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A Polyaniline-Skeleton Nickel Electrode for the Potentiometric Detection of Nitrate and Nitrite

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Abstract: A modified electrode obtained by the electrochemical depositon of polyaniline from aqueous acid solutions on a rough substrate of skeleton nickel has been prepared and tested as potentiometric sensor. The detection properties of the skeleton Ni-polyaniline selective electrode were determined for nitrate and nitrite anions. The modified electrode presents short response time and Nernstian behaviour in the concentration range of 10^{-1} to $5{\cdot}10^{-5}$ mol L^{-1}. The selectivity coefficient for nitrate in the presence of nitrite was calculated according to the separate solution method.

Keywords: electrochemical sensor, polyaniline, skeleton electrodes, nitrate, nitrite

1. Introduction

Electrochemical sensors and detectors have gained increasingly interest for applications in environmental monitoring [1] such as on-site detection of priority pollutants in drinking water, in the food industry or wastewater treatment. Their main advantages relay on the high selectivity and sensitivity, stability, short response time and ease of use since such devices are compact and portable.

The nitrates and nitrites determination presents importance to pollution control. Nitrates and nitrites usually exists in industrial wastewaters, polluted groundwater and radioactive solutions. Nitrates are less toxic compounds than nitrites bu they can be reduced to nitrites, which are precursors in the formation of nitrosamines, compounds with potential carcinogenic effect. The clasic methods for nitrate determination are based on spectroscopic, chromatographic, and electrochemical detection [2-4]. These methods are usually complicated and insufficiently specific. Sensors on the other hand, allow a rapid detection and simple use and they suitable for analytical purposes.

Very promising materials for application in electrochemical sensors are organic conducting polymers [5]. For the detection of nitrates and nitrites several conducting polymers have been used, such as, polypyrrole, polyaniline and polydiamino-naphtalene [6-9]. Polyaniline is unique among conducting polymers in that it has a very simple acid/base doping/dedoping chemistry. It is well known that during the synthesis of polyaniline (PANI) the anions present in the reaction media are included in the polyaniline matrix as dopant anions.

By immersing polyaniline in solutions containing other types of anions an exchange equilibrium process occurs, and the dopant anions are replaced [10-12]. As a result of this behaviour it is possible to use polyaniline as anion sensor. Sensors and actuators assembled with conductive polymer nanowires have superior responding characteristics to their counterpart [13,14].

The aim of this paper is to show our results for the use of PANI-skeleton nickel electrode as potentiometric anion sensor for nitrate and nitrite. An unconventional substrate was selected for the deposition of PANI, namely skeleton nickel [15]. This kind of substrate solves the problems related to the adherence of the polyaniline film. The substrate doesn't affect the sensing properties of the modified electrode, thus, the potentiometric response is the same as in case of conventional substrates.

2. Experimental

In all experiments, freshly distilled aniline (MERCK) and sulfuric acid (MERCK) were used. The skeleton nickel electrode was prepared by thermal arc spraying technique using two different wires, one of Ni (99.2%) and one of Al (99.5%) [16]. The coating was activated by alkaline leaching with 1 mol L^{-1} NaOH solution at 80°C for 4 hours. During activation aluminum is removed from the coating, leaving a porous, three-dimensional matrix of nickel.

The PANI-skeleton nickel electrode was prepared by electrochemical deposition of PANI on a substrate made of skeleton nickel. The potential cycling was performed with a Princeton Applied Research 173 Potentiostat connected to computer via an interface. A conventional electrochemical cell was used with a skeleton nickel working electrode ($S = 1cm^2$), two graphite roads as counter electrodes and a saturated calomel electrode (SCE) as reference. The ohmic drop in the solution was minimized using a Haber-Luggin capillary placed at approximately 1 mm from the electrode surface.

PANI was deposited from an aqueous solution of 0.027 mol L^{-1} aniline in 1 mol L^{-1} sulfuric acid, by sweeping the potential between -0.2 V/SCE and 1.2 V/SCE, at 100 mV s^{-1} scan rate for 10 cycles.

Afterwards the anodic potential limit was lowered to 1.0 V/SCE and the potential cycling was continued for 10 more cycles.

The characterization of the polymer film by scanning electron microscope (Philips XL30 ESEM) coupled with energy dispersive X-ray analysis and X-ray diffraction (Philips X'Pert diffractometer) is described elsewhere [17].

The potentiometric response of the PANI-skeleton nickel electrodes was measured using a digital voltmeter E 0302 in several solutions with different concentration of NO_3^-, and NO_2^-. A silver–silver chloride electrode (Ag/AgCl) was used as reference. In all experiments the temperature was 25° ± 1°C.

3. Results and Discussion

The cyclic voltammograms recorded during the electrochemical oxidation of aniline are shown in Figure 1 (extended potential range) and Figure 2 (restricted potential range).

