A novel redox-mediated gel polymer electrolyte for high-performance supercapacitor

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ABSTRACT

A supercapacitor based on a novel redox-mediated gel polymer electrolyte (PVA–H_2SO_4–P–benzenediol) and activated carbon electrodes is assembled. The electrochemical properties of the supercapacitor are evaluated by cyclic voltammetry, galvanostatic charge–discharge, and electrochemical impedance spectroscopy techniques. It is found that the supercapacitor exhibits large specific capacitance (474.29 F g^{-1}), high energy density (11.31 W h kg^{-1}), and excellent cyclical stability. The good performance for the supercapacitor is due to the capacity-storage mechanism combination of the electrical double layer capacitance and Faradaic pseudocapacitance by p-benzenediol/p-benzoquinone in the electrolyte.

1. Introduction

The growing concerns about global warming and the fossil fuels crisis have stimulated intensive development of more sustainable energy economy. Supercapacitor, a new type of reversible electrochemical energy storage device, also known as electric double-layer capacitors, ultracapacitors, or electrochemical capacitors [1], are very attractive and arouses wide research due to their fast energy delivery, short charging time, high power capability, long durability (>10^5 cycles), and environment-friendly features [2–5].

In an effort to develop high-performance supercapacitors to meet the high-safety needs for practical application, gel polymer electrolytes [6], such as polyvinyl alcohol (PVA)–KOH [7], cellulose–chitin–AMImBr–H_2SO_4 [8], PVA–H_2SO_4 [9], polymethyl methacrylate (PMMA)–EC–PC–TEAClO$_4$ [10] and polyacrylate (PAA)–KCl [11], have been developed rapidly because they can provide high reliability without electrolyte leakage as well as thin-form and separator-free devices. However, the practical application of gel polymer electrolytes is limited. The difficulty is mainly due to their relative low ionic conductivity, which is usually lower than 10 mS cm^{-1} [12].

Recently, an innovative redox-mediated strategy for supercapacitor was reported. The quick reversible redox reaction introduced by redox mediator can efficiently enhance the ionic conductivity and bring pseudocapacitance. Iodide and iodine (I^-/I_2) is a classical redox couple mediator applied in dye-sensitized solar cells [13,14]. Yin et al. [15,16] added them into poly(ethylene oxide)/lithium aluminate and activated carbon composite for supercapacitors. It is interesting that the electrode specific capacitance of the supercapacitor is increased by 27-folds (150 F g^{-1}) compared to the system without I^-/I_2. However, the complex preparation procedure baffles its applications. We added the I^-/I_2 redox couple in the PVA–KOH gel electrolyte [17], which simplified the preparation procedure and effectively enhanced the performance of the supercapacitors. The specific capacitance of the supercapacitor is 236.90 F g^{-1}, increasing by 74.28% compared to the system without KI. Good performance for this electrolyte and supercapacitor inspire us to search for a more stable and efficient redox mediator for high-performance supercapacitors.

The stable and reversible redox reactions of p-benzenediol (PB) and its derivatives have been extensively researched in various fields, such as biomedicine [18], electroanalysis [19], and sensors [20], and in different media [21,22]. But, only few reports have emerged on the PB in gel polymer electrolyte used in supercapacitor.

Herein, a redox-mediated gel polymer electrolyte was prepared by adding PB to PVA–H_2SO_4 gel polymer electrolyte, and it was assembled with activated carbon electrodes to form a supercapacitor. The electrochemical properties and pseudocapacitive effect for the supercapacitor were investigated by cyclic voltammetry, galvanostatic charge–discharge, and electrochemical impedance spectroscopy techniques.

