

Two Reduction Processes of Conducting Polypyrrole Tosylate Film in Aqueous Solutions

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ABSTRACT: The electrochemical properties of polypyrrole tosylate [PPy(TsO⁻)] in aqueous solutions were investigated by cyclic voltammetry and ac impedance measurements. The cyclic voltammograms (CVs) of PPy(TsO⁻) show two reduction processes. Two doping sites of the counteranions in PPy(TsO⁻), site A with the counteranions located between the PPy layers and site B with the counteranions located in the PPy layers, were proposed based on the results of the electrochemical studies, and the partial counteranion exchange occurred when PPy(TsO⁻) was dipped in a 1 mol/L HNO₃ aqueous solution. The reduction of site A is accompanied by the dedoping of counteranions and the reduction of site B is carried out with the insertion of solution cations. The electrochemical kinetics of the redox processes of site A was analyzed based on the ac impedance results. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 350–355, 2001

Key words: polypyrrole tosylate; cyclic voltammograms; ac impedance; aqueous solutions; doping sites

INTRODUCTION

The electrochemical properties of conducting polymers have attracted much attention in the past 20 years,^{1–7} due to the novel doping/dedoping mechanism of its electrochemical processes and its promising electrochemical applications, such as in batteries, electrochromic displays, electrocatalysis, and electrochemical sensors. Among the conducting polymers, conducting polypyrrole (PPy) film has drawn special interest in electrochemical studies^{1,3–9} because of its high conductivity, high stability in air, and the easy preparation of PPy films by electropolymerization.

The electrochemical redox processes of PPy(ClO₄⁻) in an organic solution and PPy(NO₃⁻) in an aqueous solution have been studied extensively. A large overpotential was observed in the first reduction of PPy(ClO₄⁻) in the organic (acetonitrile or propylene carbonate) solutions, and reversible doping/dedoping of counteranions takes place in the subsequent oxidation and reduction in the cyclic voltammetry.^{4–6} The large overpotential in the first reduction results from the slow diffusion of the counteranions in the as-prepared PPy(ClO₄⁻) film and the reduction is accompanied mainly by the insertion of the solvated cations. For PPy(NO₃⁻), two doping structures corresponding to two reduction processes exist. The electrochemical reduction and reoxidation in the acidic aqueous NaNO₃ solutions are reversible and accompanied by the dedoping and redoping of the counteranions.^{3,8} For PPy(TsO⁻) prepared from an organic solution, Smyrl et al.⁹ carried out an

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electrochemical quartz crystal microbalance (EQCM) study on the electrochemical properties of the PPy(TsO⁻) film and found that both anions and cations participated in its redox processes. But for PPy(TsO⁻) prepared in an aqueous solution, only a few studies have been done on its electrochemical processes in such solutions^{10–14} and the results are only phenomenological. The mechanism of the electrochemical processes remains ambiguous.

It is well known that the conductivity and mechanical properties of PPy films prepared from aqueous solutions electrochemically are closely related to the electropolymerization conditions and especially related to the nature of the anions in the electrolyte solutions.¹⁴ The conductivity and mechanical property of PPy(TsO⁻) with the counteranions of the organic surfactant anion TsO⁻ are much better than those of PPy(NO₃⁻) or PPy(Cl⁻) with the counteranions of inorganic anions NO₃⁻ or Cl⁻. This indicates that there should be some difference between the doping structures of PPy(TsO⁻) and PPy(NO₃⁻). In fact, the difference of the doping structures and structural anisotropy between PPy(TsO⁻) and PPy(NO₃⁻) were revealed by the shrinkage and mass loss of the films after alkali treatment.¹⁵ There are two doping structures: the oxidized conjugated PPy chain with counteranions (structure **I**) and the protonic acid doping structure (structure **II**). In PPy(NO₃⁻), there are about half of the counteranions doped in structure **II**, while in PPy(TsO⁻), about 95% of its total doping structure belongs to structure **I**. The NO₃⁻ counteranions in the two doping structures of PPy(NO₃⁻) all locate between the PPy plain layers, while the TsO⁻ counteranions in structure **I** of PPy(TsO⁻) locate partly between and partly in the PPy plain layers.¹⁵ Obviously, the difference in the doping structures should result in different electrochemical doping/dedoping characteristics of the two kinds of conducting PPy films.

In this article, the mechanism of the electrochemical processes of PPy(TsO⁻) were studied by cyclic voltammetry, ac impedance, and elemental analysis. It was found that there are two doping sites in structure **I** of PPy(TsO⁻): site A with the counteranions located between the PPy layers and site B with the counteranions located in the PPy layers. The reduction of site A is accompanied by the dedoping of the counteranions, and the reduction of site B is carried out with the insertion of the solution cations. The electrochemical kinetics of the redox processes of site A was analyzed based on ac impedance measurements.

