

Polypyrrole–Carbon Fiber Composite Film Prepared by Chemical Oxidative Polymerization of Pyrrole

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ABSTRACT: Polypyrrole–carbon fiber (Ppy–CF) composite films with carbon fiber (CF) content ranging from 15 to 20 wt % have been prepared by chemical oxidative polymerization of pyrrole at the surface of a CF-covered Teflon substrate following a layer-by-layer deposition approach. The composites have a high modulus of $8\text{--}9 \times 10^{10}$ dyn/cm², high tensile strength of 200–270 kg/cm², and good thermal stability. More importantly, these composite films showed electrochemical activity in their free-standing state. Thus, they can be used as the cathode material for a rechargeable battery without conventional metallic or conducting glass sheet as the current collector. Here, carbon fibers act as an electrically conductive skeletal electrode for current collection. The charge capacity of the film with a thickness of 120 μm was tested to be 2.5 coulombs (C)/cm² and a specific capacity of 91 mAh/g. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 2149–2154, 1997

Key words: polypyrrole–carbon fiber composite film; tensile strength; battery; charge capacity

INTRODUCTION

During the last few decades, heterocyclic conducting polymers have attracted a great deal of interest owing to their remarkable electrical properties. Polypyrrole (Ppy) has been studied since it presents a high electrical conductivity, interesting redox properties, and a satisfying environmental stability. Usually, thin films of Ppy are obtained by electrochemical synthesis,¹ and powders by chemical oxidative polymerization.² The delocalized structures of Ppy yield stiff chains with strong interchain interaction. This leads to the commonly observed nonsolubility, nonmelting, and nonfusibility behavior.^{3,4} Therefore, Ppy–CF (carbon fiber) composite film cannot be prepared by conventional polymer synthesis and processing techniques. B. Coffey and coworkers have

prepared graphite fiber–Ppy composite electrodes by electrochemical polymerization.⁵ In this paper, we wish to report that the composite film of Ppy and CF can be chemically synthesized by deposition of Ppy onto a CF-covered solid substrate. Carbon fibers were introduced as the start of film preparation. The resultant material has enhanced mechanical strength and shows electrochemical activity in its free-standing state. This suggests that the composite film obtained this way can be used as the electrode for a rechargeable battery. The specific capacity of the composite film with a thickness of 120 μm was tested to be 91 mAh/g (electrode).

EXPERIMENTAL

Materials

Pyrrole (Py, 99%) was purchased from Aldrich and then distilled before use. Dehydrated FeCl₃ was a product of Jinsan Fact. (China). It was dried at 80°C under vacuum for 24 h. Analytical

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Table I Operating Conditions for the Preparation of Layer-by-Layer Ppy-CF Composite Films

Step	Operation	Medium	Duration (s)
1	Immersion in monomer solution	Py 10% in CH ₂ Cl ₂	4
2	Drying	Weak nitrogen flow	300
3	Immersion in oxidizing solution	1.5 M FeCl ₃ in methanol	6
4	Polymerization	Weak nitrogen flow	360
5	First rinsing	10 vol % methanol in acetonitrile	60
6-8	Subsequent rinsings	Acetonitrile	10
9	Drying	Weak nitrogen flow	240

All the processes were carried out at room temperature

grade pure acetonitrile (MeCN) (Zhangjin Fact., China), methanol (MeOH) (Nanjing Chem. Reg. Fact.), and dichloromethane (CH₂Cl₂) (Nanjing Chem. Reg. Fact.) were used after distillation. Purified KCl and LiClO₄ were used as supporting salts in electrochemical examinations. Carbon fibers with diameters of 5–6 μm and tensile strength of 3160 kg/cm² were obtained from Shanghai Carbon Fact. (China). A commercially obtainable 10 × 20 × 0.5-cm Teflon sheet was used as the solid substrate after having been rinsed with methanol 3 times and dried at room temperature for 4 h.

