A self-healing hydrogel electrolyte towards all-in-one flexible supercapacitors

Wen-Bin Ma1, Ke-Hu Zhu1, Shi-Fang Ye1, Yao Wang1, Lin Guo1, Xue-Yu Tao1-*, Li-Tong Guo1, He-Liang Fan1, Zhang-Sheng Liu1, Ya-Bo Zhu1, and Xian-Yong Wei2,3

1 School of Materials Science and Physics, China University of Mining and Technology, Xuzhou 221116, Jiangsu, China
2 School of Chemical Engineering and Technology, China University of Mining and Technology, Xuzhou 221116, Jiangsu, China
3 Key Laboratory of Coal Processing and Efficient Utilization, Ministry of Education, China University of Mining and Technology, Xuzhou 221116, Jiangsu, China

ABSTRACT

The self-healing electrolytes play an essential role in self-healing supercapacitors. Herein, poly (vinyl alcohol)/sulphuric acid (PVA/H2SO4) hydrogel electrolytes with self-healing properties are prepared, which has been achieved by dynamic hydrogen bonds between PVA chains. The obtained PVA hydrogel displays fast self-healing capability, reliable mechanical performance (stress at 0.29 MPa after stretching to 238%) and high ionic conductivity (57.8 mS cm−1). Based on these excellent properties, an all-in-one self-healing supercapacitor is assembled by in situ polymerization of aniline on the surface of PVA/H2SO4 hydrogel electrolyte. The assembled all-in-one supercapacitor shows outstanding capacitance performance (specific capacitance 504 mF cm−2 at current density of 0.2 mA cm−2 and energy density 35 μWh cm−2 at power density 100 μW cm−2), good cycle stability (after 5000 cycles of charging and discharging, the capacitance retention rate is 77%), excellent flexibility and considerable self-healing performance (69% capacitance retention rate after the fifth self-healing cycle). This self-healing supercapacitor will promote the development of self-healing energy storage devices in wearable electronics.

1 Introduction

Flexible electronic devices have received broaden attention due to the booming market of wearable and portable products. These equipments are often applied under various mechanical loads such as stretching and bending, which are easy to be damaged. It is a feasible solution to strengthen the flexible electronic devices and endow them with self-healing performance. On the one hand, the flexible self-healing electronic devices, including self-healing transistors [1], sensors [2], electronic skin [3], supercapacitors [4] and so on, are still competitive in

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Address correspondence to E-mail: taoxueyu@cumt.edu.cn

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wearable and portable products. On the other hand, self-healing characteristics can extend these devices’ service life under mechanical load by spontaneously healing its fracture surface after being damaged, thus healing their mechanical and electrochemical properties. These advantages will greatly affect the existing energy storage devices, which are essential in several modern electronics.

Among various flexible energy storage devices, supercapacitors have been made great progress because of their fast charging and discharging process, high power density and good cycle life [5]. In self-healing supercapacitors, the self-healing polymers serve as substrates, coating shells or electrolytes, which is the basis of healing mechanical integrity, while the healing of conductivity is based on the recovery of mechanical integrity [6]. According to previous reports, Han et al. [7] synthesized self-healing polyaniline-cellulose nanofiber electrode by combining self-healing PVA hydrogel with capacitive polymer active material. This work actually sacrifices the mass and volume of the electrode in exchange for the ability of self-healing. And Chen et al. [8] prepared the borax-crosslinked polyvinyl alcohol/nanocellulose hydrogel electrolyte, and assembled supercapacitor by clamping non-self-healing activated carbon paper electrode on the electrolyte. Although this method does not sacrifice the performance of active components, the components with self-healing performance are independent from other components, which is not conducive to the overall self-healing of devices. Based on this method, Guo et al. [9] initially constructed an integrated self-healing supercapacitor, avoiding the defects of delamination and high interface resistance in the laminated design. However, no further research has been done on the self-healing performance of the device, and the capacitance performance is not satisfactory in their research.