EXPERIMENTAL

PPy(TsO⁻) films were prepared in a pH 3, 0.1 mol/L pyrrole, 0.2 mol/L TsONa aqueous solution galvanostatically. The PPy film electrode for cyclic voltammetry was produced at 0.1 mA on a Pt disc electrode with an area of 7 mm² for 70 s. The PPy films for acid treatment were deposited at 1.5 mA/cm² on a stainless-steel plate with an area of 10 × 1.5 cm. A Pt plate was used as the counter-electrode and a saturated calomel electrode (SCE) was used as the reference electrode. The potential scan rate was 20 mV/s unless otherwise stated. The ac impedance measurement was performed at various potentials with an ac voltage of 5 mV in the frequency range from 0.01 to 100 kHz. The cyclic voltammetry and ac impedance measurement were performed with a ZAHNER IM6e electrochemical workstation.

The acid treatment was carried out by immersing the PPy(TsO⁻) films in a 1 mol/L HNO₃ solution for 10 h. After the treatment, the sample was washed with deionized water three times and then dried at 60°C in a vacuum for 8 h. The thickness of the PPy films was measured by an electronic digital micrometer (Qinghai Measuring and Cutting Tools Plant, China) with a measurement error of ±1 μm. All the experiments were performed at room temperature.

RESULTS AND DISCUSSION

Cyclic Voltammograms in Aqueous Solution

Cyclic voltammetry was performed for investigating the electrochemical properties of conducting PPy(TsO⁻) films in aqueous solutions. It was found that the shape of the cyclic voltammograms (CVs) depends on the nature of the electrolyte salts and the solution pH values. Figure 1 shows the CV of PPy(TsO⁻) film in a neutral 0.2 mol/L NaNO₃ aqueous solution. Obviously, there are two reduction processes in the potential range from 0.2 to -0.9 V. The first reduction process is between 0.2 and -0.6 V; the cathodic peak is at about -0.3 V. The second reduction process is between -0.6 and -0.9 V; the cathodic peak is at about -0.83 V. The reduction processes are reversible and the CV is reproducible in the subsequent cycles.

Figure 2 shows the potential scan rate dependence of peak currents in the CVs of PPy(TsO⁻) in a neutral 0.2 mol/L NaNO₃ aqueous solution. The

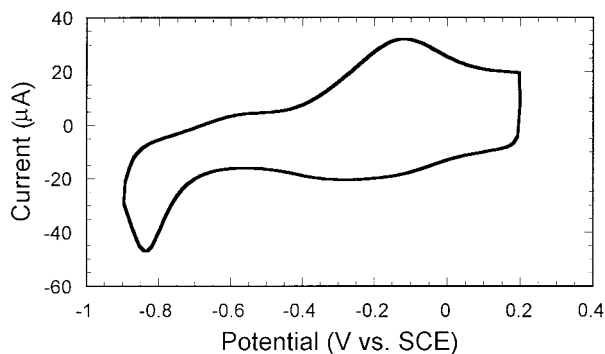


Figure 1 CV of PPy(TsO⁻) in a neutral 0.2 mol/L NaNO₃ aqueous solution.

peak currents in the reduction and reoxidation are proportional to the scan rate in the range from 10 to 40 mV/s, which indicates that the two reduction processes are both surface reactions for the thin film electrodes.

Figure 3 shows the CV of PPy(TsO⁻) in a neutral 0.2 mol/L TsONa aqueous solution. Compared with the CV in a 0.2 mol/L NaNO₃ aqueous solution, the first reduction peak disappeared and the second reduction peak remained in the CV in the 0.2 mol/L TsONa aqueous solution. The two electrolyte solutions contain the same cations of Na⁺ but different anions of NO₃⁻ and TsO⁻. This result indicates that the first reduction process

