Electropolymeric materials incorporating subsite structures related to iron-only hydrogenase: active ester functionalised poly(pyrroles) for covalent binding of {2Fe3S}-carbonyl/cyanide assemblies†

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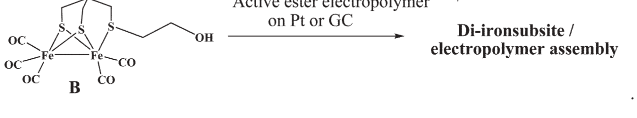
We report the assembly of the first electropolymeric materials incorporating catalytic diiron subsites related to those of the iron-only hydrogenases.

In earlier work, we have shown that iron–sulfur cluster analogues of the electron-transfer centres in the {4Fe4S}-ferredoxin redox proteins can be built into cysteinyl functionalised poly(pyrroles) and that such arrays sustain fast charge propagation through an electrode-bound polymer film.[1,2] Incorporating synthetic analogues of the catalytic machinery of iron-only hydrogenase within an electropolymer presents a greater challenge, but one which might afford new electrode materials for electrocatalysis of dihydrogen uptake/evolution. This is particularly attractive if catalysis can be matched to the conducting regime of the supporting polymer or fast electron-transfer relays are co-incorporated. Here we report some first steps in this direction: the assembly of solid-state materials with structures related to the subsite of iron-only hydrogenase confined within a poly(pyrrole) framework.

The most obvious route to electropolymer materials functionalised with diiron subsite analogues was to tag a pyrrole unit onto a {2Fe3S}-carbonyl assembly *via* the chemistry shown in Scheme 1.[3–5] The synthesis of [$Fe_2\{CH_3C(CH_2S)_2(CH_2S\{CH_2\}_2$-N-pyrrole)}$(CO)_5$] **A** is straightforward but the overall strategy fails because the diiron unit is destructively oxidised at potentials negative of that necessary for anodic polymerisation of the pyrrole unit. We therefore turned to post-polymerisation modification procedures that we had established earlier for covalent attachment of groups which are sensitive to or inhibit pyrrole electropolymerisation.[1,2] The 2-hydroxyethane derivatised diiron unit **B** was synthesised by the pathway outlined in Scheme 1.



Scheme 1 Synthesis of pyrrole (**A**) and alcohol (**B**) functionalised diiron assemblies. (i) NaH, $ClCH_2CH_2(NC_4H_4)$, MeCN; (ii) $LiAlH_4$, Et_2O; (iii) $Fe_3(CO)_{12}$, toluene; (iv) NaH, ICH_2CH_2OH, THF; (v) $LiAlH_4$, Et_2O; (vi) $Fe_3(CO)_{12}$, toluene.

The pentafluorophenolate 'active ester' monomer **C** was synthesised as we have previously described[2] and electropolymerised on platinum to give electrode bound films of the conducting polymer **Pt|C$_{poly}$** of *ca.* 100 nm thickness which are golden yellow in the reduced-state. The diffuse reflectance FTIR spectrum of **Pt|C$_{poly}$** shows the characteristic *ν*(C=O) and *ν*(C–O) bands for the pentafluorophenolate ester at 1784 and 1520 cm^{-1}, Scheme 2.[6]

Pt|C$_{poly}$ assemblies were reacted in MeCN with **B** in the presence of triethylamine, washed in MeCN, dried under a stream of nitrogen, and examined by diffuse reflectance FTIR spectroscopy, Scheme 2. The insets to Scheme 2 show: the growth of the normal ester band at *ca.* 1736 cm^{-1}; the concerted depletion of the pentafluorophenolate ester band at 1784 cm^{-1}; and the appearance of the characteristic intense *ν*(C=O) stretches of the covalently attached diiron unit[7] in the modified electropolymer, **Pt|D$_{poly}$**. The same preparative and FTIR monitoring procedures allow assembly and characterisation of glassy carbon (GC) modified electrodes, **GC|D$_{poly}$** (Scheme 3).