The anodic peak A at 0.2 V/SCE observed during the first cyclovoltammetric scan (Figure 1 – cycle 1) is related to the oxidation of the nickel substrate. The main feature in the following cycles is the appearance of four oxidation peaks (B, C, D, and E) associated with different steps of the electrochemical polymerization mechanism.

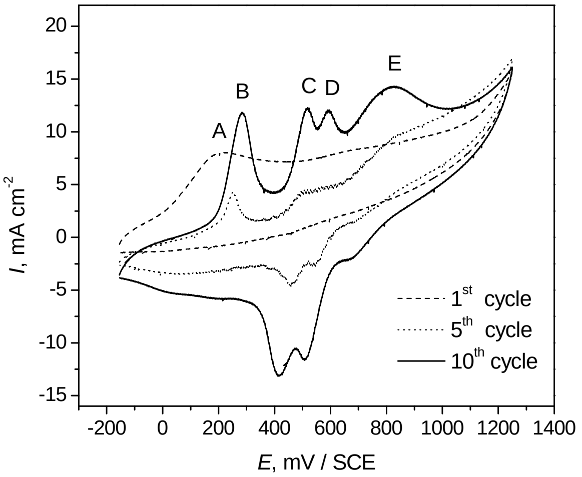

Figure 1. Cyclic voltamogramms for the electrochemical polymerization of aniline on skeleton nickel electrode, 1 mol L^{-1} H_2SO_4 + 0.027 mol L^{-1} aniline solution, scan rate 100 mV s^{-1}, potential range −0.2 ÷ 1.2 V/SCE.

Degradative oxidation reactions of the polymer backbone may be avoided by lowering the reversal potential to 1.0 V/SCE. The shape of the cyclic voltammograms is given in Figure 2.

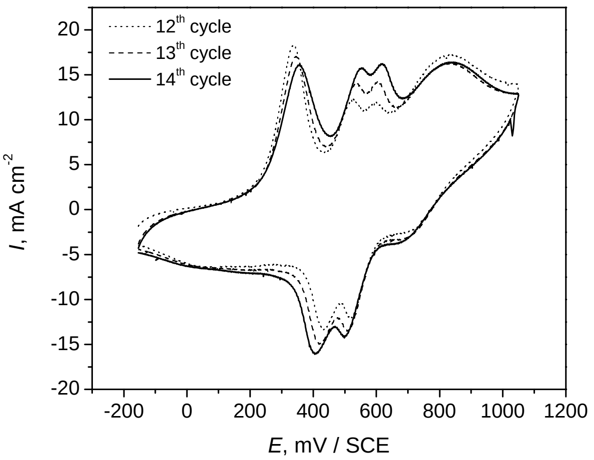

Figure 2. Cyclic voltamogramms for the electrochemical polymerization of aniline on skeleton nickel electrode, 1 mol L^{-1} H_2SO_4 + 0.027 mol L^{-1} aniline solution, scan rate 100 mV s^{-1}, potential range −0.2 ÷ 1.0 V/SCE.

The potentiometric response of the skeleton Ni-PANI electrode was measured for nitrate and nitrite anions. Before the measurements the modified electrode was conditioned for 24 hours in a 10^{-5} mol L^{-1} solution of the corresponding anion to achieve the anion exchange equilibrium. During this step the sulfate dopant anions are exchanged with nitrate or nitrite anions.

The calibration curves given in Figures 3 and 4 were obtained in $NaNO_3$ and $NaNO_2$ solution with different concentrations, ranging from 10^{-1} to 10^{-5} mol L^{-1}.

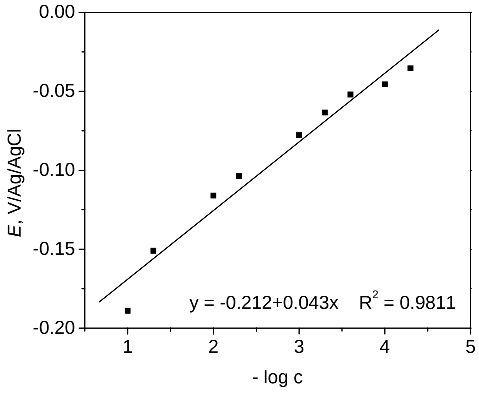

Figure 3. Potentiometric calibration curves for nitrate.

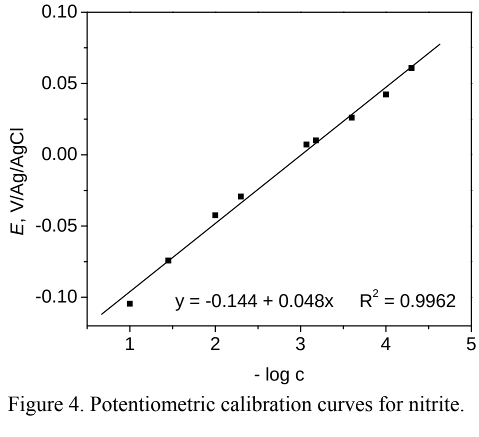

Figure 4. Potentiometric calibration curves for nitrite.

