

Preparation and Electrochemical Capacitance of Poly(pyrrole-co-aniline)

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ABSTRACT: The copolymer of pyrrole and aniline, poly(pyrrole-co-aniline), has been prepared by chemical oxidation of corresponding monomer mixtures with ammonium peroxydisulfate. Techniques of FTIR, SEM-EDS, and BET surface area measurement were used to characterize the structure and morphology of the copolymer. The electrochemical properties of the copolymer were investigated by cyclic voltammetry, galvanostatic charge-discharge, and electrochemical impedance spectroscopy. The results indicated that poly(pyrrole-co-aniline) was about

100–300 nm in diameter and showed better electrochemical capacitive performance than polypyrrole and polyaniline. The specific capacitance of the copolymer electrode was 827 F/g at a current of 8 mA/cm² in 1 mol/L Na₂SO₄ electrolyte. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 1881–1885, 2010

Key words: copolymerization; poly(pyrrole-co-aniline); electrochemistry; FTIR; electrochemical capacitance

INTRODUCTION

In recent years, more and more researchers focused on studying the synthesis and electrochemical properties of electrically conducting polymers (ECPs) including polypyrrole (PPY),^{1,2} polyaniline (PANI),^{3,4} polythiophene,^{5,6} and their derivatives,^{7,8} which represent promising electrode materials for the application of supercapacitors due to their high specific capacitance. At the same time, as electrode material for supercapacitor, the ECPs have some problems that limit their further application and industrialization.

As we know, the electrochemical behavior and charge-storage mechanism of ECPs depend on the structural characteristics and rapidly reversible doping-dedoping ability, while the application of ECPs in supercapacitors is also limited because of these. There are three reasons: (1) Because conducting polymers have low conductivity in the whole doping and dedoping state, the resistance of capacitors made by them becomes higher at the end of charge and discharge process. (2) In the process of charge and discharge, the removal-intercalation of doping ions makes the volume of polymers repeatedly expand and shrink, which would destroy the poly-

mer structure, and lead to a rapid attenuation of the electrode capacity. (3) Since doping process takes place in the fixed potential range for most conducting polymers, and the stable potential window is low, the energy density of the corresponding supercapacitor is low too.⁹

For these reasons, various measures are used to improve the structure of ECPs in order to expand their application in supercapacitors. One is to compound with other materials so as to get a good capacitive composite materials^{10–18}; another is copolymerization, which could get a new integrated polymer. The latter, however, has not drawn enough attention in the field of electrode material for supercapacitors. For example, it has been reported that poly(pyrrole-co-aniline) could be synthesized by electrochemical method¹⁹ and chemical oxidation,^{20,21} but its use in electrode material of supercapacitor was seldom reported in literature.

In this work, the copolymer of pyrrole and aniline was prepared on the basis of the literature^{20,21} and some reaction conditions have been changed for the sake of its electrochemical property. More important aim was to obtain a new polymer electrode material with good electrochemical performance. So, its capacitive behavior was examined by cyclic voltammetry (CV), galvanostatic charge-discharge, and electrochemical impedance spectroscopy (EIS). In addition, further studies on relation of copolymerization conditions, copolymer composition, and its capacitance performance will be summarized in our next study.

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EXPERIMENT

Copolymerization

Pyrrole (Py, 99%, Fluka, Switzerland) and aniline (AN, analytical purity, Tianjin Chemical Reagent, China) were purified through distillation under reduced pressure and stored refrigerated before use.

The mixtures of pyrrole and aniline were oxidized in 1 mol/L HCl with 0.25 mol/L ammonium persulfate ((NH₄)₂S₂O₈) at 0°C. The molar ratio of pyrrole to aniline was 1 : 3. After 4 h of stirring, the precipitates were separated on a filter, rinsed with 0.01 mol/L HCl, followed by acetone and dried at 60°C in a vacuum oven. For comparison, PPY and PANI, respectively, were synthesized at the same condition.

