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# Electrochemical nanogravimetric studies on the electropolymerization of indole and on polyindole

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ABSTRACT

The electrochemical quartz crystal nanobalance has been used to study the formation and redox behavior of polyindole in acid media. It was found that the redox transformations of polyindole are accompanied with the sorption and desorption of counterions. A comparison is made with the electropolymerization of 4-aminoindole and with the behavior of poly(4-aminoindole), where completely different mass change curves have been detected. Based on the results of the nanogravimetric measurements a redox mechanism describing also the pH dependence is suggested.

## 1. Introduction

Research of polymer modified electrodes and the synthesis of new conducting polymers still belong to the main branches of electrochemistry. Owing to the wide range of promising applications [1] research activity is continuously increasing [2].

Electropolymerization of indole has also been studied [3–6], and a wide range of applications of the polymer from corrosion protection via Li-ion batteries to ion sensors and electrochromic devices has been suggested [7–10]. The interesting effect of substituents on the polymerization and the properties of the formed materials make the work with these compounds even more inviting. Basic aspects such as the position of the couplings between the monomers have been disputed, but even the formation of a real polymer has been questioned [11]. For the indole derivatives different suggestions have been made for the linkages [4,12]. Theoretical considerations about the polymer structure support the C2–C3, C2–C7 connections [13,14]. Spectroscopic measurements in the case of derivatives strengthen the view that coupling occurs between the C2–C3 atoms. The formation of cyclic forms was not excluded, either [11,14].

A wide arsenal of non-electrochemical methods has been used to characterize the polymers; however, the electrochemical quartz crystal nanobalance (EQCN) has not been exploited, yet. In the present study we focus our attention on the electropolymerization of indole and the characterization of the resulting polyindole film by using EQCN technique. The difference between the formation and charge transport properties of polyindole and poly(4-aminoindole) [15] is discussed.

## 2. Experimental

The experimental setup and conditions are the same reported in our previous work [15]. Analytical grade chemicals such as $HClO_4$ (Merck), $NaClO_4$ (Merck) and indole (Sigma–Aldrich) were used as received. Doubly distilled water was used (Millipore water). Polymerization was carried out by potentiodynamic cycling at a scan rate of 10 mV $s^{-1}$ by using the solution of 1 mmol $dm^{-3}$ indole dissolved in 1 mol $dm^{-3}$ $HClO_4$. A sodium chloride saturated calomel electrode (SCE) was used as the reference electrode and a platinum wire as the counter electrode. The applied potential ranges are indicated at the discussion of the experiments. The cycling of the potential as a pretreatment of the electrode was carried out before each experiment in the supporting electrolyte, until a voltammogram characteristic to the clean Pt surface was obtained. Indole solutions were always freshly prepared and indole was dissolved in deaerated electrolytes.

Five megahertz AT-cut crystals of one inch diameter coated with platinum with titanium underlayer (Stanford Research Systems, SRS, U.S.A.) were used in the EQCN measurements. The electrochemically and the piezoelectrically active areas were equal to 1.37 $cm^2$ and 0.4 $cm^2$, respectively. The integral sensitivity of the crystals ($C_f$) was found to be $56.6 \times 10^6$ Hz $g^{-1}$ $cm^2$, i.e., 1 Hz

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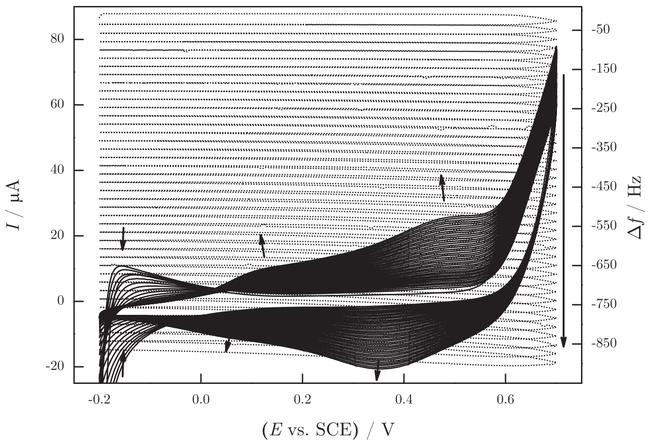

**Fig. 1.** Cyclic voltammograms and the simultaneous change of the frequency during the polymerization of indole (1 mmol dm$^{-3}$ in 1 mol dm$^{-3}$ $HClO_4$), in 40 consecutive cycles, scan rate: 10 mV s$^{-1}$.

corresponds to 17.7 ng cm$^{-2}$. The integral sensitivity was calculated by using the 'effective' charge related to the piezoelectrically active area, i.e., the total charge consumed during the calibration via silver deposition was multiplied by the ratio of the piezoelectrically active and the electrochemically active areas.

## 3. Results and discussion

### 3.1. Electropolymerization of indole

Fig. 1 shows the cyclic voltammetric and the corresponding frequency change curves during 40 consecutive cycles of polymerization. During the first cycles oxidation of the adsorbed hydrogen and the underpotential deposition (UPD) of hydrogen can be observed which were suppressed in the subsequent cycles by the growth of polyindole layer. Based on this observation it can be concluded, that the adsorption ability of indole is comparable with that of the hydrogen.

