Iron–Sulfur Clusters in Ionic Polymers on Electrodes

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Iron–sulfur clusters have been incorporated in cationic polymers at electrode surfaces; the methodology for the assembly of such structures, and their characterisation by reflectance Fourier-transform (FT) IR, EPR and electrochemical techniques, is given. The stoichiometries of the cluster–electrode assemblies are self regulated by the necessity to maintain charge neutrality during redox cycling. Thus the assembly produced by the incorporation of $[Fe_4S_4(SPh)_4]^{2-}$ in $[C_4H_4N(CH_2)_3NMe_3]^+{}_3[BF_4]^-$ polymer (C_4H_4N = pyrrol-1-yl) adopts a composition close to $[C_4H_4N(CH_2)_3NMe_3]^+{}_3[Fe_4S_4(SPh)_4]^{2-}[BF_4]^-$. Electron-transfer and ligand-exchange reactions of polymer-bound clusters have been studied. Electrostatic (ion-pairing) effects are shown to modulate redox potentials and thus $E^{\circ\prime}$ values for $[Fe_4S_4(SPh)_4]^{2-/3-}$ and other couples are generally shifted to potentials positive of those observed in solution. Chronocoulometric measurements show that apparent diffusion coefficients (D_{app}) for the one-electron reduction of $[Fe_4S_4(SCH_2Ph)_4]^{2-}$ and $[Fe_4S_4(SPh)_4]^{2-}$ are about an order of magnitude greater than that for the reduction of the corresponding trianionic cubanes. This appears to be a consequence of different mechanisms of charge propagation within the polymer films: electron hopping enhances D_{app} for the 2−/3− couples whereas for the 3−/4− process, a physical diffusional mechanism probably dominates, with D_{app} close to the value for pure diffusion. As estimated by assumption of the simple Dahms–Ruff model, the rate constant k_{ex} for the electron self exchange reaction between $[Fe_4S_4(SCH_2Ph)_4]^{2-}$ and $[Fe_4S_4(SCH_2Ph)_4]^{3-}$ within the cationic film, is relatively high at *ca.* 10^3 dm^3 mol^{-1} s^{-1}. This in turn suggests that polymer-confirmed clusters operating at the 2−/3− level might well be effective mediators for electron transfer to (co-trapped) substrate reducing sites.

Metal–sulfur clusters are ubiquitous as prosthetic groups in a wide range of proteins. Their role is associated predominantly with inter- or intra-protein electron-transfer reactions,[1] although in certain enzymes they are also involved directly in substrate binding and transformation.[2] For example, the multi-electron reduction of molecular nitrogen to ammonia catalysed by the nitrogenases and hydrogen evolution or uptake catalysed by the hydrogenases, involve substrate interactions at cluster centres.

We wish to define methods for deploying synthetic and natural metal–sulfur clusters within polymers on electrodes.[3–5] The construction of electrodes modified with metal–sulfur clusters, bound within an appropriate polymer matrix, offers the possibility of (*i*) electrocatalysing the redox reactions of small molecules such as molecular nitrogen or (*ii*) artificially mediating electron transfer to biological molecules in solution or co-entrapped within the surface-bound polymer. Additionally, such electrodes could provide a means of exploring microenvironmental effects on thermodynamic, kinetic and spectroscopic aspects of the electron-transfer chemistry of clusters.

With respect to electrocatalytic transformations, Tanaka and co-workers[6] have examined the reduction of a wide range of small molecules by FeS and MoFeS clusters in suspension in aqueous or mixed solvent electrolytes, or as solid deposits on glassy carbon electrodes. Whereas such systems may be efficient at catalysing the multi-electron reduction of some small molecules, the nature of the catalytic species remains ill defined. It is not certain that the integrity of the cluster core is maintained during turnover.[6] Nitrogen fixation by well defined metal–sulfur cluster assemblies remains elusive, although suspension of iron–sulfur and molybdenum–iron–sulfur clusters in methanol are reported to give ammonia in about 4% yield after prolonged electrolysis.[7]

With regard to microenvironmental effects, metal–sulfur clusters bound within proteins show electron-transfer and magnetic properties different from those of their synthetic analogues in solution.[8] For example: (*i*) frozen solution EPR spectroscopy shows the $\{Fe_4S_4\}^+$ oxidation level to be a magnetically pure $S = \frac{1}{2}$ system in most protein systems in which it has been studied, whereas synthetic analogues at this oxidation level display a mixture of spin states;[9] (*ii*) the redox potentials of iron–sulfur clusters bound by cysteinyl-*S* ligands in proteins vary widely, although possessing a common primary co-ordination sphere, and are usually considerably positive of those measured for synthetic analogues; hydrogen-bonding interactions between peptide NH and cluster S atoms do not adequately explain the wide variations in E° (crystal-structure data show the conservation of structural $H \cdots S$ interactions for ferrodoxins which have considerably different redox potentials[10]) and (*iii*) in certain electrolytes, four redox states of synthetic $\{Fe_4S_4\}$ cores are observable[11] whereas in proteins only two redox states of this core are usually accessible.[12] In order to try and understand the role of solvent and microenvironment on the redox properties of synthetic clusters and on natural systems various studies have been carried out. These have included[1,13] the generation of water soluble species,[14] the incorporation of clusters in micelles[15] and cyclodextrins,[16] and partial denaturation of ferredoxins in mixed solvents;[12] more recently,[1] site-directed mutagenesis has been employed to probe the role of specific amino acid residues in the neighbourhood of the iron–sulfur centres.

Electropolymerisation of pyrrole derivatives provides a means of binding reaction centres in a polymer by way of covalent, ligative or electrostatic bonding to pendant substituents at the N or 3 position of the pyrrole.[17] As a first step towards defining a methodology for building and characterising electrode structures containing clusters, we describe here the assembly and spectroscopic and redox properties of poly(pyrrole alkylammonium) modified electrodes in which a wide range of anionic, electroactive iron–sulfur clusters are incorporated in a cationic polymer matrix.[4] We have extended this approach by binding clusters in certain copolymers *via* cysteinyl ligation[5] and this will be described in detail elsewhere.

Results and Discussion

Cluster–Electrode Assemblies.—Electrodes coated with the ion-exchange polymer prepared from I were exposed to MeCN solutions of the various iron–sulfur cluster anions listed in Table 1. The incorporation of the clusters in the polymer films was established by cyclic voltammetry and also, in certain cases, by EPR and reflectance Fourier-transform (FT) IR spectroscopy.

Fig. 1 shows a typical cyclic voltammogram obtained for $[Fe_4S_4(SPh)_4]^{2-}$ in $[C_4H_4N(CH_2)_3NEt_3]^+[BF_4]^-$ polymer (C_4H_4N = pyrrol-1-yl). There is a well defined current response at $E^{o\prime} = -1.20$ V *versus* the ferrocene–ferrocenium couple corresponding to the reversible reduction of the polymer confined dianion to the trianion. The peak separation, ΔE, for this process is *ca.* 40 mV at 20 mV s^{-1}; the theoretical ΔE value for a surface confined Nernstian process is 0 mV.[18] At a more negative potential the reduction of the trianion to the tetraanion is observed. The remarkably disparate responses for these two successive processes will be discussed in detail below. For the immediate purpose of characterisation of the cluster assemblies attention is focused on the primary redox process involving the 2−/3− couple.

