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## ORIGINAL PAPER

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# Electrochemistry and electrocatalytic activity of polypyrrole/ferrocyanide films on a glassy carbon electrode

**Abstract** Functionalized polypyrrole films were prepared by incorporation of $Fe(CN)_6^{3-}$ as doping anion during the electropolymerization of pyrrole at a glassy carbon electrode from aqueous solution. The electrochemical behavior of the $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ redox couple in polypyrrole was studied by cyclic voltammetry. An obvious surface redox reaction was observed and dependence of this reaction on the solution pH was illustrated. The electrocatalytic ability of polypyrrole film with ferrocyanide incorporated was demonstrated by oxidation of ascorbic acid at the optimized pH of 4 in a glycine buffer. The catalytic effect for mediated oxidation of ascorbic acid was 300 mV and the bimolecular rate constant determined for surface coverage of $4.5 \times 10^{-8}$ M cm$^{-2}$ using rotating disk electrode voltammetry was 86 M$^{-1}$ s$^{-1}$. Furthermore, the catalytic oxidation current was linearly dependent on ascorbic acid concentration in the range $5 \times 10^{-4}$–$1.6 \times 10^{-2}$ M with a correlation coefficient of 0.996. The plot of $i_p$ versus $v^{1/2}$ confirms the diffusion nature of the peak current $i_p$.

**Key words** Polypyrrole · Ferrocyanide · Modified electrode · Ascorbic acid · Electrocatalysis

## Introduction

Conducting polymers such as polypyrrole, polythiophene, and polyaniline prepared by an electropolymerization procedure have received much attention since 1979 when Diaz et al. [1] synthesized polypyrrole on the surface of an electrode. These polymers were used as modifiers for the construction of chemically modified electrodes which find applications in many fields such as biosensors [2], electrocatalysis [3], ion-selective electrodes [4], and electrochemically controlled release devices [5].

Polypyrrole has received most attention owing to its convenience of preparation, good stability, and appropriate range of applications. In order to obtain films with the expected properties, functionalized polypyrrole films are prepared. One method is to attach a functional group to the pyrrole ring by a covalent bond and then polymerize electrochemically [6, 7]. Sometimes these polymers do not display the desired electronic conductivity of polypyrrole [7]. In addition, it appears that steric hindrance and cross-linking effects prevent growth of the polymerization of species with just one pyrrole group. An alternative strategy is the preparation of polypyrrole films with anion-exchange properties by grafting cationic groups on to the polymer and binding an anionic functional group to the polymer electrostatically [8–11].

The ability of anions to incorporate into the polypyrrole matrix as doping ions provides a fast and simple method of preparing functional polypyrrole films [12–21]. Ferrocyanide and some other anions have generally been incorporated into polypyrrole films during the polymerization process of pyrrole [13, 22, 23]. Mao and Picup [11] believe that the method is not effective for ferrocyanide, suggesting that polypyrrole has a low permeability even to highly charged anions such as $Fe(CN)_6^{4-}$ and $Ru(CN)_6^{3-}$. Further, the anions are lost from the film during reduction since the polypyrrole becomes neutral and will no longer bind anions. However, we anticipate that the concentration of $Fe(CN)_6^{4-}$ incorporated in polypyrrole during the electropolymerization of pyrrole in an aqueous solution of $K_4Fe(CN)_6$, pyrrole, and $LiClO_4$ with optimized concentration will be high enough to exert its own mediator activity. Further, its mediator activity may be used in aqueous solution in the potential range 0–1.3 V where polypyrrole is always in doped form and the ferrocyanide anions are not lost from the film. To our knowledge there is no report on the study of the electrochemical behavior and specially electrocatalytic activity of

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polypyrrole/ferrocyanide films. In this context we report in this paper the electrochemical behavior and electrocatalytic ability of polypyrrole/ferrocyanide on a glassy carbon (GC) electrode. The catalytic oxidation of ascorbic acid, receiving much attention during the past decade, was demonstrated as a typical example of the application of the electrode and the kinetic bimolecular rate constant $k_{app}$ was determined by rotating disk electrode (RDE) voltammetry. Here we refer to the polypyrrole film with ferricyanide incorporated as PPy/FCN.

