

Articles

Electropolymerization Mechanism for Poly(*o*-phenylenediamine) (PPD) and Its Electrocatalytic Behavior for O₂ Reduction

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o-Phenylenediamine (*o*-PD) was electropolymerized on glassy carbon electrodes under a potential cycling condition. The resulting polymer films mediated electrons for the reduction of molecular oxygen at pH=1.0. It was found from the RDE, RRDE, and cyclic voltammetry experiments that the modified electrodes reduce oxygen to hydrogen peroxide at about 300 mV lower potential than the bare glassy carbon electrode. The polymer film consisted of more than two components. Among those, only one component was active in oxygen reduction, which was formed mainly in the earlier stage of the electropolymerization. 2,3-diaminophenazine, a cyclic dimer of *o*-PD, was also active in the oxygen reduction reaction, from which it was suggested that the active polymeric component has a structural unit similar to the cyclic dimer. Finally, the electropolymerization mechanism for the formation of the active and inactive components has been proposed.

Introduction

The synthesis and chemical, physical and electrical properties of π -conjugated polymers are subjects of recent interest. Much of the research on such systems focuses on their basic electrical properties and on their connection to a variety of potential applications.¹⁻²¹ The ladder-type polymers such as poly(*o*-phenylenediamine) (PPD)¹⁹ and poly(*o*-aminophenol) (PAP)²¹ have been electrochemically prepared, and their possible applications to electron transfer mediators for oxygen reduction, pH sensitive electrodes,^{15,16} electrochemical diodes,¹⁴ corrosion inhibitions,^{17,18} and permselective detection of anions^{12,15} have been sought.

Oyama *et al.*¹⁴ reported that PPD exhibits an electrocatalytic behavior for oxygen reduction and contains a phenazine unit in its backbone. Even though they provided detailed kinetic parameters including reaction rate constant, the identity of the polymeric species responsible for O₂ reduction was not clearly demonstrated. Also, the electropolymerization mechanism was not fully studied.

The principal purpose of this study was to draw a more detailed picture on those aspects. For this purpose, we chemically synthesized 2,3-diaminophenazine, the fully oxidized cyclic dimer of *o*-PD and its electrocatalytic activity for oxygen reduction was investigated. With the finding that the dimer also showed electrocatalytic activity for oxygen reduction, we proposed that the active polymeric species has a structural unit similar to the cyclic dimer. A plausible mechanism for the formation of the active and inactive components was also provided.

Experimentals

Materials. *o*-Phenylenediamine (Fluka Co. 98%) was purified by recrystallization from water and dried under reduced pressure. All other chemicals were of reagent grade and used without further purification.

Synthesis of 2,3-diaminophenazine.²² A cyclic dimer of *o*-PD was prepared as follows: 7.1 g (44 mmol) of FeCl₃ was dissolved in 100 mL water and the resulting solution was poured into a stirred solution containing 2.16 g (20 mmol) of *o*-phenylenediamine and 1.4 mL of HCl in 100 mL water at room temperature. A red precipitate formed immediately. For the recrystallization, the precipitate was filtered and dissolved in hot water and allowed to be cooled. The crystal was then collected and washed with diethylether. The needle-type crystal was dissolved in methanol and neutralized with NaOH solution. The solvent was removed using a rotary evaporator and recrystallized from methanol. This material was characterized by NMR spectroscopy and turned out to be 2,3-diaminophenazine, the fully oxidized cyclic dimer of *o*-PD, as depicted in the inset of Figure 1.

Apparatus. A standard three-electrode electrochemical cell was used for the voltammetric experiments. The working electrode was a glassy carbon electrode (Pine Co. area=0.2 cm²), and Pt foil was used as the counter electrode. As a reference electrode, saturated calomel electrode (SCE, Aldrich Co.) was used throughout the cyclic voltammetry experiments and saturated silver/silver chloride electrode was used for the hydrodynamic experiments (RDE and RRDE). The glassy carbon electrode was polished with diamond paste (0.2-1 μ m). All the electrochemical measurements were performed with a Model AFRDE4 bipotentiostat (Pine Co.). Rotation speed of the disk electrode in the hydrodynamic experiments was controlled by using an MSR speed controller (Pine Co.). The output signals were recorded on a 3025 X-Y-Y' recorder (Yokogawa Co.).

