

M.H. Pournaghi-Azar · R. Ojani

Attempt to incorporate ferrocenecarboxylic acid into polypyrrole during the electropolymerization of pyrrole in chloroform: its application to the electrocatalytic oxidation of ascorbic acid

Received: 30 July 1998 / Accepted: 3 March 1999

Abstract In this work, polypyrrole films with ferrocenecarboxylic acid incorporated (PPy/FCA) were prepared on a glassy carbon (GC) electrode in chloroform as an aprotic solvent with low dielectric constant, convenient for the preparation of the films by a precipitation mechanism. The electrochemical behaviour of the PPy/FCA-coated GC electrode was studied by cyclic voltammetry in aqueous solution with low pH. The results obtained show that the electrochemical response of FCA incorporated in polypyrrole is consistent with a reversible surface oxidation. An obvious electrocatalytic effect of PPy/FCA on the oxidation of ascorbic acid is observed in aqueous solution.

Key words Polypyrrole · Ferrocenecarboxylic acid · Electrocatalysis · Ascorbic acid · Chloroform

Introduction

Polypyrrole (PPy) has received much attention owing to its convenience of preparation, good stability and appropriate range of applications [1–5]. In order to obtain films with the expected properties, functionalized polypyrrole films must be prepared [6–24]. One method is to attach a functional group to the pyrrole ring by a covalent bond and then polymerize electrochemically [6, 14]. The ability of anions to incorporate into the polypyrrole matrix as counter-anions provides a fast and convenient method of preparing functional polypyrrole films [15–23]. We believe that ferrocenecarboxylate anions cannot be incorporated into polypyrrole film as doping ions during the electropolymerization of pyrrole in water, because owing to the electropolymerization potential of

pyrrole, ferrocenecarboxylate is oxidized to a neutral ferricinium species, which is no longer an anion.

We describe in this paper an alternative procedure for the incorporation of ferrocenecarboxylic acid (FCA) into polypyrrole. The method involves the electropolymerization of pyrrole in the presence of FCA in chloroform, because chloroform is (1) an aprotic solvent, convenient for electropolymerizations which proceed via a radical mechanism [25], and (2) a solvent with a low dielectric constant suitable for the incorporation of the less soluble ferriciniumcarboxylic acid cation FCA^+ formed at the oxidation potential of pyrrole via a precipitation mechanism. In addition, we report the electrochemical behaviour and electrocatalytic activity of polypyrrole/ferrocenecarboxylic acid (PPy/FCA) films prepared in chloroform and water in order to compare and subsequently confirm the assumed incorporation mechanism. The electrocatalytic activity of the PPy/FCA films for the oxidation of ascorbic acid as a typical example is also reported here.

Experimental

Reagents and chemicals

The solvent for electropolymerization studies was chloroform GR, used without further purification. Pyrrole was distilled prior to use. Tetrabutylammonium salts of perchlorate (TBAP), tetrafluoroborate (TBATFB), benzoate (TBABz), hydrogensulfate (TBAHS), tosylate (TBAT) and iodide (TBAI) from Aldrich were used as supporting electrolytes in chloroform. Lithium perchlorate was used as supporting electrolyte in bidistilled water. The FCA was used without further purification. The solutions were bubbled with N_2 gas (99.999%) and kept under a N_2 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

M.H. Pournaghi-Azar (✉) · R. Ojani
Electroanalytical Chemistry Laboratory,
Faculty of Chemistry,
University of Tabriz, Tabriz, Iran

FX-850. A conventional three-electrode cell with a calomel electrode as the reference electrode, a platinum wire as the auxiliary electrode and a glassy carbon (GC) disk as the working electrode ($A = 0.126 \text{ cm}^2$ from EG & G) were used. The reference electrode in chloroform was Ag/AgI (satd); 0.05 M TBAI and 0.5 M TBAP in chloroform, prepared in a separate compartment with a dense ceramic plug in the bottom, were used.