As mentioned above, self-healing polymers play a crucial role in self-healing supercapacitors. Among the various self-healing materials [10–12], Poly (vinyl alcohol) (PVA) has been studied intensively for the good hydrogel forming and physical properties, high hydrophilicity, processability and biocompatibility [13, 14]. As has been reported, PVA hydrogel can be prepared by chemically crosslinked by some crosslinkers, physically crosslinked by microcrystalline region and irradiation [13, 15]. To obtain the self-healing hydrogel, physical crosslinking is a facile method by freezing and thawing cycles. If it is not treated under low temperature cycles, the hydrogel will be too viscid to remove from mold and not stable in water solution, so it is often used in the laminated supercapacitor. On the contrary, the hydrogel will be a membrane with good mechanical property compatible with the all-in-one configuration supercapacitor. And the degree of crosslinking and the mechanical performance of PVA hydrogel are affected by cycles of freezing–thawing treatment [16]. Gupta et al. [17] prepared a PVA hydrogel through 45 freezing–thawing cycles and it possessed the stiffness of 33.25 MPa. Samadi et al. [18] prepared a triple networks hydrogel based on Agar/PVA/Graphene, and it demonstrated autonomous self-healing within a short time of 10 min. Peng et al. [19] has prepared a B-PVA/KCl/GO hydrogel electrolyte and endowed the active carbon based supercapacitor self-healing property without external stimulus. Therefore, PVA hydrogel electrolyte prepared by freezing and thawing cycles is employed as the self-healing substrate and electrolyte for the all-in-one configuration supercapacitor.

To construct a supercapacitor system, electrode materials play another important role. The capacitive materials for electrode application include carbon materials [20], metallic oxide [21], conductive polymer [22], and their composite. As one of the most widely studied conductive polymer electrode materials, polyaniline (PANI) shows the advantages of good thermal stability, biocompatibility [16], excellent capacitive property and cyclic stability. For example, Pouget et al. [23] have investigated the structure of PANI by XRD and discussed the relationship of crystallite size, protonation and the conductivity of PANI. In fact, several methods have been developed for preparing polyaniline-based electrode materials, including chemical oxidation, electrochemical polymerization, electrospinning, seeding, interfacial polymerization and 3D printing [24–28]. Lin et al. [29] grew the nano-wire PANI electrodes on the surface of carbon cloth by electrodeposition, and the two electrodes were sandwiched to a PAA hydrogel electrolyte to obtain a supercapacitor. This device exhibited a specific capacitance of 217.43 F g^{-1}. Our group has also investigated the structure, electrochemical properties of PANI and its application on hydrogel electrodes [30–32]. In addition, PANI can be easily integrated on the surface of hydrogel electrolyte by in-situ chemical oxidation...
polymerization to form an all-in-one device. Thus, PANI electrode material has been employed for the research of self-healing supercapacitor.

In many reported literatures about self-healing supercapacitors, most supercapacitor devices adopt the traditional laminated structure and need extra self-healing membrane layer, which will undoubtedly increase the interface contact resistance of devices and the risk of delamination under large deformation. Designing an all-in-one supercapacitor can solve these problems perfectly. Compared with the traditional supercapacitor with sandwich laminated structure, the all-in-one flexible supercapacitor avoids the extra healing membrane, simplifies the complicated process of assembling devices, which can theoretically reduce the interface contact resistance, improve the energy density and prolong the cycle life of devices. And self-healing hydrogel electrolyte is an important carrier to realize all-in-one configuration. However, in the reported all-in-one supercapacitors, many hydrogel electrolytes are chemically cross-linked, which is not only complicated in method, but also unsatisfactory in self-healing performance and mechanical strength [33, 34]. In contrast, physical cross-linking is a very simple method to obtain hydrogel electrolytes with strength and performance meeting the requirements of flexible supercapacitors.

In this work, we report a self-healable and tough PVA hydrogel electrolyte based on physical crosslinking network by freezing–thawing method. The physical crosslinking PVA hydrogel was prepared by freezing–thawing cycles method. In a typical process, 2.6 g of PVA powder was added to 15 mL of aqueous solution containing H2SO4 with different concentrations (0.01, 0.5, 1, 2, and 3 mol L−1). The mixture was heated at 90°C in a water bath with violent stirring until the solution was clear. The solution was ultrasonically vibrated to remove bubbles, and then poured into a Petri dish. After the liquid level was flat, the Petri dish was placed in a refrigerator at −20°C. After 3 h, the Petri dish was placed at room temperature to thaw the hydrogel. After three freeze–thaw cycles, the self-healing PVA/H2SO4 hydrogel electrolyte membrane was obtained.

2 Experiment

2.1 Materials

Polyvinyl alcohol (PVA, average molecular weight 74,800–79,200 g mol−1), aniline and ammonium persulfate (APS) were obtained from Sinopharm Chemical Reagent Co., Ltd. Shanghai, China. All reagents used in this research were analytically pure, and no further purification was needed.

