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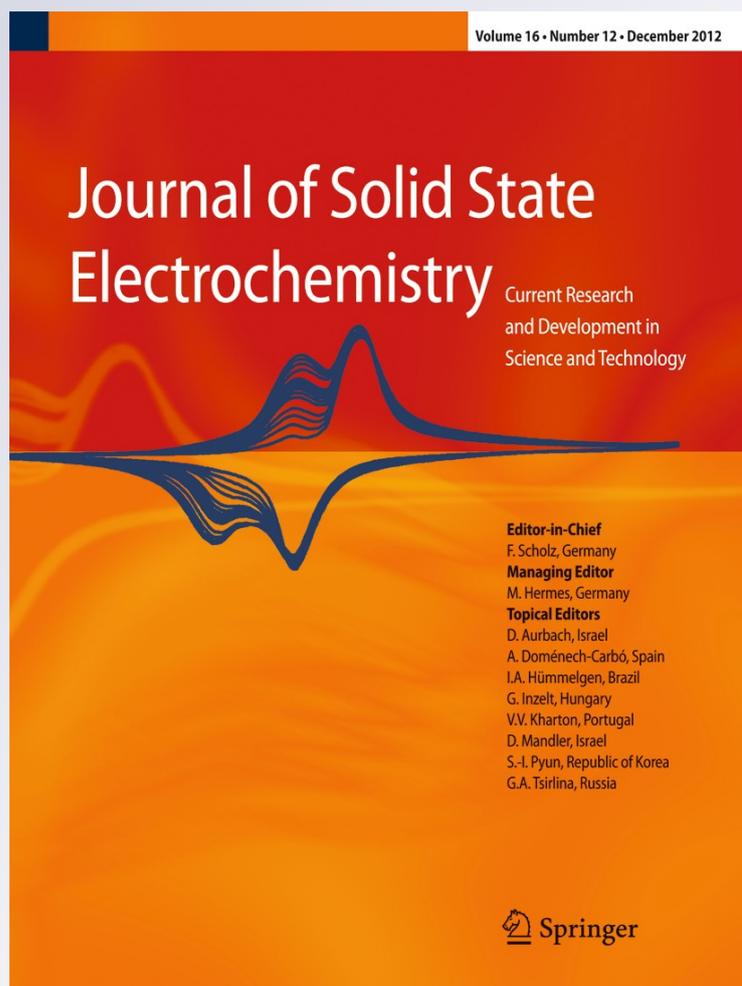
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# Incorporation of ferrocene into polypyrrole films via an ionic adduct with boron trifluoride

Abdul R. F. Al-Betar · Peter G. Pickup

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**Abstract** 1-(Ferrocenyl)ethanol has been immobilized within polypyrrole films during their electrochemical deposition, or following their deposition, via its adduct with boron trifluoride. Dissociation of  $H^+$  from this adduct, formed in a solution of boron trifluoride diethyl ether (BFEE) in acetonitrile, produces an anion that can act as a counterion for oxidized polypyrrole. Its subsequent hydrolysis produces a polypyrrole film containing neutral 1-(ferrocenyl)ethanol which was found to be strongly retained. In addition to producing a novel type of polypyrrole–ferrocene composite, this work provides clear evidence to support the efficacy of this methodology for the incorporation of neutral species within conducting polymer films.

**Keywords** Polypyrrole · Ferrocene · Boron trifluoride diethyl ether · Composite · Counterion

## Introduction

Conducting polymers can be utilized to incorporate and immobilize a wide variety of species within their matrices [1, 2]. Ferrocene has commonly been employed as a redox active modifier [1], since it provides a characteristic and well-behaved redox couple for method development, fundamental studies, and a variety of applications. For example, ferrocene-containing polypyrroles have been used to increase the sensitivity of carbon monoxide gas sensors [3], as a paramagnetic conducting polymer [4], and as electrocatalysts for the evolution of hydrogen gas [5]. Ferrocene-containing polythiophenes have been used in biosensors [6].

Composites of polypyrrole with poly(styrenesulfonate-*co*-vinylferrocene) possess increased charge capacity due to the additional electroactivity of the ferrocene groups and can be used as electrode materials for rechargeable batteries [7, 8].

Conducting polymer films are also commonly modified with large non-electroactive molecules and polymers, such as surfactants, ionomers, and steric stabilizers [2, 9, 10]. Such modification can influence the physical properties of the polymer films, such as morphology, mechanical strength, conductivity, and solubility. The large counterions can facilitate the polymerization process and stabilize the polymer by reducing the natural repulsion of the radical cations [9, 10].

