# Poly(3,4-ethylenedioxythiophene) Electrodes Doped with Anionic Metalloporphyrins

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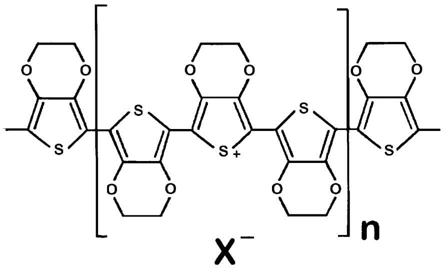
Conducting poly(3,4-ethylenedioxythiophene) (PEDT) films with metalloporphyrins incorporated as the counter ions were prepared by electropolymerization of the monomer in the presence of metal-tetra(sulfonatophenyl)porphyrin anions. Cathodic reduction of oxygen on the resulting conducting polymer films was studied. The overpotential for $O_2$ reduction on electrodes with cobalt-porphyrin complex was significantly smaller in acidic solutions than on gold. In basic solutions, the overpotential at low current densities was close to those on platinum and gold. Polymer electrode with Co-complex yielded higher limiting currents than with Fe-complex, although the Co-complex polymer electrode was a poorer electrocatalyst for $O_2$ reduction in the activation range of potential than the Fe counterpart. From the rotating ring-disk electrode experiments, oxygen reduction was shown to proceed through either a 4-electron pathway or a 2-electron pathway. In contrast to the polypyrrole-based electrodes, the PEDT-based metalloporphyrin electrodes were stable with wider potential windows, including the oxygen reduction potential. Their electrocatalytic properties were maintained at temperatures up to 80 °C in KOH solutions.

## Introduction

The search for low overpotential electrocatalysts remains a pressing challenge for workers in the field of electroreduction of oxygen because of its importance to fuel cells and other oxygen cells.[1] Overpotential for electroreduction with an appreciable current density is about 0.45 V even at the best known platinum-based catalyst electrodes. Electrodes prepared by incorporating metalloporpyrins are prospecting candidates for such applications, because they have excellent thermal, chemical, electrochemical, and photochemical stability in addition to their catalytic properties.[3,4] There have been intensive studies on the catalysis of the electroreduction of $O_2$ by porphyrin complexes.[2,5-9] Various methods of incorporating metalloporphyrins into conducting polymers have been used by numerous workers and electrocatalysis on the resulting polymer-metalloporphyrins has been studied.[10-12] However, the polymers previously adopted as the conducting host material, such as polypyrrole (PPy), have shortcomings due to lack of stability. In a previous work we examined the electrocatalytic property of metalloporphyrin-incorporated polypyrrole (PPy-MP) films.[13] Although the PPy-MP film electrodes showed significant electrocatalytic property for $O_2$ reduction, stability of polypyrrole seemed to be one limiting factor in the performance of the polymer-catalyst electrode.

Poly(3,4-ethylenedioxythiophene) (PEDT), whose chemical structure is shown below, is an exceptionally stable conducting polymer that can be prepared by electrochemical polymerization in aqueous media.[14] PEDT does not readily degrade at moderately elevated temperatures, under oxidizing conditions, or on exposure to daylight,[14-17] whereas other conducting polymers such as polypyrrole lose much of their conductivity and reversible redox properties under such conditions. This polymer has other unique characteristics, such as transparency in the oxidized state, related to its unusually low band-gap energy.[14,15]



Poly(3,4-ethylenedioxythiophene) with doped anion X⁻ (PEDT-X)

Chemically prepared PEDT, which is slightly soluble in water, is commercially available. Because of the unusual environmental stability it appears that this polymer could possibly be used to modify electrodes or immobilize electrocatalysts. In this study we incorporated metalloporphyrin moieties into PEDT by employing anionic derivatives of the porphyrins. The resulting conducting polymer-metalloporphyrin complex films were investigated for their catalytic properties in oxygen reduction in both acidic and basic aqueous media.