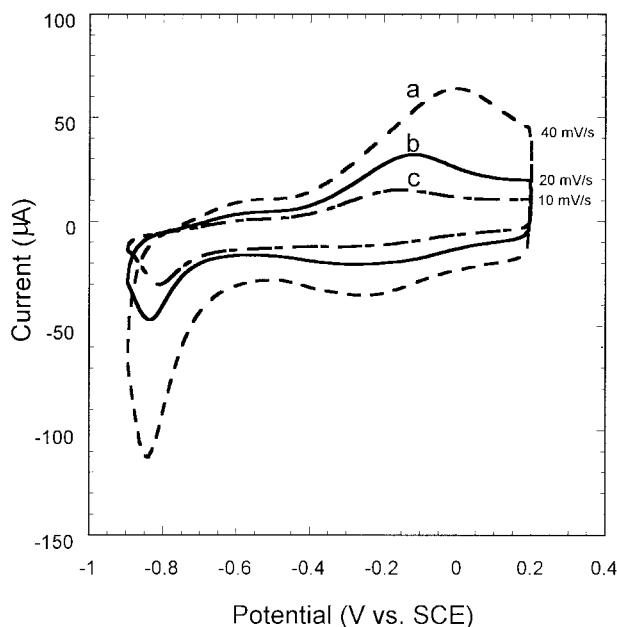


Figure 2 CVs of PPy(TsO⁻) in the neutral 0.2 mol/L NaNO₃ aqueous solution at the potential scan rate of (a) 40 mV/s, (b) 20 mV/s, and (c) 10 mV/s.

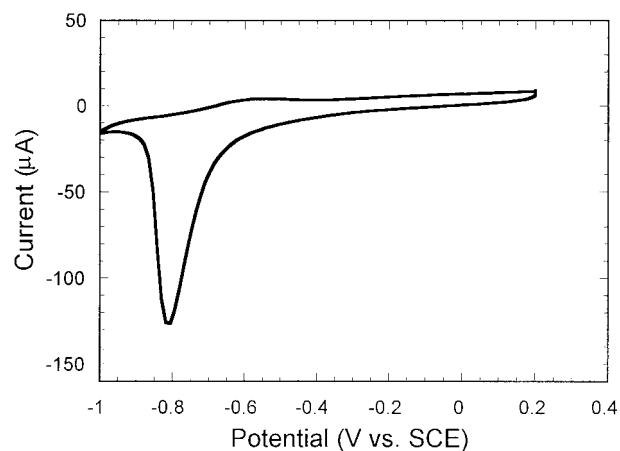
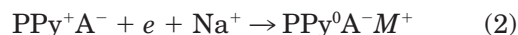


Figure 3 CV of PPy(TsO⁻) in a neutral 0.2 mol/L TsONa aqueous solution.

may be accompanied by the dedoping of the counteranions and the second reduction process probably is accompanied by the insertion of the solution cations, that is, the first reduction:



and the second reduction:



where the doped conducting PPy was written as PPy⁺A⁻ for an easy expression of the electrochemical reaction; PPy⁰ represents the neutral state of PPy.

According to the Nernst equation, the electrode potential of reaction (1) can be expressed as

$$E = E' - (RT/nF)\ln([\text{A}^-]) \quad (3)$$

The electrode potential of reaction (2) can be expressed as

$$E = E' + (RT/nF)\ln([\text{Na}^+]) \quad (4)$$

where E' includes the contribution from the standard potential E^0 and the concentration of PPy⁺, [Na⁺] and [A⁻] represent the concentrations of cation Na⁺ and anion A⁻, respectively. Thus, the reduction potential of the first reduction process should change negatively with increase of the anion concentration and that of the second reduction process should change positively with increase of the cation concentration. Figure 4 shows the CVs of PPy(TsO⁻) in 0.2 mol/L and 1.0 mol/L NaNO₃

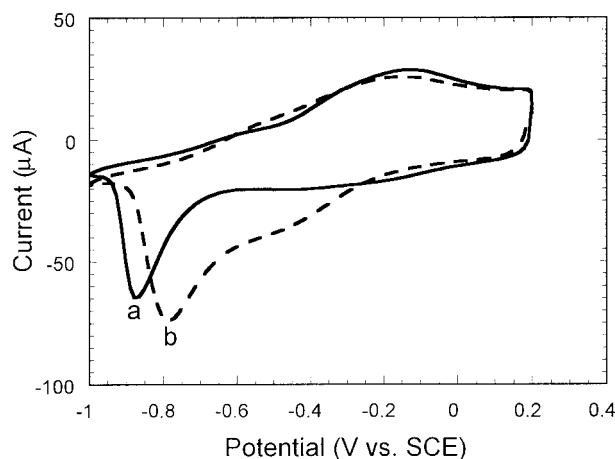


Figure 4 CVs of PPy(TsO⁻) in the neutral NaNO₃ aqueous solutions with the NaNO₃ concentration of (a) 0.2 mol/L and (b) 1.0 mol/L.

aqueous solutions. Compared with the CV in 0.2 mol/L NaNO₃ solution, the cathodic(reduction) peak potential of the CV in the 1.0 mol/L NaNO₃ solution shifted obviously: The first cathodic peak shifted negatively while the second cathodic peak shifted positively. These results agree well with the reduction mechanism proposed above.

