Development of low-cost metal oxide pH electrodes based on the polymeric precursor method


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**Abstract**

In this work, the polymeric precursor method was used to prepare low-cost solid-state sensors for pH determination based on iridium oxide as the main pH sensitive material. The iridium content was reduced with addition of TiO₂, forming the binary system IrOₓ–TiO₂, whose electroanalytical properties were evaluated in comparison with a commercial glass pH electrode. The minimum iridium content which gave suitable results was 30 mol%, and the electrode presented Nernstian and fast response in the pH range from 1 to 13, with no hysteresis effect observed. Besides, the electrode showed high selectivity in the presence of alkali ions as Li⁺, Na⁺ or K⁺. The amount of iridium in the prepared electrodes was very small (<0.1 mg), supporting the efficiency of this method on the simple preparation of functional low-cost pH electrodes.

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**1. Introduction**

pH measurements are indispensable in a wide range of control processes as well as in clinical, environmental and food industry applications. Among the various methods, the use of glass electrode has been widely adopted due to its good sensitivity, selectivity, stability and long lifetime [1]. However, glass electrodes have several disadvantages related to the intrinsic nature of the glass membrane; high impedance of the membrane, difficulty of miniaturization, mechanical fragility and chemical instability in corrosive systems can be described.

Non-glass based hydrogen ion-selective electrodes are preferred over glass electrodes where robustness is necessary. Hence, several works have investigated the possibility of using conducting polymers [2,3], and metal oxides [2,4] to build pH sensors, and metal oxides have demonstrated to be the most promising candidates. They have a number of advantages over conventional glass electrodes. They are mechanically stable and can be miniaturized for in vivo measurements [5], used in aggressive environments [6], at temperatures up to 250 °C [7] and at pressures up to 270 bar [8]. They also respond faster to pH changes, even in non-aqueous solvents [9].

Different oxides have been used to develop pH sensors such as: PtO₂ [10], IrO₂ [8,10–13], RuO₂ [10,14–17], molybdenum bronzes [18], OsO₂ [10], Ta₂O₅ [10], TiO₂ [10], PdO [10], SnO₂ [10], ZrO₂ [10], Co₂O₃ [19], WO₃ [20], PbO₂ [21], and Sb₂O₃ [22]. Among the mentioned materials, the most promising ones are RuO₂ and IrO₂ due to their chemical stability and high conductivity, which inhibit the space charge accumulation. The construction of IrO₂-pH electrodes is described in the literature using some techniques such as reactive sputtering [23–25], thermal oxidation of iridium wetted with NaOH [26], in molten potassium nitrate [7] or carbonate [27], thermal decomposition of an iridium salt [28,29], electrochemical...
oxidation of Ir electrodes [30–32], and anodic iridium oxide film (AIMOF) electrodeposition [33–35]. Other important methods used to prepare oxide films are the sol–gel routes. Among them, the polymeric precursor method [36] allows the preparation of oxides with high homogeneity and well-defined properties, even to mixed oxides or oxides with low level of doping. Moreover, it consists in a simple procedure (the sol is stable and has no problems concerning moisture) and it is still a low-cost method, since it uses cheap start reagents, such as citric acid (CA) and ethylene glycol (EG).

Aiming at the development of a more inexpensive pH electrode, our group recently proposed the use of binary systems as pH electrodes prepared by polymeric precursor method [37]. This approach was based on our experience on the study of the dimensional stable anodes (DSA®) [38–40]. DSA® were initially developed by Beer [41] and widely investigated by Trasatti [42,43]. At present, these electrodes are a very important material to the application in electrocatalysis (e.g. chloro-alkali industry). It is known that the stability of DSA® electrodes can be improved if a binary (or even ternary) composition is employed. These mixtures usually consist of an active oxide mixed with a chemically inert one. The most commonly used composition is the RuOx–TiO2 electrode [43]. In this case, the amount of RuOx in the binary system is the minimum required to guarantee the electrocatalytic activity of the electrode. Considering that RuOx is the most expensive component used in the preparation of the electrode, the RuOx–TiO2 composition is a compromise among cost, stability and activity. The important advantage of using binary systems is the reduction in the final price of the electrode since the second oxide, TiO2, is of low-cost.

In the preliminary work [37], it was demonstrated that RuOx–TiO2 electrodes could be used as a pH electrode, since they presented a Nernstian response (56 mV pH−1) and are insensitive to the presence of cations, such as Li+, Na+ and Ca2+. Though Ir salts are more expensive than the Ru salts and there is evidence showing that the IrOx has less catalytic activity than the RuO2 [44], it is known that the IrOx is anodically much more stable, being used to stabilize RuO2 in a mixture against anodic dissolution [44,45]. RuOx–pH electrode has a drawback related to its low resistance in alkaline solutions since the anodic dissolution affects its lifetime.

