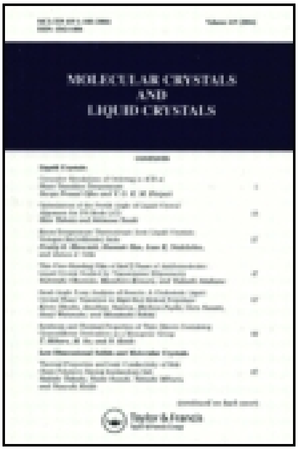

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Electrochemical Response of Poly-(3-Methyl-Thiophene) to Various Anions in Aqueous Solutions

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Electrochemical Response of Poly-(3-Methyl-Thiophene) to Various Anions in Aqueous Solutions

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Electrochemically formed films of poly-(3-methyl-thiophene), (PMeT), on platinum electrodes have been characterized by cyclic voltammetry in aqueous solutions containing KNO_3, $KClO_4$, KCl and K_2SO_4. An observed enhanced anodic current response for CVs in nitrate and perchlorate solutions compared to the responses for the other solutions, is believed to be due to the oxidizing power of the nitrate and perchlorate ions. The demonstrated effect may suggest the possibility of applying PMeT as a sensor for oxidizing ions in aqueous solution.

INTRODUCTION

Electronically conducting polymers have been widely investigated due to their interesting electrical, electrochemical and optical properties.[1] It has also been demonstrated that these materials can be used as sensors. For example, polypyrrole (PPy) has been studied as a potentiometric glucose sensor[2] and for detection of biological ions in solutions,[3] while polyaniline (PANI) has been investigated as a sensor for solvent vapours.[3]

This work is concerned with the electrochemical response of thin films of poly-(3-methyl-thiophene) on platinum electrodes towards some anions in aqueous solutions.

The present sensor concept is based on the redox properties of the conducting polymer and the corresponding insertion (removal) of counter ions into (from) the polymer material. During an anodic potential sweep the following oxidation reaction is assumed to take place[1];

$$P + X \longrightarrow (P^+)(X^-) + e^- \tag{1}$$

where P represents an electroactive center on the polymer (in this work three to four thiophene rings for each electron), and X^- is a counter ion (like NO_3^-, ClO_4^-, Cl^-, SO_4^{2-}, etc.) entering the polymer from the solution.

. Normally the electrochemical response of a given electroactive polymer for different counter ions is considered to be almost identical.[1] Electroactive polymers are, therefore, not obvious candidates for sensors that are selective to a particular anion. However, as will be demonstrated below, a strong anodic current response for nitrate and perchlorate ions is observed, which may be linked to the oxidizing power of these species. The presence of an oxidizing specie like H_2O_2 is also the key to the functioning of polypyrrole as a the glucose sensor, as suggested by Couves & Porter.[2]

EXPERIMENTAL

The working platinum disk electrode (0.196 cm^2) was polished with 1 μ diamond spray, rinsed with; acetone, distilled water and finally with ethanol. The 3-methylthiophene monomer was distilled before use, and all chemicals were of p.a. quality, except $KClO_4$ which was of puris quality.

The platinum electrode was coated with poly-(3-methyl-thiophene) by electropolymerization of 3-methyl-thiophene (0.1 M) in acetonitrile containing tetra-butylammonia-tetra-fluoro-borate (0.1 M) as a supporting electrolyte.

The polymerization was carried out by applying a constant potential of 1650 mV vs. Ag/AgCl for 60 seconds. The polymer film was thereafter reduced potentiostatically at −500 mV for 120 seconds in the formation solution. The electrode was then rinsed thoroughly in distilled water and stored in distilled water until transference of the electrode to the different solutions to be tested. Prior to each voltammogram, the PMeT film electrode was reduced at 0 mV for 2 minutes in the test solution.

Aqueous solutions containing different anions were tested, and linear sweep cyclic voltammetry (CV) was carried out with a SOLARTRON 1286 Electrochemical Interface, controlled by a microcomputer (OLIVETTI M24), using a conventional 3-electrode setup. Normally, a potential sweep rate of 10 mV/s was used (any deviation from this standard is indicated in the figure legends).

