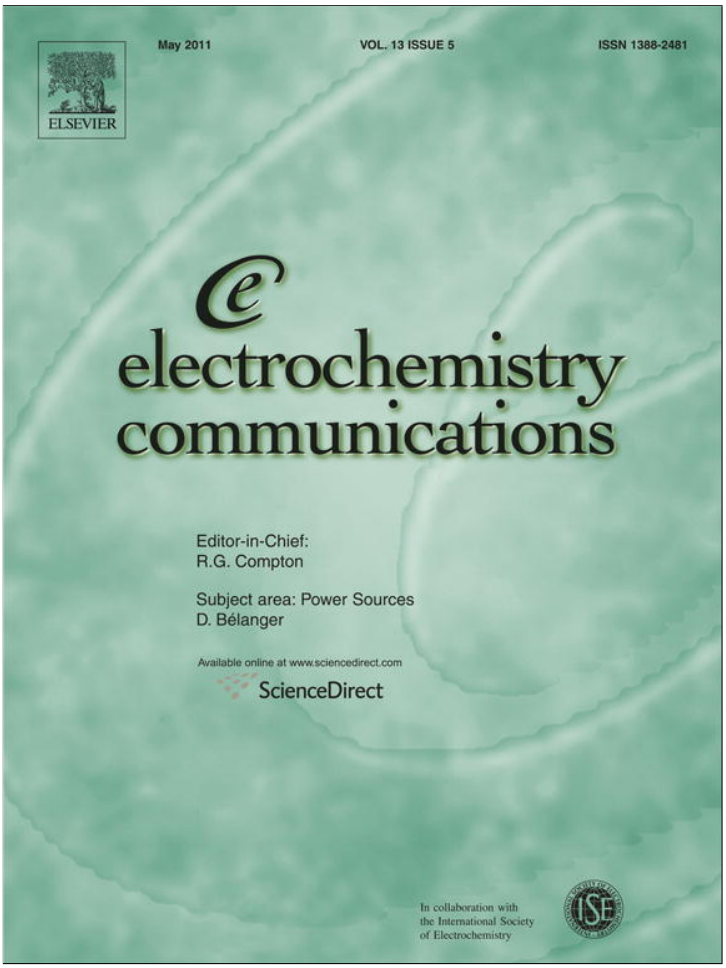

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Electrosynthesis of hollow polypyrrole microtubes with a rectangular cross-section

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ABSTRACT

We present results on the electrosynthesis of hollow rectangular microtubes of polypyrrole from neutral and alkaline solutions of salicylate. The electroactive films were prepared by electropolymerization of pyrrole on stainless steel substrate at a constant potential. The growth process of microtubes was studied by scanning electron microscopy (SEM). Deposition parameters such as salicylate concentration, monomer concentration, solution pH and electrode rotation have significant effects on the morphology of deposits. A plausible explanation for the occurrence of rectangular-sectioned microtubes is given.

1. Introduction

Micro and nanostructures of conducting polymers have been intensively investigated due to their interesting and sometimes unexpected size-dependent properties. These structures are considered as a new class of materials for several applications fields including sensors, drug delivery devices and conducting coatings [1,2]. Conducting polymers structures of reduced size have been synthesized with various morphologies such as fibers, tubes and rods [3]. Comparatively there are fewer reports in the literature concerned with the formation of rectangular tubes of conducting polymers, which are expected to have an improvement in optical, mechanical and conductivity properties. The occurrence of this type of morphology has been observed for polyaniline [4,5] and polypyrrole (PPy) [3,6], both prepared by chemical polymerization. Díez et al. were the first to report the formation of polypyrrole structures with a rectangular cross-section [7]. The polymer was chemically synthesized in aqueous solution containing β-naphthalenesulfonic acid (NSA) and ammonium peroxodisulfate as oxidant. Authors proposed that Py and NSA form at low temperature a complex that precipitates with a rod-like morphology, which acts as a template for polymerization. Yan and Han also reported the formation of rectangular-sectioned PPy tubes in a chemically polymerized PPy through a self-assembly method [6].

In the present contribution we have electrodeposited polypyrrole microtubes with a rectangular cross-section from a salicylate solution. To the best of our knowledge, the electrosynthesis of a conducting polymer film with this type of morphology has not been reported yet. The influence of some deposition parameters like deposition time, solution pH, salicylate concentration and electrode rotation on the morphology of the electrodeposits was analyzed. A possible formation mechanism is discussed.

2. Experimental

The working electrode was a disk of stainless steel 316 L embedded in a Teflon holder with an exposing area of 0.07 cm^2. Before each experiment, the exposed surfaces were abraded to a 1200 grit finish using SiC, then degreased with acetone and washed with triply distilled water. Potentials were measured against a Ag/AgCl (3 M KCl) electrode and a platinum sheet was used as a counter electrode.

