A Solid Fe$_2$O$_3$ Based Carbon-Epoxy Electrode For Potentiometric Measurements of pH

M.F.S. Teixeira[*], L.A. Ramos, E.A. Neves and E.T.G. Cavalheiro

Departamento de Química, Centro de Ciências Exatas e de Tecnologia, Universidade Federal de São Carlos, Caixa Postal 676, CEP 13.560-970 - São Carlos, SP, Brazil

Abstract

A solid of Fe$_2$O$_3$ based carbon-epoxy composite electrode was investigated for use as a potentiometric pH sensor. The electrode was constructed with a mixture of sulfated iron(III) oxide, carbon power and epoxy resin that was deposited directly onto a glass tube. The effect of composition (Fe$_2$O$_3$, carbon and epoxy resin) on the electrode response and its calibration curve (mV/pH) were investigated. The analytical behaviour of the electrode in acid-base titrations was compared with that of a glass electrode. A linear response from pH 1.7 to 12.2 with a slope of -39.7 $\pm$ 0.6 mV/pH (at 25 $^{\circ}$C) was observed.

Keywords: potentiometric pH sensor, Fe$_2$O$_3$, carbon-epoxy composite electrode.

Introduction

The use of the glass membrane electrode to find the hydrogenionic activity in aqueous solutions, as pH, consists in one of the most frequent experimental determinations in several areas of interest, as for example chemistry, biological sciences and environment. The glass electrode responds in a wide pH interval. However in extreme acid and basic conditions of the pH scale, great deviations of the nernstian behaviour are observed. In the solutions of high alkalinity, the H$_3$O$^+$ ions in the gel layer of the glass electrode can be partially or totally substituted by other cations, mainly Na$^+$ and K$^+$, leading the electrode to respond to those metal cations (alkaline error). On the other hand, in high acid concentrations the gel layer of the glass electrode suffers a decrease in adsorbed

---

[*] Corresponding author. E-mail address: funcao@dq.ufscar.br

water molecules that affects the hydrogenionic activity on its surface, responsible for the acidic error [1].

The development of alternative electrodes for pH measurement presents a considerable interest in the sense of eliminating these limitations presented by the glass electrode with the possibility of its miniaturization by improvement of the mechanical resistance. In addition to glass electrodes, metal-metal oxide electrodes have been used as acid-base indicator electrodes. Of those, the most frequently used are the antimony [2], niobium [3], copper [4], tantalum [5], stainless steel [6], iridium [7] and tungsten [8] electrodes. The feasibility of electrodeposited metal-oxides in a matrix of graphite [9,10], platinum [11,12] and other materials [13,17] was studied as potentiometric electrodes for H_3O^+. These electrodes are based in reversible redox systems such as MnO_2/Mn^{2+}, CrO_3/Cr^{3+}, PbO_2/Pb^{2+} with pH dependence of the redox equilibrium, but very sensitive to reducing agents.

The applications of Ta_2O_5, ZrO_2, Al_2O_3 and Si_3N_4 films produced on SiO_2-Si substrates as pH-sensitive membranes for ion-selective field-effect transistors (ISEFET) have also been described in the literature [18-24]. The formation of a thick metal-oxide membrane was prepared by electron gun evaporation of the metal (Ta, Zr or Al), followed by its oxidation at a high temperature in dry O_2.

Single crystals of $Li_{0.27}V_2O_{4.95}$, $Na_{0.32}V_2O_{4.95}$, $K_{0.20}V_2O_{4.95}$, $Ag_{0.33}V_2O_{4.90}$ and $Cu_{0.33}V_2O_{4.90}$, were used as sensors for measuring pH in the range 1 to 6 in the presence of large concentrations of fluoride [25]. The disadvantages of these electrodes are the low selectivity to H^+ in the presence of Li^+, Na^+, Ag^+ and Cu^{2+} ions.

Our group has developed modified carbon-epoxy electrodes for the potentiometric determination of acids and bases [26-29]. Those sensors showed a good linear response over a wide pH range with satisfactory results in the end-point detection in potentiometric titrations and in the miniaturization for flow injection analysis.

