

PREPARATION, CHARACTERIZATION AND ELECTROCHEMICAL PROPERTIES OF POLYPYRROLE-POLYSTYRENE SULFONIC ACID COMPOSITE FILM*

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Abstract Polypyrrole-polystyrene sulfonic acid (PPy-PSSA) composite films have been electrosynthesized in an aqueous solution of PSSA. The electro-active films exhibit cation exchange during the redox process. Infrared, Raman and energy-dispersive spectroscopic results demonstrated that the polyanion of PSS⁻ is co-deposited into the PPy matrix and couldn't be stripped from the film extensively by dedoping. The doping level together with dipolaron content of the PPy-PSSA composite film increases during electrochemical polymerization process. SEM images revealed that the composite film has smooth and compact morphology and AFM pictures suggested that PPy chains are possibly grown perpendicular to the electrode surface. TGA tests indicated that the composite films has much better thermal stability than that of pure PPy. Furthermore, electrochemical studies showed that the relaxation process at certain holding potential has great effect on the shape of the cyclic voltammetric curves of PPy-PSSA composite film. The composite film exhibits cation and anion exchange during the redox process after undergoing the relaxation step. It is more difficult for divalent anion to enter the polymer matrix than a univalent ion, and a large cation such as (CH₃CH₂CH₂CH₂)₄N⁺ cannot be involved in the ion exchange process.

Keywords: Polypyrrole; Polystyrene sulfonic acid; Composite; Electrochemical studies.

INTRODUCTION

Polypyrrole (PPy), a typical conductive polymer, has attracted considerable attentions because of its high conductivity, good environmental stability and biocompatibility^[1–3]. It has been widely applied in batteries^[4], supercapacitors^[5], sensors^[6], anhydrous electrorheological fluids^[7], microwave shielding, and corrosion protections^[8]. Up to now, PPy has been synthesized through a chemical or an electrochemical route, and its properties depend strongly on the synthetic conditions. For example, PPy can be easily electropolymerized in aqueous solution containing surfactants with low molecular weight. However, the films are usually rough and porous. A series of dopants has been used to improve the mechanical properties, conductivity, stability of the resulting polymers^[9, 10]. On the other hand, in order to endow some new functions, various functional components such as nanoparticles^[11, 12], large anions^[13], or bioactive materials^[14] have been introduced directly into the PPy films. Preparation of conductive polymer-polymer composites is also an effective approach to achieve high-quality and functional conductive polymeric materials^[15–19]. Electropolymerization of pyrrole in the presence of polyanion such as polystyrene sulfonate anion (PSS⁻) has been accomplished and reported previously^[20–22]. However, almost all the PPys doped with PSS⁻ were synthesized in the aqueous solution of polystyrene sulfonate salt. The introduction of polyanion into the p-type conducting polymer makes the charge of the film compensated by cation during redox process, because the immobilized anion groups incorporated into the polymer neutralize the cationic sites generated on the redoxing polymer chains.

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PPy films with small mobile anions such as tetrafluoroborate (BF_4^-) and perchlorate (ClO_4^-) exhibit mainly anion exchange behavior, whereas PPy doped with immobilized anions such as *p*-toluene sulfonate (ToS^-) or polystyrene sulfonate shows cation exchange properties that are superior in capacitance per unit volume and in diffusion of ionic species^[23, 24]. The electrochemical switching of conducting polymers from the insulating state to the conducting state is accompanied by a structural or conformational change and the relaxation of the polymer film is shown to affect the rate of the redox transformation^[25–27]. Electrochemical cyclic voltammetry is an effective technique for the characterization of ion movement in the transition process.

Here, we report the preparation of PPy-polystyrene sulfonic acid (PPy-PSSA) composite film by direct electrochemical polymerization of PPy in the aqueous solution of PSSA. As far as we know, it is the first time that PPy-PSSA composite film has been electrosynthesized in the polymeric acid medium. Smooth and compact PPy-PSSA composite films with good thermal stability and electronic conductivity were generated. The electrochemical behavior of the obtained PPy-PSSA composite films was also investigated.