Preparation of PPy and PPy/FCA films

The PPy/FCA films were prepared under the following conditions. The working electrode was polished with alumina powder (0.05 μm), then washed with water and acetone in turn and immersed in a chloroform solution containing 0.05 M pyrrole, 0.1 M FCA and 0.25 M of supporting electrolyte. The electropolymerization was performed potentiostatically by holding the potential of the working electrode at 1.2 V versus 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 [26]. The film was washed with bidistilled water before being used. For electropolymerization of pyrrole in water we used an aqueous solution containing 0.01 M FCA, 0.05 M pyrrole and 0.1 M LiClO_4 , with an adjusted pH of 6.5. The potential of the PPy/FCA-coated glassy carbon electrode was scanned for two cycles over the range -0.8 to 1.3 V in a 0.1 M aqueous solution of LiClO_4 . The PPy films were prepared under similar conditions in the absence of FCA.

Results and discussion

Electrochemical behaviour of PPy/FCA films

Prepared in chloroform

In Fig. 1A the cyclic voltammograms recorded for the PPy/FCA films in 0.5 M aqueous glycine buffer solution (pH 4) and 0.1 M LiClO_4 exhibit a less prominent pair of peaks, confused with the charging current of the film. With thicker coatings of polypyrrole the non-prominency of the peaks remained unchanged. The experimental investigations showed that a well-defined and reproducible cyclic voltammogram was obtained after scanning of the potential of PPy/FCA-coated GC electrode over the potential range -0.8 to 1.3 V for two cycles (Fig. 1B). This requirement could be attributed to the morphological change in the film, allowing improved electrolyte penetration. As seen in Fig. 1B, the voltammograms exhibit two anodic and cathodic peaks with peak potentials of 0.37 and 0.21 V, respectively. Note that a shoulder with a potential of 0.16 V preceded the anodic peak, which may be attributed to the doping of pyrrole. The comparison with the cyclic voltammograms of a PPy-coated GC electrode prepared in chloroform (Fig. 2A) and dissolved FCA (Fig. 2B) in 0.1 M LiClO_4 aqueous solution indicate clearly that the two nearly symmetric anodic and cathodic peaks relate to the redox system FCA^+/FCA in PPy. The peak separation potential ($\Delta E = E_p^a - E_p^c$) for a very low scan rate of 5 mV s^{-1} was about 42 mV. In addition, at potential scan rates over the ranges 5 – 320 mV s^{-1} the peak current was linearly dependent on the rate v , with a corre-

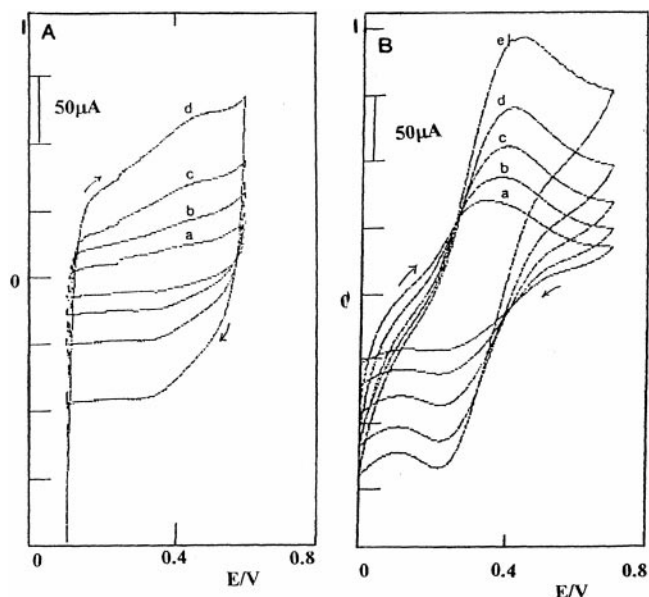


Fig. 1 Cyclic voltammograms of PPy/FCA at pH 4 in 0.5 M glycine buffer + 0.1 M LiClO_4 at a scan rate of *a* 20, *b* 40, *c* 80, *d* 160 and *e* 320 mV s^{-1} , **A** before conditioning of the film, **B** after conditioning of the film by two cycles scanning of the electrode potential between -0.8 and 1.2 V; polymer thickness 0.28 μm

