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# Reinforced conducting hydrogels prepared from in-situ polymerization of aniline in an aqueous solution of sodium alginate

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Huabo Huang,<sup>a</sup> Xiaoping Zeng,<sup>a</sup> Wan Li,<sup>a</sup> Hong Wang,<sup>b\*</sup> Qin Wang<sup>a</sup> and Yajiang Yang<sup>a\*</sup>

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By using in-situ polymerization of aniline in an aqueous solution of sodium alginate, we prepared reinforced conducting hydrogels (PANI/SA) with good conductivity ( $\sim 10^{-3}$  S/cm). SEM images indicated that the microstructure of PANI/SA hydrogels is a typical 3D nano-fiber network formed by the entanglement of the PANI and SA molecular chains, leading to a good compressive strength ( $\sim 41$  KPa). Because the system does not contain any adhesives and conducting fillers, the PANI/SA conducting hydrogels with self-supported structures can be directly employed for electrode materials of supercapacitors. A study of cyclic voltammograms indicated that the currents of anodic peak significantly increased with an increase of scan rate, implying that the electrode materials possess good responsiveness. As a reference, traditional compressive tablet electrodes were also prepared by mixing powder of PANI/SA xerogels, adhesive and conducting filler. The results of galvanostatic charge/discharge and impedance show that PANI/SA hydrogels possess longer discharge times, higher specific capacitance and lower electronic resistance in comparison with compressive tablet electrodes. After 1000 times of charge/discharge, there is almost no difference of retained specific capacitance between PANI/SA hydrogels electrodes and compressive tablet electrodes. The easily fabricated PANI/SA conducting hydrogels show great potential as electrode materials of supercapacitors.

## 1. Introduction

Electrochemical energy storage is a clean and sustainable energy resource.<sup>[1,2]</sup> Particularly, supercapacitors as novel electrochemical energy storage devices have received much attention in the past decade because of their advantage of high power density, long cycle life and fast charge/discharge.<sup>[3,4]</sup> Therefore, supercapacitors have been widely used in the fields of electric vehicles, mobile electronic products and other products that need uninterruptible power supply.<sup>[5,6]</sup> In general, the performance of supercapacitors relies heavily on electrode materials. Commercially available materials for supercapacitor electrodes mainly include: (1) carbon materials, (2) conducting polymers and (3) precious metallic oxides. However, low power density and high price of these materials restricts extensive application of supercapacitors to a certain extent.<sup>[4,7]</sup> In order to improve the power density of supercapacitors, an effective approach is to prepare materials with nano-pores or nano-structures.<sup>[8]</sup> As reported recently, polyaniline

nanomaterials,<sup>[9,10]</sup> graphene<sup>[11,12]</sup> and nano-composites of carbon materials and conducting polymers<sup>[13-16]</sup> can effectively improve the power density of supercapacitors. Yet, the aggregation of nanomaterials easily occurs during the construction of 3D nano-structures when using the above materials, leading to a decrease of the specific surface area. Another problem is the addition of adhesives and conducting fillers which are necessary for these electrode materials. The presence of adhesives and conducting fillers not only results in a complicated preparation process, but also an increase of contact resistance and a decrease of the capacitance performance.<sup>[17-19]</sup>

Conducting polymer hydrogels have been recognized an ideal electrode materials because they have the advantage of ordered 3D nano-structures, a large specific surface area and fast electron/ions transfer.<sup>[20]</sup> Particularly, such hydrogels exhibit the feature of a self-supported structure, namely no adhesives and conducting fillers need to be added in the system. Conventional conducting hydrogels are prepared by adding

some conducting polymers into the matrixes of non-conducting hydrogels.<sup>[21-24]</sup>

Recently, conducting hydrogels prepared by non-covalent crosslinking and in-situ polymerization were also reported. For instance, Pan et al. reported polyaniline hydrogels prepared by using phytic acid as non-covalent crosslinker. The resultant hydrogels showed high conductivity and good capacitance performance.<sup>[25]</sup> Dai et al. reported conducting hydrogels prepared by supramolecular self-assembly of cationic polyaniline (PANI) and anionic poly(styrene sulfonate) (PSS).<sup>[26]</sup> Another typical examples are the hydrogels with graphene.<sup>[18,19,27-30]</sup> Due to the 3D nano-structure, these hydrogels possess a large specific surface area, fast electron transfer and ion diffusion, and a large specific capacitance (>200 F/g). Such hydrogels with graphene show good rate capabilities. However, as electrode materials, improvement of two disadvantages still remains a challenge. One of them is the expensive graphene. Another is the inherent low mechanical strength of the hydrogels.

