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Impedimetric detection of dopamine on poly(3-aminophenylboronic acid) modified skeleton nickel electrodes

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ABSTRACT

Detection of biologic compounds in particular dopamine is usually based on the complexation between boronic acid groups and diols. For this reason the development of new sensors based on direct monitoring of boronic acid–diol complexation is attractive. A measurable electric response due to a change in the dopamine concentration can be achieved on electrodes modified with boronic groups. In this work a modified electrode has been obtained by electropolymerization of 3-aminophenylboronic acid in aqueous solutions on a preformed polyaniline layer electrochemically deposited on smooth and skeleton nickel electrodes. The modified electrodes have been tested as impedimetric sensors for the detection of dopamine in aqueous phosphate buffer at pH = 7.4. Both sensors gave a linear response for dopamine concentrations between 10^{-5} and 10^{-10} mol L^{-1}. Poly(3-aminophenylboronic acid) modified skeleton nickel electrode has the advantage of an increased specific surface area, that lead to a high density of boronic acid groups and hence to a better sensitivity.

1. Introduction

Electrochemical sensors based on conducting polymers offer some advantages and possibilities to detect biological compounds. One of the most intensively investigated conducting polymers is polyaniline (PANI) due to its facile synthesis, excellent stability in different solutions, good electronic properties, and strong biomolecular interactions [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 three oxidation states of PANI and it is obtained in acidic conditions (pH = 2.5–3.0). The pH sensitivity is unfavorable 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. In some studies *N*-substituted anilines were used instead of aniline and it was found that the alkyl chain, which is covalently bonded to the nitrogen atom, prevents the formation of the emeraldine base (EB) form, and finally the obtained polymer is not pH sensitive [4]. Another derivative of PANI, self-doped PANI, which is usually known as sulfonated PAI, shows redox activity even in solutions with neutral pH [5]. Sulfonated PANI was used in amperometric biosensors [6]. It has also been demonstrated that 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 polymerization of monomers containing a boron moiety leads to 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], iodide [10], saccharides [11,12], butylamine [13] and dopamine [14] based on the analyte interactions with the boronic acid functionality. Composite materials for the detection of DA have been developed, based on PABA obtained by template electrochemical polymerization [15]. Also acryloyl derivatives of 3-aminophenylboronic acid have been used to obtain copolymers in form of hydrogels with sensitivity towards glucose detection [16–18]. Most of the papers investigate the electropolymerization of aminophenylboronic acid (ABA) on noble electrodes (platinum or gold) and most of the developed sensors are either amperometric or potentiometric sensors.

In this work a method has been developed for the preparation of a sensitive electrode based on PABA for the detection of dopamine. The method consists in the electrochemical deposition of two layers of conducting polymers, first a polyaniline layer and then a sensitive PABA layer. This approach has been already used for the preparation of an amperometric protein sensor, obtained by the application of two separate polymer layers, one of polypyrole and one of poly-aminophenylboronic acid on screen-printed platinum electrodes [19]. In our work, the polymer films have been

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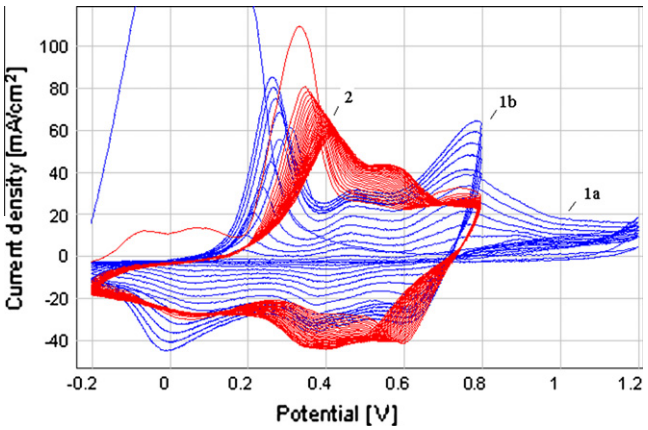

Fig. 1. Cyclic voltammograms obtained during preparation of Ni60/PABA. 1a – initiation of PANI electrodeposition in a larger potential window; 1b – subsequent PANI deposition in a narrow potential window; 2 – electropolymerization of ABA.

deposited on a non-noble substrate with high porosity (skeleton nickel), which ensures an active area much larger than the geometric surface area. This kind of surface offers at the same time high area and also highly active catalytic centers. Similar porous metallic matrices have been used for the electrodeposition of PANI films [20]. The aim of this work is to use such substrates for dopamine sensor design since a high surface area will lead to a high concentration of boronic groups and to a better sensitivity. Another advantage is that skeleton nickel substrates are more accessible from economic point of view compared to other substrates used in sensor design, such as platinum or gold.

