Modification of Antimony/Antimony Oxide pH-Sensor by a Polymer Coating

Fereydoon Gobal

Department of Chemistry, Sharif University of Technology, P.O. Box 11365-9516, TEHRAN, IRAN

An all solid state proton sensor based on potentiometric measurement was developed by coating a PVC film containing tri-n-dodecylamine as neutral carrier on an antimony/antimony oxide interface. The sensor exhibits an almost Nernstian response in the pH-range of 2-13 and the response is reasonably fast (around 3 minutes to achieve 90% of the full response). The sensor was stable in both acidic and basic media over periods of days. Impedance spectroscopy was employed to shed light on the nature of this complicated interface. Processes with different time constants and distinct sensitivities with pH and applied probing overpotentials were detected.

Antimony/antimony oxide system is known to act as a pH-sensor [1]. Although careful experimentation shows a Nernstian behaviour over the pH-range 1-10 [2], the antimony electrode is not perfectly reversible and its potential depends on the concentration of the dissolved oxygen, composition of solution, stirring, etc. So a number of modifications are elaborated [3]. However, polymeric membranes containing neutral carriers are, in principle, capable of generating a membrane potential sensitive to the pH of the solutions in contact with it [4]. The systems require reference solution which is occassionally a nuisance - hindering the miniaturization of such sensors. Recently, the use of a conducting polymer layer between the pH-selective membrane and a Pt substrate has been shown [5] to create performances superior to the proton selective coated wire electrode without this layer. The purpose of this work is to combine a proton selective membrane and electrode of the second kind using the beneficial aspects of each. Impedance spectroscopy is employed to reveal the nature and kinetics of interfacial as well as bulk processes associated with such a complex system.

MATERIALS AND METHODS

Antimony, PVC (of η = 1.4), di-nonyl phthalate, tri-n-dodecylamine, sodium hydroxide, sulphuric acid and tetrahydrofuran used in this work were all of analytical grade and used without further purification. Antimony, in the form of a rod, was covered with its oxide (oxyhydroxide) by sweeping its potential to -0.6 V/SCE in 0.1 M NaOH and keeping the potential constant until a perfect, stable and adherent surface film was formed. This was thoroughly washed, dried in air at 343°K, dipped in a solution containing 48% PVC w/w, 50% di-nonyl phthalate and 2% tri-n-dodecylamine, subsequently removed and dried in air. Repeating this dip-dry sequence upto three times gives thick polymer film. Repeating this further, too

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thick films are formed which had an adverse effect on the performance. In a number of cases, potassium tetraphenyl borate (upto a maximum of 0.2%) were added to extend the Donan exclusion limit. The improvement was found to be marginal.

Impedance studies were performed in a three electrode cell with the sensor forming the working electrode; its potential was monitored against a SCE using high impedance SM 200 digital voltmeter. A large platinum foil was used as the auxillary electrode. The cell was powered by a fully computerized EG & G electrochemical system comprizing of a 273A potentiostat/ galvanostat, a 5210 lock-in amplifier and this was run by an IBM ps/value point computer through M398 software.

RESULTS AND DISCUSSION

Figure 1 presents the response of sensors made by 1- and 3-dips in 0.1 and 0.01 M NaOH and 0.1 M H_2SO_4 solutions. The potential attained 90% of its ultimate value