In this work, conducting hydrogels were prepared by in-situ polymerization of aniline in an aqueous solution of sodium alginate (SA). The resulting conducting hydrogels (PANI/SA) were reinforced by not only the entanglement of PANI and SA molecular chains, but also by inter/intramolecular hydrogen bonding because of the large number of carboxylic groups and hydroxyl groups in the SA structure. Thus, PANI/SA conducting hydrogels show a self-supported 3D nano-structure (no adhesives and conducting fillers in the system) and could be directly used as electrode materials of supercapacitors. Due to their good capacitance performance and mechanical strength, the easily fabricated conducting PANI/SA hydrogels exhibit great potential as electrode materials of supercapacitors and actuators.

## 2. Experimental section

### 2.1 Materials

Aniline (An, chemically pure) was purchased from Sinopharm Chemical Reagent Co and was distilled before use. Sodium alginate (SA, Mw~2.1×10<sup>5</sup>, chemically pure) was purchased from Shanghai Chemical Co. and used as received. All other chemicals and solvents were analytical reagents.

### 2.2 Preparation of conducting PANI/SA hydrogels

A known amount of SA was added in deionized water under stirring for 2 h to obtain a transparent solution. A designed amount of An was added into the above solution under stirring for further 2 h. Subsequently a designed amount of oxidant (ammonium persulfate, APS) was added into the above mixture under vigorous stirring. After standing for some minutes, a stable hydrogel was formed and was kept at 4 °C for 24 h for completed polymerization of An. The resultant hydrogels (denoted as PANI/SA) were immersed into a large amount of water for 3 days to remove inorganic impurities and oligoaniline. The water was changed every 12 h. The detailed

structure characterization of PANI/SA can be found in the *Electronic Supplementary Information (ESI)*.

### 2.3 Field emission scanning electron microscope

PANI/SA hydrogels were freeze-dried by liquid nitrogen and coated by gold. Their microscopic morphologies were imaged on a scanning electron microscope (FE-SEM, Sirion 200, FEI) at an accelerating voltage of 10 kV.

### 2.4 Compressive strengths

According to the method described elsewhere,<sup>[31,32]</sup> the compressive strength of PANI/SA hydrogels was measured by using an electromechanical universal testing machine (CMT-4104, SANS) at room temperature. The cylindrical samples (φ18×8 mm) were placed between two plates. The compression speed was 2 mm/min.

### 2.5 Conductivity

In a two-electrode system, the square PANI/SA hydrogel samples with a size of 0.5×0.5×0.5 cm were sandwiched between two platinum plate electrodes. The conductivities of the samples were determined from impedance spectra measured by using an electrochemical workstation (CS350, HUST) and the data were treated by Zview software. The frequency was in the range of 100 KHz~0.01 Hz and the perturbation AC voltage was 10 mV. A three-component model was used for impedance analysis to deduce the bulk resistance *R* of the hydrogels.<sup>[33]</sup> The conductivity was calculated by the following equation:

$$\sigma = \frac{1}{R} \frac{d}{S} \quad (1)$$

where  $\sigma$  is the conductivity, *R* is the resistance, *d* and *S* is the thickness and area of the sample, respectively.

As a reference, the powder of PANI/SA xerogels was compressed into tablets under the 20 MPa. The conductivity of the tablets was measured by using a four-point-probe meter (ST2253, Suzhou Jingge Electronic Co.)