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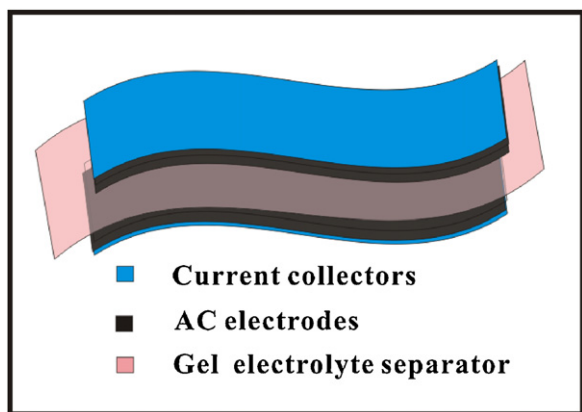*E-mail address:* jhwu@hqu.edu.cn (J. Wu).

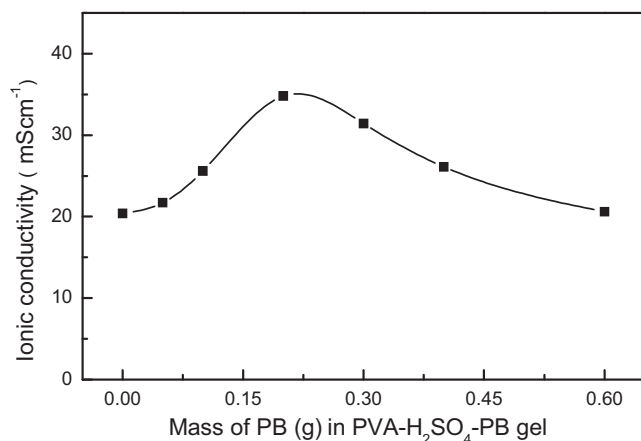**Fig. 1.** Schematic representation for the supercapacitor model.

Fig. 2. Ionic conductivity of PVA–H_2SO_4–PB gel electrolyte with different amounts of PB (PVA = 1 g, H_2SO_4 = 0.01 mol).

2. Experimental

2.1. Materials

Activated carbon (AC) was from Fuzhou Yihuan Co., Ltd. Polytetrafluoroethylene (PTFE), graphite, H_2SO_4, N-methyl-2-pyrrolidone (NMP), p-benzenediol (PB), and polyvinyl alcohol (PVA, average molecular weight 88,000, purity 87–89%) were purchased from Sinopharm Chemical Reagent Co., Ltd. All materials were commercially available and employed without further purification.

2.2. Preparation of gel polymer electrolyte

A gel polymer electrolyte was prepared in solution-casting method by modifying the procedure described in the previous literature [7]. 1 g of PVA was dissolved in deionized water with agitation at 50 °C for 4 h, until a homogeneous and low-viscous solution was formed. And then H_2SO_4 (0.01 mol) was added to the solution with a constant stirring rate. After 1 h, PB (0–0.6 g) was mixed into the above solution. Finally, the solution was evaporated at room temperature to produce a gel polymer electrolyte.

2.3. Preparation of activated carbon electrode

The electrode was composed of AC, graphite and PTFE aqueous solution with weight ratio of 85:10:5 [23]. At room temperature, AC and graphite were added to PTFE/NMP mixture and was stirred to form carbon paste, the carbon paste was pressed by Decal method to form a thin sheet. Under a pressure of 10 MPa, the thin sheet of 6 mg was pressed on a stainless steel net. After being dried at 100 °C for 24 h in a vacuum, an AC electrode was obtained.

2.4. Fabrication of supercapacitor

A two-electrode test supercapacitor was fabricated with a pair of the AC electrodes and the gel polymer electrolyte. The model of supercapacitor was shown in Fig. 1. The gel polymer electrolyte simultaneously served as separator and electrolyte.

2.5. Characterization

The ionic conductivity of the gel polymer electrolyte was measured by a conductivity meter (DDSJ-308A, Shanghai REX Instrument Factory). Electrochemical testing for supercapacitor was performed on an electrochemical workstation system (CHI 660C, Shanghai Chen Hua Co., Ltd) under ambient conditions. The electrochemical impedance spectroscopy (EIS) measurements were evaluated with the frequency ranging from 10 mHz to 100 kHz with a bias voltage of 0, 0.5, and 1 V. The cyclic voltammetry (CV) measurements were done in the potential range of −0.5 to 1 V at various scan rates from 5 to 35 mV s^{-1}. The galvanostatic charge–discharge (GCD) tests were performed between cell voltages of −0.5 to 1 V at a different current density. The supercapacitor specific capacitance (C, F g^{-1}) and electrode specific capacitance (C_s, F g^{-1}) were evaluated from charge–discharge curves according to the following equation [24]:

$$C = \frac{I \times \Delta t}{\Delta V \times m_{ac}} \qquad (1)$$
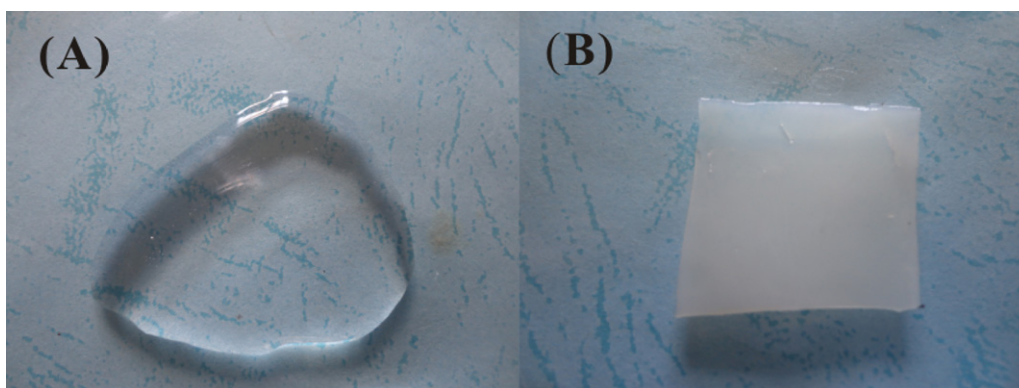
$$C_s = 4 \times C \qquad (2)$$

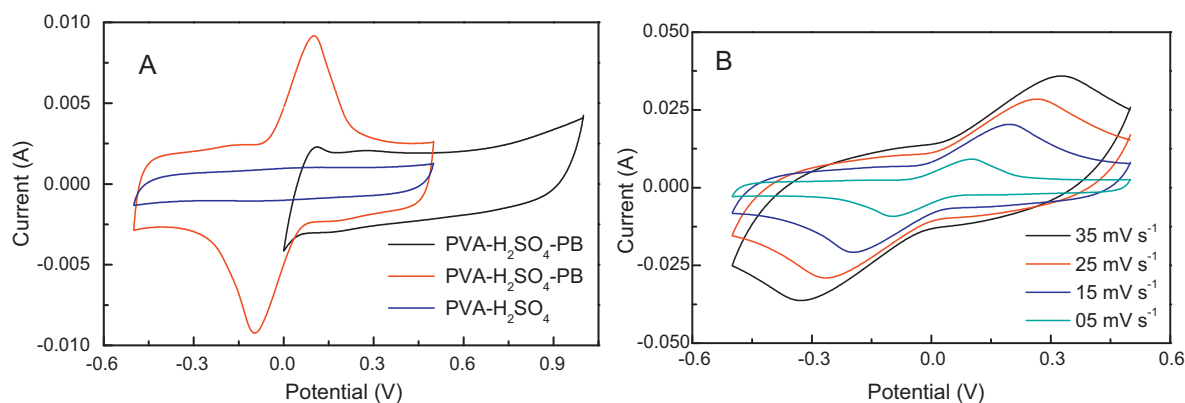**Fig. 3.** The appearance of the PVA–H_2SO_4 electrolytes with 0 g and 0.2 g PB.

Fig. 4. (A) CV curves for the supercapacitors with PVA–H_2SO_4 and PVA–H_2SO_4–PB gel electrolytes at scan rate of $5\,mV\,s^{-1}$. (B) CV curves for the supercapacitor with PVA–H_2SO_4–PB gel electrolyte at different scan rates from $5\,mV\,s^{-1}$ to $35\,mV\,s^{-1}$.

