

# Preparation of Membranes by Electropolymerization of Pyrrole Functionalized by a Ferrocene Group

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**ABSTRACT:** The preparation of dense membranes by the electropolymerization of functionalized pyrrole (Py) by ferrocene units was carried out. The synthesis of *N*-[3-(pyrrol-1-yl)propyl]ferrocene-1-carboxamide (or [(ferrocenyl)amidopropyl] pyrrole, FAPP) is described. The electropolymerization of the monomer on platinum electrode and on stainless-steel meshes was studied. The electroactivity of the grafted ferrocenyl group of the FAPP monomer was confirmed and the electrochemical properties of the electrogenerated FAPP film were investigated. The stability in potentiostatic and potentiodynamic modes of FAPP films was low and, to improve the latter, the electrochemical preparation of

the copolymer between the pyrrole and the FAPP was performed. The electrochemical characterization of the copolymer showed that it was possible to control the oxidation state of both electroactive compounds of the film. The FAPP/Py copolymer was then prepared on stainless-steel meshes to produce membranes, whose transport properties were electrochemically controllable. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 3947–3958, 2004

**Key words:** membranes; electrochemistry; films; functionalization of polymers; electrochemical impedance spectroscopy (EIS)

## INTRODUCTION

Intrinsically conducting polymers are membrane materials of interest for the detection and transport of chemical substances.<sup>1–3</sup> Nevertheless in the field of molecular recognition (i.e., chemsensor devices), the functionalization of the material is a way of enhancing their selectivity properties. Guided by this aim, the grafting of specific groups to the precursor monomer is then often chosen, even if the direct chemical functionalization of the polymer<sup>4</sup> or the incorporation of appropriate counteranions<sup>5,6</sup> would be achieved. Covalent linkage is generally preferred to encapsulation because of problems stemming from diffusing out of specific function. The functionalization of pyrrole and thiophene monomers using complexing agents like calixarene,<sup>7,8</sup> crown ethers,<sup>9–11</sup> or pyridine<sup>12</sup> and ion-exchanger functions like alkylammonium,<sup>13</sup> carboxylate,<sup>14</sup> or sulfonate<sup>2,15</sup> was then performed with respect to ionic detection, permselective transport, and retention of heavy metals or radionuclides.

In the field of molecular recognition, much attention has been focused on the electropolymerization of pyrrole and thiophene monomers in the presence of redox groups (see review article by Goldenberg

et al.<sup>16</sup>). The redox activity of electrodes modified by pyrrole or thiophene ferrocene derivative films has been intensively investigated,<sup>16–21</sup> particularly in view of their use as transducers in biosensor applications.<sup>20,21</sup>

The preparation of permselective membranes based on pyrrole functionalized by the ferrocene molecule (i.e., the [(ferrocenyl)amidopropyl]pyrrole, FAPP) is of interest for anion transport. Indeed the anion-exchanger properties of the polypyrrole<sup>22,23</sup> can potentially be increased by the immobilization of the ferrocenium positively charged function (Fig. 1). Thus, the preparation of membranes based on the pyrrole monomer functionalized by ferrocene moieties, presented in this work, is part of a larger study devoted to the elaboration of materials presenting electrocontrolled transport properties.

We report here the synthesis and the electropolymerization of *N*-[3-(pyrrol-1-yl)propyl]ferrocene-1-carboxamide (or [(ferrocenyl)amidopropyl]pyrrole, FAPP), for the preparation of supported films. With respect to membranes, the first part of this study concerns the optimization of electrosynthesis on the platinum electrode by cyclic voltammetry and characterization of the deposit by quartz crystal microbalance and electrochemical impedance spectroscopy (EIS). These results are then applied to the material electrogeneration on stainless-steel gauze, as supporting electrode of higher surface area, in view of the study of the membrane ionic transport properties under electrochemical control.

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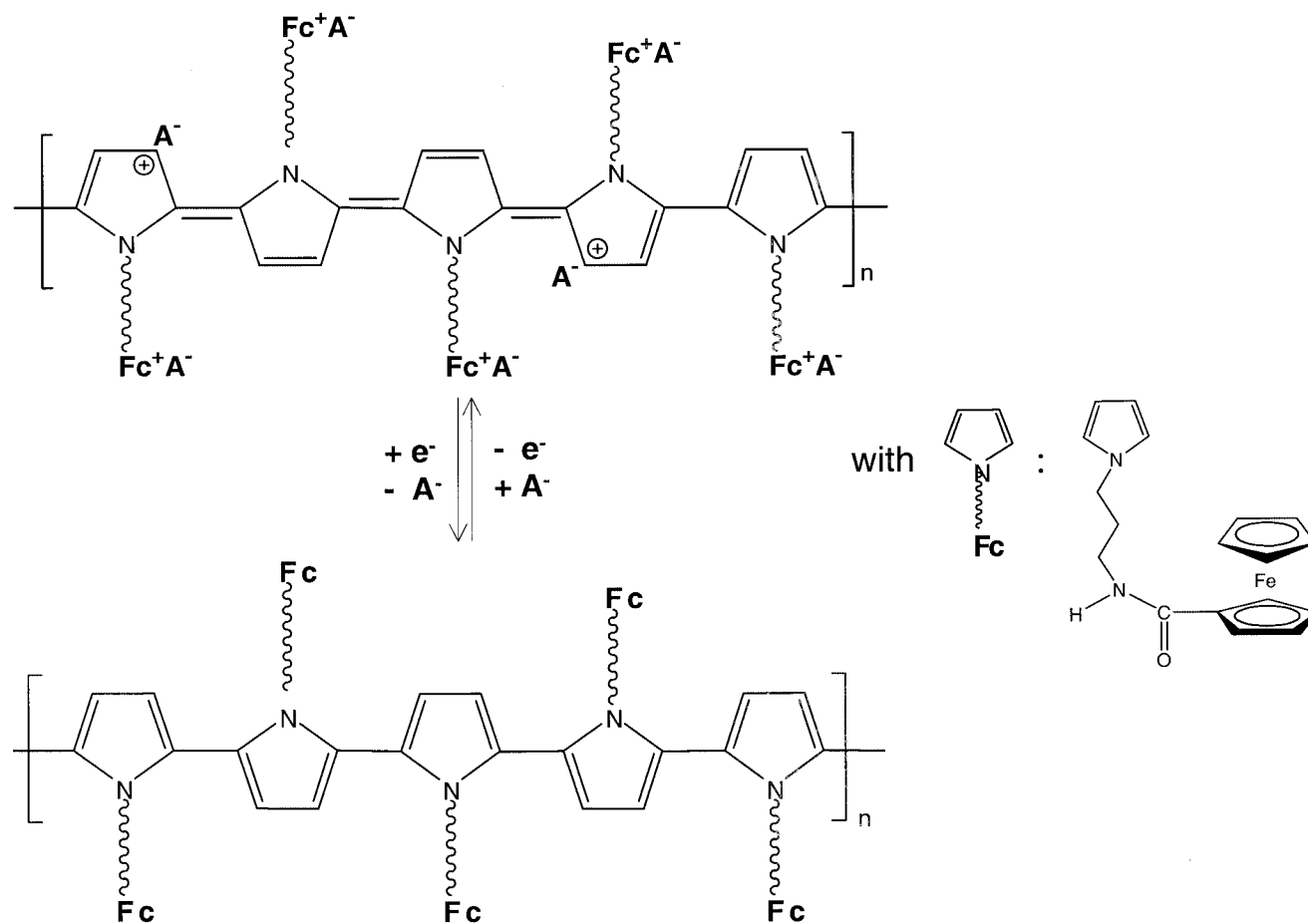


Figure 1 FAPP monomer and FAPP polymer as electro-controllable anions exchanger.

