

# A Solid Fe<sub>2</sub>O<sub>3</sub> Based Carbon–Epoxy Electrode for Potentiometric Measurements of pH<sup>1</sup>

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**Abstract**—A solid Fe<sub>2</sub>O<sub>3</sub> based carbon-epoxy composite electrode was investigated for use as a potentiometric pH sensor. The electrode was constructed using a mixture of sulfated iron(III) oxide, carbon power, and epoxy resin, which was deposited directly onto a glass tube. The effect of composition (Fe<sub>2</sub>O<sub>3</sub>, carbon and epoxy resin) on the electrode response and its calibration curve (mV/pH) were investigated. The analytical behavior 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°C) was observed.

The use of a glass membrane electrode to determine the hydrogen ion concentration in aqueous solutions is frequent chemistry, biological sciences, and environmental studies.

The glass electrode responds in a wide pH interval; however, in the acid and basic extremes of the pH scale, great deviations from the Nernstian behavior are observed. In the solutions of high alkalinity, the H<sub>3</sub>O<sup>+</sup> ions in the gel layer of the glass electrode can be partially or totally substituted by other cations, mainly Na<sup>+</sup> and K<sup>+</sup>, leading the electrode to respond to those metallic cations (alkaline error). On the other hand, in high acid concentrations, the gel layer cannot adsorb molecules of these acids increasing at the hydrogen ion activity on it. This activity increase causes a deviation of the theoretical value in the acidic media (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, besides 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] were studied as potentiometric electrodes for H<sub>3</sub>O<sup>+</sup>. These electrodes are based in reversible redox systems such as MnO<sub>2</sub>/Mn<sup>2+</sup>, Cr<sub>2</sub>O<sub>3</sub>/Cr<sup>3+</sup>, PbO<sub>2</sub>/Pb<sup>2+</sup> with pH dependence of the redox equilibrium.

The applications of Ta<sub>2</sub>O<sub>5</sub>, ZrO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and Si<sub>3</sub>N<sub>4</sub> films produced on SiO<sub>2</sub>–Si substrates as pH-sensitive membranes for ion-selective, field-effect transistors have also been described in the literature [18–24]. The formation of a thick metal-oxide membrane were prepared by electron gun evaporation of the metal (Ta, Zr, or Al), followed by its oxidation at a high temperature in dry O<sub>2</sub>.

Single crystals of Li<sub>0.27</sub>V<sub>2</sub>O<sub>4.95</sub>, Na<sub>0.32</sub>V<sub>2</sub>O<sub>4.95</sub>, K<sub>0.20</sub>V<sub>2</sub>O<sub>4.95</sub>, Ag<sub>0.33</sub>V<sub>2</sub>O<sub>4.90</sub>, and Cu<sub>0.33</sub>V<sub>2</sub>O<sub>4.95</sub> were used as sensors in solid-state pH sensitive electrodes for measuring pH in the range 1 to 6 in the presence of large concentrations of fluoride [25]. The disadvantages of these electrodes are their low selectivity to H<sup>+</sup> once these electrodes respond also to Li<sup>+</sup>, Na<sup>+</sup>, Ag<sup>+</sup>, and Cu<sup>2+</sup>.

In our group, we developed modified carbon-epoxy electrode 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 behavior when activated with small amounts of sulfate. Such property originated from the chemical modifications of the surface of the oxide with sulfate groups presents the effect of electronic induction that increases the Lewis acidity of the metallic cation (Fig. 1) [30].

In the present work, a construction of a solid Fe<sub>2</sub>O<sub>3</sub> based carbon-epoxy electrode is described for potentiometric pH detection in acid–base titrations. The electrode was constructed of a mixture of sulfated iron(III) oxide, carbon powder and epoxy resin that was depos-

<sup>1</sup>This article was submitted by the authors in English.

ited directly onto a glass tube. The effect of the composition (Fe<sub>2</sub>O<sub>3</sub>, 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.