Energy density (E, $W\,h\,kg^{-1}$), equivalent series resistance (ESR, Ω) and power density (P, $kW\,kg^{-1}$) of the supercapacitor were obtained from the following equations [24,25]:

$$E = \frac{C \times \Delta V^2}{2} \times \frac{1000}{3600} \tag{3}$$

$$ESR = \frac{iR_{drop}}{2 \times I} \tag{4}$$

$$P = \frac{I \times \Delta V}{2 \times m_{ac}} \times 1000 \tag{5}$$

where I (A) is the discharge current, m_{ac} (g) is the weight of active material (including the binder and the graphite), Δt (S) is the discharge time, $\Delta V(V)$ represents the voltage change after a full charge or discharge, and iR_{drop} (V) is defined as the electrical potential difference between the two ends of a conducting phase during charging–discharging.

3. Results and discussion

3.1. The conductivity of gel polymer electrolytes

Fig. 2 shows the effect of the amount of PB on ionic conductivity of the gel polymer electrolyte. When the amount of PB is less than 0.05 g, the increase of the ionic conductivity is not obvious. With the increase of PB from 0.05 to 0.2 g, the ionic conductivity rises quickly and reaches the highest value of $34.8\,mS\,cm^{-1}$ with the PB amount of 0.2 g. Beyond the amount of 0.2 g, the ionic conductivity gradually decreases with the increase of the amount of PB. The PB can act as plasticizer and redox shuttle in the electrolyte, when the PB amount is less, such as less than 0.05 g, PB function as redox shuttle cannot realized well, and the conductivity of the electrolyte is smaller. When the amount of PB increase to 0.20 g, the PB shows the plasticizer and redox shuttle functions, the electrolyte becomes quasi-solid state (Fig. 3) accompanied by the highest ionic conductivity. But, higher PB amount will lead to the aggregation of free ions and the crystallization of PB in PVA system, which decreases the ionic conductivity of the gel electrolyte [26]. Therefore, 0.2 g of PB was chosen to an optimal PB amount.

3.2. CV measurements

The CV curves (Fig. 4A) of the supercapacitor with PVA–H_2SO_4 gel electrolyte shows near parallelogram shape approximated to the ideal situation of electrical double layer capacitor, i.e., there is no visible redox peak from a Faradic current over the potential region.

When the PB is added to the PVA–H_2SO_4 electrolyte, a pair of broad and symmetric redox peaks (these peaks are centered at −0.1 and 0.1 V and corresponding to the oxidation and reduction of PB and benzoquinone, respectively) appears in CV curves from −0.5 to 0.5 V. The probably processes of redox reactions are presented in Fig. 5 [27,19]. But, when the potential range is changed to common potential range (0–1 V) in aqueous system [27], the CV curves of the supercapacitor with PVA–H_2SO_4–PB gel electrolyte show only a weak reductive peak at 0.1 V, which is due to that the redox reaction cannot happen in this potential window. As we known, the redox process at the electrolyte|electrode interface can give rise to pseudocapacitance for the electrode, the appearance of bumps of two CV curves of the supercapacitor with PVA–H_2SO_4–PB electrolyte reveals that the capacitive contribution due to Faradaic processes. From the above discussion, it can be inferred that the capacitance values for the supercapacitor with PVA–H_2SO_4–PB electrolyte should be the sum of the double layer capacitance and the Faradaic pseudocapacitance, since charging of the double layer is accompanied with the redox reactions, and both processes work in parallel [28].

Fig. 4B shows the CV curves for the supercapacitor with PVA–H_2SO_4–PB gel electrolyte at different scan rates from 5 to $35\,mV\,s^{-1}$. The supercapacitor shows pronounced current response over the potential window with the reductive peaks shifting positively and the oxidative peaks shifting negatively. The current response of activated carbon electrode increases with peak shifting, which is attributed to the pseudocapacitance of redox processes
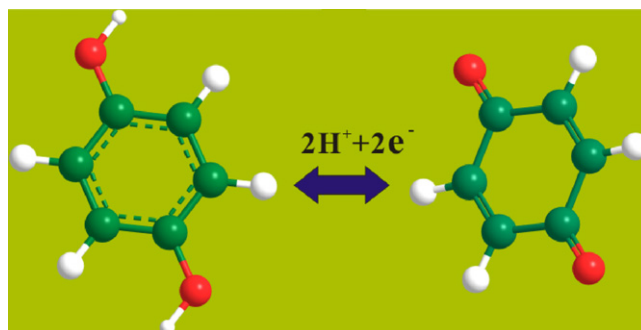

