

Short Communication

## Electrosynthesis and Performance of Poly(aniline/pyrrole) Copolymer

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In this paper, poly(aniline/pyrrole) (PANPY) copolymer was prepared in a mixed acid solution by electrosynthesis method. The molar ratio between the aniline and pyrrole monomer was found to great influence on the electrochemical performance of PANPY copolymer. When molar concentration ratio of aniline and pyrrole to be 1: 1, the PANPY copolymer exhibited highest specific capacity of 227.88 F·g<sup>-1</sup> at a current density of 4 mA·cm<sup>-2</sup>. This work indicates the potential application of PANPY copolymer as supercapacitor.

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**Keywords:** Electrosynthesis; polyaniline; polypyrrole; supercapacitance

### 1. INTRODUCTION

Polyaniline (PANI) and polypyrrole (PPy) have received great attention because of their unique electrochemical properties, such as good environmental stability, easy synthesis, high conductivity and easy doping [1-4]. These properties lead PANI and PPy have been widely applied as battery electrode material, supercapacitor and electrochemical sensor [5-8].

In the last decades, electrosynthesis method has been widely utilized to prepared PANI or PPy polymer. Shiri *et al.* [9] introduced a electrosynthesis method to prepare PPy thin film on the surface of yttrium aluminum garnet (YAG, Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>). And the specific capacitance of the PPy was calculated as 109 F·g<sup>-1</sup> at a current density of 1 mA·cm<sup>-2</sup>. Le *et al.* [10] prepared PANI films on mutilwalled

carbon nanotubes by electro-polymerization method, which show that the PANI films have a high electroactivity, and a porous and branched structure that can increase the specific surface area for biosensing application. However, the electrosynthesis and electrochemical performance of poly(aniline/pyrrole) (PANPY) copolymer has been rarely studied. And the PANPY copolymer would combine the advantages of the individual PANI or PPy polymer.

In this paper, PANPY copolymer was obtained by electrosynthesis method, and the structure and electrochemical properties of the copolymer were also investigated. It is found that, when the molar ratio between aniline and pyrrole as 1:1, the PANPY copolymer exhibited highest specific capacity ( $227.88 \text{ F}\cdot\text{g}^{-1}$ ) at a current density of  $4 \text{ mA}\cdot\text{cm}^{-2}$ . Moreover, the PANPY copolymer showed excellent cycle stability, the capacity dropped only 3.99% even after 1000 cycles. This study introduces a facile method to prepare PANPY copolymer, which have advantages, such as high specific capacity and long life cycle and stability in an aqueous electrolyte.

## 2. EXPERIMENTAL

### 2.1. Materials

Ethanol and acetone were obtained from Sinopharm Chemical Reagent Company (Shanghai, China) and purified by distillation under reduced pressure. Sodium hydroxide (NaOH), sodium carbonate ( $\text{Na}_2\text{CO}_3$ ), sodium silicate ( $\text{Na}_2\text{SiO}_3$ ), trisodium phosphate sodium phosphate ( $\text{Na}_3\text{PO}_4\cdot 12\text{H}_2\text{O}$ ), nitric acid ( $\text{HNO}_3$ ), hydrofluoric acid (HF), sulfuric acid ( $\text{H}_2\text{SO}_4$ ), p-Toluenesulfonic acid ( $\text{p-CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H}$ ) and the 304-type stainless steel plates were purchased from Chengdu Kelong chemical reagent company.

### 2.2. Electrosynthesis of PANPY Copolymers

The 304-type stainless steel plates were firstly washed by hot ethanol and acetone to remove oil on their surfaces. Then alkaline solution prepared by NaOH (20 g/L),  $\text{Na}_2\text{CO}_3$  (20 g/L),  $\text{Na}_3\text{PO}_4\cdot 12\text{H}_2\text{O}$  (20 g/L) and  $\text{Na}_2\text{SiO}_3$  (10 g/L) were further applied to remove the residual oil. After that, the plates were polished by immersed in mixed acid solution (with  $\text{HNO}_3$  and HF as 1:1) for 30~60 S at room temperature.

