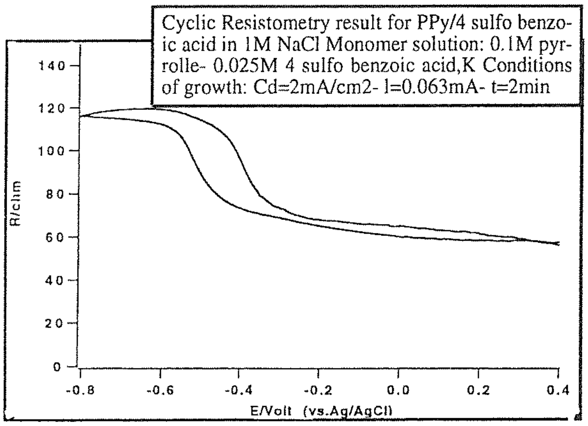
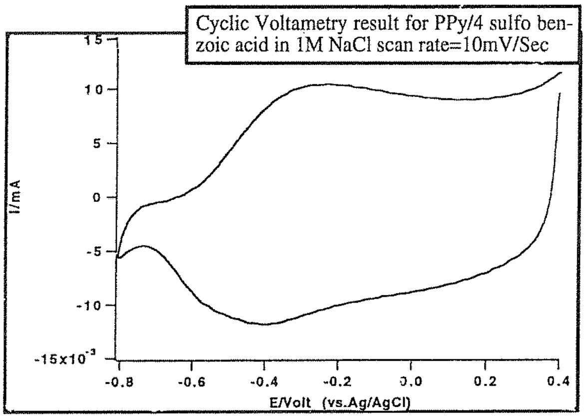


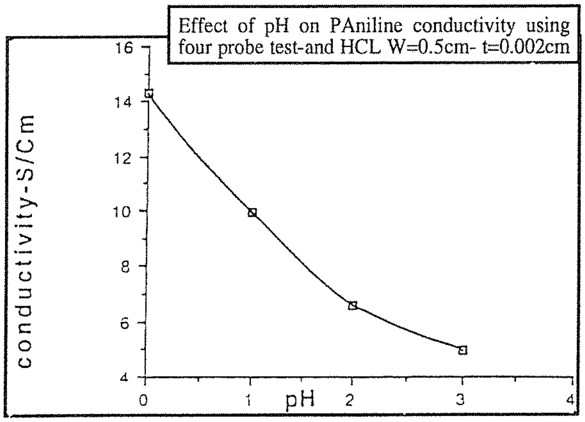
Cyclic Resistometry result for PPy/4 sulfo benzoic acid in 1M NaCl Monomer solution: 0.1M pyrrolle- 0.025M 4 sulfo benzoic acid,K Conditions of growth: Cd=2mA/cm2- I=0.063mA- t=2min

Fig (7-a)



Cyclic Voltametry result for PPy/4 sulfo benzoic acid in 1M NaCl scan rate=10mV/Sec

Fig (7-b)



Effect of pH on PAniline conductivity using four probe test-and HCL W=0.5cm- t=0.002cm

Fig (8)

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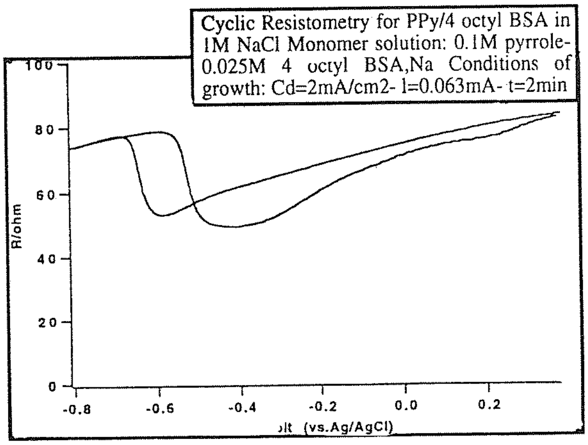


Fig (4-a)

