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Electrocatalytic oxidation of ascorbic acid on mesostructured SiO2-conducting polymer composites

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ABSTRACT

The conducting self-doping copolymer poly(aniline-co-ABA) preserves its redox activity at pH values as high as 7. This observation was the starting point to synthesize an organic–inorganic hybrid composite able to electrochemically oxidize ascorbic acid molecules at that pH. The inorganic part of the catalytic element was an ordered mesoporous electrodeposit of SiO2, which has been used as the template for the electrochemical insertion of the self-doping copolymer. The oxidation of ascorbate ions at a fixed potential on this composite was studied by means of the kinetic model proposed by Bartlett and Wallace (2001). It was observed that the effective kinetic constant K_{ME} increased significantly but, simultaneously, k'_{ME} remained almost constant when the composite was employed as the electrocatalytic substrate. These results were interpreted in the light of two combinations of kinetic constants, which strongly suggested that the increase in K_{ME} should be ascribed to the improvement in electronic conductivity of the copolymer induced by the highly ordered silica template.

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1. Introduction

Although the sol–gel synthesis of SiO2 is known from the 60s, mesostructured silica was reported only two decades ago in the form of surfactant templated particles [1]. These tailored materials were used soon as supports to immobilize catalytically active species, such as metals, peptides or enzymes [2–4]. More recently, the assembly of functional mesostructured materials based on silica, titania or zirconia has gained increasing interest from a wide range of both scientific and technologic fields [5,6]. Functionalization provides with interesting electrical, optical or catalytic properties which may be very different to those of the original constituents [7]. Specifically, the preparation of mesostructured materials as electrodes containing conducting polymers as functionalization agents has attracted attention because of its range of possibilities in optoelectronics or bioelectrochemistry, among others [8,9].

It is known that when organic molecules are inserted into host mesoporous inorganic materials, the physicochemical properties as well as the surface characteristics of the inorganic matrix such as hydrophobicity or surface charge result altered [10]. This behavior has been used to induce the adsorption or to immobilize large molecules, even proteins, on silica mesopores which significantly broadened the application of these materials [11,12]. In particular, we have shown in previous studies the electrochemical growth of polyaniline through the pores of unstructured SiO2 films deposited on glassy

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60   carbon electrodes [13]. The obtained composite materials were used recently as electrocatalysts toward some organic and
61   inorganic redox probes [14].
62   In the present contribution, we will try to take advantage of the highly oriented SiO_2 mesostructure to insert electrochem-
63   ically a self-doping conducting copolymer obtained from aniline and o-aminobenzoic acid (ABA) monomers. This composite
64   material will be used as electrode to study the oxidation of ascorbic acid molecules at neutral pH. We have observed that the
65   oxidation kinetics of ascorbate molecules on conducting poly(ani-co-ABA) films can be satisfactorily described by the kinetic
66   model proposed by Bartlett and Wallace [15]. It is expected that the application of the same model to the oxidation of ascor-
67   bate on the mesostructured SiO_2–poly(ani-co-ABA) composite electrode could clarify the role of the highly ordered silica
68   matrix on the kinetics of the electrocatalytic oxidation.

2. Experimental part

2.1. Reagents and equipment

71   Tetraethyl orthosilicate (TEOS, Sigma–Aldrich), Ascorbic acid (Sigma–Aldrich p.a.), cetyl trimethylammonium bromide
72   (CTAB, Sigma–Aldrich) and sulfuric acid (Merck, p.a.) were used as received. All the solutions were prepared with
73   18.2 MΩ cm ultrapure water obtained from an Elga Labwater Purelab system. The carboxylate-containing polyaniline film
74   was synthesized from the electrochemical copolymerization of o-aminobenzoic acid (99%, Aldrich) and aniline (Aldrich)
75   in 0.5 M sulfuric acid electrolyte with 50 mM concentration of each monomer.
76   The electrochemical experiments were performed in conventional electrochemical Pyrex glass cells. The working elec-
77   trode was a glassy carbon disk (GC, V-25 model, Carbone Lorraine). The GC electrode was carefully polished with fine emery
78   paper and alumina suspensions (Buehler, 1 μm and 0.25 μm) over cloth and then ultrasonically cleaned in distilled water. A
79   platinum wire was employed as counter electrode, and a reversible hydrogen electrode (RHE) immersed in the same elec-
80   trolyte solution through a Luggin capillary was used as the reference electrode. All the results are presented in this potential
81   scale.