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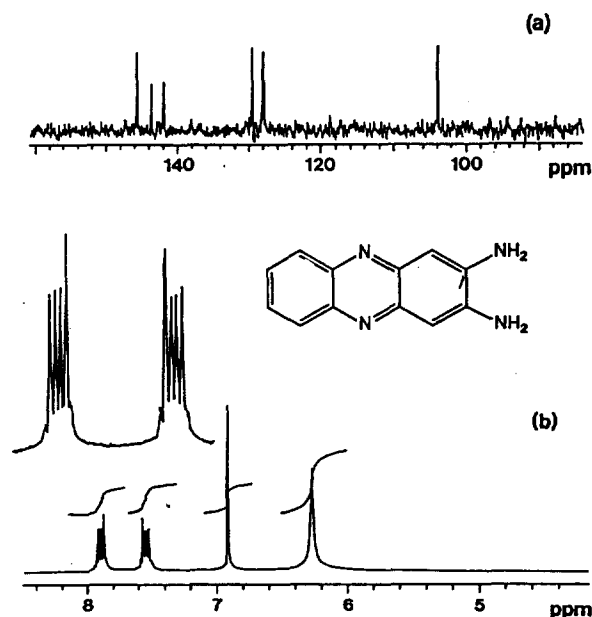


Figure 1. FT NMR spectra of 2,3-diaminophenazine. (a): ¹³C NMR spectrum; 145.64 ppm, 143.65 ppm, 142 ppm, 129.45 ppm, 128 ppm, 103.82 ppm; solvent DMSO-d₆. (b): ¹H NMR spectrum; 2H (7.9 ppm, mult), 2H (7.5 ppm, mult), 2H (6.9 ppm, s), 4H (6.25 ppm, s); solvent DMSO-d₆.

Preparation of poly(*o*-phenylenediamine). Poly(*o*-phenylenediamine) (PPD) films were prepared on glassy carbon electrodes by potential sweep electrolysis. The potential was cycled between -0.8 and 1.2 V *vs.* SCE at 50 mV/sec in 100 mL of 0.2 M Na₂SO₄ solution (pH=1.0) containing 0.5 mmol *o*-phenylenediamine. To adjust the pH of the solution, 0.2 mol of Na₂SO₄ was dissolved in 800 mL water and then sulfuric acid was added until the pH reached at 1.0 . The resulting film-coated electrodes were thoroughly rinsed with H₂SO₄ solution (pH 1.0) and then with distilled water.

Electrocatalytic activity for O₂ reduction. Electrocatalytic activities for oxygen reduction reaction were examined with cyclic voltammetry and rotating Pt ring-GC disk electrode experiments. For the latter experiment, the disk potential was scanned between 0.2 V and -1.0 V *vs.* sat. Ag/AgCl at 10 mV/sec while the ring potential was fixed at 1.0 V *vs.* sat. Ag/AgCl for the detection of the products formed on the disk electrode.

Results and Discussion

Electropolymerization of *o*-PD. The electropolymerization of *o*-PD was carried out in an aqueous solution of 0.2 M Na₂SO₄ (pH=1.0) on glassy carbon electrodes under nitrogen atmosphere. Unless otherwise specified, this solvent/electrolyte system was used throughout the work. A typical voltammogram of *o*-PD is shown in Figure 2. On the first positive sweep, at least two anodic peaks can be located between 0.6 V and 1.0 V. On the subsequent negative sweep, however, none of these peaks show complementary cathodic peaks, indicating that chemical follow-up reactions produce the species detected as peaks **c-c'** and **d-d'**. On the first

