Polymeric Sulphur Nitride Electrode: an Example of Electrocatalysis by Surface Chemical Modification

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Summary The surfaces of crystals of the anisotropic metallic conductor, polymeric sulphur nitride, $(SN)_x$, were chemically modified by pretreatment with penta-amminechlororuthenium(III) chloride; the cyclic voltammograms of the I^-/I_2 couple exhibited electrocatalysis after this pretreatment.

High conducting, analytically pure crystals of the anisotropic inorganic polymer $(SN)_x$,[1,2] which have good characteristics as electrodes,[3,4] have been chemically modified at their surfaces and shown to electrocatalyse the oxidation of iodide to iodine. Preparation of the $(SN)_x$ crystals, mounting them as electrodes, and all experimental procedures are the same as those previously described.[1,4]

A typical cyclic voltammogram for 50 mM KI solutions in 0·5 M NaCl supporting electrolyte, and 0·05 M sodium phosphate buffer (pH = 6·7) is shown by curve B of the Figure. The cyclic voltammograms for the I^-/I_2 couple were irreversible and kinetically controlled,[5] and were the same for both parallel (sides of fibre bundles exposed to solution) and perpendicular (ends of fibre bundles exposed) crystal face electrodes. However, the reversibility for $(SN)_x$ electrodes was somewhat better than that found for typical noble metal electrodes under similar conditions.[6] If the same electrodes were dipped in a 3·5 mM solution of $[Ru(NH_3)_5Cl]Cl_2$ for a few minutes, carefully rinsed several times, and then returned to the KI solution, the resulting I^-/I_2 cyclic voltammograms for perpendicular electrodes showed enhancement of the peak currents of 100 to 200%, as seen by curve C in the Figure. (There was no significant decrease, however, of the separation of the peak currents.) This catalytic effect was independent of the $[Ru(NH_3)_5Cl]^{2+}$ concentration in the pretreatment solution. For both the untreated and treated $(SN)_x$ electrodes, the anodic peak currents showed some increase with increasing scan rate (5—500 mV s^{-1}). The electrode can be cycled indefinitely after pretreatment, and there is no change in current peak heights or wave shape. On the other hand, the same pretreatment of a parallel electrode had no noticeable effect on the I^-/I_2 peak currents. $[Ru(NH_3)_5Cl]^{2+}$ does not exhibit any redox waves at either type of $(SN)_x$ electrode in the potential region employed in this study, which is contrary to its behaviour at a platinum electrode. The $[Ru(NH_3)_5Cl]^{2+}$ pretreatment has no effect on the redox waves for the reversible outersphere ferricyanide system, as expected for an outersphere reversible electron transfer reaction.[4] $[Ru(NH_3)_6]^{3+}$, which does exhibit well defined reversible waves at both types of $(SN)_x$ electrodes, shows no catalytic effect on the I^- oxidation when used instead of $[Ru(NH_3)_5Cl]^{2+}$ in the dipping pretreatment.

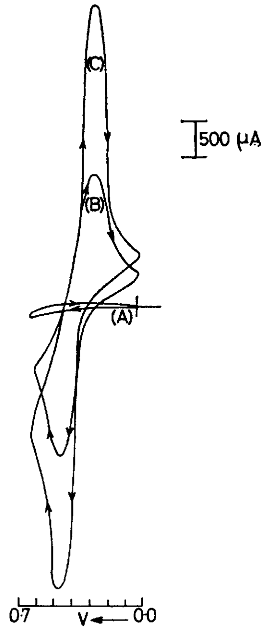

FIGURE. Perpendicular $(SN)_x$ electrode, sweep rate; 500 mV s^{-1}: (A) 0·5 M NaCl and 0·05 M phosphate buffer (pH = 6·7). (B) 0·05 M KI in 0·5 M MaCl and 0·05 M phosphate buffer (pH = 6·7). (C) Same solution after pretreatment of the electrode with $[Ru(NH_3)_5Cl]^{2+}$.

It had previously been reported that Ru^{III} was effective as a homogeneous catalyst for the oxidation of the iodide ion to iodine.[7] Thus, although *X*-ray fluorescence and a differential pulse voltammetric technique[8] failed to give positive direct evidence for ruthenium on the surface of the electrode because of signal-to-noise problems, the above evidence indicates that the $[Ru(NH_3)_5Cl]_2^+$ species does react with the perpendicular surface of the $(SN)_x$, and some type of ruthenium species is immobilized on the surface. The chemical nature and composition of the co-ordination sites on the ruthenium, as well as its valence state, are not yet known. However, the persistence of the catalytic activity, the fact that the perpendicular ends and not the π type parallel surface are affected, and the reaction is observed only for the $[Ru(NH_3)_5Cl]^{2+}$ and not the substitution inert $[Ru(NH_3)_6]^{3+}$ species, indicate that it is strongly held on the surface through co-ordinate bonding. It should be further noted that anisotropic single crystals of pyrolytic graphite, which have been found to have analogous adsorption properties with respect to certain organic redox systems (such as methylviologen), and have been suggested as comparable types of surfaces,[9] show no catalysis of the $I^-–I_2$ couple on $[Ru(NH_3)_5Cl]_2^+$ pretreatment.

Thus, the $(SN)_x$ surface may be more amenable to chemical and/or electrochemical modification for the production of surface redox catalysts than the more common solid electrode materials.

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