Electrochemistry Communications 48 (2014) 142–146

Contents lists available at ScienceDirect

Electrochemistry Communications

journal homepage: www.elsevier.com/locate/elecom

Electrochemical exfoliation in real time of natural graphite deposited onto glassy carbon. Doping and modifying carbons through ultra-thin graphite layers

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ARTICLE INFO

Article history:
Received 20 August 2014
Accepted 29 August 2014
Available online 6 September 2014

Keywords:
Graphite
Exfoliation
Graphene surfaces
Modified carbon electrodes

ABSTRACT

Natural graphite, deposited onto smooth glassy carbon, when reduced (around −2 V vs. Ag/AgCl) in the presence of tetraalkylammonium salts (TAAX) in aprotic polar solvents, leads to spectacular exfoliation processes followed in real time in the course of voltammetric scans. The method permits to get extraordinary stable modified carbon surfaces, with quite simple voltammetric responses (1 to 4 reversible cathodic steps) that strongly depend on the nature of the cations used. Those cathodic steps exhibit currents quasi perfectly proportional to the scan rate. It is expected the formation of a graphene-like substrate. Surface modifications both by ferrocene and anthraquinone could underline the originality of those new materials.

1. Introduction

Glassy carbon (GC) is considered as a convenient electrode material for achieving analysis and macro-electrolyses, especially within the cathodic domain [1]. A large panel of electro-organic reactions were carried out within a quite extended cathodic domain at negatively polarized carbon and this material remains very useful to conduct electrochemical reactions at potentials < -2 V in dry polar organic solvents. Moreover, it has been reported that GC at $E < -1.7$ V, is not longer totally inert owing the presence of ribbons of graphite-like structures [2,3]. Cathodic charging (by insertion of organic or inorganic cations) of these different “impurities” has been used for inducing specific reactions with a large palette of electrophilic reagents [4].

Independently, it is worth recalling that, when polar organic solvents are used, cathodic charge of highly oriented pyrolytic graphite [5] specifically leads to well defined insertion stages $[\mathrm{C}_n^-,\mathrm{TAA}^+]$ via concomitant insertion of electrons and tetraalkylammonium salts (TAAX). Fixed potential reduction and exfoliation of natural graphite by bulky ammonium salts have been reported [6]. The electrochemical synthesis of those “graphite salts”, rather similar to {TAA-amalgams}, has to be considered both as a novel generation of reducing species and as polynucleophilic materials (then reactive with organic reagents for modification of graphites and carbons [7]).

Under these conditions, graphite appears to be a key substrate to create via several methods graphene plans. In electrochemistry, the basic method remains the reduction of graphene oxide [8]. The cathodic reduction of commercial graphene has been achieved and 3D {graphene-GC} electrodes were described. Recently, electrochemical functionalizations of graphene were reported [9].

The early method [6] for a facile exfoliation of graphite by means of electrochemistry (reduction at about −2.0 V) remains certainly a fascinating manner to generate in situ at electrified solid substrates thin graphene layers. We here describe a new process for achieving natural graphite exfoliation concomitantly with deposition onto glassy carbon.

2. Experimental section

Voltammetries were carried out in 0.1 M solutions of tetraalkylammonium salts (TAAX) such as tetramethylammonium ($\mathrm{TMABF_4}$), tetraethylammonium ($\mathrm{TEABF_4}$), tetra-*n*-butylammonium ($\mathrm{TBABF_4}$), and tetra-*n*-octylammonium tetrafluoroborate ($\mathrm{TOABF_4}$), and dissolved in upper grade dimethylformamide (DMF). Experiments described in this work did not need special treatment of electrolytic solutions.

Potentials are referred to the aqueous $\mathrm{Ag/AgCl/KCl_{(sat)}}$. Voltammetric and coulometric measurements were performed using three-electrode cells separated with a fritted glass. The electrochemical instrumentation has been previously reported [7].

GC rod electrodes as substrates used for graphite deposition had geometric areas of 1 and 7 mm^2. All those carbon samples were purchased from Tokai Carbon C° (code: GC Rod) and Carbone Lorraine carbon vitreous VD 1500. Also, large GC plates (from Carbone Lorraine) were also employed for building flat electrodes of a much larger area.

Prior to being modified by deposition of natural graphite, GC substrates were carefully polished first with silicon carbide paper (Struers 500) and then with a thinner polishing paper (Struers 1200). Then,

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http://dx.doi.org/10.1016/j.elecom.2014.08.031

natural graphite (from Ceylon) or highly oriented pyrolytic graphite (HOPG), both first partly exfoliated by the electrolytic method already quoted [6] was disposed on a carbon planar surface. Deposition of graphite was done using glassy cardboard and the surface was rubbed by firmly polishing electrodes until obtaining a shiny aspect of carbon. The final process for deposit final exfoliation is fully described below in §3.1.

