

ELECTROCHEMICAL STUDIES ON CONDUCTING COMPOSITE FILMS FROM POLYURETHANE AND POLYPYRROLE

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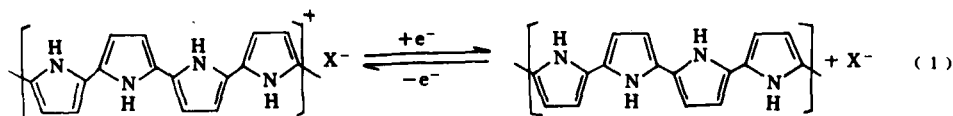
ABSTRACT

A study on the electrooxidative polymerization of pyrrole onto polyurethane-coated platinum electrodes and the electrochemical properties of the composite polyurethane/polypyrrole films (PU/PPy) as-prepared is presented. It is found that polypyrrole grows layer by layer from the polyurethane/platinum interface through the polyurethane matrix, and ca. 20 wt. % of polypyrrole will fill up the matrix. Cyclic voltammograms show that the composite films are porous, and the reduction-reoxidation (redox) rate of the composite films is limited by the diffusion of counteranions through the films. Larger anion size leads to slower diffusion process. The composite films can also act as modified electrodes.

INTRODUCTION

Electrically conducting polymers, especially those based on aromatic or heterocyclic monomers such as pyrrole, aniline, and thiophene, are getting more and more attention^[1]. A polypyrrole(PPy) film prepared by electrooxidizing the appropriate monomer shows high conductivity and stability, but it is hard and brittle with very poor flexibility^[2]. Some methods was used to improve its mechanical properties^[3]. We have recently obtained conducting composite films from polypyrrole and polyurethane^[4]. These films maintain polyurethane's super-high flexibility and polypyrrole's high stability and conductivity(10—30 S/cm).

As has been reported^[1], PPy chain, in its conducting state, bears one positive charge of unity for every 3 to 4 pyrrole rings. This charge is balanced by the counteranion from the electrolyte salt^[2,5,6]. Conducting polypyrrole can be reduced electrochemically or chemically, becoming a neutral insulating polymer. Cyclic potential scans can drive PPy to switch between its conducting and insulating state repeatedly^[7], as shown in the following scheme,



Scheme 1: The switching of PPy chain between its oxidized and neutral state

Some researches have been presented on the switching kinetics^[6,7]. Here we report the electrooxidative polymerization of pyrrole in insulating polyurethane film substrates and the electrochemical properties of the composite films so obtained. It is found that the composite films bear a porous structure, and the diffusion of counteranions into or out of the films limits the redox

rate of polypyrrole dispersed in the electrochemically inert polyurethane substrates.

EXPERIMENTAL

Polyurethane(PU) was obtained from BF Goodrich Co. as a polyester-based resin. Pyrrole was obtained from Tokyo Chemical Industries, Ltd., distilled(bp. 129—131°C) and stored under argon prior to use. Acetonitrile, ethylene glycol, and all of the electrolyte salts were domestic A.R. grade reagents. Among them acetonitrile was further purified by distilling from anhydrous P_2O_5 (81—83°C), whereas the others were used as received.

A PU/Pt electrode, i.e., a Pt slice entirely covered by a PU film (ca. 10 μ m thick if not mentioned) was prepared by depositing a 5 wt. % solution of PU in THF onto the Pt slice polished with metallographic abrasive paper and flannel, and allowing the solvent to evaporate. All of the electrochemical experiments were carried out in an undivided three-electrode cell containing 0.1*N* supporting electrolyte solution of acetonitrile/ethylene glycol(volume ratio 2:1) or water, with an aqueous KCl saturated calomel electrode(SCE) as reference, and a bare Pt slice counter electrode. On a PU/Pt working electrode (ca. 0.6cm²), pyrrole was electropolymerized under a constant potential of 1.00V for 20 to 60 minutes in an acetonitrile/glycol solution containing 0.1*M* pyrrole and 0.1*N* sodium *p*-tosylate (TsONa) supporting electrolyte to prepare a composite polyurethane/polypyrrole film (PU/PPy). The composite films as-prepared were rinsed with distilled water and then dried at 50°C. Cyclic voltammetry (CV) of a composite film was conducted with a PU/PPy/Pt as the working electrode. The electrochemical set-up used to perform these experiments has been described elsewhere^[4]. All of the electrode potential data reported are referred to SCE.