2.2 Preparation of self-healing PVA/H2SO4 hydrogel electrolyte membrane

The physical crosslinking PVA hydrogel was prepared by freezing–thawing cycles method. In a typical process, 2.6 g of PVA powder was added to 15 mL of aqueous solution containing H2SO4 with different concentrations (0.01, 0.5, 1, 2, and 3 mol L−1). The mixture was heated at 90°C in a water bath with violent stirring until the solution was clear. The solution was ultrasonically vibrated to remove bubbles, and then poured into a Petri dish. After the liquid level was flat, the Petri dish was placed in a refrigerator at −20 °C. After 3 h, the Petri dish was placed at room temperature to thaw the hydrogel. After three freeze–thaw cycles, the self-healing PVA/H2SO4 hydrogel electrolyte membrane was obtained.

2.3 Preparation of self-healing PANI-PVA/H2SO4 hydrogel membrane

The PANI-PVA/H2SO4 hydrogel membrane was prepared by in situ chemical oxidative polymerization process. Firstly, aniline and APS were dissolved in 50 mL 1 M H2SO4 solution to obtain solution A and solution B, respectively. And the molar ratio of aniline and APS was kept constant 1:1. Secondly, a piece of PVA/H2SO4 hydrogel electrolyte membrane was immersed in solution A under magnetic stirring for 30 min. Then, solution B was dropped into the mixture of hydrogel membrane and solution A to initiate polymerization of aniline. The reaction was carried out with magnetic stirring at 0–5 °C for 3 h.
Finally, the hydrogel membrane was taken out, and by-products on the surface of PANI layer were washed with deionized water and alcohol. The self-healing PANI-PVA/H$_2$SO$_4$ hydrogel membrane was obtained, and the concentrations of aniline were 0.05, 0.1, 0.2, 0.3 and 0.4 mol L$^{-1}$, respectively.

### 2.4 Material characterizations

The PVA/H$_2$SO$_4$ hydrogel membranes and PANI-PVA/H$_2$SO$_4$ hydrogel membranes were frozen in a refrigerator at $-20\,^\circ$C for 12 h and freeze-dried in a freeze dryer at $-60\,^\circ$C for 24 h to obtain lyophilized gel samples (PVA/H$_2$SO$_4$ hydrogel membranes and PANI-PVA/H$_2$SO$_4$ hydrogel membranes). The morphology of lyophilized gel samples was characterized by scanning electron microscopy (SEM, SU8220, Hitachi, Japan). And the lyophilized gel samples were subjected to X-ray diffraction (XRD) using a diffractometer (Bruker D8 ADVANCE) equipped with Cu K$_\alpha$ radiation ($\lambda = 1.5418$ Å). The infrared absorption spectrum of lyophilized gel samples was obtained by attenuated total reflection Fourier transform infrared spectrometer (ATR-FTIR, Nicolet iS5, Thermo Fisher, America) at room temperature.

### 2.5 Tensile experiments

The mechanical tensile properties of the PVA/H$_2$SO$_4$ hydrogels were studied by the Electron Universal Testing Machines (MC009-WDW-20). The hydrogel membranes were cut into strips with dimensions of 80 mm $\times$ 20 mm $\times$ 2 mm. Tensile measurement was carried out by uniaxially stretching the hydrogel strips at a rate of 50 mm min$^{-1}$. The stress ($\sigma$) and strain ($\varepsilon$) were obtained by the following formulas, respectively:

$$\sigma = \frac{P}{A} \quad (1)$$

$$\varepsilon = \frac{L - L_0}{L_0} \quad (2)$$

where $P$, $A$, $L_0$ and $L$ are the force, the cross-sectional area, the initial length and the length of the specimen in tension, respectively.

### 2.6 Fabrication and electrochemical measurements of the all-in-one self-healing supercapacitors

The PANI-PVA/H$_2$SO$_4$ hydrogel membrane was cut off the edge connection to form a PANI($x$)-PVA/H$_2$SO$_4$ supercapacitor with a size of 30 mm $\times$ 10 mm $\times$ 2 mm ($x$ is the concentration of aniline monomer). Then carbon cloth strips were used as current collection and would connect the supercapacitor and the electrochemical workstation system (CHI660 E, Shanghai ChenHua Co., Ltd, China).

Cyclic voltammetry (CV) scans were carried out from 0 to 1 V at various scan rates of 5, 10, 20, 50 and 100 mV s$^{-1}$. Galvanostatic charge/discharge (GCD) was carried out at current densities of 0.2, 0.5, 1, 2 and 3 m Ac m$^{-2}$, and the voltage ranges from 0 to 1 V. Electrochemical impedance spectroscopy (EIS) was taken at open circuit potential over the frequency range from 100,000 to 0.01 Hz with a potential amplitude of 5 mV. All electrochemical experiments were carried out at room temperature using a two-electrode system.