To prepare PANPY copolymers, different proportions (molar ratio) of aniline and pyrrole monomer was dropwised into a mixed acid solution with appearance of sulfuric acid ( $0.25 \text{ mol}\cdot\text{L}^{-1}$ ) and p-toluenesulfonic acid ( $0.25 \text{ mol}\cdot\text{L}^{-1}$ ), and the PANPY copolymers were formed on the surface of 304-type stainless steel plates. A cyclic volt-ampere (CV) method was applied to synthesis PANPY copolymers with scan range from 0 to 1.3 V, scanning laps of 30 and scanning speed of  $100 \text{ mV}\cdot\text{S}^{-1}$ .

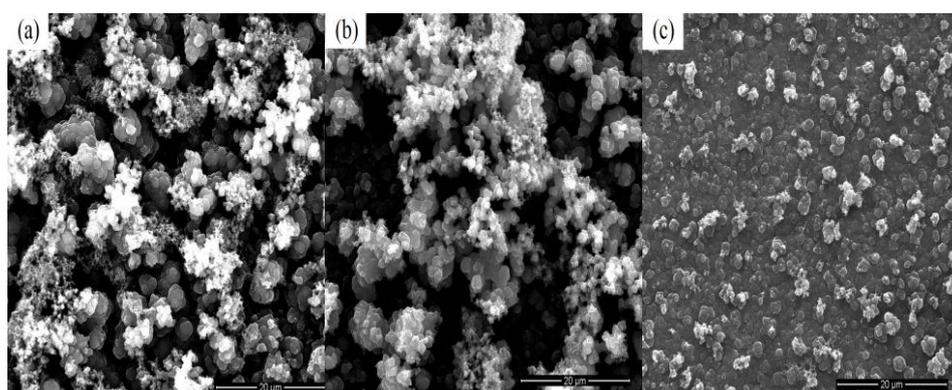
### 2.3. Characterizations

The morphologies and structures of PANPY copolymers were observed by field-emission

scanning electron microscope (FE-SEM, Ultra 55). Fourier transform infrared spectra (FTIR) of these samples were recorded on a spectrometer (Nicolet-5700, USA) using pressed KBr pellets. All of the electrochemical measurements were carried out in  $0.5 \text{ mol}\cdot\text{L}^{-1} \text{ H}_2\text{SO}_4$  using a three-electrode system. The PANPY copolymers were directly loaded on stainless steel mesh as the working electrode. Platinum foil and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. Cyclic voltammetry (CV) curves and galvanostatic charge-discharge measurements were recorded at the potential range of  $-0.2$  to  $0.8 \text{ V}$  and  $0$  to  $0.7 \text{ V}$  with IM 6 electrochemical workstation, respectively.

### 3. RESULTS AND DISCUSSION

#### 3.1. SEM measurement



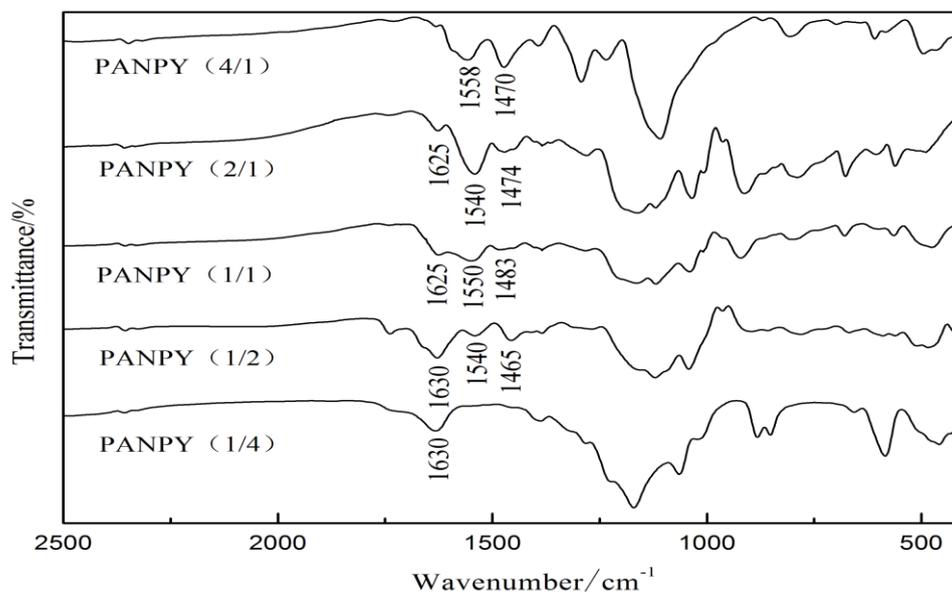
**Figure 1.** SEM images of PANPY copolymers prepared from different aniline and pyrrole monomer ratio (a) 1:1 (b) 1:2 (c) 2:1.