### 2.6 Electrochemical properties

Similar to the preparation of PANI/SA hydrogels described above, an aqueous solution of SA, An and APS was dropped onto a stainless steel mesh (1.0×1.0 cm). The resultant hydrogels were left at 4 °C for 24 h and used as working electrode (denoted as hydrogel electrode). The samples were immersed into a large amount of water for 48 h and subsequently in an aqueous solution of H<sub>2</sub>SO<sub>4</sub> (1 mol/L) for 12 h.

The electrochemical tests were carried out in a three-electrode system at room temperature. Herein, an aqueous solution of H<sub>2</sub>SO<sub>4</sub> (1 mol/L) was used as electrolyte. Platinum wire was used as the counter electrode and an Ag/AgCl electrode was used as the reference electrode. Cyclic voltammetry (CV), galvanostatic charge/discharge and electrochemical impedance spectroscopy (EIS) were recorded on an electrochemical workstation (CS350, HUST). The data

were treated by Zview software. CV curves were collected in the range of  $-0.3$  to  $0.9$  V. The scan rates were varied from  $10\sim 200$  mV/s. The galvanostatic charge/discharge was measured at a varied voltage ranging from  $0$  to  $0.80$  V. In the EIS measurements, the frequency was in the range of  $100$  kHz $\sim 0.01$  Hz, and the perturbation AC voltage was  $10$  mV.

As a reference, the working electrode was also prepared by a traditional method. Briefly, the powder of PANI/SA xerogel and acetylene black as conducting fillers and a  $1$  wt% of aqueous polytetrafluoroethylene suspension as adhesive were mixed into a slurry. The weight ratio of the three components was  $75:20:5$ . Small amounts of the slurry were coated on a stainless steel mesh and dried at room temperature. The samples were compressed under  $20$  MPa to form tablets with a size of  $1\times 1$  cm. In comparison with the hydrogels, they are defined as compressive tablets.

### 3. Results and discussion

Due to the large number of carboxylic groups and hydroxyl groups in the SA structure, SA, as a kind of polyanion, can be used not only as a polyelectrolyte with environmental response,<sup>[34,35]</sup> but also as an electrode material in the presence of conducting polymers. For instance, Xue et al. prepared PANI/SA nano-fibers by introducing An and APS into a diluted solution of SA ( $0.025\sim 0.2$  wt%) followed by oxidative polymerization.<sup>[36]</sup> Chen et al investigated the electrochemical properties of such PANI/SA nano-fibers used as electrode materials for supercapacitors.<sup>[37]</sup> However, these PANI/SA nano-fibers are unable to form membranes if not assisted by polytetrafluoroethylene as adhesive. In this work, as shown in Fig. 1a, stable conducting hydrogels can be formed within minutes after the oxidant APS was added into the highly concentrated solution of SA and An ( $2$  wt%). The chemical structures of PANI/SA hydrogels were characterized by FT-IR, UV-vis and XRD (see *Electronic Supplementary Information, ESI*). The formation of hydrogels is similar to that of PANI/PSS hydrogels.<sup>[26]</sup> Yet, the mechanical strength of PANI/PSS hydrogels is very poor, only slight agitation already leads to the collapse of the hydrogels. By contrast, PANI/SA hydrogels show excellent mechanical strength. We are able to unbrokenly take the samples out of the vessel. As shown in Fig. 1a, the samples can maintain integrated shapes even under a pressure of  $200$  grams weight. The favourable mechanical strength may be attributed to two interactions within the system due to the large number of carboxylic groups and hydroxyl groups in the SA structure. One of them is the entanglement of PANI and SA molecular chains caused by hydrogen bonding (and electrostatic) interaction. Another is inter/intramolecular hydrogen bonding within the SA chains (Fig. 1b). The synergy of both interactions leads to the increase of hydrogel strength. The spectra of FT-IR and XRD of PANI/SA (see *ESI*) indirectly supported this conclusion. For example, the shifts of  $-\text{COO}^-$  peak in SA spectra of FT-IR imply the complex formation between the protonated amino groups ( $-\text{NH}_2^+-\text{C}_6\text{H}_4^-$ ) of PANI replacing the sodium ions of SA and SA chains. The

red shift of  $\text{C}=\text{N}$  peak in PANI/SA also implies the complex formation between PANI and SA. In the spectra of XRD, all characteristic peaks of the PANI/SA xerogel are broadened in comparison with PANI. These changes are likely a result from the intermolecular interactions between PANI and SA. In this work, it was found that the strength could be even higher when higher concentrations of SA were employed. However, resulting high viscosity of the solutions makes it hard to form homogeneous hydrogels. Thus, we only used  $2$  wt% of SA to prepare all samples.