2. Experimental

2.1. Materials and reagents

3-Aminophenylboronic acid hydrochloride (ABA, 98%), aniline (⩾99.5%) and 3-hydroxytyramine hydrochloride (dopamine DA, ⩾98.5%) were purchased from Aldrich Chemical Inc. Double distilled water and analytical grade sulphuric acid (Merck, p.a., 95–97%) were used to prepare the electrolyte solutions.

2.2. Preparation of skeleton nickel electrodes (nickel Raney)

One aspect that needs to be considered in the development of the skeleton nickel substrate is to preserve the mechanical resistance of the substrate. Skeleton nickel electrodes were prepared from a smooth nickel plate, wafer, immersed in a bath of molten zinc (at 450 °C) for 30, 60 and respectively 90 min. After the thermal galvanizing step, discs with 15 mm diameter were cut out from the plate. The skeleton structure was obtained by dissolving the zinc from the Ni–Zn alloy formed during thermal diffusion

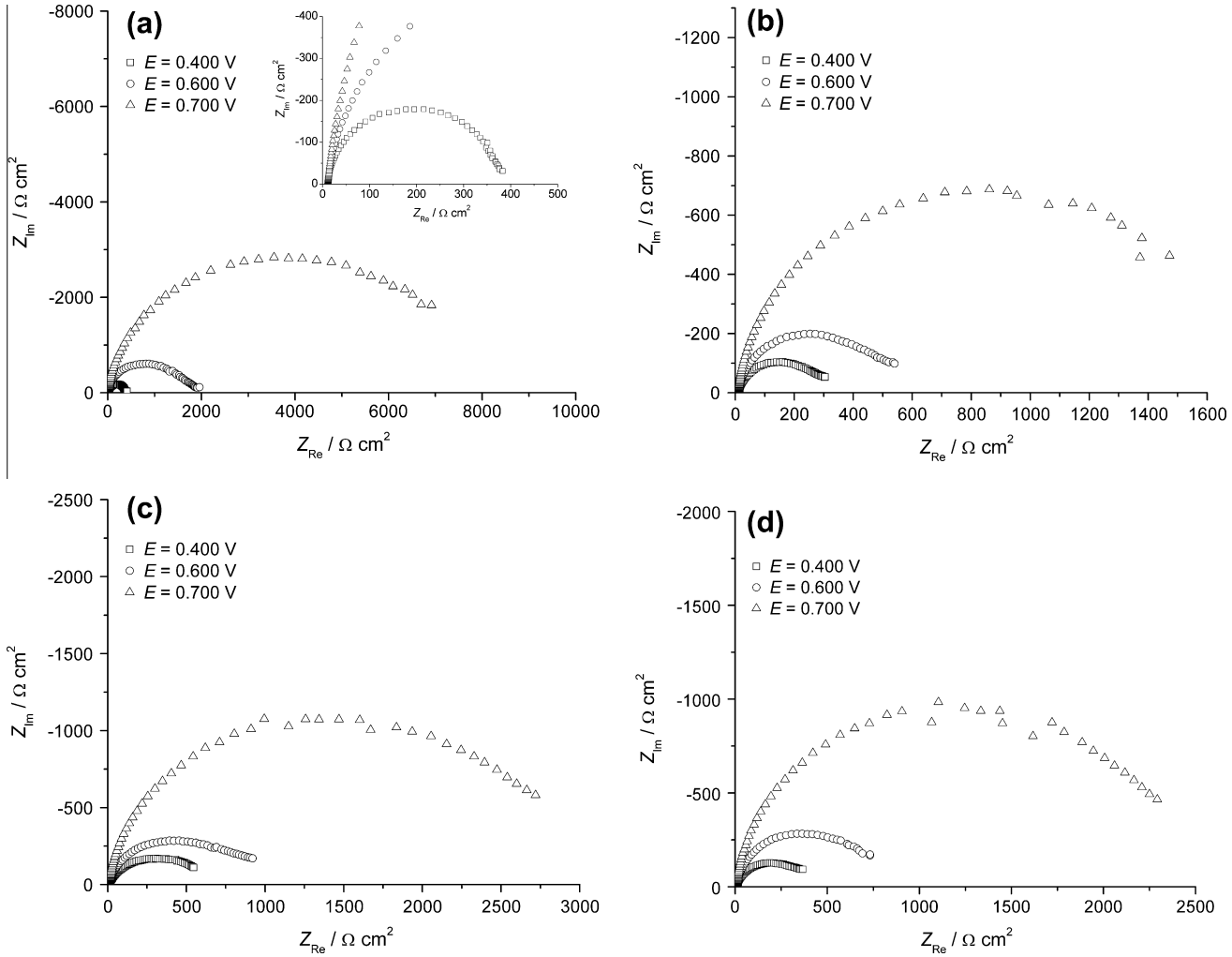

Fig. 2. EIS spectra in 0.5 M H_2SO_4 solution for Ni/PABA (a); Ni30/PABA (b); Ni60/PABA (c) and Ni90/PABA (d).