On the origin of enhanced electrochemical behavior of oxidized activated carbon

Rui Niu,^{a,c} Haibo Li,^{b,*} Yulong Ma,^{a,b,}

a College of Chemistry and Chemical Engineering, Ningxia University, Yinchuan, Ningxia 750021, P.R. China.

b Key Laboratory of Ningxia for Photovoltaic Materials, Ningxia University, Yinchuan, Ningxia 750021, P.R. China.

c State Key Laboratory Cultivation Base of Energy Sources and Chemical Engineering, Ningxia University, Yinchuan, Ningxia 750021, P.R. China

* Corresponding author. Fax/Tel: +86 0951 2062414; E-mail: lihaibo@nxu.edu.cn (Haibo Li)

Abstract

The amount of ions stored within the electrochemical double layer is dominantly determined by the surface area of porous electrode. High surface area indicates high capacitance. However, this is not the case when the pore is extremely small, ~less than 1 nm. To observe this phenomenon, we have carried out an experiment by comparatively investigating the electrochemical performance of activated carbon (AC) and sulfuric acid treated AC (SAC). The results show that the electrochemical performance of SAC involving the specific capacitance, rate capability and cycling stability is significantly increased as compared to pristine AC. These are attributed to the improved porosity by differentiating the respective contributions of electrochemical double layer capacity and pseudo-capacity from SAC and AC, respectively.

Keywords: Electrochemical double layer, Capacitor, Energy storage, Carbon

1. Introduction

The electrochemical double layer capacitor (EDLC) is a new developed energy storage device that gaining rapidly increasing attentions for completing or replacing batteries. It stores ions within electrical doubles layers formed at electrolyte-electrode interface [1-4]. The EDLC has various advantages of high power, long cycles life and remission environmental pollution [5-7]. Basically, the EDLC is made up of two layers of conductive plates coated with a porous material (eventually becoming positively and negatively charged), separated by an insulator.

According to the principle of EDLC, the amount of charge is closely related to the properties of porous electrode. The porous material ideally has an ultrahigh surface area, suitable pore structure and excellent conductivity [8]. Therefore, carbon and related materials, particularly the activated carbon (AC), are widely utilized as electrode for high performance EDLC due to their high specific surface area, porous structure, low cost, large production, good electrical conductivity and environmental-friendly [9-11]. However, the AC based EDLC often suffers a low capacitance (less than 100 F g^{-1}) due to low effective surface area (only 17%) [12]. On the other hand, it is well known that the ultra-high specific surface area of AC is mainly contributed from a large amount of micropore. However, micropore is too small for ions to penetrate and therefore do not participate in ions adsorption. Additionally, double-layer overlap in the micropores might lead to inefficient ion adsorption. Nevertheless, the recent study reveals that the micropore may plays an important role in electrochemical process since an anomalous increase in carbon capacitance at pore sizes less than 1 nm has been observed [13]. This challenges the long-held axiom that pores smaller than the size of solvated electrolyte ions are incapable of contributing to charge storage.

In the past few decades, the chemical oxidation triggered by acid, i.e. H_2SO_4 [14], HNO_3 [15] and H_3PO_4 [16] etc., is being revealed as one of the most effective alternatives to improve the electrochemical performance of carbons due to its feasibility. Through oxidation, some weakly acidic functional groups, such as $-\text{OH}$, $-\text{NH}_2$ and $-\text{COOH}$ are spontaneously coupled with carbon atoms, which may improve the ion exchange ability and introduce weak pseudo reaction. Previously, extensive researches are focus on the

oxidation, the texture change on porosity and therefore the EDLC performance is more significance.

In this work, the AC has been treated by sulfuric acid through a facile hydrothermal method. The results show that the pore size of AC shifted after the treatment. Further, the enhanced capacitance of SAC is dominantly contributed from the improved micropore volume and micropore surface area by differentiating the respective contributions from double layer capacitor and pseudo capacitor. Thus, it is believed that this study provides us an alternative way to examine the insight into functionalized carbon based EDLC.