lation coefficient of 0.999 (Fig. 3). These characteristics are expected for surface film oxidation and indicate that the charge transport within the polypyrrole is fast compared with the timescale of the potential scan rate of about 5 – 300 mV s^{-1} . Continuous cycling of coated electrodes between -0.8 and 1.3 V produced no diminution in the FCA^+/FCA redox peak currents. This suggested that the FCA^+ cation was not replaced and released by supporting electrolyte ions, and even further penetration of perchlorate anions stabilised the FCA^+ cations in the PPy films by formation of insoluble $\text{FCA}^+\text{ClO}_4^-$ ion pairs.

Effect of supporting electrolyte. The electrochemical activity of a PPy/FCA-coated GC electrode prepared in chloroform solutions of TBAP, TBATFB, TBABz, TBAHS and TBAT was investigated by cyclic voltammetry. The well-defined and reproducible cyclic voltammogram with the lowest charging current, and minimum peak separation potential $\Delta E = E_p^a - E_p^c$, was obtained in the case of TBAP. Note that in the case of TBABz the polymerization does not occur, owing to the basicity of the benzoate ion preventing the growth of polymer via a cation radical mechanism.

Prepared in water

The cyclic voltammograms of PPy/FCA films prepared in water under experimental conditions quite similar to those in chloroform are shown in Fig. 4 for potential scan rates of 10 – 40 mV s^{-1} . As seen in this figure, the

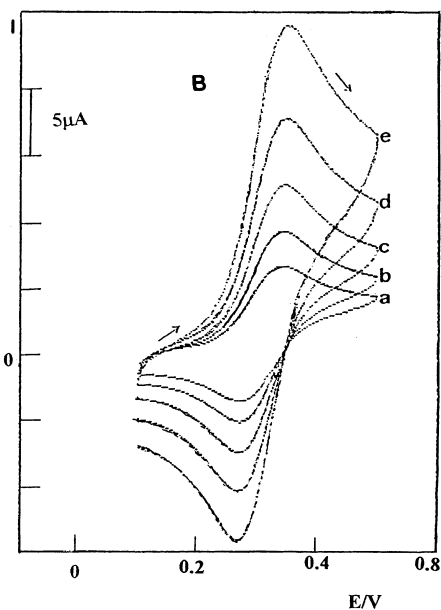
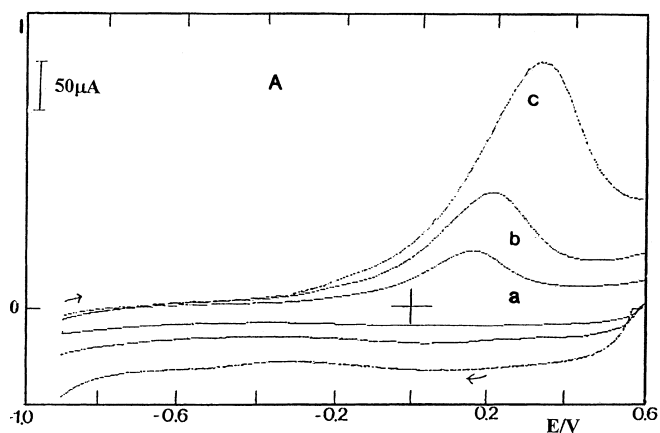


Fig. 2 Cyclic voltammograms of **A** PPy-coated GC electrode at scan rates of *a* 40, *b* 100 and *c* 200 mV s^{-1} and **B** dissolved FCA at a bare GC electrode at scan rates of *a* 20, *b* 40, *c* 100, *d* 200 and *e* 400 mV s^{-1} at pH 4 in 0.5 M glycine buffer + 0.1 M LiClO_4

quantity of FCA incorporated into the polymer was much smaller, compared with that obtained in chloroform (see Fig. 1B). The peak currents remained unchanged or even decreased with increase of the scan rate, owing to the release of FCA for repetitive scanning of the electrode potential. These observations suggest that the FCA^+ species formed in aqueous solution is very soluble in water and cannot be trapped in PPy films either as a counter-ion or as insoluble ion pairs during the electropolymerization of pyrrole.

