Improvement in electrochemical capacitance of carbon materials by nitric acid treatment

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ABSTRACT

Four commercial carbon materials, carbon nanotube, active carbon, acetylene black, and graphite, were treated by concentrated nitric acid. The surface properties and the electrochemical capacitance of the treated and the untreated carbon samples were studied by using scanning electron spectroscopy, BET surface analysis, constant current charge/discharge test, cyclic voltammetry, and alternative current impedance. It is found that the untreated samples have different specific capacitance and specific surface area, which are in the order from large to small: carbon nanotube, active carbon, acetylene black, and graphite. After treated with nitric acid, the specific surface area of these commercial carbon materials increases to different extents, and the specific capacitance of carbon nanotube, acetylene black and graphite increases proportionally to their specific surface area but the specific capacitance of active carbon decreases. The effect of acid treatment on the capacitance of the commercial carbon samples is related to their porosity structure and surface functional groups.

1. Introduction

Electrochemical capacitors are new maintenance-free energy storage devices that fill the gap between normal capacitors and secondary batteries [1,2]. They can deliver higher power in short time than batteries and store more energy than normal capacitors. Moreover, electrochemical capacitors have longer cycle life, wide work–temperature range, short charge time, and no pollution and zero emission. Due to these advantages, electrochemical capacitors find their wider and wider application in many fields, such as tools, information technology and electric vehicles. Thus they have been attracting intensive research [3–5]. Carbon materials are the main materials used as the electrodes of electrochemical capacitors [6–8]. It has been accepted that the electrochemical capacitance of carbon materials depends to a great extent on their pore structure and surface functional groups [9,10]. These properties of carbon materials can be changed by heat or chemical treatment. The purpose of this paper is to understand the effect of acid treatment on the electrochemical capacitance of four commercial carbon materials, carbon nanotube, active carbon, acetylene black, and graphite.

2. Experimental

2.1. Carbon materials

Four commercial carbon materials, carbon nanotube (CNT, Chengdu Institute of Organic Chemistry), active carbon (Tianjin Fuchen Chemical Regent Factory, A.R.), graphite (Tianjin Fuchen Chemical Regent Factory, A.R.), and acetylene black (Guangzhou Newport Chemical Industry Ltd., C.R.), were used. Before used, they were dried at 60 °C for 24 h in vacuum oven. In the treatment, the commercial carbon samples were distilled and refluxed in concentrated nitric acid (Guangzhou Donghong Regent Factory, A.R.) at 80 °C for 1 h, then filtered and washed with double distilled water until the pH of the filtrate was near 7, and dried at 60 °C for 24 h in vacuum oven.

2.2. Preparation of electrodes

Treated and untreated carbon materials were mixed with binder powder (PTFE) in a mass ratio of 9:1. The mixture was dispersed in 1-methyl-2-pyrrolidon (Sinopharm Group Chemical Reagent Co. Ltd., C.P.) ultrasonically for 30 min, coated on the cleaned nickel foam, and pressed under 20 MPa to form thin films with uniform thickness as electrodes and dried at 60 °C for 24 h in vacuum oven.

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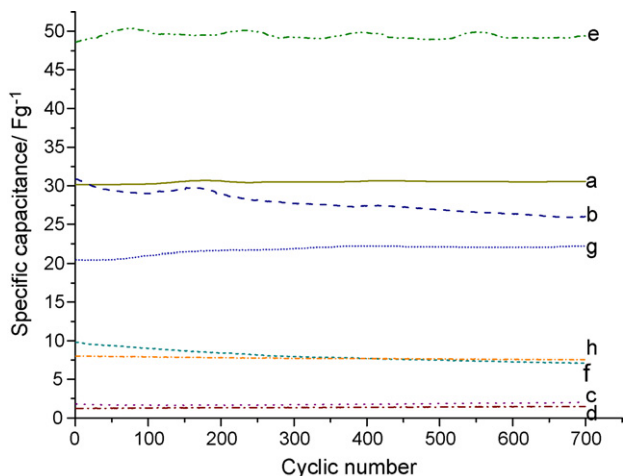E-mail address: liwsh@scnu.edu.cn (W.S. Li).

