Improving the volumetric specific capacitance of flexible polyaniline electrode: solution casting method and effect of reduced graphene oxide sheets

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ABSTRACT High volumetric specific capacitance is essential for flexible supercapacitors. In this paper, a flexible composite electrode with ultrahigh volumetric specific capacitance and good rate performance is designed and prepared. The film electrode is composed of non-porous compact polyaniline as the matrix and a small amount of reduced graphene oxide sheets as the conductive filler. The film is prepared by a newly developed solution casting method, where the casting solution is obtained by self-assembly of polyaniline and graphene oxide in a blended solution. A systematical investigation on the effect of reduced graphene oxide sheets reveals that they serve as both the conductive filler and the diffusion barrier. With the optimized reduced graphene oxide content, a large volumetric specific capacitance of 1354 F cm^{-3} at 2.4 A cm^{-3} is achieved, and good rate performance is also obtained because of the good ionic conductivity of polyaniline. This work provides a high-performance electrode for flexible supercapacitors, and the solution casting method is also valuable in fabricating other organic electrode materials.

Keywords: conducting polymer, graphene, compact film, conductivity, diffusion barrier

INTRODUCTION

Flexible energy storage devices are highly demanded with the rapid development of wearable electronic devices [1–4]. Flexible supercapacitors are an important group of flexible energy storage devices due to their high rate performance and long cycling life [5–7]. Considering the practical application, volumetric specific capacitance is essential for flexible supercapacitors [8,9]. Generally, the volumetric specific capacitance of an electrode material can be calculated from its gravimetric specific capacitance

and apparent density. For an electrode material with a certain composition, the main method of promoting its volumetric specific capacitance is to increase the apparent density, for example, by reducing the porosity. However, the interconnected pores inside the electrode serve as a “high way” for electrolyte diffusion and reducing the porosity of the electrode usually leads to a decrease in the rate performance. Therefore, it requires accurate control of the porosity and microstructure of the electrode materials to achieve a high volumetric specific capacitance at large current density.

At present, carbon materials, conducting polymers and transition metal oxides are common electrode materials in supercapacitors [10–12]. Among these materials, polyaniline/reduced graphene oxide (PANI/RGO) composites have attracted considerable attention because PANI provides large pseudocapacitance *via* redox reactions and RGO sheets form conducting path for electron transport [13–16]. More importantly, as a hydrophilic polymer, PANI is highly solvated in the electrolyte and thus has large ion conductivity, which allows the PANI-based electrode to possibly maintain a high rate performance even at low porosity [17–20]. Conventional methods of fabricating the PANI-based film electrode are mainly based on *in-situ* polymerization of aniline on a flexible matrix. For example, *in-situ* polymerization in hydrogel yields flexible and porous PANI composite hydrogel [21,22]. However, these methods are designed for depositing PANI into a porous matrix or onto the surface of the substrate. They are not suitable for preparing a high-density PANI/RGO composite with low porosity and high volumetric specific capacitance. Also, by the *in-situ* polymerization, it is difficult to control the compo-

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sition of the prepared PANI/RGO electrode. Obviously, a novel method is desirable to develop PANI/RGO electrode materials with high volumetric specific capacitance.

In this paper, we fabricated flexible PANI/RGO composite films with an ultrahigh volumetric specific capacitance, by using a newly developed solution casting method. Stable solutions of PANI/GO are obtained by self-assembling of PANI and graphene oxide (GO) in a blended solvent of *N*-methyl-2-pyrrolidone (NMP) and water, and they are cast into large-area, uniform and non-porous PANI/RGO films with high apparent density. This method also allows us to accurately control the content of RGO over a wide range (0–100%) and systematically study the effect of RGO on the capacitive performance. Our results confirm that besides as the conductive filler to enhance the mechanical strength, RGO sheets also play a role of diffusion barriers to the electrolyte. Systematical investigation finds that 10 wt.% RGO in composite films leads to the highest volumetric specific capacitance of 1354 F cm^{-3} and good rate performance.

