



Preparation and electrochemical stability of graphene/polyaniline composites with polylactic acid as biodegradable adhesive

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ABSTRACT

Conductive polymer polyaniline (PANI) is a hot research topic in pseudocapacitor electrode materials due to its low preparation cost and high specific capacitance. In this work, graphene/polyaniline composites (Gr/PANI) were prepared by in situ chemical oxidation polymerization. The morphology and structure of the materials were characterized by SEM, TEM, EDS, XRD and FTIR. Additionally, Gr/PANI capacitors were prepared using PLA and PVDF as adhesives, and the electrochemical behavior was studied by galvanostatic charge–discharge (GCD) and cyclic voltammetry (CV). Furthermore, the 500 cycle stability and the degradation of PLA on capacitance performance of 90 days were carried out in both acidic and neutral solutions. Results show that the specific capacitance of PANI compounded with 50 mg graphene (P-50) is higher than that of pure PANI at current density of 0.5 A/g. Electrode has higher specific capacitance and better cycle stability in acidic solution than in neutral solution. The specific capacitance of P-50 + PLA is 332.3 F/g in sulfuric acid solution, which is 37.4% higher than that of 241.8 F/g in sodium sulfate solution. The cycle stability shows that capacitance retention of P-50 + PLA (71.1% content) was 14.4% less than that of P-50 + PVDF (85.5%) after 500 number cycles. Degradation of PLA on capacitance studies show that the capacitor (P-50 + PLA) displays relatively stable adhesion performance within 20 days in acidic solution and performs stable adhesion property within 90 days in neutral solution. It reveals that the PLA may be used in energy storage devices as environmental-friendly adhesive.

1 Introduction

The energy crisis has attracted worldwide attention with the rapid development of society and the massive consumption of non-renewable energy [1]. In addition, the use of fossil energy produces greenhouse gases and leads to global warming. Therefore, it is imperative

to develop renewable, green and clean energy storage devices [2, 3]. Energy storage devices, such as batteries [4, 5] and capacitors [6], have been widely studied and applied increasingly widespread recently for their advantages of energy storage performance [7]. Typically, supercapacitors with many advantages such as fast charge and discharge [8], long service life [9],

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wide temperature range [10] have been widely used in many areas [8, 11]. Meanwhile, the extensive application of capacitors may cause serious environmental pollution for the difficulty in regenerating electrode material. One of the main reasons is that the use of non-degradable adhesives make it difficult to decompose and regenerate large electrode materials [12].

Polyaniline (PANI) is an ideal electrode material for pseudocapacitors because of its simple preparation method, high yield and large specific capacitance [13, 14]. There are three different oxidation states of PANI, namely, the oxidation state, the reduction state and the half-oxidation-half-reduction state [15]. It is worth noting that only PANI in the half-oxidation-half-reduction state by doping with aqueous protonic or functionalized acids can display redox property well [16]. The mechanical properties of single PANI are poor and significant volume changes are involved in the oxidation and reduction reaction, resulting in poor cycle stability [17]. Therefore, PANI is often combined with other materials to improve its electrochemical properties. Graphene (Gr), with large theoretical specific capacitance and high specific surface area, can be used as electric double-layer capacitor electrode to provide capacitance through the double layers of the electrode–electrolyte interface [18, 19]. It has been shown that excellent electrochemical properties can be obtained by combining Gr with PANI, in which can inhibit the structure fracture caused by volume change during charging and discharging [20]. The Gr can further improve the electrochemical performance of PANI [21]. Li et al. [22] prepared graphene/polyaniline composites modified with carbon nanodots by supramolecular in situ self-assembly technique, which reduced the agglomeration of Gr and had low charge transfer resistance, and presentable cycling performance.

The application of biocompatible and biodegradable materials in the fabrication of electronic devices is one of the most interesting research topics of the recent years [12]. PLA is a typical biodegradable and environmentally polymer [23], derived from renewable resources, such as corn, potato or wheat [24], making it a compelling alternative to traditional synthetic polymers. It can be used as the flexible substrate to develop novel degradable and flexible PANI-based composites [25]. Due to the high pseudocapacitance and electrical conductivity properties, PANI can significantly boost the electrochemical performance of the electrodes. At the same time, mechanical flexibility and biodegradability of PLA offer structural support

and environmental benefits [26]. In recent years, much attention has been paid on the preparation of green flexible supercapacitors (SC) using PLA as polymer substrate [27]. For instance, Wang [28] designed a kind of self-supporting composite electrode, using chemical oxidation of aniline in presence of porous polylactic acid/carbon nanotube as degradable substrate. It has excellent mechanical strength, good cycle stability and specific capacitance of 510.3 F/g in 1.0 mol/L sulphuric acid electrolyte. However, polylactic acid has some problems such as high water sensitivity and fast hydrolysis rate [29, 30]. The application of PLA as an adhesive in supercapacitor electrodes needs further study because it may degrade to lactic acid over time [31], which may affect the electrochemical properties of electrode materials.

In this work, Gr/PANI composite was prepared by in-situ chemical polymerization using APS as oxidant in the presence of hydrochloric acid. Gr/PANI electrodes were prepared using PLA or PVDF as adhesives of the active materials. The capacitance performance of grapheme/PANI was studied. Further, the effect of PLA degradation of 90 days on capacitance performance was discussed, compared with that using PVDF as adhesive. Results reveal that PLA can be used as adhesive in capacitor and the detailed application needs to be further explored.

