



Asymmetrical modification of carbon microfibers by bipolar electrochemistry in acetonitrile



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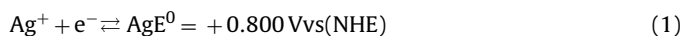
ABSTRACT

This contribution presents the asymmetrical modification of carbon microfibers (CMF) with gold and polythiophene, by bipolar electrochemistry (BPE) in acetonitrile (ACN). At first, the electrochemical behavior of AuCl_4^- in ACN was examined by cyclic voltammetry, in order to determine the deposition mechanism and the electric field threshold, beyond which bipolar electrochemistry allows metal deposition in such a medium. It is demonstrated that, by using suitable BPE conditions in ACN, it is possible to deposit asymmetrically species characterized by a difference in redox potential as high as 3V. The modified CMFs are characterized by SEM, FEG-ESEM and EDS.

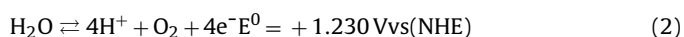
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1. Introduction

Bipolar electrochemistry (BPE) occurs when faradaic reactions are driven on electronic conductors not directly connected to an electrical power source, but in contact with a dielectric (typically a solution) which is polarized under the influence of an applied electric field. [1–5]. If the polarization is strong enough and suitable redox species are dissolved in the dielectric medium, electrochemical reactions at the opposite sides of the substrate are triggered, with an oxidation process occurring at one end of the substrate and a reduction process at the opposite one so that the conductive substrate acts as a bipolar electrode. As a first approximation, the magnitude of the polarization must be greater than the difference between the standard potentials (E^0) of the two involved redox species. For example, if one wants to functionalize asymmetrically a substrate by depositing metallic silver at one end, the standard potential of Ag^+ :



and of water oxidation, at the opposite side, must be considered:



It follows that in this case, the electric field must generate a minimum potential difference of approximately 0.430 V between the two ends of the substrate.

The substrate can be any kind of conducting material and, in principle, with any shape or dimension. Bipolar electrochemistry can induce, like conventional electrochemistry, all kind of electrochemical processes. Moreover, the possibility to disperse the substrate in the electrolyte solution, makes bipolar electrochemistry a truly three-dimensional technique, allowing the scale-up of the production of asymmetric particles [6–8].

In the case when bipolar electrochemistry is used to perform electrodeposition processes onto bipolar electrodes, the amount of deposited material can be increased by maximizing the fraction of electric current flowing through the electrodes themselves. The flow of current in the cell, during a BPE experiment, follows a rather complex pathway which can be modeled by an equivalent circuit composed of multiple resistors connected in series and in parallel, corresponding to the resistances of the electrolyte solution, bipolar electrodes and relevant interfaces [3,4]. In order to increase the yield of material deposited on the bipolar electrodes one should take into account that, in the vicinity of the substrate, the overall current is divided into two fractions, one flowing through the conducting object and the other through the solution [9].

It follows that the ratio between these two currents is correlated with the resistance of the bipolar electrode and the solution, respectively [10]. In the case of electrodeposition, it is

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advantageous to work with a highly conductive object dispersed in a highly resistive medium. In this case, the majority of the current passing through the cell will flow through the conducting object.

In order to drive correctly a bipolar electrodeposition one must take into account the size of the bipolar electrode and the polarization potential (ΔV). Indeed, for an anisotropic particle such as a nanowire, ΔV is related to its length (l) and the applied electrical field (E) by the following equation [1,11]:

$$\Delta V = El \quad (3)$$

This equation has been confirmed empirically by Goodridge et al. [2] and illustrates that large electric fields are needed for substrates with small dimensions [2,12]. When anisotropic particles are used, the polarization also induces an orientation of the particles in the electric field with the longitudinal axis parallel to the field lines. This means that no precautions have to be taken to control their orientation during the BPE experiment [6]. Moreover, in order to generalize BPE for various electrodeposition applications, it is essential to extend the number of materials which can be deposited, and this can require high potential differences between the two sides of the substrate, achieved by imposing a high potential difference between the feeding electrodes. This is facilitated by decreasing the conductivity of the solution, and avoiding water reduction/oxidation at the feeder electrodes by substituting water with aprotic organic solvents, as demonstrated by Bradley and Ma [13]. On the other hand, aprotic or scarcely polar solvents present heavy drawbacks related to potential evaporation of the medium due to ohmic heating [13,14]. Because of its electrical stability, capability to solvate and dissociate both suitable metal complexes and organic compounds, easy purification, as well as relatively low cost, acetonitrile (ACN) has been chosen as a good candidate to this aim. The goal of this work is the asymmetrical modification of carbon microfibers (CMFs) with electroactive materials which need large potential differences in order to trigger BPE, namely gold and polythiophene (PT). PT is a conducting polymer which can be obtained by electrochemical oxidation of thiophene (C_4H_4S) in ACN solution [15,16]. As far as Au is concerned, a precursor of this metal which is soluble in acetonitrile is used, namely its tetraethylammonium salt tetrachloridoaurate(III) [TEA(AuCl₄)]. Since the electrochemical behavior of the redox species is greatly influenced by the solvent in which the experiments are carried out, it is important to study the electrochemical systems that are going to be exploited in the BPE experiments in order to define as precisely as possible the voltage threshold beyond which BPE is achieved. Therefore both, [TEA(AuCl₄)] and thiophene have been first studied by cyclic voltammetry (CV), and were then used in BPE to modify asymmetrically carbon microfibers. The approach used here can provide useful operative guidelines in order to rationally plan BPE deposition experiments.

