Iron–Sulphur Clusters in Ionic Polymers on Electrodes

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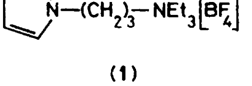
The cluster $[Fe_4S_4(SPh)_4]^{2-}$ can be incorporated in electrode-bound ion-exchange polymers based on *N*-substituted poly(pyrroles) and such electrode assemblies show well defined redox behaviour in MeCN, MeOH, and aqueous electrolytes; electrostatic binding in the polymer matrix is shown to exert a considerable influence on its primary and secondary reduction potentials, which are shifted about 180 mV positive of their solution values, suggesting that in principle ion–ion interactions could provide a mechanism for modulating cubane redox potentials in a biological matrix.

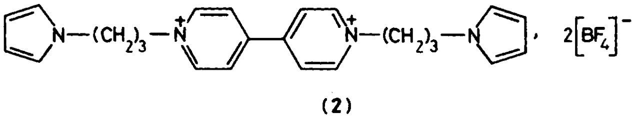
Electropolymerisation of the tetra-alkylammonium derivatised pyrrole (**1**) on platinum or glassy carbon in MeCN containing 0.1 M $[NBu_4][BF_4]$ proceeds in an expected and well behaved fashion to give an adherent film of the cationic polymer on the electrode surface.[1,2] Immersion of such a coated electrode in a solution of $[Fe_4S_4(SPh)_4]^{2-}$ in MeCN (10—15 min) leads to the binding of the di-anionic cluster in the polymer matrix by anion exchange with $[BF_4]^-$.[3]

The incorporation of intact cluster in the polyelectrolyte film was established by cyclic voltammetry of the modified electrodes in 0.1 M $[NBu_4][BF_4]$–MeCN. Voltammograms are well defined and show the two successive reversible reduction processes which are characteristic of the cluster (Figure 1). The separation of 0.67 V between the first and second reduction potentials $[{}^1E^{\circ\prime} - {}^2E^{\circ\prime}]$ for the polymer-confined material corresponds closely to the difference measured for the (2−/3−) and (3−/4−) couples of the cubane in solution at bare electrodes.[4] Coulometric measurements show that the ratio of the mono-cationic alkylammonium groups of the polymer to the di-anionic cluster is about 3:1 and this is indicative of a high loading.

The binding of the cluster in the cationic matrix considerably perturbs the redox potentials of the (2−/3−) and (3−/4−) couples. Shifts of ${}^1E^{\circ\prime}$ and ${}^2E^{\circ\prime}$ to values about 180



(**1**)



(**2**)

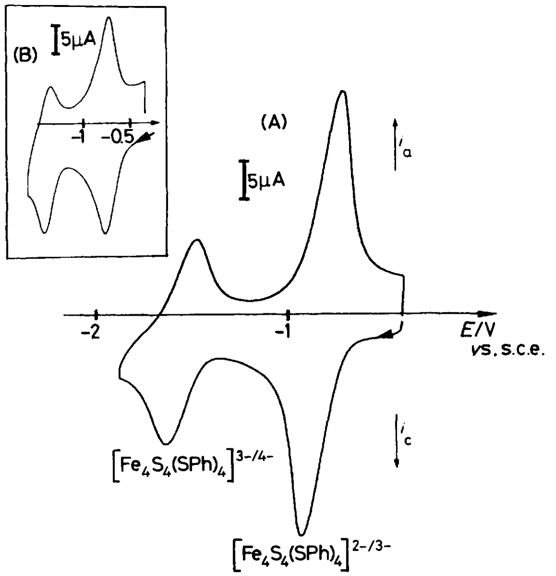


Figure 1. Cluster-polymer (**1**) film electrodes. Cyclic voltammograms recorded at 100 mV s^- on a glassy carbon disc electrode of diameter 2.5 mm in 0.2 M $[NBu_4][BF_4]$–MeCN. Voltammogram (A) shows the $[Fe_4S_4(SPh)_4]^{2-/3-}$ and $[Fe_4S_4(SPh)_4]^{3-/4-}$ couples in a thick film (1.15×10^{-7} mol alkylammonium cm^{-2}). [The importance of film thickness in determining the differential response of the successive couples is illustrated by the voltammogram obtained on a thinner film (B, inset, 5.4×10^{-8} mol alkylammonium cm^{-2}): evidently counter-ion mobility is important in determining the relative electron-transfer rates of the couples (s.c.e. = saturated calomel electrode).]

