

Oxygen Reduction Catalysis at Anthraquinone Centres Molecularly Wired *Via* Carbon Nanotubes

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Multi-walled carbon nanotubes (MWCNTs) have been chemically derivatised via the reduction of anthraquinone-1-diazonium chloride with hypophosphorous acid to attach 1-anthraquinonyl groups to the MWCNTs, most likely at edge plane like defects. The covalently attached quinone moiety attached to the nanotubes ('molecular wire') acts as an effective mediator for the electrocatalytic reduction of oxygen.

Keywords: Anthraquinone, Oxygen reduction, Multi-walled carbon nanotubes, Edge plane defects

INTRODUCTION

The electrochemical reduction of oxygen on carbon electrodes receives significant attention due to the importance in hydrogen-oxygen fuel cells, for example, in the use of high surface area carbon materials for supports for noble metal catalysts [1]; electrode catalysts which promote oxygen reduction with high efficiency with long operating lifetimes are sought. The immobilisation of catalytic materials is advantageous since they reduce the typically large overpotentials that are required at most electrode substrates [2]. It has been shown that modification of the electrode surface by quinones *via* adsorptive attachment enhances the rate of oxygen reduction [1]. However quinones can desorb from the surface during long-term operation, especially in alkaline solution [1]. It is more beneficial to attach the quinone moiety covalently to the surface [3-5], but only a few oxygen

reductions have been explored due to the lack of simple grafting [1]; covalent modification can be achieved by electrochemically reducing the required diazonium salt [1,4,6,7]. An alternative is to initiate chemisorption by direct reduction with hypophosphorous acid which has been shown to provide an easy methodology for the derivatisation of carbon powder [8,9].

Carbon nanotubes have seen a large expansion of interest recently due to their unique properties such as high mechanical strength and electrical properties, but also as promising materials for their possible technological applications [10-12]. It is also suggested that carbon nanotubes represent a well-defined chemical system with easy access to meaningful molecular-scale interrogation and benefits in applications requiring assembly, such as in fuel cells [13]. In the present context we seek to exploit CNTs as 'molecular wires' linking quinoid electrocatalytic centers with a macroelectrode, which serves to pass the current in and out of the centers.

We report the chemical derivatisation of multi-walled

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carbon nanotubes with 1-anthraquinonyl groups using chemical (as opposed to electrochemical or physical) attachment through the reduction of anthraquinone-1-diazonium chloride using hypophosphorous acid and describe the use of the resulting modified MWCNTs for the electrocatalytic reduction of oxygen. CNTs have been previously modified to improve their response such as increasing their solubility in organic solvents [14] or their electrochemical applicability [15]. All these modifications have been facilitated *via* electrochemical reduction, in contrast to the approach used in this report where the reduction of the anthraquinone-1-diazonium chloride occurs in homogeneous solutions.

EXPERIMENTAL

Voltammetric measurements were carried out using a μ -Autolab III (ECO-Chemie, Utrecht, The Netherlands) potentiostat. All measurements were conducted using a three electrode cell. Basal plane pyrolytic graphite electrodes (bpgg, eppg, Le Carbone, Ltd. Sussex, U.K.) were polished according to a literature methodology [13]. The counter electrode was a bright platinum wire, with a saturated calomel electrode completing the circuit. All solutions were prepared with deionised water of resistivity not less than 18.2 M Ω cm (Millipore water systems, UK).

All chemicals used were of analytical grade and used as received without any further purification. Multiwalled carbon nanotubes (purity > 95%, diameter 30 ± 15 nm, length 5-20 μ m) were purchased from Nano-Lab Inc. (Brighton, MA, USA) and were used without further purification. The orientation of the nanotube is such that the term “bamboo-like” [16] has been coined to describe the fact that the planes of the graphite sheets are at an angle to the axis of the tube itself; the analogy is that of paper cups stacked one inside the other. The MWCNTs were derivatised by stirring 50 mg of MWCNTs into 10 cm³ of a 5 mM solution of anthraquinone-1-diazonium chloride, to which 50 cm³ of H₃PO₂ (50% w/w in water) was added. The solution was filtered by water suction, carefully washed with deionised water and acetonitrile and allowed to air-dry for 12 h. AQ-MWCNTs were attached to a freshly prepared basal plane pyrolytic graphite electrode *via* abrasive immobilisation [17].

