EDLC Characteristics of Carbon Materials Prepared from Coal Extract

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ABSTRACT

HPC is an ashless coal obtained via the thermal extraction of coal and is soluble in organic solvents. In this study, carbon powder was prepared from the HPC/pyridine solution via precipitation using water as a poor solvent and was subsequently carbonized via heat treatment at 900°C. The evaluation of the pore characteristics of the obtained carbon powders revealed that the carbon powders mainly contained micropores. The average pore diameter (D_{pw}) of the micropores was 0.75 nm, suggesting that they are super-micropores or ultra-micropores. The applicability of the carbon powder was verified by examining the EDLC characteristics. The capacitance of the EDLC containing the aqueous solution of H_{2}SO_{4} as the electrolyte was 170 F cm^{-2} (200–210 F g^{-1}) at a current density of 50 mA g^{-1}, denoting a capacitance similar to that of the activated carbon powder (YP-50F). The capacitance was 140 F cm^{-3} (170 F g^{-1}) even when the current density increased from 50 to 5000 mA g^{-1}, indicating a high retention rate of approximately 80%. Subsequently, the capacitance became 210 F cm^{-2} (260 F g^{-1}) when the CO_{2} activation treatment was conducted for 60 or 90 min. Therefore, a high yield of carbon powders with extremely fine pores can be easily obtained via precipitation using HPC as the raw material.

Keywords : Hyper Coal, EDLC Characteristics, CO_{2} Activation, Precipitation Method

1. Introduction

The electric double-layer capacitor (EDLC) is an electric storage device that stores electric charge by adsorbing the electrolyte ions at the interface between the electrodes and the electrolyte to form an electric double layer.1,2 Unlike secondary batteries, electric storage batteries have a long life span and are self-discharging.3,4 Therefore, high-speed charge and discharge are possible, and the capacitance does not considerably decrease due to the small reaction. Therefore, high-speed charge and discharge are possible, and the capacitance does not considerably decrease due to the small repeated charge and discharge. The capacitance is mainly dependent on the electric double layer formed on the electrode surface; therefore, it is dependent on the specific surface area of the electrode material. Hence, a material having a high specific surface area and exhibiting electrical conductivity is preferable as an EDLC electrode material. Various researchers have used porous carbon materials exhibiting excellent electrical conductivity and abundant pores as the EDLC electrode materials.5,6,9,10,11 In addition, the EDLC characteristics are considerably dependent on the specific surface area and the pore structure.7,8 In particular, the materials containing micropores have been reported to exhibit high capacitance in aqueous and nonaqueous EDLCs.10,11 Therefore, the porous carbon materials that mainly contain micropores exhibit a high capacitance and can be potentially used as electrode materials. Among the materials containing micropores, the materials that mainly contain very fine super-micropores (0.7–2.0 nm) and ultra-micropores (<0.7 nm) are observed to exhibit high capacitances.12–14 Chmiola et al. (2006) reported that when the solvated electrolyte ions were adsorbed into the micropores (<1 nm) in a nonaqueous EDLC in which TEABF_{4}/AN was considered to be the electrolyte, they were de-solvated based on the sieving effect. The electrolyte ions formed from an electric double layer exhibiting a very short distance between the pore wall and the ion center result in high capacitance.15 In addition, Raymundo-Piñero et al. (2006) showed that nonaqueous EDLCs using TEABF_{4}/AC as the electrolyte have high capacitance with a micropore having a size of approximately 0.8 nm. Water-based EDLCs using H_{2}SO_{4} or KOH aqueous solution show high capacitance with a micropore having a size of approximately 0.7 nm.16 Other research groups have confirmed that high volumes can be achieved using these micropores.17,18 However, in case of a porous carbon material having pores of smaller than 0.7 nm, the contribution of the pores to the capacitance of the aqueous EDLCs may vary considerably when compared with that of the nonaqueous EDLCs. Xu et al. (2013) denoted that a porous carbon material mainly containing micropores with sizes of approximately 0.55 nm showed high capacitance in an aqueous EDLC in which the KOH aqueous solution was used as an electrolyte; however, it exhibited extremely low capacitance in nonaqueous EDLC using Et_{4}NBF_{4}/PC as the electrolyte.19 This result can be attributed to the fact that the pores with sizes of approximately 0.55 nm are so small that even the desolvated electrolyte ions in the nonaqueous electrolyte were not adsorbed. Therefore, it is very important to consider the size of the electrolyte ion with respect to the micropores to achieve a high capacitance, indicating that the presence of extremely fine micropores can significantly improve the performance of the EDLC in an appropriate electrolyte. Generally, a physical or chemical activation treatment or a template method is used to prepare porous carbon materials that can be used as the EDLC electrode materials.20–23 Kierzka et al. (2004) prepared microporous activated carbon with a specific surface area of greater than 3000 m^{2} g^{-1} by chemical activation treatment using KOH. A material containing abundant micropores can be obtained; however, the carbonization yield decreases in this case, which is a disadvantage. Furthermore, in the template method, MgO can be used as a template to develop materials with a regular pore structure not only in micropores but also in mesopores and macropores;24–26 however, in this case, a...
template elution step is required using an acidic solution. Therefore, the preparation of porous carbon materials by the activation treatment or template method increases the production cost and the complexity associated with the process. Hence, obtaining a porous carbon material without using the activation or template method can increase productivity, and porous carbon materials can be manufactured at a low cost owing to the high carbonization yield and the simplification of the manufacturing process.

