

In-situ Electrical Measurements of Conductive-Electroactive Polymers during their Redox Processes: A Case Study of Polypyrrole/p-Toluene Sulphonic Acid

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ABSTRACT

Cyclic resistometry, CR, is an in-situ resistance measurement which is applied during the electrosynthesis of polypyrrole/para toluene sulfonate and also subsequent to polymer growth. The resistance changes during cyclic voltammetry of the PPY/PTS characterise the effect of polymerisation and post-polymerisation conditions.

Key Words

resistometry, characterisation, conducting polymers, oxidation, reduction

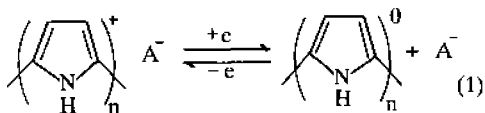
INTRODUCTION

To utilise the potential of conductive, electroactive polymers (CEPs) in sensor applications, it is necessary that processes occurring at the polymer solution interface are well characterised. It has previously been shown how crucial it is to characterise and control the dynamic nature of these polymers and the effect of incorporated counterions on their electronic and electrochemical properties [1-3]. To investigate the effect of polymerisation and post polymerisation conditions on the electrical and electrochemical properties of CEPs, polypyrrole para toluene

sulfonic acid was investigated as a case study in this paper.

The switching ability of conducting polymers such as polypyrroles between the reduced and oxidised states has attracted the immediate attention of energy technologists who realise the potential to be gained from lighter weight batteries and of those involved in electronics who realise that bistable polymer devices could be made in any shape or size. More recently, the importance of this switching behaviour has been utilised in sensing and membrane separations technologies

[4-6]. This process for polypyrroles can be described as:



Where A^- is PTS in our case. The importance of this electrochemical process has resulted in many studies on the subject. However, to date, the tools available to study the process have been limited. Only electrochemical techniques such as cyclic voltammetry, chronopotentiometry and chronoamperometry provide direct, in-situ information on the process. However, these techniques are only capable of monitoring the electrochemical processes (changes in potential or current flow) occurring. More recently an in-situ technique that does provide additional information has been developed. This technique has been denoted "Cyclic Resistometry", CR, which is based on applying a current pulse and measuring the potential between the reference and the working electrode which is related to the resistance of the system [7-8].

Examples of how this technique is useful in the study of even a simple system such as PPy/PTS are given below.

EXPERIMENTAL

All reagents were analytical reagent (AR) grade quality unless otherwise stated.

Pyrrole, sodium chloride, calcium chloride, lithium chloride and sodium para toluene sulfonate were obtained from Aldrich.

Instrumentation

A home made galvanostat was used for galvanostatic polymerisation. A bio analytical system (BAS) model CV-27 was used for potentiostatic and potentiodynamic electro-deposition. The resistometer was purchased from CSIRO (Division of Mineral Products), Melbourne, Australia. Data collection was carried out using a Macintosh computer.

Procedure

Electrodeposition was carried out in a three electrode system electrochemical cell using a Pt substrate as the working electrode and a Ag/AgCl as the reference electrode. A Pt electrode was also used as the counter electrode. Different techniques (potentiostatic and potentiodynamic) were employed in this investigation and the monomer solution contained 0.1M pyrrole and 0.025M PTS salt in Milli-Q deionised water otherwise stated. Resistance changes were simultaneously monitored during polymer growth by using the resistometer and CV 27 potentiostat. Resistometry after polymer growth was conducted in 1M NaCl supporting electrolyte unless stated.

RESULTS AND DISCUSSION

A. The effect of parameters involved during polymerisation on the polymer resistivity

The effect of thickness on the electrical properties of the polymer has been studied by using a potentiostatic method to grow polymers. This is a simple technique by which the polymer is grown at constant potential taking into consideration the different time in which we can grow polymers with different charges resulting in polymers with different thicknesses. As it can be observed in Figure 1, the thicker the polymer, is the more conductive it is at positive potentials (oxidised form). This is to be expected since by more polymer deposition we create a bigger surface area. In fact, we found that the bare electrode has a little bit more resistive background than the modified electrode in 1M NaCl [3].

