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SHORT COMMUNICATION

Permeation and electrocatalytic reduction of oxygen by poly(*o*-phenylenediamine) incorporated into Nafion® film

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1. Introduction

A number of conductive polymers can be easily synthesized by electropolymerization on the electrode surface [1–3]. Most of these conducting polymer films become neutral under electroreduction and are highly hydrophobic in nature. Under these conditions, the charge and counter ion migration within the film become the limiting factors for catalytic applications. In an effort to improve the performance of polymer coated electrodes conducting polymers have been incorporated into Nafion® film [4–6]. However, direct applications have not so far been reported. Nafion® film exhibits some degree of phase segregation, which leads to unusual stability towards dissolution while providing a microheterogeneous environment to the adsorbed molecules [7–8]. In this communication, we report the preparation of poly (*o*-phenylenediamine) (PPD) incorporated into a Nafion® film coated electrode. The conducting polymer PPD formed within the Nafion® film showed a greatly enhanced electrocatalytic reduction of oxygen coupled with the permeation of oxygen through the Nafion® film.

2. Experimental details

A three electrode cell with a 0.07 cm^2 glassy carbon working electrode, a 1 cm^2 platinum plate counter electrode and a saturated calomel reference electrode (SCE) was used for the electrochemical experiments. A Nafion® (Aldrich) coated electrode was prepared by spreading a known volume of 2% Nafion® solution on the glassy carbon electrode. The solvent was then allowed to dry at room temperature and the Nafion® coated electrode was dipped in water for 30 min (represented as GC/Nf). The PPD incorporated into the Nafion® film coated glassy carbon electrode was prepared by continuous scanning between −0.8 and 1.2 V or applying a potential of 1 V vs SCE using a mixture containing 0.05 M *o*-phenylenediamine (thrice recrystallized), 0.2 M Na_2SO_4 and 0.1 M H_2SO_4 (represented as GC/Nf/PPD). The Nf/PPD electrode was thoroughly rinsed with 0.1 M H_2SO_4 and distilled water. The total film thickness of the Nf/PPD film was calculated by considering the individual film thickness of Nafion® [9] and PPD [3, 10] films by knowing the amount of Nafion® and PPD coated on the electrode. The volume concentration (C_p) and the apparent diffusion coefficient (D_app) were calculated by measuring the amount of electroactive PPD using coulometry and chronoamperometry [3]. The electrochemical measurements were made on an EG&G 273A PAR potentiostat/galvanostat equipped with a RE 0151 recorder. Hydrogen peroxide was estimated by titrimetry and spectro-photometry methods [11, 12].

3. Results and discussion

3.1. *Formation and electrochemical characterization of PPD incorporated into the Nafion®* film

The continuous cyclic voltammograms recorded using GC and GC/Nf electrodes dipped in a mixture containing 0.05 M *o*-phenylenediamine, 0.2 M Na_2SO_4 and 0.1 M H_2SO_4 under deaerated condition showed the oxidation of monomer *o*-phenylenediamine at 0.525 V vs SCE in the first cycle. In the follow up cycles, the oxidation current decreased rapidly at 0.525 V vs SCE with a simultaneous appearance of a redox wave at −0.150 V vs SCE. This clearly shows the oxidation of the monomer and the formation of PPD at GC [10] and GC/Nf electrodes. The PPD film formed on the plain GC electrode by electropolymerization was always limited to around 1 μm in thickness. The chronocoulometric data showed that the amount of PPD formed at the GC/Nf electrode was always much higher than that at the plain GC electrode. The PPD film coated onto the GC electrode did not show any colour; whereas the PPD film prepared by using the GC/Nf electrode was light yellow and the colour did not disappear when the electrode was dipped or washed with 0.1 M H_2SO_4 or water. This suggests that the adsorbed monomer is polymerized within the Nafion® film. A similar observation was reported for a polyaniline intercalated clay coated electrode [13].

The cyclic voltammograms and the chronoamperometric plots recorded for GC/PPD and GC/Nf/PPD in 0.2 M Na_2SO_4 and 0.1 M H_2SO_4 are shown in Fig. 1. The electrochemcial data obtained for both GC/PPD and GC/Nf/PPD electrodes at different film thicknesses are summarized in Table 1. The chronoamperometric plots clearly show that the PPD is reversible at both GC/PPD and GC/Nf/PPD electrodes (Fig. 1). The reversible behaviour observed for the GC/Nf/PPD electrode at all film thicknesses shows the homogeneous distribution of PPD

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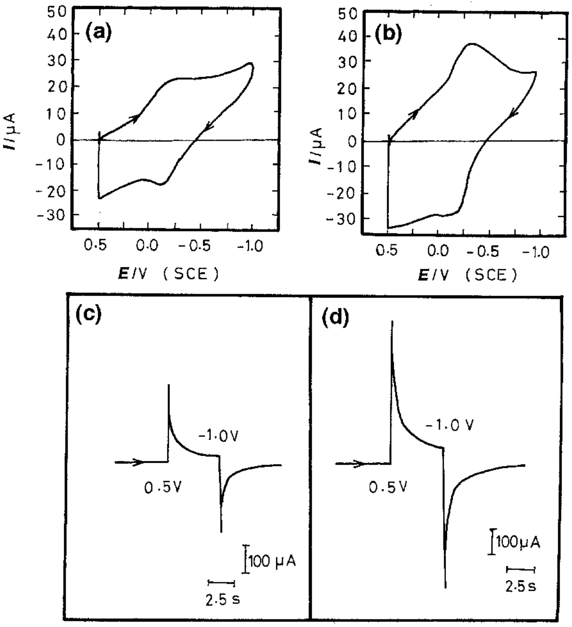


Fig. 1. Cyclic voltammograms of (a) GC/PPD and (b) GC/Nf/PPD electrodes in a mixture containing 0.2 M Na_2SO_4 and 0.1 M H_2SO_4 under deaerated condition. Scan rate: 50 mV s^{-1}. Potential-step chronoamperometric current–time response for the oxidation and reduction processes of (c) GC/PPD and (d) GC/Nf/PPD electrodes.

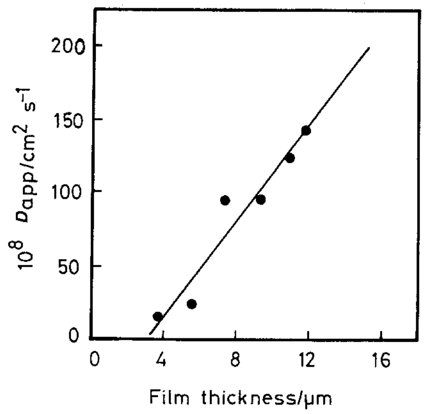
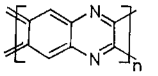
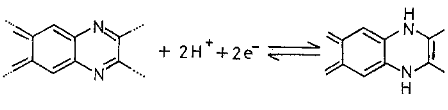


Fig. 2. the plot of apparent diffusion coefficient (D_{app}) vs film thickness of GC/Nf/PPD electrode. Experimental conditions are same as in Fig. 1.


PPD


(1)

throughout the Nafion® film. The Nafion® film contains hydrophilic sulfonate ionic clusters, a hydrophobic fluorocarbon region and an interfacial region formed between these two [7, 8]. It has been reported that small molecules such as neutral ferrocence [14] are adsorbed into the interfacial region of the Nafion® film. In the present investigation, it is suggested that the monomer *o*-phenylenediamine occupies the interfacial region and, upon oxidation, the neutral PPD forms within the Nafion® film. The PPD polymer is neutral in both oxidized and reduced forms and protons are involved in this redox process [3, 10] (Equation 1).

