

Electrocatalytic Reduction of Molecular Oxygen at Poly(1,8-diaminonaphthalene) and Poly(Co(II)-(1,8-diaminonaphthalene)) Coated Electrodes

Hyun Park, Tae-guen Kwon, Deog-Su Park, and Yoon-Bo Shim*

Department of Chemistry, Pusan National University, Busan 609-735, Korea. *E-mail: ybshim@pusan.ac.kr
Received July 20, 2006

The application of poly(Co(II)-(1,8-diaminonaphthalene))(poly(Co-DAN)) and poly(1,8-diaminonaphthalene) (Poly(1,8-DAN)) to the electrocatalytic reduction of molecular oxygen was investigated, which were electrochemically grown by the potential cycling method on the glassy carbon electrodes. The reduction of oxygen at the polymer and its metal complex polymer coated electrodes were irreversible and diffusion controlled. The Poly(1,8-DAN) and Poly(Co-DAN) films revealed the potential shifts for the oxygen reduction to 30 mV and 110 mV, respectively, in an aqueous solution, compared with that of the bare electrode. Hydrodynamic voltammetry with a rotating ring-disk electrode showed that Poly(1,8-DAN) and Poly(Co-DAN) coated electrodes converted respectively 84% and 22% of O₂ to H₂O via a four electron reduction pathway.

Key Words : Conductive polymer, Metal complex polymer, Electrocatalytic reduction of O₂

Introduction

The catalytic oxygen reduction has been one of the most important electrochemical reactions in the practical, economical, and theoretical point of view.¹⁻⁵ One of the challenging problems in electrocatalysis involves the reduction and generation of O₂ at low and moderate temperatures in aqueous media. Despite over a century of effort to find out effective catalytic materials for this system, further developmental needs are required.

Two important approaches to be adopted for the electrocatalysis are (a) using metal surfaces which would catalyze the oxygen reduction through the peroxide elimination reaction (*e.g.*, at carbon electrodes) and (b) using functional groups on the surface of the electrode at which oxygen would undergo specific reactions. In general, macrocyclic transition metal complexes have been found to possess catalytic activity for the oxygen reduction reaction. Several research groups have reported describing the use of transition-metal macrocyclic compounds for the catalytic reduction of molecular oxygen, such as iron and cobalt phthalocyanines or porphyrins and hemins^{6,7} adsorbed on the electrode surface. Jansinski *et al.*^{8,9} first reported O₂ electrocatalysis with a transition metal macrocycle, the cobalt(II) phthalocyanine, adsorbed on carbon and nickel substrates. There are some reports^{10,11} for the electrocatalysis with a complex formed between Cu and phenanthroline derivative adsorbed strongly and irreversibly on the surface of graphite electrodes. Besides these, some reports have mentioned the electrocatalysis of O₂ with various kinds of chemicals, including amine neurotransmitters¹² and ascorbic acid,¹³ metal complexes,^{14,15} polymers,^{16,17} and others.^{18,19}

The electrical conducting polymers have been receiving much attention due to their unique electrical properties and several proposed applications to practical devices.²⁰⁻²⁴ Of these, the conducting polymers prepared from aromatic

diamine compounds have interesting in applications due to their multifunctional groups. The compounds having polyamine groups can react with metal ions to form a complex followed by polymerization through the removal of an electron from nitrogen of amine groups.²² The modification of electrode surfaces with the conducting polymers containing transition metal complexes is an interesting area in electrochemical research. Previously, a diaminonaphthalene-copper complex appended conducting polymer have been reported for the electrocatalytic reduction of O₂.²⁵ However, there is no report for the preparation and application to the electrocatalytic reaction with the conducting metal complex polymer prepared from its monomer until now.

In the present study, we investigated the electropolymerization of Poly(Co-DAN) films, and the application to the electrocatalytic reactions on the reduction of molecular oxygen with Poly(1,8-DAN) and Poly(Co-DAN) films, which were feasible in catalyzing the reduction of molecular oxygen by N=N- bonds and a metal-oxygen bonding. The metal complex was synthesized from Co(II) nitrate hexahydrate and 1,8-diaminonaphthalene. Upon complex formation between the monomer and the metal ion followed by subsequent polymerization on the electrode surface, the catalytic effect on the reduction of molecular oxygen was investigated by cyclic voltammetry, rotating disk electrode (RDE), and rotating ring disk electrode (RRDE) experiments in various pH media.

