# Redox-active Films of Ferrocene Covalently Attached to Polypyrrole

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Thin films of an electroactive polymer may be obtained from the anodic electropolymerisation of an N-substituted ferrocenylpyrrole. Direct electropolymerisation yields a film which exhibits rectifying behaviour but whose electroactivity decays. Co-polymerisation with N-methylpyrrole gives a film with a stable Fc–Fc$^+$ response.

The incorporation of redox centres in thin films of poly(pyrrole) may be achieved readily by functionalising the pyrrole monomer at nitrogen with the molecular electroactive species. Anodic electropolymerisation yields a material which is both a 'redox-conductor' and a semi-conductor (σ_{298} typically 10^{-3}–10^{-5} S cm^{-1}). Several different examples of N-alkylpyrroles bearing metal bipyridyl[1] or phenanthrolyl[2] centres have been reported, and some preliminary examples of ferrocenyl-substituted films have also been described.[3–5] In reports of these ferrocene-containing materials,[3,4] the characterisation and stability of the polymeric films has been rather neglected. In this work, the polymeric films have been examined both electrochemically and by surface analytical methods, with particular attention to their stability to electrochemical cycling. A preliminary report of some of this work has been given.[5]

The monomer N,N'-bis-[3-(pyrrol-1-yl)propyl]ferrocene-1,1'-dicarboxamide (1) was prepared by reaction of N-(3-amino-

(1)
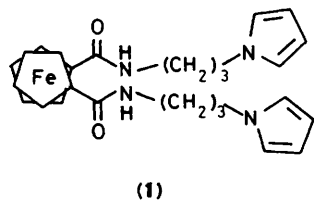
propyl)pyrrole, in the presence of triethylamine, with ferrocene-1,1'-dicarbonyl chloride. A single-sweep cyclic voltammogram of (1) (2 × 10^{-3} mol dm^{-3}) in acetonitrile solution, in the presence of 0.1 mol dm^{-3} Bu$_4$NClO$_4$ or Bu$_4$NBF$_4$, showed a reversible ferrocene–ferricenium wave at $E^{\ominus}$ 0.78 V (*versus* s.c.e.) and an irreversible oxidation peak at *ca.* +1.26 V, arising from pyrrole oxidation. Golden films of a polymeric material were deposited on the electrode surface (glassy carbon, Pt or indium–tin oxide) either by repeated cycling between −0.1 and +1.3 V or by controlled potential electrolysis at +1.3 V. A single-sweep cyclic voltammogram, in monomer-free solution, for a film deposited by controlled-potential electrolysis (c.p.e.) (Γ_{app} 4 × 10^{-9} mol cm^{-2}) reveals a ferrocene–ferricenium wave at +0.78 V, (Figure 1). At a sweep rate of 10 mV s^{-1}, a peak splitting of 30 mV (FWHM 160 mV) for this redox couple was observed and i_a/i_c was unity in good agreement with the value expected for a surface-immobilised electroactive film for which charge transfer is reversible and is rapid with respect to the experimental timescale.[6] Thicker films were obtained with longer electrolyses—up to an apparent molar coverage of 3.8 × 10^{-8} mol cm^{-2} on a glassy carbon electrode. Using the approximation that one molecular layer corresponds to a coverage of *ca.* 10^{-10} mol cm^{-2},[7] this coverage is equal to 380 layers.

Dry-state electronic conductivity measurements showed the film exhibited unusual rectifying behaviour (Figure 2) impeding
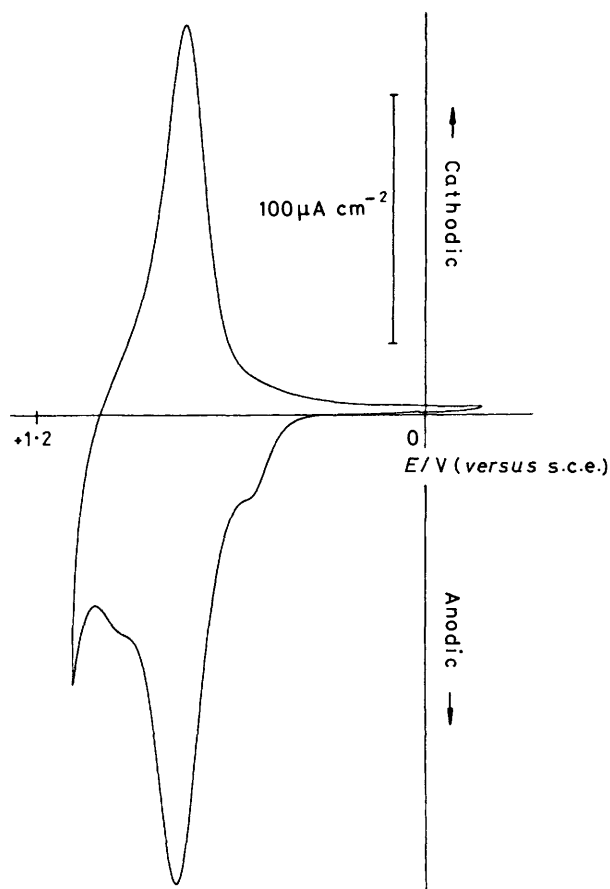

