

Communication

# High Power Density Electric Double Layer Capacitor with Improved Activated Carbon

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The improvement on commercial activated carbon (AC) through the reactivation under steam in the presence of  $\text{NiCl}_2$  catalyst leads to the increases of both energy and power densities of electric double layer (dl) capacitors. When AC was treated at 875 °C for 1 h, its discharge specific capacitance increases up to  $53.67 \text{ F} \cdot \text{g}^{-1}$ , an increase of about 25% compared to the as-received AC. Moreover, a significant increase in high rate capability of electric dl capacitor was found after the improvements. Surprisingly, both the treated and untreated AC samples showed similar specific surface area and pore size distribution, but some changes in the surface groups and their concentrations after reactivation were verified by X-photoelectron spectra. Thus, it is reasonable to conclude that the decrease in the surface concentration of the carbonyl-containing species for the improved AC results in an increase of accessibility of the pores to the organic electrolyte ion, causing the enhancements of both the specific capacitance and high rate capability.

**Keywords**    activated carbon, electric double layer capacitor, high-rate capability, surface group

## Introduction

Recently, there has been an increasing interest in the development of electric double layer capacitors (EDLCs) using highly porous carbons as the electrode materials due to their possible technological applications as energy storage devices possessing high power density capability.<sup>1,2</sup> The main advantages of such devices are their possible high rate capability and long cycle life as compared to rechargeable batteries, but its energy density is lower than that of rechargeable batteries. In order to obtain the required energy and power density, EDLC electrode materials must have a large specific surface area, suitable pore size distribution (PSD), good electrical conductivity and wettability by the electrolytes.<sup>3,4</sup> To meet these requirements, carbonaceous materials such as activated carbons, carbon aerogels/xerogels and carbon nanotubes have been extensively studied as the electrodes in EDLCs.<sup>5-8</sup> Among them, AC should be especially attractive for EDLCs from the economical point of view.

Usually, the specific surface area of AC determines the thermodynamics of electric charge stored within the pores,

and the dl charging/discharging kinetics is mainly controlled by PSD.<sup>9</sup> It is known that ACs with a large surface area, a high mesoporous ratio as well as good electrical conductivity are required for the fabrication of practical EDLCs. However, it is not easy to find a commercial AC satisfying these requirements. Thus, improvement on AC is always needed for the development of EDLC. Recently, some researchers have focused on the preparation and modification of carbon materials so that the pore structure can be improved, which may lead to the desirable specific energy and power density of the EDLCs.<sup>10-12</sup> As reported in literature,<sup>13,14</sup> the physicochemical properties of AC, such as specific surface area, PSD, and porous structure could be improved by the catalytic gasification under  $\text{CO}_2$  and steam from carbon precursor or by secondary activation of the commercial AC. The main purpose of this work is to improve an inexpensive commercial AC under steam so that the dl capacitance and high rate capability of the EDLCs could be increased.

## Experimental

Improvement of a commercial AC was performed through secondary activation under steam in the presence of  $\text{NiCl}_2$  in the temperature range of 800—925 °C. The commercial activated carbon (Kureha Chemical Co., Japan) with a specific surface area of *ca.*  $1050 \text{ m}^2 \cdot \text{g}^{-1}$  was blended with 0.43 wt%  $\text{NiCl}_2$  in aqueous solution and stirred at about 80 °C for 4 h. It was then dried at 110 °C overnight and heated in a tube furnace under Ar or  $\text{N}_2$  for 2 h at a desirable reaction temperature. After that, the gas was switched to steam and reactivation was continued for 1 h. The reactivated AC was then cooled to room temperature under Ar or  $\text{N}_2$  and served as the active material for EDLC.

To prepare the polarizable electrodes, an electronic conductor (LB-300H) was added to AC in order to ensure good conductivity. An AC/LB-300H mixture was then added to PVdF/NMP [poly(vinylidene fluoride)/1-methyl-2-pyrrolidinone] solution to form a carbon slurry, where the weight ratio of AC:LB-300H:PVdF was 8:1:1. After mixing, the slurry

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was sprayed on an aluminum foil collector (20  $\mu\text{m}$ ) using a doctor-blade and dried at 130  $^{\circ}\text{C}$  for 30 min to form the carbon layer. The sheet-type electrode pellets (geometric area: 2  $\text{cm}^2$ ) were dried under vacuum at 130  $^{\circ}\text{C}$  for more than 3 h before use. Each electrode contained about 12 mg of AC.

