

DEPENDENCE OF EFFECTIVE DIFFUSION COEFFICIENTS OF PPy FILM ON PREPARATION PROCESS

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ABSTRACT

Conjugated polymers are promising materials for the use as soft actuators or as electrodes in batteries and the actuation mechanism of such polymers highly depends on the diffusion of counter ions into these polymers during the redox process. Among several conjugated polymers, polypyrrole doped with large immobile dodecylbenzene sulfonate anions (PPy/DBS) operating in aqueous electrolytes has been identified as one of the successful systems suitable for the use as artificial muscles. The insertion and expulsion of counter ions into PPy/DBS films when operating in aqueous electrolytes determines the speed of response of such films and is quantitatively measured by the parameter, the effective diffusion coefficient. The objective of the present work is to determine the effective diffusion coefficients for PPy/DBS films prepared by different preparation processes in order to compare the yield values. For this PPy/DBS films were electropolymerized on Pt wire under galvanostatic mode and electrochemically cycled in 0.1M LiCl aqueous electrolytes. The effective diffusion coefficient for 10 μm PPy/DBS films prepared as a single layer was found to be $3.315 \times 10^{-12} \text{M}^2 \text{S}^{-1}$. Whereas it was $9.9433 \times 10^{-12} \text{M}^2 \text{S}^{-1}$ when the same thickness film was prepared as 2 μm layer by layer rather than single layer. This finding indicates that the speed of response PPy/DBS films improves considerably when it is prepared as layer by layer

Keywords: Conducting polymers, Polypyrrole, Cyclic Voltammetry, Effective Diffusion Coefficient

1. INTRODUCTION

Conducting polymers are novel type of organic materials which have unique characteristics as compared with other types of organic materials. Generally, conducting polymer is an innate semiconductor in its neutral state but becomes an electronic conductor in its highly doped state [1]. During the doping processes of CPs, counter ions are incorporated or expelled from the polymer backbone and this can be achieved electrochemically [2]. The ability to be electrochemically switched between different states at low voltage causes very large changes in properties i.e. the conductivity changes, color changes and volume changes [3]. The volume change is the primary mechanism for the use of this CPs as soft actuators or artificial muscles and this type of actuators are attractive because they can electrochemically be controlled. The volume change of conjugated polymers depends on several experimental conditions such as synthesis condition, driving voltage, surrounding ions and fluids, cycle history, etc. Besides, ionic motion into these polymers is mainly responsible for this volume change [4] and determines the speed of response when such polymers are in use [5]. This is quantitatively measured by a parameter called effective diffusion coefficient and the aim of investigation was to accurately determine the effective diffusion coefficient of a selected conducting polymer.

Among several CPs, polypyrrole (PPy) films have been found to be useful to fabricate soft actuators. The present work is focused on PPy films doped with large surfactant anions, dodecyl benzene sulfonate (DBS), operating in aqueous

electrolytes, since the films have been shown to be a promising system for use in soft actuators [6,7]. The main aim of this work is to determine the effective diffusion coefficients for PPy/DBS films prepared by different preparation processes in order to compare the yield values. The effective diffusion coefficients for 10 μm PPy/DBS films prepared, as a single layer and layer by layer, were found using cyclic voltammetry techniques.

2. METHODOLOGY

The cyclic voltammetry is more sensitive technique which describes the redox process and it contains fingerprint information about the nature of ions and solvent. The voltammogram also gives the information about the kinetics of the process, and the change of voltammogram as a function of the sweep rate can be analyzed in terms of effective diffusion coefficient of ions in the polymer film. In order to determine the diffusion of ions quantitatively, the diffusion of counter ions into the polymer film is assumed to follow Fick's law of diffusion. It was adopted to a method proposed by West et al. to determine effective diffusion coefficient in intercalation electrode materials. In the present context, transport in PPy/DBS coatings will be treated as a planar diffusion, and in the potential range investigated here a linear relationship between charge insertion and potential during the cathodic scan will be assumed. Under these assumptions, the relationship between cathode utilization U (defined as the ratio of the charge accumulated in the electrode relative to the maximal charge that can be accumulated under equilibrium conditions), and sweep rate α is derived by West et al [8].

