REVIEW

Study of capacitive properties in supercapacitor for copolymer of aniline with *m*-phenylenediamine

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Abstract The copolymers were synthesized with different molar ratios of *m*-phenylenediamine to aniline (*R* for short) by a chemical oxidation method. The products were first used as electrochemical activity materials of the supercapacitor. Capacitive behaviors of the prepared copolymers in 1 mol·L^{-1} H$_2$SO$_4$ electrolyte were examined by electrochemical impedance spectroscopy, cyclic voltammeter, and galvanostatic charge/discharge. The relationship of molar ratios with capacitive property of the prepared products was investigated too. The results showed that the product with *R* of 2:98 displayed better electrochemical properties than that of the other products. Compared with the synthesized polymer in the absence of *m*-phenylenediamine, the polymerized copolymer with *R* of 2:98 exhibited the initial specific capacitance value of 475 F·g^{-1}, which increased by nearly 10.1% than that of the former at a current density of 200 mA·g^{-1} in 1 mol·L^{-1} H$_2$SO$_4$ electrolyte in the potential range of −0.3 to 0.7 V. The discharge specific capacitance value of the copolymer remained 300 F·g^{-1} after 1,000 cycles, exhibiting a good cycling performance and the structure stability.

Keywords Copolymer · Aniline · *m*-phenylenediamine · Capacitive properties

Introduction

In recent years, a research interest has focused on supercapacitor because of its particular properties of high power density and potential applications in the fields of hybrid electric vehicles and electronic equipments and so on [1]. Performance of the supercapacitor is closely related to the electrode material, so researching and developing new electrode material is an important way to improve the performance of the supercapacitor. Among the numerous supercapacitor electrode materials, polyaniline (PANI) has received a great deal of attentions due to its advantages, such as material being easily obtained, being easily synthesized, excellent environmental stability, and higher energy storage [2–4]. It is well known that PANI would degrade at high potentials, which has seriously restricted the application in the field of supercapacitor [5]. So many studies have been done in the fields of defending against degradation of PANI and enhancing its structure stability. Over the years, there were some reports on the interesting copolymers of aniline with aromatic diamines, *p*-, *m*-, or *o*-phenylenediamine [6–11]. Most methods adopted by the above authors were electrochemical method; compared with chemical method, the latter has the advantages such as simple equipment requirement, good repeatability and so on. Moreover, the copolymers of aniline with aromatic diamines (namely, *p*-, *m*-, or *o*-phenylenediamine) which were obtained by above authors have not been used as electrode material. So in this work, the copolymers of aniline with *m*-phenylenediamine, which were synthesized by a chemical oxidation method, were used as electrode material for the supercapacitor in the aqueous electrolyte, and the capacitive properties were first studied. Moreover the copolymers were also synthesized with different molar ratios of *m*-phenylenediamine to aniline, and the capacitive properties were compared with each other. The *m*-phenylenediamine was used due to its two aminos at the metapositions of benzene ring, which may be easy to generate new branch chains, leading to improve the

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structure stability of polymers and the discharge specific capacitance.

Experimental

Preparation of copolymer samples

Aniline and *m*-phenylenediamine were dissolved in 20 mL 1 mol·L^{-1} hydrochloric acid at a certain molar ratio. The mixture was put in ice bath (0–5 °C) and the polymerization reaction was started by adding 25 mL 1 mol·L^{-1} anmoium persulfate. After 24 h, the precipitate was filtered, washed repeatedly with 1 mol·L^{-1} hydrochloric acid and acetone sequentially and dried at 60 °C under vacuum for 24 h. Copolymers were prepared with the same method by using the mixtures of aniline and *m*-phenylenediamine with various molar ratios.

Characterization of copolymer samples

Powder X-ray diffraction (XRD) data were collected on a Rigaku D/MAX-rA diffractometer with Cu Kα radiation, operating at 40 kV and 100 mA. The Fourier transform infrared (FT-IR) spectra were recorded by a Nicolet 170SX spectromete with KBr pellets.

Electrochemical measurements

Preparation of electrodes

The mixture was prepared by mixing 80 wt.% copolymer powders, 15 wt.% acetylene black and 5 wt.% PVDF, which was dissolved by NMP. (NMP is short for *N*-methyl pyrrolidine.) The copolymer electrodes were prepared by pressing the mixture onto stainless steel grids and then dried under infrared lamp.