EXPERIMENTAL

Polystyrene sulfonic acid (PSSA, a 18 wt% aqueous solution) was purchased from Aldrich and used as received. Sodium polystyrene sulfonate (NaPSS) was prepared by neutralizing PSSA with aqueous NaOH. Pyrrole (available from Chinese Army Medical Institute) was distilled before use. The electrosynthesis was carried out at room temperature in a one compartment cell (5 cm³) by using of a Model 283 potentiostat-galvanostat (EG&G Princeton Applied Research) under computer control. The working and counter electrodes used to prepare polymer films were two stainless steel sheets (AISI 321) with a surface area of 0.5 cm² each and placed 0.5 cm apart. The working electrode used to study the electrochemical behavior of the composite film was a platinum wire with a diameter of 0.5 mm and an effective length of 8 mm. All potentials were referred to a saturated calomel electrode (SCE). The solutions were deaerated by dry nitrogen stream and maintained under a slight overpressure during the experiments. The typical electrolyte was an aqueous solution of 0.5 mol L⁻¹ pyrrole and 0.5 mol L⁻¹ repeat units of PSSA. In order to eliminate the influence of gas bubbles generated at the counter electrode on the morphology of film, a small partition was placed between the working and counter electrodes. The composite films were generated by the chronoamperometry, chronopotentiometry or the cyclic voltammetry technique.

The infrared spectra of polymers were recorded on a Spectrum GX FT-infrared spectrometer (Perkin-Elmer) with KBr pellets. Raman spectra were recorded by using a RM 2000 microscopic confocal Raman spectrometer (Renishaw PLC., England) employing a 633 nm laser beam. The SEM images and energy-dispersive spectroscopy (EDS) of the composite film were recorded by using a KYKY 2800 scanning electron microscope with a FINDER-1000 energy-dispersive spectrometer (Beijing Scientific Instrument Company, China). The thermal stability of the samples was tested by a thermogravimetric meter (Instrumental TGA 2050) at a heating rate of 20 °C min⁻¹ under nitrogen atmosphere and the decomposition temperature was determined automatically by a TGA equipment. The dedoped PPy films were obtained by immersing the film in 25% (by weight) ammonium hydroxide for 24 h followed by water wash and vacuum dry before characterization. Atomic force microscopic (AFM) images were obtained by using a SPA-300 microscopy (Seiko Instruments, Inc., Chiba, Japan).

RESULTS AND DISCUSSION

Electrochemical Polymerization

The anodic polarization curves of 0.5 mol L⁻¹ pyrrole in the aqueous solution containing 0.5 mol L⁻¹ repeat units of PSSA (1) or NaPSS (2) are shown in Fig. 1(a), respectively. The virgin oxidation potentials of pyrrole in the two media are nearly the same (~ 0.7 V). However, the current density in the acidic medium of PSSA is much larger than that in the NaPSS aqueous solution, which suggests that the acidic electrolyte can promote the polymerization. Figure 1(b) illustrates the successive cyclic voltammograms (CV) of 0.5 mol L⁻¹ pyrrole in an

electrolyte containing 0.5 mol L^{-1} PSSA. A regular increase of the anodic and cathodic current densities indicated the growth of an electroactive polymer film on the surface of working electrode. The anodic ($\sim 0.3 \text{ V}$) and cathodic ($\sim -0.2 \text{ V}$) waves show the expulsion and insertion of H^+ ion from the film. It is believed that the polyanion of PSS^- is trapped inside the polymer matrix, and is not directly involved in the redox process. The obtained polymer composite is homogeneous and can be peeled off from the electrode surface as a free-standing state. On the other hand, the successive cyclic voltammograms of 0.5 mol L^{-1} pyrrole in an electrolyte containing 0.5 mol L^{-1} NaPSS show much lower current density of polymerization (Fig. 1c) than that in the aqueous PSSA solution (Fig. 1b), and the redox waves of the polymer were not found. The polymerization rate of pyrrole in this medium was fairly slow and no apparent polymer film was observed on the electrode in the initial several tens cycles. These results indicate that the aqueous acid solution is a better medium than the widely used aqueous solution of NaPSS for electrosynthesis of PPy-PSS $^-$ composite film.