## Experimental Section

**Deposition of PEDT with Metalloporphyrins**. PEDT

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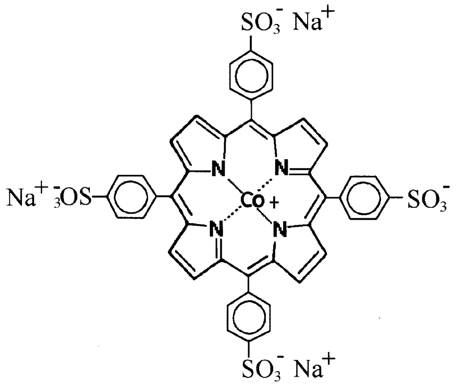
films doped with anionic metalloporphyrins were prepared by anodic electropolymerization of the monomer 3,4-ethylenedioxythiophene (EDT). Aqueous solutions containing 10 mM EDT and 1.0 mM of the appropriate salts of anionic metalloporphyrins were used. EDT (from Bayer AG, Germany) was purified by vacuum distillation. The anionic metalloporphyrins that were used have the following structure shown for a Co-complex as an example.



Co(III) Tetra(4-sulfonatophenyl)porphyrin,
Tri-Sodium Salt

Sodium salts of cobalt-tetra(sulfonatophenyl)porphyrin (CoTSP) anion and iron-tetra(sulfonatophenyl)porphyrin (FeTSP) anion purchased from Midcentury Chemicals were used as received. No electrolyte other than the porphyrin salts was added to the solutions during the electropolymerization. Water was distilled and deionized for use in the preparation of the solutions.

A three-electrode two-compartment glass cell and a bipotentiostat (Pine Instruments) or a galvanostat (Amel) were employed in the voltammetric and the electropolymerization experiments. All electrolyte and monomer solutions were purged with nitrogen before and during the polymerization. The electrodes used for electropolymerization and voltammetric experiments were glassy carbon disk electrodes polished with 0.1 $\mu$m alumina powder and then washed in an ultrasonic bath. Each of the working electrodes had a geometric surface area of 0.164 $cm^2$. A sodium chloride-saturated calomel electrode (SSCE) was used as the reference electrode. All potentials reported in this article are referred to this electrode. The counter electrode was a spiral piece of platinum wire.

Cyclic voltammograms during electropolymerization were recorded to monitor the growth of the polymer film with the potential cycles. However, the PEDT-metalloporphyrin (PEDT-MTSP) electrodes used later in the voltammetric experiments were prepared by constant-current electropolymerization. Current density of 0.60 mA $cm^{-2}$ was applied for about 2 min for the polymerization. The total coulombic charge was such that the thickness of the deposited film was approximately 0.15 $\mu$m with an approximate density of 1.5 g $cm^{-3}$. Adhesion of the deposited films to the substrate electrodes was good enough to permit voltammetric experiments both on the stationary and rotating electrodes.

**Reduction of Oxygen**. Reduction of molecular oxygen was studied with rotating disk electrode (RDE) or rotating ring-disk electrode (RRDE, Pine Model AFMT28), whose disk parts were covered with the deposited PEDT-metalloporphyrin films. Most of the experiments were conducted at room temperature except when the temperature was specified as otherwise.

## Results and Discussion

**Electropolymerization and incorporation of metalloporphyrin**. Figure 1 shows cyclic voltammograms obtained with a glassy carbon electrode in solutions of 10 mM EDT and 1.0 mM MTSP (where M = Co, Fe). The current increased with successive potential scans, indicating progress of electropolymerization of EDT with the MTSP anions being incorporated. These cyclic voltammograms are similar to those reported for the electropolymerization of PEDT in other solvents and with other electrolytes.[15] Rapid polymerization ensued at potentials above 0.8 V. The upper limit of the applied anodic potential was 1.2 V. The PEDT-MTSP polymers obtained did not show degradation of conductivity on application of this potential, in contrast to PPy reported in the previous paper.[13] When PPy was subjected to potential cycles whose upper limit was higher than 0.8 V in 0.05 M $H_2SO_4$ or 0.0 V in 0.1 M KOH in the previous study, the anodic current at the upper limit increased drastically on the first anodic sweep, after which the current decreased continuously over the whole potential range on subsequent poten-