## EXPERIMENTAL

### Organic synthesis

#### Instrumental

$^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra were recorded using a Bruker AC 250 spectrometer (Bruker, Darmstadt, Germany). Chemical shifts are given in ppm downfield from the internal tetramethylsilane standard. Mass spectra were obtained on a Platform II Micromass spectrometer using positive electrospray ionization in a  $\text{CH}_3\text{CN} : \text{water} : \text{formic acid}$  mixture (49 : 49 : 2 vol %). The source temperature was  $50^\circ\text{C}$ , the eluant flow was  $10 \mu\text{L}/\text{min}$ , and the cone voltage was 30 V.

#### *N*-[3-(Pyrrol-1-yl)propyl]ferrocene-1-carboxamide

In the following sections, the product is designated [(ferrocenyl)amidopropyl]pyrrole or FAPP. This monomer was prepared by condensation of *N*-(3-aminopropyl)pyrrole with ferrocenecarbonyl chloride. *Preparation of N*-(3-aminopropyl)pyrrole.<sup>24</sup> A solution of 1-cyanoethylpyrrole (0.041 mol) in anhydrous ether was added to a suspension of  $\text{LiAlH}_4$  (0.1 mol) in anhydrous ether (300 mL) and the mixture was re-

fluxed for 20 h. After cooling, the excess hydride was neutralized by the successive addition of water (3.4 mL), a solution of 15% NaOH (3.4 mL), and water (10.2 mL). The solution was heated to  $40^\circ\text{C}$  for 2 h and filtered on celite before being allowed to dry. A yellow oil was obtained. Yield: 92%. ES-MS  $m/z = 125$ .

$^1\text{H}$ -NMR  $\delta$  ( $\text{CDCl}_3$ ): 1.90 (m, 2H,  $\text{CH}_2$ -2), 2.70 (t, 2H,  $\text{CH}_2$ -3), 3.95 (t, 2H,  $\text{CH}_2$ -1), 6.14 (d, 2H, CH- $\beta$ ), 6.65 (d, 2H, CH- $\alpha$ );  $^{13}\text{C}$ -NMR  $\delta$  ( $\text{CDCl}_3$ ): 35.5 ( $\text{CH}_2$ -2), 39.7 ( $\text{CH}_2$ -3), 47.7 ( $\text{CH}_2$ -1), 108.4 (C- $\beta$ ), 120.9 (C- $\alpha$ ).

*Preparation of ferrocenecarbonyl chloride.* A solution of ferrocenecarboxylic acid (21.74 mmol) in benzene (150 mL) was treated with 26.08 mmol of phosphorus chloride, under nitrogen at room temperature for 4 h. The solution was filtered and the residue allowed to dry. The residue was solubilized in water and extracted by ether, and a red oil was obtained. Yield: 66%.

$^1\text{H}$ -NMR  $\delta$  ( $\text{CDCl}_3$ ): 4.35 (s, Cp), 4.55 (t, H- $\beta'$ ), 4.90 (t, H- $\alpha'$ );  $^{13}\text{C}$ -NMR  $\delta$  ( $\text{CDCl}_3$ ): 70.4 (C- $\alpha'$ ), 71.2 (C- $\beta'$ ), 71.7 (Cp), 73.3 (Ci), 178.3 (CO).

*Preparation of FAPP.* A solution of ferrocenecarbonyl chloride (0.0157 mmol) and of *N*-(3-aminopropyl)pyrrole (0.017 mmol) was stirred at room temperature in anhydrous THF (150 mL) for 20 h. The solution was

then filtered, the residue allowed to dry, and subsequently purified by chromatography on alumina (eluant =  $\text{CH}_2\text{Cl}_2/\text{AcOEt}$ , 90/10). An orange solid was obtained. Yield: 55%.  $F = 145\text{--}146^\circ\text{C}$ . ES-MS  $m/z = 337$ .

$^1\text{H-NMR}$   $\delta$  ( $\text{CDCl}_3$ ): 2.18 (m,  $\text{CH}_2\text{-2}$ ), 3.14 (t,  $\text{CH}_2\text{-3}$ ), 4.05 (t,  $\text{CH}_2\text{-1}$ ), 4.18 (s, Cp), 4.35 (t, H- $\beta'$ ), 4.60 (t, H- $\alpha'$ ), 5.40 (el, NH), 6.25 (d, H- $\beta$ ), 6.75 (d, H- $\alpha$ );  $^{13}\text{C-NMR}$   $\delta$  ( $\text{CDCl}_3$ ): 32.1 ( $\text{CH}_2\text{-2}$ ), 37.8 ( $\text{CH}_2\text{-3}$ ), 48.8 ( $\text{CH}_2\text{-1}$ ), 68.5 (C- $\alpha'$ ), 70.1 (C- $\beta'$ ), 70.7 (Cp), 76.3 (Ci), 109.2 (C- $\beta$ ), 120.9 (C- $\alpha$ ), 170.7 (CO).

#### *N*-[3-(Pyrrolidine-1-yl)propyl]ferrocene-1-carboxamide (ferrocenylamidoethylpyrrolidine)

A solution of ferrocenecarbonyl chloride (8.73 mmol) and of *N*-(3-aminopropyl)pyrrolidine (0.01 mol) was stirred, at room temperature, in anhydrous THF (150 mL) for 20 h. The solution was filtered, the residue allowed to dry, and subsequently purified by chromatography on alumina (eluant =  $\text{CH}_2\text{Cl}_2/\text{AcOEt}$ , 90/10). An orange solid was obtained. Yield: 42%.  $F = 171\text{--}172^\circ\text{C}$ . ES-MS  $m/z = 327$ .

$^1\text{H-NMR}$   $\delta$  ( $\text{CDCl}_3$ ): 1.80 (m,  $\text{CH}_2\text{-}\beta$ ), 2.60 (m,  $\text{CH}_2\text{-}\alpha$ ), 2.75 (t,  $\text{CH}_2\text{-1}$ ), 3.50 (q,  $\text{CH}_2\text{-2}$ ), 4.20 (s, Cp), 4.35 (t, H- $\beta'$ ), 4.70 (t, H- $\alpha'$ ), 6.40 (el, NH).  $^{13}\text{C-NMR}$   $\delta$  ( $\text{CDCl}_3$ ): 23.9 ( $\text{CH}_2\text{-}\beta$ ), 38.5 ( $\text{CH}_2\text{-2}$ ), 54.3 ( $\text{CH}_2\text{-}\alpha$ ), 55.1 ( $\text{CH}_2\text{-1}$ ), 68.6 (C- $\alpha'$ ), 70.1 (Cp), 70.6 (C- $\beta'$ ), 77.9 (Ci), 170.7 (CO).

#### Electrochemical instrumentation

All electrochemical studies were performed with an EG and G 273 A potentiostat-galvanostat. Cyclic voltammetry experiments were performed in a glass cell (10 mL) with a three-electrode assembly. A Pt mesh of  $2 \times 1$  cm was used as counter electrode (CE) and a KCl saturated calomel electrode (SCE) as the reference. (All potentials are given according to the SCE reference.) The working electrode (WE) consisted of a Pt disc (area  $0.07\text{ cm}^2$ ) fitted into a holder made from polytetrafluoroethylene. The working electrode was polished with 1 and  $0.1\text{ }\mu\text{m}$  diamond paste before each deposition experiment. All solutions were deoxygenated with  $\text{N}_2$  before the measurements.

