Voltammetric Behaviour, Homogeneous Charge Transport Dynamics and Electrocatalytic Properties of an Os$^{2+}$ Functionalised Pyrrole Monomer

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Abstract

Modified electrodes that contain transition metal polypyridyl complexes have attracted a great deal of interest with their catalytic activities towards hydrogenation [1], photochemical reactions [2, 3], oxidation of organics [4,5] and carbon dioxide reduction [6,7]. Also films containing these transition metal complexes have been employed in electroanalytic sensors [8]. There exists two main methods of surface immobilisation, namely incorporation of the ionic complexes into a suitable polymeric matrix [9,10] or the electropolymerisation of the bipyridine complex that has been covalently grafted to reactive functional groups such as pyrroles and thiophenes. In this contribution the Os$^{2+}$ functionalised pyrrole monomer, Osmium-bis-N,N'-(2,2'-bipyridyl)-N-(pyridine-4-yl-methyl)-(8-pyrrole-1yl-octyl)-amine-chloride, $\textbf{1}$, has been synthesised and characterised by spectroscopic (UV/Vis, $^1$H NMR, IR spectroscopy) techniques and cyclic voltammetry. Solution phase studies of $\textbf{1}$ gave a redox couple associated with the Os$^{3+/2+}$ and an irreversible wave associated with the oxidation of the pyrrole moiety. Attempts to form stable polymeric films of $\textbf{1}$ onto vitreous carbon electrodes, by homopolymerisation, proved unsuccessful. However electroactive films of $\textbf{1}$ were obtained by the electrooxidation of $\textbf{1}$ through the Os$^{3+/2+}$ couple in low dielectric media such as toluene/acetonitrile mixtures. The efficiency of film deposition and properties depend upon the supporting electrolyte and the solvent employed. Films formed in mixtures of acetonitrile and low dielectric constant solvents (dichloromethane and toluene) are electrochemically active and exhibit a redox couple associated with the Os$^{3+/2+}$ system. The voltammetric behaviour of these solid state films was investigated in both aqueous and non-aqueous solvents with a variety of supporting electrolytes. Upon redox switching between the Os$^{3+/2+}$ redox states the solid-state charge-transfer processes are coupled to the insertion/expulsion of anions from/to the solution phase. Scanning electron microscopy reveals that films formed in the presence of acetonitrile exhibit different morphology than films formed in acetonitrile-free solutions. Slow and fast linear sweep voltammograms have been employed to provide an absolute determination of the fixed site concentration as 1.5M and an apparent diffusion coefficient of $5.2 \times 10^{-12}$ cm$^2$ s$^{-1}$ in 0.3M KCl. Electroactive films of $\textbf{1}$ were then investigated for their electrocatalytic ability towards the oxidation of ascorbic acid in acidic medium. The anodic oxidation peak current was linearly dependent on the ascorbic acid concentration and a linear calibration curve was obtained in the range 0.1 – 2x10$^{-3}$ M of ascorbic acid with a correlation coefficient of 0.9993. The detection limit (3σ) was found to be 5.5 x 10$^{-5}$M.

References