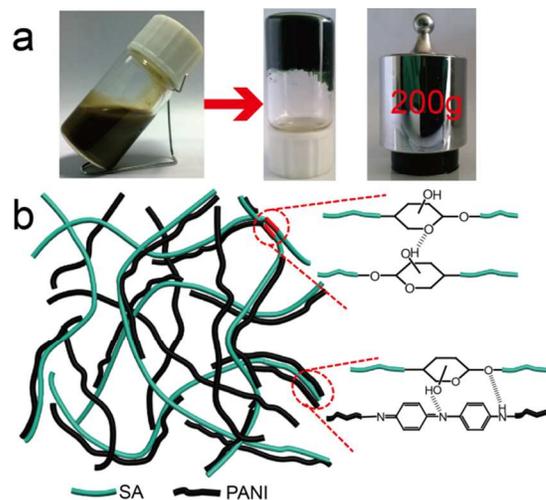


Fig. 1 (a) Photographs of PANI/SA hydrogels formation. (b) Schematic illustration of interactions within the PANI/SA hydrogels.

Conventional hydrogels cannot be used as electrode materials because of their inherent poor strength. Fig. 2 shows the compressive strength of PANI/SA hydrogels as a function of An content. We note that solution of  $2$  wt% SA itself is unable to form hydrogels, thus it has no any strength (curve 5). Herein, hydrogels can be formed only in the presence of An and consequent polymerization leading to a comparatively high strength (curve 1~4). This further verifies the above discussion, namely, the interaction between PANI and SA molecular chains provides the hydrogels with certain strength. It was found that the compressive strength of PANI/SA hydrogels is not in proportion to the content of An. For example, the compressive strength of PANI/SA hydrogels is  $\sim 41$  KPa when An of  $0.2$  mol/L was employed (curve 1). Yet it decreased to  $\sim 9$  KPa when An of  $0.8$  mol/L was employed (curve 4). The reason could be attributed to the in-situ polymerization of An in the network of SA. In the case of low content of An, the in-situ polymerized PANI may interact with part of the carboxylic groups and hydroxyl groups of SA. The other part of the carboxylic and hydroxyl groups may take part in the formation of inter/intramolecular hydrogen bonds within SA, leading to a high crosslinking degree and high strength. In the case of a high content of An, SA chains are entangled with PANI chains and most of carboxylic and hydroxyl groups are covered by PANI chains. In this case, the opportunity for formation of inter/intramolecular hydrogen bonding could be decreased,

leading to the low compressive strength. This conclusion will be further discussed based on the SEM images of PANI/SA hydrogels.

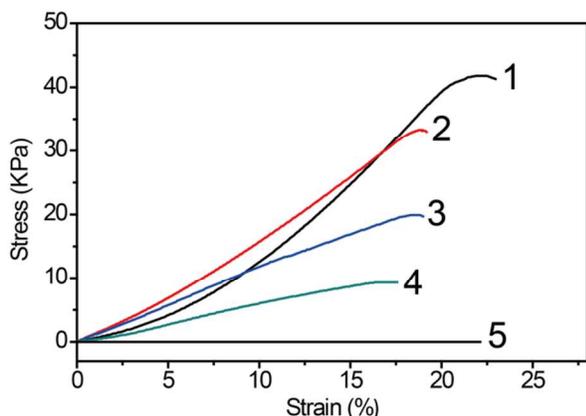


Fig. 2 Diagram of compressive stress/strain of PANI/SA hydrogels prepared with varied content of An: 0.2 mol/L (1), 0.4 mol/L (2), 0.6 mol/L (3), 0.8 mol/L (4) and 0 mol/L (5).

