



Mini review

Electrochemical conversion of glassy carbon into a poly-nucleophilic reactive material. Applications for carbon chemical functionalization. A mini-review

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ABSTRACT

During the last decade, various carbon modifications were achieved via radical addition of substituted aryl radicals produced at the surface by chemical or/and electrochemical reduction of corresponding aryldiazonium salts. Very recently, surface reactivity of carbons toward electrophilic halo-derivatives with long alkyl chains had been developed. Surface nucleophilicity of carbons was induced by their specific cathodic charge (at $E < -1.7$ V in non-aqueous electrolytes) affecting the nano-crystallites (mainly graphite) contained in glassy carbons due to the mode of its manufacturing (high temperature carbonization of phenolic resins). This new paradigm of surface decoration was successfully applied using alkyl halides, carbon dioxide, dioxygen, sulfonyl chlorides etc. and proved efficient with allotropic varieties of carbon (in particular graphites and graphene).

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1. Introduction

For the electrochemical community, glassy carbon (GC) is primarily a convenient electrode material for carrying out analyses and electrolyses within the cathodic range [1,2]. Very often, this material was considered as non-reactive and was used as an advantageous substitute of mercury and platinum [3]. However, most of the materials named glassy carbons, produced by carbonization of phenolic resins [4] at temperatures up to

2500 °C, were reported to contain large amounts of graphite-like inclusions. They should therefore be regarded as complex materials containing reticulated C_{sp3} zones in contact with the areas where sp^2 carbon atoms predominate. Recent studies, focalized on large nano- and micro-inclusions of graphitized, graphenized, and fullerenized incorporates in the body of tetrahedral carbons, emphasize this point [5,6]. Structure and conductivity of commercial GCs are thus strongly dependent on the mode of their manufacturing and especially on the carbonization temperatures. There follows that common glassy carbons correspond to complex redox conglomerates gathering aromatic structures that provide the conductivity by electron hopping between them.

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As a matter of fact, in polar aprotic solvents most of GCs can show their own cathodic response very similar to that of highly oriented pyrolytic graphite (HOPG) and more generally to that of natural graphites. Thus, under cathodic polarization, graphites are well known to be charged with Li^+ [6]. More recently, HOPG was reversibly charged (or “reduced”) in the presence of tetraalkylammonium salts (TAA⁺) to form intercalation compounds leading to well-defined structures depending on applied potentials ($E < -1.7$ V vs. Ag/AgCl) and on the bulkiness of TAA⁺ cations used [7]. These carbon insertion stages [C_pTAA^+] formed by electron uptake and concomitant insertion of tetraalkylammonium salts were considered as “graphite salts”, rather similar to TAA amalgams, and used (under inert atmosphere) as reducing species and poly-nucleophilic materials. Large exfoliation of graphite [8] and subsequently the exposure of the formed carbon salts, acting as nucleophilic species, to CO_2 permitted, for the first time, carboxylating HOPG to a large extent [9].

Electrochemical properties of HOPG can easily be transposed to GC, almost counter-intuitively bearing out that the latter can manifest a great deal of interfacial reactivity of graphite. In other words, the GC surface could be perceived as a zone with strong nucleophilic reactivity when quite negative potentials (-1.7 V) are reached. In fact, this is not so surprising when considering aromatic inclusions in GC as more loaded congeners of benzenoid aromatics (benzene, anthracene etc.) whose reduction to give nucleophilic species is well documented [10]. Therefore, the reactivity of GC interface (ET versus $\text{S}_\text{N}2$ -like reactions) toward electrophilic organic derivatives is worth being re-considered. Given the above said, new paradigm of nucleophilic modification of carbons can be developed using this chemistry.

2. Evidence of cathodic charge of carbons at $E < -1.7$ V

The presence of graphite nano-crystallites in many kinds of glassy carbons is well-recognized [1], but the intrinsic cathodic behavior of GC (i.e. its cathodic charge, principally in the interfacial area) is rarely considered or taken into account. A specific charge/discharge process beyond -1.7 V at a Carbone-Lorraine GC macro-electrode helps to interpret the way of trapping primary alkyl iodides [11]. Fig. 1A exhibits

the charge of such CG electrodes compared to curves B where a much poorer in (but not void of) $\text{C}_{\text{sp}2}$ inclusions GC surface is covered by a thin layer of natural graphite (curve 2). The almost perfect correspondence of voltammetric responses in A and B2 is striking. Let us remark that a large presence of graphite in GC would provide an advantage for obtaining very dense coverages of grafting on carbons. Charging phenomenon, analogous to that of graphite, was also observed for graphenes deposited on carbons (and also on Au, Ag, Cu or Pt; in the latter case, very dry organic solvents are needed). However, fullerenes and carbon nanotubes did not exhibit any cathodic charging before -2.3 V [12] because surface-related ion-pairing in these systems, akin to the stabilization of the anion radicals of aromatic hydrocarbons by cations of the supporting salts [13], is less efficient for negative charge stabilization than charging with in-depth TAA⁺ insertion.

