

THE INFLUENCE OF PREPARATION CONDITIONS ON THE ELECTRICAL CONDUCTIVITY OF POLY N-METHYLPYRROLE FILMS

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ABSTRACT

Electro-active poly N-methyl pyrrole (PNMP) films have been galvanostatically polymerized under a range of conditions. The influence of the conditions used in electropolymerization, such as electrolyte concentration, current density, type of doping anion and temperature during polymerization on the electrical conductivity has been investigated. The conductivity was measured by the in-situ method using a specially prepared two-band microelectrode. The current density used during the polymerization has a considerable influence on the conductivity, as earlier observed for polypyrrole in non-aqueous electrolytes. The conductivity changes with the size of the anion and the concentration of the electrolyte as well as on the temperature at which the polymerization was carried out. Polymer films formed at relatively higher temperatures had lower conductivities and were not able to insert as many counterions, indicating that the films formed were less perfect. At higher temperatures the increased rates and numbers of side reactions may be competing with the ideal one-dimensional polymerization process.

Key words: poly N-methylpyrrole, electronically conducting polymers, conjugation, electrical conductivity.

1. Introduction

Electronically conducting polymers are of interest to solid state ionics because their properties are determined by the presence and motion of ions. Most of these polymers are insulators intrinsically and become conducting only when doped with counterions by electrochemical or chemical processes. On doping, the counterions do not enter the polymer matrix by substitution for atoms in the polymer, but only associate themselves at available sites along the polymer chain. Therefore conducting polymers can be made to switch between conducting and non-conducting states easily by doping and dedoping with counterions.

Among the electronically conducting polymers, polypyrrole (PPy) and its derivatives have attracted considerable attention because of their stability and potential use in sensors, batteries, capacitors, etc [1-6]. In spite of the tremendous amount of work on these systems, there are still considerable differences between the results reported in the literature. It is a well-known fact that the properties of polypyrrole and other conducting polymer films are strongly influenced by the method of preparation, counterions and conditions used during synthesis [7-9]. However, the role played by the counterions and solvents in determining the properties of these polymers is yet to be resolved.

Our earlier systematic studies on electropolymerized PPy films in non-aqueous electrolytes have shown that the current density used during polymerization plays a crucial role in determining the properties of pyrrole [7, 10]. Based on this study, two types of PPy were identified: low current density form ($i = 300 \text{ } \mu\text{A cm}^{-2}$ in dry propylene carbonate) and high current density form ($i = 500 \text{ } \mu\text{A cm}^{-2}$ in dry propylene carbonate). The low current density form, which showed a detailed structure with narrow peaks in the cyclic voltammograms, was of the highly conjugated nature expected for nearly ideal polypyrrole films and had higher conductivity and crystallinity

than the high current density form [10, 11]. This well-defined low current density form has been used to investigate the influence of different ions and electrolyte solvents on the properties of polypyrrole [12].

It was considered of interest to extend these studies to poly-N-methylpyrrole (PNMP), to verify the applicability of the results obtained for PPy. However, the reported conductivities are very low [6]. In this paper we report a systematic study of the in-situ conductivity as a function of doping levels on PNMP prepared under a range of conditions in aqueous media. A clear understanding of the influence of the various parameters used during the preparation may lead to the synthesis of PNMP films with desired conductivities.

2. Experimental

2.1 Polymerization and Cyclic Voltammetry Studies

The monomer (N-methylpyrrole, Aldrich) was purified by distillation and kept cool in the dark prior to use. Water was doubly distilled.

All synthesis of polymer films was performed galvanostatically at normal ambient conditions on 1 cm long x 0.5 mm diameter platinum (Pt) wire electrodes sealed in a glass tube, using a standard three electrode cell. Pt wire and standard calomel electrode (SCE) were used as counter and reference electrodes, respectively. The electropolymerizations for all the investigations other than the current density dependence study were carried out with $62.5 \text{ } \mu\text{A cm}^{-2}$ in aqueous electrolytes having a concentration of 0.5 M LiClO_4 and adjusted to pH = 4.5 with perchloric acid. The monomer concentration used was 0.1 M. The thickness of the films (usually 0.25 μm) was calculated assuming that 240 mC cm^{-2} leads to 1 μm film as assumed for poly pyrrole [13]. The working electrode was removed from the cell soon after the synthesis and then washed thoroughly by the respective electrolyte solution to remove monomer molecules. The films were characterized using cyclic voltammetry. Typically, cyclic voltammograms were obtained in the -0.5 V to 0.60 V vs SCE potential window at a sweep rate of 100 mV s^{-1} .

