

Capacitance Performances of Supramolecular Hydrogels Based on Conducting Polymers*

Ting-yang Dai, Rong Tang, Xiao-xiao Yue, Liang Xu and Yun Lu**

Department of Polymer Science and Engineering, State Key Laboratory of Coordination Chemistry, Key Laboratory of High Performance Polymer Materials and Technology of Ministry of Education, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China

Abstract The capacitance performances of poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT-PSS) supramolecular hydrogels have been investigated systematically. The materials show a specific capacitance of 67 F/g and display excellent rate capability at the scan rate as high as 5000 mV/s in the cyclic voltammogram measurements, accompanied by good cycle stability. On the basis of the measurements of the microscale morphologies, specific areas and electrical conductivities, the mechanisms for the improvement of the electrochemical properties are discussed and ascribed to the novel porous microstructures of the hydrogels and the synergetic effect of the rigid PEDOT and soft PSS components. Furthermore, polyaniline (PAn) is compounded with the PEDOT-PSS hydrogels through an interfacial polymerization process, endowing the hydrogel materials with a higher specific capacitance of 160 F/g at the scan rate of 5000 mV/s. The significance of this work lies in the demonstration of a novel method to solve the problems of conducting polymers in electrochemical applications.

Keywords: Conducting polymers; Hydrogels; Capacitance performances; Rate capability; Supercapacitors.

INTRODUCTION

The electrode materials in the supercapacitors have been widely studied since the properties of the electrode materials directly influence the performances of the supercapacitors^[1–3]. Among many electrode materials, conducting polymers (CP) have been attracting increasing attention because the CPs exhibit high conductivity, high energy density as well as low cost^[4–6]. However, in comparison with traditional carbon materials, of which the energy storage is based on an electrochemical double-layer process, the charge is stored in the bulk of the CP-based electrode materials *via* faradaic reaction, resulting in relatively low rate capability and poor cycle-life^[7, 8]. In particular, their insufficient rate capability could not afford enough power density to meet the demand for many high-rate applications such as hybrid electric vehicles, portable electric tools and power backup^[9], which has already been a great obstacle for the practical use of the CP-based electrode materials. Extensive effort has been devoted to increasing the power density in order to compensate the low rate capability of the electrode materials, but usually at the expense of more energy consumption^[10, 11].

To solve the problem, micro/nanostructures of conducting polymers have been synthesized to create

* This work was financially supported by the National Natural Science Foundation of China (Nos. 21174059 and 21374046), China Postdoctoral Science Foundation (No. 2013M530249), Program for Changjiang Scholars and Innovative Research Teams in Universities, Open Project of State Key Laboratory of Supramolecular Structure and Materials (No. SKLSSM201416) and the Testing Foundation of Nanjing University.

** Corresponding author: Yun Lu (陆云), E-mail: yunlu@nju.edu.cn

Received October 31, 2014; Revised December 31, 2014; Accepted January 1, 2015

doi: 10.1007/s10118-015-1647-6

excellent electrode/electrolyte interfaces and shorten the diffusion length^[12–16]. As an example, poly(3,4-ethylenedioxythiophene) (PEDOT) nanotubes prepared by the electrochemical method in a porous alumina membrane have been reported, which show a rectangular cyclic voltammogram at the scan rate of 1000 mV/s and retain about 70% of the capacitance when the scan rate is increased by 10 times^[17]. Besides, composite materials containing conducting polymers have also been produced by combining the characteristics of different materials in order to boost the capacitance properties^[18–21]. Nevertheless, the properties of CP-based electrode materials should be further improved, and more convenient preparation approaches are still desired.

On the other hand, hydrogels based on conducting polymers have drawn a lot of scientific interest in the past decades because the materials present the mechanical and swelling properties of gels added to the specific transport properties of conducting polymers^[22]. Recently, a kind of PEDOT-S/PEDOT aerogel has been reported to be used as the electrode materials of the supercapacitors, which shows the capacitance retention of 58% when the scan rate is increased from 1 mV/s to 100 mV/s^[23]. Moreover, a kind of polyaniline (PAn) hydrogel displaying low capacitance loss with the increase of the current density has also been described^[24]. In our lab, we have developed an effective method to synthesize conducting hydrogels based on poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT-PSS) *via* supramolecular self-assembly between polymer chains and multivalent cations^[25]. Such hydrogels are intrinsically a semi-interpenetrating polymer network (semi-IPN)^[26] in which PEDOT (linear) is entrapped within the PSS network physically-crosslinked with Fe^{3+} ions. A series of conducting hydrogels with remarkable mechanical strength has also been exploited^[27–29].

In the present work, the capacitance performances of the as-prepared PEDOT-PSS supramolecular hydrogels are studied in detail for the first time. The materials present outstanding rate capability and good cycle stability. Based on the systematical measurements of the electrochemical property, microscale morphology, specific area and electrical conductivity, the mechanisms for the improved electrochemical behaviors have been discussed. Additionally, an interfacial polymerization method is employed to combine the PAn component with the PEDOT-PSS hydrogels to fabricate a kind of composite hydrogels with enhanced specific capacitance. The present study gives valuable hints for further optimizing the capacitance properties of CP-based materials to satisfy the requirements in industrial applications.

EXPERIMENTAL

Materials

3,4-Ethylenedioxythiophene (EDOT) and poly(sodium 4-styrenesulfonate) (PSS, $M_w \approx 70000$) were purchased from Aldrich. Aniline monomer (An, Beijing Chem. Co., China) was distilled under reduced pressure before use. All other chemicals (analytical grade) were obtained from Shanghai Chem. Co. (China) and used as received.

