New Processes and Materials Based on Electrochemical Concepts at the Microscopic Level Symposium, MicroEchem 2013

Modification of carbon electrodes by anodic oxidation of organic anions

Dulce M. Hernández, Miguel A. González, Pablo D. Astudillo, Lindsay S. Hernández, Felipe J. González*

Departamento de Química del Centro de Investigación y Estudios Avanzados del IPN, Av. IPN 2508, C.P. 07360, Distrito Federal, Mexico

Abstract

Functionalization of carbon surfaces was first carried out in electrode pre-treatments under drastic electrolysis conditions. As a result of these treatments, the electrode carbon surfaces were modified without selectivity with a wide variety of oxygenated functional groups. However, this lack of selectivity was partially overshot with some electrochemical strategies of covalent immobilization, such as the reduction of aryldiazonium, arylsulfonium and iodonium salts, the oxidation of amines, alkynes and arylacetates. In a variant of these direct methods, the oxidation of the carbon surfaces in presence of alcohols and alkyltrimethylsilanes has also been developed. This sort of derivatization has opened the possibility to incorporate a wide variety of functional groups according to the desired applications. In the majority of these methods, reactive intermediates such as organic free radicals and carboxylation are generated, which react with the sp² carbon atoms of the surface to produce covalently modified electrodes. In the particular case of the oxidation process of carboxylates, the loss of carbon dioxide is accompanied with the formation of free radicals and by analogy, it is proposed in this work that other organic anions are also susceptible to be oxidized to yield free radicals that could be covalently attached to carbon electrodes.

Keywords: Carbon surfaces, Covalent grafting; Carboxylates; Nitroindol; Cyclodextrins

1. Introduction

The covalent modification of carbon electrodes with organic groups, for applications in chemical sensing and materials science, has been well recognized and recently reviewed.¹ ³ Due to the great stability and chemical
properties of the grafted organic layers, several organic electrochemical reactions have been used as a tool to attach a wide variety of organic groups to carbon surfaces. For example, by using the well known reduction of aryldiazonium,4 arylyodonium and arylsulfonium salts.5, 6 Alternatively, the electrochemical oxidation of amines,7, 8 alcohols,9 and arylacetates10 have also been used for the same purpose. Nevertheless the highest number of papers on electrochemical covalent grafting involves aryldiazonium salts, the oxidation of carboxylates allows also the chemical attachment of several organic groups onto carbon surfaces. Although this oxidation method is based on salts of accessible carboxylic acids, it has only been explored for a limited number of compounds.10-14 There are two methods available to carry out the grafting of a carbon surface by oxidation of carboxylates. One of them is based on the direct oxidation of the carboxylate, which considers the intervention of a Non-Kolbe process, in which a generated carbocation can react in solution, either with the acetonitrile to afford acetamides or acylamides,15, 16 or with the sp² carbon atoms of the electrode surface (Scheme 1). In this way, glassy carbon and HOPG electrodes have been grafted with arylmethyl groups by using the direct method.10-14

In a previous study on the direct oxidation of a series of aliphatic carboxylates (acetate-octanoate) on glassy carbon electrodes, it was demonstrated that carbocations were also involved in the mechanism,15 however, the grafting of alkylic groups on the surface was not possible. This restriction of the direct method as a tool to graft surfaces from oxidation of aliphatic carboxylates, was however overcome by implementing an indirect oxidation method.17-19 In this particular case, acetate oxidation was induced by the oxidized form of ferrocene as redox catalyst, being methyl radicals the responsible of the grafting process. The attachment of alkylic groups through C-N (amine oxidation) and C-O (alcohol oxidation) bonds has been reported previously, however, this is the first method of modification of carbon electrodes allowing the anchoring of alkylic moieties through C-C bonds. Considering that the oxidation of organic anions would give rise to radicals that would react with carbon surfaces, the concept of grafting by carboxylate oxidation was extended to the case amine and alcohol derived anions. In this way, this work is divided in three parts that illustrate diverse possibilities to graft carbon surfaces by using an oxidative method, that is, the direct and mediated oxidation of carboxylates and the oxidation of 5-nitroindol and β-cyclodextrin derived anions as examples for the families of amines and alcohols.

2. Grafting of carbon surfaces by direct and mediated oxidation of carboxylates

The modification of carbon electrodes by direct oxidation of carboxylates (RCOO⁻) has been performed mainly by using arylacetates,10-13 carboxylates and carboxylates containing quinone groups.14 The oxidation mechanism occurs according to Figure 1.

![Figure 1. Mechanism of direct oxidation of carboxylates and carbon surface modification](image)

The stepwise nature of the oxidation and cleavage of carbon dioxide was demonstrated in the case of tetrabutylammonium oxalate and substituted benzylic carboxylates.13, 20 This process give rise to free radicals (R') which are more easily oxidized than the carboxylate itself, allowing the formation of carbocations (R⁺). Due to the fact that acetonitrile is a nucleophilic solvent, these intermediates can react in solution to produce acetamides and/or acylamides or with the carbon surface to graft it. This last process permits the covalent attachment of the organic groups to the surface through C-C bonds, which can only be removed by polishing.

When the phenyl group is separated from the carboxylate structure by several methylene groups, the carbon surface grafting process also occurs, however it fails for totally saturated aliphatic structures.15 This contrasting
behaviour indicates that the presence of unsaturations in the carboxylate structure is essential to develop the grafting process. To demonstrate this point, a comparison among the voltammetric behaviour of tetrabutylammonium salts of pentanoic, pentenoic and pentynoic acids was performed.\textsuperscript{21} With these examples, it was demonstrated that even when the alkene and alkyne groups are separated from the carboxylic function by several methylen groups, the electrode inhibition participates in the mechanism,\textsuperscript{21} while the saturated compound only afford acylamides in solution as products.\textsuperscript{15} The presence of the alkene on the modified electrode was demonstrated by incorporating nitrophenyl groups by a Heck reaction, while the alkyne by a Click reaction in which ferrocene was chemically attached.