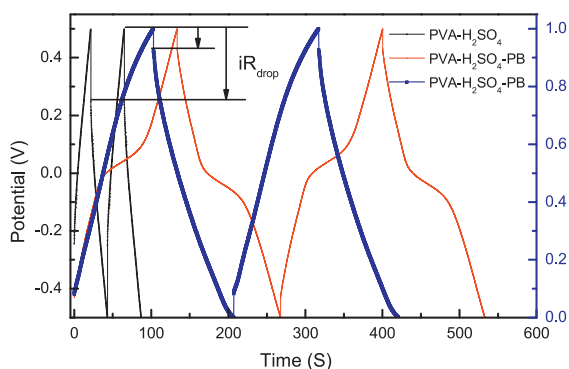**Fig. 5.** Representation of the redox processes in the electrode|electrolyte system.

Fig. 6. GCD curves for the supercapacitors with PVA–H$_2$SO$_4$ and PVA–H$_2$SO$_4$–PB gel electrolytes, charge–discharge current density at 0.83 A g^{-1}.

at the electrolyte|electrode interface through the p-benzenediol/p-benzoquinone reaction.

3.3. GCD tests

The resistance and capacitance of the supercapacitors with PVA–H$_2$SO$_4$ and PVA–H$_2$SO$_4$–PB gel electrolytes were evaluated by GCD tests and shown in Fig. 6. The supercapacitors with PVA–H$_2$SO$_4$–PB gel electrolyte in two potential ranges exhibit a smaller iR_{drop} than the supercapacitor with PVA–H$_2$SO$_4$ gel electrolyte, and the ESR are calculated as 2.45 and 8.64 Ω cm^2, respectively. It is due to the PVA–H$_2$SO$_4$–PB gel electrolyte has higher ionic conductivity than the PVA–H$_2$SO$_4$ gel electrolyte shown in Fig. 2.

From the charge–discharge curves (red) detected in the potential range of −0.5 to 0.5 V, the supercapacitor with PVA–H$_2$SO$_4$–PB electrolyte exhibits nonlinear charge–discharge behavior. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.) The inclined parts in the charging potential from 0 to 0.1 V and the discharging potential from 0 to −0.1 V indicate that redox reactions are superimposed in the charge–discharge process, which are consistent with the cyclic voltammograms in Fig. 4. But in the potential range of 0–1 V, the charge–discharge curves (blue) is nearly linear symmetry expect a little bump in the terminal of discharge line, which is due to no redox reaction happened in the potential window of 0–1 V. Because of these superimposed redox reactions, the charge–discharge time of the supercapacitor with PVA–H$_2$SO$_4$–PB electrolyte in two potential ranges are longer than that of the supercapacitor with PVA–H$_2$SO$_4$ electrolyte.

According to Eq. (2), the C_s for the supercapacitors based on electrolyte PVA–H$_2$SO$_4$–PB and PVA–H$_2$SO$_4$ gel electrolytes were calculated to be 474.29 F g^{-1} (−0.5 to 0.5 V), 374.20 F g^{-1} (0 to 1 V), and 129.29 F g^{-1} (−0.5 to 0.5 V), respectively, at the current density of 0.83 A g^{-1}. Obviously, the C_s of the supercapacitors with PVA–H$_2$SO$_4$–PB electrolyte are larger than that of the supercapacitor with PVA–H$_2$SO$_4$ gel electrolyte. It is concluded that the redox mediator can greatly improve the capacitive property of the supercapacitor.