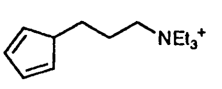
The replacement of the BF_4^- counter ion by $[Fe_4S_4(SPh)_4]^{2-}$ was confirmed by reflectance FTIR spectroscopy on thick films. Fig. 2 shows the spectrum of the polymer film before and after saturation with the cluster. The intense absorption of the $[BF_4]^-$ ion is attenuated and new bands associated with aromatic C–H bends appear at 745, 694 and 620 cm^{-1}.

The integrity of the cluster centres within the polymer film was further confirmed by EPR spectroscopy. The reduced core $\{Fe_4S_4\}^+$ is EPR active at liquid-helium temperatures and this provides a means of detecting the confined $[Fe_4S_4(SPh)_4]^{3-}$ cluster spectroscopically. A large platinum gauze electrode was coated with $[C_4H_4N(CH_2)_3NEt_3]^+[BF_4]^-$ polymer and $[Fe_4S_4(SPh)_4]^{2-}$ incorporated by ion exchange. The confined cluster was electroreduced in a MeCN electrolyte to the trianion $[Fe_4S_4(SPh)_4]^{3-}$. The reduced assembly was transferred to an EPR tube as described in the Experimental section and the EPR spectrum recorded at 10 K is shown in Fig. 3. The spectrum corresponds to the presence of a single $S = \frac{1}{2}$ spin system with axial symmetry ($g_\perp = 2.0$ and $g_\parallel = 1.9$ with $g_{av} = 1.95$). The data are typical of those observed for $\{Fe_4S_4\}^+$ centres within

Table 1 Redox potential data for various clusters*

Cluster couple	X	$E^{o\prime}_{sol}$/V	$E^{o\prime}_{polymer}$/V	ΔE/mV
$[Fe_4S_4X_4]^{2-/3-}$	Cl	−1.32	−1.00	320
	SPh	−1.40	−1.20	200
	SCH_2Ph	−1.60	−1.48	120
	SEt	−1.68	−1.54	140
	SBu^t	−1.72	−1.60	120
$[Fe_2S_2Cl_4]^{2-/3-}$		−1.04	−0.98	60
$[Fe_4S_4Cl_4]^{2-/3-}$		−1.32	−1.00	320
$[Fe_6S_6Cl_6]^{3-/4-}$		−1.24	−0.92	320

* Relative to the ferrocene–ferrocenium couple in an MeCN electrolyte.



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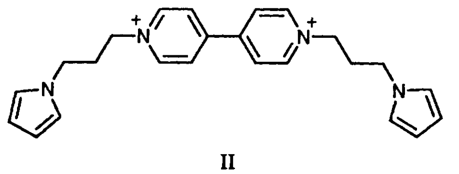

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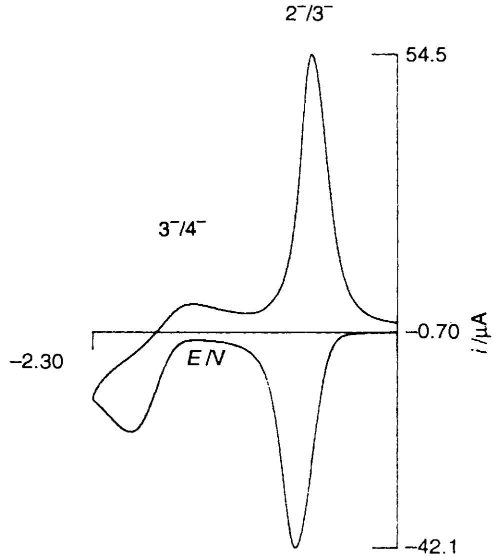


Fig. 1 Cyclic voltammogram of $[Fe_4S_4(SPh)_4]^{2-}$ in the cationic polymer on a platinum disc electrode at *ca.* 25 °C. Bathing electrolyte, MeCN–0.05 mol dm^{-3} $[NBu_4][BF_4]$; scan rate, 75 mV s^{-1}; potentials are relative to ferrocene–ferrocenium

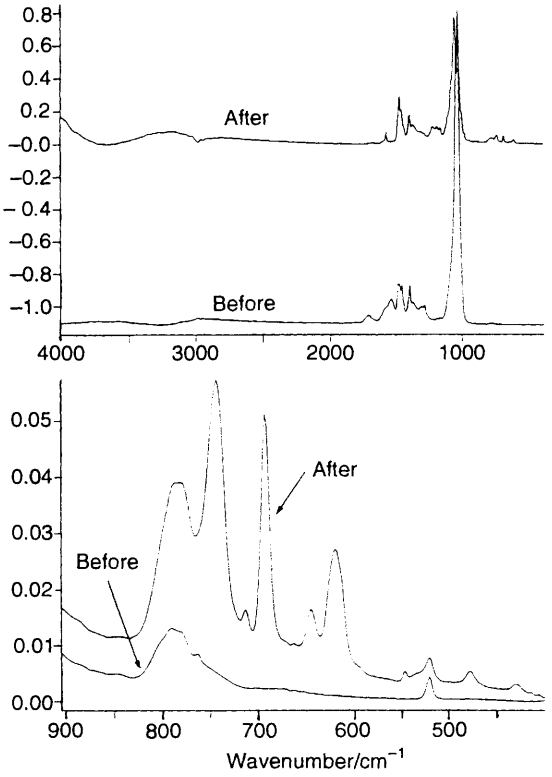


Fig. 2 Reflectance FTIR spectra of a platinum disc electrode before and after soaking in $[Fe_4S_4(SPh)_4]^{2-}$. The top spectra illustrate the dramatic attenuation of v(BF), the lower spectra the appearance of aromatic bending modes (spectra offset)

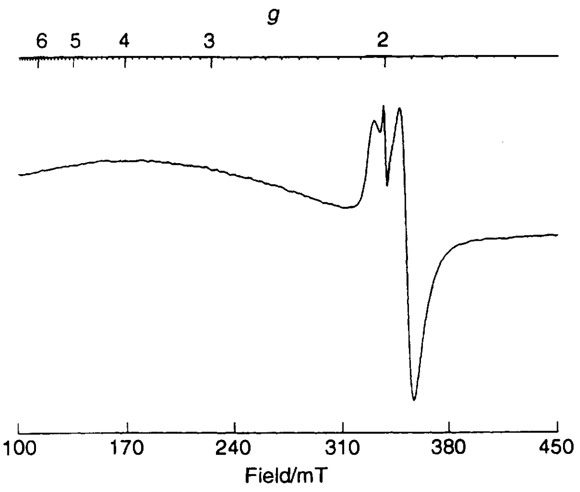


Fig. 3 EPR spectrum of the paramagnetic $[Fe_4S_4(SPh)_4]^{3-}$ cluster in the cationic polymer at 10 K

proteins and is consistent with the presence of paramagnetic $[Fe_4S_4(SPh)_4]^{3-}$ in the polymer film. There is no evidence for the presence of species with higher order spin states, $S = \frac{3}{2}, \frac{5}{2}$ *etc.*[9] The charge injected to reduce the dianion to the EPR-active state (measured coulometrically) was in reasonable accord with the spin concentration, as estimated by double integration of the EPR signal.

In frozen solution, synthetic clusters of the type $[Fe_4S_4(SR)_4]^{3-}$ (R = alkyl or aryl) generally display a mixture of spin states with the relative proportions of $S = \frac{1}{2}, \frac{3}{2}$ or $\frac{5}{2}$ species dependent on the nature of R, the counter ion and the solvent system. The relationship between the structure of $[Fe_4S_4(SR)_4]^{3-}$ salts, as determined in the solid state by X-ray crystallography and their observed EPR spectra in frozen matrices are poorly understood, but it is clear that the electronic and magnetic properties of the $\{Fe_4S_4\}^+$ core are markedly sensitive to perturbation by microenvironmental effects.

