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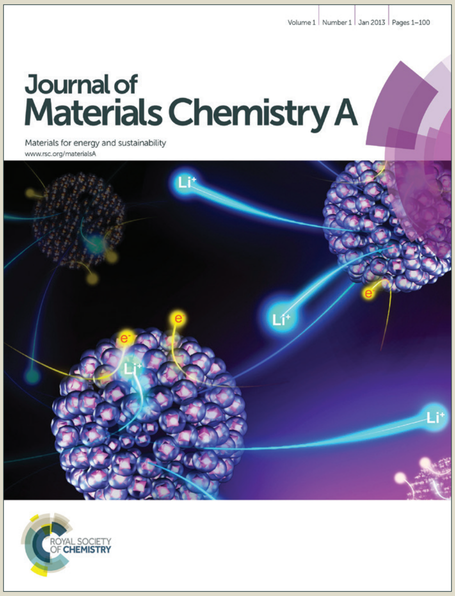

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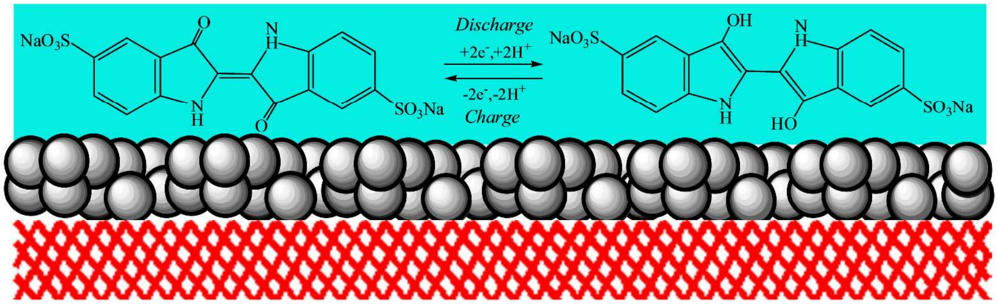

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ARTICLE TYPE

Redox Mediator Doped Gel Polymer as Electrolyte and Separator for High Performance Solid State Supercapacitor

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A stable and effective redox-mediator gel electrolyte has been prepared by doping indigo carmine (IC) into polyvinyl alcohol sulfuric acid polymer system (PVA-H_2SO_4), and a high performance solid state supercapacitor is fabricated by utilizing activated carbon as electrodes and the prepared gel polymer (PVA-H_2SO_4-IC) as electrolyte and separator. The PVA-H_2SO_4-IC gel polymer has excellent bending, compressing and stretching mechanical properties. As expected, the ionic conductivity of the gel polymer electrolyte increased by 188% up to 20.27 mS cm^{-1} while introducing IC as the redox mediator in PVA-H_2SO_4 gel electrolyte. Simultaneously, 112.2% of specific capacitance (382 F g^{-1}) and energy density (13.26 Wh kg^{-1}) are also increased. Furthermore, the fabricated device shows superior charge-discharge stability. After 3000 cycles, its capacitive retention ratio is still as high as 80.3%. This result may be due to the fact that the IC can act as plasticizer and redox mediator, and the supercapacitor combines the double-layer characteristic of carbon-based supercapacitors and the faradaic reactions characteristic of batteries energy-storage processes.

1. Introduction

Supercapacitors also called electrochemical capacitor have been studied as one type of efficient, clean and sustainable candidates for next generation energy conversion and storage, as the concern about global warming and the fossil fuels crisis grows.[1] Compared with electrostatic capacitors or batteries, electrochemistry supercapacitors have several advantages, such as large specific capacitance, high power density, long cycle life and rapid charging-discharging rates. Therefore, much attention has been focused on supercapacitors since they have the capability to meet the requirements of end users in many applications (i.e., hybrid electric vehicles, mobile phones, notebook computers, automatic door and window locks and so on), especially where one needs a high power density and desirable energy density. [2-5] However, to become primary devices for power supplication, the performance for supercapacitor must be improved further for their low energy density.[5,6] Supercapacitors can be classified into three types double layer capacitors (EDLCs), pseudo or redox capacitors and asymmetric or hybrid capacitors on the basis of their charge storage mechanism.[3,7] In electrical EDLCs, the capacitance is related to accumulation of charge as a double layer between the electrode and electrolyte interface via a non-faradaic process. In pseudo or redox capacitors, however, the capacitance comes from a charge transfer reaction between the electrode and electrolyte ions through a fast faradaic reaction and this capacitance is called pseudocapacitance.[8-10] To improve the electric conductivity and electrode specific capacitance of the supercapacitors, these two mechanisms usually work together,[11] namely the third type of supercapacitors which are named as asymmetric or hybrid supercapacitors that can store the energy through combination of electric double layer capacitance and pseudocapacitance.[8]