Experimental

1,8-Diaminonaphthalene (Aldrich 99%, 1,8-DAN) was recrystallized twice from ethanol-water mixture under nitrogen atmosphere and dried under vacuum before use. Co(II)-1,8-DAN complex was prepared by the following way: 1,8-DAN in acetonitrile was slowly added to Co(NO₃)₂·6H₂O in acetonitrile (Co(NO₃)₂·6H₂O:1,8-DAN =

1 : 2 mole ratio) under nitrogen atmosphere at room temperature. While the mixed solution was being stirred continuously, dark brown precipitates of Co(II)-1,8-DAN were obtained. After filtering, the precipitates were washed with acetonitrile for several times and dried at room temperature for 24 hours under vacuum. The complex composition was confirmed with elemental analysis. The results of the elemental analysis and AA for Co(II)-1,8-DAN complex were as follows; Calc. C 44.86%, H 4.53%, N 15.70%, Co 11.0%, Found C 45.63%, H 3.96%, N 16.32%, Co 12.86%.

Tetraethylammonium perchlorate (TEAP, Fluka Co) and potassium nitrate (reagent grade) were recrystallized twice from absolute ethanol and dried under vacuum at 60°C. Aldrich's anhydrous DMF and all other chemicals were used as received without further purification. Aqueous solutions were prepared with doubly distilled water (Millipore, Milli-Q™ Water System). The buffer media used were acetate (pH 3-6) and ammonia (pH 7-10).

A three electrode system with an auxiliary electrode separated by a fine fritted glass was used for voltammetric measurements. Electrochemical experiments were carried out with Kosentech PT-2 potentiostat/galvanostat and Pine Instrument Model AFRDE 5 bipotentiostat. A glassy carbon electrode (area: 1.13 cm², GCE) was used as a working electrode, while a platinum wire and Ag/AgCl (sat'd KCl) were used as auxiliary and reference electrodes, respectively. The GCE was polished to a mirror finish with 0.1-0.3 μm alumina powder, rinsed with water, and dried before each experiment. Infrared spectra were taken with a Polaris FT-IR spectrometer (Mattson Co.). To identify the composition, a Vario EL analyzer (Heraeus Co.) and an Atomic Absorption spectrometer (Thermo-Jarrel Ash Co.) were used.

Prior to the preparation of the Poly(1,8-DAN) film, the GCE was kept at 0 V for 3 min in an 0.1 M HCl solution containing 1.0 mM DAN. The polymer was electrochemically prepared on the electrode by cycling the potential between -0.10 and 0.80 V at a scan rate of 50 mV/s. After the polymer was prepared, the film was kept at 0 V for another 3 min before it was rinsed with 0.1 M HCl and water, successively. Similarly, the Poly(Co-DAN) film was obtained from DMF solution containing 1.0 mM Co(II)-DAN monomer and 0.1 M TEAP by cycling the potential between -1.40 and 0.80 V at a sweep rate of 50 mV/s. After the polymer was prepared, the film was kept at 0 V for another 3 min before it was rinsed with DMF and water successively.

Results and Discussion

Preparation of poly(1,8-DAN) and poly(Co(II)-(1,8-DAN)) films. Figure 1(a) shows the cyclic voltammogram recorded during the anodic polymerization of 1.0 mM 1,8-DAN in a 0.1 M HCl solution. An oxidation peak appeared at about 0.62 V during the first potential scan to the upper limit of +0.80 V. As the potential scan continues, the oxidation peak for 1,8-DAN shifted in a more positive direction. The polymer film formed during the early few