In contrast, the EPR spectra of a wide range of $\{Fe_4S_4\}^+$ ferredoxin centres in proteins show a single $S = \frac{1}{2}$ spin state.[1,8] Where the protein structure is partially disrupted, for example by exposure to urea which alters hydrogen-bonding interactions and solvent or ion access, mixed spin states are observed.[1,12] Insofar as the $[Fe_4S_4(SPh)_4]^{3-}$–poly(pyrrole alkylammonium) assembly displays a unique EPR signal, we believe that the cluster is distributed in the polymer film in such a way that the local interactions around the individual $[Fe_4S_4(SPh)_4]^{3-}$ centres are essentially uniform throughout the film. The sharp superimposed signal close to $g = 2$ constitutes less than 5% of the total spin concentration and its origin is unknown. It is possibly an impurity arising from degradation of the cluster; oxidative damage of clusters in proteins give EPR signals near $g = 2$ which have been attributed to Fe_3S_4 centres.[1]

Redox Regulation of the Stoichiometry of the Cluster–Ionic Polymer Assembly.—The charge injection, $Q_{cluster}$, corresponding to the reversible reduction of the polymer-confined cluster and that associated with the reversible oxidation of the poly(pyrrole) backbone, $Q_{polymer}$, can be measured independently. This provides a means of determining the ratio of alkylammonium to cluster groups in the assembly.

Thus $Q_{polymer}$ and $Q_{cluster}$ were estimated as follows. Polymer films were prepared by anodic oxidation on vitreous carbon and the charge consumed in converting the fully reduced poly(pyrrole) backbone to the fully oxidised conducting form, $Q_{polymer}$, was determined coulometrically. The primary oxidation of the poly(pyrrole) backbone is reversible and data for the reduction of the oxidised poly(pyrrole) backbone to the reduced form gave $Q_{polymer}$ data concordant with that obtained by oxidation. The polymer films were exposed to $[Fe_4S_4(SPh)_4]^{2-}$ and the loading of the cluster was determined by coulometry and also by reversal coulometry on $[Fe_4S_4(SPh)_4]^{3-}$. Measurements of $Q_{cluster}$ were made after equilibration of the assembly: this was effected by taking the cluster couple through three redox cycles whereafter a stable voltammetric response was observed (see below). The average ratio of polymer-NMe_3^+ to $[Fe_4S_4(SPh)_4]^{2-}$ groups was found to be 3.2 ± 0.2 from eight independent determinations of the ratio $Q_{polymer}:Q_{cluster}$ on films grown from *ca.* 1 to 5μ thick. Thus, after redox cycling, the assembly has a composition close to a polymer of $C_4H_4N(CH_2)_3NMe_3]_3^+$ $[Fe_4S_4(SPh)_4]^{2-}[BF_4]^-$.

This stoichiometry was supported by quantitative reflectance FTIR spectroscopy. The band intensity of ν(B–F) in the reflectance FTIR spectrum of a platinum disc electrode coated with $[C_4H_4N(CH_2)_3NMe_3]^+[BF_4]^-$ polymer was estimated by integration before and after cluster incorporation. The observed 70% reduction in band intensity is in good agreement with the expected decrease of 66%.

The composition of the polymer and redox centre assembly is ideally set-up to allow the stoichiometric export of one $[BF_4]^-$ anion on reduction and its import on re-oxidation, so as to maintain charge neutrality within the film. This is not serendipidous but is a direct consequence of the redox cycling of the assembly which *self regulates* the composition of the cationic polymer–dianionic cluster assembly. On the first voltammetric scan of the polymer with a saturated loading of the cluster, the charge injection for the reduction of $[Fe_4S_4(SPh)_4]^{2-}$ exceeds that observed for the re-oxidation; on the second cycle the charge injection for the reduction is diminished and more closely approaches that observed for the re-oxidation; on the third and subsequent cycles the system approaches the equilibrium composition. Evidently cluster is reduced and expelled into solution from the polymer in the early reduction cycles so as to maintain charge neutrality in the polymer. It is not re-imported on re-oxidation during cycling because its concentration in the electrolyte is vanishingly small; instead $[BF_4]^-$ maintains the charge balance. It is in this way that the polymer–cluster assembly adjusts to the observed stoichiometry. Similar examples of the self regulation of ionic polymer–redox ion stoichiometry have been noted.[19,20] For example, Anson *et al.*[20] have recently shown that the anionic polymer Nafion incorporates a dicationic ruthenium centre in a stoichiometry which mirrors that of the cationic polymer–dianionic cluster assembly reported here.

Ligand Exchange at Clusters within Polymer Films.—Thiolate ligands bound at $[Fe_4S_4(SR)_4]^{2-}$ centres can be exchanged in solution *via* reactions with thiols; thus R′SH displaces RSH and the core is substituted by R′S.[13] Such reactions can also take place within the polymer film. Fig. 4 shows the cyclic voltammogram of a $[C_4H_4N(CH_2)_3NEt_3]_3^+[Fe_4S_4(SBu^t)_4]^{2-}[BF_4]^-$ polymer coated platinum disc electrode before and after soaking in MeCN containing 2% $PhCH_2SH$. The primary redox response of the bound couple $[Fe_4S_4(SBu^t)_4]^{3-/2-}$ is displaced and a new couple appears at a potential which corresponds to that of the polymer-bound $[Fe_4S_4(SCH_2Ph)_4]^{3-/2-}$ couple. The conversion, as estimated from comparison of the charge associated with each forward peak, is essentially quantitative. The enhanced peaks observed upon scan reversal after substitution reflect the greater stability of $[Fe_4S_4(SCH_2Ph)_4]^{4-}$ with respect to the tetraanion $[Fe_4S_4(SBu^t)_4]^{4-}$. Substitution reactions of clusters are not limited to thiols but also occur with phenols. Fig. 5 shows the FTIR reflectance spectra of a $[C_4H_4N(CH_2)_3NEt]_3^+[Fe_4S_4(SBu^t)_4]^{2-}[BF_4]^-$ polymer coated platinum disc electrode before and after soaking in MeCN containing 2% 3-cyanophenol. After exposure to the cyanophenol, the appearance of ν(CN) is clearly evident together with the sharp aromatic C–H bending modes below 1000 cm^{-1}; notably ν(OH) is absent. In a control experiment, the cluster-free polymer was similarly exposed to the cyanophenol and ν(CN) was not observed.

These results further confirm that the integrity of the cluster centres within the polymer electrode assembly are conserved. They also show that the reagents (phenylmethanethiol or 3-cyanophenol) are able to penetrate the polymer and react with the clusters, and that the neutral substitution products are free to diffuse away.

Influence of Polymer Environment on the Redox Potentials of Bound Clusters.—Table 1 lists redox potential data measured for various clusters confined in ionic polymers together with corresponding data determined for the same species diffusing freely in the electrolyte solution: the difference in redox potential between the solution-free and polymer-bound $[Fe_4S_4(SR)_4]^{2-/3-}$ couples are listed as ΔE. In each case, the apparent redox potential of the cluster in the polymer film is substantially positive of that measured in solution. This effect can be viewed directly by cyclic voltammetry on thin films of the polymer with pin-hole effects:[17b] reversible one-electron reduction of the SPh cluster at the naked electrode and within the film are observed as discrete processes, Scheme 1.[4] Parallel although less marked trends are observed for the solution and polymer confined 3–/4– couples.