Solid acids have been investigated and used as catalysts or support in the petrochemical and several chemical industries. The iron oxide exhibits acid behaviour when activated with small amounts of sulphate. Such property originated from the chemical modifications of the surface of the oxide with sulphate groups presents the effect of electronic induction that increases the Lewis acidity of the metal cation (Fig. 1) [30].

In the present work the construction of a potentiometric pH sensor is described on the basis of using a solid matrix electrode consisting of Fe_2O_3 carbon-epoxy. It has been found very convenient for acid-base titrations. The electrode was constructed with a

mixture of iron(III) oxide sulphated, carbon power and epoxy resin that was deposited directly onto a glass tube. The effect of composition (Fe_2O_3, carbon and epoxy resin) on the electrode response and its calibration curve (mV/pH) were investigated. In addition, the proposed electrode has been successfully used in the determination of end-points in potentiometric acid-base titrations.
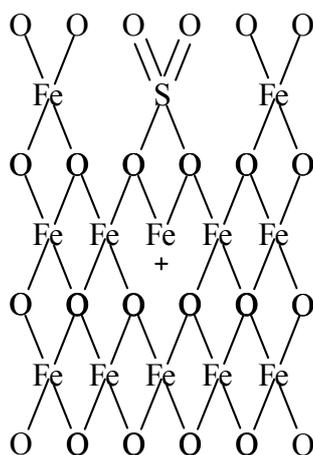
Figure 1. Proposed structure of the sulfated iron(III) oxide [30].

Experimental

Reagents and solutions

All the solutions were prepared with deionized water. Chemicals of analytical-reagent grade were used without further purification, unless stated otherwise. The solutions used in the acid-base titrations were 0.1 mol L^{-1}: phosphoric acid, hydrochloric acid, acetic acid, sodium hydroxide and ammonia (NH_3 solution). The ionic strength of the solutions was adjusted to 0.50 mol L^{-1} with KCl. All solutions were previously standardized.

Epoxy resin, pure carbon powder (Carbono Lorena), iron(III) chloride (Merck), ammonium sulfate (Merck) and a glass tube were used in the electrode construction.

Preparation of the sulfated iron(III) oxide

The method reported by literature [30,31] for the preparation of Fe_2O_3 sulphated was adopted. Initially, 5 g of $FeCl_3.6H_2O$ were treated with a 1.0 mol L^{-1} ammonia solution. The precipitate obtained was filtered in a 10-15 μ (medium porosity) sintered glass Gooch filter, washed several times with distilled water and dried at 130 ^{o}C for 4 hours in order to obtain the iron oxide. In the preparation of the Fe_2O_3 sulfated, the iron oxide

powder was mixed with 100 mL of ammonium sulphate 1.0×10^{-2} mol L^{-1} for 1 hour and dried in an oven at 90 $^{\circ}$C. Soon after, the mixture was treated at 600 $^{\circ}$C for 4 hours, under air atmosphere, for total elimination of ammonia. The percentage of sulfated Fe_2O_3 was approximately 4.5 % in sulphate mass in the final product.

Construction of the solid electrode Fe₂O₃ based carbon-epoxy conductor

The active composite material used in this electrode was prepared by mixing iron oxide sulfated, carbon powder and epoxy resin (a mixture of resin and catalyst in a 1:0.2 weight proportion) in the following percentage compositions (m/m): a) 0 % Fe_2O_3, 50 % carbon and 50 % epoxy resin; b) 20 % Fe_2O_3, 30 % carbon and 50 % epoxy resin; c) 25 % Fe_2O_3, 25 % carbon and 50 % epoxy resin; d) 30 % Fe_2O_3, 20 % carbon and 50 % epoxy resin; e) 35 % Fe_2O_3, 15 % carbon and 50 % epoxy resin. The different Fe_2O_3 carbon-epoxy composites thus obtained were inserted in glass tubes (external diameter 10 mm, internal diameter 8mm and length 13 cm) so as to be 10 mm high. The other end of the electrode was connected to a coaxial cable (which prevents external noise) and left to cure for 24 hour. The electrode surface was activated with a simple polish with a 600 sandpaper before being used. The final electrode assembly is presented in Fig. 2.
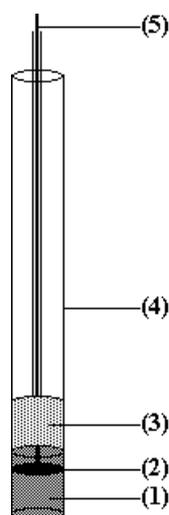
Figure 2. Schematic illustration of the electrode: (1) Different Fe_2O_3 carbon-epoxy composites; (2) copper disc; (3) sticking tape; (4) glass tube (external diameter 10 mm, internal diameter 8 mm and length 130 mm); (5) coaxial cable wire length 150 mm and diameter 2 mm.