2 Materials and methods

2.1 Materials and characterizations

Aniline (AN) was purchased from Damao chemical reagent factory in Tianjin, and distilled under reduced pressure before used. Graphene (Gr) was provided by Daewoo Chemical Co., Ltd. PLA was prepared by ring-opening polymerization of L-lactide with $M_w = 185$ kDa and $PDI = 1.85$ in the laboratory. Ammonium persulfate (APS) was obtained from Tianjin BASF Chemical Co., Ltd. N-Methyl pyrrolidone (NMP, 99%) and N, N-Dimethylformamide (DMF, 99%) were supplied by Tianjin Opusheng Chemical Co., Ltd. The other reagents used were all analytical grade reagents.

SEM images and EDS mapping of the composites were obtained on a field-emission scanning electron microscope (SEM, JSM-IT500) and TEM images were collected on a HT7700 transition electron microscopy. Specific surface and porosity analysis was provided by

surface area and porosimetry system (BET, Micromeritics ASAP 2020Plus). Fourier transform infrared spectroscopy (FTIR) measurements were carried out on a Nicolet IS10 spectrometer from potassium bromide pellets. The crystallinity of the nanocomposites were assessed by X-Ray polycrystalline diffractometer (XRD, D8ADVANCE) with Cu-K α radiation ($\lambda = 0.154$ nm) at 40 kV and 40 mA current with 2θ ranging from 10° to 90° , step size 0.02° , and counting time 0.1 s. The electrochemical performances were performed on a CHI620B electrochemical workstation (CH Instruments, Inc). Galvanostatic charge/discharge performances were conducted on a battery test system (Neware DW-P530).

2.2 Synthesis of PANI

Polyaniline was synthesized by in-situ chemical oxidation polymerization of AN. In a typical procedure, 0.05 mol APS was dissolved in 100 mL HCl (1 M) to prepare solution A. 0.05 mol AN was added to 50 mL HCl (2 M) to obtain solution B. the solution B was stirred in ice bath for about 30 min. After the temperature was stabilized at 0°C , solution A was added slowly. The drip time was controlled within 1 h, and then continue to react for 12 h. After the reaction, the product was repeatedly washed with water and anhydrous ethanol until the filtrate becomes colorless, and then vacuum-drying at 80°C to obtain dark green polyaniline.

2.3 Synthesis of Gr/PANI nanocomposites

The preparation process of Gr/PANI composites is similar to that of PANI. Amount of Gr (20 mg, 50 mg and 80 mg) was added into 0.05 mol AN, and the mixture was dispersed by ultrasonication for 30 min. Then, 50 mL HCl (2 M) was added to the above solution, and the mixture was dispersed by ultrasonication for another 30 min, and then kept in ice bath for stirring. Further, the APS solution was added into above solution and repeat the operation described in synthesis of PANI process. Composite materials with different Gr contents were obtained., named P-20, P-50 and P-80, respectively.

2.4 Preparation of electrodes

The pre-processing of nickel foam (NF): Cut the NF into 1×2 cm, then put it into 1 mol/L HCl, distilled water and

absolute ethanol to wash by ultrasonic, put it into the oven and dry. Carbon cloth is treated in the same way.

2.4.1 Preparation of electrode with PVDF as adhesive

The electrode was prepared by mixing the active substance, acetylene black and PVDF with a mass ratio of 8:1:1. The mixture with some NMP was ground for 30 min to obtain a uniform black electrode slurry. The electrode was prepared by coating amount of electrode slurry on the weighed NF and dried under vacuum at 80°C for 24 h. The dry electrode was pressed under 10 MPa. The mass of the active material was calculated according to the difference of the mass before and after the current collector (NF or carbon cloth). The coating area is 1 cm^2 and the mass of active substance is about 4 mg.

2.4.2 Preparation of electrode with PLA as adhesive

The electrode was prepared by mixing the active substance, acetylene black and PLA with a mass ratio of 8:1:1, 8:1:2 and 8:1:4. Typical procedure as follows: PLA solution of 0.0125 g/mL was prepared by dissolving PLA in mixed solvent (dichloromethane/DMF = 1:1). Amount of PLA solution was added in mixture of PANI (P-50) and acetylene black. Further procedure was followed as that of PVDF electrode but dried at 60°C .

2.5 Electrochemical performance test

The electrochemical performance of the material was tested in 1 M Na_2SO_4 solution and 0.5 M H_2SO_4 solution using three-electrode mode, platinum plate as the counter electrode, the saturated calomel electrode (SCE) or the silver chloride electrode (Ag/AgCl) as the reference electrode and active substance as the working electrode. The specific capacitance of single electrode can be calculated by cyclic voltammetry (CV) curve and constant current charge–discharge (GCD) curve. The formula [10] was as follows:

$$C_p = \frac{A}{2\Delta Vmk} \quad (1)$$

$$C_m = \frac{I \times \Delta t}{m \times \Delta V} \quad (2)$$

where A is the area enclosed by the CV curve, AV; ΔV is the voltage of the discharge curve, V; m is the

mass of the active substance on the electrode, g; K is the scanning rate, v/s; I is the discharge current, A; Δt is the discharge time, s; P and C_m are specific capacitance, F/g.