Fig. 3 shows SEM images of PANI/SA hydrogels prepared with a varied content of An. It was found that their microscopic morphology is a porous 3D network structure formed by the entanglement of nano-scale polymer fibers. This is a typical self-supported structure because no adhesive was used. Upon increasing the content of An, the uniform size of these fibers seems to be increased from  $\sim 80$  nm to  $\sim 170$  nm. This phenomenon may involve the entanglement state of PANI and SA molecular chains. In the case of a low content of An, the amount of PANI is too small to entangle the SA chains, resulting in a small size of the fibers (70–100 nm) (Fig. 3a). In the case of a high content of An, more PANI chains are entangled with SA chains, leading to a large size of the fibers ( $\sim 170$  nm). Apart from the PANI entangled with SA, a part of PANI will also aggregate into the particles dispersed in the network of the PANI/SA hydrogels (Fig. 3d).

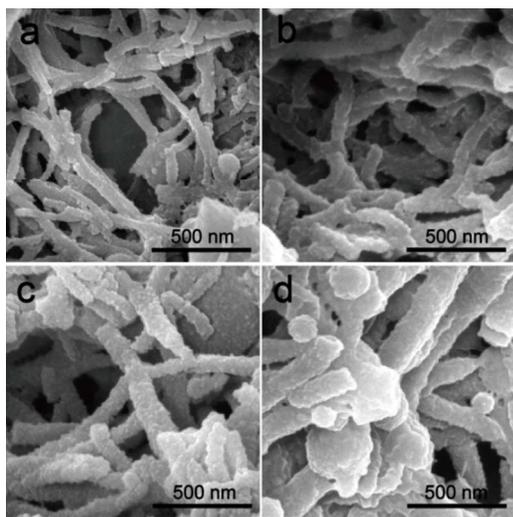


Fig. 3 SEM images of PANI/SA xerogel prepared with a varied content of An: 0.2 mol/L (a), 0.4 mol/L (b), 0.6 mol/L (c) and 0.8 mol/L (d).

For the electrode materials, a certain conductivity is an essential requirement. The conductivity of PANI/SA hydrogels was found to be about  $10^{-3}$  S/cm by the method of impedance. We note that this conductivity is an intrinsic conductivity because inorganic impurities and oligoaniline have been removed by purification. As a reference, the powder of the PANI/SA xerogels was compressed into the tablets. The conductivity of the tablets was measured by using a four-point-probe meter. The conductivity was found to be 0.31 S/cm (in the presence of 0.4 mol/L An) which is higher than that of PANI/phytic acid hydrogels (0.23 S/cm)<sup>[25]</sup> and PANI/PSS hydrogels (0.22 S/cm)<sup>[26]</sup> reported elsewhere. Hence, the PANI/SA hydrogels possess a favorable conductivity.

In addition, as shown in Fig. 3, the continuous 3D nano-fiber network structure provides a high specific surface area, so that the Faraday reaction of PANI will have enough active sites and thus increasing the electrochemical utilization of PANI. Because there are no adhesives and conducting fillers in the system, PANI/SA hydrogels can be directly used as electrode materials. Thus, we evaluated their electrochemical performance by using cyclic voltammetry, galvanostatic charge/discharge and impedance spectra.

Fig. 4 shows the cyclic voltammetry of stainless steel electrodes coated with PANI/SA hydrogels. An aqueous solution of 1 mol/L  $H_2SO_4$  was used as electrolyte. Distinct electrochemical redox peaks can be clearly observed in the range of  $-0.3$ – $0.9$  V. In order to clearly observe the CV curves at low scan rates, an enlargement of CV at 10 and 20 mV/s of scan rate was inserted into Fig. 4. The observed two pairs of redox peaks are assigned to the transition between the leucoemeraldine base state of PANI to an emeraldine state, and a further transition to a pernigraniline state.<sup>[38]</sup> This implies that PANI/SA hydrogels as electrode materials possess the feature of Faraday capacitance. Additionally, the maximum peak current of oxidation was found to be  $1.6 \times 10^{-2}$  A/cm<sup>2</sup> at 10 mV/s of scan rate. It increased to  $10.3 \times 10^{-2}$  A/cm<sup>2</sup> at 200 mV/s as the scan rate, 6.4 times higher than that of the former. The distinct increase of the peak current with an increase of scan rate indicated that PANI/SA hydrogels as electrode materials possess an excellent electrochemical response. It was also found that the anodic peaks shifted to negative and cathodic peaks shifted to positive, which is caused by the inherent resistance of electrode materials.<sup>[38–40]</sup>