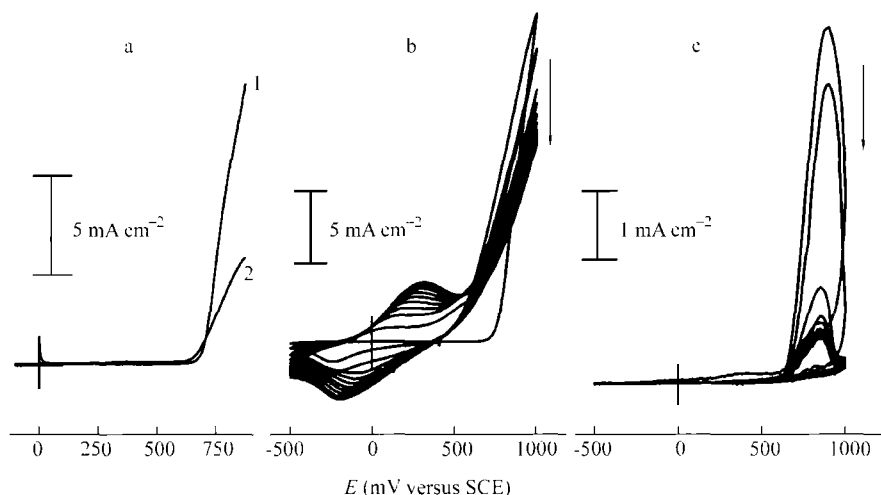


Fig. 1 Anodic polarization curves (a) and successive cyclic voltammograms of 0.5 mol L^{-1} pyrrole in an aqueous solution containing 0.5 mol L^{-1} repeat units of PSSA (b) or NaPSS (c) at a potential scan rate of 20 mV s^{-1}

FT-infrared and Raman Spectroscopic Characterizations

Figure 2 shows the FT-infrared spectra of PSSA and PPy-PSSA composite film. The spectroscopic results of the PPy film are similar to those of the PPy obtained by other method^[20, 28]. The characteristic band corresponding to SO_3^- group resulting from the dopant of PSSA was observed at 1035 cm^{-1} in Fig. 2(b), indicating the PPy was doped by PSSA. The spectrum of the dedoped PPy film (Fig. 2c) resembles that of doped PPy (Fig. 2b). This is mainly due to the fact that the large size of PSS^- means that the anions cannot be stripped from the film extensively. The energy-dispersive spectrum of the dedoped PPy sample, as well as that of the PPy film electrosynthesized in the aqueous PSSA solution, also show a sulfur peak, which supports the conclusion described above. In addition, no band close to 1700 cm^{-1} was found in Fig. 2(c), implying the PPy film was not overoxidized during the course of polymerization.

The Raman spectra of PPy-PSSA composite films with different thickness and a dedoped sample are shown in Fig. 3. The spectroscopic features of the PPy-PSSA composite film are similar to those reported previously^[29]. The strong band at ca. 1600 cm^{-1} is attributed to the stretching vibration mode of $\text{C}=\text{C}$ bonds of PPy. The double peaks at ca. 1050 and 1080 cm^{-1} are assigned to the $\text{C}-\text{H}$ in-plane deformation vibration. The other double peaks at ca. 1320 and 1380 cm^{-1} are attributed to the ring stretching vibration mode of PPy. However, the 1080 cm^{-1} band is associated with the oxidized PPy^[29], which indicates that the composite films were made of PPy in the oxidized (conductive) state. With the increase of film thickness, the 1080 cm^{-1} band intensifies in comparison with the 1050 cm^{-1} band (cf. Fig. 3a to g). Furthermore, the band at ca. 940 and 990 cm^{-1} are assigned to the ring deformation vibration mode associated with dication (dipolaron) and radical cation (polaron), respectively^[29, 30]. The intensity ratio of 940 cm^{-1} to 990 cm^{-1} band increases with the increase of film

thickness. These results demonstrate that the doping level together with dipolaron content of the PPy-PSSA composite film increases during electrochemical polymerization process, which is in agreement with the PPy film synthesized in other systems^[29]. The dc conductivity of the composite films was measured to be in the range of 0.5–15 S cm⁻¹. There are no evident bands at 1080 and 1380 cm⁻¹ in the spectrum of the dedoped PPy film (Fig. 3h), which suggests that the PPy doped by large anion PSS also can be dedoped into the neutral state.

