Polymeric Sulphur Nitride: a New Electrode Material

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Summary Crystals of the anisotropic metallic conductor polymeric sulphur nitride, $(SN)_x$, employed as electrodes with and without depolarizer present yield well defined cyclic voltammograms similar to those obtained with other solid electrodes, but with unusual electrode process characteristics which depend on crystal orientation.

HIGHLY conductive analytically pure crystals of the anisotropic inorganic polymer $(SN)_x$ have been employed as electrodes in a cyclic voltammetric study of the redox reactions of lead. A wide region of low residual current exists in 0·1 M KNO_3 supporting electrolyte (pH 5) which is not dependent on the crystal face exposed (Figure 1A). Decomposition of the $(SN)_x$ rather than electrolysis of the solvent appears to be responsible for the steep rises in the currents observed at the extremes of the potential scan.

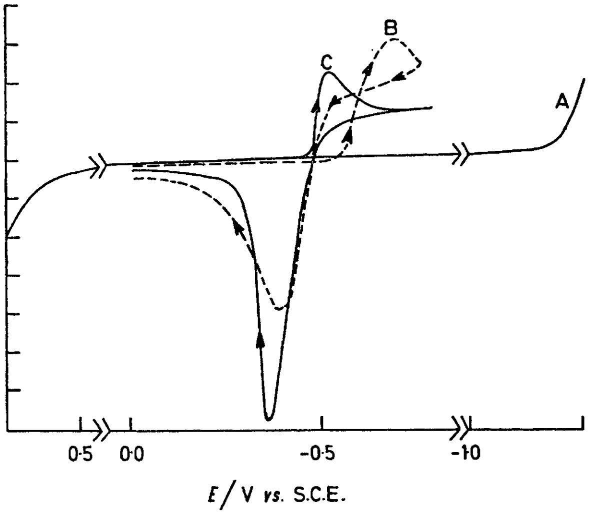

FIGURE 1. (A) 0·1 M KNO_3, pH 5, v 70 mV s^{-1}, i 100 μA/division; (B) parallel electrode: 0·1 M KNO_3 20 mM $Pb(NO_3)_2$, pH 4, v 15 mV s^{-1}, i 10 μA/division; (C) perpendicular electrode: same conditions as (B).

Cyclic voltammograms obtained for 20 mM lead ion-supporting electrolyte solutions differ markedly for parallel (sides of fibre bundles exposed to solution) (Figure 1B) and perpendicular (ends of fibre bundles exposed) (Figure 1C) crystal faces in that the latter are more reversible and more closely resemble cyclic voltammograms obtained under similar conditions employing other solid electrodes (*e.g.*, Ag[2], C[2], Au[2], Pt[3]). Cyclic voltammograms for lead obtained using parallel electrodes exhibit a more negative cathodic maximum than those with Ag, Cu, Au, or Pt, and significant hysteresis upon reversal, typical of a slow rate-limiting step in the mechanism,[4] is observed.

New parallel electrodes or those which have been cycled previously in lead ion solutions can be made to yield cyclic voltammograms identical to those obtained with perpendicular electrodes by exposure to 0·1 M $Hg(NO_3)_2$ at pH 2·5 for 2 min prior to electrolysis. No additional waves are observed for these cyclic voltammograms. However, for a perpendicular face pretreated in the same manner, a large complex cathodic wave is observed at −0·2 V *vs* SCE on the first negative scan in 0·1 M KNO_3 or lead ion solutions. The actual waves for lead, however, are unaffected by pretreatment of the perpendicular electrodes.

Scanning electron microscopy reveals the nature of electrodeposited lead on untreated perpendicular electrodes (Figure 2A) and those which had been pretreated with Hg^{2+} ion (Figure 2B). In the former, the three-dimensional deposit of lead is restricted to the ends of the fibres while the latter has three-dimensional crystallites of lead on the sides as well as the ends of the fibres. ESCA studies indicate that lead deposits as a metallic species on perpendicular and Hg^{2+} ion-pretreated parallel electrodes.

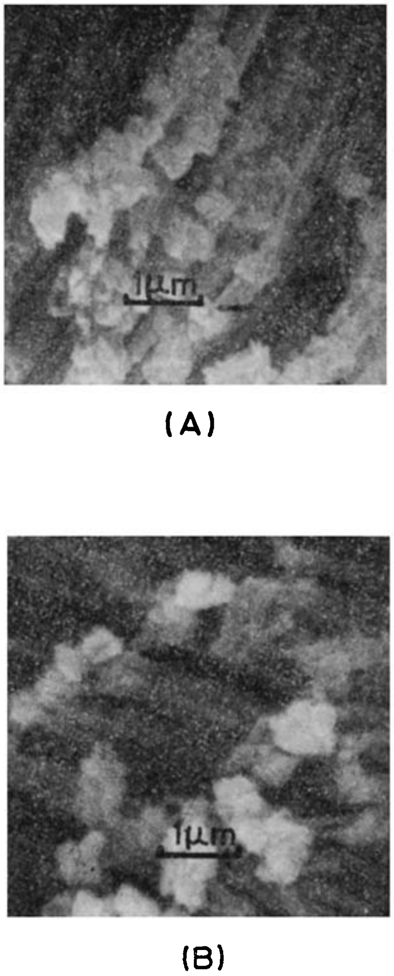

FIGURE 2. Scanning electron micrographs of electrodeposited lead on untreated (A) and Hg^{2+} ion pretreated (B) perpendicular $(SN)_x$.

These preliminary results indicate that this electrode material which is unique in its strong surface interactions with ions in the electrolyte phase exhibits unusual heterogeneous electrode process properties. Furthermore, these surfaces may be more amenable to chemical or electrochemical modification for the production of selective redox catalysts than graphite,[5] tin oxide,[6] or noble metal[7] electrodes.

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