Electroactive polymeric thin film based on polypyrrole incorporating metallophthalocyanine polymer

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Thin films of polypyrrole doped with polymeric nickel phthalocyanine were grown on a platinum substrate by the electrochemical oxidation of pyrrole from aqueous solution containing 0.01 M pyrrole and 0.1 M sodium salt of polymeric nickel phthalocyanine as the only supporting electrolyte. The film thus prepared was characterized by i.r., u.v.-vis., e.s.c.a. and by conductivity measurements. The electrochemical behaviour of the electrode was studied by cyclic voltammetry in aqueous and non-aqueous electrolytes. The film exhibits stable conductivity and reversible electrochemical behaviour in the range of the potential investigated.

(Keywords: polyphthalocyanine; conducting polymer; electrochemical activity; cyclic voltammogram)

Introduction

Metallophthalocyanines and their polymers possess aromatic conjugated structures and have excellent thermal, chemical, electrochemical, hydrolytic and photochemical stabilities[1–3]. They have therefore received considerable attention in recent years as suitable candidates for making environmentally stable electrically conductive materials. By varying the substituents on the ring of the macrocyclic phthalocyanine moiety, it is possible to improve the properties of the system[2–8]. Proper choice of the substituent is needed in order to obtain highly extended conjugated structures. The presence of these structures in the polymer could reduce the band gap, E_g, which governs the intrinsic electrical and optical properties of the system. Because of the presence of rigid structures, these polymers have poor processability. The electrochemical method is one of the easiest techniques adopted for making thin films of uniform thickness. Previous reports have described the electrochemical preparation[9] and use of monomeric phthalocyanines entrapped in a polypyrrole matrix as electrocatalysts and stable conducting materials[10,11]. It is known that polymeric phthalocyanines are better electrocatalysts than monomeric ones. The electrochemical activity of phthalocyanine polymers dispersed in an insulating matrix such as poly(*N*-vinyl carbazole) and polyimide was shown to depend on the amount of phthalocyanine in the composite. It was also shown that the charge carrier mobility is interrupted by the insulating polymer matrix[12]. We therefore reasoned that replacement of the insulating polymer matrix by conducting polymers such as polypyrrole, which are easily prepared by electrochemical polymerization[13], should be beneficial from the point of view of making thin films possessing both processability and improved electrochemical activity.

In view of the importance of these materials for various microelectronic applications, we report the electrochemical incorporation of polymeric phthalocyanine possessing peripheral carboxyl groups into a conducting polypyrrole matrix. Details of the electrochemical investigation are also presented here.

Experimental

Materials. Polymeric nickel phthalocyanine containing peripheral carboxyl groups of the structure shown in *Figure 1* has been prepared by the method reported elsewhere[6,14]. Sodium salt was prepared by reacting the acid with an equimolar amount of sodium hydroxide and precipitating the salt with alcohol. Pyrrole (Fluka AG) was dried and distilled prior to use. Tetraethylammonium perchlorate (Fluka) and potassium chloride (Glaxo) were used as received. Triply distilled water was used for all cyclic voltammetric experiments.

Measurement techniques. The i.r. spectra of the polymer were obtained with a Perkin Elmer spectrophotometer model 283. The cyclic voltammograms were recorded using an EG & G PAR (model 273A) potentiostat. Photoelectronic spectroscopic measurements were performed using a VG-ESCALAB MK-II instrument using MgKα 300 W ($h\nu = 1253.6$ eV). The electrical conductivity of the polymer was measured by pressing the powdered samples between two stainless steel anvils of known area in an insulating die of diameter ~2.5 mm and length ~10 mm by the method reported previously[6].

Preparation of film. Polypyrrole-poly(nickel phthalocyanine) (PPy-PPC) thin film was prepared from aqueous solution containing 0.01 M pyrrole and 0.1 M sodium salt of polymeric nickel phthalocyanine as the only supporting electrolyte. The film was grown on a platinum substrate by the electrochemical oxidation of pyrrole at 0.8 V with saturated calomel electrode and a platinum coil as the counterelectrode. The film adhered well to the platinum substrate. The film thickness was controlled by measuring the charge passed during the electropolymerization. The electrode was then washed thoroughly with