However, electrolyte, as an important component, plays a fundamental role during charge-discharge process in the three types supercapacitors, and an electrolyte with good electrochemical properties is very significant for an efficient supercapacitor.[12,13] In the last few decades, different kinds of electrolytes, namely aqueous (before 1980s), organic (from 1990s) and ionic liquids (from 2000s), have been used for supercapacitors. [2,3] Santamaría has found redox mediator hybrid electrolyte system that can increase the storage of electrical energy, because it combines two energy-storage processes: the double-layer formation characteristic of carbon-based supercapacitor and the faradaic reactions characteristic of batteries.[14] Some redox mediator or mediators or compounds such as p-phenylenediamine,[15] m-phenylenediamine,[16] hydroquinone,[14,17] KI[18]and $VOSO_4$[19] were introduce into liquid electrolytes to enhance the specific capacitance and energy density of the supercapacitor through their electron transfer redox reactions. However, liquid electrolytes are commonly diminished by certain problems such as electrolyte leakage, corrosion and packing.[13,20] These issues can be skirted by utilizing polymer based electrolytes. Recently, supercapacitor based on gel polymer electrolytes have been explored by several authors, such as PVA-H_3PO_4[21], PVA-H_2SO_4[22], gelatin-acetic acid[23], PAA-KCl[24], PEG-PMMA-EMI-TFSI(1-ethyl-3-methylimidazolium bis(trifluoromethane sulfonyl)imide)[25] and PVA-KOH[26]. However, some of the supercapacitor deliver low capacitance and energy density compared to liquid electrolytes.

The strategy using redox mediator in gel polymers is not well explored so far, and hence, this kind of versatile approach opened up a new avenue to identify the novel redox mediator.[27] Among the various classifications of host polymers, polyvinyl alcohol (PVA) is a good candidate for gel polymers, because of its excellent chemical stability, mechanical property, and nontoxicity.[13,28] on the other hand, the indigo carmine (IC) and its derivatives have been extensively researched in various fields, such as chemical analysis, electroanalysis and food processing because its reversible redox reactions performance. [29, 30] Therefore IC probably can be an appropriate redox additive for gel polymer electrolyte for high performance supercapacitor.

In this work, we made an attempt to incorporate redox mediator IC into PVA host to prepared a gel polymer electrolyte (PVA-H_2SO_4-IC), and a solide-state supercapacitor was assembled using the gel polymer as electrolyte and separator, activated carbon as electrode. It was found that, the introduction of IC not only increases the conductivity, but also promote quick faradaic reactions to imporve the specific capacitance of the carbon-based supercapacitor. The combination of the capacitance of the supercapacitor with that provided by the redox reaction of the electrolyte will lead to an increase in overall capacitance. Thus, the energy density also been imporved.

2. Experimental

2.1. Materials

Polyvinyl alcohol (PVA, Aladdin Co., China, molecular weight 44.05 MW, alcoholysis: 99.8-100%), Sulfuric acid (H_2SO_4, Beijing north fine chemicals co., China), Indigo carmine (IC, Tianjin Kaixin Chemical industry co., China), Activated carbon (AC, Shanghai Sino Tech Investment Management Co., China). All materials were commercially available and employed without further purification.

2.2. Preparation of gel polymer electrolyte

A series of PVA-H_2SO_4-IC gel polymers were obtained using a simple solution-mixing/casting method.[26] Typically, the synthesis procedure for PVA-H_2SO_4-IC gel with different content of IC as follows: First, 1 g PVA was dissolved in 10 mL deionized water with agitation at 80 °C for 2 h to obtain a clear solution. Then, 10 mL aqueous solution containing H_2SO_4 (1.0 g) and IC (0-0.14 g) was added to the above solution to form a homogeneous viscous mixture under constant stirring. Finally, this homogeneous viscous solution was poured into a 90 mm plastic petri dish to frozen at -25 °C for 12 h and thawed at room temperature for 12 h. The freeze-thaw cycles were repeated for 2 times to obtain the PVA-H_2SO_4-IC gel polymer.