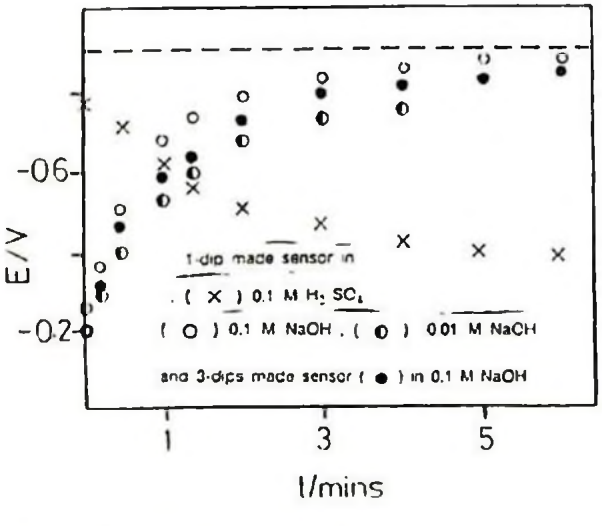


Fig. 1 - Response - time characteristics

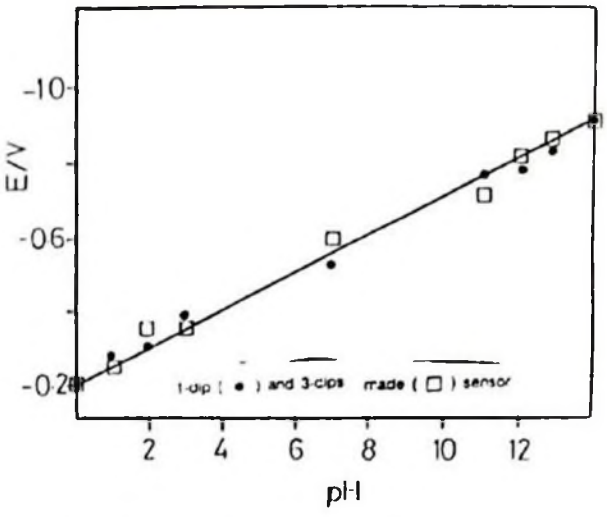


Fig. 2 - pH - potential characteristics

in about 3 minutes in the descending pH direction while the response time was considerably larger in the ascending direction. Figure 2 presents the pH-potential behaviour of sensors made by 1- and 3-dips in the range of 2 < pH < 13. The behaviour is linear but the slope is nearly 50 mV/pH - slightly less than Nerstain. Slight instability was experienced over a period of two weeks in the form of random drifts and slowness of response in the case sensor made by 1-dip in 0.1M NaOH solution. The sensor was stable in deionized water over a period of weeks.

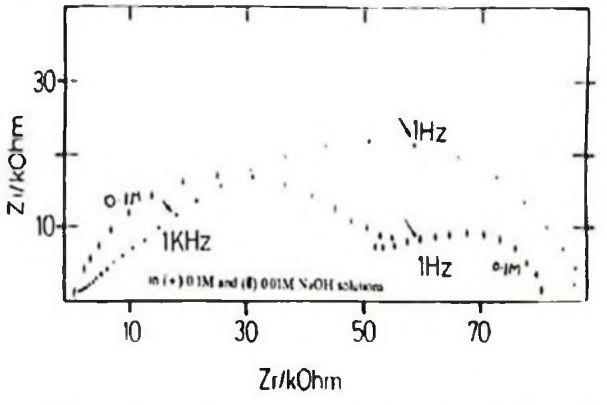


Fig. 3 - Impedance characteristics of the Sensor made by 1-dip at OCP
(+) 0.1M and (■) 0.01M NaOH solutions.

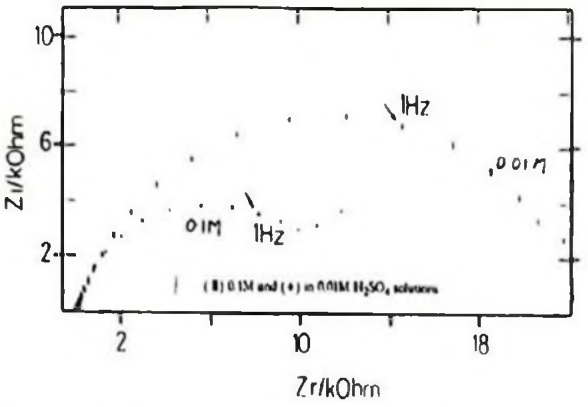


Fig. 4 - Impedance characteristics of the Sensor made by 1-dip at OCP
(■) 0.1M and (+) in 0.01M H_2SO_4 solutions.

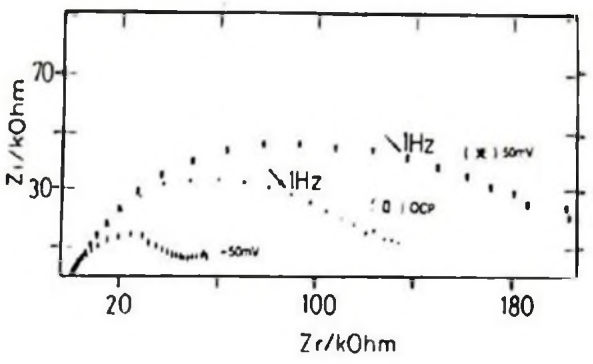


Fig. 5 - Impedance characteristics of the Sensors made by 3-dips
0.1M NaOH solution at (■) OCP,
(+) +50 mV and (*) -50mV off-sets.

Figure 3 presents the impedance characteristic of the 1-dip made sensor in the form of the Nyquist plots recorded in the frequency range of 100KHz to 10 mKHz in 0.1 and 0.01M NaOH solutions with the sensor held at its corresponding open circuit potential (OCP). Similar results at the corresponding acidic solutions are presented in Fig. 4. The sensors made by 3-dips behaved almost similarly but possessed impedances nearly twice as high. The Nyquist plots obtained in 0.1M NaOH solutions with the sensor at OCP, OCP + 50 mV and OCP - 50 mV are presented in Fig. 5. The sensor made by 1-dip was slightly unstable at the potentials under study. So a sensor made by 3-dips has been employed in this study. The software developed by Boukamp [6] for fitting the data to equivalent circuit was employed for the analysis of the results. In general, a maximum of five semi-circles corresponding to different processes of various time constants can be resolved. The entire system can be considered as consisting of a number of circuit elements presented below.