Impedance data were measured with an EG and G 5210 frequency analyzer coupled with the potentiostat and driven by EG and G M270 software. Measurements were performed in the 10-mL glass cell described, in the frequency range  $10^5\text{--}10^{-1}$  Hz with a 5-mV amplitude perturbation.

A Seiko (QCA-917) electrochemical quartz crystal microbalance (EQCM; Seiko Instruments, Tokyo, Japan), coupled with the potentiostat, was used for mass change measurements. The device was equipped with a counter platinum electrode wire and Ag/AgCl reference electrode. The EQCM cell content was about 0.5 mL and the quartz crystal (frequency oscillation

= 8.88 MHz) was covered by a  $0.196\text{-cm}^2$  Pt deposit. The frequency variations measured by an oscillator were converted to mass difference by means of the Sauerbrey equation.<sup>25</sup> The oscillator was able to detect a mass difference of  $10^{-9}$  g.

#### Reagents

All solvents and salts used were pure analytical grade. Pyrrole and 1-cyanoethylpyrrole (Aldrich, Steinheim, Germany) were used as received.

## RESULTS AND DISCUSSION

### Electrochemical properties of the monomer

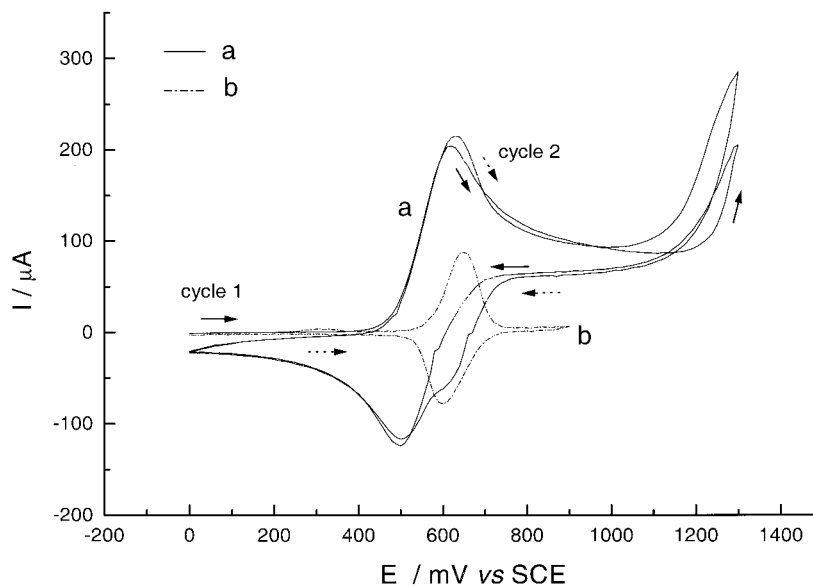
The cyclic voltammogram on Pt electrode of FAPP ( $2 \times 10^{-2}$  mol/L) in  $\text{CH}_3\text{CN}$ , with 0.1 mol/L of  $\text{Bu}_4\text{NPF}_6$  as supporting electrolyte, was performed from 0 to 0.8 V/SCE to avoid pyrrole oxidation. The obtained voltammogram was typical for the reversible oxidation of the ferrocene moiety.<sup>19</sup> The oxidation and reduction potential peaks associated with the electroactivity of the ferrocenyl group were located at 0.62 and 0.5 V/SCE, respectively. The formal potential  $E^{\circ'}$  [ $(E_{\text{ox}}^{1/2} + E_{\text{red}}^{1/2})/2$ ] was 0.565 V. Under these conditions the  $E^{\circ'}$  value of the free ferrocene/ferricinium redox couple was located at 0.41 V. The positive shift observed for the ferrocene grafted on pyrrole was attributed to the attractive effect of the amido group. The potential difference between the oxidation and the reduction peaks of 120 mV was quite high for a one-electron-transfer redox system. This shift could be explained by the ohmic decrease caused by the use of  $\text{CH}_3\text{CN}$  as solvent.

The monomer voltammetric study was also performed at different scan rates, from 10 to  $100\text{ mV s}^{-1}$ . The oxidation peak intensity of the ferrocenyl group is a linear function of the square root of the scan rate ( $R^2 = 0.9989$ ). Thus, under these conditions, the redox process in  $\text{CH}_3\text{CN}$  using  $\text{Bu}_4\text{NPF}_6$  as electrolyte was limited by the diffusion of the FAPP monomer.

### Preparation and characterization of the homopolymer

#### Electrochemical activity of the ferrocenyl group

The film was deposited by two cycles from 0 to 1.3 V/SCE (minimal electrodeposition potential in our conditions) at  $100\text{ mV s}^{-1}$  [Fig. 2(a)]. As previously observed, the oxidation peak of the ferrocenyl group was present at 0.62 V. At 1.1 V, the oxidation of the pyrrole group began, leading to film formation. During the first return scan one peak was observed at 0.5 V, attributed to the reduction of the ferrocenyl group of the FAPP monomer. During the second return scan two reduction peaks were observed: the first one, at



**Figure 2** Cyclic voltammogram: 0.1 mol/L of  $\text{Bu}_4\text{NPF}_6$  in  $\text{CH}_3\text{CN}$ , 100 mV/s, Pt electrode, WE 0.07  $\text{cm}^2$ . (a) Electropolymerization of FAPP monomer ( $2 \times 10^{-2}$  mol/L) in two cycles; (b) FAPP film transferred to the monomer-free electrolyte.

0.63 V, was attributed to the reduction of the ferrinium immobilized into the polymer chain. Transferring the FAPP film to a monomer-free solution [Fig. 2(b)] provided further evidence of this assignment. Under these conditions, the formal potential of the ferrocene/ferrinium couple was 0.62 V. The positive shift of 0.055 V, relative to the position of the redox couple in the solution of monomer, confirmed that the polymerization modified the electronic density of the ferrocenyl group.<sup>18,19</sup> It should be noted that the redox activity of the polypyrrole (generally around 0.4 V/SCE under these conditions) was not visible on the voltammogram. As previously described by Moutet et al.,<sup>18,19</sup> the polypyrrole redox peaks were screened by the ferrocene response.

After the electrosynthesis step, the modified electrode was transferred to a monomer-free solution and a voltammetric study was performed on the film as a function of the scan rate. From 10 to 150  $\text{mV s}^{-1}$ , the oxidation and the reduction charges were equal, thus proving the high reversibility of the redox system. Moreover, the oxidation peak intensity of the voltammograms is a linear function of the scan rate ( $R^2 = 0.9986$ ). Therefore, it seems that the charge transfer is the limiting step of the redox process in  $\text{CH}_3\text{CN}$  with 0.1 mol/L of  $\text{Bu}_4\text{NPF}_6$  for the FAPP polymer.

