活性炭二次活化对其电化学容量的影响

江　奇 [1,*]　　赵晓峰 [1]　　黄　彬 [1]　　杜　冰 [1]　　赵　勇 [1,2]

([1] 西南交通大学超导研究开发中心, 材料先进技术教育部重点实验室, 成都　610031;

[2]School of Materials Science and Engineering, University of New South Wales, Sydney　2052 NSW, Australia)

摘要：　为进一步提高作为电化学超级电容器电极材料活性炭的电化学容量, 采用 KOH 作为二次活性剂, 将所得活性炭进行二次化学活化处理, 从而得到二次活化活性炭. 将原始活性炭材料与二次活化活性炭材料都分别经过系列处理, 组装成电化学超级电容器进行电化学性能测试. 测试结果表明, 二次活化活性炭材料的电化学容量达到 145.0 F·g⁻¹(有机电解液), 远远大于原活性炭材料的容量(45.0 F·g⁻¹). 为研究二次活化活性炭材料电化学容量大幅提高的原因, 将这两种材料分别进行微观结构数据测试, 包括比表面积、N_2 吸脱附等温曲线和孔径分布. 研究结果表明, 二次活化处理大大增加了二次活化活性炭材料在孔径为 2–3 nm 的中孔分布, 从而证实对于有机电解液, 电极材料在 2–3 nm 的中孔对其电化学容量的提高具有重要意义.

关键词：　活性炭；　二次活化；　电化学超级电容器；　电化学容量

中图分类号：　O646；　TM911；　O63

Effect of the Activated Carbon Reactivation on Its Electrochemical Capacitance

JIANG Qi[1,*]　　ZHAO Xiao-Feng[1]　　HUANG Bin[1]　　DU Bing[1]　　ZHAO Yong[1,2]

([1]*Key Laboratory of Advanced Technologies of Materials (Ministry of Education of China), Superconductivity R&D Center, Southwest Jiaotong University, Chengdu　610031, P. R. China*;　[2]*School of Materials Science and Engineering, University of New South Wales, Sydney　2052 NSW, Australia*)

Abstract：　To enhance the electrochemical capacitance of activated carbon (AC), which is used as the electrode material for electrochemical super capacitors (ESC), the AC material was reactivated using chemical activation method and KOH as reactivation agent. The obtained material was designated as reactivated AC. Pristine AC and reactivated AC were both used as ESC electrode materials and simulated ESCs were assembled to test their electrochemical performance. Results showed that the electrochemical capacitance of the reactivated AC was enhanced up to 145.0 F· g⁻¹ in organic electrolyte, while the pristine AC only obtained a value of 45.0 F·g⁻¹. To determine the reason for the enhancement of the samples electrochemical capacitance, the specific surface area, N_2 adsorption-desorption isotherms, and pore diameter distributions were investigated. Results showed that reactivation treatment enhanced the pore distribution content of 2 to 3 nm (pore diameter). Pores with diameters from 2 to 3 nm (pore diameter) are thus important in the carbon material′s electrochemical capacitance using organic electrolyte.

Key Words：　Activated carbon；　Reactivation；　Electrochemical super capacitor；　Electrochemical capacitance

　　In recent years, great interest has been focused on the electrochemical super capacitors (ESC) for their practical applications as high power devices since they have large capacitance (several to hundreds of Farads). Compared with the normal capacitors, long

cycling life is about ten thousand times for their novel "double-electric-layer" energy storage mechanism, and the merit of charging and discharging with large electric current, especially[1–5].