There has been growing interest over the past decade in the use of boron trifluoride diethyl ether (BFEE) as a solvent for the polymerization of aromatic monomers [2, 11, 12]. For polypyrrole, the Lewis acidity of the BFEE must be decreased by dilution in a donor solvent in order to prevent ring opening and formation of non-conjugated polymers [11]. For example, high quality polypyrrole films have been prepared from isopropyl alcohol (IPA) containing BFEE and poly(ethylene glycol) (PEG) [13]. Use of protic solvents (HD), and dissociation of the resulting protic acid complexes (Eq. 1), eliminates the need for a supporting electrolyte.



Polymerization of pyrrole in an HD plus BFEE will result in incorporation of  $(D:BF_3)^-$  into the polymer matrix as the counterion, which provides the opportunity to incorporate highly basic anion ( $D^-$ ) or neutral species (HD following hydrolysis) into polypyrrole matrices. This was demonstrated in the work noted above [13], in which PEG was incorporated into the polypyrrole films as a steric stabilizer to provide

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enhanced mechanical stability. Templated polypyrrole nanowires [14] and polypyrrole films for electrochemical actuators [15, 16] have also been prepared using this solvent system, with sodium dodecylsulfonate also added in one case [16].

Although the incorporation of neutral donor molecules into polypyrrole films via deprotonated  $\text{BF}_3$  adducts offers massive scope for the development of new composite materials, it has been barely explored. As far as we know, there is no direct proof that the donor molecule (PEG) was actually incorporated into the materials discussed above, and there has been no quantification or extension to other donor molecules. We therefore report here on the incorporation, quantification, and electrochemistry of an electroactive donor molecule, 1-(ferrocenyl)ethanol. A ferrocene moiety was used because its facile electrochemistry allows its incorporation and retention to be easily tracked by cyclic voltammetry, and because of the potential applications (outlined above) that it brings.

## Experimental

### Materials

Pyrrole (Py, Aldrich, 98 %) was purified on a dry aluminum oxide column. Acetonitrile ( $\text{CH}_3\text{CN}$ ; Aldrich, HPLC grade), boron trifluoride ethyl etherate (BFEE, Aldrich, 46 %  $\text{BF}_3$  basis), polyethylene glycol (PEG-400, Fluka; analytical grade,  $M_n=400 \text{ g mol}^{-1}$ ), sodium perchlorate ( $\text{NaClO}_4$ ; Alfa Aesar, 98 %), tetraethylammonium perchlorate ( $\text{Et}_4\text{NClO}_4$ ; Alfa Aesar), 1-(ferrocenyl)ethanol (FcOH; Fluka, 97 %), and Alizarin Red S (3,4-dihydroxy-9,10-dioxo-2-anthracenesulfonic acid sodium salt; Sigma-Aldrich), were used as received unless otherwise stated. All aqueous solutions were prepared with deionized water.

### Electrochemistry and deposition of the polymer films

Electrochemical experiments were carried out in conventional three-compartment glass cells under a nitrogen atmosphere at  $23 \pm 2 \text{ }^\circ\text{C}$ . A  $0.071 \text{ cm}^2$  glassy carbon (GC) disc working electrode, Pt wire counter electrode, and a saturated calomel electrode (SCE) reference electrode were used. All potentials are quoted with respect to the SCE. All cyclic voltammograms were recorded under nitrogen.

### Atomic absorption spectroscopy (AAS)

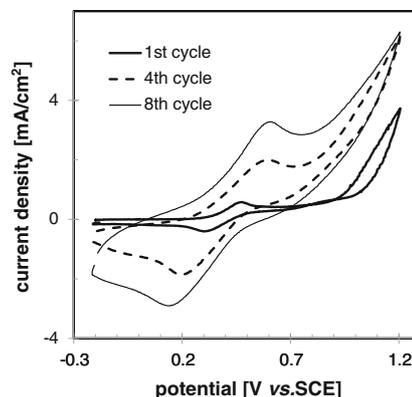
For determination of their Fe contents by AAS, polymer films were deposited on indium-tin oxide (ITO)-coated glass electrodes. Films were peeled from the electrode, weighed, and then dissolved in 5 ml aqua regia ( $\text{HNO}_3/\text{HCl}$ , 1:3). Solutions were diluted to 25 ml with 50 %  $\text{HCl}(\text{aq})$  prior to analysis.