2.2 Conductivity Measurements

For the electrical conductivity measurements, polymer films were prepared on a specially made two-band microelectrode with narrowly separated gold plates. The design of this micro-electrode was based on the electrode used by Schiavon et al [14] and its construction was described elsewhere [10]. The films were deposited on the electrode by galvanostatic polymerization as described above to have a calculated thickness of 5 μm . During the conductivity measurements the film was brought to the desired potential in the range -0.5 V to 0.6 V (measured with respect to Ag/AgCl and converted to scale with SCE) using a DC power supply. The electrode was equilibrated at this potential for 15 minutes, and AC impedance spectra were obtained using a Solartron 1260 frequency analyzer, scanning in the frequency range 10^6 Hz to 5 mHz with an applied signal amplitude of 20 mV. Resistance of the films was obtained by analyzing the impedance data using the EQUIVCRT ac-impedance data analysis program [15]. It should be noted that since the conductivity values were evaluated using the calculated thickness for the films and assuming an idealized geometry, the conductivity values might not be exact. Nevertheless, the values can be used to study the variation of the conductivity with doping level.

3. Results and Discussion

3.1 Current Density Dependence

Fig. 1 shows the cyclic voltammograms for the samples obtained in 0.5 M LiClO_4 aqueous electrolytes for a series of films prepared using different current densities. All films have the same

voltammograms do not have well defined sharp anodic and cathodic peaks. This may be partially due to steric hindrance caused by the bulky CH_3 groups being repelled by H-atoms on the pyrrole ring. This would prevent perfect coplanarity between adjacent monomers. The resulting polymer would then not be able to create quite as regular an environment for the inserted counterions. However, the PNMP shows completely reversible redox behaviour as polypyrrole. It can be observed that while the cyclic voltammograms for the low current densities of 62.5 and $125 \mu\text{A cm}^{-2}$ seemed to be almost identical, those of the high current densities differ considerably. This indicates that the current density used during polymerization has a strong influence on the resulting polymer and that the films formed with high current densities may be either less conjugated or formed with low efficiency.

Fig. 2 shows the in-situ electrical conductivity variation with applied potential (doping levels) for films prepared with three different current densities. The conductivity remains very low until the high conductivity switching occurs at about 0.12 V and increases steadily. The values of the conductivity should rise and eventually become constant when conducting state is reached at high potentials as observed for PPy [10]. This cannot be checked for the PNMP because of the problem of disintegration of the polymer at such high potentials. In the conducting state, the film prepared with lower current density had higher conductivities than those of the films prepared with high current densities. When larger current densities are used the polymerization occurs quickly resulting in imperfect films with shorter conjugation. On the other hand, when low current densities are used, polymerization may occur slowly resulting in more perfect films with longer conjugation lengths for the polymer chain. This is similar to the results observed for pure pyrrole films in non-aqueous electrolytes. The value of the conductivities of PNMP films is about 10^5 times smaller than that of the corresponding PPy films in non-aqueous electrolytes. As in the case of PPy, there is evidence that low current densities ($< 125 \mu\text{A cm}^{-2}$) results in better conjugated PNMP films. Therefore, for all other investigations films prepared with the low current density of $62.5 \mu\text{A cm}^{-2}$ were used.

3.2 Electrolyte Concentration Dependence

The cyclic voltammograms for films prepared using electrolytes having different concentrations are shown in Fig 3. These films were all prepared using the low current density of $62.5 \mu\text{A cm}^{-2}$ to have a thickness of $0.25 \mu\text{m}$. The cycling was done in 0.5 M LiClO_4 aqueous solution at room temperature. For lower concentration the anodic peak becomes sharper and shifts towards lower potentials. The area of the curves increases with decrease in electrolyte concentration.

The corresponding variations in the electrical conductivity are shown in Fig 4. The films prepared with lower concentrations clearly shows higher conductivity values. Similar results were reported for the PNMP films prepared in non-aqueous electrolytes [8]. As the overall reaction rate is fixed by the current density, this effect is most likely linked to an increased amount of side reactions at higher electrolyte concentrations. It is not clear whether these are caused by impurities introduced together with the electrolyte salt or by oxidation or branching induced by perchlorate ions.