All electrode potentials are referred to the Ag/AgCl reference electrode (which has a potential of +0.22 vs SHE).

The experiments were carried out in an open cell-system at room temperature (~295 K).

The presented cyclic voltammograms have not been corrected for IR drop in the solution. However, due to the relative small currents, this would (except maybe for the 10^{-4} molar solutions, with their low conductivities) only give small corrections).

RESULTS AND DISCUSSION

Figure 1 shows cyclic voltammograms (CVs) of the PMeT film electrode in a 0.1 M KNO_3 solution and in a 0.1 M KCl solution.

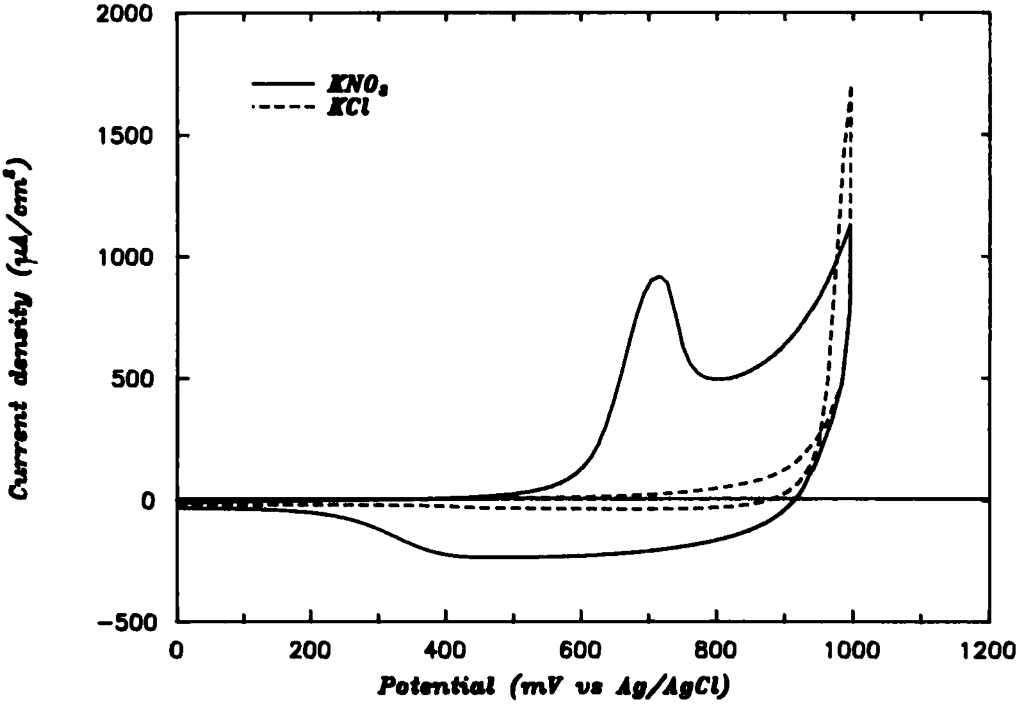

FIGURE 1 Cyclic voltammogram for PMeT film electrode in 0.1 M KNO_3 solution (—) and in a 0.1 M KCl solution (- -).

The anodic current peak starting around 600 mV in the nitrate solution is absent or shifted several hundred millivolts to more anodic potentials in chloride solutions.

The difference in the current response for nitrate and chloride solutions in the potential range 600–900 mV is our basis for suggesting PMeT as a sensor for nitrate ions. In the present work cyclic voltammograms were normally limited to the potential range 0 to 700 mV to avoid the irreversible oxidation of the polymer taking place above 1–1.2 V.[1]

Figure 2 shows the effect of nitrate ion concentration on the current response in the CVs. A similar strong anodic current response is also observed for perchlorate ions, while sulphate ions behaves more like chloride ions, as demonstrated in Figure 3 which gives the C.V. for experiments with the 0.1 M solutions of these four anions.