### EXPERIMENTAL

**Reagents and solutions.** All the solutions were prepared using deionized water. Chemicals of an analytical-reagent grade were used without further purification, unless stated otherwise. The solutions used in the acid–base titrations were 0.1 mol/L: phosphoric acid, hydrochloric acid, acetic acid, sodium hydroxide, and ammonium hydroxide. The ionic strength of the solutions was adjusted to 0.50 mol/L with KCl. All solutions were previously standardized.

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

**Preparation of the sulfated iron(III) oxide.** The method reported in the literature [30, 31] for the preparation of sulfated Fe<sub>2</sub>O<sub>3</sub> was adopted. Initially, 5 g of FeCl<sub>3</sub> · 6H<sub>2</sub>O was treated with a solution of ammonium hydroxide 1.0 mol/L. The precipitate obtained was filtered in a 1–15 μm (medium porosity) sintered glass Gooch filter, washed several times with distilled water and dried at 130°C for 4 hours in order to obtain of the iron oxide. In the preparation of the sulfated Fe<sub>2</sub>O<sub>3</sub>, the iron oxide powder was mixed with 100 mL of ammonium sulfate 1.0 × 10<sup>-2</sup> mol/L for 1 hour and kept in an oven at 96°C until the dryness. Soon after, the mixture was roasted in a muffle furnace at 600°C for 4 hours, under air atmosphere, for the total elimination of the ammonium. The percentage of Fe<sub>2</sub>O<sub>3</sub> sulfated was of approximately 4.5% in sulfate mass in the final product.

**Construction of the solid electrode.** The active composites 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<sub>2</sub>O<sub>3</sub>, 50% carbon and 50% epoxy resin; (b) 20% Fe<sub>2</sub>O<sub>3</sub>, 30% carbon and 50% epoxy resin; (c) 25% Fe<sub>2</sub>O<sub>3</sub>, 25% carbon and 50% epoxy resin; (d) 30% Fe<sub>2</sub>O<sub>3</sub>, 20% carbon and 50% epoxy resin; (e) 35% Fe<sub>2</sub>O<sub>3</sub>, 15% carbon and 50% epoxy resin. The different Fe<sub>2</sub>O<sub>3</sub> carbon-epoxy composites thus obtained were inserted in a glass tubes (external diameter 10 mm, internal diameter 8 mm 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 hours. The electrode surface was activated by polishing with a 600 sandpaper before being used. The final electrode assembly is presented in Fig. 2.

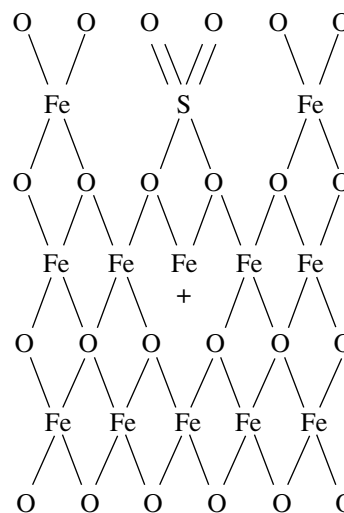


Fig. 1. Proposed structure from the sulfated iron(III) oxide.

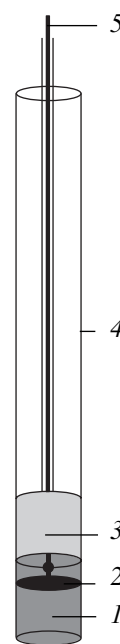
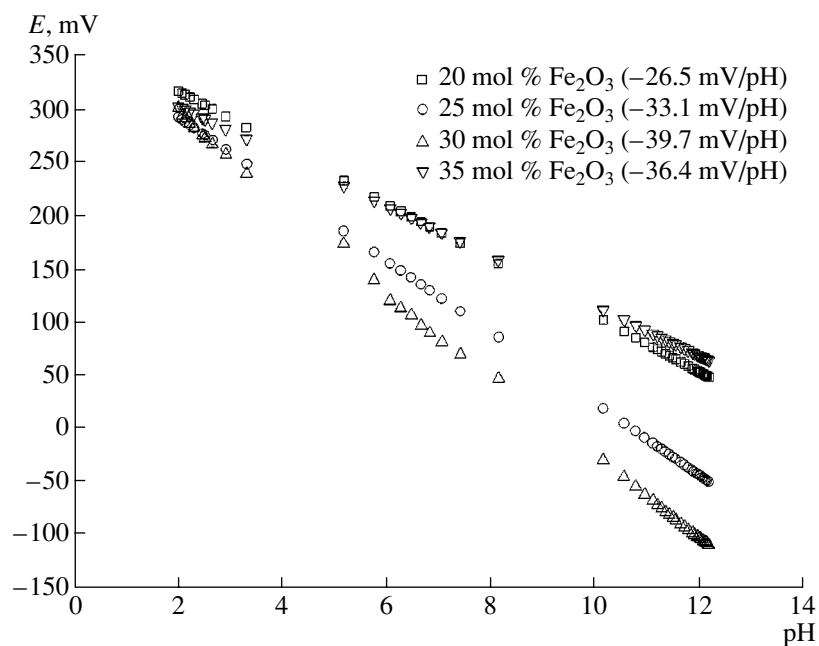


