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Polypyrrole Doped with Sulfonate Derivatives of Metalloporphyrin: Use in Cathodic Reduction of Oxygen in Acidic and Basic Solutions

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Incorporation of metalloporphyrins into polypyrrole (PPy) film was achieved either by electropolymerization of pyrrole in the presence of metal-tetra(sulfonatophenyl)porphyrin anion (MTSPP, M=Co, Fe) or by metalizing hydrogenated tetra(4-sulfonatophenyl)porphyrin anion (H₂TSPP) doped into PPy through ion-exchange. Electrochemical reduction of oxygen on the PPy doped with metallo porphyrin (PPy-MTSPP) was studied in acidic and basic solutions. Oxygen reduction on PPy-MTSPP electrodes appeared to proceed through a 4-electron pathway as well as a 2-electron path. In acidic solutions, the overpotential for O₂ reduction on PPy-CoTSPP electrode was smaller than that on gold by about 0.2 V. In basic solutions the overpotential of the PPy-CoTSPP electrode in the activation range was close to those of Au and Pt. The limiting current was close to that of Au. However, polypyrrole doped with cobalt-tetra(sulfonatophenyl)porphyrin anion (PPy-CoTSPP) or with iron-tetra (sulfonato phenyl) porphyrin anion (PPy-FeTSPP) was found to have limited potential windows at high temperatures (above 50 °C), and hence the electrode could not be held at the oxygen reduction potentials in basic solutions (pH 13) without degradation of the polymer.

Introduction

The search for efficient and cost-effective electrocatalysts for cathodic oxygen reduction other than platinum and its alloys has been intensive because of their importance in applications such as fuel cells and metal/air batteries.¹⁻³ Metal porphyrins and metal phthalocyanines are among the best candidates because they have excellent thermal and chemical stabilities,⁴ and they exhibit excellent catalytic properties.^{1,5,6} Incorporating porphyrins into a conducting polymer is one efficient technique for making electrodes with immobilized metalloporphyrins. Incorporation of metalloporphyrin into conducting polypyrrole (PPy) can be achieved by one of three different methods: i) polymerization of pyrrole in the presence of a metalloporphyrin that is derivatized with an anionic group so that the porphyrin anion is incorporated into the polymer matrix as counter-ions for the positively charged polymer;⁷⁻¹⁰ ii)

Polymerization of porphyrin-substituted pyrrole;^{11,12} iii) Ion exchange into polymer of *N*-alkylammonium pyrrole salt.^{13,14}

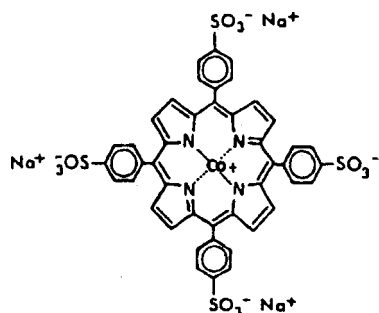
We adopted the first method, *i.e.* incorporation of metalloporphyrins with attached anionic groups into PPy by polymerizing the monomer pyrrole in the presence of the functionalized porphyrins. Cathodic reduction of oxygen on the resulting polymer electrode was studied in acidic and basic aqueous electrolytes using a rotating ring-disk assembly.

Experimental

Deposition of polypyrrole doped with metalloporphyrin. Polypyrrole films doped with metalloporphyrins were prepared by anodic electropolymerization on platinum, gold, or glassy carbon (GC) disk electrodes in aqueous solutions containing 0.1 M pyrrole and 1 mM of the appropriate salt of anionic metalloporphyrin. The anionic metalloporphyrins have a structure shown by the following example of a sulfonated Co-porphyrin.

Sodium salts of cobalt-tetra(sulfonatophenyl)porphyrin anion (CoTSPP), iron-tetra(sulfonato phenyl)porphyrin anion (FeTSPP), and tetra(sulfonatophenyl)porphyrin anion

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Sulfonated Porphyrin Cobalt Complex.

