energy gap of 11 kcal/mol only between the two configurations (Table I). This result was a first clue to the possibility of a nondiamagnetic ground state for $(\mu\text{-NO})_2(CoCp)_2$. Further evidence had to be gained from direct calculations on the triplet configuration $[2]^2[1]^1[3]^1$ and on the associated covalent singlet state described in the first approximation by the two-configuration expansion $[2]^2[1]^2[3]^0 - [2]^2[3]^2[1]^0$. The calculation on the triplet state was carried out by means of a one-configuration open-shell SCF calculation and the singlet state was independently optimized through a MCSCF treatment taking as reference states the two closed-shell configurations $[2]^2[1]^2[3]^0$ and $[2]^2[3]^2[1]^0$. This formalism allows a determination of the singlet–triplet splitting accounting for both the exchange term $2K_{ab}$ and the superexchange contribution.[18] Moreover, the set of MOs is allowed to relax independently for the singlet and the triplet states.

Both the triplet and the two-configuration singlet states were found to be lower in energy by about 120 kcal/mol than the individual $[2]^2[1]^2[3]^0$ and $[2]^2[3]^2[1]^0$ configurations (Table I). The triplet state appears to be lower in energy than the two-configuration singlet by 0.0013 hartree (280 cm^{-1}). This relative ordering is in agreement with the almost opposite weights (respectively 0.7095 and –0.7047) of the $[2]^2[1]^2[3]^0$ and $[2]^2[3]^2[1]^0$ configurations obtained in the MCSCF expansion.[18]

It must be kept in mind, however, that the reported calculations were carried out on an isolated molecule assuming a perfectly planar and undistorted geometry. The narrow singlet–triplet energy gap can be affected by the crystal packing forces and more specifically by the slight deviations from planarity observed in the crystal (0.004 Å).[1] Even if the high-spin character of the title compound is not definitely established by the present work, it appears that the singlet–triplet separation will remain weak. This means that the two extra electrons of the d^9–d^9 complexes have almost pure metal character, but they are globally nonbonding with respect to the metal atoms. This result is in perfect agreement with the observed stability of the metal–metal distances in d^8–d^8 and d^9–d^9 complexes, but it clearly questions the reported diamagnetism of $(\mu\text{-NO})_2[CoCp]_2$. A careful survey of the literature indicates that the only report on the magnetic behavior of $(\mu\text{-NO})_2[CoCp]_2$ is due to Brunner.[9] The diamagnetism was deduced only from the proton NMR spectrum.[9] No report of the temperature dependence of the magnetic susceptibility was provided, and it therefore seems that a ferromagnetic or antiferromagnetic interaction cannot be ruled out. In view of the present theoretical results, we therefore suggest a careful reinvestigation of the magnetic susceptibility of $(\mu\text{-NO})_2[CoCp]_2$.

Acknowledgment. All calculations have been carried out on the IBM 3081 of the Centre de Calcul de Strasbourg-Cronenbourg. We thank the staff for cooperation.

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(18) The singlet–triplet splitting can be expressed as $E_S - E_T = 2K_{ab} - [(\epsilon_1 - \epsilon_2)^2/(J_{aa} - J_{ab})]$, where J_{aa}, J_{ab}, and K_{ab}, computed on the triplet MO basis, are positive coulomb and exchange integrals, ϵ_1 and ϵ_2, representing the orbital energies of the open shells. The second term is the superexchange contribution, which is accounted for by the separate MCSCF optimization of the singlet state. This contribution vanishes for the degenerate case corresponding to equal values for ϵ_1 and ϵ_2 and to opposite expansion coefficients in the MCSCF treatment, thus yielding a positive value for $E_S - E_T$.[19]

(19) See, for example: Hay, P. J.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1975**, *97*, 4884. de Loth, P.; Cassoux, P.; Daudey, J. P.; Malrieu, J. P. *J. Am. Chem. Soc.* **1981**, *103*, 4007.

Electrically Controlled Release of $Fe(CN)_6^{4-}$ from Polypyrrole

Larry L. Miller,* Baruch Zinger, and Qin-Xin Zhou

Contribution from the Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455. *Received August 25, 1986*

Abstract: The anodic polymerization of pyrrole onto glassy carbon in the presence of aqueous $K_4Fe(CN)_6$ gave a polypyrrole which incorporated $Fe(CN)_6^{3-}$ (PP/FCN). The polymerization process for PP/X$^-$ (X = ClO_4, Cl, BF_4, PF_6) and PP/FCN was studied using chronoamperometry and showed nucleation and growth kinetics. The concentration of electrolyte and pyrrole governed the nucleation and growth rates. It was shown that stirring inhibits both nucleation and growth, suggesting the involvement of soluble species in film formation. Higher electrolyte concentrations gave films with larger electrical capacities as evaluated by cyclic voltammetry. The extent of incorporation of $Fe(CN)_6^{3-}$ depended on the relative concentration of $Fe(CN)_6^{4-}$ and ClO_4^- in the solution from which the film was grown. In these PP/FCN films, the FCN does not readily exchange with other ions in aqueous solution and can only be flushed out of a film (formed with Q = 2 mC cm^{-2}) into aqueous 0.1 M NaCl solution at potentials more negative than –0.4 V vs. SCE. A thinner film which had been formed with Q = 0.22 mC cm^{-2} gave release into 0.1 M NaCl only at –0.6 V. It is shown that little FCN is cathodically released into aqueous CsCl or tetraethylammonium chloride solutions. X-ray photoelectron spectroscopy indicates instead that Cs$^+$ is bound into the reduced PP/FCN film. It was demonstrated that repetitive 5-s pulses to –0.4 V from open circuit gave controlled release of FCN into a small volume of solution. PP/FCN films changed, giving smaller release amounts, when they were allowed to dry.

