Pergamon

Talanta, Vol. 41, No. 2, pp. 323–325, 1994

0039-9140/94 $6.00 + 0.00

BIFUNCTIONALITY OF CHEMICAL SENSORS BASED ON THE CONDUCTING POLYMER POLYPYRROLE

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(*Received* 27 *January* 1993. *Revised* 22 *March* 1993. *Accepted* 12 *July* 1993)

Summary—Responses of polypyrrole based ion-selective chloride electrode were investigated in chloride and redox media. Bifunctional character of the potentiometric response of the polypyrrole films doped with chloride ions was observed being sensitive both to chloride ions and to the redox potential of the solution, however the redox response seems to predominate.

Investigations in the field of analytical application of the conducting polymers—including polypyrrole—led to the construction of potentiometric sensors for chloride ions,[1,2] perchlorate ions,[3] as well as to the presentation of the redox potentiometric sensor based on the conducting polypyrrole film.[4] Dependence of ionic responses of polypyrrole films doped with chloride ions on the preparation time as well as on the tested electrolyte was recently reported.[5]

Polypyrrole based chloride sensitive electrodes[1,2] were prepared by anodic polymerization of pyrrole in the presence of chloride ions. Thus prepared polypyrrole films are characterized by linear Nernstian response to chloride ions and some applications for this electrode were presented.[2]

In this study is shown the bifunctional character of potentiometric response of polypyrrole based sensor which exhibits both: ionic and redox sensitivity.

EXPERIMENTAL

Reagents

Pyrrole was purified by vacuum distillation and kept in a refrigerator under nitrogen; other used reagents were of analytical grade and were used without purification. Deionized water was used throughout this work.

Apparatus

Polymerization of polypyrrole films was done using potentiostat EP20A, Poland. Potentiometric measurements were conducted with Solarton LM 1604 DC Digital Voltameter, Switzerland.

Preparation of polypyrrole electrodes

Polypyrrole chloride electrodes were prepared[1] by cyclic voltammetry in a conventional three electrode cell. A KCl–saturated silver/silver chloride electrode was used as a reference. Polymerization conditions were: scan rate 50 mV/sec, potential range 0.45–0.95 V, polymerization time 20 min. Films were polymerized from 0.1 mol/l pyrrole and 0.1 mol/l LiCl solution.

Thus prepared polypyrrole electrodes were conditioned for about 50 hr in 0.1 mol/l KCl solution before measurements.

Potentiometric measurements were carried out *vs* the KCl–saturated silver/silver chloride electrode with the 0.1 mol/l Na_2SO_4 liquid junction bridge.

RESULTS AND DISCUSSION

The ionic characteristics of the polypyrrole chloride electrode was measured in potassium chloride solutions in the concentration range from 10^{-5} to 3 mol/l. The slope of the electrode characteristics, recorded in potassium chloride solutions of various ionic strengths, was close to -50 mV/dec (Table 1, Fig. 1).

The redox characteristics of the tested electrode was measured in redox buffers of different redox potentials, prepared from potassium hexacyanoferrate(II) and potassium hexacyanoferrate(III) mixed in ratios from 1:10

Table 1. Slopes for calibration curves of the polypyrrole electrode doped with chloride ions. The polypyrrole films were calibrated *vs* chloride ions and *vs* redox buffer in the absence and in the presence of interferents: redox buffer or chloride ions, respectively

Calibration medium	Slope ± S_D (*mV/dec*)
KCl without redox buffer	−47.6 ± 0.90
in 0.0001 mol/l redox buffer	−38.8 ± 3.60
in 0.001 mol/l redox buffer	4.5 ± 1.20
in 0.01 mol/l redox buffer	1.5 ± 0.90
in 0.1 mol/l redox buffer	−1.0 ± 0.48
Redox buffer without KCl	59.0 ± 1.30
in 1 mol/l KCl	58.0 ± 0.80

