



Polymer Films on Electrodes

13. Incorporation of Catalysts into Electronically Conductive Polymers: Iron Phthalocyanine in Polypyrrole

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Abstract

Tetrasulfonated iron phthalocyanines (FePcS) can be incorporated into electronically conducting polypyrrole by electrochemical polymerization of pyrrole in the presence of FePcS. The FePcS modified glassy carbon electrodes catalyzed the reduction of O_2 at potentials 250 to 800 mV less negative than at bare glassy carbon or at polypyrrole-coated glassy carbon not containing FePcS. Rotating ring-disk experiments indicated some hydrogen peroxide formation at most pH's. However, at high pH essentially exclusive reduction of O_2 to H_2O was observed at potentials 250 mV less negative than at a non-catalyzed electrode.

(end of abstract)

One of the main motivations for the preparation of modified electrodes, including those covered with polymer films, is the incorporation of electrocatalysts onto the electrode surface. For example, catalysts have been covalently attached to the substrate, irreversibly adsorbed, and introduced into polymer films via electrostatic binding (1). Of particular interest have been electrocatalysts for the reduction of oxygen (2-5); these often are based on metal porphyrins and phthalocyanines. Among the problems arising in the utilization of catalytic modified electrodes are the limited effectiveness on monolayers (6), instability of the attached or adsorbed materials, and low rate of charge transport through non-electronically conductive films. We suggest here the incorporation of a catalyst into a conductive polymer layer by electrochemical polymerization in the presence of catalyst and briefly describe the characteristics of such an electrode for the reduction of oxygen.

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Key Words: catalysis, polymers, voltammetry, electrodes

The conductive polymer chosen was polypyrrole (PP); a number of electrochemical studies of this material have demonstrated that this can be readily deposited by electrochemical oxidation of pyrrole from nonaqueous or aqueous solutions (7-10). The catalyst was tetrasulfonated phthalocyanine incorporating iron (FePcS) and the substrate was glassy carbon (GC). The advantages of this system include ease of preparation, and both high conductivity and high porosity of the PP film (11), leading to rapid transport of both charge and solution substrate within the electrode structure.

Polypyrrole films were deposited from aqueous 0.05 M sodium trifluoroacetate solutions (NaTFA) (pH 1-7) that were 0.1 M in pyrrole by anodic oxidation at +0.7 V vs. SCE at GC. Polymer film thicknesses were estimated by taking 24 mC/cm² of charge to be equivalent to a 1 μ m film (8c). GC/PP/FePcS films were prepared by an identical procedure except that the solution contained only 1 mM FePcS and 0.1 M pyrrole. Oxidation of pyrrole in the presence of FePcS was necessary for catalyst incorporation. Control experiments in which a GC electrode was held at +0.7 V vs. SCE in a FePcS solution not containing pyrrole showed no O_2 - reduction catalysis. PP films deposited in the absence FePcS and then cycled through the PP redox waves in a solution containing FePcS also showed no catalytic activity.

CV Experiments.--A typical cyclic voltammogram (CV) of a FePcS/PP film (0.1 μ m thick) is shown in Fig. 1a for a 0.1 M NaTFA electrolyte (pH 1.7) saturated with N_2 . The small waves for FePcS reduction and re-oxidation are superimposed on the large PP background; the large background currents have been ascribed to capacitive charging of the highly porous PP film (11). An estimate of the amount of electroactive FePcS in the polymer from the CV, assuming $n=1$ for Fe(III)/Fe(II) couple

is 2 to 6×10^{-11} moles/cm² geometric area. The FePcS redox waves were stable to cycling within the potential limits imposed by PP. Scanning to potentials sufficiently negative for PP reduction (i.e. out to -0.3 to -0.5 V vs. SSCE) resulted in a decrease in the peak currents (i_p) for the FePcS waves. Potentials positive enough for irreversible PP oxidation (+0.8 V vs. SSCE at pH 1 to +0.4 V at pH 13) also decreased i_p for the FePcS redox waves, although the film still remained on the electrode surface.

