



# Nucleation of metals on conductive polymers: Electrodeposition of silver on thin polypyrrole films



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## ABSTRACT

The electrodeposition of silver was examined under conditions that excluded a possibility of electroless formation of polypyrrole and silver crystallites. The polymer layers were appropriately prepared; after finishing the polymerization and before the silver reduction they were oxidized. A comparison of the theoretical chronoamperograms with the experimental data, appropriately corrected for the induction time, revealed that the progressive nucleation took place for all examined polymer films and deposition potentials. For lower overpotentials the Ag nuclei were mainly formed under the polymer layer and in its pores. An explanation was given for why the Ag crystallites cannot be completely oxidized from the polypyrrole films.

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## 1. Introduction

The composites containing conducting polymers (CP) and nano- and micro-particles of metals are very interesting materials due to, among others, their catalytic properties [1–6]. Many electroless and electrodriven methods of synthesis are described in literature. Electroless methods are based on the spontaneous red-ox reaction between the monomers and the metal ions present in the same solution [7,8] or on the reaction occurring at the liquid–liquid interphase [9,10]. The electrodeposition of polymer and metallic particles from two separated solutions: one containing the monomer and the other the metal salt [1,11,12], and the electrooxidation of the monomer in a solution containing colloidal metal particles [13,14] are popular electrochemical methods of synthesis of composites. The electrodeposition of both components independently from one solution is also possible [15]. Finally, electrodeposition of metal on the polymer layer functionalized by pendant redox-active centers was proposed [16].

Potentiodynamic and potentiostatic technics allow modification of composition and structure of composites by controlling electrode potential, current intensity and time of electrodeposition. The catalytic properties of these materials depend, to a considerable degree, on amount and dispersion of noble-metal deposit and on method of inserting metal particles into the polymer layer [17–19]. However, the mechanism of deposition of metals on the

surface of conducting polymers using the electrochemical technics is not quite clear. The growth of the metallic phase is preceded by the nucleation step. The theory of nucleation of metals on surfaces proposed by Scharifker and Hills (SH) [20,21] was widely used for the examination of the process of electrodeposition of metals such as Au, Ag, Pt, Pd, Ni and Cu on the carbon- [22–25], silicon- [26,27] and metallic substrates [28–32]. As it was demonstrated by Scharifker et al., this theory is also applicable in the case of deposition of metals on thin three-dimensional substrates such as conducting polymer layers [33]. However, the number of papers dedicated to the nucleation on polymers is relatively small [34–36]. Moreover, a possible influence of the electroless deposition of metals on the nucleation process was not discussed at all.

In this paper we report on the study of the mechanism of silver electrocrystallization on thin polypyrrole (PP) layers. The proposed procedure of completing the polymerization process and pre-oxidation of PPy films allowed the elimination of the spontaneous reaction of electroless deposition of silver and the examination of the undisturbed process of the electroreduction of Ag<sup>+</sup> ions on the polymer surface. The mechanism of silver nucleation was determined according to the SH model. The scanning electron microscopy was used in analysis of metallic deposits on the PPy films.

## 2. Experimental

### 2.1. Apparatus and reagents

All electrochemical experiments were performed using the three electrode system and a PAR VersaSTAT 4 potentiostat. A glassy

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carbon (GC) disk electrode with diameter of 3.0 mm and a large-area platinum electrode were used as the working- and the counter electrode, respectively. All potentials were referred to the saturated calomel electrode (SCE). Before each deposition of the conducting polymer, the GC electrode was polished with 1.0- and 0.3- $\mu\text{m}$  alumina powders and rinsed with deionized water.

Structure and composition of the PPy/Ag composites were examined using scanning electron microscopes (SEM, model LEO 435 VP and Merlin, Zeiss) equipped with an energy-dispersive spectrometer (EDS, Roentec and Bruker, respectively).

Pyrrole (Aldrich), silver nitrate (POCH),  $\text{NaClO}_4$  (Fluka) as supporting electrolyte and deionized water obtained from Ultrapure Milli-Q system (water resistivity: 18.2  $\text{M}\Omega\text{cm}$ ) were used for the preparation of the solutions. All reagents used were of analytical grade purity. Pyrrole was distilled before use. The solutions were deoxygenated and the experiments were carried out at room temperature.