to 10:1, in the absence and in the presence of 1 mol/l KCl (Fig. 2). The total concentration of the redox buffer was in the range from 0.50 to 0.55 mol/l. This couple was selected in experiments because it is not directly influenced by the chloride ions and is considered as being reversible with standard potential in the middle of the polypyrrole electrode potential range. The potential response was fast, being linear *vs* the logarithm of ox/red ratio with the nearly Nernstian slope (Table 1). Although tested solutions contained 1 mol/l potassium chloride the recorded characteristics was typically redox, the presence of the chloride ions did not influence the slope of the calibration curve *vs* redox potential. Nevertheless comparison of the two lines from Fig. 2 indicates that the calibration graphs of polypyrrole based chloride ion-selective electrode in the presence of potassium chloride is shifted parallel because of differences of the E^0 values of both systems.

Thus the electrode behaviour is characteristic for a bifunctional sensor, which depending on the conditions may act as a redox or as an ion-selective electrode. The redox sensitivity of the polypyrrole membrane is in a better agreement with theoretical slope prediction than the ionic one.

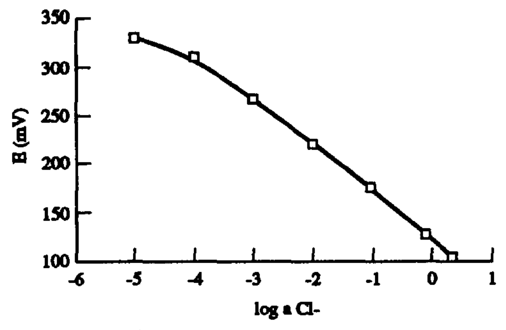

Fig. 1. Calibration of the polypyrrole based chloride selective electrode in potassium chloride solutions.

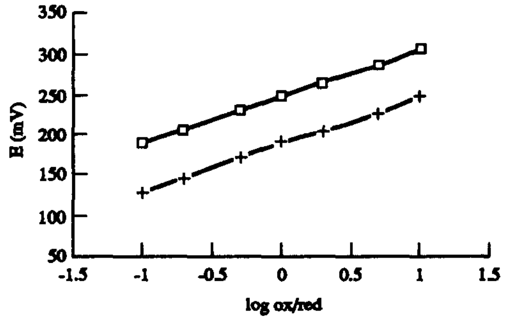

Fig. 2. Calibration of the polypyrrole based chloride selective electrode in redox buffer in presence (+) and in absence (□) of 1 mol/l KCl.

From the point of view of the redox sensitivity of the electrode the ionic response could be interpreted as an interference and from the point of view of the chloride ion selective electrode one could interpret redox sensitivity as a redox interference.

Both approaches are possible depending what kind of response of polypyrrole electrode is considered as the main. Moreover the electrode exchanges ions with the solution in the case of ionic response and exchanges electrons with the solution when the redox sensitivity is discussed, thus both are connected with charged species transfer between the polymer film and the solution.[6] Therefore the redox and ion sensitivity cannot be separated and only conditions in which one of these effects dominates should be properly established.

In order to estimate conditions when polypyrrole film doped with chloride ions could be regarded as a selective chloride electrode, measurements in the presence of various concentration of redox buffer were carried out. In all calibration measurements (Fig. 3) the ox/red ratio was constant and equal to one (log[ox/red] = 0). The total concentrations of the used redox buffers changed from 0.1 to 0.0001 mol/l. Thus the redox potential corresponds to E^0 of the hexacyanoferrate redox couple. For each redox buffer concentrations of potassium chloride were changed from 0.002 to 0.02 mol/l, which corresponds to the tested chloride sensitivity range of the electrode.

