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Electropolymerization of polyaniline on high surface area carbon substrates

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Abstract

Electropolymerization of polyaniline (Pani) was carried out on different high surface area carbon substrates: carbon fiber and reticulated vitreous carbon (RVC™). Due to the different morphology of the RVC™ substrate, a modification of a well established aniline electrodeposition methodology is proposed. The electrical and morphological characteristics of the resulting Pani films were strongly affected by the chosen substrate and are analyzed, using electrochemical impedance spectroscopy and scanning electron microscopy, in terms of the current penetration profile within the RVC™ electrode. For the films grown on RVC™ the voltammetric waves were wider, the charge-transfer resistance was higher and the morphology more compact.

Keywords: Reticulated vitreous carbon (RVC™); Carbon fiber; Polyaniline; Electropolymerization; Electrochemical impedance spectroscopy

1. Introduction

The electrochemical deposition of conducting polymers on carbon substrates has been studied with the goal of improving the mechanical properties of these polymers so as to use them as electrodes in different applications: batteries, sensors, capacitors or electrochromic displays [1,2]. Polyaniline (Pani) is a conducting polymer largely studied for these applications and several composites have been proposed to improve its performance [3]. Good results have been obtained with functionalized Pani in gas sensors and corrosion protective coatings [4]. Other examples are the use of Pani combined with Prussian blue as an electrochromic material [5] and the proposition of Pani doped with 2,5-dimercapto-1,3,4-thiadiazole (DMcT) as an alternative material for high-energy cathodes in lithium batteries [6,7].

However, for a material to be used in electronic devices, the relationship between electrode mass and electrochemical activity is an important parameter, where a high activity must be achieved with a minimum electrode mass. In order to reduce the electrode mass, the polymeric film should be removed from metallic substrates, but sometimes this is limited by the mechanical properties of the polymeric film. If the substrate has to be maintained in the electrode structure, then the choice of a light, porous and high surface area material is extremely important. These properties are easily found in carbon electrodes, which have been intensively studied as electrode materials for energy storage applications such as batteries and capacitors [8].

Among the carbon substrates found in the literature, carbon fiber (CF) and reticulated vitreous carbon (RVC™) are well known for presenting a high surface area and, therefore, have been used for conducting

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polymer deposition [1,7,9]. Films of polypyrrole [1] and polyaniline [7] electrodeposited on carbon fiber substrates presented stable and high discharge capacities when tested as cathodes in lithium rechargeable batteries. For electroanalytical purposes, the effect of the electrodeposition conditions of polypyrrole films on RVC™ substrates on the remediation of Cr(VI) in aqueous media has been analyzed [10]. Composites of RVC™/polypyrrole have been prepared either to recover Cu(II) from dilute acidic solutions [11] or to separate and recover gold and other metal ions with a high degree of efficiency and selectivity [12]. RVC™ electrodes have also been employed as host substrates for the electrochemical deposition of heparin-doped polypyrrole, resulting in a new method for the purification of thrombin [13].

Carbon fiber is usually considered to have a two-dimensional structure, assuming that its thickness is not significant when compared to that of RVC™. On the other hand, the RVC™ foam is a three-dimensional electrode, whose properties are critically dependent on the potential distribution generated within its structure [14,15]. Though various studies using RVC™ as the substrate for electropolymerization can be found in the literature, not many concerns about the dependence of the final electrode properties on the 3-D features of the substrate have been reported. Therefore, in this work we report that the use of two different carbon forms as high-area substrates strongly affects some properties of the electropolymerized polyaniline films. Furthermore, their differences in the voltammetric, electrical and morphological characteristics are analyzed in terms of the current penetration profile within the RVC™ electrode. In addition, due to the different micro-texture of CF and RVC™, a change in the methodology used for polyaniline electrodeposition on CF [7] is proposed for its deposition on RVC™.

2. Experimental

Aniline (Merck, analytical grade) was distilled under low pressure and stored in the dark before use. H_2SO_4 (Mallinckrodt, analytical grade) was used without further purification. Deionized and twice distilled water was employed to prepare all solutions. Carbon fiber (PWB-3, from Stackpole, USA) was treated at 450 °C for 1 h and washed in hot aqueous H_2SO_4 50% v/v; RVC™ (80 ppi, from ERG Materials and Aerospace, USA) was electrochemically treated by cyclic voltammetry between −0.6 and 0.8 V (vs. SCE), at 10 mV s^{-1} (5 cycles), in a 0.5 mol L^{-1} H_2SO_4 aqueous solution. The CF electrodes were made from 1.0 cm × 1.0 cm pieces of a 0.3-mm thick tissue exposed to the electrolyte, while the RVC™ electrodes were made from small parallelepipeds (1.2 cm × 0.8 cm × 0.8 cm).

An optimized methodology for electrodeposition of porous polyaniline, with potential use as a rechargeable battery electrode, has been reported previously [16]. Pani films were grown onto CF or RVC™ in 0.5 mol L^{-1} H_2SO_4 + 0.1 mol L^{-1} aniline aqueous solutions under an N_2 atmosphere by cyclic voltammetry, using the following methodology: (a) first cycle – cycling between −0.3 and 0.8 V (vs. SCE), at 2 mV s^{-1}; (b) other cycles (up to 300) – cycling between −0.3 and 0.69 V (vs. SCE), at 100 mV s^{-1}. All electrochemical measurements were carried out at room temperature (ca. 25 °C) in a conventional three-electrode Pyrex-glass cell containing CF or RVC™ as the working electrode, a cylindrical Pt grid as the counter electrode and a saturated calomel electrode (SCE) as the reference, to which all potentials in this work are referred.

After the preparation of the CF/Pani and RVC™/Pani electrodes, their electrochemical behavior was assessed by cyclic voltammetry between −0.3 and 0.69 V at 100 mV s^{-1} for 200 cycles. Electrochemical impedance spectra were obtained potentiostatically in the range −0.2 to 0.6 V at 0.10 V steps, for freshly prepared electrodes; the ac signal, with an amplitude of 10 mV (rms), was varied in the 10 mHz to 10 kHz frequency range. Both the voltammetric and the electrochemical impedance measurements were carried out in a 0.5 mol L^{-1} H_2SO_4 aqueous solution without the aniline monomer. An Autolab PGSTAT 20 potentiostat/galvanostat, controlled by the GPES software, was used to carry out the voltammetric experiments; the electrochemical impedance spectra were obtained using an Autolab FRA2 module, coupled to the PGSTAT20 potentiostat/galvanostat.

The morphological features of the freshly prepared samples, removed from the cell at the limiting negative potential, were assessed using a 960 DSM Zeiss scanning electron microscope.

3. Results and discussion

3.1. Pani electrosynthesis and electrode voltammetric characteristics

The potentiodynamic electrosynthesis of polyaniline was carried out according to previous studies [16], i.e., imposing a slower sweep rate and a wider potential range only for the first cycle, which is essential to activate a higher number of aniline cation radicals necessary to initiate the oligomeric formation. Fig. 1 shows these initiation cycles for both substrates: carbon fiber (Fig. 1(a)) and reticulated vitreous carbon (Fig. 1(b)). Fig. 1(a) shows an increase of the current at 0.7 V in the first positive sweep, showing the aniline oxidation and consequent cation radical formation to initiate the polymeric growth. On the other hand, when RVC™ was used as