

In-Situ Cyclic Voltammetry and Cyclic Resistometry Analyses of conducting Electroactive polymer membranes

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ABSTRACT: Organic conducting polymers are usually used as electrode deposited film, powder or free standing films. The electrochemical properties (e.g. electroactivity) of conducting polymers are usually studied as very thin deposited films (thickness < 1 micron). In this research, a special cell design was employed for simultaneous characterization of electroactivity and resistometry of the conducting electroactive polymers prepared as free standing film or membrane. PPy membranes doped with some benzene sulfonates were synthesized electrochemically, then the electrical conductivity and electroactivity of the films was measured after synthesized.

Key words: Polypyrrole, electropolymerisation, electroactivity, cyclic resistometry, cyclic voltammetry.

INTRODUCTION

Polypyrrole conducting polymers are easily synthesized using a broad range of electrolytes (as dopant) from aqueous and non-aqueous solvents electrochemically [1, 2]. Among the conducting polymers known to date, ones based upon PPy have attracted special interest because of their high conductivity (10^1 – 10^3 Scm^{-1}), their ease and high flexibility in preparation, high environmental and thermal stabilities and good mechanical properties. The electrical conductivity of PPy is the product of two important factors, the number of carriers (e^- or holes) and charge carrier (polaron and by polarons) mobility. The positive charges created on the polymer backbone (commonly termed polarons) are the charge carriers for the electrical conduction. Higher mobilities will occur with more crystalline, better oriented, defect free materials. The bipolaron model has been shown to provide a coherent and unified picture of the properties of doped conducting

polymers and the possibility of a small band gap has been pointed out.

In order to prepare PPy, the monomer is first dissolved in a salt solution (where the electrolyte is highly dissociated and which are slightly acidic) with low nucleophilicity and solution resistance. When the solvent is nucleophile, a mild acidic condition is preferred for electropolymerisation. Oxidation of pyrrole yields cationic charged polymer products with incorporated anions. During polymerization of pyrrole, electroneutrality of the polymer matrix is maintained by incorporation of anions (called dopant) from the reaction solution, corresponding to one anion for every 3-4 monomer units, making up 30-40% of the final weight of the polymer depending on the type (size, charge) of the dopant anion. The overall electropolymerisation of polypyrrole can simply be shown as in Figure 1:

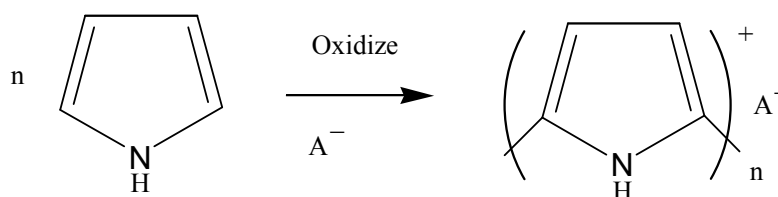


Fig. 1 Overall polymerization reaction of polypyrrole conducting polymers

Where A^- is the counterion incorporated into the polymer during polymerization in order to achieve electroneutrality [3]. A counterion (in this case an anion, typically termed a dopant anion) stabilises the charge on the polymer but is not very mobile within the dry material. Thus these polymers are truly electronic and not ionic conductors. Electropolymerisation of PPy can be carried out using different techniques including potentiostatic, galvanostatic and potentiodynamic (e.g. pulsed potential). More reproducibility in synthesis is normally obtained using galvanostatic method. Final properties (e.g. conductivity, mechanical) of the resulted polymer are dependent on various parameters such as preparation or synthesis conditions (e.g. technique of synthesis, current density or potential of electrodeposition, temperature, solvent, thickness of the film, nature of dopant, and electrodes). Even a minor change in synthesis conditions may result in a great change in the final properties of the polymer product. For example we have frequently observed that even the cell design and geometry or configuration and the sequence of deposition all can affect the quality of the product. Therefore, it is not easy to optimize all of these parameters. For example it was frequently observed that during preparation of polymer membrane from a single cell, the first grown polymer films or membrane showed higher conductivity than the others. The cell solution is colored after a few depositions, which is mostly due to the soluble oligomers produced during polymerisation. Trapping of these unwanted byproducts into the polymer matrix is believed to decrease the conductivity and mechanical properties of the prepared polymer. Multicharge anions are not usually suitable or preferred dopants because of disturbance of charge balance in polymer and also their higher nucleophilicity of the anions with increasing the charge. As a result poor quality of the polymer with regard to electrical conductivity and electroactivity, the two basic properties of these materials are obtained which is not desirable.