Preparation of PEDOT-PSS Hydrogels

PEDOT-PSS hydrogels were synthesized according to the method described before^[25]. Briefly, EDOT monomers were added into 15 mL of PSS aqueous solution. The concentrations of EDOT and PSS were calculated to be 0.06–0.6 mol/L and 0.1–1.0 mol/L, respectively. The mixture was treated in mild ultrasonic for 30 min, and then 15.3 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (38 mmol) dissolved in 3 mL of deionized water was added. After being stirred for 1 min to ensure complete mixing, the system was allowed to react at room temperature for 24 h without agitation. Finally, the products were purified in a large amount of distilled water for about 1 week in order to wash out low molecular weight components of the system.

Preparation of PEDOT-PSS/PAn Composite Hydrogels

PEDOT-PSS/PAn composite hydrogels were produced *via* the interfacial polymerization process^[30]. Typically, PEDOT-PSS hydrogels were immersed in an aqueous solution containing 0.2 mol/L ammonium peroxydisulfate (APS, as the oxidant for the polymerization of An) and 1 mol/L hydrochloric acid (HCl, as the dopant for PAn) for 1 day until equilibrium was reached. After the redundant solution on the surface of the hydrogel was carefully removed, the samples were immersed in a hexane solution containing 0.15 mol/L An for 6 h to

accomplish the polymerization of An and the formation of the composite hydrogels. Finally, the samples were purified in a large amount of 1 mol/L HCl aqueous solution for about 1 week in order to wash out low molecular weight components of the system.

Characterization

The morphologies of the as-prepared hydrogels were observed using scanning electron microscopy (SEM, LEO-1530 VP, JEOL Co., Japan). The BET-specific area measurements were performed with an ASAP 2020 instrument (Micromeritics, USA). Samples were freeze-dried before SEM and BET measurements. The electrical conductivities were measured *via* the four-probe method at room temperature by inserting the four probes into cuboidal samples with the dimension of 5 mm × 5 mm × 1 mm (RTS-8 4-point probes resistivity measurement system, Probes Tech., China).

Electrochemical Measurements

A three-electrode system was equipped with a glassy carbon electrode as the working electrode, a platinum plate as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The electroactive materials (8.0 mg) and acetylene black (1.5 mg) were dispersed in the mixed solution of 8 ml of H₂O and 50 μ L of Nafion (1 wt%) to obtain a composite slurry. Then 10 μ L of the slurry was transferred onto the surface of the glassy carbon electrode. Electrochemical performance was determined by the cyclic voltammogram (CV), galvanostatic charge/discharge (CD) and electrochemical impedance spectroscopy (EIS) tests using a CHI660E electrochemical analyzer system (Shanghai CH Instrument Company, China) in 1 mol/L NaNO₃ aqueous solution. EIS measurements were carried out in the frequency range from 10⁵ Hz to 0.01 Hz with the amplitude of 5 mV. Cycle stability was evaluated with a LAND cell-testing system (CT2001A, Wuhan, China).

The average specific capacitance values were calculated from the area of the CV plot according to equation of $C = i/m \times \Delta V^{[31]}$, where m was the mass of the electroactive material, ΔV was the sweep potential and i was the charge obtained through integrating the area of the CV curve.

RESULTS AND DISCUSSION

As the capacitance performances of the supercapacitors are closely related to the microstructures of the electrode materials^[32], SEM measurements are first carried out to investigate the morphologies of the PEDOT-PSS hydrogels prepared with different reagent concentrations. Figures 1(a)–1(e) display the SEM images of the hydrogels synthesized with 0.1 mol/L PSS and EDOT with different concentrations from 0.06 mol/L to 0.6 mol/L. With the increase of the EDOT concentration, the microscale morphologies evolve from connected films (Figs. 1a and 1b) to a three-dimensional network structure (Figs. 1c and 1d), and finally to a worm-like microstructure (Fig. 1e), which may be due to the spatially-repulsive effect^[33] of the excess formed PEDOT. That is, when an excess amount of PEDOT fills in the physically crosslinked three-dimensional network of PSS^[25], the network would partially split on account of the limited space and thereby achieve a steady state by reducing the energy of the system. Besides, the open pores take appearance in Fig. 1(b) and become larger when more EDOT is added (Figs. 1c and 1d), suggesting that the spatially-repulsive effect is more notable with the enhanced amount of PEDOT. Interestingly, when the [EDOT]/[PSS] is further increased to 6:1, the pores inversely become small (Fig. 1e), possibly resulting from the fact that the redundant PEDOT fills up the space of the split fracture. The micrographs of the PEDOT-PSS hydrogels synthesized with a fixed EDOT concentration of 0.48 mol/L and increased PSS concentrations from 0.3 mol/L to 1.0 mol/L are also shown (Figs. 1f–1i). As we can see, when more PSS is employed, the hydrogels present similar three-dimensional network microstructures and the open spacer becomes a little smaller, suggesting that the soft PSS component may not induce the breaking of the PEDOT-PSS systems.

Cyclic voltammograms are measured to evaluate the specific capacitance and the rate capability of the PEDOT-PSS hydrogels as the electrode materials of the supercapacitors. Figure 2(a) exhibits the typical CV curves of the PEDOT-PSS hydrogel prepared with 0.48 mol/L EDOT and 0.1 mol/L PSS at different scan rates. The shape of the CV plot is rectangular even at the scan rate as high as 5000 mV/s, indicating the ideal capacitor

behavior and the fast charge/discharge process characteristics^[34]. Furthermore, the material shows a specific capacitance of 67 F/g at the scan rate of 5000 mV/s, corresponding to the capacitance retention of 56% with the scan rate increasing from 50 mV/s to 5000 mV/s (Fig. 2b). According to our knowledge, this value is the highest among the CP-based electrode materials for the supercapacitors.