Fig. 2. Schematic illustration of electrode: (1) Different Fe<sub>2</sub>O<sub>3</sub> carbon-epoxy composites; (2) copper disc; (3) sticking tape; (4) glass tube (external diameter 10 mm, internal diameter 8 mm and length 130 mm); (5) coaxial cable wire 150 mm long and 2 mm in diameter.

**Apparatus.** All potentiometric measurements were carried out at 25 ± 0.2°C in a thermostated glass cell with the Fe<sub>2</sub>O<sub>3</sub> based carbon-epoxy electrode and a R684 model Analion Ag/AgCl double junction reference electrode (Brazil), either attached to an EA940 model Orion pH/ion meter (USA) with +0.1 mV precision.

All pH measurements were made with the same pH meter and a 10/402/3092 model Ingold glass membrane



**Fig. 3.** pH dependence of the equilibrium potentials (at 25°C) of Fe<sub>2</sub>O<sub>3</sub> based graphite-epoxy electrodes with different compositions. Titration of a 0.1 mol/L H<sub>3</sub>PO<sub>4</sub> solution with a 0.1 mol/L NaOH solution.

electrode (USA), previously calibrated. Calibration curves were obtained by the addition of acid and/or base of the same ionic strength using an E274 model Metrohm microburette. In the response time, stability of electrode and life time studies, the signals were recorded on a two-channel strip-chart recorder (Cole Farmer, model 12020000-USA).

## RESULTS AND DISCUSSION

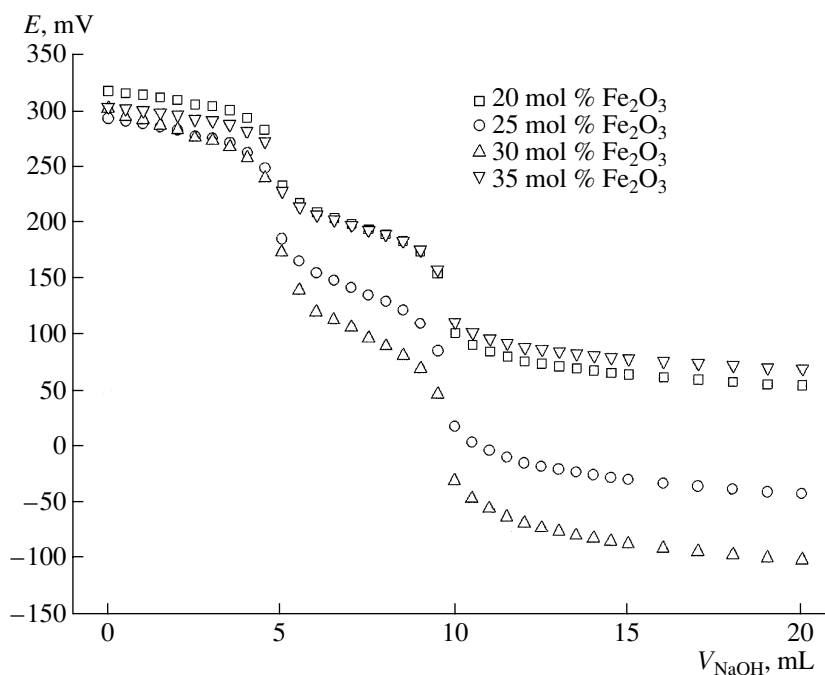
Several parameters were investigated in order to evaluate the performance of the Fe<sub>2</sub>O<sub>3</sub> carbon-epoxy electrode in terms of composition, calibration curve slope (mV/pH), reproducibility and end-point potentiometric acid-base titrations.