#### Electrosynthesis of the film

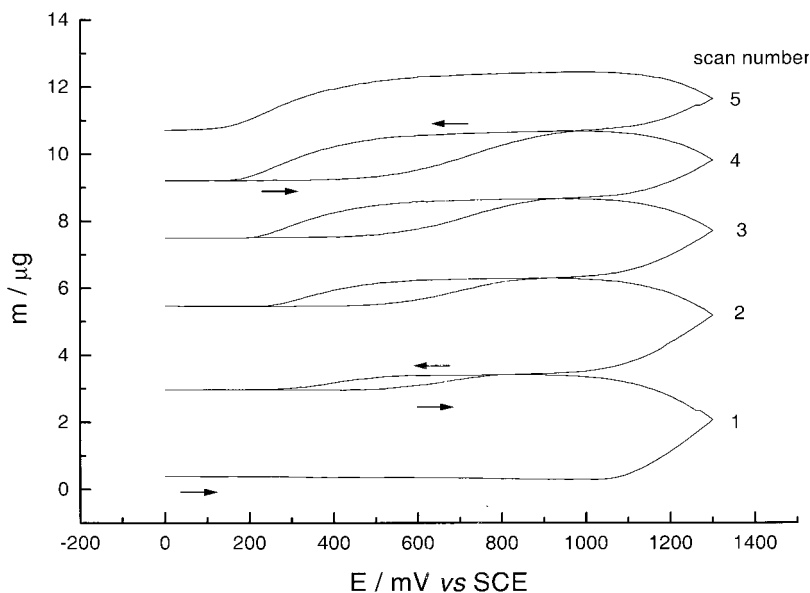
Preparation of the films was performed mainly by cyclic voltammetry, followed by EQCM from 0 to 1.3 and 1.4 V/SCE. Figure 3 shows the recording of the mass deposition as a function of the potential from 0 to 1.3 V/SCE for a monomer concentration of  $2 \times 10^{-2}$

mol/L. The optimal electrogeneration potential is 1.3 V because of the most uniform deposition around 2  $\mu\text{g}/\text{cycle}$  from scan 2 to scan 4. When cycling at 1.4 V/SCE, the mass deposited per cycle decreased during the second scan because of the passivation of the film resulting from overoxidation of the polypyrrole. The use of such a high oxidative potential would thus not be possible.

From 0 to 1.3 V/SCE, three areas are visible in Figure 3:

1. For the first scan, after the monomer oxidation, a mass deposit is observed at 1.1 V.
2. For the return scan, an increase of the mass between 1.3 and 1 V is attributed to the polymer formation. Nevertheless, between 0.6 and 0.3 V, a mass loss is attributed to anions ejected outside the film to maintain the electroneutrality of the material during the reduction process.
3. For the following scans, the mass increase starts around 0.5 V because of the anions inserted inside the film to conserve the electroneutrality of the material during the oxidation of both the pyrrole and the ferrocenyl groups.

Figure 4(a) and (b) show the response of the modified platinum electrode after transfer to a monomer-free solution, during a scan from 0 to 1 V/SCE. A very slight peak is observed at 0.35 V on the voltammogram [Fig. 4(a)], which could be a result of the polypyrrole activity. The associated mass variations are not visible on the EQCM recording [Fig. 4(b)]. The mass variations observed on Figure 4(b) are therefore principally attributed to the ferrocene electroactivity.



**Figure 3** EQCM measurements of the mass growth of FAPP polymer (monomer concentration  $2 \times 10^{-2}$  mol/L), on Pt electrode (WE  $0.196 \text{ cm}^2$ ) in  $\text{CH}_3\text{CN}$  (0.1 mol/L of  $\text{Bu}_4\text{NPF}_6$ ) at 100 mV/s.

The shift of the oxidation and reduction peaks and of the formal potential of the ferrocene/ferricinium couple should be noted, compared with the results obtained in solution and on thinner films (synthesized in only two cycles). This shift is essentially ascribed to the ohmic decrease of the cell induced by the resistivity of the FAPP film.

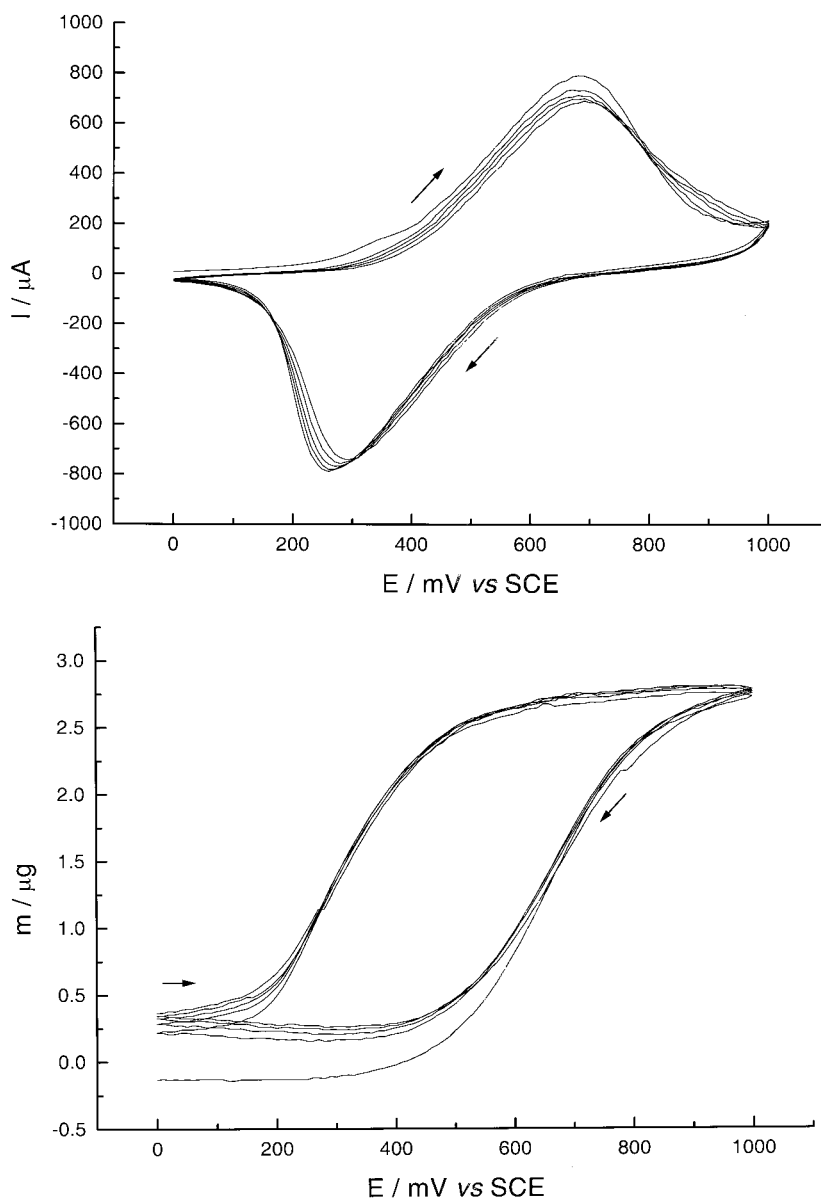
#### Stability of the homopolymer

*Potentiodynamic mode study.* Three different oxidative potentials were applied by cyclic voltammetry (CV) on the film previously prepared at 1.3 V/SCE and transferred to a monomer-free solution. Variation of the mass of the film as a function of time (i.e., potential) is given Figure 5. When cycling from 0 to 1.1 or 1.2 V/SCE, the quantity of anions entrapped during the oxidation was almost equal to the quantity of anions ejected during the reduction (except during the first scan). Nevertheless, as shown by Figure 5, when cycling from 0 to 1.3 V/SCE, the quantity of exchanged anions decreased as a function of the cycle number (i.e., time). The mass loss (deduced from the EQCM recordings) and the polymer oxidation charge for each cycle (deduced by integration on the CV recordings) are summarized in Table I. The decrease of polymer oxidation charge was induced by the material over-oxidation, leading to the loss of a part of the exchanger sites. Because the minimal electrogeneration potential was 1.3 V/SCE, it is clear that film formation is always coupled with film degradation. Moreover, as shown by the following part of the study, after synthesis, an applied potential  $< 1.3$  V/SCE can lead to a degradation of the film.