Screw-type cells were assembled in an argon-filled glove box and used as model cells for the electrochemical measurements. A pair of polarizable electrodes were separated by one glass fiber in between. The electrolyte used was 1.0 mol/L  $(\text{C}_2\text{H}_5)_4\text{NBF}_4(\text{TEABF}_4)$  in propylene carbonate (PC).

AC impedance measurements were performed with a Solartron Frequency Response Analyser combined with a Solartron 1286 Electrochemical Interface. Impedance spectra were obtained by applying an ac voltage of 10mV amplitude at open circuit potential (OCV) over the frequency range from 60 kHz to 10 mHz. Before the measurements, the screw-type cells were left at OCV for more than 4 h. Unless stated otherwise, the cells were charged and discharged at a constant current density of 0.4  $\text{mA}\cdot\text{cm}^{-2}$  with a cut off voltage of 0 to 3.0 V.

X-Photoelectron spectroscopic (XPS) experiments were carried out on an Escalab Mark II spectrometer using Mg K $\alpha$  X-ray radiation. Binding energy was calibrated with respect to  $\text{C}_{1s}$  at 284.6 eV with accuracy within  $\pm 0.2$  eV. Prior to the measurements, the samples were kept in the preparation chamber at a pressure of less than  $6.2 \times 10^{-7}$  Pa in order to desorb any volatile components present on the samples. The experimental data were curve-fitted with Gaussian peaks after subtracting a linear background.

All the measurements were performed at about 30  $^{\circ}\text{C}$ .

## Results and discussion

Fig. 1 shows the galvanostatic charge-discharge curves for the two AC samples at the 50th cycle. The charge-discharge curves exhibit the typical capacitive behavior and the capacity of improved AC is higher than that of original AC, indicating that the capacity of AC was increased after the improvement. When AC was treated at 875  $^{\circ}\text{C}$  for 1 h, its discharge capacity at the 50th cycle is about 44.73  $\text{mA}\cdot\text{h}\cdot\text{g}^{-1}$ , corresponding to the specific capacitive value of 53.67  $\text{F}\cdot\text{g}^{-1}$ , an increase of about 25% compared to the original AC. Fig. 2 shows the cycle performances of EDLCs made from the two AC samples. It can be seen that the capacity at any cycle for the improved AC is higher than that for the untreated AC, and the coulombic efficiency is close to 100% for both EDLCs. Furthermore, the specific capacitive values of all AC samples treated in the temperature range of 800–925  $^{\circ}\text{C}$  are higher than the value of the untreated AC. It was also found that the performances of EDLCs was independent of the amount of catalyst in the range of 0.20–2.5 wt%. Considering the specific capacitance and high rate capability of the EDLCs as well as the yield during the reactivation process, the suitable treatment conditions for AC should be heating at about 875  $^{\circ}\text{C}$  for 1 h. Under these conditions, the yield from the reactivation of commercial AC is about 78.4%. Similar-

ly, Kim *et al.*<sup>15</sup> recently reported the improvement of AC under  $\text{CO}_2$ . The obtained capacitive value of the improved AC is about 151  $\text{F}\cdot\text{g}^{-1}$  in aqueous electrolyte, which is much higher than our result, but the working voltage range is too low. Simon *et al.*<sup>16,17</sup> studied various ACs used for EDLCs and found that the specific capacitance of the best AC sample with a specific surface area of 2315  $\text{m}^2\cdot\text{g}^{-1}$  is about 125  $\text{F}\cdot\text{g}^{-1}$  at a working voltage of 0–2 V, which is higher than our data, but its high rate capability is not as good as ours.