Equivalence volumes (mL) obtained for acid-base titrations using the Fe<sub>2</sub>O<sub>3</sub> based graphite-epoxy electrode compared to a glass electrode ( $n = 3$ ;  $P = 0.95$ )

Acid	Base	Fe <sub>2</sub> O <sub>3</sub> electrode	Glass electrode	Relative error (%)
CH <sub>3</sub> COOH	NaOH	5.67 ± 0.03	5.67 ± 0.01	0
HCl	NaOH	5.28 ± 0.02	5.27 ± 0.01	+0.19
H <sub>3</sub> PO <sub>4</sub>	NaOH	4.76 ± 0.01	4.75 ± 0.01	+0.21
		9.71 ± 0.02	9.69 ± 0.01	+0.21
HCl	NH <sub>3</sub>	5.28 ± 0.03	5.30 ± 0.01	+0.38

**Effect of the electrode composition.** The effect of electrode composition on the response of the pH electrode (mV/pH) was initially evaluated in triplicate (see Fig. 3). For these determinations, titrations of a  $1.1 \times 10^{-1}$  mol/L H<sub>3</sub>PO<sub>4</sub> with a  $1.1 \times 10^{-1}$  mol/L NaOH solution using a glass electrode (pH measurements) and the Fe<sub>2</sub>O<sub>3</sub> based carbon-epoxy indicator electrodes (mV measurements) were carried out. The following electrode responses in mV/pH for each % Fe<sub>2</sub>O<sub>3</sub> content were observed for a 1.1–12.7 pH range: 20%: -26.5; 25%: -33.1; 30%: -39.7 and 35%: -36.4. As can be seen, the best pH-potential response was obtained with an electrode composition of 30% (m/m) Fe<sub>2</sub>O<sub>3</sub> plus 20% graphite with the a slope of -39.7 mV/pH unities with a correlation coefficient of  $r = 0.9998$ . A 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<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, 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 pK values (the surface dissociation constants) is less than about 4 [32].

Some doubtful 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, the use of the electrode composition with only 15% (m/m) Fe<sub>2</sub>O<sub>3</sub> causes a remarked improvement in the stability of the potentiometric response to pH, certainly due to its affinity for hydrogen ions. At Fe<sub>2</sub>O<sub>3</sub>



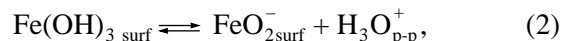
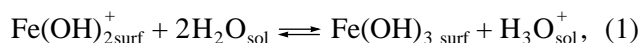
**Fig. 4.** Effect of the electrode composition on the potentiometric response of the Fe<sub>2</sub>O<sub>3</sub> graphite–epoxy electrode. Titration of a 0.1 mol/L H<sub>3</sub>PO<sub>4</sub> solution with a 0.1 mol/L NaOH solution.

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 behavior is similar with that of electrodes containing silica gel or metal oxides [26, 27]. When a nonsulfated iron oxide is used in the preparation of the electrode, the maximum amount of the material that can be used was lower than 30%. This fact is probably due to the higher acidity of the sulfated iron 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.

Figure 4 shows the effect of the electrode composition on the potentiometric titration response. Sharper jumps in the phosphoric acid: sodium hydroxide system are observed for 30% (m/m) of Fe<sub>2</sub>O<sub>3</sub>, in agreement with the slopes shown in Fig. 3.

