Electrocatalysis of Poly(2,3-diaminonaphthalene)-filmed Electrodes for Reduction of Oxygen

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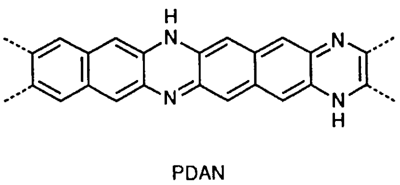
Poly(2,3-diaminonaphthalene)(PDAN)-filmed glassy carbon electrode, which can be prepared *in situ* by electropolymerization of the corresponding monomer, shows excellent electrocatalytic activity for O_2 reduction to H_2O_2 in an acidic aqueous solution (pH 1.0), with an activation overpotential which is *ca.* 300 mV lower than that of the bare electrode.

Electrocatalysis for the reduction or oxidation of a substrate is one of the most interesting functions of electropolymerized film-coated electrodes which can be prepared *in situ* by electropolymerization of a variety of aromatic compounds. The use of these modified electrodes as a new type of electrocatalyst is of much current interest because of their preparation *in situ* by electropolymerization with fine control of the thickness and homogeneity, great variation of polymers prepared, electrocatalytic properties of the films themselves, potential entrapping of other catalysts in their matrices, *etc.* Several papers have appeared on the electrocatalysis of electropolymerized film-coated electrodes for reduction and/or oxidation of O_2,[1,2] amine neurotransmitters and ascorbic acid,[3] metal complexes[2,4,5] and others.[5,6]

In this communication, we report preliminary results concerning the electrocatalytic activity of poly(2,3-diaminonaphthalene) (PDAN)-filmed electrodes for O_2 reduction, which can be prepared *in situ* by electrooxidative polymerization of the corresponding monomer (DAN) in acidic aqueous solution. The preparation, electrochemical properties and molecular structure (a double-stranded ladder structure with phenazine rings as electroactive moieties) of PDAN have been recently reported by our research groups.[7]

According to a previous procedure,[7] the electrooxidative polymerization of DAN was carried out using a three-electrode, two-compartment cell. Typically, film formation was achieved at a glassy carbon (GC) or Pt electrode in 0.2 mol dm^{-3} $NaClO_4$ aqueous solution (pH 1.0) containing $HClO_4$ and 20 mmol dm^{-3} DAN by potential-sweep electrolysis at 50 mV s^{-1} [Fig. 1 (curve *A*)]. The cyclic voltammetric behaviour observed at the GC electrode during the electropolymerization as well as the redox response (curve *B*) of the PDAN film prepared ($E^{o\prime} = -0.20$ V *vs.* SCE; $E^{o\prime}$ = formal potential; SCE = saturated calomel electrode) are essentially the same as those previously obtained at the basal-plane pyrolytic graphite (BPG) electrode.[7] A similar redox response was also obtained at the Pt electrode (curve *E* and see curve *E* in Fig. 2). Thus, the present and previous results[7] suggest that a ladder-structured polymer with phenazine rings as electroactive moieties may be formed on GC and Pt electrodes, as in the case of the BPG electrode.

It can be seen that curve *C* in Fig. 1, observed in O_2-saturated solution, shows a greatly enhanced reduction current and a positive shift in the cathodic peak potential of about 300 mV, compared to the bare electrode (curve *D*). This fact demonstrates the catalytic reduction of O_2 *via* the mediating phenazine redox couple in the PDAN film. The O_2 reduction to H_2O_2 is electrochemically an irreversible process in acidic aqueous solutions.[8,9] The peaks in the anodic scans in curves *B* and *C* correspond to the oxidation of the reduced forms that are formed during the cathodic scans. The anodic peak in curve *C* is smaller than that in curve *B*, because a part of the reduced forms take part in the electrocatalytic reduction