PPy conducting polymer and can also undergo good reversibility between its conducting (oxidized form) and insulating state (reduced or neutral form). Electroactive behaviour of the PPy is unique because the redox of polymer is accompanied by both electron and ion exchange properties as well as a change in the electrical properties of the polymer from insulating (reduced) to an electrical conductor (oxidized) forms as shown in Figure 2. Polypyrrole conducting electroactive polymers undergo ion exchange during oxidation/reduction process for maintaining charge balance in the polymer. The ion exchange properties of these polymers during redox reaction proposed many applications such as drug release, sensors, rechargeable batteries and controlled potential separation [4-8]. Cyclic voltammetry (CV) technique has been widely used for measuring the electroactivity of conducting polymers [9]. The nature of ion exchange is also dependent on the size of the dopant [9-11].

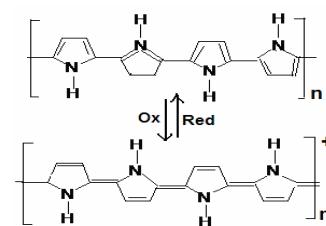


Fig. 2 Neutral and oxidized redox states of PPy.

EXPERIMENTALS

Pyrrole (obtained from Sigma) was used after distillation. Electropolymerization was carried out in aqueous solution. Electropolymerization was carried out galvanostatically using a current density of 2 mA/cm^2 , from a solution containing 0.2M pyrrole as monomer and 0.05M of sodium salts of p-toluene sulfonate (PTS), p-hydroxybenzene sulfonate (HBS), and p-dodecylbenzene sulfonate (DBS) as dopant electrolytes in distilled water. The time of polymerisation was 12 min. A single compartment electrochemical cell employing a three electrode system was used for preparation of ppy membranes [10]. Reticulated vitreous carbon (RVC), a carbonaceous, chemically inert conducting material with a large surface area was used as the auxiliary electrode. Mirror finished stainless steel plate was used as the working electrode, and a silver/silver chloride reference electrode was used as reference electrode for monitoring potential of working electrode.

The electrolyte and monomer solutions were prepared freshly and the cell solution was deoxygenated using high purity nitrogen gas before electropolymerization. The electrode coated by polymer was peeled from the electrode after soaking in distilled water for 15 minutes using a sharp blade. The membranes washed thoroughly with distilled water in order to remove any remaining monomer, electrolyte, and any impurities such as oligomers and finally dried at room temperature. The thickness of the polymer was 6 microns.

Instrumentation

A Princeton Applied Research (PAR) potentiostat/Galvanostat Model 363 was employed for electropolymerization. Electrical stimuli were applied to the polymer via ring shaped metal contacts (stainless steel). A Resistometer was used for the in-situ measurement of the resistance changes of polymers during oxidation/reduction. A solution of 0.2 M KCl was used as supporting electrolyte for CV and CR analyses. Cyclic voltammetry experiments (CV) were carried out using a Bio-Analytical Systems (BAS) 100A Electrochemical Analyser, an Electrolab, or a BAS CV-27 with the MacLab and a recording system (Macintosh computer). The electrochemical cell used for characterization of the polymer membrane is shown in Figure 3. Electrical stimuli were applied to the polymer membrane via metal contacts (ring shaped stainless steel).

