Colloid Polym Sci 275:953–957 (1997)

ORIGINAL CONTRIBUTION

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The electrochemical behavior of colloidal polypyrrole

Received: 13 December 1996
Accepted: 24 May 1997

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Abstract The electrochemical behavior and charge transport of colloidal polypyrrole particles (without stabilizer) modified electrode have been investigated. The voltammetric results show that the electrochemical behavior of colloidal polypyrrole is different from that of polypyrrole synthesized electrochemically. The strong adsorption of the colloidal particles on substrate makes it easy to form a polypyrrole modified electrode. The charge transport of polypyrrole is controlled by the diffusion of counterions.

Key words Polypyrrole – colloid – electrochemistry – charge transport – modified electrode

Introduction

The research on the processability of electronically conducting polymers has received attentions recently, which leads to the birth of soluble polyaniline [1] and polypyrrole [2]. However, more chemists concentrate on the preparation of electronically conducting polymer colloids and inorganic–organic hybrid materials, their properties and applications in the material science. Wallace et al. have prepared an electroactive colloidal polypyrrole with stabilizer of soluble polymers [3], and they found it is possible to electroplate polypyrrole onto the surface of electrode by cathodic polarization. Armes et al. [4–6] have prepared hybrid materials with a substrate of SiO_2 particles and composite of polymer grafts. These works lay a foundation for the application of conducting polymer colloids on electrochromatography [7, 8], preparation of ion-exchange membrane [9], electrochromism [10] and control release [11]. At the same time, Baker et al. have prepared the polypyrrole colloids without stabilizer [12]. It is notable that the redox behavior of the colloidal polypyrrole is very different from the polypyrrole synthesized electrochemically [13], which is apparently related to the process of preparation. Further investigation on the electrochemical behavior and charge transport of this type of polypyrrole colloids will be helpful not only to understand the polypyrrole, but also to promote its application on electrochromism, photochromism, electrocatalysis and so on.

In this paper, we report the electrochemical behavior of polypyrrole colloids without stabilizer, and compare it with that of polypyrrole prepared electrochemically.

Experimental

Pyrrole (Fluka), $K_2S_2O_8$, ethanol and H_2SO_4 (Beijing Reagent Corp.), K_2SO_4 (Tianjin Reagent Corp.) were used. The experiments were carried out using computer-controlled EG&G PARC 273A with 5210 lock-in-amplifier, and electromagnetic stirrer (Zhejiang Equipment Corp.). Pt disk electrode was used as working electrode (area = $0.00196\ cm^2$), Ag/AgCl as reference electrode and Pt plate as counter electrode.

The alternating current (AC) impedance experiment was carried out at the bias of -0.4 V (formal potential), frequency range of $0.1 \sim 10$ kHz and the AC amplitude of 5 mV. First, the system was kept in open-circuit state for 60 s, and then switched to the bias for 120 s to equilibrate the electrochemical system. The data was recorded by the computer automatically. The nonlinear least-squares fitting was done by using the software of Boukamp.

The preparation of pyrrole colloids was referenced from Baker's method [12]. 75 ml ethanol, 25 ml H_2O and 0.5 ml H_2SO_4 were mixed in 250 ml plane-bottom flask. The solution was purged with N_2, electromagnetically stirred, heated to 80 °C, and kept at this temperature. 0.3 μl pyrrole and 0.0002 g $K_2S_2O_8$ (in solution) were added. The reaction was proceeded for 3 h. The mixture was then cooled with ice bath and filtered. The filtrate (3 ml) was mixed with doubly distilled water (7 ml). The solution was centrifuged at 3000 rpm for 20 min. The pellet was washed with doubly distilled water, and centrifuged twice, which assured the salts and soluble oligmer to be dispelled. The pellet was redispersed in ethanol–water solution (10 ml) for electrochemical experiments.

TEM graphs were obtained using diluted redispersed latex dried down on carbon-coated copper grids and gold foils. A JEM 2010 transmission electron microscrope was employed.

Results and discussion

Figure 1 shows the transmission electron micrograph of the colloidal particles. It is found that the size of the particles is between 30 and 50 nm, and there exists coagulation which leads to the formation of large size of particles. The cyclic voltammogram of the colloid in the electrolyte is presented in Fig. 2a. It is a quasi-reversible reaction with the anodic potential at −0.32 V, the cathodic potential at −0.53 V, and the formal potential is −0.42 V. The electrocoagulation [3] and the growth of the colloidal particles at the surface of the electrode was not found after the potential steps from +0.1 V to −1.4 V. The electrode was taken out of the electrolyte, and the next experiment was carried out in 0.2 M K_2SO_4 aqueous solution without colloidal particles. The voltammetric results show that the peak–peak potential difference is ca 80 mV, the formal potential is 0.4 V, and both cathodic and anodic peak currents are proportional to the scan rates and the square root of scan rates within different scan-rate ranges. The resulted voltammogram is similar to that obtained in the colloidal solution (see Fig. 2b). The above evidence proves the adsorption of colloidal particles occur at the electrodic surface, which has been found by Nagaoka et al. in the investigation of polyaniline colloid [9]. Owing to the strong adsorption of colloidal polypyrrole on substrate, one can obtain the polypyrrole modified electrode conveniently.

