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Electrochemical oxidation of primary amine in ionic liquid media: Formation of organic layer attached to electrode surface

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ABSTRACT

Electrochemical oxidation of primary amine in ionic liquid media has been investigated. The ionic liquid chosen for this study was 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide. Two primary amine compounds are used for this study; 4-nitrobenzylamine and 2-aminoethylferrocenylmethylether. The oxidation of the amino compounds in ionic liquid conduces to the modification of the electrode surface. The modified electrodes were characterized by cyclic voltammetry and XPS analysis. Both techniques support the presence of an organic layer strongly attached onto the electrode surface. The surface concentration of the attached group obtained in this media was found to be around 1 to 3×10^{-10} mol cm^{-2}. The use of ionic liquid as media for the grafting leads to decrease of the surface concentration of the grafted layer; and the formation of less dense layer compared with classical solvent such as acetonitrile.

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1. Introduction

The attachment of organic molecules onto electrode material is at present an ordinary process which enables the control of the interfacial structures. A large arsenal of methods is available to form defectless mono- and multilayered structures and to control their physicochemical properties. During the last 20 years, the diazonium-based chemistry has been used to produce modified surface [1]. The procedure of the electrografting involves the electrochemical reduction of a phenyldiazonium cation leading to the attachment of phenyl group to the electrode surface [2]. This approach constitutes an interesting field for building novel interfaces for applications ranging from molecular electronics, photovoltaic devices and catalysis to chemical or biochemical sensing [3–5].

In this connection, another process has been described to perform the electrochemical modification. This process could be considered the opposite of the reduction of the diazonium cation and is based on the oxidation of amino groups. This reaction was reported for R-NH_2 compounds and success was obtained with the oxidation process to perform the grafting of organic layers [2,6]. The principle is similar to that described for the reduction of the diazonium but occurs on oxidation. Thus, the oxidation of the amine leads to the formation of the corresponding radical in the vicinity of the electrode material that quickly reacts with the surface leading to the attachment of organic layer [7].

The occurrence of such grafting was evidenced by following the electrochemical signal of electroactive groups such as nitro or ferrocene groups, and it was possible to observe the reversible signal of nitrobenzyl or ferrocene groups [8]. In addition, the grafting was also demonstrated by XPS and IR analysis [9]. This reaction has been studied in organic solvent such as acetonitrile [10]. The main goal with this reaction is to improve the control of thickness of the deposited layer. For this reason several strategies were proposed to improve the quality of the attached layer and to obtain an organic monolayer [11]. In our recent work, case of the electroreduction of the diazonium, we have shown that the use of ionic liquid leads to a better control of the amount of the grafted molecules [12]. Room temperature ionic liquids (RTILs) are receiving increasing interest for their possible use as alternative reaction media to organic volatile solvents [13]. The RTILs present several characteristics such as large electrochemical window, high ionic conductivity; they also present large potential interest as solvents for electrochemical applications because they can be used without the need of any added supporting electrolyte thanks to their intrinsic ionic conductivity [14]. The special characteristics of RTILs make these solvents attractive media for electrochemical investigations. The previous electrochemical works realized in ionic liquids demonstrates that the information obtained by transient electrochemical methods are valid and mainly remain similar with those observed in organic molecular solvents [15]. One of the differences by comparison with the organic molecular solvent is the low diffusion coefficient due to the high viscosity of the ionic liquid [16,17].

In the present work, we purpose to investigate the electro-oxidation of the primary amine in ionic liquid media. The

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attachment of the organic moieties onto the electrode surface was achieved in the ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [EMIM][TFSI] by cyclic voltammetry. Two amino compounds are used for this study 4-nitrobenzylamine and 2-aminoethylferrocenylmethylether. Cyclic voltammetry and XPS analysis were used to characterize the grafted molecules onto the electrode surface.

2. Experimental section

2.1. Chemicals

RTILs ([EMIM][TFSI]), 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, was prepared from aqueous $LiN(CF_3SO_2)_2$, [Li]–[TFSI] (Solvionic), and the corresponding bromide or iodide salts according to standard procedures [18]. The samples were purified by repeated washing with H_2O and filtered over neutral alumina and silica. Prior to each experiment, vacuum pumping carefully dried RTILs overnight and the amount of residual water was measured with Karl Fischer titration (Karl Fischer 652 Metrohm). The amount of water measured in our samples ranged from 100 to 200 ppm. The amino compounds used for this study are 4-nitrobenzylamine and 2-aminoethylferrocenylmethylether which were synthesized using a previously published procedure [9,19].

3. Electrochemical experiments

For the electrochemical experiments a conventional three-electrode cell was used. Platinum wire was used as auxiliary electrode, Ag wire (immersed in HCl prior to the measurements, then rinsed thoroughly with water and ethanol) as reference electrode. The potentials were checked versus the ferrocene/ferrocenium couple and all the potentials were scaled against the SCE electrode. Carbon electrode (0.07 cm^2) and indium tin oxide ITO (1 cm^2) were used as working electrode. The potentiostat used in this study was CHI 660C (CH instruments).