2. Experimental Section

2.1 Synthesis of SAC

The SAC was prepared by a facile hydrothermal method. At the beginning, 2 g of AC was dispersed into 25 mL 98% sulfuric acid and then subjected to a hydrothermal reactor at 120 °C for 10 h. After the mixture was cooled down to the room temperature, 500 mL distilled water was added, followed by filtrating and rinsing repeatedly using distilled water until the sulfate ion was no longer detected in the product water. After that, the SAC was obtained by simply filtrating through a vacuum filtration system. Finally, the product was placed in an oven for overnight at 80°C.

2.2 Fabrication of electrode

The electrode was fabricated by mixing 80% of SAC, 10% of carbon black and 10% of polyvinylidene fluoride (mass ratio) in ethanol with addition of a few drops of dimethylformamide. Please note that the mixture should be vigorously grinded for several minutes until it became homogenous. Subsequently, the mixtures were casted onto the graphite sheet by a medical blade, followed by drying at 80°C for 10 h in a vacuum oven.

2.3 Characterization

The morphology and structure were studied by scanning electron microscopy (SEM, SU8020). The pore size distribution and Brunauer-Emmet-Teller (BET) specific surface area were deduced from the N₂ physical adsorption measurement data (AutoChem II2920).

X-Ray photoelectron spectroscopy (XPS, Thermo ESCALAC250Xi) spectra was collected on a monochromatized Al Ka X-ray source (1486.6 eV). The functional groups on SAC were detected by Fourier transform Infrared spectra (FT-IR, TENSOR 27).

2.4 Electrochemical measurement

The electrochemical performance including cyclic voltammetry (CV), galvanostatic charging-discharging (GCD) and electrochemical impedance spectroscopy (EIS) were characterized through an electrochemical workstation (CHI 660A) by using three electrodes method in 1M KCl aqueous solution. Basically, the SAC, Pt and a saturated calomel electrode were employed as the working electrode, the counter electrode and the reference electrode, respectively. CV measurements were performed at various scan rates ranging from 1 to 100 mV s⁻¹. GCD measurements was carried out in the voltage window of -0.4-0.6 V at various current densities ranging from 1 to 3 A g⁻¹. The specific capacitance (C_s) of AC and SAC were estimated from CV and GCD curve based on the below equations, respectively [17]:

$$C_s = \frac{Q}{\Delta Vm} = \frac{\int idt}{\Delta Vm} \quad (1)$$

$$C_s = \frac{i\Delta t}{m\Delta V} \quad (2)$$

Where Q is the voltammetric charge in one sweep (C), ΔV is the potential window (1.0 V), m is the mass (g) of the sample being coated on the graphite electrode, v is the scan rate (V s⁻¹), i is the current (A) used for charging-discharging, Δt is the time for average of charge-discharge. Therefore the specific energy density (SE , Wh kg⁻¹) and the specific power density (SP , W kg⁻¹) can be separately obtained from equations (3) and (4) [17].

$$SE = \frac{1000C_{s,T}(\Delta V)^2}{7200} \quad (3)$$

$$SP = \frac{3600SE}{t} \quad (4)$$

3. Results and Discussion

Fig.1 (a), (b) and (c), (d) show the SEM image of AC and SAC in low and high magnifications, respectively. Obviously, both AC and SAC exhibit rock like shape with a

large number of holes. Meanwhile, it can be seen that the surface of SAC is smoother than that of AC. These are mainly resulted from the dehydration by sulfuric acid.

Fig. 1 SEM images of (a), (b) AC and (c), (d) SAC in different magnifications

The N_2 adsorption-desorption isotherm and corresponding pore size distribution of AC and SAC are presented in Fig.2 (a) and (b), respectively. They exhibit representative type I curves with obvious capillary condensation steps above $P/P_0=0.4$, implying the existence of mesopores which guarantees a huge space for ion accommodation. Furthermore, the texture parameters associated with AC and SAC are summarized in Table 1. The BET surface area of AC and SAC are 1477.2 and $1244.7 \text{ m}^2 \text{ g}^{-1}$, respectively. Accordingly, the micropores volume and surface area of AC and SAC are 0.17 , $0.22 \text{ m}^3 \text{ g}^{-1}$ and 336.5 and $411.8 \text{ m}^2 \text{ g}^{-1}$. These values demonstrate that the sulfating do not change the pore texture of AC except for introducing more micropores.