Cyclic voltammetry tests

The cyclic voltammetry tests were performed with a three-electrode cell equipped with a working electrode, a platinum foil counter electrode and a saturated calomel reference electrode (SCE), and carried out with LK2005 electrochemical work station system.

Electrochemical impedance tests

Electrochemical impedance spectra of the copolymer electrodes were measured with a three-electrode cell in which copolymer electrodes were used as a working electrode, a platinum foil counter electrode and a saturated calomel reference electrode. The tests were performed with Potentio-

stat Gal-vanostat PGSTAT302 (The Netherlands) in 1 mol·L^{-1} H$_2$SO$_4$ solution. The frequency limits were set between 10 kHz and 0.01 Hz, and the amplitude of the signal is 5 mV.

Charge/discharge tests

The charge/discharge tests were performed with a two-electrode cell in which the copolymer electrode was used as both positive electrode and negative electrode at a current density of 200 mA·g^{-1} in 1 mol·L^{-1} H$_2$SO$_4$ solution, and carried out with Neware battery program-control testing system.
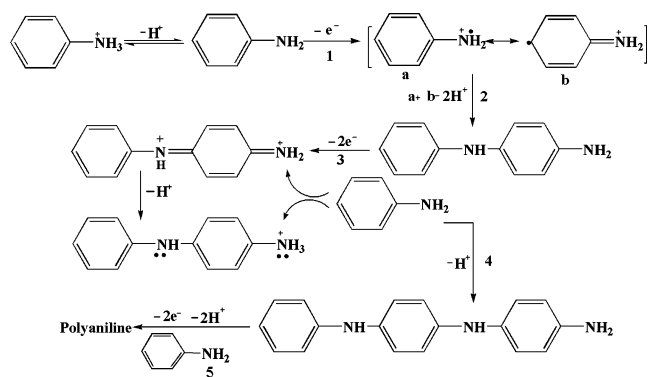
Results and discussions

IR analysis

Figure 1 shows the IR spectra of the samples ranging from 2,500 to 400 cm^{-1}, the molar ratios of *m*-phenylenediamine
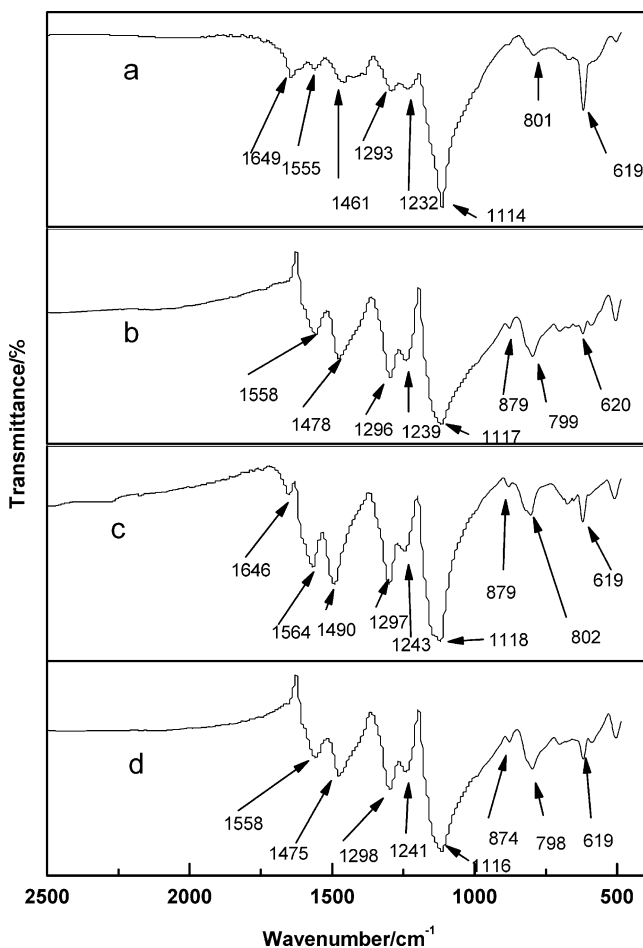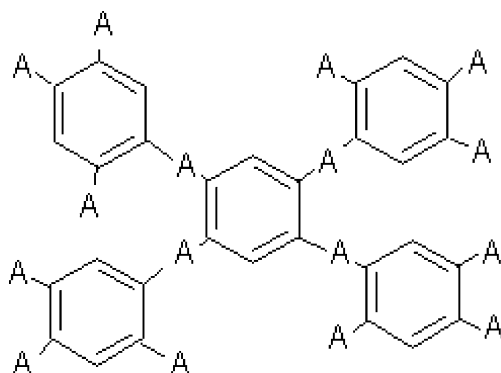