The electrochemical grafting was performed by cyclic voltammetry. For each experiment 5 cycles were performed and the potential was scanned between 0 and 1.8 V/SCE, at scan rate 0.1 V s^{-1}. This procedure was used for both electrodes carbon and ITO and for both amino compounds. The oxidation of the amino groups in the ionic liquid was performed at room temperature 25 °C.

4. Results and discussion

The electrochemical oxidation of amino compounds in the ionic liquid was investigated using cyclic voltammetry. Fig. 1 shows the voltamogramme of 10^{-3} M of 4-nitrobenzylamine in ionic liquid [EMIM][TFSI] on a carbon electrode.

The CV exhibits an irreversible oxidation wave at a potential around 1.5 V/SCE. By analogy with the previous results reported in the literature, this anodic peak corresponds to the oxidation of the amine group leading to the formation of the corresponding radical [20]. This first result indicates the possibility to oxidize the primary amine in ionic liquid media. Consequently, the electrochemical oxidation of 4-nitrobenzylamine could conduce to the attachment of amino-nitrobenzyl moieties onto the carbon surface.

One of the easiest ways to evidence the presence of organic layer attached onto carbon electrode is to characterize the modified electrode by electrochemistry thanks to the presence of the nitro groups. Indeed, the modified electrode was removed from the grafting solution and was systematically rinsed with ACN to remove the weakly adsorbed molecule. Following that the electrode was transferred to solution containing only 0.1 M of H_2SO_4. The CV recorded of the modified carbon electrode in this solution is presented on Fig. 2a.

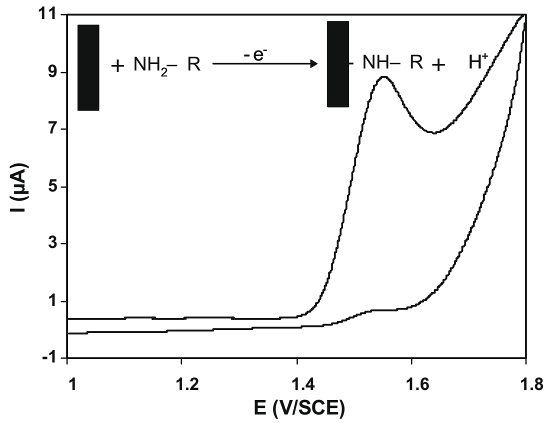

Fig. 1. Cyclic voltamogramme at room temperature, 25 °C, of 10^{-3} M of 4-nitrobenzylamine in ionic liquid [EMIM][TFSI] on a carbon electrode. Scan rate 0.1 V s^{-1}. Inset: Grafting of organic group through the electrochemical oxidation of primary amine.

The data shows the presence of irreversible reduction wave, at potential $E_p = -0.6$ V/SCE, very close to that of the reduction wave of nitrobenzene in solution. During the reverse scan an anodic wave at $E_p = 0.16$ V/SCE is observed. Upon the second scan new reversible system appears with standard redox potential $E =$ 0.12 V/SCE. By analogy with the previous work achieved in acidic media, this reversible system has been attributed to the couple NHOH/NO [21]. This behavior indicates that the reduction of the attached nitro groups, at potential −0.6 V/SCE, could occurs at $4e^-$ or $6e^-$ leading to the formation of NHOH groups or NH_2 groups, respectively [22]. The drastic diminish of the reduction wave, at $E_p = -0.6$ V/SCE, during the second scan followed by complete disappearance upon further cycles, indicate that the grafted NO_2 groups are totally reduced. All these results suggest that the amino-nitrobenzyl groups are immobilized on the carbon electrode.

The electrochemical grafting based on the oxidation of amino groups in ionic liquid has been also investigated with 2-aminoethylferrocenylmethylether onto ITO electrode. The grafting was performed following the procedure presented in the experimental part. Similar behavior as shown on Fig. 1 was obtained indicating the oxidation of the amine at ITO electrode. This result suggests the occurrence of the grafting on different electrodes materials and with several primary amines.

The modified electrode was transferred into an electrolytic solution containing 0.1 M of Bu_4NBF_4 in ACN. Fig. 2b shows the electrochemical characterization of the modified electrode. The recorded CV shows electrochemical reversible system at around 0.45 V/SCE which is assigned to the electrochemical response of the Fc^+/Fc redox system. The peak-to-peak separation is around 40 mV, and the ratio of anodic to cathodic peak currents is close to unity. This behavior is characteristic of immobilized system to the surface. Moreover, linear dependence of the current versus the scan rate in the range 0.001–5 V s^{-1} was observed. This linearity is indicative of a process where the electroactive species do not diffuse to and from the electrode and thus demonstrate that the Fc groups are grafted onto the ITO electrode. We point out that the electrochemical signal of Fc groups does not disappear after ultrasonic cleaning of the electrode in ACN, confirming the strong attachment between the organic layer and the ITO surface. In addition, the modified electrode was investigated using XPS analysis. The high resolution spectrum of *Fe* 2*p* is composed of two peaks located at 708.4 and 721.0 eV, corresponding to *Fe* $2p_{3/2}$ and *Fe* $2p_{1/2}$ signals, respectively. These values are perfectly consistent with

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