The colloidal solution was diluted to half concentration of its original, and then the electrode pretreated electrochemically was dipped into this solution. The electrode was taken out after 5 min, as in the above experiment. It is found that this colloid-modified electrode system gives a couple of sharp-peak-shaped curve as shown in Fig. 3. The sharp peaked curve may be attributed to coagulation of the colloidal particles at higher solid concentration, which increases the size of the particles and the modified layer becomes thicker, thereby, the cyclic voltammogram shows a diffusional controlled characteristics; when the concentration of the colloidal particles is lower, there is no (or less) coagulation, the size of the particles is small, and the modified layer is thinner, which results in the characteristics of kinetic control-like redox reaction in cyclic voltammogram. At lower scan rates, both cathodic and anodic peak currents are proportional to scan rate; at higher scan rates, they are proportional to the square root of the scan rate, which are given in Fig. 4. The characteristics of the surface wave at lower scan rate is caused by the total electrolysis of the colloidal polypyrrole at the surface of the electrode, and the characteristic of diffusion at higher scan rate can be ascribed to the diffusion control of counterions [14]. The advantage of the colloid-modified electrode is that there is no effect of large charging current.

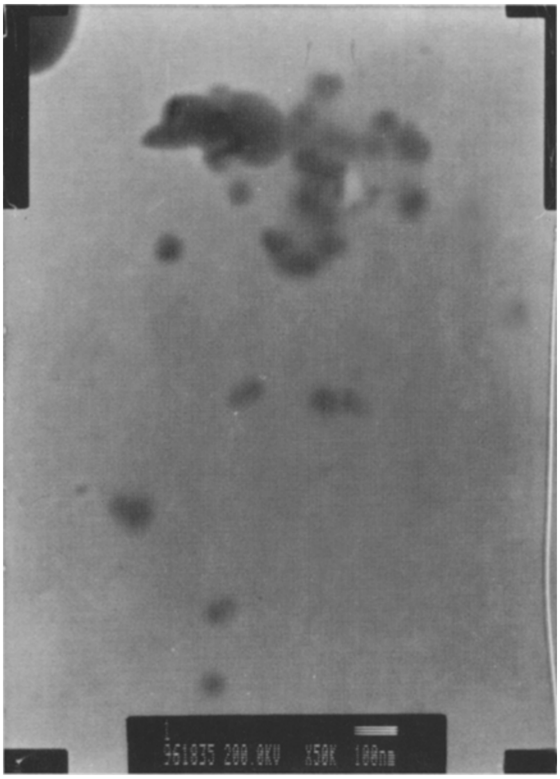

Fig. 1 Transmission electron micrograph of polypyrrole colloid

The experiments also showed that this colloid-modified electrode can be developed to sensors, because the