Fig. 1. The relationship of discharge specific capacitance with cycle number for carbon samples under charge and discharge rate of 100 mA g^{-1} between 0 V and 1.2 V (vs. open circuit potential). (a) Untreated CNT, (b) untreated active carbon, (c) untreated acetylene black, (d) untreated graphite, (e) treated CNT, (f) treated active carbon, (g) treated acetylene black, and (h) treated graphite.

Table 1
Properties of carbon samples before and after nitric acid treatment

Sample[a]	Average specific capacitance (F g^{-1} at 100 mA g^{-1})	Specific surface area (m^2 g^{-1})	Faradaic resistance (Ω)
a	30.50	334.4	1.3
b	27.80	264.2	1.7
c	1.79	66.4	4390
d	1.38	9.7	35.5
e	49.47	343.8	0.6
f	8.04	432.7	2.5
g	21.74	152.4	0.9
h	7.74	18.9	3.0

[a] (a) Untreated CNT, (b) untreated active carbon, (c) untreated acetylene black, (d) untreated graphite, (e) treated CNT, (f) treated active carbon, (g) treated acetylene black, and (h) treated graphite.

2.3. Assembly of electrochemical capacitors

A symmetrical capacitor consisting of two identical electrodes was set up. Two electrodes were separated by a fiber separator and
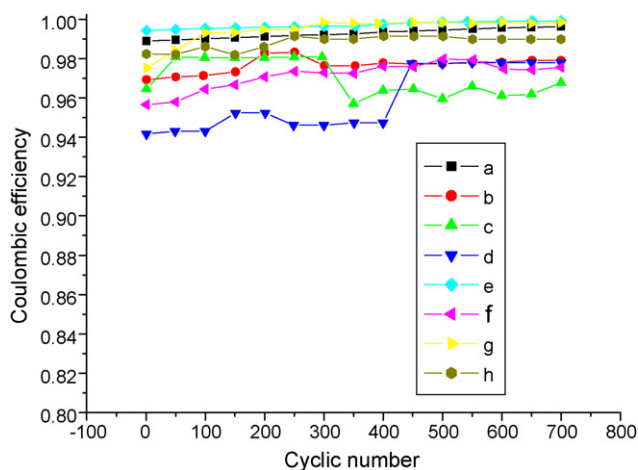

Fig. 2. Variation of coulombic efficiency with cycle number. (a) Untreated CNT, (b) untreated active carbon, (c) untreated acetylene black, (d) untreated graphite, (e) treated CNT, (f) treated active carbon, (g) treated acetylene black, and (h) treated graphite.

Fig. 3. Relation of specific capacitance of carbon samples with discharge rate. (a) Untreated CNT, (b) untreated active carbon, (c) untreated acetylene black, (d) untreated graphite, (e) treated CNT, (f) treated active carbon, (g) treated acetylene black, and (h) treated graphite.
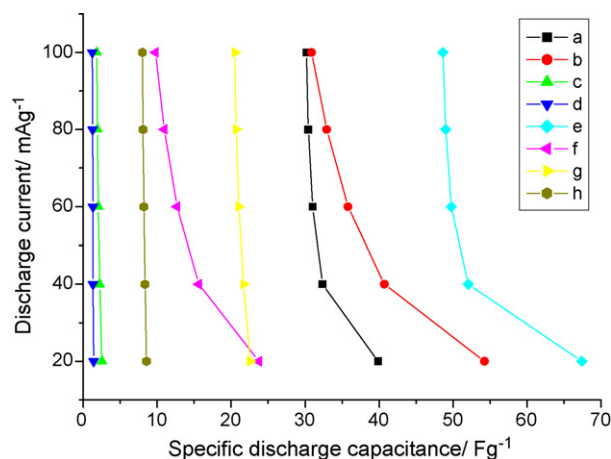
the electrolyte was 6 mol l^{-1} KOH solution. Before test, the cell was immersed in the electrolyte for 24 h.