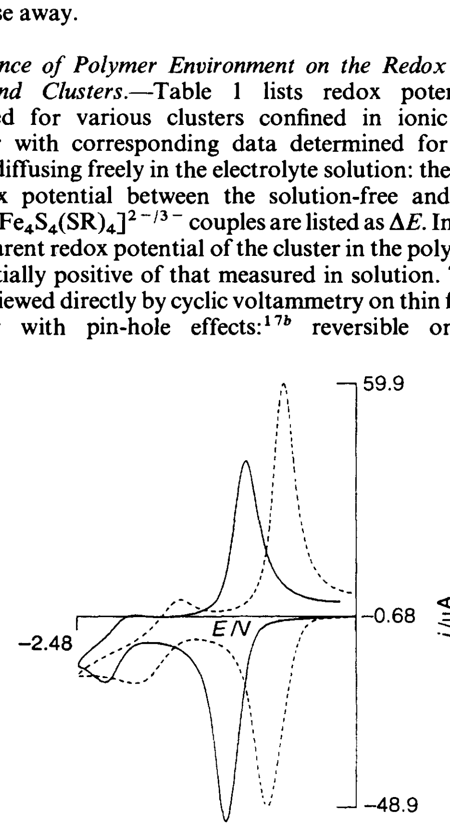


Fig. 4 Thiolate ligand exchange at cluster centres within the cationic polymer. The solid line illustrates the voltammetric response for $[Fe_4S_4(SBu^t)_4]^{2-}$ before exposure to $PhCH_2SH$ and the dashed line the voltammetry observed after exposure. The dashed curve is identical to that observed for polymer-bound $[Fe_4S_4(SCH_2Ph)_4]^{2-}$ Conditions are as for Fig. 1

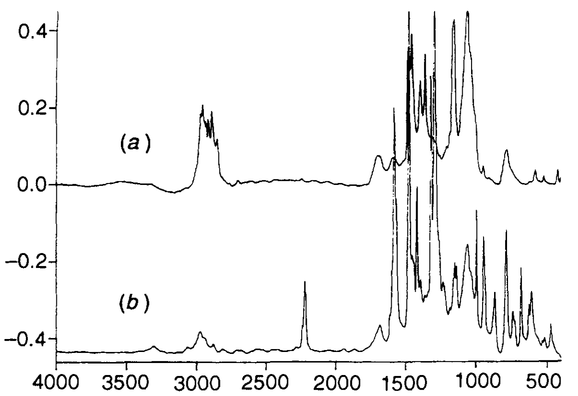


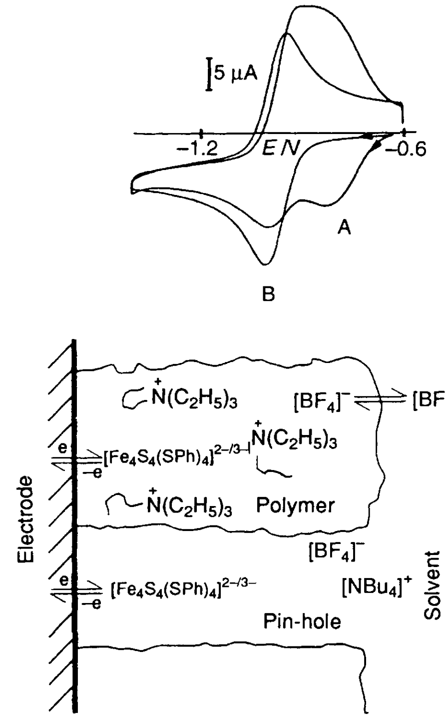
Fig. 5 Reflectance FTIR spectra of the cationic polymer coated platinum disc electrode loaded with $[Fe_4S_4(SBu^t)_4]^{2-}$ before (*a*) and after (*b*) exposure to 3-cyanophenol. Note the apperarance of ν(CN) at 2220 cm^{-1}, the diminution of ν(CH) near 3000 cm^{-1} (Bu^t) and the absence of a band at *ca.* 3400 cm^{-1} which would otherwise indicate the presence of free, unreacted 3-cyanophenol in the polymer: spectrum (b) offset

The origin of the positive shifts in potential of the bound clusters relative to those measured in solution, ΔE, are now considered. The intrinsic values of $E°$ in solution and in a film could be the same with the (non-zero) values of ΔE arising from a Donnan equilibrium. To test whether such an effect contributes significantly to the measured ΔE values the following experiments were undertaken.

The monomers **I** and **II** were co-polymerised under conditions which gave a film containing a low concentration of redox-active alkyl viologen groups distributed in a predominantly tetraalkylammonium polymer matrix. The low concentration of the redox-active centres ensures that the change in the concentration of $[BF_4]^-$ bound within the polymer that results from the addition or removal of charge is negligible. The primary reduction potential of the covalently bound viologen groups was measured for electrolyte solutions bathing the film which ranged from 0.02 to 1.0 mol dm^{-3} $[NBu_4][BF_4]$. The linear plot of $E°_{app}$ *versus* $\log([BF_4]^-/\text{mol dm}^{-3})$ is shown in Fig. 6 from which the slope, $dE°_{app}/d\log([BF_4]^-)$, is estimated to be −36 mV per decade. Were the film to act as a permselective membrane, then this slope should be about 59 mV per decade change in the concentration of $[BF_4]^-$.[21]

The monomer **II** free in solution shows the same small shift in redox potential with respect to the ferrocene–ferrocenium couple when measured in 0.02 and 1.0 mol dm^{-3} $[NBu_4][BF_4]$. Similarly, $E°$ for $[Fe_4S_4(SPh)_4]^{2-/3-}$ when measured in solution shows a minimal dependence on the concentration of the electrolyte. From these observations we suggest that Donnan effects do not contribute significantly to the large values of ΔE observed for the clusters and that the polymer film does not behave as an ideal permselective membrane but that it probably has a structure which is porous to electrolyte, *i.e.* the bulk electrolyte solution phase permeates the polymer film.

The large positive shifts in redox potential of the clusters can



Scheme 1 Behaviour of confined and solution-free $[Fe_4S_4(SPh)_4]^{2-}$ at a thin, pin-hole electrode, from ref. 4 and schematic representation of process

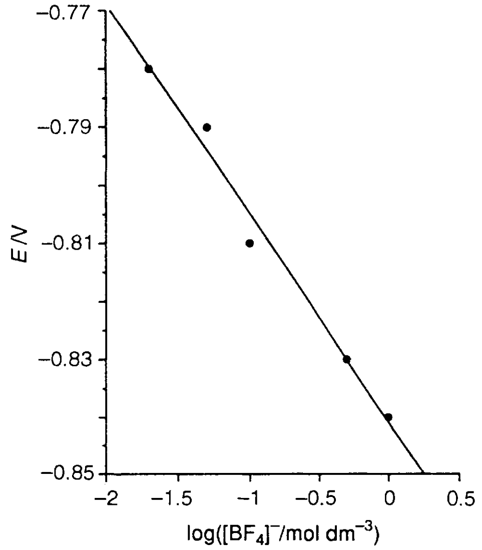


Fig. 6 Plot of observed primary reduction of alkyl viologen derivatised alkylammonium co-polymer *versus* concentration of $[BF_4]^-$ in the bathing solution. The co-polymer ratio **I** : **II** was estimated to be 70 : 1 from $Q_{\text{co-polymer}} : Q_{\text{viologen}}$ measurements. Slope of plot = −36.0 mV

be attributed to their electrostatic adsorption at the pendant cationic groups on the polymer backbone, *i.e.* ion-pairing interactions. Thus the addition of an electron to a (neutral) ion-paired aggregate is easier than addition to the solvated dianion. Conversely, the removal of an electron from the (neutral) ion-pair stabilised, trianion aggregate is correspondingly more difficult. Shifts in potential parallel to those observed for the bound clusters are found when the $[Fe(CN)_6]^{3-/4-}$ couple is incorporated in the same polymer,[4] when it is contained in macrocyclic dialkylammonium receptor molecules[22] or when it is bound in a protonated aminosiloxane polymer.[23] That the ion-pairing interactions between the anionic clusters and the pendant cationic groups on the polymer chain primarily determine the magnitude of $\Delta E_{2-/3-}$ is supported by the dependence of this parameter on the specific nature of the cluster, Table 1 (see below) and also by the following observations.

