



# A study of the modification of glassy carbon and edge and basal plane highly oriented pyrolytic graphite electrodes modified with anthraquinone using diazonium coupling and solid phase synthesis and their use for oxygen reduction



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## ABSTRACT

The oxygen reduction reaction was investigated at bare and anthraquinone modified glassy carbon and edge and basal plane highly oriented pyrolytic graphite electrodes. Anthraquinone was attached to the graphite electrodes through a  $-NHCH_2C_6H_4-$  linker using electrochemical reduction of the corresponding Boc (Boc is tert-butyloxycarbonyl) protected diazonium salt, removal of the Boc protection and subsequent solid phase coupling to anthraquinone-2-carboxylic acid. In each case electrochemical reduction of the Boc protected diazonium salt leads to blocking of the surface. Following deprotection and coupling the apparent surface coverage of anthraquinone is found to be greatest on the edge plane electrode and lowest on the basal plane with the glassy carbon surface intermediate between the two. The immobilized anthraquinone is stable at the surface and catalyzes the reduction of oxygen to hydrogen peroxide.

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## 1. Introduction

The attachment of organic functionalities to the surface of carbon based materials such as glassy carbon (GC) [1–4], highly ordered pyrolytic graphite (HOPG) [5–7], carbon nanotubes [8] and graphene [9] has attracted considerable interest over the last two decades. This is because these materials have applications in many scientific fields such as biosensing, electrocatalysis, optical devices, molecular electronics, and information storage [10–12]. As an electrode material, edge plane (EP) graphite is frequently claimed to be more active for electron transfer and adsorption than basal plane (BP) graphite for most redox couples [13–19] however recent work by the groups of Unwin and Macpherson [20] contradicts this view and this remains an area of debate. The low reactivity of basal plane graphite has been attributed to the low density of electronic states [21,22] and the lack of functional groups and adsorption sites as compared to edge plane graphite and glassy carbon.

The electrochemical reduction of oxygen has been extensively studied by researchers because it is an essential reaction in fuel

cells, metal-air batteries, gas sensors and in the electrosynthesis of  $H_2O_2$  [23–25]. Unmodified carbon electrodes are considered to be very poor electrodes for electrochemical reduction of  $O_2$ , whereas carbon electrodes modified with appropriate quinone derivatives show excellent catalytic behaviour for  $O_2$  reduction at neutral pH [26–29]. As a consequence, various types of carbon electrodes modified with quinones or other classes of organic compounds have been used for oxygen reduction such as highly oriented pyrolytic graphite (HOPG) [30,31], pyrolytic graphite [32], glassy carbon (GC) [33–38] and carbon nanotubes [39–42]. Considerable experimental [43] and theoretical effort [34,44] has been expended to examine the mediation of oxygen reduction by anthraquinone and to identify the rate determining step at unmodified and quinone modified carbon electrodes [26]. It has been suggested that surface quinone functional groups are involved because the electrocatalytic activity is enhanced with increasing the quinone surface coverage [45]. Also these studies show that the peak potential for  $O_2$  reduction is more positive at glassy carbon and edge plane graphite as compared to basal plane graphite.

A wide range of organic functionalities are attached to the carbon surface, such as carboxyl, phenolic, hydroxyl and quinone derivatives [46], depending on the pre-treatment and history of the electrode. However the precise nature of the functional groups that actually participate in the oxygen reduction reaction is unclear.

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Recently, our group reported a flexible, generic approach to covalently attach monolayers of different organic species to glassy carbon [47], carbon nanotube [48] and gold surfaces [49] by a combination of electrochemical grafting and solid phase synthesis. Boc-protected (where Boc is tert-butyloxycarbonyl)  $-C_6H_4CH_2NH-$  linkers were grafted onto electrode surfaces using reductive electrochemical diazonium coupling. The Boc protecting group is readily removed in acid solution leaving the amine groups available at the electrode surfaces for further modification with various organic species using solid phase amide coupling chemistry. The advantage of using this modification approach rather than the direct coupling of anthraquinone to the surface by diazo coupling is that multilayer formation, which is widely observed at the surfaces modified with anthraquinone by electrochemical reduction of the corresponding diazonium salt [50], is suppressed. This is because the bulky Boc protecting group hinders further coupling to the aryl groups already grafted to the surface. It is therefore interesting to investigate the effect of anthraquinone coverage and of the choice of carbon electrode on oxygen reduction. To the best of our knowledge the only work which has looked at the effect of coverage is that of Sarapu et al. for glassy carbon where they found that in 0.1 M KOH increasing anthraquinone coverage led to lower oxygen reduction currents at the prewave indicating that the anthraquinone blocks access of oxygen to the glassy carbon surface and the native glassy carbon sites [51].

In the present work, a linker,  $-C_6H_4CH_2NH-$ Boc, bearing a protected amine group was electrochemically immobilised to glassy carbon (GC) and edge plane (EP) and basal plane (BP) HOPG electrodes by electrochemical reduction of the corresponding diazonium salt. Following deprotection anthraquinone-2-carboxylic acid was coupled to the linker using solid-phase chemistry. The surface coverage and stability of the immobilised anthraquinone redox centres was investigated by cyclic voltammetry together with the effect of pH. The electrocatalytic activity of the different anthraquinone modified electrodes towards the  $O_2$  reduction reaction was studied by cyclic voltammetry at stationary and rotating disc electrodes.