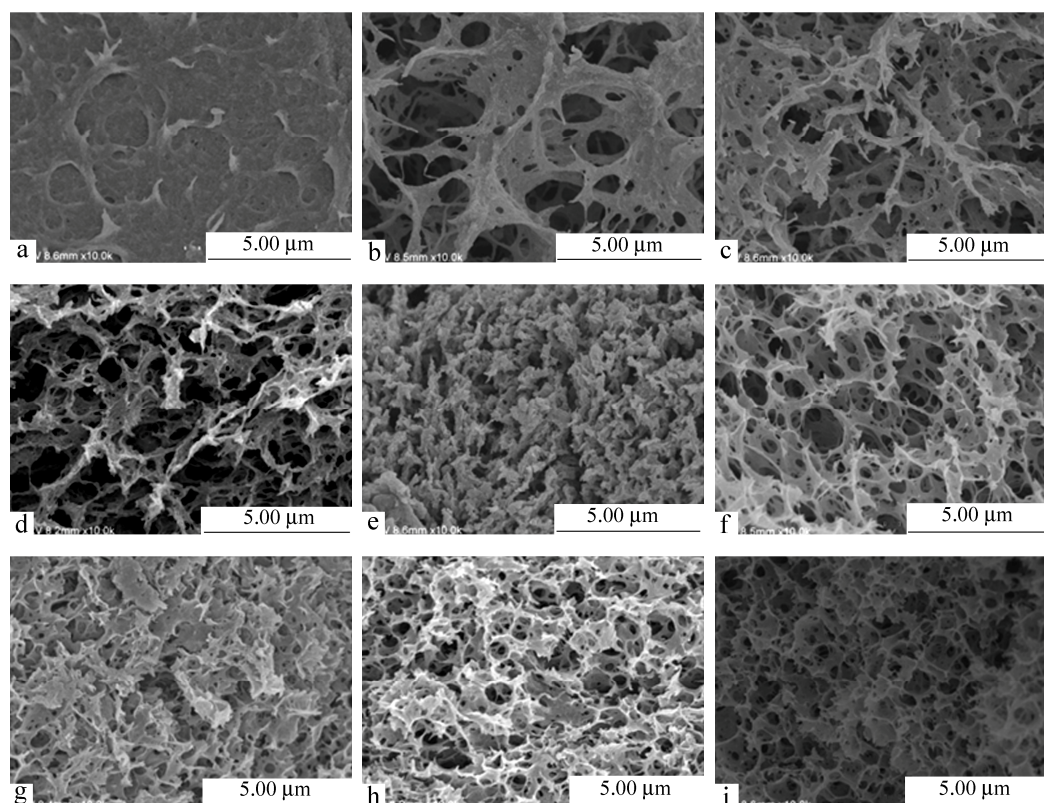
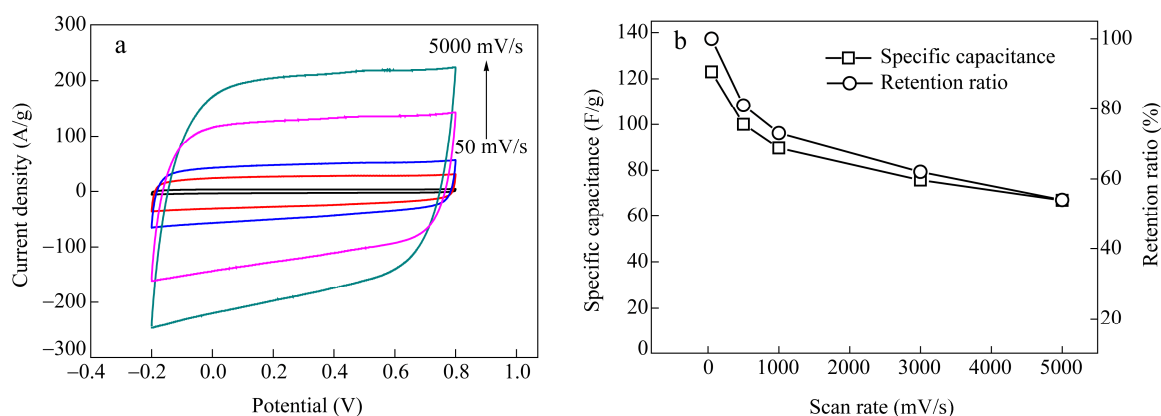


Fig. 1 SEM images of the PEDOT-PSS hydrogels prepared with (a) 0.06 mol/L EDOT and 0.1 mol/L PSS, (b) 0.18 mol/L EDOT and 0.1 mol/L PSS, (c) 0.3 mol/L EDOT and 0.1 mol/L PSS, (d) 0.48 mol/L EDOT and 0.1 mol/L PSS, (e) 0.6 mol/L EDOT and 0.1 mol/L PSS, (f) 0.48 mol/L EDOT and 0.3 mol/L PSS, (g) 0.48 mol/L EDOT and 0.5 mol/L PSS, (h) 0.48 mol/L EDOT and 0.8 mol/L PSS, (i) 0.48 mol/L EDOT and 1.0 mol/L PSS (Samples are freeze-dried before SEM measurements.)



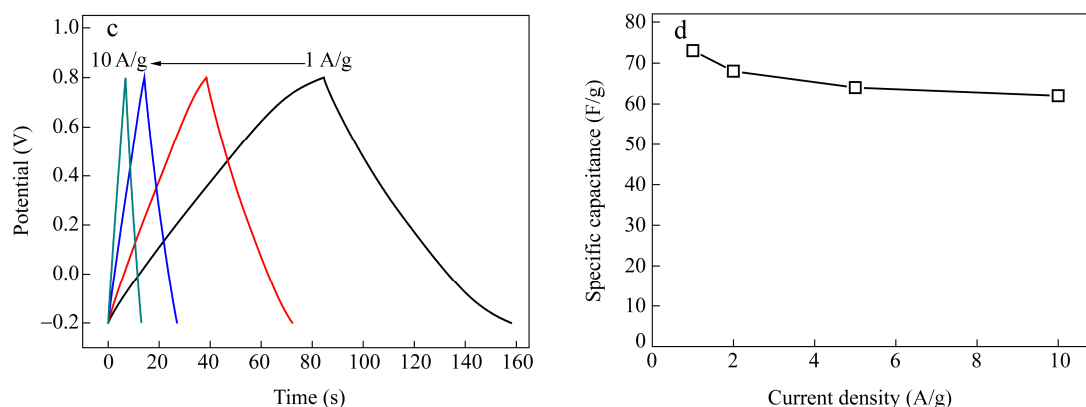


Fig. 2 (a) CV curves of the PEDOT-PSS hydrogel at the scan rates of 50, 500, 1000, 3000 and 5000 mV/s; (b) Plots of the specific capacitance and the retention ratio versus the scan rate; (c) Galvanostatic charge/discharge profiles at the current densities of 1, 2, 5, 10 A/g; (d) Summary plot of the specific capacitance values versus the current density

The hydrogel is synthesized with 0.48 mol/L EDOT and 0.1 mol/L PSS. The measurements are carried out in 1 mol/L NaNO_3 aqueous solution.