2.4. Electrochemical measurement

Cyclic voltammetry, constant current charge/discharge test and alternative current impedance were carried out on Solartron 1480. The cell capacitance was obtained from the slope of the discharge curve with Eq. (1):

$$C = \frac{I \Delta t}{\Delta V} \tag{1}$$

where C is the cell capacitance in Farad (F), I is the discharge current in ampere (A) and $\Delta t / \Delta V$ is the slope of the discharge curve (V s^{-1}) [11,12].

The electrochemical capacitors set up in this paper were in a symmetrical system. However, the weight of the active materials could not be kept exactly the same for the two electrodes. Thus the average weight of two electrodes was used to calculate the specific
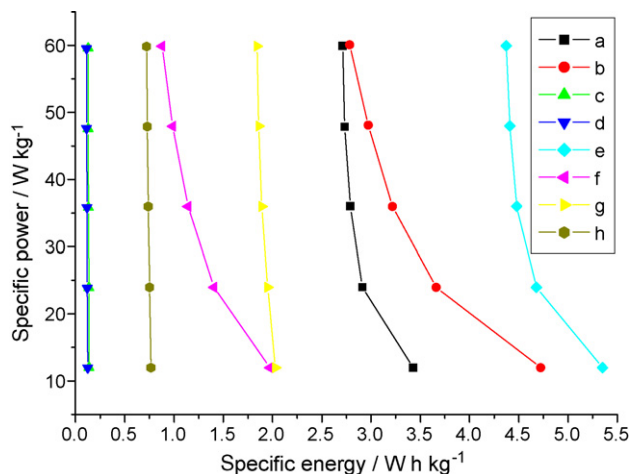

Fig. 4. Plot of specific power vs. specific energy (Ragon plot). (a) Untreated CNT, (b) untreated active carbon, (c) untreated acetylene black, (d) untreated graphite, (e) treated CNT, (f) treated active carbon, (g) treated acetylene black, and (h) treated graphite.

Fig. 5. Voltammograms of carbon samples, sweep rate: $10\,mV\,s^{-1}$.