The cyclic voltammetric behavior was also affected by the pH values of the electrolyte solutions. Figure 5 shows the CV of PPy(TsO⁻) in a pH 2, 0.2 mol/L TsONa aqueous solution. The cathodic current peak is much weaker than that in Figure 3, which indicates that the solution cation insertion into PPy is sluggish in the acidic solution. Probably, protons in the acidic solution adsorbed on the surface of the PPy film, which impedes the insertion of solution cations.

Two Doping Sites of Counteranions in PPy(TsO⁻)

To investigate the doping characteristics of PPy(TsO⁻) and to understand the anionic exchangeability in the doping structure, HNO₃ acid treatment was performed for the PPy(TsO⁻) film. The composition change and volume change of the film after the treatment are tabulated in Table I. It can be seen from Table I that 53% of the TsO⁻ counteranions in PPy(TsO⁻) was exchanged with NO₃⁻ after the HNO₃ treatment. The mass change of PPy(TsO⁻) after alkali treatment and water treatment revealed that about 95% of its total doping structure belongs to structure I and the TsO⁻ counteranions in structure I of PPy(TsO⁻) locate partly between and partly in the PPy plain layers.¹⁵ The thickness of the film was reduced by

17%, while the length and width of the film only was reduced by about 3–5% after the counteranion exchange in the acid treatment, as shown in Table I. Obviously, the counteranions between the PPy layer were exchanged with the smaller anion of NO₃⁻, which results in the reduction of the film thickness. For the convenience of discussion, here we define the doping site where the counteranions are between the PPy layer of PPy(TsO⁻) as site A and the doping site where the counteranions are in the PPy layer of PPy(TsO⁻) as site B. In this way, structure I of PPy(TsO⁻) includes two doping sites of site A and site B; the TsO⁻ counteranions in site A are exchangeable with the smaller anions such as NO₃⁻, while those in site B are not.

Based on the experimental results mentioned above, it was proposed that the first reduction (between 0.3 and -0.4 V) corresponds to site A, which is easily reduced and its counteranions are loosely combined with the oxidized PPy chain. The reduction of site A is accompanied by the dedoping of the counteranions. The second reduction between -0.4 and -0.9 V corresponds to site B, which is less easily reduced and its counteranions are tightly combined with the oxidized PPy chain. The reduction of site B is accompanied by the insertion of the solution cations. The EQCM results of PPy(TsO⁻) in an organic solution⁹ indicate that the PPy(TsO⁻) film prepared from an organic solution may also contain the two doping sites mentioned above.

Impedance Analysis

The results of the CVs of PPy(TsO⁻) mentioned above indicate that the redox processes of doping

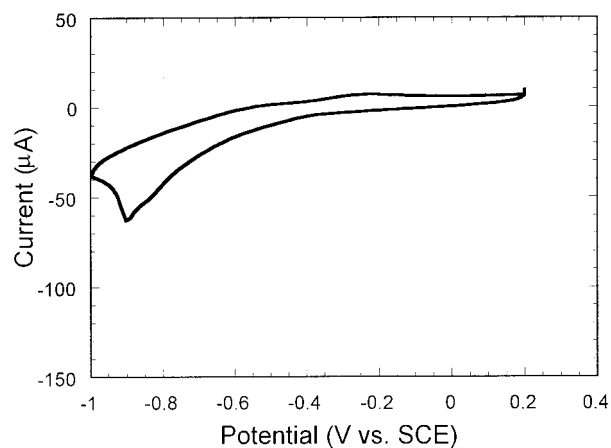


Figure 5 CV of PPy(TsO⁻) in a pH 2, 0.2 mol/L TsONa aqueous solution.

Table I Elemental Analysis of Conducting PPy Films

PPy Samples	Treatment	Ratio of the Elements ^a						Volume Change ^b		
		C	H	N	TsO ^{-c}	NO ₃ ⁻	Cl ⁻	<i>l</i> /cm	<i>w</i> /cm	<i>d</i> /μm
PPy(TsO ⁻)	As-prepared	4	3.36	1.0	0.32			4.42	1.45	76.4
PPy(TsO ⁻)	1 mol/L HNO ₃	4	3.19	1	0.14	0.17		4.20	1.40	63.7
								(-5%)	(-3.4%)	(-17%)
PPy(Cl ⁻)	1 mol/L HNO ₃	4	3.19	1		0.28	0.02			

^a The content of oxygen was not analyzed.