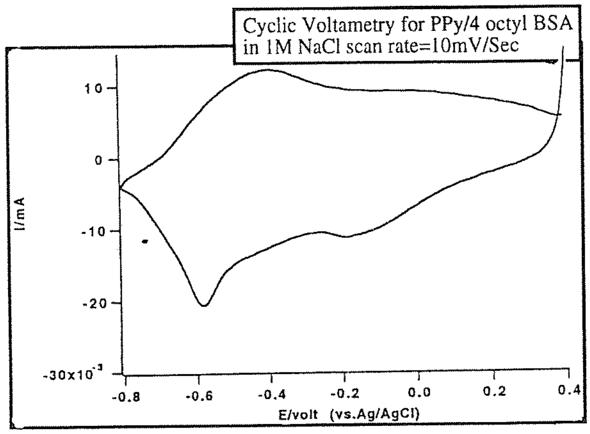


Fig (4-b)

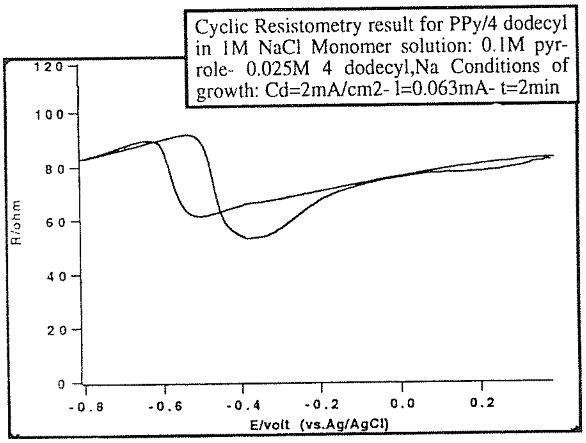


Fig (5-a)

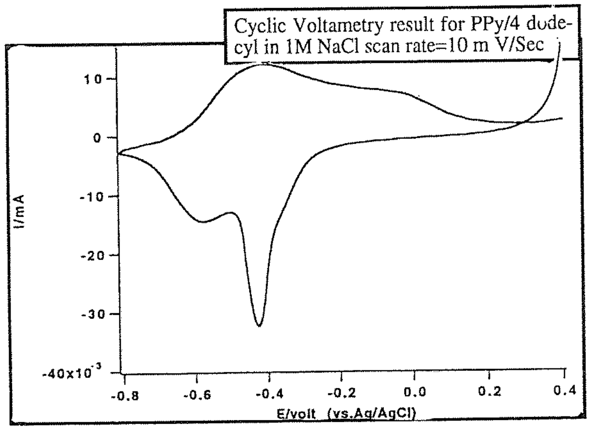


Fig (5-b)

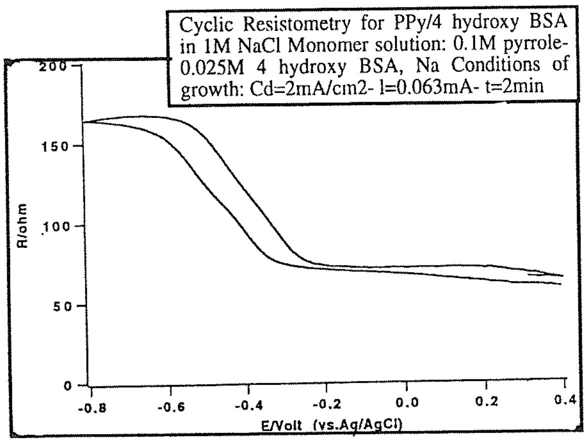


Fig (6-a)