The high rate capability of the PEDOT-PSS hydrogels is also testified by the galvanostatic charge/discharge measurements. As shown in Fig. 2(c), the curves are symmetric, indicating a high charge/discharge efficiency^[17]. When the current density increases from 1 A/g to 10 A/g, the specific capacitance only decreases from 73 F/g to 62 F/g (Fig. 2d). The capacitance retention is as high as ~85%, also suggesting the excellent rate capability.

The influence of the reagent concentrations on the electrochemical behaviors of the resulting PEDOT-PSS hydrogels has been investigated systematically. As shown in Fig. 3(a), when the PSS concentration is kept to be 0.1 mol/L and the concentration of EDOT is enhanced from 0.06 mol/L to 0.6 mol/L, the initial specific capacitance, measured at the scan rate of 50 mV/s, increases first and then dramatically decreases to low values, while the tendency of the rate capability, determined from the data measured at the scan rate of 5000 mV/s, is in the opposite. The largest initial specific capacitance and lowest capacitance retention appear at the point with 0.48 mol/L EDOT, displaying the specific capacitance of 123 F/g and the capacitance retention of 56%.

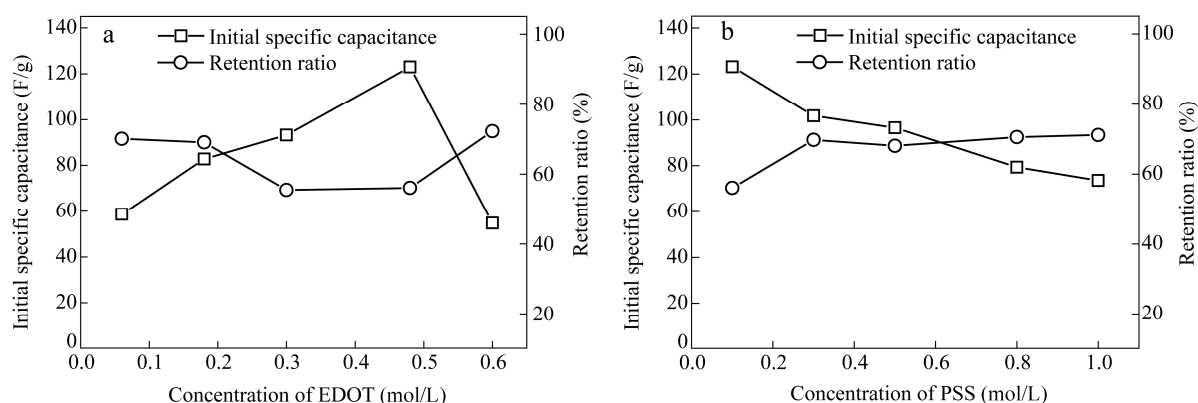


Fig. 3 Plots of the initial specific capacitance and retention ratio of the PEDOT-PSS hydrogels: (a) Samples prepared with 0.1 mol/L PSS and different EDOT concentrations; (b) Samples prepared with 0.48 mol/L EDOT and different PSS concentrations

The initial specific capacitance is measured at the scan rate of 50 mV/s. The retention ratio is determined from the data measured at the scan rate of 5000 mV/s. The measurements are carried out using the CV method in 1 mol/L NaNO_3 aqueous solution.

Such results may be explained by the morphological transformation of the materials. As shown in Fig. 1(d), compared with others, the PEDOT-PSS hydrogel synthesized with 0.48 mol/L EDOT and 0.1 mol/L PSS is rich in inter-connected open macropores and has a bigger surface area, which is also detected by the BET measurements (Table 1), resulting in a higher specific capacitance at low scan rates^[35]. However, excessive macropores may disturb the carrier transport and hence generate the relatively poor rate capability^[36]. For the sample prepared with 0.6 mol/L EDOT, the hydrogel displays an electrical conductivity of 4.6×10^{-3} S/cm, much lower than that of the sample prepared with 0.48 mol/L EDOT (9.7×10^{-3} S/cm). In this case, it is deduced that the charge storage process only takes place on the surface layer of the hydrogel, resulting in relatively low initial specific capacitance and high retention ratio.

On the other hand, if the EDOT concentration is kept at 0.48 mol/L and the PSS concentration is varied from 0.1 mol/L to 1.0 mol/L, the specific capacitance of PEDOT-PSS hydrogels monotonously decreases from 123 F/g to 71 F/g, while the capacitance retention increases from 56% to 71% and then approximately keeps constant (Fig. 3b). These results imply that the existence of more PSS in the PEDOT-PSS hydrogels is disadvantageous to the specific capacitance but beneficial to the rate capability. The polyelectrolyte (PSS) is expected to be capable of improving the electrochemical stability of the related electrodes in supercapacitors, leading to a higher rate capability^[37]. In such a case, the reduction of the specific capacitance of the PEDOT-PSS hydrogels might be attributed to the decreasing surface area^[35], as shown in Table 1, as well as the lower [PEDOT]/[PSS] ratio, which results in less faradaic pseudocapacitance^[17].