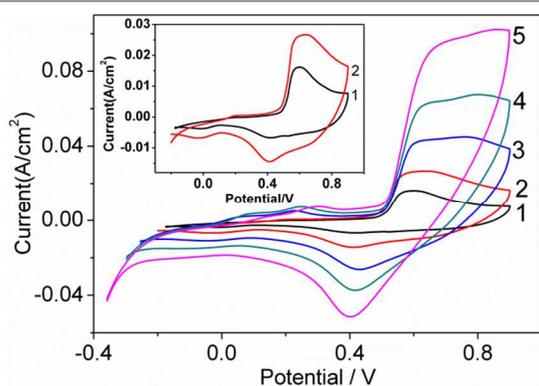


Fig. 4 Cyclic voltammograms of PANI/SA hydrogels in 1M H<sub>2</sub>SO<sub>4</sub> at scan rates of 10 (curve 1), 20 (curve 2), 50 (curve 3), 100 (curve 4) and 200 mV/s (curve 5). All samples were prepared in the presence of 0.4 mol/L An.

Fig. 5a shows the galvanostatic charge/discharge behavior of PANI/SA hydrogels (red curves) at varied current densities (0.5, 1, 2, 5 and 10 A/g). As reference, galvanostatic charge/discharge curves of compressive tablets prepared by xerogels (see experimental section) were also measured (black curves). For the charge/discharge, generally, the larger the current densities, the shorter the time of charge/discharge needed. It was found that the discharge time of PANI/SA hydrogels was obviously longer than that of compressive tablets, implying that PANI/SA hydrogels possess a better capacitance performance in comparison with that of compressive tablets.

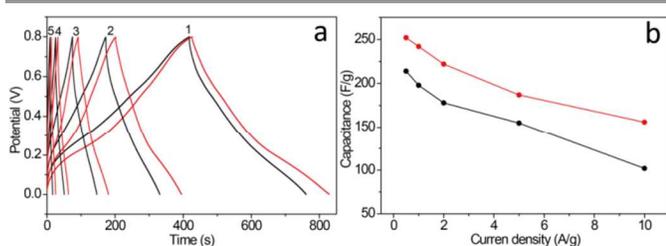


Fig. 5 (Plot a) Galvanostatic charge/discharge curves of PANI/SA hydrogel (red curves) and PANI/SA compressive tablet (black curves) electrodes in 1M H<sub>2</sub>SO<sub>4</sub> at current densities of 0.5 (curves 1), 1 (curves 2), 2 (curves 3), 5 (curves 4) and 10 A/g (curves 5). (Plot b) Values of specific capacitance as a function of current densities. All samples were prepared in the presence of 0.4 mol/L An.

Based on the data of galvanostatic charge/discharge, the specific capacitance of electrode materials can be calculated by the following equation:<sup>[38]</sup>

$$C = \frac{It}{\Delta Vm} \quad (2)$$

where  $C$  is the specific capacitance of the electrode (F/g),  $I$  is current (A),  $t$  is the total time of discharge (s),  $\Delta V$  is 0.8V and  $m$  is the dry weight of the hydrogels in the electrode (g). Fig. 5b shows values of specific capacitance of two types of electrode materials as a function of current densities. Generally, the capacitance of the electrode decreases with an increase of the current density due to the slow diffusion of electrolytic ions when a high current density was employed. In this case, doping and dedoping of PANI in the system is not completed, only part