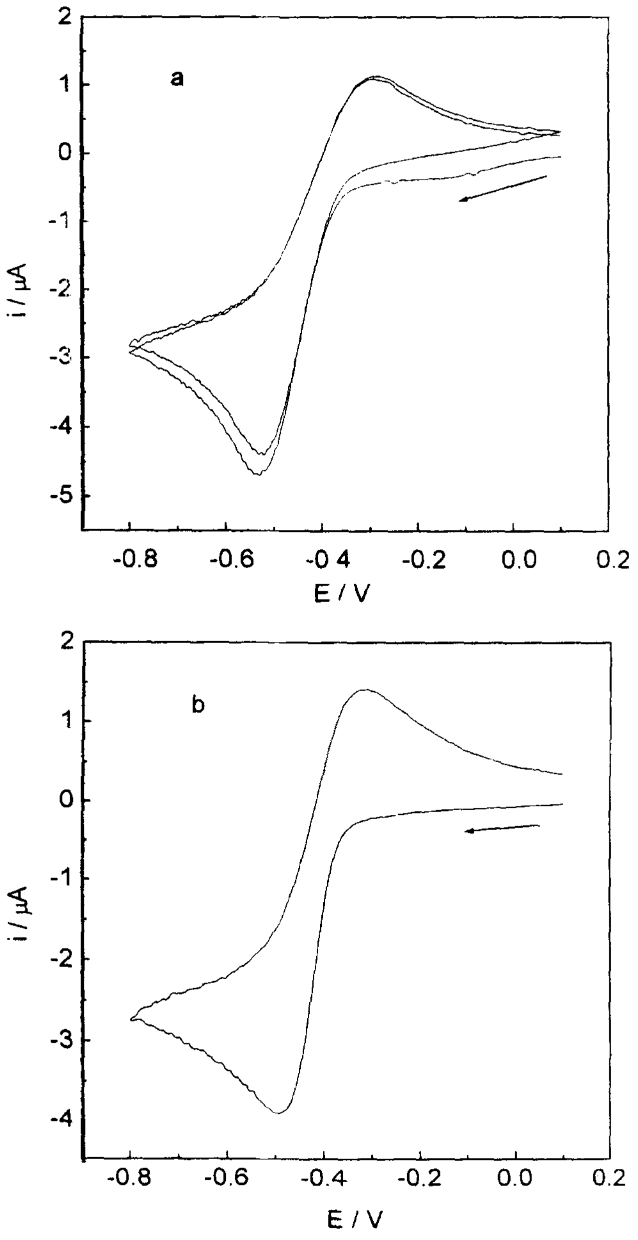

Fig. 2 The cyclic voltammogram of polypyrrole. (a) in the colloid solution of ethanol–water (3 : 1) containing 0.05 M K_2SO_4. (b) in the solution of 0.2 M K_2SO_4 v = 100 mV/s

ion-sieving effect was observed. It was found that the redox behavior did not change much if the experiments were performed in the solutions containing small size ions. On the contrary, no redox current could be obtained if the experiments were carried out in the solutions containing large-sized ions, such as sodium toluenesulfate, etc. This is because the size of the pore of polypyrrole is small, and the large ions cannot penetrate. The small-size counterions in polypyrrole migrated out of the film and were diluted so

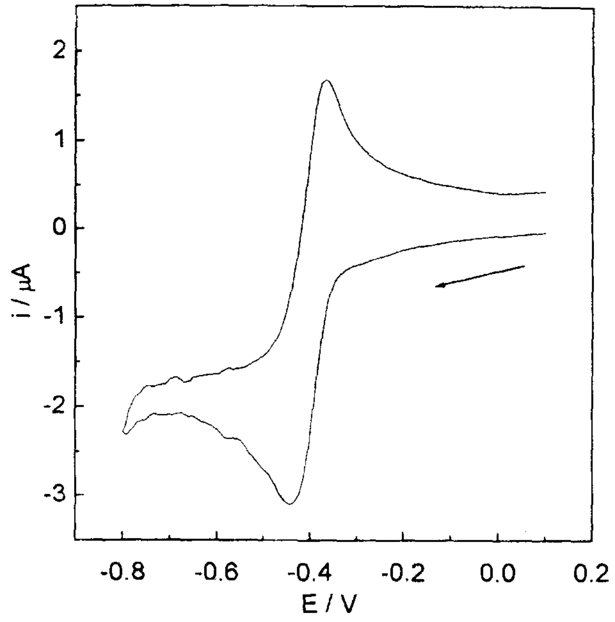

Fig. 3 The cyclic voltammogram of polypyrrole colloid modified electrode in the 0.2 M K_2SO_4 aqueous solution v = 100 mV/s

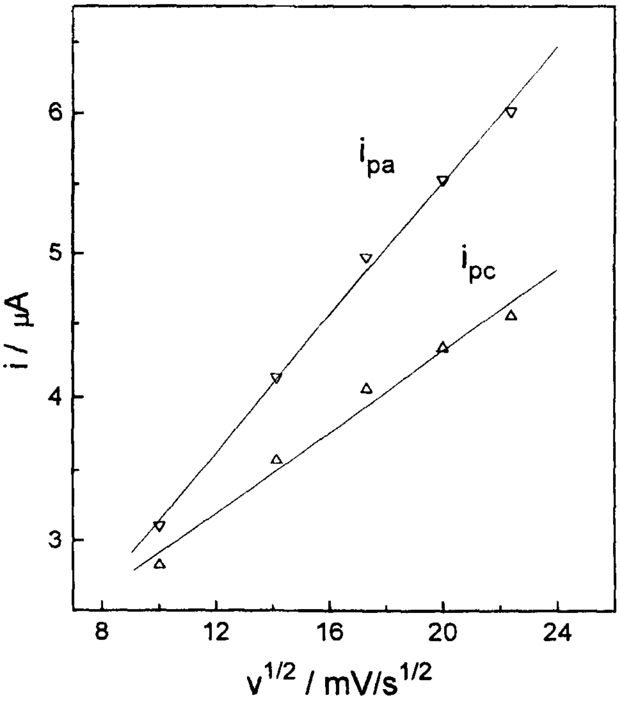

Fig. 4 The dependence of peak current on scan rate (data taken from Fig. 3)

that the sequenced elecrochemical responses could not be detected. In the potential step, it was found that a positive intercept in the plot of i–$t^{-1/2}$ could be obtained when the potential changed from the oxidized state to the reduced

