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DEVELOPMENT OF POLYRROLE THIN FILM BASED SOLID-CONTACT ION-SELECTIVE ELECTRODES FOR NITRATE AND NITRITE

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ABSTRACT

The solid-contact ion-selective electrodes for nitrate and nitrite were successfully constructed by using a conductive polypyrrole as ionic-to-electron transducer in combination with a plasticized PVC based membrane containing tetraoctylammonium bromide and cyanoaqua-cobyrinic acid heptakis (2-phenylethyl este) as nitrate and nitrite ionophores, respectively. The potentiometric response characteristics of those were evaluated using a steady-state measurement setup and a wall-jet flow cell system. In this study, it was found that the stability of electromotive force (EMF) response and selectivity of the resulting solid-contact ion-selective electrodes for nitrate and nitrite depend on electropolymerized conditions of conducting polymer thin films. The designed sensors exhibited excellent selectivity for the primary ion and a Nernstian response over a linear range of concentrations between 0.01 mM and 100 mM of the nitrate and nitrite with a slope of 58.8 mV.decade^{-1} and 59.1 mV.decade^{-1}, respectively. A new generation of this kind of developed sensors showed a fast response and a relatively high robustness.

Keywords: Conjugated polymer, electro-polymerization, and flow injection analysis, solid-contact ion-selective sensor.

Introduction

Nitrite and nitrate are widely used in foods, fertilizers and chemical processes. Their presence in environmental samples can indicate the extent of pollution of natural waters.[1-3] The determination of nitrite and nitrate concentration in a variety of matrices has increased interest in the development of novels sensors for these ions[4-6].

Clearly, the ability to make direct or indirect measurements in complex samples without concern about sample color or turbidity and the fact that such measurement require relatively inexpensive equipment make ion-selective electrodes (ISEs) very attractive analytical tools for environmental monitoring and food analysis[7]. However, the current development of analytical sciences has led to a need for maintenance-free, robust and reliable ion sensors. One common approach towards maintenance-free ion sensors is to eliminate the inner filling solution and create all solid-state contact electrodes.[8-13] Also, the miniaturization is easier for electrodes without any liquid components than for the more traditional ones with inner filling solution.

In the present work, the solid-contact ion-selective electrodes for nitrate and nitrite employing electropolymerized polypyrrole film as internal solid-contact layer between the reference element and the ion sensing membrane, instead of the conventional design with internal filling solution, have been investigated. The ion-selective membranes, which were based on plasticized PVC membrane containing nitrate and nitrite ionophore, respectively, are formed on top of a layer of the conducting polypyrrole, working as ionic-to-electron transducer. The potentiometric response characteristics of solid-contact ISEs were evaluated using a steady-state measurement setup and a wall-jet flow cell system.

Experimental

Reagents

All reagents were of analytical grade. Standard and buffer solutions were prepared with Milli-Q water. Pyrrole purchased from Fluka was redistilled under vacuum prior to use and covered with aluminium foil in the refrigerator in order to prevent UV degradation.

Tetraoctylammonium bromide (TOABr), cyanoaqua-cobyrinic acid heptakis (2-phenylethyl este) (nitrite ionophore I, Fluka, Buchs, Switzerland), 2-nitrophenyl octyl ether (o-NPOE), high molecular weight polyvinyl chloride (PVC), and tetrahydrofuran (THF) were obtained from Fluka (Buchs, Switzerland).

Electropolymerization of conducting polypyrrole

Polypyrrole (PPy) synthesis and characterization were performed in a conventional three electrodes system consisting of a 2 mm i.d. glassy carbon (GC) disc working electrode (6.1204.110 GC, Metrohm, Switzerland), a platinum wire gauze auxiliary electrode and an Ag/AgCl (3M NaCl) reference electrode. A homemade microgalvanostat was used for the electropolymerization. Chronopotentiograms were recorded by this microgalvanostat with the support of a data acquisition system. Cyclic voltammetric measurements of the conductive polymer were done by a PC-controlled system for Voltammetry (Model 757 VA Computrace, Metrohm, Switzerland).

Before polymerization, the surface of the glassy carbon working electrode was polished on a polishing cloth with alumina slurry (0.05μm) and then cleaned with double distilled water and finally in a water-filled ultrasonic bath for 30 seconds. The polypyrrole film was prepared by anodic galvanostatic electropolymerization of the pyrrole monomer from aqueous solution (0.5 M) onto the electrode surface. The counterion solution used for polymerization was deoxygenated with nitrogen for 5 minutes to remove any trace of oxygen from the solution, before the polymer synthesis. A current density of 2 mA.cm^{-2} was used to achieve electropolymerization.

