

EFFECT OF PYRIDINE ON THE POROSITY AND REDOX PROPERTIES OF POLYTHIOPHENE

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(Received October 26, 1988; revised May 10, 1988)

ABSTRACT. Polythiophene (PS) was electrodeposited on carbon electrode by electrochemical oxidation of the thiophene monomer in aqueous sulfuric acid solution. Transfer of PS film to aqueous acid solution containing pyridine appear to have effect on the PS redox properties as demonstrated by the change in the shape of PS cyclic voltammogram (CV).

When 0.01 M ammonium ferrous sulphate was added to the pyridine-acid mixture, peaks attributed to ferrous/ferric redox couple were observed in the resultant cyclic voltammogram, indicating that the film is porous to metal ions.

Another important observation was that the reduction potential of the metal ion was altered significantly by its incorporation in the polymer matrix.

INTRODUCTION

Electronically conducting polymers serve as the basis of studies pertaining to molecular electronics. This unique family of organic conductors include polythiophene (PS), polyaniline (PAN) and polypyrrole (PP). These polymers can be subjected to a wide range of applications and for that reason a lot of research is devoted to their study (1-7).

Studies on polythiophene (PS) conducted in aqueous media reveal improved redox properties and enhanced stability under ambient conditions. Most of the electrochemical studies on PS have traditionally been done in non-aqueous media.

Preliminary results obtained from studies involving PS in aqueous acid media indicate that the added pyridine has significant effect on the shape of the cyclic voltammogram.

The incorporation of metal ions by the pyridine treated film is useful as most of these organic conductors are known to be permeable only to counter ions in the form of anions and alkali metal cations. Thus, such results will serve as an anchor in comparative studies on how the polymer interior influences the redox properties of metal ions as opposed to macrocyclic systems.

EXPERIMENTAL

Reagent grade acids and chemicals were used as received. The thiophene was doubly distilled under reduced pressure yielding a colorless liquid. All the solutions were prepared using triply distilled water. The cyclical potential scan was obtained using PAR Model 175 Universal programmer in conjunction with PAR Model 173 potentiostat/galvanostat. Glassy carbon was used as the working electrode, and prior to use, it was polished with alumina on a felt polishing cloth. Polythiophene was electrodeposited on the carbon electrode

by cycling the potential between -0.2 to 0.9 volts, in a solution containing 1.0 M sulfuric acid and 0.1 M thiophene. The solutions were de-gassed using argon during and between the experiments. Saturated calomel electrode (SCE) and platinum wire were used as reference and auxiliary electrodes respectively.

RESULTS AND DISCUSSION

Fig. 1 shows the redox wave obtained during the potentiostatic oxidation of thiophene monomer in a solution containing 0.1 M thiophene and 1.0 M sulfuric acid. We observe the oxidation wave at 0.38 volts and the reduction wave at 0.22 volts. We also observe less intense redox peaks at 0.44 and 0.40 volts. It is observed that the oxidation peak is much sharper than the reduction peak. Also the charging current on the conducting end (positive potentials) is larger than that at the insulating end (negative potentials). This is in accordance with the switching of the polymer from an insulating to a conducting state. We also observe an irreversible pre-anodic shoulder at the onset of oxidation at 0.18 V, a peak which is probably the result of the switching of the polymer from a non-conducting state.

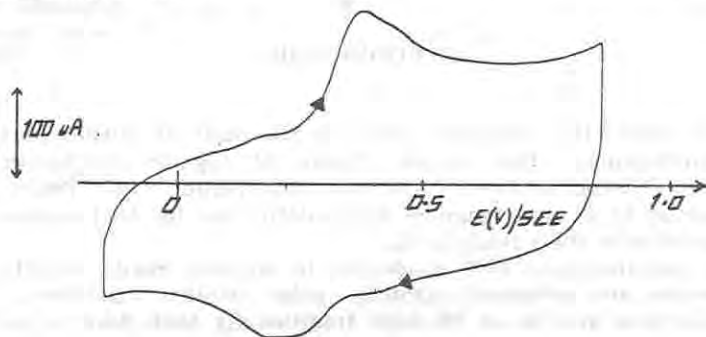


Fig. 1 Steady state cyclic voltammetric response in a solution containing 0.1 M thiophene and 1.0 M sulfuric acid. Scan rate, 200 mV/sec.