Possible overoxidation of the film was reported [9]. To avoid this phenomenon the positive potential limit was kept at 0.7 V during the deposition. Oxidation of indole in the first cycle starts at 0.52 V. The anodic current corresponding to the oxidation of the monomer increases in the course of further cycles. The frequency decrease caused by the deposition is uniform from cycle to cycle. The total frequency change within one cycle increases with the increase of film thickness. This refers to the movement of ions between the solution and the film, i.e., in the case of thicker films more and more counterions are needed to compensate the charge on the polymer chains.

Under these circumstances two pairs of peaks corresponding to the redox transformations of the forming polyindole develop gradually. The resulting layer is uniform and has a gold color (Fig. 2).

Fig. 3 shows a typical frequency vs. charge plot. The total charge was calculated integrating the current obtained from the cyclic voltammograms (CVs). The plot contains the charge values belonging to the reduced state of the film ($E = -0.2$ V) and the corresponding frequency change values (an ordered pair from every CV). In this way the charges and frequency changes related to the redox processes of the film are neglected, i.e., only the charge and frequency decrease belonging to the film growth are taken into account. A function $\Delta f = (13.49 \pm 0.30) + (25.298 \pm 0.074) \times 10^3 \times Q^{0.92617 \pm 0.00084}$ perfectly fits the measured points. Taking the first derivative of this function $d\Delta f/dQ$ the variation of the apparent molar mass during the deposition can be determined. It was calculated from the following equation: $M = -d\Delta f/dQ \times nFA/C_f$, where $n$ is the number of electrons transferred in the reaction, $F$ is the Faraday constant, $A$ is the electrode surface area, $C_f$ is the integral sensitivity of the quartz crystal used. This curve is plotted in Fig. 3 as well. Assuming that the apparent molar mass value should be constant, its decrease can be the result of the decrease of the efficiency of the deposition. The apparent molar mass value is calculated for $n = 2$, and it falls from 194 to 144 g mol$^{-1}$ assuming 100% charge efficiency. Since the molar mass of indole is $M_{\text{indole}} = 117.15$ g mol$^{-1}$ it can be assumed that certain amount of solvent and counterions also remain in the film at the end of each cycle.

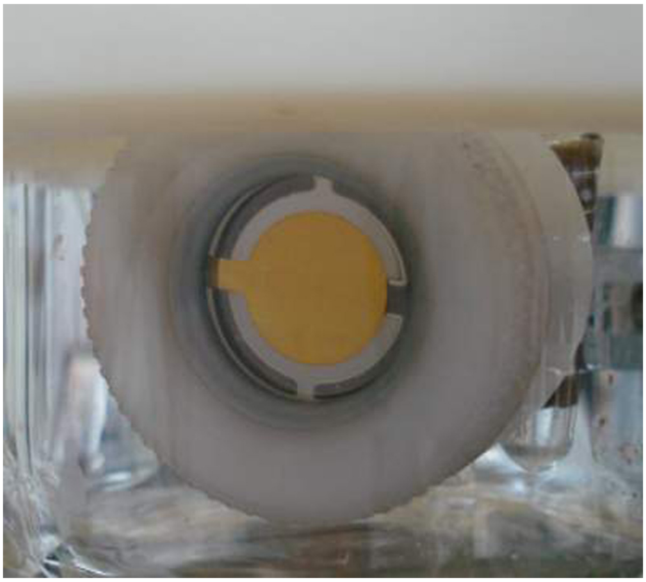

**Fig. 2.** Picture showing the golden polyindole layer on a platinum EQCN electrode.

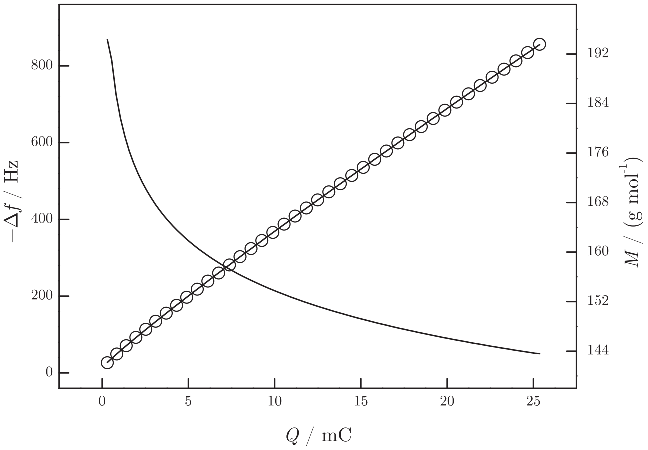

**Fig. 3.** Frequency change vs. charge curve together with its derivative. The charge values were obtained from the cyclic voltammograms, and they correspond to the end of each cycle, i.e., to the reduced, neutral state of the polymer. A power function was fitted to the points, from whose derivative the apparent molar mass values were calculated.

### 3.2. Comparing the electropolymerization of indole and 4-aminoindole

The case of these two molecules, which only differ in an amino-group from each other, is a salient example, how largely a small change in structure may influence the polymerization process. The presence of adsorbed 4-aminoindole on Pt surface is already noticeable in the first cycle of polymerization [15]. As seen in Fig. 4