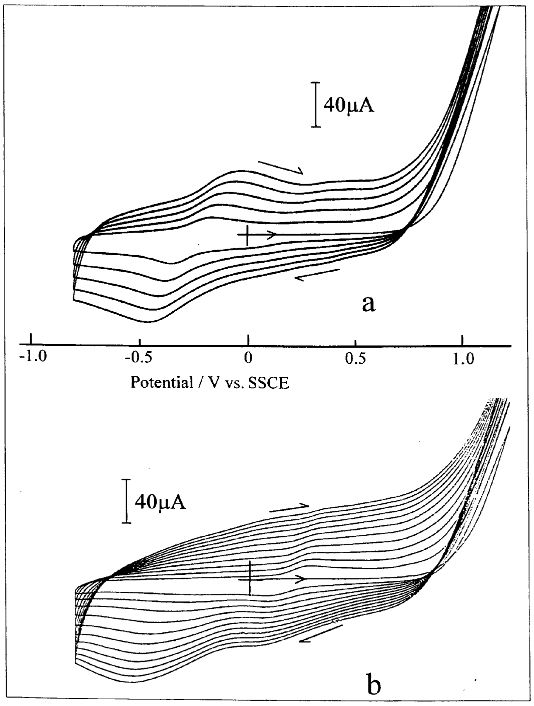


**Figure 1**. Electropolymerization of EDT on GC electrode with cyclically scanned potential in aqueous solution of 10 mM EDT and 1.0 mM FeTSP (a) or 1.0 mM CoTSP (b). Scan rate: 50 mV $s^{-1}$.

tial cycles.

The incorporation of the metalloporphyrin anions into the polymer film was confirmed by absorption spectra obtained from films deposited on ITO glass slides. The spectra showed slightly shifted Soret band peaks at 430 nm and 410 nm in the case of Co-TSP and Fe-TSP, respectively, similar to the case of incorporation of the metalloporphyrins into PPy reported previously.[13] Examination by quartz crystal microgravimetry experiments revealed that the metalloporphyrin anions once incorporated are not expelled from the polymer film on negative scan of the potential. Instead, the countercation $Na^+$, was inserted into the film to maintain the electroneutrality within the film as evidenced by decreasing frequency of the crystal oscillation.[18] The mole ratio of EDT monomer to CoTSP in the polymer film was estimated to be about 5 from the coulombic charge of polymerization and mass increase during polymerization. The EDT/FeTSP mole ratio was about 8. If it is assumed that about 3 monomer units in the polymer have one positive charge in the doped state as is the case with PPy and related conducting polymers and that there are three negative charges to a MTSP anion, the EDT/MTSP mole ratio should be around 9. The smaller ratios, 5 to 8 may reflect that the MTSP salts are not fully ionized.

**Oxygen reduction**. While the disk electrodes covered with PEDT-CoTSP and PEDT FeTSP films were rotated at 2000 rpm, oxygen was bubbled through 0.05 M $H_2SO_4$ or 0.1 M KOH solutions. Cyclic voltammograms (CV) were obtained with a scan rate of 50 mV $s^{-1}$. The results are shown in Figures 2 and 3 for $H_2SO_4$ and KOH solutions, respectively. CVs obtained at Au and Pt electrodes were also shown for comparison. The CVs obtained with the polymer electrodes show initial rapid rises in the reduction currents with negative going potentials. Limiting currents due to the diffusion-limited mass transfer of oxygen were obtained at more negative potentials. The hysteresis-like current loops are due to the double layer charging and the redox contribution of the polymer, as evidenced by the background CV for $O_2$-free solution shown in Figure 2. It can be seen in Figure 2 that the half-wave potential of $O_2$ reduction at the PEDT-CoTSP electrode is shifted to the positive side from the half-wave potential of $O_2$ at the Au electrode by more than 0.1 V. The limiting current at the PEDT-FeTSP electrode was larger than that at the Au electrode and was close to that at Pt. The half-wave potential of the PEDT-FeTSP electrode was close to that of Au.