of the electroactive materials takes part in the process of charge/discharge.<sup>[9]</sup> Thus Faraday capacitance does not completely develop, leading to the low electrode utilization. Under the condition of the same current density, however, the specific capacitance of PANI/SA hydrogels is obviously higher than those of compressive tablets. For example, the specific capacitances of PANI/SA hydrogels and compressive tablets were found to be 252 and 216 F/g, respectively, at a current density of 0.5 A/g. When 10 A/g of current density was employed, the specific capacitances decreased to 156 and 102 F/g, and retained specific capacitances of 62 and 48%, respectively. It is indicative that PANI/SA hydrogels possess a better rate capability in comparison with compressive tablets. As discussed above, this should be attributed to porous 3D nano-fibers network structure as shown in their SEM images. By contrast, the compressive tablets were prepared by using the powder of PANI/SA xerogels under 20 MPa of pressure. Although PANI/SA xerogels still remain porous structure after freeze-dry, the porous structure could be damaged and compressed after subsequent mill to powder and thermo-compression formation. Therefore, the compressive tablets possess comparatively small surface area and pore volume.

Since no adhesive and conducting fillers were employed, as electrode materials, PANI/SA hydrogels with self-supported structure are beneficial for the transfer of electrons and electrolytic ions, resulting in a high electrochemical efficiency of the electrode.<sup>[20]</sup> The results obtained from galvanostatic charge/discharge suggest that PANI/SA hydrogels will possess great potential application as high power density electrode materials.

Fig. 6 shows electrochemical impedance spectra (EIS) of PANI/SA hydrogels (red curve) and compressive tablets (black curve) as electrode materials. The inserted plot is an enlargement of EIS in the area of high frequencies. The EIS of both electrodes in the area of high frequencies shows a typical semicircle, the diameter of this semicircle corresponds to charge-transfer resistance. By contrast, the semicircle diameter of PANI/SA hydrogels was found to be definitely smaller than that of compressive tablets, indicating that PANI/SA hydrogels possess low resistance.<sup>[26]</sup> As mentioned above, it is ascribed to the absence of adhesive and conducting fillers which may induce contact resistance. The continuous 3D nano-fiber structure within PANI/SA hydrogels provides a good charge-transfer pathway. Furthermore, the straight lines in the area of low frequencies correspond to pure capacitance behavior. By contrast, the slope of the straight line for PANI/SA hydrogels is larger than that of a compressive tablet, implying more ideal capacitance behavior.<sup>[18,26]</sup> The results of EIS further indicate that PANI/SA hydrogels could be favorable candidates for electrode materials of supercapacitors.

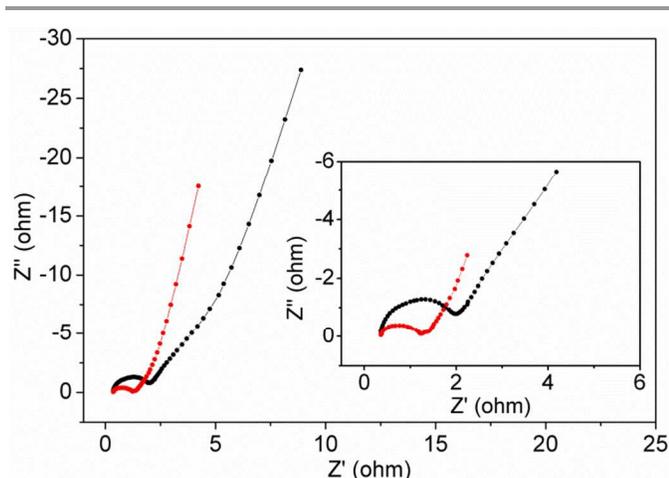


Fig. 6 Impedance spectra of PANI/SA hydrogel (red curve) and PANI/SA compressive tablet (black curve) electrodes. The inset plots show the enlarged region of high frequency. All samples were prepared in the presence of 0.4 mol/L An.