Figure 4 shows the CV for a mixture of 10^{-4} M KNO_3 + 0.1 M KCl, including the CV for pure 0.1 M KNO_3 and for 0.1 M KCl, for comparison. As indicated by the results in Figure 4, an addition of 10^{-4} M KNO_3 seems to be detectable in a 0.1 M KCl solution.

In Figure 5 the current response at 700 mV from different CVs is plotted as a function of (log of) concentration for the above mentioned salts. As indicated by Figure 5, the difference in current response for the CVs in nitrate and perchlorate solutions compared to the responses in chloride and sulphate solutions seems to increase for increasing salt concentrations.

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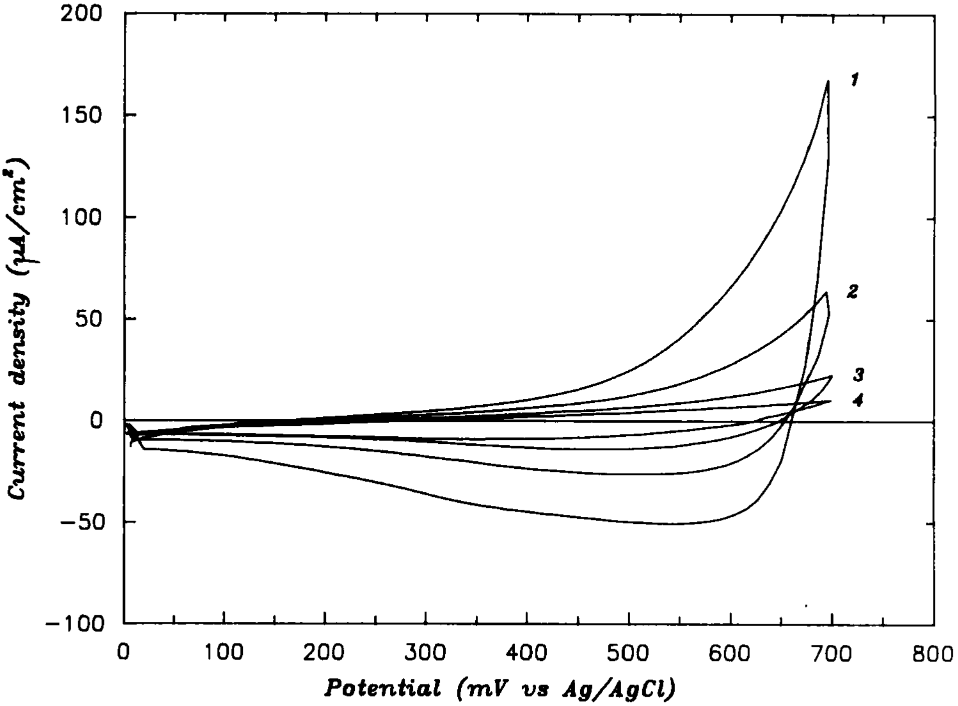

FIGURE 2 Cyclic voltammograms for PMeT film electrode in KNO_3 solutions 10^{-1} mol/l (1), 10^{-2} mol/l (2), 10^{-3} mol/l (3), and 10^{-4} mol/l (4).

