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# Oxygen electroreduction on chemically modified glassy carbon electrodes in alkaline solution

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Dedicated to Professor David J. Schiffrin on the occasion of his 65th birthday and in recognition of his contribution to electrochemistry.

## Abstract

The electrochemical reduction of oxygen on glassy carbon (GC) electrodes modified with aryl groups has been studied using the rotating disk electrode (RDE) technique. The GC electrodes were grafted by electrochemical reduction of diazonium salts. The diazonium derivatives of benzene, naphthalene and anthracene were used in surface modification. The blocking behaviour of aryl layers towards oxygen reduction was investigated. An unexpected order of blocking efficiency of the aryl moieties was observed for $O_2$ reduction in 0.1 M KOH. The phenyl-modified GC electrode was less active than those electrografted with naphthalene and anthracene. Comparative measurements were carried out in 1 mM $K_3Fe(CN)_6$. A much larger extent of blocking was evident for the $Fe(CN)_6^{3-/4-}$ couple. This effect was explained by a significant difference in size between the $Fe(CN)_6^{3-/4-}$ ions and $O_2$ molecule. A mixed film of anthraquinone (AQ) and phenyl groups was formed by diazonium reduction and its relevance in the kinetics investigations was discussed. The kinetic parameters of oxygen reduction were determined using a surface redox catalytic cycle model for quinone-modified electrodes.

*Keywords:* Oxygen reduction; Barrier properties; Glassy carbon; Diazonium; Anthraquinone; Hexacyanoferrate

## 1. Introduction

There has been an increased research activity in the modification of carbon electrodes by electrochemical reduction of diazonium salts since the first report on the application of this method [1]. The details of this process and the properties of the modified electrodes have been reviewed by Downard [2] and more recently by Pinson and Podvorica [3]. The surface modification by the reduction of diazonium salts is shown in Scheme 1.

The diazonium cation ($ArN_2^+$) is reduced and the formed aryl radical ($Ar^{\cdot}$) reacts with the carbon surface giving a strong covalent (C–C) bond [4,5]. Glassy carbon (GC) [1,4,6–19], highly oriented pyrolytic graphite (HOPG) [4,6,20,21], boron-doped diamond (BDD) [21–23], carbon nanotubes (CNT) [24,25] and other carbon materials have been successfully grafted using the diazonium reduction method. A large variety of surface modifiers can be attached to carbon surfaces. Among other compounds, several quinones have been grafted to carbon electrodes [4,26–30]. The quinone-modified electrodes showed a high electrocatalytic activity for the two-electron reduction of oxygen as reported by Schiffrin and co-workers [21,26–30].

Barrier properties of electrochemically grafted aryl moieties have been of considerable interest during the recent decade [2,3,10–13,19,20]. Various compounds have been covalently attached to carbon electrode surfaces and their effect on the electron transfer kinetics has been

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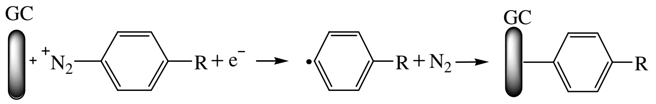
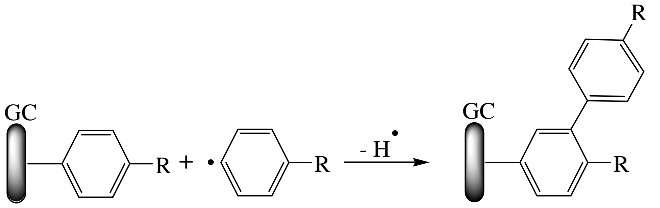


Scheme 1. Electrografting of glassy carbon with aryl groups by diazonium reduction.

investigated. In this respect, the structure of the modifier film is a major concern. It is important to know whether (sub)monolayer or multilayer films are formed [2,3]. In case of submonolayers the determination of the modifier orientation is a rather complicated task. There is also experimental evidence that in many cases multilayer films are formed [13,20,31–34].