The considerable current interest in conducting polymers has led to a number of apparent applications and to the beginnings of understanding of the structure and properties of these materials.[1] Our interest is in the electrochemical properties of conducting polymers and their use for the controlled release of chemicals, especially drugs.[2,3] The basic concept of this application is to bind the drug into a polymer film on an electrode and release the drug as needed by passing a small current through the polymer.[4] A simple approach to this problem is to bind ionic drugs into an ionic redox polymer coated on an electrode and then force the drug ion out by neutralizing the charge on the polymer. Specifically, one should be able to bind anions into a cationic polymer like polypyrrole and release the anion by reducing the cationic backbone. Because the polymer is conductive, it should allow binding and release throughout thick films, in turn allowing relatively large amounts of ions to be released. The detailed structure of polypyrrole (PP) is not well established, and it is not

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(1) For an extensive current review see: *Handbook of Conducting Polymers*; Vol. I, II; Skotheim, T. A., Ed.; Marcel Dekker: New York, 1986.

(2) Zinger, B.; Miller, L. L. *J. Am. Chem. Soc.* **1984**, *106*, 6861.

(3) Blankespoor, R.; Miller, L. L. *Chem. Commun.* **1985**, 90.

(4) See: Zinger, B.; Miller, L. L. *J. Electroanal. Chem.* **1984**, *181*, 153 and references therein to papers describing cathodic release of covalently bound dopamine, glutamate, and GABA.

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entirely stable. It did, however, seem to provide a prototype for studies of ionic binding and release. The electroactive polyanion $Fe(CN)_6^{4-}$ was chosen for incorporation. As revealed in a preliminary communication,[2] it is possible to prepare polypyrrole containing ferricyanide/ferrocyanide (PP/FCN) and to flush ferrocyanide out by reducing the film.

The incorporation of an electroactive anion into PP was first reported by Bull et al.[5] who prepared PP containing tetrasulfonated iron phthalocyanine. They used these films for oxygen reduction catalyzed by the anion. Several other groups have considered the possibility of delivering ions from redox polymers. Martin and co-workers[6] used a polyvinylferrocene/polystyrene/polystyrene sulfonate terpolymer to control the binding of cations. Shimidzu has bound a variety of anions including polynucleotides into PP and substituted polypyrroles.[7] In this context, the reports by Burgmayer and Murray[8] on the transport of chloride through a PP membrane are also of interest because it can be imagined that PP could allow more rapid drug anion transport when oxidized than when reduced. Finally, it is recognized that there is a very large literature which describes the electrochemistry of redox-polymer-coated electrodes.[9] In these studies, the ions move into and out of the film and are bound to a greater or lesser extent. The aspect of ion binding has received little explicit attention, although the recent approaches to metal ion analysis[10] are based in part on this idea.

The present paper describes a study of several aspects of PP/FCN electrochemistry. Our main goal was to gain an understanding of FCN binding and release, but several related issues provoked limited study. A central issue here is ion migration in redox polymers during an oxidation/reduction cycle. Extensive studies have been reported where the electrochemical current has been measured and taken as a measure of ionic flux. However, the counterion contents of a redox-polymer layer on an electrode and the amounts of ions actually released or incorporated into a redox-polymer film in response to an electrochemical event have not been carefully studied. Since our interest was in the amount of bound/released ions, we have analyzed for FCN in the film as well as for released FCN in the solution near the electrode. We have also assayed film content in a qualitative manner by using X-ray photoelectron spectroscopy (XPS). These results are of interest with regard to literature claims concerning cation binding into PP.

The anionic content of oxidized PP has always been acknowledged. There is, however, a report[11] which suggests that reduced PP might contain cations. In that study, weight changes during a potential cycle were measured by using a quartz crystal microbalance. The weight loss when a highly reduced film in THF was oxidized was attributed to lithium ions in the reduced film which were forced out by oxidation. In the present study, we show using XPS that reduced PP films can, indeed, bind salts from aqueous solution. If PP/FCN is used, however, small cations like lithium are the least likely to be bound.

Experimental Section

Commercial samples were used without purification except for pyrrole, which was vacuum distilled at 30–40 mmHg. It was stored under argon in the dark, and samples were removed through a septum.

Cyclic voltammetry and chronoamperometry were carried out by using a Princeton Applied Research (PAR) potentiostat, Model 173, in conjunction with a PAR universal programmer Model 175 and a Houston Model 2000 recorder. The bipotentiostat was from Pine Instruments, RDE-3. XPS experiments were performed by using a Physical Electronics Model 555 instrument.