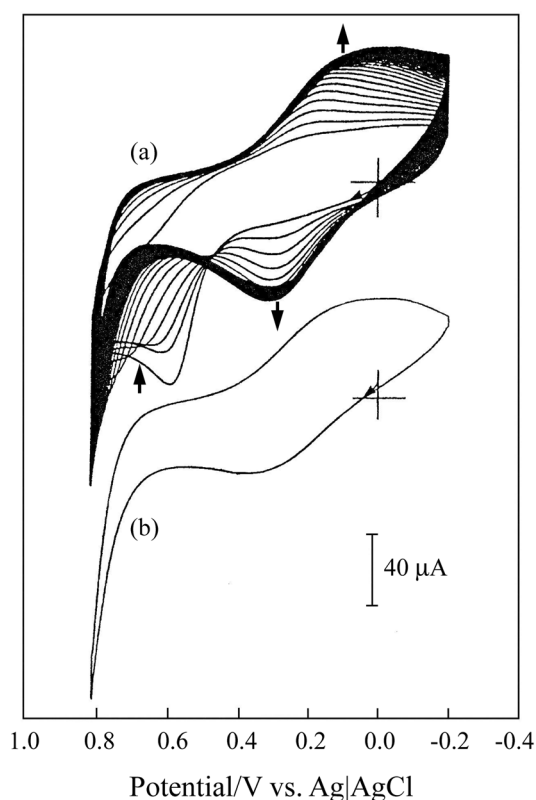


Figure 1. The cyclic voltammograms recorded for (a) the electropolymerization of Poly(1,8-DAN) in a 0.1 M HCl solution containing 1.0 mM 1,8-DAN at the potential range of +0.8 ~ -0.2 V for 15 min with the scan rate of 50 mV/sec and (b) Poly(1,8-DAN) coated GCE in a 0.1 M HCl blank solution.

potential cycles did not appear to be electroactive, and thus the film formed during the early stages resulted in the increase of the overpotential for the monomer oxidation. This might be because the products formed at the beginning had small molecular weights, such as oligomers, and the film was somewhat soluble and poorly conductive. Upon further scanning, a slow increase in small oxidation/reduction peak currents was observed at 0.30/0.18 V, which indicated an accumulation of the electroactive polymer film on the electrode surface as shown in Figure 1(b).

Cyclic voltammograms recorded during electropolymerization of 1.0 mM Co(II)-(1,8-DAN) in a DMF solution containing 1.0 mM TEAP are shown in Figure 2(a). On the immediate scan to the negative potential from at the early stage, no characteristic cathodic peak, corresponding to the reduction of products generated, appeared. Upon further potential cycling, however, a continuous increase in oxidation/reduction currents was observed at 0.1-0.3 V, which might be the oxidation/reduction peak of Co(II)/Co(III) couple, and the oxidation/reduction peak of Co(I)/Co(II) couple could be seen at -0.8 ~ -1.1 V. The cathodic peak around -0.8 V also increased by continuous potential cycling, which might be due to the reduction of the free Co(II) ion captured in polymer matrices. The cathodic peak corresponding to the reduction of Poly(Co-DAN), however, decreased when the potential was continuously cycled in a

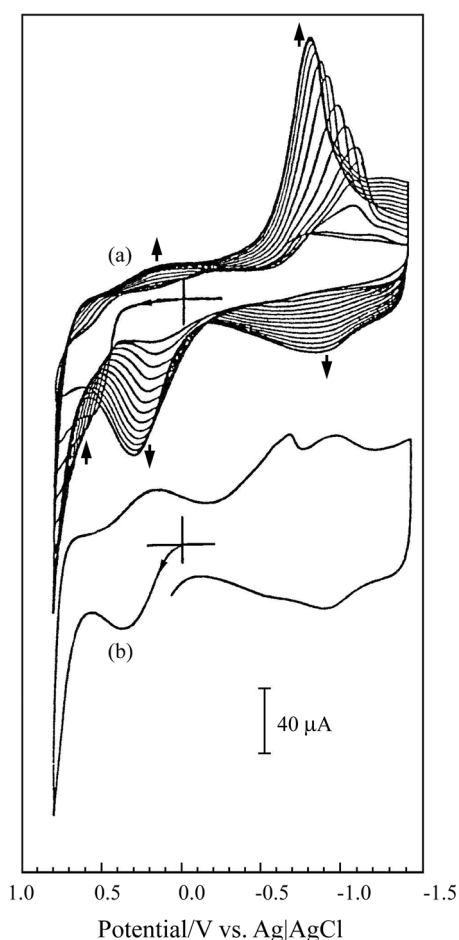


Figure 2. The cyclic voltammograms recorded for (a) the electropolymerization of Poly(Co(II)-1,8-DAN) in a DMF solution containing 0.1 M TEAP and 1.0 mM Co(II)-1,8-DAN at the potential range of +0.8 ~ -1.4 V for 15 min with the scan rate of 50 mV/sec, and (b) Poly(Co-DAN) coated GCE in a DMF solution containing 0.1 M TEAP only.

blank DMF solution containing 0.1 M TEAP as shown in Figure 2(b).