Catalytic oxidation of ascorbic acid on the PPy/FCA-coated GC electrode

It has been previously shown that ferrocene is able to electrocatalyze the oxidation of ascorbic acid both via a

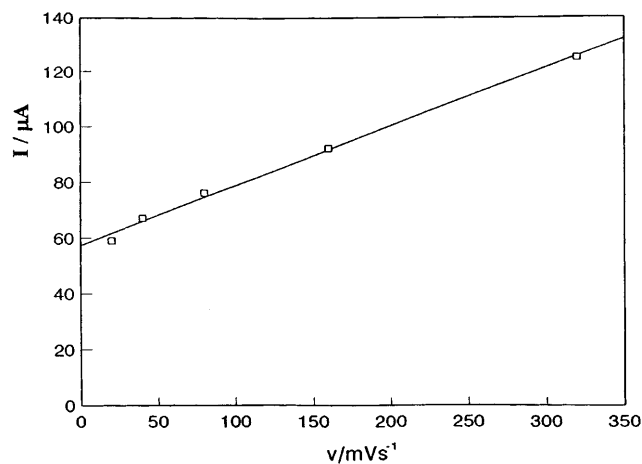


Fig. 3 Dependence of the anodic current of the cyclic voltammograms (Fig. 1B) on the scan rates

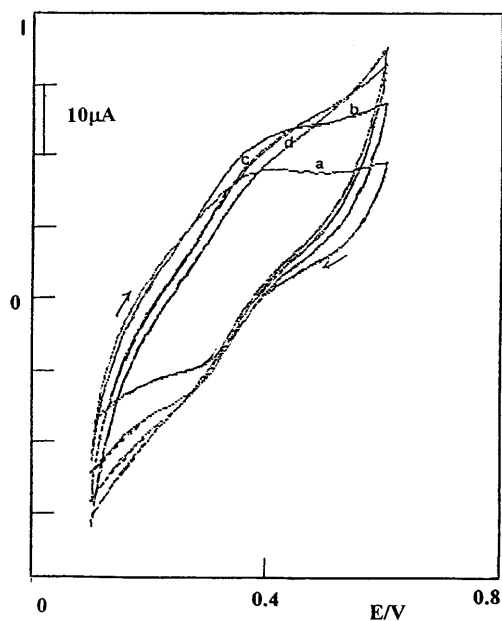


Fig. 4 Cyclic voltammograms of PPy/FcA prepared in water at pH 4 in 0.5 M glycine buffer + 0.1 M LiClO_4 at scan rates of *a* 10, *b* 20, *c* 30 and *d* 40 mV s^{-1}

homogeneous process, when ferrocene is present in dissolved form [27, 28], and heterogeneously, when a polyvinylferrocene film is covalently bound to a platinum electrode [29] or ferrocene adsorbed at the graphite electrode [30]. Accordingly, in this paper we report the ability of FCA incorporated into PPy, described above, to catalyze the ascorbic acid oxidation. In a previous paper, we have reported that the electrocatalytic effect of FCA in dissolved form for ascorbic acid oxidation on the GC electrode is maximum at pH 4 in 0.5 M glycine buffer [27]. The cyclic voltammograms obtained for a 5 mM ascorbic acid solution on the bare and PPy/FCA-coated GC electrodes are shown in Fig. 5. The oxidation of ascorbic acid on the bare GC