Fig. 1 IR spectra of the samples. **a** $R=0:100$, **b** $R=1:99$, **c** $R=2:98$, **d** $R=4:96$ (R expresses the molar ratios of *m*-phenylenediamine to aniline)
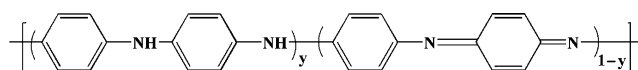
Fig. 2 Polymerization mechanism of PANI. *1* Aniline was slowly oxidized to generate radical cations. *2* Two radical cations formed dipolymer in a head to tail arrangement way. *3* The dipolymers were fleetly oxidized to quinoid structure. *4* The quinoid structure dipolymers and aniline were polymerized to form a tripolymer. *5* The tripolymer molecule continued to grow to form higher polymerization degree polymer in a head to tail arrangement way

to aniline (*R*) are 0:100 (Fig. 1a), 1:99 (Fig. 1b), 2:98 (Fig. 1c), and 4:96 (Fig. 1d), respectively. It can be seen from Fig. 1a that two main absorption bands located at 1,649 and 1,461 cm^{-1} can be attributed to the benzenoid ring stretching frequency. The absorption band at 1,555 cm^{-1} is related to quinoid ring stretching frequency. The peaks approximately around 1,293 and 1,232 cm^{-1} should be attributed to C–N stretching vibration of the aromatic amine nitrogen. The 1,114 cm^{-1} peak can be assigned to a vibration mode of the –NH$^+$=structure, which should occur during protonating. The C–H out of plane bending vibration band of 1,4-disubstituted benzene ring appears at 796 cm^{-1} [12–14]. However, compared the IR spectra of Fig. 1a with that of Fig. 1b, c, and d respectively, we can find that there is a new absorption band at approximately 879 cm^{-1}, which should relate to the C–H


Fig. 4 One base of the polyaniline (A)

bending out of plane vibration band of 1,2,4,5-substituted benzene ring [15–17]. According to aniline polymerization mechanism, which can be seen from Fig. 2, aniline was slowly oxidized to generate radical cations firstly, and two radical cations formed dipolymer in a head to tail arrangement way. Then, the dipolymers were fleetly oxidized to quinoid structure, and the quinoid structure dipolymers and aniline were polymerized to form a tripolymer. The tripolymer molecule continued to grow to form higher polymerization degree polymer in a head to tail arrangement way [18–20]. So the structure of copolymer may be speculated as Fig. 3.

According to the speculated structure above, the delocalization effect of π electron should be enlarged, and the peak positions of the copolymer should shift to the lower wave number direction. However, we can see from the IR spectra of copolymer that the peak positions have shifted to the higher wave number direction. The peak shift might have a close relationship with new substituent on the benzene ring, resulting in a spatial effect, which caused infrared absorption peak shift to the higher wave number direction [16] and this is in agreement with the literature reports. Both π electron effect and spatial effect made the

Fig. 3 The possible structure of copolymer (where A expresses one base of the polyaniline)
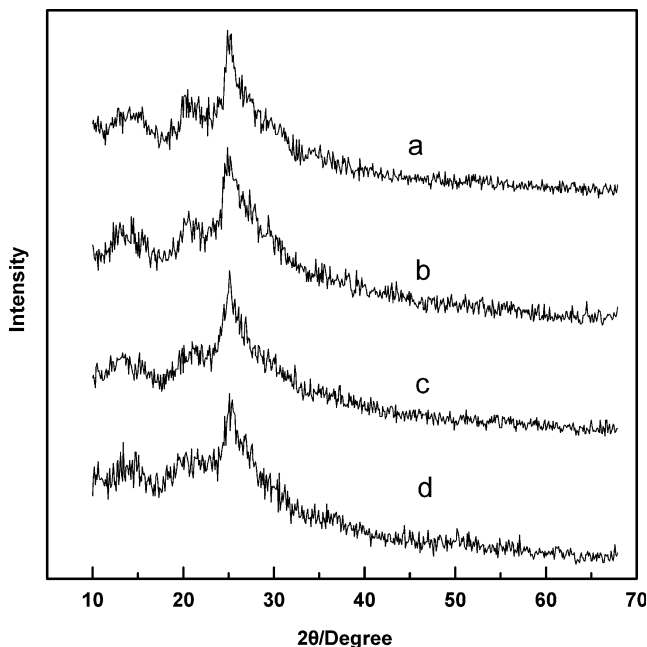
Fig. 5 X-ray diffraction patterns of copolymer samples with the different *R*. *a R*=0:100, *b R*=1:99, *c R*=2:98, *d R*=4:96