It should be noted that working electrodes made from carbon cloth as current collector, were tested in H_2SO_4 solution using SCE as the reference electrode and the others using nickel foam as current collector were tested in Na_2SO_4 solution using Ag/AgCl as the reference electrode.

3 Results and discussion

3.1 Morphology and element analysis

The morphologies of pure PANI and PANI-Gr composite (P-50) were characterized by SEM and TEM as presented in Fig. 1. As can be seen from Fig. 1a, PANI particles spaced closely and aggregated together seriously. Compared with PANI, P-50 (Fig. 1b) shows fiber-like structure with obvious surface, indicating that the addition of Gr effectively reduces the agglomeration of polyaniline. It may be attributed to the fact that Gr provides more active sites for polyaniline, making it easier to form nanorod-like structures. The microstructure of P-50 was further confirmed by TEM in Fig. 1c and d. It shows that Gr nanosheets embedded in the P-50 polyaniline matrix well and no Gr sheets were observed obviously. P-50 exhibits rough surface and large porosity properties. These analyses

confirm the effective dispersion and structural modification of Gr on polyaniline. This is conducive to the penetration of electrolytes and increases the contact area between the electrode and the electrolyte, implying that Gr enhances electrical conductivity.

The elemental analysis of P-50 composite materials was determined by EDS energy spectrum. Figure 2 shows the relatively uniform distribution of carbon, nitrogen, sulfur, and chlorine in the material. As the analysis of P-50 polymer, nitrogen atoms are part of the structure of polyaniline. A small amount of sulfur and chlorine occurs, which originates from the doping of sulfate and chloride ions. It reveals that Gr nanosheets are dispersed well in polyaniline. The EDS studies confirm that Gr is successful loaded in polyaniline matrix with good dispersibility, which is consistent with the TEM results.

3.2 BET analysis

The porous structures of PANI and P-50 were comprehensively characterized by Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) analysis. As shown in Fig. 3a, the BET N_2 absorption and desorption isotherm shows an obvious IV pattern, indicating that PANI and P-50 are mesoporous materials[10]. The specific surface area of PANI and P-50 is $15.5\text{ m}^2/\text{g}$ and $22.4\text{ m}^2/\text{g}$, respectively, indicating that the addition of Gr increases the specific surface area of PANI. The analysis of BJH aperture distribution further illustrates the aperture distribution of PANI and P-50 in Fig. 3b. As seen, the pore-size distributions of both PANI and P-50 have wide aperture distribution from 6 to 100 nm, and predominantly concentrated at 6–30 nm. The average apertures of PANI and P-50 are 23.6 nm and 25.6 nm, and the cumulative pore capacity is $0.083\text{ cm}^3/\text{g}$ and $0.123\text{ cm}^3/\text{g}$, respectively. It indicates that there are mid-holes suitable for electrolyte diffusion and charge transfer. In contrast, the P-50 shows a wider aperture distribution. It further approves that the addition of Gr potentially improves the surface area and the accessibility of molecular adsorption and diffusion.

3.3 FTIR analysis

Figure 4 shows the FTIR spectra of PLA, PANI, P-50 and P-50 + PLA. As can be seen in spectrum of PLA, a strong absorption band at 1759 cm^{-1} occurs, which can be attributed to C=O stretching vibration in the