Exposure of a cationic polymer film loaded with the cluster $[Fe_4S_4(SPh)_4]^{2-}$ to a concentrated electrolyte solution, 1.4 mol dm^{-3} $[NBu_4][BF_4]$–MeCN or $[NBu_4][BF_4]$–toluene (1 : 3),[11] has two consequences. First, the redox response of the $[Fe_4S_4(SPh)_4]^{2-/3-}$ couple within the polymer film becomes diffusional in character as $[BF_4]^-$ displaces the ion-paired cluster dianion into the solution phase of the polymer network. In this situation, the value of E° is close to that observed for the cluster when free in solution. Secondly, the displaced cluster is rapidly lost from the solution phase of the polymer matrix by leaching into the bulk electrolyte. A similar effect is observed when $[Fe_4S_4(SPh)_4]^{2-}$ is electrostatically bound in the electroactive dicationic viologen polymer **II**. Charge neutralisation of this polymer by two successive one-electron reductions also results in a value of $\Delta E_{2-/3-}$ close to zero, in accord with the release of the cluster into the solution phase of the polymer matrix and from which it is rapidly lost to the bulk electrolyte phase by migration.

From these results we suggest the following model for the electrode assembly: (*i*) anionic clusters are ion paired with cationic sites and this results in a major perturbation of redox potentials with respect to those observed in solution; (*ii*) ion pairing of the clusters to the pendant alkylammonium groups is disrupted by high concentrations of the $[NBu_4][BF_4]$ electrolyte which permeates the solution phase of the polymer matrix; and (*iii*) cluster so released into the solution phase of the polymer is free to diffuse to the electrode where it undergoes electron transfer at a potential corresponding to that observed at a bare electrode, or to migrate from the polymer matrix into the bulk electrolyte solution, the diffusion gradients being such that the cluster is rapidly leached into the bulk solution phase.

Dependence of ΔE *on the Nature of the Cluster.*—The value of ΔE shows a dependence on the nature of the thiolate ligands on the cubane core. It ranges from +320 mV for the Cl cluster to +120 mV for the SBu^t and SCH$_2$Ph substituted compounds, Table 1.

If the model of the adsorption of the anionic clusters at the cationic polymer sites is correct, then for the series of clusters examined we might expect that those with the more polar substituents will have the strongest ion-pairing interactions and hence the greatest perturbation of $E^{\circ\prime}$ from their solution values. Insofar as ΔE values for the Cl and SPh clusters are greater than for the alkanethiolate derivatives this is the case.

Steric factors may be also important in determining the magnitude of ΔE. The ion-pairing contact distance may depend upon the substituent groups; ΔE for the SBu^t ligated cluster is considerably smaller than that for the Cl ligated species and is marginally smaller than the SEt derivative. Another effect which may contribute to the magnitude of ΔE is the extent of interactions of substituents with the non-polar hydrocarbon regions of the polymer. Such interactions might be expected to stabilise the less charged 2− anion with respect the 3− conjugate and so diminish ΔE.

The cluster $[Fe_6S_6Cl_6]^{3-}$ shows a relatively large shift in its primary reduction potential in the cationic polymer with respect to that observed in solution, $\Delta E = +320$ mV. In contrast the smaller $[Fe_2S_2Cl_4]^{2-}$ cluster has a value of $E^{\circ\prime}$ only marginally shifted from its solution value, $\Delta E = +60$ mV. As discussed in the preceding section, Donnan potential contributions to ΔE appear to be negligible in the viologen doped ion-exchange co-polymer and we assume that this is also the case for the homopolymer of **I** loaded with cluster anions.

Propagation of Charge through the Polymer: Electron-hopping and Diffusional Processes in the Sequential Reduction of $[Fe_4S_4(SCH_2Ph)_4]^{2-}$ *to the Trianion and then the Tetraanion.*—Cyclic voltammetry of the polymer-bound clusters $[Fe_4S_4(SR)_4]^{2-}$ at scan rates < 0.05 V s^{-1} showed a peak–current response for the primary reduction which varied linearly with the scan rate. Such behaviour is consistent with a thin-layer response of the surface-confined redox couple in which the diffusion layer extends to the boundary between the polymer film and the bulk solution. At faster scan rates the response is non-linear because this condition is not satisfied.

At moderate scan rates, there is a striking difference in the voltammetric response for the successive reversible reductions of $[Fe_4S_4(SCH_2Ph)_4]^{2-}$ and $[Fe_4S_4(SCH_2Ph)_4]^{3-}$ within the polymer film, as compared with their behaviour in solution. The corresponding SPh couples show a quite similar response as illustrated by Figs. 1 and 7. In solution, the peak currents for the successive one-electron processes are of comparable magnitude because the diffusion coefficients of the 3− and 2− species are close, $D_{\text{sol}(2-)} = 6.7 \times 10^{-6}$ cm^2 s^{-1} and $D_{\text{sol}(3-)} = 9.1 \times 10^{-6}$ cm^2 s^{-1}. In the cationic polymer, the peak currents for the secondary process are substantially smaller than those for the primary process; additionally, the shape of the voltammetric response for the reduction of the trianion has a diffusional character. Comparable peak currents for the two successive reductions are only observed at slow scan rates in thin films where thin-layer conditions exist for both processes.

The disparate voltammetric behaviour of the dianion and trianion clusters within the cationic film is a consequence of different rates of charge propagation and we account for these in the following way. In the ionic polymer, charge propagation can take place by migration of the redox-active material to the electrode surface and this diffusional process is driven by the concentration gradient set up by its removal at the electrode surface. However, provided the concentration of the electroactive material in the polymer is sufficiently high and the rate constant for electron self exchange between redox states is sufficiently large, then an electron-hopping mechanism can also contribute to the overall rate of charge propagation. This results in a peak–current response that is enhanced relative to that which would be observed if charge propagation was purely controlled by physical diffusion.

We propose that rapid electron self exchange between clusters localised in the polymer makes a significant contribution to the overall rate of the 2 – cluster whereas electron self exchange between the 3 – and 4 – redox states is comparatively slow and the diffusional process dominates the rate of charge propagation. The following evidence provides some support for this interpretation. Fig. 7 shows voltammograms for the SCH_2Ph cluster freely diffusing in solution and confined in the ionic polymer, together with the voltammogram of a cluster co-ordinated by polymer-bound SCH_2 groups within a cationic co-polymer.[5] There is a dramatic attenuation of the peak current response for the 3 – /4 – couple relative to that of the 2 – /3 – couple on progressing from the solution to the co-ordinatively bound situation.