Scheme

(H₂TSPP) purchased from Midcentury Chemicals were used as received. Pyrrole (Aldrich Chemicals) was purified by distillation over calcium hydride. No electrolyte other than the porphyrin salts were added into the solutions for the electropolymerization. All electrolyte/monomer aqueous solutions were purged with nitrogen prior to and during the polymerization. Each of the working electrodes had a geometric surface area of 0.164 cm², and was previously polished with 0.1 μm alumina powder and then washed in an ultrasonic bath. The reference electrode used was a sodium saturated calomel electrode (SSCE). All potentials reported in this article refer to this electrode. The counter electrode was a spiral piece of platinum wire. Electropolymerization with cyclically scanned potential was done to monitor the growth of the polymer film with the potential cycles. However, the PPy-metalloporphyrin (PPy-MTSPP) electrodes used later in the voltammetric experiments were prepared by galvanostatic polymerization. Current density of 400 μA cm⁻² was applied for about 10 min for the galvanostatic polymerization.

Insertion of Co²⁺ into PPy doped with H₂TSPP.

Films of PPy doped with tetra (sulfonatophenyl)porphyrin anion (H₂TSPP) were prepared by electropolymerization from a solution containing 0.1 M pyrrole and 1 mM sodium salt of H₂TSPP. The PPy film thus formed (denoted henceforth as PPy-H₂TSPP) containing no central metal atom was transferred to a monomer-free solution containing 0.1 M CoCl₂ and the potential was scanned between -0.4 V and 0.4 V for 1 hour to obtain PPy doped with CoTSPP (denoted henceforth as PPy-CoTSPP).

Cathodic reduction of molecular oxygen was studied with a rotating disk electrode (RDE) or rotating ring-disk electrode (RRDE, Pine Model AFMT28), whose disk parts were covered with the deposited PPy-MTSPP films. Most of the experiments were conducted at room temperature except when other temperatures were specified.

Results and Discussion

Deposition of PPy-metalloporphyrin films. Figure 1 shows cyclic voltammograms obtained during formation of PPy film from a solution of 0.1 M pyrrole and 1 mM CoTSPP or 1 mM FeTSPP. The current increased with increasing numbers of the potential cycles indicating successive accumulation of polypyrrole formed by elec-

tropolymerization. The only anion present in the electrolyte that can be incorporated into the polymer was the metalloporphyrin tetrasulfonates. No distinguishable reduction-oxidation peaks other than those of polypyrrole appeared in the cyclic voltammograms with the cobalt porphyrin (Figure 1A). However, with the iron porphyrin (Figure 1B) distinguishable peaks attributable to Fe²⁺/Fe³⁺ appeared in addition to those of PPy.

To verify the incorporation of metalloporphyrin by spectroscopic examination, PPy was deposited from the same solutions on transparent glass slides coated with indium-tin oxide (ITO). The absorption spectra of the deposited films were compared with those of Co-TSPP and Fe-TSPP in solution and also with PPy doped with only a ClO₄⁻ ion, as shown in Figure 2. The sharp peak near 400 nm corresponding to the Soret band of porphyrins in each of the spectrum, slightly red-shifted and broadened, clearly indicates that the anionic metalloporphyrins (MTSPP) are incorporated into the polypyrrole film. The red-shift and asymmetric broadening of the Soret band are known to be due primarily to aggregation and stacking of porphyrin molecules in the polymer.¹⁵ Thus, metalloporphyrins with Fe or Co central atoms were confirmed to be incorporated into PPy by electrochemical polymerization from aqueous solutions. Similar incorporations of porphyrins⁷⁻¹⁰ and phthalocyanines^{16,17} from methanolic and aqueous solutions were reported.

Insertion of Co²⁺ in PPy doped with H₂TSPP.