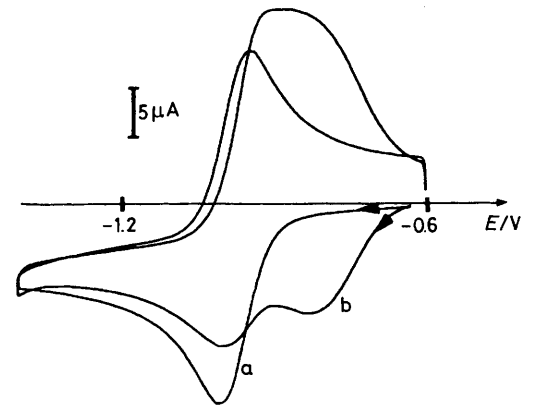


Figure 2. Perturbation of $E^{\circ\prime}$ of cluster. Cyclic voltammograms recorded at 100 mV s^{-1} of $[Fe_4S_4(SPh)_4]^{2-}$ in 0.1 M $[NBu_4][BF_4]$–MeCN on (a) a bare platinum disc of diameter 5 mm and (b) at a 'pin-holed' film (5.3×10^{-9} mol alkylammonium cm^{-2}) of polymer (**1**) on the same electrode.

mV less negative than those measured for the free cluster are observed. We can view this effect directly by cyclic voltammetry on thin (pin-holed) films of the polymer;[5] reversible one-electron reduction of cluster at the naked electrode and within the film are observed as discrete processes (Figure 2).

The perturbation of the redox potentials probably owes its origin to a strong electrostatic interaction of the cluster anions with the cationic $\{-CH_2NEt_3^+\}$-groups of the polymer. To test this we prepared ferrocyanide-modified electrodes of electropolymerised (**1**) and also cluster-modified electrodes of electropolymerised (**2**), a viologen derivative.[6]

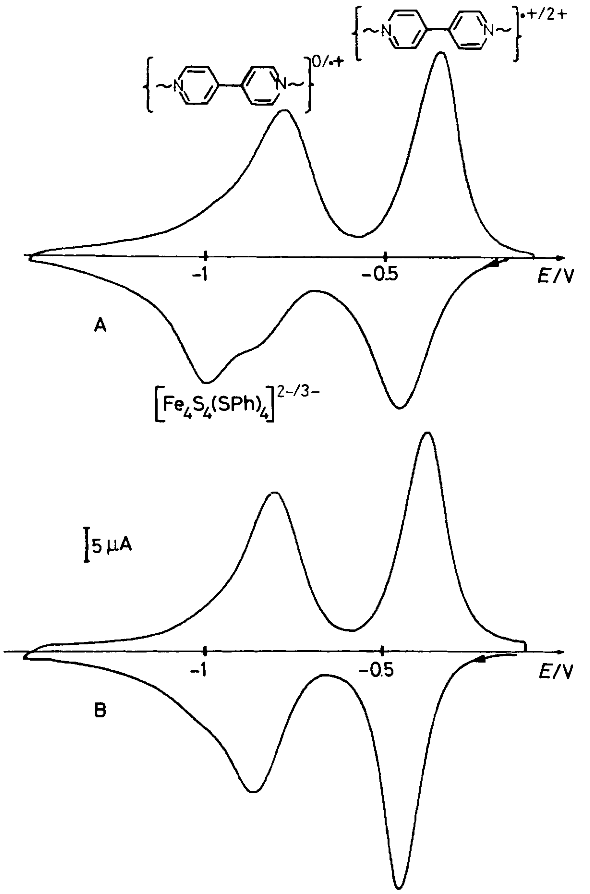


Figure 3. Generation of neutral film containing cluster. Cyclic voltammograms recorded at 100 mV s^{-1} of a platinum disc electrode of diameter 5 mm modified with polymer (**2**) (2.6×10^{-9} mol viologen cm^{-2}) containing $[Fe_4S_4(SPh)_4]^{2-}$. Voltammogram (A) shows the first cycle with (3–/2–) couple of the cluster; voltammogram (B) is the second cycle response which shows the loss of the cluster from the neutral polymer.