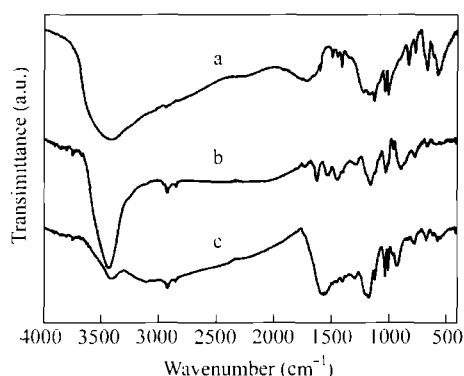


Fig. 2 Infrared spectra of PSSA (a) the PPy-PSSA film in the doped state (b) and dedoped state (c)

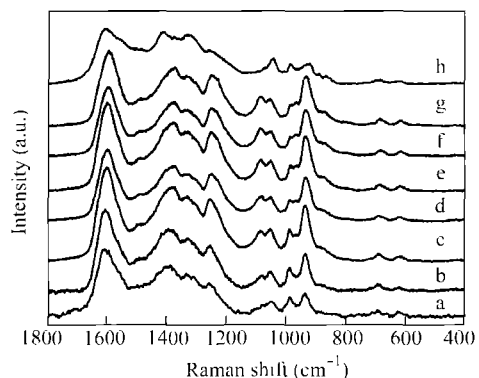


Fig. 3 Raman spectra of PPy-PSSA composite films prepared galvanostatically at 1.3 mA cm⁻² for different charge density (a, 7; b, 13; c, 27; d, 40; e, 67; f, 133 and g, 200 mC cm⁻²) and the dedoped g sample (h)

TGA Analysis of the PPy-PSSA Composite Film

Figure 4 demonstrates the TGA analysis results of PPy-PSSA composite films. It is obvious in these curves that the PPy films obtained by electrolysis of pyrrole in PSSA aqueous solution have good thermal stability with decomposition temperature higher than 320 °C. This value is much higher than that of ClO₄⁻ doped PPy (~200 °C)^[31] and PPy-coated PSSA microspheres (< 250 °C)^[32]. The highest decomposition temperature appears at 334 °C for the composite film prepared in the electrolyte containing 0.5 mol L⁻¹ PSSA. These results indicate that the introduction of polymeric acid can effectively improve the thermal stability of PPy. With the increase of PSSA concentration from 0.1 to 0.5 mol L⁻¹ repeat units, the decomposition temperatures of PPy films gradually increase, mainly due to the increase of PSSA concentration in the electrolyte and thus enhances the doping level of PSSA in the PPy matrix. However, as the concentration of PSSA is increased to 0.7 mol L⁻¹, the

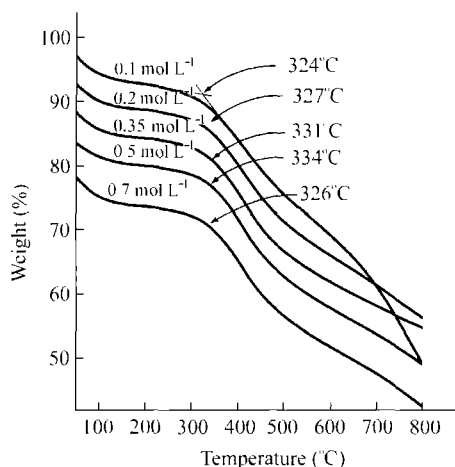


Fig. 4 TGA curves of PPy-PSSA composite films obtained by electrolysis of 0.5 mol L⁻¹ pyrrole at 0.7 V in the medium with different PSSA concentrations

decomposition temperature of the prepared PPy film is decreased slightly to 326°C. This is probably due to the fact that the high acidity of this medium leads to the fast polymerization of pyrrole and produces some defects in PPy-PSSA chains.

Morphology of PPy-PSSA Composite Film

Figure 5 illustrates the SEM images of a PPy-PSSA composite film and a β -naphthalene sulfonic acid doped PPy film (PPy-NSA) for comparison. As it can be seen from this photo PPy-PSSA composite film has a smooth and compact morphological structure (Fig. 5a, b). The grain size of the film surface is small and has a diameter less than 0.1 μm (Fig. 5a), while PPy-NSA film has a rough and porous surface and its grain size is about 2–5 μm (Fig. 5c). Furthermore, comparing the SEM cross-sectional images of PPy-PSSA film (Fig. 5b) and PPy-NSA film (Fig. 5d), the structure of the former film is compact and tight, while that of latter film is loosely piled up. The characteristics of flatness and compactness are typical for the PPy-PSSA composite film. This is similar to that of PPy composite film electropolymerized in the aqueous polystyrenesulfonate salt solution^[21].