In this context, in this work, titanium oxide was used as the “chemically inert” material completing the binary system IrOx–TiO2 to develop all-solid-state pH sensors. In fact, TiO2 is not sensitive to pH changes in solution, but it presents a very sub-Nernstian response over a comparative narrow linear range [46,47]. Thus, in this work, we investigated the possibility of using IrOx–TiO2 thin films as pH electrodes using the polymeric precursor method. It is well known that IrOx is more resistant than RuOx in alkaline solution concerning its chemical stability. We prepared a second generation of our Pechini synthesized pH electrodes associating the chemical stability of IrOx instead of RuOx, and the low-cost with addition of TiO2 to the oxide system. Also, in the development of these polymeric precursor titanium–iridium oxide films (PTIROF), we looked for the minimum IrOx content that grants suitable sensor properties although the large component of the binary system is TiO2. Besides, the use of a cheaper substrate, such as titanium, leads to a really cheaper and more convenient fabrication process than other electrodes.

2. Experimental

2.1. Electrode preparation and evaluation

The electrodes were prepared using the polymeric precursor method (also called Pechini method) [36]. Firstly, a solution containing citric acid and ethylene glycol in a 1:4.65 (CA/EG) molar ratio was prepared under stirring at 60 °C. Following, the metallic precursors iridium chloride (Aldrich) and/or titanium (IV) isopropoxide (Hull-AG) were slowly added. Both stirring and temperature were kept constant until the complete dissolution of the complex. As a first step in the study, an electrode containing only IrOx in the composition was prepared and evaluated. Subsequently, other electrode compositions were tested using the binary system IrOx–TiO2 in order to diminish the iridium content. To prepare the binary oxide, two salt solutions (Ti and Ir) were prepared separately and later mixed. Table 1 shows the compositions of the electrodes that were studied and the denomination used in the text.

Several 10 mm × 10 mm × 0.5 mm (surface area of 1.0 cm²) titanium plates with purity of 99.7% (Ti-Brazil) were used as substrate. The substrate was treated by sandblasting, followed by a chemical treatment in hot 5% (w/v) oxalic acid solution for 10 min. Finally, the electrodes were washed with Milli-Q water and dried at 150 °C. The precursor solutions were painted over the substrate and thermally treated at 110 °C during 30 min (to promote the polymerization), followed by 20 min at 250 °C (to improve the adhesion of the oxide), and finally calcined at 400 °C during 10 min. This deposition/calcination procedure was repeated 10 times in order to increase the oxide layer thickness.

A digital multimeter HP 34410A (Agilent Technologies, United States) was used in the evaluation of the oxide electrodes vs. a saturated calomel electrode (SCE). Simultaneously, the pH of the solution was monitored with a commercial glass electrode using a Corning 320 model pH meter. The characterization of the pH electrodes was done adding aliquots of 0.1 and 1.0 mol L−1 HCl solutions to a tris(hydroxymethyl)amino-methane (Tris) 0.1 mol L−1 solution. Tris allows the study of a wide pH range using a background electrolyte with no interfering alkaline cations. The effects of the interfering ions Li+, Na+, and K+ were evaluated using titration curves. The fixed interference method was used to estimate the selectivity coefficients [48]. This method is recommended when the electrode exhibits a Nernstian response to both principal and interfering ions [48].

<table>
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<th>Table 1 – PPTIROF electrodes compositions studied in this work</th>
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<td>IrOx–TiO2 (%)</td>
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Also, acid-base titrations were performed by adding sodium hydroxide to a phosphoric acid solution in order to observe the metal oxide pH electrode performance, which was compared to a commercial glass electrode. The phosphoric acid titration curves present two discernible inflections referring to two H+ dissociation constants (pK1 = 2.16 and pK2 = 7.21).

3. Results and discussion

Firstly, the electrode containing only iridium was evaluated in the titration of a Tris buffer solution. The tests showed that the electrode has average super-Nernstian sensitivity, presented in Table 2, in a pH range from 1 to 13. This super-Nernstian behavior is quite different from the usually reported for IrOx electrodes prepared by thermal treatment [28,29], which normally produces anhydrous iridium oxides – “dry films” – with Nernstian behavior. On the other hand, hydrated iridium oxide films [49,50] are found in electrodes prepared by electrochemical oxidation, usually showing a super-Nernstian behavior ranging from 61 to 83 mV pH−1 at room temperature [50]. The super-Nernstian response could be related to the mechanism of one transferred electron per 1.5 H+ ion [51]. Dry iridium oxide films supported on titanium with unexpected super-Nernstian behavior were also found [11]. In fact, there is evidence that some of the outer oxyxation species at the thermally prepared oxide–solution interface are both hydrated and acidic in character [11,52]. The usual Nernstian response is determined by the anhydrous material, though the potential values are probably mixed potentials, resulting from the contributions of the hydrous and anhydrous phases. This could be accepted assuming that the charge capacity of the hydrous species, at the partially hydrated surface layer, is quite small and is in contact with a much thicker, inner, anhydrous film [11]. On the other hand, this super-Nernstian behavior could also be related to the oxidation state of the oxide Io2O–TiO2film. O’Hare et al. found evidence showing that thermal iridium oxide films are composed of complex mixtures of different oxidation states [52]. They also found in the oxide voltammogram the characteristic peak attributed to the Ir(III)/Ir(IV) transition obtained for AIROF electrodes, which is only apparent after at least 2 days soaking in deionized water [52]. It has been accepted, for AIROF electrodes, that differences in fabrication conditions lead to different oxidation states and extent of hydration [49], bearing in mind that the higher the oxidation state is, the higher the slope [53].