RESULTS AND DISCUSSION

Figure 1 (Curve A) shows a typical stable voltammetric response recorded in a pH 2.5 buffer solution. Well-defined reduction and oxidation peaks are observed at -0.21 V and -0.23 V (*vs.* SCE) respectively which corresponds to the electrochemical almost-reversible reduction of the quinone species as observed previously [18-20]. The stability of the modified electrodes have been characterised separately [19] where highly reproducible voltammetric signals can be achieved. The voltammetric scan rate was varied at 10, 25, 50, 75 and 100 mV s⁻¹ and is depicted in Fig. 2. A plot of peak current *vs.* scan rate was found to produce a linear response [($I_p/A = 4.68 \times 10^{-4} (\text{V}^{1/2} \text{s}^{-1/2})$ $R^2 = 0.98$)] indicating that the anthraquinone species is surface bound. The surface coverage of the immobilised anthraquinone on the MWCNTs was next evaluated *via* the following equation:

$$\Gamma = Q/nFA \quad (1)$$

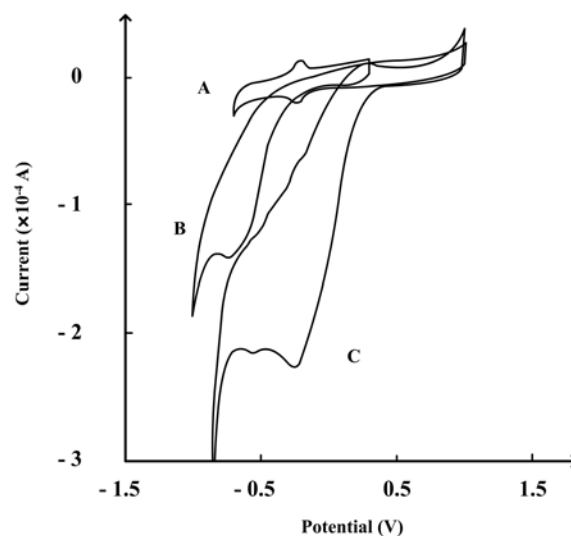


Fig. 1. Cyclic voltammograms for, (A) AQ-MWCNTs abrasively attached to a basal plane pyrolytic graphite electrode, (B) a bare basal plane pyrolytic graphite electrode in a saturated oxygen solution and (C) AQ-MWCNT in the presence of a saturated oxygen solution. All scans run at 10 mV s⁻¹, in a pH 2.5 phosphate buffer solution.

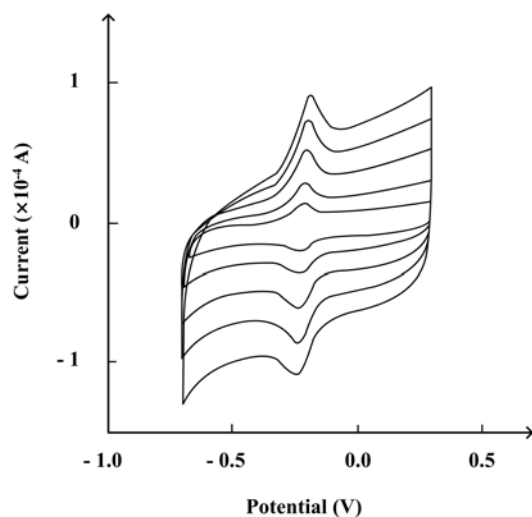
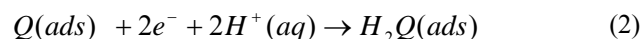


Fig. 2. Abrasively attached AQ-MWCNT onto a basal plane Pyrolytic graphite electrode in a pH 2.5 buffer solution at, 10, 25, 50, 75 and 100 mV s^{-1} .

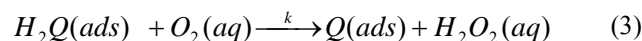
where A is the electrode area, n is the number of electrons per reactant molecule, F is the Faraday constant and Q is the charge obtained from integration of the cathodic peak. The surface coverage was consequently found to be $2.04 \times 10^{-10} \text{ mol cm}^{-2}$. This coverage is similar to that reported by Tammeveski *et al.* who has studied the electrochemical modification of glassy carbon with anthraquinone-1-diazonium chloride [1].

The variation of the peak potential with pH was next explored. The cathodic and anodic waves were observed to shift toward more negative potentials from increasing the pH. A plot of formal potential against pH was observed to be linear over the entire pH range (1.0-14.0) studied with the gradient found to be 59.3 mV per unit ($E_p = -0.153 - 0.0593 \text{ pH}$) which suggests an n -electron, n -proton process where n is likely to be 2. It is worth noting that when the anthraquinone moiety was studied in solution, the variation in peak potential with pH was found to be linear from pH 1 to 10 with a gradient of 53 mV per pH unit, which was then found to be non-linear over pH 10.5. This is attributed to the removal of the first proton, ($pK_{a1} = 10$) while the pK_a for the removal of the second proton is *ca.* $pK_{a2} = 12$. At pH values greater than pH 10, the reduced form of anthraquinone may be deprotonated causing a change in variation of peak potential with pH. However, no such deviation from linearity is

observed for the AQ-MWCNTs over the pH range of 1-14, concluding that derivatisation onto the surface of the MWCNT changes the pK_a of the 1-anthraquinonyl moiety. This has consequently been exploited for pH sensing opportunities [19]. Overall the voltammetry in Fig. 1 can be described *via* the following equation:

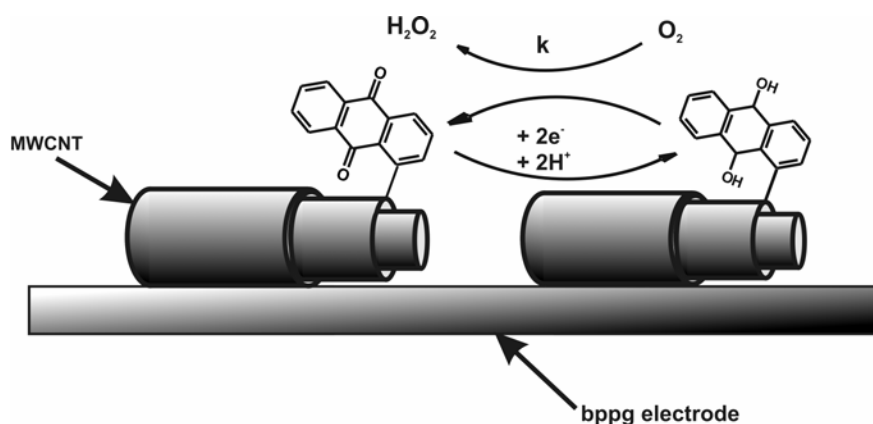


Next the electrocatalytic activity of the AQ-MWCNTs was explored. Using a pH 2.5 buffer oxygen saturated solution the voltammetric response was sought. Figure 1 shows the response for the bare basal plane pyrolytic graphite electrode (curve B) with an oxygen reduction wave at *ca.* -0.77 (vs. SCE) compared with the AQ-MWCNT modified basal plane pyrolytic graphite (bppg) electrode (curve C) exhibiting a reduction wave at -0.29 V (vs. SCE). A bppg electrode abrasively modified with MWCNTs (no anthraquinone) exhibited a reduction wave at *ca.* -0.6 V. Note that this reduction in overpotential when comparing the CNT modified bppg and the bare bppg electrode is probably due to the edge plane sites which occur at the ends and defects of the carbon nanotubes [21]. For the AQ-CNT modified electrode, a large shift to a less negative potentials with an increase in the current suggests that the chemically derivatised AQ-MWCNTs are electrocatalytic to oxygen reduction. This suggests that the mechanism is likely to involve the surface bound anthraquinone being reduced to hydroquinone, which reacts with oxygen to form hydrogen peroxide while regenerating the anthraquinone (see scheme 1) as described by equation (2) and (3) [18,22]:



Scheme 1 shows a pictorial representation of multiwall carbon nanotubes where the tubes fit one inside the other [12], with the anthraquinone moieties likely to reside on the ends of the nanotube, specifically at the edge plane sites/defects. Note that pH 2.5 was used to study the electrochemical reduction of oxygen since this pH value was found to be the best, in terms of the most positive potential and peak magnitude.

The electrocatalytic rate constant for oxygen reduction at the AQ-MWCNT was determined using Andrieux and Savéant



Scheme 1. Pictorial representation of anthraquinone derivatised MWCNTs on a basal plane pyrolytic graphite electrode showing the suggested mechanism of the electrocatalytic reduction of oxygen.

theory [23], where cyclic voltammograms are run at slow scan rates (5, 10, 15, 20, 25, and 30 mV s⁻¹) in the presence of oxygen. From the corresponding plot of peak height vs. square root of scan rate ($I_p/A = 1.67 \times 10^{-3} \text{ (V}^{1/2} \text{ s}^{-1/2})$, $R^2 = 0.98$) and from knowing the surface coverage of the anthraquinone on the electrode surface *via* equation (1), the electrocatalytic rate constant (see scheme 1 and equations 2 and 3) can be deduced. The rate constant was found to be $8.6 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ in comparison with the value of $4.7 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ found by Tammeveski and co-workers for oxygen reduction *via* 1-anthraquinonyl groups attached to a glassy carbon electrode [1]. It is noted that the AQ-MWCNT exhibits excellent electrochemical stability and comparable electrocatalytic activity as that seen at other modified electrodes [18,20,22] but of course the vastly increased catalyst coverage possible with CNT modified electrodes as compared with a modified GC electrode means that much improved catalytic rates (s⁻¹) are achievable.

In conclusion we have shown the modification of MWCNT with anthraquinone-1-diazonium chloride produces electro-catalytically active mediator sites for the reduction of oxygen.

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