2.2. Preparation of SiO_2 layers on glassy carbon electrodes

83   Either microporous or mesoporous silica layers were obtained from two silica precursor solutions:
84   Solution 1 for the microporous SiO_2: 2 mL of TEOS is mixed with 2.75 mL ethanol and 2 mL of a 0.46 M KCl/0.01 M HCl
85   solution. The resulting solution was stirred in a closed vial for 15 min in an ultrasound bath.
86   Solution 2 for the mesoporous SiO_2: 13.6 mmol TEOS and 20 mL ethanol were added to a vessel containing 20 mL 0.1 M
87    $NaNO_3$ in 10^{-3} M HCl. This solution was stirred and then 4.35 mmol CTAB were added. The resulting mixture was stirred for
88   2.5 h.
89   The precursor solution (solution 1 or solution 2) was placed in an electrochemical cell in which the electrodeposition of
90   the silica was performed. The SiO_2 layer is electrochemically deposited on glassy carbon electrode during the application of a
91   very negative potential (−0.9 V/RHE) for 10 s where the reduction of water is produced. This reaction decreases the concen-
92   tration of protons in the vicinity of the electrode surface, inducing the collapse of colloids in the precursor solution and
93   favouring the silica deposition [12,13,16]. If solution 1 is used, the obtained SiO_2 layer is microporous [16]. If the solution
94   2 is used, a mesoporous SiO_2 layer is obtained on the glassy carbon electrode because it has been demonstrated previously
95   that CTAB induces the ordering of the SiO_2 layers [12]. The CTAB is removed from the electrode by treating the mesoporous
96   film electrode in an ethanol solution containing 0.1 M HCl under stirring for 5 min [12]. The counter electrode was a plat-
97   inum wire and a silver wire was used as a pseudo-reference electrode but the reported potentials are referred to the RHE
98   scale.

3. Results and discussion

3.1. Synthesis and characterization of mesostructured SiO_2-conducting polymer composites

101   Two identical glassy carbon electrodes were used as the support for the electrochemically assisted deposition of SiO_2 lay-
102   ers. The experimental procedure is explained comprehensively in the previous section and it has been also described else-
103   where [12]. One of these electrodes was submitted to the deposition of an ordered mesoporous silica film through the
104   template route whereas the other was used for the deposition of microporous SiO_2. Structural differences between both silica
105   layers can be observed clearly in the TEM micrographs presented in Fig. 1. The addition of CTAB to the synthesis medium
106   leads to the well-arranged growth of silica mesostructures showing parallel channels of about 2–3 nm width perpendicular
107   to the electrode surface [12]. On the contrary, a microporous silica deposit is obtained for the glassy carbon electrode
108   immersed in the CTAB-free precursor solution. The potentiostatic growth of a conducting polymer such as polyaniline
109   through the pores of the microporous, electrochemically synthesized SiO_2 film has been reported previously [13]. It was
110   shown there that the polymerization reaction takes place initially inside the pores of the SiO_2 structure. These pores fill
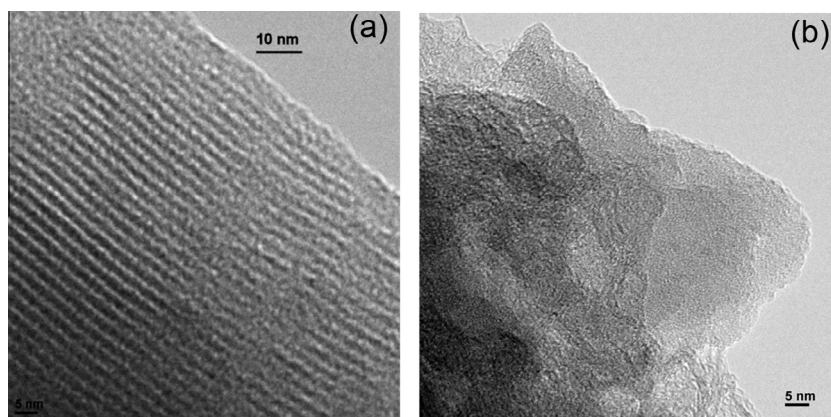
Fig. 1. TEM micrographs acquired at the same magnification after the electroassisted deposition of either a SiO$_2$ film with highly oriented mesostructure (a) or a microporous SiO$_2$ film (b) on glassy carbon substrates.