Apparatus

All potentiometric measurements were carried out at 25 ± 0.2 °C in a thermostated glass cell with the electrode of Fe_2O_3 based carbon-epoxy and a R684 model Analion Ag/AgCl double junction reference electrode (Brazil), both connected to an EA940 model Orion pH/ion meter (USA) with ± 0.1 mV precision.

All pH measurements were made with the same pHmeter and a 10/402/3092 model Ingold glass membrane electrode (USA), previously calibrated. Calibration curves were obtained by addition of acid and/or base using an E274 model Metrohm microburette, in the same ionic strength. In the response time, stability of electrode and life time studies, the signals were recorded on a two-channel strip-chart recorder (Cole Parmer, model 12020000-USA).

Results and Discussion

Several parameters were investigated in order to evaluate the performance of the Fe_2O_3 carbon-epoxy electrode in terms of composition, calibration curve, slope (mV/pH), precision and end-point potentiometric acid-base titrations.

Effect of the electrode composition

The effect of electrode composition on the electrode response (mV *vs*. pH) was initially evaluated in triplicate (see Fig. 3). For these determinations, titrations of a 1.1×10^{-1} mol L^{-1} H_3PO_4 with a 1.1×10^{-1} mol L^{-1} NaOH solution using a glass electrode (pH measurements) and the Fe_2O_3 sensor (mV measurements) were carried out. The following electrode responses in mV/pH for each % Fe_2O_3 content were observed for a 1.1 - 12.7 pH range: 20 %, -26.5; 25 %, -33.1; 30 %, -39.7; 35 %, -36.4. As can be seen, the best pH-potential response was obtained with an electrode composition of 30 % (m/m) Fe_2O_3 plus 20 % graphite with a slope of -39.7 mV/pH unities with a correlation coefficient r = 0.9998. The slope lower than 59 mV/pH (predicted by the Nernst equation) for n=1, was also found at other metal oxide/aqueous electrolyte interfaces such as SiO_2, Al_2O_3 and ZnO. The potentiometric response of those oxides depends on the interfacial equilibrium (electrical double layer) and the Nernst equation is approximately obeyed provided the difference in the p*K* values (the surface dissociation constants) is less than about 4 [32].
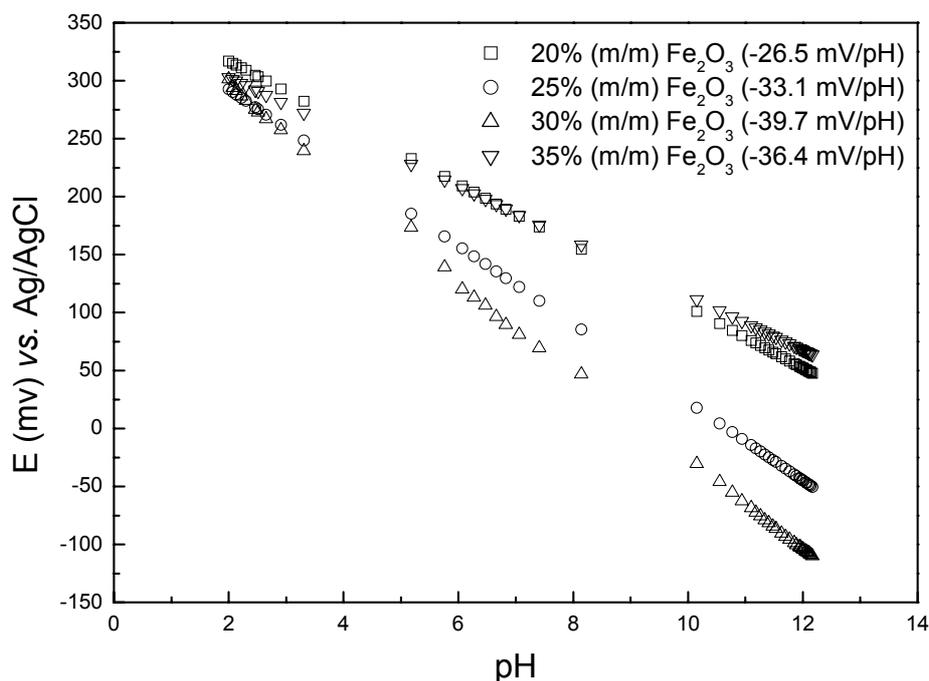
Figure 3. pH dependence of the equilibrium potentials (at 25 ^{o}C) of Fe_2O_3 based graphite-epoxy electrodes with different compositions. Titration of a 0.1 mol L^{-1} H_3PO_4 solution with a 0.1 mol L^{-1} NaOH solution.

