

Study of Ion Mobility Characteristics and Morphology of some Electrochemically-Synthesised Polypyrroles

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Abstract: This paper reports the diffusion coefficients of various dopant counter-anions into electro synthesised polypyrrole films, the cyclic voltammetry behaviour of the doped polymers and the effects of the electrolyte on the morphology of the polymer. The diffusion properties of electrochemically-prepared poly (N-dodecylpyrrole) and polypyrrole films were investigated in electrochemical cells containing lithium perchlorate, tetra methyl ammonium chloride and sodium dodecyl benzene sulfonate, and the effects of the size of the ions on their diffusion coefficients are discussed.

Keywords: Polypyrrole, Cyclic Voltammetry, Dopant Diffusion.

I. INTRODUCTION

Among conducting polymers, polypyrrole is one of the most extensively studied because the monomer (pyrrole) is easily oxidized, water-soluble and commercially available. Polypyrrole presents several advantages including environmental stability, good redox properties and the ability to give high electrical conductivities. Since pyrrole has a relatively low oxidation potential, electro polymerisation can be carried out in aqueous electrolytes, which is not possible for thiophene or benzene [1-3].

The ion exchange behaviour during the charging and discharging processes of conducting polymer electrodes has been investigated in recent years [4,5]. The kinetics depends on many factors such as polymerisation conditions [4,6] and the type and size of the counter-ions incorporated during the polymerisation process. In addition, the thickness of the polymer film has a remarkably large effect on the ion exchange [7].

The diffusion of dopants into conducting polymers can be measured electrochemically. The transport of ions into or out of a film can be followed by passing a short current pulse to create an excess of dopant counter-ions at the surface of a film immersed in an electrolyte solution. By following the relaxation of the surface potential as the concentration of counter-ions returns to equilibrium throughout the polymer, it is possible to determine the diffusion kinetics. A plot of working electrode potential versus $(1/\sqrt{\text{time}})$ has a linear region; its slope can be used to calculate the diffusion coefficient [8].

During the equilibration, a plot of electrode potential, E , against $t^{-1/2}$ should follow a straight line if the diffusion behaviour is governed by Fick's law. As a convention, if the polymer electrode is made more positive, the process would be called 'doping' and the potential becomes more negative in 'dedoping'. The following expression is used for the estimation of the diffusion coefficient for the ions into and out of the electrode material:

$$\exp\left(\frac{(E_t - E_0)F}{RT}\right) - 1 = \frac{IP}{(1-y)FAC_0\sqrt{\pi Dt}}$$

For small potential changes, a plot of $(E_t - E_0)$ versus $t^{-1/2}$ follows a straight line of slope S , given by:

$$S = \frac{IPRT}{(1-y)F^2AC_0\sqrt{\pi D}}$$

from which:

$$D = \frac{I^2P^2R^2T^2}{(1-y)^2F^4A^2C_0^2S^2\pi} \text{ (cm}^2\text{s}^{-1}\text{)}$$

where I is the strength of the current pulse (A), P is the duration of the pulse (s), R is the universal gas constant ($8.314 \text{ J mol}^{-1}\text{K}^{-1}$), T is the experimental temperature (K), F is Faraday's constant (96487 C mol^{-1}), A is the area of the polymer coated electrode (cm^2), C_0 is the dopant concentration in the polymer film (mol cm^{-3}), $(1-y)$ is the concentration correction factor and E_0 is the final equilibrium potential of the electrode [9].

This method is preferred because, while measuring diffusion, no current is applied through the electrode material. As a result, no correction has to be made for electron transfer kinetics or variable ohmic (IR) potential differences.

II. EXPERIMENTAL

A. Materials and Apparatus

Pyrrole 98% (Sigma Aldrich), used for the synthesis of PPy films, was purified by distillation over calcium hydride under vacuum and stored in the dark at low temperature. 1-bromododecane 97%, 1,6-dibromohexane 96%, potassium t-butoxide 95% were also obtained from Sigma Aldrich. The electrolyte salts used were of reagent grade: sodium dodecyl benzene sulfonate (Acros), methyl orange (Alfa Aesar) aluminon (Lancaster), xylenol orange (Fluka), tetrabutyl ammonium perchlorate (TBAP) (Aldrich).