There has been a report on the metallization of PPy incorporated with sulfonated porphyrin without a central metal atom (H₂TSPP), by refluxing in aqueous 0.1 M cobalt(II) acetate solution heated to 90 °C for several minutes.⁶ We in-

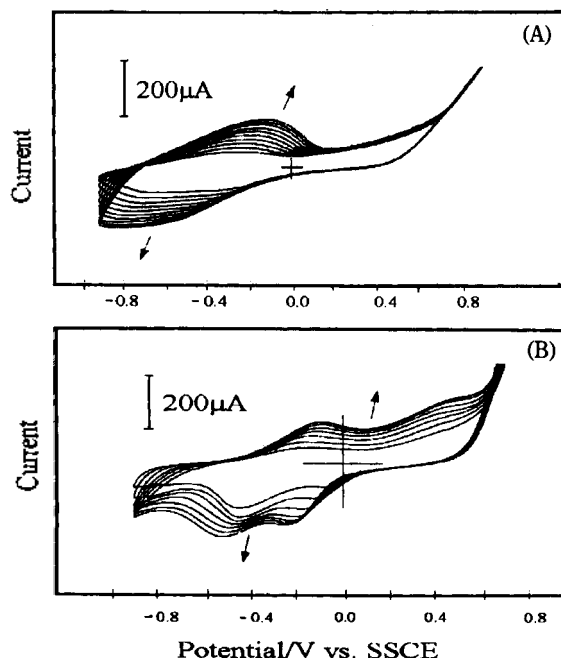


Figure 1. Cyclic voltammograms(CV) during formation of PPy-MTSPP by electro polymerization from aqueous solutions of 0.1 M pyrrole and tetra(sulfonatophenyl) metalloporphyrin salt on Au disk electrodes of 0.164 cm². Scan rate: 50 mV sec⁻¹. (A) 1.0 mM CoTSPP (Na₃), (B) 1.0 mM FeTSPP (Na₃). Scan rate: 50 mV sec⁻¹

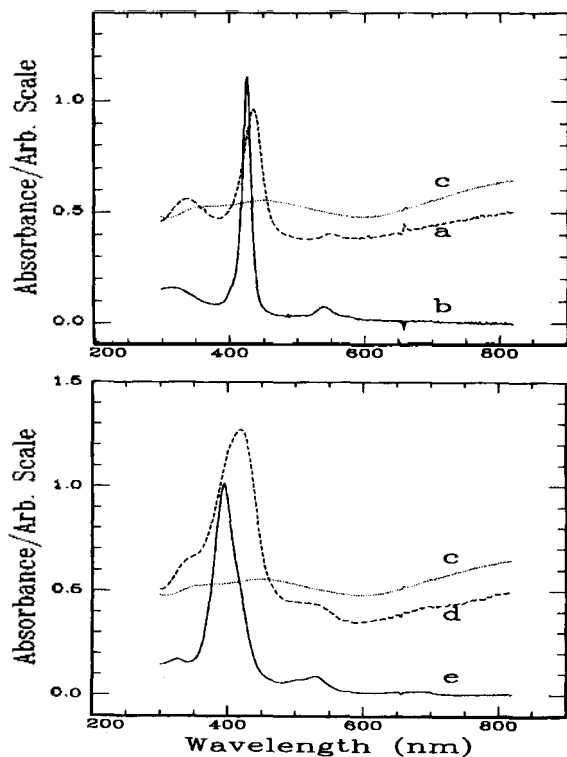


Figure 2. Absorption spectra of PPy-MTSP films deposited on ITO electrodes compared to those of PPy-ClO₄ and the porphyrin complexes dissolved in aqueous solutions. (a) ITO/PPy-CoTSPP, (b) CoTSPP, (c) ITO/PPy-ClO₄, (d) ITO/PPy-FeTSPP, (e) FeTSPP.

incorporated a Co(II) ion into PPy-H₂TSPP in a more convenient way. After a PPy-H₂TSPP film was prepared from a solution containing 0.1 M pyrrole and 1 mM H₂TSPP, it was transferred to a 0.1 M aqueous CoCl₂ solution. The potential of the film electrode was cycled between -0.4 V and 0.4 V for 1 hr. The insertion of Co atoms into the porphyrin moiety in the treated film was confirmed by an increase in the reduction current in an O₂-saturated 0.05 M H₂SO₄ solution. PPy-H₂TSPP is inactive toward O₂ reduction above 0.0 V (Figure 3A), whereas the O₂ reduction is clearly facilitated at the film treated in the CoCl₂ solution (Figure 3B). The incorporation of the cobalt ion into PPy-H₂TSPP film can be explained by the ion transport property of the polypyrrole doped with metalloporphyrin anion. Ionic migration in polypyrrole doped with the large size metalloporphyrin anion is cation-dominant in neutral solutions which is confirmed by separate experiments using electrochemical quartz crystal microbalance (EQCM). Thus, the cobalt cation moves into the polypyrrole film on reduction of the cationic polymer to compensate the anionic charge to be eventually bound to the center of the macrocycle replacing hydrogen. It was shown also by EQCM that the metalloporphyrins once incorporated into the polymer film are not replaced on repeated potential cycles in the cathodic and anodic directions.

