Formation of Electronically Conductive Thin Films of Metal Phthalocyanines *via* Electropolymerization

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Oxidative electropolymerization of cobalt and nickel complexes of tetra-aminophthalocyanine in dimethyl sulphoxide rapidly leads to electrode modification, and the thin polymeric coatings obtained by this method are highly electronically conductive under a wide variety of conditions.

Metal phthalocyanines have received much attention recently in several contexts, owing in large part to their intriguing conductivity properties[1,2] as well as their capacity for the electrocatalytic reduction of O_2 and CO_2.[3—6] In particular, a number of studies have focused on the attachment of metal phthalocyanines to electrode surfaces by a variety of methods.[7—10] Based on the elegant work from Murray's laboratory concerning the electropolymerization of metalloporphyrins,[11,12] we reasoned that similar behaviour might be expected for the analogous metallophthalocyanines, and the resultant polymer films may possess useful electrocatalytic properties. We report that very thin films of the Co and Ni complexes of 4,4′,4′′,4′′′-tetra-aminophthalocyanine (TAPc) can be readily prepared *via* electropolymerization and that the polymeric coatings produced in such a manner exhibit electronic conductivity over a wide potential range.

Cobalt and nickel TAPc complexes were synthesized and characterized according to established literature procedures.[13,14] The electrochemical behaviour of these compounds could be conveniently examined in either dimethylformamide (DMF) or dimethyl sulphoxide (DMSO), and results obtained in both solvents were very similar. A typical cyclic voltammogram of the cobalt derivative is shown in Figure 1. The reversible couple centred at −0.52 V can be tentatively assigned to the $Co^{2+/+}$ couple, while the quasireversible couple at +0.17 V most likely corresponds to $Co^{3+/2+}$. The rather surprising lack of complete reversibility in the $Co^{3+/2+}$ couple has been previously noted for other cobalt phthalocyanine complexes, and attributed to surface adsorption effects.[15] The assignment of the reversible couple at −1.66 V is less clear, having been variously attributed to $Co^{+/0}$ and $Pc^{2-/3-}$ in previous reports on related cobalt phthalocyanines.[15—17] We tentatively assign the waves at −1.66 V to the $Pc^{2-/3-}$ couple, in accord with the bulk of the literature and with data obtained on other metallophthalocyanines.[18] A quasireversible couple also appears at very negative potentials (~ −2.2 V, quite close to the cathodic solvent limit), which may result from a second one-electron reduction of the ligand. Finally, two quasireversible couples are observed at +0.5 and ~ +0.7 V, and it is these oxidation processes, presumably localized on the Pc ring and/or the aniline moieties, which lead to the electropolymerization of CoTAPc shown in Figure 2. Upon repetitive cycling from −0.2 to +0.9 V at 200 mV/s, a gradual increase in the faradaic current was observed. This behaviour is similar to that reported for Co(tetra-aminophenylporphyrin)[11,12] and is indicative of the oxidative electropolymerization of CoTAPc and the subsequent deposition of the resultant electroactive polymer onto the electrode surface. These coatings can be seen by eye, and their precise colour depends on a variety of factors in the treatment of the electrode. The u.v.–visible spectrum of a green film of poly-CoTAPc which was coated on an optically transparent electrode (indium oxide/glass) resembles that of the corresponding monomer in solution, but exhibits extreme broadening.

The electrochemical behaviour of NiTAPc in DMSO/0.1 M tetraethylammonium perchlorate (TEAP) is also readily interpretable. Three reversible couples are observed, at +0.23, −1.00, and −1.45 V. Since no metal-centred reductions are expected in this potential region, the processes occurring at −1.00 and −1.45 V can be confidently assigned to ligand-based one-electron reductions. The origin of the waves at +0.23 V has not been absolutely determined, but literature reports suggest that it may be due to the $Ni^{3+/2+}$ couple.[19] Our observation that no electropolymerization occurs when NiTAPc is repetitively cycled from −0.2 to +0.6 V *vs.* saturated sodium calomel electrode (SSCE) supports this assignment. On the other hand, repetitive cycling from −0.2 to +0.8 V *vs.* SSCE induces ring oxidation (an anodic wave is observed at ~ +0.7 V), and efficient electropolymerization is observed.