## Results and discussion

### Preparation of ferrocene-modified polypyrrole films

The system used to produce ferrocene-containing polypyrrole (PPy-FcOH) films utilized BFEE in acetonitrile to activate and ionize the hydroxyl group of FcOH as shown in Eq. 1 (with  $D=\text{FcO}$ ). Since no electrolyte was added, the conductivity of the polymerization solution should have been due predominately to  $\text{H}^+$  and  $(\text{FcO}:\text{BF}_3)^-$ . As the dominant anion in the system,  $(\text{FcO}:\text{BF}_3)^-$  was expected to be incorporated into the polypyrrole films as the counterion. However, whether this happens or not is complicated by the concurrent oxidation of the ferrocene moiety to yield a neutral (zwitterion) species, and the presence of anions such as  $\text{BF}_4^-$ , and  $(\text{HO}:\text{BF}_3)^-$  produced by reaction of  $\text{BF}_3$  with trace water in the system [12]. The conductivity of commercial BFEE is reported to be ca.  $1 \text{ mS cm}^{-1}$ , indicating that there are appreciable concentrations of these ions [12].

Figure 1 shows voltammograms of the electrochemical polymerization of Py in the presence of FcOH and BFEE, with three non-consecutive cycles (first, fourth, and eighth) presented. The first cycle shows a reversible wave due to the Fe(III/II) couple of the ferrocene at a formal potential of ca.  $0.4 \text{ V}$  (the peak separation is presumably high due to the solution resistance), as well as irreversible oxidation of the pyrrole at potentials above ca.  $0.9 \text{ V}$ . The appearance of a nucleation loop (higher currents on the reverse scan) in the first pyrrole oxidation wave is characteristic of polypyrrole deposition on the electrode. The fourth and eighth cycles shown in Fig. 1 exhibit larger and increasing waves for ferrocene oxidation, as well as the development of much broader oxidation and reduction currents between  $-0.2$  and ca.  $+1.0 \text{ V}$  that can be attributed to polypyrrole electrochemistry. These voltammograms therefore provide good evidence that a ferrocene-modified polypyrrole film was being deposited.



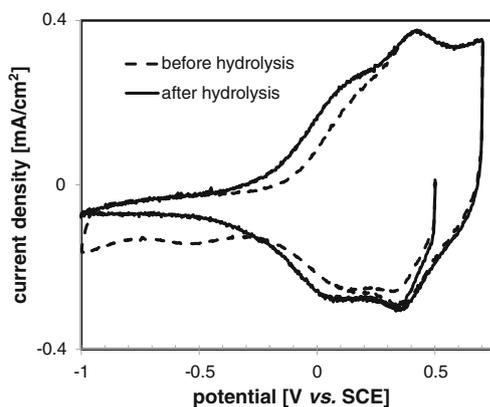
**Fig. 1** Cyclic voltammograms ( $0.1 \text{ V s}^{-1}$ ) of a GC electrode of a solution containing  $0.1 \text{ M}$  Py,  $10 \text{ mM}$  FcOH and  $20 \%$  (v/v) BFEE in  $\text{CH}_3\text{CN}$

## Characterization

Electrodes coated with PPy-FcOH films either potentiodynamically, as described above, or using potentiostatic or galvanostatic methods were characterized following rinsing with acetonitrile (for measurements in acetonitrile) and water (for measurements in aqueous solutions). Rinsing with acetonitrile would be expected to leave the  $(\text{FcO}:\text{BF}_3)^-$  in the film intact, while rinsing with water should cause hydrolysis to FcOH and various  $(\text{HO})_x\text{BF}_{4-x}^-$  anions.

Figure 2 shows voltammograms in acetonitrile of a PPy-FcOH film before and after hydrolysis by immersion in 0.5 M  $\text{NaClO}_4(\text{aq})$  for ca. 1 min. Both voltammograms show oxidation and reduction peaks at ca. 0.4 V superimposed on the broad polypyrrole waves (with a formal potential of ca. 0.1–0.2 V) that can be attributed to FcOH incorporated into the film. Hydrolysis improved the polypyrrole electrochemistry significantly, lowering the formal potential and greatly decreasing the cathodic background current at potentials below  $-0.3$  V, but did not significantly influence the ferrocene electrochemistry. This more facile polypyrrole electrochemistry can be attributed to the smaller anions produced by hydrolysis and possibly hydration of the PPy chains.

