Electrochemical polymerization of indole

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Electrochemical oxidation of indole, C_8NH_7, in a non-aqueous medium, such as a solution of $LiClO_4$ or $LiBF_4$, dissolved in acetonitrile, leads to the formation of polyindole, an air stable conducting polymer that exhibits electrochromic properties. The room temperature electrical conductivity, in the range 5×10^{-3}–8×10^{-2} S cm^{-1}, depends slightly on the nature of the counterion.

(Keywords: polyindole; conducting polymer; electrochromic properties)

Introduction

A large number of publications are devoted to the characterization of polyheterocyclic conducting polymers, such as polypyrrole, polythiophene and derivatives (for a general review, see ref. 1). Only a few preliminary studies deal with polyindole, a conducting polymer obtained by anodic oxidation of indole, C_8NH_7, in aprotic electrolytes[2–4]. Owing to the lack of precise characterization of this polymer and to the absence of published electrochemical curves, we have started a systematic study of the experimental conditions for obtaining polyindole, using electrochemical techniques of polymerization such as intensiostatic potentiometry and cyclic voltammetry carried out in different electrolytes[5]. The stoichiometry of doped polyindole has been obtained by elemental analysis and the evolution of the electrical conductivity during storage of the polymer in air has been studied. The efficient electrochromic properties of polyindole and its processability are currently being studied in order to optimize the characteristics of this interesting material; full results will be published in a forthcoming paper[6].

Experimental

Electrochemical synthesis was carried out in a classical three-electrode cell. The working electrode was a polished metal plate (platinum, gold or nickel). The counter-electrode was a platinum wire, while the reference electrode was a typical saturated calomel electrode (SCE).

Acetonitrile (Fluka), stored over $CaCl_2$ or P_2O_5, was vacuum distilled just before utilization. $LiBF_4$ and $LiClO_4$ (Alfa) were heated under vacuum at 150°C and 180°C, respectively, for water removal. Indole (Fluka) was used as received.

The electrochemical cell was maintained in an inert atmosphere of argon or nitrogen.

The electrical conductivity measurements were carried out on pellets of polyindole powder pressed under 2 T cm^{-2} using the method described by Van der Pauw[7].

Results and discussion

Figure 1 presents the variation of potential of the working electrode as a function of time, obtained under galvanostatic conditions in a one-compartment cell. The electrolytic solution consists of acetonitrile (30 ml), $LiClO_4$ (0.18 M) and indole (0.45 M). The current density is equal to 166 μA cm^{-2}. A film of polyindole is thus formed at the surface of a platinum electrode 2.2 cm^2 in area. The initial potential, close to 0.09 V vs. SCE, increases sharply up to 0.85 V when the electrolysis current is applied, and then decreases to a potential plateau at 0.66 V. Further cyclic voltammetry experiments indicate that this stable potential corresponds to the monomer polymerization. The polymer film deposited on the platinum electrode is khaki-green in colour.

Figure 2 presents several cyclic voltammograms. They have been recorded between -0.05 V and 1 V at a sweep rate of 10 mV s^{-1}. The increase of the intensities of both anodic and cathodic current peaks with the increase of the cycle number is consistent with the growth of a polyindole surface phase occurring for each anodic wave. This behaviour is very similar to the polymerization of pyrrole onto a metal electrode[8]. Potential sweeps inside selected domains show that the anodic peak a_1 is associated to the cathodic peak b_1, and that the anodic wave a_2 is related to the cathodic wave b_2.

Figure 3 shows the voltammogram, at 10 mV s^{-1}, of a polyindole film in a solution of $LiClO_4$ (0.25 M) – acetonitrile. Anodic and cathodic peaks (E_a and E_c)

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Table 1 Elemental analyses (wt%) of polyindole doped with perchlorate and tetrafluoroborate anions

	C	N	H	Cl	O	B	F	Total
ClO_4^- doping	62.79	9.39	3.645	7.825	14.595			98.245
BF_4^- doping	65.91	9.69	3.41			2.25	15.80	97.06

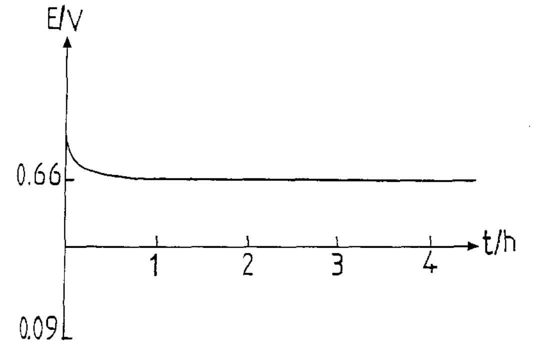

Figure 1 Potential *versus* time constant current curve corresponding to the polymerization of indole in acetonitrile – $LiClO_4$ (0.18 M) – indole (0.45 M) solution (electrolysis current density = 166 μA cm^{-2}; potentials are given against SCE electrode)

