

Ni(Salen)-based polymer modified electrodes as sensors for metal ions

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Nickel complexes with salen-type ligands have long been recognized to have interesting catalytic properties (1). Incorporation of these redox functionalities in polymeric systems (poly[Ni-salen]) is possible and such polymer modified electrodes have been described by several research groups (2),(3),(4),(5). These systems are interesting from a fundamental viewpoint, since they contain discrete localized redox entities (the Ni centres) and delocalized redox centres (associated with an extended conjugated system in the polymeric ligand). Accordingly, we have used spectroscopic (6) and nanogravimetric (7) methods to probe the electron transfer mechanism and the associated mobile species population and structural changes.

In an extension of this work, we are now exploring the properties of these Schiff base complexes substituted with macrocyclic receptor groups, particularly crown ethers. The notion we explore is that the electrochemistry of the parent [Ni-salen] group will be sensitive to the complexation state of a crown ether in close proximity—this would then be the basis of a sensor. This idea is widely recognized for monomeric Schiff-base complexes in solution, but is poorly developed for surface-immobilised polymeric complexes. The latter offer many advantages, for example in terms of detection and sensitivity, but present the additional complication of the electroactivity of the polymeric ligand. With these issues in mind, we now report the preparation and electrochemical / acoustic wave characterisation of polymer films based on a salen-type Ni(II) complex functionalised with a benzo-15-crown-5 moiety.

Monomeric [Ni(3-MeOsalophen-benzo-15-crown-5)] was prepared by standard methods and polymerized potentiodynamically ($-0.3 < E/V$ (vs Ag/AgCl) < 1.2 ; $v = 0.02$ or 0.10 V s^{-1} , according to desired film thickness) on Pt electrodes exposed to monomer solutions in acetonitrile. The resultant films were characterized in monomer-free solutions using cyclic voltammetry. The film electrochemical responses were then determined upon injection of Ba^{2+} and Gd^{3+} . Analogous experiments using films on Pt electrodes supported on 10 MHz AT-cut quartz crystals were used to determine the corresponding acoustic wave responses.

Polymerization results in a complex voltammetric response: ultimately we are able to resolve four anodic peaks (at 0.19, 0.43, 0.78 and 1.04 V) and three distinct cathodic peaks (at 0.19, 0.69 and 0.89 V). Continuous increases in all peak currents are seen up to at least 150 electropolymerization cycles. Upon transfer to background electrolyte, film redox charge for even the thickest of these films was independent of potential scan rate for $v < 100 \text{ mV s}^{-1}$. This allowed

simple control and assay of electrode coverage with polymer. Electrodes modified with films obtained using different numbers of polymerisation scans showed a linear increase of the electroactive coverage ($0.11\text{--}12 \text{ nmol cm}^{-2}$) with the number of polymerization scans (1-100). Coulometric assay (based on irreversible polymerization and reversible redox charges) yields a number of reversibly transferred electrons per monomer unit, $n = 0.5$; this indicates a ligand-based (cf. Ni-based) redox process, with one electronic charge delocalised over two monomer units.

Crystal impedance spectra of the films acquired during deposition showed them to be acoustically thin (“rigid”) for the first ca. 25 polymerization scans; thereafter, a progressive drop in admittance (by up to a factor of two) indicated the appearance of viscoelastic characteristics with increasing film thickness. Hence crystal frequency responses for thinner films may be interpreted in gravimetric terms according to the Sauerbrey equation. The derived film mass data implies inclusion of some solvent, but not sufficient to cause the films to become viscoelastic.

Injection of small amounts of solutions of Ba^{2+} or Gd^{3+} (to give final metal ion concentrations in the micromolar region) resulted in significant changes in film electrochemical and acoustic (gravimetric) responses. A new voltammetric peak develops, the location and amplitude of which moves systematically with added metal ion. Corresponding shifts in QCM resonant frequency (but not admittance) are observed. The qualitative characteristics of these responses will be discussed.

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