Figure 1. illustrates the morphologies and structures of PANPY copolymers synthesized from different molar ratio between aniline and pyrrole monomer. The PANPY (1/1) copolymer shows more uniform surface morphology, the mushroom clouds-like PANPY copolymers could be observed on the surface of stainless steel plates which have larger surface area. A smoother surface of PANPY (2/1) copolymer was observed, indicating the specific surface area of the copolymer was remarkably decreased, which is detrimental to ion insertion/de-insertion ability. The PANPY (1/2) copolymer shows similar surface structure with PANPY (1/1) copolymer, however, the binding force of the copolymer film was rather weak, which is very easy to fall from the stainless steel plates.

#### 3.2. FT-IR spectra

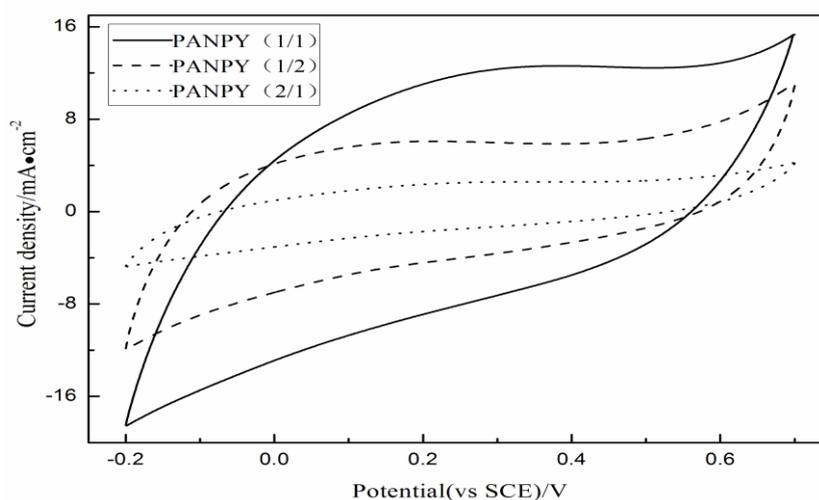
Figure 2. shows the FTIR spectrums of PANPY copolymers. As shown in Figure 2., the PANPY (2/1), PANPY (1/1), PANPY (1/2) copolymers exhibited a quinone structure  $\text{C}=\text{N}$  stretching vibration peak at  $1540 \text{ cm}^{-1}$ , and a benzene structure of  $\text{C}=\text{C}$  stretch vibration of PANI peak at  $1474 \text{ cm}^{-1}$  [11, 12]. The absorption peak at  $1625 \text{ cm}^{-1}$  could attribute to  $\text{C}=\text{C}$  stretching vibration of pyrrole

rings of Ppy [12]. For PANPY (1/4) copolymer, the spectrum of benzene and quinone-type peaks almost disappeared. Similarly, IN PANPY (4/1) copolymer, the strength of C=C absorption peak was noticeably reduced. This is because a greater concentration of monomer, the polymerization is dominant in the solution, and the monomer yield pure PANI or Ppy.



