Structural Feature and Double-Layer Capacitive Performance of Porous Carbon Powder Derived from Polyacrylonitrile-Based Carbon Fiber

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A microporous carbon powder derived from pulverizing a polyacrylonitrile-based activated carbon fiber showed an excellent performance serving as electrodes for symmetric electric double-layer capacitors using sulfuric acid as the electrolyte. In comparison with conventional activated carbon powders derived from a phenol-formaldehyde resin, this fiber-derived carbon showed a large ultimate capacitance value and could still retain a high capacitance at high current rates. Quantitative characterization on the pore structure of these carbons was conducted. The electrochemical impedance spectra of the carbons were adequately fitted to an equivalent circuit containing a Warburg element. The fiber-derived carbon was found to have a greater effective diffusivity for electrolyte transport due to its smaller tortuosity factor, which had a value of 4–7 times smaller than those of the conventional carbon powders. The results of oxygen chemisorption on the carbons suggested that the pore walls of the fiber-derived carbon were more populated with graphite-like crystallite edges. This feature would lead to a stronger specific adsorption and thus a higher double layer capacitance.

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Electric double-layer capacitors (EDLCs), which are fabricated using porous carbons as the electrodes, are considered promising energy storage devices due to their high energy and power densities.1-17 The capacitance in double-layer capacitors is purely electrostatic in origin due to the separation of electron and ionic charges across the electrode/electrolyte interfaces.18,19 Both the capacitance distribution along the pore axis and rate of double-layer buildup are strongly affected by the resistance of electrolyte migration in the pores.20-22 Thus, the limitation on electrolyte transport imposed by the pore structure of the carbons has been considered one of the key issues affecting the energy and power densities of the resulting capacitors. Activated carbon fiber was reported to contain micropores with minimum diffusion restriction and exhibit its high efficiency in adsorption.23-25 The present work intends to examine and characterize the pore-structural feature of a fiber-derived activated carbon for its application in double-layer capacitors.

Carbon fibers with a large surface area (>1500 m²/g) are mainly microporous. Micropores, which possess large overlapping potentials and provide the majority of surface area, were considered the major location allowing compound adsorption.26-27 The accessibility of micropores is limited by the configuration or length of the passage for molecule transport. The accessibility for the formation of the double layer would be somewhat analogous to that for adsorption,28-33 because the development of the double layer is initiated by forming a layer of solvent dipoles and specifically adsorbed ions attaching to the solid surface (i.e., the inner Helmholtz layer), followed by layers of solvated ions.2

The pore structure of porous carbons is dependent on the arrangement of graphitic crystallites in the carbon precursors. The pores of powdered activated carbon are generally distributed with macropores or mesopores situated in the outer zone with micropores at the core zone,24 because the pore development during physical activation (with CO₂ or steam) starts from the outer zone. In contrast, activated carbon fibers, with an anisotropic crystallite arrangement, contain micropores opening directly to the outer surface.25 This feature significantly minimizes the transport restriction in the porosity and thus promotes the adsorption efficiency. However, the large electrical contact resistance between the fiber sheaths, which is composed of the basal planes of the crystallites, has restricted the use of this carbon in fabricating electrodes for double-layer capacitors.8,9

Within the above scope, we overcame the conductivity issue by pulverizing a polyacrylonitrile (PAN)-based activated carbon fiber into a powder, while it still remained the low transport resistance feature of the fiber. This fiber-derived carbon was effective in double-layer formation in comparison with conventional activated carbon powders. The physical and chemical characteristics of the micropores were explored, especially with electrochemical impedance spectroscopy, for the above carbons to elucidate how the effectiveness in energy storage was achieved by the fiber-derived carbon.