## Experimental

### Reagents and chemicals

The solvent used for electropolymerization and electrochemical studies was doubly distilled water. Pyrrole (Merck) was distilled prior to use. Lithium perchlorate (Fluka) was used as supporting electrolyte. All other reagents were of analytical grade. The solutions were bubbled with $N_2$ gas (99.999) and kept under a nitrogen atmosphere during the electrochemical experiments.

### Instrumentation

Polymerization and other electrochemical experiments were carried out using an EG & G potentiostat/galvanostat model 273 coupled with an IBM PC and connected to an Epson printer, model FX-850. A conventional three-electrode cell with a calomel electrode as reference electrode, a platinum wire as auxiliary electrode, and a GC disk as working electrode ($A = 0.126$ cm$^2$ from EG & G) were used. A pH meter model 654 (Metrohm) was used to adjust the pH of the buffer solutions.

### Preparation of PPy/FCN films

The PPy/FCN films were prepared in the following way. The working electrode was polished with alumina powder (0.05 μm), then washed with water and acetone in turn, and immersed in aqueous solution containing 0.05 M pyrrole, 0.01 M K$_4$[Fe(CN)$_6$], and 0.05 M LiClO$_4$ as electrolyte. The electropolymerization was performed potentiostatically by holding the potential of the working electrode at 0.7 V vs. the reference electrode for a required time. The charge passed was determined by chronoamperometry and the thickness of the film was obtained according to Diaz and Castillo's method [24]. The film was washed by doubly distilled water before being used. The potential of the PPy/FCN-coated GC electrode was scanned for two cycles over range −0.8 to 1.3 V and then held at 1.3 V for 30 s in 0.01 M K$_4$[Fe(CN)$_6$] with 0.05 M LiClO$_4$ as supporting electrolyte.

## Results and discussion

### Cyclic voltammetry of PPy/FCN film

Preliminary experiments showed that the oxidation of Fe(CN)$_6^{4-}$ occurs at a potential about 400 mV less positive than the oxidation potential of pyrrole on a GC electrode. Thus during the electropolymerization of pyrrole at the conditions mentioned above, Fe(CN)$_6^{4-}$

was oxidized to Fe(CN)$_6^{3-}$ which was incorporated in the polypyrrole. The experimental investigations showed that well-defined and reproducible cyclic voltammograms were obtained when the film (1) is prepared in 0.01 M Fe(CN)$_6^{4-}$, 0.05 M pyrrole, and 0.05 M LiClO$_4$ and (2) conditioned by two cycles scanning of the coated GC electrode potential over the range −0.8 to 1.3 V and then holding at 1.3 V for 30 s. The latter requirements could be due to morphological changes in the film, allowing improved electrolyte penetration. Figure 1a shows the cyclic voltammogram of PPy/FCN film in 0.5 M glycine buffer aqueous solution (pH 4) with 0.1 M LiClO$_4$ as supporting electrolyte. As seen in this figure, the voltammogram exhibits two nearly symmetric anodic and cathodic peaks related to the redox system Fe(CN)$_6^{3-}$/Fe(CN)$_6^{4-}$ in PPy. The comparison with the cyclic voltammogram of Fe(CN)$_6^{3-}$/Fe(CN)$_6^{4-}$ in aqueous solution, shown in Fig. 1b, indicates clearly that the peak separation potential ($E_{pa} - E_{pc} = \Delta E_p$) decreased from 80 to 35 mV with the same formal potential when Fe(CN)$_6^{4-}$ was incorporated into PPy (Fig. 1a). Such symmetry is expected for surface film oxidation. In addition, at low scan rates (5–20 mV s$^{-1}$) the peak current of the cyclic voltammograms (Fig. 2A) was linearly dependent on the scan rate, with a correlation coefficient of 0.999, while for scan rates higher than 20 mV s$^{-1}$ its value decreased to 0.939, where $i_p$ becomes proportional to $v^{1/2}$ and the voltammograms exhibit a shape indicative of diffusion control (Fig. 2B). These characteristics indicate that the charge transport within the polypyrrole is fast compared with the time scale of the potential scan (5–20 mV s$^{-1}$).
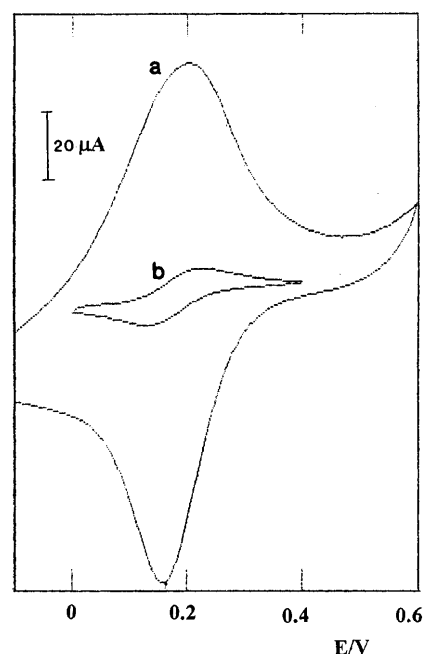