Table 1. BET surface areas and average pore diameters of the PEDOT-PSS hydrogels

Reagent concentration (mol/L)		Surface area (m ² /g)	Average pore diameter (nm)
EDOT	PSS		
0.06	0.1	2.88	6.7
0.18	0.1	27.8	24.7
0.30	0.1	29.5	25.6
0.48	0.1	63.0	27.1
0.6	0.1	63.9	21.3
0.48	0.3	43.4	16.0
0.48	0.5	39.0	16.2
0.48	0.8	29.0	15.6
0.48	1.0	33.4	16.8

Figure 4(a) presents the Nyquist plot of the PEDOT-PSS hydrogel synthesized with 0.48 mol/L EDOT and 0.1 mol/L PSS. At the low frequency, the impedance plots exhibit a slightly tilted vertical line, which is a characteristic feature of the ideal capacitance behavior^[38]. At the high frequency, there is no semicircle, indicating that the interfacial charge-transfer resistance is significantly low, which may lead to a high rate capability^[39]. The cycle-life test of the PEDOT-PSS hydrogel as the electrode material is performed at a constant current density of 1 A/g in the potential range between -0.2 V and 0.8 V (Fig. 4b). The hydrogel electrode retains 70% of the initial capacitance during 1500 charging-discharging cycles and the value remains higher than 60% after 3000 cycles, which is outstanding among the CP-based electrode materials^[4, 40]. The good cycling performance may be resulted from the synergetic effect of the rigid PEDOT and the soft PSS, which could bring out improved mechanical properties for the materials^[29], enabling the electrode to accommodate the swelling and shrinking movements of the polymer during the doping/dedoping (charging/discharging) process^[24].

As a comparison, a sample of PEDOT-PSS powder is prepared using the same method as for the PEDOT-PSS hydrogel synthesized with 0.48 mol/L EDOT and 0.1 mol/L PSS, and the only difference is that the powder is produced under mechanical stirring at a rate of 300 r/min. Its SEM image presents that the morphology of the sample is mainly irregular particles (Fig. 5a), which differs distinctly from that of the hydrogel (Fig. 1d). According to BET tests, the surface area and average pore diameter of as-prepared powder are 1.94 m²/g and 5.3 nm, respectively, much lower than those of the hydrogels (Table 1). The CV curves of the PEDOT-PSS powder turn into fusiformis and only 25% of the capacitance retains when the scan rate increases from 50 mV/s

to 5000 mV/s (Fig. 5b). Again, the three-dimensional network microstructure of the hydrogels is proved to be significant to the improved capacitance performance. Concretely speaking, the porous structure of the hydrogels may promote the diffusion of counter-ions into/out of the polymer (the doping/dedoping processes) at the interface of the electrode and the electrolyte solution, leading to the high capacitance at the fast scan rates^[41]. Interestingly, similar to the PEDOT-PSS hydrogels, the powder sample also presents good charging-discharging cycle stability. With a current density of 1 A/g, PEDOT-PSS powder maintains 68% of the initial capacitance after 1500 cycles, possibly because the synergetic effect between the PEDOT and PSS components may also exist and take functions in the powder sample.

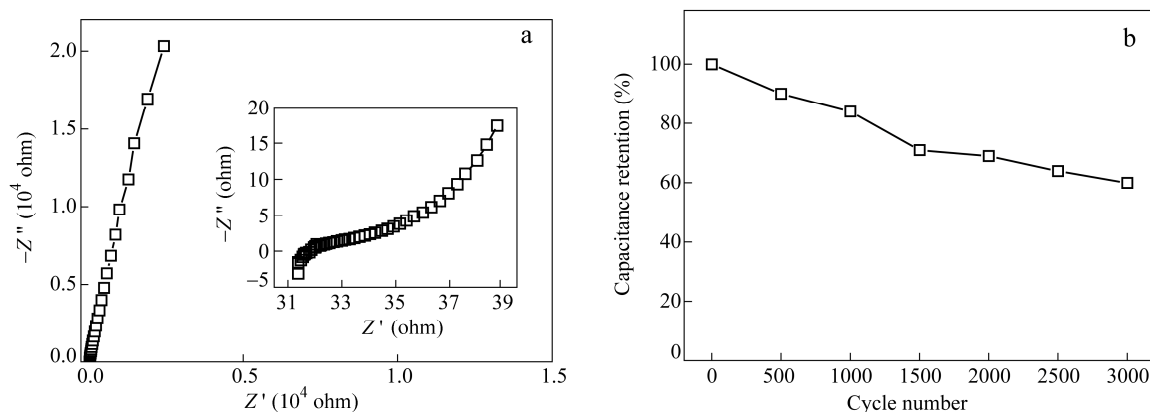


Fig. 4 (a) Nyquist plot of the PEDOT-PSS hydrogel (The inset is the detail with enlarged scale.); (b) Cycle stability at the current density of 1 A/g in the potential range between -0.2 V and 0.8 V (The hydrogel is synthesized with 0.48 mol/L EDOT and 0.1 mol/L PSS.)