In O₂-saturated solutions the current at the FePcS² wave was greatly increased (Fig. 1b); this is attributed to the catalyzed reduction of O₂. In all cases significantly higher reduction currents were found at more positive potentials at GC/PP/FePcS than at GC/PP or bare GC electrodes. For example, under the conditions of Fig. 1b, O₂ reduction at GC/PP occurs at about -0.8 V vs. SSCE. The effect of pH on the potentials for catalyzed O₂-reduction was similar to that found for the FePcS waves themselves. At pH < 3, the shift of E_d was 45 mV/pH unit. As with the FePcS redox waves themselves, the waves attributed to O₂ reduction disappeared upon irreversible PP oxidation.

RRDE Experiments.--Reduction of O₂ at bare and modified GC disk electrodes with detection of products (e.g. H₂O₂) via oxidation at a Pt ring electrode provided additional information about catalysis by incorporated FePcS (Fig. 2). At a bare GC electrode O₂-reduction occurred to produce a mass transfer controlled wave, with the limiting current, i_l , increasing with angular rotation velocity, ω . For GC/PP electrodes a wave at similar potentials was observed, but i_l reached a limiting value at about 1000 rpm. The collection efficiencies, N, found for GC and GC/PP electrodes (for O₂ reduction at the disk and H₂O₂ oxidation at the ring) were generally 0.26-0.30; this is less than the collection efficiency found with this electrode and a soluble redox couple such as Fe(CN)₆^{3-/4-}, where N = 0.39. For a GC/PP/FePcS disk electrode, the reduction of O₂ essentially coincided with the FePcS reduction wave and occurred at less negative potentials compared to GC and GC/PP electrodes, similar to the CV results. At most pH's anodic ring currents were observed when O₂ was reduced at the disk (e.g. at pH = 6.5, E_d = -0.6 V; E_r = +1.0 V vs. SSCE), demonstrating that some H₂O₂ is produced. Typical results for a 0.12 μm PP/FePcS film in O₂-saturated 0.1M NaTFA (pH 6.5) are given in

Fig. 2a. Strict correspondence to the Levich equation (i_p vs. $\omega^{1/2}$) was not found with this electrode, perhaps because of interference from the background processes of PP. The reduction of O₂ at GC/PP/FePcS in 0.1 M NaOH did not lead to anodic ring currents until the disk potential attained values where direct O₂ reduction of GC/PP occurs. Typical RRDE voltammograms are given in Fig. 2b. After an initial "break-in period" during which the reduction current decreased, the current between -0.1 and -0.3 V was independent of ω . No ring currents were observed at these values of E_d. When E_d reached -0.35 V, the onset potential for O₂ reduction at bare GC, anodic current became apparent. Note, however, that even at these potentials the anodic currents were very small, so that N-values in this region were two orders-of-magnitude smaller than for catalyzed O₂ reduction at lower pH. These results suggest that FePcS catalyzes the decomposition of H₂O₂ in 0.1 M NaOH solution.

In general, over the pH range of 1.7 to 13, N-values for GC/PP/FePcS electrodes were always smaller than those for bare GC electrodes at the same pH. However, at lower pH, N was nearly the same as that for the bare electrode. At pH 13, N was two orders of magnitude less than at a bare GC electrode, even at potentials where peroxide is produced at GC.

The stability of FePcS-PP films depended on the pH and the cathodic scan limits. If the PP films were reduced, O₂-reduction activity decreased. As a result, limiting currents and i_p vs. $\omega^{1/2}$ data could not be obtained. This was particularly so at low pH, where PP reduction began at only slightly negative potentials. The stability of the catalyst-film during O₂ reduction and in the presence of reduction products, e.g. H₂O₂, is also of interest. Successive O₂-reduction scans, especially at low pH, resulted in a gradual decrease in the disk current. After prolonged O₂ reduction the initially shiny blue-black FePcS-PP film changed to a gray particulate deposit that was easily removed from the electrode. At this point, little O₂ reduction activity was observed and, after N₂ saturation, no FePcS redox activity was found. The addition of H₂O₂ to the electrolyte also brought about rapid delay of catalytic activity.

In conclusion, this method of incorporation of catalysts via conductive polymers onto an electrode surface appears to be a promising one. For the GC/PP/FePcS electrodes we have observed significant

catalytic activity for O_2 reduction at potentials 250 to 800 mV² less negative (depending on pH) than at bare GC or GC/PP electrodes. Moreover, the observed current densities for O_2 reduction based on the geometric area of the electrode appear to be larger than those reported for similar catalysts adsorbed on electrodes (2,5). This can probably be attributed to the high conductivity and porosity of the PP matrix, making a larger number of catalyst centers accessible per unit area of electrode to dissolved O_2 .