*Potentiostatic mode study.* For the films synthesized by cyclic voltammetry at 1.3 V/SCE (monomer concentration  $2 \times 10^{-2}$  mol/L), a potential  $< 1.3$  V/SCE was applied for different times: the film was maintained at 0.9 V in a monomer-free solution, for 0, 5, 15, and 35 min, and scanned from 0 to 0.9 V. Decreases of the oxidation ( $I_{\text{ox}}$ ) and of the reduction currents ( $I_{\text{red}}$ ) were observed [ $I_{\text{ox}} = -1.154t + 109.33$ ,  $R^2 = 0.994$ ; and  $I_{\text{red}} = -1.177t + 118.27$ ,  $R^2 = 0.9990$ , with  $I$  ( $\mu\text{A}$ ) and  $t$  (min)]. This study was completed by electrochemical impedance spectroscopy measurements realized at different potentials.

*Voltammetric coupled impedance spectroscopy study.* This study was performed as a function of the potential. Before impedance measurements, the polymer was held for 5 min (to reach the stationary state) at the corresponding potential before imposing the ac perturbation. The impedance measurements were obtained with a decreasing frequency scan and an increasing scan from  $10^5$  to  $10^{-1}$  Hz to verify the reproducibility of the data.

The film used for the voltammetric coupled impedance spectroscopy study was synthesized from a solution at  $2 \times 10^{-2}$  mol/L of FAPP by cyclic voltammetry from 0 to 1.3 V/SCE (7 cycles), on Pt electrode ( $0.07 \text{ cm}^2$ ), in  $\text{CH}_3\text{CN}$  with 0.1 mol/L of  $\text{Bu}_4\text{NPF}_6$ . The voltammogram of the modified electrode after transfer to the monomer-free solution is given in Figure 6(a). After impedance measurements in reductive conditions (applied potential: 0.1 V/SCE), the cyclic voltammogram shows a reduction current similar to those measured at the initial stage and an oxidation current slightly higher than this latter [Fig. 6(b)]. In oxidative conditions, oxidation and reduction currents are al-

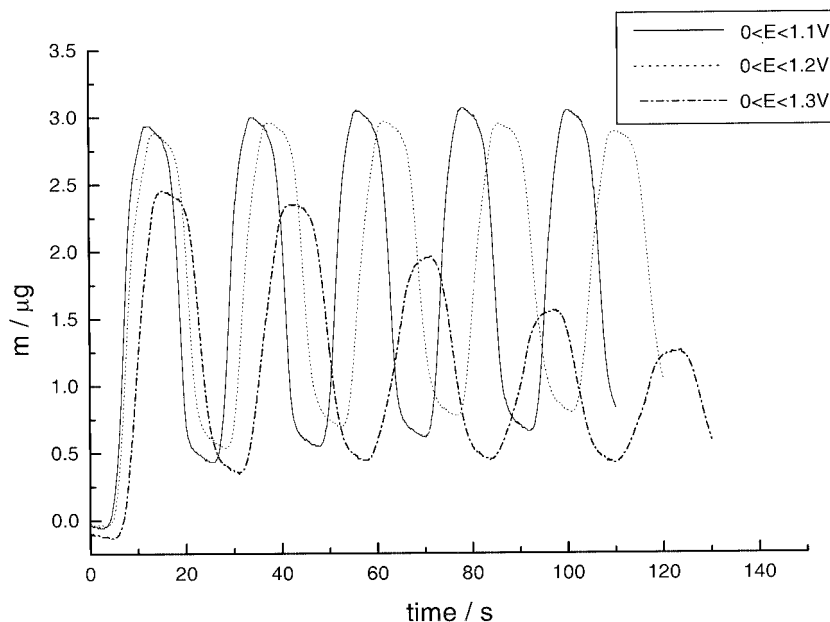


**Figure 4** Electrochemical characterization of FAPP film, on Pt electrode (WE 0.196 cm<sup>2</sup>) in CH<sub>3</sub>CN (0.1 mol/L of Bu<sub>4</sub>NPF<sub>6</sub>) at 100 mV/s: (a) cyclic voltammogram; (b) EQCM measurements.

most equal to those measured at the initial step for applied potentials from 0.4 to 0.7 V/SCE [Fig. 6(c)]. The slight differences observed for the oxidation peaks are, from our point of view, not significant, given that the reduction peaks were equal whatever the applied potential from 0.1 to 0.7 V/SCE. Nevertheless, for higher potentials (i.e., after impedance measurements at 0.9, 1, and 1.1 V/SCE), an irreversible degradation of the redox properties of the film may be noted [Fig. 6(d)–(f)]. Impedance measurements recorded, in oxidative conditions, at 0.5, 0.6, 0.7, 0.8, and 0.9 V/SCE are given in Figure 7. The total ohmic resistance  $R_T$  of the system was deduced from the data at the intersection of the low-frequency part of the diagram with the real axis. For each potential,

$R_T$  is presented in Figure 7. The total resistance  $R_T$  of the system decreases between 0.5 and 0.6 V (optimal oxidative condition). From 0.6 V/SCE, the film resistance increases because of the overoxidation of the polymer. EIS coupled with CV is a method well adapted to investigate the film stability. Indeed, at 0.7 V, the cyclic voltammogram presents no change before and after impedance measurements; nevertheless, as shown by the Nyquist representation at this potential, the total resistance  $R_T$  of the system is significantly higher than that at 0.6 V, proving that degradation of the film starts at this relatively low oxidative potential.

As seen previously [Fig. 4(a)], only a slight oxidative peak that is related to the polypyrrole electroactivity is visible on the voltammograms at 0.35 V. It is then pos-



**Figure 5** EQCM measurements of the mass variation of FAPP polymer on Pt electrode as a function of time for different applied potentials.

sible that the polypyrrole electrochemical behavior is perturbed by the ferrocenyl group because of the high repulsive interactions between the ferrocenium positive groups of the FAPP film. To decrease these interactions, we propose introduction of a spacer in the FAPP polymeric chain by electrogenerating a copolymer between the pyrrole and the FAPP monomers.

#### Preparation and characterization of the copolymer FAPP/Py

This study was performed under the experimental conditions previously used in the case of FAPP (Pt electrode of  $0.07 \text{ cm}^2$  area, in  $\text{CH}_3\text{CN}$  with  $0.1 \text{ mol/L}$  of  $\text{Bu}_4\text{NPF}_6$ ). Different FAPP/Py ratios were tested:  $10^{-2}/5 \times 10^{-3}$ ,  $10^{-2}/10^{-2}$ , and  $10^{-2}/2 \times 10^{-2} \text{ mol/L}$ . Films were synthesized in 10 cycles by cyclic voltammetry from  $-0.4$  to  $1.3 \text{ V/SCE}$  and then transferred to

