High-density Pd nanoparticles distribution on PEDOT obtained through electroless metal deposition on pre-reduced polymer layers

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A B S T R A C T

Pd electroless deposition is carried out at the expense of oxidation of pre-reduced poly(3,4-ethylene dioxythiophene) (PEDOT)-coated electrodes. Two largely differing potentials for deep and mild pre-reduction of PEDOT are chosen and correspond to initial low (deep pre-reduction) and, correspondingly, high (mild pre-reduction) conductive states of the polymer material. The role of organic doping ions (polysterene sulfonate, PSS or dodecyl sulfate, SDS) used in the course of PEDOT synthesis for the electroless deposition of Pd is also investigated. PEDOT-supported Pd catalysts with high-density homogeneous distribution of Pd nanoparticles (NPs) with sizes ranging between 4 and 12 nm are obtained. The amount of deposited metal depends significantly on the pre-reduction potential of PEDOT whereas the surface density of the metal NPs is largely influenced by the doping ions used to obtain the PEDOT material. Evidence for irreversible structural transformation obtained upon deep pre-reduction of PEDOT:SDS is obtained.

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1. Introduction

Conducting polymers (CPs) may take different interconvertible oxidation states and therefore provide the opportunity for chemical (electroless) deposition of metals at the expense of the polymer oxidative transition from lower to higher oxidation state. This spontaneous process occurs without additional reductants in the solution and becomes driven by the difference in the initial potential of the CP-coated electrode (when put into contact with the metal ions solution) and the equilibrium potential of the depositing metal ions. This approach for metal deposition is used for noble metals such as Au, Ag, Pd, Pt and also for Hg that that have equilibrium potentials positive enough with respect to the potentials of oxidative transitions of the CP materials (see review papers [1–3] and literature cited therein).

There are basically two directions in the studies of electroless metal deposition on CPs: i/to use the process for removal of metal ions from waste or contaminated solutions [4–11] or ii/to obtain catalytic materials with well dispersed metallic phase [12–21]. Whereas in the first case the main task is to obtain materials with high loading capacity and possibility for subsequent recovery of the metal phase, in the second one the main aim is to control the amount and dispersion (size and surface distribution) of the metallic particles in order to ensure optimal catalytic properties and high mass activity with respect to given electrocatalytic reactions.

Palladium alone or in combination with other metals is a catalytic metal that is largely used for electrochemical reactions such as reduction of oxygen or oxidation of hydrazine, glycerol, ethanol, methanol, formic acid, etc. Electroless deposition of Pd on conducting polymer-coated electrodes is studied by using polyaniline [7,13,18,22,23], polypyrrole [12,24], and poly(3,4-ethylene dioxythiophene) (PEDOT) [14–17,21,25,26] as supports. Although the electroless process seems in many cases a suitable alternative to other methods for metal particles deposition in CPs there are still no abundant studies in this field and basically there is little understanding on how to affect the characteristics of the metallic phase. In general, different factors may influence the process originating from the characteristics of both the polymer support and the metal plating solution. For instance, in the case of Pd the role of the surface morphology of electrochemically synthesized PANI layers was studied by Mourato et al. [13]. The surface structure was intentionally modified by using two different potentiodynamic polymerization regimes. Thus, it was found that for a more compact PANI surface, Pd clusters with an average size of 20 nm and also larger particles with a size distribution between

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80 and 200 nm are formed. In the case of a more porous surface morphology, smaller clusters (15 nm) with very narrow size distribution were observed, together with larger particles in the 100–200 nm range. A series of studies on the electroless deposition of Pd (from PdCl$_2$ solution) were carried out on PEDOT obtained in acetonitrile in the presence of ClO$^-_4$ as doping ions [16,26]. Microscopic pictures have shown the availability of Pd nanoparticles (with sizes between 10 to 20 nm) that are preferentially located on the protruding morphological features of a largely porous structure (50 to 200 nm large pores). The reductive pretreatment of PEDOT was completed at a potential corresponding presumably to the high conductive state of PEDOT. In a recent study [21] focused on the possibility to use Pd/PEDOT as a catalyst for glycerol oxidation a much more negative potential was used for pre-reduction of PEDOT in order to increase the amount of deposited metal. The size of the deposited Pd NPs was estimated to be 12 nm. Apart from these individual observations there are no studies revealing the role of the potential used in the pre-reduction step for the electroless deposition of Pd. Therefore one of the aims of this investigation is to study, at otherwise identical conditions, Pd electroless deposition at two largely differing pre-reduction potentials of PEDOT chosen in a way to correspond to the range of low and high conductive initial state of this polymer material.

Furthermore, in recent studies on the electroless deposition of silver on PEDOT [27,28] it was demonstrated that the difference in the polymer doping may influence markedly the electroless deposition process by affecting both the amount and characteristics of the obtained metallic particles. In these studies PEDOT layers were obtained in the presence of perchlorate and either polysterene sulfonate (PSS) or dodecyl sulfate (SDS) ions, i.e. the properties of the CP layers were influenced by inorganic/organic ions doping. The second aim of the present study is to investigate the role of individual organic doping ions (PSS or SDS) used in the course of PEDOT synthesis for the electroless deposition of Pd. For this purpose two types of PEDOT coatings are obtained by using aqueous EDOT solutions containing either sodium polysterene sulfonate or sodium dodecyl sulfate as salts. Previous investigations [29,30] have already shown that PEDOT coatings obtained under these conditions have markedly different surface morphology and viscoelastic properties, with significant stiffness imparted by the dodecyl sulfate anions. It was established that upon reduction cationic ingress is characteristic for PEDOT:PSS whereas mixed anionic and cationic transport is observed for PEDOT:SDS with cationic ingress prevailing at more negative potentials [30]. Another important difference between both type of layers is the lower amount of water molecules exchanged upon reduction/oxidation that corresponds to the high stiffness of PEDOT:SDS and reflects the hydrophobic nature of the PEDOT:SDS material. The role of different polysulfonic acids used to dope PEDOT for the spectroelectrochemical characteristics of the obtained polymer materials was recently studied [31]. Hydrophobic/hydrophilic interactions of the PEDOT chains with the different doping polyanions were discussed in order to explain the observed differences in the spectroelectrochemical behavior.

