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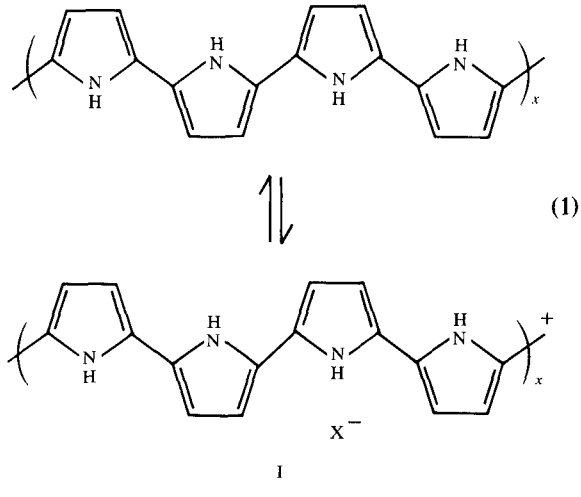
# [Pt]Polypyrrole: A New Organic Electrode Material

*Films of $BF_4^-$-doped polypyrrole grown on platinum, hereafter termed [Pt]polypyrrole, were used as electrodes in a series of reactions. These organic electrodes are found to be quite stable and nonporous; they generally do not perturb the redox reactions of dissolved species and they display rapid surface-substrate electron-transfer kinetics. The polypyrrole films are sensitive to the presence of Lewis bases in solution, which apparently act as nucleophiles, leading to degradation of the electrode properties.*

## Introduction

With the formation of stable conducting polymeric films during electropolymerization of aromatic compounds such as pyrrole, a new class of organic electrodes has become available [1a]. These polypyrrole films are readily formed on platinum surfaces by electro-oxidation of pyrrole in a wide variety of solvents. The films are produced in the oxidized state and consist of densely packed insoluble materials that strongly adhere to the metal and show metal-like conductivity [1b]. These films are of interest both as new electrode materials and because of the generality of the preparation procedure, which allows one to conveniently modify the polymer by simply derivatizing the monomer. For example, electropolymerization of N-methylpyrrole (in the presence of $BF_4^-$) generates films of poly-N-methylpyrrole in the oxidized form with a lower conductivity and higher oxidation potential than polypyrrole. These films consist of about 70% polymer (cationic) and 30% $BF_4$ anion, by weight, and the ratio of pyrrole units to $BF_4^-$ is $\approx$ 4:1. While the insoluble nature of these films has not allowed a precise determination of the chemical structure, available evidence indicates a linear $\alpha,\alpha'$-disubstituted pyrrole polymer, where the unsaturated polymer backbone is fully conjugated [see Structure I in Eq. (1)].



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Preliminary experiments using polypyrrole as an electrode [1a, c] reveal that such films are quite stable and could have wide application as nonmetallic electrode materials [2–4]. For these reasons we proceeded to test the electrode behavior of the polypyrrole-$BF_4$ electrode in acetonitrile ($CH_3CN$), using various reactions to better determine the limits of application. Three redox reactions

known to have reversible electrochemistry on a metal surface were used as test cases to determine whether the polymeric electrode has any influence on the thermodynamic redox potentials $E^0$ and the kinetics of the heterogeneous electron-transfer processes [see Eqs. (2)-(4)].

$$\text{ferrocene} \rightleftharpoons \text{ferricenium}^+ \quad (2)$$

$$\text{phenothiazene} \rightleftharpoons \text{phenothiazenium}^+ \quad (3)$$

$$\text{chloranil} \rightleftharpoons \text{chloranil}^- \quad (4)$$

Our results show that the redox reactions of solubilized electroactive species occur only at the electrode surface, with no evidence of either absorption or adsorption; the $E^0$ values are not different from those obtained on Pt surfaces. These reactions, however, became quasi-reversible when driven by the [Pt]polypyrrole electrode. The influence of the electrode on the electrochemical reversibility of the reactions was estimated semiquantitatively by applying Nicholson's treatment for measuring the heterogeneous standard rate constants $k_s$ for the simple quasi-reversible electrochemical reactions [5] of ferrocene, phenothiazine, and chloranil [see Eqs. (2)-(4)].

## Experimental section

Chloranil, ferrocene, and phenothiazine [6] were purified by recrystallization, whereas benzoquinone [6], toluenesulfonic acid [7], and glycine [7] were used without further purification. Electrolytic grade tetraethylammonium tetrafluoroborate ($Et_4NBF_4$) [8] was dried at 70°C before use. The pyrrole [6] was distilled and stored under nitrogen. Anhydrous acetonitrile ($CH_3CN$) was prepared by distillation under nitrogen from phosphorous pentoxide.