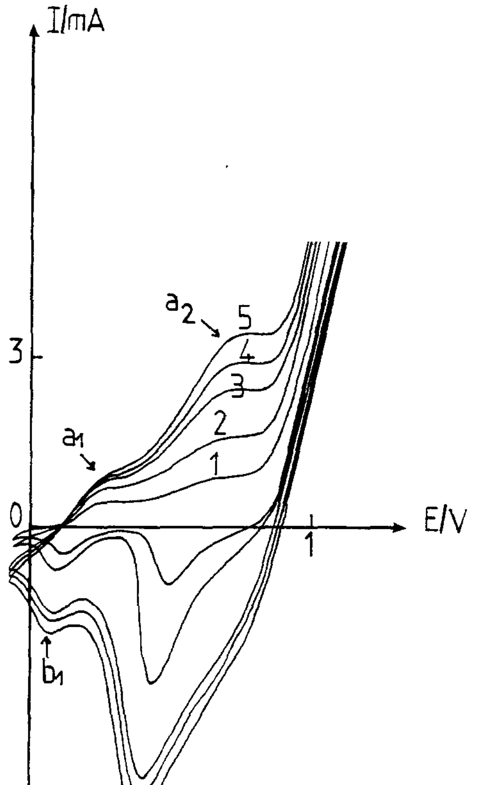

Figure 2 Cyclic voltammograms of polyindole growth in acetonitrile – $LiClO_4$ (0.17 M) – indole (0.15 M). Numbers 1 to 5 refer to the cycle numbers (sweep rate = 10 mV s^{-1})

correspond to doping and dedoping of the polymer, respectively. The potential of this redox reaction, $E = 1/2\ (E_a + E_c)$, is equal to 0.56 V vs. SCE. The reduced (undoped) polymer is yellow in colour. Polyindole, in the doped state, exhibits good air stability; continued air storage for several months does not modify its colour and weight. Moreover, the room temperature conductivity measured on pellets of polyindole powder pressed under 2 T cm^{-2}, using the Van der Pauw method[7], is constant *versus* time during air exposure. Thus, after 2 months of air exposure, the average room temperature electrical conductivity is equal to $(7.7 \pm 0.4) \times 10^{-2}$ S cm^{-1}.

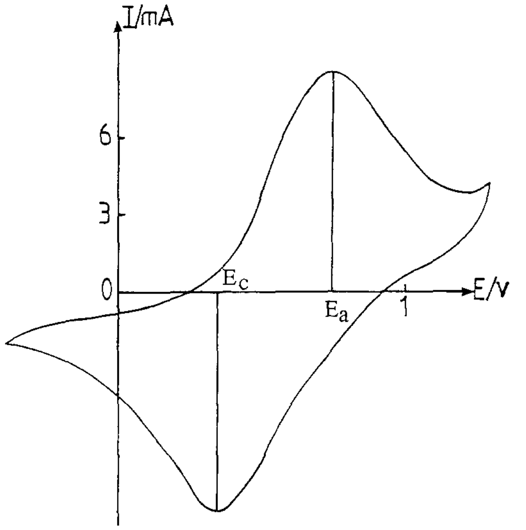

Figure 3 Cyclic voltammogram of polyindole at 10 mV s^{-1} in acetonitrile – $LiClO_4$ (0.25 M) solution

Electropolymerization of indole in $LiBF_4$–acetonitrile solutions leads to electrochemical curves comparable to those obtained in $LiClO_4$–acetonitrile electrolyte. The room temperature electrical conductivity of the doped polymers, measured after compression at 2 T cm^{-2}, is equal to 7.7×10^{-2} S cm^{-1} for ClO_4^- doping and 5.4×10^{-2} S cm^{-1} with BF_4^- as counterion.

Elemental analysis of ClO_4^- and BF_4^- doped polyindole synthesized at a constant potential of 0.8 V, carried out by the Centre d'Analyses du CNRS, Vernaison, are presented in *Table 1*. From these data, the formulas of the doped polymers can be written as follows:

$$[(C_8NH_5)_3^+(ClO_{4.1})^-]_x \quad \text{and} \quad [(C_{7.94}NH_{4.93})_{3.33}^+(BF_4^-)]_x$$

It appears that the maximum monomer unit to counterion ratio is in the range 3–3.5, a value comparable to those observed in parent polymers such as polypyrrole.

Spectroscopic characterization of polyindole (infra-red, e.s.c.a., ^{13}C n.m.r.) as well as X-ray diffraction studies will be published elsewhere.

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