For comparison purpose, the gel polymer PVA-H_2SO_4 without IC was also prepared under the same conditions.

2.3. Preparation activated carbon electrode and fabrication solid state supercapacitor

The activated carbon (AC) electrode was prepared as follows: Initially, the activated carbon (16 mg, 80%), acetylene black (2 mg, 10%) and polytetrafluoroethylene (2 mg, 10%) were mixed and dispersed in 0.4 ml of N-methyl-2-pyrrolidone (NMP) to produce a homogenous slurry.[31] Then, the resultant slurry was coated on the stainless steel net (thickness = 0.06 mm) with an area of 1.5 cm^2. After being dried at 60 °C for 24 h, the AC electrodes for supercapacitors were obtained and the mediator material loading was (including carbon black and polytetrafluoroethylene) to be 3 mg on each electrode.

The fabrication details of solid state supercapacitor is shown in Figure 1. The prepared gel electrolyte was coated on the surface of the electrodes and assembled together by face-to-face. The two carbon papers with the electrode material used as current collectors and the polymer gel electrolytes were used as both separator and electrolyte.

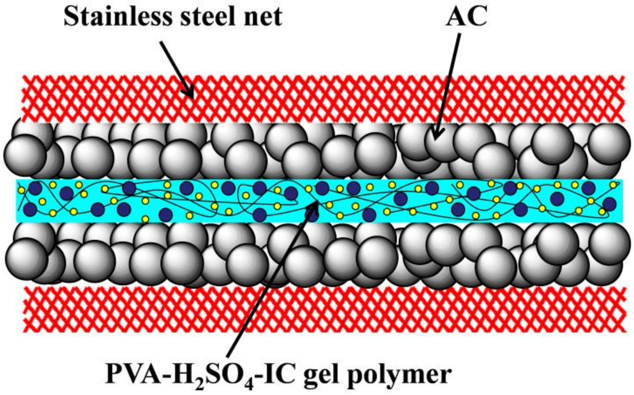

Figure 1. Schematic diagram of fabricated supercapacitor (black line, blue circle and yellow circle correspond to PVA polymer, IC molecule and H_2SO_4 molecule).

2.4. Characterizations

The mechanical performance of the redox mediated gel polymer was tested via bending, compressing and stretching. The gel polymer membrane was cut into a ribbon of 0.8 cm width and 3.0 cm length and the deformation was caused under proper forces.

The electrochemical properties of the supercapacitor were studied through cyclic voltammetry (CV) for potential of 0-1 V and galvanostatic charge-discharge (GCD) test for potential of 0-1 V at different current densities from 0.3 to 2 A g^{-1}. Electrochemical impedance spectroscopy (EIS) was carried out at open circuit potential (OCP) by applying AC potential with 5 mV amplitude in the frequency ranges from 0.1 Hz to 10^5 Hz. Moreover, cycle life was tested at current density of 1 A g^{-1} for 1000 cycles. For comparison, the CV and GCD of the three-electrode system based 1 mol/L H_2SO_4 contains 0.1 g IC were also studied. All the above electrochemical studies were carried out at room temperature using an electrochemical workstation system (CHI 660D, Chenghua, Shanghai, China).

3. Results and discussions

3.1. Mechanical Properties of Gel Polymer Electrolyte

The PVA-H_2SO_4-IC gels polymer have excellent mechanical properties. From Figure 2(a) it can be observed, the gel polymer ribbon can be elastically stretched to more than 2 times length than its original, and from Figure 2(b), a prepared cylinder of

$PVA-H_2SO_4$-IC gel polymer can be greatly compressed. From Figure 2(c) and (d), the gel polymer ribbon is easy twisted into a spiral and bent into a circle without fracturing. The ribbons and the cylinder are able to quickly recover its original length and shape after the external force was removed which exhibit outstanding mechanical properties. This result may be due to the fact that the IC can act as plasticizer, and to help the mechanical properties of the gel polymer.