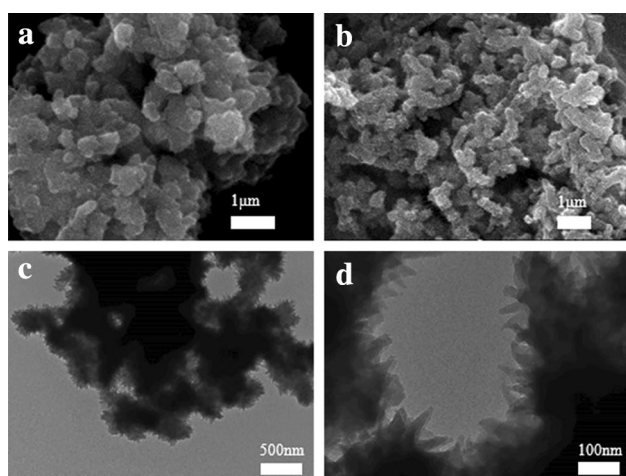
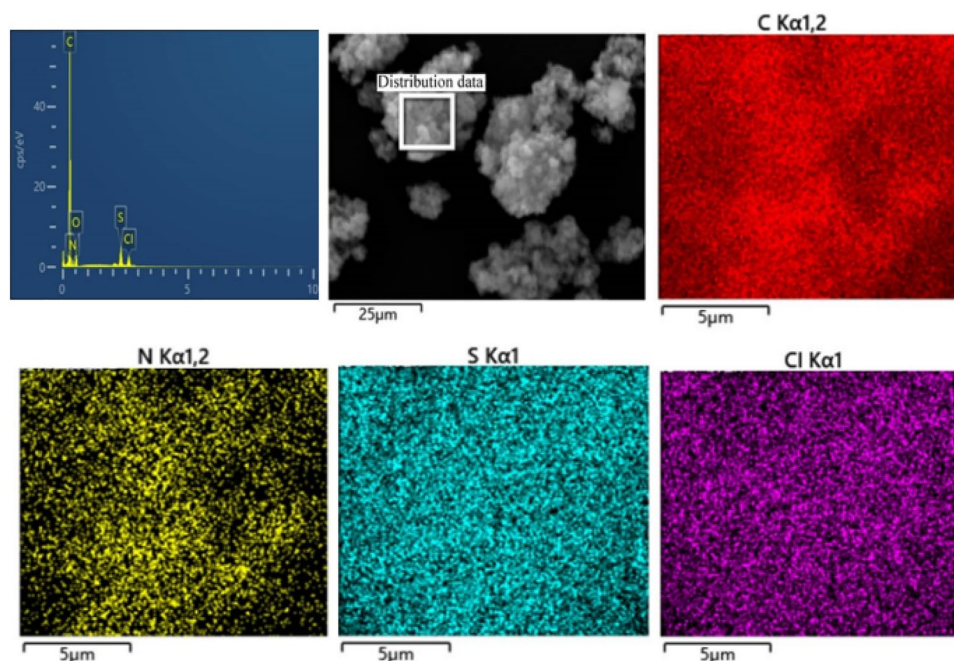
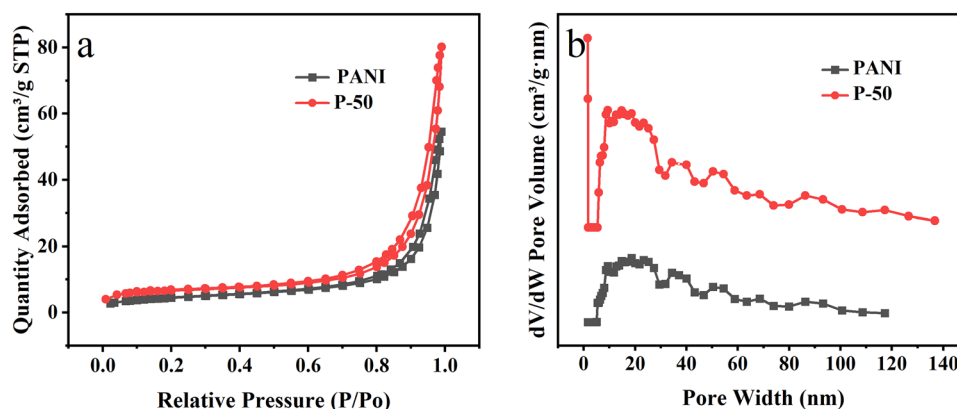


Fig. 1 SEM morphological images of **a** PANI and **b** P-50. **c–d** TEM images of P-50

Fig. 2 EDS spectrum and elemental mapping of P-50**Fig. 3** **a** BET N_2 adsorption–desorption isotherms and **b** BJH pore-size distribution plots of PANI and P-50

PLA chain [32]. The absorption bands at 1184 cm^{-1} and 1091 cm^{-1} are due to C–O stretching and in-plane bending of O–H bond, respectively [23]. In the PANI, P-50 and P-50 + PLA spectra, the absorption bands at 1666 cm^{-1} , 1135 cm^{-1} and 1106 cm^{-1} are from the C=C skeleton vibration on the benzene ring, the C–N stretching vibration in quinone structure and benzene structure, respectively [33]. In the P-50 + PLA spectrum, it can be seen that the absorption band at 1759 cm^{-1} also appears with significantly reduced absorption amplitude. This can be attributed to the lower content of polylactic acid in the composite, which leads to a decrease in C=O content, resulting in lower absorption band intensity.

3.4 XRD analysis

The XRD patterns of PANI, P-50 and P-50 + PLA are represented in Fig. 5. The sharp diffraction peaks of PANI at $2\theta = 14.8^\circ$, 20.2° , 25.3° belong to the crystallinity structure of polyaniline. The diffraction peak of $2\theta = 20.2^\circ$ is generated by the amorphous PANI, corresponding to the parallel (020) plane of the PANI backbone, and the diffraction peak of $2\theta = 25.3^\circ$ corresponds to the orthogonal (200) plane of the backbone [34], indicating that PANI and P-50 has superior regularity. The diffraction peaks of P-50 are similar to that of PANI for the small content of Gr in the polymer matrix, but a slight peak at $2\theta = 26^\circ$ comes out from the typical graphite structure