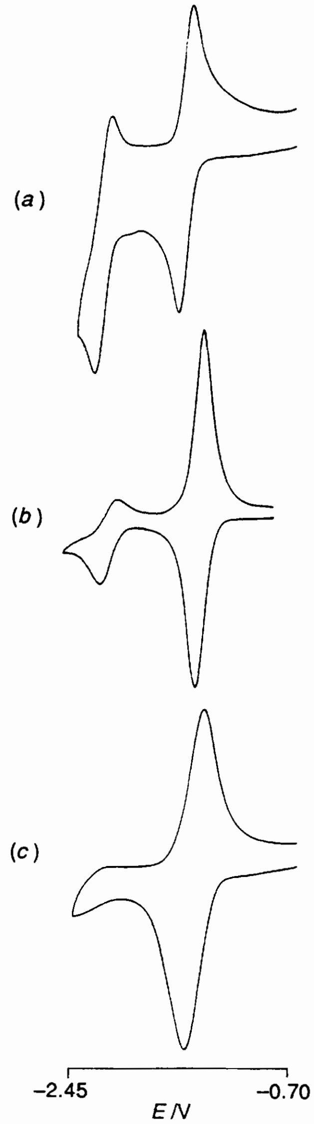


Fig. 7 Cyclic voltammograms of (*a*) $[Fe_4S_4(SCH_2Ph)_4]^{2-}$ at a platinum electrode freely diffusing in 0.1 mol dm^{-3} $[NBu_4][BF_4]$–MeCN; (*b*) the same anion electrostatically bound within the cationic polymer of **I**, bathing solution 0.05 mol dm^{-3} $[NBu_4][BF_4]$–MeCN; and (*c*) $[Fe_4S_4(SCH_2\text{–})_4]^{2-}$ units covalently bound within a cysteinyl derivatised co-polymer (see ref. 5). The current scales are arbitrarily set for clarity of comparison

The tightly bound polymer-ligated cluster cannot diffuse to the electrode surface and propagation of charge through the film can only take place by electron hopping between the localised redox centres within the polymer matrix. The redox response for the reduction of the 2 – centres is well defined but that for the reduction of the 3 – centres is all but absent. Clearly, electron self exchange between the 3 – and 4 – states must be considerably slower than for the 2 – /3 – self exchange.

If the relative rates of electron self exchange for the 2 – /3 – and 3 – /4 – centres in the polymer-ligated cluster parallel those of the ionically bound SCH_2Ph cluster, then the redox response of the 3 – /4 – couple in the ionic polymer can be primarily attributed to a diffusional process whereas that for the 2 – /3 – couple involves both diffusional and electron-hopping elements. Chronocoulometric experiments were undertaken in order to obtain semi-quantitative information on the propagation of charge through the cluster-loaded ionic films. The *Q versus t* plot of Fig. 8 shows that there is nothing unusual in the electron stoichiometry of the reductions. Terminal values of *Q* are equivalent whereas the rates of reduction of $[Fe_4S_4(SCH_2Ph)_4]^{2-}$ and $[Fe_4S_4(SCH_2Ph)_4]^{3-}$ are clearly different, as expected from the voltammetry.

Apparent diffusion coefficients, D_{app}, associated with charge propagation through a polymer film can be estimated from the slope Φ (in C $s^{-\frac{1}{2}}$) of plots of *Q versus* $t^{\frac{1}{2}}$ using equation (1) where

$$D_{app} = \pi[\Phi/(2FAc)]^2 \qquad (1)$$

A is the electrode area. Such an analysis is appropriate because charge transport can be regarded as equivalent to a diffusional process with Cottrell-type behaviour at short times. Taking the density of the polymer film to be 1.2 g cm^{-3} the concentration (*c*) of the cluster in the idealised stoichiometry, $[C_4H_4N(CH_2)_3NMe_3]_3{}^+$ $[Fe_4S_4(SCH_2Ph)_4]^{2-}[BF_4]^-$, is estimated to be 1.4 mol dm^{-3}. Fig. 9 shows typical *Q versus* $t^{\frac{1}{2}}$ plots obtained for the reduction of the 2 – SCH_2Ph cluster and thence the 3 – cluster in a cationic polymer. For a value of *c* approaching the ideal stoichiometry (1.34 mol dm^{-3}), $D_{app(2-/3-)}$ and $D_{app(3-/4-)}$ were calculated to be *ca.* 7.6×10^{-12} and 8.1×10^{-13} $cm^2\ s^{-1}$ respectively. If we assume that electron hopping makes a negligible contribution to the reduction of the 3 – cluster as discussed above, then $D_{app(3-/4-)}$ will be essentially the physical diffusion coefficient $D_{polymer(3-)}$ for $[Fe_4S_4(SCH_2Ph)_4]^{3-}$ within the cationic polymer, *i.e.* $D_{app(3-/4-)} \approx D_{polymer(3-)} = 0.81 \times 10^{-12}$ $cm^2\ s^{-1}$. This may be compared with the value of $D_{soln(3-)} = 6.7 \times 10^{-6}$ $cm^2\ s^{-1}$ determined for the freely diffusing cluster in the electrolyte

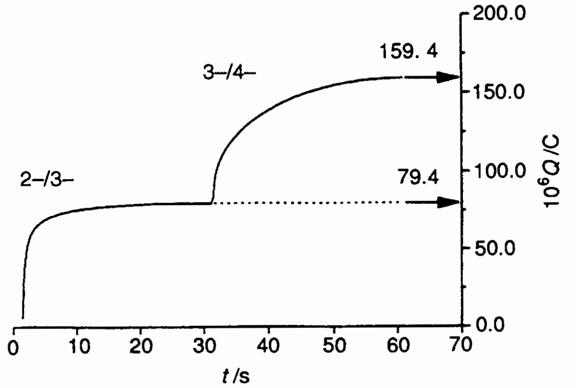


Fig. 8 Successive potential step chronocoulometric responses of $[Fe_4S_4(SCH_2Ph)_4]^{2-}$ and $[Fe_4S_4(SCH_2Ph)_4]^{3-}$ bound in a cationic polymer. The waveform was initial potential –0.5 V stepped to –1.58 V and held at this value for 30 s then stepped to –2.30 V for > 30 s. Potentials are relative to ferrocene–ferrocenium: bathing solution, 0.05 mol dm^{-3} $[NBu_4][BF_4]$–MeCN. Note that terminal *Q* values are nearly identical for the successive one-electron steps but the rates of approaching stoichiometric reduction are clearly different

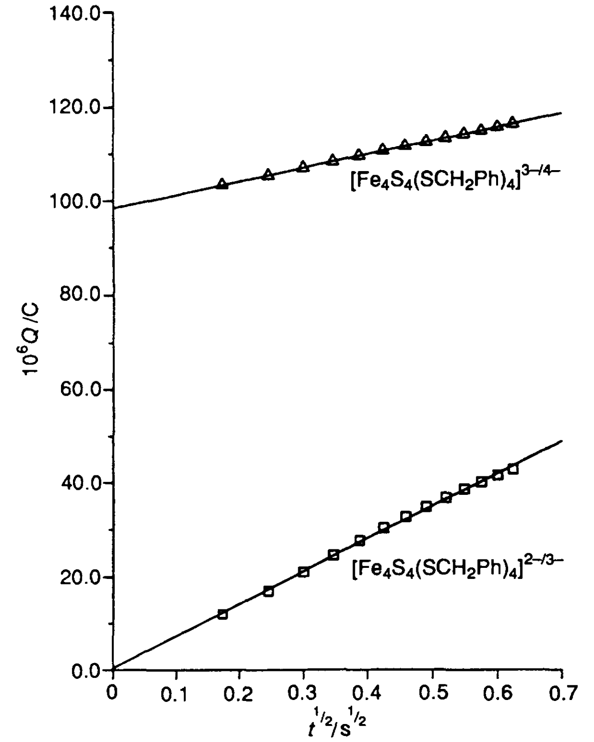


Fig. 9 A typical plot of Q *versus* $t^{\frac{1}{2}}$ for the cationic polymer confined $[Fe_4S_4(SCH_2Ph)_4]^{2-}$ to $[Fe_4S_4(SCH_2Ph)_4]^{3-}$ process illustrating Cottrell-type behaviour. The D_{app} values were calculated from the slopes of such plots (upper, 30×10^{-6} C $s^{-\frac{1}{2}}$; lower 70×10^{-6} C $s^{-\frac{1}{2}}$) using equation (1). Electrode area, 0.2 cm^2; nominal cluster concentration, 1 mmol dm^{-3}; ratio of cluster to alkylammonium groups 1 : 44