Many materials have been found suitable for using as the electrode materials of the ESC by far, which can be classified into four types based on the material component: carbon series, transition metal oxide series, electronically conducting organic polymer series, and others[6–11]. Among the carbon series, activated carbon (AC, which exhibits a large specific surface area, a wide and easy way to prepare, and a low price) has been widely used as the electrode material of the ESC[12]. However, some AC electrochemical capacitances are not very high because of the shortcoming that not all the specific surface area is available, only part is used in the process of charging-discharging. That is because considerable pores of the AC are micro-pores (though the pores with the pore diameter less than 2 nm are also important to the electrochemical capacitance[13,14]), which lowers the electrochemical capacitance performance of the ESC made from the activated carbon[15]. Especially, the ESC made with organic electrolyte (which is famous for its high working voltage and high power in recent years though its capacitance maybe much lower than that with aqueous electrolyte, normally about 10 to 100 percent)[1]. To improve the electrochemical capacitance performance of the ESC, many researches were applied to prepare good ACs with suitable pore distributions from many raw materials, such as coal, fibers and so on. Of course, they had many excellent researching results, but the operation processes from these raw materials to the products (ACs) were relative complicated for ensuring the suitable pore distribution[16–19]. In fact, we can easy obtain the AC by the commercial channels. But the problem is the poor electrochemical capacitance performance of the AC. So if we can find an easy method to enhance the electrochemical capacitance performance of the AC, the problem can be resolved. In this paper, a relative simple method to enhance the electrochemical performance of the obtained AC is brought forward, which is the reactivation method to the AC using KOH as the activating agent.

1 Experimental

The activated carbon (pristine AC) was obtained by commercial channels (made from fruit shell, Wuhan, China). The reactivation of the AC (reactivation AC) was performed in a horizontal-chamber reactor with an electron auto control temperature system. The AC and the activating agent (KOH, AR degree) were exactly weighted as the proportion ($m_{KOH}:m_{AC}$=2:1) and mixed adequately in an agate mortar. After that, the mixture was placed in a ceramic boat and inserted into a ceramic tube (diameter 3 cm, length 80 cm) in the reactor. Then the reactor temperature was heated from the room temperature to 1123 K at a rate of 10 K·min^{-1}, while N_2 (99.99%) flowing through the ceramic tube with a rate of 240 mL·min^{-1}. Once the temperature reached 1123 K, held the temperature for 1 h. At last, the reactor was naturally cooled to room temperature. During the operation, the N_2 flowed

through the ceramic tube until the temperature cooled to room temperature. The obtained sample was washed to a pH of 7 with distilled water and dried in air at 393 K for 48 h.

In order to study the obtained sample electrochemical performance as the electrode materials of ESC, the simulated ESCs based on the two samples (pristine AC and reactivation AC) were assembled. Both of the two samples were made into electrodes as that they were mixed as 80% (*w*, mass fraction) of the sample, 10% (*w*) of acetylene black and 10% (*w*) of binding substance (polyvinylidene fluoride). Then, they were coated on a clean Al foil and made into pellets, followed by drying at 423 K under vacuum for 4 h. A micro porous separator (Celgard 2400) was sandwiched between the same two sample electrodes. These pellets and the micro porous separator were both entirely wetted using 1.0 mol·L^{-1} lithium perchlorate ($LiClO_4$) dissolved in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1 by volume). The process of the assembly was performed in a glove box filled with dried argon gas. The performances of the ESC were tested with cyclic voltammetry (CV, ZF-9 potentiostat, Shanghai Zhengfang), electrochemical impedance spectroscopy (EIS, IM6 electrochemical tester, Germany) and galvanostatic charging-discharging cycling testing (DC-5 Cell tester, Shanghai Zhengfang).

The electrochemical capacitance performance was tested with constant current (3.3 A·m^{-2}) charging-discharging model between 0.01 and 3.00 V at 298 K on the battery-testing instrument. The absolute capacitance of the ESC was calculated by the discharging curve of the simulated ESC using the following equation:

$$C=It/U$$

In this equation, the result of the discharging time (*t*) multiplied by the discharging current (*I*) is the discharging coulomb capacitance. The result of the coulomb capacitance divided by the discharging voltage (*U*) is the absolute capacitance (*C*, in F) of the simulated ESC. The specific capacitance of the single electrode (C_s, in F·g^{-1}, namely the specific capacitance of the pristine AC or reactivation AC) is calculated as:

$$C_s=2C/m$$

where *m* is the mass of the single electrode.