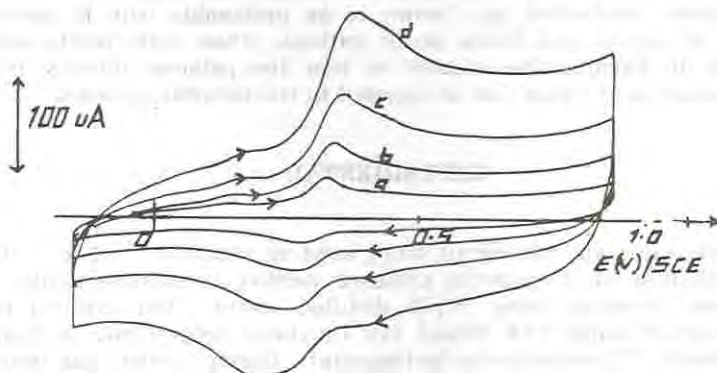


Fig. 2 Polythiophene film in a solution containing 1.0 M sulfuric acid, in the absence of thiophene monomer.
Scan rate: a) 20 mV/sec b) 50 mV/sec c) 100 mV/sec d) 200 mV/sec

The above film was then rinsed with triply distilled water, and then transferred to a solution containing 1.0 M sulfuric acid in the absence of thiophene monomer. We then observe that the peak current varies linearly with the scan rate, implying that the redox process is not diffusion - controlled. The absence of peak tailing further supports the above conclusion (see Fig. 2).

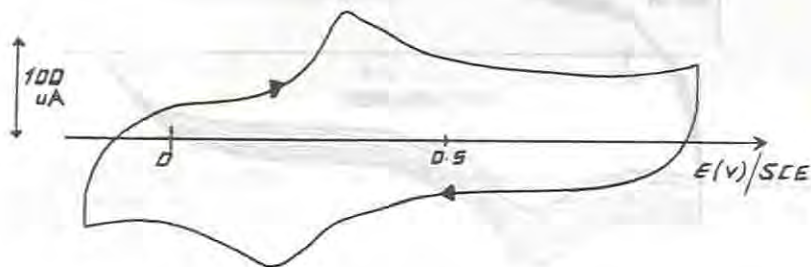


Fig. 3 Steady state cyclic voltammetric response obtained in a solution containing 1.0 M sulfuric acid and 0.01 M pyridine. Scan rate, 50 mV/sec.

When this film was transferred to a solution containing 0.01 M pyridine and 1.0 M sulfuric acid, one observes that the oxidation and reduction peaks are about equally sharp, as opposed to the earlier case where the reduction peak was much broader as compared to the oxidation peak (see Fig. 3).

The oxidation - reduction peaks have now shifted by 40 and 20 mV respectively towards negative potentials. The irreversible pre-anodic shoulder has now vanished. This shift in the redox wave potentials is not surprising since pyridine with an unshared pair of electrons on the nitrogen atom is a base and is largely protonated in acidic conditions. Thus, in a high pH solution the shift towards negative potentials was expected. Such shifts have been observed in other conducting polymers (4).

On continuous cycling in this pyridine containing media (in the absence of thiophene monomer) we observe continued growth of the PS redox was as illustrated in Fig. 4. This is strange since in the absence of thiophene monomer, we do not expect to observe further film growth. A possible explanation to this phenomenon is that the thiophene monomer trapped in the film prior to the transfer is being electropolymerized.

It is also possible that the presence of pyridine alters the electron dynamics in the film in a direction as to favour enhanced oxidation - reduction of PS. The verification of this assertion will require detailed studies on the electron transfer kinetics in these films.

When the film was transferred to solution containing 0.01 M ammonium ferrous sulphate, 1.0 M sulfuric acid, and 0.01 M pyridine, the resultant cyclic voltammogram (Fig. 5) depicted a redox wave with oxidation wave occurring at 0.50 V and the reduction wave at 0.40 V. These peaks probably represent the ferrous/ferric ion redox couple (Fig. 5, curve B). Cyclic voltammetric response recorded in bare glassy carbon electrode revealed an oxidation peak at 0.50 V and a reduction peak at 0.30 V, respectively. We observe that the reduction peak was shifted towards negative potentials by 100 mV, whilst the oxidation peak is invariant. Thus, it appears that the incorporation of the metal ion in the polythiophene matrix does not alter the oxidation potential of the metal ion.

