

Trapping of Dopant Anions in Two-layer Polypyrrole Films

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A new method to decrease leaching out of dopant ions from conducting polypyrrole films using a two-layer system is presented.

Over the past few years, the electrosynthesis and the electrochemical properties of conducting polymers have been widely studied.¹ In particular, it has been shown that the incorporation of dopant anions necessary to maintain the electroneutrality of the film can be exploited to confer new properties on the polymer. For example, redox couples such

as ferro/ferricyanide^{2,3} or halogen/halides⁴ have been incorporated to stabilize the potential of the film for photoanode corrosion protection or as new battery electrode material, respectively. Recently, the range of dopants incorporated has even been extended to large biological molecules such as the enzyme glucose oxidase.⁵ The development of these modified

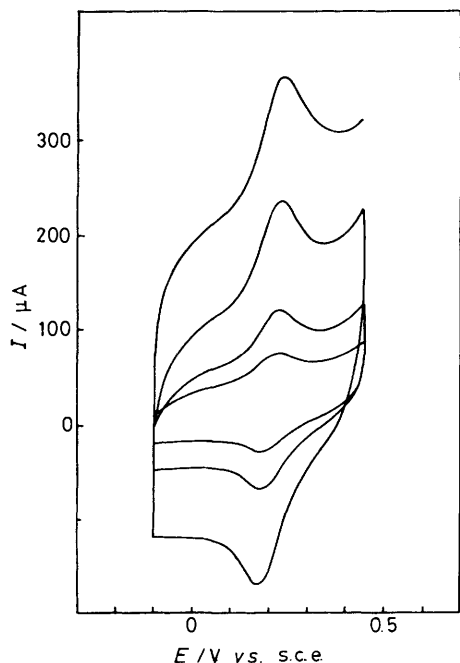


Figure 1. Cyclic voltammogram of PP/Fe(CN)₆³⁻ film (ca. 500 nm) in 0.25 mol dm⁻³ KCl aqueous solution; sweep rates 0.01, 0.02, 0.05, and 0.1 V s⁻¹.

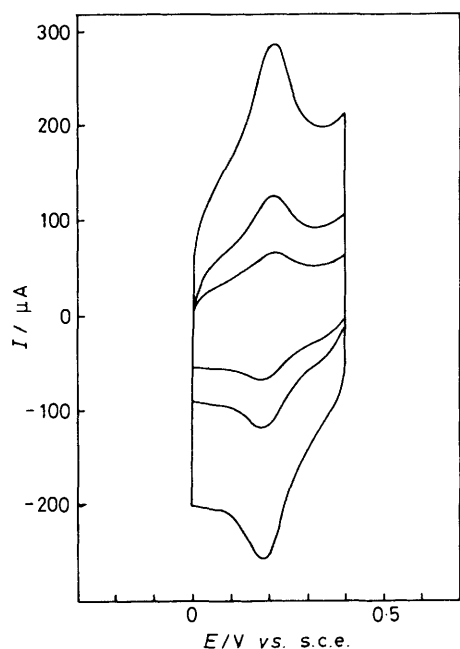


Figure 2. Cyclic voltammogram of a two-layer (PP/Fe(CN)₆³⁻/PP/Cl⁻) film (ca. 500 + 500 nm) in 0.25 mol dm⁻³ KCl aqueous solution; sweep rates 0.01, 0.02, and 0.05 V s⁻¹.

conducting polymer electrodes has been hindered however by the short lifetime of the film caused by the gradual leaching out of the active species into the solution.

The purpose of the present communication is to show that this leaching-out process can be minimized by using the ion-sieving properties of electrosynthesized polypyrrole

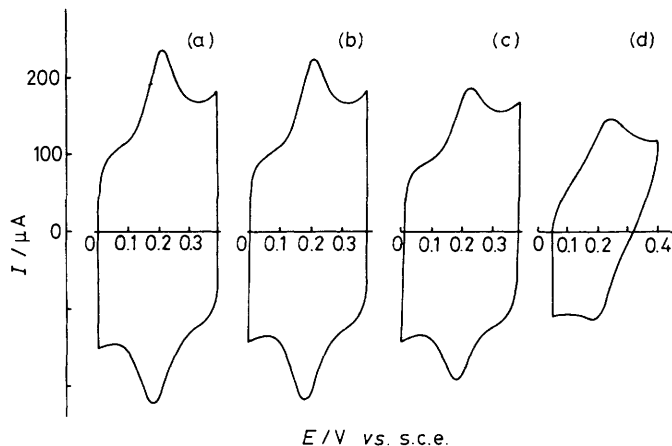


Figure 3. As Figure 2 after (a) 1, (b) 2, (c) 3, and (d) 8 days in the KCl solutions; sweep rate 0.05 V s⁻¹.

