ELECTROCHEMICAL SYNTHESIS OF POLY-3-AMINOPHENYL BORONIC ACID IN SULFURIC ACID SOLUTION

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ABSTRACT

Sensors based on the complexation of boron groups with diols are an attractive alternative to detection of biologic compounds in particular dopamine. The electropolymerisation of 3-aminophenylboronic acid (APBA) in aqueous solutions on Pt electrodes has been investigated. The obtained poly-3-aminophenylboronic acid is used for the potentiometric detection of dopamine.

INTRODUCTION

Electrochemical sensors based on conducting polymers offer many advantages and new possibilities to detect biologically significant compounds. A most intensively investigated conducting polymer due to its excellent stability in different solutions, good electronic properties, and strong biomolecular interactions is polyaniline (PANI) [1]. Various sensors and biosensors, such as enzyme sensors, DNA sensors and immunosensors based on PANI are reported.[2,3] The emeraldine salt (ES) form is the only conducting state among the four basic states of PANI and can be obtained in acidic conditions (pH = 2.5 ~ 3.0). The pH sensitivity seems unfavourable for application in biosensors, because most bioassays must be performed in neutral or slightly acidic conditions. In order to overcome this disadvantage, functionalization strategies were adopted. Some research used N-substituted anilines instead of PANI and reveals that the alkyl chain, which is covalently bounded to the nitrogen atom, prevents formation of the EB form, and finally the obtained polymer do not have pH sensitivity [4]. Another derivative of PANI, self-doped PANI, which is usually known as sulfonated PANI, shows redox activity even in solutions with neutral pH [5]. Sulfonated PANI was used in amperometric biosensors [6]. It has also been demonstrated that the blends of PANI that included negatively charged co-components such as sulfonic acid or polyacrylic acids exhibit redox activity in neutral aqueous solutions [7]. The presence of boron moiety in PANI chain generated poly(aniline boronic acid) PABA [8] a polymer which exhibits redox activity also in solutions with neutral pH. PABA was used in the detection of fluoride [9], saccharides [10], and dopamine [11] based on analyte interactions with the boronic acid functionality. In this work, PABA has been electrochemically synthesized and explored as a sensing material for dopamine.

MATERIALS and METHODS

Materials and reagents

3-Aminophenylboronic acid hydrochloride (APBA), aniline, dopamine (DA) and sodium fluoride were purchased from Aldrich Chemical Inc. Double distilled water and analytical grade sulphuric acid was used to prepare the electrolyte solutions.

PABA electropolymerization

The electrochemical polymerization of APBA was carried out by cyclic voltammetry using an Autolab PGSTAT 302N. All measurements were performed in a conventional one-compartment, three-electrode electrochemical cell equipped with a Pt disc working electrode (A = 1 cm^2), two graphite rods as counter electrode and an Ag/AgCl electrode as reference electrode. Cyclic voltammograms were recorded at a scan rate of 100 mV s^{-1} in 0.5 M H_2SO_4 solutions with 0.3 M NaF and 0.01 M APBA and respectively 0.03 M APBA.

For the first ten cycles the potential range was from –0.2 V to 1.2 V to allow the initiation of the polymerization process, afterwards the reversal potential was decreased to 0.8 V to avoid the overoxidation reactions of the polymer chain.

The redox activity of the PABA film was investigated by cyclic voltammetry in a monomer free 0.5 M H_2SO_4 solution.

RESULTS

The cyclic voltammograms recorded during the electropolymerization of APBA in 0.5 M H_2SO_4 solution are given in Figure 1. The anodic potential limit was set to 1.2 V for the first 10 scans to initiate the polymerization process, afterwards it was lowered to 0.8 V and the potential was cycled between –0.2 and 0.8 V for the next 20 scans. It has been observed that in the absence on NaF no oxidation of the monomer took place.