Some precarious pH responses for the electrode without iron oxide are possible due to the presence of traces of carboxylic acids, quinones or phenolic groups in the carbon powder at the electrode surface [33]. However, an electrode composition as low as a 15 % (m/m) in Fe_2O_3 causes a remarkable improvement in the stability of the potentiometric response to pH, certainly due to its affinity to hydrogen ions. At Fe_2O_3 content higher than 35 % (m/m), the slope of the electrode response decreases due to the increase of the electric resistance caused by the lower graphite content, since the iron oxide is a bad-conducting material. This behaviour is in agreement with that of electrodes containing silica gel or metal oxides [26,27]. When a non sulfated iron oxide is used in the preparation of the electrode the maximum amount of the material that can be used was below 30 %. This fact is probably due to the higher acidity of the iron sulfated oxide which, according to Lee and Park [30], is caused by the formation of a complex surface containing sulfur with a covalent double bond S=O and its electronic inductive effect that improves the Lewis acid character of the metal cation.

Fig. 4 shows the effect of the electrode composition in the potentiometric titrations response. Sharper jumps in the phosphoric acid - sodium hydroxide system are observed for 30 % (m/m) of Fe_2O_3, in agreement with the slopes determined in Fig. 3.
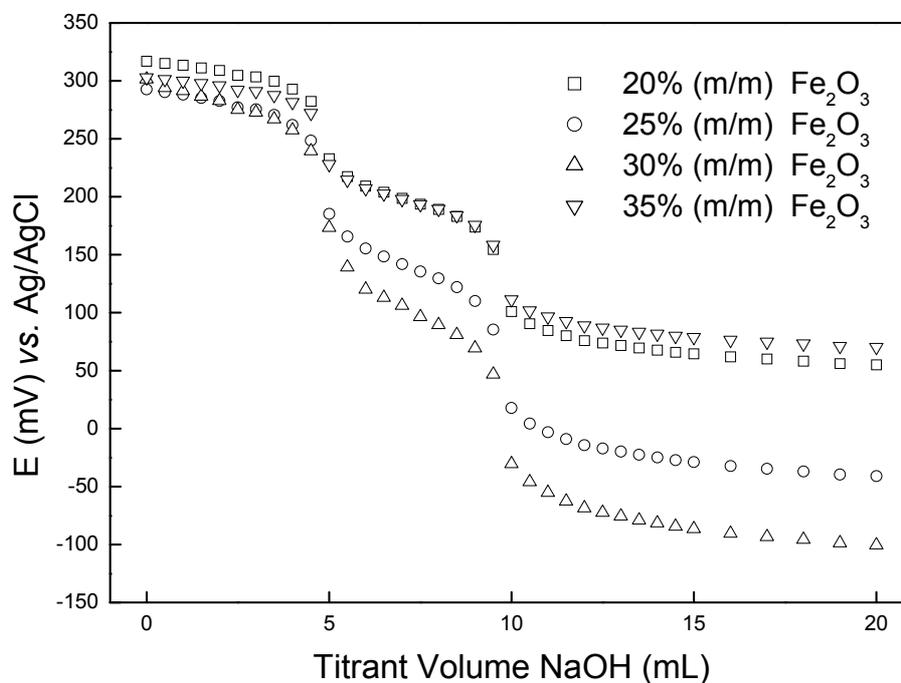
Figure 4. Effect of the electrode composition on the potentiometric response of the Fe_2O_3 graphite-epoxy electrode.