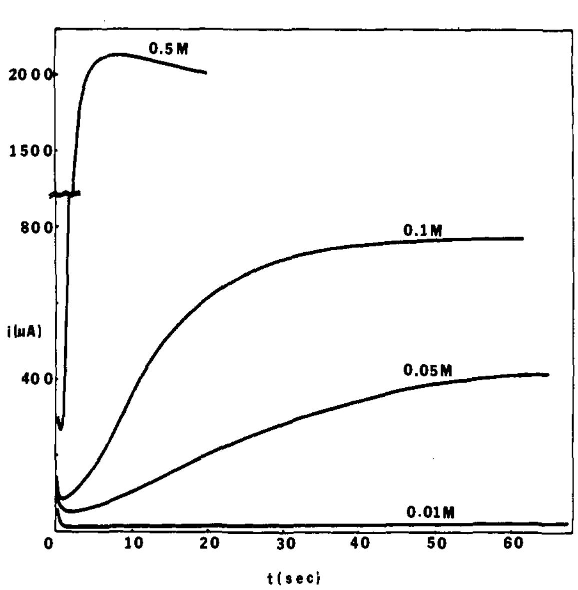

Figure 1. Chronoamperograms for 0.05 M pyrrole with varying concentrations of $LiClO_4$. $E = 0.7$ V.

Polymerizations were conducted by using a single-compartment cell containing a saturated calomel electrode (SCE) as a reference electrode. The counter electrode was a graphite rod. The working electrode was the glassy carbon disk (0.46 cm^2) of a ring-disk electrode from Pine Instruments. It was cleaned on polishing cloth (Fisher) using 0.3 μm alumina (obtained from Buehler, Ltd., Evanston, IL), wiped with a tissue, and then washed successively with distilled water.

Results and Discussion

In spite of the extensive number of publications on polypyrrole and its analogues, there is little kinetic information in the literature on the growth of these films. Therefore, first reported are chronoamperometric data concerning the growth of polypyrrole (PP) and PP/FCN films on glassy carbon electrodes. Second are results on the release of ferrocyanide from PP/FCN films on glassy carbon.

Growth of PP Films. Polymerization of pyrrole was carried out in an unstirred aqueous solution of pyrrole and supporting electrolyte. A SCE was used as reference electrode, and all the potentials are reported relative to SCE. The reproducibility of the results was improved substantially by using pyrrole which had been vacuum distilled and stored under argon. Unless extreme precautions were employed, the pyrrole became yellow.

Electropolymerizations were conducted by using either constant current or constant potential conditions. The former led to somewhat more reproducible results in terms of release characteristics. The latter was of interest in order to try to understand the process of film growth. After film formation at constant E (described in detail below), the films were analyzed by using cyclic voltammetry (CV), in aqueous 0.1 M $LiClO_4$ over the range −0.4 to +0.4 V. PP gave CV results in qualitative agreement with the literature. PP/FCN gave current peaks attributed to the iron(III/II) couple superimposed on the large PP current. It is especially noted that the peaks attributed to the $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ couple in PP/FCN were unchanged by repeated cycling of the potential in this range even over a period of several hours.

Consider now the constant potential deposition process and the corresponding current–time (i–t) curves for polymerization of pyrrole to PP. This part of the study expands on the results of Pletcher et al.[12] who investigated PP growth in aqueous KNO_3. They found i–t curves characteristic of nucleation and growth kinetics. In our studies films were grown by stepping the electrode potential to 0.7 V in a solution containing 0.05 M pyrrole and 0.1 M electrolyte. Typical i–t behavior at 0.7 V is shown in Figure 1. Tetraethylammonium fluoroborate ($TEABF_4$), lithium perchlorate, and ammonium hexafluorophosphate (NH_4PF_6) all

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(5) Bull, R. A.; Fan, F.-R.; Bard, A. J. *J. Electrochem. Soc.* **1984**, *131*, 687.

(6) Espenscheid, M. W.; Martin, C. R. *J. Electroanal. Chem.* **1985**, *188*, 73.

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(9) For a review, see: Murray, R. W. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, 1984; Vol. 13.

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(12) Asarapiriyanont, S.; Chandler, G. K.; Gunawardena, G. A.; Pletcher, D. *J. Electroanal. Chem.* **1984**, *177*, 229.

behaved very similarly with maximum currents of 1.2–1.6 mA cm^{-2}. Sodium chloride gave smaller currents, 0.2 mA cm^{-2} maximum. With all four salts, it was observed that immediately after the anodic step there was a sharply dropping current, followed by a rising transient and eventually a steady-state current. This results because time is required to nucleate the film. During this period, pyrrole is being oxidized, but the film is not forming. Later, nucleation and growth of the film proceeds and the current increases. After passage of 7.8 × 10^{-2} C cm^{-2}, the growth was terminated and the films were studied by recording cyclic voltammograms (CV) at 200 mV s^{-1} in 0.1 M $LiClO_4$. The voltammograms which were obtained were as expected from the literature and indicated that the film from NaCl solution had the smallest charging current. Measured at 0.0 V, the difference between the anodic and cathodic currents was $LiClO_4$, 95 $\mu A/cm^2$; NH_4PF_6, 109 $\mu A/cm^2$; $TEABF_4$, 68 $\mu A/cm^2$; and NaCl, 13.6 $\mu A/cm^2$. Clearly, even though the same charge was passed in forming these films, they had somewhat different electrochemical characteristics. NaCl gave low currents in polymerization and lower film currents. Since chloride is the most easily oxidized anion, it is possible that chloride is being oxidized during PP film formation at 0.7 V. If this process does not lead to polymer, but consumes some monomer, the film growth rate (current) could be smaller and the final film thinner. Other explanations are also possible.