Structure characterization

Fourier transform infrared spectroscopy (FTIR) was recorded with BRUKER-EQUINOX-55 spectrometer in the range of 2000–500 cm⁻¹. Scanning electron microscope (SEM) analysis was conducted with a JSM-35C instrument (JEOL, Japan) equipped with an energy-dispersive spectrograph (EDS). The BET specific surface areas were determined by nitrogen adsorption method (Micromeritics, ASAP2400).

Preparation of electrodes

The electrode of the copolymer was prepared by mixing 75 wt % active materials, 15 wt % carbon blacks, and 10 wt % polytetrafluoroethylene (PTFE). After mixing thoroughly, the mixture was pressed on the graphite electrode (1 cm²), which was used as a current collector. Then the electrode was dried at 60°C for 8 h before use. At the same time, the PPY and PANI electrode were also prepared according to the above procedure.

Electrochemical tests

All electrochemical tests were carried out in a three-electrode cell configuration, a platinum counter electrode, and a standard calomel reference electrode (SCE). The electrolyte was 1 mol/L Na₂SO₄.

The electrochemical behaviors of the copolymer electrode were evaluated by CV, galvanostatic charge-discharge, and EIS techniques with CHI660 electrochemical workstation at room temperature. CV test was performed in the potential window ranged from -0.2 to 0.8 V (vs. SCE), and the galvanostatic charge-discharge test was from 0.005–1 V (vs. SCE) at different current density. EIS measurement was performed at open-circuit potential with the frequency range of 0.005 to 10⁵ Hz.

RESULT AND DISCUSSION

Structural characteristics

SEM image and elemental analysis results of the copolymer are shown in Figure 1 and Table I, respectively. As shown in Figure 1, the copolymer is granular and about 100–300 nm in diameter. The distribution of particle size is uniform, which indicates that these small particles may belong to one kind of substance rather than mixture of PPY and PANI. In the process of synthesis, of course, it is inevitable that some PPY and PANI were included in the product, but we can see from the SEM image that the impurity content is very low. In addition, agglomeration can be seen in some area, which results to a request of dispersant in the process of electrode preparation.

Because in the process of synthesis some Cl⁻ and S₂O₈²⁻ were doped or remained in the product, the elements of Cl, S, and O could be examined by EDS. Besides, from the Table I it can be seen that the mass composition of C and N is very close to the predesigned theoretical values, which indicate that the experiment of copolymerization has achieved expected effect.

The specific surface area of the poly(pyrrole-co-aniline) measured by isothermal N₂ adsorption-desorption experiment was 38.2 m²/g (PPY and PANI was 40.8 m²/g and 36.5 m²/g, respectively). As an electrode material for supercapacitor, it is favorable that the copolymer has high surface area, which can produce high double-layer capacitance.

The FTIR spectra of PPY, PANI, and the copolymer are presented in Figure 2. It can be seen that the infrared spectra of poly(pyrrole-co-aniline) is very close to the PANIs, which is consistent with the literature report.²⁰ As it has been reported, with increasing of aniline monomer in the process of the copolymerization, the infrared spectra of the copolymer were more and more close to the PANIs. But the difference also exists, for example, the main characteristic peaks of PANI were assigned as follows: the bands at 1568 cm⁻¹, 1486 cm⁻¹ correspond to quinone and benzene stretching-ring-deformation, and the bands at 1293 cm⁻¹, 1137 cm⁻¹ belong to C–N stretching mode and N=Q=N (Q represents the quinoid ring), respectively. While the corresponding peaks in the spectrum of the copolymer are at 1544 cm⁻¹, 1476 cm⁻¹, 1300 cm⁻¹, and 1147 cm⁻¹. Moreover, the above difference, by analogy with the reported literature and the spectrum of PPY, was caused by the presence of neighboring aniline and pyrrole constitutional units in the copolymer.²⁰ This experiment thus confirms that aniline and pyrrole are indeed able to copolymerize.