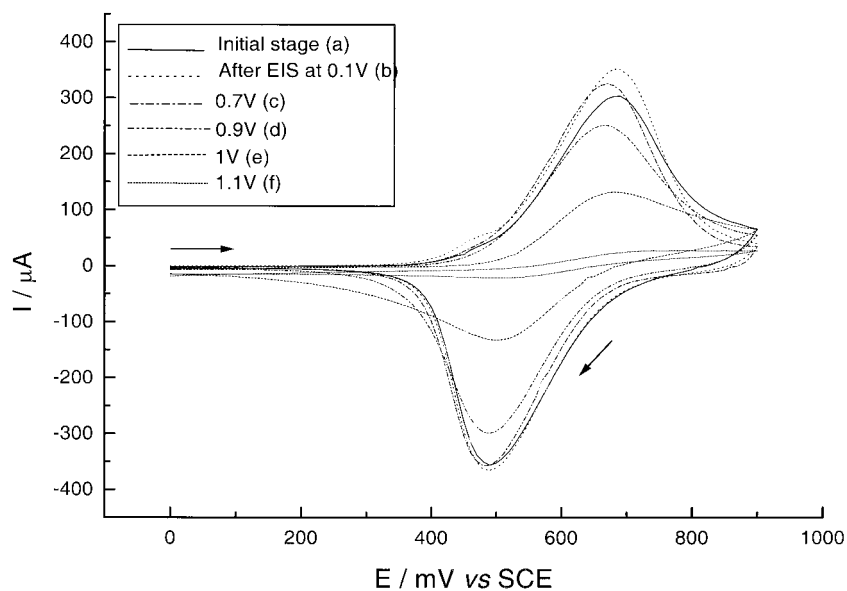
a monomer-free solution. The electropolymerization of the film and its redox activity are given for the FAPP/Py ratio  $10^{-2} \text{ M}/10^{-2} \text{ M}$  in Figure 8(a) and (b), respectively. The different waves, corresponding to the electrooxidation of FAPP and of the pyrrole are distinguishable. For the  $10^{-2}/10^{-2}$  ratio, current steps at  $0.2$  and  $0.7 \text{ V}$  are related to the polypyrrole and to the FAPP oxidations, respectively. It should be noted that the ratio  $I_{\text{ox}}(\text{FAPP})/I_{\text{ox}}(\text{Py})$  agrees with the concentration ratio; furthermore, the reduction polypyrrole peak, masked for a high FAPP/Py ratio ( $10^{-2}/5 \times 10^{-3}$ ) is visible when the latter is decreasing ( $10^{-2}/10^{-2}$ ). Moreover, the first potential scan [Fig. 8(a)] presents a single principal oxidation peak starting at  $1.2 \text{ V}$ , corresponding to the oxidation of both monomers in the solution. This result is in accordance with the electrosynthesis of a FAPP/Py copolymer and not a mixture of polypyrrole and polyFAPP.

Nevertheless, to complete the study that concerns formation of the copolymer, attempts of electropolymerizations of pyrrole ( $5 \times 10^{-3} \text{ mol/L}$ ) first in the presence of a nonelectropolymerizable compound (ferrocenylamidoethylpyrrolidine at  $10^{-2} \text{ mol/L}$ ) and second in the presence of the molecule of ferrocene ( $10^{-2} \text{ mol/L}$ ) were performed. The voltammograms related to the electropolymerization showed the typical redox waves of the polypyrrole with an oxidation step around  $0.1 \text{ V/SCE}$ . The redox peaks of the non-electropolymerizable ferrocenyl group were also observed with an oxidation peak at  $0.7 \text{ V}$  in the case of ferrocenylamidoethylpyrrolidine and at  $0.4 \text{ V}$  in the case of the ferrocene molecule. Moreover, after trans-

**TABLE I**  
Variations of the Exchanged Anion Quantity ( $\mu\text{g}$ ) and of the Polymer Oxidation Charge (mC) for the Different Cycles (n)<sup>a</sup>

<i>n</i>	<i>m</i> ( $\mu\text{g}$ )	<i>Q</i> (mC per cycle)
1	2.37	3.12
2	1.57	2.55
3	0.746	1.775
4	0.429	1.485
5	0.308	1.346

<sup>a</sup> (Scanning potential from  $0$  to  $1.3 \text{ V/SCE}$ ). Film synthesized by cyclic voltammetry in 10 cycles ( $0$  to  $1.3 \text{ V/SCE}$ ) from a solution of  $2 \times 10^{-2} \text{ mol/L}$  of FAPP (Pt,  $0.196 \text{ cm}^2$ ).

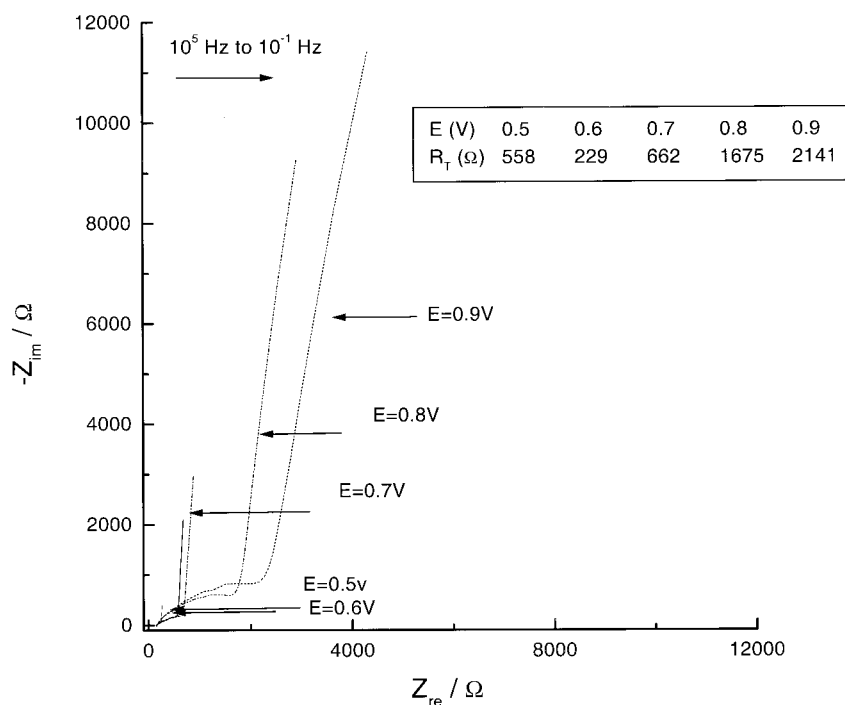


**Figure 6** Cyclic voltammogram recorded after EIS at (b) 0.1 V, (c) 0.7 V, (d) 0.9 V, (e) 1.0 V, and (f) 1.1 V, where (a) is the initial response of the film.

fer in a monomer-free solution, the voltammograms of both types of modified electrodes did not show the redox activity of the ferrocenyl group, which proves that the ferrocene molecule and especially the ferrocenylamidoethylpyrrolidine molecule cannot be trapped in the polymer film. As a consequence, we can affirm in the case of the FAPP/Py film preparation that the

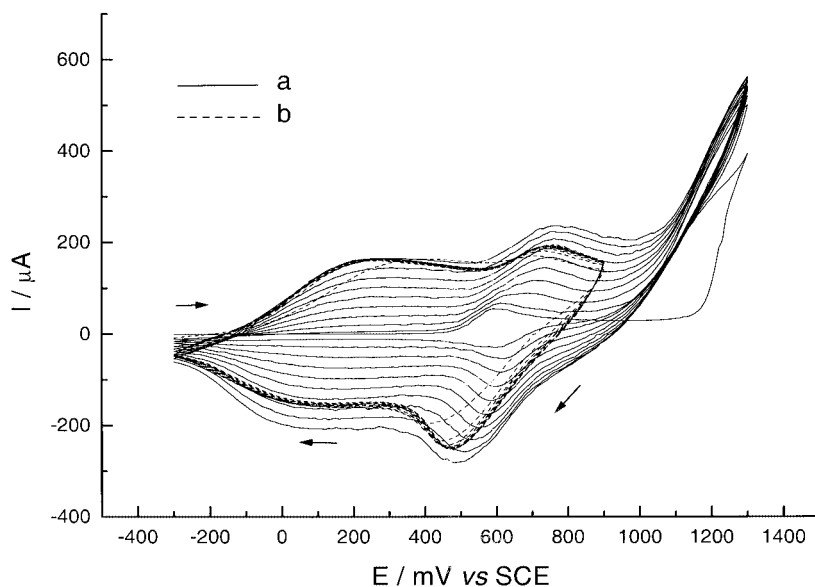
FAPP molecule is polymerized and not simply inserted in a polypyrrole film.