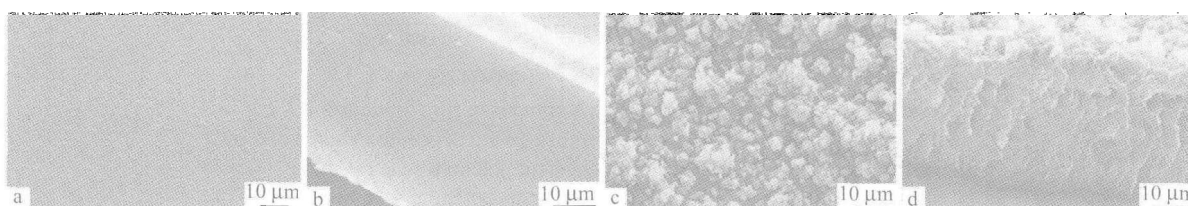


Fig. 5 SEM images of a PPy-PSSA composite film (a, b) and a PPy-NSA film (c, d). Both films have nearly the same thickness and were formed potentiostatically at 1.2 V in an aqueous solution of 0.5 mol L⁻¹ pyrrole and 0.5 mol L⁻¹ PSSA or β -naphthalene sulfonic acid (NSA); Scale bars: 10 μm

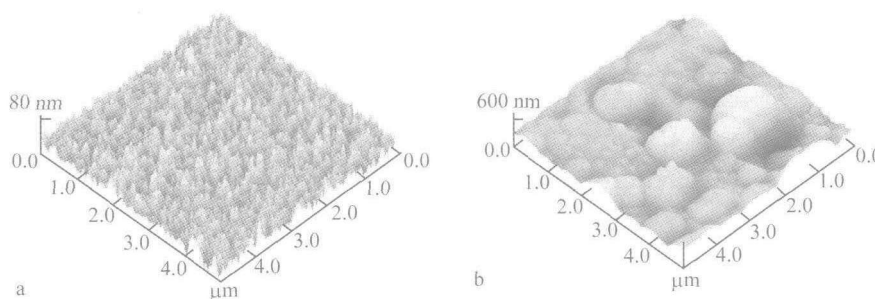


Fig. 6 AFM images of the PPy-PSSA composite film (a) and PPy-NSA film (b) electrodeposited from 0.5 mol L⁻¹ PSSA and NSA, respectively

The surface morphology of PPy-PSSA composite film was also investigated by using atomic force microscopy (AFM). As shown in Fig. 6, the surface of the PPy-PSSA film has a columnar structure, whereas that of PPy-NSA film consists of irregular-shaped microspheres, suggesting that PPy-PSSA composite film is grown perpendicularly to the electrode surface and PPy-NSA film is deposited in a random way. The growth of PPy-PSSA film is similar to the polymerization of ethylenedioxythiophene in an electrolyte containing long-chain surfactant^[33]. Furthermore, the roughness of the PPy-PSSA composite film is about 50 nm, which is much lower than that of PPy-NSA film (ca. 600 nm).

Cyclic Voltammetric Studies of PPy-PSSA Composite Film

The electro-activity of PPy-PSSA composite film was tested in 0.1 mol L⁻¹ aqueous LiClO₄ solution after rapid washing with water. Figure 7 illustrates the cyclic voltammograms (CVs) of PPy-PSSA composite film deposited electrochemically from the medium of 0.5 mol L⁻¹ PSSA. The steady-state CVs show broad anodic

and cathodic peaks. The currents are proportional to the scan rate (Fig. 7, inset), indicating a redox couple attached to the electrode. Furthermore, the films can be cycled repeatedly between the conducting (oxidized) and insulating (neutral) state without significant decomposition of the materials. The redox process is fairly reversible, and the anodic and cathodic current densities are almost the same.