There are some reports concerning the copolymerization mechanism of pyrrole and aniline.^{22–24}

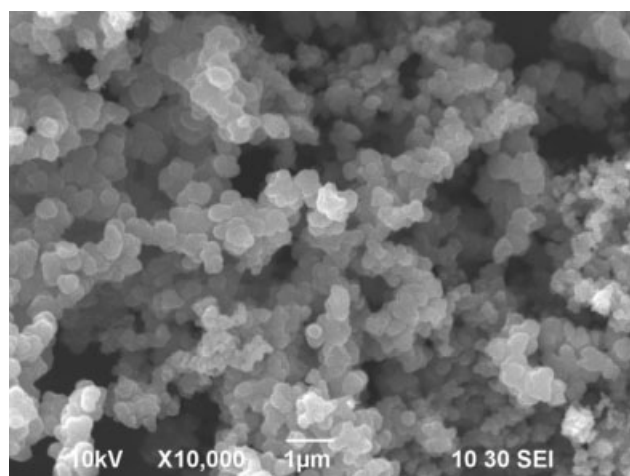


Figure 1 SEM image of poly(pyrrole-co-aniline).

General perspective is that the copolymerization reaction is the coupling of radical cations, and the structure of the copolymers is determined by monomer reactivity ratio.²⁴

Electrochemical performance

The cyclic voltammograms for poly(pyrrole-co-aniline), PPY, and PANI electrode in 1 mol/L Na₂SO₄ are shown in Figure 3. For PPY and PANI electrodes a pair of redox peaks can be found, while in the CV curve of the copolymer there are two pairs of redox peaks, which were attributed to the doping-dedoping processes of anion. Because these polymers were polymerized and evaluated at same conditions, and the redox potentials of the copolymer are different from that of PPY and PANI, it is believed that the "copolymer" is indeed poly(pyrrole-co-aniline) rather than simple mixture of PPY and PANI.

Regarding the copolymer, it can be observed that it shows better capacitive performance than PPY and PANI. One reason is that high specific surface area of the copolymer can produce high double-layer capacitance. Another, may be more important, is that the polymer with improved structure results in high redox capacitance.

Figure 4 shows the charge-discharge curves of PPY, PANI, and the copolymer electrode in the 1 mol/L Na₂SO₄ solution at a constant current of 10 mA/cm². The discharge time increased in the order of PPY < PANI < Poly(pyrrole-co-aniline), which is consistent with the result of CV test. Moreover, it

TABLE I
EDS Result of Poly(pyrrole-co-aniline)

Mass composition (%)	C	N	Cl	O	S
Measured values	69.94	12.05	2.51	14.83	0.66
Theoretical values	78.3	19.2	–	–	–

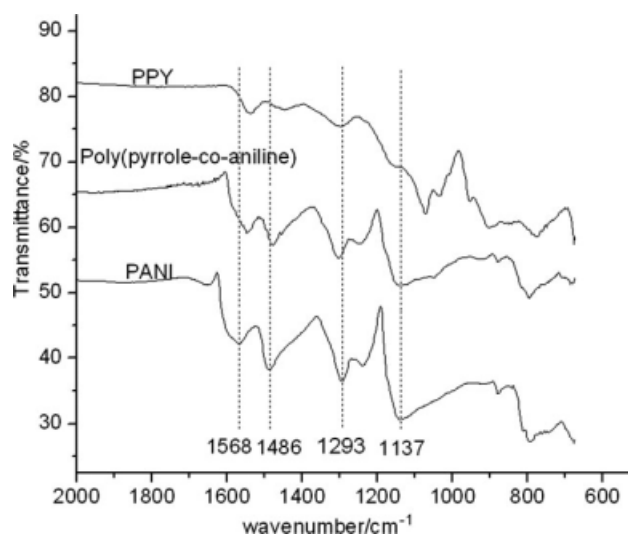


Figure 2 FTIR spectra of PPY, poly(pyrrole-co-aniline), and PANI.

can also be calculated based on Figure 4 that the specific capacitance of PPY, PANI, and the copolymer electrode are 163 F/g, 246 F/g, and 489 F/g, respectively. It is obvious that the copolymer electrode shows higher specific capacitance, which may be due to its high specific surface area and improved structure.