EXPERIMENTAL SECTION

Materials

Natural graphite powder (325 mesh) was bought from Qingdao Huatai Lubricant Sealing S&T Co. Ltd. Potassium permanganate (AR), sodium nitrate (AR), hydrogen peroxide (30%), sulfuric acid (H_2SO_4 , 98%), hydrochloric acid (HCl, AR), aqueous ammonia (28%), and ammonium persulfate (AR) were purchased from XiLong Scientific Co., Ltd. Aniline and 1-methyl-2-pyrrolidinone (AR) were the products of Aladdin Industry Co., Ltd. All the chemicals were used as received without further purification. GO was prepared by oxidation of natural graphite powder according to a modified Hummers' method [23]. PANI was synthesized by chemical oxidation polymerization [24], and then converted into the emeraldine base state by ammonia treatment to increase its solubility in NMP. The dried PANI powder was dissolved in NMP by agitation at room temperature, and the obtained solution was filtered, giving a PANI stock solution of $\sim 37.1 \text{ mg mL}^{-1}$.

Preparation of PANI/RGO composite films

PG_x denotes a PANI/RGO composite film with x representing the weight percentage of GO over PANI+GO in the sample preparation. In order to prepare PG_{30} , 0.566 mL of PANI stock solution (37.1 mg mL^{-1}) was diluted by adding 28.375 mL of NMP, and then 1.059 mL of GO aqueous dispersion (9.4 mg mL^{-1}) was added into

the above PANI solution under violent agitation. The produced homogeneously mixed dispersion was poured into a ceramic or poly(tetrafluoroethylene) (PTFE) mold, and dried at 75°C in air for 8 h, yielding a free-standing PANI/GO film. The film was chemically reduced by soaking in hydroiodic acid (45%) for 1 h and repeatedly rinsing with ethanol and water to remove residual iodine. After being dried at room temperature, PG_{30} film was prepared. To prepare other PANI/RGO films, the volume of PANI solution and GO dispersion was adjusted to the corresponding values. The RGO film was prepared following the same procedure, except that only GO aqueous solution was used in the casting. Pure PANI film was obtained by directly drying the PANI solution in NMP at 75°C .

Fabrication of flexible solid-state device

The poly(vinyl alcohol) (PVA)/ H_3PO_4 gel electrolyte was prepared as follows: 6 g of PVA powder was added in 60 mL of deionized water and heated to 95°C under agitation, until the solution became clear. After the solution cooled down, 3.2 mL of phosphoric acid was added. The mixed solution was spread onto a culture dish and dried at 50°C for 5 h to form a PVA/ H_3PO_4 gel film [25]. The PVA/ H_2SO_4 gel electrolyte was prepared by dissolving 6 g of PVA powder and 3.28 mL of H_2SO_4 in 60 mL of deionized water at 95°C [26]. The PG_{10} film was cut into two rectangular pieces ($1 \text{ cm} \times 1.5 \text{ cm}$) and put on the gold-coated polyimide substrate. The PVA/ H_2SO_4 gel electrolyte aqueous solution was slowly dropped onto the PG_{10} films and dried in the ambient environment for 12 h. Then the two electrodes were pressed together with PVA/ H_3PO_4 gel electrolyte film as a separating membrane between two electrodes.

Electrochemical measurements

The electrochemical performance of the PANI/RGO composite film was tested in a three-electrode system. $1 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ was used as the electrolyte and Pt foil was used as a current collector. The counter electrode was an RGO hydrogel [27] and the reference electrode was an saturated calomel electrode (SCE). The PANI/RGO composite film was cut into a $1.5 \text{ cm} \times 1.5 \text{ cm}$ square as the working electrode. The film was immersed in the electrolyte solution for 12 h before the test to allow the complete infiltration of electrolyte into the electrode materials. The electrochemical impedance spectroscopy (EIS) was recorded under their open circuit potential. The specific capacitance of the film was calculated by galvanostatic charge discharge (GCD) tests using the equation:

$$C = I \Delta t / K(\Delta U - IR), \quad (1)$$

where I is the constant discharge current, t is the discharging time, K is the mass (for gravimetric specific capacitance) or the volume (for volumetric specific capacitance) of the composite film, U is the potential range of the working electrode (from 0 to 0.8 V), and IR is the voltage drop upon discharging.