Fig. 6 The charge/discharge curves of 20th cycle for the copolymer electrodes with the different R at a current density of 200 mA·g^{-1} in 1 mol·L^{-1} H$_2$SO$_4$ electrolyte. *a* $R=0:100$, *b* $R=1:99$, *c* $R=2:98$, *d* $R=4:96$
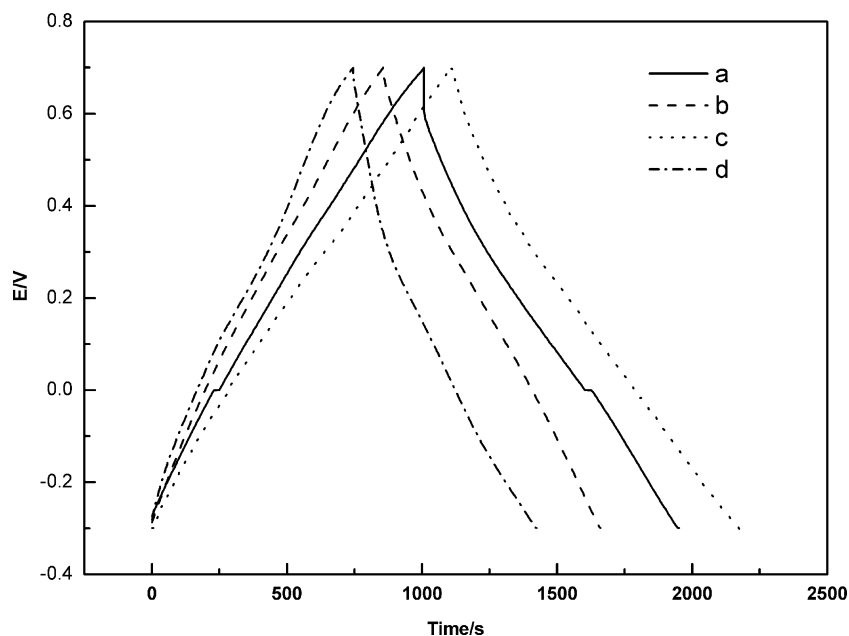
peak positions not shift to the lower wave number but to the higher wave number (Fig. 4).

XRD analysis

Figure 5 illustrates the XRD spectra of copolymer samples with different R. The results indicate that all of the products have the similar structure and there are three diffraction peaks at 15°, 20°, and 25°, of which 20° and 25° are two characteristics diffraction peaks of copolymer samples,

respectively. It can be attributable to the parallel polymer chain and the perpendicular polymer chain [21].

Charge and discharge analysis

Figure 6 displays the 20th cycle charge/discharge curves of the copolymer electrodes at a current density of 200 mA·g^{-1} in 1 mol·L^{-1} H$_2$SO$_4$ electrolyte. As shown in Fig. 6, a good linear variation of potential vs. time is observed for all charge/discharge curves. The charge curves

Fig. 7 The charge/discharge curves of 200th cycle for the copolymer electrodes with the different R at a current density of 200 mA·g^{-1} in 1 mol·L^{-1} H$_2$SO$_4$ electrolyte. *a* $R=0:100$, *b* $R=1:99$, *c* $R=2:98$, *d* $R=4:96$
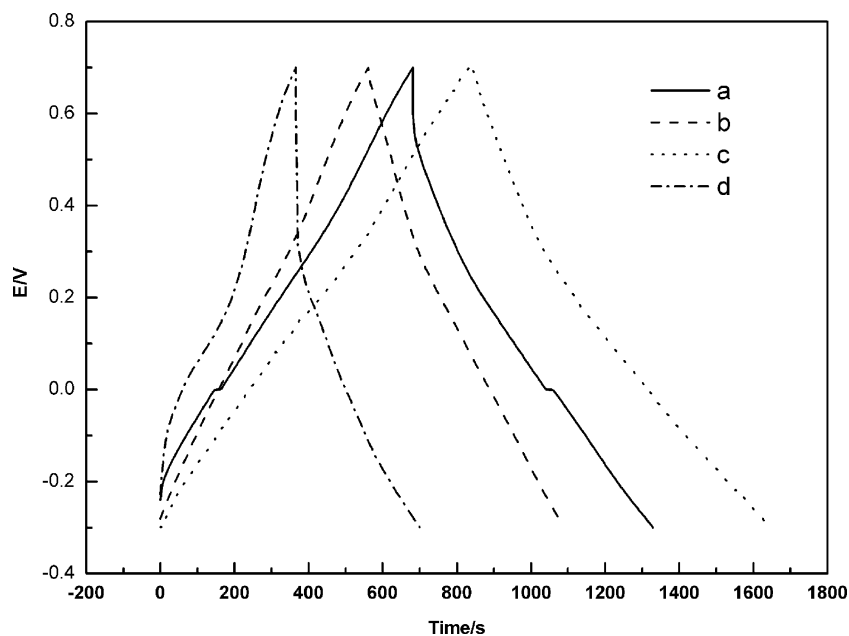
Table 1 The discharge specific capacitance of the copolymer electrodes with the different R at 200 mA·g^{-1} in 1 mol·L^{-1} H$_2$SO$_4$ electrolyte