Fig. 6. SEM images of carbon samples. (a) Untreated CNT, (b) untreated active carbon, (c) untreated acetylene black, (d) untreated graphite, (e) treated CNT, (f) treated active carbon, (g) treated acetylene black, and (h) treated graphite.
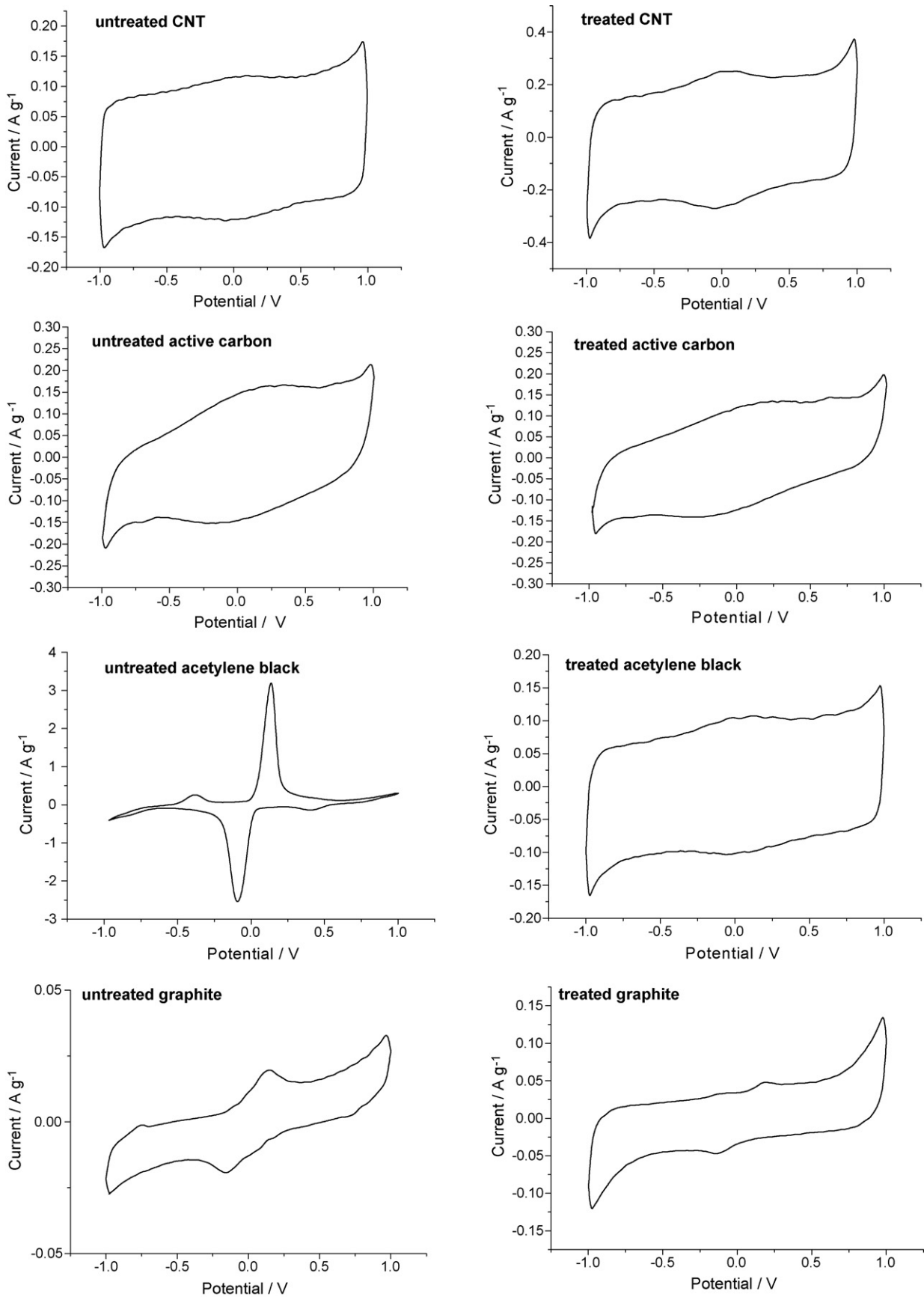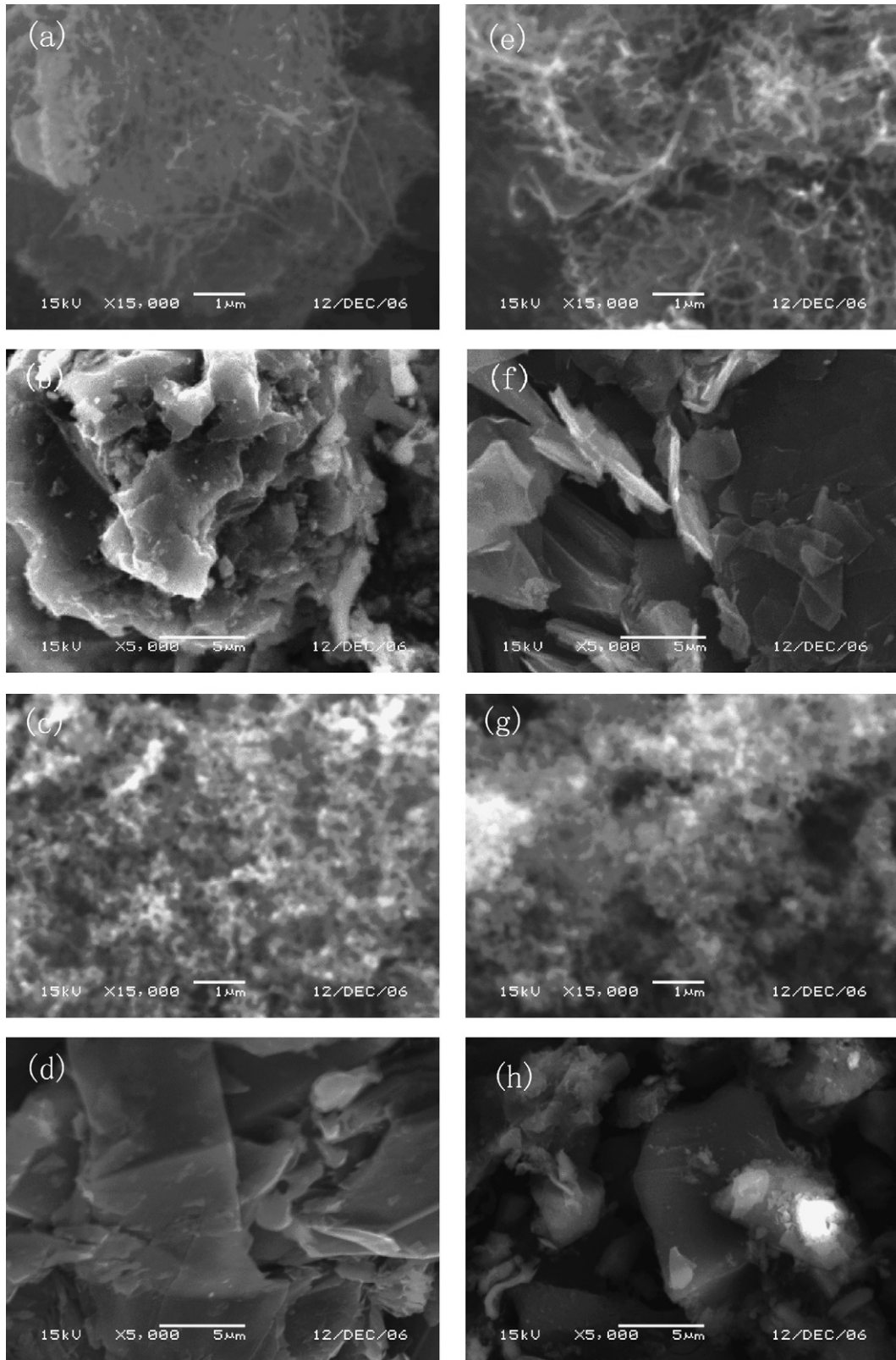
capacitance C_m (Fg^{-1}) [13]:

$$C_m = \frac{2C}{m} \tag{2}$$

where C is the cell capacitance and m is the average weight (g) of the active material.

In the alternative current impedance measurement, the frequency was from 10^5 Hz to 10^{-2} Hz and the potential magnitude was 5 mV.

2.5. SEM observations and BET specific surface area determination

SEM images were observed with JSM-6380LA (Rigaku). Specific surface area was determined by N_2 adsorption–desorption at the temperature of 77 K with BET analyzer (ASAP 2020, Micromeritics).

3. Results and Discussion

Constant current charge/discharge test was used to obtain the capacitance behavior of the carbon samples. Fig. 1 presents the variation of discharge specific capacitances of the treated and the untreated samples with cycle numbers under a charge and discharge current of 100 mA g^{-1}. It can be seen from Fig. 1 that the specific capacitance of four untreated samples is very different from each other. The initial capacitance of active carbon is the biggest, but its capacitance decreases gradually with cycling. The initial capacitance of CNT is a little smaller than that of active carbon but its capacitance has less change with cycling. The initial capacitance of acetylene black and graphite is far smaller than that of active carbon or CNT and their capacitance is hardly influenced by cycling. The average specific capacitance of the samples during 700 cycles is tabulated in Table 1.

The change of the specific capacitance with cycle numbers for the treated samples is similar to that for the untreated samples. However, the specific capacitance of the samples except active carbon is improved significantly by the acid treatment. It can be seen from Table 1 that the increase magnitude of the specific capacitance is different, by 62%, 1115% and 461%, for CNT, acetylene black and graphite, respectively. Different from these samples, the specific capacitance of active carbon decreases by 71% due to the acid treatment.

Fig. 2 shows the variation of coulombic efficiency with cycle numbers. It can be seen from Fig. 2 that coulombic efficiency of carbon samples is different from each other and can be influenced by the acid treatment. CNT shows its high coulombic efficiency and the acid treatment improves its coulombic efficiency. Compared with CNT, active carbon, acetylene black and graphite have poorer coulombic efficiency when they are untreated. Coulombic efficiency is improved significantly for acetylene black and graphite but less influenced for active carbon by the acid treatment.