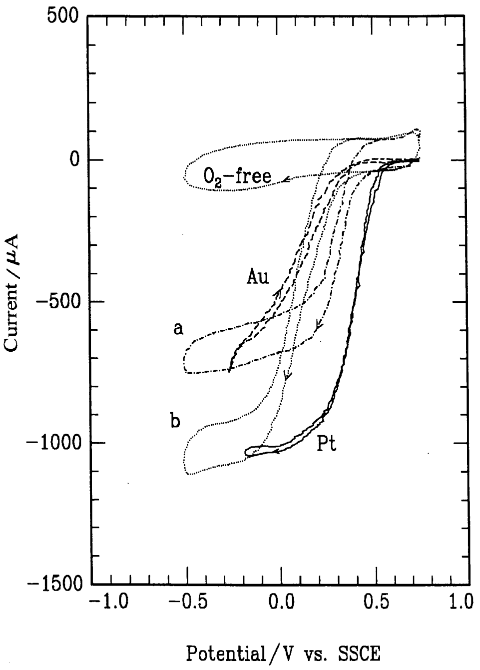


**Figure 2**. $O_2$ reduction currents at rotating PEDT-CoTSP (a), PEDT-FeTSP (b), Pt, and Au electrodes in $O_2$-saturated 0.05 M $H_2SO_4$. Scan rate: 50 mV $s^{-1}$; Rotation rate: 2000 rpm; Electrode area: 0.164 $cm^2$.

It can be seen that the PEDT-CoTSP electrode has smaller overpotential than the Au electrode for oxygen reduction in the acidic solution, although the limiting current was only as large as that on gold, on which the current is known to be limited by 2-electron reduction of oxygen.

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$$

The PEDT-FeTSP electrode on the other hand exhibited overpotential that is as large as that on gold. However, the limiting current was as large as that of the platinum electrode, which is one of the best known catalyst facilitating 4-electron transfer, reducing oxygen directly to $H_2O$.[1]

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

Therefore, it seems that 2-electron reduction prevails on PEDT-CoTSP and 4-electron reduction prevails on PEDT-FeTSP. The polymer films were thick enough, approximately 0.15 μm for both PEDT-CoTSP and PEDT-FeTSP, to prevent intervention of the underlying electrode metals.

In the basic solution, the overpotential for $O_2$ reduction at

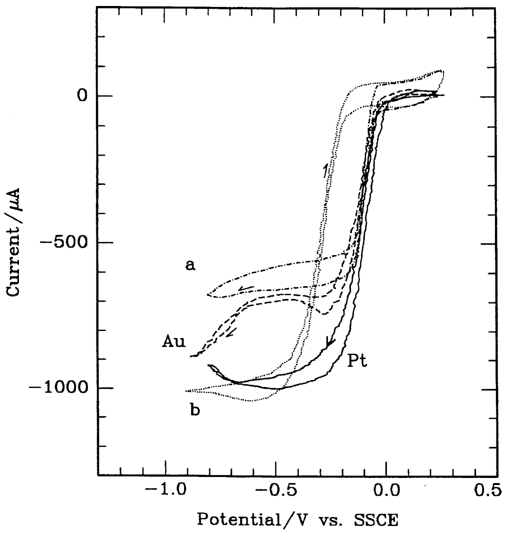


**Figure 3**. $O_2$ reduction currents at rotating PEDT-CoTSP (a), PEDT-FeTSP (b), Pt, and Au electrodes in $O_2$-saturated 0.1 M KOH. Scan rate: 50 mV $s^{-1}$; Rotation rate: 2000 rpm; Electrode area: 0.164 $cm^2$.

the PEDT-CoTSP electrode was close to that at the Au or Pt electrodes (Figure 3). However, the limiting current was slightly smaller than on Au. The PEDT-FeTSP electrode showed larger overpotential than the precious metals by about 0.2 V although the limiting current was as large as on Pt. In both the acidic and basic solutions PEDT-CoTSP seemed to be a reasonably good electrocatalyst comparable to Pt at low current levels, but is less satisfactory at larger polarization since the reduction of oxygen seems to proceed mostly through a 2-electron transfer process. PEDT-FeTSP is a good electrode material in the sense that it facilitates a 4-electron process as the Pt electrode, but is poorer as an electrocatalyst than Pt or PEDT-CoTSP because the overpotential for $O_2$ reduction is larger. The voltammetric characteristics of PEDT-MTSP electrodes are similar to those of MTSP-doped polypyrrole (PPy-MTSP), reported previously.[13] Such a similarity between the PPy-based and the PEDT-based MTSP electrodes indicates that the catalytic activities of these electrodes derive from the metalloporphyrins instead of the polymers. The polymers are media for immobilizing the catalysts. One significant difference between the PPy-based and the PEDT-based MTSP electrodes is that at the PPy-FeTSP electrode the limiting currents were not larger than that of Au, whereas at PEDT-FeTSP the limiting currents approached that of Pt. The larger limiting current at the PEDT-based electrodes is perhaps due to better stability of PEDT. It is known that conducting PPy tends to degrade and loose part of its electronic conductivity when high anodic potentials are applied or on prolonged exposure to oxygen. It is also possible that PPy is degraded by hydrogen peroxide produced by the 2-electron transfer reaction. PEDT does not show any appreciable deterioration when the potential is scanned to anodic range as high as 1.0 V *vs.* SSCE, in agreement with the result of Yamamoto *et al.*[19]