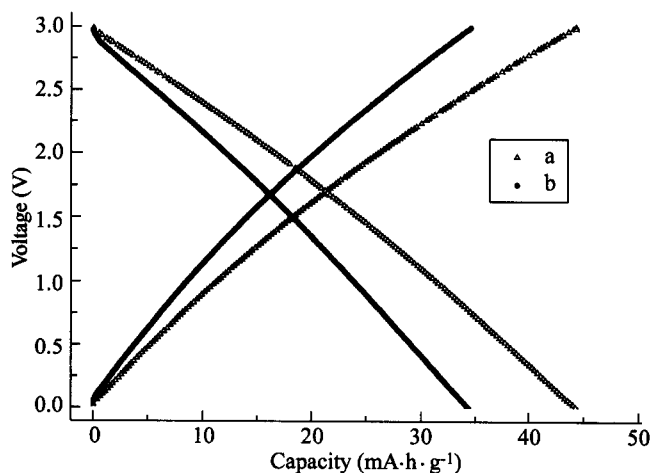


Fig. 1 The 50th charge-discharge curves for polarizable electrodes fabricated with (a) AC improved at 875  $^{\circ}\text{C}$  for 1 h and (b) original AC. Cycling was carried out at 0.4  $\text{mA}\cdot\text{cm}^{-2}$ .

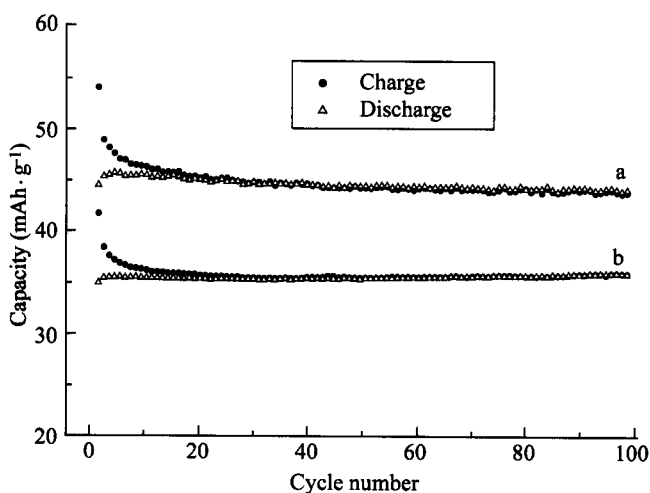


Fig. 2 Cycling performance of EDLCs made with (a) improved AC at 875  $^{\circ}\text{C}$  and (b) original AC.

Fig. 3 depicts the typical impedance spectra in Nyquist form obtained from the improved and as-received AC electrodes in 1.0 mol/L  $\text{TEABF}_4/\text{PC}$  solution. The shape of the impedance spectra is the characteristic of porous carbon materials and has been discussed with equivalent circuits.<sup>12,18</sup> In the high-frequency region (60000–60 Hz), the depressed arcs for both AC samples are found as a result of the porous and inhomogeneous character of the composite electrodes,<sup>18</sup> indicating that they are not ideal polarized electrodes. In the

low frequency region (less than 0.1 Hz), the imaginary component abruptly increases, indicating a capacitive behavior of the AC electrode. The impedance spectra should theoretically be a vertical line in this region for ideal EDLC. Comparison of the imaginary lines for two EDLCs shows that the inclined line for the improved AC is closer to a theoretical vertical line than that of the original AC, suggesting that the improvement of the AC may increase the pore accessibility to the electrolyte. From Fig. 3, the electrolyte resistances of two EDLCs are nearly identical, but the contact resistances are quite different. For the improved AC, the contact resistance is lower than that using the original AC, suggesting that the electrical conductivity of AC was increased significantly after improvements. From the slope of the linear relationship between the imaginary component of the impedance,  $Z_{\text{imag}}$ , and the reciprocal of the angular frequency,  $\omega^{-1}$ , the specific capacitance of the AC electrode can be calculated. As a result, the specific capacitance of the improved AC is  $59.67 \text{ F}\cdot\text{g}^{-1}$ , which is higher than that of the as-received AC with a specific capacitance of  $47.30 \text{ F}\cdot\text{g}^{-1}$ . By extrapolating the low frequency impedance lines to the real axis, the equivalent series resistances (ESRs) of two EDLCs can be obtained.<sup>19</sup> Thus, the capacitance resistance (RC) time constant of the two capacitors can be estimated from the ESR and the accumulated capacitance.<sup>19</sup> For EDLCs with the improved AC and untreated AC as the active materials, the RC time constants are about 1.74 and 4.73 s, respectively, indicating that the high rate capability of EDLC with the improved AC was enhanced greatly.

is less than about  $10 \text{ mA}\cdot\text{cm}^{-2}$ . When the current density is more than  $10 \text{ mA}\cdot\text{cm}^{-2}$ , its discharge capacitance remains almost constant. These results clearly proved that the EDLCs with the improved AC could be cycled at very high current densities. The high rate capability of the EDLC with improved AC is much better than the recently published results.<sup>2,17</sup> Thus, the improved AC seems to be a suitable material for the fabrication of the EDLC with high power density.