recently described by Shinohara *et al.*⁶ These authors have shown that the incorporation of anions during electropolymerisation leads to the formation of pores of a diameter similar to that of the dopant anions. We therefore expected that by using a two-layer polypyrrole film it would be possible to entrap any target species in the first layer if the top layer was electropolymerised with an anion having a diameter smaller than that of the target species itself. As an example, we have studied the redox behaviour of a two-layer system containing a ferro/ferricyanide-doped polypyrrole covered by a chloride-doped polypyrrole film {Stokes radii: $r[\text{Fe}(\text{CN})_6^{3-}] = 2.74 \text{ \AA}$, $r(\text{Cl}) = 1.21 \text{ \AA}$ }.⁷

The ferro/ferricyanide-doped polypyrrole was synthesized on a polished Pt disc (0.126 cm²) by electrochemical oxidation of an aqueous solution of 0.1 mol dm⁻³ doubly distilled pyrrole and 0.25 mol dm⁻³ potassium ferrocyanide. A typical cyclic voltammogram for such a system shows a first peak at 0.310 V corresponding to the oxidation of ferrocyanide and a more anodic wave corresponding to the oxidation of pyrrole. In order to be able to estimate film thicknesses, the film was deposited by sweeping the electrode potential from 0 to +0.9 V vs. s.c.e. at 50 mV s⁻¹, the thickness of the film being monitored by integration of the current corresponding to the pyrrole oxidation using the correlation between charge and thickness proposed by Diaz.⁸ Ferricyanide solution was not used directly for this electrolysis because this anion oxidises pyrrole in the aqueous bulk solution giving black polypyrrole flakes.

The presence of redox anions in the polypyrrole film was monitored by cyclic voltammetry in a 0.25 mol dm⁻³ KCl solution. Figure 1 shows the results for a one-layer film (thickness ca. 500 nm). The linear dependence of peak height on sweep rate for values below 50 mV s⁻¹ confirms that the redox species are surface-bound. The small shift of the peak potential with the sweep rate decreases with the film thickness and can therefore be attributed to iR drop within the film. The amount of capacitive current shown in Figure 1 depends on the history of the electrode in the polymerisation solution. It was observed that small values can be obtained if the electrode is left on open circuit to equilibrate and even cycled between -0.8 and 0.5 V (vs. s.c.e.) for a few minutes. Larger capacitive currents were obtained when the electrode was removed and washed directly after the polymerisation. If the electrode is left for a few hours in the KCl solution the redox anion will partition with the electrolyte; consequently the film loses its redox activity.

In order to study the ion-sieving property of a second film, similar experiments were carried out on a two-layer polypyrrole electrode. The deposition of the second layer was carried out in an aqueous solution of 0.1 mol dm^{-3} doubly distilled pyrrole and 0.25 mol dm^{-3} KCl, by cycling the electrode potential between 0.6 and 0.9 V vs. s.c.e. until the chosen film thickness was obtained.

Figure 2 shows the redox activity of the two-layer film under the same conditions as used for Figure 1. Apart from an increase of the capacitive background current, the two curves are similar, with reproducible peak height values (corrected for the background level). The main differences between the one-layer unprotected electrode and the two-layer electrode is that the redox activity of the latter remains for days.

Figure 3 shows the redox behaviour of the two-layer polypyrrole electrode after 1, 2, 3, and 8 days immersion in a $0.25 \text{ mol}^{-1} \text{ dm}^{-3}$ KCl solution. Although the background capacitive current appears to decrease with time the oxidation of ferrocyanide remains, showing that this anion cannot escape the film to partition with the electrolyte. It can therefore be concluded that the electropolymerisation of a second polypyrrole film with anions smaller than those present in the first layer hinders the leaching out of the dopants from the modified electrode.

Similarly, it has been observed that a two-layer film prepared as described can be reduced at -0.8 V for a few hours and still show redox activity.

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References

- 1 G. K. Chandler and D. Pletcher, Royal Society of Chemistry Specialist Periodical Report, 'Electrochemistry,' vol. 10, 1985.
 - 2 R. Noufi, D. Trench, and L. F. Warren, *J. Electrochem. Soc.*, 1981, **128**, 2596.
 - 3 L. E. A. Berlouis and D. J. Schiffrin, *Trans. IMF*, 1986, **64**, 42.
 - 4 G. Mengoli, M. M. Musiani, R. Tomat, S. Valcher, and D. Pletcher, *J. Appl. Electrochem.*, 1985, **15**, 697.
 - 5 M. Umana and J. Waller, *Anal. Chem.*, 1986, **58**, 2979.
 - 6 H. Shinohara, M. Aizawa, and H. Shirakawa, *J. Chem. Soc., Chem. Commun.*, 1986, 87.
 - 7 R. A. Robinson and R. H. Stokes, 'Electrolyte Solutions,' 2nd edn., Butterworth, London, 1959.
 - 8 A. F. Diaz, J. I. Castillo, J. A. Logan, and W.-Y. Lee, *J. Electroanal. Chem.*, 1981, **129**, 115.
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