Research on the application of functional materials as a starting material for the development of hyper coal (HPC) is still ongoing. HPC is an ashless coal obtained via the thermal extraction of coal.19 Because HPC can dissolve in an organic solvent, a carbon fiber precursor can be prepared as a free-standing film by electrospinning and a carbon fiber with micropores can be obtained through heat treatment.30,31 Furthermore, a maximum surface area of 1000 m² g⁻¹ can be achieved without activation. The carbon fiber prepared using this method is obtained in a non-woven fabric state in which long fibers are observed to be entangled and can be directly used as an electrode without a binder at the time at which the electrode is produced. When this carbon fiber with a specific surface area of 600 m² g⁻¹ was applied as an EDLC electrode, the capacitance was 300 F g⁻¹ (50–55 µF cm⁻²) at a current density of 50 mA g⁻¹ in a 40% H₂SO₄ electrolyte, which was considerably high and exceeded the capacitance of the activated carbon powder (YP-50F) (260–280 F g⁻¹; 20–22 µF cm⁻²). In particular, the capacitance per area was more than twice. This is because the capacitance per unit weight of the carbon fiber exceeded that of the activated carbon powder even though the specific surface area of the carbon fiber was smaller than that of the activated carbon powder. Further, the capacitance per volume of carbon fiber was 40 F cm⁻³, which is smaller than that of the activated carbon powder (150–170 F cm⁻³). The low capacitance per volume can be attributed to the fact that the electrode density of the carbon fiber was smaller than that of the activated carbon powder. An increase in the capacitance per volume is a very important factor because it considerably contributes to the miniaturization of the devices. In this study, to improve the capacitance per volume, carbon powder was prepared from the HPC solution, and we attempted to increase the density of the electrodes. The precipitation method was used to obtain carbon powder from the HPC solution. In this method, solubility was reduced using a poor solvent, and HPC was precipitated in the poor solvent. The HPC solution was prepared by adding the HPC described in section 2.1 to pyridine (Wako Pure Chemical Industries Ltd., purity: 99.5%). The weight ratio of HPC to pyridine was 1:10. The solution was subsequently stirred at room temperature for 1 h.

2.3 Preparation of the carbon precursor powder from the HPC solution
The carbon precursor powder was prepared from the HPC solution via precipitation using water as a poor solvent. The 10-wt% HPC solution prepared in the previous section was poured into water, which is a poor solvent, to precipitate HPC in water. The precipitated carbon precursor powder was collected via suction filtration, and the precipitate was vacuum-dried at 110°C for 12 h. The yield of the recovered carbon precursor powder was subsequently calculated using the following equation.

\[ Y_1 = 100 \times \frac{M_p}{M_{HPC}}. \]  

where \( Y_1 \) denotes the yield (%) of the recovered carbon precursor powder, \( M_{HPC} \) denotes the weight of HPC dissolved in pyridine, and \( M_p \) denotes the weight of the recovered carbon precursor powder after precipitation.