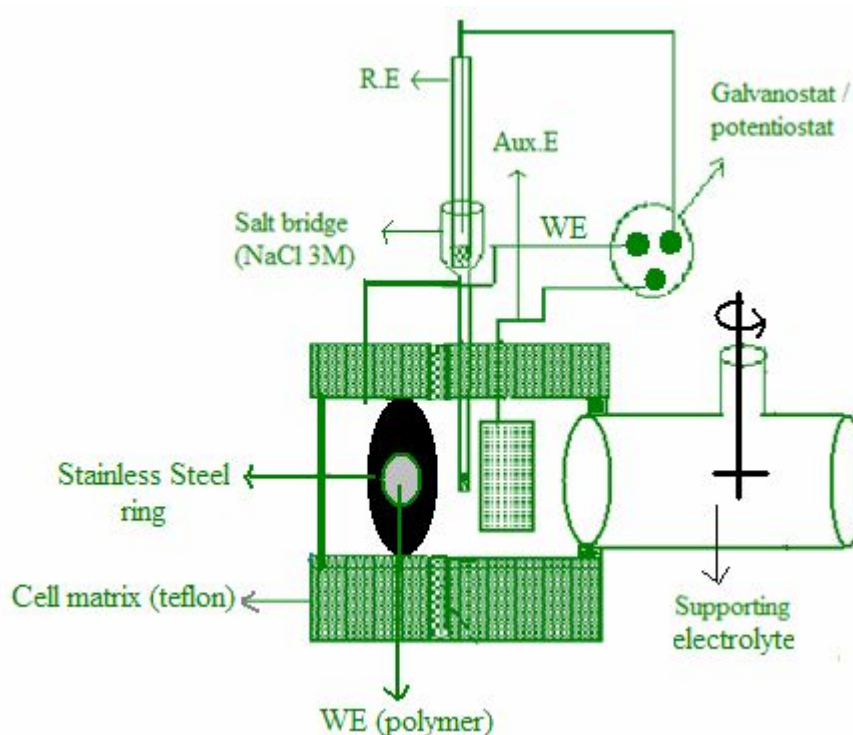


Fig. 3 Electrochemical cell set up used for in-situ cyclic voltammetry and resistometric characterizations of conducting polymer membranes.

RESULTS AND DISCUSSIONS

The cell design showed in Figure 3 permits the polymer to be characterized for its electrochemical properties as free standing films. Electroactivity, one of the most important properties of conducting polymers is usually determined as a thin film coated on the surface of electrodes such as glassy carbon or platinum. However; in some applications of these polymers such as membrane separation, the

polymer is used as free standing films, so it is needed to be characterized as it is applied. Simultaneous in-situ CV and CR recorded for PPy/PTS membrane is shown in Figure 4.

Resistometry was used to measure the resistance changes of the polymer as it is switched between the oxidised and reduced states (Fig. 4). Using these techniques the suitable switching potentials can also be ascertained.

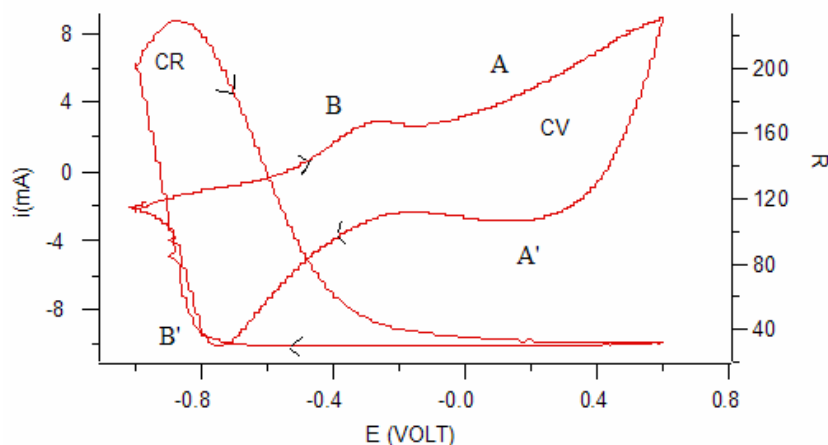


Fig. 4 Simultaneous CV and CR of PPy/PTS membrane. Scan rate = 5mV/sec. The film thickness was 6microns. Resistance (ohm) was measured using a resistometer.