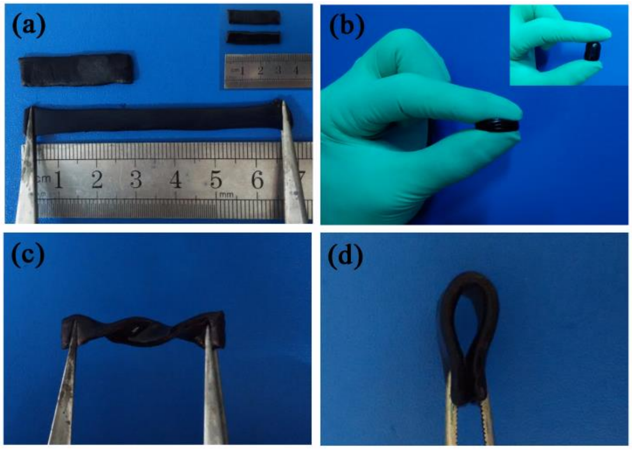

Figure 2. Photographs of flexible $PVA-H_2SO_4$-IC gel polymer.

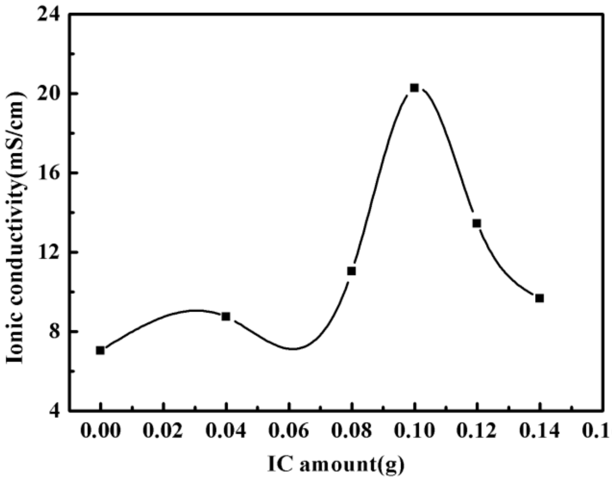

Figure 3. Ionic conductivity of $PVA-H_2SO_4$-IC gel electrolyte with different contents of IC.

3.2. Ionic conductivity of gel polymer

The ionic conductivity of gel polymer electrolyte is crucial to the performance of supercapacitors, and it is determined from impedance spectrum. The ionic conductivity (σ, S cm^{-1}) of the gel polymer can be calculated by the following equation[31]:

$$\sigma = L/(Rb \times S) \qquad (1)$$

where L (cm) is the distance between the two pieces of stainless steel net, S (cm^2) is the contact area of the electrolyte film with stainless steel net during the experiment, and they were manually measured for several times. Rb (ohm), obtained from the curves of EIS, is the bulk resistance. The effect of IC amount on the ionic conductivity of gel polymer electrolyte is shown in Figure 3. As can be seen, the ionic conductivity of the gel polymer electrolyte increased with an increase in the amount of IC, and attained the maximum 20.27 mS cm^{-1} at the amount of IC is 0.1 g, then decreases gradually with the increase of IC amount, which means that the ionic conductivity of the gel polymer electrolyte can be improved with the appropriate doping amount of IC. This result may be due to the fact that the IC can act as redox mediator in the gel polymer, when the IC amount is less, such as less than 0.1 g, IC functions as redox mediator cannot realize well, and the conductivity of the gel polymer is smaller. However, when the IC amount is more than 0.1 g, it will lead to the aggregation of free ions and the crystallization of IC in $PVA-H_2SO_4$ system, which decreases the ionic conductivity of the gel polymer[32]. Therefore, 0.1 g IC is optimal content in $PVA-H_2SO_4$ gel polymer.

3.3. Cyclic voltammetry measurements

Cyclic voltammetry for the supercapacitors with $PVA-H_2SO_4$, $PVA-H_2SO_4$-IC gel polymer, and its liquid electrolyte without PVA at scan rate of 10 mV s^{-1} in the potential window range 0 to 1 V are presented in Figure 4. The CV curves of the supercapacitor with $PVA-H_2SO_4$ polymer shows an almost rectangular behavior without visible redox peaks that infers the capacitance is stored by an accumulation of ions between the electrolyte|electrode interfaces which is known as electric double layer capacitance.[33]