2. Experimental

2.1. Chemicals and materials

ACN was dried by distillation with phosphorus pentoxide (P_2O_5) in N_2 atmosphere. Pyrrole (C_4H_5N) and thiophene were also distilled before use. Lithium perchlorate ($LiClO_4$) and tetraethylammonium chloride [(TEA)Cl] were dried overnight at $50^\circ C$ under vacuum. The solvent soluble gold salt [(TEA)AuCl₄] was synthesised as follows. An equimolar mixture of tetraethylammonium hydroxide [(TEA)OH] and tetrachloroauric acid ($HAuCl_4$) were vigorously stirred in a biphasic mixture of water and dichloromethane (ratio 1:1). After the yellow coloration was entirely transferred to the organic layer, the phases were separated. The solvent was removed from the organic fraction, and the resultant crystalline yellow solid [(TEA)AuCl₄] was dried under vacuum [17].

2.2. Electrochemical apparatus and devices

All the voltammetric analysis were performed using a CH 660 B potentiostat in a conventional three electrodes cell, in N_2 atmosphere. Nitrogen, used to remove dissolved oxygen from the working solution, was previously passed through sulphuric acid to remove traces of water. A glassy carbon (GC) electrode disc, 3 mm diameter, was employed as working electrode and two platinum coils were used as counter and pseudo-reference electrode. The GC electrode was mirror polished prior to each experiment with 0.3 and $0.05 \mu m$ alumina slurries on soft pads. After each set of measurements, a microvolume of ferrocene (Fc) solution in ACN was added as an internal standard of the potential scale, according to the IUPAC guidelines [18]. In order to do this, the cyclic voltammogram of ferrocene (Fc)/ferricinium (Fc^+) couple was recorded at $50 mV s^{-1}$ ($\Delta E_p = 60 mV$) and its $E_{1/2}$ value was determined as $[(E_{pf} + E_{pb})/2]$ [19]. The $E_{1/2}$ is centered at 0.040 V with respect to the Pt pseudo-reference electrode. All the other potential values reported in the following are referred to the $E_{1/2}$ of the Fc/Fc⁺ couple.

2.3. Bipolar electrochemistry apparatus and reagents

Fig. 1 (a-b) shows a schematic representation and a picture of the custom made bipolar electrodeposition glass cell. It is composed of one reaction compartment in which the substrates and the reagents are located. This central chamber is separated by two glass septums (thickness 3 mm, porosity G2) from the two electrode compartments. These separators are needed in order to limit the effects of the high potentials applied to the electrodes, such as bubble formation and convection due to ohmic heating. Using this configuration, the electric field can be imposed for a relatively long time (in the order of a few minutes) without experiencing significant problems. The central compartment is filled with a suspension of microfibers in a solution containing the redox species to

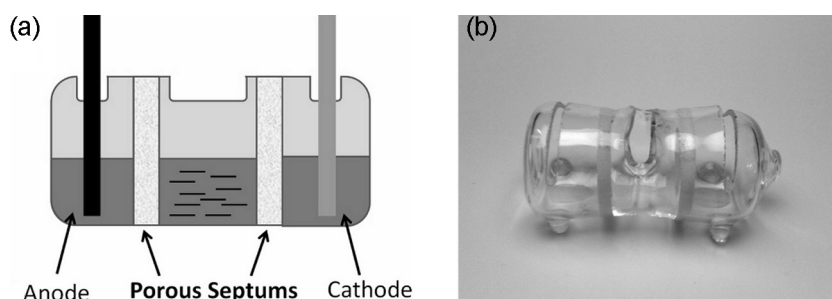


Fig. 1. a) scheme and b) photograph of the cell; the distance between the electrodes is 4 cm and between the porous sectums is 1.5 cm.

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