The electrosynthesis and the electroactivity of the copolymer films were characterized by EQCM for different concentration ratios. These experiments were performed under the same experimental conditions as previously described. We present the recording of the



**Figure 7** Impedance spectra of FAPP film (Pt electrode, WE 0.07 cm<sup>2</sup>, 0.1 mol/L of Bu<sub>4</sub>NPF<sub>6</sub> in CH<sub>3</sub>CN), in the frequency range 10<sup>-5</sup> to 10<sup>-1</sup> Hz, at 0.5, 0.6, 0.7, 0.8, and 0.9 V/SCE.





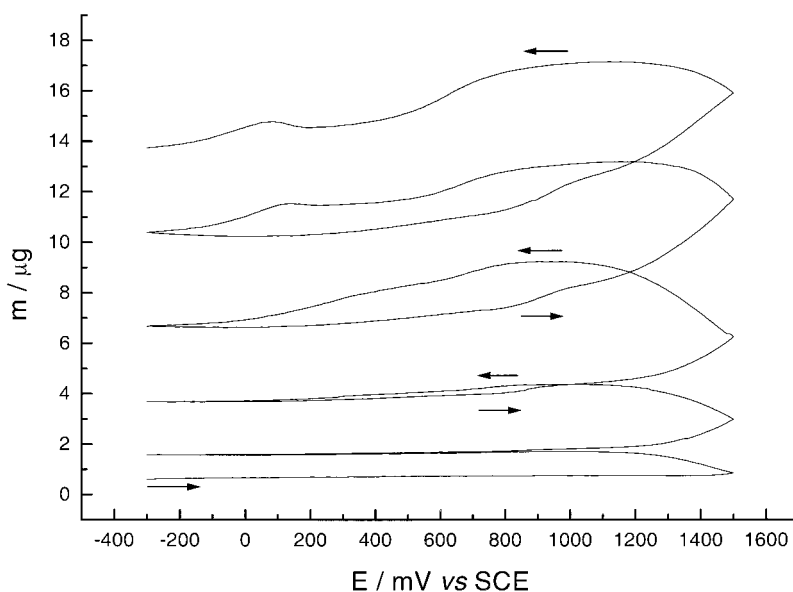
**Figure 8** Cyclic voltammogram: 0.1 mol/L of  $\text{Bu}_4\text{NPF}_6$  in  $\text{CH}_3\text{CN}$ , 100 mV/s, Pt electrode, WE 0.07  $\text{cm}^2$ : (a) electropolymerization of FAPP and pyrrole in the FAPP/Py concentration ratio of  $10^{-2}/10^{-2}$  (—); (b) FAPP/Py copolymer film in the transfer solution (---).

mass deposit as a function of the potential for the FAPP/Py ratio  $10^{-2}/10^{-2}$  (Fig. 9). After five cycles, the mass deposition was 3.2, 10.7, and 17  $\mu\text{g}$  for FAPP/Py concentration ratios of  $10^{-2}/2 \times 10^{-3}$ ,  $10^{-2}/5 \times 10^{-3}$ , and  $10^{-2}/10^{-2}$ , respectively, which proves the rather high regularity of the deposition for such a number of cycles.

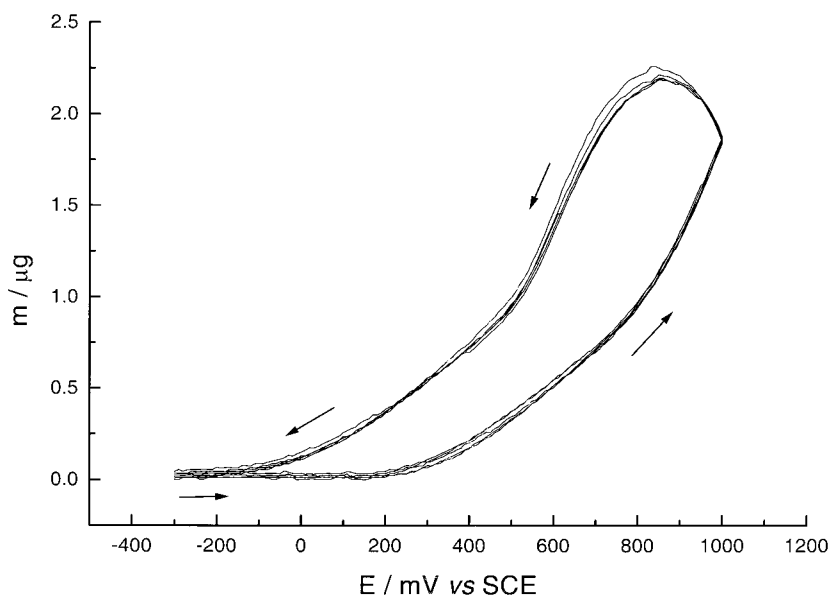
After transfer to a monomer-free solution, the redox waves related to the polypyrrole and to the ferrocenyl group were distinguishable. The variations of the

mass of the film determined by EQCM as a function of the potential (Fig. 10) allowed us to specify the different ionic motions involved in the redox processes:

- Between 0.2 and 0.8 V/SCE, an anion insertion is necessary to maintain the electroactivity of the polypyrrole in the copolymer.
- Between 0.8 and 1 V, an anion insertion allows the cation ferrocium to be neutralized. The mass increases up to 1 V and in the return scan, to 0.85 V.



**Figure 9** EQCM measurements of the mass growth of FAPP/Py copolymer in the FAPP/Py concentration ratio of  $10^{-2}/10^{-2}$  (0.1 mol/L of  $\text{Bu}_4\text{NPF}_6$  in  $\text{CH}_3\text{CN}$ , 100 mV/s, Pt electrode, WE 0.196  $\text{cm}^2$ ).



**Figure 10** EQCM measurements of FAPP/Py copolymer on Pt electrode (WE 0.196 cm<sup>2</sup>) in CH<sub>3</sub>CN (0.1 mol/L of Bu<sub>4</sub>NPF<sub>6</sub>) at 100 mV/s (film synthesized under the conditions defined in Fig. 9).

- Between 0.85 and 0.6 V, a mass loss and consequently an anion expulsion is attributed to the reduction of the cation ferrocenium in the copolymer.
- Between 0.6 and -0.2 V, the mass loss, observed on a different slope, is linked to the reduction of the polypyrrole in the copolymer.

The high reversibility of the ionic exchange proves that the electroactivity of the polypyrrole and the ferrocenyl group remained in the copolymer film. Thus, it is possible to control the oxidation state of both electroactive compounds in the film. This property should allow us to use the material as an electrocontrollable membrane for ionic transport.