Experimental

A PAN-based activated carbon fiber, supplied by Challenge Carbon Technology Co., Taiwan, was pulverized into a powder to serve as the electrode material for EDLCs in the present work. This fiber-derived carbon powder is designated as FIB. Conventional activated carbon powders (ACs) were prepared from 900°C carbonization of a phenol-formaldehyde resin and subsequent 900°C activation of the residual carbon in CO₂ to different extents of burn-off. The resin, supplied by Chang-Chung Plastics, Taiwan, is of the resol type with a molecular weight of 700–1000. Prior to any characterizations or measurements, the carbon was heated treated in helium at 900°C to remove the surface oxides, which were shown to significantly enhance the pseudo-capacitance of carbon electrodes.34-37 These carbons had a particle size of 10–40 µm.

Specific surface areas and pore volumes of the carbons were determined by N₂ adsorption at 77 K. An adsorption apparatus (Micromeritics ASAP 2010) was employed for these measurements. The apparent surface area (Sₐpp) and micropore volume (Vₘ) of the specimens were evaluated with the application of the Brunauer-Emmett-Teller (BET) and Dubinin-Radushkevich (DR) equations,26 respectively. The amount of N₂ adsorbed at relative pressures near unity (p/p₀ = 0.96 here) was employed to determine the total pore volume (Vₚ), which corresponds to the sum of the micropore and mesopore volumes.38 Due to the slit shape of carbon micropores, the DR theory is used to determine the characteristic energy (Eₒ) of the microporosity (Vₘ),39-41 and the micropore average width (Lₒ) and surface area (Sₒ) are calculated according to

\[
Lₒ(\text{nm}) = \frac{10.6}{Eₒ(\text{kJ mol}^{-1}) - 11.4}
\]
The sum of somewhat misleading. The porosity of the fiber-derived carbon rafluoroethylene binder monitored with a nondispersive infrared analyzer. in an aqueous solution of 4 M H2SO4, and then discharging to 0 V double-layer capacitance was obtained by charging the cells to 1 V, used to examine the electrochemical performance of the carbon ing at 80°C for 8 h under vacuum. Two-electrode capacitor cell was used to and any approach based on S is well known that the BET equation overrates the surface area of microporous carbons and any approach based on S could be somewhat misleading. The porosity of the fiber-derived carbon (FIB) was situated within the range of those for the ACs. Apart from the physical characteristics of the particulate carbon specimens determined from N2 adsorption are summarized in Table I. The conventional activated carbon powders, AC1 and AC2, were obtained with carbon burn-off levels of 64 and 81%, respectively. The pore volumes of the carbons were predominantly contributed by micropores. The values of S were much smaller than those of S_{BET}. It is well known that the BET equation overrates the surface area of microporous carbons and any approach based on S_{BET} could be somewhat misleading. The porosity of the fiber-derived carbon (FIB) was situated within the range of those for the ACs. Apart from the numerical values of pore structure obtained from the adsorption analysis, the arrangement of the graphite-like crystallites, which would eventually determine how pores are constructed, was disclosed with HRTEM inspection. Figure 1a shows the image of FIB. The image presents a zone corresponding to the cross section of the original carbon fiber. The cross section is composed of groups of concentric graphene sheets, which are known to elongate along the fiber axis because carbon fibers are produced under a controlled tension. This anisotropic feature renders a high electrical conductivity parallel to the axis while the conductivity measured perpendicular to the axis is small. Figure 1b shows the image of AC2. The structure, on the contrary, was isotropic in the crystallite arrangement because the AC specimens were produced with no tension applied. The lattice fringe can be clearly observed from the image, showing a random distribution of coherent domains (L_a × L_c). We previously reported the electrochemical performance of PAN-based carbon fibers serving as electrodes for EDLCs. As expected, the interfiber electrical resistance based on ac impedance measurements was large and presented as the major contribution to the overall resistance of EDLCs. Under this circumstance, the resistance resulting from electrolyte migration in micropores was considerably small in comparison with the interfiber resistance. By pulverizing fibers into powders (such as FIB) the interfiber resistance

### Table I. Pore structure of the pulverized activated carbon filter (FIB) and the activated carbon powders (AC1 and AC2).