The potentiometric response of the Fe_2O_3 carbon-epoxy electrode in aqueous solutions of different pH is determined by a charge transfer reaction at the Fe_2O_3 /aqueous solution interface. The mechanism by which the surface charge is established may be viewed qualitatively as a two-step process, which is the surface hydration followed by dissociation of the surface hydroxide [34]. This mechanism may be represented schematically as shown in Fig. 5. The surface reactions involved in the establishment of a surface charge may be represented formally by the following equations:

$$Fe(OH)_2^+\text{ (surface)} + 2H_2O_\text{ (l)} \rightleftarrows Fe(OH)_3\text{ (surface)} + H_3O^+\text{ (aq)} \qquad (1)$$

$$Fe(OH)_3\text{ (surface)} \rightleftarrows FeO_2^-\text{ (surface)} + H_3O^+\text{ (aq)} \qquad (2)$$
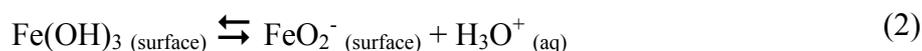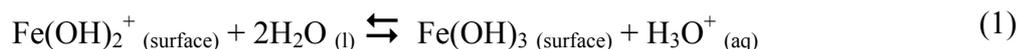
where $Fe(OH)_3$ (surface) represents the uncharged surface site which by adsorbing a proton becomes positive $[Fe(OH)_2^+]$ or by desorbing a proton becomes negative.

$$\mathrm{-\!\!\overset{|}{\underset{|}{Fe}}OH_2^+} \quad \underset{+H^+}{\overset{-H^+}{\rightleftarrows}} \quad \mathrm{-\!\!\overset{|}{\underset{|}{Fe}}OH} \quad \underset{+H^+}{\overset{-H^+}{\rightleftarrows}} \quad \mathrm{-\!\!\overset{|}{\underset{|}{Fe}}O^-}$$

$$\xrightarrow{\hspace{3cm} \text{pH} \hspace{3cm}}$$
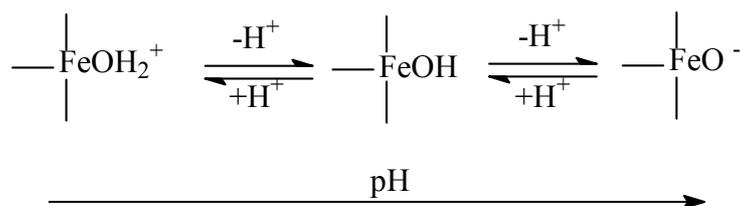
Figure 5. Schematic illustration of the surface hydration and dissociation of the surface hydroxide in the ferric oxide.

Potentiometric determination of acids and bases

A comparison of equivalent volumes obtained in acid-base titrations using glass and the Fe_2O_3 based graphite-epoxy electrode is presented in Table 1 for acetic, hydrochloric and phosphoric acids. Fig. 6 shows the potentiometric curves obtained in the titration of 5 mL of 1.3×10^{-1} mol L^{-1} acetic acid and 1.1×10^{-1} mol L^{-1} hydrochloric acid with a 1.1×10^{-2} mol L^{-1} NaOH and ammonia solution using the Fe_2O_3 based graphite-epoxy electrode in different compositions. As can be seen, the equivalent volumes obtained using the developed electrode are in good agreement with those equivalent volumes obtained with the glass electrode. The relative errors are in an acceptable range, suggesting that this electrode is viable and practical for use in detection of end-points in acid-base potentiometric titrations.

Table 1. Equivalent volumes (mL) obtained for acid-base titrations using the Fe_2O_3 based graphite-epoxy electrode compared to a glass electrode (average of 3 measurements).

Acid	Base	Fe_2O_3 electrode	Glass electrode	Relative error (%)
H_3CCOOH	NaOH	5.67 ± 0.03	5.67 ± 0.01	0
HCl	NaOH	5.28 ± 0.02	5.27 ± 0.01	+0.19
H_3PO_4	NaOH	4.76 ± 0.01	4.75 ± 0.01	+0.21
		9.71 ± 0.02	9.69 ± 0.01	+0.21
HCl	NH_3	5.28 ± 0.03	5.30 ± 0.01	-0.38

The effect of several species such as LiCl, NaCl, $MgCl_2$, $CaCl_2$, $NaNO_3$ and Na_2SO_4 in high concentration (0.50 mol L^{-1}) on the potentiometric response of the electrode was

also evaluated. The presence of all these cations and anions investigated did not cause any depletion in the potentiometric curves during acid-base titrations.