2.4 Preparation of the carbon powder
The carbon powder was prepared by heat-treating the carbon precursor powder prepared in section 2.3. The carbon precursor powder obtained by the precipitation method was infusibilized and carbonized using an electric furnace (Isuzu Seisakusho Co., Ltd., KRR-24HH). During the infusibilization process, the temperature was increased to 300°C at a rate of 1°C min⁻¹ when air was supplied into the furnace at a flow rate of 1.0 dm³ min⁻¹ using an air pump, and this temperature was maintained for 1 h. Subsequently, the mixture was naturally cooled to room temperature. During the carbonization treatment, the furnace was replaced with a nitrogen atmosphere by flowing nitrogen gas at room temperature for 4 h at a flow rate of 0.1 dm³ min⁻¹ and the temperature was increased to 900°C at a heating rate of 200°C h⁻¹. The temperature was increased for 30 min, and the furnace was then naturally cooled to room temperature. The carbon powder yield was calculated using Eq. (2).

\[ Y_2 = 100 \times \frac{M}{M_0}, \]  

where \( Y_2 \) is the yield (%) of the carbon powder, \( M_0 \) is the weight of the carbon precursor powder before heat treatment, and \( M \) is the weight of the carbon powder after heat treatment.

2.5 Activation of carbon powder
The carbon powder was subjected to activation treatment using CO₂. The procedure for the activation of carbon powder is as follows. After \( N_2 \) was flown into the furnace at room temperature for 4 h at a flow rate of 0.1 dm³ min⁻¹, the temperature was increased to 900°C at a heating rate of 200°C h⁻¹. This temperature was maintained for 30 min, and the temperature was subsequently increased from 900°C to 950°C at a heating rate of 200°C h⁻¹. When the temperature reached 950°C, CO₂ gas was supplied into the furnace. At this time, \( N_2 \) and CO₂ gases were supplied into the furnace at a flow rate of 0.05 dm³ min⁻¹ to ensure that the total flow rate became 0.1 dm³ min⁻¹. The activation time was 30–120 min at 950°C in a mixed atmosphere of \( N_2 \) and CO₂. The sample code is HPC- (activation time/min). The sample code is HPC- (activation time/min) such as HPC-30 (activation time of 30 min).
potential window, and the current density ranged from 50 to 5000 mA g⁻¹. The capacitance per volume \( C_v \) (F cm⁻³) and the capacitance per weight \( C_m \) (F g⁻¹) at each current density as well as the discharge curve were obtained by conducting the galvanostatic charge/discharge measurement. The ranges of the aforementioned parameters can be calculated using Eqs. (3) and (4).

\[
C_v = \frac{(\Delta t)}{(d\Delta V)} \quad \text{(3)}
\]

\[
C_m = \frac{(\Delta t)}{\left(m\Delta V\right)} \quad \text{(4)}
\]

where \( I \) is the magnitude of the current (A), \( \Delta t \) is the discharge time (s), \( \Delta V \) is the potential range (V), \( d \) is the volume of the electrode (cm³), and \( m \) is the weight of the electrode. The capacitance retention ratio \( C_m \) in the current density range of 50–5000 mA g⁻¹ was calculated using Eq. (5).

\[
C_m = 100 \times \frac{C_{5000}}{C_{50}} \quad \text{(5)}
\]

where \( C_{50} \) indicates the capacitance at a current density of 50 mA g⁻¹ and \( C_{5000} \) indicates the capacitance at a current density of 5000 mA g⁻¹.

3. Results and Discussion

3.1 Preparation of the carbon powder via the precipitation method

The carbon powder precursor was obtained by pouring the HPC/pyridine solution into water; then, HPC was precipitated in water, followed by suction filtration of the precipitate. Finally, the adsorbed water was dried under vacuum at 110°C. At this time, the yield of the recovered carbon powder precursor was 95%, suggesting that the HPC that dissolved in pyridine was completely precipitated in water and that it could be recovered. The carbon powder was obtained by infusing the carbon powder precursor at 300°C and then carbonizing it at 900°C. At this time, the carbonization yield was 60%–65%, higher than that obtained by the normal activation or template method; thus, high productivity is expected. Figure 2(a) shows an overall image of the carbon powder obtained via the precipitation method, whereas Fig. 2(b) shows a partially enlarged view. From Fig. 2(a), particles having sizes of 5–6 \( \mu \)m can be observed. When the particle surface was partially enlarged (Fig. 2(b)), fine uniform submicron-sized particles having sizes of approximately 10 nm or slightly higher were observed in an aggregated state. This indicates that the carbon powder can be obtained via precipitation as secondary particles around which the nanoparticles are aggregated.