Electrochemical measurements were done using a potentiostat–galvanostat Autolab/PGSTAT128N. A dual stage ISI DS 130 SEM was used to examine the morphology of the deposits. Measurements were performed in solutions containing pyrrole (Py) (0.05–0.25 M) and sodium salicylate (0.1–0.5 M) in a purified nitrogen gas saturated atmosphere at 25 °C. The pH of the solution was adjusted by addition of NaOH. Pyrrole (Sigma-Aldrich) was freshly distilled under reduced pressure before use.

3. Results and discussion

The pyrrole electrooxidation was performed under potentiostatic conditions. Fig. 1 shows the i–t curves obtained at 0.8 V in solutions containing 0.5 M salicylate and 0.25 M pyrrole at pH 7 and 12. The increasing current obtained in neutral solution is characteristic of

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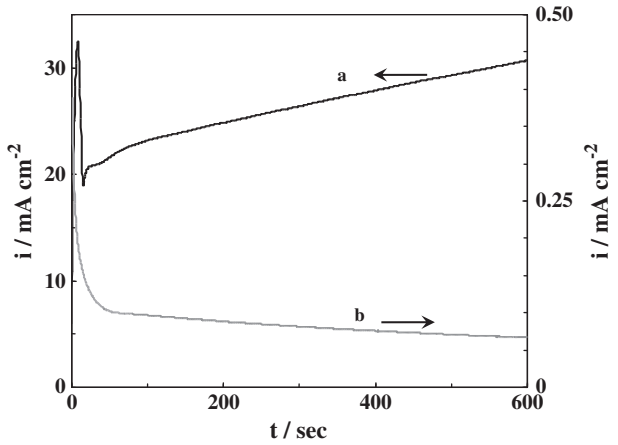

Fig. 1. Chronoamperometric curves obtained at 0.8 V in 0.5 M salicylate solution containing 0.25 M Py. Solution pH: 7 (curve a) and 12 (curve b).

phase formation on electrode surfaces. In the case of the alkaline solution the current continuously decreases. A strongly adherent black film was deposited at the end of the experiment in neutral solution while no film was formed in the alkaline medium. In the latter case, potentials higher than 1.3 V must be applied to deposit the coating.

The morphology of the film electrodeposited after 600 s in the neutral solution is presented in Fig. 2. Different regions can be distinguished, each one constituted by an ensemble of closely packed microtubes with the same orientation (Fig. 2A) The magnified image reveals that most of the structures have rectangular cross-section with side length varying between 1 and 5 μm (Fig. 2B and C). Some of them are well-defined rectangular microtubes and others are more irregular in shape. It is also visible that the microtubes have a hollow interior. Their inner side surface is smooth while the external surface is rougher, covered by the typical globular structure of PPy. A lateral view of the film shows aligned microtubes with a length of about 60 μm (Fig. 2D). The hollow interior of the tubes is visible from some broken structures. It should be mentioned that the obtained microtubes are very similar to those synthesized by chemical oxidation of pyrrole [3].

Morphologies observed at shorter times are presented in Fig. 3. After 30 s of deposition two distinctive morphologies are observed on the surface (Fig. 3A). The PPy appears to be composed of small grains homogeneously distributed on the whole substrate surface. Several structures growing between the grains are observed, which can be viewed as nascent microtubes. When the polarization time is increased to 60 s, a large amount of microtubes in a variety of sizes were formed (Fig. 3B). Further prolonging the deposition time to 120 s results in microtubes covering the whole surface (Fig. 3C). The morphology of the film prepared for 300 s is almost the same as that for 600 s (Fig. 3D).

The wall thickness of the tubes is estimated to be 0.1 μm. The microtubes grow in their length without modification of the wall thickness. On the other hand, cyclic voltammetry of the thinner films in a monomer-free solution presents redox current peaks indicating that the deposited polymers are electrochemically active (Fig. 4).