The effects of pyrrole and electrolyte concentration on the electropolymerization of pyrrole were investigated by varying either the concentration of $LiClO_4$, from 0.01 to 0.5 M with a constant concentration of pyrrole (0.05 M), or varying the concentration of pyrrole, from 0.01 to 0.15 M with a constant concentration of $LiClO_4$ (0.1 M). The kinetics of these polymerizations were rather sensitive to the electrolyte and pyrrole concentrations as illustrated in Figure 1. Nucleation started sooner and growth was more rapid when the concentration of pyrrole or $LiClO_4$ was higher. The resulting PP films had similar CV in shape, but the film charging currents increased as the $LiClO_4$ concentration used for preparation was increased, even though the same amount of charge was used for the preparation of the films.

Perhaps the most important result was the observation that *no PP (or PP/FCN) was formed from stirred solutions.* The chronoamperograms showed no rising transients, and no visual evidence of a film was obtained. This indicates that an oxidized product, free in the solution so it can be swept away by stirring, is involved in nucleation. If film growth was started in an unstirred solution and then stirring commenced, the current decreased, indicating that film growth was slowed. This indicates that there are soluble species (oligomers?), which are necessary for both nucleation and growth.

Pletcher et al. have studied PP growth under similar conditions and reported that the rising transient i depends linearly on t^2.[12] Our studies sometimes gave such behavior, but the results were quantitatively irreproducible and did not give t^2 behavior every time. We had hoped to make some quantitative studies of the rate, but this proved impossible. The qualitative facts remain clear. (1) The rate increases with the potential and the concentration of either pyrrole or electrolyte. This is quite reasonable since the film is composed of pyrrole and anions. (2) The unexpected discovery is that stirring inhibits nucleation.

Growth of PP/FCN Films. To incorporate ferricyanide into polypyrrole, $K_4Fe(CN)_6$ was used together with pyrrole and/or a supporting electrolyte in the aqueous polymerization system. It was mentioned above that the electropolymerization was sluggish when only 0.1 M NaCl was used as electrolyte in the aqueous pyrrole solution. However, the electrolysis of the three-component solution (0.05 M pyrrole/0.01 M FCN/0.1 M NaCl) gave a fast deposition of PP. These two cases are compared in Figure 2 (still oxidizing at 0.7 V). Addition of $Fe(CN)_6^{4-}$ to the solution gave higher currents at all times but most specifically gave a rising transient at much shorter times than in its absence; i.e., it aided nucleation. Since $Fe(CN)_6^{4-}$ is being oxidized at this potential, it is also of interest to know the current obtained from $Fe(CN)_6^{4-}$ alone. Clearly, the falling transient of the three-component system over the first 10 s is primarily due to the glassy carbon charging current and the diffusion-controlled $Fe(CN)_6^{4-}$ oxidation. Only at later times is film growth occurring.

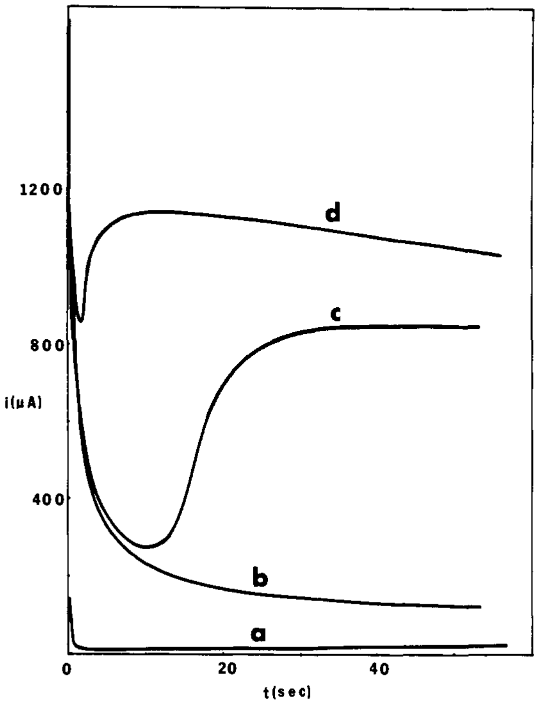

Figure 2. Chronoamperograms for (a) 0.05 M pyrrole, 0.05 M NaCl; (b) 0.05 M NaCl, 0.01 m $K_4Fe(CN)_6$; (c) 0.05 M pyrrole, 0.01 M $K_4Fe(CN)_6$, 0.05 M NaCl; (d) 0.05 M pyrrole, 0.01 M $K_4Fe(CN)_6$, 0.05 M $TEABF_4$. E = 0.7 V.

Table I. CV Data for PP/FCN Films Grown from Solutions Containing Various Electrolytes

electrolyte	i_{ch}, μ_A[b]	i_p, μA[b]
NaCl	283.0	17.5
$LiClO_4$	255.0	42.5
NH_4PF_6	259.4	55.0
$TEABF_4$	281.3	58.0
nil[c]	209.0	42.5

[a] PP/FCN films formed using 0.05 M pyrrole, 0.01 M FCN, and various 0.1 M electrolytes and then analyzed by CV at 100 mV s^{-1} in aqueous 0.1 M $LiClO_4$. [b] See Figure 5 for definitions. [c] Only 0.01 M FCN.