Ppy-CF Composite Film Preparation

Carbon fibers were spread parallel on the surface of a Teflon sheet. Their free ends were attached to the substrate surface with two plastic adhesive tapes. The chemical oxidative polymerization of Py on a platelike CF-covered Teflon substrate occurs by an alternate immersion of the substrate in solution of pyrrole and in an oxidant solution of FeCl₃. The operating conditions for one cycle of polymer deposition are summarized in Table I. The synthesis was carried out in a glove box flushed with nitrogen gas. A film with thickness of 120–150 μm was formed by performing 1, 2, 3, 4, 5, and 20 deposition cycles. Ppy was obtained in its oxidized Cl⁻ and FeCl₄⁻ doped conductive forms. Then the composite film was peeled off from the solid substrate and dried under vacuum and at 80°C for 24 h. The flow chart of preparation of the Ppy-CF composite film with one CF layer is illustrated in Figure 1. The film with three CF layers was prepared by spreading one more CF layer on the composite surface after each 20 poly-

mer deposition cycles until 60 deposition cycles were performed.

Film Property Tests

The tensile strength of Ppy-CF composite film was measured by using an electronic stretching machine (WD-1, Changcun) at a stretching rate of 5 cm/min. Dynamic mechanical tests were carried out on a dynamic viscoelastometer Rheovibron DDVII-EA at a frequency of 3.5 Hz. Differential scanning calorimetry (DSC) measurements were carried out on a Perkin-Elmer thermal analysis calorimeter at a temperature scan rate of 20°C/min. Scanning electron microscopy pictures were obtained using an X-560 electron micrographer. Electrochemical examinations were carried out on an EG&G potentiostat (Princeton Appl. Research Co.) under computer control. All the solutions were deaerated by nitrogen gas. A free-standing composite film was used as a working electrode, a platinum sheet with the same size was used as a counter electrode, and an Ag/AgCl wire was used as a reference electrode. The charge capacity of the film was determined by transferring the

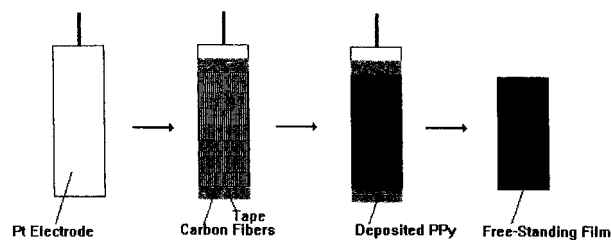


Figure 1 Flow chart of the processes for preparation of Ppy-CF composite film.