CV of molecular oxygen reduction with the polymer electrodes. Figure 3 shows (a) a CV recorded for a bare GCE in a 0.1 M KNO₃ solution saturated with molecular oxygen, (b) CV of molecular oxygen recorded for the Poly(1,8-DAN) film coated electrode in a 0.1 M HCl solution, and (c) the CV of molecular oxygen was recorded for the Poly(Co-DAN) film in a DMF solution containing 0.1 M TEAP. The reduction potential of molecular oxygen on the Poly(1,8-DAN) film coated electrode was -0.39 V, which has shifted in the positive direction by about 30 mV. On the other hand, the reduction potential of molecular oxygen on the Poly(Co-DAN) film coated electrode was -0.28 V, which has shifted to the positive potential by about 110 mV. The results indicate that Poly(Co-DAN) acts as an effective catalyst on the molecular oxygen reduction reaction, however, the catalytic effect on the oxygen reduction with Poly(1,8-DAN) was minimal.

To investigate the pH effect on the catalytic process, the reduction potentials of molecular oxygen on Poly(Co-DAN)

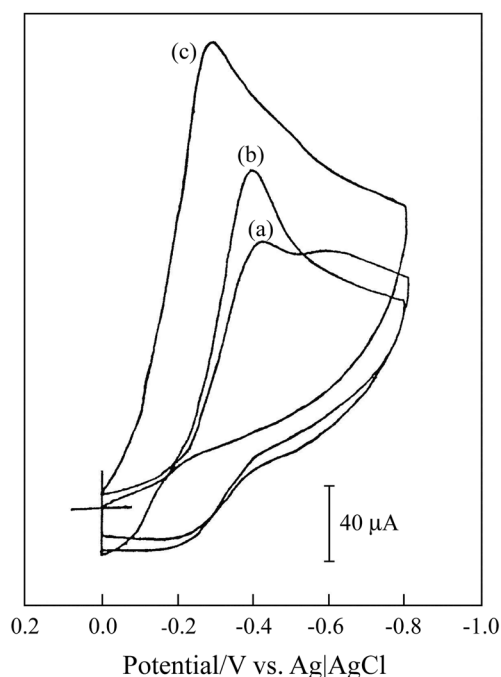


Figure 3. The cyclic voltammograms recorded during the reduction of molecular oxygen at (a) the bare GCE, (b) Poly(1,8-DAN) coated GCE, and (c) Poly(Co(II)-1,8-DAN) coated GCE in 0.1 M KNO₃ solution saturated with O₂.

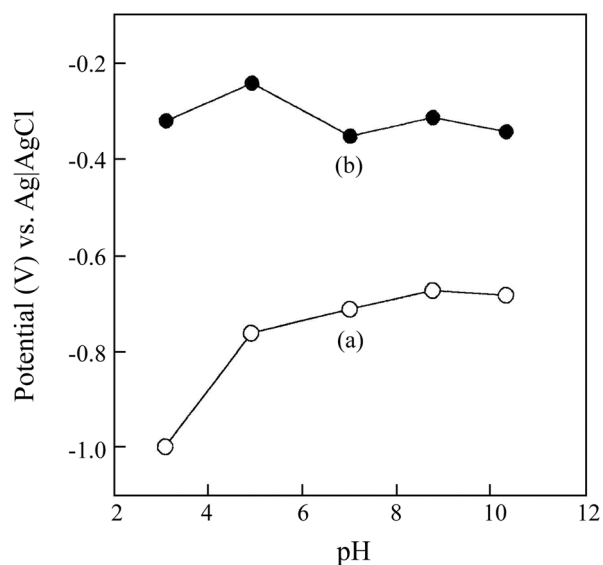


Figure 4. The pH dependence of the reduction peak potential of molecular oxygen on (a) the bare GCE, (b) Poly(Co-DAN) coated GCE in various pH media saturated with O₂.