The polypyrrole-$BF_4$ films were prepared by electrooxidation of freshly distilled pyrrole in a tenth molar (0.1 M) solution of $Et_4NBF_4$ in 99:1 $CH_3CN$:$H_2O$. The films were grown in a one-compartment cell using a 0.5-$cm^2$ Pt working electrode, a gold wire counter electrode, and a sodium chloride standard calomel electrode (SSCE). The films were grown at a fixed potential of 0.9 V. The charge density-thickness relationship was approximately linear; with our electrode-cell conditions, 190 $\mu C/cm^2$ produces a 0.5-$\mu$m-thick film. The films (deposited on Pt surfaces) were subsequently washed with copious amounts of $CH_3CN$ and dried at 75°C for 3 h.

All measurements were performed in a one-compartment cell using $CH_3CN$ containing 0.1 M $Et_4NBF_4$ and with 70-80% *iR* compensation, and the diffusion coefficients were measured chronocoulometrically, as previously described [9a]. All the electrochemical equipment used in this study was designed and built in these laboratories [10].

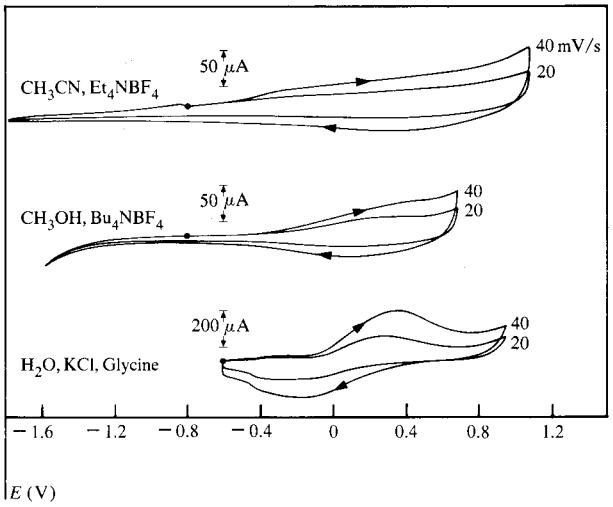



**Figure 1** Cyclic voltammogram of 0.5-$\mu$m polypyrrole-$BF_4$ film on platinum *vs.* a sodium standard calomel electrode (SSCE).

## Results and discussion

• *Studies in supporting electrolyte (no electroactive species in solution)*

The electrochemical analyses were performed using cyclic voltammetry, where the current response is plotted against the potential of the working electrode as that potential is varied linearly from some initial value $E_1$ to a second value $E_2$ and the back to the first value $E_1$.

The cyclic voltammogram produced when using a polypyrrole-$BF_4$ electrode in pure (blank) electrolyte is different from that observed with a Pt electrode. Only a broad background current is observed [1] with the thicker films (0.8-5 $\mu$m), while thinner films ($\approx$0.1 $\mu$m) give broad peaks near −0.2 V [9b] that are due to the oxidation and reduction reactions of the films [Eq. (1)]. Films of intermediate thickness (0.5-2 $\mu$m) produce cyclic voltammograms that are consistent with this (see Fig. 1).

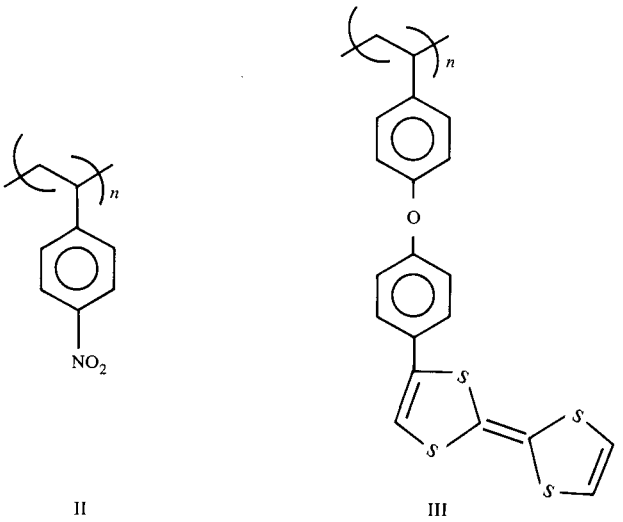
The electrochemical reaction of the thin polypyrrole films (0.1 $\mu$m) in supporting electrolyte was previously described [9b]. In this reaction, it is the extended $\pi$-system of the polymer that is oxidized and the film switches from the neutral to the oxidized state, which involves a $\pi$-delocalized radical cation structure [see Eq. (1)]. This reaction is accompanied by a visible color change, where the neutral film is yellow and the oxidized film is brown-black. The redox reaction is quite sensitive to the nature of the electrolyte since it involves movement of the anion (a counter ion to the incipient cationic polymer chain) in and out of the film.

The voltammograms of the thick films (0.5–2 $\mu$m) used in this study are sensitive to the treatment given to the film. For example, films prepared by electropolymerization of pyrrole, washed with $CH_3CN$, and dried in air at 75°C for 3 h produce voltammograms like those shown in Fig. 1. Films that are used directly without this heat treatment give a different voltammogram; the difference between the currents in the cathodic and anodic regions is much larger and broad peaks centered at −0.2 V appear. In fact, such films slowly transform to the stable heat-treated form.

