



# Facile cathodic surfacial carboxylation of glassy carbon by means of immobilized alkanic acids chains

Viatcheslav Jouikov<sup>a</sup>, Jacques Simonet<sup>b,\*</sup>

<sup>a</sup> UMR 6510, Université de Rennes 1, Campus de Beaulieu, 35042 Rennes Cedex, France

<sup>b</sup> Laboratoire MaCSE, UMR CNRS 6226, Université de Rennes 1, Campus de Beaulieu, 35042 Rennes Cedex, France

## ARTICLE INFO

### Article history:

Received 22 June 2011

Received in revised form 19 July 2011

Accepted 25 July 2011

Available online 11 August 2011

### Keywords:

Glassy carbon

Surface grafting

Carboxylation

Bromo-alkanoic acids

## ABSTRACT

The reduction of  $\omega$ -bromoalkanoic acids  $\text{Br}(\text{CH}_2)_n\text{COOH}$  at glassy carbon cathodes in aprotic polar solvents (acetonitrile, *N,N*-dimethylformamide or propylene carbonate) in the presence of tetraalkylammonium salts at  $E < -1.7$  V vs. Ag/AgCl results in a dense organic layer, covalently attached to carbon, which progressively covers the electrode surface. It was evidenced that the immobilization of alkyl chains occurs via the scission of C-Br bonds permitting an efficient coverage of the carbon surface with the layers built of alkyl links  $\{\text{CH}_2\}_n$  ( $3 \leq n \leq 11$ ) terminated with COOH groups. The carboxyls immobilized this way were easily transformed into electroactive esters or into amides by reacting with phenols or amines, respectively. Thus grafted  $\pi$ -acceptor groups allowed estimating the carboxylation level as very high, ca.  $(1-5) \times 10^{-9}$  mol/cm<sup>2</sup> when taking into account the starting surface area. In aqueous media, the immobilized films with long alkyl linkers visibly behave as hydrophobic layers.

© 2011 Elsevier B.V. All rights reserved.

## 1. Introduction

Glassy carbon (GC) is considered to be a convenient and “inert” carbon electrode material for electroanalytical and electrosynthetic purposes. This complex material, industrially prepared by carbonization of phenolic resins at high temperatures [1], contains ribbons of graphite-like structures intermittent with “crystallite” boundaries [2]. GC can be also considered as a patchwork of conducting carbon zones containing fullerene-like areas [3]. This complex nature of GC accounts for the graphite capability to be electrochemically charged (or chemically doped) at quite negative potentials ( $E < -1.7$  V) [4].

Furthermore, free organic radicals electrogenerated from aryl-diazonium salts [5] or activated halides [6] are easily grafted on GC surfaces at the potentials where these radicals are not reduced (about  $E > -1.2$  V). Cathodic activation of GC was recently discussed [7] which, under polarization at  $E < -1.7$  V could form nucleophilic centers at the GC surface [see also the carboxylation of graphite by  $\text{CO}_2$  [8] as a model] capable to induce interfacial reactions with electrophilic species RX resulting in deposition of alkyl chains.

Exploiting these phenomena might enable a cheap, simple and efficient way of preparing new chemically modified materials that can be used in catalysis by immobilizing simple functional groups to GC. In the present report, this has been achieved using aliphatic precursors ended on one side by a halogen (X, electrophilic center) and on the

other side by a versatile function (Y) capable to be chemically transformed afterwards with high conversion efficiency:



Here X is Br or I, while Y could be chosen as nitrile, sulphonate, sulphinate or carboxylate groups, all being good anchoring sites for further modifications. Obviously, Y might not be a redox center in order to avoid any reaction of its reduced form(s) with RX resulting either from internal electron transfer and/or nucleophilic substitution [9]. The reported approach specifically concerns  $\omega$ -bromoalkanoic acids  $\text{Br}-(\text{CH}_2)_n-\text{COOH}$  with  $n = 3$  (**1**), 5 (**2**), 9 (**3**) and 11 (**4**). 3-Bromopropionic acid ( $n = 2$ ) was found not to be suitable for the present project because in non-aqueous unbuffered media it readily decomposes to acrylic acid in the contact with electrogenerated bases present at the electrode vicinity. The experimental conditions for achieving the grafting concern simply polar aprotic organic solvents (such as DMF) containing tetraalkylammonium salts.

