METAL INCORPORATION IN CONDUCTING POLYMERS BY ELECTROLESS DEPOSITION

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ABSTRACT

The incorporation of metals in organic conducting polymers by electroless deposition is demonstrated for Ni-P on electropolymerized polyaniline films.

The creation of starting catalytic conditions for effective nickel electroless deposition is discussed and the influence of the electropolymerization conditions on the metal particles dispersion is analysed. Nickel electroless deposition has been carried out on polymer films built up to various thicknesses in order to produce several metallic contents and / or different sized Ni-P particles. The so-obtained modified electrodes have been characterised including its redox behaviour.

Key Words: Surface Modified Electrodes; Conducting Polymers; Polyaniline; Electroless; Ni-P

INTRODUCTION

During the last decade a lot of work has been devoted to the preparation of surface modified electrodes [1,2]. A considerable part of these investigations is concerned to the use of conductive organic polymers [3,4] being one of the most interesting aspects the incorporation of metals in the polymeric matrix [5-8]. Actually, there exist several potential applications for these promising materials in the areas of catalysis, photocatalysis, sensor development and in other specific fields making use of metal-polymer-metal composites.

There are different methods of manufacturing polymer modified electrodes containing metal particles but most of the published studies are related to classical metal electrodeposition [5,9] and therefore mainly focused on noble metals. Also, the possible spontaneous and sustained reduction of gold [6], palladium [10] and silver [11] on Polyaniline films has been demonstrated; although this process presents obvious importance either in the field of extractive metallurgy or to obtain modified electrodes for electrocatalysis, it is restricted to metals which deposit at potentials coping with the range where the spontaneous deprotonation of the polymer (e.g. protonated emeraldine) occurs.

Recently we have reported [12] a novel procedure to obtain modified electrodes containing metal particles. Electroless nickel deposition, from a hypophosphite based solution, has shown to be

a suitable method to incorporate Ni-P into Poly-3-methylthiophene films. Indeed a satisfactory particle dispersion has been observed and the presence of the metal was seen not to deteriorate the pristine polymer redox features.In the present work, we expand the methodology to Polyaniline films.

EXPERIMENTAL

From a solution containing 0.1 mol dm^{-3} aniline in 0.5 mol dm^{-3} H_2SO_4, the polyaniline (PANI) films were grown potentiodynamically at $v = 20$ mV s^{-1} [13] and galvanostatically at $i_g = 0.15$ mA cm^{-2} on a specpure Pt disk (0.196 cm^2 geometric area), being illustrated in figure 1 the cyclic voltammograms and potential profile recorded during the polymer growth.
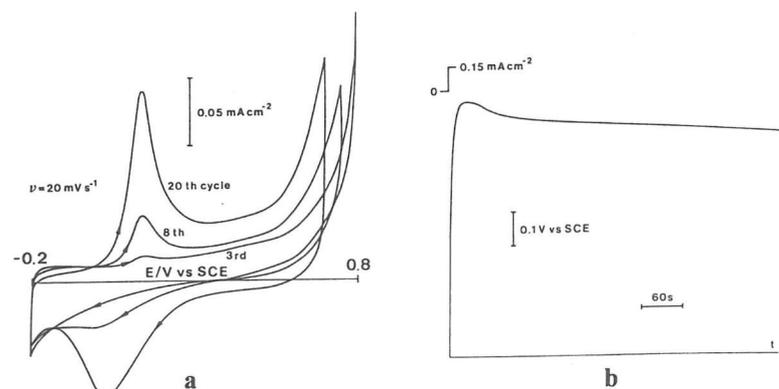
Fig. 1 - Electrochemical growth of PANI under potentiodynamic (a) and galvanostatic (b) control.

After polarisation of the polyaniline films at 0.5V in a 0.5M H_2SO_4 solution for 30s, the incorporation of catalytic nuclei of Ni was carried out by a potentiostatic pulse to -1.0V for 5s in a solution containing 0.2 mol dm^{-3} $NiSO_4$. The electroless deposition of Ni-P was performed by immersion of the PANI/Ni modified electrodes in a solution containing 0.2 mol dm^{-3} $NiSO_4$ and 0.5 mol dm^{-3} NaH_2PO_2 for 60s.

The metal dispersion on the polymer was checked by optical microscopy and the modified electrodes were characterised by cyclic voltammetry at $v = 20$ mV s^{-1} in a 0.5M H_2SO_4 solution. The electrocatalytic activity of the modified electrodes for the hydrogen evolution reaction was evaluated performing steady state polarisation curves in an aqueous solution containing 0.1 mol dm^{-3} NaCl.

With the exception of the electroless Ni-P deposition which was carried out at 70°C, all the experiments were performed at room temperature in a three electrode two compartment cell, being

the solutions thoroughly deoxygenated directly in the cell with high purity Ar prior to measurements. The electrode potentials are referred to the saturated calomel electrode (SCE).