The observed background currents are dependent on the potential region, the polarity of the solvent, and the sweep rate. For example, in the region anodic of (more positive in potential than) about −0.3 V, the current is approximately twice that observed in the region cathodic of (more negative in potential than) this value. The background current does not change in going to less polar solvents such as methylene chloride but does increase in protic solvents such as methanol. In aqueous solutions, the background current appears as a broad peak centered at −0.2 V. Finally, the background current scales linearly with sweep rate, indicative of charging in the surface-localized polymer film. There are no noticeable changes in the background current when other supporting electrolytes are used (tetra-n-propylammonium-$BF_4$, tetraethylammonium perchlorate, tetra-n-butylammonium perchlorate, tetra-n-butylammonium-$BF_4$, or toluenesulfonic acid). Considerably smaller background currents were observed when redox species were present in the solution (see next section). These species apparently act as charge-transport agents, allowing charge dissipation in the films. These background currents appear to be the only inconvenience involved in using these materials as electrodes in aprotic solvents since otherwise they function very well in the potential range of −2 to +1 V.

The redox reactions of polypyrrole become much slower and less efficient in the presence of oxygen and the effect is greater with thinner films. The effect of oxygen on the polymer is of interest and requires additional discussion. The redox reaction of the film shows only a very weak broad signal after the surface has been exposed to air. Electron scattering analyses (ESCA) of these surfaces reveal that exposure of the polymer produces oxygen-containing groups, *e.g.*, carbonyl groups [1c]. It is possible that formation of such groups along the polymer chain could generate a variety of nonequivalent electroactive polymer segments with differing $E^0$ values, thus producing what appears to be a broad background signal. Further studies of these films in the presence of oxygen are needed to better understand the mechanisms involved.

The films are quite stable and do not undergo additional change on standing in air or with continued use for several weeks. The polypyrrole electrodes generate reproducible voltammograms without an initial hysteresis or conditioning effect when used with blank electrolyte or with electrolyte containing electroactive species. This behavior apparently results from the improved electrical conductivity of the Pt-polymer system produced by the preparative procedure used. (This conductivity is dependent on such factors as electrical contact between the polymer chains and the Pt surface and the ready availability of solvent and electrolyte ions within the film.) Observations on other polymer-coated electrodes [11, 12] [polynitrostyrene (II) and tetrathiafulvalene-substituted polystyrene (III)] have indicated the presence of these

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conditioning and hysteresis effects; in fact, the initial scans have actually been used to charge the films. This occurs in the reduction of the linear polymer poly-p-nitrophenylstyrene (II) in dimethylformamide (DMF) [11] and in the oxidation of the tetrathiafulvalene moiety when attached to linear polystyrene (III) in $CH_3CN$ [12]. The different behavior of the polypyrrole electrodes is perhaps due to the fundamental chemical differences between polypyrrole and these other polymers, which contain saturated backbones in which the redox centers are isolated on pendant groups. In contrast, the backbone on the polypyrrole polymer is an extended $\pi$-system, which is itself electroactive.

- *Studies with dissolved redox species*

The large background currents observed do not interfere with the electrochemical measurements in aprotic solvents using cyclic voltammetry. As mentioned previously, the background currents are reduced in the presence of soluble redox species. See Fig. 2, which shows

cyclic voltammograms of several compounds [ferrocene, Eq. (2); phenothiazene, Eq. (3); chloranil, Eq. (4); and benzoquinone, Eq. (5)]

$$\text{benzoquinone} \rightleftharpoons \text{benzoquinone}^- \qquad (5)$$

known to undergo reversible electrochemical reactions on metal electrodes. It is known that these reactions are electrochemically reversible in the voltage range considered here (−1 to +1 V). Organic compounds with these general structures are reported to have $k_s$ values of 0.005–1 cm/s for reactions of the type shown in Eqs. (2)–(5) when metal electrodes are used [13, 14].

As can be seen in Table 1, the formal potentials $E^0$ for the redox reactions of the dissolved species are not significantly different from those measured with a Pt electrode. Peak heights vary linearly with the sweep rate $\nu^{1/2}$ from 10 to 100 mV/s, as expected for a diffusion-limited process, and the ratio of the peak heights $i_{pa}/i_{pc}$ is always close to unity. Both the 0.5- and 2-$\mu$m films provide the same $i/AC(\nu)^{1/2}$ values ($A$ is the electrode area), indicating that the signal amplitudes do not depend on film thickness. Furthermore, the values measured with these films, which have 0.5-cm$^2$ geometric surface areas, agree within 10% with the values measured on a 0.2-cm$^2$ surface of platinum. Thus, the electrode properties of the polymeric film do resemble those of a metal: the formal potentials are not influenced, there is no evidence of absorption or adsorption on the polymer surface (indicated by the fact that $i/AC(\nu)^{1/2}$ remains constant in the potential sweep range tested), and the geometric area is a fair estimate of the actual area. This latter point is important because it indicates that the polymer (film) electrode is not porous to the electroactive species, as has been the case with other polymer-coated and nonmetal electrodes [2, 3, 15].