Solution pH has an influence on the electropolymerization process. It was demonstrated that good PPy films were synthesized on the steel at 0.8 V in an alkaline solution containing molybdate and nitrate [8], but the polymerization does not occur at this potential in the presence of salicylate. Voltammetric results indicate that the presence of salicylate produces a positive shift of the pyrrole oxidation. Thus, in alkaline medium there is a competition between salicylate oxidation

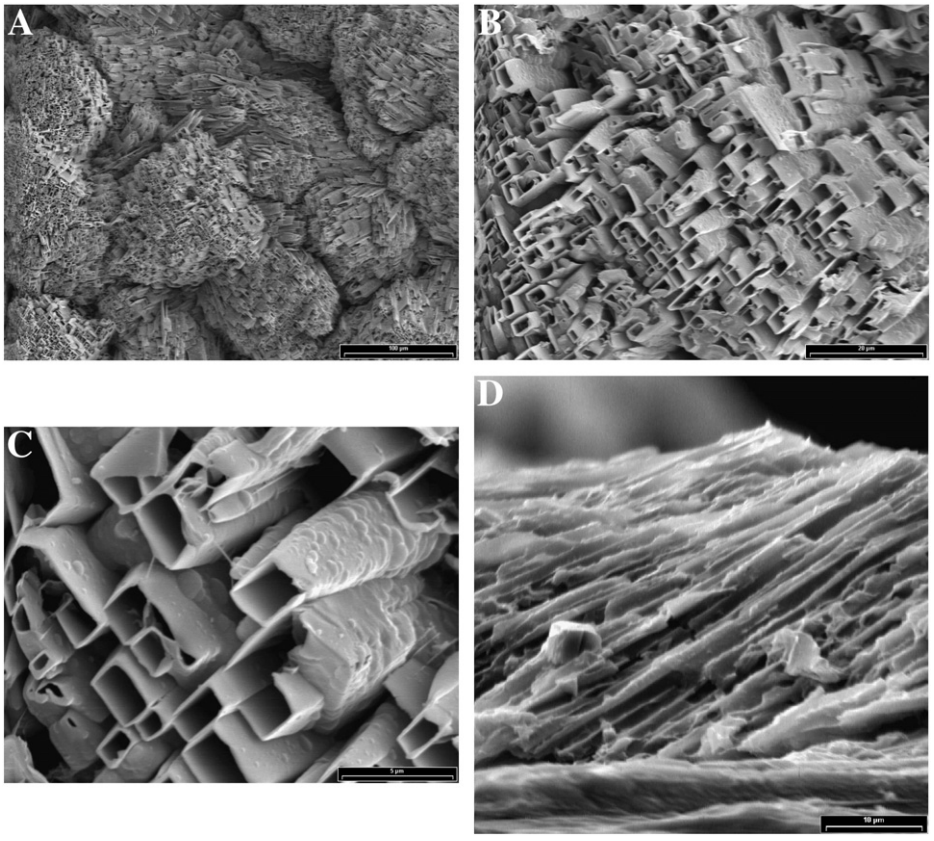

Fig. 2. (A) SEM image of the PPy film deposited at 0.8 V during 600 s in 0.5 M salicylate solution containing 0.25 M Py at pH 7; (B) and (C) Amplified images of (A); (D) SEM lateral view of the deposit.

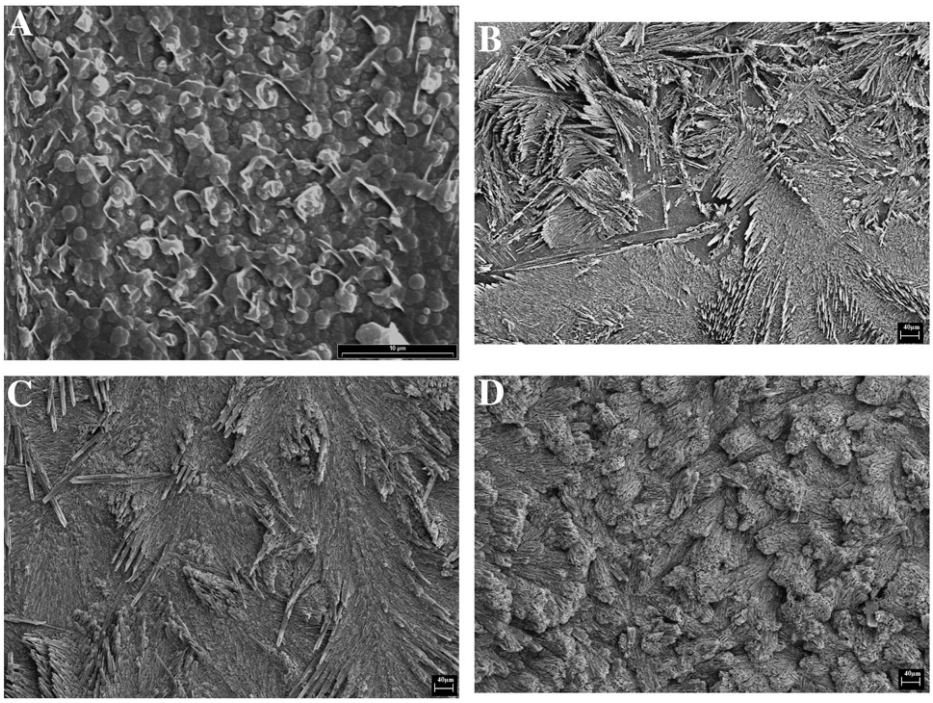

Fig. 3. SEM images of the PPy film electrosynthesized at 0.8 V in 0.5 M salicylate solution containing 0.25 M Py at pH 7. Polarization time: (A) 30, (B) 60, (C) 120 and (D) 300 s.