and bare electrodes were plotted as a function of pH in aqueous media as shown in Figure 4. The potential at a bare electrodes shifted to the positive direction as the pH increased, while a little change at a Poly(Co-DAN). In neutral and basic media, however, the peak potential was similar to each other. The largest potential difference was shown in pH 3.1. This might be that these polymer films did not work as an effective catalyst for O₂ reduction by the two

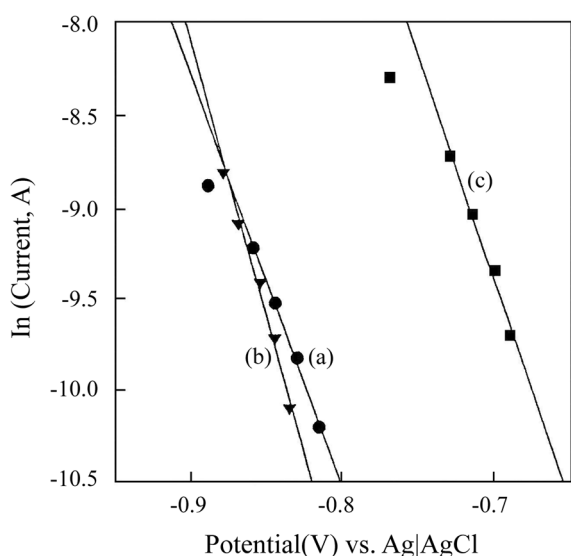


Figure 5. The plot of logarithmic plot of currents for the reduction of molecular oxygen according to the peak potential with (a) the bare GCE, (b) Poly(1,8-DAN) coated GCE, and (c) Poly(Co(II)-1,8-DAN) coated GCE in 0.1 M KNO_3 solution saturated with O_2 .

or four electron pathway in an acidic medium.

Determination of kinetic parameters for the electrocatalytic process. We plotted the oxygen reduction current, i_p obtained for a bare and polymer coated electrodes according to $v^{1/2}$ (not shown). The peak current for the polymer electrodes showed linearity to the square root of the scan rate, indicating that the molecular oxygen reduction reaction on the electrodes was controlled by diffusion. A higher current obtained for the polymer electrode than that for a bare GCE indicates that the electrocatalytic molecular oxygen reduction reaction took place more likely on the polymer coated GCE surface. To attain the kinetic data for the molecular oxygen reduction reaction, the plot of E_p vs. i_p was made from the following equation (1)²⁶ and represented in Figure 5.

$$i_p = 0.227nFAC^*k^0 \exp[-(\alpha n_a F/RT)(E_p - E^0)] \quad (1)$$

Kinetic parameter, αn_a and k^0 values were obtained from

the slope and intercept shown in Figure 6, respectively. αn_a ²⁷ values were 0.745 for the Poly(1,8-DAN) electrode, 0.617 for the Poly(Co-DAN) electrode, and 0.563 for a bare GCE. Standard rate constant, k^0 values were determined to be 1.107×10^{-12} (cm/sec) for Poly(1,8-DAN), 3.531×10^{-10} (cm/sec) for Poly(Co-DAN), and 5.619×10^{-11} (cm/sec) for the bare electrode using 1.70×10^{-5} (cm^2/sec) of D_0 ²⁸ and C_0 of 1.38×10^{-6} (mole/ cm^3).²⁹ This shows that the exchange rate constant was higher on the Poly(Co-DAN) coated electrode than on a bare electrode. On the other hand, the exchange rate constant obtained for the Poly(1,8-DAN) coated GCE was similar to that on a bare GCE.