The specific areal capacitance ($C_A$) of the supercapacitors based on single PANI electrode calculated from GCD curves is respectively derived from the equations:

$$C_A = \frac{2 \times I \times t}{A \times V} \quad (3)$$

where $I$, $t$, $A$, and $V$ are the discharge current, discharge time from GCD curves, electrode area and voltage window, respectively.

The Energy density ($E_A$) and Power density ($P_A$) of the supercapacitors are obtained based on Eqs. (2) and (3), respectively:

$$E_A = \frac{1}{2} \times C_A \times V^2 \quad (4)$$

$$P_A = \frac{E_A}{t} \quad (5)$$

The ionic conductivity ($\sigma$) of the PVA/H$_2$SO$_4$ hydrogel electrolyte is examined by the equation:

$$\sigma = \frac{d}{R \times S} \quad (6)$$

where $d$ and $S$ are the thickness and area of the PVA/H$_2$SO$_4$ hydrogel electrolyte sample, respectively. $R$ is the bulk resistance obtained from EIS, which is the intercept on the real impedance axis in high frequency area of the Nyquist plot.
2.7 Self-healing test

A hydrogel electrolyte or an all-in-one supercapacitor were cut off and then the fracture surfaces were contacted for 20 min to repair themselves. The ionic conductivity of healed electrolyte was tested and then compared with the initial value to study its self-healing performance. And the CV, GCD and EIS were used to test the healed supercapacitor to investigate whether its electrochemical performance was repaired.

3 Results and discussion

The self-healing PVA/H$_2$SO$_4$ hydrogel electrolyte was facilely synthesized by physical crosslinking with hydrogen bonds. The preparation process was shown in Fig. 1. PVA powder was dissolved in H$_2$SO$_4$ aqueous solution under vigorous stirring until the blend solution became clear. Then the hydrogel was formed after three freezing–thawing cycles, which was shown in Fig. 1a–d. For a freezing–thawing cycle, the blend was frozen at $-20^\circ$C for 3 h and then thawed at room temperature for 1 h. During the freezing–thawing cycles, as shown in Fig. 1e, hydrogen bonds were formed gradually between a large number of hydroxyl groups (–OH) on PVA. As shown in Fig. 1f, when the hydrogel was freeze–thawed, the peak of hydroxyl group was redshifted from 3364 cm$^{-1}$ to 3355 cm$^{-1}$. These results confirm the hydrogen bonding crosslinking in PVA/H$_2$SO$_4$ hydrogel.

Moreover, the crystal characteristic of PVA was detected by XRD spectra. The peak in the 2$\theta$ range 18°–21° corresponds to 101 crystal plane of PVA, suggesting the microcrystalline regions in PVA hydrogel. This result is consistent with the reports of the crystallinity of freezing–thawing PVA hydrogels of Rosa et al. [38, 39].

The self-healing procedure of PVA hydrogel is shown in Fig. 2. A piece of PVA hydrogel was cut into two halves, then the hydrogel was healed successfully when the two halves were put contact and the fracture surfaces were overlapped. Even being lifted up, the healed specimen would not be broken again. In this test, the healing surface is formed by the fracture surfaces coming from the same specimen. To study the self-healing characteristics of fracture surfaces of different specimens, two pieces of hydrogels were cut in half, one of which was dyed red by rhodamine B to show the difference (Fig. 2b). Subsequently, the four cut pieces were brought into contact alternately and healed immediately. Even being lifted up and bent, the healed specimen assembled with different parts would not be broken again. These results show the outstanding self-healing performance of the PVA/H$_2$SO$_4$ hydrogel. On the one hand, the self-healing process can be realized at room temperature without any external stimulation (ultraviolet light, alternating current or pH value). On the other hand, even between two different fracture surfaces, there is still self-healing activity. Therefore, based on the above results, the self-healing process can be illustrated in Fig. 2c. When the hydrogel is cut off, PVA networks in Fig. 1e will be damaged and the PVA chains will cleavage and/or slippage. Then, the hydroxyl groups on the polyvinyl alcohol chains will be free, which endows the fracture surface with reactivity for healing. According to the self-healing model studied by Antonella et al. [40], on the fracture surface, hydroxyl groups which were originally in equilibrium state due to hydrogen bond breaking now become non-equilibrium state. After reassembling the cut pieces, the hydroxyl groups on different fracture surfaces will reassociate by diffusion of PVA chains to reform hydrogen bonds to re-establish the equilibrium state. For different fracture surfaces, there are also reactive
hydroxyls on them, thus the self-healing behavior can still be effective.