Table II. Amounts of FCN Released into Electrolytes with Different Cations[a]

salt	FCN, mol × 10^{-7}	salt	FCN, mol × 10^{-7}
LiCl	1.6 ± 0.1	RbCl	1.1 ± 0.2
NaCl	2.4 ± 0.1	CsCl	0.3 ± 0.2
KCl	1.8 ± 0.1		

[a] PP/FCN films grown from 0.05 M pyrrole, 0.05 M NaCl, and 0.01 M $K_4Fe(CN)_6$ using Q = 2 C cm^{-2}. Used in the small-volume cell with a 70-L droplet of 0.1 M electrolyte. Released at 0.8 V for 60 s. Data are averages from two or more films, with three analyses on the ring for each film.

The effect of FCN on promoting the deposition current was found not only in the system with NaCl as electrolyte but also in those with other electrolytes, e.g., $LiClO_4$, $TEABF_4$, and NH_4PF_6, which didn't have a sluggish PP-deposition process like NaCl when they were used as electrolytes with pyrrole.

The CV behavior of PP/FCN films formed after passage of 7.8 × 10^{-2} C cm^{-2} using various electrolytes is shown in Table I. Two aspects are of interest, the peak current (i_p) due to the $Fe(CN)_6^{4-/3-}$ couple centered at ca. 0.1 V and the size of the charging current i_{ch} from PP (see Figure 3). The latter was relatively invariant as the electrolyte was changed. The amount of electroactive FCN which was incorporated was, however, quite variable. The data in Table I indicate that with NaCl, the PP film had the lowest amount of active FCN and with $TEABF_4$ the

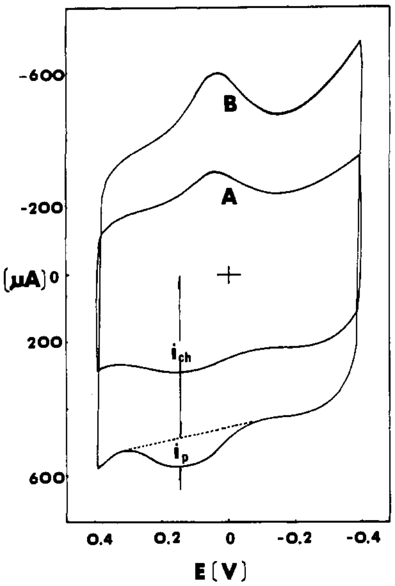

Figure 3. Cyclic voltammograms for PP/FCN in aqueous 0.1 M $LiClO_4$ at (A) 100 mV s^{-1} and (B) 200 mV s^{-1}.

highest amount of FCN. One explanation for this phenomenon involves a competition between $Fe(CN)_6^{3-}$ and X^- for incorporation as the counteranion where Cl^- has the highest affinity to PP^+ among the four electrolytes and BF_4^- has the lowest affinity. This would be consistent with release results reported below.

As shown in Figure 1, different concentrations of $LiClO_4$ in aqueous pyrrole solution caused great differences in the chronoamperometric behavior in absence of FCN. The effect of changing $LiClO_4$ concentration was much diminished when 0.05 M $K_4Fe(CN)_6$ was present. The phenomena were similar, but it seems clear that higher electrolyte concentrations (whatever the electrolyte) will always lead to faster kinetics; i.e., the onset of the current rise is sooner, and the steady-state current is larger. From the CV of the resulting PP/FCN films, increasing the concentration of $LiClO_4$ from 0.0 to 0.2 M gave two results: i_{ch} increased from 209 to 279 μA; i_p decreased from 43 to 19 μA. The first result is similar to that for where increased electrolyte concentrations give larger charging currents. The second result may be ascribed to the competition for incorporation of ClO_4^- or $Fe(CN)_6^{3-}$.

Increasing the $K_4Fe(CN)_6$ concentration from 0.001 to 0.03 M also gave increased film growth currents. The behavior observed results from a combination of film growth and $Fe(CN)_6^{4-}$ oxidation. The CV's of the films which result (constant Q for film formation) show that the larger currents lead to films with less electroactive FCN. This most probably results because a substantial fraction of the current goes to produce $Fe(CN)_6^{3-}$, some of which is not incorporated in the film.

Finally, variation of the pyrrole concentration from 0.05 to 0.15 M for the formation of PP/FCN had little effect on the chronoamperograms and resulting PP/FCN film CV's. Use of 0.01 M pyrrole did, however, produce films with decreased charging current and FCN peak currents.

Release of $Fe(CN)_6^{4-}$ from PP/FCN. As indicated above, the release of FCN by reduction of PP/FCN was chosen as a model system because FCN was strongly bound in the PP film, because it could be cathodically released and because it could be easily analyzed in the solution by using a third electrode. The instability of reduced PP, especially in air, was recognized to be a problem at the outset—especially if the film was to be reduced repetitively. We chose to accept that shortcoming rather than use more restricted experimental conditions. In this study, a small-volume cell was invented for the rapid analysis of released FCN which maximized the concentration of released FCN. This cell allowed us to rapidly set up the experiment with many different PP/FCN films and to change many variables. It was simply constructed by placing a glassy carbon disk electrode 1.0 mm above a ring–disk electrode (glassy carbon disk–platinum ring). The PP/FCN was polymerized onto the disk. A droplet of aqueous electrolyte (typically 70 μL) was syringed into the gap, covering all three electrodes. A glass capillary leading to an SCE reference was then inserted into the droplet for a reference electrode. This cell was surrounded by a glass vessel, the interior of which was lined with wet filter paper to ensure that the volume of the aqueous droplet did not diminish due to evaporation during the experiment. The use of standard solutions containing $K_4Fe(CN)_6$ in the droplet and CV on the ring demonstrated the stability of the electrochemical response on the ring and provided a linear i_p/concentration standardization curve for FCN analysis in the solution. It was found that the distance between the upper and lower electrodes was not critical as long as the three electrodes were all covered with solution. There were, however, many other variables, and an extensive study ensued to get reproducible results. Eventually we were able to get acceptable quantitative results for single-pulse release as well as short multiple pulses using potentiostatic control. Controlled current pulses were not useful. Unless otherwise noted, the PP/FCN films for these experiments were grown from a solution of 0.05 M pyrrole, 0.05 M NaCl, and 0.01 M $K_4Fe(CN)_6$ at 0.7 V onto the glassy carbon disk of the ring–disk electrode.