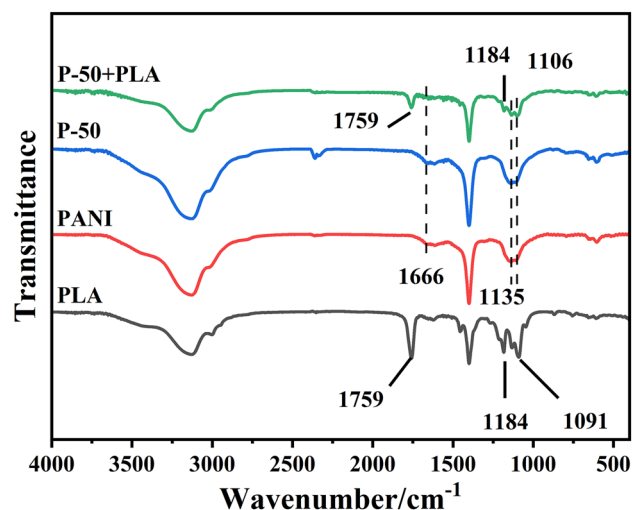


Fig. 4 FTIR spectra of PLA, PANI, P-50 and P-50 + PLA

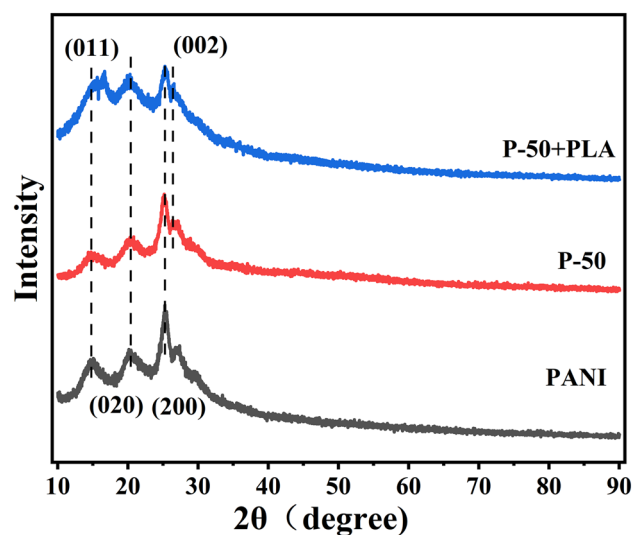


Fig. 5 XRD spectra of PANI, P-50 and P-50 + PLA

[22], which is the (002) plane of the hexagonal graphite carbon, illustrating the Gr sheets are well wrapped in PANI. In all of the spectra, the wide diffraction peaks from 10° to 30° appear, which shows the amorphous region of polyaniline, suggesting polyaniline with low crystallinity structure are obtained. The diffraction peak of P-50 + PLA at $2\theta = 16^\circ$ belongs to the amorphous structure of PLA [35], which confirms the successful addition of PLA.

3.5 Electrochemical performance analysis

In order to investigate the electrochemical behavior of the electrode materials, the cyclic voltammetric curves of the samples are determined at a sweep rate of 0.01 V/s at a potential window of -0.4 – 1.2 V, and the results are shown in Fig. 6a. As can be seen in the figure, there are distinct redox peaks at all the electrodes, which are derived from the redox of polyaniline, indicating the pseudocapacitive properties of the electrodes. According to formula (1), it can be inferred that under the same potential window and scanning speed, the capacitance of samples with the same mass of active substances is approximately proportional to the area enclosed by the CV curve. By combining Fig. 6a and formula (1), it can be inferred that the specific capacitance of P-50 is higher than that of the others.

The charge–discharge curves of PANI, P-20, P-50 and P-80 in 1 M Na_2SO_4 electrolyte under the potential window of -0.4 V to 0.6 V at current density of 1.0 A g^{-1} are shown in Fig. 6b. It can be observed that the charge and discharge of all samples are not in a straight line, which confirms the pseudo-capacitance property of the electrodes. At the current density of 1 A/g , the specific capacitance of PANI is increased by adding proper amount of Gr. According to the formula (2), the specific capacitance of the sample at different current densities is calculated and the ratio curve of Fig. 4c is obtained. At the current density of 0.5 A/g , the specific capacitance of P-50 is 348.1 F/g , which is 27.8% higher than that of PANI (272.4 F/g). It is observed from the ratio curves that the specific capacitance of P-50 is larger than that of other samples when the current density is no more than 2.0 A/g , indicating that the electrochemical properties of PANI are improved by adding Gr.

The influence of PLA contents on the electrochemical behavior of Gr/PANI composites was further studied. The cyclic voltamphere curves of the electrodes prepared by mixing PLA and P-50 with different proportions at 0.01 V/s scanning speed are depicted in Fig. 7a. It can be observed that no new redox peaks appear with the increase of PLA contents, but the strength of the peak decrease. The area surrounded by CV curves are also reduced, indicating a decreased in specific capacitance. It can be attributed to that with the content of PLA (a non-conductive polymer) increasing, the conductivity of the electrode material decrease, leading the reduction of specific capacitance [27].