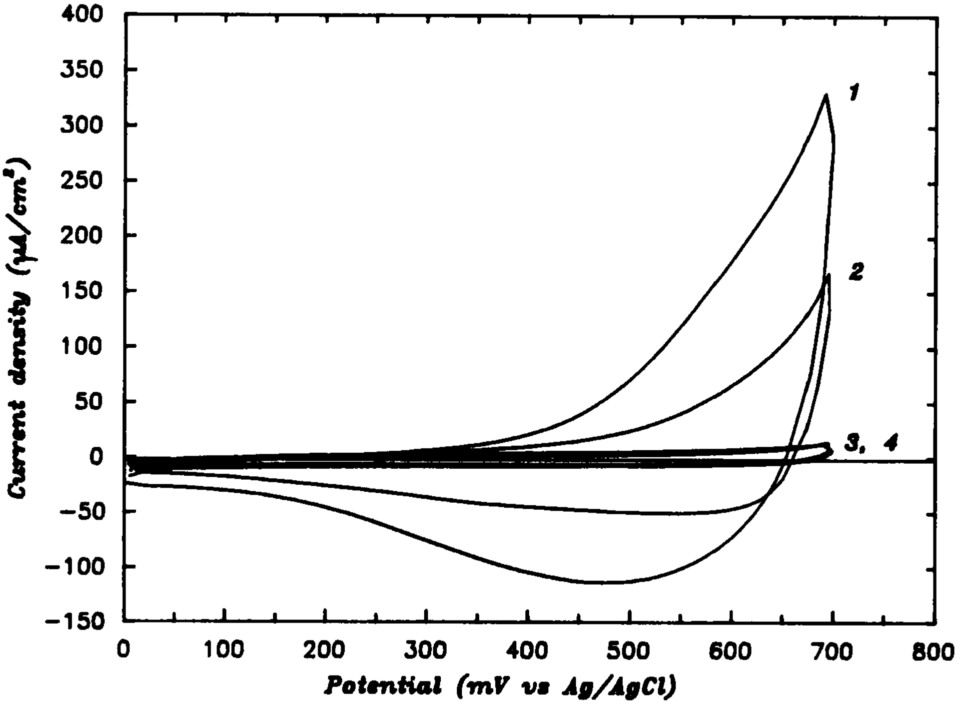

FIGURE 3 CVs for PeMeT film electrode in 0.1 M $KClO_4$ (1), 0.1 M KNO_3 (2), 0.1 M KCl (3) and 0.1 M K_2SO_4 (4) solutions.

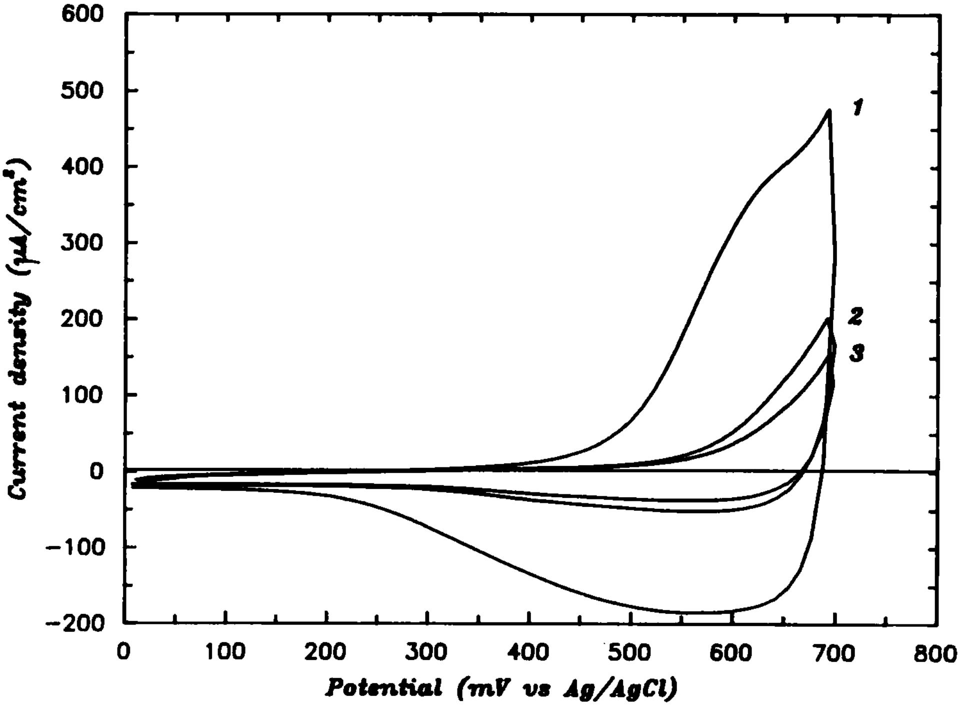

FIGURE 4 CVs of PMeT film electrode in a mixture of 0.1 M KCl + 10^{-4} M KNO_3 (2), and pure solutions of 0.1 M KNO_3 (1), and 0.1 M KCl (3).