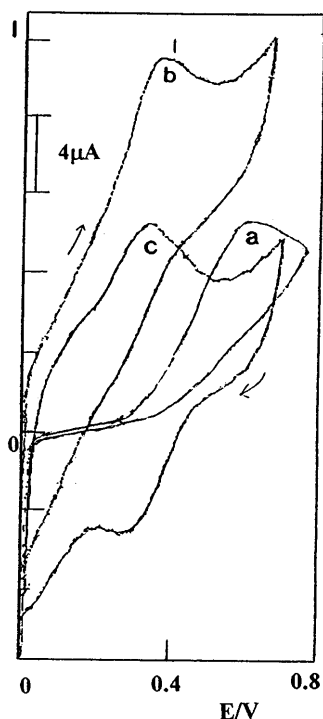
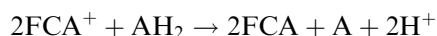


Fig. 5 Cyclic voltammograms of 0.5 mM ascorbic acid solution at *a* bare GC electrode and *b* at PPy/FCA-coated GC electrode (film thickness of 0.28 μm) *c* cyclic voltammogram of PPy/FCA-coated GC electrode in electrolyte solution of 0.5 M glycine buffer pH 4 + 0.1 M LiClO_4 ; scan rate: 10 mV s^{-1}

electrode occurred irreversibly with a peak potential of 0.64 V vs. SCE under the solution conditions (curve *a*), while its oxidation peak on the PPy/FCA-coated GC electrode appeared at 0.34 V oxidation potential of the FCA (curve *b*). Therefore the ferrocene catalytic effect is 300 mV. As seen in curve *b*, the anodic current was increased over that ordinarily observed just for the incorporated FCA^+/FCA couple, while the corresponding cathodic peak was substantially depressed on the reverse-scan. This behaviour is typical of that expected for electrocatalysis, and the following EC steps are involved:



where AH_2 and *A* represent ascorbic acid and dehydroascorbic acid, respectively.

The anodic peak current for cyclic voltammograms with a scan rate of 10 mV s^{-1} was proportional to the ascorbic acid concentration within the limited range 5×10^{-4} – 5×10^{-3} M (Fig. 6).

Stability of the film

The stability of the PPy/FCA film and reproducibility of its electrochemical behaviour were investigated by cyclic voltammetry after exposing the film to air or storing it in

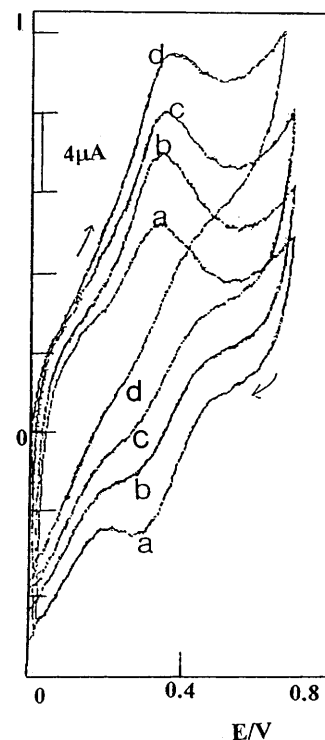


Fig. 6 Cyclic voltammograms of PPy/FCA-coated GC electrode in 0.5 M glycine buffer, pH 4, + 0.1 M LiClO_4 *a* in the absence of ascorbic acid (AH_2), and in the presence of *b* 0.5, *c* 1.00 and *d* 2.00 mM AH_2 ; polymer thickness: 0.28 μm

glycine buffer at pH 4 for several weeks. According to the results obtained, the current response of the electrode was not changed by storing in glycine buffer for three days, but decreased to 70% of the initial value of the current response after storing it for a week. In contrast, the current response of the film was not changed by exposing it to air for more than two weeks. Furthermore, the reproducibility of the electrocatalytic effect of the PPy/FCA-coated GC electrode was examined by repetitive recording of the cyclic voltammograms in ascorbic acid solution. A small decrease in height of the voltammograms was observed for 20 cycles of potential scanning over the range 0–0.8 V. However, the primary catalytic activity of the film was drastically decreased after prolonged use.

Conclusion

The simultaneous oxidation of FCA during the anodic polymerization of pyrrole in chloroform solution allowed the formation of PPy film which incorporated $\text{FCA}^+\text{ClO}_4^-$ by a precipitation mechanism. Several cycles of potential scan between –0.8 and 1.3 V to minimize the charging current of the PPy matrix is required. The redox reaction of FCA^+/FCA in the polymer matrix shows a reversible surface oxidation behaviour at low scan rates.