2 Results and discussion

Fig.1a denotes the charging-discharging curves of the ESC based on the two carbon materials. The charging-discharging current (*I*) and mass (*m*) of the single effective electrode material (the carbon samples) are 0.2 mA and 0.0018 g, respectively. From Fig.1a, it can be seen that the relationships between the charging-discharging voltage and the charging-discharging time of the ESC based on the two carbon samples are both linear variation, which is the ESC typical characteristic[20]. Moreover, the charging-discharging time in one cycle of the ESC based on the reactivation AC is much larger than that of the pristine AC at the same charging-discharging current and electrode material mass, indicating that the electrochemical capacitance of the ESC based on the reactivation AC is much larger than that of the ESC
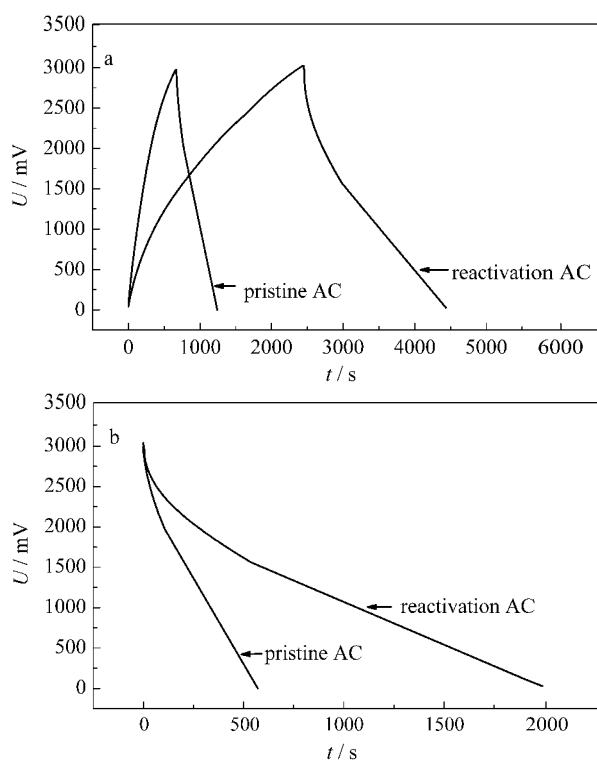
Fig.1   Charging-discharging curves (a) and discharging curves (b) of the two carbon samples with organic electrolyte

I=0.2 mA, *m*=0.0018 g

based on the pristine AC.

In order to further study the two electrode material capacitances exactly, the two discharging curves based on the two electrode materials are showed in Fig.1b. From Fig.1b, it can be seen that the discharging time of the ESC based on the pristine AC is about 610 s when the discharging voltage changes from 3000 to 10 mV. Whereas the discharging time of the ESC based on the reactivation AC is 1960 s, which is over 3 times that of the pristine AC. Based on the electrochemical capacitance calculation equation mentioned above, we can obtain the two electrode material electrochemical specific capacitances. The electrochemical specific capacitances of the reactivation AC and pristine AC are 145.0 and 45.0 F·g^{-1}, respectively. So, we can see that the electrochemical specific capacitances of the reactivation AC is much larger than that of the pristine AC, which is about 3.2 times that of the pristine AC, indicating that the electrochemical capacitance of the carbon sample can be greatly enhanced after being treated by the reactivation treatment mentioned above.