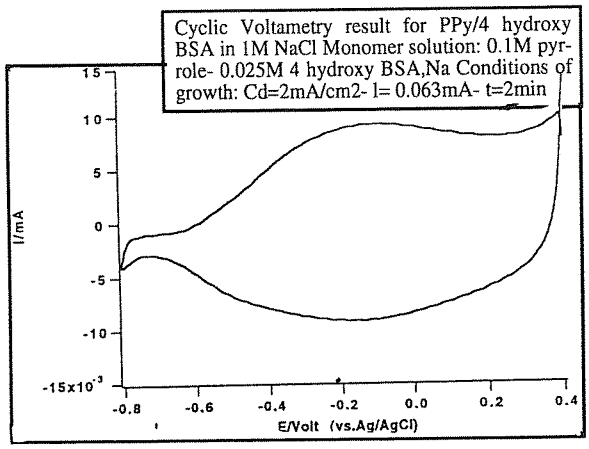
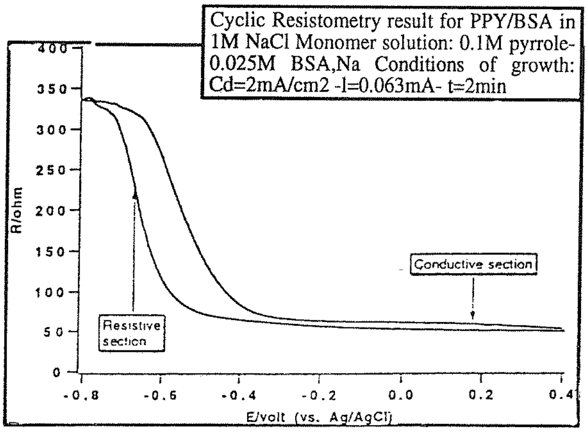


Fig (6-b)

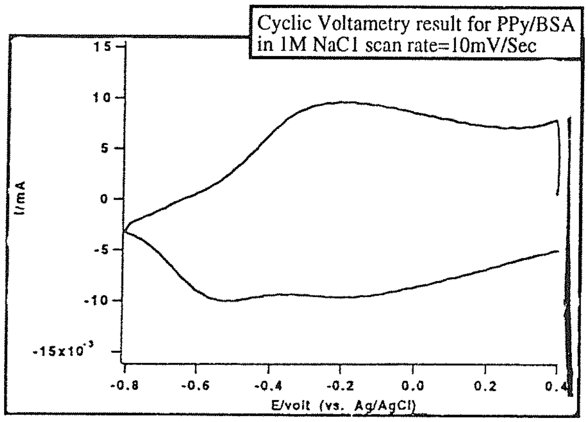
Conclusions:

Amongst the important behaviour of conducting polymers is their inherent sensing capabilities. This behaviour varies with different counterions, polymers and solution matrices. It has been demonsteated that by changing these parameters it is possible to make versatile sensors which can be used in different ranges of voltage and current. Further it has been shown that it is possible to create dual sensors by employing intelligent polymers.



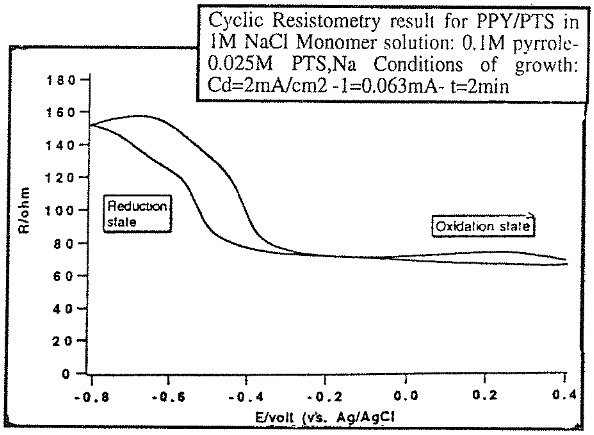
Cyclic Resistometry result for PPY/BSA in 1M NaCl Monomer solution: 0.1M pyrrole-0.025M BSA,Na Conditions of growth: Cd=2mA/cm2 -I=0.063mA- t=2min

Fig (1-a)