3.2 Pore characteristics of the carbon powder obtained by precipitation method

Figure 3(a) shows the \( N_2 \) gas adsorption/desorption isotherm of the carbon powder obtained via the precipitation method. Based on the adsorption isotherm, the total specific surface area \( (S_{\text{total}}) \), micropore specific surface area \( (S_{\text{micro}}) \), external specific surface area \( (S_{e}) \), and average pore diameter \( (D_{v}) \) of the micropores calculated via the \( \alpha_s \) analysis are presented in Table 1. From the isotherm (Fig. 3), the amount of \( N_2 \) adsorbed increased to 80 cc g⁻¹ around the low-relative-pressure region \( (P/P_0 = 0) \), suggesting the presence of micropores. Further, the amount of adsorption was observed to increase in the high-relative-pressure region \( (P/P_0 = 0.8–1.0) \), indicating the presence of mesopores. However, based on the \( \alpha_s \) analysis results (Table 1), \( S_{\text{micro}}/S_{\text{total}} = 0.71 \), indicating the dominance of the micropores and a considerably small proportion of mesopores in the carbon powder. A logarithmic-scale adsorption–desorption isotherm was plotted and shown in Fig. 3(b) to conduct a detailed investigation of the adsorption behavior in the low-relative-pressure region corresponding to the adsorption by the micropore of the carbon powder. We observed that adsorption by carbon powder had already started in the low-relative-pressure region at a relative
pressure ($P/P_0$) of $10^{-1}$. This may be attributed to the enhanced adsorption field (micropore filling) caused by the overlapping of the wall potential effect of the pore walls of the micropores, promoting the adsorption of the N$_2$ molecules with respect to the micropores. Therefore, very fine super-micro pores (0.7–2.0 nm) or ultra-micro pores (<0.70 nm) were formed in the carbon powder obtained via precipitation from HPC. $D_{ave}$ was calculated by $c_{eq}$ analysis to be 0.75 nm (Table 1), indicating that super-micropores and ultramicropores were present in the carbon powder. Thus, the carbon powder obtained by the precipitation method using HPC as the starting material mainly contained micropores. It should be noteworthy that porous carbon can be obtained without activation. In addition, the fine pores formed by the precipitation method were very fine pores because $D_{ave}$ was 0.75 nm.

### 3.3 EDLC characteristics of the carbon powder obtained from the precipitation method

An electrode was fabricated using the obtained carbon powder, and the EDLC characteristics were evaluated. Figure 4(a) shows the charge/discharge curve at a current density of 50–5000 mA g $^{-1}$ when carbon powder was used as the electrode. The charging process from 0.8 to 1.0 V in Fig. 4(a) is curved because of the contribution of the invalid Faraday current. Further, the linearity of the obtained charge/discharge curve improved with an increase in the current density. Based on these results, a high-speed charge/discharge behavior peculiar to EDLC was observed, and the capacitance (EDLC) owing to the adsorption and desorption of the electrode surface as well as the electrolyte ions were the main contributing factors. The capacitance per volume at each current density was calculated using Eq. (3) (described in the experiment) around the 0.2–0.8-V region of the discharge curve, and the relation between the capacitances with respect to the current density is shown in Fig. 4(b). The obtained capacitance per volume (150–170 F cm $^{-3}$) was 170 F cm $^{-3}$ (200–210 F g $^{-1}$) at 50 mA g $^{-1}$, equivalent to the capacitance per volume of the activated carbon powder (YP-50F). Furthermore, the capacitance per weight was 200–210 F g $^{-1}$ although the specific surface area of the carbon powder used as the electrode was 400 m$^2$ g $^{-1}$; therefore, the capacitance per area of the carbon powder was high (55 µF cm $^{-2}$). This suggests that the electrolyte ions in the H$_2$SO$_4$ aqueous solution can be easily adsorbed and desorbed inside the extremely fine micropores of the carbon powder, which form an electric double layer. Although the capacitance decreased with increasing current density, the capacitance was observed to be 140 F cm $^{-3}$ at a current density of 5000 mA g $^{-1}$; therefore, the rate of decrease was small, and a high capacitance retention rate (approximately 80%) was observed at current densities of 50–5000 mA g $^{-1}$. The excellent rate characteristics may be attributed to the fact that some mesopores were formed in the carbon powder, facilitating the adsorption and desorption of
the electrolyte ions into the micropores. Furthermore, the initial capacitance is maintained at 95% even when the charge and discharge mechanisms are repeated 10,000 times at a current density of 5000 mA g\(^{-1}\). Thus, the carbon powder obtained by the precipitation method clearly exhibits a high capacitance in aqueous EDLC using H\(_2\)SO\(_4\) as the electrolyte. This can be attributed to the fact that the extremely fine micropores formed in the carbon powder became adsorption sites, thereby forming an electric double layer exhibiting high capacitance. Therefore, the capacitance per volume of the carbon powder exceeded the capacitance of the activated carbon powder (YP-50F) due to the formation of fine pores owing to the activation treatment.