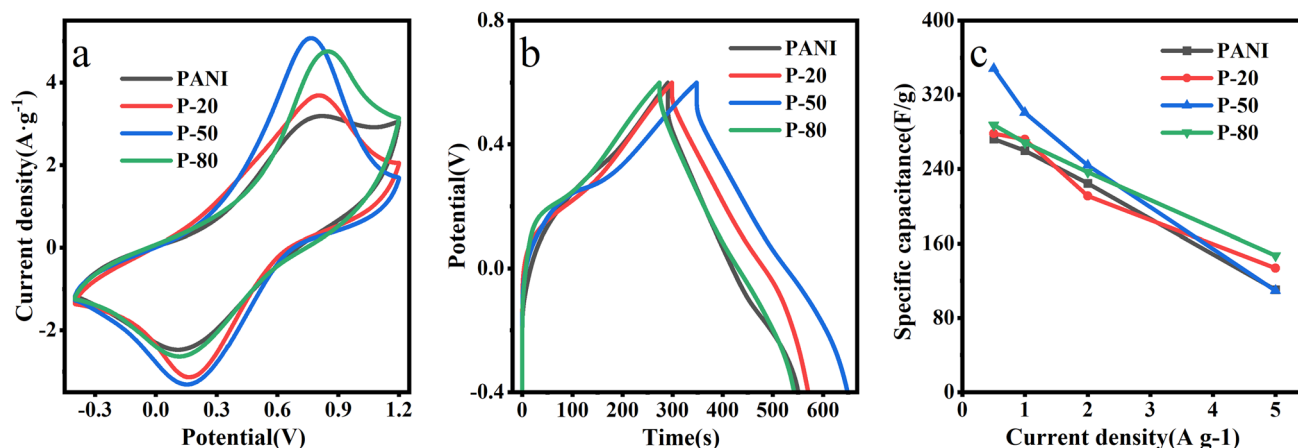


Fig. 6 **a** CV curves at a scan rate of 0.01 V s⁻¹, **b** GCD curves at current density of 1.0 A g⁻¹, **c** the specific capacitances at different current densities of the PANI, P-20, P-50 and P-80 in 1 mol L⁻¹ Na₂SO₄ solution

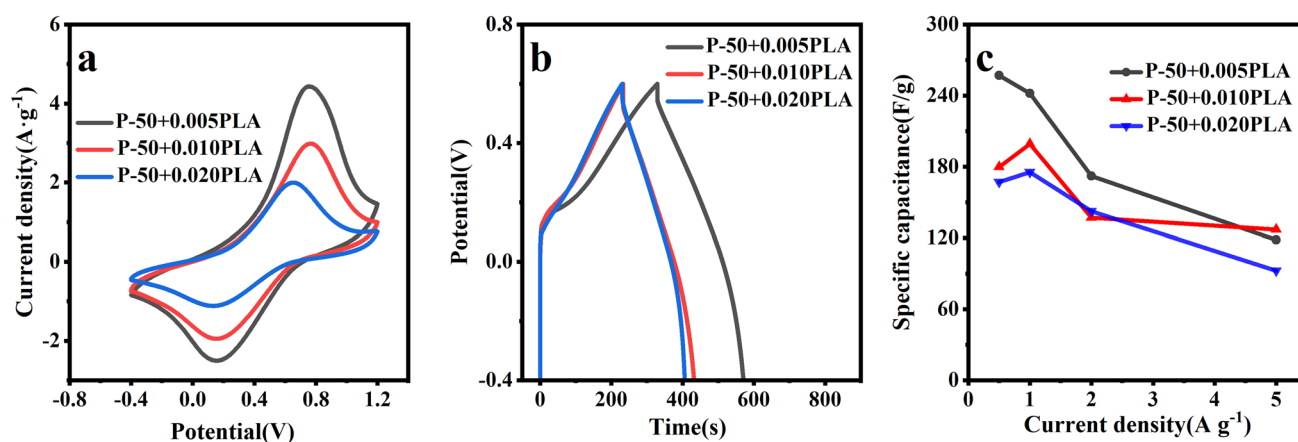


Fig. 7 **a** CV curves at a scan rate of 0.01 V s⁻¹, **b** GCD curves at current density of 1.0 A g⁻¹, **c** The specific capacitances at different current densities of P-50 + 0.005PLA, P-50 + 0.010PLA and P-50 + 0.020PLA in 1 mol L⁻¹ Na₂SO₄ solution

The charge–discharge performance of the materials is examined using the GCD technique. Figure 7b shows that there are no new charging and discharging platforms on the GCD curves with the increase of PLA content. Further, excessive PLA does not display pseudo-capacitance. It is consistent with the results of the CV. The specific capacitance values of P-50 + 0.005PLA, P-50 + 0.010PLA and P-50 + 0.020PLA at 1.0 A g⁻¹ current density are 241.8 F/g, 199.2 F/g and 175.5 F/g, respectively. Both CV and GCD studies indicate that no obvious oxidation–reduction occurs of PLA in the charge–discharge process, showing reasonability of using polylactic acid as an adhesive. Figure 7c shows the charge–discharge ratio diagram, drawn by calculating the specific capacitance of the electrode at

different current densities. The specific capacitance of the electrode tends to decrease with increasing current density. This is similar to the behavior of capacitors using PVDF as adhesive.

The electrochemical behavior of Gr/PANI composites was further studied with the mass ratio of P-50, acetylene black and PLA (PVDF) 8:1:1 in 0.5 mol/L H₂SO₄ solution. The specific capacitance studies of P-50 + PVDF and P-50 + PLA at different current densities are shown in Fig. 8. As seen, the GCD curves of P-50 + PVDF and P-50 + PLA are nearly symmetrical triangles, indicating that the electrode has excellent electrochemical reversibility. At the current density of 1.0 A/g, the specific capacitance of P-50 + PVDF in the acid electrolyte is 367.3 F/g, which is 22.4% higher