**Rotating Ring-Disk Electrode Experiments.** To detect $H_2O_2$ that may be produced during oxygen reduction, RRDE experiments were carried out in both acidic and basic solutions described above. PEDT-MTSP films were deposited on the disk part of the RRDEs. The RRDEs all had platinum rings. As the disk potential was scanned, the ring potential was fixed at 1.00 V in acidic solutions and at 0.60 V in basic solutions to detect the oxidation current of $H_2O_2$. Both in the acidic (Figure 4) and basic (Figure 5) solutions, the ring current associated with the PEDT-CoTSP disk electrode indicated continuous production of $H_2O_2$ during oxygen reduction, whereas the small ring current associated with the PEDT-FeTSP disk electrode indicated only small amount of $H_2O_2$ produced in the range of small overpotential. These observations support the assumption that at the Co-complexed electrode a 2-electron transfer process occurs to a large extent, while at the Fe-complexed electrode the reduction proceeds mostly through a 4-electron transfer process.

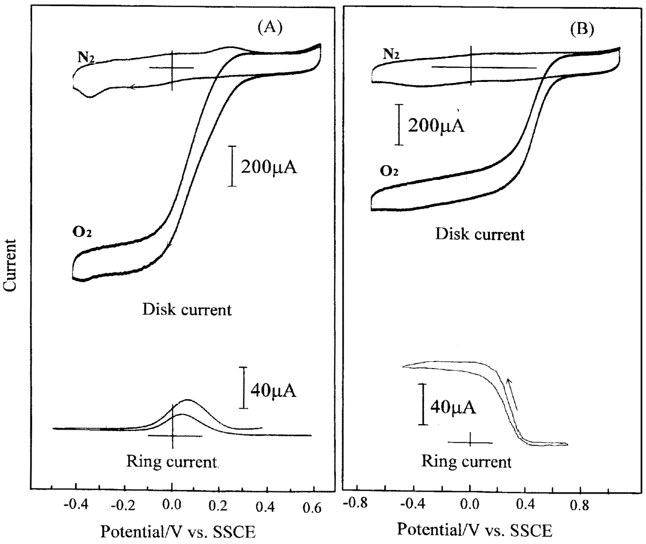


**Figure 4**. RRDE currents with oxygen reduction at PEDT-MTSP disk electrodes in $O_2$-saturated 0.05 M $H_2SO_4$. (A) PEDT-FeTSP, (B) PEDT-CoTSP. Scan rate: 50 mV $s^{-1}$; Rotation rate: 2000 rpm.

The fraction of the reduction current used for $H_2O_2$ formation was estimated from the ratio of the ring currents to the disk currents and from the collection factor of the ring-disk electrode used. Table 1 summarizes the results. The fractions of current consumed for $H_2O_2$ production at the PEDT FeTSP electrodes were small. A large part of the reduction current seems to be consumed in reduction of $O_2$ to water or hydroxide by a 4-electron process at PEDT-FeTSP. The por-