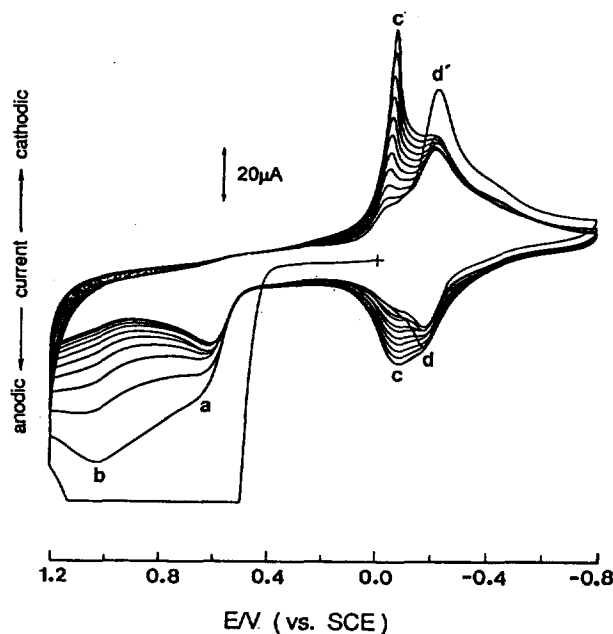


Figure 2. Cyclic voltammograms for the electropolymerization of *o*-PD under nitrogen atmosphere. Electrolyte; aqueous solution of Na₂SO₄ (pH=1.0), concentration of *o*-PD; 5 mM, electrode; glassy carbon, and potential scan rate; 50 mV/sec.

sweep, the intensity of peak **d-d'** is much larger than that of peak **c-c'**. On the following 2-3 sweeps, peak **c-c'** (peak I) increases whereas peak **d-d'** (peak II) diminishes. After the 4th scan, however, both peaks keep increasing with the faster growing rate for peak I as compared to peak II.

After about 50 sweeps, the resulting polymer-deposited electrode was washed with distilled water and potential-cycled in the same electrolyte without *o*-PD (Figure 3-b). The two peaks can still be seen on the cyclic voltammogram. From this, it can be said that *o*-PD is electropolymerized on the electrodes and the polymer is composed of at least two components.

Cyclic voltammetry in O₂ saturated solution. Cyclic voltammetry of the PPD-film coated GC electrode was carried out in an aqueous solution of 0.2 M Na₂SO₄ (pH=1.0) saturated with/without oxygen to examine its catalytic activity in oxygen reduction. In Figure 3, the curve **a** corresponds to the cyclic voltammogram traced with a bare glassy carbon electrode in O₂ saturated solution. The cathodic current peak located at -0.55 V *vs.* SCE can be identified as the oxygen reduction current. The voltammogram **b** was observed with the PPD-coated electrode under nitrogen atmosphere. The curve **c** was traced with the PPD-coated electrode in O₂ saturated solution. The voltammogram **c** shows an enhanced cathodic current at about -0.25 V, which is identified as the polymer-mediated oxygen reduction current. This illustrates that the overpotential for oxygen reduction is reduced by 300 mV by modifying the electrode with PPD. Also immediately apparent in the voltammogram **c** is that the cathodic peak current of component II is much increased, but that of component I remains essentially the same as compared to the voltammogram **b**. This manifests itself that only component II is active in the electrocatalytic O₂ reduc-

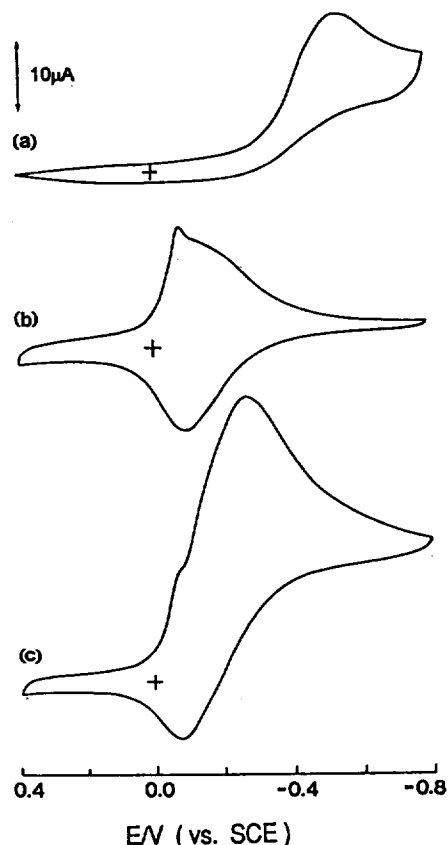


Figure 3. Cyclic voltammograms of the PPD-coated GC electrode in 0.2 M Na_2SO_4 solution (pH=1.0). Voltammogram (a) was traced with a bare GC electrode. Potential scan rate; 10 mV/sec. (a) and (c); in O_2 saturated solution and (b); in N_2 saturated solution.