up slowly with polyaniline and, finally, the polymer chains reach the outer layer of the silica and spread out on its surface. In that stage, a quicker polyaniline autocatalytic growth is observed.

Since we are interested in the effect of silica mesostructure on the electrocatalytic properties of poly(ani-*co*-ABA), a glassy carbon electrode was modified with an oriented SiO$_2$ layer obtained as in Fig. 1a and that material was then used as a template for the growth of the conducting copolymer. The template electrode was immersed at controlled potential in an acidic polymerization solution containing 50 mM aniline and 50 mM *ortho*-aminobenzoic acid. The potential was then stepped up to 1.05 V/RHE and the chronoamperogram shown in Fig. 2a was recorded. According to the profile of this curve, it can be deduced that the polymerization is restricted to the inner mesostructure of the silica layer below, roughly, 1200 s [13]. The exponential shape of the chronoamperogram recorded beyond that point reveals that poly(ani-*co*-ABA) grows out of the silica pores. Accordingly, in the present study we have limited the polymerization time to 1200 s in order to fill up all the mesopores of the silica structure and to minimize the amount of polymer sticking out of the pores.

Once synthesized, the composite electrode obtained as in Fig. 2 but during 1200 s has been tested in both sulfuric acid and pH 7 phosphate buffer solutions and the results presented in Fig. 3. The materials were submitted to repeated oxidation–reduction cycles till the voltammetric curves show a steady profile and it was checked that the structure of the SiO$_2$ film remained after cycling. The characteristic shape recorded in H$_2$SO$_4$ electrolyte shows, as the main features, the redox transition of the copolymer from leucoemeraldine to emeraldine redox state at around 0.5 V and a pair of peaks of uncertain nature in the vicinity of 0.75 V. This curve is similar to that obtained during the copolymerization of aniline and ABA monomers on a bare glassy carbon electrode [17]. Obviously, this voltammetric profile changes significantly when the composite electrode is cycled in neutral medium, as it is observed in Fig. 3b. There, only a pair of redox peaks appears in the voltammetric curve at around 0.6 V. Nevertheless, the presence of aminobenzoic units in the copolymer chains provides this material with self-doping properties and preserves its redox activity in pH 7 medium. Such behavior makes the poly(ani-*co*-ABA)/SiO$_2$ composite electrode an interesting material to study the catalytic oxidation of ascorbic acid molecules in phosphate electrolyte and to establish whether or not the mesostructured silica improves the kinetics of the electrocatalytic oxidation.
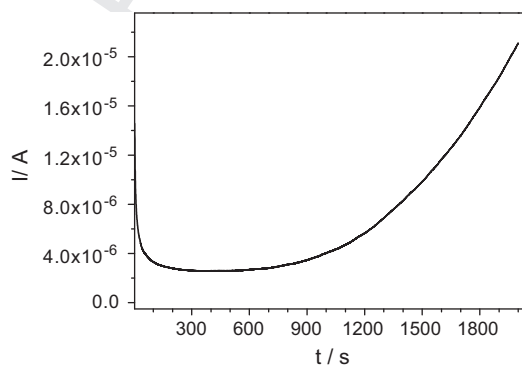