The specific capacitance of the film in a flexible device was calculated by GCD tests using the equation:

$$C = I \Delta t / K(U_M - IR), \quad (2)$$

where K is the total mass (for gravimetric specific capacitance) or the volume (for volumetric specific capacitance) of two electrodes, U_M is the highest working voltage of the device.

The volumetric energy density of the electrode material in the flexible device was determined by the following equation:

$$E = I / V \int_{\text{discharge}} U dt, \quad (3)$$

where V is the total volume of the two electrodes, U is the voltage of the device. The volume of the film electrode was calculated from the area and the thickness, which was determined by averaging the thicknesses measured from the cross-sectional SEM image at different positions. The volumetric power density (P) was calculated by:

$$P = E / \Delta t, \quad (4)$$

where t is the corresponding discharge time.

Characterization

All the electrochemical measurements were performed on a 660E electrochemical workstation (CHI, China). The morphology of the composite films was observed on a SU-70 field emission scanning electron microscope (SEM, Hitachi, Japan) at 10 kV. All the samples were sputtered with an Au layer for SEM observation. Raman spectra were collected by using XPLORA Raman spectrometer (Horiba, Japan) with a 532-nm laser as a light source. The X-ray diffraction (XRD) was measured on a D8 X-ray diffractometer (Bruker, USA) with Cu K α source. X-ray photoelectron spectroscopy (XPS) was collected on the Escalab 250Xi X-ray photoelectron spectroscopy (Thermo Fisher, USA) using monochromated X-rays from an Al K α source. The conductivity was tested on a dual-electric test four-probe conductivity meter (Guangzhou four-probe electronic, China).

RESULTS AND DISCUSSION

Fig. 1a shows the solution casting method, where a

blended solution of PANI/GO in NMP/water was obtained by mixing the solution of PANI in NMP and the GO aqueous dispersion. GO is a two-dimensional (2D) surfactant and soluble in both water and NMP. PANI chains can self-assemble onto the GO sheets *via* π - π stacking and hydrogen bond. Meanwhile, PANI in the emeraldine base state is partially doped by the carboxyl groups on GO, and forms electrostatic interaction with GO. Therefore, PANI and GO were dispersed homogeneously in the mixed solvent and the solution homogeneity was stable over several weeks (Fig. S1). The blend solution was cast and dried on a PTFE or alumina ceramics substrate, producing a uniform PANI/GO film, which was then reduced by hydroiodic acid to give a pristine PANI/RGO film. During the reduction process, PANI in the emeraldine base was also doped by hydroiodic acid, and thereby the final product is emeraldine salt/RGO composite film.

To optimize the capacitance performance of PANI/RGO films, the content of GO in the composite was controlled from 0 to 100 wt.%, and its effect on the properties of PANI/RGO composite films was investigated systematically. With the novel casting method, it is easy to fabricate large-area PANI/RGO film as long as a large casting mold is available. Here a 900-cm² PG₃₀ film is demonstrated in Fig. 1b, and the large-area film is expected to provide more possibilities in the practical applications.

Fig. 1c–j and Figs S2–S4 are the SEM images of the as-prepared PANI/GO and PANI/RGO films. The corresponding PANI/GO and PANI/RGO films have similar morphology, and thus the hydroiodic acid does not change the morphology and structure of the films. All the PANI/RGO films have a compact and smooth surface. Films with high RGO contents (Fig. 1c, d) have wrinkles on their surfaces, which is the characteristic of RGO. As the RGO content decreases (Fig. 1e, f), the wrinkles on the surface become less, and only small grains appear, which are the typical surface feature of a polymer film. In the cross-sectional view (Fig. 1g–j), the lamellar structure was observed for all the films, even when the PANI content was as high as 90 wt.%. The similar lamellar structures were also found in other RGO/polymer composite films [28], attributed to the lyotropic liquid crystal property of GO sheets. These lamellar structures can efficiently enhance the mechanical strength of the composite film [29–31]. No PANI aggregates or/and pores were detected in the SEM observations. The nitrogen, carbon, and oxygen element signals were homogeneous in the energy-dispersive X-ray spectroscopy (EDS) mapping of