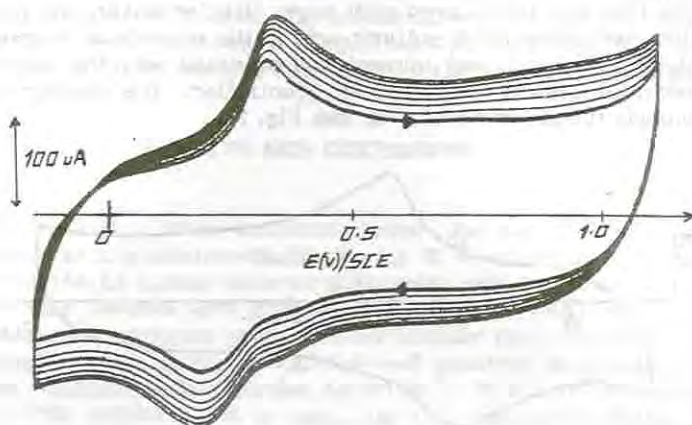


Fig. 4 Cyclic voltammetric response showing film growth during continuous cycling in a solution containing 1.0 M sulfuric acid and 0.01 M pyridine, in the absence of thiophene monomer. Scan rate, 50 mV/sec.

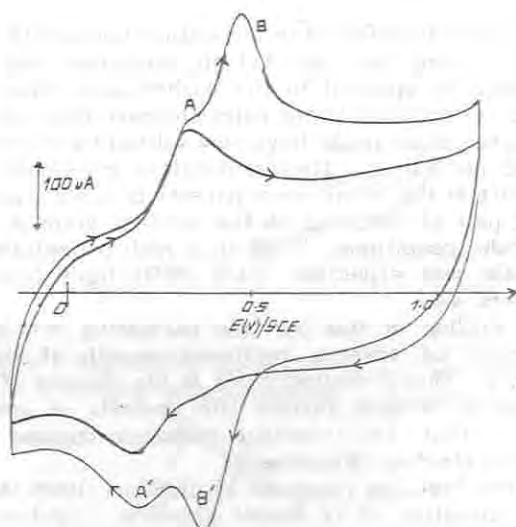


Fig. 5 Cyclic voltammetric response in a solution containing 1.0 M sulfuric acid, 0.01 M pyridine and 0.01 M ammonium ferrous sulphate. Curve A - A' and curve B - B' represents the PS and ferric/ferrous ion redox peaks respectively. Scan rate, 50 mV/sec.

We also observe that the peak current varies linearly with the scan rate, for the ferric/ferrous couple.

The PS and ferrous/ferric ion redox couples appear side by side at different formal potentials. This is an indicator to the non equivalence of the redox sites.

When the reduced film was returned to the growth solution containing 1.0 M sulfuric acid and 0.1 M thiophene after allowing to stay in triply distilled water for 24 hours, the resultant cyclic voltammogram showed only the PS

redox wave, implying that the metal ions were expelled from the film, a result which could be due to protonation of the film in the reduced state or due to unfavourable electrostatic interactions between the metal ions.

Studies on the effect of pH is still in progress but results obtained so far, indicate that the PS redox wave shifts in the direction of negative potential as the pH is raised. It is further observed that the electrochemical response was not degraded in high pH conditions.

CONCLUSION

This modification by pyridine of the electrochemical behaviour of polythiophene still needs further investigation so as to ascertain its possible effect on charge transfer in PS and possibly other conducting polymers. Work also is in progress to try and ascertain whether in addition to affecting the porosity of polythiophene, the pyridine is necessary to attract the Fe(II) ion.

The observation that the redox property of the metal ion is altered significantly when it is incorporated into the polymer matrix, will serve as a useful basis for comparative study on how such a robust polymer matrix compares to a macrocyclic - typical of biological systems, in its ability to alter the redox properties of a metal ion.

ACKNOWLEDGEMENT

This work was supported by a grant from the Royal Society of Chemistry.

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