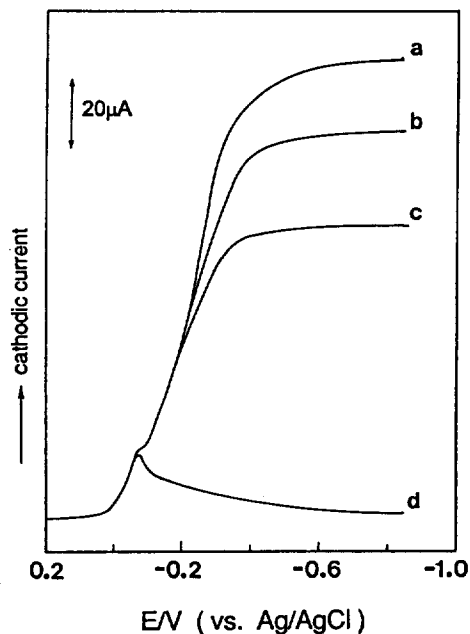


Figure 4. Rotating disk voltammograms for the PPD-coated GC electrode in O_2 saturated solution at various rotation speeds (rpm): a; 1600, b; 900, c; 400, and d; 1600 (in N_2 saturated solution).

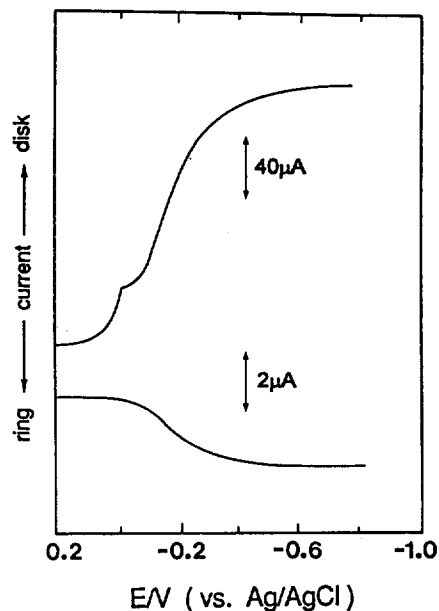


Figure 5. Current-potential curves for the reduction of O_2 with a rotating PPD-coated GC disk-Pt ring electrode in 0.2 M Na_2SO_4 solution (pH=1.0). Rotation speed was 100 rpm.

tion.

Rotating disk electrode (RDE) experiments with PPD/GC electrode. The concurrent electrochemical behavior of the polymer films was observed with a rotating disk electrode experiment (Figure 4). As illustrated in Figure 4, the limiting currents of peak II are increased in O_2 saturated solution as compared to that traced under nitrogen atmosphere, and the limiting current corresponding to component II becomes larger at higher rotation speeds. The current for component I, however, remains the same regardless of the atmosphere and rotation speed. This fact again demonstrates that only component II is active in O_2 reduction reactions.

Rotating ring disk electrode (RRDE) experiments with PPD/GC electrode. Based on the results from the cyclic voltammetry and RDE experiments, it has been claimed that only component II is an active electron mediator in O_2 reduction. In order to ascertain this fact further and to identify the nature of the reduction products, RRDE experiment was performed, where the potential of the Pt ring electrode was held at 1.0 V vs. sat. Ag/AgCl to detect hydrogen peroxide that might possibly be formed at the disk electrode during the cathodic sweep. As shown in Figure 5, the ring current stays at zero in the potential range encompassing peak I, but significantly grows in the potential range where peak II develops. This clearly indicates that only component II plays an active role in oxygen reduction and hydrogen peroxide is formed in this potential range.

As illustrated in Figure 2, component II is formed dominantly in the earlier stage of the polymerization whereas component I becomes dominant later. This fact leads us to infer that the active polymer unit be located mainly near the electrode surface. If this were true, it could be deduced that the electrocatalytic reduction of oxygen mediated by component II would be more difficult as the film thickness increa-

