

Electropolymerization and Ion Exchange Properties of a Polypyrrole Film Doped by *para*-Toluene Sulfonate

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ABSTRACT: Electropolymerization and ion exchange properties of the polypyrrole film doped by *para*-toluene sulfonate (PPy/pTS) were investigated in aqueous solutions. The film with a column-like surface morphology was galvanostatically synthesized at 3 mA/cm² during 1800 s. Cyclic voltammetric measurements of the PPy/pTS film in sodium *para*-toluene sulfonate (NapTS), tetraethylammonium chloride ((C₂H₅)₄NCl), and NaCl aqueous solutions showed a cation exchange property, an anion exchange

property, and a combination of them, respectively. Moreover, the large ions could decrease the transport of the small ions coexisting in the same solution, and the redox processes were proved to be electrochemically irreversible and ion transport-limiting reactions. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 2518–2522, 2006

Key words: polypyrrole; cyclic voltammetry; electron microscopy; ion exchange

INTRODUCTION

Many reports revealed that conducting polymers, such as polypyrrole, polythiophene, polyaniline, etc., can be used as sensors, ion exchange resins, and actuators. Among them, polypyrrole was extensively investigated because of its stability and easy chemical or electrochemical polymerization.^{1–11} When compared with other conducting polymers based on polypyrrole, polypyrrole/*para*-toluene sulfonate (PPy/pTS) composites were proved to be very suitable for practical applications, because of their good physical, chemical, mechanical properties and long-term stable redox cycling.^{9–13}

It is well known that PPy composites can be doped and dedoped by anions or cations, inducing the electronic, chemical, and physical changes of the polymers, which were regarded as the basis for nearly all practical applications. However, those processes are related to the ion exchange properties in essence. Therefore, in recent years, the ion exchange properties of the PPy composites have been the focus of many investigations,^{2,4,6,9,11} which are very helpful to deeply understand the inner working mechanism of the sensors, actuators, and electrically switched ion exchange resins. However, though the study on the ion exchange properties has been carried out for more than two decades, there still exist two main problems that

have puzzled the investigators in practical application of PPy composites. One is the low ion exchange rate. As well known, the electropolymerized PPy film usually has a relatively flat surface, and ion transport in the polymer matrix is not easy because of the compactness of the film, and the redox sites in the matrix cannot be reached in short time. The other problem is the functions of electrolyte ions in the redox processes. The electroactivity of conducting polymer is dependent on the ion exchange between the solution and the composites matrix. The influence of the nature of electrolyte ions on ion exchange property has not been discussed completely.

For enhancing the ion exchange rate of the PPy/pTS composites, in this study, we electrochemically synthesized a typical conducting PPy film with a large specific surface area. In addition, to better understand the ion exchanging mechanism of the electrolyte ions in aqueous solutions, in this study we investigated the redox processes of the PPy/pTS film to determine the influence of the electrolyte ion size on the ion exchange properties.

EXPERIMENTAL

Pyrrole (99%) was twice distilled prior to use. Other reagents such as NaCl, *para*-toluene sulfonate (NapTS), *para*-toluene sulfonate acid (HpTS), and (C₂H₅)₄NCl were AR grade and used as received. All reagents were purchased from Chinese National Reagents Group in Shanghai, China. Solutions were prepared with deionized water and purged with nitrogen before use. The volume of solution in the cell was 100

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mL containing 0.1M pyrrole monomer, 0.05M NapTS, and 0.05M HpTS during polymerization. The synthesis processes were carried out in conventional three-electrode system in single compartment electrochemical cell, in which the working electrode was a 1-cm² platinum plate, the auxiliary electrode was a 5-cm² platinum flag, and the reference electrode was a saturated calomel electrode (SCE). The temperature of polymerization was kept at 0°C. After polymerization, the PPy/pTS film obtained was soaked in 0.5M NaCl aqueous solution for 24 h. Then, the film was twice cleaned using distilled water and kept in distilled water saturated with high purity N₂ gas until use.

The electroactivity characterization was performed in the same electrochemical cell with the PPy/pTS film attached on a 1-cm² Pt plate as a working electrode at room temperature of 25°C, which was obtained through galvanostatic polymerization at 3 mA/cm². The counter and reference electrodes were similar to those used during polymerization.