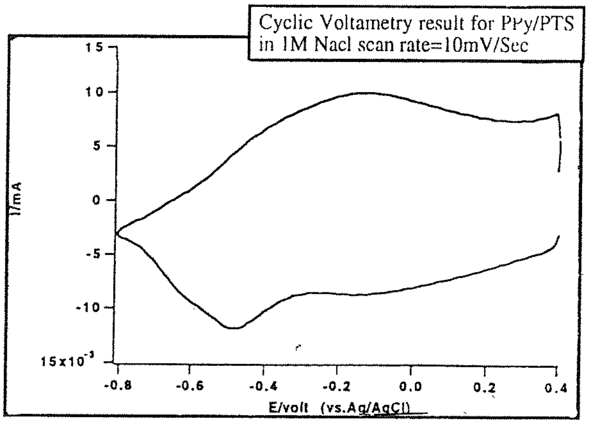
Cyclic Voltametry result for PPy/BSA in 1M NaCl scan rate=10mV/Sec

Fig (1-b)



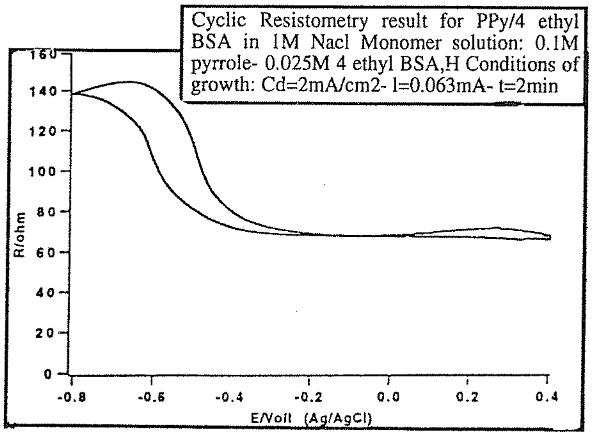
Cyclic Resistometry result for PPY/PTS in 1M NaCl Monomer solution: 0.1M pyrrole-0.025M PTS,Na Conditions of growth: Cd=2mA/cm2 -I=0.063mA- t=2min

Fig (2-a)



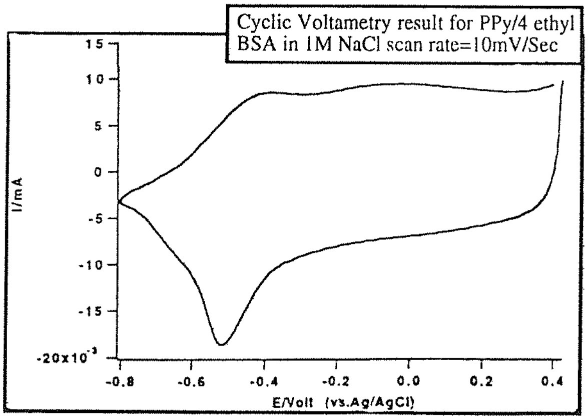
Cyclic Voltametry result for PPy/PTS in 1M Nacl scan rate=10mV/Sec

Fig (2-b)



Cyclic Resistometry result for PPy/4 ethyl BSA in 1M Nacl Monomer solution: 0.1M pyrrole- 0.025M 4 ethyl BSA,H Conditions of growth: Cd=2mA/cm2- I=0.063mA- t=2min

Fig (3-a)



Cyclic Voltametry result for PPy/4 ethyl BSA in 1M NaCl scan rate=10mV/Sec

Fig (3-b)

For all the above-mentioned counterions cyclic voltametry and cyclic resistometry results were plotted and are shown in Figures 1-7. Looking at the results for counterions No. 1 and 2, one can see how the polymer becomes more conductive through methyl substitution of the counterions in the para position. The maximum resistance of polypyrrole/benzenesulfonic acid is more than 300 ohm whereas the resistance of the polypyrrole/p-toluenesulfonic acid is 150 ohm.

This is very important in the switching application area when the amount of resistance, which is related to the current flow through the polymer as a response, is the main interest. It is also possible to make more a conductive polymer by adding another carbon to the counterion in the para position and by changing themethyl functional group to ethyl.