R value	0:100	1:99	2:98	4:96
Cs (F·g^{-1})	390	391	434	290

R the molar ratio of m-phenylenediamine to aniline, Cs the discharge specific capacitance

are very symmetric to their corresponding discharge counterparts. Especially, the voltage drop is not observed when the current direction is changed, indicating that at the beginning of the charge/discharge, all of the copolymer electrodes show ideal electrochemical properties. Based on the following formula, the discharge specific capacitance (C_s) of the copolymer electrodes can be calculated from the discharge curves:

$$C_s = \frac{2i \times \Delta t}{\Delta V \times m} \qquad (1)$$

Where i (A), ΔV (V), Δt (s), and m (g) are the discharge current, discharge potential range, discharge time consumed in the potential range, and the active material mass of the single electrode, respectively. The results are listed in Table 1. As can be seen in Table 1, the specific capacitance value is the largest when R is 2:98, and the specific capacitance values almost have no differences when R are 0:100 and 1:99. The specific capacitance value is smallest when R is 4:96, which is in accordance with the result obtained by cyclic voltammetry tests. Figure 7 gives the 200th cycle charge/discharge curves of the copolymer electrodes at a current density of 200 mA·g^{-1} in 1 mol·L^{-1} H$_2$SO$_4$ electrolyte. As shown in Fig. 7, a good linear

variation of potential vs. time is observed for charge/discharge curves when R are 2:98 and 1:99, but when R are 0:100 and 4:96, the voltage drop is observed when the current direction is changed, indicating that the internal resistance is bigger. We can also clearly see from Table 1 that when R is 2:98, the discharge specific capacitance of the copolymer electrodes increased by nearly 10.1% and the cycle performance has been greatly improved.

Figure 8 describes the curves of charge/discharge efficiency vs. cycle number for the copolymer electrodes with different R. As can be seen from Fig. 8, charge/discharge efficiency is in the order of c>b>a>d. When R is 2:98, the charging and discharging efficiency of the copolymer electrodes is the highest (about 98%), revealing that the electrode material has good reversible charge/discharge performance.

Figure 9 illustrates the cycling performance of the copolymer electrodes in 1 mol·L^{-1} H$_2$SO$_4$ electrolyte at a current density of 200 mA·g^{-1}. It is clearly observed that copolymer electrodes exhibited the worst cycling performance when R is 4:96, and when R is 2:98, copolymer electrodes exhibited the best cycling performance. Initial discharge specific capacitance value is up to 475 F·g^{-1}, and the value remains 300 F·g^{-1} after 1,000 cycles. This can be attributed to two factors: (1) The π electron delocalization effect of the copolymer is enhanced because of appropriate R, and this can reduce the charge transfer resistance of copolymer material and increase electronic conductivity of the copolymer, improving the discharge specific capacitance to a certain extent. (2) The copolymer produces some branch chains due to adding m-phenylenediamine, which could play a role of structural stability. But when R is more