Electropolymerization of pyrrole was performed using a Potentiostat/Galvanostat (EG and G Princeton Applied Research 263A), which was also used to measure the electrochemical properties of PPy/pTS composites by cyclic voltammetry. The potential ranged from -1.0 to 0.6 V versus SCE. Unless otherwise mentioned, all potentials are referred to the SCE. The charges consumed during the redox processes were recorded to quantitatively estimate the amount of ion exchange. SEM pictures were taken using JSM-5600LV.

RESULTS AND DISCUSSION

Electropolymerization and surface morphology

The surface morphology of conducting PPy film varies with the different electrosynthesized parameters such

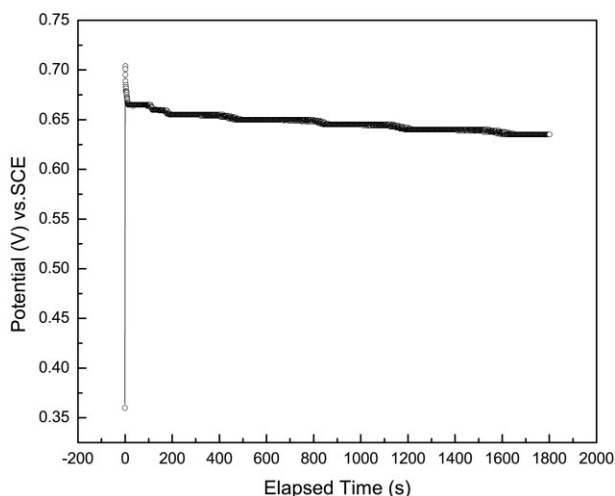


Figure 1 Potential variation with time during the galvanostatic polymerization in aqueous solution.

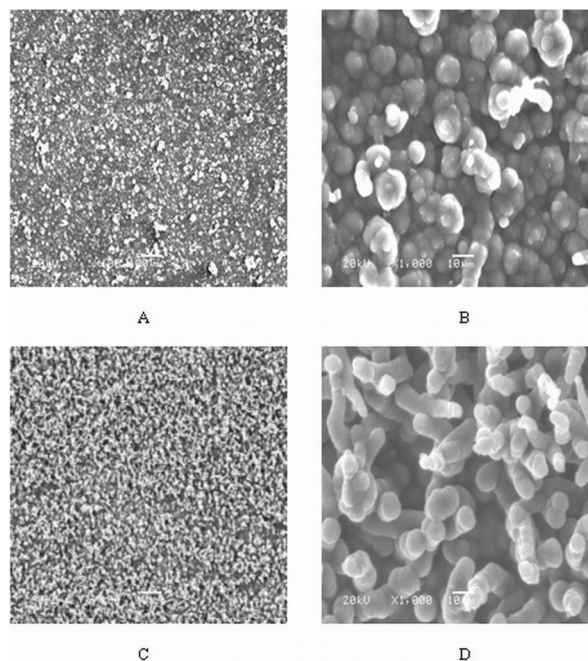


Figure 2 SEM pictures of PPy/pTS composites obtained in aqueous solution containing 0.1M pyrrole monomer, 0.05M NapTS, and 0.05M HpTS. For (A) and (B), polymerization time was 600 s; for (C) and (D), 1800 s. The scale bar of (A) and (C) is 100 μm; (B) and (D) for 10 μm.

as applied current density/potential, solvent, nature of electrolyte, electrode substrate, etc.^{14,15} Different film morphology can largely influence the ion movement between PPy matrix and solution¹⁵⁻¹⁷ and thus influence its practical applications. In this study, PPy/pTS composite films were electrochemically synthesized on platinum electrode during different polymerization time at constant current density of 3 mA/cm².

As shown in Figure 1, the potential has a sharp increase at the initial stage of synthesis, which is in good agreement with other previously published works. After that, the potential decreases step by step, which is supposed to correspond to the growth of the polymer.