Fig. 2. Chronoamperometric curve showing the potentiostatic growth of poly(ani-*co*-ABA) through an oriented silica mesostructure. Initial potential: 0.05 V/RHE; Final potential: 1.05 V/RHE; [ani] = 0.05 M [ABA] = 0.05 M. Supporting electrolyte: 0.5 M H$_2$SO$_4$.
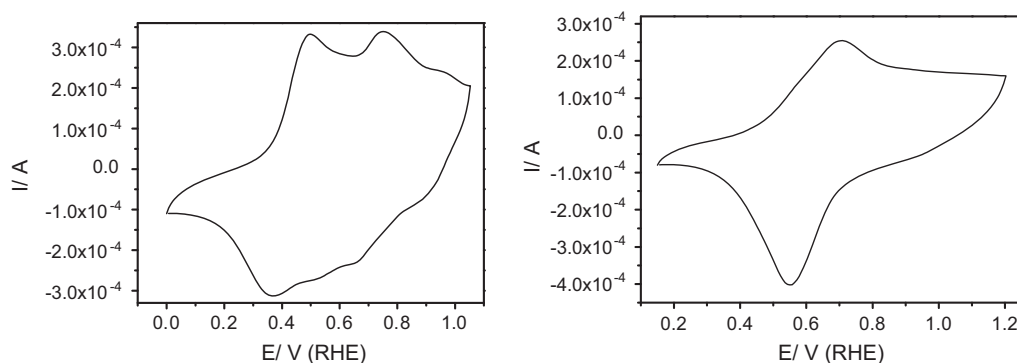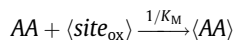
Fig. 3. Stabilized cyclic voltammograms recorded in (a) 0.5 M H_2SO_4 and (b) pH 7 phosphate buffer solutions for a composite electrode obtained as in Fig. 2 but during 1200 s. Scan rate 50 mV s^{-1}.

It is worth mentioning that ascorbic acid is not oxidized on a microporous SiO_2–poly(ani-co-ABA) composite. This result is similar to that reported previously by Walcarius et al. [18] for zeolite modified electrodes, which was associated to a molecular sieving effect. For this reason, in the following sections only mesostructured silica modified electrodes have been studied.

3.2. Electrocatalytic oxidation of ascorbic acid on mesostructured SiO2–poly(ani-co-ABA) composite electrodes

The oxidation of ascorbic acid (AA) as a model molecule has been the subject of numerous studies owing to its significance in biological processes. It has been reported that the electrocatalytic oxidation of AA can be favored on conducting polymers as opposed to carbon or metal electrodes because no strongly adsorbed residues are formed in the organic polymer substrates [19]. Consequently, lower overpotentials and better reproducibility are usually found for the former electrodes [17]. In a recent contribution we have shown that ascorbic acid molecules can be readily oxidized on poly(ani-co-ABA) films [17]. Besides, it was stated that the surface active sites for the oxidation of ascorbic acid were, specifically, the rings showing full quinoid character in the copolymer backbone. The existence of electrostatic repulsions between the attached carboxylate self-doping anions and AA was also demonstrated at pH values above the pK_a of ascorbic acid, which is 4.25. The accepted mechanism for the electrochemical oxidation of AA on polyaniline derivatives has been previously described [15,17,20] and it involves a Michaelis–Menten kinetics for which the overall reaction can be divided in the following two stages:

$$AA + \langle site_{ox} \rangle \xrightarrow{1/K_M} \langle AA \rangle$$

$$\langle AA \rangle \xrightarrow{k_{cat}} \langle site_{red} \rangle + Product$$

Firstly, the formation of the reaction adduct $\langle AA \rangle$ between the Ascorbic Acid molecule and the catalytic site in its oxidized form, whose kinetic constant parallels the reciprocal of the Michaelis constant, K_M. In the second step, charge transfer takes place from the molecule to the site which is then reduced. This second step is governed by the rate constant for the catalytic reaction, k_{cat}.

