Modification of a Tin Oxide Electrode by Attachment of Iron–Sulphur Clusters

By ROGER J. BURT, G. JEFFERY LEIGH, and CHRISTOPHER J. PICKETT*
(*Agricultural Research Council, Unit of Nitrogen Fixation, University of Sussex, Brighton* BN1 9QJ)

Summary By appropriate thiolsilylation of a tin oxide electrode and subsequent exposure to an iron–sulphur cluster we have been able to attach the cluster to the electrode surface and study its redox behaviour.

THE chemical modification of electrode surfaces by covalent attachment of organic functions[1–3] can allow a more sophisticated control over the course of electro-oxidation or reduction of a substrate dissolved in the electrolyte. For example Miller *et al.*,[1] have shown that by attaching an optically active amino-acid ester to a graphite electrode by a covalent bond, chiral reduction of ketones in aqueous media is possible.

Attaching ligated metal centres to an electrode could afford additional electrode specificity; for example, metal redox centres could behave as electron-transfer mediators to a solution substrate by outer-sphere or inner-sphere pathways. The latter can be viewed as the provision of binding sites for the substrate on the electrode. We communicate here evidence for the attachment of iron–sulphur cluster groups $[Fe_4S_4(SR)_4]^{2-}$ to an electrode surface *via* covalently bonded thiolate ligands, an example of a metal redox centre attached to an electrode surface.

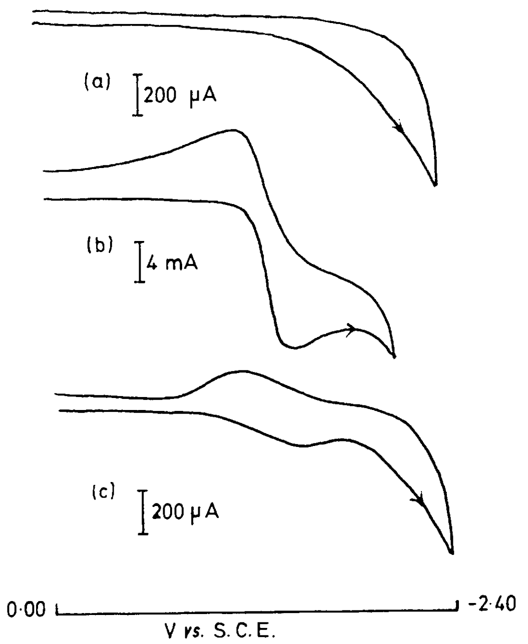
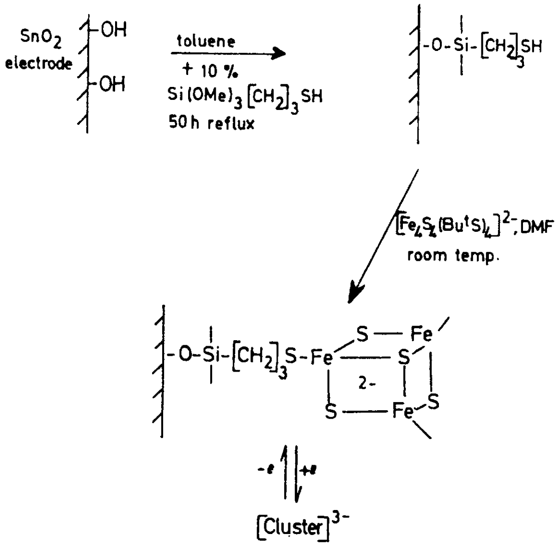


FIGURE. Cyclic voltammograms at tin oxide electrodes in 0·2M $[Et_4N][BF_4]$–dmf. Cell volume *ca.* 10 ml, geometric electrode area 1·76 cm,[2] scan rate 0·9 V s^{-1}. (a) untreated electrode; (b) thiolsilylated electrode +2·0 mg ml^{-1} $[Et_4N]_2[Fe_4S_4(Bu^tS)_4]$, current axis 20 × less sensitive than (a) and (c); (c) removal of cluster solution and washing 5 × 10 ml dmf electrolyte. $\frac{1}{2}[Ep^c + Ep^a]$ for the cluster in solution at an untreated electrode was *ca.* 50—100 mV more negative than at the thiolated electrode.

Antimony-doped tin(IV) oxide electrodes were prepared by passing air saturated with water vapour through a 10% solution of $SbCl_5$ in $SnCl_4$ and allowing the resultant vapour to react on soda glass plates maintained at 300 °C. The Figure (a) shows a typical *i–V* response in 0·2M $[Et_4N][BF_4]$–dimethylformamide (dmf), for the tin oxide electrodes in an electrochemical cell. Using the method of Murray *et al.*,[2] the residual surface hydroxyl-groups of the tin oxide electrodes were silylated with $(MeO)_3Si[CH_2]_3SH$ (**1**) (Scheme), to introduce surface thiol groups, and the electrodes were reexamined by cyclic voltammetry in the dmf electrolyte. The *i–V* response was essentially similar to that of the untreated tin oxide electrode of Figure (a). As the t-butyl thiolate groups of $[Fe_4S_4(SBu^t)_4]^{2-}$ can be readily exchanged by reaction with thiol ligands, this cluster species was allowed to react with the electrode in the cyclic voltammetry cell in dmf. The Figure (b) shows a typical cyclic voltammogram for the iron cluster solution at a thiol electrode.[4] The cluster solution was removed from the cell after 15 min, and the electrode washed *in situ* with fresh electrolyte solution. Re-examining the *i–V* response by cyclic voltammetry revealed an adsorbed species which underwent reversible reduction [Figure (c) and Scheme]. The peak current varied ***linearly*** with the voltage scan rate over the range 0·01 to 1·5 s^{-1}. The $\frac{1}{2}$ $[Ep^c + Ep^a]$ potential for this process occurs at −1·34 V *vs.* the saturated calomel electrode (S.C.E.). The surface coverage corresponded to *ca.* 2×10^{15} molecules cm^{-2}. When a non-thiolated tin oxide electrode was left in contact with the cluster solution and then washed, a similar intrinsic redox process was not observed. The redox potential of the adsorbed species is close to that of the cluster $[Fe_4S_4(S\{CH_2\}Si(OMe)_3)_4]^{2-}$, $E_{\frac{1}{2}} = -1{\cdot}36$ V [generated by the reaction of an excess of the mercaptosilane (**1**) with the t-butyl thiolate cluster].



SCHEME

Clearly it is not possible to determine the degree of substitution of the t-butyl thiolate groups by surface thiols using electrochemical methods alone. The electrodes employed in this study have high surface resistances, precluding detailed characterisation of electron transfer rates.

Using this technique we are preparing analogous thiolated electrodes with various hydrocarbon chain lengths to investigate the rates of electron transfer *via* hydrophobic tunnels to the biologically significant Fe_4S_4 cluster species.[5]

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