Figure 2 presents the SEM pictures of PPy films. Figure 2(A, B) are the same film obtained during polymerization time of 600 s. Figure 2(C, D) corresponds to the film obtained during 1800 s. The magnification factor of Figure 2 (B, D) is 10 times as large as that of 2(A, C), respectively. Obviously, PPy/pTS film A is the typical nodular shape which was widely reported in other researchers' studies;^{14,15,17} however, C has a column-like morphology, which was reported by few investigators. As well known, for practical application of PPy composites, such as ion exchange materials and electrochemical sensors, a high specific surface area was of the most importance, which can improve the kinetics of ion exchange. As shown in Figure 2, obviously, the surface of C is tougher than that of A, i.e.,

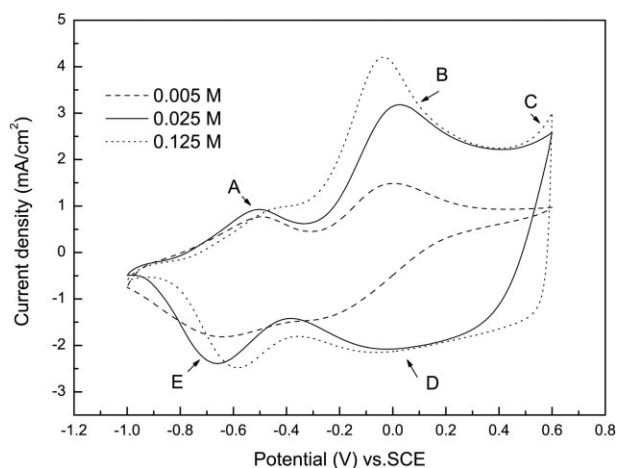


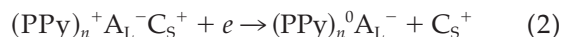
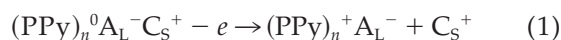
Figure 3 CVs of the film in NaCl aqueous solution. Film was electro synthesized in 0.1M pyrrole monomer, 0.05M NapTS, and 0.05M HpTS aqueous solution at constant current density of 3 mA/cm² for 1800 s. Scan rate: 5 mV/s.

the film C has a larger specific surface area and would be much more beneficial to the ion exchange processes. In this study, we assumed that the possible reason for the formation of the column-like morphology would be the continuous growth of the nodules on the surface of the film A.

Ion exchange properties

Electroactivity of the PPy/pTS film was certified by cyclic voltammetry, which was also used to determine the ion exchange properties. During the redox processes carried out in the PPy/pTS polymer, the electrolyte ions not only act as the conducting media, but also participate in the reaction. It should be noted that the cyclic voltammograms (CV) in this study are very stable after 10 cyclings from -1.0 to $+0.6$ V in 0.1M NaCl aqueous solution. The scan rate was 5 mV/s, at which the redox processes could be performed completely. Figure 3 presents the dependence of the electrolyte concentration on the CV shape. Clearly, the CV curves could be divided into five regions. The explanation is as follows: because pTS anions in PPy/pTS composite can partially leak out of the PPy matrix, the film has two main structures. One is $(\text{PPy})_n^+(\text{pTS})^-$ and the other is $(\text{PPy})_n^0$. The regions near the peaks A and E correspond to the expulsion and insertion of cations Na^+ , as shown in reactions (1) and (2), respectively. The peaks B and D represent the incorporation and expulsion of anions Cl^- in reactions (3) and (4), respectively. Thus, accompanied by the anions and cations movement, the PPy/pTS composite film shows the combination of both anion and cation exchange properties in NaCl. Needless to say, these explanations discussed here have been accepted widely.^{4,6,9,10,18–24} However, the discussion to region C has

been neglected. Though the reaction corresponding to the region C is uncompleted, it is also supposed to relate to Cl^- incorporation. Similarly, peak D should be the combination of reaction (4) and reduction process of region C.



where, generally, $n = 3-9$;¹⁸ A_S^- (small size anion), A_L^- (large size anion), and C_S^+ (small size cation) correspond to Cl^- , pTS⁻, and Na^+ in this study, respectively.

It is well known that oxidation process at a high potential (for instance 1.0 V) could induce the overoxidation and the loss of electroactivity of the PPy film. Li and Qian showed that region C was corresponding to the OH^- attack due to the electrolysis of water and the overoxidation of PPy film was dependent on the solution pH.²⁵ In this study, evidences supported that region C is also related to the concentration and nature of the electrolyte anions. As shown in Figure 3, the area of region C increases with the increased concentration of Cl^- , even at the same pH. Moreover, Figure 4 also gives evidence that region C is directly related to the electrolyte anion Cl^- . Thus, we can draw a conclusion that region C is somehow caused by the Cl^- incorporation.