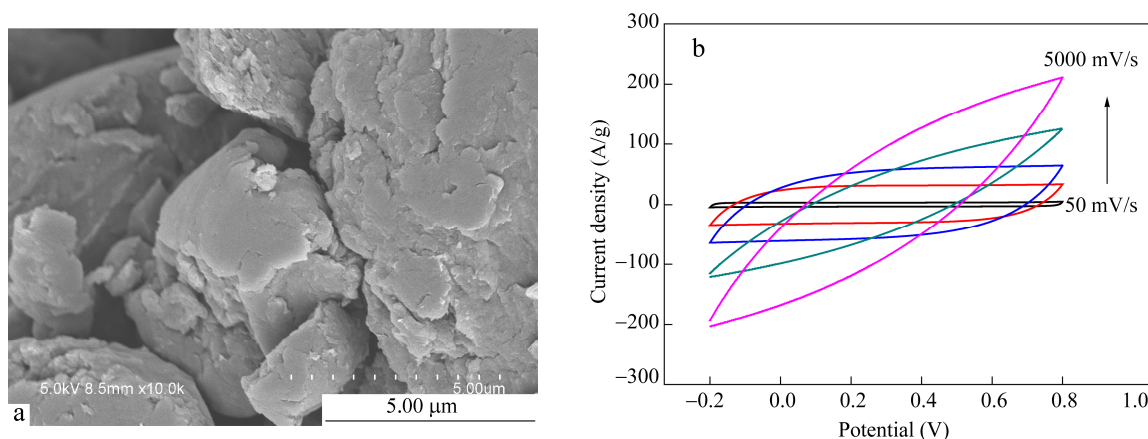


Fig. 5 (a) SEM image of the PEDOT-PSS power; (b) CV curves of the PEDOT-PSS power at different scan rates of 50, 500, 1000, 3000 and 5000 mV/s (The sample is synthesized with 0.48 mol/L EDOT and 0.1 mol/L PSS under mechanical stirring.)

To further enhance the specific capacitance of the materials, PAN, which is a kind of conducting polymer possessing much higher theoretical specific capacitance than PEDOT^[42], is compounded with the PEDOT-PSS hydrogels through an interfacial polymerization process^[30]. From the SEM image (Fig. 6a), PAN granules with the size of 200–800 nm are successfully combined with the three-dimensional network of the PEDOT-PSS hydrogel matrix (Fig. 1c). Although the network structure can not be directly observed, it seems from the SEM image with a higher magnification (Fig. 6b) that there are abundant small pores in the formed granules. According to the BET tests, after the introduction of PAN, the surface area of the hydrogel decreases from

29.5 m^2/g to 10.0 m^2/g , while the average pore diameter decreases from 25.6 nm to 17.2 nm. In the electrochemical processes, the pathway for the diffusion of the ions is believed to be unobstructed for the PEDOT-PSS/PAn composite hydrogel, despite PAn fills the space of the PEDOT-PSS matrix.

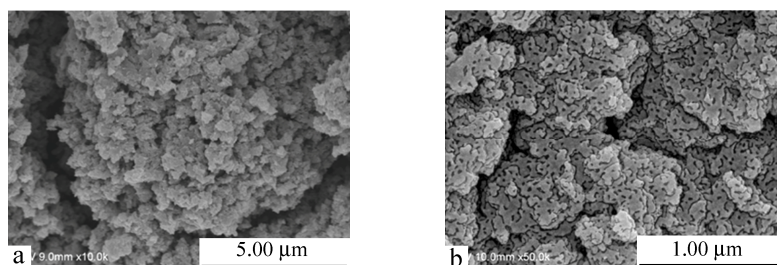


Fig. 6 (a) SEM image of the PEDOT-PSS/PAn composite hydrogel and (b) SEM image with a higher magnification

PEDOT-PSS hydrogel matrix is produced with 0.3 mol/L EDOT and 0.1 mol/L PSS. The composite hydrogel is prepared with 0.2 mol/L and 0.15 mol/L An *via* the interfacial polymerization process.

The preparation process of the PEDOT-PSS/PAn composite hydrogels includes the fabrication of the PEDOT-PSS hydrogel matrix and sequentially the interfacial polymerization of An. The loading amount of the PAn component can be easily controlled in the interfacial polymerization simply by modulating the concentrations of APS in the aqueous phase and An in the organic phase. On the basis of the systematical investigation of the samples synthesized with different reagent concentrations, it is found that the composite hydrogel prepared with 0.3 mol/L EDOT, 0.1 mol/L PSS, 0.2 mol/L APS and 0.15 mol/L An, which possesses a PAn content of 15.2 wt% in its dry weight, has the optimal electrochemical behaviors. In the CV curves of the PEDOT-PSS/PAn composite hydrogel (Fig. 7a), redox peaks at the potential of 0.5–0.6 V are detected, which is ascribed to the faradaic transformation of emeraldine-pernigranline of the PAn component and indicates the presence of the redox capacitance in the composite material^[43]. Moreover, the composite hydrogel exhibits a larger inner integrated area than the PEDOT-PSS hydrogel, implying the higher energy density of the composite^[44]. At the scan rate of 50 mV/s, the specific capacitance of the PEDOT-PSS hydrogel is calculated to be 95 F/g, while the value for the corresponding PEDOT-PSS/PAn composite hydrogel is 258 F/g. When the scan rate increases to 5000 mV/s, the composite hydrogel still presents a specific capacitance as high as 160 F/g, and the CV curve displays a rectangular shape (Fig. 7b), suggesting excellent rate capability of the material. Additionally, for the composite hydrogel, the charge/discharge curves are symmetric, and the specific capacitance only decreases from 137 F/g to 129 F/g with the growth of the current density from 1 A/g to 10 A/g (Fig. 7c). In the impedance spectrum, the plots present a slightly tilted vertical line at low frequencies (Fig. 7d). All of these electrochemical measurements represent the ideal capacitance performances of the composite materials^[17, 38]. The combination of PAn not only provides the hydrogel with redox capacitance, but also enhances the electrical conductivity of the material (from 5×10^{-3} S/cm to 7×10^{-2} S/cm), which jointly improves the capacitance properties of the materials. Another possible reason for the improvements is the modification of the pore structure at the nanometer scales^[34], which has been testified by the BET measurements. After the combination of PAn, the capacitance retention during 1500 charging-discharging cycles slightly decreases to 64%, compared to the value of 70% for the PEDOT-PSS matrix hydrogel. The cycle stability of the PEDOT-PSS/PAn hydrogel remains at a high level, indicating that the composite hydrogel possesses good mechanical toughness to sustain the swelling and shrinking movements in the charging/discharging process, which results from the synergetic effect between the soft and rigid components in the materials^[29]. In the present case, the soft component is PSS, while the rigid components contain not only PEDOT but also PAn.