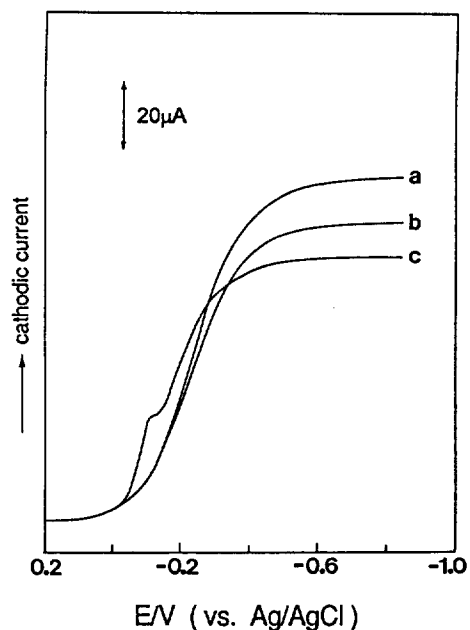


Figure 6. Rotating disk voltammograms traced with the PPD-coated GC electrodes. The film thickness was expressed as the potential cycling numbers; rotation speed=400 rpm. a; after 3 cycles, b; after 13 cycles, and c; after 40 cycles.

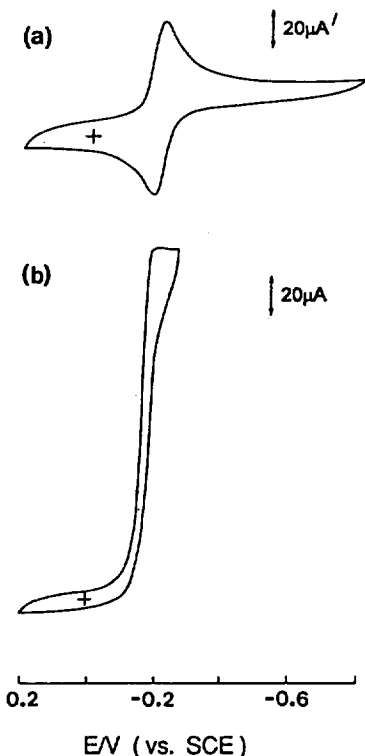


Figure 7. Cyclic voltammograms of 2,3-diaminophenazine in 0.2 M Na₂SO₄ solution; potential scan rate=10 mV/sec, concentration of 2,3-diaminophenazine; 0.05 mM. (a); in N₂ saturated solution and (b); in O₂ saturated solution.

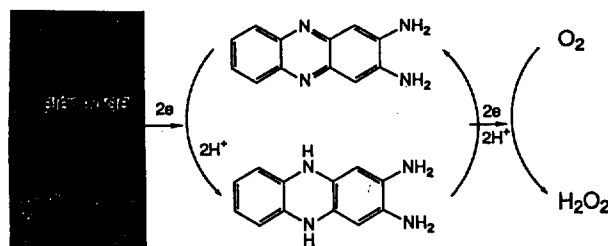


Figure 8. Schematic drawing which illustrates the electron mediation by 2,3-diaminophenazine in oxygen reduction to hydrogen peroxide.¹⁹

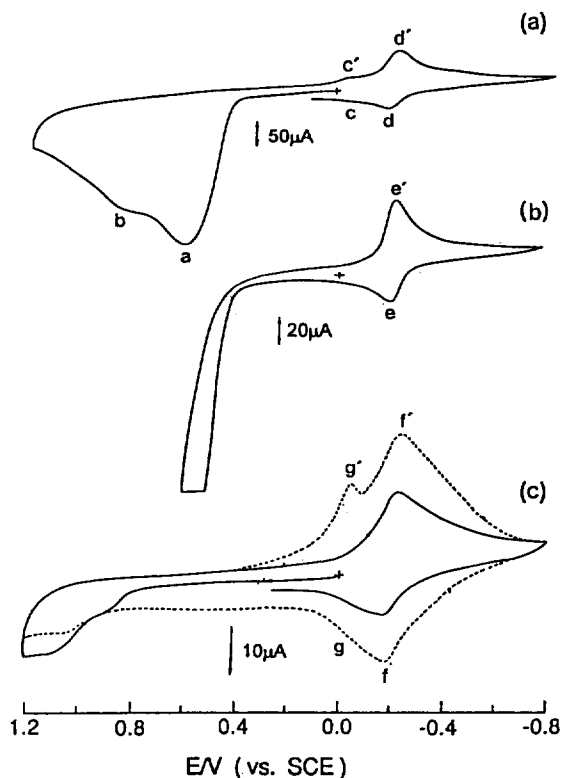


Figure 9. Cyclic voltammograms traced with *o*-PD (a and b) and DAP (c). In c: solid line; 1st scan and dashed line; 9th scan.

thesis, rotating disk voltammograms with the PPD-coated electrodes of different film-thickness were traced and presented in Figure 6. The film thickness was expressed by the scan numbers since it was too thin to measure. The result shows that the reduction currents with thicker films are smaller as expected.