For the polymer electrode materials of supercapacitors, electrochemical stability is an important parameter. In general, conducting hydrogels appear to have poor cycling stabilities because they easily expand and shrink during the charge/discharge. Therefore, their mechanical strength and Faraday capacitance show a tendency to decline after certain cycles of charge/discharge.<sup>[4,25]</sup> As shown in Fig. 7, almost no difference of retained specific capacitances was found between PANI/SA hydrogels (red curve) and compressive tablets (black curve) electrodes after 800 times of cycling. A little difference can be found after 1000 times of cycling, in which, the retained specific capacitances of PANI/SA hydrogels and compressive tablets were found to be 71% and 76%, respectively. The good cycling stability of PANI/SA hydrogels can be attributed to their substantial mechanical strength. As discussed above, the hydrogen bonding interactions within the system and 3D nano-fibers network efficiently overcome the tendencies to expand and to shrink during the process of charge/discharge.

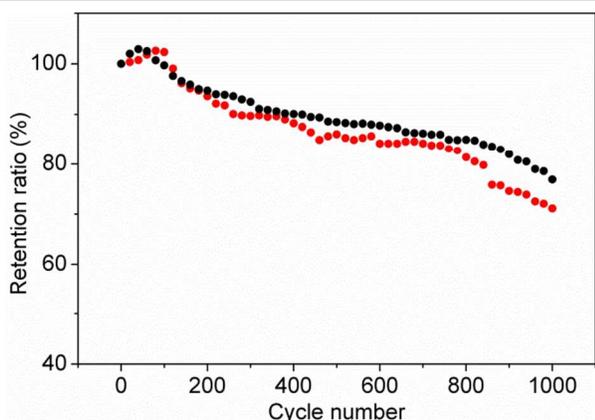


Fig. 7 Cycling stability of PANI/SA hydrogel (red dots) and of the compressive tablet electrodes (black dots) at 2 A/g current density. All samples were prepared in the presence of 0.4 mol/L An.

## 4. Conclusions

In this work, reinforced conducting hydrogels were prepared by in-situ polymerization of aniline in aqueous solutions of sodium alginate. Due to the hydrogen bonding interactions between polyaniline and sodium alginate, both polymer chains are entangled, leading to the formation of a 3D nano-fiber network structure and a consequent relatively high mechanical strength. In comparison with conventional conducting polymer electrodes, the PANI/SA hydrogels are a kind of self-supported materials because of the absence of adhesive and conducting fillers in the system. The study of cyclic voltammetry, galvanostatic charge/discharge, electrochemical impedance spectroscopy and cycling stability indicate that PANI/SA hydrogels show a fast electrochemical responsivity, high specific capacitance and low resistance, and a good cycling stability. The preparation of the present PANI/SA hydrogels provides a novel kind of electrode materials for supercapacitors.

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## Notes and references

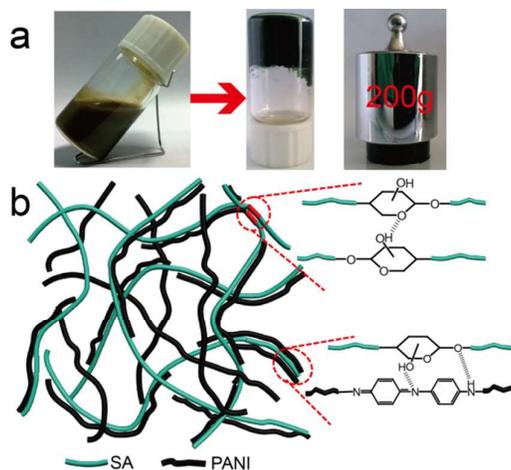
a Key Laboratory for large-format battery materials and systems, Ministry of Education  
 b School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan 430074, China  
 † Electronic Supplementary Information (ESI) available: The characterization of chemical structure of SA, PANI/SA. See DOI: 10.1039/b000000x/

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Graphical Abstract for

**Reinforced conducting hydrogels prepared from in-situ polymerization of aniline in an aqueous solution of sodium alginate**



Reinforce of PANI/SA conducting hydrogels is attributed to interaction of PANI–SA chains and inter/intramolecular hydrogen bonding within the SA chains.