The capacitance values and retention ratio of activated carbon electrode are shown in Fig. 7. When in the potential range of −0.5 to 0.5 V, the supercapacitor with PVA–H$_2$SO$_4$–PB gel electrolyte exhibits the highest C_s of values at scan rates of 0.83, 1.67, 2.5, 4.17 and 8.33 A g^{-1}, which are counted to be 474.29, 464.29, 460.90, 439.59, and 398.95 F g^{-1}, respectively. For the potential range of 0 to 1 V, the C_s are calculated to be 374.20, 331.29, 318.99, 309.16, and 296.36 F g^{-1}, respectively. Similarly, in the potential range of −0.5 to 0.5 V, the C_s for the supercapacitor with PVA–H$_2$SO$_4$ gel electrolyte at scan rates of 0.83, 1.67 and 2.5 A g^{-1} are 129.29, 106.63
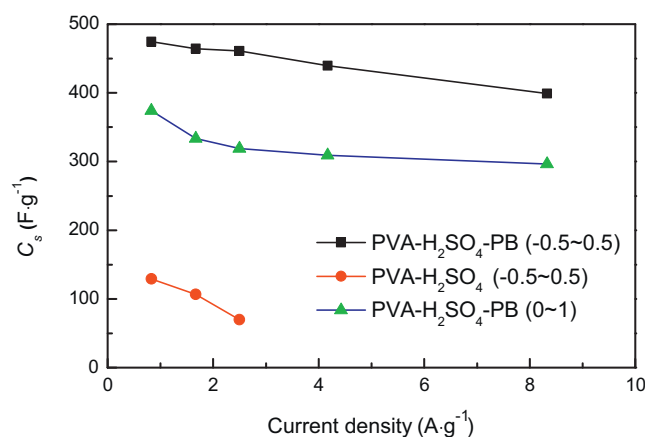

Fig. 7. C_s of the supercapacitors with PVA–H$_2$SO$_4$ and PVA–H$_2$SO$_4$–PB electrolytes at different charge–discharge current densities.
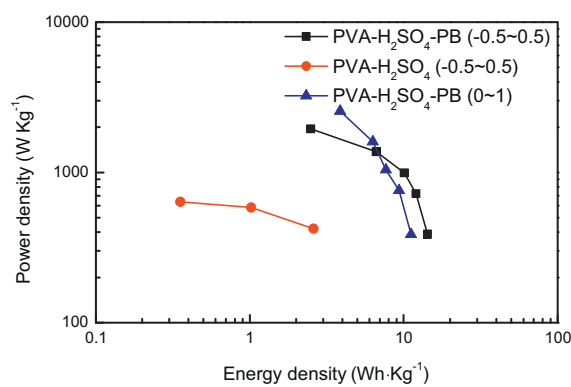

Fig. 8. Ragone plots related to energy and power densities of the supercapacitors with PVA–H$_2$SO$_4$ and PVA–H$_2$SO$_4$–PB gel electrolytes.

and 69.84 F g^{-1}, respectively. The decrease in C_s of the supercapacitor based on PVA–H$_2$SO$_4$–PB gel electrolyte with increasing current density is significantly less than that of the supercapacitor with the PVA–H$_2$SO$_4$ gel electrolyte. It suggests that the supercapacitor with PVA–H$_2$SO$_4$–PB gel electrolyte has a better rate behavior compared to the supercapacitor with PVA–H$_2$SO$_4$ gel electrolyte. The better performances may be due to the quicker ions diffusion rate and more adequately electrode|electrolyte interfacial contact, which are enhanced by the redox reaction of p-benzenediol/p-benzoquinone during charge–discharge process.
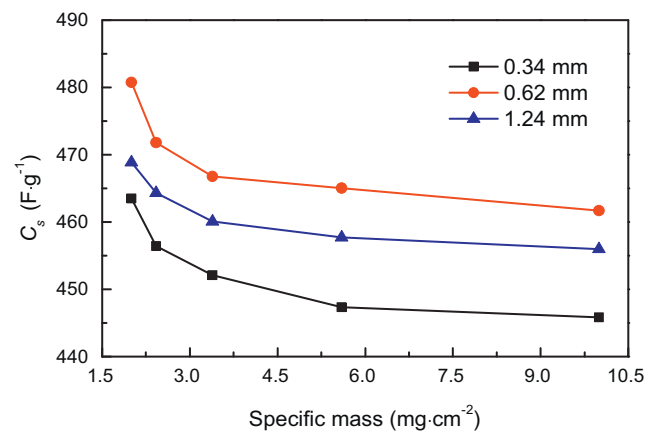