A comparison of the amount of the electrografted material determined by charge integration and the data on film morphology measured by atomic force microscopy (AFM) was made by Brooksby and Downard [31]. An atomically flat pyrolyzed photoresist film (PPF) was used as a substrate material and the authors concluded on the basis of their data that an incompact layer was formed. The experimentally determined surface concentration of nitrophenyl corresponded to 21% of a close-packed monolayer [31]. This is crucially important in the electron transfer kinetics research. If the layer is not compact enough, then the redox active species can reach the underlying substrate and therefore the modifier film does not provide an effective blocking of the electrode surface. By contrast, for a compact monolayer the electron transfer can occur only by tunnelling through the film and obviously its rate depends on the thickness of the monolayer film. Systematic investigations in this field using monolayers of variable thicknesses (from 0.59 to 1.4 nm) have been carried out by Yang and McCreery [10]. For several organic redox systems studied, the presence of a monolayer had little effect on the value of $k^0$ as compared to the one of the polished GC. For instance, only 50% decrease of $k^0$ was observed for methyl-viologen on the GC electrode modified with nitrophenyl groups. For chlorpromazine, the value of the tunnelling parameter ($\beta$) was found to be 0.2 $\text{Å}^{-1}$. However, when interpreting these results, one must be concerned about the compactness and ordering of the chemisorbed monolayers on glassy carbon.

The formation of multilayer films by diazonium reduction has been reported by Kariuki and McDermott [13,20]. These authors have examined the surface morphology of electrografted GC [13] and HOPG [20] electrodes by scanning probe microscopy (SPM) and the formation of modifier films thicker than a monolayer was clearly seen. Multilayer growth can be explained by the following mechanism (Scheme 2).



Scheme 2. Schematic representation of multilayer formation by diazonium reduction.

The radical formed by diazonium ion reduction may attack an already attached group by abstracting H atom and this surface bound radical may react with another radical causing the second layer and subsequent layers to be formed. It was found that a longer deposition time (at least 10 min) at constant potential results in a thicker film formation. The preferential growth of the films occurred on defect sites of HOPG. The formation of "humps" was also seen, which reveals the three-dimensional (3D) growth of the film on HOPG. The height of these features was 5–15 nm above the substrate surface [20]. Surprisingly, the relatively thick films studied did not present such barrier properties as expected on the basis of the exponential decrease of the rate constant with the film thickness. Obviously, other electron transfer mechanism than tunnelling has to be considered. The authors have highlighted the importance of organic film defects in the overall charge transfer process. The topography of the films examined by SPM techniques was non-uniform. The surface blocking of HOPG by diethylaniline was thoroughly studied. It was found that the $k^0$ value of the $\mathrm{Fe(CN)}_6^{3-/4-}$ couple was significantly reduced after the first electrografting cycle. This was explained by the initial anchoring of the modifier molecules to the defect sites of HOPG. It is considered that the charge transfer process of $\mathrm{Fe(CN)}_6^{3-/4-}$ ions is facilitated by the defect sites. During further grafting cycles the film gradually covers the HOPG surface as evidenced by SPM.

The barrier properties of covalently attached phenyl layers have been studied in several laboratories [8–12,19]. This is the thinnest blocking layer, which can be formed by the diazonium reduction method. The estimated thickness of the phenyl monolayer is 0.59 nm, however, the "average thickness" of the layer is less than that, due to defects and disorder in the modifier monolayer. The phenyl monolayer was found to decrease the rate of electron transfer reactions of certain redox species (for example, the $\mathrm{Fe(CN)}_6^{3-/4-}$ couple [12,19]), whereas for others (e.g. methyl-viologen) the redox process was not significantly influenced by the surface modifier [12].

It is of considerable interest to study the reduction of oxygen on GC electrodes modified with barrier layers of various organic compounds. The blocking behaviour of these films is of paramount importance in many fields, including electrocatalysis and electroanalysis. Up to now, there have been only a few studies of $O_2$ reduction on self-assembled monolayer-modified gold electrodes (SAM/Au) [36–39] and a single report on the reduction on 4-methylphenyl-modified GC electrodes [35]. The blocking action for $O_2$ reduction was also observed for fullerene monolayers on gold electrodes [40]. The purpose of the present work was to investigate the reduction of oxygen on glassy carbon electrodes electrografted with phenyl,