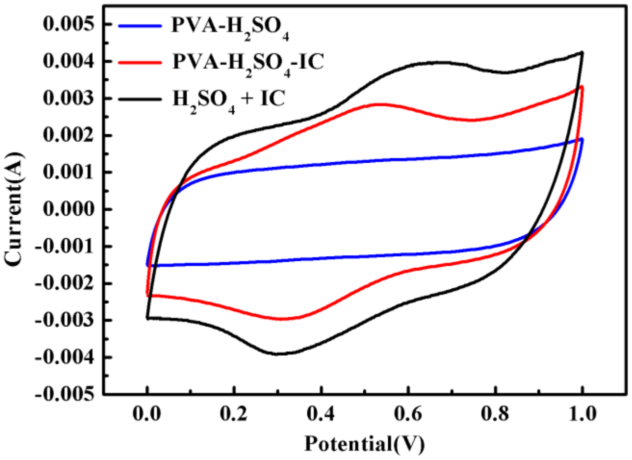

Figure 4. CV curves for the supercapacitors with $PVA-H_2SO_4$, $PVA-H_2SO_4$-IC gel polymer, and liquid electrolyte without PVA at scan rate of 10 mV s^{-1}.

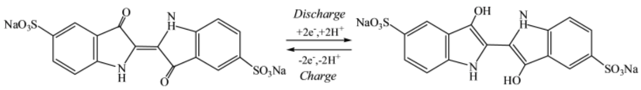

Figure 5. Representation of the redox processes in the electrode|electrolyte system.

However, the supercapacitor that utilized $PVA-H_2SO_4$-IC gel polymer as electrolyte and separator shows a rectangular CV curve with a pair of broad and symmetric redox peaks centered at around 0.4 V, as well as the supercapacitor based H_2SO_4-IC liquid electrolyte. From Figure 4, the CV curve area of the supercapacitor based H_2SO_4-IC liquid electrolyte is larger than that of the supercapacitor based $PVA-H_2SO_4$-IC gel polymer on the basis of equal quality of IC for PVA big molecular which makes the transfer space of ions decrease. The appearance of the redox peaks are attributed to the introduction of IC in the electrolytes system that causes a redox processes on the electrolyte|electrode interface. The probably processes of redox reactions are presented in Figure 5.[29]

3.4. Galvanostatic charge-discharge measurements

The resistance and capacitance of the supercapacitor with PVA-H_2SO_4, PVA-H_2SO_4-IC gel polymer, and H_2SO_4-IC liquid electrolyte evaluated by galvanostatic charge-discharge tests are shown in Figure 6. Here, all curves of the supercapacitors show good coulombic efficiency[34] as that nearly equivalent charge time and discharge time. Besides, the second in two potential ranges exhibits a smaller iR_{drop}. The equivalent series resistance (ESR) are calculated as 37.22, 24.44, and 37.22 Ω cm^2, respectively, which enhances the power output of supercapacitor in principle.[33] The ESR can be calculated by the following equation[35]:

$$ESR = iR_{drop} / (2 \times I) \qquad (2)$$

where I (A) is the discharge current and iR_{drop} (V) is defined as the electrical potential difference between the two ends of a conducting phase during charging-discharging. The ESR is the sum of the intrinsic resistance of all materials and the contact resistance between them. The reduction of that probably because of: (a) the improvement of the ionic conductivity of the gel polymer electrolytes; and (b) the enhanced conjunction between the gel polymer electrolyte and electrodes via electron transfer between the mediators.[36] Compared with the linear charge-discharge behavior of the supercapacitor with PVA-H_2SO_4 gel polymer and H_2SO_4-IC liquid electrolyte, the supercapacitor with PVA-H_2SO_4-IC gel polymer displays a nonlinear charge-discharge behavior after adding IC to PVA-H_2SO_4 gel polymer system. The inclined parts in the charging potential and the discharging potential indicate that redox reactions are superimposed in the charge-discharge process,[37] which are consistent with the cyclic voltammograms in Figure 4. Such characteristics represent a deviation from the ideal triangular shape and are known to be typical effects of pseudocapacitive contributions. Besides, the charge-discharge time of the supercapacitor with PVA-H_2SO_4-IC gel electrolyte is much longer than that of the supercapacitor with PVA-H_2SO_4 gel electrolyte, revealing great improvement by IC on the electrochemical performances of the supercapacitor. Charge-discharge time for the supercapacitors with PVA-H_2SO_4-IC and H_2SO_4-IC liquid electrolyte are larger than PVA-H_2SO_4 electrolyte, the reasons may be the additional contribution of reversible redox reactions of IC and the decrease of transfer space which has been interpreted aforementioned.

