



Oxygen reduction on thick anthraquinone films electrografted to glassy carbon



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ABSTRACT

Multilayer 9,10-anthraquinone (AQ) films on the surface of glassy carbon (GC) electrodes were prepared by electrochemical reduction of the corresponding diazonium cations in acetonitrile. The surface concentration of AQ was varied in the range of $(1-6) \times 10^{-9}$ mol cm⁻² using different modification procedures. X-ray photoelectron spectroscopy (XPS) was used to analyse the composition of AQ films. The XPS study revealed the presence of azo linkages within the film. The oxygen reduction reaction was investigated employing the rotating disk electrode (RDE) method. The RDE results indicated that the reduction of oxygen follows a two-electron pathway on thick AQ films.

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1. Introduction

The oxygen reduction reaction (ORR) is one of the most widely investigated electrochemical reactions, because it plays a significant role in various systems including fuel cells, sensors, corrosion of metals and alloys or electrosynthesis of hydrogen peroxide [1]. Depending on several factors (e.g. electrode material, experimental conditions) this reaction proceeds either by a four-electron pathway to water or by a two-electron pathway to H₂O₂ [2–5].

During last three decades, the reduction of oxygen has been widely studied on quinone-modified electrodes due to their good electrocatalytic properties for the two-electron reduction of O₂ to H₂O₂ [6–51]. These electrodes can be employed for the electrochemical synthesis of hydrogen peroxide [51]. There are many ways how to modify the electrode surface with quinone groups (e.g. physisorption, chemical attachment or electrochemical grafting). An interesting grafting method involves the electrode surface modification via electroreduction of the corresponding diazonium salts. This method is well established because it is easily feasible and leads to a strong covalent bond between the organic groups and carbon electrode surface [52–58]. Depending on the modification conditions (for instance electrolysis time at constant potential, potential range, number of potential cycles, scan rate, concentration of diazonium salts, etc.), it is possible to achieve monolayer or multilayer aryl films. The formation of mono- or multilayers

can be determined by measuring the layer thickness using various surface characterisation methods (e.g. atomic force microscopy, X-ray photoelectron spectroscopy, ellipsometry) or it can be estimated also by measuring the surface concentration of aryl groups by electrochemical means [56]. For the surface-confined quinone groups, the determination of the surface concentration can be easily performed by the charge integration under the cyclic voltammetry peaks [59]. According to Ernst et al. [60] the surface coverage for closely-packed monolayer of anthraquinonyl groups is 3.45×10^{-10} mol cm⁻².

In our previous studies, the anthraquinone (AQ) modified carbon electrodes have shown high electrocatalytic activity towards the ORR in alkaline media [17–29]. In these experiments, the electrografting of AQ groups was performed in various conditions to yield the surface concentration below 1×10^{-9} mol cm⁻². Sarapuu et al. [22] studied the reduction of oxygen on AQ-modified highly oriented pyrolytic graphite electrodes with the AQ surface concentration even lower than 1×10^{-10} mol cm⁻².

The reduction of oxygen on quinone-modified carbon electrodes follows an electrochemical-chemical (EC) mechanism according to [11,17]:



followed by a chemical step



The superoxide ion can undergo disproportionation:

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or further reduction to peroxide



where Q is the surface quinone species. Reaction (II) is the rate determining step and in this reaction model, the overall rate is determined by the surface concentration of Q^- [11,17]. Reactions (III) and (IV) are considered to be fast and lead to the formation of peroxide. The EC mechanism of O_2 reduction on quinone-modified electrodes, highlighting the extremely high activity of semiquinone radical ions, has been confirmed using cyclic voltammetry [33].

Efforts have been made to increase the surface concentration of covalently bound AQ groups [61,62]. Daasbjerg and co-workers demonstrated that sweeping the potential to more negative values during the electrografting of AQ diazonium salts leads to the formation of thicker films [63–65]. It was of particular interest to use this modification procedure in the present work.

Herein, the main objective was to study the electrochemical reduction of oxygen on AQ-modified glassy carbon (GC) electrodes of high surface concentration in alkaline solution. X-ray photoelectron spectroscopy (XPS) was used to characterise the AQ films on GC surface. The electrochemical behaviour of the GC/AQ electrodes was studied using cyclic voltammetry (CV) and the rotating disk electrode (RDE) method. The kinetic parameters of O_2 reduction on the GC/AQ electrodes were determined.

2. Experimental

2.1. Electrode preparation and surface modification

Glassy carbon (GC) electrodes with a geometric area (A) of 0.196 cm^2 were prepared by mounting GC disks (GC-20SS, Tokai Carbon) into Teflon holders. The electrodes were polished to a mirror finish with 1.0 and $0.3 \mu\text{m}$ alumina slurries (Buehler) and cleaned by sonication in Milli-Q water (Millipore, Inc.), isopropanol (Sigma–Aldrich) and acetonitrile (ACN, Sigma–Aldrich) for 5 min.