Cyanation of {2Fe3S}-carbonyls generally proceeds smoothly in solution to give di-cyanide species such as [$Fe_2\{CH_3C(CH_2S)_2(CH_2SCH_2R)\}(CO)_4(CN)_2]^{2-}$ *via* monocyanide and bridging carbonyl intermediates.[7] In the polymer film only a limited reaction is observed because these types of polymers tend to exclude penetration of alkylammonium counter ions which are necessary to maintain charge neutrality within the film.[2,3]

To overcome this problem, the cationic tetra-alkylammonium monomer **E**[8] was co-electropolymerised with **C** to produce **Pt|{C:E}$_{copoly}$** and **GC|{C:E}$_{copoly}$** films.[1,8–11] Diffuse reflectance FTIR spectra of co-polymer films show *ν*(B–F) for the BF_4^- counter-ion near 1060 cm^{-1} in addition to the bands of the active ester at 1784 cm^{-1} and 1520 cm^{-1}. The co-polymer films were reacted as before with **B** then subsequently with [Bu_4N][CN] in MeCN (Scheme 3).

The ratio of the alkylammonium active ester groups in the polymer can be coarsely controlled by varying the ratio of the monomer precursors, **C** : **E**. At *low* **C** : **E** ratios monosubstitution

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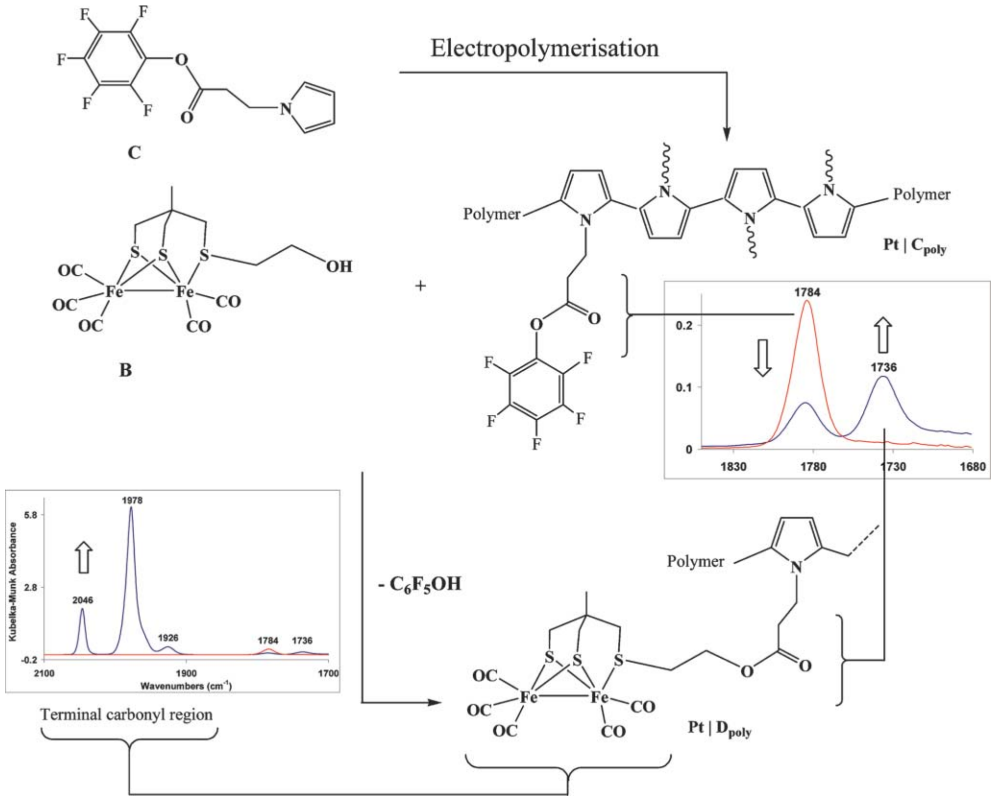
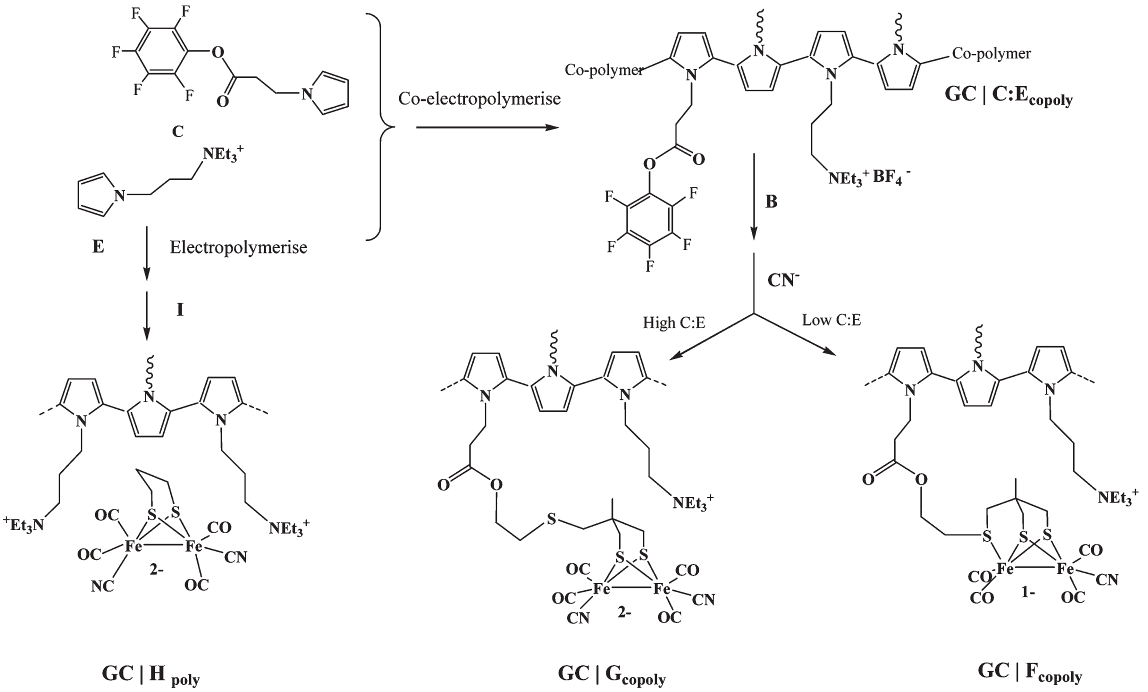
† Electronic supplementary information (ESI) available: Scheme S4. Diffuse reflectance FTIR spectra for (a) covalently linked carbonyl subsite, **GC|D$_{poly}$**; (b) covalently linked monocyanide **GC|F$_{copoly}$**; (c) covalently linked dicyanide **GC|H$_{poly}$**; (d) ionically bound polymer subsite assembly **GC|H$_{poly}$**. See DOI: 10.1039/b617399c



