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Synthesis of polyaniline nanostructures by electrochemical deposition on niobium

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ABSTRACT

Nanostructured polyaniline films have been electrochemically synthesized on passivated niobium substrate by potentiodynamic method in 0.5 and 1 mol L^{-1} H_2SO_4 solution and different aniline/acid molar ratios. The niobium oxide particles formed during passivation induce the nucleation of polyaniline nanofibers via adsorbed phenazine nucleates. The infrared spectra of polyaniline nanofibers showed the presence of vibrations attributed to phenazine-units in the polymer chain which support the phenazine nucleates theory for polyaniline nanofiber growth. The morphology of polyaniline is also influenced by acid concentration and a branched structure consisting of polyaniline nanofibers with a mean diameter of 70 nm is observed for 1 mol L^{-1} sulfuric acid solution. The shape of the impedance spectra is controlled by charge transport through ion diffusion, with higher diffusion resistances for granular polyaniline. The capacitance increases with the polymer layer thickness and has higher values for nanofibrilar than for granular polyaniline.

1. Introduction

Nanostructured conducting polymers, especially polyaniline (Pani) have been intensively studied in the last years due to their potential applications in micro- and nanoelectronics and for the construction of sensors, biosensors and biomedical devices [1,2]. It is expected that nanostructured polyaniline will show net superior properties compared to amorphous polyaniline, or even unique properties. Several studies have recently shown that going down to nano-level dimensions, together with a marked increase of the specific surface area, can bring further improvement of several other properties like conductivity, processability and sensing properties. Several methods have been proposed to synthesize polyaniline nanostructures. Most of them are chemical oxidative methods which include the use of insoluble hard templates such as zeolites or polymer membranes with controlled pore size or soluble soft templates such as macromolecules, surfactants [3] or nanofibers such as Mn_2O_3 that acts as both guiding template and oxidant [4]. Alternative synthesis methods include nanoseeding which is usually done with other nanostructured organic or inorganic materials like carbon nanotubes [5,6], polyaniline [7], graphene oxide [8] vanadium oxide nanofibers [5]. Attempts have been made to develop template free synthesis methods including chemical interfacial polymerization [9–13]. Chemical synthesis can be also applied as template free method to produce polyaniline nanostructures by changing the reaction conditions, e.g. the monomer/oxidant ratio [14] and the rate of oxidant addition [15], by using milder oxidants [16–18] or by the homo- or co-polymerization of aniline dimers [19].

Despite the net advantage of chemical method in producing large scale quantities of polyaniline, the electrochemical method in turn allows a more rigorous control of synthesis parameters and offers a very convenient way to study the electrochemical properties of polyaniline nanofibers. Nanostructured conducting homo- or copolymers of polyaniline have been obtained by template free electrochemical methods such as cyclic voltammetry [20–22], galvanostatic [23,24] or potentiostatic [25] methods, pulse galvanostatic or potentiostatic methods [26,27]. The results point out that the nanofibrilar morphology might be an intrinsic property of electrochemically synthesized polyaniline [25], however it is strongly affected by synthesis conditions. One of the factors reported to influence the morphology [28], as well as the diameter and length of nanofibers [23] is the scan rate in potentiodynamic methods.

It is generally accepted that the substrate plays a special role in the formation and growth of polyaniline nanofibers, however there are only scarce studies regarding the effect of electrode material on the formation and growth of electrochemically deposited

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polyaniline nanofibers. Generally, the electrochemical synthesis of polyaniline nanofibers is carried out on conventional substrates such as platinum, gold or stainless steel. The electrochemical deposition of granular polyaniline is reported on a large variety of electrode materials including nickel, graphite, glassy carbon, carbon fibers, indium tin oxide.

In this study a novel substrate has been selected for the electrochemical polymerization. To the best of our knowledge, there are no studies devoted to the electrochemical deposition of either granular nor nanostructured polyaniline on niobium substrate. A special interest has been given to this metal due to its property to form vertically oriented nanofibers of niobium oxide during thermal treatment [29]. It is expected that during the electrochemical oxidation of niobium, nanoseeds of niobium oxide will form with a key role in the nucleation and growth of polyaniline nanofibers.

2. Experimental

Aniline (puriss., p.a., ≥99.5% GC from Fluka) was freshly distilled under reduced pressure and stored in dark at low temperature. Double distilled water and analytical grade sulfuric acid (95–97% from Riedel de Haen) were used to prepare the electrolyte solutions.

The potentiodynamic polymerization of aniline was performed in a standard three-electrode electrochemical cell connected to an Autolab PGSTAT 302N. The working electrode was a Nb disc ($A = 1$ cm^2), two graphite rods were used as counter-electrodes and a saturated calomel electrode (SCE) as reference electrode. Special attention has been paid to the mechanical preparation of the Nb substrate. Before each measurement the Nb electrode was mechanically polished with SiC paper of different grades from 400 to 2400 and then mirror polished with diamond sprays with different grain size (6, 3 and 1 μm). The freshly prepared electrode was immediately immersed in the electrolyte solution and a cyclic voltammogram was taken. Cyclic voltammograms (CV) were recorded at a scan rate of 50 mV s^{-1} in a potential range from −0.500 V to 1.200 V to initiate the polymerization process. After the initiation cycles the potential range was limited from −0.350 up to 0.800 V to avoid the overoxidation reactions of the polymer chain. Pani samples were prepared at two different concentrations of the sulfuric acid solution (0.5 and 1 mol L^{-1}) and at aniline/acid ratio of 0.2, 0.4 and respectively 0.6. An overview of the corresponding synthesis conditions is given in Table 1.

