Preparation and Capacitive Performance of Mesoporous Carbon with Short Time CO₂ Activation

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ABSTRACT
The porous carbon material was prepared from sawdust impregnated with a 0.1 M FeCl₃ aqueous solution with CO₂ activation at 800°C. Pores were found to develop with increasing activation time. The BET surface area, average pore diameter and volume of the mesopores also became greater with increasing activation time. The ratio of the mesopore to total pore volume in the activated carbon was more than 90% after 5 min of activation. Precise control of the pore size distribution is possible by finely tuning the activation time. The porous carbonized material was examined for use in electric double layer capacitor (EDLC) electrodes. The charge and discharge characteristics of EDLC electrodes using these carbonized materials were studied. Cyclic voltammetry and rate performance indicated good correlation between the pore structure of the carbonaceous materials and the magnitude of the electrolyte. These relationships were in good agreement with the Nyquist plot obtained by measuring the impedance. These results were also in accordance with pore structure analysis obtained using the nitrogen adsorption method. It is suggested that the Nyquist diagram characterizes the pore structure of porous carbon from the viewpoint of ion transfer.

Keywords : CO₂ Activation, Mesopore Diameter Control, Capacitance, Nyquist Plot

1. Introduction

Electric double layer capacitors (EDLCs) have been studied for their potential applications as energy storage devices due to their high power densities, long lives and ability to reduce loads of secondary cells by hybridization. Activated carbon is usually used as the electrode material, because it has high surface area, high electric conductivity and chemical stability. EDLCs store electric charge in the electric double layer at the electrode/electrolyte interface. The electric storage performance depends on the pore structure of the carbon electrode and electrolyte. A microporous carbon with a high specific area exhibits a large capacitance.1–5 Non-aqueous EDLC systems using organic electrolytes (e.g., propylene carbonate) have been widely investigated because their electrochemical windows can improve the cell voltage and total stored energy for EDLCs. However, if the ionic radius of the electrolyte is larger than the pore radius, the ions cannot penetrate into the carbon pores and the surface of the interface cannot store the charge.1–5,6–9 Therefore, the pore structure of the electrode carbon can be considered to be one of the most important factors determining the capacitance of EDLCs. In particular, mesoporous carbon (MC) has attracted interest as an electrode material due to its high specific surface area, fast mass transfer and ion diffusion for non-aqueous and ionic liquid (IL) EDLCs with larger ions.10,11 However, the specific capacitance of MC is still relatively low for practical EDLCs.12,13

Although sophisticated carbon aerogels,14 carbon nanotubes,15 and porous carbon prepared by the template method16 or catalytic activation17 to penetrate mesoporous carbon have been developed, their capacitance is still not satisfactory due to their low specific surface area. Ideally, the carbon electrode for high performance EDLCs should have both a high surface area and a suitable pore size for electrolyte ions. Therefore, carbon electrode materials must be designed with pores that are large enough for the electrolyte to access completely, but small enough to ensure a large overall surface area.18 Fuertes et al. reported that mesoporous carbons with graphitic structures fabricated by using iron-impregnated polymer showed good performance as EDLC electrode19 due to high electro conductivity and rapid mass transfer in the porous carbon.

In this paper, we report a simple method for preparing mesoporous carbon by catalytic activation with iron ions. The pore distribution drastically changes for short activation times. The porous carbon material having different pore structure was slightly prepared by changing the activation time from the same raw material. These porous materials was advantageous to analyze the movement of ions in the pores. The capacitive performance was measured by the conventional galvanostatic charge and discharge procedure and cyclic voltammetry. Impedance spectroscopy was measured for small and large ions for non-aqueous electrolytes.

2. Experimental

2.1 Materials

Sawdust (a Japanese oak) which was supplied by Yonebayashi Milling Co., Ishikawa Prefecture, Japan was used as a raw material. Its ash content was 2.1 mass% by thermogravimetric analysis. The diameter of the sawdust was ca. 0.5–2 mm. FeCl₃ (special grade, Wako Pure Chemical Industries, Ltd.) was purchased for use as a catalyst for production of mesopores. Two kinds of ionic liquids were used as electrolytes. Table 1 shows the features of the ionic liquids used in this study. These reagents were purchased from Wako Pure Chemical Industries, Ltd. and used without further
purification. Electrolyte solutions were prepared by diluting these ionic liquids with propylene carbonate (PC) (Kishida Chemical Co., Ltd., capacitor grade). The three ionic liquids of alkyl imidazolium salts differ in alkyl group and anion. Molecular weights and ionic diameters calculated by Win Monstar are shown in Table 1. Pure water was used to prepare FeCl₃ aqueous solution.