## 2. Experimental

### 2.1. Materials and chemicals

All solutions for electrochemical experiments were prepared using deionised water (18 M $\Omega$  cm) from a Whatman RO80 system coupled to a Whatman "Still Plus". 4-(N-Boc-aminomethyl)benzenediazonium tetrafluoroborate salt was synthesised following procedures described earlier [52]. Anthraquinone-2-carboxylic acid, N,N-diisopropylethylamine (DIEA) and tetrabutylammonium tetrafluoroborate (NBu<sub>4</sub>BF<sub>4</sub>) were purchased from Aldrich. Glacial acetic acid, H<sub>3</sub>PO<sub>4</sub>, HCl, dimethylformamide (DMF), dioxan and ethanol were obtained from Fisher Scientific. Sodium acetate and NaOH, was purchased from BDH Chemicals. O-benzotriazol-1-yl-N,N,N',N'-tetramethyluronium hexafluorophosphate (HBTU) and acetonitrile (ACN) were obtained from Merck, and Rathburn Chemicals, respectively. All chemicals were used as received without any further purification.

Glassy carbon working electrodes (GC, rod 0.071 cm<sup>2</sup>, HTW Germany) were sealed in glass and connected to copper wires using indium (Aldrich) or were commercial rotating disc electrodes (0.196 cm<sup>2</sup>, Pine). The edge (EP, 0.105, 0.20, 0.25 and 0.31 cm<sup>2</sup>) and basal plane (BP, 0.09 and 0.20 cm<sup>2</sup>) graphite electrodes were embedded in epoxy resin (Struers, Epofix Kit) and connected to steel rods using silver epoxy. Prior to each experiment, the conductivity of each electrode was checked to ensure good electrical connection. Before modification, the glassy carbon and edge plane

graphite electrodes were polished with silicon carbide polishing paper (DTC, grade 1200) then with 1  $\mu$ m and 0.3  $\mu$ m alumina (Buehler) and rinsed thoroughly with deionised water and eventually dried under an argon stream. This polishing procedure leads to a mirror-like surface for glassy carbon electrodes and low surface roughness for edge plane electrodes. All current densities below are calculated with respect to the geometric area of the corresponding carbon electrode [53]. The basal plane graphite electrodes were prepared by cleaving the surface with adhesive tape before each experiment. Rotating disc experiments were carried out with a Pine Instruments rotator and 5 mm diameter glassy carbon rotating disc electrode.

All electrochemical measurements were performed with Autolab PGSTAT30 Potentiostat/Galvanostat and controlled using the general purpose electrochemical system (GPES) software. The electrochemical cell was a conventional three-electrode system with a 1 cm<sup>2</sup> platinum gauze counter electrode and a home-made SCE or Ag/AgCl reference electrode. Apart from the studies of the influence of pH on anthraquinone electrochemistry and oxygen reduction, all electrochemical measurements were conducted in 0.1 M acetate buffer at pH 4.8. To investigate the effect of dissolved oxygen concentration the solutions were sparged with mixtures of pure oxygen and argon prepared using Smart-Trak mass flow controllers to blend the two gasses in the desired ratio. The electrochemical measurements were made at 23 °C.

### 2.2. Electrochemical modifications of glassy carbon and HOPG electrodes with linker and anthraquinone groups

Electro-grafting of the Boc-NHCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>- linker to the edge plane, basal plane and glassy carbon surfaces was carried out by electrochemical reduction in a solution containing 5.0 mM of the corresponding diazonium salt dissolved in 0.1 M TBATFB in acetonitrile. The attachment was performed by cycling the electrode in the range from 0.4 to  $-1.0$  V for GC, from 0.6 to  $-1.0$  for EP electrodes and from 0.5 to  $-1.5$  V for BP electrode vs. Ag/AgCl at a scan rate of 50 mV s<sup>-1</sup> until complete blockage of the current was observed (within 10 cycles).

To remove the Boc protecting group the edge plane, basal plane and glassy carbon electrodes modified with the Boc-NHCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-linker were suspended in a solution of 4.0 M HCl in 1,4-dioxane at room temperature for 1 h. The electrodes were then washed by DMF, deionised water and ethanol prior to anthraquinone coupling. Anthraquinone-2-carboxylic acid (252 mg, 1.0 mmol), HBTU (450 mg, 1.2 mmol) and DIEA (4.2 mmol) were dissolved in DMF and the mixture was heated at 60 °C for 15 min with magnetic stirring to obtain a homogeneous solution. All modified electrodes were then suspended in this solution at room temperature and stirred for 16 h. The electrodes were then washed with DMF and ethanol before electrochemical characterisation.

## 3. Results and discussion

### 3.1. Electrochemical coupling of linkers

Fig. 1 shows cyclic voltammograms recorded at 50 mV s<sup>-1</sup> for the electrochemical attachment of the BocNHCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>- linker from solution containing 5.0 mM BocNHCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub> diazonium salt in 0.1 M TBATFB in acetonitrile for edge plane, basal plane and glassy carbon electrodes.

As seen in Fig. 1 in each case there is a rather broad irreversible peak for the reduction of the BocNHCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub> diazonium salt to give the aryl radical which then reacts with the electrode surface. On the second cycle, the reduction peak is absent indicating blocking [47] of the electrode surface by the attached, Boc protected, linker.

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