3.4 EDLC characteristics of the carbon powder by CO\(_2\) activation

Figure 5(a) shows the charge/discharge curves at a current density of 50 mA g\(^{-1}\) for the original carbon powder prepared by the precipitation method (without CO\(_2\) activation treatment (HPC-0)) and the carbon powder activated with CO\(_2\) for 30 and 90 min. At a current density of 50 mA g\(^{-1}\), the linearity of the charge curves for HP-0, HP-30, and HP-90 was less than that in 0.8–1.0 V. This indicates the existence of a resistance component during the charging process. However, in the discharge curve, the HPC-0 curve was linear, suggesting the contribution of the resistance component and a small pseudo-capacitance owing to the oxidation–reduction reaction during the discharge process. Therefore, the capacitance of the electrode using HPC-0 can be mainly attributed to the adsorption and desorption of the electrolyte ions on the electrode surface. However, the linearity slightly decreased at around 0.4–0.6 V of the discharge curve for the samples activated for 30 and 90 min. This slight decrease in linearity may be attributed to an increase in the resistance component, which was presumed to be due to the presence of the oxygen-containing functional groups in the carbon powder. The linearity decreased with an increase in the activation time, suggesting that oxygen-containing functional groups were introduced on the surface of carbon powder via CO\(_2\) activation. In case of temperature-programmed desorption analysis, the total amount of oxygen-containing functional groups in HPC-90 was 3700 mmol g\(^{-1}\), which is higher than the amount of 3300 mmol g\(^{-1}\) observed in case of HPC-0. At this time, the increase in the amount of oxygen-containing functional groups owing to CO\(_2\) activation can be mainly attributed to the fact that the amount of carboxyl group
increased from 200 to 450 mmol g\(^{-1}\). The amount of acid anhydride increased from 250 to 350 mmol g\(^{-1}\) before and after CO\(_2\) activation. Although the presence of the oxygen-containing functional groups increased the resistance, the wettability of the carbon powder electrode may have been enhanced. Using Eqs. (3) and (4) (described in the experiment), the capacitances of HPC-0, HPC-30, and HPC-90 in the 0.2–0.8-V region of the discharge curve at 50 mA g\(^{-1}\) were 170 F cm\(^{-3}\) (200 F g\(^{-1}\)), 190 F cm\(^{-3}\) (230 F g\(^{-1}\)) and 210 F cm\(^{-3}\) (260 F g\(^{-1}\)), respectively. The capacitance increased with increasing activation time. Figure 5(b) shows the relation between the current density and the capacitance per volume at each current density. The capacitance per unit volume was observed to increase as the current density increased. The capacitance with respect to each current density of HPC-0 increased with an increase in the activation time. In particular, the activation times of 60 and 90 min showed the largest capacitance (210 F cm\(^{-3}\)) at 50 mA g\(^{-1}\), which was greater than the capacitance per volume (150–170 F cm\(^{-3}\)) of activated carbon (YP-50F). However, HPC-120 with the longest activation time showed the lowest capacitance per volume among the samples with different activation times, indicating that excessive treatment time may decrease the capacitance per volume. The effect of electrode density will be discussed in section 3.6. Thus, the capacitance per unit volume of the carbon powder obtained via precipitation can be increased to 210 F cm\(^{-3}\) (260 F g\(^{-1}\)) by performing CO\(_2\) activation for 60–90 min. The capacitance was approximately 1.4 times that of the activated carbon (YP-50F).

