Potentiometric behavior of graphite-epoxy electrochemical transducers towards anions, cations and pH in aqueous media

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In the present work, a study of the effect of anions, cations and pH in the potentiometric response of a graphite-epoxy composite is reported. The results obtained indicate a better response for anionic than for cationic ions, with those of greater magnitude being towards OH^- and H^+ respectively. It is possible to give an explication that is in agreement with the results obtained, for some behaviors in the response of chemical sensors and biosensors based on the study of this transducer; likewise some interesting direct and practical applications, are suggested and explored.

Keywords: Electrochemical transducers; graphite-epoxy- composites; potentiometry.

En el presente trabajo se reporta el estudio del efecto de aniones, cationes y pH, en la respuesta potenciométrica de un composite grafito-epoxi. Los resultados obtenidos indican mayor respuesta aniónica que catiónica, siendo las de mayor magnitud hacia OH^- y H^+ respectivamente. Conforme a los resultados obtenidos, es posible explicar algunos comportamientos en la respuesta de sensores químicos y biosensores basados en el transductor estudiado; asimismo se sugieren y exploran algunas aplicaciones directas y prácticas de interés.

Descriptores: Transductores electroquímicos; composites grafito-epoxi; potenciometría.

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1. Introduction

Although the electrochemical behavior of carbon electrodes has been widely described in the scientific literature [1,2], because of the new developments in materials science and the variety of materials used for their construction, these studies continue to be of scientific interest. Particularly for potentiometric response, it is well-known that these electrodes are sensitive to pH, anions and/or cations due to adsorption processes and ionic exchange governed by reactions of the functional superficial groups of carbon with the chemical species present in the aqueous solution [1-6]. The nature of the functional groups depends on the manufacture process of the electrode, as well as the chemical conditions (temperature, solvent, ionic strength, etc.). Thus, in the present work, the potentiometric behavior in shown of a graphite-epoxy transducer, widely used in the development of diverse chemical sensors and biosensors [7-9], is shown.

2. Experimental

The transducer was constructed as described previously [10,11], using an acrylic tube as body (length = 10 cm, inner diameter = 8.5 mm), which is glued to another acrylic tube (length = 2 cm, inner diameter = 4 mm). A shielded cable that is soldered to a copper disc (diameter = 8 mm) in is passed inside across the thinner tube, and the disc is placed on the internal acrylic tube leaving a space of 0.5 cm. A graphite-epoxy mixture is then deposited in the space created between the external acrylic tube and the copper disc. The weight proportion of graphite-epoxy is 50% graphite powder (Aldrich) and 50% resin:catalyst mixture. One hundred parts of resin (Araldyt HY956 Ciba Geigy) are mixed with 20 parts in mass of catalyst (REM 001 Ciba Geigy), previous to the graphite load. The composite is allowed to cure for 24 hours at 40°C, and once the material is hardened, it is polished to obtain a shining, flat surface.

The potentiometric calibration and titration curves were obtained by means of a PHM 250 (Radiometer-Copenhagen) potentiometer. All the potential measurements were made using a Ag/AgCl double junction reference electrode with NaCl to 10% w/w as external reference solution (E=SCE). All the reagents used were analytical grade. The solutions were prepared with deionized water.

3. Results and discussion

In order to study the effect of the anions on the electrode response, calibrations curves were done for Na^+ and K^+ salts. In both cases the graphite-epoxy electrode showed an anionic response close to the Nernstian behavior, from 1 to 3 pSalt, being more sensitive to OH^- (Fig. 1, Table I). According to

TABLE I. Potentiometric response of graphite-epoxy transducers towards different sodium and chloride salts in aqueous medium at room temperature.

Salt	m(mV/decade)	%RSD	Eo (mV)	%RSD	r^2	LRR(pSalt)
Sodium salts						
NaCl	51.3	0.5	12.7	18.6	0.9998	1-3
$NaNO_3$	53.6	0.7	155.6	2.4	0.9973	1-4
Na_2SO_4	38.6	1.8	234.6	3.4	0.9995	1-3
$NaClO_4$	53.7	1.0	150.8	2.0	0.9949	1-4
NaOH	68.4	5.0	1047.1	2.8	0.9949	1-5
Chloride salts						
HCl	36.1	8.8	104.8	13.5	0.9992	2-4
KCl	50.3	0.9	13.8	4.5	0.9999	1-3
NaCl	51.3	0.5	12.7	18.6	0.9998	1-3
LiCl	52.4	0.4	53.0	9.9	0.9993	1-3

%RSD= percentage of relative standard deviation m= average slope. Eo= intercept. r^2= linear correlation coefficient. LRR= linear response range. Statistic obtained from calibration curves of three different electrodes.