With increasing current density, as can be seen from Figure 5, the discharge duration of copolymer electrode decreases. When current densities are 8, 10, and 12 mA/cm², the corresponding specific capacitances are 827 F/g, 489 F/g, and 375 F/g. Although at higher current density, 12 mA/m² for example, capacitance value is lower than that of lower current density, it is still higher than that of most other polymer materials for supercapacitors.^{1,2} Therefore, it can be concluded that the poly(pyrrole-co-aniline) is suitable for electrode material of supercapacitor.

The impedance responses of PPY, PANI, and the copolymer electrode are displayed in Figure 6, which was carried out at the open circuit potential in the frequency range of 0.005 to 10⁵ Hz with ac-voltage amplitude of 5 mV. For three different polymers, all the typical Nyquist plots consist of two parts: a single semi-circle in the high-frequency region and a straight line in the low-frequency region. The intercept of the semicircle in the high-frequency region at the real axis represents the internal resistance, which was related to the intrinsic electrical resistance of the active materials, the electrolyte resistance, and the contact resistance at the interface between the active material and current collector.²⁵ As these polymers were polymerized at same conditions, the internal resistance differs slightly and the difference is caused by active

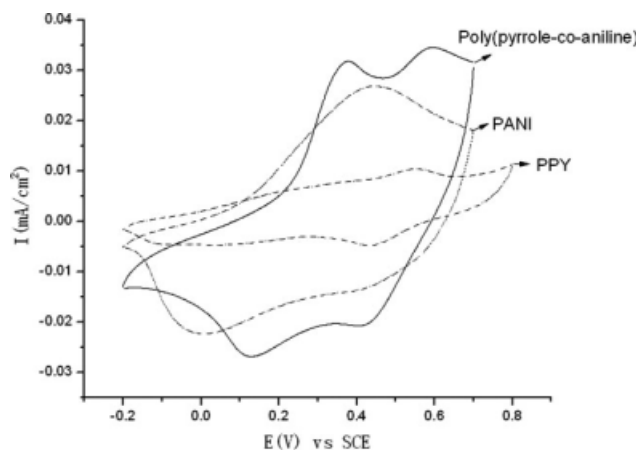


Figure 3 Cyclic voltammograms of poly(pyrrole-*co*-aniline), PPY, and PANI electrode in an electrolyte solution of 1 mol/L Na_2SO_4 . Scan rate: 5 mV/s.

material. Moreover, the value of the copolymer is lowest, which indicates that the electrical conductivity of poly(pyrrole-*co*-aniline) is higher than PPY and PANI.

In the high- and medium-frequency regions a semi-circle can be observed, which was generally attributed to the double layer charging process and also to the charge transfer step.³ As shown in Figure 6, the radius of semicircle in spectra of the copolymer is smaller than other two polymers, which illustrates that the electrochemical performance of the copolymer are better when compared with PPY and PANI.

Lastly, in the low-frequency region, the impedance spectra exhibit a quasi-linear behavior that is attributable to diffusion processes. As the linear region of the copolymer leans more toward imaginary axis, it