^b *l* represents length; *w*, width; and *d*, thickness.

^c Calculated based on the content of sulfur; the content of C and H was considered.

site A are strongly related to the nature of the anions in the electrolyte solutions. The phenomenon could be elucidated further with a kinetic study of the processes. Thus, the ac impedance measurements were carried out to study the electrochemical kinetics. Figure 6 shows the impedance plot of PPy(TsO⁻) in a 0.2 mol/L NaNO₃ aqueous solution at -0.2 V. There is a flattened semicircle in its high-frequency range and a sharply rising tail in its low-frequency end in the impedance plot. The charge-transfer resistance R_{ct} can be obtained from the semicircle, which is about 50 Ω and similar to the R_{ct} value of PPy(NO₃⁻) in a NaNO₃ aqueous solution in the potential range between 0.2 and -0.4 V.¹⁶ The impedance plot of PPy(TsO⁻) in an 0.2 mol/L TsONa aqueous solution at -0.2 V is shown in Figure 7. Obviously, the R_{ct} value (ca. 10 kΩ) is much larger than that in the NaNO₃ solution,

which indicates that the charge-transfer reaction in the redox processes of site A is much more sluggish in the TsONa solution in comparison with that in the NaNO₃ solution. The disappearance of the first reduction process of site A in the TsONa solution may partly result from the sluggish kinetics.

CONCLUSIONS

The following conclusions can be drawn from the experimental results mentioned above:

1. There are two doping sites, site A and site B, in the doping structure I of the conducting PPy(TsO⁻). The TsO⁻ counteranions in site A locate between the PPy layers and are loosely combined, while those in site B locate in the PPy layers and are tightly combined.
2. There are two reduction processes of PPy(TsO⁻) in the aqueous solutions with

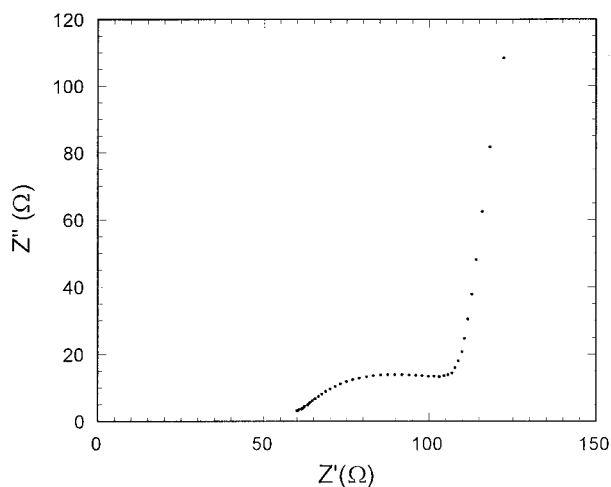


Figure 6 An ac impedance plot of PPy(TsO⁻) in a neutral 0.2 mol/L NaNO₃ aqueous solution at the potential of -0.2 V.

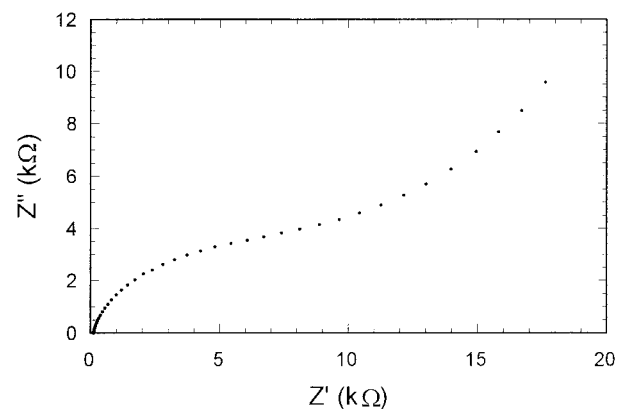


Figure 7 An ac impedance plot of PPy(TsO⁻) in a neutral 0.2 mol/L TsONa aqueous solution at the potential of -0.2 V.

smaller anions in the potential range from 0.3 to -0.9 V. The first reduction process from 0.3 to -0.4 V, corresponding to the reduction of site A, is accompanied by the dedoping of the counteranions. The second reduction processes from -0.4 to -0.9 V, corresponding to the reduction of site B, is accompanied by the insertion of the solution cations.

3. The electrochemical kinetics of the redox processes of site A of PPy(TsO⁻) was studied by ac impedance measurements. The charge-transfer reaction in the redox processes of site A is much more sluggish in the TsONa solution in comparison with that in the NaNO₃ solution.

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