On the other hand at negative potential less than -0.7volt, the thicker polymer is the less conductive it becomes. This can be explained by Fletcher's theory [9]. According to his model the conducting polymers can be simulated as an equivalent circuit which includes different impedance components in parallel and series forms. Two main components of this model are resistance of pores and resistance of the polymer itself. At the negative potential in which the polymer is almost fully reduced, the bulk polymer

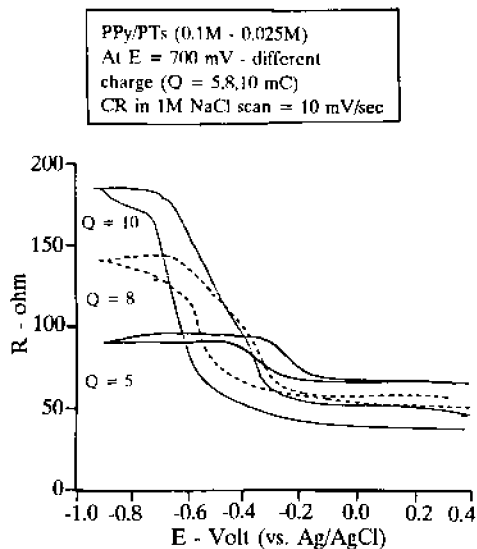


Fig.1. The effect of thickness on the resistance of the polymer.

Supporting electrolyte: 1M NaCl, Scan rate = 10 mV/sec.

Polymers are grown potentiostatically at E = 700 mV.

itself acts as an insulator and does not play any important role in the conductivity of the system. But the pores are a dominant factor for the conductivity. By making thicker polymer, the pores, which can be a simulated of series of resistors, become more resistive. In other words more resistors are involved in a series form in the thicker polymer by consuming more charge during growth. This results in a greater equivalent resistance of the pores.

The effect of thickness can also be studied by other electrochemical techniques like the potentiodynamic method. In this method the applied potential sweeps between two upper and lower potentials at a particular scan rate. Therefore, by using this technique we are able to make polymers with different thicknesses in two different ways:

- Keeping the number of sweeps constant and varying the scan rate.

The result for such an investigation has been plotted in Figure 2. By decreasing the scan rate, a thicker polymer is obtained since as there is more time for the monomer to be oxidised at its growth potential. Of course this results in more deposition on the surface of the electrode.

- Keeping the scan rate constant and changing the number of sweeps.

In this method, by using a scan rate of 100mV/sec and different sweep numbers such as 10, 20 and 50 a variety of PPy/PTS with different thicknesses were produced. By looking at Figure 3 one can see how the resistance of the polymer increases by increasing the sweep number. In fact increasing the sweep number causes more deposition as at each sweep more monomer is oxidised. By increasing the thickness of the polymer potentiodynamically similar changes to those of the potentiostatic method can be observed. This means in both cases the polymer becomes more resistive at its reduced form and more conductive at its oxidised form as it becomes thicker. However, the rate of change is different due to using two different techniques. As it can be seen for all results, the resistance of the system starts to decrease as we go to more negative potentials in the case of the polymers produced potentiodynamically. This is because with the potentiodynamic technique it is possible that some parts of the electrode are not covered by the polymer. This causes the reduction of water at the surface of electrode and creates H^+ which results in decreasing in the resistivity.

B. The effect of the parameters involved after polymerisation on the conductivity measurement.

Here the importance of the role of the supporting electrolyte and some other characterisation conditions on the relationship between redox reaction and polymer conductivity is shown. Both concentration and type of the supporting electrolyte effect the changes in the conductivity in the redox reaction. As the concentration decreases the driving force for ion

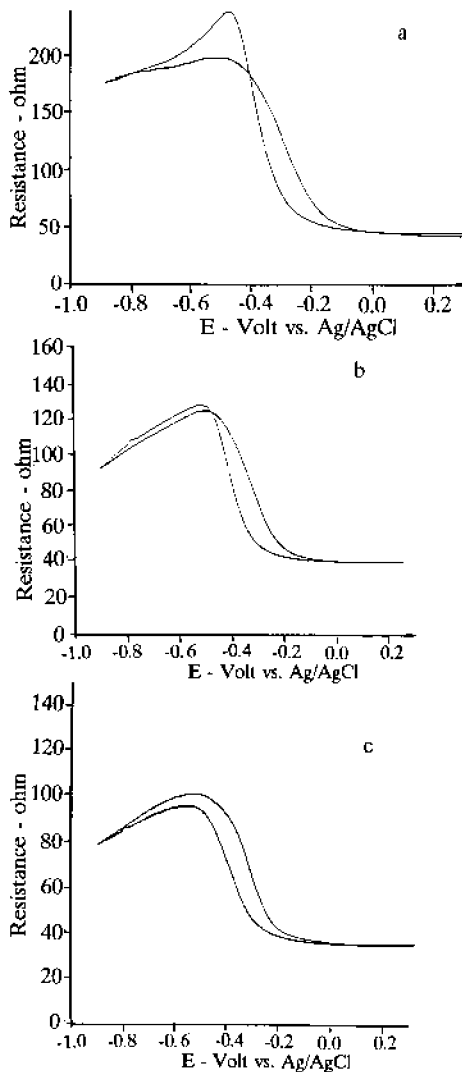


Fig.2. The effect of thickness on the resistance of the polymer.

Supporting electrolyte: 1M NaCl, Scan rate = 10 mV/sec.