3. Experimental results and procedures

3.1. Evidences for real time exfoliation procedures with natural graphite

First of all, an exfoliated graphite coating (electrolysis in DMF accordingly to reference [6] i.e. at mercury pool, potential −2.1 V, amount of electricity: 12 C/1 g of Ceylon graphite) was achieved at a GC disk and electrolyzed in DMF/$TMAClO_4$. A typical voltammetry is displayed in Fig. 1A: while the GC disk polished according to the procedure given in the experimental does not display any strong signal, an intense signal assigned to the exfoliation process is obtained from the first scan. From −1.7 V, i.e. a potential reported to correspond to the cathodic charge threshold of graphite, the huge increase of current is immediately followed (≈ −2 V) by a sudden decay. The anodic discharge, still rather intense, is observed. Furthers scans (scans 2 and 3) show a progressive crushing of charge/discharge processes until very reproducible signals (in potential and intensity) apparently specific of used TAA^+ salts. In general, with scans up to −2.3 V, peaks (their number ≤4 essentially depending on the employed TAA^+ electrolyte) are obtained. They are assigned to the electrochemical reduction (or charge) of a few remaining layers of graphite immobilized at the GC interface presumably by mean of π,π-interactions with the substrate. Exfoliation with TMA^+ is considered as a formatting process and allows testing behaviors of several ammonium salts that all exhibit specific responses. Some of them are displayed in Fig. 1B.

Reduction of graphite deposits onto GC (before exfoliation) revealed different points: in the course of the first sweep, some small reduction peaks are observed around −1 V and are assigned to electroactive edge impurities provoked by the aging of graphite in contact with air (such as ketonyl and quinonyl groups, aromatic carboxylic acids). After three scans, reversible electrochemical steps are observed at $E < -1.8$ V and assigned to stable graphitic (or graphene) layer(s). Thus, in the specific case of tetraethylammonium of salts (triflate, tetrafluoroborate or perchlorate) in DMF, three well defined reversible steps are obtained (see curve C in Fig. 1). Their peak currents are strictly proportional to the scan rate (until 1 V s^{-1}) and could be assigned to the reduction of graphene mono-layers although re-arrangement of those layers into "graphite-like" by means of π,π-interactions can reasonably envisaged. This kind of interaction could also contribute to fix graphene layers onto GC. Moreover, cathodic responses of those GC modified surfaces are particularly stable upon charge/discharge cyclings.

In $TMAClO_4$/DMF, half-peak potentials of four reduction steps are with I ($E_{I} = -1.76$ V), II ($E_{II} = -1.97$ V), III ($E_{III} = -2.10$ V) and IV

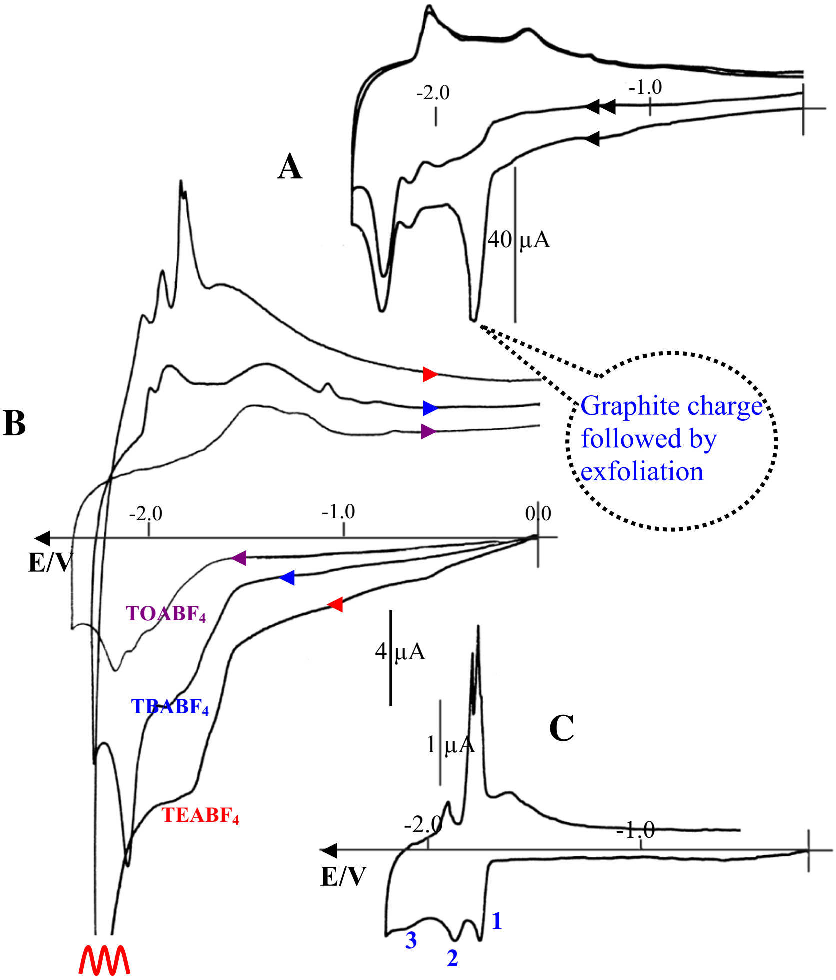

Fig. 1. (A) Process of exfoliation of GC–graphite surface by $TMABF_4$. (B and C) Examples of electrochemical charges of formatted GC–graphite electrodes shown in (A) in the presence of different tetra-alkylammonium salts. Solvent: DMF. Scan rate: 50 mV s^{-1}. Apparent surface areas of electrodes: 7 mm^2 in A and B, and 0.8 mm^2 in C.