The PP background often hindered the collection of precise peak and limiting current data for quantitative kinetic analysis. As a result, only qualitative aspects of O_2 reduction mechanisms can be discussed. The similarity of the FePcS and catalyzed O_2 reduction potentials suggests a redox-type mechanism (12). However, the voltammetric behavior and the change of N with pH suggest at least two simultaneous O_2 reduction processes. At low pH the reduction is predominantly to peroxide and N is nearly that found for an unmodified GC electrode. As the pH is raised the Tafel slopes increased and N decreased from that at an unmodified electrode. At intermediate pH, the 2e and 4e processes are competitive, but at high pH no peroxide was detected at potentials positive of O_2 reduction at GC, suggesting a direct 4e reduction to H_2O . The 4 electron process probably involves the dismutation of H_2O_2 by FePcS, as suggested for iron porphyrins in methylacrylate polymers (13). Direct reduction of H_2O_2 is also possible; however, H_2O_2 contributes to instability of PP and loss of catalytic activity. The stability of PP/FePcS catalyst increased at higher pH.

The catalytic behavior found here is qualitatively similar to those observed by Zagel et. al. (2) and perhaps involve similar mechanisms. This suggests that incorporation of FePcS into PP has essentially no effect on the mechanism or catalytic behavior. However, the conductive support enhances the effectiveness of the catalyst by providing more surface area and a larger percentage of active centers than are present in adsorbed films or catalysts in non-conducting polymers and provides a convenient method of attaching the catalyst to the substrate (14).

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14. Support of this research, a joint project with Prof. A. B. Lever, by the Office of Naval Research and by the National Science Foundation (CHE 7903729) is gratefully acknowledged.

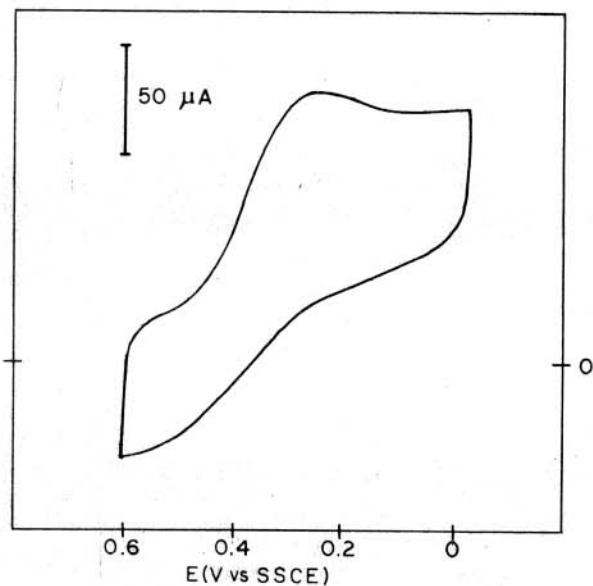
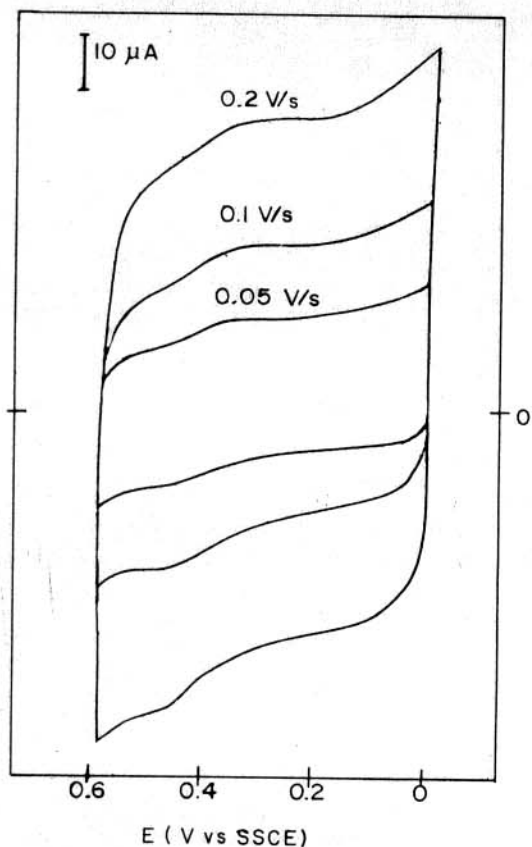


Fig. 1. Cyclic voltammetry of a $0.1 \mu\text{m}$ FePcS/PP film in 0.1M NaTFA ($\text{pH} = 1.7$); (a, top) N_2 -saturated; (b, bottom) O_2 -saturated, $v = 0.1 \text{ V/s}$.