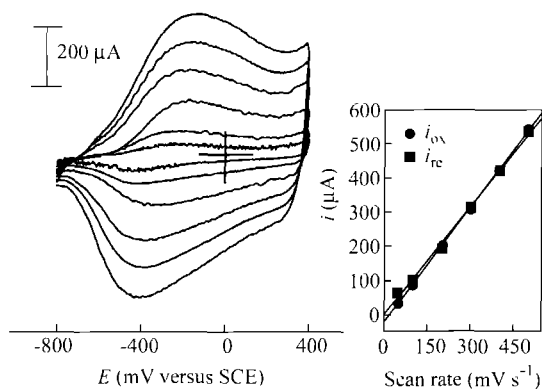


Fig. 7 Cyclic voltammograms of a PPy-PSSA composite film (obtained at 1.2 V in 0.5 mol L^{-1} pyrrole and 0.5 mol L^{-1} PSSA solution with deposition charge of 7 mC) in 0.1 mol L^{-1} aqueous LiClO_4 solution at different potential scan rates
Inset: plots of anodic or cathodic peak current versus potential scan rate

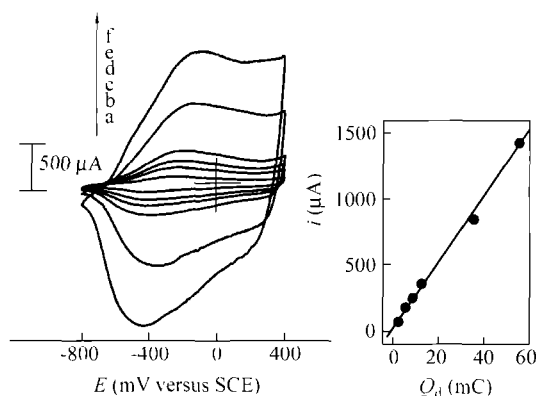


Fig. 8 Stabilized cyclic voltammograms of a PPy-PSSA composite film modified electrodes in 0.1 mol L^{-1} LiClO_4 aqueous solution with deposition charge Q_d (a, 2.6; b, 6.0; c, 8.4; d, 12.8; e, 34.8 and f, 55.2 mC)
Scan rate: 200 mV s^{-1} ; Inset: plots of anodic peak current versus deposition charge Q_d .

Stabilized CVs of PPy-PSSA composite film modified electrode with different film thickness are shown in Fig. 8. A good positive linearity between anodic wave current and film thickness is observed, indicating PPy-PSSA composite film has a uniform structure despite of the increase of the film thickness. The number of the ions insetting and expelling the polymer matrix also increases consistent with that of thickness. On the other hand, the drive force of charges (electrons or ions) is the applied potential, the potential shift of anodic peak was observed with the increase of film thickness due to the potential drop inside the film and the limitation of the charge transfer.

To confirm the cation exchange behavior of the PPy-PSSA composite film during the redox process, the CVs were carried out in 0.1 mol L^{-1} sodium dodecylbenzene sulfonate (SDBS) aqueous solution. The PPy film doped with small anion of ClO_4^- was also studied for comparison. As shown in Fig. 9, the ClO_4^- doped PPy film shows weak electrochemical responses in the electrolyte solution containing large anions, indicating the dodecylbenzene sulfonate ions cannot be incorporated into the PPy matrix because of their steric hindrance. However, the PSS^- doped film has the electrochemical responses based on doping and dedoping of the small

cations. In Fig. 9, the PPy-PSSA composite film shows a couple of redox waves at -0.2 and -0.35 V (*versus* SCE), respectively. With successive voltammetric scanning in the potential scale of -0.9 to 0 V for several hours, the electrochemical responses did not decline remarkably. Thus, both of the waves shown in Fig. 9 cannot be attributed to the film decomposition or the occurrence of some reversible side reactions. It is reasonable to conclude that the anodic peak at -0.2 V corresponds to the dedoping of the cation from the PPy-PSSA film, and the cathodic peak at -0.35 V is caused by the doping process. Therefore, PPy-PSSA composite film can be reduced and oxidized based on the doping and dedoping of cations in this electrolyte solution.