The monomer N-dodecylpyrrole was synthesised using a previously-reported method [10]. Electrochemical polymerizations, diffusion and cyclic voltammetric

measurements were performed in a one-compartment cell with three electrodes at room temperature with a Uniscan Potentiostat-Galvanostat P580. A calomel reference electrode, a platinum disk or wire working electrode and a stainless steel counter electrode were used for the preparation and electrochemical investigation of the properties of polypyrroles. Polymer films were deposited on platinum wire and the scanning electron micrographs were obtained with a SEM Zeiss EVO 50 instrument.

B. Cyclic voltammetry of polypyrroles films

Polypyrrole and poly (N-dodecylpyrrole) were electrochemically prepared from aqueous and non-aqueous solutions of 0.1M monomer in 0.1M electrolytes (NaDBS, lithium perchlorate, aluminum, xyleneol and methyl orange) deoxygenated by nitrogen bubbling for 15 min. Electro polymerisation was performed on platinum wire working electrodes under potentiodynamic conditions (-700 to +1200 mV versus calomel reference electrode, scan rate, $v = 100 \text{ mV/s}$) for the CV measurements.

C. In situ study of diffusion coefficient of polypyrrole films
In order to study the diffusion of dopants into the polymers, films of polypyrrole and poly(N-dodecylpyrrole) were synthesised electrochemically. Solutions with concentrations of 0.1M TBAP and 0.1M monomer were prepared in acetonitrile (50 ml), and polymerisation was carried out galvanostatically (0.1 mA for 10 s) on a 1 mm² Pt disc electrode. The polymer films were rinsed with distilled water in order to remove any monomer left on the film surface. The electrode coated with polymer films (working electrode) were studied in three different electrolytes: LiClO₄, TMACl and NaDBS (0.1M) solutions in acetonitrile which had been deoxygenated by nitrogen bubbling. For the diffusion measurements, a current of 10 μA was applied for 1 s; then 0 μA was applied for 60 s to provide time for the ions to return to equilibrium. By selecting the initial linear part of the graph and calculating its slope, the dopant diffusion coefficient was estimated.

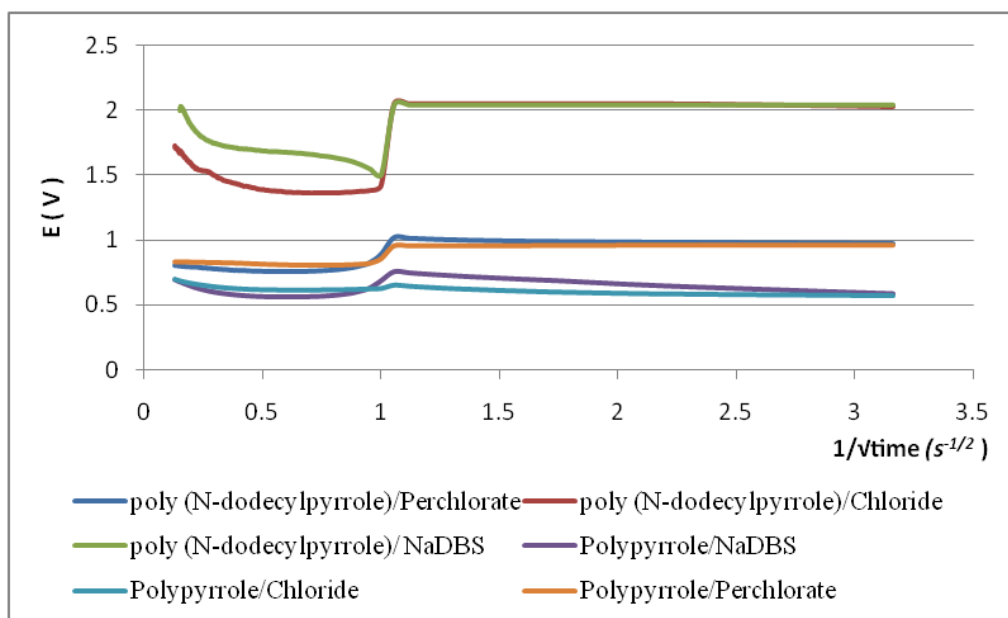


Fig. 1 Electrode potential versus $(\text{time})^{-1/2}$ for poly (N-dodecylpyrrole) and polypyrrole

III. RESULTS AND DISCUSSION

The values of diffusion coefficients for various combinations are given in Table 1. Diffusion measurements of electrochemically prepared poly (N-dodecylpyrrole) and polypyrrole films were studied in

electro chemical cells containing LiClO₄, TMACl in acetonitrile and NaDBS in water. An increase in diffusion coefficients in the order of $\text{Cl}^- < \text{ClO}_4^-$ at 296.15 K has been observed.