The electroactive properties of the polyaniline films were investigated by cyclic voltammetry and electrochemical impedance spectroscopy (EIS) in 0.5 M H_2SO_4 solution. EIS measurements were carried out using the FRA Module of Autolab 302N, in the frequency range from 0.1 Hz to 10^4 Hz and AC voltage amplitude of 10 mV. For each spectrum 60 points were collected, with a logarithmic distribution of 10 points per decade. The experimental electrochemical impedance data were fitted to the electrical equivalent circuit by a complex non-linear least squares (CNLS) Levenberg–Marquardt procedure using the ZView 3.0 software (Scribner Associates, Inc.).

Table 1
Synthesis conditions and characteristics of the first anodic peak for the prepared Pani samples.

Sample	H_2SO_4 [mol L^{-1}]	Aniline [mol L^{-1}]	Molar ratio	Nr. of scans	E^a [V]	i^a [mA cm^{-2}]	Q^a [C]
Pani1	0.5	0.1	0.2	15	0.249	5.3	4.9 × 10^{-3}
Pani2	0.5	0.2	0.4	15	0.317	16.1	23.6 × 10^{-3}
Pani3	0.5	0.3	0.6	15	0.342	57.4	88.9 × 10^{-3}
Pani4	1	0.2	0.2	15	0.362	61.2	98.0 × 10^{-3}
Pani5	1	0.4	0.4	12	0.298	55.6	113.0 × 10^{-3}
Pani6	1	0.6	0.6	12	0.375	63.5	145.0 × 10^{-3}

[a] Values are given for the last cycle.

The structure and morphology of the polyaniline films prepared on niobium were characterized by scanning electron microscopy (SEM) using a FEI INSPECT S electron microscope. The three dimensional morphology of the electrochemically passivated niobium surface was examined by atomic force microscopy using a Nanosurf® EasyScan 2 Advanced Research AFM. Fourier-transformed infrared (FTIR) spectra of prepared polyaniline were measured on KBr pellets using an IFS 66v spectrometer (Bruker Optics, Germany) equipped with a DTGS detector working at room temperature. For each spectrum 100 interferograms with a resolution of 4 cm^{-1} were sampled.

3. Results and discussion

Fig. 1 shows the cyclic voltammograms recorded for the passivation of Nb in sulfuric acid solution. A typical shape for anodic passivation curves can be observed, with three distinct regions. The first region is the so-called active region, where the current increases exponentially with the applied potential and an oxidation peak is formed at 0.2 V, corresponding to the dissolution of Nb. The second or passive region, where the anodic current reaches a plateau and is independent of the applied potential, corresponds to the electrochemical passivation of Nb according to the reaction [30]:

$$2Nb + 5H_2O \rightarrow Nb_2O_5 + 10H^+ + 10e^-$$

The third region (here not shown) corresponds to the oxygen evolution reaction which takes place on the passivating oxide layer. In the following scans, the current has a constant value closed to zero and neither additional oxidation nor reduction peaks can be seen since Nb is covered by a passivating layer of niobium oxide.

Literature data indicate different chemical composition of the passive oxide film formed on niobium, depending on the environment and treatment conditions. It seems that, for the electrochemical passivation of Nb in acidic aqueous solution, the main component of the passivating oxide film is Nb_2O_5 [30,31].

The electrochemical oxidation of aniline was further carried out on the passive niobium electrode. Representative examples of cyclic voltammograms obtained during synthesis in the two sulfuric acid solutions of different concentrations for the initiation cycles and further growth of the Pani film are given in Fig. 2 for Pani2 and Pani5.

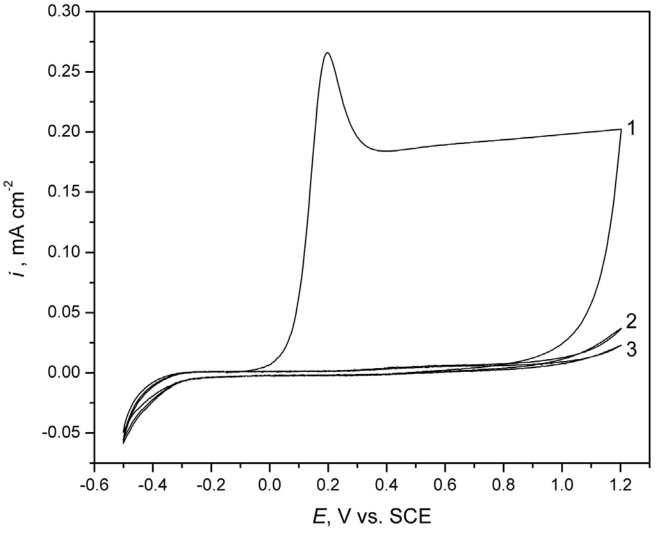

Fig. 1. Cyclic voltammogram of Nb in 0.5 M H_2SO_4, scan rate 50 mV s^{-1}.