The covalent attachment of AQ groups was performed by the electrochemical reduction of the corresponding diazonium salt, Fast Red AL salt (Sigma–Aldrich). The electrografting was carried out using a sweep rate (ν) of 100 mV s^{-1} in acetonitrile solution containing the diazonium salt and 0.1 M tetrabutylammonium tetrafluoroborate (TBABF₄, Fluka) as supporting electrolyte. Two different concentrations of diazonium salt (2 and 10 mM) were used in order to achieve the variable surface concentrations of AQ. For the same purpose, the number of potential cycles was varied: 1; 3; 10 cycles in 2 mM solution and 1; 2; 3; 5; 10 cycles in 10 mM solution. The potential cycling was carried out between 0.6 and -1.45 V . This procedure was taken from the literature [63–65]. After electrografting, the AQ-modified GC electrodes were sonicated in ACN for 5 min to remove the physically adsorbed material.

2.2. Characterisation of GC/AQ electrodes by XPS

The elemental composition of the AQ-modified GC electrodes was measured by X-ray photoelectron spectroscopy (XPS). GC plates of $1.1 \times 1.1 \text{ cm}$ were used as substrate material for the XPS studies. The preparation of samples for XPS followed the same electrografting procedures as described in Section 2.1. The XPS measurements were performed with a SCIENTA SES-100 spectrometer using an unmonochromated Mg K α radiation (incident energy = 1253.6 eV), a take-off angle of 90° and a source power of 300 W. The base pressure in the analysis chamber was below 10^{-9} Torr . The pass energy was set to 200 eV for survey and core

level spectra. The survey spectra were scanned in the range of 0–600 eV (step size of 0.5 eV) and the high-resolution N1s scans between 395 and 410 eV (step size of 0.1 eV). The atomic concentration (at.%) of nitrogen species was calculated for all the GC/AQ samples studied.

2.3. Electrochemical measurements

The electrochemical characterisation of AQ-modified GC electrodes was carried out by using cyclic voltammetry (CV) and oxygen reduction was studied using the rotating disk electrode (RDE) method. Electrochemical measurements were performed in 0.1 M KOH (p.a. quality, Merck). The solution was saturated with Ar (99.999%, AGA) or O_2 (99.999%, AGA). A continuous flow of gases was maintained over the solution during the experiments. A CTV101 speed control unit (Radiometer, Copenhagen) and an EDI101 rotator were used for the RDE experiments. The electrode rotation rates (ω) from 360 to 4600 rpm were used. The potential was applied with an Autolab potentiostat/galvanostat PGSTAT30 (Eco Chemie B.V., The Netherlands) controlled with General Purpose Electrochemical System (GPES) software. A Pt foil served as the counter electrode and the reference electrode was a saturated calomel electrode (SCE). All the potentials are referred to this electrode and all experiments were carried out at room temperature ($23 \pm 1^\circ \text{C}$).

Non-linear regression analysis (NLR) fits were performed using Origin[®] software (version 7.5, OriginLab Corporation).

3. Results and discussion

3.1. Electrografting of AQ groups onto GC electrode

Fig. 1 presents the cyclic voltammograms for electrochemical grafting of anthraquinone groups onto glassy carbon electrode by the electrochemical reduction of Fast Red AL salt in a wide potential range: 0.6 V to -1.45 V . In general, the electrografting behaviour observed is in good agreement with the recent reports on similar experiments by Daasbjerg's group [63,64]. Herein, the electrochemical grafting behaviour is discussed in brief. First of all, two different diazonium salt concentrations (2 and 10 mM) were used (Fig. 1a and b). In both cases, the first cycle showed the reduction wave of AQ diazonium cations at ca. 0.4 V, which disappeared during subsequent cycles as reported by Ceccato et al. [64] and Bousquet et al. [63]. As can be seen in Fig. 1a and b, a redox wave appeared at more negative potentials with the peak potential separation (ΔE_p) and redox potential (E°) values of ca. 0.166 V and -0.89 V , respectively. Based on the study by Ajloo et al. [66], this redox wave may correspond to the one-electron reduction of AQ to AQ^- . Similar to the study of Bousquet et al. [63] the increase in the intensity of the redox wave during the following cycles was observed (Fig. 1a and b). They suggested that this is due to a steady increase in the number of AQ groups attached to the electrode surface. Upon successive potential cycling, a small peak at ca. -0.6 V emerged and it was still visible after 10 cycles.

3.2. Surface concentrations of GC/AQ electrodes

Next, the surface concentration (Γ_{AQ}) of AQ groups attached to GC electrodes was determined in O_2 -free 0.1 M KOH solution (Fig. 2). The values of Γ_{AQ} were calculated from the following equation: $\Gamma = Q/nFA$ [59], where Q is the amount of charge consumed, n is the number of electrons involved ($n = 2$), F is the Faraday constant ($96,485 \text{ C mol}^{-1}$) and A is the geometric electrode area ($A = 0.196 \text{ cm}^2$). Baseline subtraction of CV data was used for the correct estimation of Q . The Γ_{AQ} values were determined as

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