

Substituent Effect on the Electron Transfer Rate in *N*-Arylpolypyrrole Film Electrodes

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Electronic interaction between the polypyrrole nucleus and *para*-substituents on the *N*-phenyl ring affects the electron transfer rate of polymer electrodes.

Early experiments on polypyrrole films showed that their performance as organic electrode materials varied over a wide range¹ when their electrical and electrochemical properties were modified by chemical or by anion permutation.² We now report a preliminary cyclic voltammetric study of the ferrocene redox reaction to evaluate the effect of change of substituent in some poly-*N*-*para*-substituted phenylpyrrole films used as electrodes.

The polymeric films of *N*-phenylpyrrole (1), *N*-*p*-methoxyphenylpyrrole (2), and *N*-*p*-nitrophenylpyrrole (3) were grown on a Pt surface of area 0.2 cm² by passing 20 mC/cm² in a two-electrode cell containing 0.1 M Et₄NBF₄ and the corresponding pyrrole monomer in acetonitrile solution. The oxidation of the *N*-substituted phenylpyrroles proceeds with the formation of an insoluble polymer film on the electrode as previously observed with pyrrole and other *N*-alkylpyrroles.³

The voltammetric study of ferrocene (1 × 10⁻³ M in an acetonitrile solution containing Et₄NBF₄) was carried out using thin films of the polymers of the *N*-phenylpyrroles (1)–(3) on a Pt working electrode.

Ferrocene electro-oxidation with coated Pt electrodes is *quasi*-reversible and shows small variations in the redox *E*^o potential; consequently, the chemical environment around ferrocene at the coated electrode surface must be similar to that of a clean Pt surface electrode.

The ferrocene-ferrocinium⁺ cyclic voltammograms using polypyrrole electrodes show a larger separation between *E*_{pa} and *E*_{pc} peaks than with Pt. The peak shape and the *i*_p–*v*^{1/2} relationship are in agreement with the occurrence of a reaction of a dissolved species which is not absorbed or adsorbed on the electrode.

To evaluate the effect of changes in substituent in the electrode film on the ferrocene couple reaction, the heterogeneous standard rate constants (*k*_s) values were determined by Nicholson's treatment.⁴ The changes in the film electron-transport rate observed (Table 1) are the result of the variation in the structure of the monomer. Thus, an electronic interaction between the electroactive pyrrole ring of the polymer and the *para*-substituent through the phenyl ring is observed.

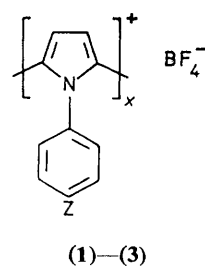


Table 1. Electron transfer rate constants *k*_s for the ferrocene redox reaction using 0.1 M Et₄NBF₄ in MeCN for the different poly-*N*-phenylpyrrole electrodes.

	Z	10 ³ <i>k</i> _s /(cm s ⁻¹)
(1)	OMe	10.47
(2)	H	12.35
(3)	NO ₂	14.70

Full details of our work will be described elsewhere but these results clearly reveal that chemical derivatization of the polymer structure is important for designing pyrrole polymers with the desired electrode properties.

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References

- 1 A. F. Díaz, K. K. Kanazawa, and G. P. Gardini, *J. Chem. Soc., Chem. Commun.*, 1979, 635.
- 2 M. Salmón, A. F. Díaz, A. J. Logan, M. Krounbi, and J. Bargon, *Mol. Cryst. Liq. Cryst.*, 1982, **83**, 265.
- 3 A. F. Díaz, J. Castillo, K. K. Kamazawa, J. A. Logan, M. Salmón, and O. Fajardo, *J. Electroanal. Chem.*, 1982, **133**, 233.
- 4 R. S. Nicholson, *Anal. Chem.*, 1965, **37**, 1351.