solution. That the diffusion coefficient in the (viscous) polymer is several orders of magnitude lower than that for the cluster in the MeCN electrolyte is not surprising: similar values are observed for cation complexes bound within anionic polymers, for example, D_{polymer} is *ca.* 10^{-12} cm^2 s^{-1} for $[Co(bipy)_3]^{2+}$ (bipy = 2,2'-bipyridine) in Nafion.[24]

We now consider the 'enhanced' apparent diffusion coefficient observed for the primary 2−/3− couple. For the reduction of the bound 2− cluster $D_{\text{app}(2-/3-)}$ is close to $D_{\text{app}(2-/3-)}$ determined for the oxidation of the 3− product for a range of polymer compositions and as is observed in solution. This serves to emphasise that the difference in the magnitudes of $D_{\text{app}(2-/3-)}$ and $D_{\text{polymer}(3-)}$ cannot merely be a consequence of a difference in the physical diffusion coefficients of the 2− and 3− species within the polymer film and that an additional mechanism of charge propagation must be operative for the 2−/3−couple, electron hopping.

In the simplest model, the contribution of propagation of charge by electron hopping to the magnitude of $D_{\text{app}(2-/3-)}$ is given by the Dahms–Ruff relationship, equation (2). This

$$D_{\text{app}(2-/3-)} = D_{\text{polymer}(2-)} + (k_{\text{ex}}/6)\delta^2 c \qquad (2)$$

assumes that the apparent diffusion constant is the sum of the physical displacement and electron-hopping diffusion coefficients. Fixed redox centres are regarded as randomly distributed over a fictitious cubic lattice whose characteristic length is equal to the hopping distance δ. In equation (2), k_{ex} is the rate constant for the self exchange of electrons, in our case between the $[Fe_4S_4(SCH_2Ph)_4]^{2-}$ and $[Fe_4S_4(SCH_2Ph)_4]^{3-}$ centres within the cationic polymer.[25]

In solution, $D_{\text{sol}(3-)} \approx D_{\text{sol}(2-)}$ and, in the polymer, $D_{\text{app}(2-/3-)} \approx D_{\text{app}(3-/2-)}$. It is therefore reasonable to assume that the physical diffusion coefficients $D_{\text{polymer}(3-)}$ and $D_{\text{polymer}(2-)}$ are also close. Thus, from equation (2), with $D_{\text{polymer}(2-)} = 0.8 \times 10^{-12}$ cm^2 s^{-1}, $c = 1.34$ mol dm^{-3} and assuming $\delta = 11$ Å gives* $k_{\text{ex}} = 2.4 \times 10^3$ dm^3 mol^{-1} s^{-1}.

In solution, the electron self-exchange rate constant for the SCH_2Ph cluster has been estimated to be about 10^8 dm^3 mol^{-1} s^{-1} by NMR spectroscopy.[26] A quite similar disparity in solution and polymer magnitudes of k_{ex} has been observed for the $[Co(bipy)_3]^{3+/2+}$ system[24] where values of 2×10^3 and 10^8 dm^3 mol^{-1} s^{-1} have been reported for polymer and solution respectively. A common argument advanced by several authors[27] to explain such differences is as follows. In solution, diffusional rates k_{diff} are fast and an electron self-exchange process is usually limited by k_{et}, the intrinsic rate constant for the electron-transfer process, rather than the rate at which the reactants come together. In a polymer, where diffusional rates are much slower, the rate constant for physical diffusion can dominate the kinetics of the hopping process. The observed rate constant, k_{ex}, is consequently related to the activation-limited electron self-exchange rate constant k_{et} and the diffusion-limited bimolecular rate constant k_{diff} by the Noyes[28] equation (3). With $k_{\text{et}} \gg k_{\text{diff}}$ then equation (4) applies. In one such[24]

$$1/k_{\text{ex}} = 1/k_{\text{et}} + 1/k_{\text{diff}} \qquad (3)$$

$$k_{\text{ex}} = k_{\text{diff}} \qquad (4)$$

approach the magnitude of k_{diff} has been calculated from the von Smoluchowski[29] equation (5) and thence compared with

$$k_{\text{diff}} = 4\pi N_A r_T D_T/10^3 \qquad (5)$$

the experimental value of k_{ex}. In this equation, r_T is the sum of the radii of the oxidised and reduced partners, D_T is the sum of their diffusion coefficients, and N_A is Avogadro's number. In our case, taking $r_T = 11$ Å and $D_T = 2D_{\text{polymer}(2-)} \approx 1.6 \times 10^{-12}$ cm^2 s^{-1} gives $k_{\text{diff}} = 1.4 \times 10^3$ dm^3 mol^{-1} s^{-1} which is reasonably close to $k_{\text{ex}} = 2.4 \times 10^3$ dm^3 mol^{-1} s^{-1} estimated from the chronocoulometric data and consistent with equation (4). However such an analysis[24] has been criticised as being fundamentally flawed because the pure diffusion element is fully accommodated by equation (2).[27] Thus for the $[Co(bipy)_3]^{3+/2+}$ system in Nafion, it has been argued that k_{ex} does not represent the diffusion limitation of the reaction kinetics as derived by von Smoluchchowsky;[29] it is actually equivalent to k_{et} and its diminished value with respect to k_{et} in solution is a consequence of pronounced, but undisclosed, matrix effects on the electron-transfer kinetics.[27]

The loading of $[Fe_4S_4(SCH_2Ph)_4]^{2-}$ was varied by exposing fresh polymer coatings to a solution of the cluster for shorter or longer times. The resulting films invariably gave excellent Cottrell plots for both the 2−/3− and 3−/4− processes from which diffusion constants were estimated as described above. Values of $D_{\text{polymer}(3-/4-)}$ decreased from 2.9×10^{-12} cm^2 s^{-1} at 0.5 mol dm^{-3} to 0.7×10^{-12} cm^2 s^{-1} at 1.45 mol dm^{-3}. A decrease in D_{app} with increasing loading has been attributed to 'single-file diffusion' effects in related systems where physical diffusion is important: as more sites are occupied migratory pathways are restricted.[24] Values of $D_{\text{app}(2-/3-)}$ on the other hand ranged from *ca.* 6×10^{-12} to 42×10^{-12} cm^2 s^{-1}, increasing rapidly to a maximum at about 0.75 mol dm^{-3} and thereafter falling off to values scattered around 10×10^{-12} cm^2 s^{-1}. Equation (2) predicts a linear increase in $D_{\text{app}(2-/3-)}$ with concentration whereas other more or less sophisticated models

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* The concentration of the cluster in the polymer was based on coulometric data and the arbitrary assumption that the density of the film is 1.1 g cm^{-3}. The densities of organic crystals are typically *ca.* 1.3 g cm^{-3}. The density of the polymer is undoubtedly less than this but detached films have a density greater than that of water. Taking other values in the range 1–1.3 g cm^{-3} would slightly modify the estimated concentrations. The centre-to-centre separation of the clusters in the film (δ) was calculated from the molar volume with the assumption of uniform distribution in a cubic lattice.

attempt to account for non-linear dependencies on c.[27,30] However, the inadequate quality of our fractional loading data does not allow further analysis in terms of these models.