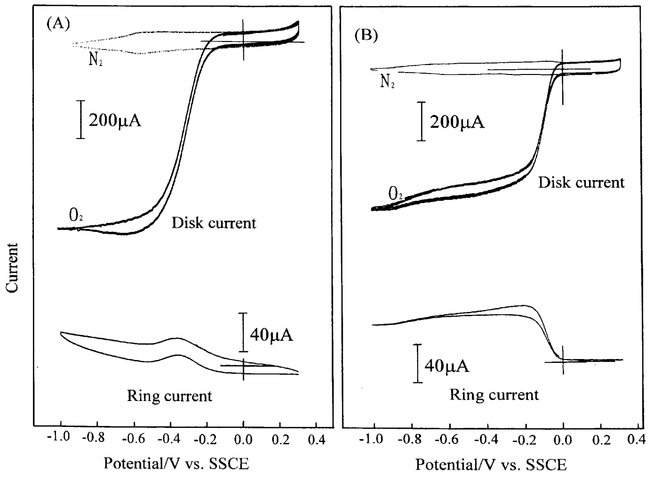


**Figure 5**. RRDE currents with oxygen reduction at PEDT-MTSP disk electrodes in $O_2$-satd. 0.1 M KOH. (A) PEDT-FeTSP, (B) PEDT-CoTSP. Scan rate: 50 mV $s^{-1}$; Rotation rate: 2000 rpm.

**Table 1**. Summary of RRDE experiments for $O_2$ reduction using a disk electrode covered with PEDT-MTSP and a Pt ring electrode (ring collection factor = 0.220, scan rate = 10 mV $s^{-1}$, rotation rate = 2000 rpm)

| Electrodes | Electrolytes | Limiting disk current density, $\mu A\ cm^{-2}$ | Fraction of current used for $H_2O_2$, % |
|---|---|---|---|
| GC/PEDT-FeTSP | 0.05M $H_2SO_4$ | 6100 | 11 |
| | 0.1M KOH | 6100 | 9 |
| GC/PEDT-CoTSP | 0.05M $H_2SO_4$ | 3900 | 39 |
| | 0.1M KOH | 3900 | 39 |
| Pt | 0.05M $H_2SO_4$ | 6200 | 2 |
| | 0.1M KOH | 6100 | 3 |

tions of the current used in the 2-electron process of $O_2$ reduction to $H_2O_2$ were larger in the case of PEDT-CoTSP electrode, but even there the fractions were less than 40%.

The present results are similar to our previous results on PPy-based electrodes,[13] but are in discrepancy with the work by Ikeda *et al.*[5] in which they reported that reduction of $O_2$ at PPy-FeTSP and PPy-CoTSP proceeded mostly through a 2-electron path in acidic solutions, and the 4-electron process occurred only at PPy-FeTSP electrode at high overvoltages.

It may be assumed that some of the $H_2O_2$ formed at the disk electrode can be further reduced to water or hydroxide ion as proposed by Ikeda *et al.*[5] However, at the PEDT-CoTSP electrodes, where the ring currents were large, the limiting disk current density was much smaller than at PEDT-FeTSP. Therefore, $H_2O_2$ once formed at the polymer electrodes is not likely to be further reduced.

The mechanism of electrocatalytic reduction by metalloporphyrins involves binding of dioxygen molecule to the central metal atom. It is generally believed that weakening of the O-O bond in oxygen facilitates 4-electron reduction. The weakening of the bond is reported to occur when oxygen is bound to two cobalt atoms in cofacial Co-porphyrins, or when oxygen is bound to a cobalt atom of a Co-porphyrin whose ring is appended by complexes of Ir or Os that can electronically enhance the porphyrin ring through back-bonding.[9] The mode of catalytic activity of the PEDT-MTSP electrodes is not understood. The polymers, PEDT used in the present study or PPy used in the previous study, are not directly involved in the reaction other than providing conductivity and playing host to the sulfonated porphyrins by securely holding them by electrostatic interaction. The polymer, however, may present occasional neighboring sites on which the metal-porphyrins arrange themselves face-to-face. An oxygen molecule can bind itself to two porphyrin metal atoms in $\mu$-peroxo form bridging the two metal atoms, resulting in a drastically weakened O-O bond.