The mechanical property plays a vital role in the application of flexible electrolyte. The PVA/H$_2$SO$_4$ hydrogel has been stretched uniaxially with a constant rate of 50 mm min$^{-1}$. Figure 3a shows its stress–strain behavior, which exhibits a soft and tough elastic deformation in the tensile fracture curve. And the tensile strength can reach 0.29 MPa, when elongation at break is 238%, which is much higher than that of hydrogels reported in other literatures (Fig. 3c). According to Hernández et al.’s study on viscoelastic properties of PVA hydrogel, the increased storage modulus of the hydrogel obtained from multiple cycles may be due to the increase of molecular chains involved in hydrogen bonding [13]. Therefore, physical crosslinking including hydrogen bonding and microcrystalline achieved by freezing–thawing process provides the hydrogel with outstanding mechanical properties. Then loading–unloading test has been carried out in order to investigate the hydrogel’s energy dissipation ability (Fig. 3b). The hysteresis loops of the hydrogel can be observed under various maximum extension ratios ($\lambda_{\text{max}}$), indicating that energy dissipation occurs inside the hydrogel when it is stretched. And the energy dissipation of the hydrogel shows a strain dependence that the hydrogel will exhibit greater.

Fig. 1 a–d Schematic of preparation process of physical crosslinking PVA/H$_2$SO$_4$ hydrogel electrolyte membrane. e The progress that PVA chains are crosslinked by hydrogen bond. f ATR-FTIR spectra of PVA hydrogel and lyophilized gel. g XRD spectra of the lyophilized gel.
energy dissipation at higher strain level. And the elastic modulus also becomes larger with the increasing of maximum extension ratios, which also be observed in the work of Yu et al. [10]. These results may be due to that the weak interactions such as hydrogen bonds will be broken primarily when the strain is small, then the entangled PVA chains will be rearranged and consume more energy as the strain increases. All these indicate good mechanical properties for the PVA/H$_2$SO$_4$ hydrogel prepared by freezing–thawing cycles.

The protons from H$_2$SO$_4$ endow PVA/H$_2$SO$_4$ hydrogel with the ionic conductivity, which is measured by EIS and shown in Fig. 4a. Various H$_2$SO$_4$ concentration has been changed from 0.01 to 3 M to be applied in PVA/H$_2$SO$_4$ hydrogel. And they do exhibit different ohmic resistance obtained from the intercept in the real axis. PVA/H$_2$SO$_4$ hydrogel
electrolyte exhibits the largest ohmic resistance when the concentration of H$_2$SO$_4$ is as low as 0.01 M. On the contrary, the PVA/H$_2$SO$_4$ hydrogels with higher H$_2$SO$_4$ concentration possess much lower ohmic resistance, indicating higher ionic conductivity. By the ohmic resistance from Fig. 4a, the ionic conductivity of various PVA/H$_2$SO$_4$ hydrogels can be calculated and displayed in Fig. 4b. As the H$_2$SO$_4$ concentration increases from 0.01 to 1 M, the ionic conductivity increases rapidly from 1.5 to 57.8 mS cm$^{-1}$. But when H$_2$SO$_4$ concentration grows from 1 to 3 M, the ionic conductivity barely increases and eventually even decreases, which may be because H$_2$SO$_4$ has been consumed by the reaction with the –OH on PVA. Thus, PVA/H$_2$SO$_4$ hydrogel with 1 M H$_2$SO$_4$ has been regarded as the most suitable hydrogel electrolyte for super capacitors.