Polymers are grown potentiodynamically between $E_1 = 0.8$ V and $E_2 = -1$ V. No. of sweeps = 10
 Scan rate = (a) 20 mV/sec, (b) 50 mV/sec, (c) 100 mV/sec.

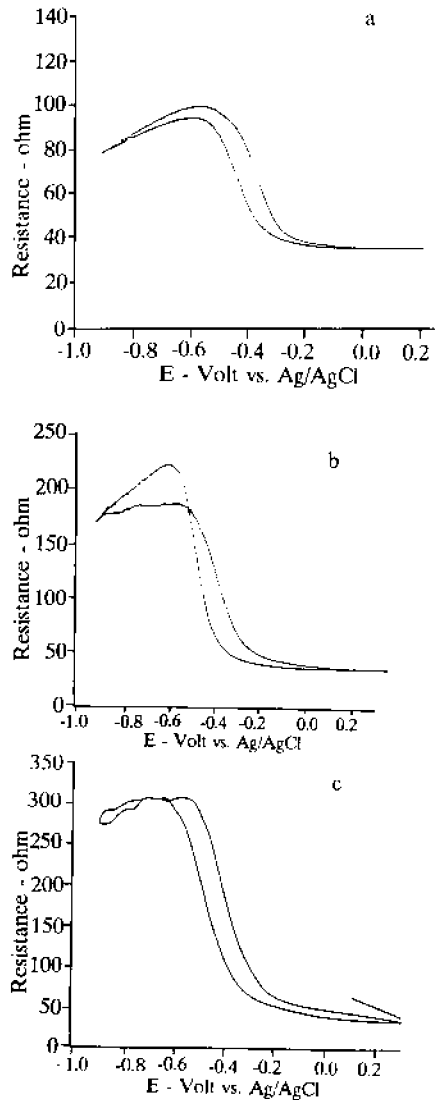


Fig.3. The effect of thickness on the resistance of the polymer.

Supporting electrolyte: 1M NaCl, Scan rate = 10 mV/sec.

Polymers are grown potentiodynamically between $E_1 = 0.8$ V and $E_2 = -1$ V. Scan rate = 100 mV/sec No. of sweeps = (a) 10, (b) 20, (c) 50.

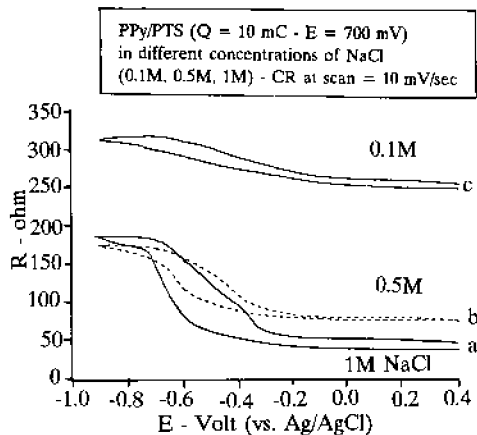


Fig.4. The effect of concentration of the supporting electrolyte on the resistance of the polymer.

Supporting electrolyte: (a) 1M NaCl, (b) 0.5M NaCl, (c) 0.1M NaCl, Scan rate = 10 mV/sec.

Polymers are grown potentiostatically at $E = 700$ mV and $Q = 10$ mC.

exchanges decreases during reduction and oxidation process. Therefore, smaller changes in the conductivity are expected (Figure 4). Smaller concentration results in a less conductive background. As discussed previously [10], the resistance measured is the combination of polymer resistance and that of the supporting electrolyte. Thus, the higher concentrated the solution, the higher is the value of conductivity.

Changing the cation in the supporting electrolyte gives very interesting results as far as the electronic properties of the PPy/PTS is concerned. By employing a double charge cation like calcium we observed more resistive materials (Figure 5). This cation could adhere to the anions in polymer and change the pore structure which results in more resistive pores. The figure reveals that the cation incorporation process induces a mechanism of resistance change different from that observed for anion expulsion. Given the well known chaotropic effects of different cations this is

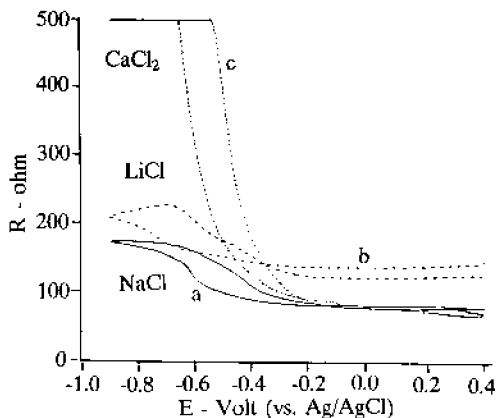


Fig.5. The effect of type of the supporting electrolyte on the resistance of the polymer.