3.3 Dependence on the Dopant Anion

To investigate the effect of the type of counterions on the properties of PNMP, ClO_4^- , CF_3SO_3^- , and Cl^- anions were used. The samples were polymerized using the low current density of $62.5 \mu\text{A cm}^{-2}$. The films were prepared and cycled in electrolytes having the same anions. The cyclic voltammograms obtained and the corresponding variations in conductivities are given in Figs 5 and 6, respectively. The cyclic voltammogram of the polymer obtained and cycled in the presence of Cl^- ions is remarkably different from the other two curves. The potential range of the

difference may be explained by differences in association between dopant ions and the polymer. A closer association will give rise to a lower oxidation potential, to peaks in the voltammogram and in cases where the insertion of dopant ions lead to changes in the conformation of the polymer, a persistent hysteresis is often observed in cyclic voltammograms. On the other hand, when the inserted charge is only associated loosely with the polymer, featureless voltammograms with high reversibility may be expected. The voltammograms on Fig 5 thus show that Cl⁻ ions interact more weakly with the polymer than does ClO₄⁻ and CF₃SO₃⁻. Fig 6 shows that the conductivity of the PNMP/Cl⁻ complex is very poor. K.M. Cheung et al [17] have reported that in PPy, larger anions produce a more regular chain structure with higher degree of conjugation, and therefore chain packing and chain perfection are probably strongly influenced by the anion used as counterion during polymer synthesis.

As can be seen, the anions greatly influence the film formation and the conductivity values. The conductivities of the films prepared with ClO₄⁻ and CF₃SO₃⁻ counterions are much larger than those of the films prepared with Cl⁻. This is in contrast to the findings reported by J.J. Kim et al [18]. They have shown that solvents (PC and water) and counterions (Cl⁻ and ClO₄⁻) have very little influence on the conductivities of PPy and PNMP films. Their films were prepared with a current density of 1-3 mA cm⁻² and therefore fall in the category of less conjugated high current density form in which Cl⁻ and ClO₄⁻ ions may not cause any significant changes to produce observable conductivity differences.

3.4 Temperature Dependence

To examine the temperature effect on the formation of PNMP, films were polymerized at temperatures in the range of 3 °C to 40 °C with a current density of 62.5 A cm⁻². The cyclic voltammograms were performed in 0.5 M LiClO₄ aqueous electrolyte at room temperature. The curves obtained are shown in Fig 7. The anodic peak position moves to the left and the area of the curves decreases as the synthesis temperature increases.

The corresponding in-situ conductivity variations are shown in Fig 8. The conductivity of the films prepared at 3 °C is very much greater than those of the films prepared at high temperatures. Similar temperature effects have been reported for PPy [9] and PNMP [19]. These results imply that the films formed at higher temperatures are not perfect and less conjugated. Lower conductivities of these polymers at higher temperatures may arise due to structural defects such as crosslinking between polymer chain, which result in small conjugated segments and thereby hindering the conduction process. Another explanation may be that at higher polymerization temperatures, unwanted side reactions compete with the desired π - π coupling reaction of the oxidized monomer units and thereby result in less uniform films. There was a suggestion by Maddison and Unsworth [20] that at higher temperatures, monomer units begin to polymerize in solution and the resulting small segments of oligomers are incorporated into the growing polymer resulting in high defect densities due to many side chains formed. At lower temperatures, the rate of such unwanted side reactions become much lower relative to the desired polymerization reaction. As a result, the films prepared at lower temperatures have less defects and high conjugation and thereby have higher conductivities.

4. Conclusions

The factors affecting the formation and the in-situ conductivity of poly N-methylpyrrole were investigated. The current density and the temperature used during the polymerization play crucial roles in determining the structure and properties of the polymer film. The films prepared with low current densities and low temperatures seemed to be more perfect with higher conjugation and therefore have high conductivities compared to those of films prepared with high current densities or at high temperatures. The conductivity of PNMP films is also affected by the concentration of

improve the packing of the polymer and thereby result in increased conductivity.