$$U = 4/3 \sqrt{\frac{(E_1 - E_2)}{\pi \tau \alpha}} \quad (1)$$

Where $E_1 - E_2$ is the potential window used for the scan and τ is the time constant for diffusion in the electrode. Assuming Fickian diffusion, plots of U versus $\frac{1}{\sqrt{\alpha}}$ For PPy/DBS films cycled in LiCl aqueous electrolyte should show that U is approximately proportional to $\frac{1}{\sqrt{\alpha}}$ Down to a critical sweep rate, and at lower sweep rates U becomes independent of α . From this plot, τ can be determined from the critical sweep rate marking; the transition between two linear regimes. Then the effective diffusion coefficient of ion movements in the polymer film can be obtained using the relation

$$D = \frac{l^2}{\tau} \quad (2)$$

Where, l is length of diffusion. If the diffusion is assumed to occur across the film uniformly, l will correspond to thickness of the film.

For this investigation, pyrrole (Aldrich 98%) monomer was distilled under nitrogen and stored in a freezer in a sealed vial prior to use. Other chemicals, sodium dodecyl benzene sulfonate (SDBS) (Aldrich, technical quality), LiCl (Merck, analar grade), were used as received. For all polymerizations, a 0.05 M SDBS aqueous solution containing 0.05 M pyrrole was used and the films were prepared using galvanostatic electropolymerization with a constant current density of 0.1 mA cm⁻². The PPy/DBS films were deposited on Pt wire, assuming that a charge of 160 mC/cm² passed during synthesis yields a 1 μm thickness film [9]. The electrochemical behaviour of the deposited films was studied in 0.1 M LiCl aqueous electrolyte. All cycling aqueous electrolytes used were thoroughly purged with nitrogen gas for an hour to remove dissolved oxygen. All electrochemical investigations were carried out using a three

electrode arrangement with a Pt sheet and a standard Ag/AgCl (3 M KCl) electrode serving as the counter and reference electrodes respectively. For this investigation, two layers of 10 μm films were used: a one layer of 10 μm film was continuously coated and characterized. The other one was coated as 2 μm layer by layer after 10 initial conditioning cycling in 0.1 M LiCl electrolytes before coating.

3. RESULTS AND DISCUSSION

Fig. 1 and 2 show a series of cyclic voltammograms at different sweep rates cycled with 0.1M LiCl. In order to facilitate the comparison of all curves the current values were divided by the sweep rates. In the resulting differential capacity versus voltage diagrams, the area under the curve is a direct measure of the charge that is cycled in and out of the film during redox cycling. Significant changes in the cyclic voltammograms are obtained with the sweep rate. The scan rate considerably affects the positions of nearly all peaks and this fact proves the important role of kinetic factors in the redox processes.