**Figure 2.** FTIR spectra of the PANPY copolymers.

### 3.3. CV copolymer film detection

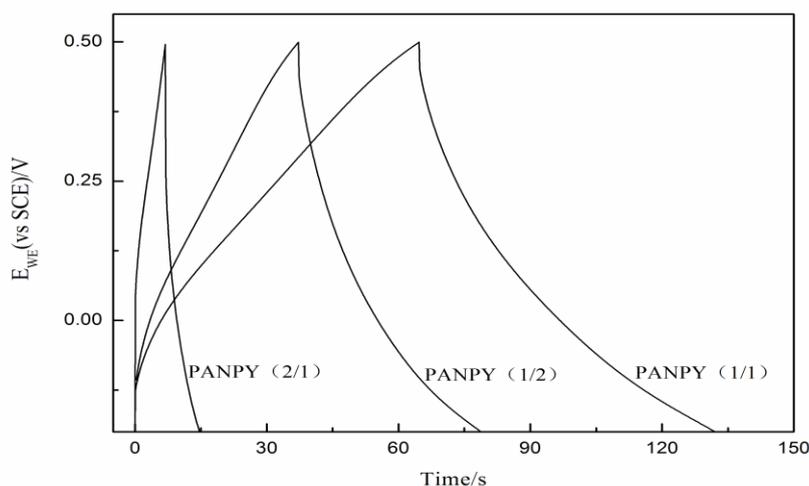


**Figure 3.** Cyclic voltammetry curves of PANPY copolymers.

As can be seen in Figure 3. the PANPY copolymers exhibit different CV performances, they all have a good reversibility during charge and discharge, the ion exchange process is relatively fast [13]. Two pairs of redox peaks were appeared for PANPY based hybrid materials, which were attributed to two transitions (leucoemeraldine/emeraldine and emeraldine/permigraniline) of PANI and PPy.

Therefore, the capacitance of PANI based hybrid materials mainly originated from pseudocapacitance. It was well known that the capacitance of electrode material was proportional to the area of CV curve, the PANPY (1/1) copolymer performed a largest CV area at a scanning speed of  $100 \text{ mV}\cdot\text{S}^{-1}$ , indicating this polymer have a greatest capacitance value.

### 3.4 Copolymer membrane charge and discharge performance test



**Figure 4.** Charge/discharge cures of PANPY copolymers.

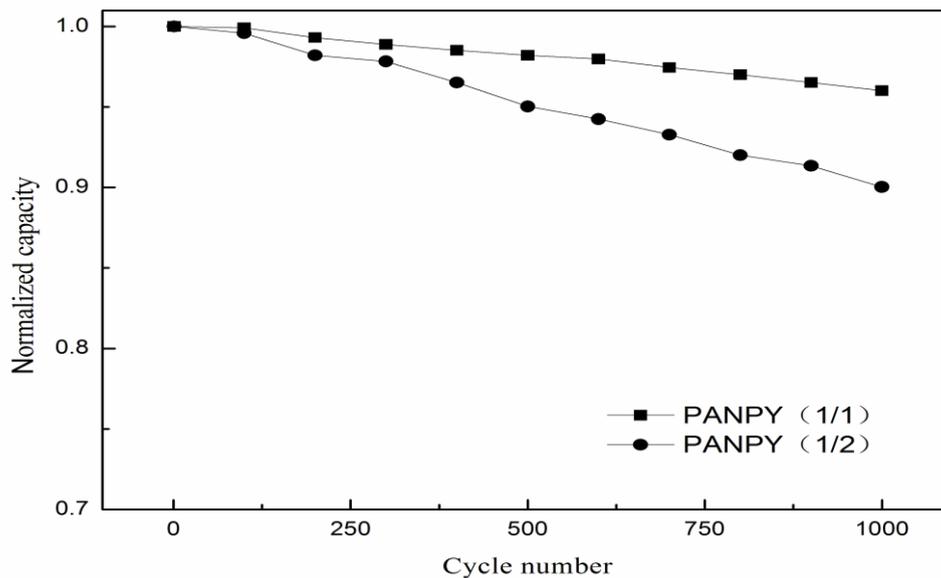
The charge-discharge curves of the PANPY copolymers in  $0.5 \text{ M H}_2\text{SO}_4$  solution at a current density of  $4 \text{ mA}\cdot\text{cm}^{-2}$  as shown in Figure 4. And which could be calculated by the formula [14]:

$$c = \frac{I\Delta t}{\Delta Vm}$$

Where  $C$  is the specific capacitance ( $\text{F}\cdot\text{g}^{-1}$ ),  $I$  is the charge-discharge current (A),  $\Delta V$  is  $0.5 \text{ V}$ , and  $m$  is the mass of active material with the electrode.

