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Influence of reactivation on the electrochemical performances of activated carbon based on coconut shell

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Abstract

Coconut shell-based activated carbon (AC) were prepared by CO₂ activation, and then the ACs with higher mesopore ratio were obtained by steam activation and by impregnating iron catalyst followed by steam activation, respectively. The AC with the highest mesopore ratio (ACₘₐₛ) shows superior capacitive behavior, power output and high-frequency performance in supercapacitors. The results should attribute to the connection of its wide micropores and mesopores larger than 3 nm, which is more favorable for fast ionic transportation. The pore size distribution exhibits that the mesopore ratios of the ACs are significantly increased by reactivation of steam or catalyst up to 75% and 78%, respectively. As evidenced by cyclic voltammetry, electrochemical impedance spectroscopy, and galvanostatic measurements, the ACₘₐₛ shows superior capacitive behaviors, conductivity and performance of electrolytic ionic transportation. The response current densities are evidently enhanced through the cyclic voltammetry test at 50 mV/sec scan rate. The electrochemical impedance spectroscopy demonstrates that the conductivity and ion transport performance of the ACs are improved. The specific capacitances of the ACs were increased from 140 to 240 F/g at 500 mA/g current density. The ACₘₐₛ can provide much higher power density while still maintaining good energy density, and demonstrate excellent high-frequency performances. The pore structure and conductivity of the ACₘₐₛ also improve the cycleability and self-discharge of supercapacitors. Such ACₘₐₛ exhibits a great potential in supercapacitors, particularly for applications where high power output and good high-frequency capacitive performances are required.

Key words: supercapacitor; activated carbon; electrochemical performance

Introduction

Supercapacitors have been attracted much attention for years, because of their excellent pulse power supply and high dynamic of charge propagation (Conway, 1999; Frackowiak and Beguin, 2001). Such supercapacitors mainly used activated carbon (AC) as electrode materials, strongly dependent on their stable physicochemical properties, good conductivity, low cost, and availability (Kötz and Carlen, 2000; Zhang and Zhao, 2009). However, AC-based supercapacitors are known to be suffering from electrode kinetic problems that are related to inner-pore ion transportation and the conductivity of carbon materials (Pandolfò and Hollenkamp, 2006). The exact mechanism of ion transportation within porous textures is very complex (Wang et al., 2006), because the pore-size distribution and shape of the pores, as well as the nature of the electrolyte and the solid-liquid interface, all have to be considered (Rolison, 2003; Lee and Pyun, 2006; Long et al., 2004). Among these factors, the inner-pore ion-transport resistance and the conductivity of electrode materials are the most important ones for high-rate power output, strongly depending on the preparation method (chemical or physical activation). Large values of these two parameters lead to a significant electrode-potential drop and a low ion-accessible surface area at large current values, thus severely reducing the performance of the supercapacitors. Because the biomass has the advantages of wide resource and availability, they have been widely applied in AC preparation (Shi et al., 2010; Alam et al., 2007; Zhao et al., 2009; Anirudhan and Sreekumari, 2011). However, most of AC usually displays the characteristics of micropore size distribution, which restrains the power output of supercapacitors. As a result, it is necessary to reactivate biomass-based AC to get the expected porous structure.

In the present work, reactivation method was adopted to exploit the influences of reactivation on the electrochemical performances of AC as electrode materials of supercapacitors. Coconut shell from Hainan, China was used as the precursor of AC. After it was carbonized,
the product was reactivated by steam and the combination of steam and catalyst, respectively. The effects on porous structure and electrochemical performances were observed.

1 Materials and methods

1.1 Preparation and Characterization of AC

After the coconut shells were dried and crushed, carbonization was performed in a horizontal furnace under nitrogen flow (flow rate of 200 mL/min). The samples were heated (10°C/min) from room temperature to final carbonization temperature of 900°C. At the final temperature, samples were maintained for 1 hr. Afterwards, CO₂ activation was carried out under CO₂ flow (flow rate of 600 mL/min) for 5 hr at the same temperature, and then cooled to room temperature in inert gas atmosphere (the sample named as AC-1). AC-1 was heated to 850°C under nitrogen atmosphere again, and then was activated for 2 hr under steam atmosphere at the same temperature (the sample named as AC-2). Furthermore, AC-1 was impregnated by the alcohol solution of ferrocene. The rest procedures were the same as the preparation of AC-2. The product was washed with 5% HCl solution to remove the Fe particles and distilled water until near pH 7. Finally, the resulting product was dried under vacuum at 120°C (the sample named as AC-3). The porous texture of all samples were probed by nitrogen adsorption-desorption analysis with Micromeritics ASAP 2010 M (Micrometric, USA).

1.2 Electrochemical performances of supercapacitors

The sheet-type electrode was prepared by mixing AC (95 wt.%) and polytetrafluoroethylene (PTFE) (5 wt.%) with ethanol to form slurry, and spreading onto a nickel foam (0.8 cm in diameter). The mass load of active material was 10–20 mg/cm². All electrochemical measurements were carried out in a two electrode coin-type cell, in which a separator soaked with 6 mol/L KOH solution was sandwiched between two carbon electrodes.

The cyclic voltammogram (CV) and electrochemical impedance spectroscopy (EIS) measurements were carried out on Solartron 1287/1260 electrochemical systems (Solartron, UK). The CV measurements were tested between 0–1.0 V voltage windows. The EIS measurements were analyzed in the range of 100 kHz to 10 mHz with alternating current (ac) amplitude of 10 mV. The galvanostatic charge-discharge tests were accomplished on BT2000 Arbin (Arbin, USA).

2 Results and discussion

2.1 Porous texture of ACs

As shown in Fig. 1a, the types of the nitrogen adsorption-desorption isotherms of the ACs present evident transformation as the different reactivation was utilized (Achaw et al., 2008; Li et al., 2011; Wang et al., 2006). The AC-1 shows type-I isotherm with mesopore ratio (Vₘesopore/V_total) of 11.54%, indicative of mainly microporous characteristics. The specific surface area and total pore volume of AC-1 are 1171 m²/g and 0.52 m³/g, which demonstrates that it is difficult for high specific surface area obtained by CO₂ activation within short activation time. After AC-1 is reactivated by the steam, the AC-2 still presents type-I isotherm with board knee. The specific surface area and total pore volume are as high as 1933 m²/g and 0.92 cm³/g, respectively. Due to the role of steam during reactivation, the micropores is widened a bit, which makes the small mesopores formed (Kim et al., 2004; Águlló et al., 2004; Kierzek et al., 2004; Qiao et al., 2005). The Vₘesopore/V_total of AC-2 is raised to 75.00%. When AC-1 is reactivated by the combination of catalyst and steam, the isotherm of AC-3 exhibits a small hysteresis loop at high relative pressure, suggesting more and larger mesopores constructed in the carbon framework. The specific surface area and total pore volume of AC-3 are 1728 m²/g and 1.45 cm³/g, respectively. The combination of catalyst and steam activation give rise to the maximum mesopore ratio of 77.93%. Therefore, the catalytic reactivation is appropriate

Fig. 1 N₂ adsorption-desorption isotherm (a) and pore structure distribution (b) of AC-1, AC-2 and AC-3. V and D represent pore volume and pore size, respectively.
to prepare the AC with high mesoporous percentage.

The density functional theory was adopted to analyze the pore size distributions of AC (Fig. 1b). AC-1 displays micropore size distributions at 0.68 and 0.80 nm (Gregg and Sing, 1982; Liu et al., 2005; Hsu and Teng, 2000; Wang et al., 2008). However, reaction obviously change the pore size distributions of the AC-1. Besides the small micropore of AC-1 reserved, the micropores and small mesopores of AC-2 between the pore sizes from 1 to 3 nm are generated a lot. The change results from carbon atoms burned off and carbon atoms reacting with the steam during steam reactivation. Compared with AC-2 and AC-1, new small mesopores for AC-3 present at 9.30 nm. The pore size distributions originate from the role of iron catalyst, which promotes carbon atoms to react with steam. As a result, abundant mesopores are developed.

### 2.2 Electrochemical performance of ACs

The influence of porous structure on ion transport behavior can be characterized by the CV method based on the evaluation of capacitive performance of supercapacitors. Generally, the desired capacitive performance requires a rectangular shaped voltammogram. Besides, the capacitive behavior can also be studied by changing the voltage scan rates to estimate the applicability for quick charge-discharge operations (Du et al., 2010; Zheng and Gao, 2011; Wang et al., 2008; Huang et al., 2011). The CV characteristics of ACs are presented in Fig. 2. The voltammograms of all ACs maintained the desired rectangular shape at voltage scan rates of 5 mV/sec. The response current of AC-3 is obviously higher than those of other ACs. When the voltage scan rate was increased to 50 mV/sec, quasi-rectangular shapes can still be remained for all AC, indicating excellent capacitive behavior even at high current intensity. At slow sweep rate, the ions have enough time to diffuse into the micropore surface, while at high voltage sweep rate the ions can only penetrate into some external large pores, which can explain why the CV curves are distorted with the variation of voltage sweep rate. The response current of AC-3 is twice as high as AC-2 at the voltage scan rate of 50 mV/sec. Meanwhile, the response current of AC-2 is twice as high as that of AC-1 as well. The cyclic voltammograms demonstrate that high ratio of mesopores is suitable for quick charge-discharge operations, suggesting a better capacitive behavior for AC-3. Generally, the faster the penetration of electrolyte ions into electrochemically active porous surface, the better the capacitive behavior at high voltage scan rate. Namely, the pores texture of AC-3 are favorable for the ionic diffusion inside the pores/channel of AC.

To evaluate clearly the capacitive behavior of AC investigated, the ratio of retained capacitance vs increased voltage scan rates is plotted in Fig. 3. The bigger the retention ratio, the better the ion transport behavior and capacitive behavior (Xing et al., 2006; Wang et al., 2008). AC-3 maintains 90% of its initial capacitance at a high voltage scan rate of 50 mV/sec, which is more than the ratio of 80% of AC-2 and 54% of AC-1. This means a better ion transport capability and capacitive behavior for AC-3 due to its abundant mesopore size. That is, the solvated ions can diffuse fast enough into the mesopores of AC-3 even at the voltage sweep rate of 50 mV/sec. Furthermore, the capacitive behavior of AC-2 is also better than that of AC-1, indicating that higher mesopore ratio will play a dominant role in determining the ion transport and capacitive behavior at high voltage scan rates. As shown in Fig. 3, the specific capacitance values decrease with the increase of sweep rate for all activated carbons investigated, which indicates that there is always less active surface area of pores being utilized at higher voltage sweep rate. AC-3 possesses the highest the ratio of retained capacitance, indicative of higher percentage of electrochemically active surface area utilized at higher voltage sweep rate, which originates from its high mesopore ration and large mesopores than 3 nm.

EIS, which distinguishes the resistance and capacitance of devices, is still considered as a powerful method to obtain dynamic ion diffusion information and reveals the resistance of the supercapacitors in the electric double-layer formation on the carbon electrodes (Du et al., 2010;
Zheng and Gao, 2011; Wang et al., 2006). The complex-plane impedance plots (Nyquist plots) of high-frequency region for these carbon materials are given in Fig. 4a. A semi-circle loop appears in the very high-frequency region before the plot transforms completely to a vertical line (the inset in Fig. 4a). This semi-circle loop was suggested to represent the total contact resistance between the active materials and between the collector and active materials (Portet et al., 2004; Nian and Teng, 2003). Generally, the decrease of semi-circle loop illuminates that the conductivity of the electrodes are enhanced (Kötz and Carlen, 2000; An et al., 2001; Song et al., 1999). In Fig. 4a, the semi-circle loops of AC-3 and AC-2 are close to each other, whereas they are distinctly smaller than that of AC-1, indicative of higher conductivity of AC-3 and AC-2 than that of AC-1. The conductivity of AC-3 is the highest, demonstrating that the reactivation is favorable to prepare the AC with higher conductivity. Because high mesopores rate is suitable for electrolyte ion to transport inside the porous structure of the AC. More inner-surfaces of pores inside the AC can be wetted by the electrolyte. Therefore, the conductivity of AC electrode is enhanced.

Generally, the knee frequency is considered to be the critical frequency where supercapacitor begins to exhibit capacitive behavior. These values for AC-1, AC-2 and AC-3 are 501, 398 and 252 Hz, respectively (Fig. 4a). Therefore, AC-3 has the capability of rapidly electric double-layer formation. When the frequency is less than the knee frequency, a straight line, nearly vertical to the real impedance axis ($Z'$), was observed, characteristic of an admirable capacitive behavior. Deviation from the vertical line is attributable to the diffusion resistance for electrolyte ions in porous channels of AC, which is strongly dependent...
on the detailed porous structure of the different samples.

In the phase angle plot (Fig. 4b), the approach to pure capacitive behavior at low frequency is usually identified with phase angle approaching to 90°. Better capacitive behavior always exhibits a plateau around 90° (Wang et al., 2006). Furthermore, the higher the frequency of the plateau, the better the performance of ion diffusion in porous channels of AC. Consequently, AC-3 possesses the best capacitive behavior. Accordingly, the frequencies of the 45° phase angle can be used to evaluate more conveniently the capability of ion diffusion in pore/channels at the medium-frequency region. That is, the higher the frequencies at the phase angle of 45°, the better the capacitive performance, and hence, the faster the ions diffusion. The frequency dependent behaviors of the phase angle are illustrated in Fig. 4b (Bode plots). The frequency of AC-3 is evidently higher than those of AC-2 and AC-1 at the 45° phase angle, indicating that the resistive behavior of the AC-3 is frequency-delayed and the capacitive behavior appears at higher frequencies. It is demonstrated that high mesopores ratio can enhance the performance of ion diffusion in pore/channels of AC. Meanwhile, high mesopores ratio is suitable for quick charge-discharge. Consequently, it is promising that AC-3 will exhibit the better performance of power discharge operations.

Some researchers have demonstrated that the imaginary part of the capacitance as a function of frequency is useful for gaining insight into the discharge time of the carbon material (Toupin et al., 2005). The minimum discharge time for a carbon electrode is an important factor, which is inversely related to the power that can be delivered during discharging. As shown in Fig. 4c, a maximum of the imaginary part of the capacitance can be observed at a characteristic frequency (f) for all ACs, which represents the minimum time (τ = 1/2πf) that could be used to evaluate the rate of the charge or discharge of the electrode material. Figure 4c shows that the frequency of the imaginary part for AC-3 is the largest. That is, the minimum discharge time of AC-3 among all ACs is the lowest, which implies that the quickest power discharge and the highest rate performance should be obtained. A shorter time constant for AC-3 should correlate with a higher number of large mesopores, which allows “connection” between the micropore areas.

To understand distinctly the electrochemical impedance behavior, the results of electrochemical impedance spectroscopy of the AC-3 electrode were fitted and simulated to analyze the characteristics of the electrochemical processes of the AC-3 electrode (Fig. 4d). The process is operated by mean of the equivalent circuit. The corresponding solid lines represent the fitting curves in terms of the equivalent circuit (inset in Fig. 4d). The fitting curves show that the equivalent-circuit models reasonably represent the electrochemical processes arising at the AC-3 electrodes. The object is that the impedance behavior on the whole frequency range of the supercapacitors of the AC-3 is described. The preceding electrochemical impedance spectroscopy suggests that an equivalent circuit corresponding to the impedance responses of the present system should involve the following elements (Portet et al., 2004; Nian and Teng, 2003): the bulk solution resistance (Rb), capacitance (Ci) at the contact interface of the AC particles, which was expected in parallel with the contact resistance (Rc) at high frequency. In addition, the capacitive nature of the AC electrode in the low-frequency region should be reasonably expressed as a low-frequency capacitance (Ci(ω)) in series with electrolyte resistance (Rb(ω)) at a particular depth of the pore. Because the impedance behavior of AC-3 consists in a semi-circle loop observed in the previous Nyquist plots, it can be represented by a parallel “RC” circuit. Namely, Rb-Ci associates with a series resistance Rb. The “RbCi” circuit could describe the current collector/AC-3 particles interface electronic properties. In this way, Rb here represents the interface resistance between the AC-3 particles as well as that between the AC-3 and the current collector, while the resistance of the current collector, considered as much lower than that of the AC-3 itself, is negligibly small. Due to the presence of non-ideal capacitive behavior, constant phase element (CPE), instead of the interfacial capacitance at the current collector/active material interface (Ciecl), should be virtually employed in the model. As a result, αi was represented to describe the consistency with the ideal behavior of this capacitance (0 < αi < 1), where depending on the Rb and Ci values. The semi-circle loop delays or blocks the capacitive behavior. Behind the depressed semi-circle loop, the 45° region (Warburg region) and the non-vertical slope line of low frequency impedance of supercapacitor are exhibited, which can be represented by a series “RbCi(ω)” circuit, traducing the supercapacitive behavior. Rb(ω) is the series resistance of the supercapacitor, depending on the frequency. Ci(ω) is the supercapacitor capacitance, also depending on the frequency. The total series resistance (R) of the supercapacitor is given by R = Rb + Rb + Rb(ω). This value strongly depends on the impedance contact at the current collector/active material interface. The 45° region is a consequence of the distributed resistance/capacitance in a porous electrode. At higher frequencies the resistance as well as capacitance of a porous electrode decreases, because only the part of the active porous layer is accessible at high frequencies (Kötz and Carlen, 2000). The supercapacitors behave like small impedance elements (Z=1/jωC) and almost no current flows deep down the pore. Consequently, resistance and double layer capacitance are reduced at high frequencies. The non-vertical slope line of low frequency range is a typical feature of electrochemical charging processes. The characteristic may be interpreted as resulting from non-uniform active layer thickness or a distribution in microscopic charge transfer rates, adsorption processes, or
surface roughness. Therefore, the non-vertical slope line of the low frequency impedance can be considered as the deviation from the ideal capacitive behavior. Based on the simulation results of the equivalent circuit, it is believed that the better electrochemical behavior of the AC-3 mainly originate from the suitable pore structure, with the concurrence of micropores and small mesopores, and better conductivity. Because the AC-2 holds the microporous characteristics of the AC-1, though it possesses more smaller mesopores than those of AC-1, the EIS behavior of the AC-2 must be inferior to that of the AC-3.

Galvanostatic charge/discharge measurements were conducted to calculate the specific capacitances and study the dependence of specific capacitance on different loading current densities in Fig. 5a. The specific capacitances of the three AC electrodes are ca. 206 F/g (AC-1), 212 F/g (AC-2) and 298 F/g (AC-3) at current density of 5 mA/g. When current density of 500 mA/g is loaded, these ACs still retain specific capacitance of 140 F/g (AC-1), 166 F/g (AC-2), 240 F/g (AC-3), respectively. It can be inferred that high mesopore ratio is helpful for ion diffusion in the meso-channels (Huang et al., 2011). The wettability and the conductivity of the electrode material are enhanced. In consequence, higher specific capacitance can be obtained at high loading current density.

The Ragone plots for the carbon materials are exhibited in Fig. 5b, which show the dependence between power output and energy density that is quite useful to determine the application potentials for different carbon materials (Wang et al., 2008; Xing et al., 2006). The energy and power densities were calculated by means of constant-current charging-discharging of a supercapacitor using a cell-voltage window between 0–1.0 V voltage windows and current densities between 0.01 and 50 A/g. The energy density ($E$, (kW·hr)/kg) and power density ($P$, (kW·hr)/kg) can be written, respectively, as:

\[ E = CV_d^2/2 \]  
\[ P = iV_d/2 \]

where, $C$ (F), $V_d$ (V), and $i$ (A) are the gravimetric capacitance of the two-electrode capacitor (1/4 single electrode capacitance), the voltage decrease in discharge, and the discharge current density. As seen from the Ragone plots, AC-3 can reach higher power density (ca. 1100 (kW·hr)/kg) while still maintaining high energy density (ca. 13 (kW·hr)/kg). Comparatively, with the increase of power output, although the energy densities of AC-1 and AC-2 only decrease a little, the performances of their power output are markedly inferior to that of AC-3. It is believed that AC-3 has excellent electrochemical properties of high energy density and power output, therefore very promising for application in the scenarios where high
power output as well as high energy capacity is required (Xing et al., 2006). This merit of AC-3 can be also ascribed to its good conductivity and developed mesopores which favors the fast transport of solvated ions during the charge-discharge process.

Durability of supercapacitor is also one of the most important feature for practical application (Kierzek et al., 2004), hence, all supercapacitors were cycled in galvanostatic charge/discharge of 500 mA/g (Fig. 5c). All ACs reveal a good cycleability. Meanwhile, AC-1 and AC-3 present a capacitance increase of 5% after 500 cycles, while the capacitance of AC-2 is almost stable during 500 charge-discharge circles. The capacitance increase may originate from the enhancement of the wettability inside micropores of AC during the cycleability of galvanostatic charge/discharge. Namely, more surfaces of AC were available and more electrolytic ions were adsorbed on the micropore surfaces of AC.

The loss of capacity during cycling is essentially connected with the values of self-discharge for supercapacitors (Kierzek et al., 2004). Such parameters for different ACs are presented in Fig. 5d. The capacitance losses of self-discharges are ca. 78% (AC-3), 73% (AC-2) and 48% (AC-1) after 12 hr, respectively. It is clear that not only the high values of capacitance are important for practical use but also stable capacitance with cycling. Self-discharge may result from the presence of the oxygen groups created on activation. This type of functionalities can be slowly reduced during cycling in a non-reversible way, via redox reactions. The superior performance of self-discharge for AC-3 results from the cooperation of the reactivation at high temperature and iron catalyst to remove the oxygen groups on AC.

3 Conclusions

ACs with high mesopore ratio were prepared by steam reactivation or the combination of catalyst and steam based on coconut shell carbon. Their capacitive behaviors and conductive characteristics were investigated based on CV, EIS and galvanostatic charge/discharge measurements. It was found that the capacitive behavior was improved as the mesopore ratio increased. The reason is believed to lie in the difference among their mesopore ratio and conductivity. High mesopore ratio is favorable for the ion diffusion in the meso/micro-pores. The process enhances the accessibility of the micropore surface area and the conductivity of AC electrode material. An electric equivalent circuit has been suggested to describe the Nyquist plots. The conducting resistance and the RC time constant of the supercapacitors decrease with the reactivation operated. It is noteworthy to underline that AC-3, with the highest mesopore ratio, has exhibited superior capacitive behavior, power output characteristics and high-frequency performance, as evidenced from cyclic voltammetry studies and frequency response analysis. Additionally, the AC-3 can provide much higher power density while still maintaining good energy density, due to its wide micropores and mesopores larger than 3 nm. The pore structure of AC-3 also improves the cycleability and self-discharge of supercapacitors. In conclusion, activated carbon with higher mesopore ratio can offer a great potential in supercapacitors, particularly for applications where high power output and good high-frequency capacitive performances are required.

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