



Short communication

Covalent attachment of alkene and alkyne groups on carbon surfaces by electrochemical oxidation of unsaturated aliphatic carboxylates



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ABSTRACT

The covalent modification of glassy carbon electrodes by oxidation of unsaturated aliphatic carboxylates is reported in this work. It is shown that the presence of π -bonds on the hydrocarbon structure is essential to develop the grafting process, which does not occur with totally saturated carboxylates. In this way, the glassy carbon surface modification with aliphatic chains containing alkene and alkyne groups was performed and the presence of such groups was demonstrated through a *Heck* and a *Click* reaction, allowing respectively a further functionalization with nitrobenzene and ferrocene groups.

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1. Introduction

In the last decades, several electrochemical methods of covalent modification of carbon surfaces have been developed and recently reviewed [1–3]. The immobilization has been attributed to the attack of free radicals or carbocationic intermediaries on the sp^2 carbon atoms existing on the basal or edge sites of the carbon surfaces. Alternatively, the generation of surface anionic sites that can react by nucleophilic substitutions has also been proposed [4,5]. Due to the strong nature of the chemical binding mode with the surface, it has been found that the stability of these covalently modified electrodes is higher than in the case of physically immobilized monolayers. This difference makes important the covalent grafting for robust applications in the field of sensors and biosensors [6], carbon–epoxy composite materials [7], in electrocatalysis [8] and for fundamental studies [9]. The grafting with organic moieties takes place on glassy carbon, but also on different substrates, such as HOPG, carbon fibers or carbon felts [10] and carbon powders by chemical means [11].

One of the grafting methods of carbon surfaces that has been scarcely studied is the anodic oxidation of carboxylates, which alternatively, is one of the most relevant reactions in electrosynthesis to form of a wide variety of organic compounds, derived from a radical (Kolbe reaction) or carbocationic (non-Kolbe reaction) chemistry [12]. These reactions has been extensively studied, however, its application for preparation of modified electrodes has been only focused to the case of the direct oxidation of substituted arylacetates [13–15] and the mediated oxidation

of other carboxylates [16]. The mechanistic analysis of the arylacetate oxidation process suggested that benzylic carbocations can react either through a Ritter reaction with the acetonitrile or they can be covalently grafted to the carbon surface [17].

Considering that alkyl carbocations are more reactive than benzylic carbocations, the oxidation of a series of tetrabutylammonium aliphatic carboxylates in acetonitrile was also tested, however no grafting process was observed, even when a carbocationic chemistry was in agreement with the nature of electrolysis products (acetamides and acylamides) [18,19]. This result suggests that the presence of an aromatic nucleus or even the only presence of π -bonds on the carboxylate structure can be an essential factor to develop the grafting process where highly reactive carbocations are involved. Thus, in this work, several aliphatic carboxylates containing single, double and triple bonds, were used to demonstrate that the presence of π -electrons on the carboxylate structure is a key factor to promote the grafting of carbon surfaces by anodic oxidation of carboxylates. Tetrabutylammonium carboxylates derived from pentanoic (**1**), 4-pentenoic (**2**) and 4-pentynoic acids (**3**) were selected to offer experimental evidence. In this series, compounds **2** and **3** allow the carbon surface functionalization with aliphatic chains containing terminal alkene and alkyne terminal groups.

2. Experimental

Acetonitrile spectral grade (Merck) was used as the solvent whereas tetrabutylammonium hexafluorophosphate 99% was the supporting electrolyte. Tetrabutylammonium hydroxide 1 M/methanol and the necessary carboxylic acids to prepare the pentanoate (**1**), 4-pentenoate (**2**) and 4-pentynoate (**3**) ions were obtained from Aldrich and used as

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received. The carboxylates were prepared in-situ by stoichiometric neutralization of the acid with tetrabutylammonium hydroxide. The carboxylate solutions were deoxygenated by argon bubbling and an argon atmosphere was maintained over the solutions during the experimental runs ($T \approx 25\text{ }^{\circ}\text{C}$).

The electrochemical apparatus consisted of a potentiostat DEA-332 (Radiometer) with positive feedback resistance compensation. A conventional three-electrode cell was used in the voltammetric experiments. The working electrode was a 3 mm diameter glassy carbon disk (Sigradur G from HTW), and the counter electrode was a platinum mesh. The reference electrode was a saturated calomel electrode (SCE). A salt bridge, containing 0.1 M $n\text{-Bu}_4\text{NPF}_6$ + acetonitrile solution, connected the cell with the reference electrode.