Unlike the behavior of these reactions on platinum, the reactions appear quasi-reversible; *i.e.*, the separation between the peaks $E_{pa}$ and $E_{pc}$ ($\Delta E$) is greater than 59 mV and increases with sweep rate. Nicholson's treatment [5] for determining $k_s$ values was used to evaluate the effect of the electrode on the various reactions. In this treatment, values for the $\psi$ parameter are obtained from the $\Delta E$ values and plotted against $\nu^{-1/2}$. For a quasi-reversible reaction at 25°C, Nicholson's empirical equation relates $\psi$ to

$$0.09k_s(nD)^{-1/2}(\nu)^{-1/2}, \qquad (6)$$

where $n$ is one electron per molecule for these reactions and $D$ is the diffusion coefficient. The change in $\Delta E$ values can be seen in Fig. 3, which shows the cyclic voltammograms at various sweep rates for the ferrocene reaction [Eq. (2)]. The relationship in Eq. (6) can be written

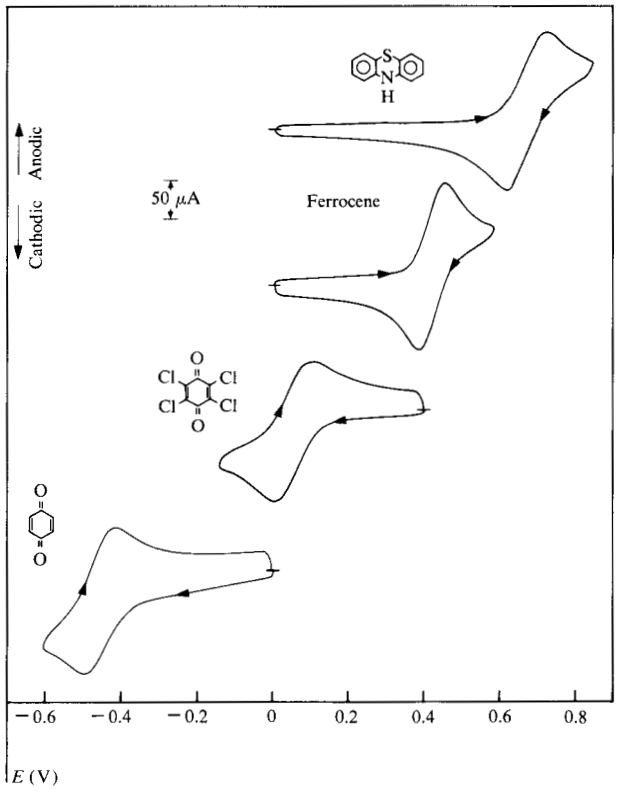


**Figure 2** Cyclic voltammograms measured using 0.5-$\mu$m polypyrrole-$BF_4$ film on platinum using 0.1 M $Et_4NBF_4$ in $CH_3CN$ *vs.* SSCE.

**Table 1** Summary of electrochemical data measured using a [Pt]polypyrrole-$BF_4$ electrode.[a]

| *Compound* | $E^0$ (mV) | $i_p/ACv^{1/2}$[b] | $i_{pa}/i_{pc}$ | $k_s$ (cm/s)[c] |
|---|---|---|---|---|
| Phenothiazine | 620 ( 620)[d] | 940 (1030)[d,e] | 1 | 0.008 |
| Ferrocene | 425 ( 440)[d] | 1250 (1410)[d,e] | 1 | 0.04 |
| Chloranil | 53 ( 55)[d] | 1150 (1200)[d,e] | 1 | 0.01 |
| Benzoquinone | −455 (−480)[d] | 1000 (1265)[d] | 1 | — |

[a]Polypyrrole-$BF_4$ film (0.5 cm$^2$) *vs.* SSCE in $CH_3CN$ containing 0.1 M $Et_4NBF_4$.
[b]A/(moles/cm$^3$)(V/s)$^{1/2}$; the same value is obtained with the 0.5- and 2-$\mu$m films.
[c]Average value with 0.5-$\mu$m film.
[d]Platinum electrode (0.2 cm$^2$).
[e]The numbers given in parentheses are from Ref. [9a].

for the redox reactions of ferrocene, phenothiazene, and chloranil. For these respective reactions $\psi = 17.1\,k_s(\nu)^{-1/2}$ ($D = 2.76 \times 10^{-5}$ cm$^2$/s); $25.5\,k_s(\nu)^{-1/2}$ ($1.38 \times 10^{-5}$); and $19.4\,k_s(\nu)^{-1/2}$ ($2.15 \times 10^{-5}$) [6a].