RDE and RRDE experiments for the molecular oxygen reduction reaction. To estimate the kinetic parameters and overall mechanism of the catalytic reaction, the hydrodynamic experiments employing the rotating ring-disk electrode (RRDE) and the rotating ring electrode (RDE) were performed. Two possible pathways were distinguished by examining the slope of from the Koutecky-Levich plot obtained from these experiments, which was inversely proportional to n . Figure 6(a) shows a series of RDE voltammograms recorded at several rotation rates, ω for the reduction of O_2 in a 0.1 M KNO_3 solution with the disk electrode modified with the Poly(1,8-DAN) film. The Levich plot in Figure 6(b) was non-linear for a catalyzed reaction, because a current-limiting chemical step precedes the electron transfer. The corresponding Koutecky-Levich plot derived from the limiting current density at -0.7 V was shown in Figure 7(c). The equation describing the Koutecky-Levich plot²⁶ is shown as follows (3):

$$1/i_{lim} = 1/i_k + 1/0.62nFAC^*D^{2/3} \nu^{-1/6} \omega^{1/2} \quad (3)$$

Where, the first term on the right-hand side is the inverse of the kinetic current density discussed below. The second term is the inverse of the Levich current density, which is limited by the mass transport of O_2 to the electrode surface. n is the number of electrons participated in the overall electrode reaction. D and C^* are the diffusion coefficients and the solution concentration of O_2 , and ν is the kinematic viscosity of the electrolyte solution. The Koutecky-Levich plot in Figure 6(c) was nearly parallel to the calculated line

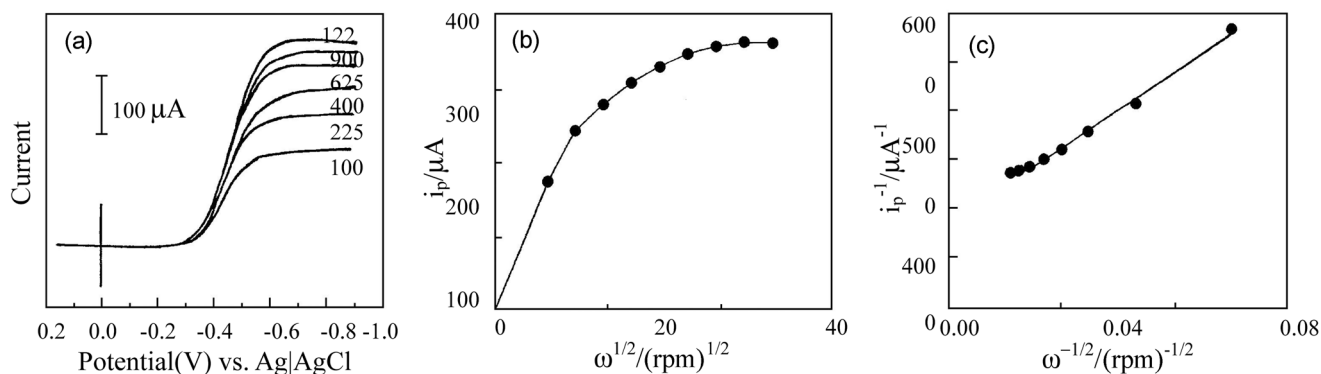


Figure 6. Electroreduction of molecular oxygen catalyzed by Poly(1,8-DAN) in a 0.1 M KNO_3 solution. (a) Rotating disk voltammograms at various electrode rotation rates, scan rate: 10 mV/sec. (b) the Levich plot of plateau currents vs. (rotation rate)^{1/2} for the curves in (a). (c) Koutecky-Levich plots of (plateau current)⁻¹ vs. (rotation rate)^{-1/2} for the data in (b).

