as to Pb^{2+} concentration responses. The experimental slopes obtained were quite close to the theoretical predictions, $\beta_1 = 0.95$ and $\beta_2 = 0.86$.

To our knowledge the pH-slope obtained in the present work is about twice the highest value found in the literature [7–9].

An interesting and unexpected result was observed in the study of the influence of the support material used for constructing the electrodes. As shown in Fig. 3, the electrodes using graphite, tungsten and gold as supports have similar analytical responses, whereas the responses for antimony and copper were almost null and unsteady. Although these results cannot be explained at present, a practical conclusion may be drawn from them: graphite, tungsten and gold are good a choice as support for the membrane.

The behavior (linearity and slope) of the electrodes tested under different storage conditions (dry, in 4.0 or 7.0 buffer solutions, or in 95% (w/w) ethanol) did not change significantly after storage for more than 3 months.

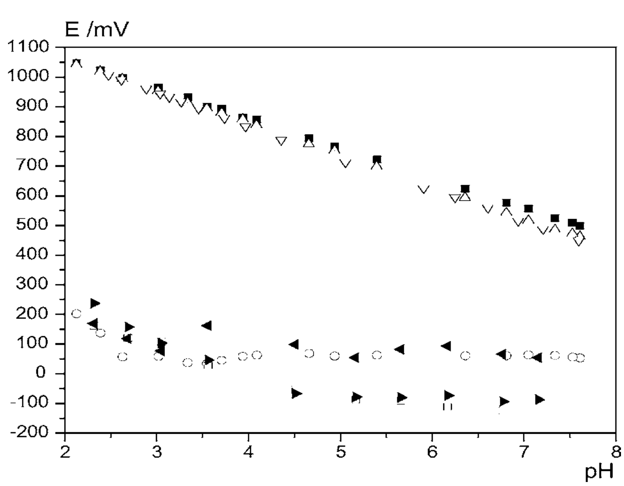

Fig. 3. Influence of the support material on the PbO_2–paraffin matrix behavior. Materials: (■) gold, (▽) graphite, (△) tungsten, (◯) copper plate, (► and ◄) copper wire, (□) antimony.

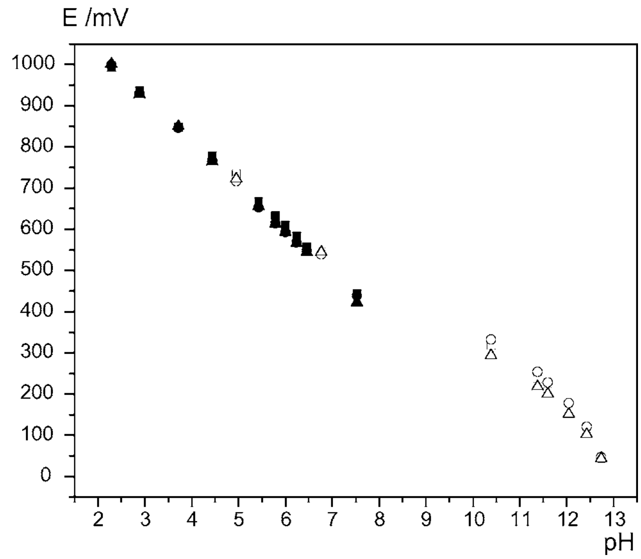

Fig. 4. Electrode potential vs. pH plots: acid way: (■) 1st, (●) 2nd, (▲) 3rd; basic way: (□) 1st, (◯) 2nd, (△) 3rd.

The study in alkaline region was accomplished by addition of NaOH after the acid-pH measurements were completed (Fig. 4). Above pH 7.5, the response presented a non-linear behavior. The mean slope in this region was 88 mV/decade, a value still greater than those given by conventional pH-electrodes. At high pH values no electrode damage was observed. Furthermore, no hysteresis was observed in various acidic–basic–acidic runs (Fig. 3).

The sensitivity of reference electrode was tested in order to guarantee its stability against changes in the surrounding conditions [12].

4. Comparison of methods

In order to compare the electrode response with that of the pH-glass electrode, measurements were made in complex matrices. Industrialized fruit juices of different brands found in the Brazilian market (listed in Table 1) were used as matrices. As seen in Table 1, a good agreement (with a maximum difference of 0.28 pH-unit) was obtained between the methods. In fact, the pH-measurements can be correlated by the linear relationship $pH_{proposed} = 0.083 + 0.993\ pH_{glass}$, with a correlation coefficient 0.97 ($n = 11$).

However, this favorable response should be seen with some care in the sense that the use of this electrode in complex media can occasionally lead to errors due to complexation or redox effects. However, the electrode could be used as a transductor in gas sensors or even in biosensors, in which cases no direct contact occurs between the sample and the transductor.

Table 1
Comparison of proposed electrode with glass pH-electrode in complex matrix samples

	Sample	Brand	pH (glass electrode)	pH (proposed electrode)	ΔpH
1	Coconut water	Kero-coco	5.34	5.19	−0.15
2	Coconut water	Trop-coco	5.41	5.42	0.01
3	Coconut water	Ducoco	5.26	5.54	0.28
4	Lemon tea	Santal Mate	3.57	3.58	0.01
5	Lemon tea	Santal Mate	3.52	3.68	0.16
6	Peach tea	Santal Mate	3.34	3.18	−0.16
7	Mango juice	Izzy	3.27	3.39	0.12
8	Mango juice	Izzy	3.38	3.42	0.04
9	Mango juice	Izzy	3.37	3.48	0.11
10	Grape juice	Santal	3.26	3.44	0.18
11	Grape juice	Santal	3.27	3.26	−0.01

5. Conclusion

A new high sensitivity potentiometric electrode, namely, a PbO_2–paraffin pH-sensor, with high sensitivity response was proposed. The sensor, made easily in the laboratory, presented the following features: (i) high sensitivity (ca. 112 mV/decade) in the acid region, (ii) high stability and (iii) reproducibility. Furthermore, hysteresis effects and influence of matrix thickness or composition were not observed. The electrode also responded to the lead (II) ion. Its low sensitivity to this ion could be well explained by the Nernstian equation for the proposed half-reaction.

The sensor was applied to pH determination in industrialized fruit juices, leading to results that correlated well ($r = 0.97$, $n = 11$) with those obtained with a conventional pH-glass electrode, thus demonstrating its feasibility as a pH-electrode.

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