The specific capacitance of carbon samples should be related to the charge/discharge rate. Fig. 3 shows the relation of specific capacitance of the treated and the untreated samples with charge/discharge rate, and Fig. 4 shows the specific energy of the corresponding capacitors with their specific power. It can be seen from Figs. 3 and 4 that the specific capacitance and the specific energy of the samples more rely on the charge/discharge rate when the samples have larger specific capacitance or when the samples are charged/discharged under smaller charge/discharge current. It is noted that among all the samples, the specific capacitance and the specific energy of active carbon, treated or untreated, is most influenced by the charge/discharge rate.

Fig. 5 shows the voltammograms of the treated and untreated samples in 6 mol l^{-1} KOH solution. It can be seen from Fig. 5 that
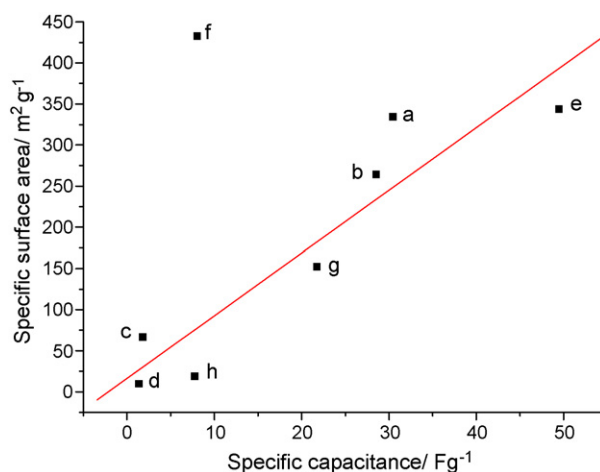

Fig. 7. Relationship of average specific discharge capacitance with specific surface area of carbon samples. (a) Untreated CNT, (b) untreated active carbon, (c) untreated acetylene black, (d) untreated graphite, (e) treated CNT, (f) treated active carbon, (g) treated acetylene black, and (h) treated graphite. The line in the plot is obtained by fitting all the points except point f.

there is different voltammetric behavior for each untreated sample. The untreated CNT has a quasi-rectangular voltammogram like a capacitor [14–16] and one couple of weak oxidation/reduction peaks at 0 V, which can be ascribed to surface functional group. The voltammetric behavior of untreated active carbon, acetylene black and graphite is different from that of CNT. The voltammogram of untreated active carbon slopes upwards towards the right hand side, indicating that this material has large internal resistance. The large internal resistance can account for the dependence of the specific capacitance and the specific energy of active carbon on the charge/discharge rate. A couple of significant oxidation/reduction peaks appear in the voltammograms of untreated acetylene black and graphite, indicating that these materials contain impurity. Cu, Ni, Co, Fe, Mn, and Zn were detected when examining these samples with ICP. The impurity may account for the unsteady coulombic efficiency.

The voltammetric behaviors of the samples are influenced to different extents by acid treatment, as shown in Fig. 5. After acid treatment, the voltammetric behaviors of CNT and active carbon are less changed but the current increases for CNT and decreases for active carbon, i.e., the capacitance increases for CNT and decreases for active carbon. This is in agreement with the constant current charge/discharge test, as shown in Fig. 1. The redox peaks from impurity disappear completely for acetylene black, indicating that the impurity in acetylene black can be removed by the acid treatment. On the other hand, the impurity in graphite is not easy to be removed because the redox peaks from the impurity in the untreated sample can still be observed in the treated sample.

Fig. 6 shows the images of SEM of the treated and untreated samples. It can be seen from Fig. 6 that before treated with nitric acid, CNT is composed of long pipelines with an average diameter of 50 nm, active carbon is composed of sheets of 100 nm thick with lots of particles on the sheets, acetylene black has a flocculent structure, and graphite also has sheet size like active carbon, but it is larger and smoother than active carbon.