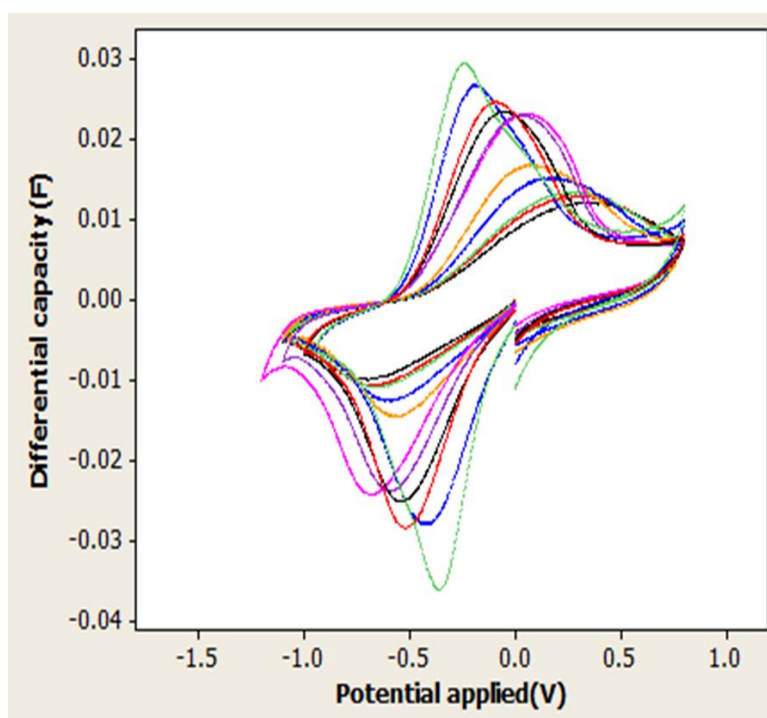


Fig. 1. A set of cyclic voltammograms for 10 μm layer by layer film cycled with 0.1M, LiCl for different sweep rates: 28, 40, 65, 80, 100, 130, 150, 200, 280, 300, 350 mV/s.

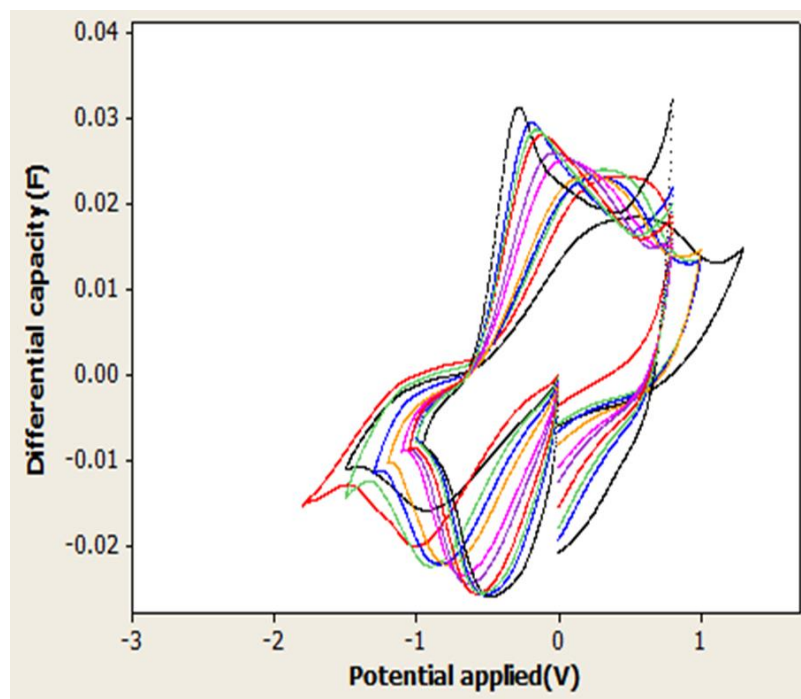


Fig.2. A set of cyclic voltammograms for 10 μ m film (one shot method) cycled with 0.1M, LiCl for different sweep rates: 20, 40, 48, 60, 80, 100, 150, 180, 200, 250, 300 mV/s.

During reduction, the sharp cathodic peak is obtained due to insertion of cations in low scan rates. It can be seen that the cathodic peaks become sharper with decreasing scan rate and shift to more negative with increasing scan rate. It is obvious that in low scan rates, more counter ions are inserted into the polymer film. During oxidation process, the peaks shift to more positive potential with increasing scan rates and also at low scan rates the peaks become sharper compared with high scan rates. Therefore, at low scan rates more cations come out from polymer film. Furthermore, all cathodic and anodic peaks are smaller at high scan rates and this interpret that the cations and anions are no longer able to participate fully in the doping/dedoping process at high scan rates, since at high scan rates, ions do not have sufficient time to be inserted or extracted to the polymer film.