The charge-discharge curves and the specific capacitance of the supercapacitors with PVA-H_2SO_4 and PVA-H_2SO_4-IC gel electrolytes at various current densities of 0.3, 0.5, 0.8, 1 and 2 A g^{-1} are displayed in Figure 7(a) and (b). The specific capacitance (C, F g^{-1}) of the supercapacitor and electrode specific capacitance (C_s, F g^{-1}) were evaluated from charge-discharge curves according to the following equation[33]:

$$C = (I \times \Delta t)/(\Delta V \times m_{ac}) \qquad (3)$$

$$C_s = 4 \times C \qquad (4)$$

where m_{ac} (g) is the weight of mediator material (including the acetylene black and the binder), Δt (s) is the discharge time, ΔV (V) is the operating voltage window of the supercapacitor. According to the above equation, the gravimetric capacitance of

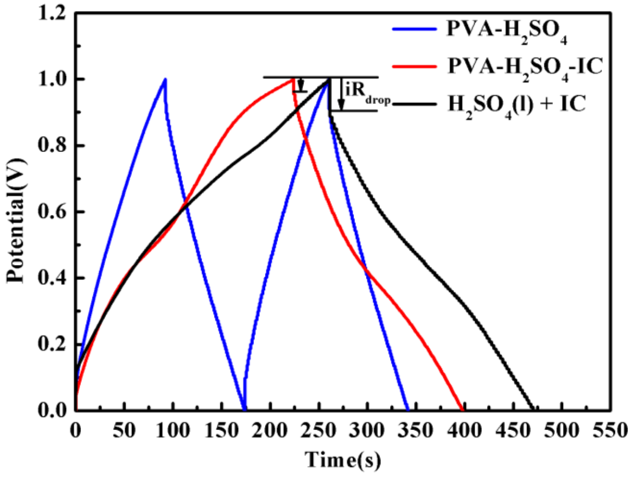

Figure 6. Galvanostatic charge-discharge curves of supercapacitors with PVA-H_2SO_4, PVA-H_2SO_4-IC gel polymer and liquid electrolyte without PVA at a current density of 0.5 A g^{-1}.

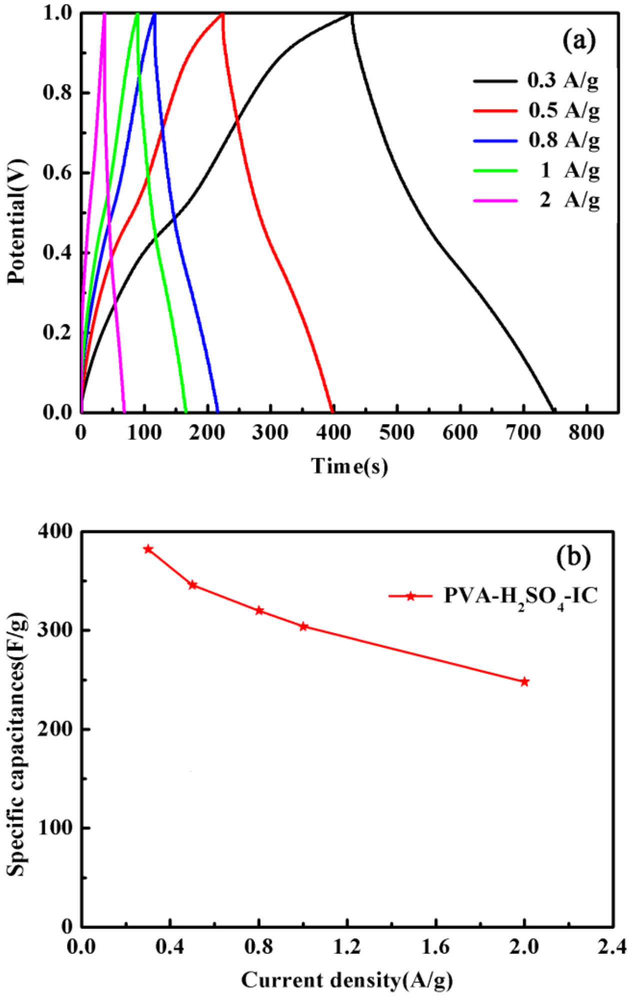

Figure 7. (a) Galvanostatic charge-discharge curves of supercapacitors with PVA-H_2SO_4-IC gel polymer at various current densities; (b) C_s of the supercapacitors with PVA-H_2SO_4-IC gel electrolyte at various current densities.