In order to evaluate the useful lifetime of the composite electrode, all the acid-base potentiometric titrations in this work were carried out along 8 months using the same electrode, without surface renovation. When a significant delay in the potentiometric response was observed, the electrode could be reactivated with a simple polishing of its surface using a thin emery paper. The electrode response of 15s was found on basis of a IUPAC recommendation [35]. This low response time can be attributed to the water absorption by oxide iron and or epoxy [36].
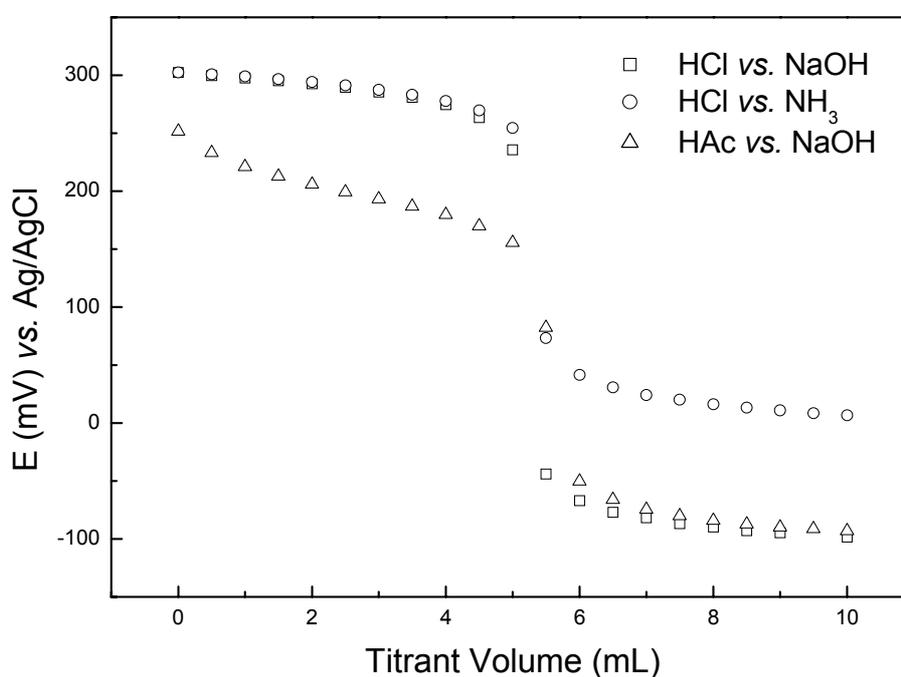
Figure 6. Acid-base potentiometric titrations using the magnesium silicate based graphite-epoxy electrode for aqueous solutions: 5 mL of 1.3×10^{-1} mol L^{-1} CH_3COOH (Δ), 1.2×10^{-1} mol L^{-1} HCl ($\square$) solutions with a 1.1×10^{-1} mol L^{-1} NaOH solution and 5 mL of 1.2×10^{-1} mol L^{-1} HCl (O) solutions with a 1.1×10^{-1} mol L^{-1} NH_3 solution.

Conclusions

This Fe_2O_3 electrode presented a linear response in the pH range from 1.7 to 12.2 with a slope of -39.7 mV/pH, a low-cost of fabrication, a long life time (8 months) and usefulness in the acid-base titrations.