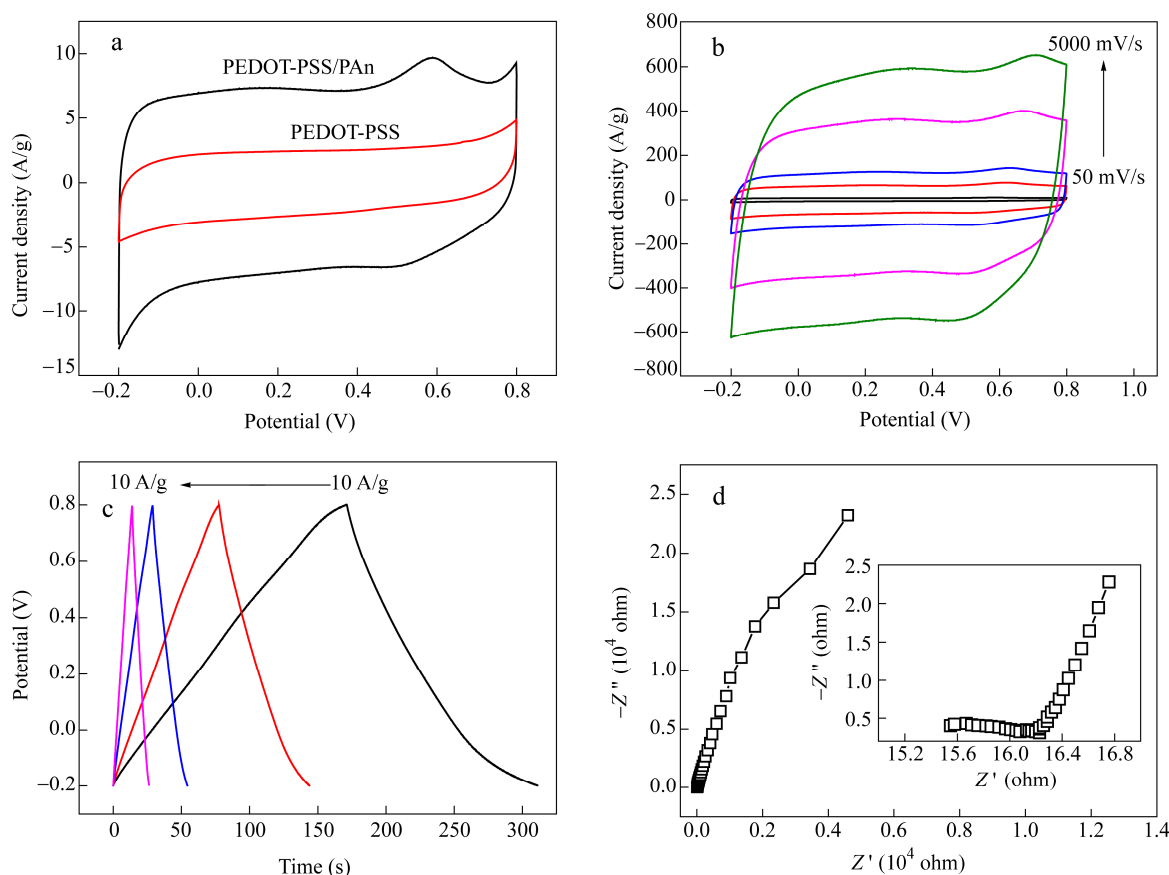


Fig. 7 (a) CV curves of the PEDOT-PSS hydrogel matrix and the corresponding PEDOT-PSS/PAn composite hydrogel at the scan rate of 50 mV/s; (b) CV curves of the PEDOT-PSS/PAn composite hydrogel at the scan rates of 50, 500, 1000, 3000 and 5000 mV/s; (c) Galvanostatic charge/discharge profiles of the composite hydrogel at the current densities of 1, 2, 5 and 10 A/g; (d) Nyquist plot of the composite hydrogel PEDOT-PSS hydrogel matrix is produced with 0.3 mol/L EDOT and 0.1 mol/L PSS.

The composite hydrogel is prepared with 0.2 mol/L and 0.15 mol/L An *via* the interfacial polymerization process.

CONCLUSIONS

In summary, the capacitance properties of the PEDOT-PSS supramolecular hydrogels have been reported for the first time. The CV plots of the hydrogels display highly rectangular curves at the scan rate as high as 5000 mV/s, implying remarkable rate capability among the conducting polymer materials. The excellent electrochemical behaviors are attributed to the porous microstructures, which promote the ion diffusion between the electrode material and electrolyte. Moreover, the PEDOT-PSS hydrogels also show good cycle stability because of the synergetic effect of the rigid PEDOT and the soft PSS. After the combination of PAn, the PEDOT-PSS/PAn composite hydrogels exhibit much higher specific capacitance and outstanding rate capability at the same time. Research is now under way to produce composite materials of conducting hydrogels and carbon materials to further enhance the capacitance performances.

REFERENCES

- 1 Wang, X.F., Lu, X.H., Liu, B., Chen, D., Tong, Y.X. and Shen, G.Z., *Adv. Mater.*, 2014, 26: 4763
- 2 Peng, X., Peng, L.L., Wu, C.Z. and Xie, Y., *Chem. Soc. Rev.*, 2014, 43: 3303