the supercapacitor with PVA-H_2SO_4-IC gel polymer is calculated as high as 382 F g^{-1} at a current density of 0.3 A g^{-1}. Even though the current density is as high as 2 A g^{-1}, the specific capacitance still maintains at a high value of about 248 F g^{-1}. However, the specific capacitance of the supercapacitor with PVA-H_2SO_4 gel polymer is only 180 F g^{-1} (0.3 A g^{-1}). It indicates clearly that the supercapacitor with PVA-H_2SO_4-IC gel polymer electrolyte shows superior electrochemical behavior.

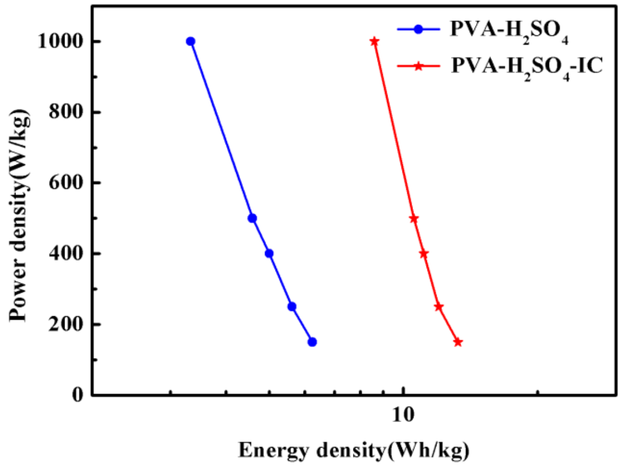

Figure 8. Ragone plots of the supercapacitors with PVA-H_2SO_4 and PVA-H_2SO_4-IC gel polymer electrolytes.

The Ragone plots for the supercapacitors with PVA-H_2SO_4 and PVA-H_2SO_4-IC gel polymer are shown in Figure 8. The energy and power densities are derived from galvanostatic charge-discharge at various current densities. The energy density (E) and power density (P) are evaluated according to the following equations[11]:

$$E = (1/2)\,CV^2 \qquad (5)$$

$$P = E/\Delta t \qquad (6)$$

As seen from the Ragone plots, the energy density of the supercapacitor with PVA-H_2SO_4-IC gel polymer can reach 13.26 Wh kg^{-1} at a power density of 150 kW kg^{-1}, and still remains 8.6 Wh kg^{-1} at a power density of 1000 kW kg^{-1}, which exhibited a large power range that can be obtained while maintaining a relatively high energy density. While the energy density and power density for the supercapacitor with PVA-H_2SO_4 gel polymer is only 6.2 Wh kg^{-1} and 3.3 kW kg^{-1}, respectively. The results illustrate that the supercapacitor with PVA-H_2SO_4-IC gel polymer have excellent electrochemical properties of high energy density and power output. Moreover, it is worth mentioning that the energy density of the supercapacitor with PVA-H_2SO_4-IC gel polymer is much higher than those of the current supercapacitors, which are usually lower than 10 Wh kg^{-1}. [12,33,35]

3.5. EIS technique

The electrochemical conductive and kinetic properties of PVA-H_2SO_4 and PVA-H_2SO_4-IC gel polymer were tested using EIS at open circuit potential in the frequency range from 100 mHz to 100 kHz. The corresponding Nyquist impedance plots are shown in Figure 9. As we can see, the two gel polymers exhibit ideal electrochemical capacitance behavior, i.e., a small depressed semicircle at higher frequency[38], a small ~45° inclined line at middle frequency which is known as diffusive or warburg resistance of ions with electrode[39] and imaginary parts of impedance at low frequency region are nearly linear[40,41]. In addition, the supercapacitor with PVA-H_2SO_4-IC polymer not only has lower inner resistance (R_i, 8.346 Ω cm^2) calculated from the point of intersecting with the x-axis in the range of high frequency, but also possesses smaller interfacial charge transfer resistance (R_{ct}, 2.843 Ω cm^2), counting from the span of the single semicircle along the x-axis from high to low frequency region[42]. In addition, Rb, the most important data used in the calculation formula of ionic conductivity, is obtained by the following method: draw a tangent line going along the slope of EIS curves in the range of low frequency until intersect with x-axis. The point of intersection is the data we need. Clearly, the performances of the supercapacitor are heightened remarkably after introducing the redox mediator (IC) into PVA-H_2SO_4 gel polymer.