### 3.5 Effect of CO\(_2\) activation on the pore characteristics

Figure 6(a) shows the adsorption and desorption isotherms of the carbon powder before and after CO\(_2\) activation. The amount of N\(_2\) adsorbed in the low-relative-pressure region (around \(P/P_0 = 0\)) was 80 cc g\(^{-1}\) for HPC-0; however, the amount of adsorption increased to 200 cc g\(^{-1}\) when the sample was activated for 30 or 60 min. Furthermore, the amount of adsorbed N\(_2\) can be increased to approximately 300 cc g\(^{-1}\) by setting the activation time to 90 or 120 min. Therefore, it was presumed that micropores were formed by activation. In addition, in case of the adsorption of HPC-120 with the longest activation time, the increase was low in the low-relative-pressure range, suggesting that the pore size increased due to the connection of micropores, which can be attributed to the increased treatment time. However, the adsorption amount increased in the high-relative-pressure range (\(P/P_0 = 0.8–1.0\)) with increasing activation time. The adsorption amount in case of HPC-0 was 500 cc g\(^{-1}\); however, it clearly increased to 700 cc g\(^{-1}\) after the sample was activated for 30 or 60 min and 1100 cc g\(^{-1}\) after the sample was activated for 90 or 120 min. Therefore, both micropores...
and mesopores were formed by the activation. However, based on the results of the EDLC characteristics of the carbon powder (section 3.3), it can be stated that the micropores mainly contributed to the high capacitance of the carbon powder. Therefore, the formation of micropores due to activation was studied in detail. Figure 6(b) shows the logarithmic-scale adsorption–desorption isotherm. With increasing activation time, the adsorption amount increased near a relative pressure of $P/P_0 = 10^{-1}$, suggesting that the activation treatment resulted in the formation of extremely fine pores. Figure 6(c) shows the effect of the activation time on the $D_{mic}$ calculated using $\alpha_3$ analysis. The $D_{mic}$ in case of HPC-0 was 0.75 nm, and no significant difference could be observed when the sample was activated for 30 or 60 min. Therefore, extremely fine pores having sizes of 0.70–0.80 nm were formed or developed by activation for 30 or 60 min. However, $D_{mic}$ slightly increased when the activation time increased to 90 min, and it further increased to approximately 0.90 nm when the activation time increased to 120 min. This suggests that activation for 90–120 min resulted in the formation of fine micropores corresponding to ultra-micropores and the formation of super-micropores. Figure 6(d) shows the activation-time-dependence of $S_{mic}$, $S_{micro}$, and $S_{total}$ calculated via $\alpha_3$ analysis based on the obtained adsorption isotherm. The total specific surface area of HPC-0 was approximately 400 m$^2$ g$^{-1}$, which increased to become approximately 1000 m$^2$ g$^{-1}$ after it was subjected to activation treatment for 30 or 60 min. The total specific surface area increased to 1550 m$^2$ g$^{-1}$ when the activation time was extended and the activation treatment was performed for 120 min. Further, the dependence of the activation time on $S_{micro}$ was examined to investigate the cause of increase with respect to $S_{total}$. The carbon powder that was not activated exhibited a total specific surface area of approximately 300 m$^2$ g$^{-1}$, which considerably increased to 700 and 900 m$^2$ g$^{-1}$ after it was activated for 30 and 60 min, respectively. This increase in $S_{micro}$ can be attributed to the formation of fine pores with sizes of 0.70–0.80 nm due to activation. In addition, $S_{micro}$ increased to 1100 m$^2$ g$^{-1}$ as the activation time increased to 90 min and reached 1200 m$^2$ g$^{-1}$ when the activation time became 120 min; however, the surface area exhibited a minimal increase when the activation time was increased from 90 to 120 min. This may be attributed to the increase in the average pore diameter of the micropores during activation for 90–120 min. Therefore, $S_{micro}$ significantly increased due to the formation of 0.70–0.80-nm pores during activation. However, when the relationship between the activation time and $S_{total}$ was examined, HPC-0 was approximately 100 m$^2$ g$^{-1}$; after 120 min of activation treatment, it became 300 m$^2$ g$^{-1}$. The increase in $S_{total}$ was minimal, indicating the small contribution of $S_{micro}$ to $S_{total}$. Based on these observations, it can be inferred that the formation of extremely fine micropores of 0.70–0.80 nm proceeded preferentially during the activation treatment process and that $S_{micro}$ increased considerably to ensure that $S_{total}$ became 1550 m$^2$ g$^{-1}$. This suggests that the EDLC capacitance increased because extremely fine micropores of approximately 0.7–0.8 nm were formed by the CO$_2$ activation of the sample.