The PPy/NO$_3$ thin film employed in the solid-contact nitrate selective electrodes was electropolymerized from electrolyte solutions containing various concentration 0.1, 0.5, and 1 M nitrate with various deposition time from 90 to 200 seconds. A PPy used in the solid-contact nitrite selective electrodes was fabricated as the following, first PPy/Cl was prepared from electrolyte solution containing 1 M of chloride and electropolymerization achievement for 250 seconds, subsequence cyclic voltammetry of PPy/Cl in an electrolyte solution containing 0.1 M nitrite was achieved.

Fabrication of the solid-contact ISEs

Solid-contact ISEs were prepared by coating GC/PPy electrodes with ion-selective membranes. Nitrate selective membrane contained 3 % (w/w) of the TOABr and 33 % (w/w) of the PVC and 64 % (w/w) o-NPOE. Nitrite selective membrane contained 1% (w/w) of the nitrite ionophore and 33% (w/w) of the PVC and 66 % (w/w) o-NPOE as plasticizer. The membrane compositions were dissolved in 1 ml THF and applied by a micropipette on the electrode to cover the PPy layer, then dried for 2 hours under a gently nitrogen atmosphere, and conditioned overnight in 10 mM of the selected primary ion solution prior to any measurements.

Potentiometric measurements

Steady-state potentiometric measurements were made while stirring at a constant rate and with the electrodes immersed to the same depth in the solution to be tested. The calibration curve was obtained by a standard addition method involving the additions of 10^{-6} M to 10^{-1} M of the primary ion.
The potentials were measured against a double junction Ag/AgCl reference electrode (Orion 90-02-00) using a 692 pH/Ions meter (Metrohm, Switzerland).

Flow injection potentiometric measurement was performed with a simple flow manifold including a four channel peristaltic pump (Ismatec - Switzerland), a low pressure six way injection valve (5020 Rheodyne)

with 100 μl sample loop and a wall-jet flow cell (Metrohm, Switzerland). The carrier eluents in the flow injection experiments for nitrate and nitrite solid-contact electrodes are phosphate buffer (0.067M, pH 5) and 2-morpholinoethanesulfonic acid monohydrate (MES) buffer (0.01 M, pH 5) containing 2 mM NaCl, respectively. Primary ions of 1 μM were added to the carrier eluent to provide the base-line stability. All measurements were carried out at room temperature.

Results and discussion

A polypyrrole film was deposited on electrode surface by oxidation of monomer from an aqueous solution containing the appropriate counterion as supporting electrolyte. In this work, the PPy thin film containing nitrate (PPy/NO$_3$) and chloride (PPy/Cl) were grown on the glassy carbon electrode surface. Chronopotentiograms were recorded during film growth. Relatively constant potential was observed throughout the polymerization, indicating the formation of a conductive polymer layer.

Since the polypyrrole film plays the role for the transfer from ionic to electronic conductivity in the solid-contact ion-selective electrode as can be seen in the Fig. 1, the estimation of the electropolymerized conditions such deposition time (t$_d$), concentration of counterion (c$_A$) in electrolyte solution, and incorporation of various counterions into the polymer film are important to the development process. Cyclic voltammograms recorded in counterion solution after growth of PPy/NO$_3$ and PPy/Cl indicate that polymers were conductive in analyze solutions of counterion. Counterion injection and release to accompany the redox cycling of electropolymerized polypyrrole films in electrolytes occurred as shown in Scheme 1.[14]

Scheme 1
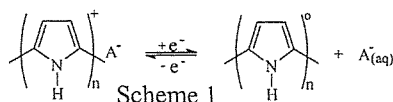
Cyclic voltammogram of PPy/Cl in electrolyte solution containing 0.1M NO$_2^-$ (PPy/NO$_2$) and MES buffer (0.01 M and pH 5) was also indicated that chloride ion in those polymer films was replaced by mean of other anion in electrolyte solutions during oxidation/reduction cycling of polypyrrole.

Potentiometric response characteristics of solid-contact ISEs for nitrate and nitrite in steady-state

The solid-contact ion-selective electrodes for nitrate and nitrite based on polypyrrole thin film layers working as an ionic-toelectron transducer were prepared. The scheme diagrams of the charge transfer process occurring in a conventional internal electrolyte ISE and in a solid-contact ISE presented in the Fig.

1. As can be seen in the Fig. 1, the charge transfer process occurring in both type of ion-selective electrodes showed similar trends.
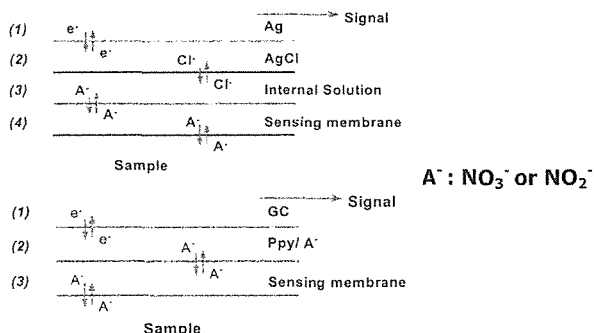
Fig.1. Charge transfer process occurring in (A) a conventional internal filling ion-selective electrode; and (B) in a solid-contact ion-selective electrode.