TABLE I Ionic diffusion coefficients in poly (N-dodecylpyrrole) and polypyrrole

System	D/cm ² s ⁻¹ Poly(pyrrole)	D/cm ² s ⁻¹ Poly (N-dodecylpyrrole)	Comments (or Literature Values)
LiClO ₄ /CH ₃ CN	1.1 x 10 ⁻¹⁰	7.8 x 10 ⁻¹¹	Mirebeau[11] obtained 5 x 10 ⁻¹² cm ² s ⁻¹ For LiClO ₄ /Poly(pyrrole) Genies and Pernaut [12] obtained 4 x 10 ⁻⁹ cm ² s ⁻¹ for LiClO ₄ /Poly(N-methylpyrrole)
TMACl/CH ₃ CN	1.5 x 10 ⁻¹²	1.2 x 10 ⁻¹²	
NaDBS/water	2.6 x 10 ⁻¹²	1.7 x 10 ⁻¹²	

The estimated values for the diffusion of ClO_4^- in poly(N-dodecylpyrrole) and polypyrrole are $7.8 \times 10^{-11} cm^2 s^{-1}$ and $1.1 \times 10^{-10} cm^2 s^{-1}$, respectively.

As can be seen from Table 1, these values are larger than those for chloride ions. The increasing diffusion coefficient with the increase in the size of the dopant anions, suggests that counter anions used during the electro polymerisation have a great effect on the diffusion process. Since ClO_4^- was used as the counter anion, it appears that the polymer matrix is probably more compatible with the structure of ClO_4^- than other anions and that makes it easier for the ClO_4^- to diffuse into the polymer. For an amorphous glassy polymer, the diffusion usually involves the hopping of molecules or ions from one region of free volume to another, which is expected to be slower (less frequent) for larger ions. Hence $D (DBS^-) \ll D (ClO_4^-)$, this is observed for both the polymers studied. However, we should expect $D (Cl^-)$ to be greater than $D (ClO_4^-)$ on this principle, since the chloride ion is small.

The reason why the chloride ion diffuses more slowly may be related to the fact that its small size causes it to be more strongly polarising (i.e. stronger electrostatic attraction to the positive polar on the polymer backbone). These results can be compared with those of Mirebeau [12] who obtained a diffusion coefficient of $5 \times 10^{-12} cm^2 s^{-1}$

for ClO_4^- , from $LiClO_4$, diffusion into and out of polypyrrole at 298 K.

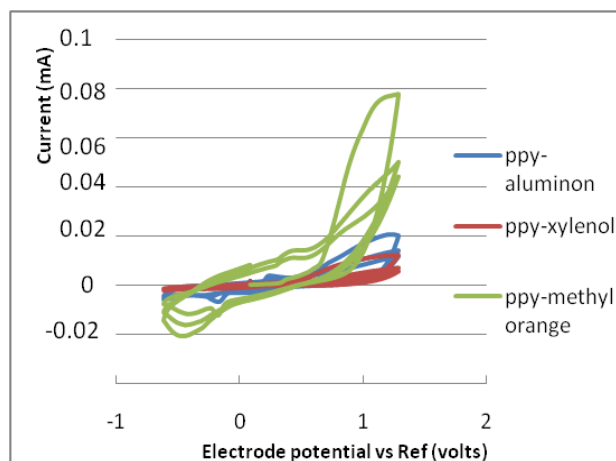


Fig. 2 Cyclic voltammetry curves for polypyrrole in aluminum, xylenol orange and methyl orange in water. Scan rate is 100 mV/s.

The voltammogram of polypyrrole in the presence of three large organic dye molecules revealed that methyl orange had the largest redox activity in comparison to aluminum and xylenol orange. It is apparent that the smaller size of methyl orange has a great effect the redox activity (Fig. 2).