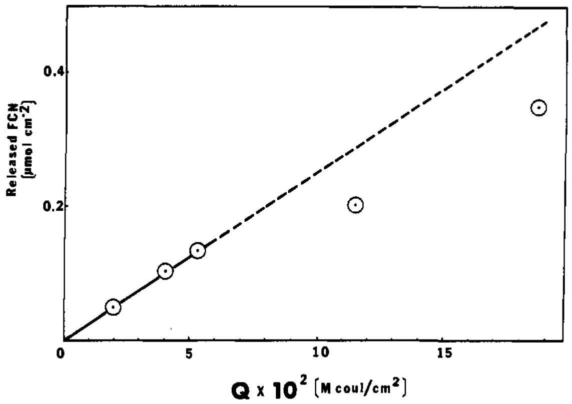

Figure 4. Amount of released FCN for PP/FCN films of varying thickness.

Consider first an experiment in which FCN was flushed from the film by progressively stepping the potential to more and more negative potentials in aqueous NaCl electrolyte solution. The film potential was stepped from 0.0 to −0.1 V for 4 s, and then the solution was analyzed by using the ring, with the filmed disk at open circuit. This analysis was followed by sequential 4-s steps, making the step 0.1 V more negative each time, and analyzing the solution between steps. With a thick film, which was formed using 2 C cm^{-2}, FCN release commenced at −0.4 V. At −0.8 V no further increase in the FCN solution concentration was measured. At this point a CV on the film showed that virtually all the FCN signal had disappeared. In a similar experiment, a thinner film which was formed using 0.22 C cm^{-2} showed release only when −0.6 V was reached.

These results were confirmed by experiments where a single film was pulsed only once. A 10-s pulse to −0.4 or −0.5 or −0.6 V was used. The results confirmed that Q = 2 C cm^{-2} films gave release at potentials more negative than −0.4 V, while Q = 0.22 C cm^{-2} films flushed out FCN only at −0.6 V, not at −0.4 or −0.5 V.

Next, the amount of FCN released from films of varying capacity was studied. The PP/FCN films were grown and then placed in aqueous NaCl. Release was accomplished by stepping the potential to −0.8 V for 2 min. The amounts of released FCN were determined from the peak current on the ring. The results are in Figure 4. It can be seen that there was a linear relationship between the capacity of the film and the amount of FCN released for thin films. Thicker films delivered less than expected. In concert with this observation, CV on the film after cathodic release showed no FCN for thin films but a substantial FCN peak for thicker ones.

Table III. Pulsed Release of FCN[a]

1		2		3		4	
Q, mC[b]	i_p, μA[c]	Q, mC	i_p, μA	Q, mC	i_p, μA	Q, mC	i_p, μA
31	1.0	36	1.5	34	1.7	38	2.0
8.8	2.4	12	2.1	9.3	2.6	13	2.6
7.1	3.7	8.4	3.1	7.9	3.6	8.3	3.4
	4.0	6.6	3.5	6.5	4.3	6.4	3.9
5.7	4.5	5.7	3.9	5.8	4.8	5.3	4.2
5.2	5.0	5.1	4.2	5.2	5.1	4.7	4.4
4.7	5.4	4.6	4.4	4.8	5.5	4.1	4.5
4.4	5.5	4.2	4.6	4.5	5.7	3.9	4.6
4.0	5.5	4.0	4.6	4.1	5.8		

[a] Four experiments on identically prepared PP/FCN films. See text for details. [b] Charge passed during cathodic pulse. [c] Current due to FCN in solution measured on ring.

The residual FCN peaks in thick films were studied further. It was found that these peaks were, in part, due to readsorption of FCN. Thus, these peaks were absent if the droplet containing released FCN was quickly replaced with fresh electrolyte solution. Further, it was shown that the amount of released FCN in the solution droplet decreased with time and reappeared in the film. A measurement of the disk potential during analysis on the ring showed that the potential rose from -0.8 to ca. -0.2 V immediately after the disk circuit was opened and then gradually shifted to 0.05 V after 25 min and to 0.14 V after 100 min. This confirmed the possibility of the reabsorption because within this potential range the neutral polypyrrole could start to be reoxidized with FCN reincorporated.

Other evidence for the reabsorption was obtained from an experiment where a bipotentiostat was to sweep the ring potential and control the potential of the filmed disk at the same time. The result showed that the FCN concentration in the droplet declined when the disk potential was kept at -0.2 V. At -0.4 V the FCN concentration in solution remained roughly constant.