RESULTS AND DISCUSSION

1. Electropolymerization of pyrrole on a PU/Pt working electrode.

One precondition of the electropolymerization of pyrrole on a PU/Pt electrode is that the electrolyte solution can swell the PU film, so that pyrrole and counteranions can penetrate through

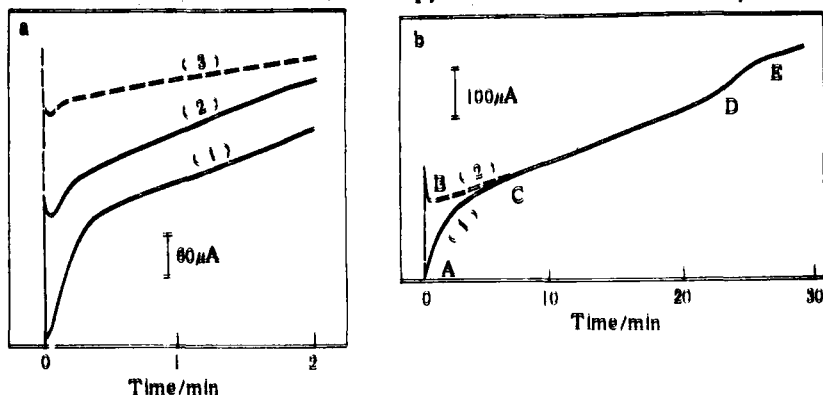


Fig.1. Electropolymerization current of pyrrole via reaction time on PU/Pt electrode under a constant potential of 1.00V in acetonitrile/glycol soln. containing 0.1*M* pyrrole,
 (a) at the initial reaction stage with the PU films pre-swollen for (1) 0 minute,
 (2) 1 minute, (3) 3 and 5 minutes;
 (b) during the whole reaction process with the PU films (1) no pre-swelling applied,
 (2) pre-swollen for 3 minutes.

the insulating layer onto the Pt surface^[4]. The pyrrole is electrooxidatively polymerized on the Pt surface and doped by the counteranions (i.e., dopant) at the same time. Reactants penetrating through the PU layer afterwards will electrodeposite onto the surface of the PPy layer that has formed. As a result, PPy grows layer by layer from the PU/Pt interface through the PU film matrix. Fig. 1a, recording the electrolysis current at the initial reaction stage, shows that previous swelling for 3 minutes and more will make the PU film fully swollen, and the current increases smoothly with the time. When the pre-swelling time is less than 2 minutes, the less the time is, the slower the reaction. But it speeds up much more quickly than the case the PU film has been fully pre-swollen especially when no pre-swelling is applied.

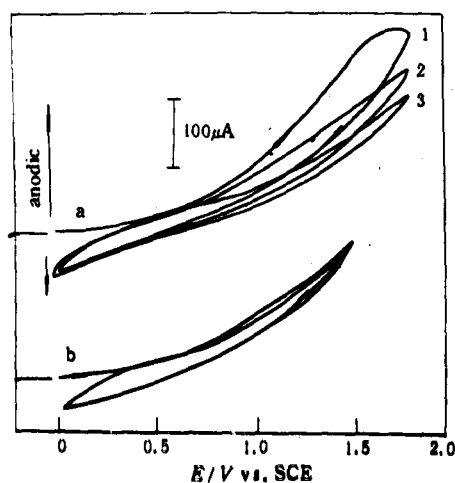


Fig. 2 CV for pyrrole on PU/Pt electrode in 0.1N TsONa, 10mM pyrrole soln. of acetonitrile/glycol (sweep rate 50mV/s.). The thickness of the PU films is (a) ca. 7 μm , (b) ca. 15 μm .

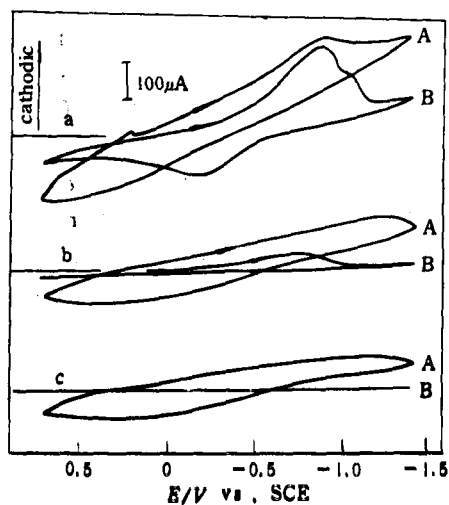


Fig. 3 CV of PU/PPy films in 0.1N TsONa soln. of (A) acetonitrile/glycol; (B) water.