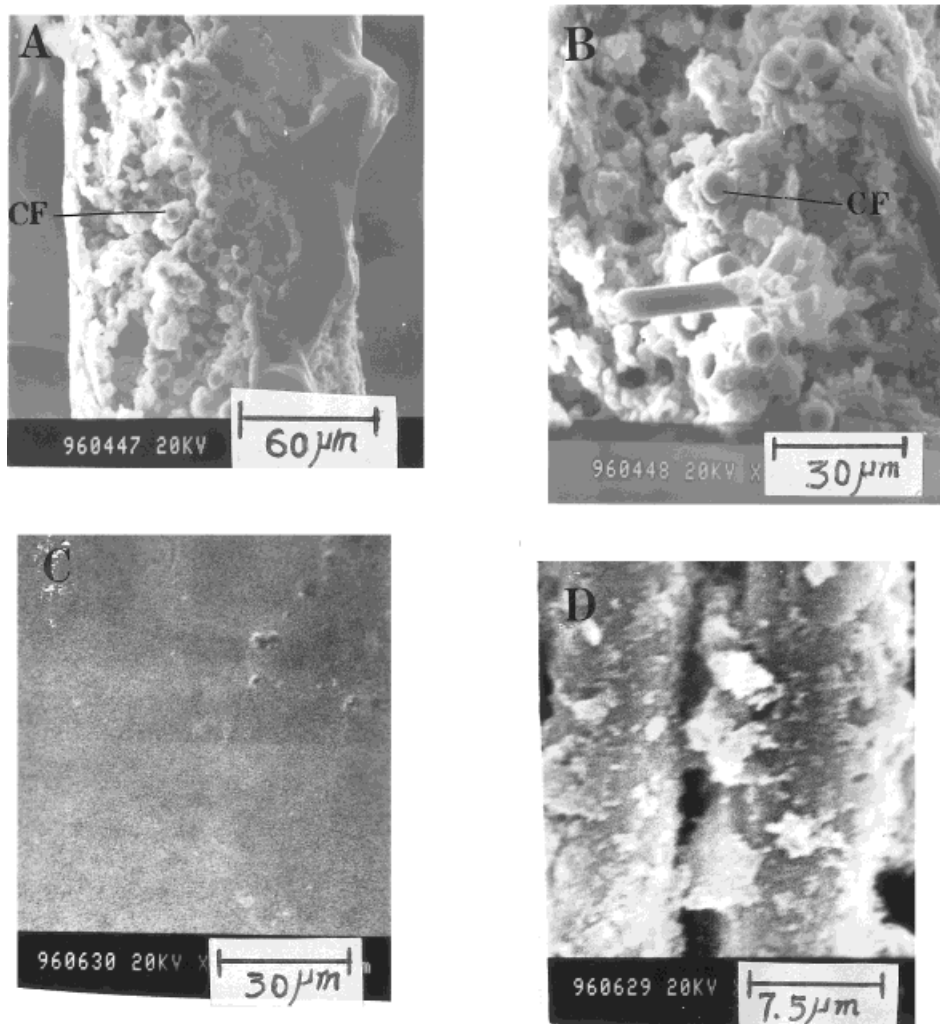


Figure 2 SEM images of the Ppy-CF composite film deposited for 20 cycles. (A) and (B) cross-sectional view; (C) the side contacted to the Teflon sheet; (D) the side exposed to the solutions.

chemically prepared composite film to a sealed cell containing deoxygenated acetonitrile and $0.5M$ $LiClO_4$ and integrating the current transients in response to a potential step for the polymer from a fully oxidized to a fully reduced state.

RESULTS AND DISCUSSION

Figure 2 shows the scanning electron microscopy pictures of the composite film prepared by a 20 deposition cycle. The cross-sectional view [Fig. 2(A,B)] of the film revealed that the film has a thickness of $\sim 120 \mu m$ and the carbon fibers were buried well in Ppy matrix. The side in contact with the Teflon sheet was very flat and compact

[Fig. 2(C)]. However, the side exposed to the solutions was rough and porous [Fig. 2(D)]. The conductivity of the composite was measured, by a conventional four-probe technique, to be $8 S/cm$. It is close to the value reported for chemically synthesized Ppy in a similar system.⁶ The tensile strength of the composite film along the fiber direction is $200\text{--}270 \text{ kg/cm}^2$. Pure Ppy film prepared by the same technique was found to be powder-like and very brittle. The results described above implied that carbon fibers enhanced greatly the strength of Ppy, however, not its conductivity. Thus, the composite films are mechanically stable and can be fabricated in large areas or cut into any shape.

Dynamic mechanical test diagrams (Fig. 3) of

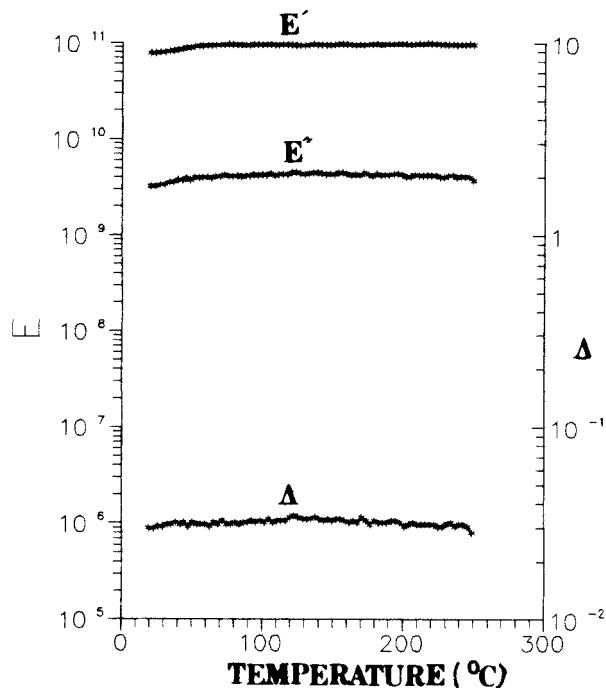


Figure 3 Dynamic mechanical test diagram of Ppy-CF composite film (0.12 mm thick) along CF-oriented direction.

the composite film showed that its real modulus (E') at room temperature in the direction of the oriented carbon fiber was very high, $\sim 8 \times 10^{10}$ dyn/cm², and this value remained almost as a constant up to 250°C. The loss modulus (E'') and loss tangent (Δ) curves of the composite film also showed no transition in the temperature scale of 20–250°C. On the other hand, the DSC test diagram of the composite showed a weak and broad transition between 148 and 197°C (Fig. 4). However, no decomposition of the composite was discovered as the temperature increased up to $\sim 250^\circ\text{C}$, indicating the film has a good thermal stability.