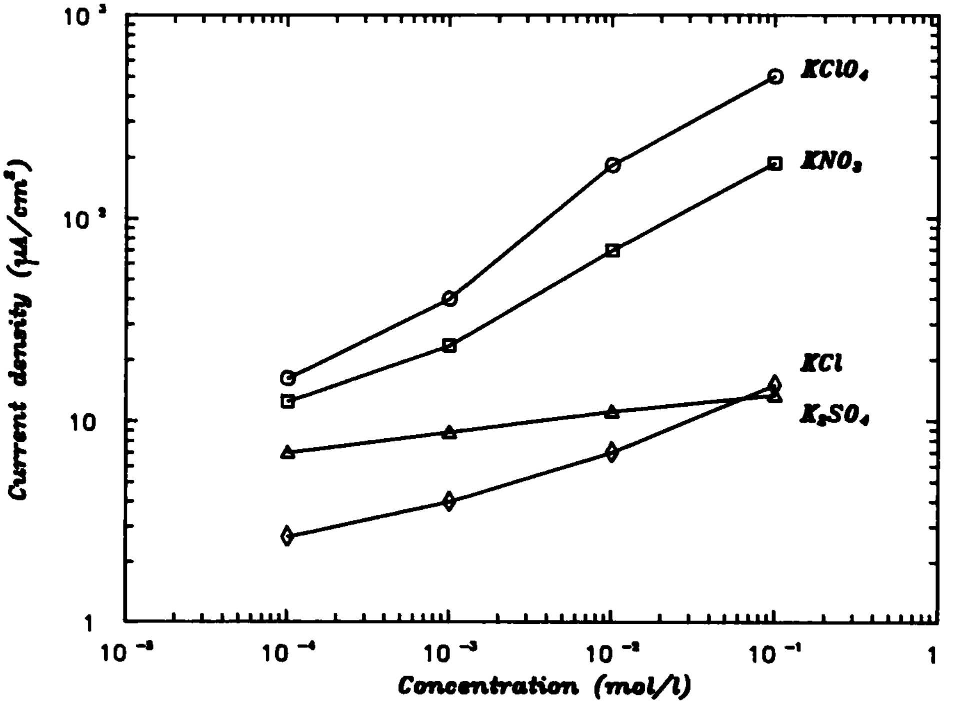

FIGURE 5 Current density measured at 700 mV (from different CVs) vs. concentration (log scale) for $KClO_4$, KNO_3, KCl and K_2SO_4.

The current response for nitrate and perchlorate ions relative to chloride and sulphate ions can be further enhanced by increasing the potential sweep rate, as can be seen from Figure 6 for the 0.1 M solutions of all four salts. The current responses for $KClO_4$ and KNO_3 increases significantly with increasing sweep rates, while there is almost no effect of sweep rate on the current responses for KCl and K_2SO_4 solutions.

A possible explanation for the observed enhanced current response for the nitrate and perchlorate solutions compared to the other solutions is given in the following.

In this work each voltammogram is started at zero vs. Ag/AgCl. At that potential PMeT is in its reduced form, which is several orders of magnitude less conductive than the oxidized form of PMeT. In the first part of a potential sweep from negative to positive potentials with electrodes coated with reduced PMeT, the current response will, due to the low conductivity of the film, normally be limited by the transport of electrons through the film.[1] At higher potentials the PMeT film starts to be oxidized, and the current will normally be limited by the transport of anions through the film. In CVs in nitrate solutions, however, the PMeT may be oxidized by the nitrate ion according to the following redox process;

$$2\,P + NO_3^- + H_2O \longrightarrow 2\,(P^+) + NO_2^- + 2\,OH^- \qquad (2)$$

where the nitrite and hydroxyl ions compete with the nitrate ions as counter ions