The CVs of the film in different electrolyte concentrations varied. Generally, the peak current increased with increasing electrolyte concentration. However, peaks A and E have less change compared with peaks

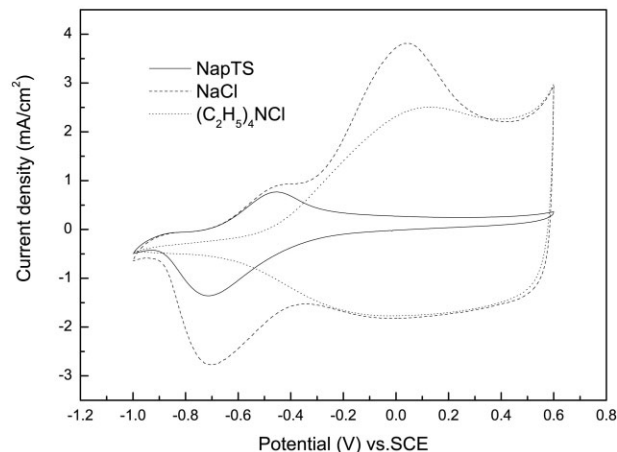


Figure 4 CVs of the film in different electrolytes aqueous solution. The concentration of electrolytes used is 0.1M. Scan rate was 5 mV/s. The film used was the same to Figure 3.

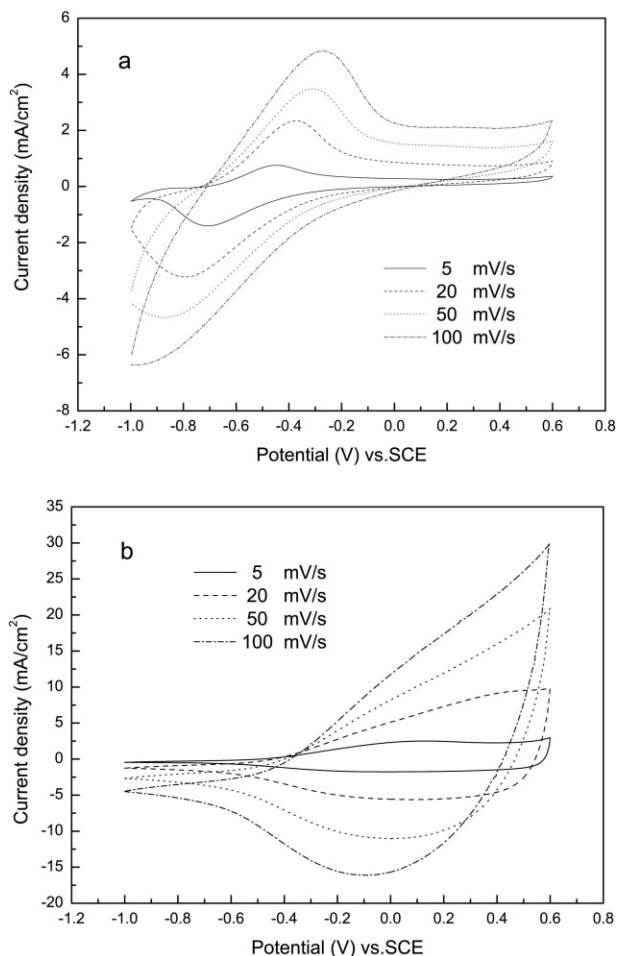


Figure 5 CVs of the film in aqueous solution at different scan rate. (a) 0.1M NapTS; (b) 0.1M $(\text{C}_2\text{H}_5)_4\text{NCl}$.

B and D. This phenomenon could result from the less redox sites in the regions near peaks A and E, so that the redox sites could be saturated even with low electrolyte concentration.

The nature of the electrolyte ions also plays a significant role in the ion exchange processes of PPy composites.^{19–23} To investigate the anion or cation exchange behavior separately (as compared with NaCl), NapTS and $(\text{C}_2\text{H}_5)_4\text{NCl}$ were chosen as the electrolytes respectively. The former has large size anions (pTS^-), and the latter has large size cations ($(\text{C}_2\text{H}_5)_4\text{N}^+$).