Fig.2 is the cycle characteristic of the ESCs based on the two carbon samples. In order to research the beginning part in detail, we only list the anterior 20 cycles. From Fig.2, it can be seen that the cycle curve of the reactivation AC lies obviously higher than that of the pristine AC. That is because that the electrochemical capacitance of the ESC based on reactivation is much larger than that of the pristine AC. Moreover, there is an up trend in the cycle curve of the reactivation AC at the beginning, which is frequently phenomenon to the cycle curve of a super
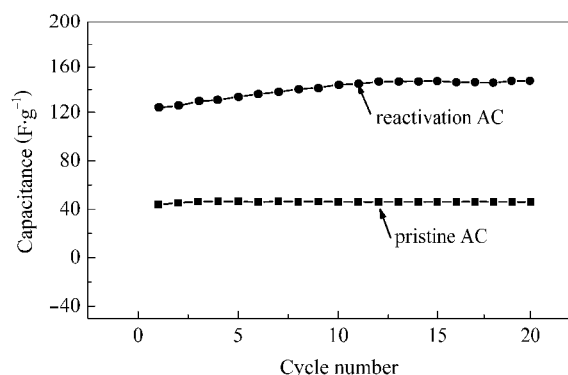

Fig.2   Relationships between the discharging capacitance and cycle number of the two carbon samples in organic electrolyte

I=0.2 mA; *m*=0.0018 g

capacitor or a battery when the specific surface area of the electrode material is much larger. The reason is that it needs more time (several charging-discharging cycle) to let the electrolyte completely enter into the pores of the electrode material[21], indicating that the specific surface area of the reactivation AC is larger than that of the pristine AC (for there is not an up trend in the pristine AC cycle curve at the beginning). In a word, both the ESCs based on the carbon samples have good cycle performance (of course, based on more cycle testing times besides the anterior 20 cycles) and the electrochemical capacitance of the reactivation AC is much larger (over 3 times as large as that of the pristine AC).

Fig.3 is the CV curves of the ESCs based on the two carbon materials. It can be seen that there are no obvious peaks on the two curves and the CV curves are very like rectangle. So, we can consider that the two carbon materials work (energy storage) mainly as the "double-electric-layer" mode. Moreover, from the fact that the rectangle based on the reactivation AC is bigger than that of the pristine AC, we can deduce that the electrochemical capacitance of the reactivation AC is higher.

Fig.4 is the EIS curves of the ESCs based on the two carbon materials. From the figure, we can see that the trends of the two curves are similar (both have a semi-circle in high frequency field and an oblique line in low frequency field). But if we exa-
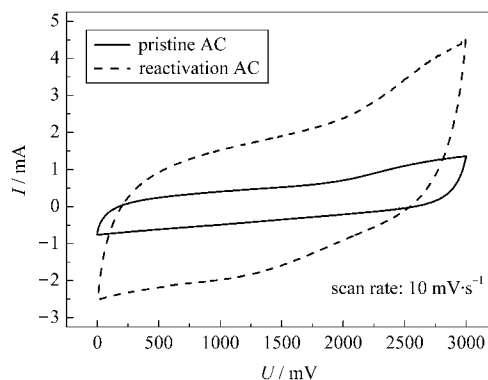
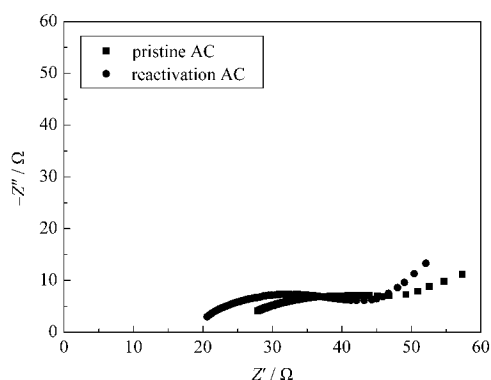**Fig.3   CV curves of the ESCs based on the two carbon materials**

Fig.4   EIS curves of the ESCs based on the two carbon materials

mine the curves carefully, we can find that the corresponding *x*-coordinates of the semi-circles are different indicating that the resistance of the ESC based on the two carbon materials is different. More importance is that the slopes of the two oblique lines are also different. The absolute value of the slope based on the reactivation AC is bigger than that of the pristine AC, indicating that the ESC based on the reactivation AC has better electrochemical capacitance than that based on the pristine AC.