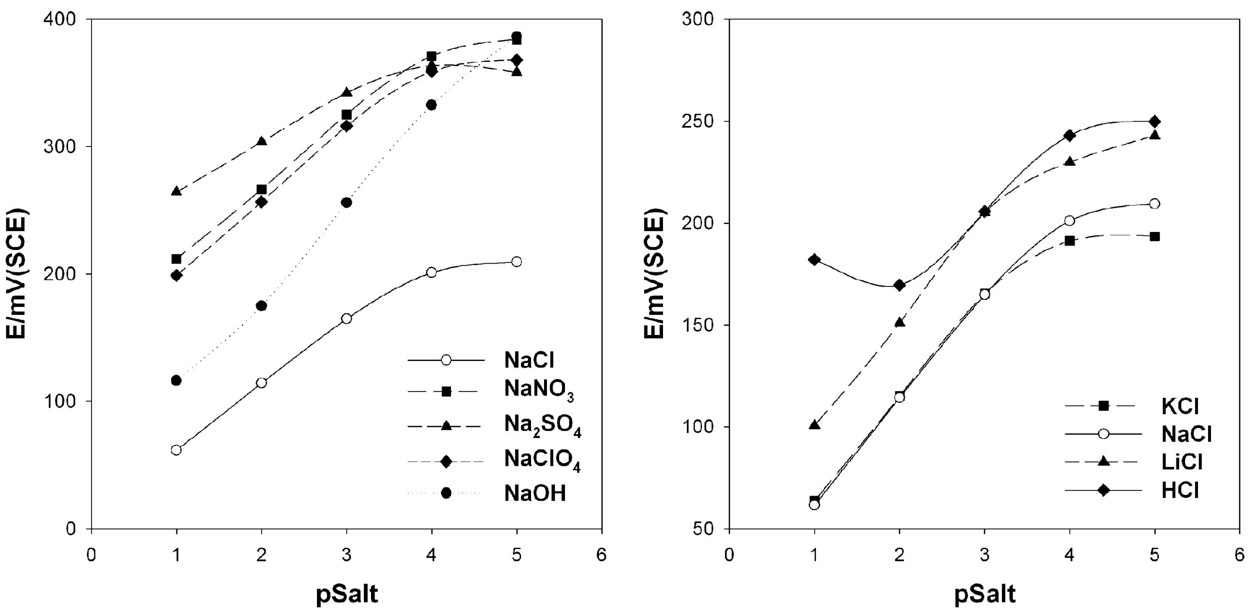

FIGURE 1. Potentiometric response of graphite-epoxy transducers towards sodium (left) and chloride salts (right).

these results, and considering the anionic response mechanisms proposed before [1,3], it is possible to suggest that the transducer response is owing to an adsorption process, that is related to an electroreduction of the adsorbed oxygen on the graphite surface in such way that an increase in the electrode potential takes place due to a change in the oxidation state (Table I).

On the other hand, the minimal response found towards Li^+, Na^+, K^+ and H^+ when chloride is the common counterion, confirms the anionic response shown by the electrode. Nevertheless, it is important to notice the lower slope value obtained with hydrochloric acid, a clearly distinguishable behavior that makes it possible to conclude that the transducer shows a greater sensitivity to protons than to other cations studied (Fig. 1, Table I). An analogous behavior in the cationic electrode response is obtained with other common anions (NO_3^-, SO_4^{2-}, ClO_4^- and OH^-). It is necessary to emphasize that the electrode response to strong acids was anionic in all cases.

The singular potentiometric behavior of the graphite-epoxy transducers was successfully applied as an indicator electrode in a potentiometric acid-base titration, obtaining equivalent results to those of a glass electrode for the end-point volume, though with a minor potential change (Fig. 2).

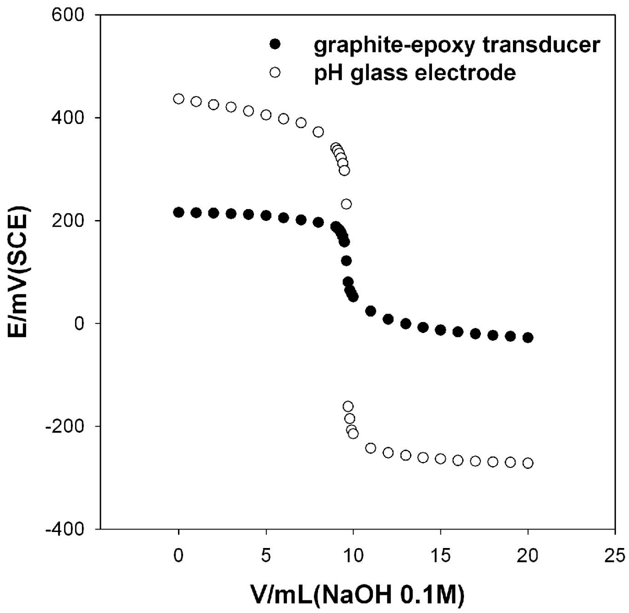

FIGURE 2. Potentiometric behavior of graphite-epoxy electrochemical transducers towards anions, cations and pH in aqueous media.

The potentiometric response characteristics of the transducer studied can also be useful for the development of potentiometric biosensors, based on the production or consumption of acid or base compounds, as a result of the interaction between the substrate and the recognition element, as in the case of the glucose biosensor (glucose oxidase) and the urea biosensor (urease).

4. Conclusions

The studies of graphite-epoxy transducers, have shown that this transducer has a different potentiometric behavior to those reported for carbon electrodes; however, the major sensitivity to hydroxide and hydronium ions with respect to other anions and cations, as well as the good response reproducibility, allow us to explore new applications of this device on the development of chemical sensors.

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