PDAN

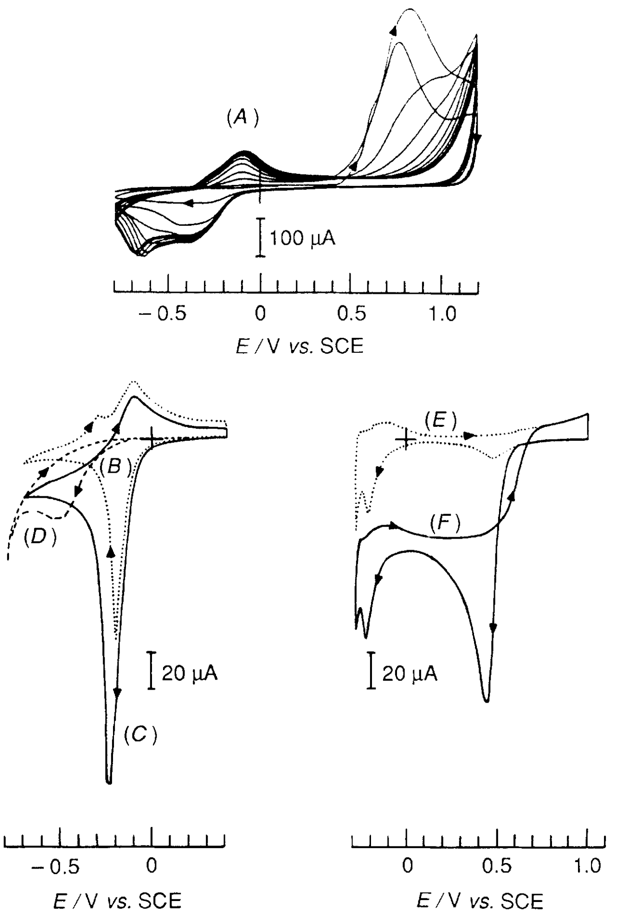


Fig. 1 (*A*) Cyclic voltammograms recorded continuously during the electropolymerization of DAN at a GC electrode (0.27 cm^2) in an acidic aqueous solution (pH 1.0) containing $NaClO_4$ (0.2 mol dm^{-3}) and DAN (20 mmol dm^{-3}) under an N_2 atmosphere. (*B*, *C*) Cyclic voltammograms of the PDAN-filmed GC electrode (prepared by repeating potential sweep 10 times as in *A*) in Na_2SO_4 (0.2 mol dm^{-3}) solution (pH 1.0) saturated with O_2 (*C*) and without O_2 (*B*). (*D*) Cyclic voltammogram at bare GC electrode in the same solution as in *B* and *C* under an N_2 atmosphere. (*E*, *F*) Cyclic voltammograms of the PDAN-filmed Pt electrode (0.27 cm^2) (prepared by repeating potential sweep 10 times between 0 and 1.2 V at 50 mV s^{-1}) in the same solution as in *B* and *C* under an atmosphere of N_2 (*E*) and O_2 (*F*). Potential scan rate: (*A*) 50 mV s^{-1}, (*B*, *C*, *D*, *E*, *F*) 10 mV s^{-1}.