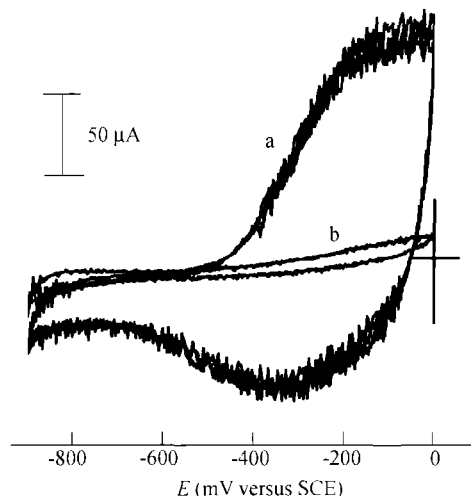


Fig. 9 Cyclic voltammograms of a PPy-PSSA film (a) and a PPy-ClO₄ film (b) (both films were electrosynthesized at 1.2 V in an aqueous solution of 0.1 mol L⁻¹ pyrrole and 0.1 mol L⁻¹ repeat units of PSSA or HClO₄) in 0.1 mol L⁻¹ SDBS solution. The deposition charge of films was 30 mC each and the potential scan rate was 50 mV s⁻¹.

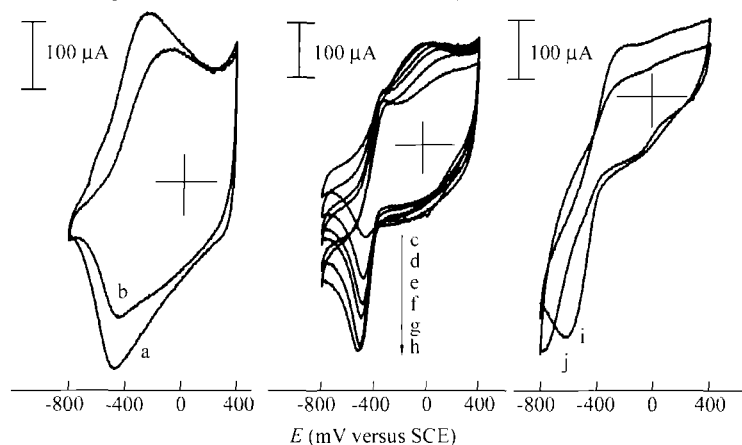


Fig. 10 Cyclic voltammograms of a PPy-PSSA composite film (8.4 mC) modified electrode in 0.1 mol L⁻¹ LiClO₄ aqueous solution at a holding potential E_w of -2 V for different waiting time t_w (a, 0; b, 5; c, 10; d, 20; e, 30; f, 40; g, 100; h, 500; i, 1000 and j, 1500 s); Scan rate = 200 mV s⁻¹

Polyanion inset into the polymer matrix is believed to be immobile, the relaxation experiments were carried out with a modified electrode coated with a thin layer of PPy-PSSA composite film (8.4 mC) to study the effect of holding potential E_w . The potential value of -2 V at which most of conductive polymers can be reduced was selected as the value of E_w . The CV curves of the PPy-PSSA composite film modified electrode in 0.1 mol L⁻¹ LiClO₄ aqueous solution (Fig. 10a) shows a couple of redox wave. The oxidation peak at -0.3 V corresponds to the expelling of Li⁺ and the reduction peak at -0.5 V is assigned to the inset of Li⁺. It is clear that the shape of

the CVs depends strongly on t_w (Fig. 10). As $t_w = 5$ s (Fig. 10b), a positive shift of the anodic peak potential at ca. -0.15 V accompanied by a decrease of peak current was observed. At the moment of $t_w = 10$ s, the cathodic peak at ca. -0.5 V corresponding to the inset of cation becomes sharper and a new weak anodic peak appears at -0.35 V. The anodic wave at -0.15 V still kept positive shift and decrease in the peak current. With the prolongation of t_w , two anodic peaks appear near -0.35 V and 0 V and two cathodic peaks corresponding to the anodic peaks were also observed. Taking the t_w of 500 s as an example (Fig. 10h), the waves at -0.5 V and -0.35 V are associated with the inseting and expelling of Li^+ , and the peaks at 0.15 V and -0.1 V are attributed to the doping and dedoping of ClO_4^- . This is different from that of the large anion (such as dodecylbenzene sulfonate, DBS) doped PPy film. The DBS doped PPy film presented simultaneous anion and cation mobility during the redox in aqueous electrolyte without the reduction of film at a holding potential^[34]. At the drive potential of -2 V, the CV behavior of the PPy film doped by polyanion of PSS^- can be changed. The anion, as well as cation, can exhibits doping and dedoping response during the redox process of the composite film. In addition, as shown in Fig. 11, the peak current (i_p) and potential (E_p) corresponding to the inset of Li^+ into the PPy matrix increase with the increase of t_w (> 10 s). This indicates that the increasing reduction of PPy-PSSA composite film at the potential of -2 V can enhance the peak current dramatically. Therefore, the polyanion doped polymer also can be reduced and its reduction level can be controlled by the waiting time t_w and the holding potential E_p . On the other hand, the increase of E_p indicates that the inset of cation into PPy matrix needs a higher drive potential with the increase of t_w .