Supporting electrolyte: (a) 1M NaCl, (b) 1M LiCl, (c) 1M CaCl_2 , Scan rate = 10 mV/sec.

Polymers are grown potentiostatically at $E = 700$ mV and $Q = 10$ mC.

understandable [11]. We also collected conductivity data by standard conductivity measurement for those three solutions used as supporting electrolytes in this cations study. These data are recorded in the following table.

Type of solution	Conductivity in 0.001 Molar of the solutions- $\mu\text{S}/\text{cm}$	Resistance-ohm at bare electrode at $E = 0.4\text{V}$
NaCl	29	122
LiCl	17	143
CaCl_2	74	80

As it can be seen with the two measurements, resistometry and standard conductivity measurement, calcium chloride is more conductive than the others. This information is useful for more detail discussion on the resistance changes in the redox reaction.

The effect of scan rate in characterisation study is the next factor to be discussed. In Figure 6 we see that by increasing the scan rate less changes

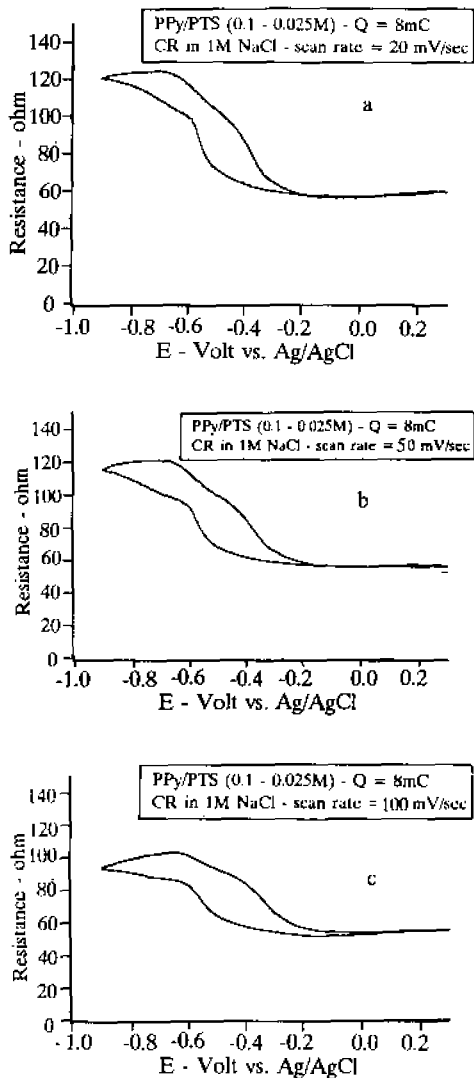


Fig.6. The effect of the scan rate on the resistance of the polymer.

Supporting electrolyte: 1M NaCl. Scan rate = (a) 20 mV/sec, (b) 50 mV/sec, (c) 100 mV/sec.

Polymers are grown potentiostatically at E = 700 mV and Q = 8 mC.

Chronoamperogram and chrono-resistogram for PPY/PTS (0.1 - 0.5M) during growth at E = 700 mV - Q = 5 mC

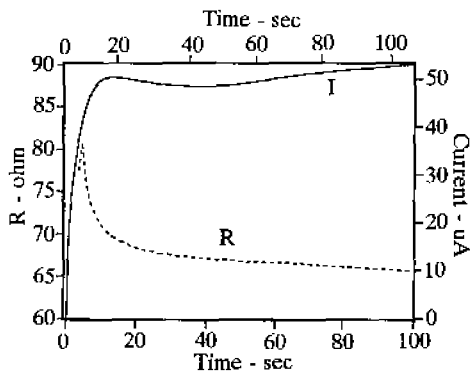


Fig.7. Current and resistance changes during the potentiostatic growth of PPY/PTS.

monomer solution: 0.1M pyrrole + 0.5M PTSNa
E = 700 mV time = 100 sec.

in the resistance occur by changing the polymer state from the oxidised form to the reduced form. This is expected because as the scan rate decreases there is more time for anions to move from the polymer to the solution and consequently less changes in conductivity can be observed.

At the end of this discussion it is essential to mention that it is difficult to monitor the resistance of the system in monomer solution while the salt concentration is so low, in our case, 0.025 M. However, to give an idea of how the changes occur during polymerisation we increased the concentration to 0.5M of PTS sodium salt in monomer solution. Figure 7 contains simultaneous current and resistance changes during potentiostatic growth. As expected, the resistance decreases during polymerisation due to increasing the surface area.

CONCLUSION

By in-situ resistance measurements, the kinetics of the electrochemical process occurring at the

interface of the modified electrode and solution can be characterised when used in conjunction with other conventional techniques. In-situ information on redox reactions may be obtained through the use of resistometry at real time in the polymers operational environment. This is important for applications of these polymeric materials in sensing technology.

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