The formation of PPD within the Nafion® film increases the volume of the interfacial region of the Nafion® film thereby decreasing the ionic cluster volume [15, 16]. It has been reported [15, 16] that the increase in hydrophobicity within a Nafion® film leads to the removal of water molecules from the ionic cluster region, resulting in an increase in acidity in the film. The presence of lower volume ionic clusters containing protons improves the electrochemical properties of PPD at the Nafion® film. The apparent diffusion coefficient (D_{app}) for charge transport measured by chronoamperometry for the GC/Nf/PPD electrode is almost 10–100 times higher than that for the GC/PPD electrode (Table 1). It has been demonstrated for other coated electrode systems that D_{app} increases when the volume concentration C_p decreases [17]. The increase in film thickness leads to a decrease in C_p [3]. In the present system,

Table 1. Apparent diffusion coefficients, D_{app}, for GC/PPD and GC/Nf/PPD electrodes at various Nf/PPD film thicknesses

ϕ/μm	$10^4\ C_p$, mol cm^{-3}	$10^8\ D_{app}$, cm^2 s^{-1}
0.36*	6.10	5.90
3.84†	1.14	15.75
5.37†	0.73	37.35
7.16†	0.39	98.00
8.95†	0.39	98.00
11.35†	0.32	126.70
11.59†	0.38	174.50

ϕ Total film thickness of Nf/PPD film
C_p Volume concentration of electroactive species in the film
* GC/PPD
† GC/Nf/PPD

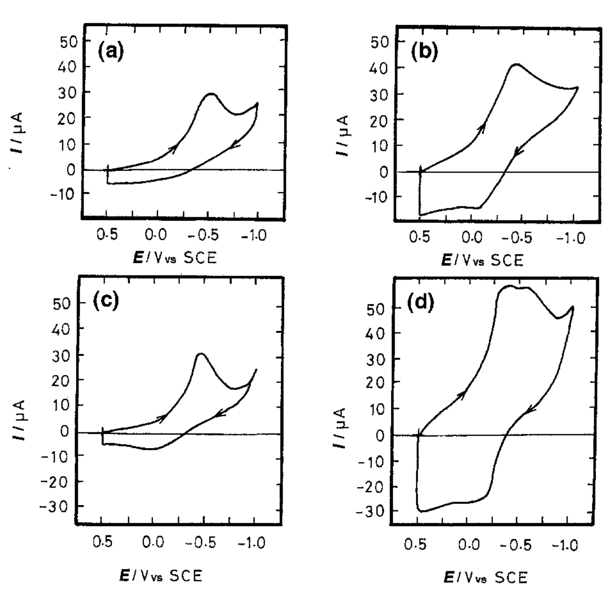


Fig. 3. Cyclic voltammograms of (a) GC, (b) GC/PPD, (c) GC/Nf and (d) GC/Nf/PPD electrodes in a mixture containing 0.2 M Na_2SO_4 and 0.1 M H_2SO_4 under oxygenated condition. Scan rate: 50 mV s^{-1}.

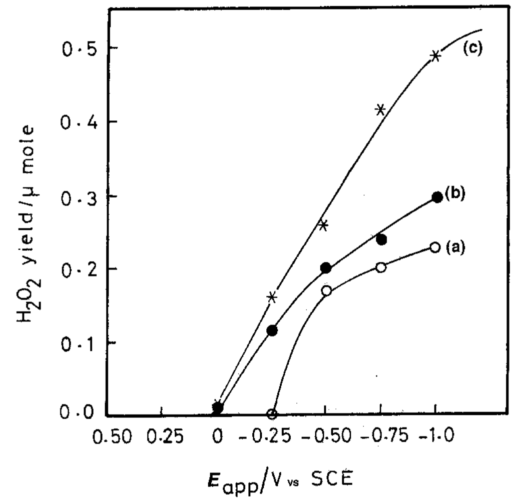
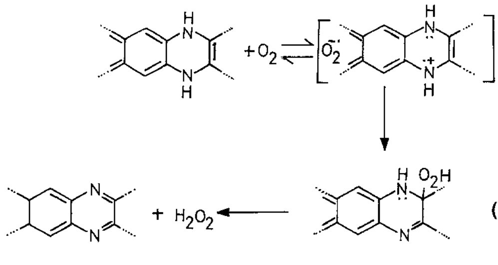