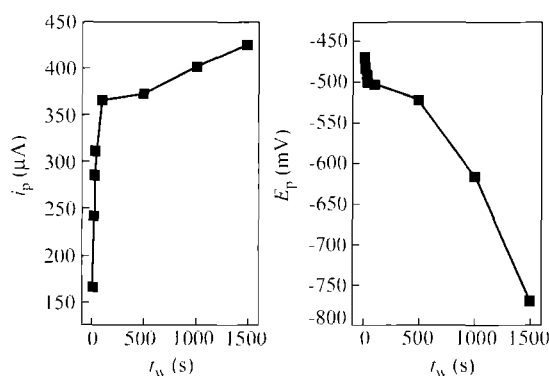


Fig. 11 Plots of i_p and E_p versus t_w for E_w of -2 V

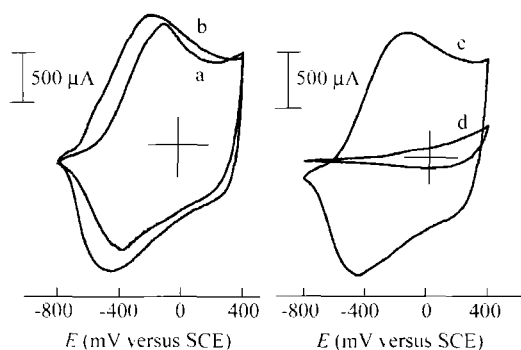


Fig. 12 Cyclic voltammograms of PPy-PSSA composite film modified electrode in 0.1 mol L^{-1} NaCl (a), CaCl_2 (b), NaBr (c) and TBAB (d) at the scan rate of 100 mV s^{-1} .

To test the exchange behavior of different cations, the CVs of PPy-PSSA composite film prepared at a constant current of 1 mA for 80 s were measured in an aqueous electrolyte of NaCl, CaCl_2 and tetrabutylammonium bromide (TBAB). The cathodic peak at ca -0.4 V and the anodic peak at -0.1 V represent the insertion and expulsion of Na^+ ion (Fig. 12a). No response corresponding to the exchange of Cl^- anions was

observed. In the electrolyte containing divalent Ca^{2+} ions, the drive potential of inseting the cations into the PPy matrix is at ca. -0.5 V (Fig. 12b). This value is higher than that of Na^+ ion although the two cations have similar size, indicating the divalent ion enters the matrix more difficult than univalent ion does. Furthermore, as a large cation was used as the exchange ion, there was no significant response and a small amount of charge can be cycled during the cyclic voltammetric process (Fig. 12d). In contrast with Fig. 12(c), there is no apparent TBA^+ ion doping and dedoping wave in Fig. 12(d). The large size and the hindrance of $(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_4\text{N}^+$ ion disable the cation to be involved in the ion exchange.

CONCLUSIONS

PPy-PSSA composite films have been synthesized by electropolymerization of pyrrole in an aqueous solution of PSSA. The free-standing composite film is electro-active and shows cation exchange during the redox process. The composite films have flat surface, compact structure, good thermal stability, and have a conductivity of $0.5\text{--}15\text{ S cm}^{-1}$. The polyanion of PSS^- can be immobilized in the PPy matrix and can only be partially removed by dedoping. The doping level together with dipolaron content of the PPy-PSSA composite film increases with the increase of deposition charge. Furthermore, the reduction at certain holding potential affects strongly on the shapes of the cyclic voltammograms of PPy-PSSA composite films. The composite film presented cation and anion exchange during the redox process after undergoing the relaxation. The univalent ion enters the polymer matrix more easily than the divalent ion. The large cation of $(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_4\text{N}^+$ is unable to be involved in the ion exchange process.

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