The Fe contents of two PPy-FcOH films were determined by AAS. The results are reported in Table 1 together with the deposition conditions employed, masses of PPy-FcOH formed and Py/FcOH mole ratios calculated assuming that the films consisted of polypyrrole (65 g/mol of pyrrole rings) and FcOH. For the 10 mM FcOH concentration used to prepare the film in Fig. 1, a Py/FcOH ratio of  $\sim 200:1$  was obtained, while a higher Fe content and Py/FcOH ratio of  $\sim 100:1$  was obtained for a film prepared using a FcOH concentration of 20 mM.



**Fig. 2** Cyclic voltammograms ( $0.05 \text{ V s}^{-1}$ ) of a PPy-FcOH coated GC electrode in 0.1 M  $\text{Et}_4\text{NClO}_4/\text{CH}_3\text{CN}$  before and after hydrolysis. The film was deposited from 0.1 M Py, 15 mM FcOH and 20 % (v/v) BFEE in  $\text{CH}_3\text{CN}$  at 0.3 mA with a deposition charge of  $0.018 \text{ C}$  ( $0.25 \text{ C cm}^{-2}$ )

The number of electrons consumed per pyrrole unit during the polymerization ( $n_{\text{pol}}$ ) was calculated from the data in Table 1 by using Eq. 2.

$$n_{\text{pol}} = Q_{\text{pol}} M_{\text{Py}} / m_{\text{Py}} F \quad (2)$$

where  $m_{\text{Py}}$  is the mass of pyrrole in the film,  $M_{\text{Py}}$  is the molar mass of a pyrrole unit ( $65 \text{ g mol}^{-1}$ ),  $F$  is the Faraday constant ( $96,485 \text{ C mol}^{-1}$ ), and  $Q_{\text{pol}}$  is the charge used for the polymerization. The value of  $n_{\text{pol}}=2.3$  for Film 1 (Table 1) is consistent with the polymerization of pyrrole under conventional conditions [17]. Since two electrons per pyrrole unit are required to polymerize pyrrole, it indicates that the polymer formed was doped (oxidized) to a level of ca. 0.3 electrons per pyrrole ring [17] (i.e., every three to four rings carry one positive charge). The higher value of 2.8 for Film 2 was presumably due to some inefficiency in the deposition, since a doping level of 0.8 would be unreasonably high.

Figure 3 shows voltammograms in 0.5 M  $\text{NaClO}_4(\text{aq})$  of PPy-FcOH coated electrodes prepared by three polymerization techniques. In all cases, there are distinct oxidation and reduction peaks at ca. 0.20 and 0.15 V, respectively, superimposed on the broad polypyrrole waves (with peaks at ca.  $-0.1$  V) that can be attributed to FcOH incorporated into the films. The Fe(III)/(II) formal potential is shifted cathodically relative to Fig. 1 due to the change in solvent from  $\text{CH}_3\text{CN}$  to water. It is clear from the data in Fig. 3 that the polymerization method does not greatly influence either the voltammetry of the resulting PPy-FcOH film or the extent of FcOH incorporation. The differences in peak currents can be attributed to differences in the amount of polymer, or film thickness, deposited in each experiment. The differences below  $-0.5$  V can be attributed to cation insertion [18, 19], which is most evident for the film prepared potentiostatically.

The compositions of the PPy-FcOH films can be roughly estimated from the voltammograms in Fig. 3 from the charges under the polypyrrole and Fe(III/II) waves. The dotted lines in the figure show how the Fe (III/II) charge was roughly separated from the polypyrrole charge ( $Q_{\text{PPy}}$ ). The number of moles of pyrrole rings ( $N_{\text{Py}}$ ) in the film was calculated with Eq. 3, where  $n_{\text{Py}}$  is the number of electron per ring involved in oxidation of the polypyrrole to the potential limit of  $+0.4$  V used for the integration (0.25 [17]).

$$N_{\text{Py}} = Q_{\text{PPy}} / n_{\text{Py}} F \quad (3)$$

Similarly, the moles of FcOH were calculated as  $N_{\text{FcOH}} = Q_{\text{Fc}} / F$ , since  $n_{\text{Fc}}=1$ . Data obtained in this way from Fig. 3 are presented in Table 2 for both oxidation

**Table 1** Fe contents and Py/FcOH mole ratios determined by AAS for PPy-FcOH films prepared on ITO electrodes from 10 % BFEE in CH<sub>3</sub>CN