Cyclic voltammetry of 2,3-diaminophenazine. 2,3-Diaminophenazine(DAP), a fully-oxidized cyclic dimer of *o*-PD (see the inset of Figure 1), was chemically synthesized by oxidative coupling of *o*-PD. A cyclic voltammogram traced with DAP is represented in Figure 7. The redox potential of DAP is almost identical to that of component II as can be seen by comparing the voltammograms in Figure 2 and 7. Even more interesting is the fact that DAP is also an active electron mediator for oxygen reduction as demonstrated in Figure 7-b. This is indicative of the fact that the structure of the active polymer unit (component II) be similar

ses since oxygen should diffuse longer distances through the inactive polymer layer. To test the validity of this hypo-

to that of DAP. In Figure 8, a schematic diagram illustrating the electron mediating action of DAP for O_2 reduction is provided.

Polymerization mechanism of *o*-PD. The polymerization mechanism of *o*-PD has not been fully understood in the literature.^{14,19,20} In order to collect useful informations concerning the electropolymerization mechanism, cyclic voltammograms separately traced with *o*-PD and 2,3-diaminophenazine (DAP) are compared (Figure 9). In the cyclic voltammogram obtained with *o*-PD, at least two anodic peaks can be located (Figure 9-a); one peak, **a**, at 600 mV and the other, **b**, at 840 mV. On the negative sweep, none of these peaks show complementary peaks, indicating that chemical follow-up reactions give products detected as peaks **c-c'** and **d-d'** on the continuing sweep. However, if the switching potential is lowered to 700 mV (before peak **b** shows up), only peak **e-e'** appears (Figure 9-b), whose redox potential is identical to that of the active polymer component (**d-d'**) and also to DAP (Figure 7-a). Characteristically, even if the cycling is repeated, the peak intensity of **e-e'** does not increase, explaining that the species giving peak **e-e'** is not deposited on the electrodes. Actually, the species giving peak **e-e'** was identified as DAP through a combination of bulk electrolysis and NMR spectroscopy. From this, it can be said that DAP is formed from *o*-PD by imposing the oxidation potential up to 600 mV.

In the cyclic voltammogram scanned with DAP as the starting material (Figure 9-c), two anodic peaks are recognized at 840 mV and 1.0 V on the positive sweep and, on the reverse scan, peak **f-f'** at the first scan and peaks **f-f'** and **g-g'** after 10 scans. The latter two peaks kept growing as the cycles repeated, indicating that the species are deposited on the electrodes. The peak potential for **f-f'** is identical to those of **d-d'** and **e-e'**, and the peak position of **g-g'** is very close to that of **c-c'**. From this, the anodic peaks at 840 mV and 1.0 V could be assigned to the oxidation of DAP to its monocation radical and consecutive oxidations to the polymeric species. Summarizing the pieces of informations, the anodic peak **a** in Figure 9-a can be accounted for the oxidation of *o*-PD to DAP, and peak **b** for the oxidation of DAP to the polymeric species.

From the results presented so far and taking account of the proposed mechanism for the anodic oxidation of anilines in aqueous solution,²³⁻²⁵ a plausible mechanism for the electropolymerization of *o*-PD has been proposed (Figure 10). *o*-PD is oxidized to the monocation radical and the resulting *o*-PD⁺ (1) is dimerized by either C-N coupling (2) or C-C coupling (3). C-N coupling is known to be dominant in the case of the anodic oxidation of anilines in aqueous solution.^{23,24} The dimer (2) can further be oxidized to either 4 or 5, and 4 can further be oxidized to 6. Based on the explanation for Figure 9-b, however, the major route seems to follow through 1, 2, and 4, and these ECE type reactions take place around 600 mV. Furthermore, 4 is easily oxidized to 6 at this potential since it is far more positive than the anodic peak potential for **e** in Figure 9-b. In the potential range of 0.84 V-1.0 V, several combinations of chemical and electrochemical reactions may occur consecutively. As one of the possible ways, DAP (6) may be oxidized to the monocation radical (6⁺), and 7 is produced by the coupling of