<table>
<thead>
<tr>
<th>Carbon type</th>
<th>S_{BET} (m² g⁻¹)</th>
<th>V₁ (cm³ g⁻¹)</th>
<th>V₉₅ (cm³ g⁻¹)</th>
<th>Sₕ (m² g⁻¹)</th>
<th>Sₘi (m² g⁻¹)</th>
<th>Sₘ (m² g⁻¹)</th>
<th>L₀ (nm)</th>
<th>E₀ (kJ mol⁻¹)</th>
</tr>
</thead>
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<tr>
<td>FIB</td>
<td>1310</td>
<td>0.63</td>
<td>0.57</td>
<td>112</td>
<td>858</td>
<td>970</td>
<td>1.33</td>
<td>19.5</td>
</tr>
<tr>
<td>AC1</td>
<td>1270</td>
<td>0.62</td>
<td>0.55</td>
<td>155</td>
<td>685</td>
<td>840</td>
<td>1.62</td>
<td>18.1</td>
</tr>
<tr>
<td>AC2</td>
<td>1550</td>
<td>0.74</td>
<td>0.66</td>
<td>218</td>
<td>777</td>
<td>995</td>
<td>1.69</td>
<td>17.8</td>
</tr>
</tbody>
</table>

\[ S_{mi} (m² g⁻¹) = \frac{2000 \; V₉₅ (cm³ g⁻¹)}{L₀ (nm)} \]  

The Barrett-Joyner-Halenda method was employed to calculate the external surface area (S_e). The total surface area (S_t) is defined as the sum of S_{mi} and S_e. The microstructure and crystallite arrangement of the carbons were explored with a high-resolution transmission electron microscope (HRTEM, Hitachi FE-2000).

Oxygen chemisorption was employed to characterize the affinity of carbon surface with adsorbate molecules. The chemisorption was conducted at 150°C in air for 10 h. A temperature-programmed desorption technique was employed to analyze the population of carbon-oxygen complexes formed on the carbons. The desorption was carried out under a helium flow, by heating the specimens from room temperature to 900°C with a linear rate of 30°C min⁻¹. The evolution of CO and CO₂ during the desorption was continuously monitored with a nondispersive infrared analyzer.

To prepare the carbon electrodes, a slurry of carbon and polytetrafluoroethylene binder (20/1 in weight ratio) was pressed on a stainless steel-foil current collector of 1 cm², with subsequent drying at 80°C for 8 h under vacuum. Two-electrode capacitor cell was used to examine the electrochemical performance of the carbon electrodes. The cell was assembled with two facing carbon electrodes, sandwiching a piece of filter paper as the separator. The double-layer capacitance was obtained by charging the cells to 1 V, in an aqueous solution of 4 M H2SO4, and then discharging to 0 V at a constant current of 1 – 100 mA. An ac impedance spectrum analyzer combined with a computer software was employed to measure and analyze the impedance behavior of the capacitors. In this work, the measurements were conducted at 0 V with an ac potential amplitude of 5 mV and a frequency range of 2 mHz to 100 kHz.

### Results

The physical characteristics of the particulate carbon specimens obtained from N2 adsorption are summarized in Table I. The conventional activated carbon powders, AC1 and AC2, were obtained with carbon burn-off levels of 64 and 81%, respectively. The pore volumes of the carbons were predominantly contributed by micropores. The values of S were much smaller than those of S_{BET}. It is well known that the BET equation overrates the surface area of microporous carbons and any approach based on S_{BET} could be somewhat misleading. The porosity of the fiber-derived carbon (FIB) was situated within the range of those for the ACs. Apart from the numerical values of pore structure obtained from the adsorption analysis, the arrangement of the graphite-like crystallites, which would eventually determine how pores are constructed, was disclosed with HRTEM inspection. Figure 1a shows the image of FIB. The image presents a zone corresponding to the cross section of the original carbon fiber. The cross section is composed of groups of concentric graphene sheets, which are known to elongate along the fiber axis because carbon fibers are produced under a controlled tension. This anisotropic feature renders a high electrical conductivity parallel to the axis while the conductivity measured perpendicular to the axis is small. Figure 1b shows the image of AC2. The structure, on the contrary, was isotropic in the crystallite arrangement because the AC specimens were produced with no tension applied. The lattice fringe can be clearly observed from the image, showing a random distribution of coherent domains (L_a × L_c).
would be minimized and the micropore resistance would become an
important factor affecting the capacitance of a resulting EDLC, es-
pecially at high charge-storage rates.