Figure 1. Cyclic voltammogram for a glassy carbon electrode modified with a film of poly (1), v 100 mV s^{-1} (0.1 mol dm^{-3} Bu$_4$NClO$_4$ in CH$_3$CN)

current flow with a positive potential, more strongly than with an applied negative potential. For none of the samples tested was a conductivity greater than 5 × 10^{-9} S cm^{-1} recorded. Such a value clearly does not support the hypothesis that film growth is sustained by high electronic conductivity in this case. However, the Fc–Fc$^+$ redox couple is *ca.* 0.48 V negative of the pyrrole monomer oxidation peak so that a film-growth mechanism involving redox conduction seems unlikely at first glance. It does seem that the iron centre plays a catalytic role in the polymerisation process. Indeed films could be formed at only +1.1 V (also observed with a copolymer). The Fc–Fc$^+$ couple is anodic with respect to the oxidation potential of the polypyrrole moiety, and could function as an electron relay sustaining film growth as the film thickness grows and builds up a finite resistance.

An ESCA spectrum of a typical film grown on a platinum flag electrode revealed that the iron is present in an electron paired environment, with the $Fe_{2p_{3/2}}$ signal centred at 708.8 eV (FHWM 3.8 eV) (Figure 3). Identical spectra were obtained with films grown from solutions of (1) over 1, 2, 4, and 8 min reaction times. For films grown in Bu_4NClO_4 electrolyte, the percentage perchlorate doping level was obtained from both the nitrogen to chlorine elemental ratios, giving 39 and 37% respectively; for films grown in Bu_4NBF_4 solution dopant anion levels of 17.6 and 18.1% were correspondingly evaluated from
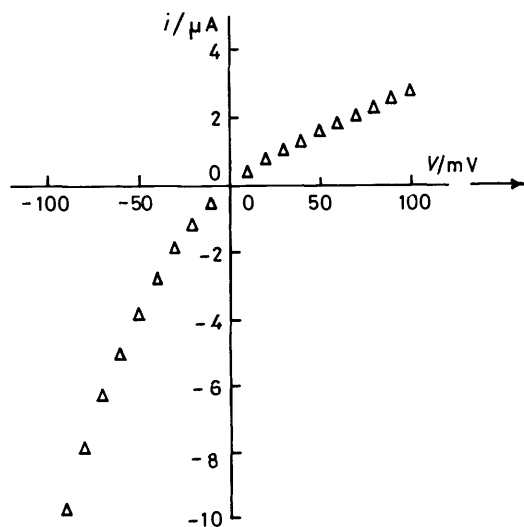

Figure 2. Current voltage plot for poly (1)

N/F and Fe/F ratios. The higher incorporation of perchlorate compared to tetrafluoroborate has been observed previously for poly(pyrrole) itself.[8] In the N_{1s} spectra the main peak may be approximated to a single Gaussian curve, although curve-fitting is complicated by the amide nitrogens which give a small positive shift from 400 eV.

Film deposition efficiencies were evaluated from the number of moles of (1) deposited (determined by cyclic voltammetry) divided by the number of moles of (1) oxidised during deposition (determined from the total charge passed during electrolysis and using a value of 5.6 for the number of electrons transferred, i.e. two for each pyrrole, one for $Fc–Fc^+$ and 2×0.3 for the monomer doping level). Deposition efficiencies were invariant with deposition time 1–10 min and average values of 6 (in 0.1 mol dm^{-3} Bu_4NClO_4) and 9% (in 0.1 mol dm^{-3} Bu_4NBF_4) were found. These are comparable to values of 60–80% found for metal bipyridyl N-substituted poly(pyrroles).[1b]