## 2.2. Preparation of polypyrrole layer

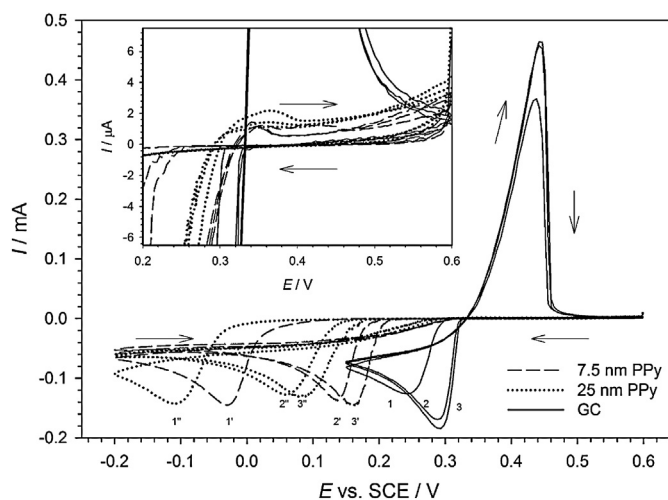
The PPy films were deposited by polarizing the GC electrode cyclically between  $-1.0$  and  $0.8$  V at  $20$   $\text{mV s}^{-1}$ . The synthesis was carried out in a 10 mM monomer solution containing 0.1 M  $\text{NaClO}_4$ . The thickness of polymer films was estimated using the procedure given in [37]. The anodic charge of deposition of PPy was calculated from CV curves after subtracting the background. The thickness of the examined PP layers, corresponding to 2 and 5 cycles of deposition, was ca. 7.5 and 25 nm, respectively. The GC substrates covered with PPy films were rinsed with deionized water, moved to a monomer-free 0.1 M supporting electrolyte solution, polarized cyclically from  $-1.0$  to  $0.8$  V to remove monomers and oligomers present in the conducting polymer layers, and finally kept at 0.6 V for 10 min to complete the polymerization reaction and to oxidize the polymer. The corresponding voltammograms can be inspected in Ref [15]. Always a new CP layer was prepared for the next  $\text{Ag}^+$  electroreduction process.

## 2.3. Silver electrodeposition on the PPy surface

The potential range of silver electrodeposition on the surface of the conducting polymer was determined from cyclic voltammograms obtained in a  $\text{AgNO}_3$  solution in 0.25 M  $\text{NaClO}_4$  using PPy in the oxidized form as the substrate. The CV curves recorded for different concentrations of  $\text{Ag}^+$  ions at selected potential sweep rates were also useful in the preliminary examination of the kinetics and mechanism of the silver electroreduction process on the PPy films. The initial potential for all recorded voltammograms was 0.6 V. Before the potential step experiments, the electrodes were kept for 30 s at 0.4 V where the electroreduction of silver could not occur.

## 3. Results and discussion

Properties and quality of the surface of the substrate are the most important factors that influence the nucleation process. When the nucleation process occurs at a polymer layer, the metal ions can be reduced either by the monomers and oligomers present in the polymer layer or by the reduced form of the polymer [38,39]. We have seen that for the as deposited PPy film. The metal nuclei formed by electroless deposition change the physical and chemical characteristics of the substrate and affect the process of electroreduction of metal ions on the surface of the polymer. That is why the CP films in the inactive form toward metal ions should be used for the examination of the process of electroreduction of metals on the polymer surface. In order to eliminate the process of electroless deposition of silver on the surface of polypyrrole, the CP



**Fig. 1.** Voltammograms obtained in 10 mM  $\text{AgNO}_3$  on bare GC and oxidized PPy electrodes;  $\nu = 20$   $\text{mV s}^{-1}$ . The first three consecutive scans are shown for each case. Signals corresponding to oxidation of silver deposited on PPy substrate are magnified in inset.

layers were prepared according to the procedure described in the experimental section. It is worth noting, that even after immersion (at open circuit) of those PPy substrates in 10 mM  $\text{Ag}^+$  for 30 min, a detectable amount of silver deposit was never found on the surface of the polymer using the SEM-EDS analysis. We have examined the open circuit potentials of the nontreated and treated polymer layers and got 0.15 and 0.45 V, respectively, while the estimated formal potential for  $\text{Ag}/\text{Ag}$  couple in the plating solution was circa 0.35 V.

Typical cyclic voltammograms for silver electroreduction on the surface of GC and on initially oxidized PPy film are presented in Fig. 1. In the case of the polymer substrate two interesting effects were noticed. First, a strong shift of the reduction peaks to more negative potentials in comparison to the peak obtained for the GC electrode and a large hysteresis in the voltammograms were observed. These results illustrated a substantial overpotential required for the electroreduction of  $\text{Ag}^+$  ions on the polymer layer. The thicker polypyrrole layer the bigger overpotential of silver deposition was. Second, only very small signals of silver oxidation from the polymer surface were observed in the reversed scan (see inset in Fig. 1). Furthermore, a decrease in the deposition overpotential was noticed for subsequent scans. This suggests that a significant part of the deposited silver was not oxidized during the anodic scan. Apparently, the silver remaining on the surface makes the electroreduction in the consecutive scans faster. However, the reduction overpotential never disappears, even after tens of cycles. Probably, to become active in the electrodeposition process the Ag crystallites remaining on the surface require the rebuilding of the electrical contact with the electrode substrate.

The next voltammetric experiments involved different  $\text{AgNO}_3$  concentrations and various scan rates (see Figs. 2 and 3). As it is seen in Fig. 2, the cathodic peaks were shifted to more negative potentials with a decrease in concentration of  $\text{Ag}^+$  ions in the solution. Contrary, a decrease in the overpotential of silver electroreduction was noticed for low scan rates (see Fig. 3). The lower scan rate means that more time is available for the formation and growth of silver nuclei. Therefore, as expected, the cathodic current corresponding to the growth of silver crystals appeared at lower overpotential when more  $\text{Ag}^+$  ions were present at the surface of electrode and when the deposition was carried out for a prolonged time. The reduction current in the backward scan apparently increased for lower scan rates, which is clearly a consequence of a substantial growth of the area of the Ag crystals.

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