2. Experimental

All electrolyte solutions were prepared with deionized water (ρ = 18.2 $M\Omega\,cm$) obtained from Millipore Synergy^{TM} Ultrapure Water Purification System. Before starting electrochemical measurements the electrolytes were de-aerated with argon for at least 20 min and kept under argon atmosphere thereafter. A computer-driven potentiostat/galvanostat (Autolab PGSTAT 12; Ecochemie, The Netherlands) was used for the electrochemical measurements. The electrochemical experiments were carried out in three electrode cells by using a platinum plate counter electrode and

a mercury/mercury sulfate reference electrode (MSE) (Hg/Hg$_2$SO$_4$/ 0.5 $mol\,cm^{-3}$ K$_2$SO$_4$). All potentials in the text are referred to MSE, $E_{MSE/K2SO4}$ = 0.66 V vs. SHE. Spectral graphite rods (Ringsdorff-Werke GMBH) with diameter 0.3 cm and exposed front surface area, S = 0.071 cm^2 were used as working electrodes. The exposed graphite surface was pre-treated with emery cloth (Buehler P5000) and rinsed with water before use.

Electrochemical polymerization of EDOT was carried out in aqueous solution consisting of 0.01 $mol\,cm^{-3}$ EDOT and either 34 $mmol\,cm^{-3}$ of sodium polystene sulfonate or 34 $mmol\,cm^{-3}$ sodium dodecyl sulfate at constant anodic potential, E_a = 0.36 V. PEDOT films with polymerization charges Q_{poly} = 5.3 mC were used in this study. The two type of PEDOT materials will be further denoted as PEDOT:PSS and PEDOT:SDS, respectively. A formal estimation of the thickness, d of the obtained PEDOT layers based on the polymerization charge and Faraday's law results in d = 0.37 μm. This is however a rather approximate evaluation of the polymer film thickness as far as at one and the same polymerization charge the thickness may vary significantly depending on the available doping ions (see e.g. [30])

After synthesis, the polymer-coated electrodes were transferred in supporting electrolyte (0.1 $mol\,cm^{-3}$ LiClO$_4$) for evaluation of their electroactivity. In the same electrolyte, the polymer layers were electrochemically reduced by keeping the working electrode at constant potential, either E = −0.66 V or E = −1.4 V, for 1200 s. These two conditions for pre-reduction of PEDOT will be further referred to as "mild" (at E = −0.66 V) and "deep" (at E = −1.4 V) reductions, respectively. In the first case PEDOT is reduced in the pseudocapacitive potential region and remains in its high conducting state whereas in the second one PEDOT suffers complete reduction. Electroless deposition of palladium was carried out by dipping the pre-reduced PEDOT layers in an aqueous solution of 2 $mmol\,cm^{-3}$ PdSO$_4$ and 0.5 $mol\,cm^{-3}$ H$_2$SO$_4$. The equilibrium potential of Pd^{2+}/Pd in this solution is $E_0(Pd^{2+}/Pd^0)$ = 0.195 V. The electroless deposition process was monitored through the change in the open circuit potential (OCP) of the PEDOT-coated electrode. The process was stopped at E_{OCP} = −0.05 V. After this step some of the specimens were used for SEM observation. Identical specimens were prepared and used to determine the mass of the deposited Pd by anodic voltammetric stripping completed in aqueous solution of 1.15 $mol\,cm^{-3}$ hydrochloric acid.

Microscopic observation of the Pd/PEDOT-coated specimens was completed by means of a JSM 7800-F device at Jeol Europe BV.

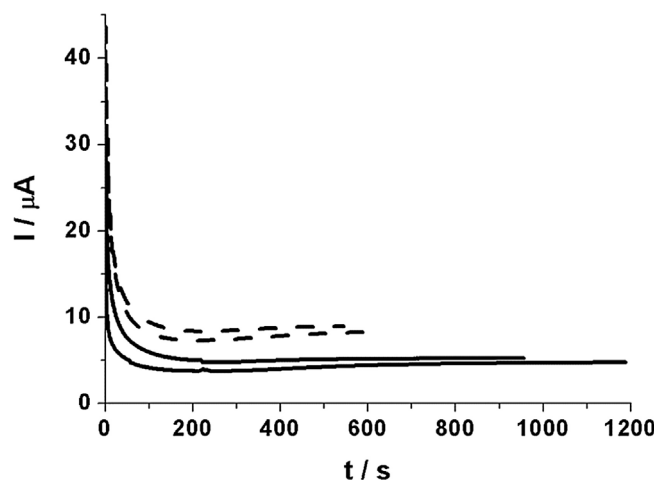**Fig. 1.** Sets of polymerization curves obtained in the presence of 34 $mmol\,cm^{-3}$ PSS (full lines) or SDS (dashed lines) in the aqueous solution of EDOT (10 $mmol\,cm^{-3}$).