## 2. Experimental

Voltammetry was carried out in 0.1 M solutions of  $\text{Bu}_4\text{NBF}_4$  or  $\text{Me}_4\text{NBF}_4$  in *N,N*-dimethylformamide (DMF), and permuted water. The experiments described in this work needed no special treatments of electrolytic solutions.

Potentials are referred to the aqueous Ag/AgCl<sub>(sat)</sub>. The electrochemical instrumentation has been previously reported [8].

The electrodes used in voltammetry had an apparent surface area of 0.8 mm<sup>2</sup> (GC1) and 7 mm<sup>2</sup> (GC3). Coulometric measurements and

\* Corresponding author.

E-mail address: jacques.simonet@univ-rennes1.fr (J. Simonet).

electrolytic deposits were performed using three-electrode cells separated with a fritted glass. The experiments were completed on  $\text{Br}(\text{CH}_2)_n\text{COOH}$  concentrations between 7 and 20  $\text{mmol L}^{-1}$ . Efficient argon bubbling was provided in all cases. Modified electrodes were sonicated (during 2 min) in water, then rinsed with acetone.

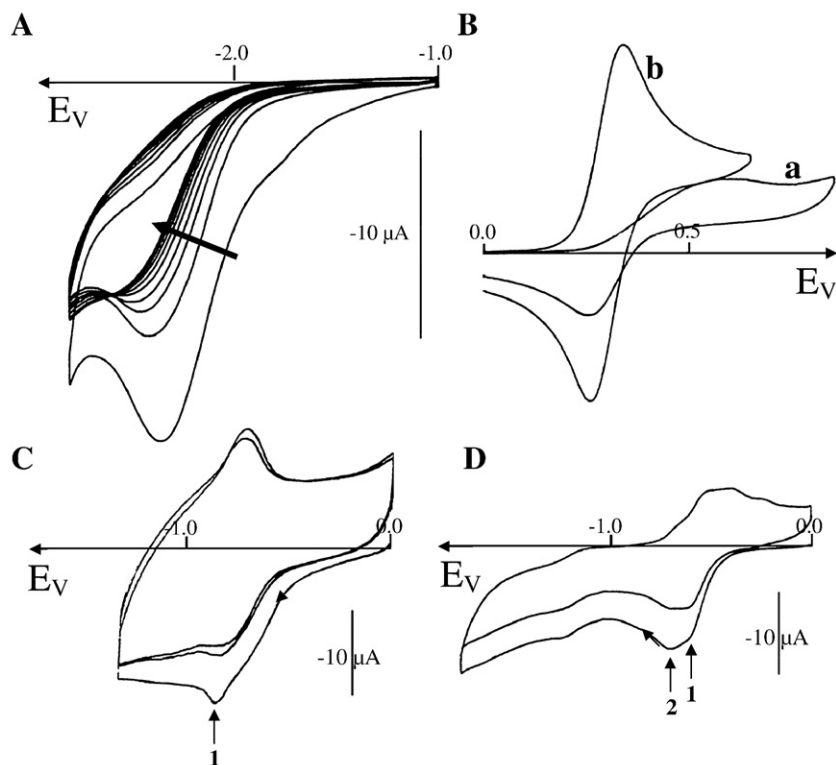
Supporting salts, solvents and the chemicals used to deposit and modify the carboxylated layers (bromoalkanoic acids, phenols and aminoaromatic ketones, bearing  $\pi$ -acceptor substituents) were purchased from Aldrich and used as such. Precise reaction modes are explicated in the text.