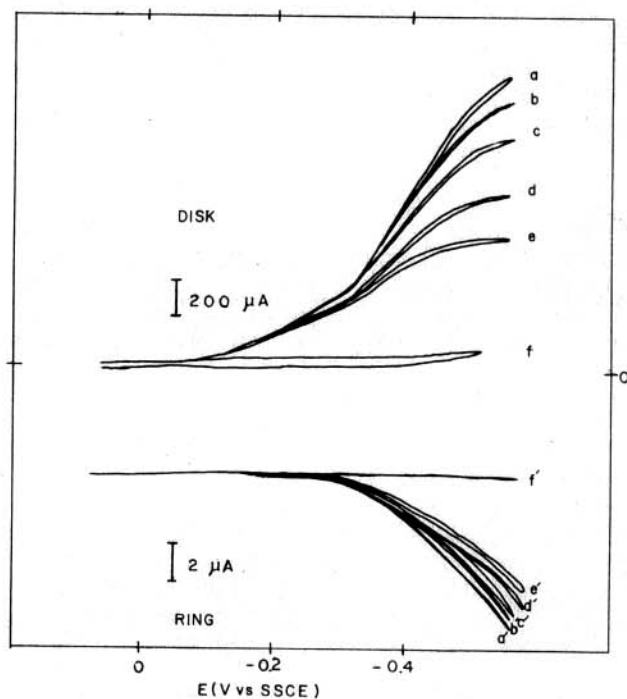
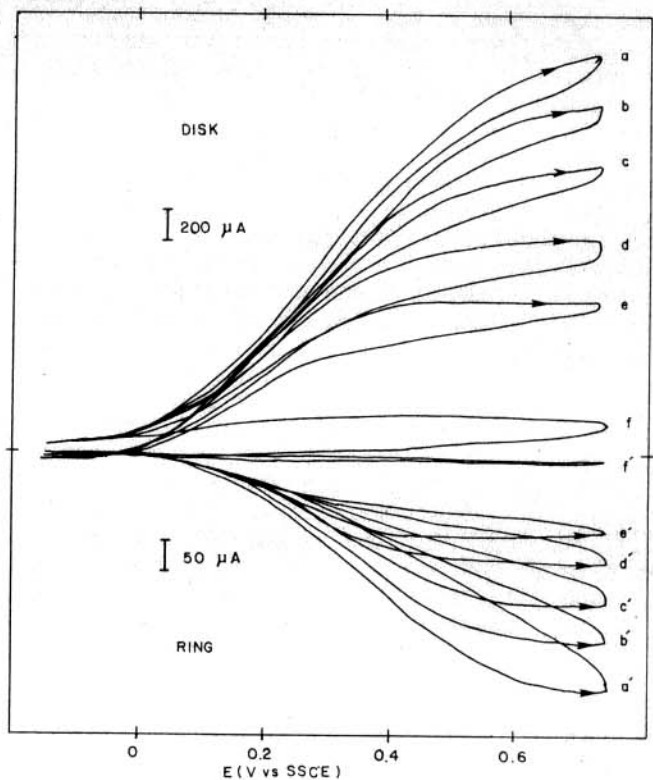


Fig. 2. Rotating ring-disk electrode voltammograms of a $0.1 \mu\text{m}$ FePcS/PP film in O_2 -saturated electrolyte at $\omega(\text{rpm})$, (a, a') 2000; (b, b') 1500; (c, c') 1000; (d, d') 500; (e, e') 250; (f, f') 2000 in N_2 -saturated electrolyte (a, top) 0.1M NaTFA ($\text{pH} = 6.5$) and (b, bottom) 0.1M NaOH.