Scheme 2 Reaction of **B** with active ester electropolymer electrode **Pt|C**$_{\mathbf{poly}}$ to give **Pt|D**$_{\mathbf{poly}}$. Red curves show FTIR spectrum in the carbonyl regions before reaction with **B**, blue curves show partial reaction with **B**.

of the diiron unit is the predominant reaction, as is evident from the observation of ν(CO) and ν(CN) bands close to those observed for $[Fe_2\{CH_3C(CH_2S)_2(CH_2SCH_2R)\}(CO)_4(CN)]^{1-}$ in MeCN solution (Scheme 3, **GC|F**$_{\mathbf{copoly}}$ and Supplementary Material, Scheme S4).[7] At *high* **C** : **E** ratios di-substitution of the diiron unit by cyanide predominantly occurs (Scheme 3, **GC|G**$_{\mathbf{copoly}}$) and the polymer film shows bands corresponding to those measured for $[Fe_2\{CH_3C(CH_2S)_2\}(CO)_4(CN)_2]^{2-}$, **I**, when this di-anion is



Scheme 3 Routes to assembly of diiron subsite analogues in electrode bound electropolymer films.

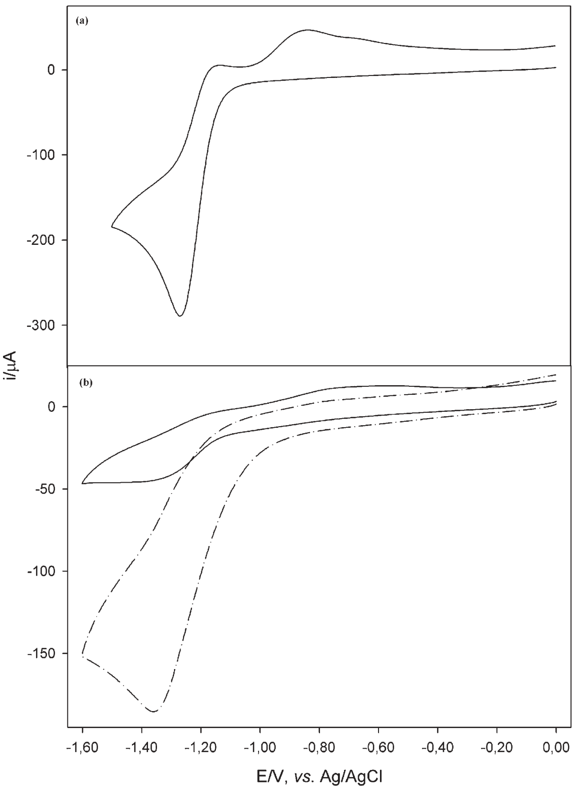


Fig. 1 Electrochemical behaviour of solution and polymer bound subsite analogues (in 0.2 M $[NBu_4][BF_4]$–MeCN). Panel (a): cyclic voltammetry of **B** at vitreous carbon electrode (15 mM complex; 100 mV s^{-1}; nominal electrode area 0.77 cm^2; RT). Panel (b): cyclic voltammetry of **GC|D$_{poly}$** in absence (solid line) and presence (dashed line) of $[LuH^+]$ = 16 mM (100 mV s^{-1}; nominal electrode area 0.77 cm^2; film thickness 0.8–1 μm; RT).

bound within a **GC|E$_{poly}$** by simple ion-exchange of BF_4^- (Scheme 3, **GC|H$_{poly}$** and Supplementary Material, Scheme S4); they are also close to those measured for $[Fe_2\{CH_3C(CH_2S)_2(CH_2SCH_3)\}(CO)_4(CN)_2]^{2-}$ in MeCN solution.[7]

Electrocatalysis of proton reduction takes place on the subsite loaded polymeric material **GC|D$_{poly}$** at a potential $E_{p/2} = -1.20$ V *versus* {Ag/AgCl, CHB$_{2B}$ClB$_{2B}$, 0.45 M [NBuB$_{4B}$][BFB$_{4B}$], 0.05 M [NBuB$_{4B}$]Cl}‡ which is essentially pinned to that for the reduction of the bound complex, $E_{p/2} = -1.22$ V. It is shifted *ca.* 120 mV positive of that observed for reduction on the subsite-free polymer, **GC|C$_{poly}$**, which is observed at $E_{p/2} = -1.32$ V, and is *ca.* 90 mV positive of that observed on unmodified glassy carbon. We estimate the current density at $E_{p/2}$ for proton reduction on **GC|D$_{poly}$** to be about six times higher than on the subsite-free polymer at equivalent $[LuH^+]$.

Several synthetic analogues of the diiron subsite are now known to electrocatalyse proton reduction in solution albeit at large overpotentials relative to the reversible potential for H^+/H_2.[12–17] Cyclic voltammetric examination of **GC|D$_{poly}$** in 0.2 M $[NBu_4][BF_4]$–MeCN showed a redox behaviour for the polymer confined diiron assembly similar to that observed for the precursor $[Fe_2\{CH_3C(CH_2S)_2(CH_2SCH_2CH_2CH_2OH)\}(CO)_5]$ free in solution, Fig. 1.[5] The non-ideal behaviour of the surface confined subsite is possibly a consequence of diffusion limited ingress of $[NBu_4]^+$ into the polymer film accompanying electron-self exchange.

The electrochemical response for **GC|D$_{poly}$** film in the presence of 2,6-dimethylpyridinium cation (LuH^+) as a source of protons is also shown by Fig. 1. In summary, we have shown that it is possible to incorporate diiron units related to the carbonyl/cyanide subsite of iron-only hydrogenase in electropolymer films grown on platinum or carbon. We have also presented preliminary results which show that one such assembly electrocatalyses proton reduction. Although this electrocatalysis occurs at an overpotential far removed from that required for a workable device, we have nevertheless taken some first steps towards establishing the principle that a functional solid-state molecular material containing covalently bound {2Fe3S}-subsite analogues can be constructed.

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Notes and references

‡ All subsequent given potentials are *versus* this same reference system; the ferrocenium/ferrocene (Fc^+/Fc) couple is at +0.51 V *versus* {Ag/AgCl, CH$_{B2B}$ClB$_2$B, 0.45 M [NBuB$_{4B}$][BF$_{B4}$B], 0.05 M [NBuB$_4$B]Cl}.

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