Data from these types of voltammograms were used in the Nicholson treatment and are listed in Table 2, along

**Table 2** Cyclic voltammogram data using a [Pt]polypyrrole-$BF_4$ electrode.[a]

| *Electrode* | $\nu$ (mV/s) | $E_{pa}$ (mV)[b] | $E_{pc}$ (mV)[b] | $\Delta E$ (mV) | $\psi$[c] | $k_s$ (cm/s) |
|---|---|---|---|---|---|---|
| *Ferrocene:* | | | | | | |
| Pt | 10–100 | 470 | 410 | 60 | — | — |
| Polypyrrole | | | | | | |
| 0.5 $\mu$m | 10 | 455 | 386 | 69 | 2.63 | 0.04 |
| | 20 | 460 | 385 | 75 | 1.66 | |
| | 30 | 467 | 382 | 82 | 1.11 | |
| | 40 | 470 | 380 | 90 | 0.80 | |
| | 50 | 475 | 378 | 97 | 0.63 | |
| | 80 | 485 | 372 | 113 | 0.42 | |
| | 100 | 490 | 370 | 120 | 0.36 | |
| 0.8 $\mu$m[d] | 20 | 450 ($E^o$) | | 90[d] | | |
| 2 $\mu$m | 10 | 480 | 409 | 71 | 2.08 | 0.01 |
| | 20 | 490 | 404 | 86 | 0.91 | |
| | 30 | 494 | 400 | 94 | 0.69 | |
| | 40 | 500 | 398 | 102 | 0.54 | |
| | 50 | 502 | 395 | 107 | 0.48 | |
| | 80 | 509 | 392 | 117 | 0.38 | |
| | 100 | 512 | 386 | 126 | 0.31 | |
| *Phenothiazine:* | | | | | | |
| Pt | 10–100 | 650 | 590 | 60 | — | — |
| Polypyrrole | | | | | | |
| 0.5 $\mu$m | 10 | 660 | 585 | 75 | 1.66 | 0.008 |
| | 20 | 662 | 580 | 82 | 1.11 | |
| | 30 | 666 | 574 | 92 | 0.74 | |
| | 40 | 670 | 570 | 100 | 0.57 | |
| | 50 | 674 | 565 | 109 | 0.45 | |
| | 80 | 680 | 556 | 124 | 0.33 | |
| | 100 | 690 | 553 | 137 | 0.26 | |
| 2 $\mu$m | 10 | 668 | 598 | 70 | 2.50 | 0.005 |
| | 20 | 670 | 595 | 75 | 1.66 | |
| | 30 | 672 | 593 | 79 | 1.25 | |
| | 40 | 675 | 590 | 85 | 0.91 | |
| | 50 | 677 | 588 | 89 | 0.83 | |
| | 80 | 678 | 585 | 94 | 0.69 | |
| | 100 | 680 | 585 | 95 | 0.66 | |
| *Chloranil:* | | | | | | |
| Pt | 10–100 | 85 | 25 | 60 | — | — |
| Polypyrrole | | | | | | |
| 0.5 $\mu$m | 10 | 90 | 15 | 75 | 1.66 | 0.01 |
| | 20 | 92 | 12 | 80 | 1.22 | |
| | 30 | 98 | 9 | 89 | 0.83 | |
| | 40 | 100 | 5 | 95 | 0.67 | |
| | 50 | 104 | 2 | 102 | 0.55 | |
| | 80 | 110 | 2 | 108 | 0.45 | |
| | 100 | 115 | 0 | 115 | 0.40 | |

[a] 0.1 M $Et_4NBF_4$ in $CH_3CN$.
[b] *vs.* SSCE.
[c] Ref. [5].
[d] Ref. [1a].

with the $k_s$ values. Rate constants obtained from several measurements agreed within 20%; the small differences between them could arise from differences in the *iR* compensation used. All of the reactions appear quasi-reversible, with reaction kinetics similar to those found using a metal electrode. It is unclear at this time whether the observed quasi-reversibility is due to the polymer itself or to the nature of the film surface [1c], which is known to have carbonyl functions (probably contained in pyrrolidone structures) [1c]. These carbonyl groups are not electroactive in this potential range, and as we have previously demonstrated, the presence of nonelectroactive

organic molecules on an electrode surface at submonolayer concentrations reduces the $k_s$ values by this order of magnitude [9a]. The presence of oxygen in the solutions did not produce any noticeable differences in the voltammograms for ferrocene or phenothiazine. It does show up in the voltammogram for chloranil, whose redox potential is closer to that of oxygen.