Fig. 8 The curves of the charge/discharge efficiency vs. cycle number for the copolymer electrodes with the different R. a R=0:100, b R=1:99, c R=2:98, d R=4:96
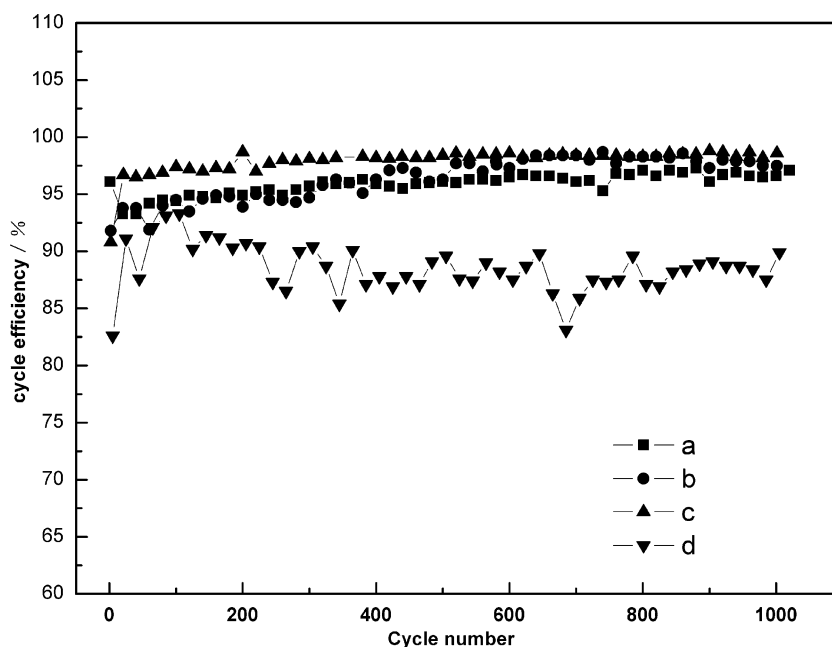
Fig. 9 Cycling performance of the copolymer electrodes with the different R in 1 mol·L^{-1} H$_2$SO$_4$ electrolyte. *a* R=0:100, *b* R=1:99, *c* R=2:98, *d* R=4:96
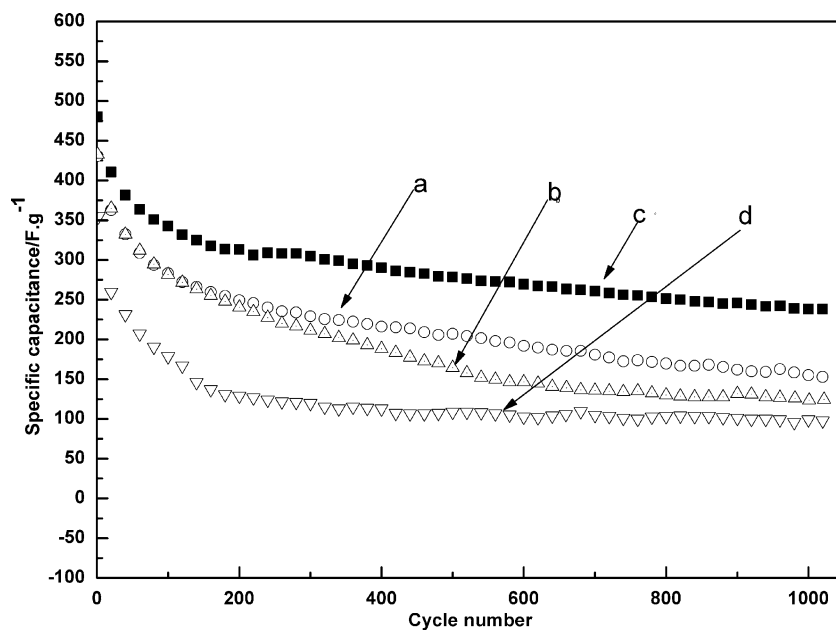
than 2:98, the copolymer exhibited the worst cycling performance. The fact may relate to generating some copolymer with low molecular weight in polymerization process.

Cyclic voltammetric analysis

To evaluate the electrochemical characteristics of the electrode for supercapacitors, current-potential response was employed to investigate the electrochemical performance of the electrode at the potential window from −0.3 to 0.7 V vs. SCE. Figure 10 illustrates the cyclic voltammeter

(CV) curves of composite electrodes measured in 1 mol·L^{-1} H$_2$SO$_4$ electrolyte at a scan rate of 5 mV·s^{-1}. The results shown in Fig. 10 reveal that the area in which the CV curve closed is in the order of c>b>a>d, in other words, the discharge specific capacitance of the copolymers is in the order of c>b>a>d. Moreover, the discharge specific capacitance of the copolymer electrodes can be also calculated from the CV curves according to Eq. (2) [22]:

$$C_s = \frac{q_a + q_c}{2m\Delta V} \quad (2)$$

Where q_a+q_c, m, ΔV are the sum anodic and cathodic voltammetric charges on positive and negative sweeps,