	[Py] (M) <sup>a</sup>	[FcOH] (mM) <sup>a</sup>	Deposition charge (C)	Polymer mass (mg)	% Fe	Py/FcOH	$n_{\text{pol}}$
Film 1	0.1	10	1.44	0.44	0.4	~200	2.3
Film 2	0.5	20	4.32	1.10	0.8	~100	2.8

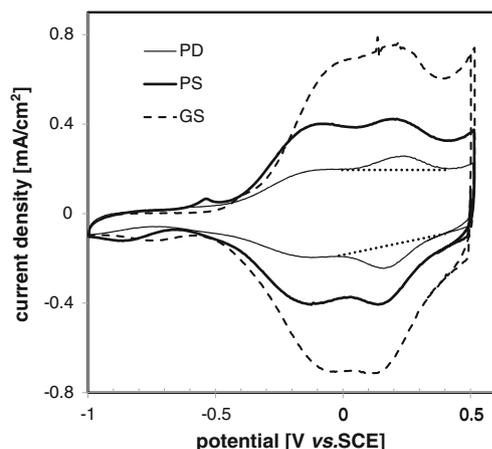
<sup>a</sup> Concentrations in the deposition solution

and reduction of the polymers, together with Py/FcOH mole ratios derived from the results. There are significant discrepancies between the results reported for the anodic and cathodic scans in Table 2 that can be attributed to the occurrence of irreversible processes and inaccuracies in the separation of the charges for the PPy and FcOH electrochemistries. However, the results do provide a useful semi-quantitative guide to how much FcOH was incorporated into the films, and they do show some differences in the Py/FcOH ratios produced by the three polymerization methods that are not readily apparent from inspection of the voltammograms. Further experiments, not reported here, suggested that this could be attributed to the differences in the amount of polymer that was deposited in each case, since the Py/FcOH ratio was found to increase as the deposition charge was increased. This is illustrated by comparison of the Py/FcOH ratio of ~200 for Film 1 ( $Q_{\text{pol}}=1.44$  C) in Table 1, with that of 71–82 for the galvanostatically deposited film in Table 2 ( $Q_{\text{pol}}=18$  mC).

The highest FcOH content achieved in these experiments of 35–59 pyrrole units per FcOH is much lower than the typical doping level of polypyrrole of ca. 4 pyrrole units per

dopant anion. This indicates that most of the doping charge of the polypyrrole must have been compensated by other counterions, presumably  $\text{BF}_4^-$  and  $(\text{HO}:\text{BF}_3)^-$  originally present in the BFEE [12], and the series of  $((\text{HO})_x\text{BF}_{4-x})^-$  anions resulting from the reaction of  $\text{BF}_3$  with adventitious water (including water in the CH<sub>3</sub>CN) prior to film deposition. The low  $(\text{FcO}:\text{BF}_3)^-$  doping levels are presumably due largely to the concurrent oxidation of  $(\text{FcO}:\text{BF}_3)^-$  to the neutral  $\text{FcO}:\text{BF}_3$  species during polypyrrole deposition. It is also noteworthy that the yield of polypyrrole produced during galvanostatic deposition of PPy-FcOH on GC using a charge of 18 mC, determined from the PPy reduction charge in Fig. 3 and  $n_{\text{pol}}=2.3$ , was only 17 %. This indicates that much of the oligo-/poly-pyrrole produced was not deposited on the electrode, presumably due to the deficiency of available counterions (see below).

Figure 4 shows cyclic voltammograms of PPy and PPy-FcOH films deposited galvanostatically from solutions containing various concentrations of FcOH. These voltammograms show an increasing FcOH content in the polymer with increase concentration in the deposition solution as well as curious peak shapes for the Fe oxidation wave when 20 or 30 mM FcOH was used. For the film prepared at 30 mM FcOH, the ratio of the charges for PPy and Fe oxidation yield and approximate Py/FcOH ratio of ca.14:1. The voltammogram in Fig. 4 of the film deposited using 40 mM FcOH does not show any evidence of PPy electrochemistry, suggesting that it consists of primarily of FcOH molecules, which may be linked in some way by pyrrole based moieties. The origins of the sharp peak at ca. 0.35 V for the films prepared with 20 or 30 mM FcOH is unknown, but can perhaps be ascribed to some type of charge trapping phenomenon [20].