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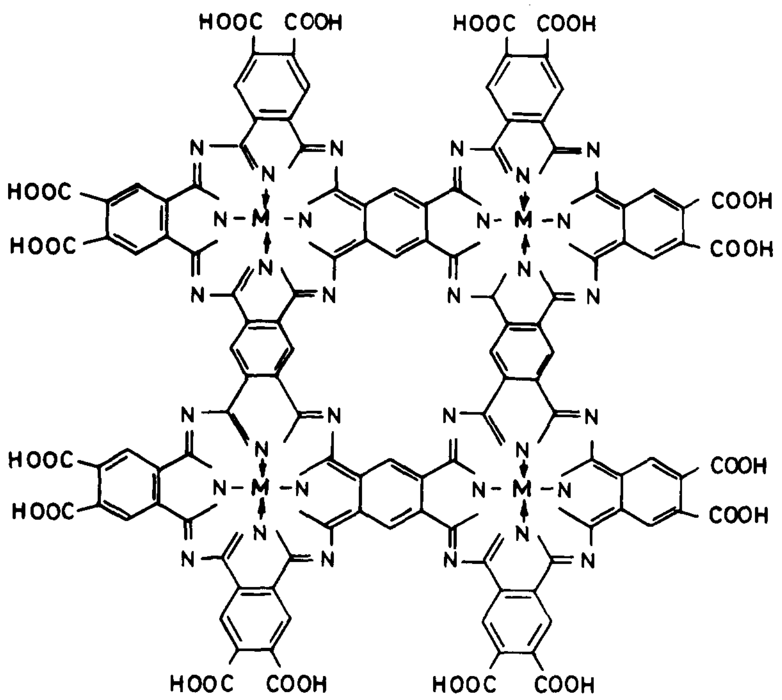

Figure 1 Structure of metallophthalocyanine polymer, M = Ni

distilled water till the washings were free from adsorbed phthalocyanine. It was then allowed to dry at room temperature.

Results and discussion

The i.r. spectrum of PPy-PPC film shows bands at 750, 885, 925, 1015, 1070 and 1140 cm^{-1}, which are attributed to the phthalocyanine skeleton[6,14,15], in addition to bands at 3480, 1710, 1680, 1640, 1560, 1480 and 1380 cm^{-1}. The u.v.-vis. spectrum of the limited soluble portion of the polymer in concentrated sulfuric acid shows absorption peaks characteristic of substituted phthalocyanine at 739, 690, 655 and 630 nm. These data prove that phthalocyanine polymer is incorporated into polypyrrole matrix. The presence of phthalocyanine in the film was further confirmed by the observed characteristic core-binding energies of Ni(2p$_{3/2}$) at 845.5 eV, Ni(2p$_{1/2}$) at 872.0 eV along with the binding energies of carbon (1s), nitrogen (1s) and oxygen (1s) centred at 285, 400, and 531 eV, respectively, in the x.p.s. spectra of the PPy-PPC polymer[6]. The PPy-PPC polymer exhibits a room temperature electrical conductivity of 2.5×10^{-3} S cm^{-1} which remains stable even after keeping the samples under ambient conditions. The value is about four orders of magnitude larger than that of undoped or non-heat-treated polymeric phthalocyanines[6] and is about two orders of magnitude lower than that of polypyrrole doped with other anions[16].

The electrochemical characteristics of the PPy-PPC film were studied using the modified electrode by cyclic voltammetry (*Figure 2*) in 0.01 M HCl. Upon reduction of the film, the polymeric phthalocyanine carboxylate anion, being large, remains in the matrix so that an electrolyte countercation can be released from or penetrate into the matrix to conserve the electroneutrality of the film. With the following oxidation, the remaining phthalocyanine anion can be incorporated again, followed by the release of the cation from the matrix. This is analogous to the behaviour of polypyrrole doped with large anions[16,17]. In PPy-PPC film the redox process can also occur via injection of electrons at the metal/polymer interface, followed by the transfer of charge through the film and by the incorporation of charge-compensating cations through the polymer/electrolyte interface. The charge-compensating cations (protons in the case of HCl) might be easily attached to the weakly basic aza nitrogen atoms of the phthalocyanine moieties, as is known to occur in thin films of polymeric phthalocyanine as such, or incorporated into an insulating matrix[12,18,19]. The film shows a near square root dependence of peak current with scan rate, indicating that the cation intercalation follows diffusion-controlled kinetics. This is analogous to the behaviour of octacyano phthalocyanine dispersed in an insulating polymer matrix[18].

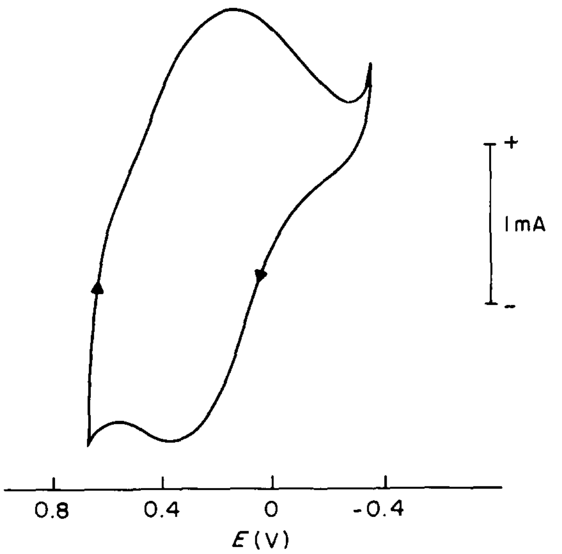

Figure 2 Cyclic voltammogram of PPy-PPC film on Pt in 0.01 M HCl. Sweep rate = 100 mV s^{-1} using SCE reference electrode