The composites contain a) 0.25, b) 0.20, c) 0.15 C/0.6cm² of PPy in the PU substrate of ca. 6 μm thick.

Fig. 1b, which records the electrolysis current during the whole growth process of PPy in the PU matrix, shows that the curves in Fig. 1a coincide after point C. In Section CD, the current increases smoothly, because as PPy grows continually, the PPy layer in the PU matrix thickens gradually and the diffusion distance of reactants through the PU film shortens correspondingly. PPy may have just filled up the inside of the PU film nearby point D, and the following polymerization reaction occurs directly on the PPy exposed to the solution from the outer surface of the PU film, so it is remarkably accelerated (See Section DE). An evidence for this mechanism is that the inner surface (close to the electrode) of the composite PU/PPy film as-prepared is conducting as soon as electropolymerization occurred, while the outer surface (close to the solution) is insulated if the reaction time is less than 20 minutes, but become more and more conductive after Point D. The current integral between A and D is ca. 0.35C. The weight percentage of PPy of a composite PU/PPy film can be estimated using the following equation (suppose the final PPy chains bear a charge of unity for every 4 pyrrole unit),

$$\text{PPy-TsO}^- \text{ wt. \%} = \frac{\frac{Q}{2.25F} \times (M(\text{pyrrole}) + 0.25M(\text{TsO}^-)) \times 100}{\frac{Q}{2.25F} \times M(\text{pyrrole}) + 0.25M(\text{TsO}^-) + V \times d} \quad (1)$$

where Q is the charge consumed during the electropolymerization, e.g. 0.35C; $V \times d$ is the original weight of the PU film, e.g. $(0.6\text{cm}^2) \times (10\mu\text{m}) \times (1.11\text{g/cm}^3)$; M is the molar mass; and F , Faraday constant. The calculated weight percentage of PPy of a composite film whose PU substrate is just full of PPy is 20%, close to the result obtained by weight analysis (16.9%).

To get some more information on the electropolymerization process of pyrrole, cyclic triangular potential waves between 0 and +1.5 or +1.8V were applied to a PU/Pt working electrode immersed for 2 to 3 minutes in the electrolyte solution of acetonitrile/glycol containing 10mM pyrrole and 0.1N TsONa. On the PU/Pt electrode, pyrrole began to be electrooxidatively polymerized at ca. 0.8V, an anodic peak (P_a) emerges at ca. +1.7V (See the first cycle in Fig.2a). At the potential range of 0 to +1.5V, the CV-curves coincide well when the thickness of the PU film is $15\mu\text{m}$, and the oxidative current at +1.5V remains 0.42mA/cm^2 (Fig.2b). For a thinner PU film or a higher positive potential limit, the oxidative current will drop as the potential scan goes on repeatedly (See Fig.2a). On the contrary, when the PU film is thicker than $15\mu\text{m}$, the anodic current increases as the potential scan goes on repeatedly in the range of 0 to +1.5V. A high positive potential may cause partial oxidative decomposition of PPy, lower the activity of the electrode, and thus reduce the polymerization rate of pyrrole. The existence of a PU layer acts like a series resistance in an electric circuit which leads to the decrease of the effective electrode potential. The thicker the PU layer is, the higher its resistance will be.

2. Electrochemical behavior of a PU/PPy composite film in a background supporting electrolyte solution

Fig. 3 shows cyclic voltammograms (CV) for composite films in a 0.1N TsONa solution of acetonitrile/glycol (i.e., background solution) compared with those obtained in a 0.1N TsONa aqueous solution. The CV of a composite film in the background solution with its outer surface conducting bears a cathodic peak (P_c) and an anodic peak (P_a). The two peaks are broad and have a very large value of ΔE_p (peak separation). No notable capacitive current is observed. When cathodic potential surpass E_p , the relevant current will not decline rapidly as the case for a pure PPy film^[5,6]. In the second scan, P_c becomes broader and I_{P_c} drops, whereas P_a changes little. Both I_{P_c} and I_{P_a} for the same film in TsONa aqueous solution are lower than those mentioned above (Fig.3a). As the PPy concentration in a composite decreases, this difference becomes more remarkable. If a composite film contains less than $0.20\text{C}/0.6\text{cm}^2$ of PPy in the PU substrate of $6\mu\text{m}$ in thickness, no redox reaction can be observed in aqueous solution (Fig.3c). PPy less than $0.20\text{C}/0.6\text{cm}^2$ has not filled up the PU matrix, its outer surface is still insulating. An aqueous solution can not swell the PU film to permit electrolyte to penetrate into or out of the film, so the reaction shown in Scheme(1) will not occur. However, an acetonitrile/glycol solution can swell the PU matrix. Figure 3a indicates that when PPy has grown out of the surface of PU substrate, anions in aqueous solution can diffuse through the composite film to conduct the redox reaction of PPy. The swelling in acetonitrile/glycol solution facilitate this diffusion process, bringing about a faster reaction (Fig.3a). Nevertheless, the diffusion process is still a limiting step, which causes a large ΔE_p and a cathodic current declining