In order to study the reason that the reactivation AC has better electrochemical capacitance performance, the microstructure of the two carbon samples (including specific surface area, pore volume, pore diameter distribution, and adsorption-desorption isotherms) are characterized by an automatic nitrogen gas adsorption analyzer at 77 K. The specific surface area and the pore diameter distribution are calculated by the BET equation and the BJH method, respectively. The pore volume is calculated by the *t*-plot and estimated to be the liquid volume of nitrogen at a relative pressure of about 0.999. These testing results are also listed in Table 1. Table 1 is the characteristics of the pristine AC and reactivation AC. From the table, it can be seen that the specific surface area of the reactivation AC is about 1587 $m^2 \cdot g^{-1}$, which is much larger than that of the pristine AC (about 1072 $m^2 \cdot g^{-1}$). And the pore volume of the carbon sample increases from 0.61 to 1.07 $cm^3 \cdot g^{-1}$ after being reactivated with KOH, indicating that the reactivation operation can change the microstructure of the pristine AC.

Fig.5 denotes the nitrogen adsorption and desorption isotherms of the pristine AC and reactivation AC tested by the N_2 adsorption analyzer at 77 K. From Fig.5, it can be seen that the adsorption amount of the pristine AC adsorption isotherm increases rapidly at ultra-low pressure and then holds at a relative stable level, which belongs to the type I[22]. And this fact also indicates that there are lots of micro-pores in the pristine AC. At

the same time, there is a relative small hysteresis loop between the adsorption and desorption isotherms of the pristine AC, which is the result of meso-pores. So, from the analysis results mentioned above, we can deduce that the pristine AC has lots of micro-pores and some meso-pores.

Whereas, the adsorption and desorption isotherms of the reactivation AC are typical type II from the trend of isotherm curve and there is a relative big hysteresis loop between the adsorption and desorption isotherms, indicating that the reactivation AC has lots of meso-pores and some macro-pores[22,23]. So, we can see that the reactivation operations in our experiments have the result of increasing amount of meso-pores and macro-pores of the carbon sample. Moreover, the reactivation treatments increase the adsorbing amount of the treated activated carbon material, from the fact that the isotherms of the reactivation AC are obviously higher than those of the pristine AC. The larger adsorbing amount indicates that the reactivation AC has larger specific surface area and pore volume than the pristine AC, which is proved by the specific surface area and pore volume data of the two samples listed in Table 1.

From Table 1, it can be seen that the specific surface area and pore volume of the pristine AC are about 1072 $m^2 \cdot g^{-1}$ and 0.61 $cm^3 \cdot g^{-1}$, respectively. And the specific surface area and pore volume of the reactivation AC are about 1587 $m^2 \cdot g^{-1}$ and 1.07 $cm^3 \cdot g^{-1}$, respectively. The specific surface area and pore volume of the reactivation AC are about 1.5 and 1.7 times that of the pristine AC. However, the electrochemical capacitance of the reactivation AC is about 3.2 times that of the pristine AC. As we know, the electrochemical energy storage mechanism of the AC material is mainly "double-electric-layer" mechanism[1]. This is difficult to explain the relationship between the electrochemical capacitance and the specific surface area only from the data of the specific surface area. So, the pore diameter distributions of the pristine AC and reactivation AC are studied.