Binding of Cations into Reduced PP/FCN

So far the importance of electrolyte in the loading and release process was only related to the anions used for preparing polypyrrole. However, it was noticed that cations in the receptor droplet had a surprising effect on FCN release. With $Q = 2$ C cm^{-2} films, the supporting electrolyte (0.1 M) was changed in the sequence of LiCl, NaCl, KCl, RbCl, and CsCl. The number of coulombs passed during release was the same 0.2 ± 0.1 C cm^{-2} for all the electrolytes. The amount of released FCN from these identically prepared PP/FCN films showed a striking, progressive decline (Table III) for large cations. For tetraethylammonium fluoroborate, an electrolyte with an even larger cation, the FCN release was zero. These facts demonstrated that the electrolyte cations were not passively present in the system, and it was hypothesized that the larger cations were incorporated into the film upon reduction. Thus, the reduced film still contained FCN, and it incorporated cations to balance the charge.

In order to test the hypothesis that reduction of PP/FCN in CsCl solution could lead to incorporation of Cs^+, several X-ray photoelectron spectroscopy (XPS) analyses were performed.[13] The PP/FCN samples were in each case prepared in aqueous 0.05 M Py, 0.05 M NaCl, and 0.01 M FCN by passing 3.92 mA cm^{-2} until 4.1 C cm^{-2} was consumed. The freshly prepared film showed XPS peaks at 707 and 720 due to iron in addition to C, N, O, and weak Na peaks.

When an identically prepared film was reduced in 0.1 M LiCl solution and then analyzed by XPS without reoxidation, the intensities of the Fe peaks were substantially reduced and no lithium was detected.

When an identically prepared film was reduced in 0.1 M CsCl and then analyzed by XPS, intense Fe peaks remained and Cs^+ peaks were now observed at 725 and 739 eV. Simply soaking a film in aqueous CsCl lead only to a trace of Cs^+ incorporation.

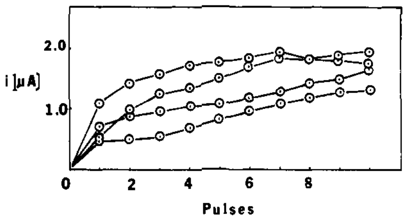

Figure 5. Pulsed release of FCN. Released using 1-s pulses to -0.8 V, holding disk $E = -0.2$ V. FCN current measured at ring electrode.

In view of the suggestion that Li^+ was incorporated into reduced PP,[11] an additional XPS experiment was made using PP/ClO_4. A PP/ClO_4 film sample was electrochemically prepared in aqueous 0.1 M $LiClO_4$ solution. By use of XPS, an intense peak of Cl at 209 eV was found. As expected, no Li peak was observed. An identical PP/ClO_4 film was electrochemically reduced in aqueous 0.1 M NaCl solution. XPS analysis showed the Cl peak at 209 eV disappeared. No Na peak at 1072 eV could be observed. It is concluded that after reduction of PP^+/ClO_4^-, ClO_4^- anion is released from the polymeric film, and Na^+ cation from the electrolyte does *not* reside in the polymer.

Release of FCN Using Consecutive Pulses of Current. FCN can be released in a controlled manner from PP by using short pulses of current.[2] This aspect was studied further using the small-volume cell and a droplet of 0.1 M NaCl. The films were prepared using a constant current, $i = 3.9$ mA cm^{-2}, from a solution of 0.05 M pyrrole, 0.01 M $Fe(CN)_6^{3-}$, and 0.05 M NaCl. In a typical experiment, the PP/FCN disk electrode potential was pulsed cathodically for a second, then the solution droplet was analyzed by using the ring electrode, then a second cathodic pulse was applied to the disk, etc. The concentration of FCN in the droplet increased with further pulses. Initial experiments showed the difficulty of getting reproducible release results. The following experiments indicate several approaches to improving this situation, which were ultimately fairly successful.

With a film formed using $Q = 0.22$ C cm^{-2}, the disk potential was stepped from 0 to -0.8 V for 1 s and then back to 0.0 V. The disk circuit was opened, and the ring voltage was swept for analysis. Similar results were obtained when a bipotentiostat was used, and the disk potential was controlled at all times. Thus, the disk was pulsed from -0.2 to -0.8 V for 1 s and then back to -0.2 V. That potential was held while the ring was swept for analysis. The results of four experiments are shown in Figure 5. It can be seen that the first pulse gives quite variable amounts of release: the later pulses tend to even this out. It was also noted that the final amount was lower than expected from an experiment with one long pulse to -0.8 V.

In these experiments, we realized that there was a very large anodic current pulse going through the film when the disk E was returned to -0.2 V. Thinking that this might cause a problem, further experiments were performed in which the disk potential went from open circuit to -0.8 V and back to open circuit. This improved the net amount released. On the other hand, the first two pulses essentially completed the release.

Since these -0.8-V open-circuit experiments were controlled manually, it was desirable to lengthen the time spent on the cathodic pulse so that the time could be more accurately controlled. This was accomplished by using a less negative E for release. The experimental protocol was open circuit to -0.6 V for 5 s and then open circuit (wait 60 s and then analyze on the ring). The results were more satisfactory since the final amount was still relatively large and there was a controlled release, with each pulse adding to the concentration in solution over the first seven or eight pulses.