A constant current charge-discharge cycling was conducted to
measure the capacitance of the EDLCs made of FIB and ACs. The
specific discharge capacitance \( C \) is calculated according to
\[
C = \frac{2It}{M \Delta E}
\]  
[3]
where \( I \) is the discharge current, \( t \) is the discharge time, \( M \) is the
mass of an electrode (carbon plus binder), and \( \Delta E \) is the potential
difference in discharge, excluding the portion of IR drop. The factor
of 2 comes from the total capacitance measured from the test cells
being the addition of two equivalent single-electrode capacitors in
series. Figure 2 shows the variation of the relative capacitance (com-
pared to the ultimate value obtained at 1 mA (C1)) with the discharge
current. The C1 value of AC2 was larger than that of AC1, prin-
cipally due to the larger surface area for AC2. However, it was of
interest to observe that FIB exhibited a larger C1 value than AC2,
though the porosity of FIB was smaller. Moreover, Fig. 2 shows that
the relative capacitance decrease with current for FIB was less dra-
matic than those for ACs, even if the pore size of FIB was smaller (Table I).
A relative capacitance of ~0.7 could still be achieved for FIB at a discharge current as high as 100 mA, while less than 0.6 for
AC2. This reflects a smaller pore resistance for FIB to allow effi-
cient charge storage at large operating currents.

Ac impedance spectroscopy, which distinguishes the resistance and capacitance of a device, was further employed to analyze the
electrochemical behavior of the capacitor cells. The obtained imped-
ance spectra of these cells are shown in Fig. 3, which depicts the
standard Nyquist plots scanned at 0 V. For each cell there is a semi-
circle intersecting the real axis in the high frequency region (see the
inset of Fig. 3). The plot transforms to a vertical line with the de-
creasing frequency. The semicircle is typical of a RC circuit that
represents an interface resistance in parallel with an interface
capacitance. In the low frequency region where nearly complete
penetration of ions into pores would be allowed, the vertical line
(with a slight tilt) reflects the domination of the capacitive behavior.
Between the semicircle and straight line, there appears a transition
zone corresponding to the restricted motion of electrolyte ions in
carbon micropores. Accordingly, the equivalent circuit for these
electrodes should have elements involving the bulk solution resis-
tance, \( R_e \), the capacitance and resistance due to the contact interface,
\( C_i \) and \( R_i \), a Warburg diffusion element attributable to the diffusion
of ions, \( Z_W \), and the double-layer capacitance inside pores, \( C_d \).
Hence, an equivalent circuit combining these elements is proposed
in Fig. 4 to simulate the impedance spectra shown in Fig. 3.

The overall impedance, \( Z \), of the equivalent circuit in Fig. 4 is
given by
\[
Z = R_e + \frac{1}{j\omega C_i + \frac{1}{R_i + Z_W}} - j\omega C_d
\]  
[4]
\[
Z_W = \frac{W}{\sqrt{j\omega}}
\]  
[5]
where \( W \) is the Warburg parameter in units of \( \Omega \cdot s^{1/2} \). This param-
ter is an increasing function of the resistance for electrolyte trans-
port in a porous electrode. At sufficiently high frequencies, the
overall impedance can be reduced to
\[
Z = R_e + \frac{1}{j\omega C_i + \frac{1}{R_i}}
\]  
[6]
The above equation corresponds to a locus showing a semicircle that
intercepts the real axis at \( R_i \) and \( R_i + R_e \) in the Nyquist plot.

Figure 2. Variation of the relative capacitance with discharge current for the FIB, AC1 and AC2 capacitors in 4 M H2SO4. The relative capacitance was obtained by dividing the specific capacitance with the value obtained at 1 mA (C1). The capacitors have been charged to 1 V prior to discharge.