Following, a reduction of the iridium content in the composition of the oxide film was carried out with the substitution of iridium by titanium to form the IrOx–TiO2 oxide binary system. Thus, new compositions were prepared and tested, aiming at getting electrodes with better, or at least, the same electroanalytical properties of the sensor containing only iridium. Table 1 shows the tested compositions of the binary system. The electrode IrO2–TiO2 70–30 mol% presented Nernstian sensitivity, observed in Table 2, within the same linear pH range from 1 to 13. The introduction of titanium in the oxide composition improved the electroanalytical properties of the sensor, at least with regard to sensitivity, presenting ideal responses. Other two compositions were tested and the results are presented in Table 2. One can observe that a reduction of the Ir content from 70 to 20 mol% does not affect the titration curve slope of the prepared electrodes, since there is no significant difference between its values by performing a t-test with a 95% confidence level. In order to clarify the importance of the presence of a minimum iridium content in the binary system to achieve better pH responses and to show the very sub-Nernstian behavior of the titanium oxides, a new electrode was prepared containing only titanium (pure TiO2/Ti system). This electrode presented a narrow linear pH range from 2 to 6 and a slope of 25 mV pH−1. The values of standard deviation denote average errors around 3.5% and are below the 6.2 mV dec−1 reported by Kinlen et al. [24] for thermally oxidized iridium electrodes, although the proposed preparation method is completely manual. This good reproducibility of the electrodes is also demonstrated by the standard deviation presented in the variation of E′′, which is lower than reported by Hitchman and Ramanathan [54], who observed that the variation of this parameter was greater than 100 mV for a batch of thermally prepared IrOx electrodes. The value presented for the composition IrO2 100 mol% in Table 2 is superior to that reported for the standard E° (926 mV vs. SHE) [49]. The data were calculated assuming that saturated the calomel reference electrode potential is 241.2 mV vs. SHE at 25°C. However, similar values had been found by Hitchman and Ramanathan [54] for thermally prepared electrodes. The addition of titanium to the mixture decreased the value of E′′ to around 850 mV and did not vary with the subsequent reduction of the amount of iridium to 20 mol%, since there is no significant difference between the values of each composition by performing a t-test with a 95% confidence level. This value is close to the one presented for the pure TiO2/Ti electrode (811 mV vs. SHE) [46]. Kinlen et al. [24] obtained similar results for iridium oxide films thermally deposited on a titanium substrate. The electrode surface properties such as potential, charge or catalytic properties are determined by the amount of active material on the surface. De Paoli and Trasatti [55] observed a constant E′′ for electrodes containing at least 4% Ir on the system IrO2–SnO2 and demonstrated differences between surface composition and nominal composition by voltammetric and Auger electron spectroscopy (AES) data. Thus, it could be possible that E′′ does not change and the electrode with mixed oxides behaves as a pure electrode considering the iridium concentration at the electrode surface higher than the nominal concentration [55]. All electrodes also presented the same linear pH range from 1 to 13 when used in a titration of a Tris buffer solution. In compar-

<table>
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<th>Table 2 – Electroanalytical characterization of the PPTIROF pH electrodes related to their composition (n = 6)</th>
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<td>IrOx–TiO2 (%)</td>
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a The data was calculated by assuming that saturated calomel reference electrode potential is 241.2 mV vs. SHE at 25°C.
ison to the RuO₂–TiO₂ electrode [37], the iridium electrodes presented better sensitivity, similar precisions, and a wider linear working range.

Since the reduction of the iridium content down to 20 mol% did not change significantly the sensitivity or the parameter $E^\prime$, other parameters were investigated for each electrode such as the selectivity and the response time. The selectivity was evaluated by the fixed interference method from the most common interfering cations as Na⁺, Li⁺ and K⁺. Redox interference is also known to be a problem for metal oxide electrodes. Unlike glass electrodes, metal oxide electrodes usually undergo redox interference due to the fact that metal oxides are mixed conductors and both electrons and ions may determine the potential. Thus, a relevant redox system, such as ascorbic, was tested in the present work to evaluate the redox interference.