Oxygen reduction. Cathodic reduction of oxygen at rotating disk electrodes of PPy doped with metal tetrasulfonatophenyl porphyrin anion (MTSP, M=Co, Fe) was examined by cyclically scanning the electrode potential in O₂-

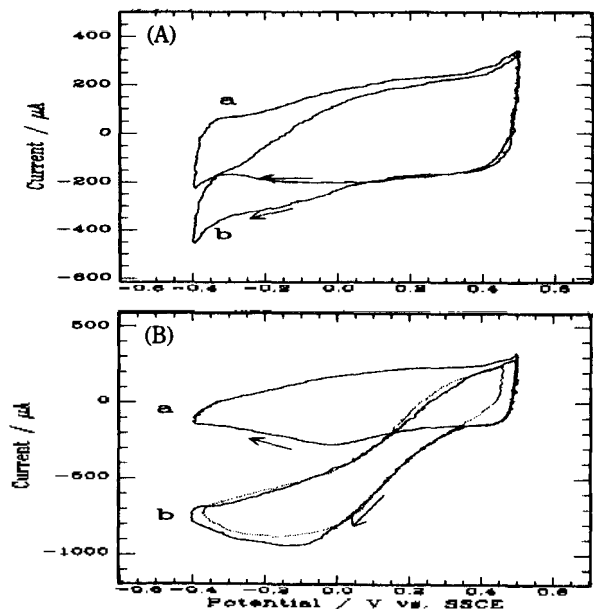


Figure 3. Cyclic voltammograms at rotating disk electrodes of (A) PPy-porphyrin and (B) Cobalt-inserted PPy-porphyrin, in 0.05 M H₂SO₄, in the absence (a) and presence of O₂ (b). (—) PPy-H₂TSPP after Co insertion, (.....) PPy-CoTSPP. Scan rate=50 mV/sec, rotation rate=2000 rpm.

saturated sulfuric acid or potassium hydroxide solutions. The substrate for the deposited PPy-MTSP was disks of glassy carbon. Replacing the glassy carbon disk with a gold or platinum disk did not affect the current response of the polymer electrodes. This shows that the reactions occur only at the polymer surface and not on the substrate. The cyclic voltammograms (CV) of rotating PPy-MTSP electrodes are compared with those obtained at rotating bare Pt, Au, and glassy carbon electrodes in Figures 4 and 5.

In 0.05 M H₂SO₄ solution (Figure 4) both the PPy-CoTSPP and PPy-FeTSPP covered disk electrodes exhibited much larger limiting currents for O₂ reduction and lower overpotential at low current densities than the glassy carbon electrode by about 500 to 600 mV. The overpotential of the PPy-CoTSPP electrode was smaller than that of the Au electrode by about 200 mV in the activation-controlled range. The limiting currents were somewhat higher than that at Au. The potential-current relation of the PPy-FeTSPP electrode was close to that of Au. It is generally accepted that at the Au electrode the oxygen reduction goes via 2-electron reaction,² and the limiting current is about half of that at the Pt electrode where the reduction proceeds by a 4-electron path.² In basic solutions (Figure 5) the overpotential of the PPy-CoTSPP electrode was close to those of Au and Pt. The limiting current was close to that of Au. The PPy-FeTSPP electrode exhibited larger overpotential than Au. In summary, the electrocatalytic effects of PPy-CoTSPP and PPy-FeTSPP are markedly larger than that of glassy carbon. The PPy-CoTSPP electrode is a better catalyst than Au in 0.05 M H₂SO₄ and equally as good a catalyst as Au in 0.1 M KOH.