Fig. 4. The yield of hydrogen peroxide at different applied potentials measured at (a) GC/Nf, (b) GC/PPD and (c) GC/Nf/PPD electrodes dipped in 0.1 M H_2SO_4 and 0.2 M Na_2SO_4 solution.

D_{app} increases with increasing Nf/PPD film thickness (Fig. 2). In addition, the microheterogeneous environment provided by the Nafion® film contributes in improving the charge migration aided by proton and counter ion movement within the Nafion® film. The electrochemical properties such as the redox potentials and peak separations are not affected by the Nafion® film environment at the GC/Nf/PPD.

3.2. *Electrocatalytic reduction of oxygen at GC/Nf/PPD electrode*

The cyclic voltammograms recorded for oxygen reduction at GC, GC/PPD, GC/Nf and GC/Nf/PPD in a mixture containing 0.2 M Na_2SO_4 and 0.1 M H_2SO_4 supporting electrolyte are shown in Fig. 3. In all electrode systems, oxygen reduction was observed. In comparison to GC and GC/Nf electrodes, an anodic shift was observed for the reduction of oxygen at GC/PPD and GC/Nf/PPD electrodes. It has already been reported that the PPD coated electrode catalyses oxygen reduction [10]. It was found that the rate of oxygen reduction was enhanced when the GC/Nf/PPD electrode was used and this was confirmed by measuring the reduction product, hydrogen peroxide, at different times. This observation clearly indicates that catalytic reduction of oxygen to hydrogen peroxide is mediated by the protonated form of reduced PPD in the GC/Nf/PPD electrode (Equation 2). The migration of protons and supporting electrolyte ions is enhanced in the Nf/PPD film when compared with the PPD film.



(2)

In addition to the catalytic reduction of oxygen by Nf/PPD, an irreversible reduction of oxygen was also observed (Fig. 3). This can be explained on the basis of the permeation of oxygen through the Nafion® film. The cyclic voltammogram recorded for the GC/Nf/PPD electrode with different film thicknesses (3.8–11.6 μm) clearly showed two reduction waves at −0.275 V and −0.5 V vs SCE indicating the catalytic reduction of oxygen by Nf/PPD and direct reduction of oxygen by permeation, respectively. The reduction of oxygen by two different processes can be understood on the basis of the Nafion® film structure. It has already been reported that the permeation of oxygen at Nafion® films occurs effectively and the concentration of oxygen inside the Nafion® film is also much higher than in water [18, 19]. The PPD incorporated into the interfacial region of the Nafion® film mediates oxygen reduction catalytically and the oxygen permeated through the interfacial region of the Nafion® film undergoes direct irreversible reduction. The yield of hydrogen peroxide estimated [11, 12] at different applied potentials was plotted and is shown in Fig. 4. A 10% increase in hydrogen peroxide yield was found at the GC/PPD electrode when compared to the GC electrode. The amount of hydrogen peroxide observed at GC/Nf/PPD is 35–40% higher than that observed at GC/PPD. At higher negative potiential (> −0.5 V vs SCE), the amount of hydrogen peroxide was found to be much higher than that of the GC/PPD electrode and shows the direct reduction of permeated oxygen in addition to the Nf/PPD catalysed oxygen reduction process. This observation is supported by the fact that the D_{app} value measured for the GC/Nf/PPD electrode is almost 100 times higher than that for the GC/PPD electrode.

Acknowledgement

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