The influence of a large incorporation of graphite (or graphene) in the GC may quite certainly influence the reduction potentials of acceptors (here, electrophiles like 1-iodoalkanes [14]) in non-aqueous solvents as shown in Fig. 1, C1–C2. This undermines a widespread view of GC as an almost perfect material without any catalytic activity compared to other electrode materials such as silver, palladium or copper. Thus, curve C1 (Tokai carbon having lower graphite content) has $E_{1/2} = -1.92$ V while graphite-rich GC (Carbone-Lorraine) provokes an anodic shift, $E_{1/2} = -1.78$ V. In the latter case (C2), the threshold of graphite charging and the reduction potential of 1-iodoalkane are identical (-1.6 V) meaning that graphite charge may induce a kind of redox-catalytic interface. This assumption was entirely verified with gold electrodes with deposited thin layers of natural graphite or graphene.

3. Surface modifications based on GC cathodic charge

Nucleophilic surface modification of GC takes on different aspects: i) an irreversible prodding of the initial surface by charge and ii) TAA⁺ cation insertion to burst the graphite inclusions in the vicinity of the surface along with iii) chemical reactivity of nano-nucleophilic centers disposed at (or very close to) the interface. This phenomenon has been clearly demonstrated [9] during the charge of HOPG in the presence of

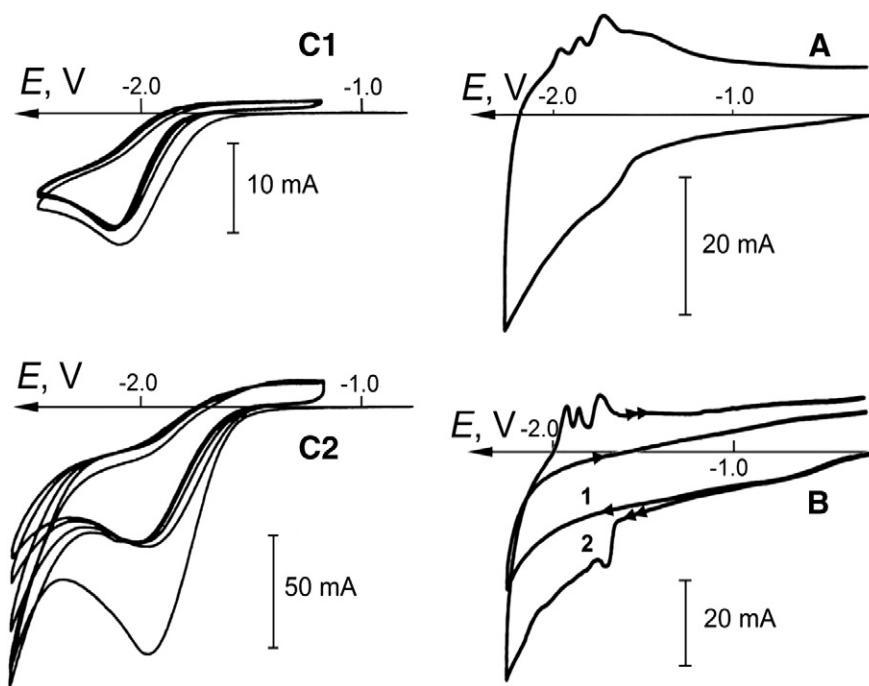


Fig. 1. Voltammetry of glassy carbons under cathodic charge. DMF/0.1 M Et_4NBF_4 . Scan rate: 50 mV s^{-1} . (A) Carbone-Lorraine GC electrode (7 mm^2). (B) Poorer in graphite Tokai GC: bare (curve 1) and covered by an ultra thin layer of natural Ceylon graphite (curve 2). (C) Reduction of 1-iodo-octane (11 mmol L^{-1}) at two different GCs. (C1) Tokai GC (0.8 mm^2); (C2) Carbone-Lorraine GC (7 mm^2).

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