**Fig. 3** Cyclic voltammograms ( $0.1 \text{ Vs}^{-1}$ ) in  $0.5 \text{ M NaClO}_4(\text{aq})$  of PPy-FcOH coated GC electrodes prepared potentiodynamically (PD; light; 5 cycles between  $-0.2$  and  $1.2 \text{ V}$ ), galvanostatically (GS; dashed;  $3 \text{ mA}$  ( $0.018 \text{ C}$ )) and potentiostatically (PS; bold;  $1.0 \text{ V}$  for  $1 \text{ min}$ ) from solutions containing  $0.1 \text{ M Py}$ ,  $10 \text{ mM FcOH}$  and  $20 \text{ \% (v/v) BFEE}$  in  $\text{CH}_3\text{CN}$

#### FcOH retention

One of the crucial points for incorporation of electroactive species into a polymer matrix is to understand the retention and release of that species. In order to understand the nature of the interactions between FcOH and the polypyrrole matrix, various methods were employed in attempts to expel the FcOH from the films, such as cycling in aqueous and non-aqueous solutions, and

**Table 2** Py/FcOH mole ratios determined by cyclic voltammetry for PPy-FcOH films prepared on GC electrodes from 0.1 M Py, 10 mM FcOH and 20 % BFEE in CH<sub>3</sub>CN

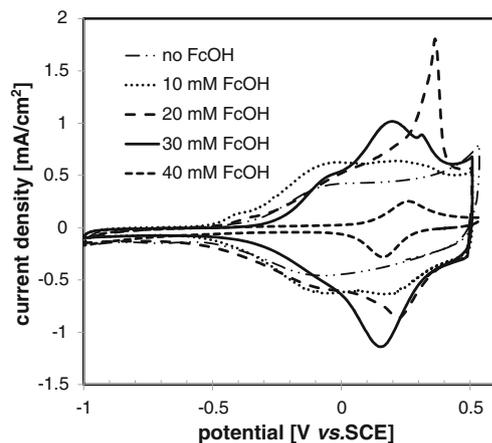
Deposition method	Scan direction	Moles of Py	Moles of Fe	Py/FcOH ratio
Potentiodynamic	Anodic	$4.5 \times 10^{-9}$	$7.7 \times 10^{-11}$	59
	Cathodic	$5.0 \times 10^{-9}$	$1.4 \times 10^{-10}$	35
Potentiostatic	Anodic	$8.2 \times 10^{-9}$	$8.8 \times 10^{-11}$	93
	Cathodic	$9.0 \times 10^{-9}$	$1.4 \times 10^{-10}$	66
Galvanostatic	Anodic	$1.2 \times 10^{-8}$	$1.7 \times 10^{-10}$	71
	Cathodic	$1.4 \times 10^{-8}$	$1.7 \times 10^{-10}$	82

polarizing them at positive or negative potentials. None of these approaches were entirely successful, indicating that the FcOH was either physically trapped between the polymer chains or had formed a covalent or other type of strong bond with the polypyrrole.

Figure 5 shows cycling of a PPy-FcOH polymer film between 0.5 and -1.0 V in an aqueous solution. During cycling, the voltammogram showed only minor changes, with only small decreases in currents after the first cycle. The Fe(III) peaks did not decay significantly when account is taken of the changes the PPy currents. The conclusion here then is that the ferrocene is quite strongly bound or trapped within the polypyrrole film, and that the loss during the 10 cycles shown in Fig. 5 was insignificant.

#### (FcOBF<sub>3</sub>)<sup>-</sup> uptake by preformed polypyrrole

Modification of polypyrrole with FcOH can also be achieved by ion exchange following its electrodeposition onto an electrode surface. Here preformed polypyrrole films with either ((HO)<sub>x</sub>BF<sub>4-x</sub>)<sup>-</sup> or Alizarin Red S counterions (A<sup>-</sup>) were immersed in a solution containing 10 mM FcOH and 20 % (v/v) BFEE in CH<sub>3</sub>CN, and the potential was cycled,

**Fig. 4** Cyclic voltammograms (0.1 Vs<sup>-1</sup>) in 0.5 M NaClO<sub>4</sub>(aq) of PPy and PPy-FcOH films deposited galvanostatically at 0.3 mA (0.018 C) from solutions containing various concentrations of FcOH as indicated, 0.1 M Py and 20 % (v/v) BFEE in CH<sub>3</sub>CN

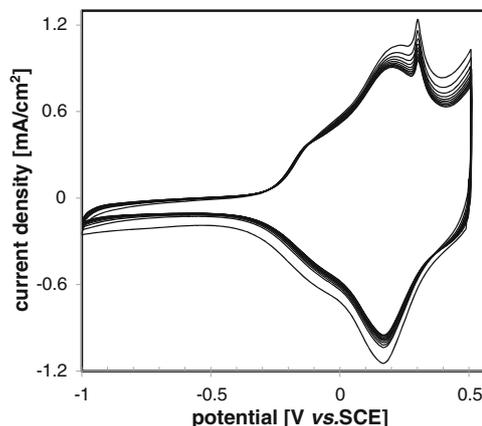
or held at a particular value, in order to promote ion exchange according to Eq. 4.