**Fig. 1** Cyclic voltammograms of *a* PPy/FCN film (thickness of 0.28 μm) on the GC electrode, *b* $2 \times 10^{-3}$ M FCN solution at the bare GC electrode. Electrolyte solution: 0.5 M glycine buffer (pH 4) and 0.1 M LiClO$_4$. Scan rate: 10 mV s$^{-1}$
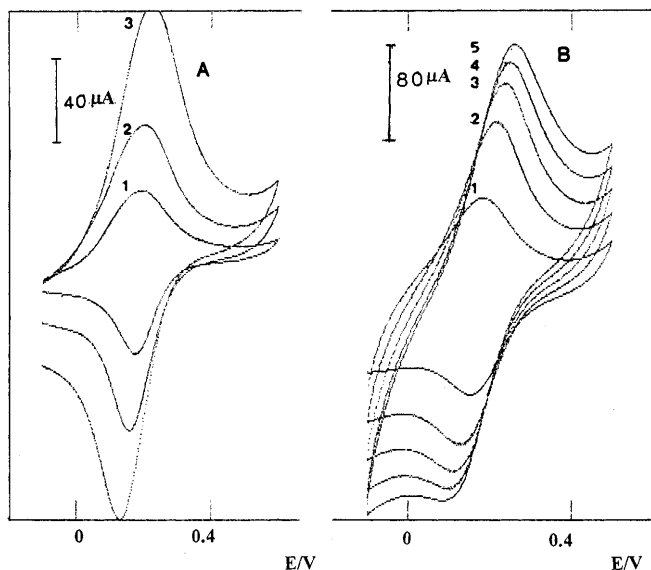
**Fig. 2** Cyclic voltammograms of PPy/FCN at pH 4 in 0.5 M glycine buffer, 0.1 M LiClO$_4$ at two ranges of scan rate: **A** 5, 10, and 20 mV s$^{-1}$, **B** from 20 to 100 in 20 mV s$^{-1}$ intervals. Polymer thickness: 0.28 μm

## Influence of pH on the film behavior

The electrochemical response of ferrocyanide in aqueous solutions is pH dependent because $H_2Fe(CN)_6^{2-}$ is a di-acid with two acidic constants: $pK_{a1} = 2.22$ and $pK_{a2} = 4.17$. Therefore the redox waves of $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ recorded for a $10^{-3}$ M solution of $Fe(CN)_6^{4-}$ shifted positively as the pH of the solution decreased from 4.2. Similar results were observed for PPy/FCN films. Figure 3 shows the voltammograms of PPy/FCN film with a thickness of 0.225 μm in solution with different pH values. From these voltammograms at a pH value lower than 2.2 an $E°$ versus pH graph was obtained which showed that the $E°$ of the redox couple $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ depends linearly on the pH of the solution with a slope of about 0.115 V, very close to the theoretical value of $2 \times 0.059$ V at 25 °C. For a pH value greater than 4.7 the $E°$ remains approximately constant.

The dependence of the redox couple $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ on the pH of the solution is an important factor affecting its catalytic activity when it is used as a mediator both via homogeneous and heterogeneous media. This behavior shows why greater attention must be paid to the optimization of the pH of the catalytic reaction media.