Figure 1 Preparation and morphology of the PANI/RGO composite films. (a) Schematic illustration of the preparation procedure (HI represents hydroiodic acid). (b) Photograph of a 900-cm² PANI/RGO film. (c–f) SEM images of the top surface view of RGO (c), PG₉₀ (d), PG₅₀ (e), and PG₁₀ (f). (g–j) SEM images of the cross-sectional view of RGO (g), PG₉₀ (h), PG₅₀ (i), and PG₁₀ (j). (k–n) EDS mapping of C (l), N (m), and O (n) elements on the cross-section of PG₅₀.

the cross-section of the film (Fig. 1k–n), suggesting a uniform distribution of PANI and RGO in the film. It is difficult for conventional *in-situ* polymerization method to produce a uniform and free-stranding PANI/RGO composite film with very high PANI content, while the novel casting method can easily achieve the high uniformity, which improves the electrochemical energy storage performance.

Fig. 2a shows the PG₃₀ survey XPS spectrum, indicating the iodine 3d_{5/2} peak at 617 eV and iodine 3d_{3/2} at 629 eV [32]. This iodine can be attributed to the iodide ions, which are the counter ions of the doped PANI. The deconvolution of PG₃₀ C 1s lines (Fig. 2b) show the bonds of

C–C/C=C (284.6 eV), C–O (285.2 eV), C–O (286.1 eV), C=O (287.3 eV), and O–C=O (289.9 eV) [33], where the intensity of C–O and C=O peaks from the PG₃₀ film is much lower than that in the corresponding PANI/GO film, indicating GO is successfully reduced by hydroiodic acid. The structure of the composite film was further investigated by XRD. As shown in Fig. 2c, RGO film has a broad diffraction peak around 24.5°, corresponding to the interlayer spacing of 0.36 nm of the RGO sheets [34]. As the PANI content increases, this peak becomes weaker, showing that PANI is intercalated between the RGO. The XRD patterns confirm that the RGO sheets and PANI are uniformly distributed. For all the films, the absence of

Figure 2 Structure and property of PANI/RGO films. (a) Survey (a) and (b) C 1s XPS spectra of the PG₃₀ film before and after hydroiodic acid reduction. (c) XRD patterns of RGO, PANI, and PANI/RGO films. (d) Electric conductivities of PANI/RGO, RGO, and PANI film.

diffraction peak associated with GO ($\sim 11^\circ$) again reveals the complete reduction of GO. Raman spectra of the composite films (Fig. S5) also show the characteristic bands of the doped PANI. In summary, all the results confirm the successful preparation of uniform PANI/RGO films.

Electric conductivities of the PANI/RGO composites were measured to evaluate the reduction level of RGO and the charge transport ability of the composite. As shown in Fig. 2d, the pure PANI film has a small conductivity of $8.7 \times 10^{-2} \text{ S cm}^{-1}$, but for the PG₁₀ (10 wt.% GO feeding ratio), the conductivity increases to 1.3 S cm^{-1} . The improvement in film conductivity further confirms the successful reduction of GO by hydroiodic acid [35]. The conductivity of PANI/RGO film increases with the RGO content, and reaches 109.4 S cm^{-1} for PG₉₀. Although high RGO content increases conductivity, high RGO content decreases the specific capacitance of the composite film due to a decrease in the PANI content. Therefore, the RGO content should be optimized for practical application.

The electrochemical performance of the PG_x films was

tested in a three-electrode cell. Fig. S6 shows the cyclic voltammetric (CV) curves of pure PANI film, pure RGO film, and PANI/RGO composite films with a scanning rate of 50 mV s^{-1} at a potential range of -0.2 – 0.8 V vs. SCE (all the potential was referenced to SCE unless otherwise stated). The CV curve of the pure RGO film has a rectangular shape, showing the characteristics of electric double-layer capacitance. The CV curves of the PANI/RGO composite films show a pair of redox peaks at $\sim 0.5 \text{ V}$, corresponding to the redox of oligoanilines [36], as indicated by Fig. 3a. The oligoanilines are typical electrochemical decomposition products of PANI, but they have larger specific capacitance than PANI. Fig. 3b shows the GCD curves of the PANI/RGO films measured under the preset maximum potential of 0.8 V at the current density around 1 A g^{-1} (see Figs S7–S13 for GCD curves at other current densities). The plateau at $>0.7 \text{ V}$ in the charge curve indicates slight over-oxidation of PANI, which generates oligoaniline [36]. The shoulder in each discharging curve of the PANI/RGO composite films between 0.4 – 0.5 V is attributed to the redox of oligoaniline.