Fig. 2 (a) Nitrogen adsorption-desorption isotherms of AC and SAC, (b) pore size distribution.

Table 1 Porosity texture of AC and SAC

Sample	S_{BET} (m^2g^{-1})	$V_{\text{micropore}}$ (cm^3g^{-1})	$S_{\text{micropore}}$ (m^2g^{-1})	$D_{\text{averagepore}}$ (nm)
AC	1477.2	0.17	336.5	0.17
SAC	1244.7	0.22	411.8	0.17

FTIR spectra shown in Fig.3 (a) is recorded to evaluate the functional groups. The FTIR spectrum of AC shows three intense bands at 3428 cm^{-1} , 1632 cm^{-1} and 1132 cm^{-1} , which are assigned to -O-H stretching vibration of hydroxylic groups [10], -C=O stretching vibration of carbonyl groups [18] and -C-O stretching vibration [11], respectively. Remarkably, there are three new peaks at 1388 cm^{-1} , 1013 cm^{-1} and 618 cm^{-1} appearing on SAC spectrum as compared to pristine AC, in which the peak at 1388 cm^{-1} is attributed to -O-H bending vibration [19] while the peak at 1013 cm^{-1} and 618 cm^{-1} confirm the presence of -SO₃H [20, 21]. It is necessary to mention that the intense water containing groups as well as -O-H and -SO₃H are beneficial to improve the hydrophilicity of SAC, resulting in better electrochemical effective interface and therefore the performance. The XPS spectrum of AC and SAC depicted in Fig.3 (b), (c) and (d) are employed to examine the insight into chemical bond. It can be observed from the Fig.3 (b) that the SAC exhibits C1s, O1s and S2p, indicating the successfully doping of sulfur. Fig.3 (c) shows the C1s peak of AC and SAC. The broad carbon peaks are observed in the binding energy ranging from 282 to 292 eV. Deconvolution of the C1s spectra of AC and SAC could generate five peaks at 284.8, 286.2, 287.8, 289.1, and 291.0 eV, corresponding to C-C or C=C, C-O or C=N or C-S, C=O, O-C=O, and π - π^* [10,14,22,23], respectively. Fig.3 (d) shows the S2p spectra of AC and SAC. As compared to AC, the S2p peak of SAC can be divided into two doublets having different binding energies: one doublet with lower binding energy arising from electron-rich ($2p^{2/3}$) sulfur, and another with higher binding energy arising from electron-poor ($2p^{1/2}$) sulfur, which is mainly caused by different environments around sulfur atoms [14,21]. Table 2 summarizes the intensities of various peaks in terms of corresponding components. The intensity of the peak at 286.2 eV is enhanced after the treatment due to the involvement of C-SO₃H or C-OSO₃H. In contrast, the intensity of the peak at 289.1 eV is decreased. This is probably attributed to the fact that the sulfuric acid

react with $\text{O}-\text{C}=\text{O}$ yielding $-\text{O}-\text{SO}_3\text{H}$ [14]. According to the literature [14], it is recognized that the H^+ derived from the $-\text{SO}_3\text{H}$ or $-\text{OSO}_3\text{H}$ is possibly to exchange with K^+ during the electrochemical process and thereby enhance the specific capacitance.

Fig. 3 (a) FT-IR, (b) XPS, (c) C1s and (d) S2p spectra of AC and SAC.