As may be anticipated from the above discussion, these film electrodes also influence irreversible reactions. For example, the proton reduction reaction of toluenesulfonic acid

$$H^+ \rightleftharpoons H_2 \tag{7}$$

produces a peak at −0.6 V (50 mV/s) on platinum when an acetonitrile solution containing $10^{-3}$ M toluenesulfonic acid plus 0.1 M $Et_4NBF_4$ is used. With the [Pt]polypyrrole-$BF_4$ electrode (0.5 $\mu$m), the peak, although small and broad, appears at −1.6 V. Likewise, the peak for the reduction of tropylium ion $C_7H_7^+$ in acetonitrile electrolyte solution [Eq. (8)]

$$C_7H_7^+ \rightleftharpoons C_7H_7^{\cdot} \tag{8}$$

shifts from −0.18 V (50 mV/s) on platinum to −0.26 V with the polymer film electrode. Even the irreversible oxidation of pyrrole [see Eq. (9)]

$$\text{pyrrole} \rightleftharpoons \text{pyrrole}^+ \tag{9}$$

in acetonitrile-electrolyte solution is influenced by the film. With the Pt electrode, the peak appears at +1.22 V (60 mV/s), while with the film electrode it appears at about +1.6 V. This latter value is found to vary with the solution concentration of pyrrole.

Completely different behavior was observed when a relatively long-lived Lewis base was produced. For example, the nitrobenzene redox reaction

$$\text{nitrobenzene} \rightleftharpoons \text{nitrobenzene}^- \tag{10}$$

becomes electrochemically irreversible on the [Pt]polypyrrole-$BF_4$ surface. While the formal potential is not changed from that on platinum, the peak separation is 230 mV at 100 mV/s and the peaks broaden and separate further with continued scanning.

Because of the sensitivity of these films to Lewis bases, they were next treated with amine bases to determine the generality of the behavior. Using the ferrocene reaction [Eq. (2)] to test the effect, it was observed that films immersed in acetonitrile solutions containing i-propylamine, n-hexylamine, and pyridine (primary amines) and rinsed before use produced cyclic voltammograms that had a greater $\Delta E$ and broader peaks for $E_{pa}$ and $E_{pc}$. From the resulting altered cyclic voltammograms, $k_s$ values approximately equal to $10^{-2}$ cm/s were calculated for the ferrocene reaction. These results suggest that Lewis bases may undergo nucleophilic reactions with the films.

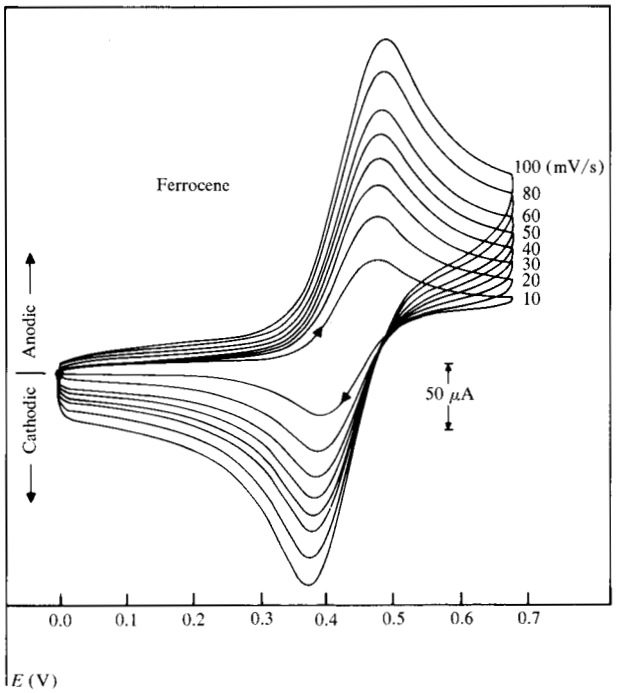


**Figure 3** Cyclic voltammogram of the ferrocene oxidation reaction measured using a 0.5-$\mu$m polypyrrole-$BF_4$ film on platinum *vs.* SSCE.

The electrochemical behavior described here in $CH_3CN$ is also observed in other conventional aprotic solvents such as butanone, methylene chloride, and benzonitrile. In aqueous solutions, however, the background currents make it difficult to perform a quantitative study by cyclic voltammetry. For studies in this solvent, techniques that reduce the effects of large background currents, *e.g.*, ac second harmonic voltammetry, become necessary [1a]. In spite of this consideration, a brief study with $K_4Fe(CN)_6$ in aqueous 0.1 M KCl plus 0.1 M glycine indicates that the films can be used in aqueous solutions. The peaks for the redox reactions of $K_4Fe(CN)_6$,

$$Fe(CN)_6^{2-} \rightleftharpoons Fe(CN)_6^{3-}, \tag{11}$$

appear superimposed on the background signal and are centered at +0.193 V (+0.195 V on Pt) with $\Delta E$ equal to 97 mV (72 mV on Pt) at 50 mV/s.

