

Electrosynthesis of polypyrrole nanotubules using particle track-etched membranes as template

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RÉSUMÉ

Du polypyrrole a été électrosynthétisé dans les pores de membranes "track-etched" nanoporeuses, en utilisant deux types d'anions dopants (poly 4-styrènesulfonate de sodium et perchlorate de lithium). La morphologie et les propriétés électrochimiques des nanomatériaux obtenus par cette méthode de synthèse ont ensuite été étudiées.

Mots-clés : Polypyrrole, Synthèse électrochimique, Nanomatériaux.

ABSTRACT

Polypyrrole has been electrochemically synthesized inside the pores of nanoporous polycarbonate particle track-etched membranes. The morphology and the electrochemical properties of the obtained nanomaterials, using two types of doping anions (poly (sodium-4-styrenesulfonate) and lithium perchlorate) has been studied.

Key words : Polypyrrole, Template electrosynthesis, Nanomaterials.

INTRODUCTION

Currently there is a considerable interest in nanoscale materials, since they exhibit novel properties largely as a consequence of their finite small size. Moreover, nanomaterials have wide-ranging implications to a variety of areas, including chemistry, physics, electronics, optics, materials science and the biomedical sciences. A possible chemical approach for building such nanoscale objects involves the use of nanoporous host materials as templates [1]. Although there exists a wide range of nanoporous materials, many studies were performed using particle track-etched membranes and anodic porous alumina membranes [2-4]. In this method, thin fibrils of metals and conducting polymers are chemically or

electrochemically synthesized within the pores of the template membrane. Recently, in parallel to the development of preparation process and characterization techniques of polycarbonate nanoporous particle track etched membranes (PC nano PTM) [5-7], we considered the use of these nano PTM as templates for the synthesis of nanoscale polymers. In this paper, we report on the electrosynthesis of pyrrole nanotubes, using two types of doping anions.

EXPERIMENTAL

The present work was carried out in aqueous solutions. Pyrrole (Janssen) was distilled under low pressure prior to use. The poly (sodium-4-styrenesulfonate) (NaPSS, Acros) and the lithium perchlorate (LiClO_4 , Aldrich) were used without any prior purification. The microporous polycarbonate Particle Track-etched Membranes (PTM) used in this work were obtained by a procedure described earlier [4-6]. For this study, we prepared and used microporous PC PTM with a pore density of 4×10^8 pores cm^{-2} and pores diameters of 200 nm. A rather thick layer (± 500 nm) of gold was deposited on one side of the template membrane using a vacuum coating. This metal film was used as an anode to electrochemically synthesize the polymer within the pores of the membrane. All experiments were carried out in a conventional one compartment cell with a Pt counter electrode and a saturated calomel reference electrode, at room temperature. Scanning electron microscopy (SEM) was performed using a high resolution FEG Digital Scanning Microscope 982 Gemini from Leo.

RESULTS AND DISCUSSION

It is well established that the supporting electrolyte used to synthesize a conducting polymer affects its morphology and some of its properties. For this reason, we used either a small size anion (ClO_4^-) or a polyelectrolyte (PSS^-) as doping agent during the electropolymerization of pyrrole inside the pores of a PC membrane. Aqueous solutions containing 0.1M pyrrole and either 0.1M LiClO_4 or 0.1M NaPSS were used as electropolymerization solutions. Polypyrrole was generated by polarizing the working electrode at 0.8V *vs SCE* for a defined polarization time. The filling of the pores can be easily monitored by measuring the plating current. Indeed, as the first polypyrrole tubules emerge from the surface, the current increases very rapidly due to the formation of caps associated to a three-dimensional deposition. The morphologies of the template synthesized

polypyrrole nanostructures obtained by electropolymerization using the two different doping anions were analyzed using SEM after dissolution of the PC membrane. The SEM images presented on Figures 1 and 2, clearly show that in both cases, nanotubes are obtained. Nevertheless, the PPy-PSS nanotubes present much thicker walls than the PPy-ClO₄ ones.