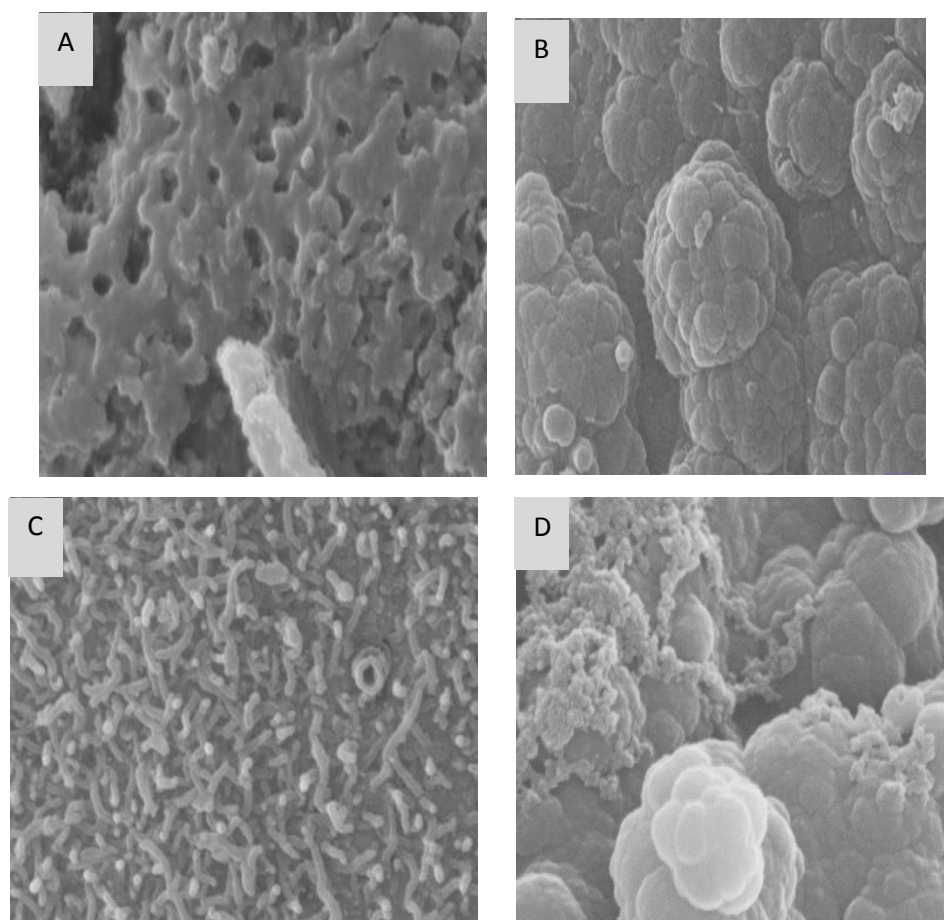


Fig. 3. SEM photos of poly (N-dodecylpyrrole) and polypyrrole (200 nm)
A: polypyrrole in aluminon dye, B: polypyrrole in $LiClO_4$, C: polypyrrole in 3,5-dinitrosalicylic acid,
D: poly (N-dodecylpyrrole) in TBAP

Figs. 3 A and C show SEM images of polypyrrole films electrochemically synthesized on the platinum electrode in the presence of aluminon and 3,5-dinitrosalicylic acid respectively. It was found from the experimental results that in the presence of aluminon a porous structure can be obtained. Aluminon, which contains three negative sites, acts as a template during polymerisation and induces an increase of the empty spaces in the polymer structure. Synthesis of polypyrrole in the presence of 3,5-dinitrosalicylic acid revealed a vermicular morphology. Such porous structure can be seen in the work of Yang et al; they obtained polypyrrole nanotubes in the presence of methyl orange. Methyl orange plays a role of active sites for the growth of polypyrrole [12].

Fig. 3D shows the SEM micrograph of poly (N-dodecylpyrrole) electrochemically synthesised on the platinum working electrode. This photo shows a more complex morphology rather than the cauliflower-like appearance of polypyrrole (Fig. 3 B). Since the oxidation potential of N-dodecylpyrrole monomer is higher than pyrrole monomer, it is possible that over oxidation happens and creates such a complex structure.

IV. CONCLUSION

A wide variety of morphologies were obtained, depending on the electrolyte and on the conditions used. The diffusion coefficients of several dopant counter-ions were estimated using a galvanostatic pulse technique. All the polymers were synthesised using a per chlorate salt electrolyte, which gave a relatively smooth, low-area surface. It was found that the diffusion coefficient for ClO_4^- was much greater than for DBS^- , which was attributed to the sizes of these two ions. However the smaller Cl^- ion had a very low diffusion coefficient. This may be due to the more strongly polarising effect of the small ion, causing it to be trapped by the electrostatic field of the positive polarons. Alternatively the internal morphology of the ClO_4^- polymer may contain holes or channels that are especially compatible with the ClO_4^- dopant ions, and allow them to move very easily in the polymer film.

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