Fig. 10 Cyclic voltammograms of the copolymer electrodes with the different R in 1 mol·L^{-1} H$_2$SO$_4$ electrolyte at a scan rate of 5 mV·s^{-1}. *a* R=0:100, *b* R=1:99, *c* R=2:98, *d* R=4:96
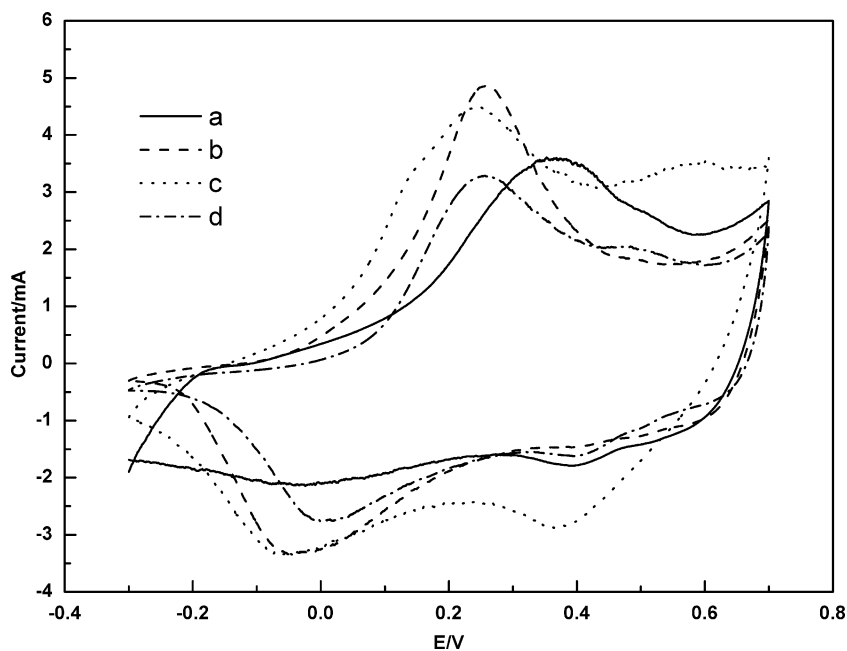
Table 2 The discharge specific capacitance of the copolymer electrodes with the different R at a scan rate of 5 mV·s^{-1} in 1 mol·L^{-1} H$_2$SO$_4$ electrolyte

R value	0:100	1:99	2:98	4:96
C_S(F·g^{-1})	421	456	589	373

R the molar ratio of m-phenylenediamine to aniline, C_s the discharge specific capacitance

mass of the copolymer electrodes, and the potential range of CV, respectively. The results are listed in Table 2, as can be seen from Table 2, the discharge specific capacitance values of the copolymers is in the order of c>b>a>d, but the values of the discharge specific capacitance are larger in comparison with that in Table 1, which may be caused by different testing systems. Obviously, the capacitive performance of composite electrodes was improved by adding m-phenylenediamine, which is ascribed to the enhancement of conductivity. Some important information could also be noticed from Fig. 10c. Two pairs of redox peaks located at −0.1 and 0.25 V should correspond to the exchange between leuco-emeraldine and emeraldine states of PANI [23], while redox peaks of 0.38 and 0.5 V should be associated with degradation products of PANI [24–26]. The CV curves of copolymer electrodes also show that the first redox peak current ratio is the minimum when R is 2:98. This shows that copolymer electrodes have good electrochemical reversibility and good pseudo-capacitance. These data support the results of the charge/discharge tests.
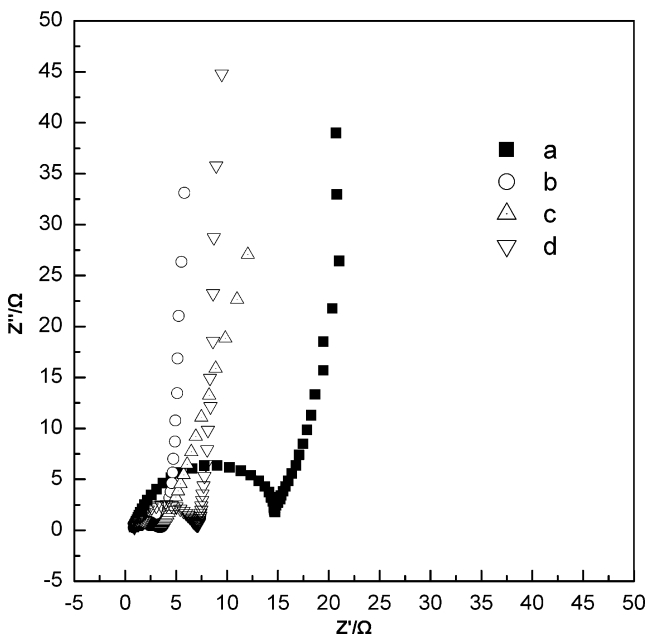
Fig. 11 The alternating current impedance spectra of the copolymer electrodes with the different R in 1 mol·L^{-1} H$_2$SO$_4$ electrolyte. *a* R= 0:100, *b* R=1:99, *c* R=2:98, *d* R=4:96