In the methyl cyanide electrolyte the $E^{\circ\prime}$ of the polymer-bound $[Fe(CN)_6]^{3-/4-}$ couple is about 160 mV positive of that measured at a bare glassy carbon electrode. This is consistent with redox potential perturbations reported for ferrocyanide bound within macrocyclic dialkylammonium receptor molecules (+130 to +165 mV)[7] and when it is in a protonated aminosiloxane polymer (+140 mV),[5] and parallels the shifts observed for the rather larger cubane.

Electropolymerised (**2**) in its dicationic form also acts as an ion-exchange coating and binds the dianionic cluster.[8] The dicationic polymer containing the bound cluster is readily converted to a neutral polymer by two successive one-electron reductions of the pendant viologen groups, as is shown by the voltammogram of Figure 3. In this neutral form there can be no electrostatic interactions between the confined cluster and the polymer and accordingly we find that the redox potential of the (2–/3–) couple is essentially unperturbed from that measured in solution. The weak binding of the trianionic cluster to the neutral form of the viologen polymer is revealed upon the second and subsequent voltammetric scans; the peaks associated with the reversible reduction of the cubane are lost and those for the viologen sharpened, presumably because the electrorelease of the bulky cluster facilitates ionic migration and/or intramolecular electron-transfer within the viologen polymer.

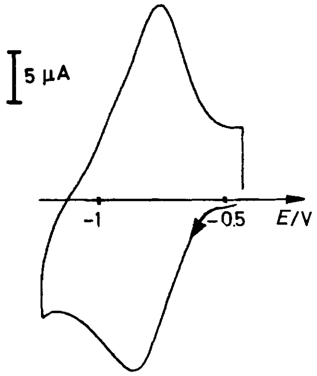


Figure 4. Cluster-polymer (**1**) film electrode in aqueous buffer. Steady-state voltammogram (11th scan) for a cluster-modified glassy carbon electrode, diameter 2.5 mm, in a phosphate buffer at pH 8; the scan-rate was 100 mV s^{-1} and the surface concentration was *ca.* 10^{-8} mol alkylammonium cm^{-2}.

The poly(tetra-alkylammonium pyrrole) electrode provides a means of interfacing the hydrophobic tetra-thiophenolate cluster with hydroxylic environments. Preliminary measurements show that in methanol containing 0.1 M $[NBu_4][BF_4]$ the (2–/3–) couple is very stable; similarly in aqueous phosphate buffers of pH 4—9 reproducible steady-state cyclic voltammograms can be obtained with $E^{\circ\prime}$ at −0.73 V relative to the saturated calomel electrode, Figure 4.

The construction of such cluster-coated electrodes offers the prospect of studying, in a range of media, the electron-transfer reactions of the surface-confined cubane centres with substrates such as H^+, acetylenes, and carbon monoxide.[9] Hitherto surface studies have been limited to reactions of somewhat ill-defined cluster deposits on glassy carbon electrodes. These show poorly resolved voltammetric properties and it is by no means certain that the integrity of the cubane core is conserved in operation.[10]

Finally, we note that whereas hydrogen-bonding, local dielectric, and solvation effects are often cited as the 'extrinsic' factors which influence the potentials of clusters within proteins[11] and somewhat set them apart from those of their synthetic analogues,[4] our results show that at least in principle, ion–ion interactions might provide a mechanism for modulating cubane redox potentials in a biological matrix.

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