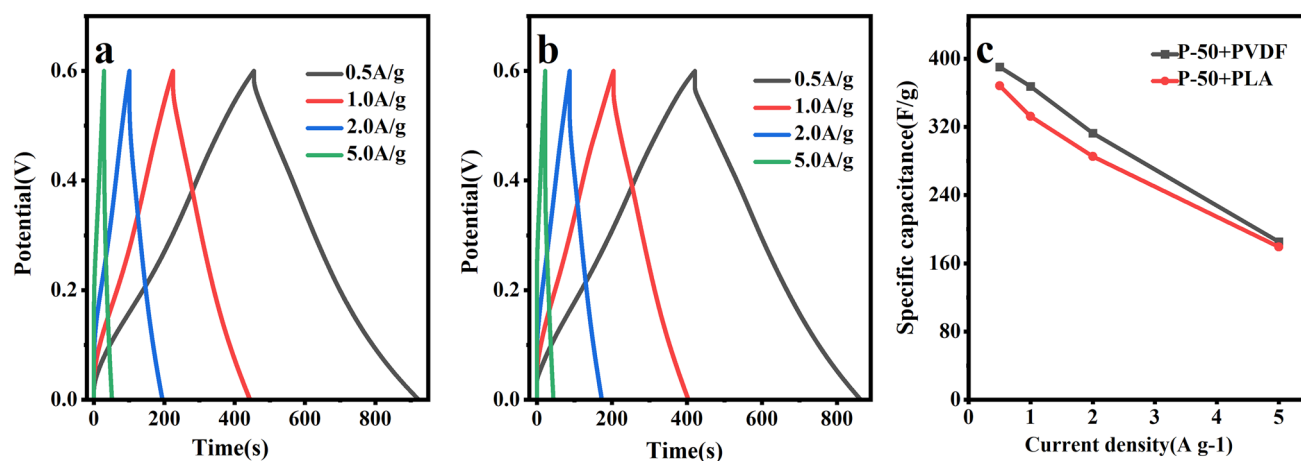


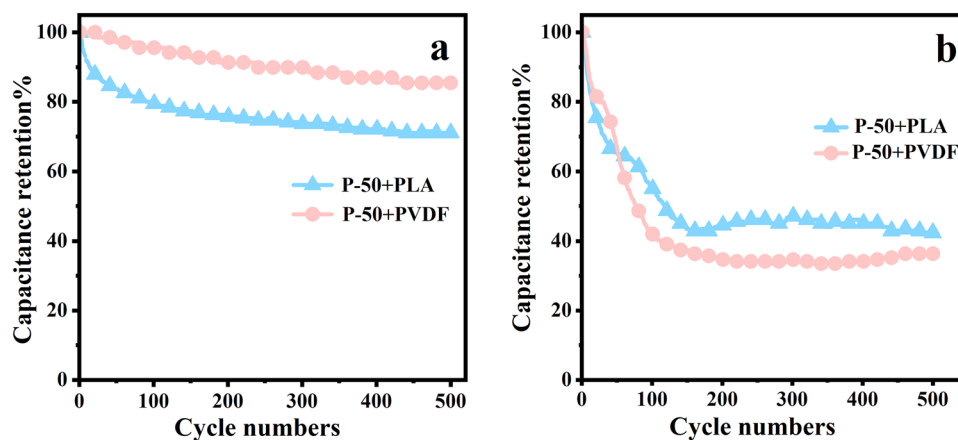
Fig. 8 GCD curves of **a** P-50+PVDF and **b** P-50+PLA at different current densities. **c** The specific capacitances at different current densities of P-50+PVDF and P-50+PLA

than that under neutral conditions, while the specific capacitance of P-50+PLA is 332.2 F/g, which is 37.4% higher than that of neutral conditions. Therefore, the electrochemical performance of the electrode in an acidic solution is better than that of the neutral electrolyte, which is determined by the doping mechanism of polyaniline. Polyaniline is easier to protonize under acidic conditions and can quickly switch between different oxidation states, which enables the charge to be stored and released efficiently, resulting in higher than capacitance [17, 36]. Meanwhile, it is observed that the specific capacitance values of P-50+PLA is a little smaller than that of P-50+PVDF at all current density from 0.5 to 5.0 A/g, which further supports the feasibility of polylactic acid as an electrode adhesive.

The electrochemical stability of prepared samples (P-50+PVDF and P-50+PLA) was tested by applying of 500 charge–discharge cycles at the current

density 1 A g⁻¹ under neutral and acidic conditions. The dependence of capacitance retention ratio on the cycle number is given in Fig. 9. As can be seen, the capacitances of P-50+PVDF and P-50+PLA are more stable in acidic solution than in neutral solution. The capacitance retention rates of P-50+PVDF after 500 cycles in acidic and neutral solutions are 86% and 42%, respectively, while the capacitance retention rates of P-50+PLA are 71% and 36%, respectively. All behaviors are due to the polyaniline of P-50 is easy to deprotonate in the neutral solution in the charge–discharge process, while the acidic solution helps to maintain the protonization state of PANI in P-50 [17]. Meanwhile, the hydrolysis and degradation reactions of polylactic acid are accelerated under acidic conditions, resulting in a decrease of adhesive strength of PLA and subsequent detachment of active substances. Therefore, the stability of the P-50+PLA cycle is slightly poor than

Fig. 9 The cyclic stability of P-50+PLA and P-50+PVDF in 0.5 mol L⁻¹ H₂SO₄ solution (**a**) and 1.0 mol L⁻¹ Na₂SO₄ solution (**b**)



that of P-50 + PVDF. However, after 500 revolutions, it still has a considerable specific capacitance.