slowly after P_c . On the basis of Figure 3b, $0.20C/0.6cm^2$ of PPy has just filled up a PU matrix with thickness of $6\mu m$. This value corresponds to 19.3% of PPy in the composite according to Equation(1).

3. Electrochemical properties of a composite film in aqueous solutions

The electrochemical behavior of an outer surface-conducting PU/PPy composite film is independent of electrolyte cations but dependent on the kind of anions in aqueous solutions as shown in Figures 4 through 7. In the CV obtained from a TsONa supporting electrolyte solution(Fig.4a), P_c consists of a main peak followed by two shoulders with strong peak current (-1.1 to $-1.4V$), P_a is weak, $E_{Pa} = ca. -0.25V$. In the second scanning cycle, I_{Pc} declines by a half, while I_{Pa} declines a little. Cycling for about 15 times, both I_{Pc} and I_{Pa} stabilize. At that moment, the two values are very low, and the cathodic peak becomes a single peak, E_{Pc} equals ca. $-1.3V$. In $NaClO_4$ solution(Fig.4b), P_c is similar to that in TsONa solution during the first scanning cycle, but I_{Pc} is much stronger. In the second cycle, I_{Pc} declines by ca. a third, P_a broadens and declines a little. When the CV stabilizes after ca. 13 cycles, P_c is still composed of a main peak followed by one shoulder, yet P_a disappears. the CV obtained from KCl, $NaNO_3$ or Na_2SO_4 solution are similar to that from $NaClO_4$ solution except for a little change of E_p and I_p , which will be considered later.

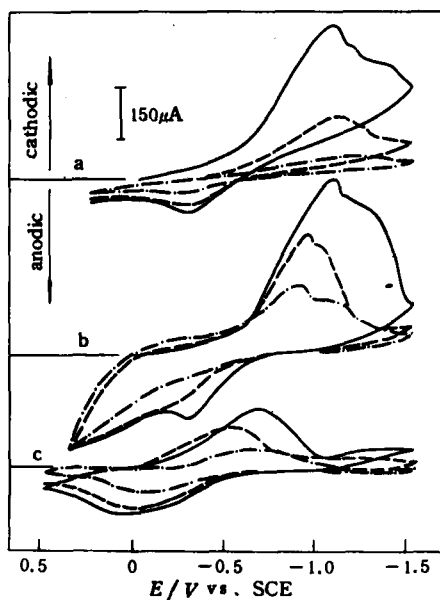


Fig.4 CV for composite PU/PPy films in aqueous soln. of 0.1N (a) TsONa, (b) $NaClO_4$, (c) NaOH. The composites contain $0.4 C/cm^2$ of PPy, in the PU substrates of ca. $10\mu m$ in thickness.

The sweep rate is 20mV/s

————: the first cycle; ----: the second cycle; - · - · - : the stabilized CV-curves after about a dozen of cycle.

The redox property of a composite film in NaOH aqueous solution is peculiar. In its CV, P_c , composed of a single peak, is much weaker than those mentioned above, E_{Pc} equals ca. $-0.6V$. P_a is very broad, E_{Pa} equals ca. $0V$ (Fig.4c).

In aqueous solutions of varied supporting electrolytes, the redox reaction of a composite PU/PPy film all bears $I_{pc} \propto v^{1/2}$, indicating that they are diffusion-controlled. Within low scanning rate limits, I_{pc} tend to be proportional to V (See Fig.5), i.e. to take on the trait of a pure PPy thin film[6]. Figure 6 shows that in the low concentration scope of supporting electrolytes, cathodic peak current drops rapidly as the concentration reduces, and the lower concentration, the more rapidly. Whereas in high concentration region, the peak current changes little as the concentration increases, especially for those supporting electrolyte anions with large molecular sizes.