Both poly-CoTAPc and NiTAPc exhibit a stable electrochemical response to repeated cycling following transferral of the coated electrode to a solution containing only fresh electrolyte. However, the most prominent feature in the resulting voltammograms is a large background current, the magnitude of which depends linearly on scan rate (see Figure 3). Such behaviour is reminiscent of polypyrrole,[20,21] but the

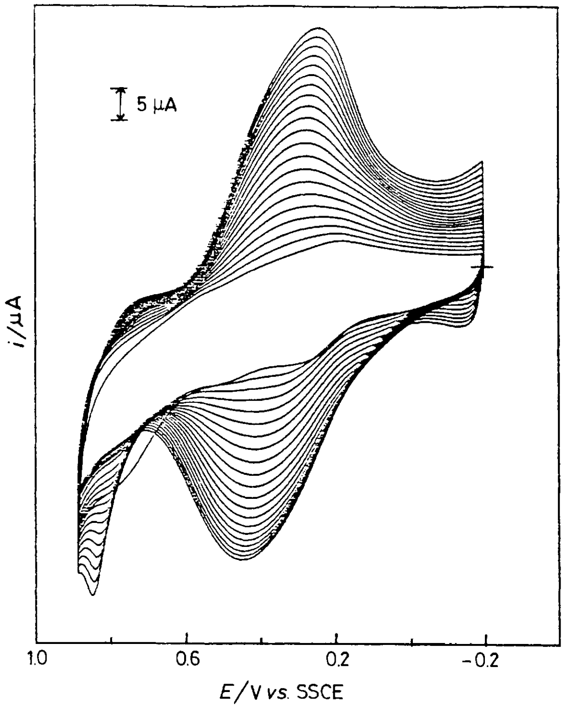

Figure 2. Repetitive cyclic voltammograms (−0.2 → +0.9 V *vs.* SSCE) of a 1 mM CoTAPc solution in DMSO/0.1 M TEAP at a glassy carbon electrode. Scan rate 200 mV/s; every fifth scan is recorded.

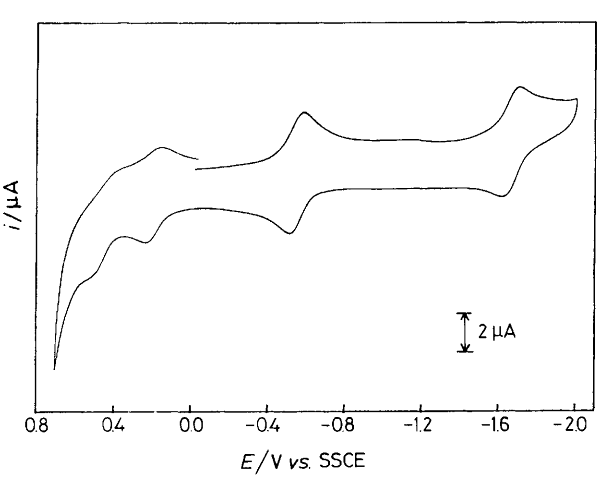

Figure 1. Cyclic voltammogram of CoTAPc (1 mM) in DMSO/0.1 M Et_4NBF_4 at a glassy carbon working electrode. Scan rate 20 mV/s.

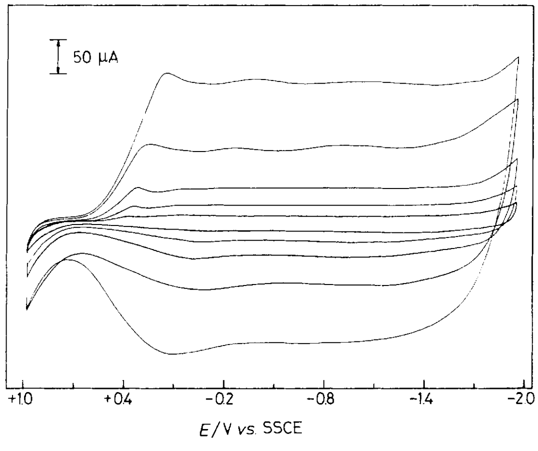

Figure 3. Cyclic voltammograms (+1.0 → −2.0 V *vs.* SSCE) recorded using a NiTAPc-coated glassy carbon working electrode in DMSO/0.1 M TEAP. Scan rates are 400, 200, 100, 50, and 20 mV/s.