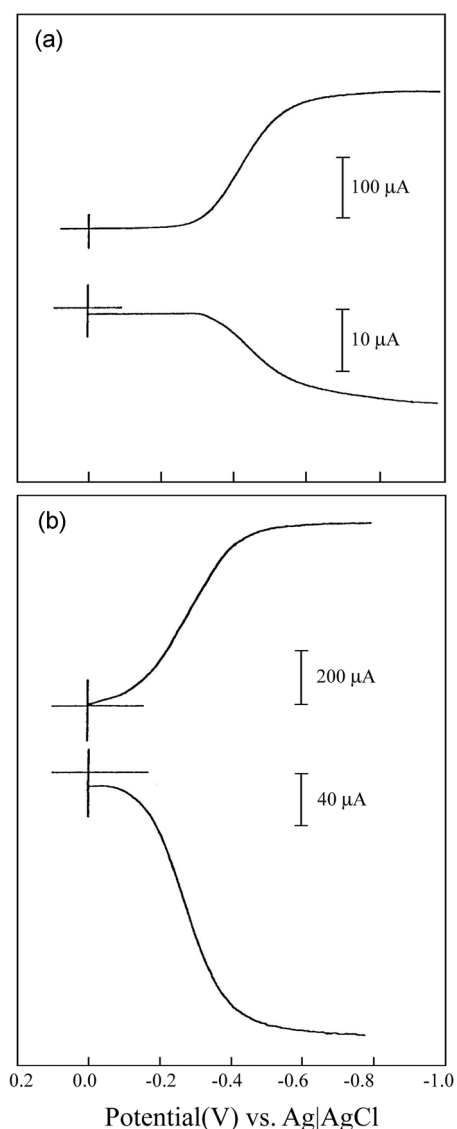
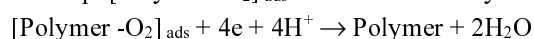
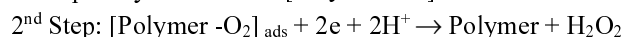
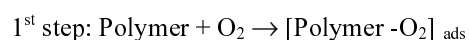


Figure 7. The current-potential curves recorded during the reduction of O_2 at a rotating GC ring-disk electrode in a 0.1 M KNO_3 solution saturated with O_2 . The GC disk electrode was modified with (a) Poly(1,8-DAN) and (b) Poly(Co-DAN). The potentials of the GC ring electrodes were held at +1.0 V vs. Ag/AgCl.

for the reduction of O_2 by four electrons, indicating that the adsorbed catalyst almost accomplishes the reduction pathway of O_2 to H_2O .

A rotating GC ring-disk electrode was employed to determine the relative proportions of two- and four-electron reductions of O_2 which occurred at the Poly(1,8-DAN) film coated disk electrode. As shown in Figure 7(a), hydrogen peroxide generated during molecular oxygen reduction on a rotating GC disk electrode coated with Poly(1,8-DAN) was detected on the ring electrode, when the potential of the GC ring electrode was held at 1.0 V vs. Ag/AgCl. At -0.35 V, the current on the rotating disk and ring electrodes increased simultaneously. In the case of the two electron reduction reaction of O_2 to H_2O_2 , the N^{-1} value and I_D/I_R should be the

same, theoretically. From the experimental result, we obtained $N^{-1} = 2.54$ and $I_D/I_R = 16.15$. By quantitative calculation, the efficiency of O_2 to H_2O_2 through the two-electron reduction process is only 16%. Thus, the presence of the Poly(1,8-DAN) film catalyzed the reduction of O_2 by about four fifths through a four-electron reduction pathway, the remainder may take place through the two-electron reduction to H_2O_2 or H_2O_2 degradation reaction. Similarly, a rotating GC ring-disk electrode was employed for Poly(Co-DAN) film. The result is shown in Figure 7(B). From the experimental result, we obtained $N^{-1} = 2.54$ and $I_D/I_R = 3.67$. The efficiency of O_2 to H_2O_2 catalytic conversion through the two-electron reduction process was 78%. Thus, the reduction mechanism of molecular oxygen might be followed by two different pathways:



Where, Polymer includes PolyCo-DAN and PolyDAN.

Conclusively, electropolymerization of Co(II)-(1,8-DAN) in a DMF solution containing 1.0 mM TBAP was successfully performed with the metal complex monomer followed by the reaction between Co(II) ion and 1,8-diaminonaphthalene. The polymer films of 1,8-DAN and Co(II)-(1,8-DAN) grown on the electrode were tested for the catalytic characteristic to the reduction process of molecular oxygen. The relative proportions of two- to four-electron reductions of O_2 were determined to be 16% at the Poly(1,8-DAN) film and 78% at the poly(Co-DAN) film. The Poly(1,8-DAN) electrode revealed smaller effects on the electrocatalytic reduction of molecular oxygen than poly(Co-DAN).