• *Other polymeric electrodes*

The performance of the polypyrrole film as an electrode compares well with other polymeric electrodes investi-

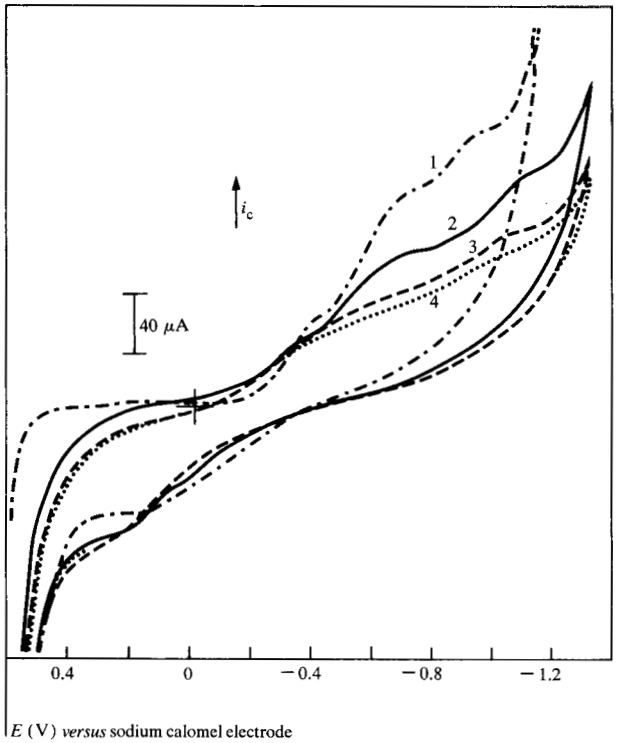


**Figure 4** Cyclic voltammogram in 0.5 M $NaClO_4$. Scan number is indicated on each curve. Scan rate 50 mV/s; from Ref. [2c].

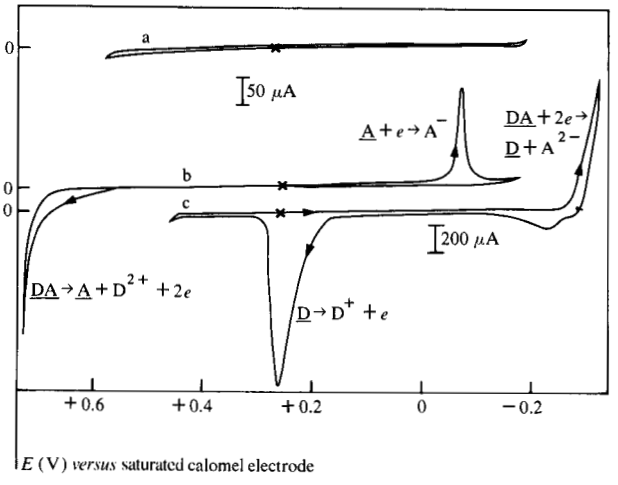


**Figure 5** Cyclic voltammogram of the TTF-TCNQ electrode in 1 M lithium acetate at a scan rate of 5 mV/s: (a) stable potential region; (b) oxidation of the electrode surface and resultant peak on reversal; (c) reduction of the electrode surface and resultant peak on reversal. In this figure A and D represent TCNQ and TTF, respectively. Insoluble or slightly soluble species are underlined. Scans start at potenital marked by ×. Figure is redrawn with permission from Fig. 1 of Ref. [3]. Copyright 1980 American Chemical Society.

gated. For example, crystals of the metallic conductor polysulfur nitride $(SN)_x$ were used as electrodes for electrochemical studies in aqueous solutions [2]. This material shows good electrode properties from −1.5 to +0.5 V. These potential limits are established by electrochemical decomposition of the polymer. The electrochemical behavior of this electrode was found to depend on cell conditions such as the pH, the nature of the electrolyte, the time elapsed since the initial scan, and the solvent. The $(SN)_x$ electrode displays anisotropic behavior that depends on whether the exposed electrode surface consists of fibral chain ends or sides of fiber bundles. The cyclic voltammograms (see Fig. 4) obtained for the electrochemical reduction of lead ion,

$$Pb^{2+} \rightleftharpoons Pb, \tag{12}$$

are different for these two surfaces. The reaction is more reversible on the surface containing the ends of the fibers. These results are consistent with the anisotropy of conductivity $\sigma$, which is about 300 times greater along the fiber chains than in a direction perpendicular to the fibers.

More recently, pressed pellets of $(SN)_x$ powder were tested as electrodes and found to show good electrode properties [2d]. These produced good cyclic voltammograms for the reactions of ferrocene and chloranil [Eqs. (2) and (4)]. With this electrode, the reactions show quasi-reversible behavior and $E^0$ values comparable to those observed on Pt. Again, the $i$-$\nu^{1/2}$ dependencies in the cyclic voltammograms are consistent with the reaction involving dissolved species and occurring on the surface of the polymer pellet.

Pressed disks [17–21 MPa (2500–3000 psi)] of the crystalline tetrathiafulvalene-tetracyanoquinodimethane complex (TTF-TCNQ) have also been used as electrodes for electrochemical studies in aqueous solutions [3]. This material is quite stable from −0.2 to +0.5 V, where TCNQ is reduced and TTF is oxidized, respectively. Thus, the potential range that can be investigated with this material is more limited than with polypyrrole or $(SN)_x$. With this electrode, reversible cyclic voltammograms are produced (see Fig. 5) for the redox reactions of several dissolved species known to have reversible behavior on Pt electrodes.