Voltammograms for ring and disk electrodes were obtained in O₂-saturated 0.05 M H₂SO₄ and 0.1 M KOH solutions using RRDE whose disk part was covered with deposited PPy-metallo porphyrin. The Pt ring was maintained

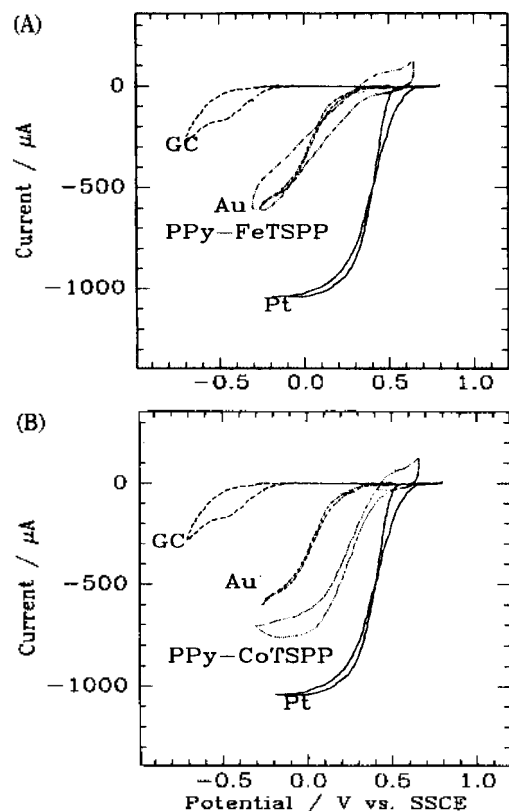


Figure 4. O_2 reduction at rotating (A) PPy-FeTSPP (B) PPy-CoTSPP electrodes in O_2 -saturated 0.05 M H_2SO_4 solution compared to those at Pt, GC, and Au (electrode area= 0.164 cm^2 , scan rate= 10 mV sec^{-1} , rotation rate= 2000 rpm).

at 1.0 V in the acid and 0.6 V in the basic solution to oxidize H_2O_2 produced at the disk. The disk and ring currents are shown in Figures 6 and 7. The thickness of the deposited polymer was about $0.5 \mu\text{m}$. The slight change of geometry at the gap between the disk and ring by the deposited film might have affected the hydrodynamic flow near the surface and hence the collection factor of the ring electrode. We have, however, neglected the effects of the geometry change by the deposited polymer in the treatments of the ring current data because the thickness of the film is much smaller in comparison to the gap between the disk and ring. The results are summarized in Table 1.

The fact that ring currents were observed in all cases indicates formation of hydrogen peroxide from reduction of oxygen at the disk electrodes. From the ratio of the ring currents to the disk currents, and from the collection factor of the particular ring-disk electrode used, the fraction of the reduction charge used for H_2O_2 formation was calculated. The percentage was no more than 30% in all cases. It may be assumed that some of the H_2O_2 formed at the disk electrode can be reduced further to water or hydroxide ion as proposed by Ikeda *et al.*⁸ However, when we measured reduction current densities in 1 mM H_2O_2 solution at a PPy-CoTSPP electrode and a Pt electrode the reduction current at PPy-CoTSPP was found to be less than 1/5 of that at a Pt electrode in the limiting current range. Therefore, H_2O_2 once formed at the polymer electrodes is not likely to be reduced further. A large part of the reduction current was