Figure 3. Nyquist impedance plots of the FIB, AC1 and AC2 capacitors in 4 M H2SO4 with the frequency ranging from 3 mHz to 100 kHz at an applied potential of 0 V. The inset shows the magnification of the high frequency region of the impedance spectra.

Figure 4. Equivalent circuit for the simulation of the impedance spectra of the carbon electrodes shown in Fig. 3.
On the other hand, a decrease in frequency can transform Eq. 4 to
\[
Z = R_s + R_c + \frac{W}{\omega} = \frac{1}{\omega} \left[ \frac{W}{\omega} + \frac{1}{C_\omega} \right].
\]

The observed slight tilt on the vertical line at low frequencies can be ascribed to the existence of the \( W \omega^{-1/2} \) term that would have caused the slight increase in the Re(Z) value as the frequency approaching zero.

Equation 4 together with the impedance data in Fig. 3 were employed to calculate the values of the elements constituting the equivalent circuit. The simulation results are summarized in Table II. In Fig. 3 the lines represent the best-fit curves in terms of the equivalent circuit. The simulation results are summarized in Table II. The mean error of modulus was smaller than 0.3% on the basis of the least squares method. The bulk solution resistance \( (R_s) \) was found to be of \( \sim 1 \) \( \Omega \) for each cell. The contact resistance \( (R_c) \) was small for all the carbon electrodes and had values of \( \sim 1 \) \( \Omega \). Our previous studies showed a \( R_c \) value of larger than 14 \( \Omega \) for a capacitor using PAN-based activated carbon fibers as the electrodes. Because of the large \( R_c \), the Warburg transition region was invisible for the systems using carbon fabrics as the electrode. In the present work the Warburg element well simulated the transition zone between the semicircle and vertical line of the Nyquist plots, reflecting the significant role of pore resistance involved in the double-layer formation.

Table II shows that the value of the Warburg parameter for FIB was much smaller than those for ACs, indicating that the pore resistance was smaller for FIB. This could contribute to the lesser extent of capacitance decrease with the discharge current for FIB shown in Fig. 2. As to the double-layer capacitance \( (C_\omega) \) responsible for the low-frequency impedance, it showed an order of FIB > AC2 > AC1, inconsistent with that obtained from the constant current discharge measurements. Because the values of \( C_\omega \) were obtained on the basis of simulation to considerably low frequencies, it was reasonable to obtain the \( C_\omega \) values that were larger than those obtained for \( C_1 \) at the 1 mA discharge.

Still, the pore structure of the carbons shown in Table I cannot provide explanations for the smaller pore resistance and the larger capacitance exhibited by FIB.

Discussion

A small diffusion resistance for PAN-based activated carbon fibers in adsorption systems has been well known. This small-resistance feature was also observed for FIB. We intended to give a quantitative characterization on the diffusion in the carbon micropores by analyzing the Warburg parameter determined from the impedance measurements. The Warburg parameter can be correlated with the diffusion coefficient of electrolyte ions by
\[
W = \frac{RT}{n^2F^2Ac\sqrt{D_e}}
\]
where \( R \) is the gas constant, \( T \) is the absolute temperature, \( n \) is the number of electron transferred, \( F \) is the Faraday constant, \( A \) is the geometric electrode area, \( c \) is the electrolyte concentration, and \( D_e \) is the effective diffusivity for electrolyte motion in carbon micropores. Although there was no electron transfer involved during double-layer formation, an equivalent value for \( n \) could be assigned to account for this charge coupling process at the carbon/electrolyte interface. According to Eq. 8, the difference in \( W \) for different carbons principally resulted from the difference in \( D_e \).

The effective diffusivity for electrolyte motion in porous media can be estimated according to
\[
D_e = \frac{D}{\tau}
\]
where \( D \) is the intrinsic diffusivity of the electrolyte ion, \( \tau \) is the tortuosity factor, which is a measure of deviation from the straight-pore postulation, \( \varphi \) is the size ratio of electrolyte ion to pore, \( F_1 \) is the steric partition coefficient, and \( F_2 \) is the hydrodynamic hindrance factor. Because sulfuric acid was used as the electrolyte, the electrolyte ion considered in the following calculation was the hydrated \( SO_4^{2-} \), which is more restricted in transport than the hydrated \( H^+ \). An intrinsic diffusivity of 8.3 \( \times 10^{-4} \) \( \text{cm}^2 \text{s}^{-1} \) (at 298 K) and a diameter of 0.533 nm for the hydrated \( SO_4^{2-} \) were used in the present calculation.

By assuming a tortuosity factor of unity (i.e., a straight-pore configuration) for FIB, one can obtain tortuosity values of 4.5 and 6.5 for AC1 and AC2, respectively, according to Eq. 8 and 11. The tortuosity factor for activated carbons is normally within a range of 2–7, which coincidently includes the above values calculated for AC1 and AC2. This coincidence suggested that FIB should have a tortuosity factor close to unity. On the basis of the straight-pore assumption for FIB, the parameters involved in Eq. 9 are summarized in Table III. The large tortuosity ratio of AC1 or AC2 to FIB implicitly explains why the electrolyte motion in FIB was less restricted, even though the porosity was smaller or the \( \varphi \) value was larger for FIB. We also conducted experiments using NaCl and NaOH as the electrolyte. The tortuosity ratios for the carbons based on NaCl and NaOH as the electrolyte are similar to those obtained using \( H_2SO_4 \). The straight-pore feature must be responsible for the higher relative capacitance of the FIB capacitor (see Fig. 2).

The micropore configuration of an activated carbon can be affected by the crystallite and defect arrangements of the carbon precursor. Because carbon fibers from carbonization of the PAN polymer are rather long and rich in defects (including heteroatoms as N, H, and O and nonaromatic bondings), during activation the micropore development toward the fiber core would be directed by the defects. Thus, the passage for electrolyte motion from the outer surface to the interior would be rather straight for a PAN-derived carbon like FIB. As to a phenol-formaldehyde resin-derived carbon like ACs, activation is to open the isolated original pores. For this type of porosity, it would be necessary to make a detox for electrolyte penetration into the carbon interior created with varying pore cross section. This would have led to a larger tortuosity factor and thus a more restricted diffusion for ACs than FIB (as shown in Table III), even if the mean micropore sizes of ACs were larger. The difference in diffusion resulting from the different pore configurations is illustrated in Fig. 5. Both the varying direction of diffusion and
varying pore cross section affect the value of the tortuosity factor. Because the pores in ACs are formed by opening the isolated pores, the variation of the pore cross section would be great.

Apart from the straight-pore feature, FIB had a larger capacitance value than both ACs, though the surface area of FIB was smaller than that of AC2. Differences in the structure of pore walls may have affected the specific adsorption and thus the degree of double-layer formation. We have suggested above that the micropores in FIB were created by eliminating the defects distributed over the graphene layers. The TEM image of FIB in Fig. 1a faintly shows the presence of some ruptured spots on the stacked graphene layers. Thus, the micropores in FIB would intersect the basal-plane layers and be expected to have walls highly populated with the crystallite edges, which were polar in nature and considered the active sites of carbon.\textsuperscript{49,50} Under this circumstance, the micropore walls of FIB would have a strong tendency to adsorb ions, thus to create the inner Helmholtz plane of the electric double layers.\textsuperscript{2} Carbons derived from phenol-formaldehyde resin, on the other hand, were reported to contain a high population of closed pores that are encircled by the basal planes of graphite-like crystallites.\textsuperscript{44} The basal planes are less active and would have a weak affinity with ions for specific adsorption. This situation would cause a less effective formation of double layers on ACs.

In order to estimate the population of the edge sites, the oxygen chemisorption experiment was conducted for the carbons at 150°C. Because oxygen chemisorption to form carbon surface oxides can occur only on the edge of the graphene sheets, the amount of the oxides formed would serve as an index reflecting the edge-site population on the micropore walls of the carbons. Figure 6 shows the temperature-programmed desorption spectra of the carbons oxidized at 150°C in air for 10 h. Both the CO and CO\textsubscript{2} evolution spectra show that FIB had larger amounts of oxides formed on the surface than the ACs. This result was supportive for the argument that the pore wall of FIB was more highly populated with the edge sites. The difference in the ultimate capacitance per unit surface area between these two types of carbons could arise from this surface difference.

The accumulated amounts of CO and CO\textsubscript{2}, as well as the total O, evolved during the programmed desorption were calculated and are given in Table IV. The amounts of the oxides evolved from ACs were found to be proportional to the surface area. Furthermore, the CO/CO\textsubscript{2} ratio of the accumulated evolution had a value of 2.4 for the two ACs. The above results explicitly reflect that AC1 and AC2 had surfaces similar in chemical characteristics though their exposed areas were different. On the other hand, FIB accommodated more surface oxides per unit surface area than ACs and exhibited a larger

<table>
<thead>
<tr>
<th>Carbon type</th>
<th>CO evolution (mmol g\textsuperscript{-1})</th>
<th>CO\textsubscript{2} evolution (mmol g\textsuperscript{-1})</th>
<th>Total O evolution (mmol g\textsuperscript{-1})</th>
<th>CO/CO\textsubscript{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>FIB</td>
<td>0.32</td>
<td>0.11</td>
<td>0.54</td>
<td>2.9</td>
</tr>
<tr>
<td>AC1</td>
<td>0.17</td>
<td>0.071</td>
<td>0.31</td>
<td>2.4</td>
</tr>
<tr>
<td>AC2</td>
<td>0.21</td>
<td>0.086</td>
<td>0.38</td>
<td>2.4</td>
</tr>
</tbody>
</table>

Figure 5. The illustration of the diffusion path for ions from the bulk solution to the interior of the carbon specimens: (a) FIB with a small-tortuosity configuration; (b) ACs with a large-tortuosity configuration.

Figure 6. Evolution profiles of CO and CO\textsubscript{2} by temperature-programmed desorption for different carbons (FIB, AC1 and AC2) treated in air at 150°C for 10 h. The desorption was carried out under a helium flow, by heating the specimens from room temperature to 900°C with a linear rate of 30°C min\textsuperscript{-1}.

Table IV. Accumulated amounts of CO, CO\textsubscript{2} and total O evolutions from the temperature-programmed desorption of the carbons oxidized in air at 150°C for 10 h.
CO/CO₂ ratio (2.9). The CO evolution, mainly at high temperatures, results principally from desorption of the carbonyl group, which has a less space-restricted configuration in comparison with others like the carboxylic group for CO₂ evolution. The intimate stacking of the graphene-sheet edges on the FIB surface may have caused the high population of the carbonyl group produced during the oxygen chemisorption.

Conclusion

By pulverizing a PAN-based activated carbon fiber to eliminate the external contact resistance, a microporous carbon powder exhibiting a small pore diffusion resistance and a large ultimate double-layer capacitance was obtained. On the basis of the analysis using electrochemical impedance spectroscopy, the fiber-derived carbon showed a large effective diffusivity for electrolyte ions in comparison with conventional activated carbon powders. The tortuosity factor of the micropores in the fiber-derived carbon was found to be more than four times smaller than those in the conventional carbons. This straight-pore feature for the fiber-derived carbon resulted in the small pore resistance and, therefore, a lesser extent of capacitance decrease at high discharge rates. As to the large ultimate capacitance of the fiber-derived carbon, it was attributed to the anisotropic arrangement of graphite-like crystallites. This arrangement led to formation of micro pores with surface highly populated with crystallite edges, which would induce stronger specific adsorption and thus a higher degree of double-layer formation. This fiber-derived carbon was considered an excellent electrode material for double-layer capacitors with high performance.

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