The electrode modification was performed with successive cycles until the total disappearance of the voltammetric oxidation peak. Between each cycle, the solution was stirred by argon bubbling. The functionalization of the modified electrodes with alkene and alkyne groups was performed following the basic principles of the Heck and Click chemistry [20,21]. The electrode modified by oxidation of **2** was placed in 15 mL of DMF containing 10 mg of palladium acetate and 25 mg of triphenylphosphine during 10 min. After this time, 19 mg of 1-bromo-4-nitrobenzene and 650 mg of K_2CO_3 were added under argon atmosphere and the mixture was kept in reflux during 20 h. Concerning the electrode modified by oxidation of **3**, it was placed in 15 mL of isopropanol:water (2:1) containing 2.5 mg of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 6.7 mg of sodium ascorbate and 26 mg of synthesized azidomethylferrocene [22]. This mixture was kept in the dark under stirring at room temperature during 1 h. Once both functionalization procedures were completed, the electrodes were rinsed with different solvents in an ultrasonic bath. These electrodes were electrochemically tested in a solution containing only acetonitrile and the supporting electrolyte to register respectively the surface voltammetric signals of nitrobenzene and ferrocene.

3. Results and discussion

Fig. 1 shows a comparison between the voltammetric behavior of pentanoate (**A**), pentenoate (**B**) and pentynoate (**C**) ions, which possess the same aliphatic length chain. Repetitive cycles, separated each one by stirring of the solution, were registered. In each case, the chemically irreversible behavior observed was in agreement with the fact that the first electron transfer process is followed by fast decarboxylation [17,19]. In the particular case of the saturated carboxylate **1** (Fig. 1A), all the cycles are closely equivalent, meaning that the oxidation process occurs without the interference of electrode inhibition effects. Contrary, in the case of the unsaturated carboxylates **2** and **3**, the current peak decreases with the number of cycles, which implies that the electrode surface is being gradually blocked, reaching finally a total inhibition state after several cycles (Fig. 1B–C). This surface process provokes the decrease of the active surface toward the electron transfer and it is manifested in the voltammograms by the fast decrease of current upon repetitive cycling and the typical curvature after the reverse potential [23], which is different to the case of the saturated carboxylate **1** where the electrode inhibition is absent.

A comparison among these three carboxylates is shown in Fig. 2 in terms of the peak current of the first cycle registered as a function of the carboxylate concentration at a fixed value of scan rate. In the case of the saturated aliphatic carboxylate **1**, the current peak presents a linear behavior with the concentration, which is in agreement with a process occurring only under diffusion and chemical control [24]. Alternatively, in the case of the unsaturated aliphatic carboxylates **2** and **3**, a tendency which deviates from the linear behavior was observed. The degree of deviation is proportional to the predominance of grafting effect. Thus high carboxylate concentrations afford the more important deviation and consequently the highest rate of electrode inhibition, which is more significant for the carboxylate structure containing the terminal alkyne group. This conclusion is supported by an analysis

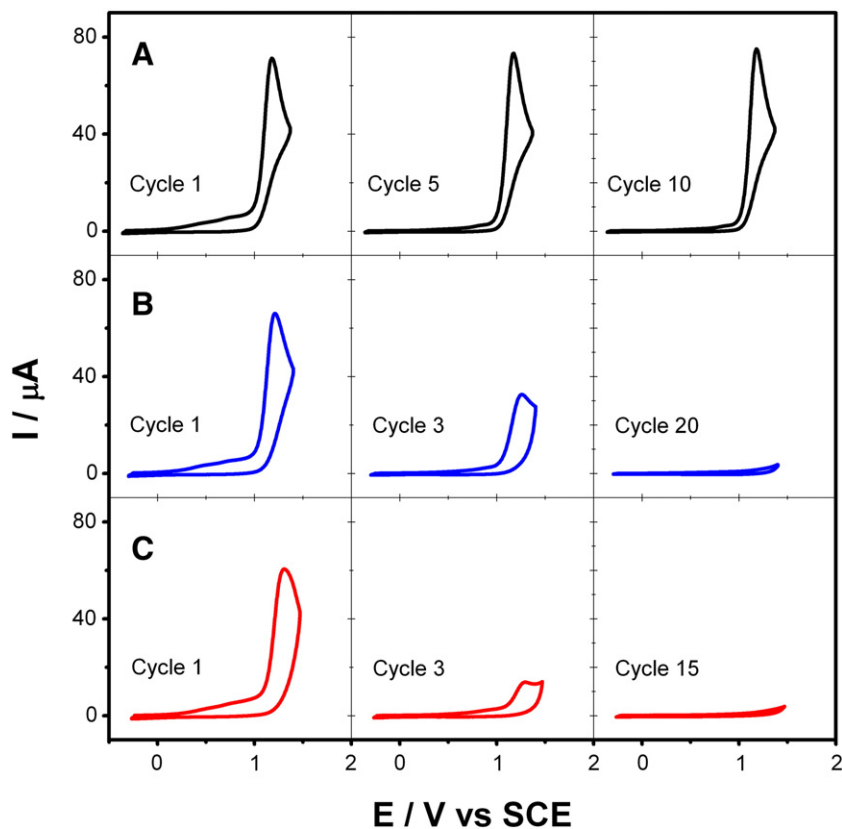


Fig. 1. Repetitive cyclic voltammetry of 4 mM of tetrabutylammonium pentanoate (A), 4-pentenoate (B) and 4-pentynoate (C) ions in acetonitrile + 0.1 M $n\text{-Bu}_4\text{NPF}_6$ on glassy carbon electrodes at 0.1 V s^{-1} . The solution was stirred between each one of the successive cycles.

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