## Catalytic oxidation of ascorbic acid

It has been previously shown that $Fe(CN)_6^{4-}$ is able to electrocatalyze the oxidation of ascorbic acid both via a homogeneous process when ferrocyanide is present in dissolved form [25] and heterogeneously when electrostatically attached to an alkylamine-siloxane polymer film on a Pt electrode [26] or a 5% poly(4-vinylpyridine)
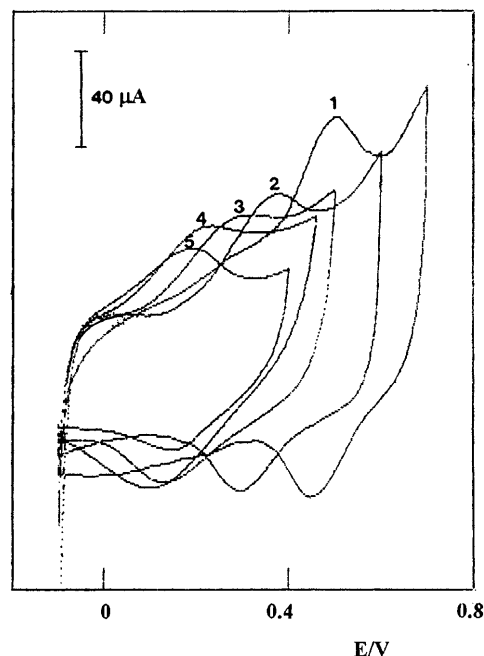


**Fig. 3** Cyclic voltammograms of PPy/FCN film in buffer solutions with different pH values at a scan rate of 20 mV s$^{-1}$: *1* 2 M HCl (pH −0.3), *2* 0.1 M HCl (pH 1), *3* 0.5 M glycine (pH 3.2), *4* 0.5 M acetate (pH 5.2), and *5* 0.5 M phosphate (pH 7.2). Polymer thickness: 0.225 μm

carbon paste electrode [27] or bent electrostatically on to a poly[1-methyl-3-(pyrrolylmethyl)pyridinium] coated Pt electrode [11]. Accordingly, in this paper we report the ability of $Fe(CN)_6^{4-}$ incorporated into PPy to catalyze ascorbic acid oxidation. In a separate experiment we found that the electrocatalytic effect of $Fe(CN)_6^{4-}$ in dissolved form, for ascorbic acid oxidation on a GC electrode, is maximum at pH 4 in a glycine buffer.

Cyclic voltammograms obtained for a 5 mM ascorbic acid solution on the bare and PPy/FCN-coated GC electrodes with a surface coverage of $5 \times 10^{-8}$ M cm$^{-2}$ ferrocyanide are shown in Fig. 4. The oxidation of ascorbic acid on the bare GC electrode occurred irreversibly with a peak potential of 0.5 V vs. SCE under the solution conditions (curve a), while its oxidation peak on the PPy/FCN-coated GC electrode appeared at 0.2 V, the oxidation potential of $Fe(CN)_6^{4-}$ (curve c). Therefore the ferrocyanide catalytic effect (CE) is 300 mV, which is 80 mV greater than the CE value when ferrocyanide is present in dissolved form in solution (curve d). As seen in curve c, the anodic current was increased over that ordinarily observed just for the incorporated $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ couple (curve b), while the corresponding cathodic peak was substantially depressed on the reverse scan. The anodic peak current observed for the modified GC electrode was linearly dependent on the ascorbic acid concentration in the range $5 \times 10^{-4}$–$1.6 \times 10^{-2}$ M (Fig. 5) and the plot of $i_p$ versus $v^{1/2}$ is linear, suggesting that the peak current is diffusion controlled. This behavior is typical of that expected for electrocatalysis, and the following EC steps are involved:
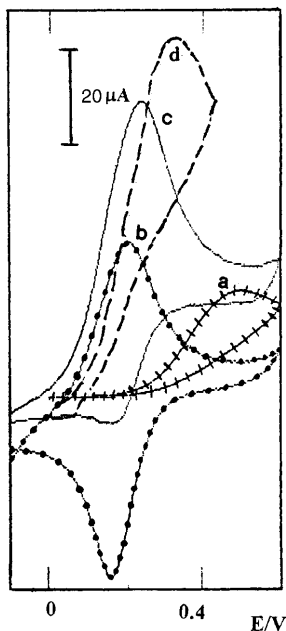
**Fig. 4** Cyclic voltammograms of *a* bare GC electrode in $5 \times 10^{-3}$ M ascorbic acid, *b* PPy/FCN-coated GC electrode in glycine buffer only (pH 4), *c* same electrode as *b* with addition of $5 \times 10^{-3}$ M ascorbic acid, *d* same electrode as *a* with addition of $2 \times 10^{-3}$ M $Fe(CN)_6^{4-}$. Surface coverage: $4.68 \times 10^{-8}$ mol cm$^{-2}$; scan rate: 5 mV s$^{-1}$
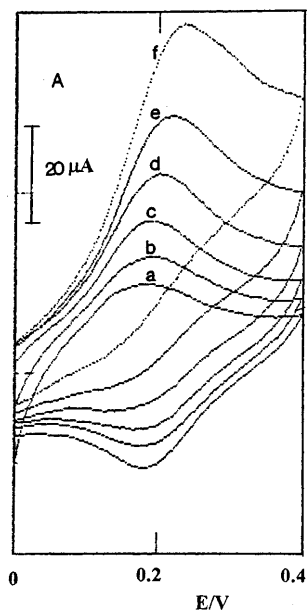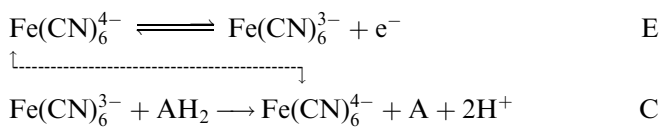