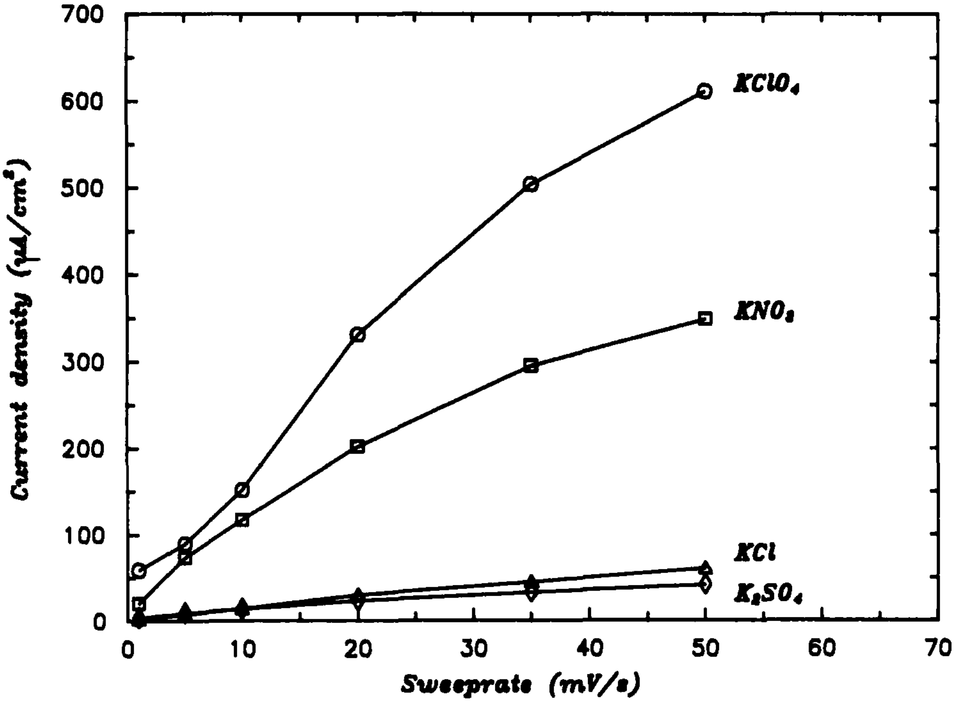

FIGURE 6 Effect of potential sweep rate on the current density measured at 700 mV (from different CVs) for (pure) 0.1 M solutions of $KClO_4$, KNO_3, KCl and K_2SO_4, respectively.

in the film. (A similar redox reaction is believed to take place with perchlorate ions and other oxidizing anions).

The red-ox reaction (2) partly oxidizes the polymer (probably equivalent to ordinary chemical doping of electroactive polymers), thereby increasing the conductivity of the film at much lower potentials than in solutions with only non-oxidizing anions. Although the redox reaction (2) drains electrons from the polymer (which reduces the net anodic current), the results of reaction (2) is an increased conductivity of the PMeT film, thereby enhancing the rate of the anodic reaction (1) at extraordinary low potentials. At higher potentials the current probably becomes limited by the transport of anions through the film also for CVs in aqueous solutions with oxidizing anions.

Work in progress seem to support the proposed explanation of the enhanced current response for aqueous solutions with oxidizing anions.[4]

CONCLUSION

It has been demonstrated that a PMeT covered platinum electrode in aerated aqueous solutions gives an enhanced current response for oxidizing ions like nitrate and perchlorate ions, while non-oxidizing ions like chloride and sulphate ions give significantly lower current responses in the cyclic voltammograms.

The current responses for the oxidizing ions can be further enhanced by increasing the potential sweep rate to more than 10 mV/s.

This effect suggests the possibility of using the poly-(3-methyl-thiophene) film electrode as a sensor for oxidizing ions in aqueous solutions (which should be free of interfering oxidizing agents).

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