The performance of these solid-contact ISEs was tested in steady-state. Principle electrode characteristics such as Nernstian slope, dynamic linear range, detection limit and potentiometric selectivity coefficients, were estimated.

The potentiometric response of three solid-contact nitrate selective electrodes (a), (b), (c) employing different PPy/NO3 thin films which were electropolymerized from electrolyte solutions containing 0.1 M, 0.5 M, and 1 M nitrate, respectively, with the deposition time of 150 seconds, was showed in the Fig 2. As can be seen in Fig. 2, both electrodes (b) and (c) give almost a Nernstian response with slopes of -58.8 and -55.1 mV.dec^{-1}, respectively, excluding electrode (a) exhibited a super-Nernstian slope. However, the linear part of calibration curve for electrode (b) observed from 10^{-5} to 10^{-1} M, while the electrode (c) exhibited a linear part in range from 3×10^{-5} to 10^{-1} M of nitrate ions. The effect of the electropolymerized time for growth of conducting polymer thin film to the potentiometric response of solid-contact nitrate selective electrodes was also investigated and no significant effect was observed with various deposition times in range from 90 to 200 seconds. Almost solid-contact nitrate selective electrodes show a Nernstian response in the linear range from 10^{-5} to 10^{-1} M of nitrate concentration.
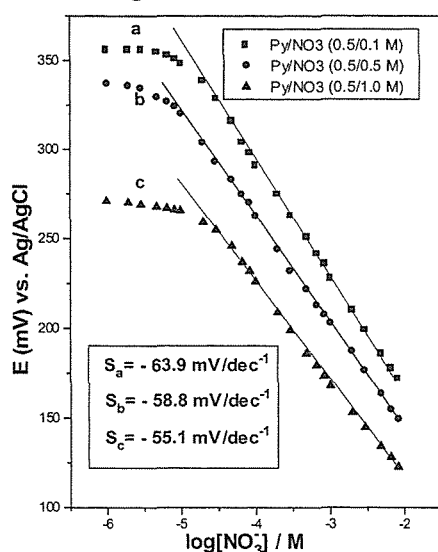

Fig.2. Calibration curves for the conducting polymer based solid-contact nitrate selective ISEs employing different polypyrrole thin films, which were polymerized in the different electrolyte solution containing (a) 0.1 M nitrate; (b) 0.5 M nitrate; and (c) 1.0 M nitrate
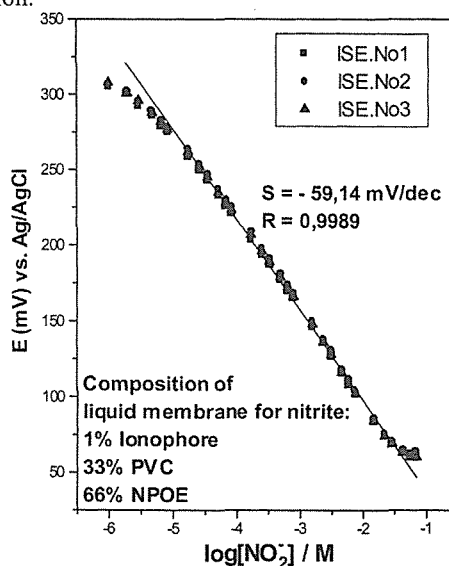
Fig.3. Calibration curves for the conducting polypyrrole based ion-selective electrodes to nitrite solution in MES buffer containing 2 mM NaCl.

The potentiometric response of the solid-contact ISEs for nitrite in steady-state is shown in the Fig. 3. The calibration plots were recorded from 10^{-1} M to 10^{-6} M NaNO2. The slopes of the linear part of the calibration plots ($4 \times 10^{-2} \sim 1 \times 10^{-5}$ M) for the solid-contact nitrite selective electrodes are 59.1 mV.dec^{-1}. Furthermore, this study also indicated that a sub-Nernstian response at nitrite concentrations > 100 mM was observed for these solid-contact ISEs due to the inherent attributes of the ion-selective liquid membrane based on a polar plasticizer, such as o-NPOE. However, that effect is not concerned to the sensor development process. Since the concentration in the environmental samples are shown less than 100 mM and the improving of lowering detection limit of nitrite ISEs is much more importance in the sensor development.

The potentiometric response of the solid-contact ISEs was very stable in the measured concentration range of primary ion, which is believed to be the result of a better-defined interfacial potential between the sensing membrane and the solid electrode contact. Response time of solid-contact ISEs was also

investigated, because it is an important factor in terms of the practical use of these ion sensors. The time taken for the both electrodes to attain 90 % of the steady-state response was typically a few seconds, suggesting that this electrode is ideal for a flow injection measurement.