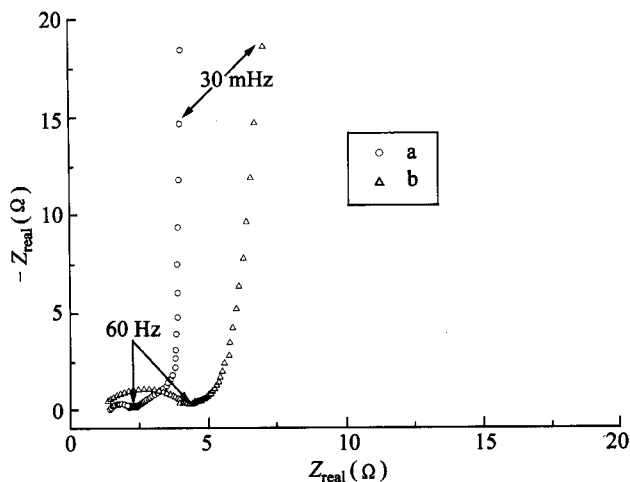


Fig. 3 AC impedance spectra of EDLCs fabricated with (a) improved AC at  $875 \text{ }^\circ\text{C}$  for 1 h and (b) original AC measured at OCV.

Fig. 4 presents the dependence of the discharge capacitance of two AC samples on the current density. As shown in the figure, the discharge capacitance of the EDLC with the original AC continuously decreases with the increase of current density. However, for the EDLC with the improved AC, its discharge capacitance shows only a slight decrease with the increase of discharge current density when the current density

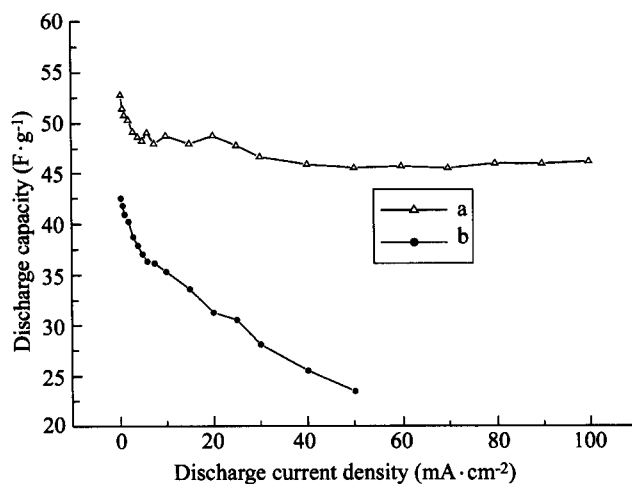


Fig. 4 Dependence of the specific discharge capacitance of polarizable electrodes with (a) improved AC at  $875 \text{ }^\circ\text{C}$  for 1 h and (b) original AC on the discharge current density. Cycling was carried out between 0 and 3 V.

The usual explanation is that the increases in both the specific capacitance and high rate capability of EDLC with the improved AC should be due to the increasing mesoporous ratio. To explain the increased performance of EDLC with the improved AC, the specific surface area and PSD of both kinds of AC samples were first determined by multi-points  $\text{N}_2$  adsorption isotherms at 77 K using a Gemini 2375 instrument. It is very interesting that the specific surface area and PSD for the two AC samples are almost the same, which is similar to the recent published results.<sup>15</sup> For example, the specific surface area of AC reactivated under optimized conditions is about  $1044 \text{ m}^2\cdot\text{g}^{-1}$ , which is nearly the same value as the original AC. The results proved that the markedly enhanced high rate capability of the EDLCs with the improved AC is not relevant to the increased mesoporous ratio. A possible reason for the enhancements of both dl capacitance and high rate capability of the EDLCs may be the changes in the surface carbon groups after the improvement. In order to clarify the possible changes in the surface groups, the two AC samples were subjected to XPS measurements. The obtained XPS spectra as well as their Gaussian peak simulation are shown in Fig. 5. From the figure, five peaks for both AC samples can be found. Although the positions of the five peaks for both samples remained unchanged, the changes in relative intensities were found. As reported in the literature,<sup>20,21</sup> the first two peaks should be assigned as C—C or graphitic carbon (peak 1) and C—OH (peak 2), the latter three peaks could be