**Stability of PEDT-MTSP catalysis**. We examined the change in the current of oxygen reduction at PEDT-MTSP electrodes with time at room temperature. The potentials were fixed in the diffusion limited ranges in oxygen-saturated acidic and basic solutions. The results are shown in Figure 6. The current at the PEDT-FeTSP electrode decreased rapidly in acidic solutions and somewhat slowly in 0.1 M KOH, but in 1 M KOH the current did not decrease significantly. The current at the PEDT-CoTSP electrode dropped initially in the acidic solution, but subsequent decrease was slight. In basic solution the decrease was only slight from the beginning. The stronger basic solution (1 M KOH) seemed to be beneficial for long-term stability of the electrocatalysis although the current level is usually smaller in basic solutions. In those cases where the current decreased significantly, the changes were irreversible. Also, concomitant increases in the ring current were observed. The degradation of the activity of the polymer-metalloporphyrin electrodes may be attributed to oxidation of the polymer by $H_2O_2$ produced as was proposed by Be' lange *et al.*[20] However, the degradation occurred more in the case of PEDT-FeTSP at which less $H_2O_2$ was produced than at PEDT-CoTSP. Therefore, it is possible that the degradation is at least partly due to the central metals being released from the macrocyclic center. Fe is known to be detached more easily than Co in strongly acidic solutions.[21]

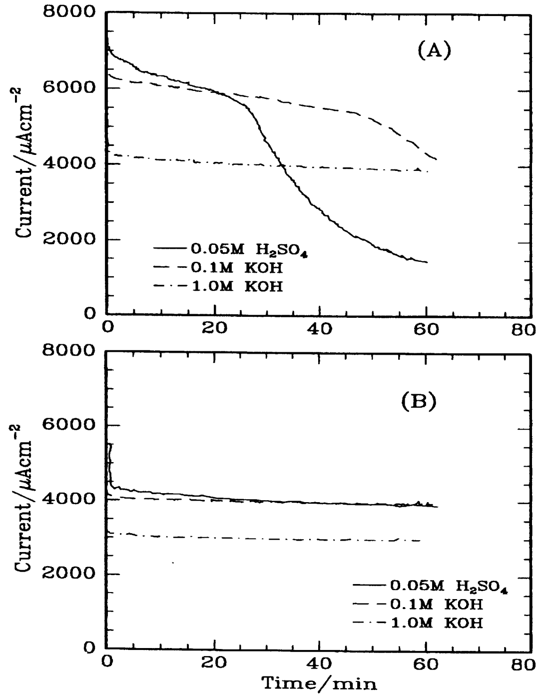


**Figure 6**. Changes in the limiting currents of oxygen reduction with time at PEDT-MTSP electrodes in $O_2$-saturated solutions. (A) PEDT-FeTSP, (B) PEDT-CoTSP. The potential was fixed for diffusion-limited current in each case

Anodic oxidation of PEDT itself is another factor that might contribute to the degradation of the electrocatalytic property, especially at elevated temperatures. To test the stability of the electrodes at elevated temperatures cyclic potential scans were continued for 30 min on the rotating disk electrodes at 50 °C, and 80 °C in 1 M KOH. The oxygen reduction current at PEDT-FeTSP decreased as much as 42% after 30 min. However, the current decrease at PEDT-CoTSP was only about 1% at both 50 °C and 80 °C. Degradation of the polymer itself, therefore, does not seem to be the primary cause of the current decrease.

**Comparison with polypyrrole-MTSP**. The electrochemical properties of PEDT-MTSP, including the catalytic effect toward oxygen reduction, are similar to those of polypyrrole doped with metalloporphyrins (PPy-MTSP).[13] However, PEDT showed greater stability over wider potential range. Both PEDT and PPy have upper potential limits above which there is a steep rise in oxidation current and the CVs subsequently diminish rapidly, indicating degradation of the polymers. The upper potential limit of PEDT was 0.8 V in 0.05 M $H_2SO_4$ at room temperature and 0.3 V in 0.1 M KOH at temperatures up to 80 °C. In contrast, the anodic limit of potential that can be applied to the PPy electrode in 0.05 M $H_2SO_4$ without deterioration of the conducting property was 0.5 V at room temperature. In 0.1 M KOH, the upper limit was 0.0 V at room temperature, decreasing to -0.2 V at 50 °C and to -0.3 V at 80 °C.[13] Thus, PEDT has the upper potential range at least 0.3 volt higher than PPy in any condition.

Due to this stability of PEDT electrodes, the catalytic property of the PEDT-MTSP electrodes was maintained for longer periods under the conditions relevant for practical applications, such as in alkaline fuel cells.

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