When films deposited by c.p.e. were examined by cyclic voltammetry as a function of time, a steady decrease in the current response with cycle number was observed (Figure 4). This decay process was repeatedly found regardless of the supporting electrolyte used to grow or test the films. Plots of i_a or i_c against cycle number (v 10 mV s^{-1}) showed a linear dependence, implying that the degradation process has a zero order dependence on the ferrocene concentration. The rate of decay was increased by increasing the anodic potential limit of the cyclic voltammetry (c.v.), but was independent of the concentration of dissolved oxygen: experiments performed in oxygen-saturated solution rather than in an argon purged solution showed no variation. Examination by ESCA of several films which had undergone exhaustive cycling revealed that all of the iron was present in the +3 oxidation state ($Fe_{2p_{3/2}}$ 711.5 eV) and there was also an increase in the oxygen to carbon ratio
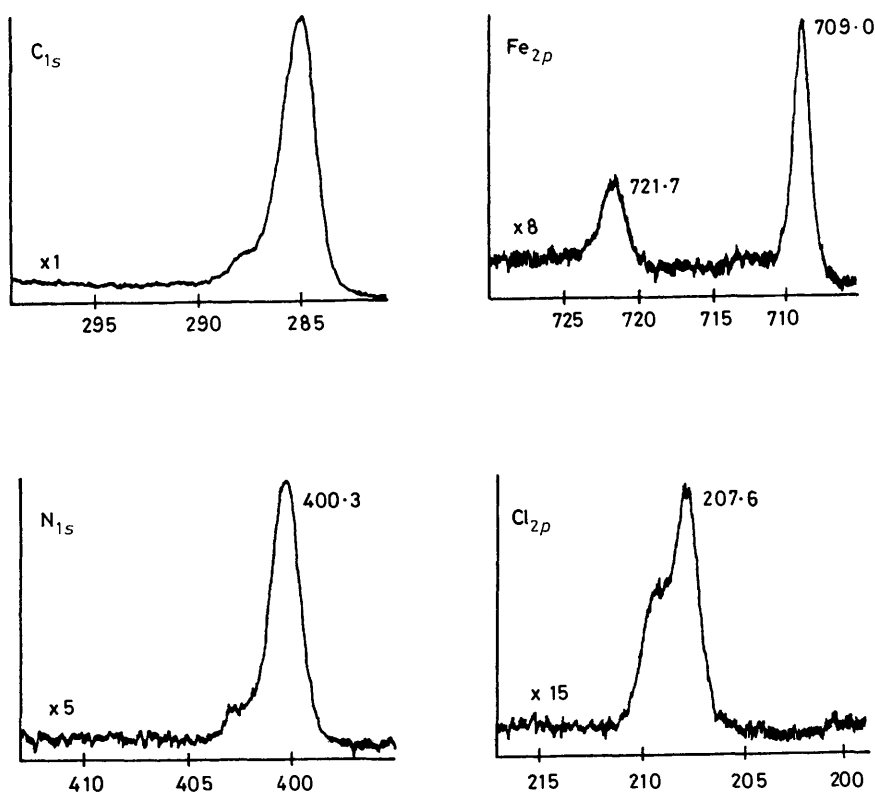