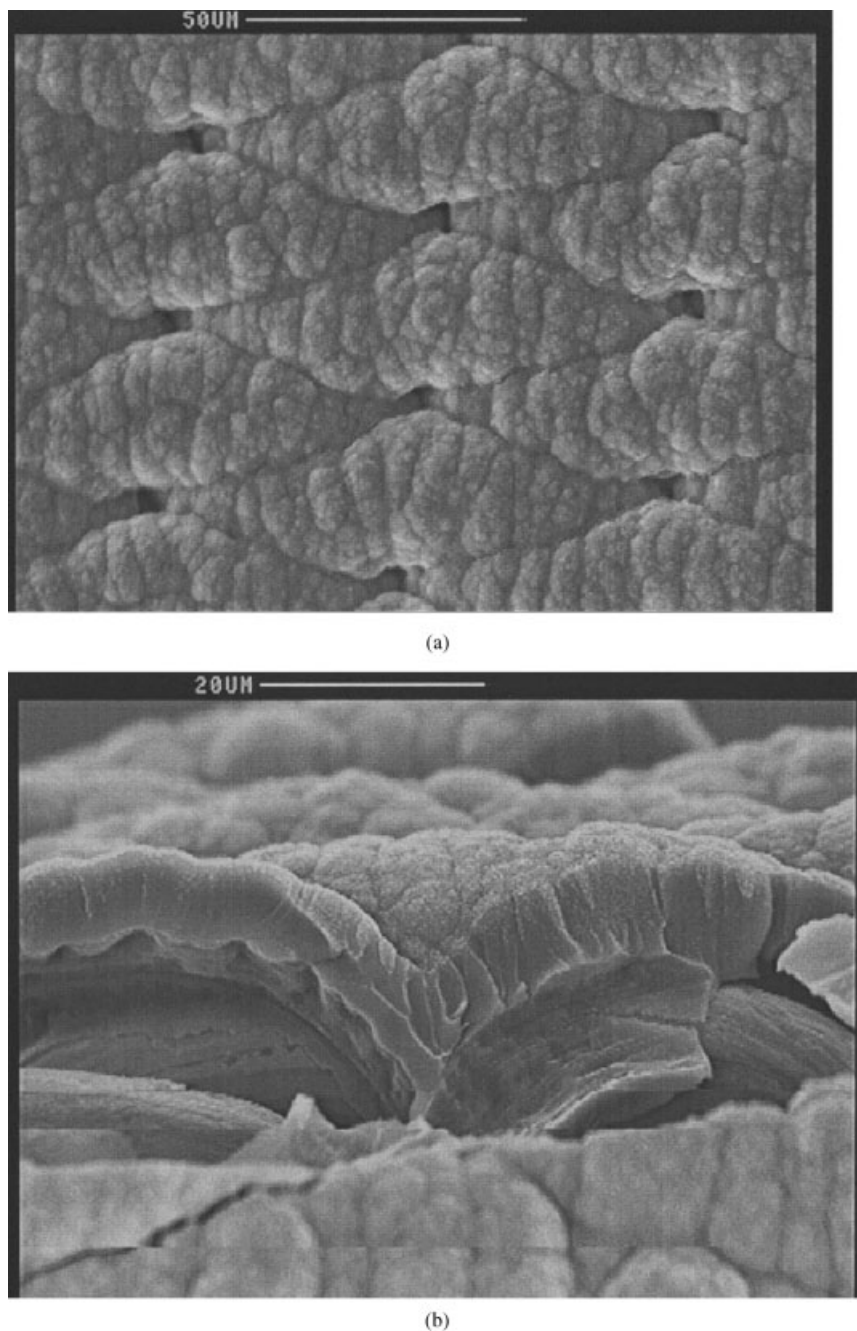
### Preparation of membranes

With respect to membrane applications, both faces of the film must be accessible and the surface of the

polymer must be high enough to permit sufficient transfer of the compound. Therefore, we initially studied the FAPP/Py electrodeposition on stainless-steel meshes of around 2 cm<sup>2</sup> area. Electrogeneration of the film was performed from a solution of pyrrole and FAPP in the FAPP/Py concentration ratio of 10<sup>-2</sup>/10<sup>-2</sup> by cyclic voltammetry (10 cycles) from -0.4 to 1.3 V/SCE under the classical experimental conditions (CH<sub>3</sub>CN, 10<sup>-1</sup> M Bu<sub>4</sub>NPF<sub>6</sub>, V = 100 mV s<sup>-1</sup>). As previously observed on Pt electrode, two redox waves were distinguishable. Current steps, located at 0.5 and 1.05 V, were attributed to the polypyrrole and the FAPP oxidations, respectively. The shift of the oxidation potentials observed on stainless-steel meshes was essentially attributed to the nature of the electrode. SEM analysis showed a homogeneous coating of the fibers (thickness 1 μm), although the porosity apparently remained. To develop thicker films, it was necessary to perform the electropolymerization in the potentiostatic mode. The optimization of the experi-

**TABLE II**  
Characteristic and Elaboration Conditions of FAPP/Py Copolymer Films Prepared in Potentiostatic Mode on Stainless-Steel Meshes (2 cm<sup>2</sup>) in CH<sub>3</sub>CN (0.1 mol/L Bu<sub>4</sub>NPF<sub>6</sub>)

Applied potential (V versus SCE)	Concentration ratio FAPP/Py (mol/L <sup>-1</sup> )	Electrolysis duration (min)	Film aspect	Thickness (μm)
1.2	10 <sup>-2</sup> /5 × 10 <sup>-3</sup>	5	Partial coating of the mesh	0.5
—	—	10	—	0.8
—	—	30	Total coating with cracks	3
—	10 <sup>-2</sup> /10 <sup>-2</sup>	5	Partial coating of the mesh	1
—	—	10	Total coating with cracks	1.5
—	—	30	—	9
1.3	10 <sup>-2</sup> /5 × 10 <sup>-3</sup>	5	Partial coating of the mesh	0.9
—	—	10	—	2.5
1.3	10 <sup>-2</sup> /5 × 10 <sup>-3</sup>	5	Total coating	10



**Figure 11** SEM surface (a) and cross section (b) micrographs of FAPP/Py copolymer prepared on stainless-steel mesh by potentiostatic mode at 1.3 V/SCE for 30 min with a FAPP/Py concentration ratio of  $10^{-2}/5 \times 10^{-3}$  in  $\text{CH}_3\text{CN}$  (0.1 mol/L of  $\text{Bu}_4\text{NPF}_6$ ). The thickness of the film is about 10  $\mu\text{m}$ .

mental conditions is summarized in Table II. Micrographs obtained under more suitable conditions are presented in Figure 11. The thickness of the coating is around 10  $\mu\text{m}$  and the porosities of the meshes are completely filled. With respect to transport applications, the next stage is the preparation of plane circular membranes ( $\sim 50$  mm diameter) on the same support using our previously described laboratory cell.<sup>26</sup> Such experiments were recently successfully performed in our research group, for example, in the case of the

electrocopolymerization of mixtures of pyrrole and crown ethers functionalized pyrrole.<sup>27</sup>

## CONCLUSIONS

The synthesis of *N*-[3-(pyrrol-1-yl)propyl]ferrocene-1-carboxamide (FAPP) was carried out. The electrochemical study confirmed the redox electroactivity of the ferrocenyl group in the functionalized monomer,

by cyclic voltammetry between 0 and 0.8 V/SCE. The preparation of the polyFAPP, by cyclic voltammetry from 0 to 1.3 V/SCE, showed a positive shift of the ferrocene unit formal potential when polymerization occurred. This is probably attributable to the modification of the electronic density of the ferrocenyl group in the polymer. EQCM measurements on the electro-synthesized FAPP-based films confirmed that mass variations are essentially attributable to the electrochemical activity of the ferrocenyl group. Nevertheless, the stability of the film was low in potentiostatic and in potentiodynamic modes almost certainly because of the electrostatic interactions between the ferrocenium units. Copolymerization of pyrrole and FAPP, to increase the stability, allowed the preparation of a film for which the electroactivity of both pyrrole and FAPP are conserved and controllable. Films of about 2 cm<sup>2</sup> area were synthesized on stainless-steel meshes for membrane applications. The optimal way to obtain dense and homogeneous membranes was determined to be by electropolymerization in potentiostatic mode at 1.3 V/SCE in a FAPP/Py concentration ratio of  $10^{-2}/5 \times 10^{-3}$  mol/L, in CH<sub>3</sub>CN (0.1 mol/L of Bu<sub>4</sub>NPF<sub>6</sub>). Ionic transport experiments under electrochemical control using such membranes are now in progress.

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