### 3. Results

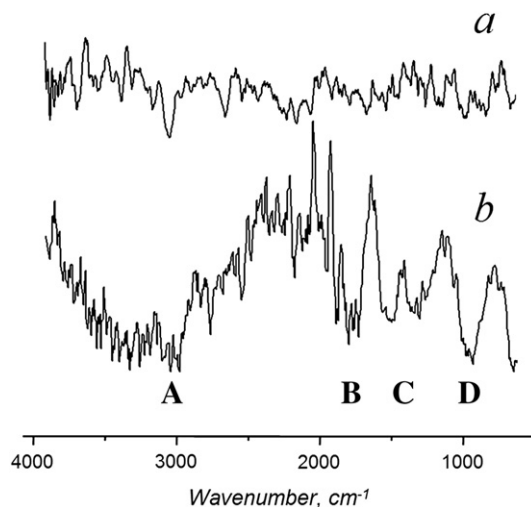
Repetitive scans between  $-1.0$  V and  $-2.8$  V at a GC electrode (in  $\text{DMF} + \text{Bu}_4\text{NBF}_4$ ) in the presence of the long chain bromo-acid **4** provoked a rapid decay of the peak limiting currents assigned to the C-Br bond scission, and a progressive shift towards very negative potentials (Fig. 1, curve A).

With moderately large concentrations (about 15  $\text{mmol L}^{-1}$ ) of the bromo-acid, this peak may totally disappear. This fact could have probably arisen from the action of electro-generated bases in the vicinity of the electrode surface, but the voltammetry in the presence of  $\text{Me}_4\text{NOH}$  as a base showed that the reduction step of **4** remains, even if clearly shifted.

The appearance of a dense deposit at the carbon surface was evidenced by the loss of reversibility of potassium ferrocyanide oxidation as shown in Fig. 1 (curve B a). The hampering of electron transfer at the same electrode is even stronger when its surface was treated with  $\text{Me}_4\text{NOH}$  (assigned to the presence of ammonium carboxylate), or by esterification with a long chain alcohol (n-butanol or n-octanol). Other bromo-acids considered in the present study behave similarly, but the decay of the alkyl chain length affects the inhibiting character of the deposit that may be quite small with **1**.



**Fig. 1.** Voltammetry of  $\text{Br}-(\text{CH}_2)_n-\text{COOH}$  at GC electrodes. Solvent:  $\text{DMF} + \text{TBABF}_4$ . (A). Bromo-acid with  $n = 11$ . Concentration: 12  $\text{mmol L}^{-1}$ .  $\nu = 50 \text{ mV s}^{-1}$ . Surface area of electrode: 0.8  $\text{mm}^2$ . Nine recurrent scans. (B) Voltammetry (a)—of a solution of potassium ferrocyanide in aqueous KCl solution at a GC electrode modified according to (A) compared to (b)—the bare GC electrode ( $\nu = 100 \text{ mV s}^{-1}$ ). (C) Layer from bromo-acid ( $n = 5$ ). Cathodic scan after reaction with 1-aminoanthraquinone ( $\nu = 200 \text{ mV s}^{-1}$ ). (D) Coverage of GC by bromo-acid ( $n = 3$ ). Functionalization with p-nitrophenol ( $\nu = 50 \text{ mV s}^{-1}$ ). See text.



**Fig. 2.** FTIR of the GC electrode (reflectance mode). (a) Bare GC; (b) GC modified with **4**. A: Broad band at  $3400 \text{ cm}^{-1}$  ( $\text{H}_2\text{O}$ );  $3100\text{--}2800 \text{ cm}^{-1}$   $\nu(\text{O—H})$  of H-bonded associated acids. B:  $1780 \text{ cm}^{-1}$ , stretching  $\nu(\text{C=O})$ . C:  $1420$  and  $1150 \text{ cm}^{-1}$ ,  $\delta(\text{C—H})$  and  $\nu(\text{C—O})$ . D:  $950 \text{ cm}^{-1}$ , characteristic  $\delta(\text{O—H})$  of H-bonds.

The deposits onto GC, after ultrasonic rinsing and washing with acetone and alcohol, were analyzed by FTIR spectroscopy. The results clearly show that these layers contain hydrogen-bonded carboxylic functions (see Fig. 2, with a deposit obtained with **4**). Therefore, grafting of bromo-acids on GC according to the reaction (1) in Scheme 1 appears quite reasonable. In order to specify the reactivity of carboxylic groups in this layer, these functions were marked with  $\pi$ -acceptors.

First of all, the amidation was used (Equation 2). At a GC3 electrode, the deposition was achieved with **2** at  $-2.55$  V and stopped after

Download English Version:

<https://daneshyari.com/en/article/180211>

Download Persian Version:

<https://daneshyari.com/article/180211>

[Daneshyari.com](https://daneshyari.com)