[9] and PPy deposition. The formation of PPy is favored when the potential is raised to 1.3 V and rectangular sectioned microtubes were found to be the final product.

The formation of the rectangular microtubes also depends on the hydrodynamic conditions. When the electrode was rotated at 500 rpm, two distinctive morphologies were observed on the surface. Microtubes deposition prevails at the disc edge while the usual globular morphology was observed at the center of the rotating disc electrode. At a rotation rate of 1000 rpm only the globular structure was generated.

It was also found that if the concentration of salicylate was lower than 0.1 M with all other parameters remaining constant, only the globular PPy morphology was observed in the sample. On the other hand, when the monomer concentration is reduced to 0.05 M, tubes similar to that previously described were obtained although they are more variable in size and shape (Fig. 5). Their mean length is higher, some as long as 500 μm.

The chemical nature of the substrate does not affect the formation of rectangular microtubes because their formation was also observed on a vitreous carbon electrode under the same conditions used for the steel substrate. It is reasonably considered that the presence of a template is the necessary conditions for the growth of tubes [10]. Therefore, the deposition of rectangular microtubes can be attributed to a template process as was postulated for the chemically synthesized tubes [3]. Possibilities include the initial formation of salicylic acid crystals. A local pH decrease at the interface owing to the release of protons during polymerization produces the protonation of salicylate anion [11]. Salicylic acid crystallizes due to its low solubility in water. The fact that the structures were not generated at low salicylate concentrations supports this hypothesis. On the other hand, rotation of the electrode prevents the decrease in pH and as a consequence only the usual granular morphology of PPy was obtained under this condition. Microtubes formation was also observed in samples grown in pH 12. In this case the generation of protons should also lead to a local pH change that facilitates the precipitation of the acid.

4. Conclusions

In summary, rectangular-sectioned PPy microtubes can be generated by electropolymerization of Py in aqueous neutral and alkaline solutions of salicylate. The rectangular structures having side

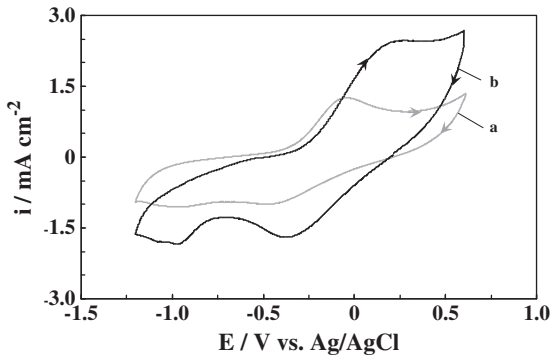

Fig. 4. Cyclic voltammograms of the PPy film at 0.05 Vs^{-1} in 0.5 M salicylate solution. The polymer film was electrosynthesized in the same solution containing 0.25 M Py at 0.8 V for: (a) 30 s and (b) 60 s. The 10th cycle is displayed.

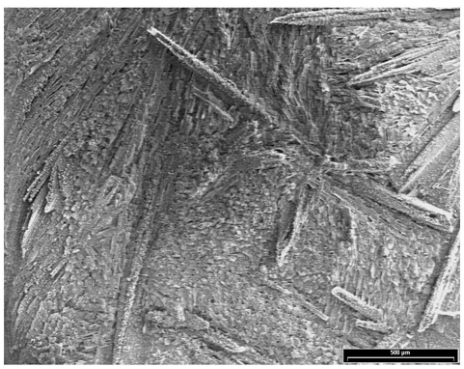

Fig. 5. SEM image of the PPy film deposited at 0.8 V during 3600 s in 0.5 M salicylate solution containing 0.05 M Py at pH 7.

dimensions in the range of 1–5 μm emerge at an early stage of electropolymerization. The microtubes are identical to those synthesized by chemical routes.

A successful synthesis requires a high salicylate concentration in a stagnant solution. In alkaline media the oxidation of salicylate makes more difficult the electrodeposition process. It is tentatively proposed that salicylic acid crystals precipitate on the electrode surface, providing a favorable template for subsequent polymer deposition.

The electrosynthesis allows preparing the coating in a one-step method and in a short time. The described structures can provide a high surface area and their internal cavities can be used for the immobilization of other materials. Our result will be a starting point for further research in these areas.

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