The surface morphology of the samples is changed when they are treated by acid. After acid treatment, the surface of CNT becomes rough, as shown in Fig. 6e, indicating that some carbon–carbon bonds are broken by nitric acid. This change should cause the increase of the surface area. The particles on the untreated active carbon disappeared after treatment, as shown in Fig. 6f. This should cause the decrease of surface area. It can be seen from Fig. 6g and
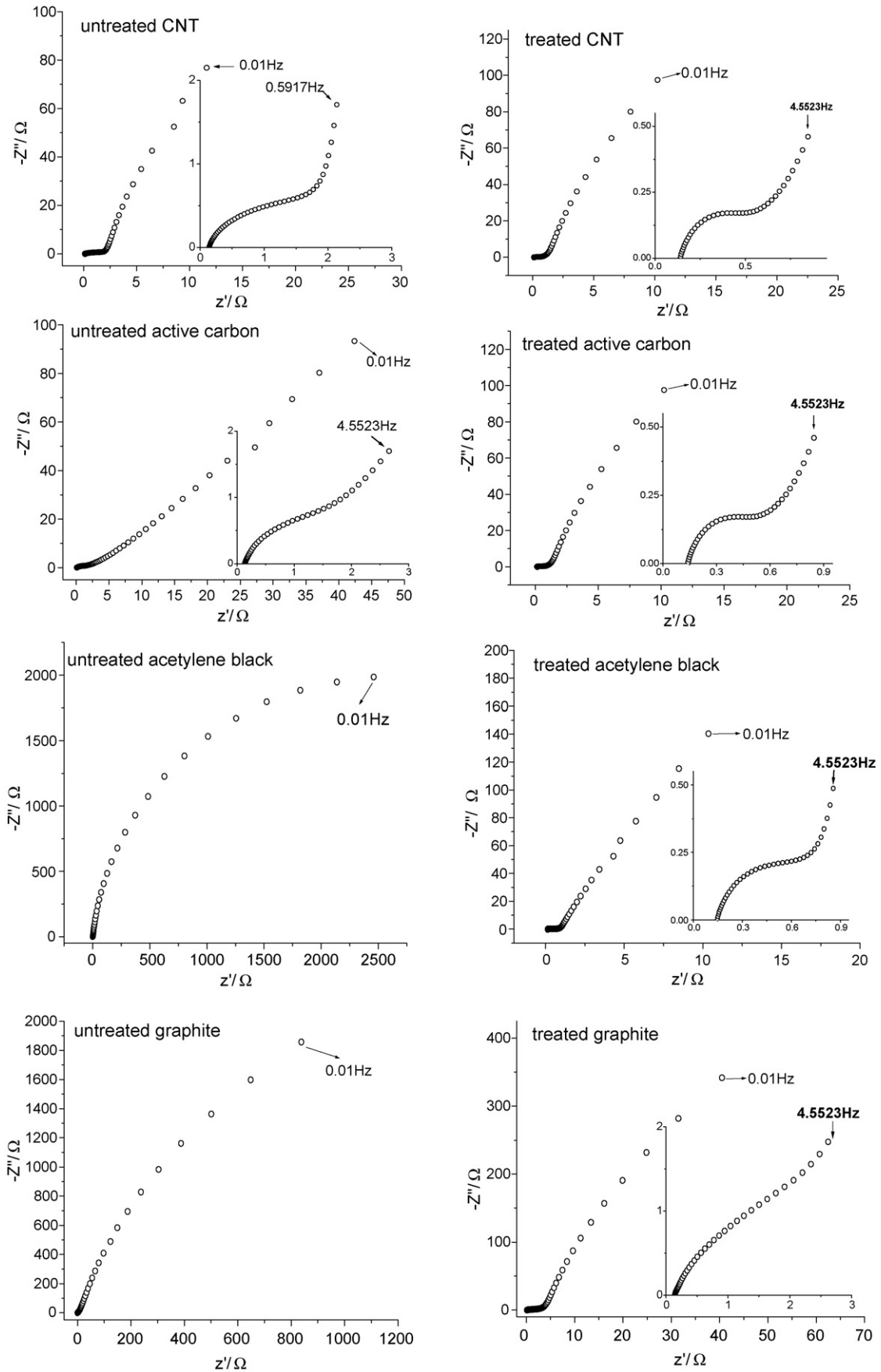
Fig. 8. Alternative current impedance spectra of carbon samples from 10^5 Hz to 10^{-2} Hz at open circuit potential.

h that acetylene black and graphite are etched due to the acid treatment. This should cause the increase of the surface areas. The change in specific surface area for the samples due to the acid treatment can be confirmed by BET measurement, as shown in Table 1.

