

Electrocatalysis of O₂ Reduction at Poly(*o*-phenylenediamine)- and Poly(*o*-aminophenol)-coated Glassy Carbon Electrodes

Takeo Ohsaka,^{a,*} Takashi Watanabe,^a Fusao Kitamura,^a Noboru Oyama^b and Koichi Tokuda^a

^a Department of Electronic Chemistry, Graduate School at Nagatsuta, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 227, Japan

^b Department of Applied Chemistry, Faculty of Technology, Tokyo University of Agriculture and Technology, 2-24-16 Naka-machi, Koganei, Tokyo 184, Japan

Poly(*o*-phenylenediamine)-coated glassy carbon electrodes possess much greater catalytic activity for O₂ reduction in acidic aqueous media (pH 1.0) than poly(*o*-aminophenol)-coated electrodes, the coated electrodes being prepared *in situ* by electropolymerization of the corresponding monomers, as a result of the different reactivity of 1,4-diazine and 1,4-oxazine rings as electroactive moieties with O₂.

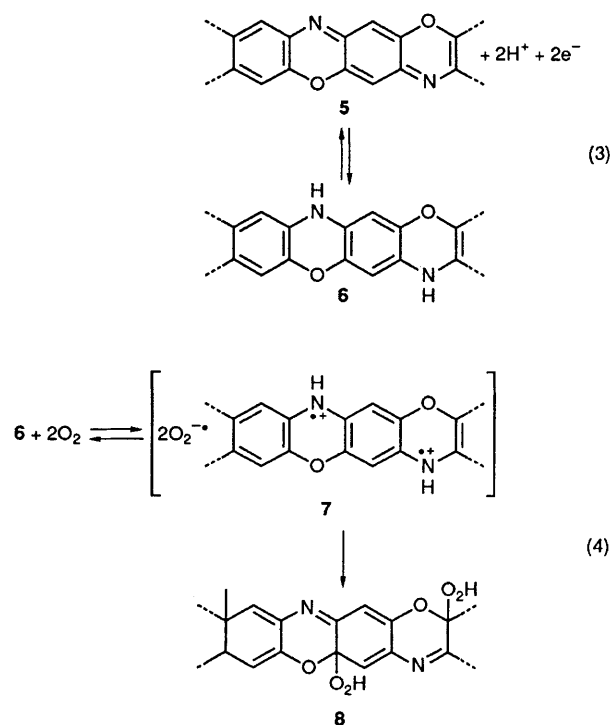
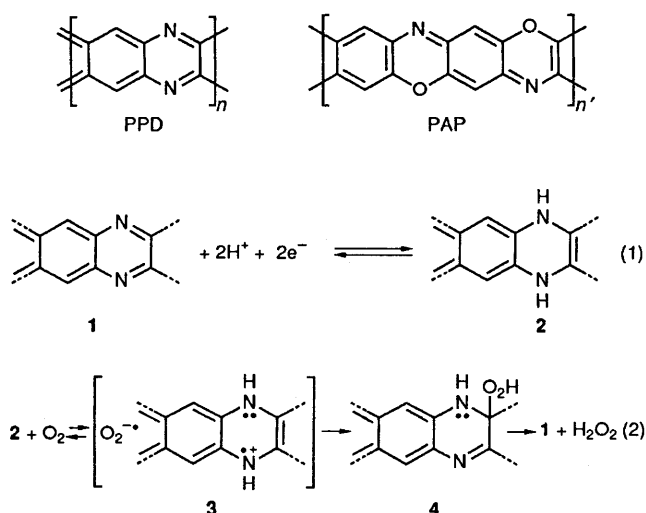
Recently, electropolymerized film-coated electrodes, which can be prepared *in situ* by electropolymerization of a variety of aromatic compounds, have become of great interest as a new type of electrocatalyst.¹

In this communication, we report on the electrocatalysis of poly(*o*-phenylenediamine) (PPD)- and poly(*o*-aminophenol) (PAP)-coated glassy carbon (GC) electrodes for O₂ reduction in acidic aqueous media. The greater catalytic activity for O₂ reduction of the PPD-coated electrode in comparison with the PAP-coated electrode is demonstrated on the basis of their cyclic voltammetric behaviour. The *in situ* preparation of PPD- and PAP-coated electrodes by electrooxidative polymerization of the corresponding monomers and their unique structures (*i.e.* double-stranded ladder polymers with 1,4-diazine and 1,4-oxazine rings as electroactive moieties) and electrochemical properties have been recently reported by our research groups²⁻⁶ and Barbero *et al.*⁷

The PPD- and PAP-coated GC (area: 0.27 cm²) electrodes were prepared by potential-sweep electrolysis at 50 mV s⁻¹ in the potential range of -0.8 to 1.2 and -0.4 to 1.0 V *vs.* a saturated calomel electrode (SCE), respectively, in 0.2 mol dm⁻³ Na₂SO₄ aqueous solution (pH 1.0) containing 50 mmol dm⁻³ *o*-phenylenediamine or *o*-aminophenol under an atmosphere of nitrogen. The PPD- and PAP-coated GC electrodes thus prepared show a reversible redox response at *ca.* -0.15 and 0.05 V *vs.* SCE, respectively (Fig. 1 voltammograms *a* and *c*). The voltammogram *b*, observed in O₂-saturated solution, shows a greatly enhanced reduction current and a positive shift in the cathodic peak potential of about 300 mV in comparison with that (voltammogram *f*) obtained at a bare GC electrode. This fact demonstrates the catalytic reduction of O₂ *via* the mediating 1,4-diazine redox couple in the PPD-film, as in the case of poly(2,3-diaminonaphthalene) (PDAN)-coated electrode, where PDAN also contains 1,4-diazine rings as electroactive moieties.^{1,8,9} In