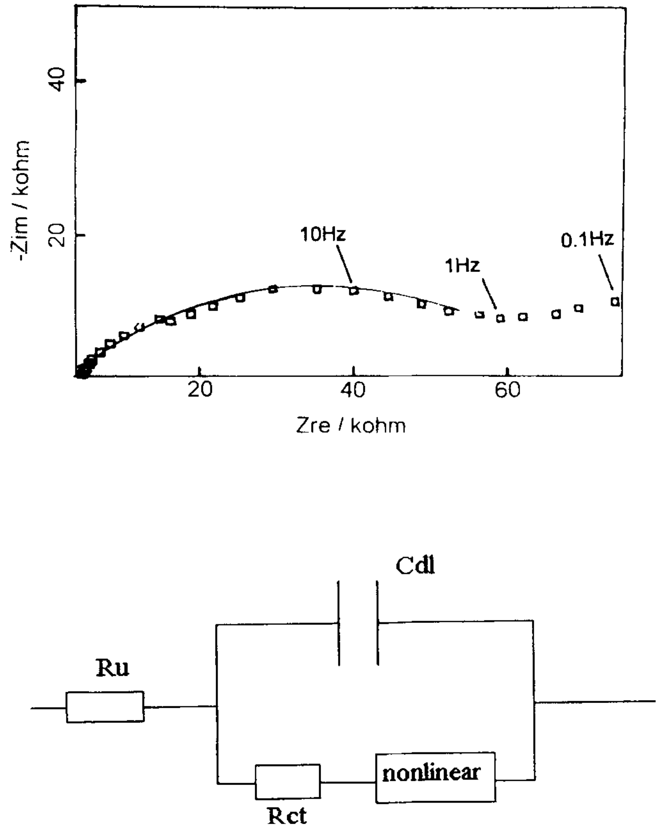

Fig. 5 The Nyquist plot of polypyrrole colloid at the formal potential, the solid line is the simulated results (top), the equivalent circuit (bottom)

state, while a negative intercept may be caused by the charging current [13, 14], if the potential changed from the reduced state to the oxidized state. The chronocoulometry can give positive intercept in the Q–$t^{-1/2}$ plot. However, the thickness of the film is unknown, the D_{app} of the charge transport cannot be obtianed [15].

Figure 5 gives the Nyquist plot. It shows a charge transfer resistance related to the kinetic control, but the diffusional characteristic [16] is not observed clearly. The heterogeneous electron transfer rate-parameter k_0 can be obtained in this plot, however, the AC responses do not form a semicircle but a depressed semicircle which was found in the polypyrrole prepared electrochemically and was explained by the coarseness of the electrodic surface [17, 18]. In the process of nonlinear least-squares fitting, a constant phase angle element (CPE) parallels a resistance of charge transfer was found to be suitable to simulate the charge-transfer resistance part. The CPE can be described by [19]

$$Z = R_0 + R/(j\tau\omega)^n , \tag{1}$$

where R_0 is the ohmic resistance, τ is the character time constant, ω is the frequency, n is a variable parameter ($0 < n < 1$). CPE is a capacitance when $n = 1$, a Warburg when $n = 0.5$. The fitting results showed that $n = 0.63$. The equivalent circuit apparently shows that the charge transfer resistance part does not correspond to a pure electron transfer reaction, it contains component of diffusion which comes from the counterions' coupling movement, and this leads to the nonlinear AC responses of the polypyrrole modified electrode. The coarseness of the electrodic surface will not influence the parameter n so much. The modified equivalent circuit considering the effect of nonlinearity is also given in Fig. 5. R_u is the uncompensated resistance, C_{dl} is the double-layer capacitance, and R_{ct} is the charge-transfer resistance. The component denoted by nonlinear stands for the contribution of the counterions.

Conclusions

The electrochemical behavior of electrodes modified by colloidal polypyrrole is different from that with polypyrrole prepared electrochemically. The broad redox curve cannot be found in the oxidized state of colloidal polypyrrole. Both redox reactions of the polypyrrole colloids and the electrochemically prepared polypyrrole are quasireversible. The charge transport of the colloid-modified electrode is controlled by diffusion of counterions. The coupling movement of counterions at higher frequency affects the AC high-frequency response of colloidal polypyrrole.

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