Fig.6 denotes the pore diameter distributions of the pristine AC and reactivation AC. From Fig.6, it can be seen that both the pristine AC and reactivation AC have considerable micro-pores (pore diameter less than 2 nm), which are about 28% and 25%, respectively. As we know, when the electrolyte is organic elec-
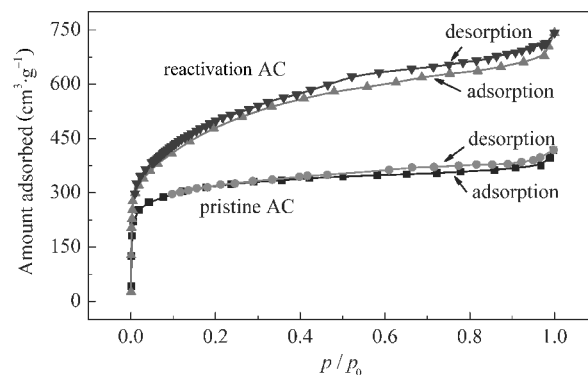
Table 1   Characteristics of the pristine AC and reactivation AC

AC	Yield(%)	C_s/(F$\cdot$g^{-1})	S_{BET}/(m$^2\cdot$g^{-1})	V/(cm$^3\cdot$g^{-1})
pristine	–	45.0	1072	0.61
reactivation	75	145.0	1587	1.07

S_{BET}: BET surface area; V: pore volume; C_s: capacitance of the electrode material
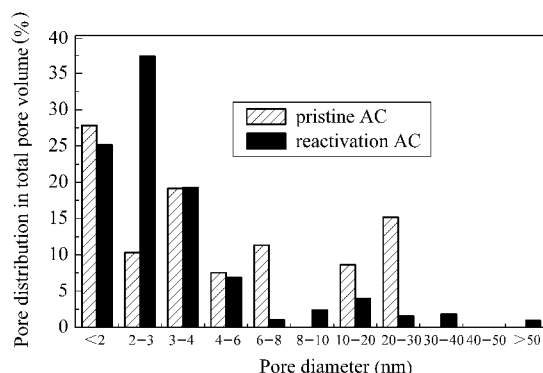

Fig.5   Nitrogen adsorption-desorption isotherms of the two carbon samples at 77 K

Fig.6　Pore diameter distributions of the pristine AC and reactivation AC

trolyte, the most efficient pores using to store energy are meso-pores and macro-pores[1,12]. So, in this paper, the meso-pore and macro-pore diameter distributions of the two carbon samples are studied in detail. Compared with the contents of meso- and macro-pores, it can be seen that most pores of the reactivation AC lie with their pore diameter from 2 to 6 nm (about 64%), whereas the content percentage of the pristine AC in same pore diameter scope is only about 35%. The most pores of the pristine AC lie with their pore diameter from 2 to 30 nm. Especially, the pores with the diameter from 2 to 3 nm of the reactivation AC have about 37% of the pore distribution, which is the maximum distribution. The pores with the diameter from 2 to 3 nm of the pristine AC only have about 11% of the pore distribution and the maximum distribution is from 3 to 4 nm. Moreover, the pore distribution scope from 2 to 3 nm of the reactivation AC is the only distribution scope (where two samples both have distributions) that the pore content percentage is higher than that of the pristine AC, which is about 3.4 times that of the pristine AC.

Considering that the reactivation AC electrochemical capacitance is about 3.2 times that of the pristine AC and the electrochemical capacitance has close correlation with the pore diameter distribution based on the "double-electric-layer" energy storage mechanism[12,13], we have the result that the pores with their diameter distribution from 2 to 3 nm have the most important contribution to the carbon sample electrochemical capacitance in our system. And the reason that the reactivation treatment can greatly enhance the carbon sample electrochemical capacitance (from 45.0 to 145.0 F·g^{-1} in organic electrolyte) is that the reactivation treatment greatly enhances the pores the pore distribution contenten of 2 to 3 nm (pore diamter).

3　Conclusions

Several conclusions can be drawn from the experimental results and discussion mentioned above, including:

Firstly, reactivation treatment can greatly enhance the obtained carbon sample electrochemical capacitance by modifying the sample microstructure (including the specific surface area,

pore volume, and pore diameter distribution).

Secondly, the pores with their diameter from 2 to 3 nm are the most important pores to the energy storage in organic electrolyte system.

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