In order to find the effective diffusion coefficient of PPy/DBS films, the cathodic electrode charge versus inverse square root of the sweep rates was plotted as shown in Fig. 3 and 4.

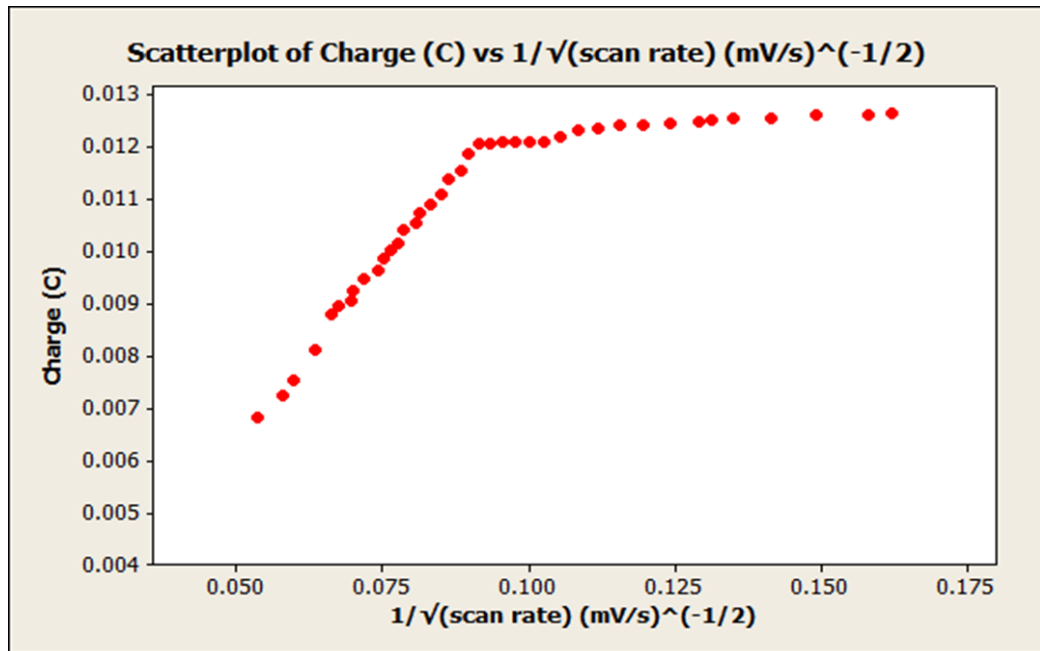


Fig. 3. The cathodic electrode charge versus inverse square root of the sweep rates for 10 μm layer by layer film