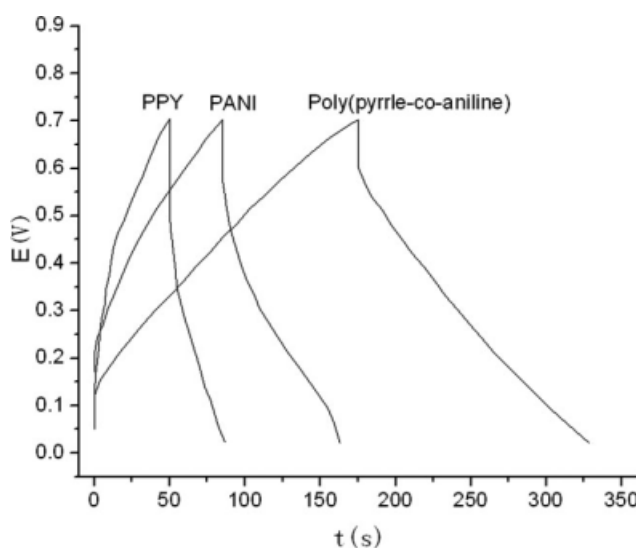


Figure 4 Galvanostatic charge-discharge curves of PPY, PANI, and poly(pyrrole-*co*-aniline) electrode at a current density of 10 mA/cm².

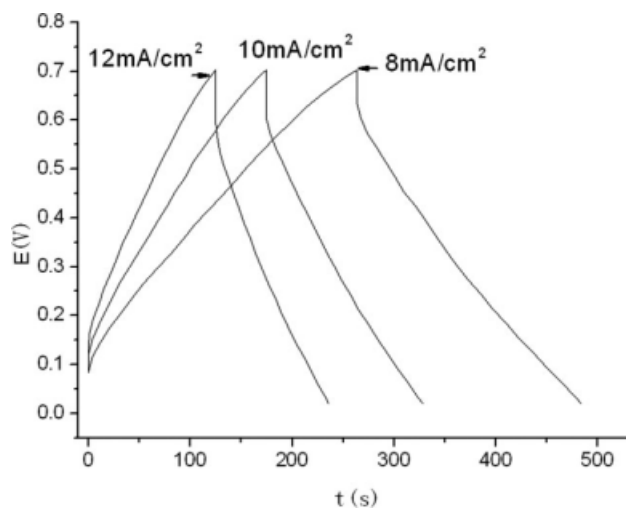


Figure 5 Galvanostatic charge-discharge curves of poly(pyrrole-*co*-aniline) electrode at current density of 8, 10, and 12 mA/cm².

leads to a conclusion that poly(pyrrole-*co*-aniline) shows better electrochemical capacitance than PPY and PANI.

CONCLUSIONS

A novel capacitive material for supercapacitor, poly(pyrrole-*co*-aniline), has been prepared by joint oxidation of the corresponding monomer mixtures. The copolymer was granular and about 100–300 nm in diameter. FTIR, SEM-EDS, and CV tests proved that the product was copolymer instead of mixture of PPY and PANI. Electrochemical tests indicated that poly(pyrrole-*co*-aniline) had better capacitive performance than PPY and PANI. The specific capacitance of the pyrrole-aniline copolymer was

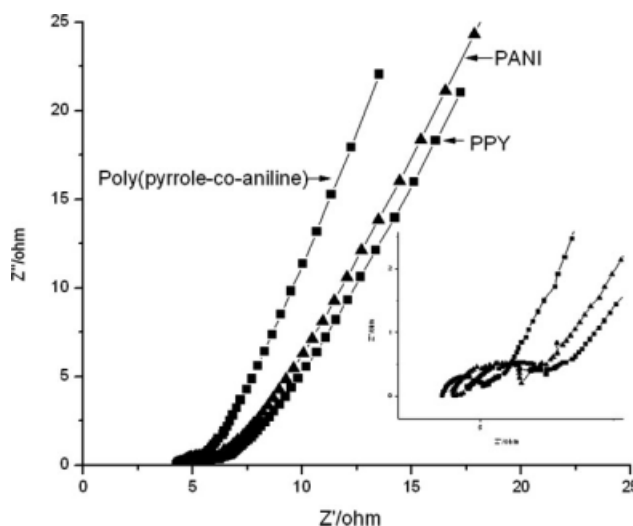


Figure 6 Nyquist diagram of PPY, PANI, and poly(pyrrole-*co*-aniline) electrode in 1 mol/L Na_2SO_4 at open circuit potential.

827 F/g in 1 mol/L Na₂SO₄ at a current density of 8 mA/cm². Moreover, this study provided a new idea for the application of conducting polymer in supercapacitor.

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