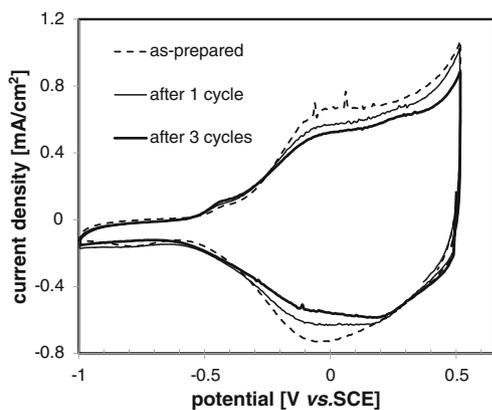


As seen in Fig. 6, cyclic voltammograms of the PPy ((HO)<sub>x</sub>BF<sub>4-x</sub>) film in 0.5 M NaClO<sub>4</sub>(aq) show that there had been some uptake of FcOH, although it was quite limited. Much greater uptake was observed (Fig. 7) for PPy doped with the large aromatic anion, Alizarin Red S, which was employed here because it is known from our unpublished work to form a much more porous film. These results clearly demonstrate that polypyrrole can be loaded with neutral species by ion exchange of their hydrolysable adducts with BFEE.

#### Use of PEG as a steric stabilizer

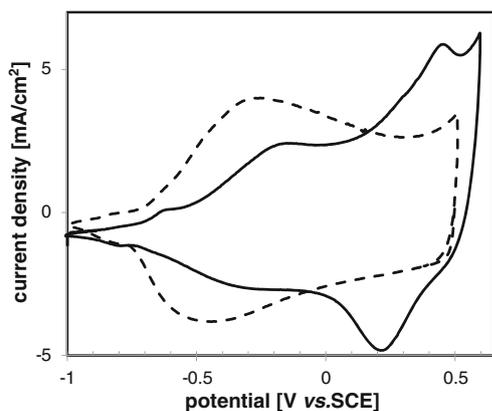
Using a steric stabilizer, such as polyethylene glycol (e.g., PEG-400), during the electrochemical deposition of polypyrrole can improve the polymer film properties [13]. In order to investigate whether addition of PEG-400 would be beneficial in the present case, PPy-FcOH films were

**Fig. 5** Cycling of a PPy-FcOH film in 0.5 M NaClO<sub>4</sub> at 0.1 Vs<sup>-1</sup>. The film was deposited on a GC electrode from 0.1 M Py, 30 mM FcOH and 20 % (v/v) BFEE in CH<sub>3</sub>CN at 0.3 mA (0.018 C)

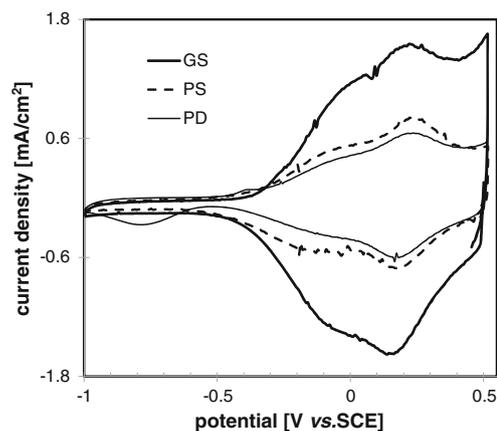


**Fig. 6** Cyclic voltammograms at  $0.1 \text{ V s}^{-1}$  in  $0.5 \text{ M NaClO}_4$  of a PPY film that had been loaded with  $(\text{FcO}:\text{BF}_3)^-$  following deposition. The polymer film was deposited from  $0.1 \text{ M Py}$  and  $20 \%$  (v/v) BFEE in  $\text{CH}_3\text{CN}$  at  $0.3 \text{ mA}$  with a deposition charge of  $0.018 \text{ C}$ , then cycled in a solution of  $10 \text{ mM FcOH}$  and  $20 \%$  (v/v) BFEE in  $\text{CH}_3\text{CN}$  between  $0.5$  and  $-1.0 \text{ V}$  for the indicated number of cycles