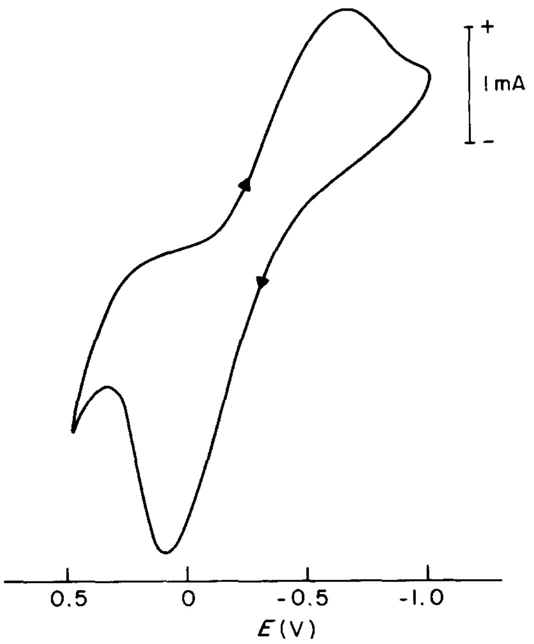

Figure 3 Cyclic voltammogram of PPy-PPC film deposited on Pt in aqueous solution containing 0.01 M sodium salt of nickel phthalocyanine polymer. Sweep rate = 100 mV s^{-1} using SCE reference electrode

The electrochemical characteristics of the film were also investigated by cyclic voltammetry in aqueous solution containing the sodium salt of nickel phthalocyanine polymer (*Figure 3*). A blank cyclic voltammogram run in aqueous solution of sodium salt of polymeric nickel phthalocyanine using platinum electrodes shows only the charging current. *Figure 3* therefore reflects the oxidation–reduction behaviour of the incorporated anion. E_p^a shifts more positively and E_p^c shifts more negatively as sweep rate (v) increases, indicating that the process resembles a quasi-reversible behaviour. The anodic and cathodic peak separation was found to increase with increasing sweep rate. The film has a ΔE value of 242 mV (at $v = 200$ mV s^{-1}), which is more positive than that of polypyrrole doped with other anionic polyelectrolytes[16]. The peak currents show square root dependence with scan rate, indicating the occurrence of diffusion-controlled migration of charge carriers in the system. The polymer electrode is swollen enough to facilitate the process.

When these films are immersed in acetonitrile solution with tetraethylammonium perchlorate as the supporting electrolyte, they behave in a similar manner and exhibit stable cyclic voltammetric responses. The peak currents do not vary much, even after repeated cycling.

The voltammetric behaviour of the electrode in acqueous HCl (0.01 M) remains unchanged without any loss of electrochemical activity, even after keeping it overnight in HCl with no applied potential. The improved electrochemical activity of the film appears to be due to the large electron-accepting nature of the phthalocyanine polymer and the electrical conductivity of both the base polypyrrole matrix and the polyphthalocyanine units. Thus PPy-PPC film exhibits stable electrical conductivity and behaves as a charge-controllable membrane specific to cations. The phthalocyanine moiety appears to be coordinated to the pyrrole ring through the pyrrole nitrogen. This is proved by carrying out electrochemical cyling of poly(nickel phthalocyanine) incorporated poly(*N*-methyl pyrrole) in supporting electrolytes such as lithium perchlorate and tetrabutylammonium fluoroborate. The latter exhibits exchange of phthalocyanine carboxylate anions with the electrolyte anions which occur due to the hindrance of complexation of pyrrole to the central metal atom. This behaviour is similar to that of polypyrrole doped with monomeric sulfonated cobalt phthalocyanines[11]. The interaction between the N–H proton of polypyrrole and the phthalocyanine ring could facilitate intimate affinity between the base polymer and phthalocyanine moiety, thereby making the system highly stable. Since phthalocyanine moieties are tied to the polypyrrole matrix via the above interaction, the system behaves similarly to the so-called self-doped system.

The electrochemical activity of the film in a redox electrolyte indicates that it behaves like platinum. The cyclic voltammogram of the electrode surface yielded nearly reversible peaks for the ferri/ferrocyanide couple in neutral aqueous media.

Conclusions

Metallophthalocyanine polymer has been incorporated into polypyrrole matrix by electrochemical means. The resulting polymer film has been characterized by i.r., u.v.-vis., e.s.c.a. and conductivity measurements. The film exhibits stable electrical conductivity and reversible electrochemical behaviour. The electrochemical behaviour has been explained based on the reversible incorporation of cations from the electrolyte on to the polymeric film.

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