**Fig. 5** Cyclic voltammograms of ascorbic acid oxidation at a PPy/FCN-modified electrode at various concentrations: *a* 0.5, *b* 1, *c* 2, *d* 4, *e* 8, and *f* 16 mM. Solution conditions: 0.5 M glycine buffer (pH 4) with 0.1 M LiClO$_4$. Scan rate: 10 mV s$^{-1}$

$$Fe(CN)_6^{4-} \rightleftharpoons Fe(CN)_6^{3-} + e^- \qquad\qquad E$$

$$Fe(CN)_6^{3-} + AH_2 \longrightarrow Fe(CN)_6^{4-} + A + 2H^+ \qquad C$$

where AH$_2$ and A represent ascorbic acid and dehydroascorbic acid, respectively.

*Kinetic investigations*

Subsequently, in order to evaluate the kinetics involved in the catalytic sequence, the RDE approach previously described by Oyama and Anson [28] and Kuo and Murray [26] was employed. In this approach, steady-state current measurements are made at constant potential for a given chemically modified electrode surface coverage and ascorbic acid concentration as a function of the electrode rotation rate. The observed current is related to the electrode rotation rate $\omega$ and bimolecular rate constant $k_{app}$ by the Koutecky-Levich equation:

$$I^{-1} = (nFAk_{app}\Gamma_f C)^{-1} + (0.62nFAD^{2/3}v^{-1/6}\omega^{1/2}C)^{-1}$$

where $\Gamma_f$ refers to the electrode surface coverage of FCN calculated by $Q/nFA$ ($Q$ was determined from the area under the anodic cyclic voltammograms of the PPy/FCN-modified electrode), $C$ is the solute concentration, and the other terms have their usual meanings. Thus a plot of $\bar{i}^{-1}$ versus $\omega^{-1/2}$ should provide a $y$-intercept which describes the current limited by the rate of the electrocatalytic reaction and from which $k_{app}$ can be directly obtained. The experimental investigations showed that an evident and repeating catalytic effect of $Fe(CN)_6^{4-}$ in polypyrrole film was observed when the surface coverage for $Fe(CN)_6^{4-}$ was increased up to approximately $5 \times 10^{-8}$ mol cm$^{-2}$. Figure 6A shows a typical Levich plot obtained from RDE voltammograms for a PPy/FCN-coated GC electrode with a surface coverage of $4.68 \times 10^{-8}$ mol cm$^{-2}$ and ascorbic acid concentration of $5 \times 10^{-3}$ M, which exhibited the expected activation-limited plateau at higher rotation rates. This plot was constructed using the measured currents at 0.24 V vs. SCE, the peak potential of the electrocatalyzed ascorbic acid oxidation. The corresponding reciprocal plot shown in Fig. 6B is linear ($r = 0.999$). The value of the rate constant $k_{app}$ measured in the conditions mentioned above was 86 M$^{-1}$ s$^{-1}$, which is comparable with that obtained for $Fe(CN)_6^{4-}$ bonded to polyvinylpyridine and used in a carbon paste electrode [27].