The PANPY (1/1) copolymer showed largest capacitor of  $227.88 \text{ F}\cdot\text{g}^{-1}$ , which is larger than the value of PANPY (2/1) copolymer and PANPY (1/2) copolymer. It was clearly shown that the PANPY (1/1) copolymer exhibited a highest discharge capacitance than PANPY (2/1) and PANPY (1/2) copolymers, indicating that the former electrode material owned a relatively higher energy and power density. However, the specific capacitance decreased with the increase in charge-discharge current density, which was attributed to the fact that the redox reaction rate and the charge diffusion could not match the rapid increase in the current densities.

### 3.5 Stability testing cycle copolymer film



**Figure 5.** Cycling performance of the PANPY copolymers.

To examine the cycling performance of the PANPY copolymers, these polymers were measured by charge-discharge cycling at a current density of  $4 \text{ mA}\cdot\text{cm}^{-2}$  for 1000 cycles. As shown in Figure 3, the results show that the capacity of PANPY (1/1) copolymer dropped only 3.99%. It is more stable than the PANPY (1/2) copolymer which dropped 9.97% after 1000 cycles. The mushroom clouds-like PANPY (1/1) copolymer exhibited evidently higher stability than PANPY (1/2) copolymer, which derived from the synergistic effect of the individual PANI and PPy; and the mushroom clouds-like structure provided a larger contact surface area for the intercalation/deintercalation of protons into/out of active materials and shortened the path length for electrolyte ion transport.

#### 4. CONCLUSIONS

In this paper, PANPY copolymers were successfully synthesized by electrosynthesis method with different aniline and pyrrole ratios. And their electrochemical performances were thoughtfully characterized. The results prove that the PANPY (1/1) copolymer exhibits a highest specific capacitance ( $227.88 \text{ F}\cdot\text{g}^{-1}$ ) and well cycle stability, which could maintain 96% after 1000 cycles. We believe that the PANPY copolymers could be a promising supercapacitor electrode material.

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#### References

1. X. J. Xu, R. H. Liu and L. D. Li, *Chem. Commun.*, 51 (2015) 16733-16749.
2. K. Wang, H. P. Wu, Y. N. Meng and Z. X. Wei, *Small*, 10 (2014) 14-31.

3. O. Inganas and S. Admassie, *Adv. Mater.*, 26 (2014) 830-847.
4. S. M. Chen, R. Ramachandran, V. Mani and R. Saraswathi, *Int. J. Electrochem. Sci.*, 9 (2014) 4072-4085.
5. O. A. Kozarenko, V. S. Dyadyun, M. S. Papakin, O. Y. Posudievsky, V. G. Koshechko and V. D. Pokhodenko, *Electrochim. Acta*, 184 (2015) 111-116.
6. B. Thakur, C. A. Amarnath, S. H. Mangoli and S. N. Sawant, *Sensor Actuat B-Chem.*, 207 (2015) 262-268.
7. H. N. Yu, Y. C. Pang and J. Y. Tang, *Int. J. Electrochem. Sci.*, 10 (2015) 8353-8360.
8. L. Wilson, J. V. Wyk, C. Rassie, N. Ross, C. Sunday, H. R. Makelane, M. Bilibana, T. Waryo, S. Mapolie, P. G. Baker and E. I. Iwuoha, *Int. J. Electrochem. Sci.*, 10 (2015) 3207-3222.
9. H. M. Shiri, A. Ehsani and J. S. Shayeh, *RSC Adv.*, 5 (2015) 91062-91068.
10. T. H. Le, N. T. Trinh, L. H. Nguyen, H. B. Nguyen, V. A. Nguyen, D. L. Tran and T. D. Nguyen, *Adv. Nat. Sci-Nanosci.*, 4 (2013).
11. Q.-F. Lü, M.-R. Huang and X.-G. Li, *Chem. Eur. J.*, 13 (2007) 6009-6018.
12. C. F. liang, N. M. xia, M. J. yuan and D. X. yun, *Synthetic Met.*, 16 (2002) 167-172.
13. G. H. Yu, *Abstr. Pap. Am. Chem. S*, 246 (2013).
14. P. Dallas and V. Georgakilas, *Adv. Colloid Interface Sci.*, 224 (2015) 46-61.

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