RESULTS AND DISCUSSION

The current transients of the potentiostatic incorporation of Ni on PANI films with approximately the same thickness (compared by the oxidation charge displayed by the voltammetric analysis) but synthesised by different electrochemical modes - figure 2 - reveal two stages of nickel deposition. While over the galvanostatically synthesised film a dense and homogeneous dispersion of small nuclei is observed, on the potentiodynamically grown PANI a less uniform dispersion of larger nuclei is obtained.
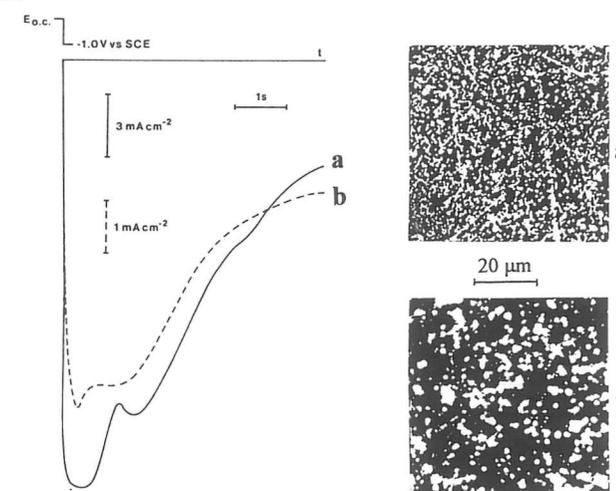
Fig. 2 - Current transients of the potentiostatic incorporation of Ni in PANI synthesised galvanostatically with $Q_g = 36$ mC cm^{-2} (a) and potentiodynamically with 20 cycles of growth (b). Also shown the photomicrographs of the obtained electrodes.

For films deposited under galvanostatic control, the effect of the polymer thickness in the electrodeposition of nickel is displayed in figure 3; for a thin film the current transient displays two waves related to the different stages of Ni electrodeposition, and a uniform dispersion of metallic nuclei is achieved, in contrast with the one-step process which takes place in the thick polymer, leading to a deposition of large metallic clusters. This observation suggests that the polymer becomes more dense with the thickening - in agreement with the electrode potential decrease observed during the galvanostatic growth - with the correspondent decrease of the number of the active sites for metallic reduction. The two current waves displayed during the electroreduction of Ni in porous films will be later related to the deposition over the surface and within the pores of the polymer.

The redox behaviour of the modified electrodes is presented in figure 4, showing that electrodissolution of nickel occurs in two steps. For thin films, a structured voltammogram is
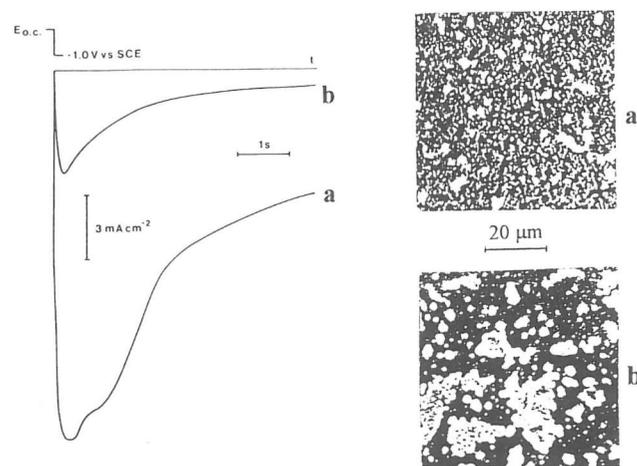
Fig. 3 - Current transients of the potentiostatic incorporation of Ni in PANI synthesised galvanostatically with Q_g = 18 (a) and 72 mC cm^{-2} (b). Also shown the photomicrographs of the obtained electrodes.

observed with one or two anodic waves preceding the main oxidation peak. As for the thick film only the peak at E ≈ 0.15V occurs, we can presume that the anodic waves taking place at E < 0.10V are related with the electrooxidation of the metal embedded in the pores of the polymer, occurring the oxidation of the metal deposited at the surface, at higher electrode potentials.
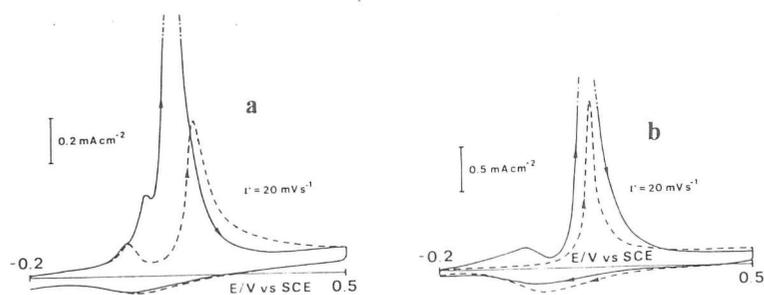
Fig. 4 - Cyclic voltammograms of PANI / Ni modified electrodes in 0.5M H$_2$SO$_4$. (a) PANI (i$_g$) 18 mC cm^{-2} (——) and PANI (CV$_g$) 20 cycles (-----); (b) PANI (i$_g$) 36 mC cm^{-2} (——) and 72 mC cm^{-2} (-----).