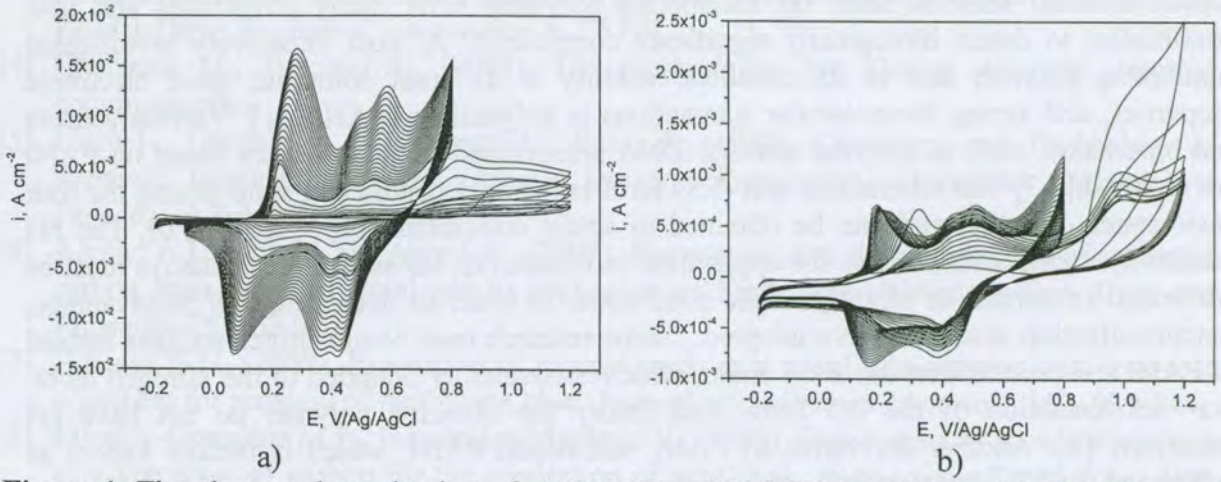


Figure 1. The electropolymerization of a) 0.03 M and b) 0.01M APBA in 0.5 M H_2SO_4 and 0.3M NaF.

The complexation of fluoride with the boronic acid moiety substantially reduced the oxidation potential required for polymerization process.

The shape of the cyclic voltammograms for APBA polymerization resembles closely that of aniline polymerization. For higher monomer concentration the first anodic peak increases during consecutive cycling which is an indication of the polymer film growth. At lower

monomer concentration, the first anodic peak increases to a smaller extent, indicating that the polymerization rate is proportional to the monomer concentration.
The redox behavior of PABA film was recorded in monomer free electrolyte solutions (Figure 2). The three redox peaks corresponding to redox transitions similar to PANI indicate that the obtained film is electroactive. Its color changes from light green to dark blue in dependence of the applied potential.

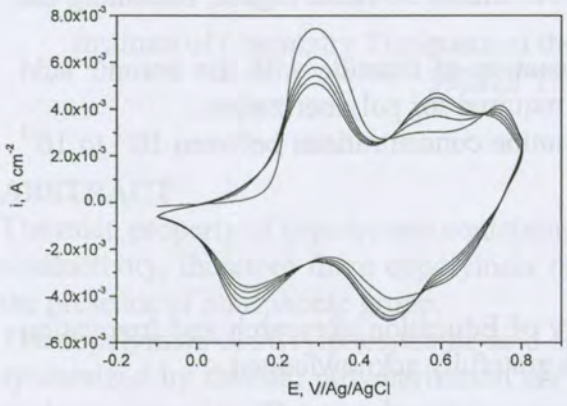


Figure 2. Cyclic voltammograms of PABA in 0.5 M H_2SO_4 solution at 100 mV s^{-1} scan rate.

The obtained PABA film was tested as a sensor for dopamine. The potentiometric calibration curve obtained in dopamine solutions with different concentrations is given in Figure 3.

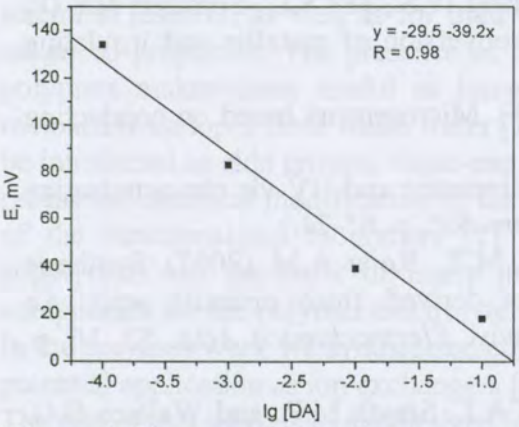
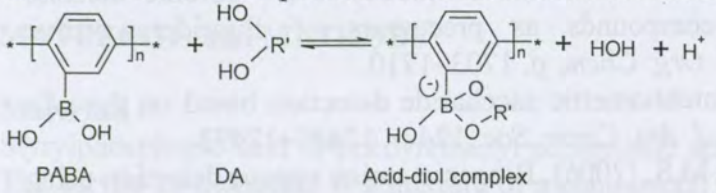


Figure 3. The potentiometric response of PABA electrode for dopamine

The gradual change in potential observed in Figure 3 is due to the effect of boronic acid complexation on the electrochemical potential, due to the increase in electron density ortho to the boronate complex, affecting the *K*a of the protonated amine [12]. At micromolar range concentration of DA used in this study, the formation of a small amount of anionic ester induce an observable potential shift as a result of boronic acid-diol complexation (Scheme 1).



Scheme 1

The electrochemical potential is sensitive to the change in the pKa of the PABA, the response for DA concentration is linear between 10^{-1} to 10^{-4} mol L^{-1}.

CONCLUSIONS

- the electrochemical polymerization of APBA on platinum takes place similarly to the electrochemical synthesis of polyaniline.
- at lower monomer concentrations the first anodic peak doesn't increase linearly with the number of scans, indicating that the film growth is obstructed.
- at higher monomer concentrations the peak current is almost 30 timer higher, indicating the formation of a much thicker polymer film.
- the presence of NaF is necessary because complexation of fluoride with the boronic acid moiety substantially reduced the oxidation potential required for polymerization,
- the PABA sensor shows a linear response for dopamine concentrations between 10^{-1} to 10^{-4} mol L^{-1}.

Acknowledgments

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