Table 2 XPS data of AC and SAC

Sample	Peak position (eV)	Percentage (%)	
		AC	SAC
C1s	284.8 (C-C/C=C)	79.94	78.68
	286.2 (C-O/C=N/C-S)	9.65	10.66
	287.8 (C=O)	1.84	2.92
	289.1 (O-C=O)	4.89	3.06
	291.0 ($\pi-\pi^*$)	3.68	4.78
S2p	168.5 ($2p^{1/2}$)	34.18	
	169.3 ($2p^{2/3}$)	65.82	

The CV curves of SAC measured at scan rate ranging from 1 to 100 mV s^{-1} in 1 M KCl solution within potential window of -0.4-0.6 V are showed in Fig.4 (a). Regardless of the

scan rate, the CV curves of SAC show an almost rectangular shape without redox peak, indicating the SAC has an ideal capacitive behavior. According to Eq. (1), the C_s can be obtained and depicted in Fig.4 (b). At each scan rate, the C_s of SAC is much larger than that of AC, evidencing the improved EDLC performance. For comparison, the capacitance of SAC electrode was 232 F g^{-1} whereas the AC was 219 F g^{-1} at the scan rate of 1 mV s^{-1} , showing an incensement of 6%. When the scan rate was increased from 1 to 100 mV s^{-1} , the C_s of AC decreased from 219 to 75 F g^{-1} with a drop by $\sim 66\%$. In contrast, the C_s of the SAC electrode only dropped by $\sim 35\%$ from 232 to 150 F g^{-1} , indicating better scan rate dependence.

The GCD curve of SAC are shown in Fig.4 (c). Obviously, all the curves are symmetrical and linear continuous at different current densities from 1 A g^{-1} to 3 A g^{-1} , indicating that the electrode has excellent electrochemical reversibility and charge-discharge quality. Meanwhile, the iR drop is very small at 3 A g^{-1} , implying better conductivity of SAC. The C_s of AC and SAC electrode obtained from the GCD process according to Eq. (2) were depicted in Fig.4 (d) for comparison. It can be clearly seen that C_s decreased as the current density ranging from 1 to 3 A g^{-1} . When the current density was increased from 1 to 3 A g^{-1} , the C_s of AC electrode decreased from 67.0 to 40.5 F g^{-1} with a drop by $\sim 40\%$. In contrast, the C_s of SAC electrode only dropped by $\sim 17\%$ from 111.1 to 91.8 F g^{-1} , demonstrating the better electrochemical behavior.

Fig. 4 (a) CV curves of SAC at various scan rates, (b) mass normalized specific capacitance of AC and SAC with respect to the scan rates, (c) GCD curves of SAC under

different current densities, (d) gravimetric capacitance of AC and SAC with respect to the current density.

Previously, it is well known that the pores smaller than the size of solvated electrolyte ions are incapable of contributing to charge storage. However, Chmiloa *et al* have explored the impact of pore size on the electrochemical performance of carbons [13]. Their findings classified three pore size distribution areas, in which the dependence of normalized capacitance on average pore size is different (referring to Fig.5). When pores were substantially larger than twice the size of the solvated ions, there was a contribution to capacitance from compact layers of ions residing on both adjacent pore walls. In this case, the capacitance is proportional to surface area (Fig.5 (a)). When the pore size is decreased less than twice the solvated ion size, it would reduce the normalized capacitance because compact on layers from adjacent pore walls impinged and the surface area usable for double layer formation was reduced (Fig.5 (b)). This trend reversed with a further decrease in the pore size to less than that of the solvated ion size. Decreasing the pore size to a value approaching the crystal graphic diameter of the ion would result in 100% increase in normalized capacitance (Fig.5 (c)). From table 1, it is read that the $V_{\text{micropore}}$ and $S_{\text{micropore}}$ of SAC are larger than that of AC (Fig.5 (d) and (e)). Thus, SAC may provide as much as tunnels for penetrating ions.

Fig. 5 Drawing of solvated ions residing in pores with distance between adjacent pore walls (a) greater than 2 nm, (b) between 1 and 2 nm, (c) less than 1nm, (d) AC, and (e) SAC