The redox peaks labelled A/A¹ and B/B¹ is attributed to anion and cation movement respectively. The cyclic voltammograms (CV) of electropolymerised polypyrrole revealed the normal oxidation/reduction processes according to:

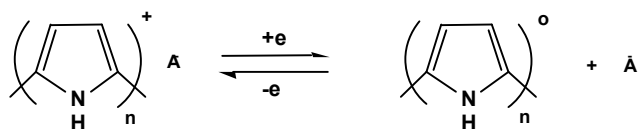


Fig. 5: Redox behaviour of PPy conducting electroactive polymers

The auxiliary electrode reactions, during the redox reactions of polymer at the working electrode, will be the reduction of water or oxidation of water. The electrochemical reaction of PPy involves the transport of ions in and out of the polymer in order to compensate the cationic nature of oxidised polymer [9]. Therefore, the redox reaction of PPy involves both electron-transfer reaction and mass transport [11]. As our CV analysis shows, the peak separation and broadening increases with increasing the thickness. Since the redox reaction of the film becomes more difficult, as the thickness increases. Well defined redox peaks are usually observed when a thin electro deposited film is analyzed. In this work it was also found that in spite of the great differences in the surface morphology of the growth (porous structure) and plate side (very smooth) in PPy films, the CV data obtained from both sides of the polymer did not show any

significant differences. In resistometry, the resistance changes of polymers may be measured as the potential of the electrode is varied [12]. This new technique allows resistance changes during doping/undoping to be measured in-situ. Pulse resistometry analysis of PPy/PTS membrane is shown in Figure 6.

As our analysis shows, the resistance of polymer increases when the polymer is switched to negative potentials (reduction) and back to its initial value upon subsequent oxidation. The increase in resistance is attributed to the changing of PPy from oxidised (PPy⁺) form to reduced (PPy⁰) which is accompanied by anion expulsion and/or cation incorporation. The large increase in resistance of the polymer occurs at a potential where the cation insertion peak appears and the resistance decreases as the cation is expelled. The resistance changes with potential is reversible if reasonable anodic potentials is applied ($E < 1.0V$). At anodic potentials more positive than 1.0V will result to an irreversible conductivity or electroactivity decay [9, 12].

CONCLUSIONS

Electrical conductivity of PPy films is strongly affected by the nature of its electrolyte dopant solution used for preparation. The cell design introduced in this paper make it possible to in-situ analyses of cyclic voltammetry and resistometry (pulsed or cyclic) of conducting electroactive polymers prepared and used as free standing films or membranes. Therefore, the proper potentials needed to be applied on the polymer sample used as stand alone membrane in a specific application can be ascertained using the introduced cell design.

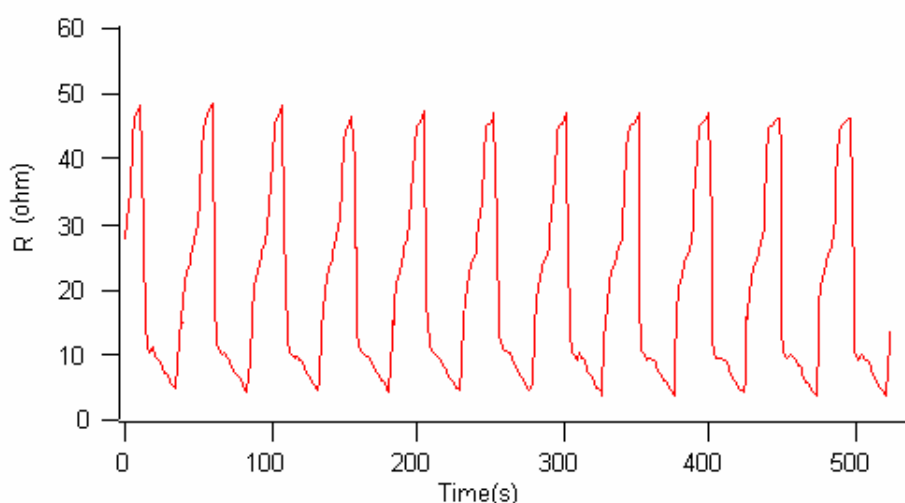


Fig. 6: The resistance changes (Ohm) recorded for PPy/PTS membranes during application of pulse potentials (pulse width=25sec). Electrochemical cell used was as shown in Figure 3. Pulsed potential applied were +0.6 V and -1.0 V. 0.2 M KCl was used as supporting electrolyte.

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