3.6 Degradation behavior analysis of P-50 + PLA/P-50 + PVDF

In order to study the effect of PLA degradation on electrodes, multiple electrodes were prepared and immersed in sodium sulfate (sulfuric acid) electrolyte. The specific capacitance of the electrodes was measured at different time intervals, and the specific capacitance time curve was obtained as shown in Fig. 10.

As seen in Fig. 10a, the specific capacitance behaviors of P-50 + PVDF and P-50 + PLA are similar in the first 20 days in acid electrolyte. After soaking for 20 days, the specific capacitance of P-50 + PLA decreases rapidly, while the specific capacitance of P-50 + PVDF decreases slightly. P-50 + PVDF still has a specific capacitance of 300 F/g after 90 days of soaking, which only decreases by 10%, suggesting the relatively electrochemical stability of PANI in acid condition. The specific capacitance of P-50 + PLA is still stable in the first 20 days of soaking, but it has a significant decreasing trend from 20 to 90 days. This indicates that the degradation of PLA has little effect on the adhesive strength of the material in the first 20 days' soaking. Subsequently, as the soaking time increases, the adhesive strength of PLA decreases for the degradation of PLA, resulting in critical detachment of active substances and a larger decrease in specific capacitance.

As seen, the capacitance of P-50 + PVDF is basically stable at 303 F/g for the first 10 days, with a slight increase to 313.2 F/g on the first 3 days, followed by a gradual decrease in Fig. 10b. After 90 days, the specific

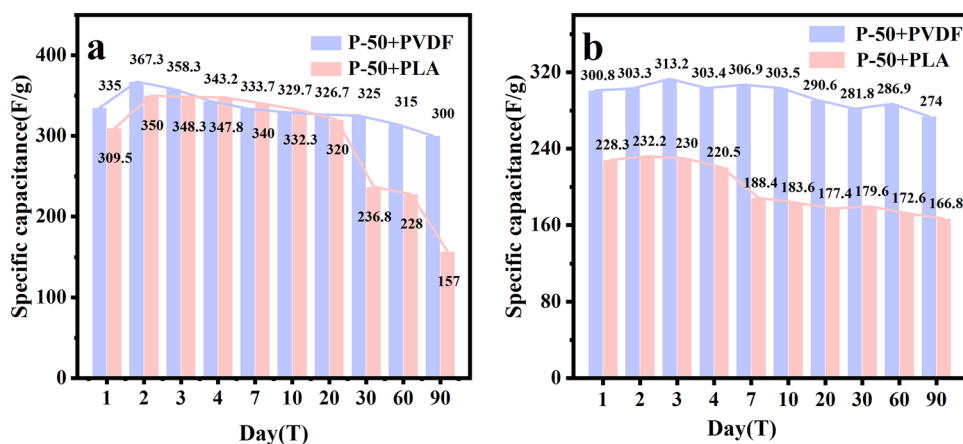
capacitance decreased by about 9%, indicating that the electrochemical properties of electrode materials with PVDF were stable. Further, the specific capacitance of the electrode material was studied using PLA to replace PVDF, as adhesive. The specific capacitance values of P-50 + PLA increase after two days immersion. It is due to the long soaking time in the electrolyte, which allows the electrode to come into full contact with the electrolyte and increases the active substances involved in the electrode reaction. The specific capacitance of the P-50 + PLA decrease seriously in the first 7 days (decreased by 18%) and fluctuated less after the 10th day (decreased by 9%). After soaping for more than 10 days, the specific capacitance of P-50 + PLA declined at a rate similar to that of P-50 + PVDF.

Compared with these results, it can be confirmed that the capacitors prepared with PLA display stable adhesion performance within 20 days in acidic solution, further soaking may cause the detachment of active material for the degradability of PLA[37]. In neutral solution, the capacitors prepared with PLA perform stable adhesion property within 90 days, and the specific capacitance of P-50 + PLA decreases much, which is due to the loss of protons during charging and discharging process of PANI.

4 Conclusions

To sum up, Gr/PANI composites have been successfully synthesized using an in-situ chemical polymerization method with APS as the oxidant in the presence of hydrochloric acid. The morphological characterization and BET analysis show that the P-50 display fiber-like

Fig. 10 The specific capacitance of P-50 + PVDF and P-50 + PLA in 0.5 mol L⁻¹ H₂SO₄ solution (a) and 1.0 mol L⁻¹ Na₂SO₄ solution (b) changes with time



structure with specific surface area of 22.4 m²/g and a higher porosity, which lead more active materials to participate in the electrochemical reaction. Biodegradable polymer PLA and traditional PVDF were used as adhesives to prepare polyaniline capacitors, and the electrochemical behavior of polyaniline capacitors was studied. In addition, the effect of degradation time within 90 days on the specific capacitance of capacitors was studied in neutral and acidic environments. It was confirmed that the capacitor using PLA as adhesive has excellent performance within 20 days in sulphuric acid solution, while it can maintain certain adhesive stability for 90 days in neutral solution. These studies provide a new route for the preparation of electrochemical devices using biodegradable adhesives.

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Author contributions

All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by Huimin Liang. The first draft of the manuscript was written by Huimin Liang and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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Data availability

The data supporting this study's findings is available from the corresponding author upon reasonable request.

Declarations

Competing interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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