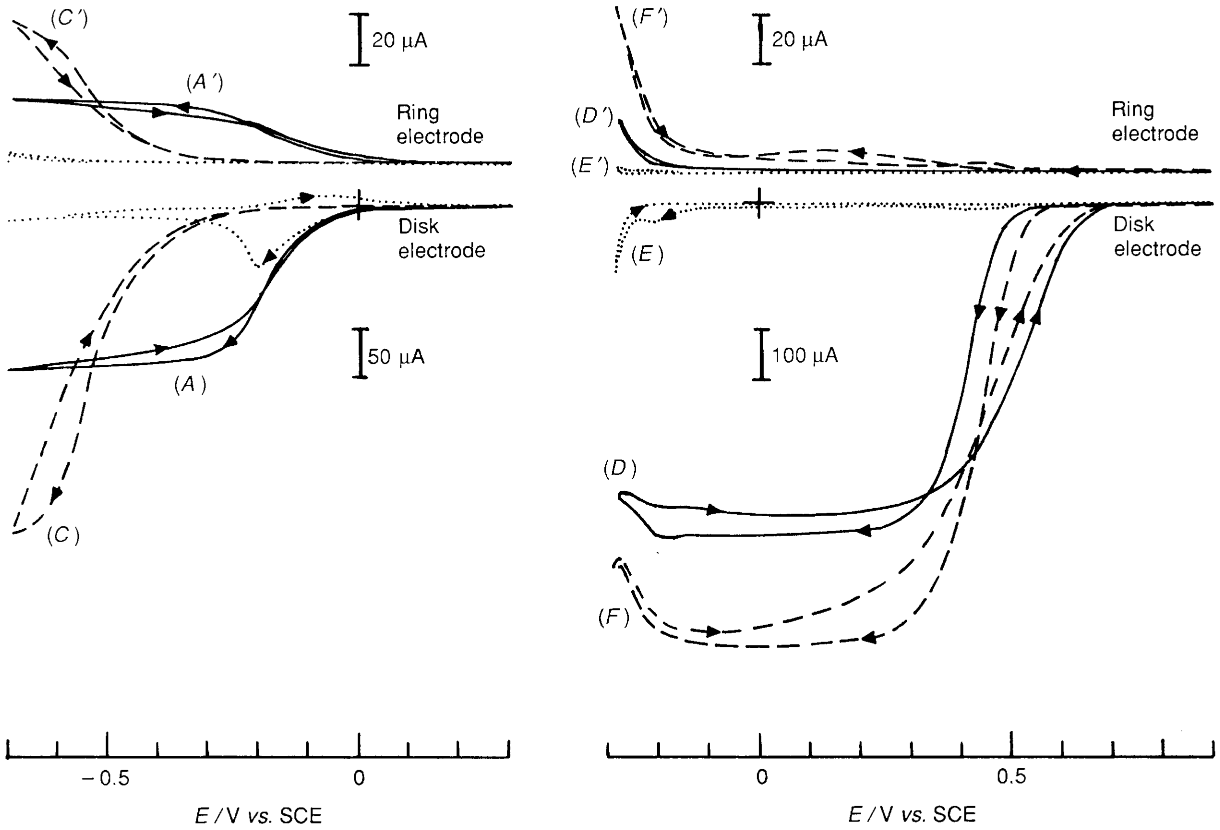


Fig. 2 Current-potential curves for the reduction of O_2 at a rotating GC (or Pt) disk–Pt ring electrode. (*A*, *B*) at PDAN-filmed GC electrode, (*C*) at bare GC electrode, (*D*, *E*) at PDAN-filmed Pt electrode, (*F*) at bare Pt electrode. Supporting electrolyte: Na_2SO_4 (0.2 mol dm^{-3}) and H_2SO_4 saturated with O_2 (*A*, *C*, *D*, *F*) and without O_2 (*B*, *E*). Rotation rate: 900 rpm. Ring electrode potential: 1.1 V *vs.* SCE. The disk potential was scanned at 5 mVs^{-1}. Ring currents *A*′, *B*′, *C*′, *D*′, *E*′ and *F*′ correspond to disk currents *A*, *B*, *C*, *D*, *E* and *F*, respectively. The PDAN-filmed GC and Pt electrodes are the same as in Fig. 1.

of O_2 and consequently they themselves are converted into the oxidized ones. The catalytic O_2 reduction is also understandable on the basis of the steady-state electrochemical behaviour obtained hydrodynamically for O_2 reduction using a rotating ring disk electrode (RRDE) (Fig. 2), where the potential of the Pt ring electrode was held at 1.1 V *vs.* SCE to detect hydrogen peroxide (H_2O_2) which might be formed at the disk electrode during the cathodic process. The positive shift of the voltammogram at the film-coated electrode (compare curves *A* and *C* in Fig. 2) indicates that the O_2 reduction is catalysed by the PDAN film (curve *B*). The fact that the limiting current is smaller than at the bare electrode may suggest that the overall rate of the catalytic reduction of O_2 is controlled by the mass-transfer process of O_2 from the bulk of solution to the film–solution interface as well as other processes in the film (*i.e.*, permeation of O_2, diffusion-like charge propagation between redox sites in PDAN film and electron cross-reaction between redox site of the film and O_2).[10] In addition, the ratio (*ca.* 8.8) of disk current (I_D) to ring current (I_R) is larger than the reciprocal of collection efficiency (N),†[11] suggesting that mainly H_2O_2 is formed, but 4-electron reduction of O_2 and/or decomposition of the H_2O_2 formed may occur.[8]

On the other hand, the situation is a little different for the PDAN-filmed Pt electrode. As usually expected for a bare Pt electrode,[9] 4-electron reduction of O_2 to H_2O occurs also at the film-coated electrode (curve *D* in Fig. 2) in the potential range more negative than *ca.* 0.5 V *vs.* SCE. This can be supported by the fact that no reduction current flows actually at the Pt ring electrode (curve *D*′). In this case, O_2 must penetrate the film to reach the electrode surface and then it can be directly reduced to H_2O. This is a reason why the limiting current at the film-coated electrode is smaller than that (curve *F*) at the bare electrode. The decreasing disk current (curve *F*) observed in the potential range of *ca.* −0.2 to −0.3 V‡ and the corresponding significant ring current (curve *F*′) may suggest that 2-electron reduction of O_2 to H_2O_2 occurs (though to a slight extent).[12] A similar RRDE behaviour was also observed at the PDAN-filmed Pt electrodes (curves *D* and *D*′). However, from the increased reduction current of the PDAN film at about −0.2 V in the presence of O_2 (curve *F* in Fig. 1) and the result obtained with the PDAN-filmed GC electrode [*i.e.*, the film electrocatalyses (mediates) 2-electron reduction of O_2 to H_2O_2], it seems likely that a direct 2-electron reduction of O_2 to H_2O_2 at the Pt-film interface as well as the 2-electron reduction mediated by the film occur concurrently.

In conclusion, the PDAN-filmed GC electrode exhibits excellent electrocatalytic activity for O_2 reduction to H_2O_2 in acidic aqueous solutions, with an activation overpotential *ca.* 300 mV lower than that of the bare electrode. Both 2- and 4-electron reductions of O_2 occur at the bare and PDAN-

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† N is a calculable geometric factor which depends on the size of disk and ring electrodes.[11] In this experiment, the radius of the disk electrode is 2.95 mm and the inner and outer radii of the ring electrode are 3.15 and 4.15 mm, respectively, and thus N^{-1} is estimated to be 2.40. If H_2O_2 is formed in 100% yield without any decomposition and further reduction to H_2O, then I_D/I_R should be equal to N^{-1}.

‡ At more negative potentials, the disk current increases again with the negative scanning of potential owing to overlapping with the proton reduction current.

filmed Pt electrodes. A quantitative analysis of the mechanism of the electrocatalytic O_2 reduction on a molecular level is currently being studied, and results will be reported later.

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