The question now is to find whether or not an electrically insulating material, as the mesostructured silica, can modify the electrocatalytic response of poly(ani-co-ABA) against ascorbic acid. Fig. 4 shows cyclic voltammograms recorded at pH 7 during the oxidation of 10 mM ascorbate at either the mesostructured SiO_2–poly(ani-co-ABA) composite (dashed line) or at the deposit of poly(ani-co-ABA) (solid line). The oxidation of AA shows a shift of about 100 mV to lower potentials using the composite material as electrode. Furthermore, it can be observed that the difference between the anodic peak and the half-wave potential ($E_p - E_{p/2}$) decreases from 0.24 V, measured for poly(ani-co-ABA), to 0.16 V when the oxidation is performed at the mesostructured SiO_2–poly(ani-co-ABA) composite. These observations can be clearly related with an improvement in the kinetics of the oxidation reaction induced by the presence of the silica ordered template. So, a kinetic study on the oxidation of ascorbic acid at both electrocatalytic materials is required in order to gain more insight on the reasons for the observed kinetic improvement. In the next section, we will use the kinetic model originally developed by Bartlett and Wallace [15], which has been successfully applied to the catalytic oxidation of ascorbic acid molecules at different conducting polymer coated electrodes [15,17,20].

3.3. Kinetic study of the ascorbic acid oxidation

Fig. 5 shows the catalytic oxidation currents recorded at a fixed potential of 0.95 V with a rotating-disk electrode for increasing ascorbic acid concentrations. The recorded current points can be well fitted with the mathematical function expressed in Eq. (1), which is derived from Bartlett's kinetic model based on a Michaelis–Menten reaction mechanism [15].
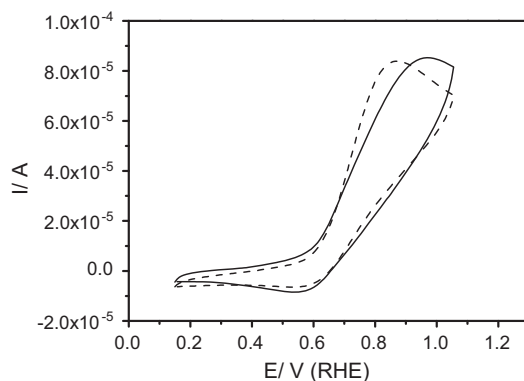
Fig. 4. Rotating-disk electrode voltammetric curves showing the electrochemical oxidation of 10 mM ascorbic acid in pH 7 phosphate buffer solutions at glassy carbon substrates covered with either a mesostructured SiO_2–poly(ani-co-ABA) composite (dashed line) or just a deposit of the poly(ani-co-ABA) copolymer (solid line). In both cases: 540 rpm rotation speed and 50 mV s^{-1} scan rate.

$$i = nFA\left[\frac{k'_D}{2}\left\{(K_{ME} + [AA]) - \sqrt{(K_{ME} + [AA])^2 - \left(\frac{4K_{ME}k'_{ME}[AA]}{k'_D}\right)}\right\}\right] \quad (1)$$