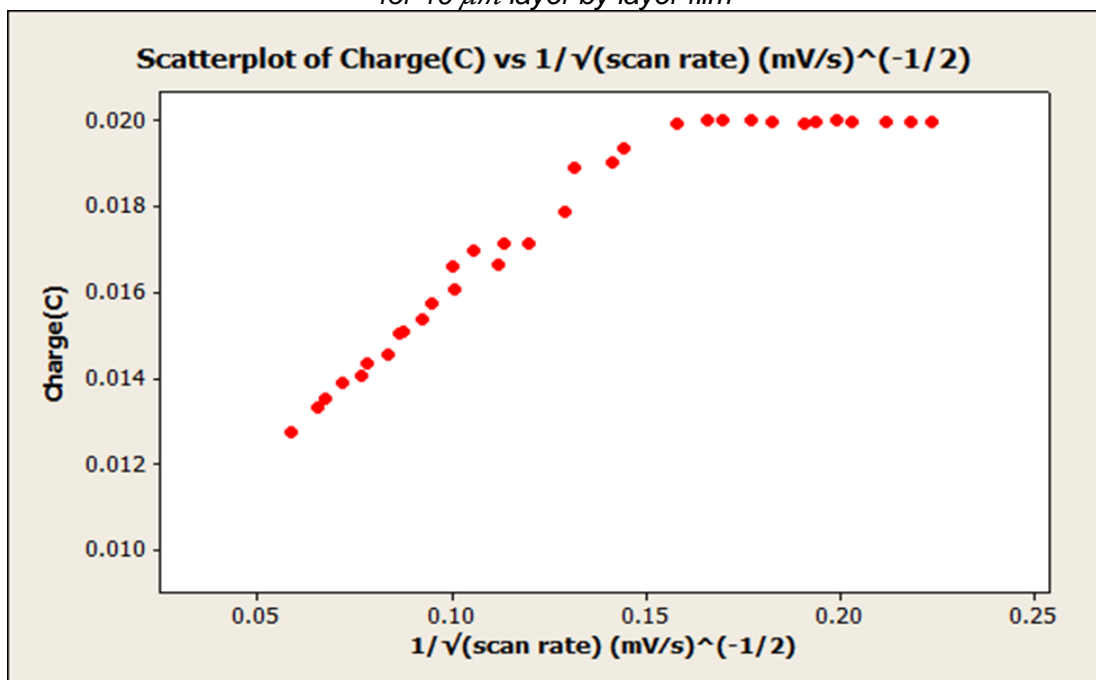


Fig. 4. The cathodic electrode charge versus inverse square root of the sweep rates for 10 μm film –single layer film.

It can be seen from Fig. 3 and 4 that the electrode charge during the cathodic scan increases linearly with the inverse square root of scan rate at high scan rates, and then reaches an approximately constant maximum value at low scan rates (high values of the inverse square root of scan rate) as predicted by West et al. The time constant (τ) can be calculated from transition between high and low scan rates. Effective Diffusion Coefficient can be calculated from equation (2). Table 1 shows the analysis of Effective Diffusion Coefficient.

Table 1. Analysis for Effective Diffusion Coefficient of 10 μm - layer by layer and single layer

Method	Critical sweep rate (α_c)	time constant (τ)	Effective diffusion coefficient (D)
Layer by layer	109.99 mV/s	10.057 s	$9.9433 \times 10^{-12} \text{ m}^2 \text{ S}^{-1}$
Single layer	44.54 mV/s	30.165 s	$3.315 \times 10^{-12} \text{ m}^2 \text{ S}^{-1}$

From Table 1, the effective diffusion coefficient of ions into the polymer film in layer by layer method is higher than single layer method which means that the ionic motion inside the polymer film is increased in layer by layer method. The improvement of effective diffusion coefficient of ions increases the speed of response in polymer film. This increment may be due to conformational changes [10] or chain confirmation relaxation [11].

The conformation arrangement of the film in layer by layer film is more stable than single layer film. Because the films were prepared as 2 μm layers and each time the films cycled with 10 mV/s for 10 cycles. This process reduces slow relaxation or memory effect of film. So the conformation arrangements become more stable in layer by layer film. This allows the ions move easily into the film compared with one shot method.

4. CONCLUSION

Polypyrrole conducting polymer films doped with large immobile anion dodecylbenzene sulfonate have been used to investigate the diffusion of counter ions during redox processes in aqueous LiCl electrolytes. The diffusion of counter ions determines the speed of response when using these films as electrodes in batteries or in artificial muscles. PPy/DBS films of 10 μm were prepared as layer by layer and a single layer and the films were characterized using cyclic voltammetry technique. The calculated values of Effective Diffusion Coefficient of PPy/DBS film prepared as layer by layer is $9.9433 \times 10^{-12} \text{ m}^2 \text{ S}^{-1}$ while it is $3.315 \times 10^{-12} \text{ m}^2 \text{ S}^{-1}$ for a single layer film. This finding indicates that the film prepared as layer by layer has a larger ionic diffusion than that of a single layer and that the speed of response of PPy/DBS film depends on preparation processes.

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