Fig. 9. C_s of the supercapacitors with various electrodes and different electrolyte thicknesses.
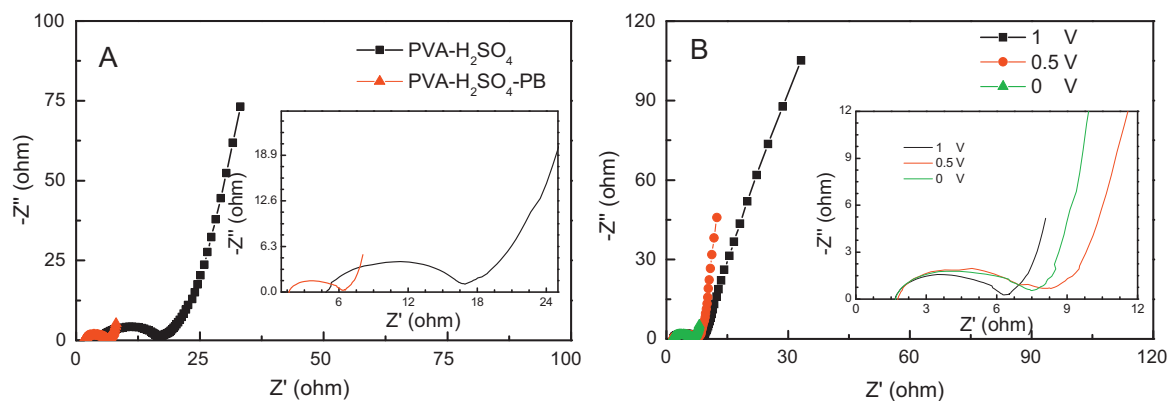
Fig. 10. (A) EIS of supercapacitors with PVA–H_2SO_4 and PVA–H_2SO_4–PB gel electrolytes, the close-up view of the left plot in high-frequency region. (B) EIS at 0, 0.5, and 1 V bias voltage on the supercapacitor with PVA–H_2SO_4–PB electrolyte, the close-up view of the left plot in high-frequency region.

The Ragone plots showing the dependence between power output and energy density are displayed in Fig. 8. The energy density and power density were derived from GCD curves by Eqs. (3) and (5) at various scan rates. The supercapacitor with PVA–H_2SO_4–PB gel electrolyte has a higher energy and power density than the supercapacitor with PVA–H_2SO_4 gel electrolyte does. Energy density and power density of the supercapacitor with PVA–H_2SO_4–PB gel electrolyte in both of potential range are about 10 W h kg^{-1} and 1000 W kg^{-1}, respectively, which are much superior to that the supercapacitor with PVA–H_2SO_4 gel electrolyte, the latter represents a normal level [29].

In order to research the influence of the content of carbon in the electrode and the thickness of electrolyte on the performance of the supercapacitor, the supercapacitors based on the electrodes with different active carbon contents (specific mass, active carbon content in unit electrode area, mg cm^{-2}) and the PVA–H_2SO_4–PB electrolytes with different thicknesses were assembled, the C_s of these supercapacitors were measured and shown in Fig. 9. The C_s of the supercapacitors has the similar tendency, which decreases with increasing specific mass from 2.0 to 10.0 mg cm^{-2}. This tendency is due to that movable ion number in an electrolyte is fixed, increasing the mass of active carbon materials in unit electrode area means decreasing the ion number in unit active carbon material, thereby, C_s decreases with the specific mass of the active carbon electrode. The supercapacitor based on PVA–H_2SO_4–PB electrolyte with a thickness of 0.62 mm has the highest C_s. It may be ascribed to that in the thinner electrolyte, the movable ion number is fewer, and the C_s is the smaller; On the other hand, in the thicker electrolyte, ions have to long-distance migrate to reach the electrolyte|electrode interface, thereby the Cs is the smaller in the thicker electrolyte.