Moreover, the self-healing property of PVA/H$_2$SO$_4$ hydrogel has been investigated by the ionic conductivity after several healing cycles (Fig. 4c and d) and the healing process is shown in Fig. 2. With the increase of the healing cycles, the intercept at the real axis gradually shifts to larger ohmic resistance in Fig. 4c. After once healing cycle, the ionic conductivity of PVA/H$_2$SO$_4$ hydrogel is 37.9 mS cm$^{-1}$, which has been restored about 71%. Even after 10th healing cycle, its ionic conductivity is still 25.9 mS cm$^{-1}$, which still meets the requirements of electrolyte. Before the 3rd healing cycle, the self-healing property decays quickly. This may be because multiple repairs lead to a gradual decrease in the active groups on the fracture surface that can form hydrogen bonds with the hydroxyl group on the other side, resulting in the decline of self-healing performance. And in the first few healing cycles, the active group density was still large, so the loss was faster, and the self-healing performance decreased rapidly. The plots in Fig. 4e displays valid application of the ionic conductive PVA/H$_2$SO$_4$ hydrogel. A piece of hydrogel membrane could be applied as a conducting wire to connect a circuit with a LED bulb. When the hydrogel membrane was cut off, the bulb turned off immediately. And after the two halves of the hydrogel have been put back together, the bulb rekindled a red light which is slightly weaker than that when the hydrogel was intact, demonstrating the hydrogel’s self-healing performance. Therefore, a...
self-healing supercapacitor can be assembled by integrated configuration based on this self-healing hydrogel electrolyte.

As shown in Fig. 5a, PANI electrode is formed by in-situ polymerization of aniline monomer on the electrolyte surface, thus forming a self-healing all-in-one supercapacitor and studying its electrochemical performance. Before oxidative polymerization, aniline and H₂SO₄ can produce aniline sulfate salt by acid–base reaction, and then APS is used as the initiator to initiate the in-situ polymerization of aniline on the surface of the electrolyte membrane, which lasts for 3 h at 0 °C to complete the reaction. The reaction formula for the polymerization of aniline to PANI is shown in Fig. 5b. The y value in the reaction formula indicates the oxidation/reduction degree of polyaniline, and different y values correspond to different oxidation states of polyaniline (y = 1, Leucoemeraldine Base; y = 0.5, Emeraldine Base; y = 0, Pernigranline Base). Among them, the Emeraldine Base is the state with the highest electrical conductivity [32]. The Emeraldine Base can be converted into Emeraldine Salt after being doped with protonic acid, and its conductivity can be improved by ten orders of magnitude or even higher. Due to the particularity of its structure, in the process of reversible doping-de-doping and redox reaction, PANI can be transformed into other structures, resulting in generating Faraday capacitance to achieve high-density charge storage. In the electrochemical reaction process, the charge can be stored in the entire conductive polymer bulk phase and not only near the surface, so that a higher specific capacitance can be obtained [41].

Figure 5c shows a piece of PANI-PVA/H₂SO₄ supercapacitor which is coated by PANI on its top and bottom surface. The micromorphology of the surface of PANI-PVA/H₂SO₄ supercapacitor is shown in Fig. 5d. The stacked staggered short rods are the typical microstructure of PANI [30], indicating that PANI has firmly grown on the surface of PVA/H₂SO₄ hydrogel membrane. After cutting off the edge connection, the cross section containing the PVA/H₂SO₄ electrolyte layer in middle is exposed in Fig. 5e. Detected by SEM, the middle part of the cross section displays a 3D network structure that belongs to the PVA/H₂SO₄ hydrogel electrolyte. This absolutely different structure confirms the sandwiched PANI electrode-PVA/H₂SO₄ hydrogel electrolyte-PANI electrode configuration. To further investigate the electrode–electrolyte interface, SEM image and line-scanning of element nitrogen has been performed through the interface (Fig. 5g). The SEM image through the electrode-electrolyte interface shows a continuous morphology without clear demarcation, indicating the firmly integrating between PANI electrode layer and PVA/H₂SO₄ hydrogel electrolyte layer. The nitrogen content is high on both sides and low in the middle from the line-scanning curve from energy dispersive spectrometer in Fig. 5h. Because nitrogen comes from PANI, the side layers contain more PANI than middle layer, which is consistent with the sandwiched configuration in Fig. 5e. By contrast, Carbon element is relatively homogeneous distributed through the cross section (Fig. S2), because both PVA and PANI contain it. Moreover, Nitrogen has also been detected in the middle layer though its content is low, which indicates that PANI or thumbnail PANI chains have embedded in the hydrogel electrolyte.

The electrochemical performance of PANI-PVA/H₂SO₄ supercapacitors with various aniline concentration (0.05, 0.1, 0.2, 0.3 and 0.4 M) have been investigated by CV, GCD and EIS. In Fig. 6a, each CV curve exhibits remarkable redox peaks attributed to the pseudocapacitance characteristics of PANI. When aniline concentration is 0.2 M, the integrated area of CV curve reaches the largest, suggesting the best specific capacitance performance.