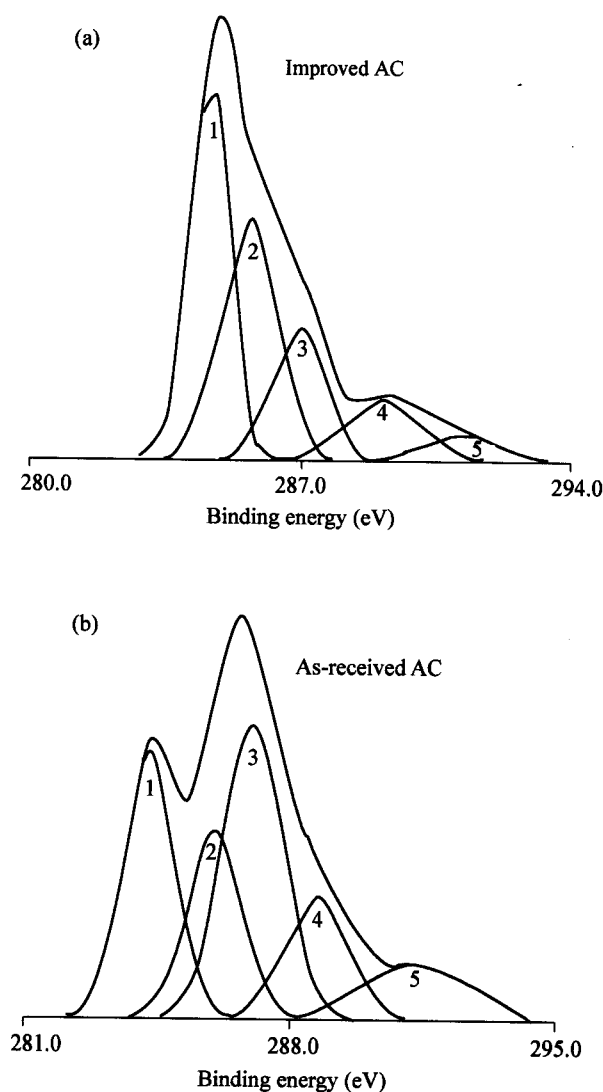


Fig. 5 XPS spectra of (a) improved AC at 875 °C and (b) original AC in the range of  $C_{1s}$  binding energy.

ascribed to  $-C=O$  (peak 3),  $-COOH$  (peak 4) and  $-COOR$  (peak 5) groups, respectively. From the figure, the relative intensities of carbonyl-containing species (peaks 3, 4 and 5) were decreased, but the surface carbon content and the concentration of  $C-OH$  group were increased after the improvement. The increase in surface carbon content could account for the good electrical conductivity of the improved AC. The increase in  $C-OH$  concentration on the surface is reasonable because the reactivation was performed with steam at high temperature, and the reduced concentration of the carbonyl-containing species may be due to the reaction of these groups with steam. Based on our experimental results, the changes in the carbon surface groups should be responsible for the increases of both specific capacitance and high rate capability. A plausible explanation is that the surface carbonyl-containing species impede the organic electrolyte ions

penetration into the pores, as a result, the low surface concentration of such species is beneficial to the increase of accessibility of the pores to electrolyte ion during the dl charging/discharging process, leading to the increases in both specific capacitance and high rate capability.

In summary, the improvement of the commercial AC with steam resulted in the increases in both specific capacitance and high rate capability of the EDLCs. Low contact resistance and enhanced accessibility of the pores to the electrolyte ion may account for the enhanced high rate capability of EDLCs with the improved AC. The increased performance with the improved AC should be attributed to the changes in the surface carbon groups.

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