5. Acknowledgements

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6. References

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Legends

- Fig. 1 Cyclic voltammograms of PNMP films prepared with different current densities (given on curves in $\mu\text{A cm}^{-2}$). Film thickness $0.25 \mu\text{m}$, electrolyte 0.5 M LiClO_4 , sweep rate 100 mVs^{-1} .
- Fig. 2 Conductivity measurements of the PNMP films prepared at different current densities. Film thickness $5 \mu\text{m}$, electrolyte 0.5 M LiClO_4 .
- Fig 3 Cyclic voltammograms of PNMP polymerized in different concentrations of LiClO_4 . Film thickness $0.25 \mu\text{m}$, synthesis current density $62.5 \mu\text{A cm}^{-2}$, sweep rate 100 mVs^{-1} . All voltammograms are obtained in 0.5 M LiClO_4 .
- Fig. 4 Variation of the conductivity of PNMP films with electrolyte concentration during polymerization. Film thickness $5 \mu\text{m}$, synthesis current density $62.5 \mu\text{A cm}^{-2}$.
- Fig5 Cyclic voltammograms of PNMP films with different anions. Film thickness $0.25 \mu\text{m}$, current density $62.5 \mu\text{A cm}^{-2}$, sweep rate 100 mVs^{-1} .
- Fig. 6 Conductivity variation of the PNMP films with different anions. Film thickness $5 \mu\text{m}$, current density $62.5 \mu\text{A cm}^{-2}$.
- Fig 7 Cyclic voltammograms of PNMP films obtained at different temperatures of the polymerization electrolytes. Film thickness $0.25 \mu\text{m}$, current density $62.5 \mu\text{A cm}^{-2}$, sweep rate; 100 mV S^{-1} .
- Fig. 8 Conductivity variation of the PNMP films electropolymerized using different electrolyte temperatures. Film thickness $5 \mu\text{m}$, current density $62.5 \mu\text{A cm}^{-2}$. Note the change in conductivity axis by a factor of 10 compared to figures 2, 4 and 6.

Fig 1:

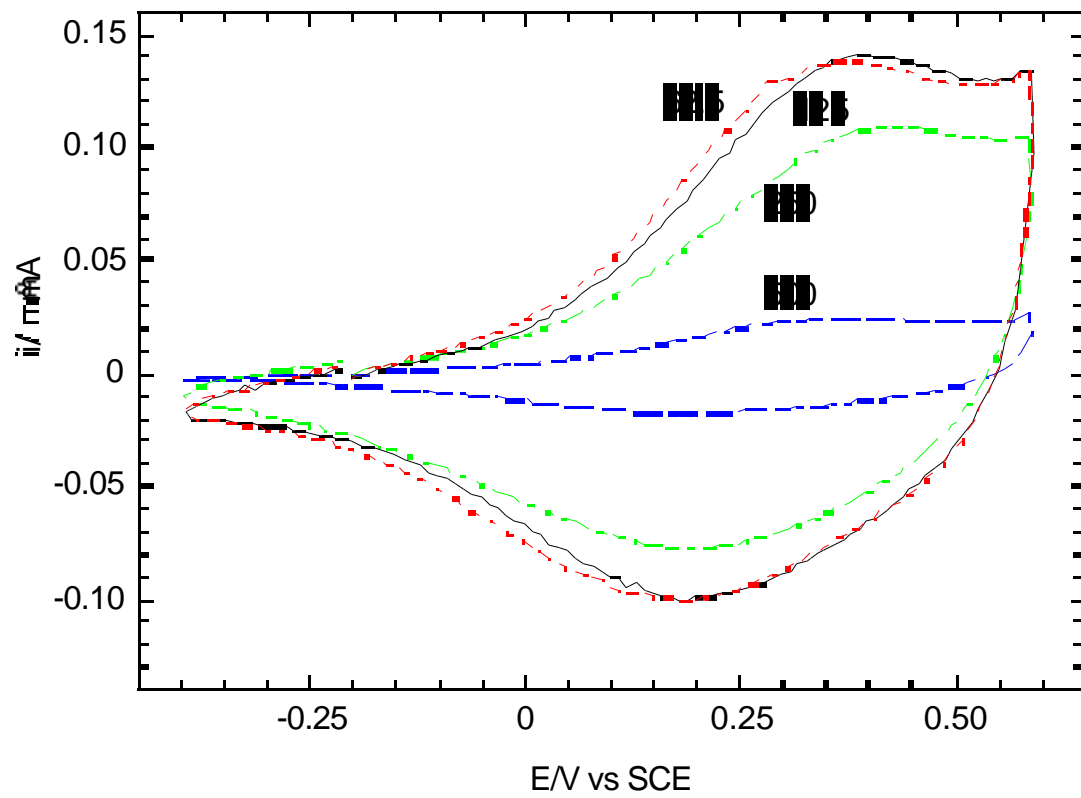


Fig 2:

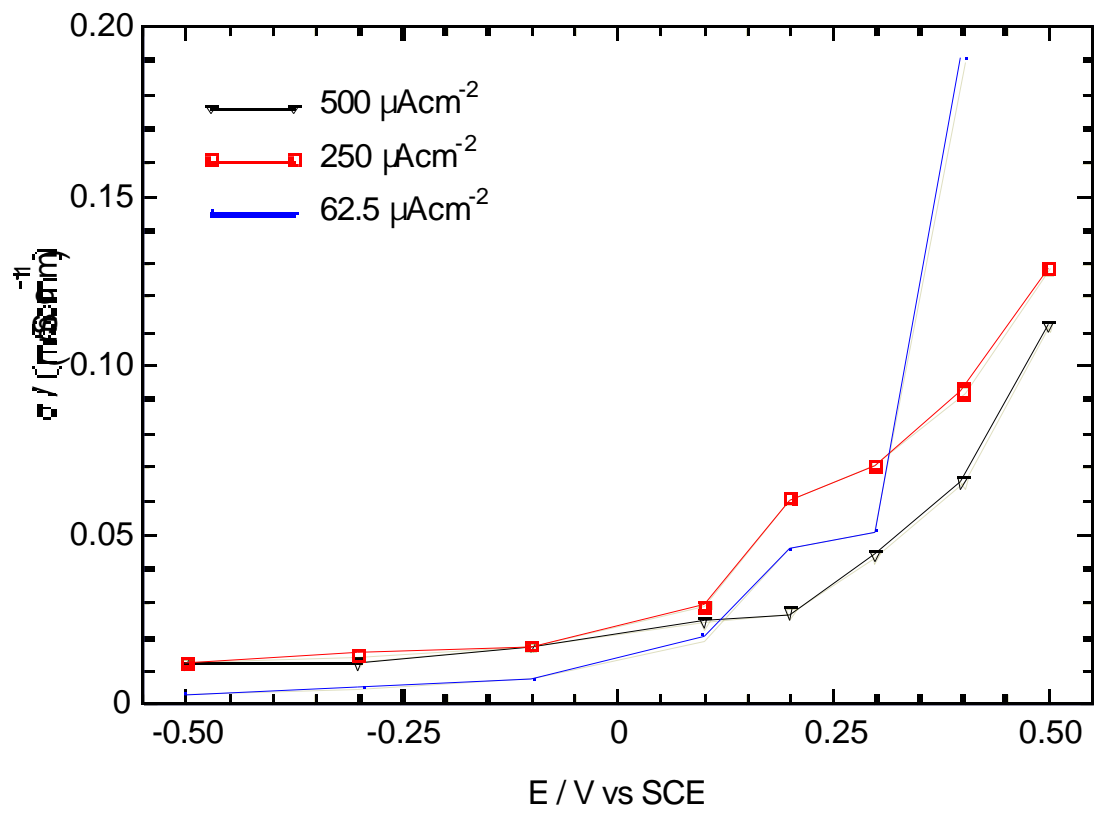


Fig 3:

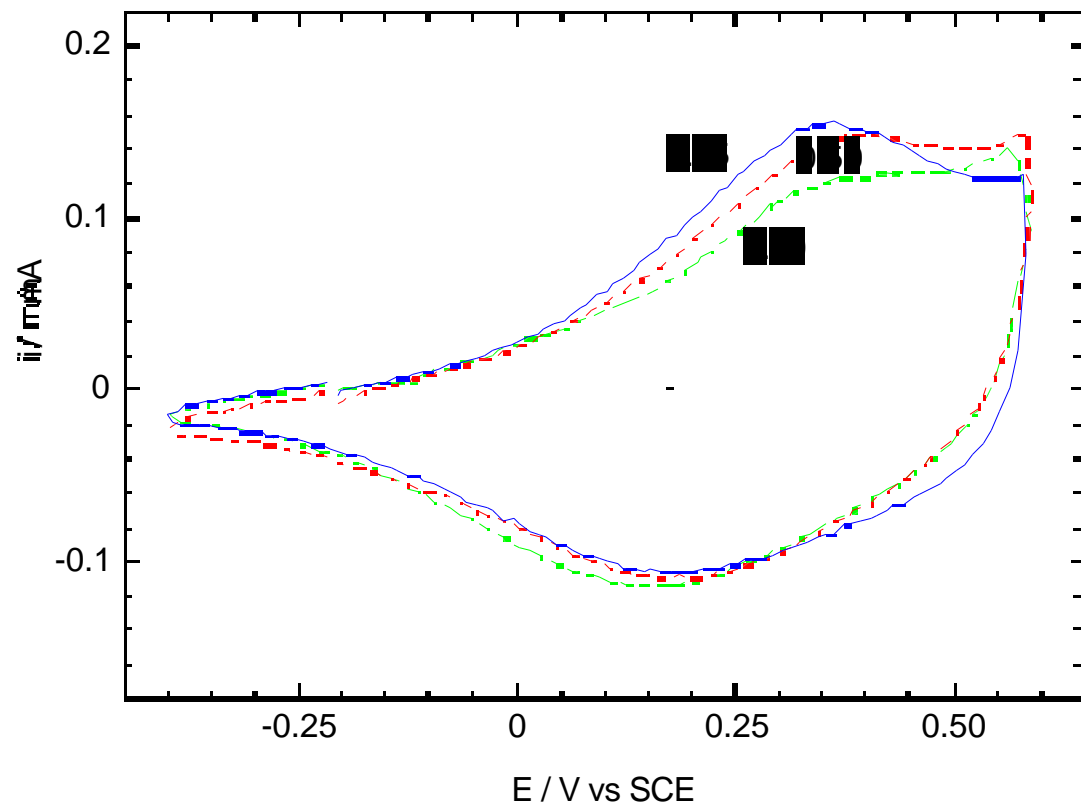


Fig 4:

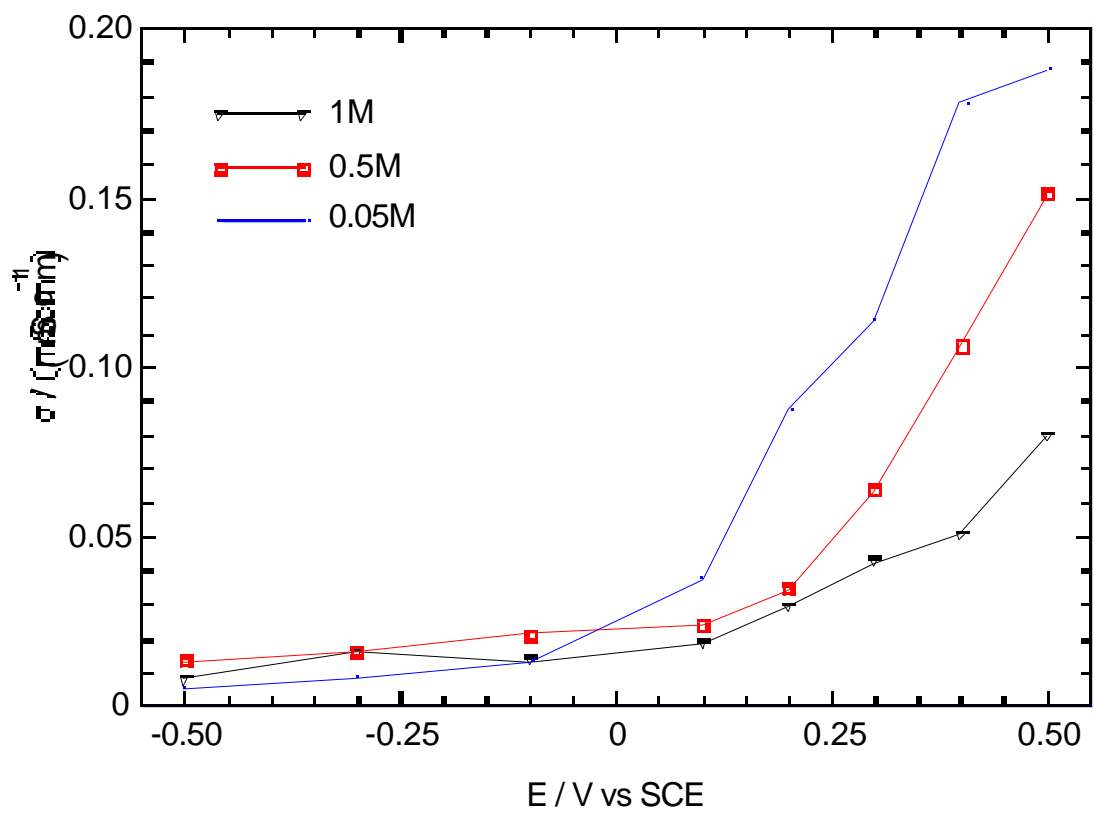


Fig 5:

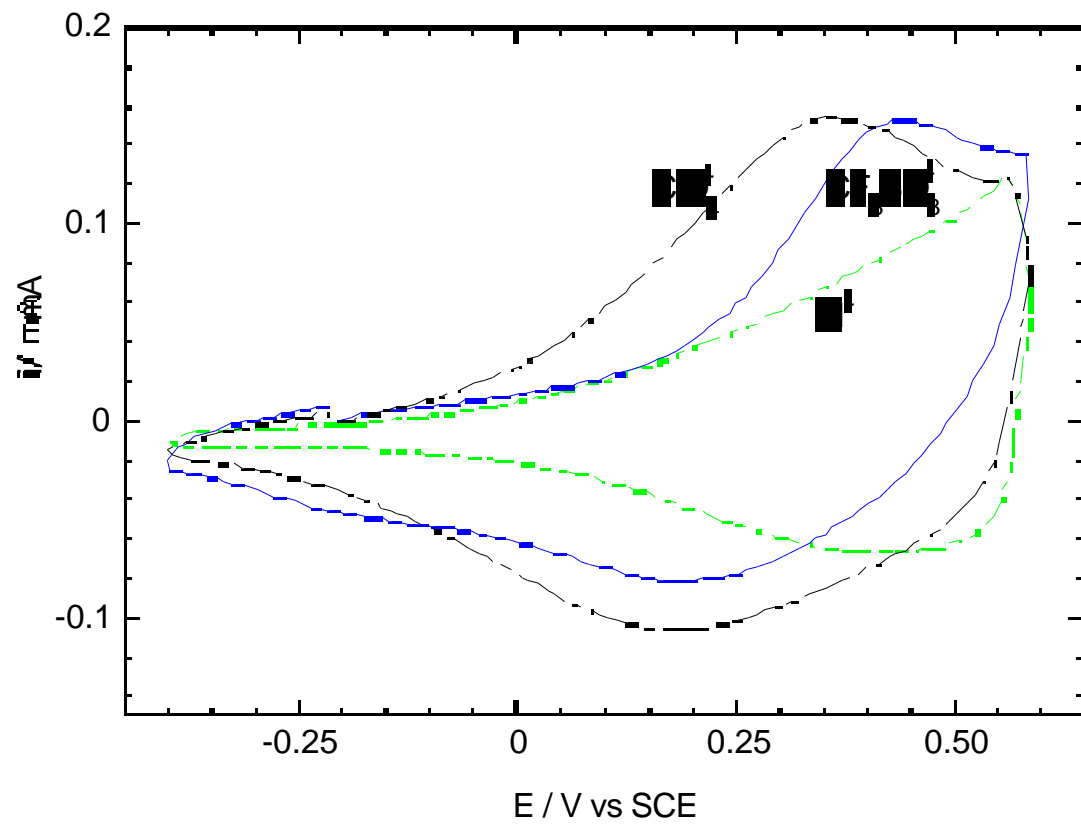


Fig 6:

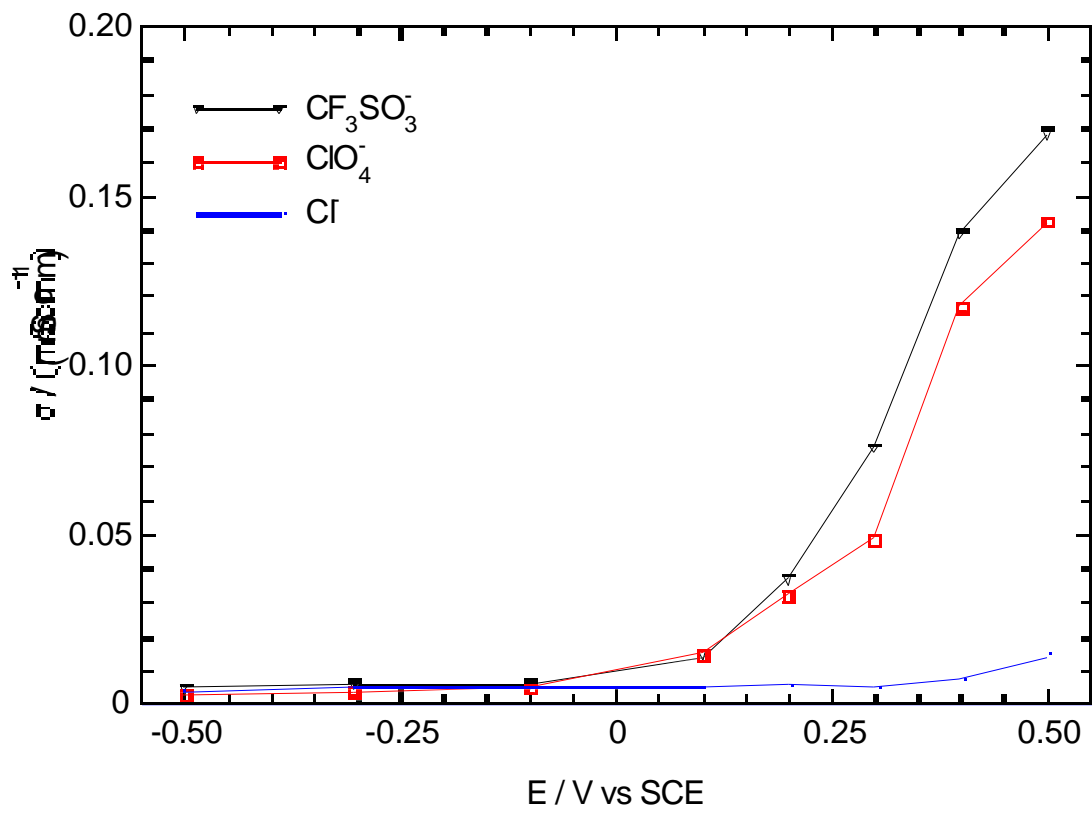


Fig 7:

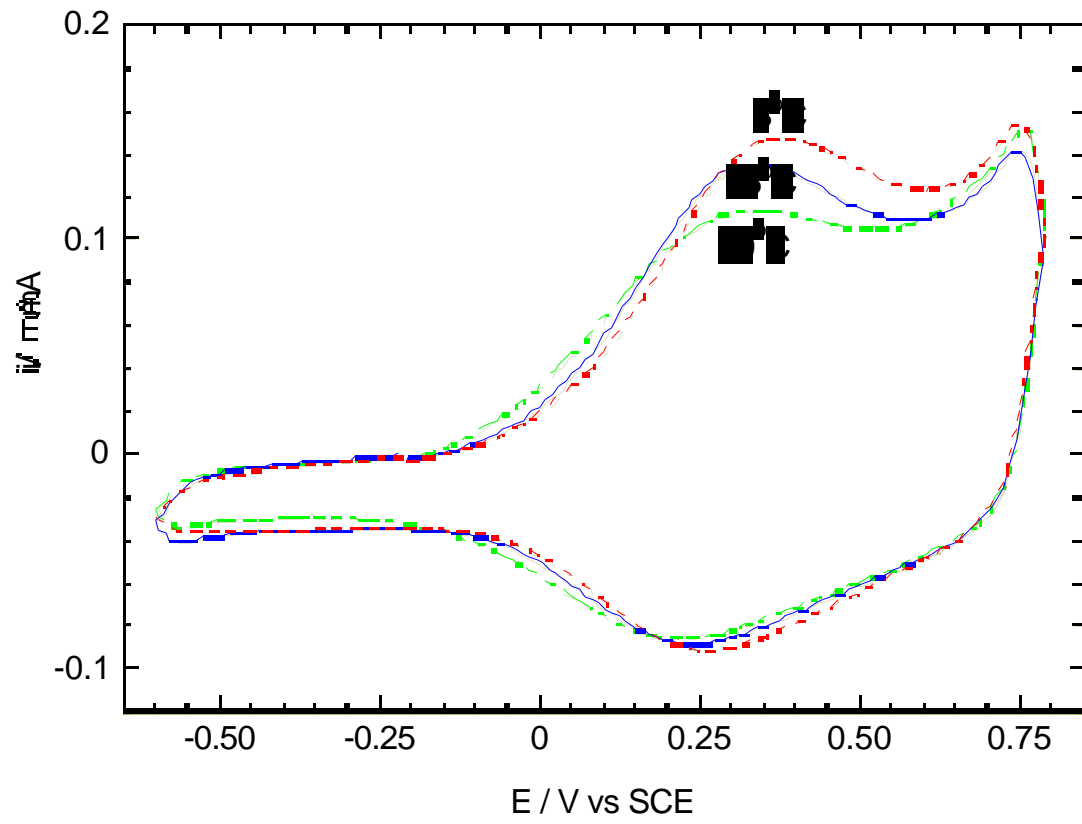


Fig 8:

