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Short Communication

Synthesis of Porous Carbon by Activation Method and its Electrochemical Performance

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For potential applications in supercapacitors, Porous carbon has been synthesized by the facile and economic activation method. The SEM and XRD are adopted to analyze the microstructure and the specific surface area. The material was tested as the electrode material for supercapacitors. With the increase of resin content, the specific capacitance of porous carbon increases gradually. When polyvinylbutyral in the compounds is 80%, the specific capacitance is 201.9 F/g, and capacitance rentention rate is 93.38% for 500 cycles. The compounds may have a good prospect in supercapacitors.

Keywords: porous carbon, specific capacitance, activation method, electrochemical, supercapacitor

1. INTRODUCTION

Recently, producing fossil fuels as much as producing energy because of the harmful effects they have on the consumption and environment has a separate precaution [1-4]. Therefore, alternative energy storage devices with high energy and power capacities are needed and intensive studies are being made to develop these devices [5-8]. Nowadays, energy accumulation and storage is one of the most important topics. Supercapacitors, also known as electrochemical capacitors or ultracapacitors, have been extensively investigated in recent years due to their potential application as power storage devices. These devices have the following advantages: long lifetime, stable performance, large current charging and discharging time, wide working temperature limit and no pollution [5, 6]. Recently, the activated carbon, graphene, carbon nanotubes and carbon aerogel are used as supercapacitor [9-15]. To today, the graphene, carbon nanotubes and carbon aerogel have the shortage of complex technology on material preparation and high cost, which would cause difficulties for the electric double layer electrode materials in industrial production [16-21]. The activated carbon is a common material and widely used in supercapacitor. Based on the energy storage principle, porous carbon electrode material is the key to improving the energy density and reducing the cost [22-29]. In the past few years, related literature reported that the size of the capacitance of electric double-layer was positively correlated with the specific surface area in the electrode material [30-39]. The relationship between specific capacitance and specific surface area was not a linear relationship. It was mattered with the pore size and the proportion of the micro hole, the middle hole and the large-hole [40-46]. The method has the shortage of complex, high cost, difficulty for industrialized production and a lower specific surface area in the real production of the porous carbon material. The porous carbon supercapacitor exhibits a superior electrochemical performance for practical applications. It may have a good prospect in supercapacitors.

2. EXPERIMENTAL

2.1 Sample preparation

The chemicals used during the synthesis process were of analytical grade. The experiment uses the method of radial activation. 48 grams of phenolic resin was dissolved in 40 ml water for 1 hour with ultrasonic, and the solution was marked as 1# turbid liquid. 1000ml of graphene aqueous solution was prepared with the concentration of 0.2 g/ml. Let it under ultrasonic treatment for 3 hours. The solution was marked as 2# aqueous solution. 0.4728 g, 4.2553 g and 17.0213 g of polyvinylbutyral was taken to phenolic resin, and dissolved in 30ml distilled water respectively. The phenolic resin was stirred with distilled water. Then they were mixed with the 2# aqueous solution respectively. Stir for 30 min rapidly and have ultrasonic treatment for 1 hour to get the 3# and 4# turbid liquid. The KOH (the mass ratio of KOH and composite carbon is 3:1, KOH is 1 M/L) was put into the solution of 1#, 2#, 3# and 4# respectively. After being heated by evaporating water, they were dried for 8 hours in the 60^oC oven. The 1#, 2#, 3# and 4# black solid powder was prepared. The solid powder was put into the tube furnace respectively. Then temperature increased from 25^oC to 800^oC under the protection of the N_2 gas. Those compositions were kept in warm environment for 120 min and then were pulled out of the tube furnace to cool to room temperature. The compounds were washed in distilled water to neutral. After being dried, all of these materials were grinded in the agate mortar. The as-prepared proportion of the polyvinylbutyral in the compounds are 0%, 10%, 50% and 80% corresponding to 1#, 2#,3#, 4#, we mark AC_0, AC_{10}, AC_{50} and AC_{80}, respectively.

2.2 The structure characterization of the material

For surface analysis, Scanning electron microscope (SEM) measurement was carried out with a scanning electron microanalyser (JSM6510LV) at 15.0 kV. X-ray diffraction (XRD) experiments were conducted in a D/MAX-IIIC X-raydiffractometer with Cu Kα radiation. The specific capacitance can be calculated from the discharge curves with the following equation: $C_{sp}= I*\Delta t/(m*\Delta V)$, where C_{sp}, I, Δt, m and ΔV are the specific capacitance (F g^{-1}), discharge current (A), discharge time (s), mass of the active material (g) and potential window (V), respectively.

2.3 The preparation of electrodes

The prepared sample, the acetylene black (produced in the United States, AR), and the Teflon (PTFE, 30% of the water emulsion, produced in Dalian) was mixed with the mass ratio 80:5:15. Anhydrous ethanol was added as liquid additives evenly. After being fully stirred into the dough, these materials were rolled into pieces. The porous carbon materials were pressed into 1cm*1cm diameter.

2.4 The test of electrochemical performance

The high-precision supercapacitor tester CHI660 (made by the Shanghai ChenHua Lim. Co.) was adopted for constant current charge-discharge measurement. The test conditions: the current is 0.5 mA and the voltage is 0 to 1V. The discharge specific capacitance can be calculated by charging and discharging curve for 500 times. The ratio of the last discharge specific capacitance and the first discharge specific capacitance is the cycle performance. The areal and volumetric capacitance values in the three-electrode configuration were calculated with the cyclic voltammetry curve. The scanning voltage is 0~1V and the scanning rate is 10 mV/s.

3. THE RESULTS AND DISCUSSION

3.1 The structure and characterization

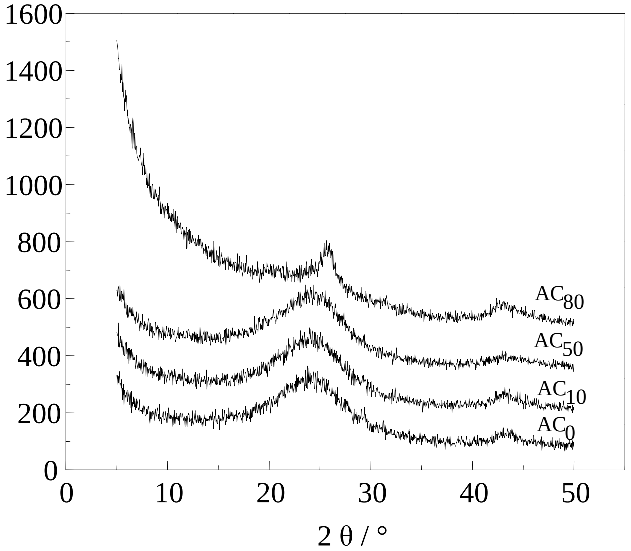

Figure 1. The XRD diagram of AC_0, AC_{10}, AC_{50} and AC_{80} (the polyvinylbutyral in the compounds are 0%, 10%, 50% and 80%)

Fig. 1 is the XRD diagram of AC_0, AC_{10}, AC_{50} and AC_{80}. The diffraction peaks of the samples are all near the 002 (26.5°). With the increasement of the content of porous carbon, the sample AC_0, AC_{10} and AC_{50} have the similar diffraction peak shape. It shows that the materials have amorphous disordered structure. While the sample AC_{80}'s peak shape is sharp, it shows that the sample material has a better crystallinity, and most of the carbon material will increase their degree of disorder by the activator. It illustrates that the sample AC_{80} is different from most of the porous carbon materials in structure. It also shows that as the temperature increases, the samples' diffraction peak shifts to the left gradually and the deviation angle is small. Porosity for good electrolyte mobility is helpful to delivering a high specific capacitance at high current densities and maintaining a stable cycle life [41-46].

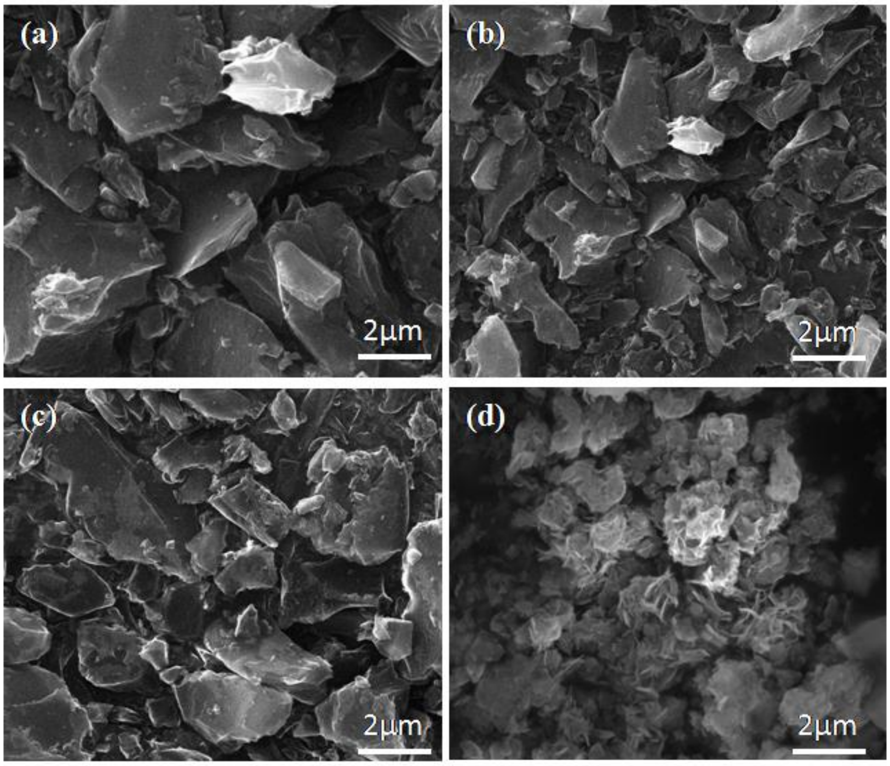

Figure 2. The SEM image of porous carbon (a)AC_0, (b)AC_{10}, (c)AC_{50}, (d)AC_{80} (the polyvinylbutyralin the compounds are 0%, 10%, 50% and 80%)

Fig.2 is the SEM image of porous carbon (a)AC_0, (b)AC_{10}, (c)AC_{50}, (d)AC_{80}. From Fig. 2 (a), (b) and (c), we can know that AC_0, AC_{10} and AC_{50} have the flocculent structure. As shown in the Fig. 2(d), the particles are dispersed and the structure is loose. These holes are caused by potassium hydroxide activation. The AC_{80} has smooth honeycomb structure and is more regular compared to the reports of reference [8] and [13]. The material holds significant potential for applications in other fields, for instance in chemical and electrochemical sensing, solar cells, catalysis, and field emission.

3.2 The electrochemical properties

From Fig. 3 (a) and (b), we can see that with the increase of current, the charging time of AC_{50} and AC_{80} decreased gradually. It shows that the supercapacitor's capacity has also decreased gradually. The reasons are as follows: the electron is not fully adsorbed on the surface when the current is large.

The symmetry of the charge-discharge curves is great, which proves that the electric double layer effect is good. When polyvinylbutyral in the compounds is 50%, the specific capacitance is 170.4 F/g. When polyvinylbutyral in the compounds is 80%, the specific capacitance is 201.9 F/g. The capacitance rentention rate is 93.38% for 500 cycles. The result is much better than the report of the reference [13], especially enhancement of the charge-discharge performance.

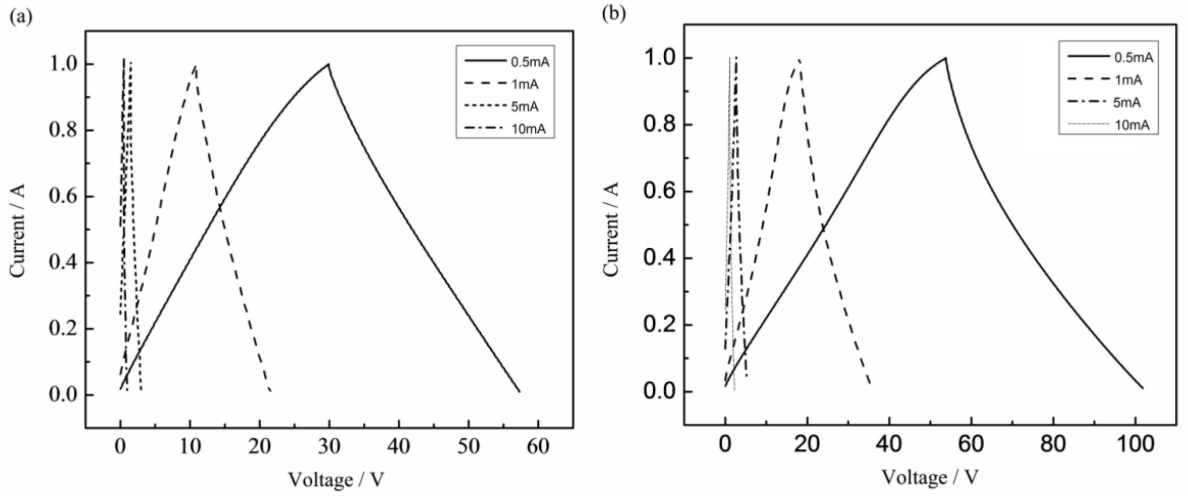

Figure 3. Charge and discharge curve of the materials of carbon electrode (a)AC_{50}, (b)AC_{80} at the current of 0.5, 1, 5, 10 mA (the different line segments show current)