4-Octylbenzenesulfonic and Dodecylbenzenesulfonic acids showed quite surprising changes in the amount of polymer resistance over the selected range of potentials. These polymers can be employed as dual switches. In other words they can be switched between E=0.2 volt to E=-0.4 volt and between E=-0.4 volt to E=-0.8 volt. In the first potential range (0.2 to -0.4) when the potential changes from the more positive to the less positive the conductivity of this material increases. The behaviour within the second potential range (-0.4 to -0.8) is the inverse of this. This versatility is of extreme importance for electronic devices and their applications. Although these two counterion results are very similar to each other, there are some differences in the hysteresis areas of the cyclic resistommogram. The rate of changes in resistance between the positive and negative potentials differ between these two polymers.

The results for the 4-Hydroxybenzenesulfonic acid and the 4 Sulfobenzoic acid counterions indicate that a polymer can be made even more conductive with hydroxy and carboxy functional groups attached to the counterions. This suggests that hydrophilicity and hydrophobicity readily affect the counductivity.

B. Polyaniline

Polyaniline for conductivity studies in different media was made chemically as described in the literature [20-21]. The process of making polymer strips involved two different main stages: chemical polymerisation and casting on glass. The chemical polymerisation was carried out in a controlled temperature cell at T=-3 °C. Polymerisation was completed within 2 hours. The product was collected after filtration and washed four times with lM HCl. In the casting stage the blue polymer first was dissolved in NMP. To do this polymer powder emeraldine was added to the solvent very slowly with vigourous stirring. It has been suggested that the polymer should be treated with ammonium hydroxide to make the emeraldine base form. After such a treatment the colour of the polymer turned from deep blue to pale copper. In the next stage the polymer dissolved in NMP and the polymer solution was spread over a glass which already was rinsed with methanol and acetone. Then the glass covered with solution was dried at T=60 °C overnight. The glass was removed from the oven and was soaked in 1M HCl for 24 hours. the film was then seperated from the glass readily and dried in the oven at T=50 °C. The film was cut into strips with dimensions suitable for four point probe conductivity measurments [1-3]. the data obtained after treatment at the different pH are recorded in Figure 8.

Results and Discussion

According to the conductivity results. polyaniline can be used as a switch between two different pH's. Because the resistance of the polymer is great in the basic solutions this polymer is recommended as a acid-base sensor. According to the conductivity plot (Figure 8) polyaniline is very resistive at pH greater than 3. In other words, in basic media there is no current due to lack of conductivity of polyaniline in the basic environment whereas in acidic media it conducts, and thereby provides an analytical signal.

A. Polypyrrole

Instrumentation

Voltammetric data were obtained using a BAS CV27 Voltammograph (Bio Analytical Systems, Larayette, P.A.U.S.A). Data were collected using MacLab (Analog Digital Instruments, Sydney, Australia) interface and an Apple computer. A resistometer, developed at CSIRO Division of Mineral Products, Melbourne, Australia, was employed to measure the resistance of polymers.

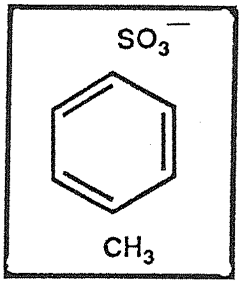
The electrochemical cell used during polymer deposition comprised a platinum working electrode (D=2mm), platinum gauze auxiliary electrode and a Ag/AgCl/ KCl_{sat} reference electrode. Two different sort of cells were designed for voltammetric and resistometric experiments in order to reduce IR drop by making the gap between the reference and working electrodes for the resistometry experiments very small. 1M NaCl was used as a supporting electrolyte in these experiments.

All polymers were deposited at the working electrode using a current density of 2 mA/cm^2 for 2 minutes. The monomer solution was 0.1 M pyrrole and 0.025 M counterions (dopants) in water. A home-made galvanostat was employed for this process.

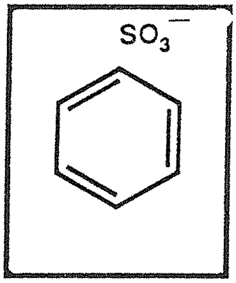
Results and Discussion

Benzenesulfonic acid and its six different para-substitued derivatives, as incorporated counterions, were used to investigate how the nature of the switching behaviour between oxidation and reduction states varied. These counterion structures are as follows:

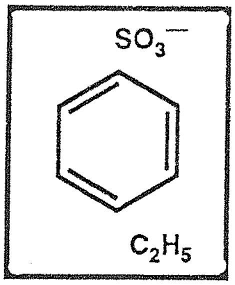
1. Benzenesulfonic acid



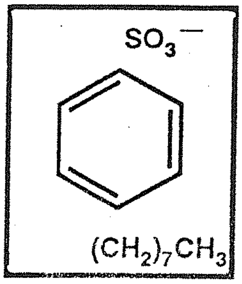
2. P-Toluenesulfonic acid



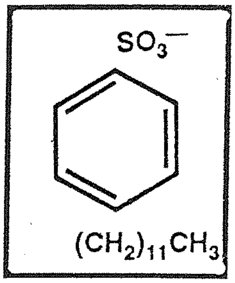
3. 4- Ethylbenzenesulfonic acid



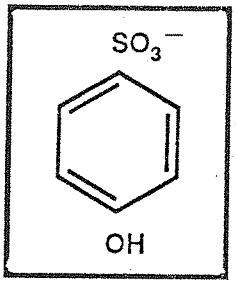
4. 4- Octylbenzenesulfonic acid



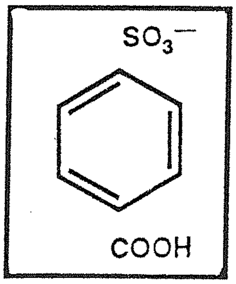
5. Dodecylbenzenesulfonic acid



6. 4-Hydroxybenzenesulfonic acid



7. 4-Sulfobenzoic acid



Technical Note

Novel Conducting Polymers as Versatile Electrochemical Sensors

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Abstract:

The switching properties of the solution-cast films of chemically prepared polyaniline and electrochemically prepared polypyrrole have been studied by means of a four-point probe conductivity method and a new in situ resistance measurement technique called cyclic resistometry. These two polymers, polyaniline and polypyrrole, can be used as electrochemical switches in the form of free-standing films or modified electrodes respectively. It has been suggested that the molecular structures of the counterions incorporated in the polymers play an important role in the electronic properties of conductive, electroactive polymers.

Introduction:

Conducting polymers such as polypyrrole can be switched between oxidised and reduced states. The redox process for this polymer is usually described as follows:

$$\underset{\text{Oxidised form}}{PPy^{+}C^{-}} \rightleftharpoons \underset{\text{Reduced form}}{PPy^{\circ} + C^{-}}$$

The reduced form of this polymer is less conductive than its oxidised form. There are many references which describe dry conductivity measurements for conducting polymers with the four point probe technique [1-3]. There are however, few in situ conductivity measurement studies for such as these materials [4-5].

A new technique has recently been developed to monitor the in situ resistance and has been employed for conductive electroactive polymers [6-11]. This technique allows electrochemists to measure the in situ resistance of a polymer during cyclic voltammetry in a conventional electrochemical cell. This method has been employed to introduce polypyrrole as a flexible electrochemical switch which can be used between two appropriate voltages in the less conductive and more conductive regions of the polymer. Polyaniline, a black conductive electroactive polymer, has been examined for many years and obtained by both chemical [12-13] and electrochemical methods. [14]

Conductivity of polyaniline, unlike polypyrrole, depends on not only the degree of oxidation but also the degree of protonation [15-17]. As a result, this polymer has been used for PH sensing [18-19]. In this paper it is described how polyaniline can behave as another type of acid-base form.

Experimental

All reagents were of analytical grade quality unless otherwise stated. Pyrrole and aniline were obtained from Sigma and redistilled prior to use. Other chemicals also obtained from Sigma unless otherwise mentioned. Ammonium persulphate and ammonium hydroxide were supplied by BDH chemicals. 1 methyl 2 pyrrolidinone (NMP) was bought from Aldrich. All solutions were made up in deionised (Milli-Q) water. Nitrogen was used for deoxygenation whenever required.