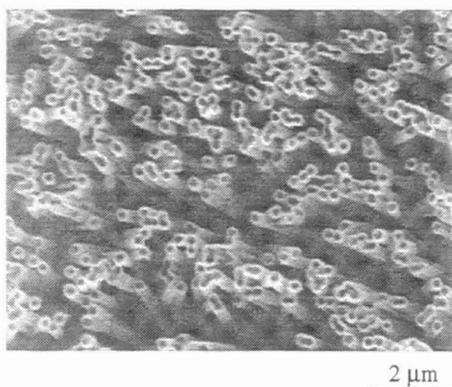


Figure 1 : SEM image of PPy-ClO₄ nanotubes obtained by electrochemical synthesis

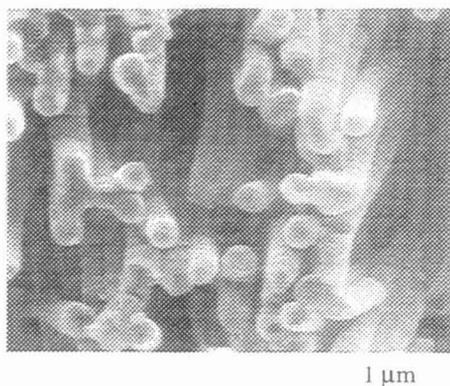


Figure 2 : SEM image of PPy-PSS nanotubes obtained by electrochemical synthesis

Both types of polypyrrole nanotubes (PPy-PSS and PPy-ClO₄) show redox reactions typical of the parent polymer in the bulk form. Like the parent polymer, the tubules can be reversibly switched between electronically insulating and electronically conductive states. In Figure 3, we present the cyclic voltamogram of PPy-PSS tubules recorded in 0.1M LiClO₄ / H₂O at a scan rate of 50 mV/s. It is interesting to note that electrochemical deposition of polymer naturally leads to the formation of tubules while it produces solid wires in the case of metal deposition. Martin *et al.* [2,3] propose to explain this phenomenon by the electrostatic attraction between the growing polycationic polymer and anionic sites along the pore walls of the polycarbonate membrane. Although, we agree with that argument, we think that the formation of tubules may also result from a limited diffusion of the monomer and the electrolyte inside the pores. Indeed, at the beginning of the electropolymerization process, the monomer contained in the pores is rapidly consumed. As the growing of the chain along the pore walls is very fast, the first

tubules emerge rapidly from the surface and progressively cover the opening of the pores. When the pores are completely corked with polypyrrole, the diffusion of the reagents is stopped and consequently it is no more possible to thicken the tubules walls. In order to confirm this hypothesis, the influence of different synthesis parameters (the applied potential, the monomer and electrolyte concentration) as well as the influence of pores walls modification prior to electropolymerization are now under investigation.

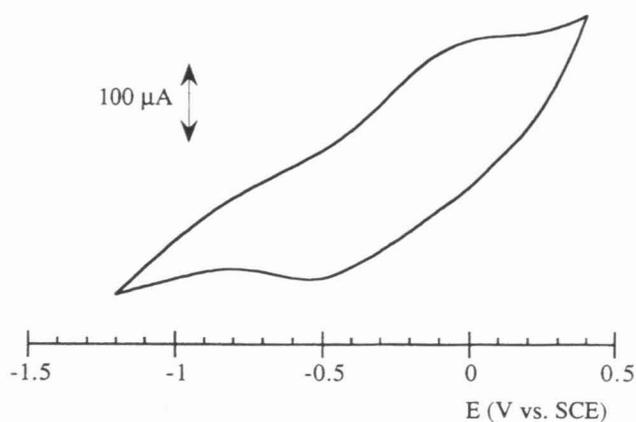


Figure 3 : Cyclic voltamogram of PP-PSS nanotubules recorded in 0.1M LiClO₄ / H₂O at a scan rate of 50 mV/s

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