Thin films of metal-free, zinc, and nickel phthalocyanine prepared by evaporation of the corresponding phthalocyanines onto platinum surfaces represent another class of materials in electrochemical studies as semiconductor electrodes [4]. In aqueous solution, these electrodes show a flat background response between −1.0 and +0.8 V (see Fig. 6). The electrodes can be used to drive the reaction of dissolved redox couples and show

semiconductor behavior. In the case of metal-free phthalocyanine, only those reversible redox couples having oxidation potentials more positive than +0.65 V have reversible behavior; *e.g.*, $Fe(OP)_3^{2+}$ and $Fe(BP)_3^{2+}$ (where OP is 1,10-phenanthroline and BP is 2,2′-bipyridine). Couples having $E^0$ values between +0.25 and +0.65 V show quasi-reversible behavior, *e.g.*, $Fe(DMP)_3^{2+}$ and $Fe(TMP)_3^{2+}$ (where DMP is 4,7-dimethyl-1,10-phenanthroline and TMP is 3,4,7,8-tetramethyl-1,10-phenanthroline). Those having $E^0$ values more negative than 0.25 V are irreversible, *e.g.*, $Fe(CN)_6^{4-}$ and $Fe(EDTA)^{2-}$ (where EDTA is ethylenediaminetetraacetate). These electrodes are sensitive to light in the region cathodic of +0.35 V, where photoenhanced currents are observed upon irradiation.

A different electrode application for conducting polymers was recently reported using polyacetylene $(CH)_x$ [16]. This material was used as a photoelectrode in a photoelectrochemical cell (photogalvanic cell). The open fibrillar microstructure of this material makes it particularly suitable for this application because of its large exposed surface area (≈40 $m^2/g$). The photogalvanic cell contained sodium polysulfide and $(CH)_x$ as the photoelectrode and has an open-circuit voltage of about 0.3 V and a short-circuit current of about 40 $\mu A/cm^2$ under illumination of 1 sun (AM1, 100 $mW/cm^2$).

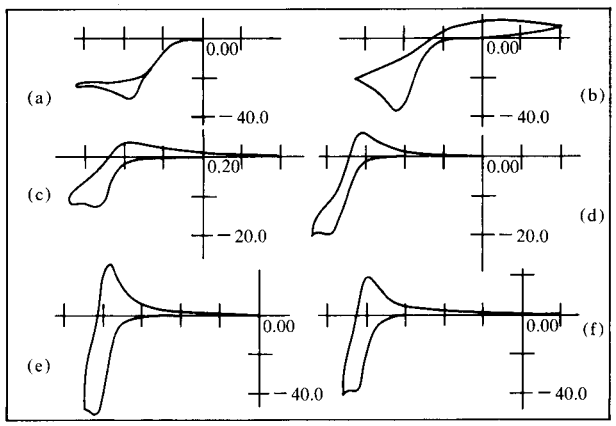


**Figure 6** Cyclic voltammograms of six iron (II) complexes on a 50-nm-thick metal-free phthalocyanine electrode. All scans start at the negative potential limit and sweep at 100 mV/s. Potentials are *vs.* a standard calomel electrode (SCE) and a unit on the potential (horizontal) axis is 0.2 V. The vertical axes are all located at zero potential and are current $i$ in $\mu A$. (a) $1.00 \times 10^{-3}$ M $Fe(EDTA)^{2-}$ in 1 M $KNO_3$. (b) $1.00 \times 10^{-3}$ M $Fe(CN)_6^{4-}$ in 1 M $KNO_3$. (c) $4.5 \times 10^{-4}$ M $Fe(TMP)_3^{2+}$ in 0.5 M $K_2SO_4$. (d) $5.5 \times 10^{-4}$ M $Fe(DMP)_3^{2+}$ in 0.5 M $K_2SO_4$. (e) $1.00 \times 10^{-3}$ M $Fe(BP)_3^{2+}$ in 1 M $KNO_3$. (f) $1.00 \times 10^{-3}$ M $Fe(OP)_3^{2+}$ in 1 M $KNO_3$. Figure is redrawn with permission from Fig. 3 of Ref. [4]. Copyright 1980 American Chemical Society.

## Conclusion

Several laboratories are developing applications for conducting organic materials. Many of the applications will likely make use of the special characteristics of these new polymeric electrode materials. In this regard, the [Pt]polypyrrole films may find useful applications as nonmetallic electrodes, especially in view of such attractive features as their stability while in use in a wide variety of solvents or during storage and their rapid electron-transfer kinetics at the surface-solution interfaces. Furthermore, the electrode properties of these materials can be varied, in principle, by modifying the chemical structure of the polymeric films.

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