Improved reproducibility and enhanced total release amounts were obtained by employing strict control over the film handling. In particular, the films were treated like ion-exchange resins, which are not allowed to dry. Trial experiments showed that films which were allowed to dry for 4 min in air at room temperature after preparation gave smaller FCN release amounts for each pulse and only about 70% of the total release amount after a long pulse,

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[13] A similar approach has been used to clarify ion content in prussian blue films during redox switching. Itaya, K.; Ataka, T.; Toshima, S.; Shinohara, T. *J. Am. Chem. Soc.* **1982**, *104*, 4767.

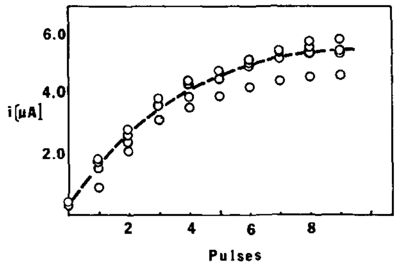

Figure 6. Pulsed release of FCN. Released using 5-s pulses at −0.4 V. FCN current measured at ring with disk at open circuit.

compared to films that were kept wet. In the following experiments, the film was soaked in water for 8 min after preparation, and then while wet it was placed in the small volume cell geometry. The droplet of aqueous solution was then added immediately. The films were used as above, keeping the times carefully regulated. This was successful. In one example, this protocol was used on a thicker film which was grown using $Q = 1.2$ C cm^{-2} using open circuit to −0.40 V (5 s), with careful control of the times involved (Figure 6).

Some electrochemical observations are pertinent here. First, during the period that the freshly prepared PP/FCN electrode was soaked in water, the rest potential did not rest but drifted from 0.7 to 0.22 V. Second the number of coulombs passed in each cathodic pulse during the release experiment is considered. Such values were routinely determined, and in general it was found that Q decreased as the number of pulses increased. Because the PP itself is electroactive regardless of FCN content and oxygen can be reduced, Q was substantial even at the end of the experiment. Typically, Q would decrease by 30–80% depending on the pulse sequence employed. Presumably, the first pulse Q is larger in part because it starts from a more positive potential. We have found no useful quantitative correlation of Q and release amount in these experiments, and the instability of PP makes the proposition doubtful. For this reason we have not pursued experiments in which a constant small amount (presumably coulometrically controlled) would be released on each pulse.

Conclusions

The goal of this study, to demonstrate that an anion could be strongly bound into a cationic, highly conducting polymer and released in quantifiable amounts in response to cathodic current pulses, was accomplished. This had not been shown previously. Some understanding of factors which influence pulsed release have been revealed. Of these, the most significant in terms of generality may be keeping the film wet. These films are porous ion-exchange membranes, and they may be fragile. The materials and the small-volume cell used here have some advantages for an initial exploratory investigation which have been mentioned in the introduction. They also have disadvantages. Reduced polypyrrole is not stable, especially in air, so reproducible pulsed release is extremely difficult. Better results might have resulted in a nonaqueous medium or in an inert atmosphere, but we were mainly interested in more common conditions. The difficulties are enhanced with this small-volume-cell design and electrochemical analysis because the released FCN is held at high concentration in contact with the reduced film. Under these conditions FCN was shown to be reabsorbed as the film potential drifted anodically. These aspects can be improved upon, and our continuing investigations employ better polymers and alternative analytical methods.

The electrochemistry of PP/FCN has a number of interesting aspects. Consider first that when potential changes occur in the range positive of −0.4 V, a great deal of redox chemistry and ion movement across the film is taking place. It is not known what ions are involved or if there is some net irreversible electrolysis taking place. It is quite clear, however, that the highly charged FCN, which was lodged in the film during polymerization, is not excluded by any changes occurring at potentials more positive than −0.4 V. FCN is flushed out only at potentials more negative than −0.4 V for a "thick" film and −0.6 V for a "thin" film. This difference is surprising since it might have been expected that the thicker, more resistive films would have required a more negative E. In any event, the potential of FCN release corresponds approximately to the potential where the cathodic PP current drops to background and PP becomes an insulator. Clearly, FCN is very strongly bound.

In contrast to this successful release behavior, the reduction of PP/FCN in aqueous CsCl gives primarily incorporation of Cs and retention of FCN. This is crudely envisaged as generating a reduced film of neutral PP containing $Cs_4Fe(CN)_6$. Like Cs^+, other large cations are preferentially taken up by reduction of PP/FCN. Since the larger cations should diffuse more slowly and tend to disrupt PP/FCN more, these factors must not be dominant in determining the relative rates of cation binding and FCN release. Instead, it is proposed that large cations are incorporated because of their "soft" acidity. One can imagine the reduced PP/FCN film to be hydrophobic but polarizable so that these soft cations prefer the film to water.

The above indicates the complexities that can occur with PP/FCN, and the XPS results indicate that similar effects of anion exclusion or soft cation incorporation are observed with PP/ClO_4. The phenomena deserve more study but with polymers that are better behaved.

Finally, we note how little is understood about the electrochemical polymerization of pyrrole. Our results show qualitatively that high electrolyte concentrations give more rapid nucleation and growth as well as films with a larger capacity. This can be understood because the electrolyte is incorporated into the polymer, the salt concentration leads to conducting polymer formation, not other reactions. A fascinating observation is that stirring inhibits nucleation and slows growth. Obviously, some soluble intermediates are involved. After so many publications, it might have been expected that more would be known about PP electrochemistry. At present, it must be said that the polymerization mechanism is not known, the structure is poorly elucidated, and the nature of the electrochemical charging–discharging process is unclear even in terms of which species are moving in and out of the film.

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