- 3 Cheng, J.P., Zhang, J. and Liu, F., *RSC Adv.*, 2014, 4: 38893
- 4 Snook, G.A., Kao, P. and Best, A.S., *J. Power Sources*, 2011, 196: 1
- 5 Wang, K., Wu, H.P., Meng, T.N. and Wei, Z.X., *Small*, 2014, 10: 14
- 6 Zhang, H.M. and Wang, X.H., *Chinese J. Polym. Sci.*, 2013, 31(6): 853
- 7 Iranagh, S.A., Eskandarian, L. and Mohammadi, R., *Synth. Met.*, 2013, 172: 49
- 8 Holze, R. and Wu, Y.P., *Electrochim. Acta*, 2014, 122: 93
- 9 Cho, S.I. and Lee, S.B., *Acc. Chem. Res.*, 2008, 41: 699
- 10 Chiolerio, A., Bocchini, S. and Porro, S., *Adv. Funct. Mater.* 2014, 24: 3375
- 11 Patil, D.S., Pawar, S.A., Devan, R.S., Mali, S.S., Gang, M.G., Ma, Y.R., Hong, C.K., Kim, J.H. and Patil, P.S., *J. Electroanal. Chem.*, 2014, 724: 21
- 12 Shi, Y., Pan, L.J., Liu, B.R., Wang, Y.Q., Cui, Y., Bao, Z.N. and Yu, G.H., *J. Mater. Chem. A*, 2014, 2: 6086
- 13 Yu, P.P., Li, Y.Z., Zhao, X., Wu, L.H. and Zhang, Q.H., *Langmuir*, 2014, 30: 5306
- 14 Fan, L.S., Zhang, N.Q. and Sun, K.N., *Chem. Commun.*, 2014, 6789
- 15 Wu, L.P., Zhang, L., Lu, L.M., Duan, X.M., Xu, J.K. and Nie, T., *Chinese J. Polym. Sci.*, 2014, 32(8): 1019
- 16 Jiang, X., Li, B.C., Song, Y.H., Gao, Z.L. and Nan, B.B., *Chinese J. Polym. Sci.*, 2014, 32(1): 35
- 17 Liu, R., Cho, S.I. and Lee, S.B., *Nanotechnology*, 2008, 19: 215710
- 18 Tian, Y.Y., Cong, S., Su, W.M., Chen, H.Y., Li, Q.W., Geng, F.X. and Zhao, Z.G., *Nano Lett.*, 2014, 14: 2150
- 19 Meng, Y.N., Wang, K., Zhang, Y.J. and Wei, Z.X., *Adv. Mater.*, 2013, 25: 6985
- 20 Wang, J., Wu, Z.C., Yin, H.B., Li, W. and Jiang, Y., *RSC Adv.*, 2014, 4: 56926
- 21 Gao, L.L., Mao, X.H., Zhu, H., Xiao, W., Gan, F.X. and Wang, D.H., *Electrochim. Acta*, 2014, 136: 97
- 22 Rolison, D.R., Long, R.W., Lytle, J.C., Fischer, A.E., Rhodes, C.P., McEvoy, T.M., Bourga, M.E. and Lubers, A.M., *Chem. Soc. Rev.*, 2009, 38: 226
- 23 Xu, Y., Sui, Z., Xu, B., Duan, H. and Zhang, X., *J. Mater. Chem.*, 2012, 22: 8579
- 24 Pan, L., Yu, G., Zhai, D., Lee, H.R., Zhao, W., Liu, N., Wang, H., Tee, B.C.K., Shi, Y., Cui, Y. and Bao, Z., *P. Natl. Acad. Sci. USA*, 2012, 109: 9287
- 25 Dai, T.Y., Jiang, X.J., Hua, S.H., Wang, X.S. and Lu, Y., *Chem. Commun.*, 2008, 4279
- 26 Siddhanta, S.K. and Gangopadhyay, R., *Polymer*, 2005, 46: 2993
- 27 Dai, T.Y., Qing, X.T., Lu, Y. and Xia, Y.Y., *Polymer*, 2009, 50: 5236
- 28 Dai, T.Y., Qing, X.T., Zhou, H., Shen, C., Wang, J. and Lu, Y., *Synth. Met.*, 2010, 160: 791
- 29 Dai, T.Y., Shi, Z.Q., Shen, C., Wang, J. and Lu, Y., *Synth. Met.*, 2010, 160: 1101
- 30 Dai, T.Y., Qing, X.T., Wang, J., Shen, C. and Lu, Y., *Compos. Sci. Technol.*, 2010, 70: 498
- 31 Reddy, A.L.M., Shaijumon, M.M., Gowda, S.R. and Ajayan, P.M., *Nano Lett.*, 2009, 9: 1002
- 32 Dai, T.Y. and Jia, Y.J., *Polymer*, 2011, 52: 2550
- 33 Campbell, A.I., Anderson, V.J., Duijneveldt, J.S. and Bartlett, P., *Phys. Rev. Lett.*, 2005, 94: 208301
- 34 Jia, Y.J., Jiang, J.C., Sun, K. and Dai, T.Y., *Electrochim. Acta*, 2012, 71: 213
- 35 Kelly, T.L., Yano, K. and Wolf, M.O., *ACS Appl. Mater. Inter.*, 2009, 1: 2536
- 36 Zheng, C., Qi, L., Yoshio, M. and Wang, H., *J. Power Sources*, 2010, 195: 4406
- 37 Kim, B.C., Ko, J.M. and Wallace, G.G., *J. Power Sources*, 2008, 177: 665
- 38 Li, L., Liu, E., Li, J., Yang, Y., Shen, H., Huang, Z. and Li, W., *J. Power Sources*, 2010, 195: 1516
- 39 Han, Y., Ding, B., Tong, H. and Zhang, X., *J. Appl. Polym. Sci.*, 2011, 121: 892
- 40 Li, W., Chen, J., Zhao, J., Zhang, J. and Zhu, J., *Mater. Lett.*, 2005, 59: 800
- 41 Wang, J., Xu, Y., Sun, X., Li, X. and Du, X., *J. Solid State Electrochem.*, 2008, 12: 947
- 42 Ryu, K.S., Kim, K.M., Park, N.G., Park, Y.J. and Chang, S.H., *J. Power Sources*, 2002, 103: 305
- 43 Zhang, L.J. and Wan, M.X., *Nanotechnology*, 2002, 13: 750
- 44 Chen, L., Yuan, C.Z., Dou, H., Gao, B., Chen, S.Y. and Zhang, X.G., *Electrochim. Acta*, 2009, 54: 2335