

Electrodeposition of silver on ultra thin polypyrrole films.
 Approach to unusual nucleation of metal.
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The interest in polymer-metal composites is growing recently, especially due to their ability of electrocatalytic oxidation of alcohols [1,2] that can be used in fuel cells. The application of a composite for electrochemical purposes requires earlier modification of the electrode surface with a layer of that composite. The properties of these materials depend on their composition and structure. The electrochemical methods of synthesis give a good control of the content of both components [3].

In this presentation we illustrate the mechanism of electrodeposition of silver on ultra thin polypyrrole layers that modify the surface of glassy carbon electrodes. The electrochemical techniques and scanning electron microscopy were used to examine the early stages of the formation of silver crystals on the surface of the conducting polymer.

Well defined properties and quality of the surface of the substrate are very important for the electrodeposition. A key problem for solving before the electroreduction of Ag^+ ions on the polymer film was to inhibit the spontaneous reaction of the electroless deposition of silver. A procedure of preparation of PPy layers for electrochemical experiments that consist of potentiodynamic and potentiostatic pre-oxidation of the conducting polymer were proposed.

Cyclic voltammetry was used to determine the potential range of silver electrodeposition on the thin PPy films. The dependencies of cathodic peak potential on concentration of Ag^+ ions and scan rate were also examined.

In the case of three dimensional polymer layers the solution containing metal ions can penetrate the pores of the polymer substrate. SEM analysis of silver deposits obtained for different overpotentials showed that Ag^+ ions could be reduced inside the polymer film and directly on the PPy surface. This resulted in two possible structures of the silver crystals: dendrites and grains.

The mechanism and kinetics of Ag nucleation were examined for two thicknesses of the PPy layers: 7.5 and 25 nm. Typical nucleation curves were obtained. The formation and growth of silver nuclei on the surface of the polymer was preceded by the induction process. Induction time was correlated with overpotential and PPy layer thickness. A detailed analysis of chronoamperograms and polypyrrole-silver composites showed (see Fig. 1) unusual course of the nucleation process. We observed that under-layer metal deposition occurs during the induction process and does not affect the currents corresponding to metal nucleation on the surface of polymer.

The theory of nucleation of metals proposed by Scharifker and Hills [4] was used to determine the mechanism of formation and growth of silver nuclei on thin PPy films. Furthermore, the influence of deposition overpotential and thickness of polymer film on the nucleation density was observed.

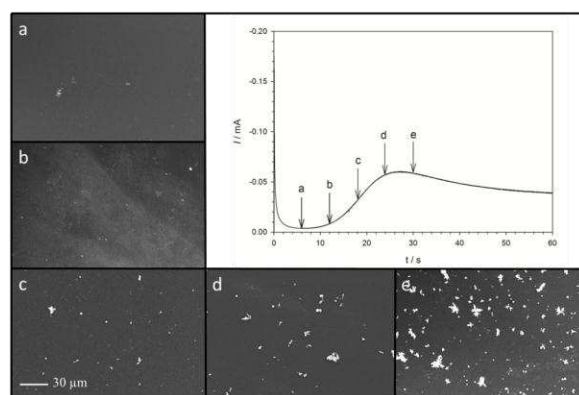


Figure 1
 Consecutive stages of Ag nucleation and growth on 25 nm PPy layer at potential +0.050 V vs. SCE. SEM images correspond to deposition times marked by arrows on the chronoamperogram.

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