Films of nickel containing polyaniline exhibit catalytic properties for electroless Ni-P plating. Autocatalytic nickel deposition from an hypophosphite containing solution was carried out over the

so modified electrodes. The amount and dispersion of electrodeposited Ni reflects the PANI structure induced by the electrochemical mode followed to prepare the polymer, and determine the subsequent incorporation of Ni-P. The incorporation of Ni-P in the film gives rise to an increase in the dimension of the metallic particles by a 3D growth on the starting nickel nuclei as illustrated in figure 5.
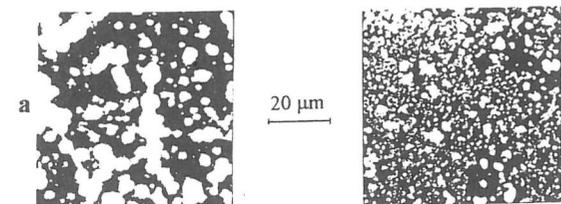
Fig. 5 - Photomicrographs of PANI / Ni-P modified electrodes. (a) PANI (CV$_g$) 20 cycles and (b) PANI (i$_g$) 36 mC cm^{-2}.

The electrochemical behaviour of PANI/Ni-P films - figure 6 - reveals an increase of the metallic content both at the surface and within the pores. For PANI films with approximately the same thickness and synthesised under different electrochemical modes, the increase of the currents of the peaks at E < 0.1V, which are ascribed to the oxidation of Ni-P and to the respective Ni starting nuclei, suggests that the deposition of Ni-P occurs on the pores of the polymer. In the potentiodynamically grown film the extent of the deposition inside the polymer is smaller, likely due to a lower pore dimension. On the other hand, in the galvanostatically synthesised film, a higher concentration of Ni-P in the pores of the polymer is achieved resulting in a peak at E = - 0.04V followed by the oxidation of nickel starting nuclei at E = 0.02V. On this modified electrode it is also possible to discriminate the oxidation of surface deposited Ni-P.
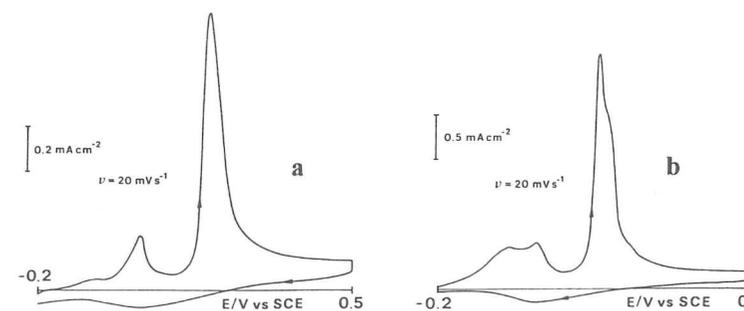
Fig. 6 - Cyclic voltammograms of PANI / Ni-P modified electrodes in 0.5M H$_2$SO$_4$. (a) PANI (CV$_g$) 20 cycles and (b) PANI (i$_g$) 36 mC cm^{-2}.

The PANI/Ni-P modified electrodes exhibits catalytic activity for the hydrogen evolution reaction - figure 7 - being the best results (similar to those obtained for a solid electrodeposited nickel electrode with the same geometric area [12]) achieved for high porous, medium thick films, where good dispersions of small Ni-P particles have been observed.
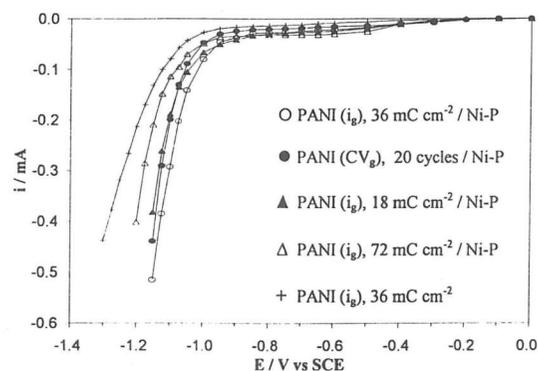
Fig. 7 - Steady state polarisation curves of the modified electrodes for the HER in 0.1 mol dm^{-3} NaCl.

CONCLUSIONS

The electroless incorporation of Ni-P in electrosynthesised polyaniline films can be achieved providing that some starting nuclei of nickel has been dispersed in the polymer. The autocatalytic deposition occurs on the nickel clusters and is a 3D - growth process.

The potentiostatic incorporation of nickel in PANI takes place both over the surface and within the pores of the polymer. The amount and dispersion of the metal is dependent on the structure of the polyaniline which is induced by the electrochemical mode of growth and by the synthesis conditions.

The PANI / Ni-P modified electrodes reveal good catalytic activity towards the hydrogen evolution reaction, providing that a good dispersion of the Ni-P particles over the polymer is achieved.

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