Acknowledgement. This study was supported by the grant of Pusan National University (2005-2006).

References

- Yeager, E. *Electrochimica Acta* **1984**, 29, 1527.
- Zagal, J.; Bindra, P.; Yeager, E. *J. Electrochem. Soc.* **1980**, 127, 1506.
- Jeong, E. D.; Won, M. S.; Shim, Y.-B. *Bull. Korean Chem. Soc.* **1998**, 19, 417.
- Kinoshita, K. *Carbon*; John Wiley & Sons, Inc.: New York, USA, 1988; Ch. 6.
- Murphy, O. J.; Srinivasan, S.; Conway, B. E. *Electrochemistry in Transition from the 20th to the 21st Century*; Plenum Press: New York, U.S.A., 1992; Ch. 9.
- Brezina, M. *Fresenius. Anal. Chem.* **1996**, 224, 74.
- (a) Kolpin, C. F.; Swafford, H. S. *Anal. Chem.* **1977**, 50, 920. (b) Song, E.; Paik, W. *Bull. Korean Chem. Soc.* **1998**, 19, 183.
- Jasinski, R. *Nature* **1964**, 201, 1212.
- Jasinski, R. *J. Electrochem. Soc.* **1965**, 112, 526.
- Zhang, J.; Anson, F. C. *J. Electroanal. Chem.* **1992**, 341, 323.
- Zhang, J.; Anson, F. C. *J. Electroanal. Chem.* **1993**, 348, 81.
- Bull, R. A.; Fan, F. R.; Bard, A. J. *J. Electrochem. Soc.* **1984**, 131, 687.
- Saraceno, R. A.; Pack, J. G.; Ewing, A. G. *J. Electroanal. Chem.* **1986**, 197, 265.

14. Ohsaka, T.; Chiba, K.; Oyama, N. *Nippon Kagaku Kasishi* **1986**, 457.
 15. Gudavicius, A. V.; Razumas, V. J.; Kults, J. J. *J. Electroanal. Chem.* **1987**, 219, 153.
 16. O'Brien, R. N.; Santranam, R. S. V. *Electrochim Acta* **1987**, 32, 8.
 17. Ohsaka, T.; Watanabe, T.; Kitamura, F.; Oyama, N.; Tokuda, K. *Chem. Commun.* **1991**, 487.
 18. Mengoli, G.; Musiani, M. M. *J. Electroanal. Chem.* **1989**, 269, 99.
 19. Hu, N.; Howe, D. J.; Ahmaddk, M. F.; Rusling, J. F. *Anal. Chem.* **1992**, 64, 24.
 20. (a) Park, S.-M. In *Handbook of Organic Conductive Molecules and Polymers*; Nalwa, H. S., Ed.; John Wiley & Sons: New York, USA, 1997; Vol. 3, Ch. 9. (b) Park, S.-M.; Lee, H. J. *Bull. Korean Chem. Soc.* **2005**, 26, 697.
 21. Bredas, J. L. In *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Marcel Dekker, Inc.: New York, 1986; Vol. 2, Ch. 25.
 22. Lee, J.-W.; Park, D.-S.; Shim, Y.-B.; Park, S.-M. *J. Electrochem. Soc.* **1992**, 139, 3507.
 23. Jin, C. S.; Shim, Y.-B.; Park, S.-M. *Synth. Met.* **1995**, 69, 561.
 24. Jin, C. S. *Thesis, Ph.D.*, Pusan National University: Korea, 1996; unpublished work.
 25. Boophathi, M.; Won, M.-S.; Kim, Y. H.; Shin, S. C.; Shim, Y.-B. *J. Electrochem. Soc.* **2002**, 149, E265.
 26. Bard, A. J.; Faulkner, L. R. *Electrochemical Methodes*; Wiley: New York, 2001.
 27. Tan, N.; Bekaroglu, O.; Kadirgan, F. J. *Electroanal. Chem.* **1994**, 364, 251.
 28. Gubbins, K.; Walker, R. J. *Electrochem. Soc.* **1964**, 112, 469.
 29. Wilke, W. *Solubilities of Inorganic and Metal Organic Compound*; American Chemical Society: Washington, D.C. 1969; Vol. II.
-