The prepared PPy/FCA-modified GC electrode is able to catalyze the electrochemical oxidation of ascorbic acid as a typical organic compound in aqueous media with an optimized pH value using glycine buffer. The catalytic ability of the PPy/FCA films remains unchanged with time owing to the good stability of FCA in the films. However, the dynamic concentration range of the electrode is restricted, which limits the analytic applications of the PPy/FCA-modified electrodes. These findings led us to conclude that the incorporation of some mediators in the polypyrrole matrix on the basis of a precipitation mechanism in a solvent with low dielectric constant suggests a new procedure for the preparation of the modified electrodes.

References

- Diaz AF, Kanazawa KK, Gardini GP (1979) *J Chem Soc Chem Commun* 635
- Iwakura C, Kajiya Y, Yoneyama H (1980) *J Chem Soc Chem Commun* 1019
- Saraceno RA, Pack JG, Ewing AG (1986) *Electroanal Chem* 197: 265
- Dong S, Sun Z, Lu Z (1988) *J Chem Soc Chem Commun* 993
- Miller LL, Singer B (1984) *J Am Chem Soc* 106: 6861
- Grimshaw J, Perera SD (1990) *J Electroanal Chem* 281: 125
- Inagaki T, Hunter M, Yang XQ, Skotheim TA, Okamoto Y (1988) *J Chem Soc Chem Commun* 126
- Daire F, Bedioui F, Devynck J, Bied-Charreton C (1987) *J Electroanal Chem* 224: 95
- Bidan G, Divisia Blohorn B, Kern JM, Sauvage JP (1988) *J Chem Soc Chem Commun* 273
- Collin JP, Sauvage JP (1987) *J Chem Soc Chem Commun* 1075
- Bettelheim A, White BA, Raybuck SA, Murray RW (1987) *Inorg Chem* 26: 1009
- Bedioui F, Bernard P, Moisy P, Bied-Charreton C, Devynck J (1989) *Mater Sci Forum* 42: 221
- Deronzier A, Latour JM (1987) *J Electroanal Chem* 224: 295
- Armengaud C, Moisy P, Bedioui F, Devynck J (1990) *J Electroanal Chem* 277: 197
- Ikeda O, Okaabayashi K, Yoshida N, Tamura H (1985) *J Electroanal Chem* 191: 157
- Bull RA, Fan FR, Bard AJ (1983) *J Electrochem Soc* 130: 157
- Okabayashi K, Ikeda O, Tamura H (1983) *J Chem Soc Chem Commun* 684
- Kajiya Y, Sgai H, Iwakura C, Yoneyama H (1991) *Anal Chem* 63: 49
- Keita B, Bouaziz D, Nadjo L, Deronzier A (1990) *J Electroanal Chem* 279: 187
- Shimidzu T, Ohtani A, Aiba M, Honda K (1988) *J Chem Soc Faraday Trans I* 84: 3941
- Bidan G, Lapkowsky M, Travers JP (1989) *Synth Met* 28: C113
- Keung Shiu K, Anson C (1991) *J Electroanal Chem* 309: 115
- Bull RA, Fan F-R, Bard AJ (1984) *J Electrochem Soc* 131: 687
- Skotheim TA (ed) (1986) *Handbook of conducting polymers*, vols 1 and 2. Dekker, New York
- Pournaghi-Azar MH, Ojani R (1994) *Talanta* 42: 657
- Diaz AF, Castillo JI (1980) *J Chem Soc Chem Commun* 397
- Purnaghi-Azar MH, Ojani R (1995) *Talanta* 42: 1839
- Pournaghi-Azar MH, Ojani R (1997) *Talanta* 44: 297
- Petersson M (1986) *Anal Chim Acta* 187: 333
- Kulys J, Drungiliene A (1991) *Electroanalysis* 3: 209