these cases, the formation of hydrogen peroxide (H₂O₂) was confirmed by rotating ring-disk electrode (RRDE) voltammetry. On the other hand, the situation is largely different in the case of the PAP-coated GC electrode. In this case, two well-defined reduction peaks are observed at about 0.0 and -0.65 V *vs.* SCE. The first reduction peak current is only slightly larger compared with that obtained under an atmosphere of nitrogen (voltammogram *d*) and the second reduction is fairly similar in peak potential to that obtained at a bare GC electrode. From these results, it may be concluded that the electrocatalysis of both these films for O₂ reduction is largely different, that is, the PPD-film catalyses considerably O₂ reduction, whereas the PAP-film exhibits very little such activity.

A probable explanation for the different electrocatalysis observed seems possible by considering the reaction mechanism of PPD (or PAP) and O₂ on a molecular basis, as shown by Schemes 1 and 2 for the PPD-O₂ and PAP-O₂ systems, respectively. Eqns. (1) and (3) represent the heterogeneous electron-transfer processes of the redox moieties of PPD and PAP, respectively. Both processes are electrochemically reversible as mentioned above. In the case of the PPD-O₂ system, the reduced 1,4-diazine moiety **2** first reacts directly with O₂ to give adduct **3**. The adduct is, *via* a rapid radical recombination, believed to rearrange to the hydroperoxy



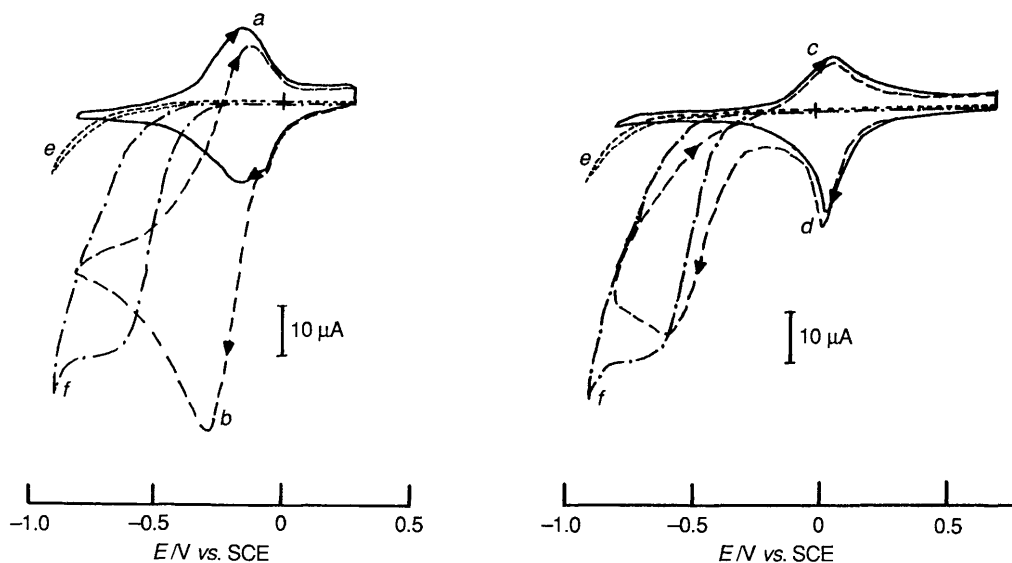


Fig. 1 Cyclic voltammograms of (a, b) PPD- and (c, d) PAP-filmed GC electrodes in $0.2 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4 + \text{H}_2\text{SO}_4$ solution (pH 1.0). (a, c, e) under N_2 atmosphere, (b, d, f) under O_2 atmosphere. Voltammograms e and f were obtained at a bare GC electrode. Potential scan rate: 10 mV s^{-1} .

derivative **4** of 1,4-diazine. Recently, it has been demonstrated that the superoxide anion radical $\text{O}_2^{\cdot-}$ is an effective oxidant of basic reducing substrates with readily transferable hydrogen atoms, e.g. reduced flavins and dihydrophenazine which have dihydro-1,4-diazine rings.¹⁰ The hydroperoxy 1,4-diazine **4** can break down intramolecularly to yield the reoxidized species **1** and H_2O_2 . Species **1**, thus regenerated, is used for a subsequent catalytic cycle [eqns. (1) and (2)]. On the other hand, the similar series of electrocatalytic cycles cannot be expected to hold for the case of the PAP- O_2 system for the following reasons. No catalytic formation of H_2O_2 via the PAP-film was confirmed by RRDE voltammetry. The reversible redox response of PAP remained substantially unchanged before and after the PAP-film had been held in its reduced state for some time (e.g. 30 min) under O_2 atmosphere, probably suggesting that the intermediate **7** is scarcely formed.[†] Such a different reactivity of 1,4-diazine and 1,4-oxazine rings with O_2 may thus be considered to be the origin of the different electrocatalysis of PPD- and PAP-films observed for O_2 reduction.

[†] From the structure of **8**, intramolecular decomposition similar to that of **4**, which results in H_2O_2 formation, would not be expected to occur.

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