deposited in the presence of various concentrations of PEG-400. These modified films (PPy-FcOH-PEG) showed enhanced electrochemical activity in both aqueous and non-aqueous solutions. Figure 8 shows voltammograms of PPy-FcOH-PEG coated electrodes in aqueous  $\text{NaClO}_4$ . In comparison with the voltammograms shown in Fig. 3, it is clear that these films had higher FcOH/Py ratios than those prepared in the absence of PEG-400. The higher overall currents also indicate that more polymer was deposited under the same conditions when PEG-400 was added. This is illustrated more clearly in Fig. 9, where voltammograms are compared for films deposited in the presence of various concentrations of PEG-400. It is clear from these voltammograms that  $1 \%$  PEG-400 provided the optimum deposition medium, while additional PEG-400 begins to inhibit film



**Fig. 7** Cyclic voltammograms at  $0.1 \text{ V s}^{-1}$  in  $0.2 \text{ M NaCl}$  of a PPY/Alizarin Red S film before (dashed) and after (solid) loading with  $(\text{FcO}:\text{BF}_3)^-$ . The polymer film was deposited from a  $0.1 \text{ M Py}$  and  $6 \text{ mM Alizarin Red S}$  aqueous solution. It was loaded with  $(\text{FcO}:\text{BF}_3)^-$  at  $0.6 \text{ V}$  ( $3 \text{ min}$ ) in a solution of  $10 \text{ mM FcOH}$  and  $20 \%$  (v/v) BFEE in  $\text{CH}_3\text{CN}$

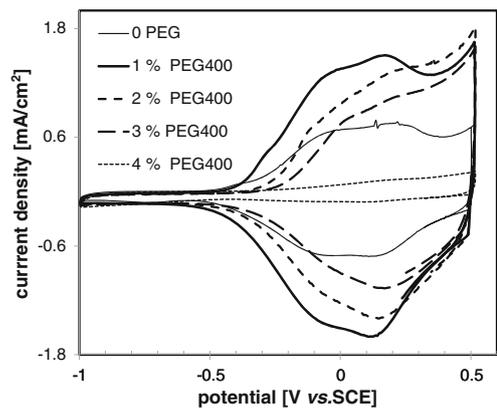


**Fig. 8** Cyclic voltammograms ( $0.1 \text{ V s}^{-1}$ ) of PPy-FcOH-PEG coated electrodes in  $0.5 \text{ M NaClO}_4$ . The films were deposited on GC electrodes from  $0.1 \text{ M Py}$ ,  $20 \text{ mM FcOH}$ ,  $20 \%$  (v/v) BFEE and  $1 \%$  PEG-400 in  $\text{CH}_3\text{CN}$ , either galvanostatically (GS) at  $0.3 \text{ mA}$  ( $0.25 \text{ C cm}^{-2}$ ), potentiostatically (PS) at  $1.0 \text{ V}$  for  $1 \text{ min}$ , or by using  $5$  cycles at  $0.1 \text{ V s}^{-1}$  between  $-0.2$  and  $1.2 \text{ V}$  (PD)

deposition. The benefit of using a small amount of PEG-400 in the deposition medium may arise in part from its ability to decrease the Lewis acidity of the BFEE and thereby stabilize the pyrrole solution [11].

## Conclusions

This work clearly shows that  $(\text{FcO}:\text{BF}_3)^-$  can be incorporated into polypyrrole films as a counterion during their deposition or by ion exchange following their deposition. This provides a novel type of polypyrrole composite, and expands the scope of the previously reported methodology [13] for incorporation of neutral species into conducting



**Fig. 9** Cyclic voltammograms ( $0.1 \text{ V s}^{-1}$ ) of PPy-FcOH and PPy-FcOH-PEG coated electrodes in  $0.5 \text{ M NaClO}_4$ . The films were deposited galvanostatically at  $0.3 \text{ mA}$  ( $0.25 \text{ C cm}^{-2}$ ) on GC electrodes from  $0.1 \text{ M Py}$ ,  $20 \text{ mM FcOH}$ ,  $20 \%$  (v/v) BFEE and PEG-400 (vol.% as indicated) in  $\text{CH}_3\text{CN}$

polymers via their ionic adducts formed with  $\text{BF}_3$ . Furthermore, it provides important evidence to show that this methodology is effective, and explores the factors that influence the uptake of  $(\text{D}:\text{BF}_3)^-$  species from their solutions in BFEE in acetonitrile.

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