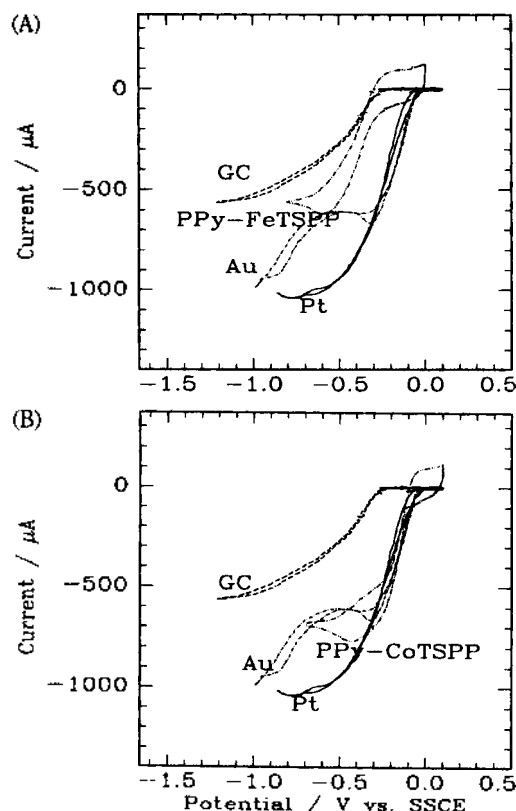


Figure 5. O_2 reduction at rotating (A) PPy-FeTSPP (B) PPy-CoTSPP electrodes in O_2 -saturated 0.1 M KOH solution compared to those at Pt, GC, and Au (electrode area= 0.164 cm^2 , scan rate= 10 mV sec^{-1} , rotation rate= 2000 rpm).

used, therefore, in the reduction of O_2 to water or hydroxide by a 4-electron process. The portion of the current used in the 2-electron process of O_2 reduction to H_2O_2 was larger in the case of the PPy-CoTSPP electrode, especially in the KOH solution. The present result is in discrepancy with the work by Ikeda *et al.*,⁸ in which they reported that reduction of O_2 at PPy-FeTSPP and PPy-CoTSPP proceeds mostly through a 2-electron path in acidic solutions, and a 4-electron process is said to occur at PPy-FeTSPP only at high overvoltages.

Stability of PPy-MTSPP. We examined the change with time of the oxygen reduction current at PPy-MTSPP electrodes at -0.1 V in oxygen-saturated 0.05 M H_2SO_4 , or at -0.5 V in 0.1 M KOH. Figure 8 shows the change of

Table 1. Summary of rotating ring-disk electrode experiments for O_2 reduction using disk electrode covered with PPy-MTSPP and Pt ring electrode (Collection factor= 0.2202 ; Scan rate= 10 mV s^{-1} ; Rotation rate= 2000 rpm)

Electrodes	Electrolytes	Disk current, A cm^{-2}	Ring current, $\mu\text{A cm}^{-2}$	Fraction of current used for H_2O_2 , %
PPy-CoTSPP	0.05 M H_2SO_4	-4100	-200	22
PPy-CoTSPP	0.1 M KOH	-3900	-250	29
PPy-FeTSPP	0.05 M H_2SO_4	-4000	-70	8
PPy-FeTSPP	0.1 M KOH	-4300	-130	14

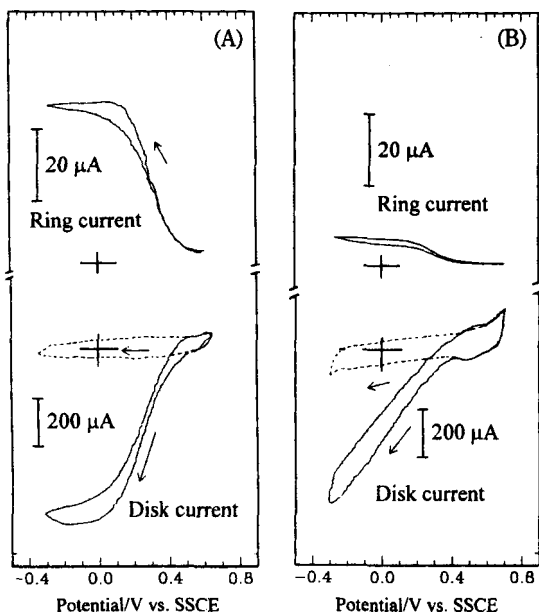


Figure 6. Ring and disk currents from RRDE experiments in O_2 -saturated 0.05 M H_2SO_4 solution. The disk electrode: (A) PPy-CoTSPP, (B) PPy-FeTSPP. The dashed curves are disk electrode CV's from O_2 -free solutions purged with N_2 . (Scan rate=10 $mV\ sec^{-1}$, rotation rate=2000 rpm, ring potential=0.6 V).