R_s = Solution Resistance
R_{sp} = Solution/Polymer
R_p = Polymer
R_{pf} = Polymer/Oxide Film
R_f = Oxide Film
R_{fm} = Oxide Film/Metal

C_{dl}= Double Layer-Capacitance
C_p = Polymer
C_{pf} = Polymer/Oxide Film
C_f = Oxide Film
C_{fm} = Oxide Film/Metal

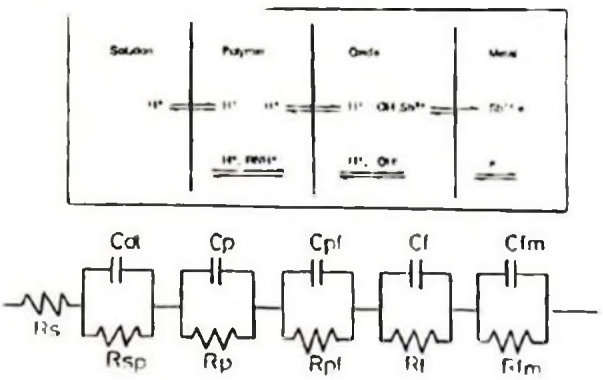
Table 1

Values of the equivalent circuit elements at two pH values

Resistance in k.ohm.cm ^{2}, Capacitance in μF.cm ^{2}

pH	R_{sp}	C_{dl}	R_p	C_p	R_{pf}	C_{pf}	R_f	C_f	R_{fm}	C_{fm}
13	10	30	15	100	40	3	15	5	1	1
2	100	50	5	500	10	50	12	4	1	1

The complex interface in the most straight forward case may be represented with Boukamp notation for the circuit.



The equivalent circuit proposed above (R(RC)(RC)(RC)(RC)(RC)) is not the unique model which fits the results. The circuit designated as (R(C(R(RC)(RC)(RC)(RC)) or (R(C(R(C(R(C(R(C(RC))))))))) creates the Nyquist plots which fits the experimentally observed results more or less equally well - with similar magnitudes of the circuit element (Fig. 6). The changes of the magnitudes of the circuit elements under different conditions (of pH and off-set potentials relative to the OCP) are

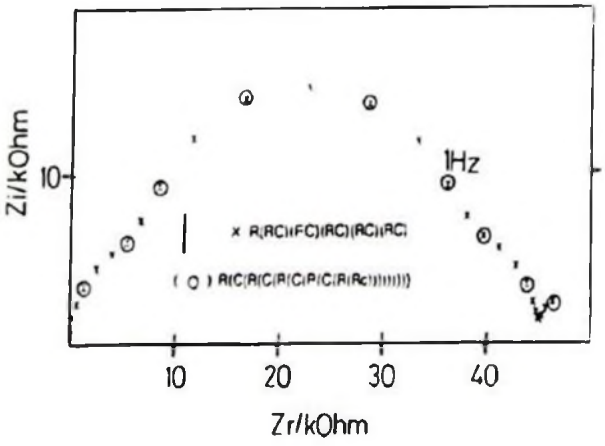


Fig. 6 - Impedance characteristics
(x) R(RC)(RC)(RC)(RC)(RC) and
(O) R(C(R(C(R(C(R(C(R(RC)))))))))

interesting and diagnostic in the assignments, (Table 1).

The two high frequency side semi-circles are highly likely to be due to the antimony/ antimony oxide part of the sensor, the magnitudes of their corresponding elements do not significantly change with pH which points to the function of this part as the internal reference electrode and its corresponding electrolyte (solid electrolyte). The changes experienced by other elements are far more significant and sensitive to the pH of the solution, (Figures 3 and 4). These changes occassionally make the two semi-circles merge to one by bringing together their time constants [7]. The expected facilitation (hindrance) factor of ion neutralization and charge transfer upon the application of 50 mV off-set is nearly 50 while the observed overall change in the real part of the impedance is only by a factor of 5 (Fig. 5). This points to the importance and slowness of ion transport across the interfaces and through the thickness of the films. The Nyquist plots obtained for antimony in 0.1M NaOH solution [8] at the potentials corresponding to those in this work have no resemblance to the Nyquist plots presented in this paper. This also signifies the importance of the new polymer/solution and polymer/oxide layer interfaces and their determining nature. The multiple interfaces of this system ensures the reversible behaviour of the entire sensor more inequivocally than that of the system consisting a conducting polymer layer [5] where the nature of interfacial reaction at the polymer/Pt is open to debate. In the present system the origin of the interfacial potentials at the complex interfaces are fairly straight-

foward. However, the slow transport across the layers and interfaces renders the system unfavourable for practical purposes.

CONCLUSIONS

On the basis of the above results and discussions the following conclusions can be arrived at :

i) The system based on the multiple interfaces of antimony/antimony oxide/PVC containing neutral carrier exhibits pH sensitivity.

ii) The sensor is stable, behaves reversibly and the nature of interfacial processes and charge carriers are clear.

iii) The showness of the interfacial and transport process renderes the sensor inappropriate for practical purposes.

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