From these results, it was considered that the attachment of saturated alkylic chains could be reached by avoiding the oxidation of the free radical R\(^{\cdot}\) at a potential lower than that of the carboxylate. To test this hypothesis, different ferrocene derived mediators were tested for the mediated oxidation of acetate ions. It was obtained that the process takes place at a potential 800 mV less positive than the direct oxidation of the acetate ions while the current was triplicated, showing the intervention of a redox catalysis process in the first two steps of the mechanism which is depicted in Figure 2. The gap between the oxidation potential of mediator and the carboxylate is too large to favour the redox catalysis reaction, however, the necessary driving force is furnished by the coupled chemical reactions involved in the overall process, such as it was demonstrated by evaluating the free energies for the individual reactions from electronic structure calculations\textsuperscript{22}

![Fig. 2. Mechanism of mediated oxidation of carboxylates and carbon surface modification](image)

The efficiency of the covalent grafting is increased by using ferrocenecarboxaldehyde, which has a redox potential closer to the potential for the direct oxidation of acetate and a similar enhancing effect was obtained for mediators containing two communicated ferrocene redox centers.\textsuperscript{18} In these cases, the grafting process yield multilayers on the surface which growth by reaction between the hydrogens on the methyl groups on the attached film and the methyl radicals generated at the interface. The morphology of the modified surfaces is independent on the chemical nature of mediator and they are enough compact to block the surface towards the entering of small molecules like molecular oxygen.

### 3. Grafting of carbon surfaces by direct oxidation of amine derived anions

One-electron oxidation of organic anions affords transient radicals, and under this principle, it has been proposed that if the oxidation process is carried out at potential values low enough, these radicals can be covalently grafted to carbon surfaces. To illustrate this proposal, deprotonation and further electrochemical oxidation of 5-nitroindole was performed in acetonitrile on glassy carbon electrodes, which allowed the covalent immobilization of nitroindole.
groups on the electrode surface. This alternative is a variant of the grafting method based on the oxidation of neutral amines, which fails for neutral indole derivatives at high potential values. Compared to the protocol for neutral molecules, the anion oxidation method provides the advantages of occurring at a lower oxidation potential, requires fewer number of potential cycles for the surface modification and it affords stable films that cannot be removed by rinsing in polar and non-polar solvents. Figure 3 shows a comparison between the grafting process by oxidation of both, the neutral and anionic 5-nitroindole.

![Fig 3. Grafting mechanism by direct oxidation of neutral and anionic amine derivatives](image)

Fig 3. Grafting mechanism by direct oxidation of neutral and anionic amine derivatives

The oxidation of the neutral 5-nitroindole (black pathway) yield a highly acidic radical cation, which is deprotonated by the solvent to generate a nitrogen centered free radical that is next covalently attached to the electrode surface. This process is not so efficient because of the relative stability of the radical cation, which can diffuse away the electrode surface where is cleaved. However, the oxidation mechanism of 5-nitroindole anions consist in the uptake of one electron from the amine nitrogen atom N1 (blue pathway), which give rise directly to a free radical possessing the spin density mainly located at the N1 and C2-C3. As a result of this density distribution, the 5-nitroindole groups can be attached on the carbon surface through two chemical contact modes. The process give rise also to multilayers on glassy carbon and HOPG surfaces and the film present the typical reversible electroactivity of 1-methyl, 5-nitroindole, which confirms the chemical nature of the groups in surface.

### 4. Grafting of carbon surfaces by mediated oxidation of β-cyclodextrin derived anions

The covalent grafting of glassy carbon and highly oriented pyrolytic graphite with compounds derived from alcohols is also based in the concept that the oxidation of organic anions generates radicals which react with carbon surfaces. In the previous case the formation of N-C(surface) bonds was possible by using amine anions, however, to induce O-C(surface) bonds, the use of alcohol anions is also possible and exemplified here for the case of cyclodextrins (CD), which are useful to prepare modified surfaces of interest in the field of sensors. For β-cyclodextrin monoanions, radical species are generated through a redox catalysis mechanism involving the anodic formation of ferrocenium ion (Fc'), which in turn oxidizes the cyclodextrin monoanion (CD') to afford an oxygen-centered free radical (CD') that ultimately reacts either in solution or with the surface, affording a strong attachment of β-cyclodextrin molecules to the carbon surface.
Fig. 4. Structure of the β-cyclodextrin anion and grafting mechanism.

The organic deposit is constituted by several layers, which cannot be removed by ultrasonic rinsing in polar and non-polar solvents. These layers are permeable and the modified electrode behaves consequently as a microelectrode array where each pinhole corresponds to an individual microelectrode. The intervention of cyclodextrin radicals was established from spectroelectrochemical EPR experiments over platinum electrodes. On the other hand, atomic force microscopy imaging showed that the attached organic layer is thick while cyclic voltammetry experiments confirmed that this modified surface can form surface inclusion complexes. This kind of modification allows incorporate cyclodextrin to an electrode surface without a binder, making the modified electrode useful to be tested in forthcoming sensor studies.

Acknowledgements

DMH, PDA, LSH, and MAG acknowledge Conacyt for a grant. The authors acknowledge also Conacyt for financial support through the project 103714 and 128411.

References