For redox buffers of concentrations 0.1, 0.01 and 0.001 no changes were observed during addition of the KCl solution. When the redox buffer concentration decreased to 0.0001 mol/l, the potential response starts to depend on the chloride concentration and the anion electrode sensitivity became predominant (Fig. 3a). Nevertheless the slope of this dependence was

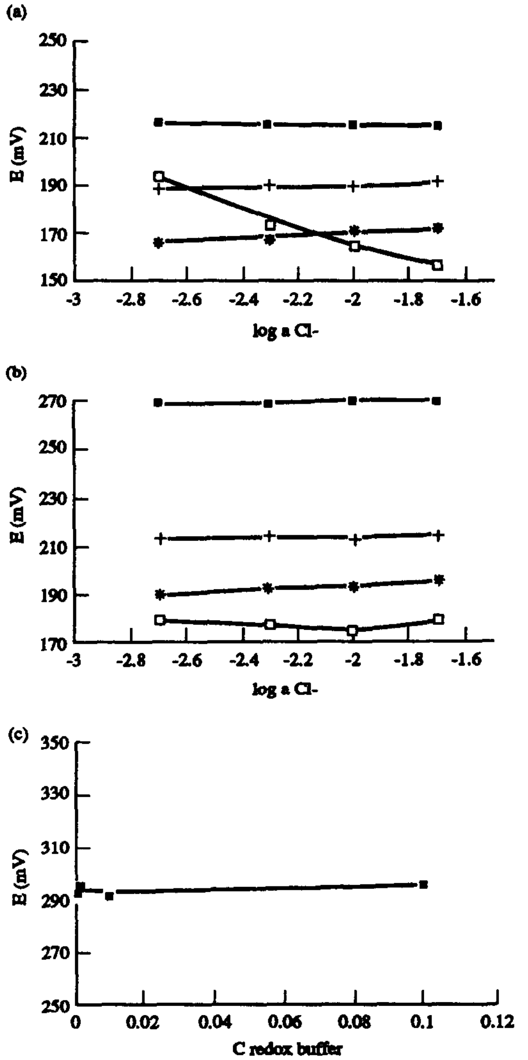

Fig. 3.(a) The response of the polypyrrole electrode doped with chloride ions electrode as the chloride selective electrode in the presence of redox buffer concentrations: (■) 0.1 mol/l, (+) 0.01 mol/l, (*) 0.001 mol/l (□) 0.0001 mol/l. (b) The response of the platinum electrode under the same conditions as in (a;). (c) The response of the platinum electrode in solutions of the same ox/red ratio but of different redox buffer concentrations, in presence of the 3 mol/l KCl solutions. Potentiometric cell in all experiments was: Ag|AgCl, sat. KCl|3 mol/l KCl|| 3 mol/l KCl + tested solution Pt/PPy-Cl or Pt.

only −38.8 mV/dec, being lower than the pure ionic response (Table 1), in the absence of the redox buffer. This suggests that the observed potential changes are not only due to the changes in chloride concentration. Thus the polypyrrole based chloride electrode can be used as a chloride electrode only when the concentration of the redox species (*i.e.* the redox buffering capacity) is lower than 0.0001 mol/l.

The differences in the recorded potential values for different concentrations of the redox buffer, within the range 0.1–0.001 are due to the changes in ionic activity and of the liquid junction potential. For comparison a similar dependence was recorded for the platinum electrode (Fig. 3b). Although when potentials of the platinum electrode were recorded in solution of different redox buffer concentrations but with constant ionic strength provided by addition of 3 mol/l KCl, no dependence of the redox species concentration was observed (Fig. 3c), as it follows from the Nernst equation.

These observations (Fig. 3a) indicate that the potential response of the polypyrrole electrode doped with chloride cannot be considered as purely ionic but it depends always also on the redox potential. The range of used concentrations suggest that the redox sensitivity of the polypyrrole film is stronger than ionic. In 1 mol/l KCl solution the Nernstian redox response was dominating while to obtain the ionic response the redox buffer concentration has to be on the level of 0.0001 mol/l or lower.

The observed redox sensitivity was tested in potential range from 180 to 310 mV but as it was described earlier[4] redox sensitivity can be observed in potential range where polypyrrole is conducting that is from about −0.5 to 1 V.

CONCLUSIONS

These experiments suggest that electrodes based on conducting polymer polypyrrole when used as ion-selective sensors usually suffer from redox interferences. This effect was until now not studied in detail and some communications on similar chloride-selective electrodes do not mention this type of interferences[1,2]. Most probably such effects should be observed with similarly prepared polypyrrole electrodes doped with perchlorate and indicated as perchlorate selective.

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