Cyclic voltammograms (CVs) of the free-standing Ppy-CF composite film in MeCN + 0.1M

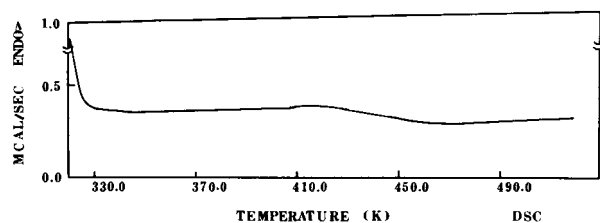


Figure 4 DSC curve of Ppy-CF composite film.

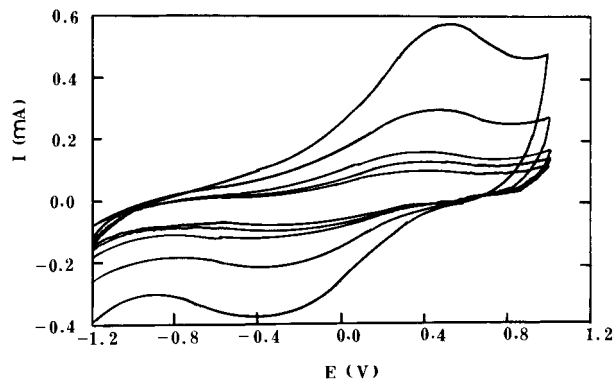


Figure 5 CV of free-standing Ppy-CF composite film in MeCN containing 0.1M LiClO₄ at potential scan rates of 30, 40, 50, 100, and 200 mV/s.

LiClO₄ are illustrated in Figure 5. These CVs are characterized by broad waves in contrast to the sharp waves associated with thin films ($< 1 \mu\text{m}$) of Ppy.^{7,8} This is due to the redox reactions of Ppy accompanying the slow doping-undoping of ClO₄⁻ anions. As can be seen from the CV curve obtained at a potential scan rate of 30 mV/s, two redox waves attributed to Ppy appeared at about -0.10 and $+0.35$ V (vs. Ag/AgCl). The half wave potential ($E_{1/2}$) was calculated to be about $+0.13$ V. This CV can be repeated for at least 100 cycles. The peak current strength of both anodic and cathodic waves increased linearly with potential scan rates. The current ratio of I_a/I_c was measured to be ~ 1.1 . The electrochemical behavior described above demonstrated that the free-standing composite film has electrochemical activity in a widely used organic solvent, and its reduction and oxidation processes were reproducible. Thus, it can be used as the electrode for a rechargeable polymer battery.

To clarify how the currents of the film were collected during the redox process, the electrochemistry of CdCl₂ at the composite film was studied. Figure 6(A) is the CV of free-standing Ppy-CF composite film in distilled water containing 0.1M KCl at a potential scan rate of 100 mV/s. As can be seen from this figure, the redox waves of Ppy were also detected at potentials of -0.18 V and -0.42 V, and its half redox potential was calculated to be -0.30 V, 0.43 V more negative than that in the MeCN system described above. The reduction wave current is almost the same as the oxidation wave. This CV also has a good repetition. Figure 6(B) is the CV of the same composite film in 0.01M CdCl₂ + 0.1M KCl at a potential scan rate of 10 mV/s. Two sharp waves attrib-

