

## Electrocatalysis of O<sub>2</sub> Reduction at Poly(*o*-phenylenediamine)- and Poly(*o*-aminophenol)-coated Glassy Carbon Electrodes

Takeo Ohsaka,<sup>a\*</sup> Takashi Watanabe,<sup>a</sup> Fusao Kitamura,<sup>a</sup> Noboru Oyama<sup>b</sup> and Koichi Tokuda<sup>a</sup>

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

<sup>b</sup> 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 O<sub>2</sub> 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 O<sub>2</sub>.

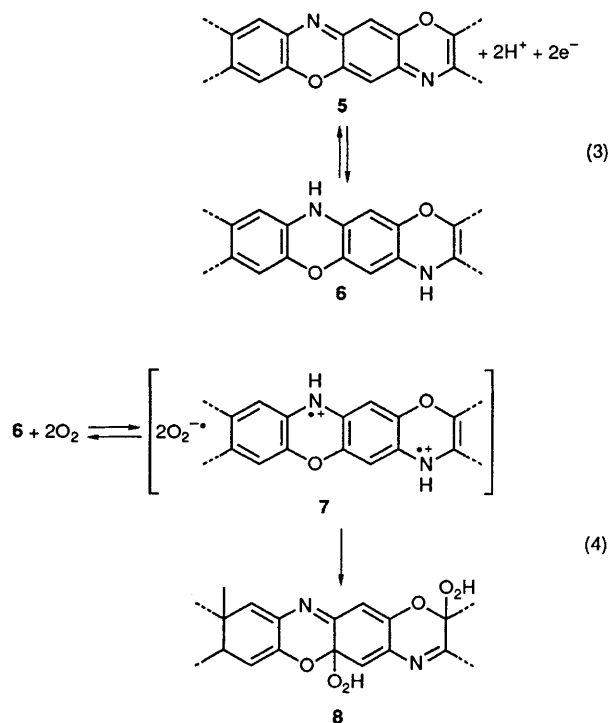
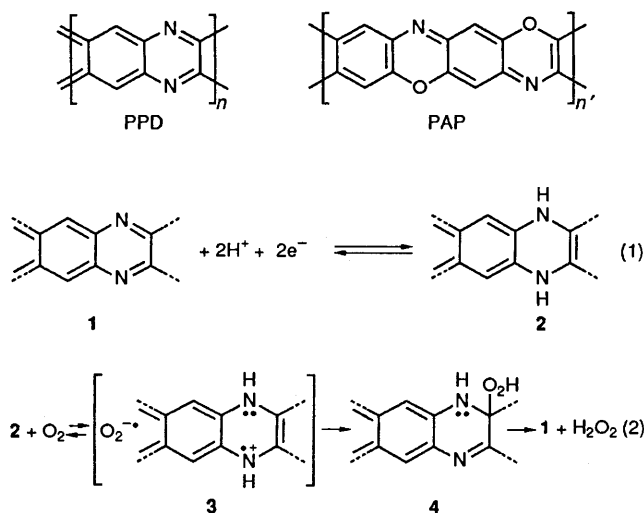
Recently, electropolymerized film-coated electrodes, which can be prepared *in situ* by electropolymerization of a variety of aromatic compounds, have become of great interest as a new type of electrocatalyst.<sup>1</sup>

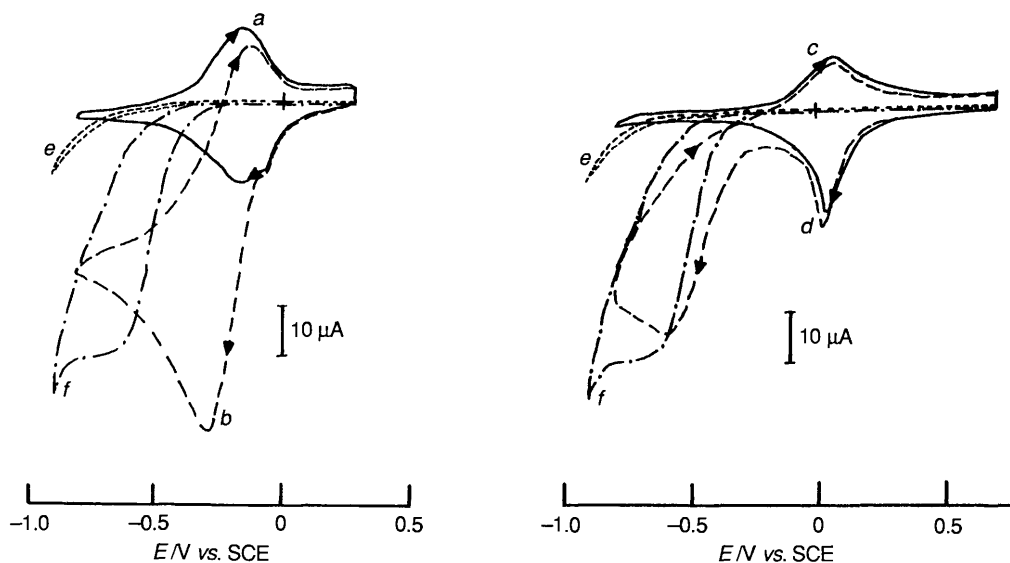
In this communication, we report on the electrocatalysis of poly(*o*-phenylenediamine) (PPD)- and poly(*o*-aminophenol) (PAP)-coated glassy carbon (GC) electrodes for O<sub>2</sub> reduction in acidic aqueous media. The greater catalytic activity for O<sub>2</sub> reduction of the PPD-coated electrode 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 groups<sup>2-6</sup> and Barbero *et al.*<sup>7</sup>