Stability of the modified electrode

The electrode stored in air at room temperature for several month yields a good cyclic voltammetric surface peak, showing a negligible loss in surface material. Our experimental investigation indicates that PPy/FCN film in the buffered electrolyte solution is relatively stable and the peak height and peak potential of the surface immobilized film by cycling of the electrode potential over the range 0.0–1.3 V remains nearly unchanged. The amount of degradation after 20 cycles was less than 10%. Furthermore, the reproducibility of the electro-
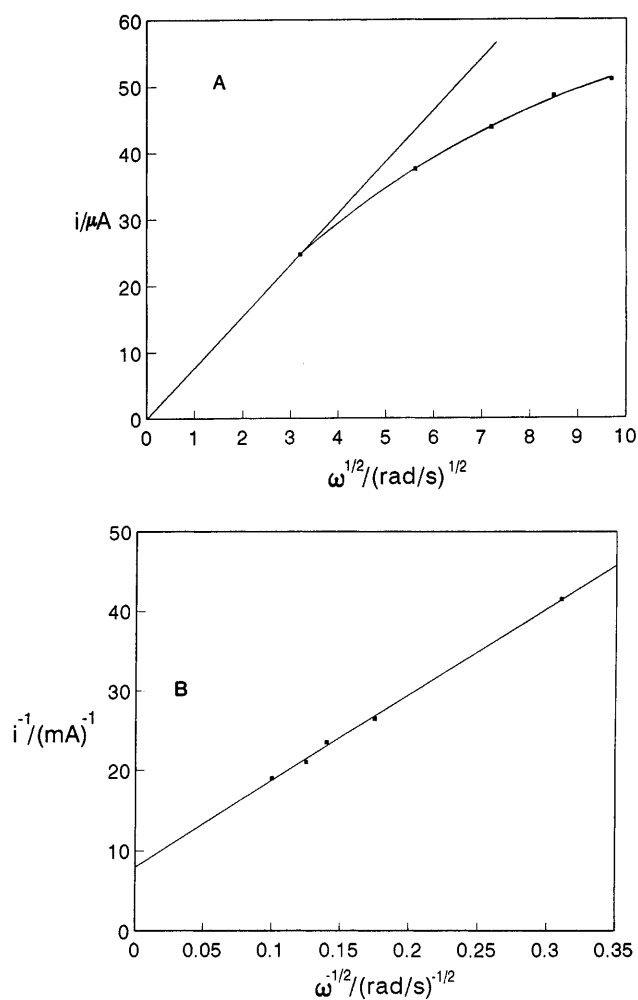
Fig. 6 A Levich and B Koutecky-Levich plots for a PPy/FCN-modified GC electrode in $5 \times 10^{-3}$ M ascorbic acid solution (pH 4). Surface coverage: $4.68 \times 10^{-8}$ mol cm$^{-2}$

−0.8 and 1.3 V to reach the steady state and hold of the electrode potential at 1.3 V vs. SCE for 30 s in order to minimize the charging current of the PPy matrix is required. The redox reaction of $Fe(CN)_6^{3-}/Fe(CN)_6^{3-}$ in the polymer matrix shows reversible behavior at a low scan rate, which is pH dependent. The prepared PPy/FCN on a GC electrode is capable of catalyzing the electrochemical oxidation of ascorbic acid as a typical substrate in aqueous media with an optimized pH value using glycine buffer. The kinetic value of bimolecular rate constant $k_{app}$ can be determined by RDE voltammetry. The PPy/FCN-modified GC electrode is suitable for the voltammetric determination of ascorbic acid in aqueous solutions.

catalytic effect of the modified electrode was examined by repetitive recording of the cyclic voltammograms in ascorbic acid solution. A small decrease in height of the cyclic voltammograms was observed; however, the modified electrodes exert their own catalytic activity for a relatively long time.

## Conclusion

The anodic polymerization of pyrrole at controlled potential at a GC electrode in 0.05 M pyrrole, 0.01 M $K_4[Fe(CN)_6]$, and 0.05 M $LiClO_4$ aqueous solution gave a polypyrrole film which incorporated $Fe(CN)_6^{4-}$ with a concentration in the film high enough to exert its own mediator activity. Two cycles of potential scan between

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