The modified electrode behaves as a second order electrode and gives a Nernstian potentiometric response in the concentration range 10^{-1} to $5\cdot10^{-5}$ mol L^{-1} according to equation (1) and (2).

$$E = E^{o'} - 2.303\frac{RT}{F}\lg a_{NO_3^-} \qquad (1)$$

$$E = E^{o''} - 2.303\frac{RT}{F}\lg a_{NO_2^-} \qquad (2)$$

Equations (1) and (2) correspond to a linear variation of the potential with the anion activity in the solution, with the general form y = a + bx, where a = ordinate ($E^{0'}$ or $E^{0''}$) and b = slope (0.059 V decade^{-1}). The slope of the calibration curves approaches the theoretical value of 0.059 V decade^{-1} for each anion. The detection range was between 10^{-1} and $5\cdot10^{-5}$ mol L^{-1} for both nitrate and nitrite anions.

In order to investigate the selectivity of the modified electrode for NO_3^- anions, with respect to NO_2^- interfering ions, the potentiometric selectivity coefficient $K_{NO_3^- - NO_2^-}$ was evaluated by the separate solution method, according to equations (3) and (4).

$$-\log K_{NO_3^- - NO_2^-} = \frac{E_2 - E_1}{2.303(RT/F)} \qquad (3)$$

$$K_{NO_3^- - NO_2^-} = \frac{a_{NO_3^-}}{a_{NO_2^-}} \qquad (4)$$

The value of the calculated selectivity coefficient is equal to 0.44. The good selectivity coefficient of the PANI-skeleton nickel electrode combined with the rapid response and stability in time, ease of preparation and insolubility of PANI in organic solvents make the electrode attractive.

4. Conclusions

The PANI-skeleton nickel electrode reveals a good sensitivity for nitrate and nitrite anions. The detection limit is $5\cdot10^{-5}$ mol L^{-1} and the electrode is stable in time. The equilibrium installs quickly and the electrode is facile to handle.

The skeleton substrate confers improved adherence of the polymeric film and is economically more attractive than conventional substrates (Pt, Au).

REFERENCES

1. Rahman Md. A., Kumar P.,. Park D.-S, Shim Y.-B., *Sensor*, **2008**, *8*, 118-141.
2. Tsikas D., Gutzki F. M., Rossa S., Bauer H., Neumann C., Dockendorff K., Sandmann J., Frölich J. C., *Anal. Biochem.*, **1997**, *244*, 208-220.
3. Davenport R. J., Johnson D. C., *Anal. Chem.*, **1973**, *45*, 1979-1980.
4. Kitamaki Y., Jin J.-Y., Takeuchi T., *J.Cromatography A*, **2003**, *1003*, 197-202.
5. Trojanowicz M., *Microchim. Acta*, **2003**, *143*, 75-91.
6. Cosnier S., Godran C., Wessel R., Montforts F.-P., Wedel M., *Sensor*, **2003**, *3*, 213-222.
7. Quan D. P., Lewis T. W., Wallace G. G., Viet P. H., *Analyt. Sciences*, **2001**, *17*, i745-i748.
8. Mazeikiene R., Malinauskas A., *Synth. Met.*, **1997**, *89*, 77-79.
9. Badea M., Amine A., Pallesci G., Moscone D., Volpe G., Curulli A., *J.Electroanal.Chem.*, **2001**, *509*, 66-72.
10. Martin C. R., Freiser H., *Anal Chem.*, **1981**, *53*, 902-904.
11. Lu Z., Sun Z., Dong S., *Electroanalysis*, **1989**, *1*, 271-277.
12. Wang J., *Synth. Met.*, **2002**, *132*, 49-52.
13. Alam M. M., Wang J., Guo Y. Y., Lee S. P., Tseng H. R., *J. Phys. Chem. B.*, **2005**, *109*, 12777-12784.
14. Ramanathan K., Bangar M. A., Yun M. H., Chen W., Mulchandani A., Myung N. V., *Nano. Lett.*, **2004**, *4*, 1237-1239.
15. Plesu N., Kellenberger A., Vaszilcsin N., Manoviciu I., *Chem.Bull.Politehnica Univ.(Timisoara)*, **2000**, *45(59)*, 198-207.
16. Vaszilcsin N., Brandl W.., Kellenberger A., Toma D., *Chem.Bull.Politehnica Univ.(Timisoara)*, **1998**, *43*, 330-339.
17. Kellenberger A., Vasilcsin N., Plesu N., *Annals of West University of Timisoara, Series Chemistry*, **2003**, *12(1)*, 17-21.