Figure 4 shows the redox behavior of the PPy/pTS film in different electrolyte aqueous solution. As for CVs obtained in NaCl solution, there are two pairs of peaks as discussed earlier. But for NapTS, only one pair of current peak appears and corresponds to the expulsion and insertion of Na^+ . Similarly, for $(\text{C}_2\text{H}_5)_4\text{NCl}$, one pair of current peaks correspond to the expulsion and insertion of Cl^- . Moreover, the amounts of charges transported were 0.42 C for $(\text{C}_2\text{H}_5)_4\text{NCl}$, 0.55 C for NaCl, and 0.1 C for NapTS, i.e.,

the amount of the charges transported in NaCl was larger than the sum of the charges transported in both NapTS and $(\text{C}_2\text{H}_5)_4\text{NCl}$. This might mean the large size ions can affect the movement of small size ions coexisting in the same solution, which can also be identified by the higher anodic peak A and cathodic peak B in NaCl solution. The possible process is that the large size ions in NapTS or $(\text{C}_2\text{H}_5)_4\text{NCl}$ can block the channel in PPy/pTS polymer matrix. Thus, the amount of small size ions (Na^+ or Cl^-) transported decreased compared with that in NaCl.

The dependence of the redox processes of the film on scan rate is also indicated in Figure 5. As can be seen, the peak potential E_p change remarkably, and the values of $E_{\text{ap}} - E_{\text{cp}}$ (E_{ap} and E_{cp} correspond to the anodic and cathodic peak potentials, respectively) have become larger with the increasing scan rate from 5 to 100 mV/s. The conducting PPy exhibited the so-called redox hysteresis, which caused electrochemical irreversibility of the film. The dependence of the value of current peaks on the scan rate is indicated in Figure 6. It should be mentioned that the anodic peak current i_{ap} in Figure 5(b) was not involved because of the loss of the anodic peaks at high scan rates. Clearly, the peak current was linearly proportional to the scan rate^{1/2}, which means that the controlling factor of the redox processes of the film was ion diffusion.

CONCLUSIONS

PPy/pTS film electrosynthesized in aqueous solution containing 0.1M pyrrole monomer, 0.05M NapTS, and 0.05M HpTS at constant current density 3 mA/cm² for 1800 s had a column-like surface morphology, which could improve the kinetics of ion exchange.

The CVs obtained in various aqueous electrolyte solutions clearly showed the different redox or ion

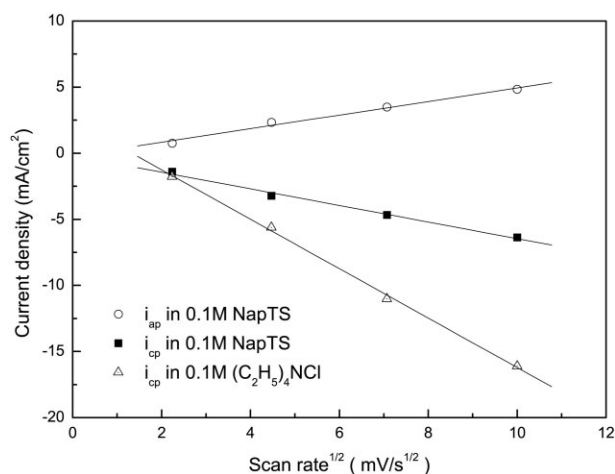


Figure 6 Relationship between peak current and the scan rate.

exchange properties. As for small size ions, such as Na^+ and Cl^- , though the amount of diffusion varies with the ion radii, valence, structure, and hydrophilic/hydrophobic nature, they can move into or out of PPy/pTS composite. However, by contrast, large size ions, such as pTS^- and $(\text{C}_2\text{H}_5)_4\text{N}^+$, can not reach the redox sites and might block the channel in the PPy/pTS matrix, thus preventing the transport of the small size ions coexisting in the aqueous solution. In that situation, PPy/pTS film was converted into anion or cation exchange material and responded only to small size anion or cation. Moreover, the redox processes of PPy/pTS composite in aqueous solution were verified to be electrochemically irreversible and diffusion-controlled reactions.

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