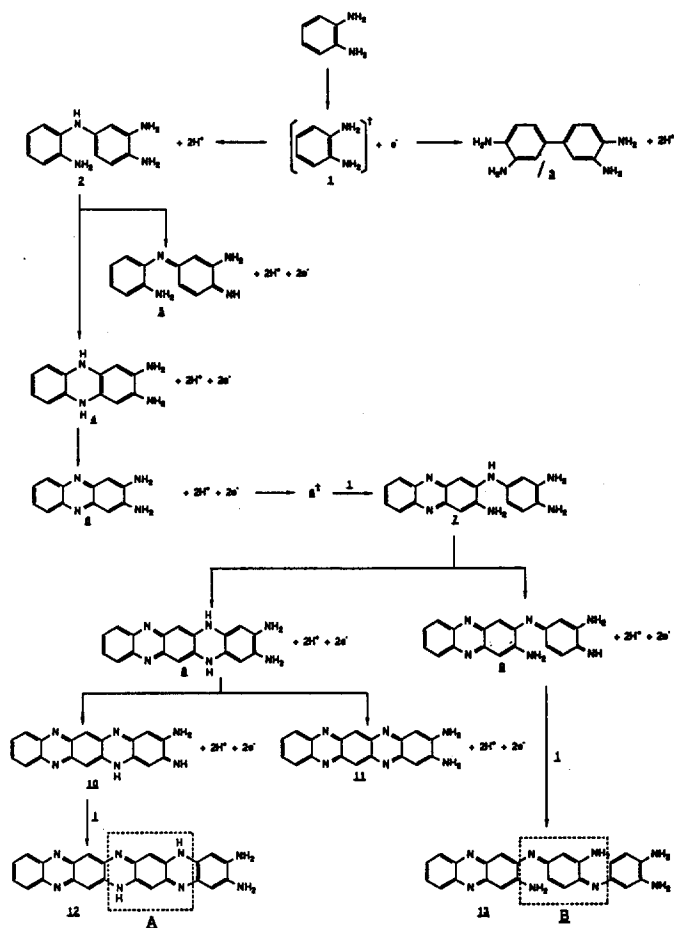


Figure 10. Proposed mechanism for the formation of the active and inactive component during the electropolymerization.

6⁺ and 1. Also, the coupling of two 6⁺s is possible as shown in Figure 9-c. However, the former would be more likely to occur since the concentration of 1 is much larger than that of the monocation radical in this potential range. The species 7 can further be oxidized to either 11 through 8, or to 10 through 8 or 9. As similar couplings are further progressed, species 12 and 13 might be prepared. Considering that the electron mediating species is the reduced state of the phenazine unit (4) as depicted in Figure 8, the inactive unit can be attributed to the cyclic unit (A) or the noncyclic unit (B). The difference between the reduced state of the phenazine unit (4) and A is the location of the protons. Component I in Figure 2 might thus be assigned to unit A or B and component II, to the phenazine unit.

In summary, it is proposed that a copolymer having different units is produced during the electropolymerization of *o*-PD. Among these, a phenazine unit seems to be produced mainly in the early stage of polymerization and the other units later. If it were true, the phenazine unit would locate near the electrode surface and the thicker film would show lower electrocatalytic activity for O_2 reduction.

Conclusion

The major goal in this study was to identify the nature

of the species responsible to the electron mediation in oxygen reduction, and to explain the mechanism for the formation of the active and inactive species during the electropolymerization of *o*-PD. Several conclusive points were listed;

(a) At least two polymeric components are produced during the electropolymerization of *o*-PD. However, only component II is active in oxygen reduction, which is formed mainly in the earlier stage of the polymerization.

(b) The chemically synthesized cyclic dimer of *o*-PD, 2,3-diaminophenazine, is also active in oxygen reduction. From this, it is proposed that the active component contains the phenazine unit. The inactive components seem likely to be the noncyclically coupled species or those whose reduced form is somewhat different from the reduced phenazine unit.

(c) The active component (peak **d-d'** in Figure 2) can also be attributed to the dimer entrapped inside the polymer. However this possibility can be excluded by two experimental results: The dimer is easily polymerized as indicated in Figure 9-c, and the cyclic voltammogram (Figure 3-b) does not change even after thorough washing of the electrodes with the supporting electrolyte solution.

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