There are four fixed factors in this expression that can be easily obtained: n, the number of electrons involved in the oxidation reaction; F, the Faraday constant; A, the surface area of the electrode and k'_D, the mass transfer rate constant of ascorbate molecules, that can be calculated from the Levich equation assuming a diffusion coefficient for AA of 6.6×10^{-6} cm^2 s^{-1}. According to the kinetic model, the *effective kinetic constants* K_{ME} and k'_{ME} depend on additional parameters such as the concentration of active sites, Γ_{site}, the electronic regeneration coefficient, k'_E, and the catalytic reaction coefficient, k_{cat} as follows [15]:

$$K_{ME} = \left(\frac{K_M}{k_{cat}} + \frac{\Gamma_{site}}{k'_D}\right)\left(\frac{1}{k'_E} + \frac{1}{k_{cat}}\right)^{-1} \quad (2)$$

$$k'_{ME} = \left(\frac{K_M}{k_{cat}\Gamma_{site}} + \frac{1}{k'_D}\right)^{-1} \quad (3)$$

The acceptable nonlinear fitting of the experimental points shown in Fig. 5 assures the applicability of the kinetic model to this system, under the conditions of the experiment, and allows K_{ME} and k'_{ME} to be obtained from Eq. (1) according to the procedure described in [17].

The values obtained for these two constants are summarized in Table 1, where it has been also included the results obtained for the electrochemical oxidation of ascorbic acid directly at poly(ani-co-ABA), i.e., at the copolymer deposited on the bare glassy carbon substrate in the absence of mesostructured SiO_2 template. As it can be observed from the two first columns in the table, the K_{ME} value obtained for ascorbic acid oxidation at poly(ani-co-ABA), 6.3×10^{-5} mol cm^{-3}, increases
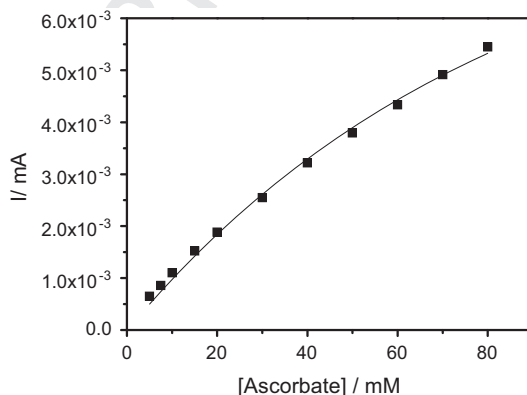
Fig. 5. Validation of the applied kinetic model: (■) experimental currents recorded at 0.95 V during the oxidation of increasing concentrations of ascorbate molecules on mesostructured SiO_2–poly(ani-co-ABA) composite electrodes. (—) Fitting curve obtained from Eq. (1). Supporting electrolyte: pH 7 phosphate buffer.

Table 1

Effective kinetic constants calculated for the oxidation of ascorbic acid at 0.95 V on glassy carbon rotating disk electrodes covered with either a mesostructured SiO_2–poly(ani-co-ABA) composite or a poly(ani-co-ABA) film. Electrolyte solution: pH 7 phosphate buffer containing 10 mM AA. ω = 540 rpm.

Modified electrode	K_{ME} (mol cm^{-3})	k'_{ME} (cm s^{-1})	K_1 ($\alpha \Gamma_{site}$)	K_2 ($\alpha k'_E$)
SiO_2–poly(ani-co-ABA)	10.3×10^{-5}	1.69×10^{-3}	3.35×10^{-3}	5.27×10^{-5}
Poly(ani-co-ABA)	6.3×10^{-5}	1.71×10^{-3}	3.28×10^{-3}	3.26×10^{-5}

by 60% when the polymer is grown within the mesostructured silica. On the contrary, the value of the other kinetic constant, k'_{ME}, seems not to be significantly affected by the presence of the ordered silica matrix.

In order to simplify the discussion on the effect of the silica matrix in the catalysis, some reasonable assumptions can be made. Among the parameters appearing in Eqs. (2) and (3), the mass transport rate, k'_D, has already been taken as a constant in the calculations of the values presented in Table 1, as diffusion within the mesoporosity is considered to be essentially conditioned by the electrolyte, without any effect of confinement. On the other hand, the catalytic reaction rate, k_{cat}, is expected to be a function of the nature of the reaction intermediate which is deemed to be unaffected by the presence of the inorganic matrix. Finally, it should be mentioned that the analysis of the experimental variables affecting the Michaelis constant, K_M, was undertaken in a previous work [17]. There, it was shown that the main changes in K_M are due to the neutral/anionic state of both the ascorbic acid and the polymer. Therefore, it is reasonable to consider that K_M is mainly a function of pH and remains constant in the present study because all the experiments are conducted at a fixed pH 7 value.