The potentiometric response of the Fe<sub>2</sub>O<sub>3</sub> carbon–epoxy electrode in aqueous solutions of different pH is determined by a charge transfer reaction at the Fe<sub>2</sub>O<sub>3</sub>/aqueous solution interface. The mechanism by which the surface charge is established may be viewed qualitatively as a two-step process: 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

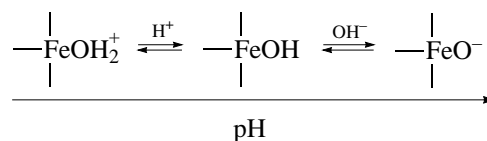
formally by the following equations:



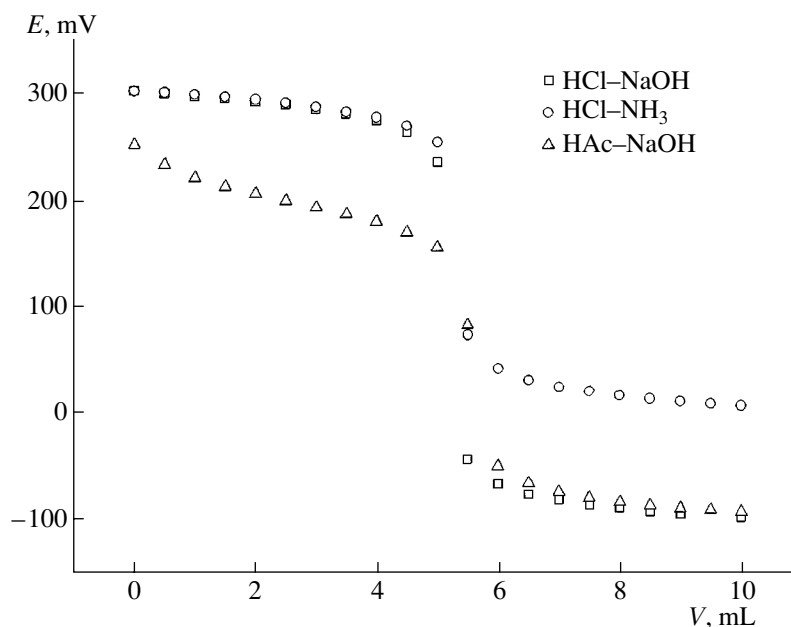
where Fe(OH)<sub>3</sub> (surface) represents the uncharged surface site which becomes positive by adsorbing a proton [Fe(OH)<sub>2</sub><sup>+</sup>] or becomes negative by desorbing a proton.

#### Potentiometric determination of acids and bases.

A comparison of equivalence volumes obtained in acid–base titrations using a glass and the Fe<sub>2</sub>O<sub>3</sub> 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<sup>-1</sup> mol/L acetic acid and 1.1 × 10<sup>-1</sup> mol/L hydrochloric acid with a 1.1 × 10<sup>-2</sup> mol/L NaOH and ammonium hydroxide solution using the Fe<sub>2</sub>O<sub>3</sub> based graphite–epoxy electrode of different compositions. As can be seen, the equivalence volumes obtained using the developed electrode are in good agreement with the



**Fig. 5.** Schematic illustration of the surface hydration and dissociation of the surface hydroxide in the ferric oxide.



**Fig. 6.** Acid–base potentiometric titrations using the magnesium silicate based graphite–epoxy electrode for aqueous solutions: 5 mL of  $1.3 \times 10^{-1}$  mol/L  $\text{CH}_3\text{COOH}$  ( $\Delta$ ),  $1.2 \times 10^{-1}$  mol/L HCl ( $\square$ ) solutions with a  $1.1 \times 10^{-1}$  mol/L NaOH solution and 5 mL of  $1.2 \times 10^{-1}$  mol/L HCl ( $\circ$ ) solutions with a  $1.1 \times 10^{-1}$  mol/L  $\text{NH}_3$  solution.

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.

The effect of several salts such as LiCl, NaCl,  $\text{MgCl}_2$ ,  $\text{CaCl}_2$ ,  $\text{NaNO}_3$ , and  $\text{Na}_2\text{SO}_4$  in high concentration, 0.50 mol/L, on the potentiometric response of the electrode was also evaluated. The presence of all the 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 for 8 months using the same electrode, without surface renewing. 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 15 s was found on basis of a IUPAC recommendation [35]. This low response time can be attributed to the water adsorption by iron oxide and or epoxy resin [36].

## CONCLUSION

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

## ACKNOWLEDGMENTS

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