Figure 3. ESCA spectra for a film of poly (1) formed in Bu_4NClO_4. Similar Fe_{2p}, C_{1s}, and N_{1s} spectra were obtained when Bu_4NBF_4 electrolyte was used
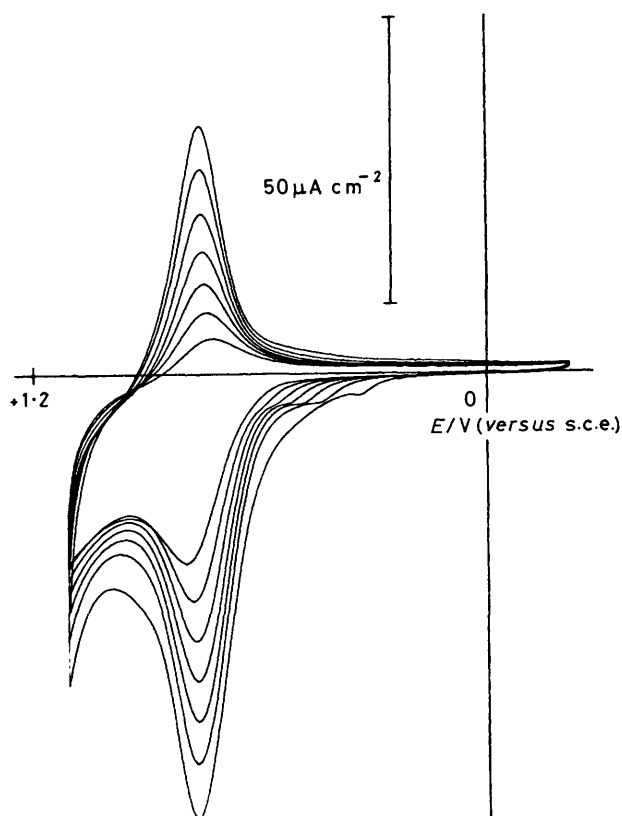
Figure 4. Decay of electroactivity of poly (1) (v 10 mV s^{-1}, 0.1 mol dm^{-3} Bu$_4$NClO$_4$ in CH$_3$CN)
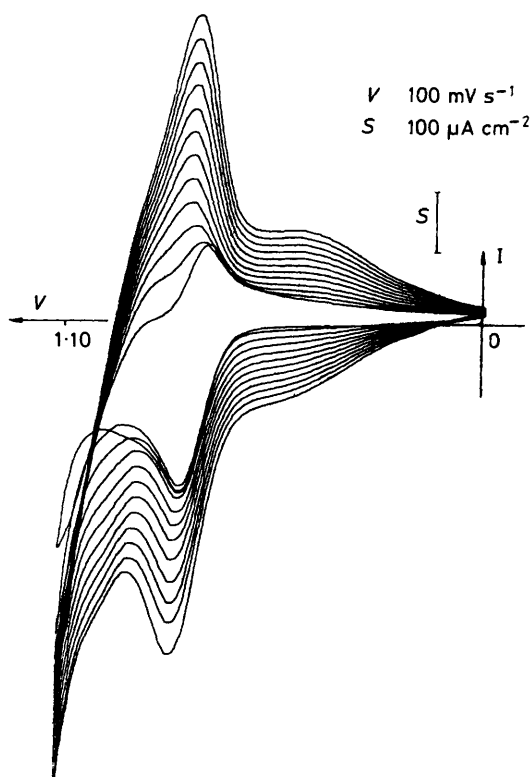

Figure 5. Growth of a stable 1 : 1 co-polymer of (1) and N-methylpyrrole, upon repeated cycling (v 100 mV s^{-1}, 0.1 mol dm^{-3} Bu$_4$NClO$_4$ in CH$_3$CN)

by a factor of between 1.4 and 2.6. The mechanism of this irreversible decay process is unclear.

When (1) was deposited onto platinum by cycling the electrode potential between -0.1 and $+1.3$ V, it was observed that the Fc–Fc$^+$ wave grew over the first few cycles but then began to decay. In an effort to evaluate the dependence of the number of c.v. cycles in determining the degree of degradation, films were deposited on an electrode for the same total deposition time, but over different numbers of cycles, by varying the sweep rate. The amount of active film was then measured from a single-sweep cyclic voltammogram in monomer-free electrolyte (v 10 mV s^{-1}). The amount of electroactive material deposited decreased with increasing sweep rate implying that the extent of film degradation increases with the number of film-forming cycles. Potentiostatting at 1.3 V a modified electrode formed by c.p.e. in a monomer-free solution, also led to a degradation in the amount of electroactive material.

A convenient way of inhibiting the decay of electroactivity of the 'redox' polymeric thin film is to co-polymerise (1) with a monomer of similar reactivity ratio. N-Methylpyrrole was adequate for this purpose and electropolymerisation of a 1 : 1 mixture (0.1 mol dm^{-3} Bu$_4$NClO$_4$) of (1) and N-methylpyrrole gave a golden film which exhibited a persistent *stable* c.v. response in monomer-free electrolyte. Growth of this copolymer was monitored by cyclic voltammetry (Figure 5), which showed that the electroactive polymer behaved almost ideally with rapid charge-transfer kinetics (*e.g.* at v 100 mV s^{-1}, i_a/i_c ca. 1, peak splitting Fc–Fc$^+$ 45 mV, FWHM 175 mV). Films with apparent molar coverages up to Γ_{app} 2 × 10^{-8} mol cm^{-2} were grown, with thinner films (Γ_{app} 5 × 10^{-9} mol cm^{-2}) exhibiting a linear response of i_a *versus* sweep rate (25→400 mV s^{-1}) while thicker films deviated from linearity as film resistance increased and charge transport became rate-limiting.[9] Similar behaviour has been defined with metal-bipyridyl functionalised thin films.[1b,8]