According to the formula \( C_A = \frac{2V}{S \times t} \), the discharge time in the GCD curves (Fig. 6b) is affected by the specific area capacitance of various PANI-PVA/H₂SO₄ supercapacitors. And discharge time also reaches the longest when aniline concentration is 0.2 M, resulting from the best capacitance performance. Then the specific area capacitance of various supercapacitors is shown in Fig. 6c. The specific capacitance increases rapidly with aniline concentration less than 0.2 M, but then goes down slowly. The influence of aniline concentration on capacitance can be explained from the following two aspects. Firstly, the thickness of active PANI layer directly affects the specific capacitance of the device. A thicker PANI electrode layer can promote the ions and electrons transmission between electrode and electrolyte interface. Therefore, a higher specific capacitance can be obtained for the supercapacitor device with thicker PANI electrode layer. This can be proved by the thickness photos of the hydrogel membranes with different PANI layers. As shown in
Fig. S3, when aniline concentration is 0.2 M, the thickness of PANI layer is the widest among these hydrogels. Therefore, after assembling the PANI (0.2)-PVA/H$_2$SO$_4$ supercapacitor device, it reaches the maximum specific capacitance of 504 mF cm$^{-2}$. When the aniline concentration is 0.3 M and 0.4 M, the thickness of the active PANI electrode layer becomes thinner, resulting in a decrease in the specific capacitance of the device. This is because the gelation of PANI at high concentration prevents the further increase of PANI loading amount [42]. Second, EIS results (Fig. 6d) can also explain the effect of aniline concentration on capacitance. In high frequency area, the intercept of the curve at real axis shows the bulk resistance of whole device. The bulk resistances of 0.1 M and 0.2 M aniline based supercapacitor device are similar (4.46 and 4.63 $\Omega$) and lower than those based on 0.3 M and 0.4 M aniline. In low frequency area, the straight line of the devices based on the 0.2 M aniline exhibit the larger slope, indicating the better capacitive property. Thus, the
PANI (0.2)-PVA/H_2SO_4 supercapacitor possesses the best capacitive performance.

The electrochemical performance of the PANI (0.2)-PVA/H_2SO_4 supercapacitor has been demonstrated (Fig. 6e and f). The shape of CV curves at different scan rate is asymmetric and nonrectangular, as a result of the combination of electric double layer capacitor and pseudocapacitor, which is proved by non-isosceles triangle of GCD curves of the PANI (0.2)-PVA/H_2SO_4 supercapacitor at different current densities (Fig. 6f). In addition, with elevated charge–discharge current, the supercapacitors display good rate capability (Fig. 6g). At the current density of 0.2 mA cm\(^{-2}\), the PANI (0.2)-PVA/H_2SO_4 supercapacitor shows the largest specific area capacitance of 504 mF cm\(^{-2}\). When the current density increases from 0.2 to 3 mA cm\(^{-2}\) (15 times), the capacitance of the PANI (0.2)-PVA/H_2SO_4 supercapacitor keeps 54%. Guo et al. [9] had also researched PVA self-healing hydrogel electrolyte and prepared the all-in-one supercapacitor with SWCNT-PANI composite electrode, but the specific area capacitance was only 15.8 mF cm\(^{-2}\) at 0.044 mA cm\(^{-2}\), which was lower than this work. Li et al. [43] had synthesized an all-solid-state supercapacitor based on polyaniline conducting polymer with the areal capacitance of 341.7 mF cm\(^{-2}\) at 0.25 mA cm\(^{-2}\). Shen et al. [44] prepared the hybridized PANI/GO/CC nanofiber arrays electrode for an all-solid-state supercapacitor, and showed a specific capacitance of 335.4 mF cm\(^{-2}\) at 1 mA cm\(^{-2}\), which was a little lower than this work. The Ragone plots in Fig. 6h show the energy density and power density of all supercapacitors. The PANI (0.2)-PVA/H_2SO_4 supercapacitor exhibits a large energy density of 35 μWh cm\(^{-2}\) when the power density is 100 μW cm\(^{-2}\). And after the power density increased by 15 times, energy density is still 18 μWh cm\(^{-2}\).

Table 1 summarizes the comparison of specific capacitance and energy density between our work and other reported supercapacitors. It can be seen that the all-in-one supercapacitor devices in this work have higher specific capacitance and energy density. Figure 6i shows the cyclic stability of the PANI (0.2)-PVA/H_2SO_4 supercapacitor based on the GCD method at the current density of 2 mA cm\(^{-2}\). With the increase of charge and discharge times, after 5000 cycles of charging and discharging, its capacitance retention rate remains about 77%, which proves its good electrochemical cycle stability.