Flow injection measurements

The solid-contact ISEs were mounted in the FIA system described in the Experimental Section. Typical flow injection peaks of solid-contact ion-selective electrodes for nitrate and nitrite obtained for series of injections of different nitrate and nitrite solutions are shown in Fig. 4, which demonstrates the high reproducibility of the observed peak heights. Significant electrode potential drifting was observed with the solid-contact nitrite selective electrodes, likely due to the slow leaching process of the inophore of this liquid membrane. However, baseline drift in the FIA mode has little effect on the calibrations since data processing can account for this when calculating peak heights. The less than Nerntian response observed for the solid-contact nitrite selective electrode in the FIA mode was due to the initial slow response of nitrite selective liquid membrane and the dispersion of the injected sample zone. However, the FIA response observed represents about 96% of the steady-state response and provides adequate analytical sensitivity. The potentiometric responses in flow system of the solid-contact selective electrodes for nitrate and nitrite were linear over the range investigated i.e., between 3×10^{-5} and 10^{-1} M l^{-1} of measured ions with Nernstian slope of 58.1 and 56.7 mV.dec^{-1}, respectively.
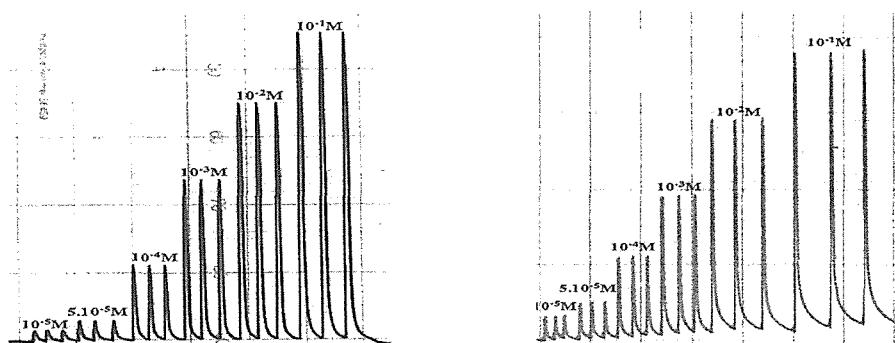

Fig. 4. Typical flow injection peaks of (A) a solid-contact selective electrode for the series injection of nitrate ion, (B) a solid-contact selective electrode for the series injection of nitrite ion; flow rate 1.5 ml/min; injected volume: 100 μL.

Fig. 5. Selectivity coefficients, log K_{ij}^{pot} for the solid-contact selective electrodes were determined in a FIA system with (a) PPy/NO$_2$/nitrite membrane and (b) PPy/NO$_3$/nitrate membrane. Flow injection conditions were as reported in the Experimental section.
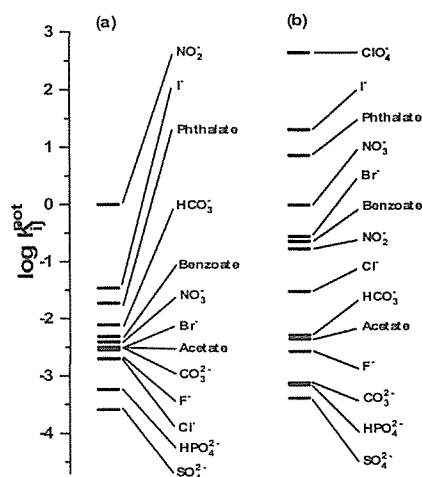
The selectivity coefficient values of solid-contact ISEs to the obtained by the separate solution method[15]. Selectivity measurements were done by injection of 0.01 M of anions into a flow injection system. The selectivity coefficient values are given in Figure 5. It has been pointed out that the ClO_4^-, I^- and organic ions are the most notable interference ions of the tested ions to both type solid-contact ISEs. Nevertheless, these solid-contact ISEs can be able to apply for determination of nitrate and nitrite in the environmental samples with little pretreatment prior to measurements.

Conclusion

The solid-contact ion-selective electrodes for nitrate and nitrite were successfully constructed by using a conductive polypyrrole as ionic-to-electron transducer in combination with plasticized PVC based membrane containing appropriate ionophores. The resulting solid-contact ISEs showed good sensitivity in concentration over the range 10^{-1} to 10^{-5} M with Nernstian slopes of 58.8mv.dec^{-1} and 59.1 mV.dec^{-1} respectively. These ISEs exhibited a fast response (5 seconds) and a relatively high robustness in both a steady-state measurement and a flow injection system. It is hoped that this study will contribute to the design and construction of planar solid-contact ISEs and their using as potentiometric detector in a miniaturized flow injection system.

Acknowledgements

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