All of the results above further confirm the porous structure of a composite film with its outer surface covered with PPy. Redox reaction of the film in aqueous medium is confined by the diffusion of counteranions through the film. This diffusion process is a slow one, which makes the reaction advance uncompletely, and ΔE_p be enlarged, furthermore, makes the content of anion in the composite films decrease as reaction is going on so that the reaction slows down gradually. The extremely strong cathodic peak current in the first potential scan cycle may result from the over-oxidation of the composite by oxygen and water during its preparation and drying processes. Cathodic current, more than one peak, further points out that the PPy chains have more than one oxidation state.

After the CV of a composite film in TsONa aqueous solution was stabilized, the solution was replaced with others containing various supporting electrolytes. Cycling times and sequence of every solution used would not affect the shape of Fig.7. This phenomenon implies that the switch of PPy chains between its oxidative and reductive state is reversible in itself. Various counteranions have different sizes and polarizations, their diffusion through the composite film will suffer distinctive resistances, which results in some differences of the CV in redox peaks. The order of cathodic peak potential in various electrolyte solutions is:

$$E_{pc}(\text{KCl}) > E_{pc}(\text{NaNO}_3) > E_{pc}(\text{NaClO}_4) > E_{pc}(\text{KPF}_6) > E_{pc}(\text{TsONa}) \quad (\text{A})$$

And their current order is:

$$I_{pc}(\text{KCl}) \approx I_{pc}(\text{NaNO}_3) \approx I_{pc}(\text{NaClO}_4) > I_{pc}(\text{KPF}_6) > I_{pc}(\text{TsONa}) \quad (\text{B})$$

These sequences demonstrate that the diffusing velocities of anions through the composite PU/PPy

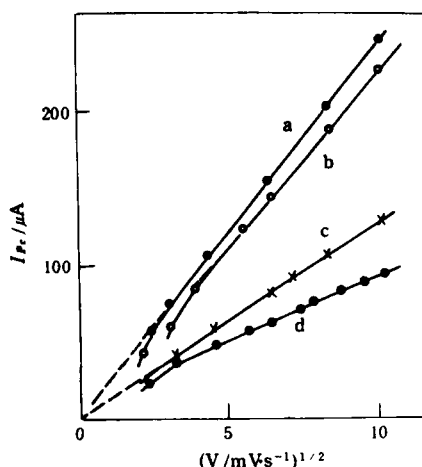
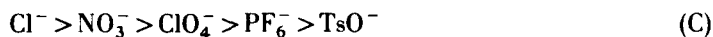


Fig.5 Cathodic peak current-square root of scan rate curve for the stabilized CV obtained in Fig.4 in 0.1N aqueous soln. of (a) KCl, (b) NaClO₄, (c) NaOH, (d) TsONa

film bear the order:



The ionic radius of the above anions may be in the opposite order of (C), so it can be considered that the diffusion rate depends directly on the anion sizes.

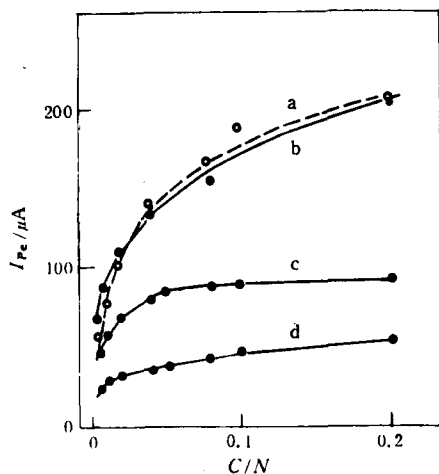


Fig.6 Curves for cathodic peak current via the concentration of supporting electrolyte from the stabilized CV in Fig.4. in (a) KCl, (b) NaClO₄, (c) NaOH, (d) TsONa aqueous soln.

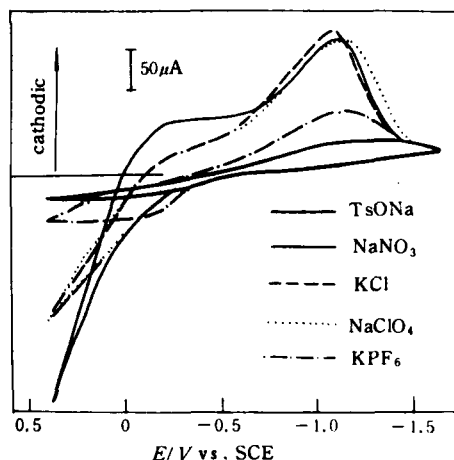


Fig.7 CV in aqueous soln. containing varied supporting electrolytes for PU/PPy films having been repeatedly redoxed for about a dozen of times in TsONa aqueous soln.