The value for k_{ex} estimated above, following the approach of Buttry and Anson,[24] must be considered with much caution because of the approximations made in the calculation and in the model employed. However, within these limitations, it nevertheless is certain that the rate constant for electron self exchange is greater for the $2-/3-$ system than it is for the $3-/4-$ process. Why the electron self exchange of the $3-/4-$ system in the polymer is (at least) an order of magnitude slower than that for the $2-/3-$ system is presumably a consequence of unfavourable spin re-arrangement or of inner- or outer-sphere structural reorganisation accompanying electron transfer.

Conclusions

Polymer electrodes in which various iron–sulfur clusters are bound electrostatically within a cationic polymer can be assembled and the films characterised by FTIR and EPR spectroscopy, cyclic voltammetry and chronocoulometry.

The cationic polymer microenvironment shifts cluster redox potentials to values more positive than those observed in solution: this is attributed to strong electrostatic interactions (ion pairing). The perturbation of E° is smallest for the $[Fe_4S_4(SBu^t)_4]^{2-/3-}$ couple and greatest for the $[Fe_4S_4Cl_4]^{2-/3-}$ couple.

Thiol–thiolate ligand exchange reactions of clusters bound within the polymeric film can be achieved.

Chronocoulometric and other data suggest that electron self exchange for the $[Fe_4S_4(SCH_2Ph)_4]^{2-/3-}$ pair is sufficiently fast to allow electron hopping to contribute significantly to charge propagation in the films whereas electron self exchange for the $[Fe_4S_4(SCH_2Ph)_4]^{3-/4-}$ pair is slow and reduction of the trianion $[Fe_4S_4(SCH_2Ph)_4]^{3-}$ takes place *via* migration to the electrode.

Finally, we note that the last conclusion has implications with respect to the design of cluster–polymer assemblies for mediating electron transfer to other molecules bound to or capable of penetrating polymeric films. The $2-/3-$ couple is intrinsically fast and stable and thus appears well suited for electron propagation to molecules which reduce at potentials positive of about -1 V *versus* a saturated calomel electrode. In this respect the $3-/4-$ couple appears much less attractive: preliminary data on the $1-/2-$ couple when bound by ion exchange or by ligation indicate that this system also suffers similar disadvantages, slow charge propagation and low stability.

Experimental

General.—All electropolymerisations and manipulations of clusters and solvents *etc.* were carried out in an inert atmosphere dry-box or by using Schlenck techniques. The various iron–sulfur clusters[13] and pyrrole monomers[17] used were prepared according to published procedures. Electrochemical measurements were carried out using an EG and G PAR model 273 potentiostat waveform generator controlled by an IBM/PC AT computer with output recorded on a Hewlett Packard HP 7470A plotter or Philips PM 8043 X-Y recorder. All software for the control and the acquisition, analysis and presentation of data were written in-house by K. S. Ryder. Coulometric data, Q, were obtained by monitoring and digitising cell current $i(t)$ and summation between $n = 0$ and $n = n$ using $Q(t) = \Delta t \Sigma i_n$ where n is the digital point number and Δt is the time interval between points.

Electropolymerisation.—A two-compartment, three-electrode cell was charged with 5 cm^3 of freshly distilled MeCN containing 0.1 mol dm^{-3} $[NBu_4][BF_4]$ and *ca.* 5 mol dm^{-3} of the pyrrole monomer. The working electrode was either a platinum disc (0.2 cm^2) or a vitreous carbon disc (0.07 cm^2). Electropolymerisation was carried out at a potential corresponding to that near the foot of cyclic voltammetric oxidation wave for the pyrrole, *ca.* 500 mV, *versus* ferrocene–ferrocenium. Cell current and charge were monitored for the 30–50 s duration of the polymerisation; typically 1.5–2.0 mC were consumed during electropolymerisation. The electrode potential was re-set after polymerisation to *ca.* -400 mV *versus* ferrocene–ferrocenium to effect the reduction of the polymer backbone; this was complete after about 60 s. The coated electrode was removed from the cell, washed in fresh MeCN and re-examined in 0.5 mol dm^{-3} $[NBu_4][BF_4]$ and $Q_{polymer}$ determined by coulometry.

Cluster Incorporation.—With the polymer in its fully reduced state, the coated electrode was immersed in a MeCN solution of the cluster, typically 1–5 mmol dm^{-3}. Saturation of the polymer film with the cluster was achieved after 10–12 min. The electrode assembly was rinsed with fresh MeCN and examined by the various electrochemical methods in a cell containing 0.02–0.05 mol dm^{-3} $[NBu_4][BF_4]$–MeCN or was allowed to dry in a stream of dinitrogen for examination by FTIR spectroscopy. Potential measurements *versus* ferrocene–ferrocenium were determined voltammetrically in the following way. The ferrocene couple was first recorded at the naked working electrode, the polymer-coated cluster assembly was prepared as described above and the electrode re-examined by cyclic voltammetry in the same electrolyte. The cluster–polymer coating was subsequently removed from the electrode surface by polishing with diamond paste and the voltammetric response of the ferrocene was then re-measured. Redox potentials of the ferrocene–ferrocenium couple relative to the silver wire pseudo-reference were within ± 5 mV before and after coating and polymer removal.

EPR of $[Fe_4S_4(SPh)_4]^{3-}$ *Confined within the Polymer Coating.*—A polymer-coated platinum gauze electrode (3 cm^3) was prepared as described above ($Q_{polymer} = 15$ mC), washed thoroughly with MeCN and transferred to a 5 mol dm^{-3} solution of $[Fe_4S_4(SPh)_4]^{2-}$ in MeCN. After 20 min the gauze was removed and washed again with MeCN. It was then transferred to a cell where the cluster was reduced completely to the trianion ($Q_{cluster} = 4$ mC) at -1.3 V relative to ferrocene–ferrocenium. The reduced modified gauze electrode was then placed in an EPR tube containing 0.5 cm^3 of fresh MeCN which was then stored in liquid nitrogen. The EPR spectra were run on a Brucker ER200-D spectrometer at 10 K.

Reflectance FTIR Measurements.—The procedure for producing the polymer–cluster electrodes was as described above except that a highly polished platinum disc of 1 cm diameter was used and thicker films were generally employed. *Ex-situ* film thickness was in the order of 1 μm as measured by scanning electron microscopy. After preparation the electrode assembly was washed with freshly distilled MeCN dried in a stream of dinitrogen and transferred to the sample holder of the spectrometer, the cavity of which was continuously purged with N_2. Reflectance FTIR spectra were recorded on a Bio-Rad FTS-7 single-beam spectrometer at a resolution of 4 cm^{-1} using a 3240-SPC data station. The spectra were ratioed against the background of the uncoated polished electrode. The experimental arrangement that we used was designed for diffuse reflectance FTIR with the Kulbelka Munck algorithm employed to relate concentration to intensity and so resolve the multiple internal reflections which occur in a powdered sample.[31] This arrangement for reflective spectroscopy was not strictly appropriate; however, reasonably good quality spectra were obtained with base-line distortion confined to the higher energy region.

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