3.6 Relation between the activation and EDLC performance

Figure 7(a) shows the dependence of the capacitance per weight and volume on the activation time at a current density of 50 mA g$^{-1}$. The capacitance per weight tended to increase with increasing activation time; however, it was observed to be saturated when the activation time became greater than 90 min. This was presumed to be due to the slight increase in $S_{micro}$ that resulted from the extremely fine micropores having sizes of 0.7–0.8 nm in the carbon powder, and the connection of pores was aided by activation for 90 min or more. In addition, the capacitance per volume peaked at 210 F cm$^{-3}$ when the activation treatment time was 60 or 90 min because an increase in the activation time to 120 min increased the pore diameter due to the connection of micropores within 0.7–0.8 nm, slightly increasing the specific surface area. The electrode density declined with an increase in the pore volume. Figure 7(b) shows the effect of activation on the electrode density and micropore volume. Further, the electrode density decreased as the activation time increased, and this result can be attributed to the increase in the micropore volume associated with the activation. In particular, the electrode density decreased considerably as the activation time increased from 90 to 120 min, and the increase in pore volume within an activation time of 90–120 min was relatively large. Therefore, the pore volume increased due to the increase in the pore diameter when activation was performed for 120 min; hence, the electrode density decreased. Thus, the capacitance could be increased to 210 F cm$^{-3}$ (260 F g$^{-1}$) by increasing the number of extremely fine micropores in 0.70–0.80 nm by activating the sample for 60 or 90 min.

4. Conclusions

In this study, a carbon powder with micropores was prepared via precipitation using the HPC obtained by the thermal extraction of coal as the starting material. The production process was easy and did not use the activation or template method, and the yield was high. The $D_{mic}$ of the micropores formed in the carbon powder was 0.75 nm, suggesting the existence of extremely fine ultra-micropores. The applicability of carbon powder was verified by examining the EDLC characteristics and considering an aqueous

![Figure 7. (a) The activation-time-dependence of the capacitance per unit mass and volume (b) effect of the electrode density and micropore volume on the activation time.](image-url)
solution of $\text{H}_2\text{SO}_4$ as the electrolyte, where the obtained capacitance per volume was 170 $\text{F cm}^{-3}$ at a current density of 50 $\text{mA g}^{-1}$. This was approximately similar to the capacitance per volume (150–170 $\text{F cm}^{-3}$) obtained in case of the activated carbon powder (YP-50F). In addition, the capacitance per weight was 200–210 $\text{F g}^{-1}$ even though the $S_{\text{total}}$ of the carbon powder was 400 $\text{m}^2\text{g}^{-1}$; therefore, the capacitance per area was 55 $\mu\text{F cm}^{-2}$, which is high. It is presumed that the electrolyte ions in the $\text{H}_2\text{SO}_4$ aqueous solution used as the electrolyte can be easily adsorbed and desorbed in the extremely fine micropores of the carbon powder, forming an electric double layer. Furthermore, the capacitance became 140 $\text{F cm}^{-2}$ when the current density was increased to 5000 $\text{mA g}^{-1}$, indicating a high capacitance retention rate (80%). The capacitance of the carbon powder, which was approximately similar to that of the activated carbon powder (YP-50F), increased to 210 $\text{F g}^{-1}$ after $\text{CO}_2$ activation for 60 or 90 min, clearly exceeding that of the activated carbon powder. This improvement in capacitance can be attributed to the extremely fine micropores (0.7–0.8 nm) formed in the carbon powder.

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