To solid our explanation, it is possible to compare the respective contribution of pseudocapacitance from AC and SAC, respectively. According to the studies by Trasatti *et al.* [24], the outer electrochemical surface, estimated from the outer charge (q_o^*), corresponds to the region touching the electrolyte directly; the inner electrochemical surface, estimated from the inner charge (q_i^*), indicates the regions of pores, grain boundaries, crevices, and crack, etc. So, the C_o^* can be gained from the extrapolation of C^* to $v=\infty$ from the plots of C^* vs. $v^{-1/2}$ (see Fig.6 (a)), the total charge (C_t^*) can be estimated from the extrapolation of C^* to $v=0$ from the plots of $1/C^*$ vs. $v^{1/2}$ (see Fig.6 (b)). Accordingly, the C_i^* can be obtained from the difference between C^* and C_t^* . Hence, C_t^* , C_o^* and C_i^* are summarized in Table 3. Due to the abundant presence of oxygen-containing functional groups, 69.99% of C_i^* comes from the pseudo-capacitance for AC. However, the corresponding percentage is only 32.60% for SAC, implying that the improved specific capacitance of SAC is mainly contributed from the double layer capacitance.

Fig. 6 Dependence of (a) C^* on $v^{-1/2}$ and (b) $1/C^*$ on $v^{1/2}$ for AC and SAC

Table 3 The total capacity (C_t^*), outer capacity(C_o^*) and inner capacity(C_i^*) for AC and SAC

Sample	C_t^*	C_o^*	C_i^*	C_i^*/C_t^*
AC	31.01	9.76	21.25	68.53
SAC	96.80	65.20	31.60	32.65

Enable to understand the EDLC power performance of SAC electrode, the kinetic features of the ion diffusion inside of the porous electrode was investigated using EIS. Fig.7 show the Nyquist plot at the frequency range from 0.01 kHz to 100 kHz for both AC and SAC electrodes with an enlarged plot for the high-frequency region and equivalent

circuit in the inset. The EIS composed of an almost vertical line in the low-frequency region indicates a good capacitive behavior and a small semicircle in the high-frequency region which from the double layer capacitance (C_{dl}) in parallel with the overall contact impedance (R_{ct}) produced by the electrical connection and the charge transfer at the contact interface. Otherwise, the R_{ct} represents overall diffusion generated from the electrolyte ions diffuse in the electrode surface and diffusion of the exchange process and electrolyte. Through simulating equivalent circuit, it can be obtained that the C_{dl} value of AC and SAC are 0.06063 and 0.1172 F cm⁻². Meanwhile, the SAC exhibits contact impedance of 1560 Ω cm², which is higher than the value of AC (219 Ω cm²). On the other hand, the R_{ct} value of SAC is 9.053 Ω cm², which is also higher than the corresponding value of AC (5.953 Ω cm²). These are ascribed to longer diffusion distance within the enlarged micropore space (referring to the N₂ adsorption-desorption results).

Fig. 7 Nyquist plot of the EIS of the AC and SAC electrodes, the inset shows the high frequency region of the plot and the equivalent circuit

The Ragone plot of the estimated specific energy and specific power for AC and SAC electrode at various charge-discharge current densities are showed in Fig.8 (a). As can be observed from the figure, the specific energy of the SAC electrode is much higher than that of AC electrode at each specific power density. Regarding to SAC electrode, as the specific power density increases from 0.56 to 1.5 kW kg⁻¹, the specific energy drops from 15.43 to 12.75 Wh kg⁻¹. On the other hand, the cycles stability of the SAC electrode was tested by continuous charge-discharge measurement in potential windows ranging from -0.4 V to 0.6 V at a current density of 2 A g⁻¹. Fig.8 (b) shows the cycling performance of

SAC electrode. As shown, the SAC electrode remained 85% capacity retention after 400 charge-discharge cycles, exhibiting good cycle ability.

Fig. 8 (a) Ragone plot of the estimated specific energy and specific power for AC and SAC electrode at various charge-discharge current densities. (b) Charge-discharge cycling test of the SAC electrode at a current of 2 A g^{-1} for 400 cycles

4. Conclusions

In this work, the sulfuric acid oxidized activated carbon (SAC) has been prepared for electrochemical double layer capacitor (EDLC). The electrochemical results show that the SAC has an improved electrochemical performance, i.e. specific capacitance and energy density, by compare to that of AC. Further, by calculating the respective contributions of double layer capacity and pseudo-capacity from AC and SAC, it is demonstrated that the improved micropore volume and surface are account for the enhanced EDLC performance.

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