Acknowledgements:

References

1. R.G. Bates, *Determination of pH, Theory and Practice*, John Wiley, New York, 1964.

2. G. Edwall, *Electrochim. Acta* 24 (1979) 595.

3. M.A.B. Gomes, L.O.S. Bulhões, *J. Electroanal. Chem*. 165 (1984) 289.

4. A.S. Fouda, *J. Electroanal. Chem*. 110 (1980) 357.

5. S. Shahine, M.S. El-Basiouny, *J. Electroanal. Chem*. 108 (1980) 271.

6. K. Nomura, Y. Ujihira, *Anal. Chem*. 60 (1988) 2564.

7. M.L. Hitchman, S. Ramanathan, *Analyst* 113 (1988) 35.

8. M.I.G. Leles, M.D. Capelato, *Química Nova* 14 (1991) 38.

9. M.D. Capelato, N.M. Cassiano, *Química Nova* 21 (1998) 494.

10. C. Efron, M. Ariel, *Anal. Chim. Acta* 108 (1979) 395.

11. H.C. Kaehelr, A. Zahilout, F. Brito, *An. Quim*. 66 (1970) 221.

12. O. Fatibello-Filho, E.F.A. Neves, W.M. Carvalho, M.D. Capelato, L.O.S. Bulhões, *IV Simp. Bras. Eletroquim. Eletroanal*. (1984) 463.

13. C.N. Wang, P.J. Kinlen, D.A. Schoeller, C.O. Huber, *Anal. Chem*. 44 (1972) 1152.

14. L.W. Niedrach, W.H. Stoddard, *J. Electrochem. Soc*. 131 (1984) 1017.

15. K. Namura, Y. Ugihia, *Anal. Sci*. 3 (1987) 125.

16. S. Glab, A. Hulanicki, S. Edwall, F. Ingman, Crit. Rev. *Anal. Chem*. 21 (1989) 29.

17. B. Centeno, M.L. Tascón, M.D. Várquez, P.S. Batanero, *Electrochim. Acta* 36 (1991) 27.

18. P. Gimmel, K.D. Schierbaum, W. Gopel, H.H. Van der Vlekkert, N.F. Rooij, *Sensors and Actuators B* 1 (1990) 345.

19. P.V. Bobrov, Y.A. Tarantov, S. Krause, W. Moritz, *Sensors and Actuators B* 3 (1991) 75.

20. Y.G. Vlasov, A.V. Bratov, *Sensors and Actuators B* 10 (1992) 1.

21. Y.G. Vlasov, A.V. Bratov, M.P. Sidorova, Y.A. Tarantov, *Sensors and Actuators B* 1 (1990) 357.

22. H.H. van der Vlekkert, N.F. Rooij, A. van der Berg, A. Grisel, *Sensors and Actuators B* 1 (1990) 395.

23. M. Klein, M. Kuisl, *VDI-Ber*. 509 (1984) 275.

24. Y.G. Vlasov, Y.A. Tarantov, V.P. Letavin, *Zhurn. Prikl. Khim*. 53 (1980) 2345.

25. V.L. Volkov, L.I. Manakova*, Zh. Anal. Khim*. 39 (1984) 2035.

26. M.F.S. Teixeira, L.A. Ramos, E.A. Neves, O. Fatibello-Filho, *Fresenius J. Anal. Chem*. 367 (2000) 86.

27. M.F.S. Teixeira, L.A. Ramos, N.M. Cassiano, O. Fatibello-Filho, N. Bocchi, *J. Braz. Chem. Soc*. 11 (2000) 27.

28. M.F.S. Teixeira, F.C. Moraes, O. Fatibello-Filho, L.C. Ferracin, R.C. Rocha-Filho, N. Bocchi, *Sensors and Actuators B* 56 (1999) 169.

29. M.F.S. Teixeira, L.A. Ramos, O. Fatibello-Filho, E.T.G. Cavalheiro, *Fresenius J. Anal. Chem*. 370 (2001) 383.

30. J.S. Lee, D.S. Park, *J. Catal*. 120 (1989) 46.

31. K. Arata, *Advances in Catalysis* 37 (1990) 177.

32. D.E. Yates, S. Levine, Healy, T.W., *J. Chem. Soc. Faraday Trans*. *I* 70 (1974) 1807.

33. K. Kinoshita, *Carbon: Electrochemical and Physicochemical Properties*, John Wiley, New York, 1988.p. 208.

34. G.A. Parks, P.L. Bruyn, *J. Phys. Chem*. 66 (1962) 967.

35. IUPAC Recommendations 1994, *Pure & Appl. Chem*. (1995) 2528.

36. ASM International Handbook Committee, Engineered Materials Handbook, Engineering Plastics, ASM international 2 (1988) 761.