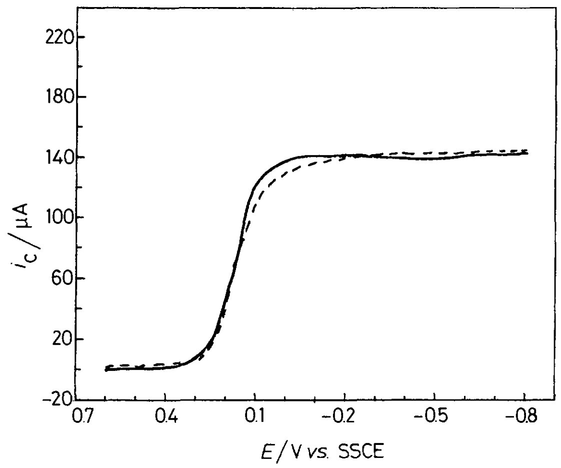

Figure 4. Hydrodynamic voltammograms for glassy carbon rotating disk electrodes in a 1 mM $K_3Fe(CN)_6$ solution (H_2O/0.1 M KCl). Scan rate = 20 mV/s; rotation rate = 900 rev./min; (---) bare electrode; (——) electrode coated with a thin film of NiTAPc prior to use.

phthalocyanine films show these large backgrounds over a much wider potential window. On the basis of the results presented herein, we attribute this large background to the charging current of the high surface area electronically conductive poly-MTAPc films.

In order to investigate further the conductivity of these films, both cyclic and rotating disk voltammetric methods were employed. In each case, the electrochemical response of the modified electrode in an electrolyte containing a dissolved redox couple was compared to that observed for a bare electrode under the same conditions. Three different solution couples, each described by a single one-electron reversible process, were examined: ferrocene$^{0/+}$/MeCN, $Fe(CN)_6{}^{3-/4-}$/H_2O, and $Ru(NH_3)_6{}^{3+/2+}$/H_2O. Formal potentials for these couples at a bare glassy carbon electrode were found to be +0.40, +0.18, and −0.12 V *vs.* SSCE, respectively.

In the cyclic voltammetry experiments, the observed response at the coated electrode appeared to be essentially that of the bare electrode superimposed on the large background current from the polymer. Peak potentials, heights, and separation were not significantly changed by the presence of the polymer coating. Likewise, data obtained from rotating disk electrode (RDE) experiments show that, at least for the reversible solution couples we examined, the coated and uncoated electrodes behave similarly. Limiting currents at the coated electrodes were equal to those observed at a bare electrode, Levich plots were linear, and $E_{1/2}$ values were virtually identical (Figure 4).

The available data are consistent with the formation of electronically conductive polymer films on the electrode surface. In particular, the large limiting currents observed in the RDE experiments rule out the possibility that reaction at the underlying electrode surface *via* substrate diffusion through cracks, pinholes, or channels makes a significant contribution to the observed current. In addition, although the porosity of these films has not yet been examined, the magnitude of the limiting current and the linear Levich plots suggest that substrate diffusion through a highly porous membrane to the metal surface is also an unlikely mechanism for the electrochemical reaction.[22,23] Finally, the constancy of $E_{1/2}$ values and the electrochemical reversibility observed for three different solution couples cannot be easily accounted for in terms of a localized hopping (redox conduction) model.[22,23] Unfortunately, free-standing MTAPc films are extraordinarily fragile, and reliable conductivity data are difficult to obtain directly. However, preliminary data using both conventional conductivity measurements and microwave reflectivity techniques support the notion of electronic conductivity in these polymers. Additional experiments, designed to probe the conductivity characteristics of the films as well as their electrocatalytic activity towards O_2 and CO_2 reduction, are in progress.

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