the oxygen reduction current at room temperature. The current at the PPy-FeTSPP electrode decreased rapidly in acidic solutions, whereas the current at the PPy-CoTSPP electrode decreased only slightly. In basic solutions, the current at PPy-CoTSPP remained almost unchanged, whereas at PPy-FeTSPP the current decreased steadily. In those

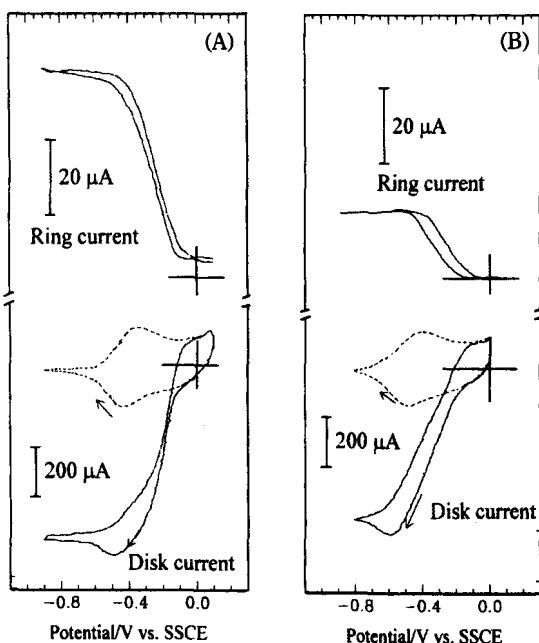


Figure 7. Ring and disk currents from RRDE experiments in O_2 -saturated 0.1 M KOH solution. The disk electrode: (A) PPy-CoTSPP, (B) PPy-FeTSPP. The dashed curves are disk electrode CV's from O_2 -free solutions purged with N_2 . (Scan rate=10 $mV\ sec^{-1}$, rotation rate=2000 rpm, ring potential=0.6 V).

cases where the current decreased significantly, the change of the electrode was irreversible. The degradation of the polymer-metalloporphyrin electrodes may be attributed to oxidation of the polymer by H_2O_2 produced as was reported by Be'lange.¹⁸ However, the degradation occurred more in the case of PPy-FeTSPP at which less H_2O_2 was produced than at PPy-CoTSPP. Therefore, it is possible that the degradation is at least partly due to the central metal atoms being released from the macrocyclic center. A Fe atom is known to be more easily detached than Co, especially in strong acidic solutions.¹⁹

Anodic oxidation of PPy itself is another factor that might contribute to the degradation of the electrocatalytic property, especially at elevated temperatures. In order to estimate the effect of raised temperature on the degradation of the polymer, cyclic voltammograms of PPy-FeTSPP, PPy-CoTSPP, and PPy- ClO_4 were obtained in 0.1 M KOH at three different temperatures, 26 °C, 50 °C, and 80 °C with various potential scan ranges. The anodic scan of potential was limited such that the CVs on repeated cycling did not shrink in current. At the higher temperatures the anodic current rose sharply beyond certain potentials after which the CVs shrank sharply. Thus the safe upper bound of potential decreased with rising temperature. The safe bounds of potential were found by repeated trial and error. Some of the representative CVs obtained at three different temperatures without significant degradation are shown in Figure 9. The PPys with the three different anionic dopants showed about the same dependence of the upper bound of potential on temperature. At 50 °C the upper bound was about -0.2 V. This is lower than the potential at which the oxygen reduction starts to occur. In view of the fact that the alkaline fuel cells of the present technology operate at temperatures near