Except the superior capacitive performance, the PANI-PVA/H_2SO_4 supercapacitor device also possesses self-healing property. In a self-healing process (Fig. 7a), a capacitor was broken into halves. And then they were connected by reassembling the fracture surface. Subsequently, the capacitor was healed integrally. This self-healing process can be illustrated by schematic Fig. 7b. After the device is broken, the PVA chains tethered on the fracture surface can move or rotate spontaneously, forcing the hydroxyl groups to re-form the hydrogen bond, thus repairing the device. In fact, PANI electrodes cannot achieve self-healing intrinsically, so the healing of the device is still dominated by PVA/H_2SO_4 electrolyte. Therefore, the PANI-PVA/H_2SO_4 membrane has been used as a conductor to connect a circuit with a LED bulb. After self-healing of PANI-PVA/H_2SO_4 membrane, the bulb rekindled with a slightly dimmed lighting indicating that the healed device remains electrical contact.

Additionally, the self-healing performance of the device has been researched by capacitance retention after several healing cycles (Fig. 8). Figure 8a shows the CV curves of the capacitor device under 0, 1, 3, 5 healing cycles at scan rate of 20 mV s\(^{-1}\). The current response is decreased as the increasing of healing cycles, indicating the increasing device resistance, which may be due to the deteriorating electric contact of PANI electrode. It can be seen from the GCD curve at the current density of 5 mA cm\(^{-2}\) in Fig. 8b, the charging and discharging time is also becoming shorter and shorter with the increase of healing cycles, but the capacitance retention rate can still reach 69% after the fifth healing cycle (Fig. 8d), showing good self-healing performance.

To investigate the electrochemical interfacial property, the device after several healing cycles has been tested by EIS and the Nyquist plots is shown in Fig. 8c. The bulk resistance represented by intercept at real axis also increases with the number of healing cycles. The healing rate based on the ionic conductivity of the electrolyte and the capacitance of device are shown in Fig. 8d for comparison. Among the three sets of data, the ionic conductivity of electrolyte decays the fastest. As for the conductivity and specific capacitance of the device, the conductivity decays faster, but there is little difference between them. Generally speaking, the healing rate of devices decreases with the increase of healing cycle, indicating the gradual deterioration of electrical contact at
the healing surface. Furthermore, according to the view of Yang et al. [52], the stability of hydroxyl groups on PVA chains exposed on the fracture surface is the key factor affecting material healing and the self-healing process will compete with the environment around the hydroxyl group. These hydroxyl groups may lose reactivity as oxidation, water competition, or changes in molecular conformation when they are exposed in the air environment as the hydrogel is damaged. After polymerization of
aniline on the hydrogel surface, from the line-scanning of nitrogen, PANI chains have diffused into the hydrogel electrolyte, which may change the chemical activity of the fracture, thus improving the reactivity of hydroxyl groups. Therefore, although the self-healing performance decreases during the healing cycles, the healing rate of supercapacitor device is slightly higher than that of pure electrolyte.

4 Conclusions

In summary, using the all-in-one configuration as the assembly strategy and PVA hydrogel as the self-healing electrolyte, we construct an all-in-one self-healing supercapacitor, which not only avoids the defects of the laminate design but also tightly combines the self-healing electrolyte with the electrode material. The PVA hydrogel electrolyte shows good mechanical properties (stress strength 0.29 MPa, strain 238%) and ionic conductivity (57.8 mS cm\(^{-1}\)), which can be content with the electrolyte application. It also shows excellent self-healing performance (after 10th healing, its ionic conductivity is still 48%). In addition, after adjusting the concentration of aniline, the supercapacitor also exhibits a high specific capacitance of 504 mF cm\(^{-2}\) at current density of 0.2 mA cm\(^{-2}\) and a large energy density of 35 μWh cm\(^{-2}\) when the power density is 100 μW cm\(^{-2}\). And it also possesses great self-healing performance (69% capacitance retention) and excellent cycling stability of 77% capacitance retention after 5000 GCD cycles, which is benefited from its all-in-one configuration. This work provides a guide for the design of all-in-one self-healing supercapacitors in wearable electronic devices.

Fig. 8  a CV curves, b GCD curves and c Nyquist plots of the PANI (0.2)-PVA/H\(_2\)SO\(_4\) supercapacitor device under 1, 3, 5 healing cycles. d Capacitance and ionic conductivity healing rate of the device under 1, 3, 5 healing cycles
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Declarations

Conflict of interest We declare that we do not have any commercial or associative interest that represents a conflict of interest in connection with the manuscript.

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