3.4. EIS technique

Fig. 10 shows the Nyquist plots for the supercapacitors with PVA–H_2SO_4–PB and PVA–H_2SO_4 gel electrolytes. Two gel electrolytes have ideal electrochemical capacitance behavior, i.e., imaginary parts of impedance at low frequency region are nearly linear, which is typical of Warburg impedance, "*W*" [30]. From the enlarged view of the higher frequency semicircles of Fig. 10A, it can be seen that the supercapacitor with PVA–H_2SO_4–PB gel electrolyte not only has lower inner resistance (R_i, 0.60 Ω cm^2), calculated from the point of intersecting with the *x*-axis in the range of high frequency, but also has smaller charge transfer resistance (R_{ct}, 1.67 Ω cm^2), which was counted from the span of the single semicircle along the *x*-axis from high to low frequency. Hence, the PB additive enhances the interaction of electrolyte|electrode interface,
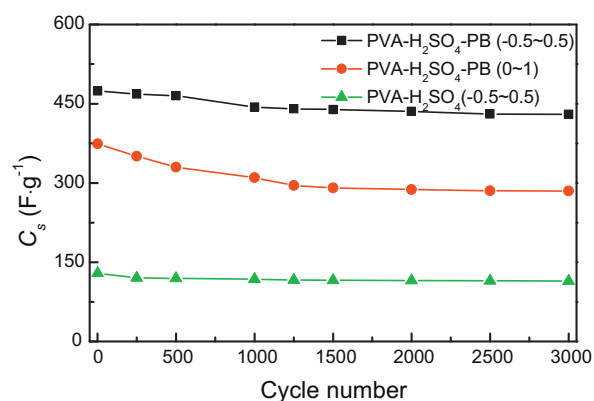

Fig. 11. The C_s of the supercapacitors with PVA–H_2SO_4 and PVA–H_2SO_4–PB gel electrolytes during long-term cycling.

which results in the high specific capacitance and good electrochemical property for PVA–H_2SO_4–PB gel electrolyte system.

Moreover, from the EIS (Fig. 10B) of the supercapacitor with PVA–H_2SO_4–PB gel electrolyte at different bias potentials from 0 to 1 V, it can be seen that the R_{ct} decline with the increase of bias potential, demonstrating the existence of redox reaction in this potential region [31].

3.5. Cycle life test

Cyclic durability is one of the most electrochemical performances of supercapacitor. The C_s variation with the cyclic times is shown in Fig. 11. The supercapacitor with PVA–H_2SO_4–PB gel electrolyte in different potential ranges has different cycle-life stability. In the potential range of −0.5 to 0.5 V, the C_s of supercapacitor with PVA–H_2SO_4–PB gel electrolyte decreases from 474.30 to 430.51 F g^{-1}, decrease about 9.23% after 3000 charge–discharge cycles, which is better than that previous report [27]. But for the range of 0–1 V, the C_s drop largely compared to the former. This change may be due to the incomplete redox reactions of p-benzenediol/p-benzoquinone in the potential range of 0–1 V. In spite of that, the PVA–H_2SO_4–PB gel electrolyte can be considered as promising electrolyte in the application of high-energy supercapacitor.

4. Conclusions

In summary, we have reported a supercapacitor based on activated carbon electrodes and a p-benzenediol-mediated

PVA–H_2SO_4 gel polymer electrolyte. With the help of the redox reaction of p-benzenediol/p-benzoquinone and its quick electron relay at the electrode|electrolyte interface, the supercapacitor shows outstanding electrochemical performances, such as, high electrode specific capacitance, high energy density, and excellent cycle life. It is believed that the idea using redox mediator has a good prospect for improving the performances of energy-storage devices.

Acknowledgements

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