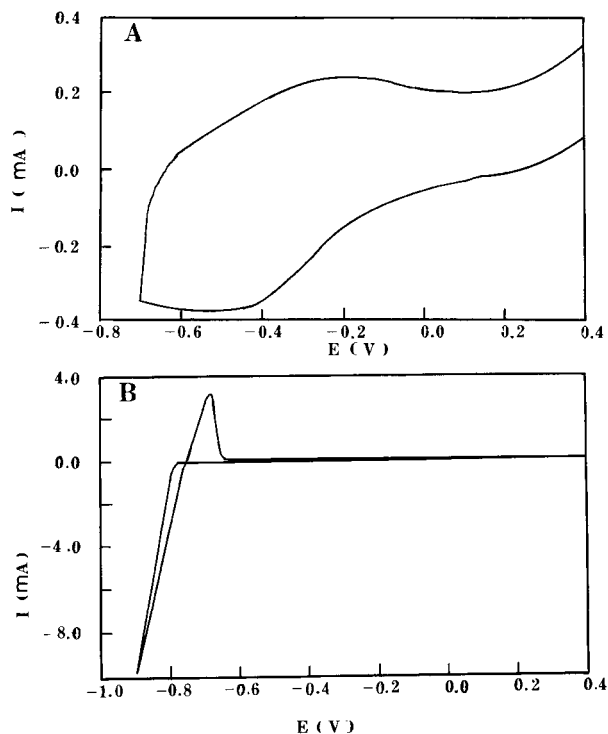


Figure 6 CV of free-standing Ppy-CF composite film in water containing 0.1M KCl (A), or in water containing 0.1M KCl and 10 mM CdCl₂ (B). For potential scan rate, see text.

uted to the Cd^{2+/0} couple appeared. These two waves were so strong that the redox waves of Ppy cannot be detected in the same current scale. At -0.6 to -0.9 V, polypyrrole is in its reduced (insulating) state. Therefore, the redox reactions of Cd^{2+/0} should have been carried out on the surface of carbon fibers. This implied that the composite film was porous and the ions of Cd²⁺ and the supporting salts diffused into the film and carbon fibers acted as a current collector.

The charge capacity of the composite electrode with a thickness of 120 μm was determined to be 2.5 C/cm², corresponding to a specific capacity of 91 mAh/g (electrode). Thus the specific capacity for electroactive polymer in the film was calculated to be ~107 mAh/g. This value was close to the expected maximum of 138 mAh/g based on a reported doping level of 0.33 electrons per repeat unit (C₄H₄N).⁵ Unfortunately, this value decreased as the film thickness was increased. The specific capacity of the composite electrode with a thickness of 460 μm was measured to be only 62 mAh/g (electrode), although its charge capacity was increased to 4.3 C/cm² (Table II). This is mainly due to the diffusion of the counter ions

into the thicker films during the polymer redox process being more difficult than into a thinner film.

The weight content of carbon fibers in the composite film strongly affects its mechanical and electrochemical properties. As the composite film contains only a small amount of CF (<5%), the property of the film is close to that of pure Ppy. It showed low strength and low electrochemical activity. The conductivity and mechanical property of the film increased with the increase in its CF weight content. However, the charge capacity of the film was decreased as the CF content was too high. This is mainly due to CF's inability to store any charges themselves. A CF weight content of 15–20% was tested to be the optimum value for the 120-μm-thick film. Thus, a suitable CF content and film thickness should be considered before a electrode selection.

The use of such a thick free-standing Ppy-CF composite film as electrode may offer several advantages for fabricating a practical polymer battery. First, the current collector of the electrode is carbon fiber, it with a low weight and volume for the whole battery. Second, the composite electrode retained a high specific capacity of 91 mAh/g even at a thickness of 120 μm. Therefore, the fabrication of a practical battery needs only a small size of film, in comparison to the usual cases with thin films (<10 μm).^{9,10} Third, the composite films have good mechanical properties and can be easily processed into desired structures.

CONCLUSIONS

Thick, lightweight Ppy-CF composite films with high charge capacity were obtainable by a chemical oxidative polymerization technique. The chemical synthesis method developed in this study is significant because it is suited for mass production, and it can facilitate the preparation of desired compositions and thicknesses of the films by adjusting the polymer deposition cycles and the CF amount and layers introduced. The composite films obtained by this method showed enhanced strength and modulus, and they can be processed easily into any shape. The films showed electrochemical activity as they are in the free-standing state. Here, carbon fibers acted as a current collector and they occupied a low weight and volume of the composite electrode. The composite film retained a high specific capacity of 91 mAh/g (cathode), even at a thickness of 120 μm. How-

Table II Compositions and Charge Capacities of Ppy-CF Composite Electrodes

Film No.	CF Layers	CF (wt %)	Film Thickness (μm)	Charge Capacity (C/cm^2)	Specific Capacity (mAh/g (electrode))
1	1	16	120	2.5	91
2	3	19	467	4.3	62

ever, the specific capacity of the thicker film with multiple carbon layers was decreased dramatically.

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