Table 1 is the comparison of the capacitance rentention rate of different carbon materials. The retention is up to 93.38%. The performance of porous carbon electrode is much better than those of compounds reported previously (see Table 1). The dispersed structure provides a conductive network for electron transporting through the overall electrode. We can conclude that porous carbon with good crystallinity, and the structures obtained were completely different from those described in previous reports [18, 35, 41]

Table 1. Comparison of the capacitance rentention rate of different carbon materials

Electrode materials	Capacitance RententionRate (%)	Reference
Porous Carbon	93.38	This work
MnO_2-CdS@NG//rGO	87	[35]
PANI nanofiber/graphene	68	[36]
Mesoporous PANI/graphene	73	[37]
PANI/graphene	64.2	[38]
PANI nanorod/graphene	67.4	[39]
PANI nanofiber/graphene	57.4	[40]
CNTs/MnO_2	70.8	[41]

Electrode materials	Capacitance RententionRate (%)	Reference
Nitrogen-doped graphene	98	[35]
Nickel Oxide/Active Carbon	90	[42]
Graphene	91	[18]

Fig. 4 is the cyclic voltammetric curves under different scan rate of AC_{80}. The scanning rate is 10, 50, 100 and 200 mV/s, respectively. The greater the scan rate is, the more the sample deviate the original rectangle is. Meanwhile, the curves keep a good symmetry. It shows that the electrode interface has a better reversible reaction in the electrolyte. The sample AC_{80} has a stability structure and a good cycle performance, which is consistent with the conclusion of charge and discharge curve. The results suggest that these particles have relatively higher capacitance as compared to the reports of reference [17] and [20].

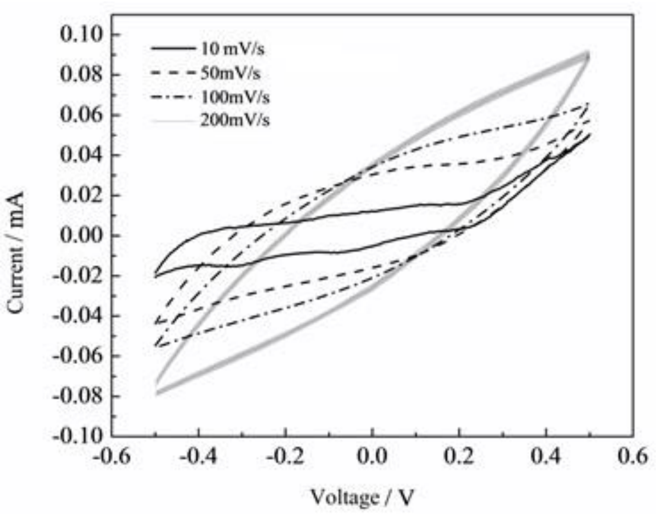

Figure 4. Cyclic voltammetric curves under different scan rate (10, 50, 100 and 200 mV/s) of AC_{80} (the different line segmentsshow scan rate)

Comparison with specific capacitance of different carbon materials is shown in the Table 2. The Specific capacitance of the as prepared electrode material (201.9 F/g) is high among the other reported supercapacitor-Ordered Mesoporous Carbon (120.0 F/g) [3], Active Carbon/RuO_2 (194.2F/g) [14], CNTs/MnO_2(260.2F/g) [41], Nitrogen-doped graphene (197F/g) [35], Nickel Oxide/Active Carbon (368F/g) [46], Graphene (185F/g) [18] as shown in Table 2, which indicates good electrode stability.

Table 2. Comparison of Specific capacitance of different carbon materials

Electrode materials	Specific capacitance (F/g)	Reference
Porous Carbon	201.9	This work
Ordered Mesoporous Carbon	120.0	[3]
Active Carbon/RuO_2	194.2	[14]
CNTs/MnO_2	260.2	[41]
Nitrogen-doped graphene	197	[35]
Nickel Oxide/Active Carbon	368	[46]
Graphene	185	[18]

4. CONCLUSIONS

In summary, we synthesize the porous carbon with the activation method. The SEM and XRD are adopted to analyze the microstructure and the specific surface area. The electrochemical performance is tested by the CHI660. It was found that such compounds are able to deliver large specific capacitance, high rate performance, and good cycling stability during charging-discharging process. When polyvinylbutyral in the compounds is 80%, the specific capacitance is 201.9F/g and the capacitance rentention rate is 93.38% for 500 cycles. The as-prepared composite therefore has promising application in high-performance supercapacitors. These structural benefits and the high product yield mean that our convenient synthesis route may also be applicable to the synthesis of other metal oxides.

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