Figure 3 Electrochemical performance of RGO, PANI, and PANI/RGO composite films. (a) Typical redox reaction of oligoaniline. (b) The GCD curves. (c) Volumetric specific capacitances at different current densities. (d) Gravimetric specific capacitances and volumetric specific capacitances of the films (current density: $1 \pm 0.5 \text{ A g}^{-1}$). (e) The comparison of volumetric specific capacitance of PG₁₀ and materials in literature. (f) Equivalent circuit of the PANI/RGO electrode. (g) Nyquist plots of the electrodes.

The gravimetric specific capacitance was calculated according to the GCD curve and depicted in Fig. 3c. The pure RGO film has a tiny specific capacitance of 0.3 F g^{-1} at 0.94 A g^{-1} . The specific capacitance of the composite films increases as the content of PANI increases (Fig. 3d), and reaches a maximum at a 90 wt.% PANI content. For PG₁₀, the gravimetric specific capacitance reaches 854 F g^{-1} at 1.5 A g^{-1} , and at a high current density of 39.0 A g^{-1} , the gravimetric specific capacitance is still

356 F g^{-1} . These values are among the highest specific capacitances of the flexible PANI-based composites. The previous study [36] confirmed that the oligoaniline produced by electrochemical degradation of PANI could contribute large pseudocapacitance, but must be with the assistance of a good electric conductive matrix. Here the RGO sheets serve as the electron conductive path in the composite and 10 wt.% RGO in the PG₁₀ composite increases significantly the capacitance to 854 F g^{-1} .

Because the films have a non-porous compact structure, they exhibit high volumetric specific capacitances. Fig. 3d shows that the highest volumetric specific capacitance is 1354 F cm^{-3} at 2.4 A cm^{-3} , and even at 62.4 A cm^{-3} , the volumetric specific capacitance is still as high as 564 F cm^{-3} . These values are much higher than other PANI-based electrode materials as shown in Fig. 3e [18,37–45]. It has been reported that PANI has a high ionic conductivity, which allows the interior of dense films to participate in electrochemical reactions. Therefore, we can use our solution-casting method to produce the compact composite film with high density, and improve the volumetric specific capacitance. However, it should be noted that although RGO sheets can improve the electric conductivity and specific capacitance of the PANI/RGO films, they may hinder the diffusion of electrolytes. This is confirmed by the EIS results (Fig. 3f, g). An equivalent circuit of the PANI/RGO electrode is shown in Fig. 3f. R_s is the series resistance of the current collector and electrolyte, C_{dl} is the electric double layer capacitance, R_t is the charge transfer resistance of the PANI redox, and T is the finite space Warburg impedance. The finite space Warburg impedance, which gives a straight line with a phase of 45° and an almost vertical line at the low-frequency region in the Nyquist plot, can be used to investigate the diffusion in the electrode. With the increase of the RGO content (Fig. 3g), the 45° -region becomes longer, corresponding to larger equivalent series resistance and a smaller diffusion coefficient of the electrolyte inside the film. While for PG₇₀, PG₉₀, and RGO film, the diffusion is so slow that the EIS

does not show capacitive characteristics. In general, the RGO content can be easily controlled to achieve a balance between the mechanical strength, capacitance, and rate performance, to meet the requirements of different practical applications. In our experiments, 10 wt.% RGO sheets can efficiently increase the conductivity of the film, but do not reduce the diffusion rate significantly. Therefore, PG₁₀ shows both high volumetric specific capacitance and good rate performance.