Fig. 7 shows the relation of the average specific capacitance of the treated and untreated samples at $100\,\mathrm{mA\,g^{-1}}$ with their specific surface area. It can be seen from Fig. 7 that, except the treated active carbon, the specific capacitance of the samples is almost proportional to their specific surface area. It is noted that, except active carbon, the increase magnitude in specific capacitance of carbon samples due to the acid treatment is larger than that in specific surface area.

In fact, specific capacitance of carbon sample is related not only to its specific surface area, but also to its electric conductivity, porosity structure and surface functional groups [17]. Only the electrolyte-wetted surface contributes to capacitance [18]. Thus, the micropores that electrolyte cannot be reached or the surfaces that contain hydrophobic groups do not contribute to capacitance. The acid treatment improves not only surface area of the carbon samples by breaking carbon–carbon bonds in the samples, but also their surface wettability by forming hydrophilic groups, such as carbonyl or carboxyl groups. As for active carbon, there are lots of sealed micropores in it. These sealed micropores are opened by the acid treatment, resulting in the significant increase in surface area. However, these opened pores are too small to be wetted, so that the acid treatment does not contribute to capacitance.

Fig. 8 shows the alternative current impedance spectra of the treated and the untreated samples at open circuit potential. It can be seen from Fig. 8 that the impedance spectrum of all the samples reflects Faradaic process at high frequency range, except the untreated acetylene black and the untreated graphite, which behave like a Faradaic process at all frequency range. The Faradaic process can be ascribed to redox reaction of functional groups on the sample surface or active impurity in the samples. The Faradaic resistance of the samples estimated by the semicircles at high frequencies, from $100\,\mathrm{Hz}$ to $50\,\mathrm{Hz}$ for all samples except the untreated acetylene black and the untreated graphite whose Faradaic resistance is estimated at the all frequencies, is tabulated in Table 1.

With the acid treatment, the Faradaic resistance of CNT decreases from $1.3\,\Omega$ to $0.7\,\Omega$. The resistance decrease can be ascribed to the increase of hydrophilic functional groups on CNT due to the acid treatment. This can be confirmed by the larger redox current of the treated CNT near $0\,\mathrm{V}$ than the untreated CNT, as shown in Fig. 5. However, the Faradaic resistance of active carbon increases from $1.7\,\Omega$ to $2.5\,\Omega$. This can be ascribed to the less wettable surface available on the treated sample than the untreated sample, although the treated sample has larger surface area than the untreated sample. The acid treatment changes the impedance of acetylene black from the reaction of impurity to that of surface functional groups whose Faradaic resistance is only $0.9\,\Omega$, which can also be confirmed by its voltammograms, as shown in Fig. 5. The impedance of graphite is also changed by the acid treatment, but the treated graphite still has larger Faradaic resistance ($3.0\,\Omega$) compared with the treated CNT or the treated acetylene black. This accounts for the difference in voltammogram between the treated graphite and the treated CNT or the treated acetylene black, as shown in Fig. 5.

4. Conclusion

The specific capacitance of carbon samples is determined by their structure and surface properties. The specific capacitances of untreated CNT, acetylene black and graphite can be improved significantly by nitric acid treatment, which is ascribed to the increase in surface area and hydrophilic functional groups due to the acid treatment. However, the nitric treatment has a negative effect on active carbon, whose specific capacitance decreases after the treatment. This negative effect results from micropore structure in active carbon, which is too small to be wetted. Therefore, it is necessary that carbon materials for the application in electrochemical capacitors should have large wettable surface.

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