The PPD- and PAP-coated GC (area: 0.27 cm<sup>2</sup>) electrodes were prepared by potential-sweep electrolysis at 50 mV s<sup>-1</sup> 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<sup>-3</sup> Na<sub>2</sub>SO<sub>4</sub> aqueous solution (pH 1.0) containing 50 mmol dm<sup>-3</sup> *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 O<sub>2</sub>-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 O<sub>2</sub> *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.<sup>1,8,9</sup> In

these cases, the formation of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) 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 O<sub>2</sub> reduction is largely different, that is, the PPD-film catalyses considerably O<sub>2</sub> 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 O<sub>2</sub> on a molecular basis, as shown by Schemes 1 and 2 for the PPD-O<sub>2</sub> and PAP-O<sub>2</sub> 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-O<sub>2</sub> system, the reduced 1,4-diazine moiety **2** first reacts directly with O<sub>2</sub> 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  $\text{N}_2$  atmosphere, (b, d, f) under  $\text{O}_2$  atmosphere. Voltammograms e and f were obtained at a bare GC electrode. Potential scan rate:  $10 \text{ mV s}^{-1}$ .

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.<sup>10</sup> The hydroperoxy 1,4-diazine 4 can break down intramolecularly to yield the reoxidized species 1 and  $\text{H}_2\text{O}_2$ . 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- $\text{O}_2$  system for the following reasons. No catalytic formation of  $\text{H}_2\text{O}_2$  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  $\text{O}_2$  atmosphere, probably suggesting that the intermediate 7 is scarcely formed.† Such a different reactivity of 1,4-diazine and 1,4-oxazine rings with  $\text{O}_2$  may thus be considered to be the origin of the different electrocatalysis of PPD- and PAP-films observed for  $\text{O}_2$  reduction.

† From the structure of 8, intramolecular decomposition similar to that of 4, which results in  $\text{H}_2\text{O}_2$  formation, would not be expected to occur.

We acknowledge financial support (No. 02805096) of this research, for T. O., from the Ministry of Education, Science and Culture, Japan, and Shimadzu Science Foundation.

Received, 20th February 1991; Com. 1/00814E

#### References

- 1 T. Ohsaka, T. Watanabe, F. Kitamura, N. Oyama and K. Tokuda, *J. Chem. Soc., Chem. Commun.*, 1991, 487 and references cited therein.
- 2 K. Chiba, T. Ohsaka, Y. Ohnuki and N. Oyama, *J. Electroanal. Chem.*, 1987, **219**, 117.
- 3 S. Kunimura, T. Ohsaka and N. Oyama, *Macromolecules*, 1988, **21**, 894.
- 4 K. Chiba, T. Ohsaka and N. Oyama, *J. Electroanal. Chem.*, 1987, **217**, 239.
- 5 T. Ohsaka, S. Kunimura and N. Oyama, *Electrochim. Acta*, 1988, **33**, 639.
- 6 N. Oyama, T. Ohsaka, K. Chiba and K. Takahashi, *Bull. Chem. Soc. Jpn.*, 1988, **61**, 1095.
- 7 C. Barbero, J. J. Silber and L. Sereno, *J. Electroanal. Chem.*, 1990, **291**, 81.
- 8 N. Oyama, M. Sato and T. Ohsaka, *Synth. Met.*, 1989, **29**, E501.
- 9 N. Oyama, M. Sato and T. Ohsaka, *Materials Res. Soc.*, 1989, **1**, 213.
- 10 E. J. Nanni and D. T. Sawyer, *J. Am. Chem. Soc.*, 1980, **102**, 7593.