A symmetric solid-state flexible device was assembled by using the PG₁₀ film as the electrodes and H_2SO_4 -PVA hydrogel as the electrolyte. The nonlinear GCD curves of the device show the character of pseudocapacitance (Fig. 4a), and the specific capacitance was calculated to be 198 F g^{-1} at 0.83 A g^{-1} , corresponding to an energy density of $15.1 \text{ mW h cm}^{-3}$ and a power density of 0.34 W cm^{-3} (Fig. S14 for Ragone plot). The average single electrode specific capacitance was calculated to be 792 F g^{-1} at 1.7 A g^{-1} . This value is slightly smaller than the three-electrode result because of the lower conductivity and weaker permeability of the gel electrolyte. When the current density increases to 4.4 A g^{-1} , the specific capacitance still remains at 124 F g^{-1} (Fig. 4b), giving the volumetric energy density and power density of 1.0 mW h cm^{-3} and 0.53 W cm^{-3} , respectively. These values are larger than those of most of the reported flexible supercapacitors [18,46–52]. Fig. S15 shows that when the supercapacitor was bent, the discharge time did not decrease, indicating good flexibility of the solid device. Fig. 4d and Movie S1 show that three series-connected devices, which have a working voltage of 2.4 V , can light a

Figure 4 Electrochemical performance of the all-solid-state device. (a) The GCD curves at different current densities. (b) Rate performance of the device. Inset: photograph of a folded device. (c) Cycle stability of the device at 3.33 A g^{-1} . (d) Photograph of an LED driven by three series-connected devices. (1) The LED before being connected to the supercapacitors. (2) The LED lightens by the supercapacitors. (3) The LED lightens by the bent supercapacitors.

2-V LED. When the devices were bent, the brightness of the LED kept stable. After 5000 charge/discharge cycles, the capacitance dropped by 50% (Fig. 4c), due to the electrochemical degradation of PANI in anode at high voltage. The above results demonstrate that the PANI/RGO films are good flexible electrodes.

The mechanical strength of the electrode materials on the capacitive performance was investigated in the present study and such property has been seldom studied yet. The present study shows that RGO sheets significantly increase the shape stability of PANI during the electrochemical test. As a high-strength 2D material, RGO sheets are reported to efficiently increase the modulus and fracture strength of various polymers [53,54]. Fig. 5 shows that the pure PANI film became shattered after 10,000 cycles of charging/discharging tests, while the PG₁₀ film maintained intact after 10,000 cycles. Clearly, composing PANI with RGO sheets makes the supercapacitor more mechanically reliable and gives it longer service life.

CONCLUSIONS

A solution casting technique was developed to fabricate flexible PANI/RGO composite films with compact PANI matrix and uniformly distributed RGO sheets, which produced large-area PANI/RGO films with precisely controlled RGO content. The RGO sheets increase the conductivity and mechanical strength of the films and the PANI provides high pseudocapacitance. Moreover, RGO sheets also play the roles of diffusion barriers to the electrolyte and mechanical reinforcer. The optimized PANI/RGO composite films containing 10% RGO exhibit the highest volumetric specific capacitance of 1354 F cm⁻³ at 2.4 A cm⁻³. Accordingly, the flexible supercapacitors

with H₂SO₄-PVA electrolyte were fabricated and showed excellent performance. These results confirm that PANI/RGO is a promising electrode material for high-density energy storage, and the solution casting method provides a new option of fabricating other organic electrode materials.

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Figure 5 Photographs of PANI and PG₁₀ films before and after the electrochemical test.

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柔性聚苯胺电极体积电容的提高: 溶液浇铸法以及还原氧化石墨烯的影响

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摘要 高体积比电容是柔性超级电容器的关键。在本文中, 我们设计并制备了一种具有超高体积比电容和良好倍率性能的柔性复合电极。该膜电极以无孔且致密的聚苯胺作为基质, 少量的还原氧化石墨烯片作为填料, 通过一种新开发的溶液浇铸法制备而成。用于浇铸的溶液是由聚苯胺和氧化石墨烯的混合溶液自组装制备得到。关于还原氧化石墨烯作用的系统研究结果表明, 还原氧化石墨烯既是导电填料又是扩散屏障。通过优化还原氧化石墨烯的含量, 电极在 2.4 A cm^{-3} 下体积比电容高达 1354 F cm^{-3} ; 同时由于聚苯胺具有良好的离子电导率, 电极也表现出良好的倍率性能。本工作为柔性超级电容器提供了一种高性能的电极, 同时溶液浇铸法有望应用于其他有机电极材料的制备。