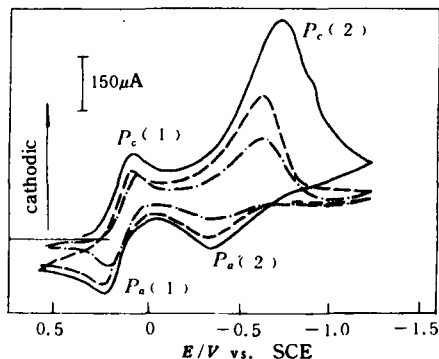


Fig.8 As in Fig.4, but note the supporting electrolyte is K₃Fe(CN)₆.

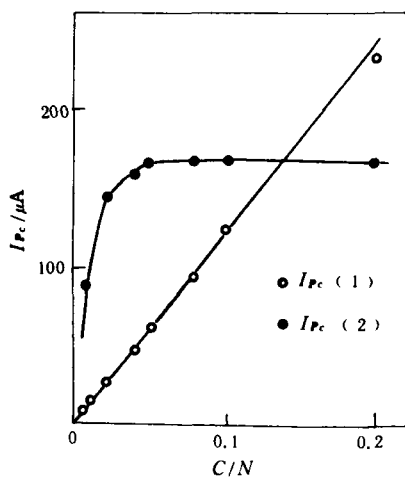


Fig.9 Curves of cathodic peak current via the concentration of Fe(CN)₆³⁻ anion for the stabilized CV obtained in Fig.8.

4. Electrochemically active species on a composite film

The CV of a composite PU/PPy film in K₃Fe(CN)₆ aqueous solution, whose outer surface is conducting, is shown in Fig.8. Two pairs of redox peaks are observed, representing reduction of

$\text{Fe}(\text{CN})_6^{3-}$ anion and oxidation of its reduction product i.e. $\text{Fe}(\text{CN})_6^{4-}$, $E_{pc}(1) = +0.1\text{V}$, $E_{pa}(1) = +0.25\text{V}$; and redox reaction of PPy chains, $E_{pc}(2) = -0.7\text{V}$, $E_{pa}(2) = -0.3\text{V}$, respectively. The latter pair of peaks are similar to those in other supporting electrolyte solutions having just been described except for a much more cathodic potential. $\text{Fe}(\text{CN})_6^{3-}$ anion can conduct redox reaction on a composite film reversibly. A little decrease of its peak current ($I_p(1)$) is only due to less activity of the composite film caused by concentration reduction of counteranions in the film after repeated potential scans. The relationship $I_p \propto v^{1/2}$ of the two pairs of redox reactions indicates both of them are diffusion-controlled reactions. Fig. 9a shows that the redox of PPy chains is intensely limited by the slow diffusing rate of $\text{Fe}(\text{CN})_6^{3-}$ anions through the film, owing to the large anion size of $\text{Fe}(\text{CN})_6^{3-}$. Yet Fig. 9b show redox of $\text{Fe}(\text{CN})_6^{3-}$ anions is controlled by the diffusion of the anions from solution bulk to the outer surface of the composite film, and the reaction occurs on the surface. In this case, the composite film acts as a metal electrode, similar to a pure PPy film^[6,9a]. The redox peak potential of $\text{Fe}(\text{CN})_6^{3-}$ anions on a composite film is close to that on a bare Pt electrode, demonstrating that the composite can be used as electrode-modifying material.

CONCLUSION

The electrochemical studies of the conducting composite films from polyurethane and polypyrrole have informed us that the two ingredients are merely mechanically combined. During the cyclic potential scan processes, the PU component maintains inert, whereas the PPy component, behaving like a pure PPy, not only can be reduced and reoxidized in itself, but also act as a electrode-modifying material to conduct electrochemical redox reaction of electro-active species on its surface. A composite film bears a porous structure. The redox rate of its PPy chains is limited by the slow diffusion process of counteranions into or out of the film. Because water can not swell the PU substrate, this diffusion process may be carried out through the pores in the composite film caused by the PPy's supporting effect^[4], note that a pure PPy film is also porous^[9]. As a modified electrode, the composite film is superior to a pure PPy film resting with its superhigh flexibility and quite good stability.

Keywords:

Polypyrrole, Conducting composite; Electrochemistry

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