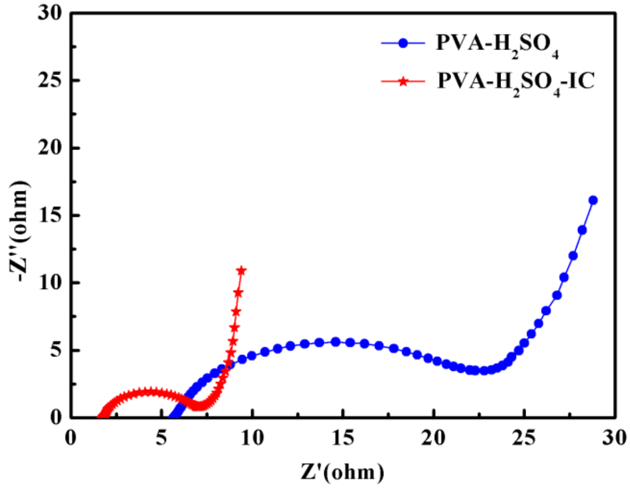

Figure 9. EIS of supercapacitors with PVA-H_2SO_4 and PVA-H_2SO_4-IC gel polymer electrolytes.

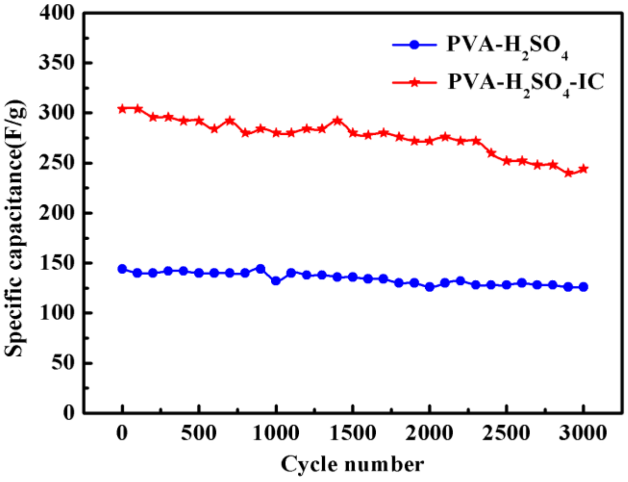

Figure 10. Cycle-life of the supercapacitors with PVA-H_2SO_4 and PVA-H_2SO_4-IC electrolytes in the long-term cycle.

3.6. Cycle-life testing

For practical applications, a supercapacitor should have extensive cycle stability. The cycling stability for the supercapacitors with PVA-H_2SO_4 and PVA-H_2SO_4-IC gel polymer was carried out by continuous charge-discharge experiments at a high current density 1 A g^{-1} for 3000 cycles, and results are shown in Figure 10. The supercapacitor with PVA-H_2SO_4-IC gel polymer exhibit good cyclic stability, after 3000 charge-discharge cycles, it can still retain a high electrode specific capacitance of 244 F g^{-1}, about 80.3% of the initial capacitance (304 F g^{-1}). This result indicates that PVA-H_2SO_4-IC gel polymer is stable, and it is concluded that the PVA-H_2SO_4-IC gel polymer can be considered as promising electrolyte in the application of high performance energy-storage devices.

4. Conclusions

In summary, we present a simple and cost effective method for enhancing the electrochemical performance of supercapacitors by introducing indigo carmine as a redox mediator into electrolyte. The supercapacitor with this redox-mediated electrolyte exhibits excellent electrochemical performance, such as, high ionic conductivity of 20.27 mS cm^{-1}, high electrode specific capacitance of 382 F g^{-1}, high energy density of 13.26 Wh kg^{-1}, and excellent cycle life that maintains 80.3% of the initial capacitance values after 3000 cycles. It can be inferred that the supercapacitor can be regarded as a novel hybrid supercapacitor that combines two energy-storage processes: the double-layer characteristic of carbon-based supercapacitors and the faradaic reactions characteristic of batteries. The simple preparation procedure, low cost and high performance for this novel idea and electrolyte can accelerate the development of supercapacitors and be applied in other electrochemical fields.

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Notes and references

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