Table 3 shows the selectivity coefficients ($K_{H,M}$) that were obtained for the metallic cations related to each studied composition. As one can see, K⁺ is the most interfering cation in the PPTIROF electrodes response. It can also be seen that there are no significant differences between the coefficients obtained for Na⁺ and Li⁺ for all compositions. However, the composition IrO₂–TiO₂ 20–80 mol% suffered great interference from the K⁺ ion, also causing a reduction of the linear pH work range for 4–11 (Fig. 1). Thus, the composition IrO₂–TiO₂ 30–70 mol% was chosen as the best electrode formulation. Quan et al. [56] found that the content of iridium oxide in a PVC composite electrode affected the pH dependence of the electrode, presenting sub-Nernstian responses with iridium content below 23 wt.%. The redox interference from the strongly reducing species ascorbate was evaluated after the electrode conditioning in a 0.1 mol L⁻¹ ascorbic acid solution. The electrodes suffered a strong influence from ascorbic acid, since the sensitivity decreased drastically to approximately 10 mV dec⁻¹. Fig. 2 shows a titration of a 0.1 mol L⁻¹ ascorbic acid solution with a 0.1 mol L⁻¹ NaOH solution using the electrode with composition IrO₂–TiO₂ 30–70 mol%. One can observe that the electrode response did not follow the pH variation, but clearly followed the composition of the redox systems present in the oxide film, showing the titration of two redox systems during the experiment, one of them having equivalence point around 60 mV (or pH 4) and the other one with equivalence point at approximately 110 mV (or pH 7). Detailed investigation on redox interference to minimize the effect of reducing agent is in progress.

The data comparing the response of the iridium based electrodes with a glass electrode are shown in Fig. 3. Slowly acid–base titrations were tested by adding sodium hydroxide to a phosphoric acid solution. The phosphoric acid titration curves present two inflections referring to two H⁺ dissociation constants (pK₁ = 2.16 and pK₂ = 7.21). The curves were very similar to those obtained with the commercial glass electrode in the pH range studied. The response of the electrodes stabilizes in a few seconds. In this case, the difference between the responses is smaller than 3%.

A typical dynamic response curve is presented in Fig. 4. The response time corresponding to the 95% change ($t_{95}$) of the potential span after a pH change [48] was evaluated. The electrode with composition IrO₂–TiO₂ 30–70 mol% presented a $t_{95}$ of 120 s for a pH change from 4 up to 12. This figure also presents the response time variation in the course of a titration in acid and base media. The average response time was about 10 s for a step change in the acidic region, whereas, in the basic region, the average response time was about 5 s. Reported data on response time usually range from a few seconds to a few minutes. Our data are in close agreement with the response times reported in the literature [49], which range from 5 to 15 s for IrO₂-coated wire pH electrodes.

![Potassium interference on the analytical response of the electrode with composition IrO₂–TiO₂ 20–80 mol%](image1)

![Redox interference presented by a titration of an ascorbic acid solution with a PPTIROF pH electrode (IrO₂–TiO₂ 30–70 mol%).](image2)

| Table 3 – Selectivity coefficients $K_{H,M}$, M = Li⁺, Na⁺ or K⁺ (n = 3) |
|-----------------|-----------------|-----------------|-----------------|
| IrO₂–TiO₂ (%)   | Li⁺             | Na⁺             | K⁺              |
| 100–0           | $-11.1 \pm 1.1$ | $-11.8 \pm 0.28$ | $-9.66 \pm 0.73$ |
| 70–30           | $-10.1 \pm 0.50$ | $-10.7 \pm 0.23$ | $-9.86 \pm 0.45$ |
| 30–70           | $-10.5 \pm 0.74$ | $-11.3 \pm 0.74$ | $-9.76 \pm 0.14$ |
| 20–80           | $-10.2 \pm 0.27$ | $-11.0 \pm 0.12$ | $-5.32 \pm 0.01$ |
4. Conclusions

This paper has described a new fabrication methodology for low-cost IrO$_2$-based pH electrodes using the polymeric precursor method and a low-cost substrate. In this work, we investigated gradual substitution of the iridium in the oxide film by titanium forming a binary system IrO$_x$–TiO$_2$ (PPTIROF) deposited over a pre-treated titanium plate. The best composition found was 30–70 mol%, which gave a Nernstian response over a wide pH range, fast response and good reproducibility, using a completely manual method. The electrode is not susceptible to the action of interfering ions such as Li$^+$, Na$^+$ and K$^+$. However, it suffers influence by strongly reducing agents such as ascorbic acid. Due to their low-cost fabrication characteristic, with excellent analytical properties, the proposed electrode shows great potential for pH sensing.

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