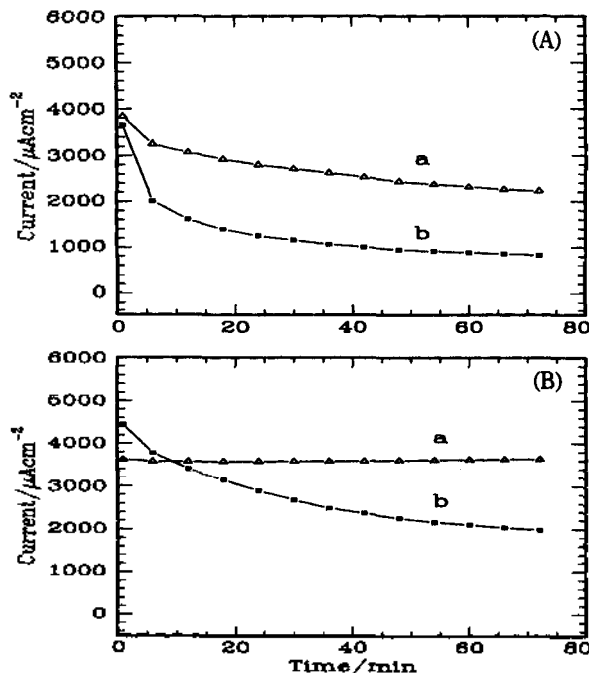


Figure 8. Change of oxygen reduction current with time at PPy-MTSPP electrodes in O_2 -saturated aqueous solutions, (A) In 0.05 M H_2SO_4 at -0.1 V, (B) In 0.1 M KOH at -0.5 V. a: PPy-CoTSPP, b: PPy-FeTSPP (rotation rate=2000 rpm).

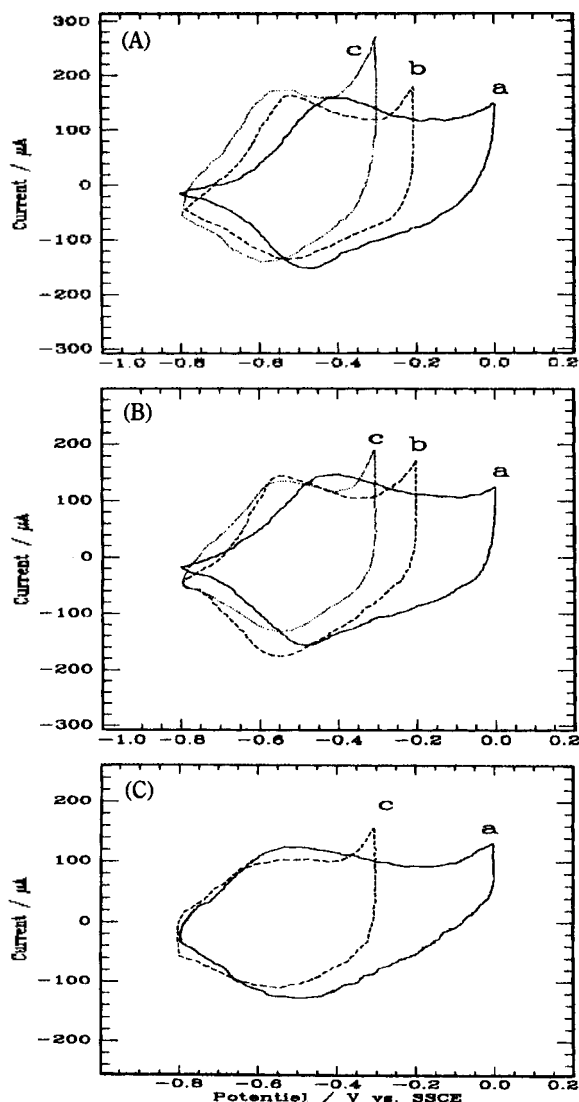


Figure 9. CV showing limits of potential scan range possible at various temperatures in 0.1 M KOH solution. (A) PPy-CoTSPP, (B) PPy-FeTSPP, (C) PPy-ClO₄. Scan rate=10 mV sec⁻¹. (a) 26 °C, (b) 50 °C, (c) 80 °C.

or higher than 80 °C, the PPy-MTSPP electrodes appear to be unsuitable for direct application in an alkaline fuel cell. The degrading part appears to be in the PPy backbone because all PPy's with any of the three different dopants including perchlorate showed similar behavior. A polymer that is more stable at a higher temperature must be sought for practical applications. In our laboratory, electrodes prepared by incorporating metalloporphyrins into a polymer of

ethylenedioxythiophene have been studied recently. This polymer is much more stable at higher temperatures and higher potentials than PPy. A report of this study is under preparation.

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