Consequently, the discussion must be focused on the influence of the concentration of active sites, Γ_{site}, and the electronic regeneration coefficient, k'_E, which is a measure of the kinetics of restoration of the active site oxidation ability. Since k'_{ME} depends only on the former parameter (Eq. (3)), it is derived that the concentration of sites should remain almost unchanged whether the polymer grows dimensionally unrestricted or within the template. An unvaried concentration of active sites, which were identified as oxidized rings with a pure quinoid character [17], is consistent as the same oxidation potential (i.e. same degree of emeraldine to pernigraniline conversion) is used in both cases. From the model, we have found a combination of constants, expressed as K_1 in Table 1, that allow the contribution of the active sites concentration, Γ_{site}, to be isolated. The fact that both materials show almost identical K_1 values (and hence, the same concentration of active sites) strongly suggests that the 60% increase observed in the K_{ME} value for the template-grown polymer must be explained in terms of an enhancement in the electronic regeneration coefficient, k'_E, which is proportional to the combined K_2 constant shown in Table 1.

The regeneration rate of the quinoid centers is essentially governed by the kinetics of electron transfer between the underlying electrode and the polymer-solution interface sites. Accordingly, it is a function of the polymer conductivity [17]. The reason for the observed increase in the regeneration rate is somehow obscure, since the silica matrix is an insulator and does not provide new paths for the electron transfer. Nevertheless, the matrix can affect the growth of the polymer modifying some of its properties. An increase in the amount/size of the crystalline domains inside the polymer and the preferential orientation of the polymer chains perpendicular to the surface are some features that can be stimulated by the inert template. The former provides the intimate packing of the chains necessary for an efficient electron transfer. In addition, a perpendicular growth of the chain bundles guarantees that the electron path from the active sites toward the electrode have a larger contribution of intra-chain electron transfer (delocalization) and a lower amount of the less favored inter-chain electron hopping. These combined effects could be at the origin of the observed increase in K_2 for the polymer confined inside the ordered silica template and, consequently, could explain the improvement in K_{ME} with no apparent effect in k'_{ME}. This interpretation is also supported by the results of Santos Pedroso et al. [21], who pointed out that the particular morphology of polyaniline grown on ordered mesoporous silica could be at the origin of the improved electrical conductivity found for this material.

4. Conclusions

Highly ordered, mesoporous, electrically insulating SiO_2 layers were deposited on glassy carbon electrodes by an electrochemically assisted deposition method. The obtained material was used as the template for the electrochemical insertion of self-doping poly(aniline-co-ABA).

The copolymer grown within the silica mesoporosity preserves its electrochemical redox activity even at pH 7. Besides, this conducting material is able to oxidize ascorbate anions with improved kinetic performance when compared with poly(aniline-co-ABA) deposited straight on bare glassy carbon substrates.

The kinetic study for the oxidation of ascorbate ions at a fixed potential revealed that the effective kinetic constant K_{ME} increases significantly and, simultaneously, k'_{ME} does not change when the catalytic reaction takes place at the SiO_2–polymer composite. The observation that the surface concentration of active sites Γ_{site} is almost the same for both poly(aniline-co-ABA) and SiO_2–poly(aniline-co-ABA) strongly suggested that the increase in K_{ME} should be ascribed to an improvement in electronic conductivity of the copolymer induced by the silica template. This hypothesis seems supported by the fact that K_2, the combination of kinetic constants proportional to k'_E, is higher for the polymer grown inside the silica template.

Acknowledgements

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