Electrochemical impedance analysis

Figure 11 presents the impedance spectra of the copolymer electrodes before cycling in 1 mol·L^{-1} H$_2$SO$_4$ electrolyte. The frequency limits were set between 10 kHz and 0.01 Hz, and the amplitude of the signal is 5 mV. The high frequency intercept on the real axis provides the solution resistance (R_s) and the diameter of semicircle provides the charge transfer resistance (R_p) of the polymer, which arises from diffusion of electrons between the electrolyte and the polymer chain [27]. As shown in Fig. 11, R_s which provides the electrolyte impedance is about 0.85 Ω and is nearly invariant with R as expected. This is because charges transfer only on the polymer electrode surface at very high frequencies and it is very difficult to transfer into internal electrode. So R_s has nothing to do with the polyaniline material [28]. From Fig. 11, we can also see that there is an increase in diameter of the semicircle with different R. The value of R_p, which is as low as 3.1 Ω when R is 2:98, increases to about 7.1 and 14.7 Ω respectively when R are 4:96 and 0:100. This is because when the frequency is lower, charges can deep into the electrode and transfer in the bulk phase of the electrode, and the charge transfer resistance of the system is displayed. At this time, the charge transfer resistance of polymer material itself can not be ignored. The straight line in low-frequency range is inclined at the angle of approximately 90° to the real axis, indicating that copolymer electrodes have a good capacitive behavior [24]. Moreover, the discharge specific capacitance of the copolymer electrodes can be calculated from Eq. (3) in low-frequency range [29].

$$C_s = \frac{1}{2\pi\, fmZ''} \qquad (3)$$

Where f, m, Z'' are the frequency of the low-frequency range (Hz), here the low frequency is 0.01 Hz, mass of the copolymer electrodes (g), and the impedance of the imaginary part (Ω), respectively. The results are listed in Table 3. As can be seen in Table 3, the discharge specific capacitance values of the copolymers is in the order of c>b>a>d, but the values of the discharge specific capacitance are larger in comparison with that in Table 1. This may be caused by different testing systems. These data

Table 3 The discharge specific capacitance of the copolymer electrodes with the different R at a frequency of 0.01 Hz in 1 mol·L^{-1} H$_2$SO$_4$ electrolyte

R value	0:100	1:99	2:98	4:96
C_S(F·g^{-1})	392	463	565	341

R the molar ratio of m-phenylenediamine to aniline, C_s the discharge specific capacitance

support the results and discussions in the charge/discharge tests and cyclic voltammetric tests.

Conclusion

In this paper, the copolymers were synthesized with different molar ratios of *m*-phenylenediamine to aniline by a chemical oxidation method. The electrochemical properties of the prepared copolymers were evaluated by cyclic voltammetry, charge/discharge test, and impedance spectra. The results showed that *m*-phenylenediamine has a great effect on the electrochemical performance of the copolymers, and when R was 2:98, the product displayed better electrochemical performance than that of the other products. In the potential range of −0.3 to 0.7 V, the copolymer exhibited the initial discharge specific capacitance value of 475 F·g^{-1} at a current density of 200 mA·$^{-1}$ in 1 mol·L^{-1} H$_2$SO$_4$ solution, increasing by nearly 10.1% compared with the polymer synthesized in the absence of *m*-phenylenediamine. After 1,000 cycles, the specific capacitance remained 300 F·g^{-1}, illustrating that the copolymer exhibited better capacity retention and cycling performance.

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