Experimental

N,N′-*Bis*-[3-(*Pyrrol*-1-*yl*)*propyl*]*ferrocene*-1,1′-*dicarbox-amide* (**1**).—Triethylamine (2.5 g, 0.026 mol) and N-(3-aminopropyl)pyrrole (1.18 g, 0.01 mol) were added to a solution of ferrocene-1,1′-dicarbonyl chloride (3.01 g, 0.01 mol) in dichloromethane (20 cm^3) and the mixture was stirred at 20 °C for 16 h. After filtration, solvent was removed under reduced pressure to yield a reddish residue which was chromatographed on neutral alumina, eluting with dichloromethane–methanol (100 : 1). An orange microcrystalline solid was obtained (3.7 g, 75%), m.p. 136 °C (Found: C, 64.5; H, 5.85; N, 11.2. C$_{26}$H$_{30}$FeN$_4$O$_2$ requires C, 64.2; H, 6.2; N, 11.5%); δ_H(CDCl$_3$) 6.74 (4 H, dd, pyrrole CH), 6.60 (2 H, br t, NHCO), 6.18 (4 H, dd), 4.38 (4 H, t, ferrocene CH), 4.33 (4 H, t, ferrocene CH′), 4.03 (4 H, t, CH$_2$N, J 6 Hz), 3.41 (4 H, dt, CH$_2$NH), and 2.08 (4 H, quint, CH$_2$CH_2CH$_2$); m/z (NH$_3$, c.i.) 487 (M^+ + 1), 486 (M^+), 485, 407, 328, 271, and 179.

Electrochemical and Conductivity Experiments.—A potassium chloride saturated calomel electrode was used as the reference. Tetrabutylammonium perchlorate and fluoroborate electrolytes were dried in a vacuum oven prior to use, and all solvents were dried immediately prior to use. Electrode deposits were formed by controlled-potential electrolysis using a Thompson Ministat

251 precision potentiostat and a Fluke 8000A digital multimeter to set the potential and measure the current. For cyclic voltammetric analysis, films were prepared by deposition from solutions that were 2×10^{-3} mol dm^{-3} in the relevant monomer onto Kel-F-shrouded platinum or glassy carbon disk electrodes. These electrodes were polished with diamond and alumina pastes, washed with distilled water and dried before use. A platinum-wire counter electrode was used. Cyclic voltammograms were recorded with a BAS CV-5B instrument, and peak areas were determined with an Apple II/e microcomputer with graphics tablet, light pen, and associated software. The areas used in apparent molar-coverage calculations were the average of at least five determinations.

Conductivity measurements were performed on films deposited onto new platinum-flag electrodes. Gold contacts (1.5 diameter) were slowly evaporated on top of the films with an Edwards vacuum evaporator. Film resistance measurements were taken with a base contact to the platinum electrode and a 'soft' spherical gold probe to the evaporated contact. Film resistance was determined from a plot of applied voltage (Time Electronics 2003S dc voltage supply) against measured current (Keithley 414A picammeter). Several films and several contacts for each film were tested. The film thickness was estimated from the charge passed during electrolysis, the electrode area, the experimentally determined deposition efficiency, and the estimate that 10^{-10} mol cm$^{-1} \approx 1$ monolayer and one monolayer ≈ 10 Å.[10] An increase in resistance with film thickness was used to test that the resistance measured was a property of the film and not of the contacts to the film.

Surface Analysis.—After preparation, films were washed in electrolyte-free solvent and dried under nitrogen and subsequently under vacuum. A Kratos ES300 electron spectrometer was used to record the ESCA spectra. Coated electrodes were mounted onto a standard Kratos probe tip with double-sided Scotch tape. Spectra were recorded with the sample positioned at an angle of 35° with respect to a plane parallel to the location of the electron analyser slits. Mg-K_α X-radiation was used. Binding energies are quoted relative to hydrocarbon C 1s at 285 eV. Surface elemental stoicheiometries were obtained from peak area ratios corrected by the appropriate elemental sensitivity factors, determined experimentally from standard samples. Curve fitting of ESCA spectra was performed manually with the graphics software of the Kratos ES300 computer system. A linear background subtraction was used. Gaussian component peaks were used exclusively, and constant peak width (FWHM) was used for all components of any one core-level spectrum.

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