### 2.2 Preparation of carbonaceous samples

Sawdust sieved to 0.1 mm average particle size was used as a raw material. The 0.1 M FeCl₃ solution was impregnated into the sawdust under low pressure for 24 hours at room temperature. The sawdust was filtered without washing and dried at room temperature. The sawdust including FeCl₃ was placed in a ceramic boat in an electric furnace with a thermocouple for temperature control. The temperature and gas flow profiles of carbonization are shown in Fig. 1. The sawdust was dried in an electric furnace for 60 min at 110°C under a stream of N₂ (300 sccm). Thereafter, the temperature was raised at a rate of 10°C/min then kept at 800°C for 60 min. The stream was quickly changed to CO₂ from N₂, and activation of the carbonaceous samples was carried out. The activation time was precisely controlled between 1–90 min. 0.1 g of the carbonized material was then poured into 20 mL of 0.1 M HCl aqueous solution at 90°C and left for 7 h to remove iron compounds from the carbon matrix. This operation was repeated until no iron ions were detected after more than 5 min activation. The pore structure of the carbonized samples was controlled to produce a uniform distribution of mesopores (10 nm to 200 nm). The pore size of the mesopores was determined by a micropore size distribution method.

### 2.3 Measurement of capacitive characteristics

The carbonized materials were crushed and selected by a test sieve (a mesh size of 75 µm, 200 mesh). The carbon material was dried at 200°C under low pressure for 4 hours to remove water in the pore. In a glove box, 0.1 g of the powdered carbon was mixed with ca. 1 mL of non-aqueous electrolyte to make a suspension. The suspension was used as an electrode and electrolyte. A schematic illustration of the test capacitor cell which was a sandwich type (two electrode system, Tomcell Japan Co., Ltd.) is shown in Fig. 2. The suspension was placed between two sheets of Pt plates (18 mm in diameter, 1 mm in thickness). A plastic mesh sheet (0.1 mm in thickness) was inserted between the Pt plates as a separator. The effective surface area of a single collector was 7.07 × 10⁻² cm². The electrochemical properties of the EDLC were studied by cyclic voltammetry, galvanostatic charge-discharge and electrochemical impedance spectroscopy, using electrochemical analyzer systems (BTS 2004W-10, Nagano, Japan, LCR 3522, 3532, Hioki E. E. Corporation, Japan).

### 3. Results and Discussion

#### 3.1 Preparation of mesoporous carbon

In this study, we investigate the change in the pore structure of carbonized materials by changing the activation time. The parameters for the pore structures of the carbonized materials used in this study are shown in Table 2. The samples are expressed as An, where “n” is activation time in minutes. For example, the microscope image of carbonized sample sieved for preparation of electrode was shown in Fig. 3. The shape of the carbonized sample (A60) was irregular and its size was almost less than 0.1 × 10⁻¹ mm. A0 was prepared without activation, that is, just carbonization under the N₂ stream. Pores develop with increasing activation time. S BET (BET surface area), dₚ (average pore diameter), and V meso (volume of mesopore) became larger with increasing activation time. The ratio of the mesopore to total pore volume for the activated carbon is more than 90% after more than 5 min activation. The pore

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### Table 1. The molecular weights and sizes of ionic liquids used in this study.

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Electrolyte</th>
<th>Alkyl group</th>
<th>Molecular weight [g/mol]</th>
<th>Ionic diameter*[^a^]</th>
</tr>
</thead>
<tbody>
<tr>
<td>EMIBF4</td>
<td>1-Ethyl-3-methylimidazolium tetrafluoroborate</td>
<td>-C₂H₅</td>
<td>197.97</td>
<td>EMI⁺ = 0.61</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>BF₄⁻ = 0.45</td>
</tr>
<tr>
<td>OMIBF4</td>
<td>1-Methyl-3-octylimidazolium tetrafluoroborate</td>
<td>-C₄H₁₅</td>
<td>282.13</td>
<td>OMİ⁺ = 0.75</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>BF₄⁻ = 0.45</td>
</tr>
</tbody>
</table>

*[^a^]: calculated by Win Monstar
EMI⁺: 1-Ethyl-3-methylimidazolium; OMİ⁺ = 1-Methyl-3-octylimidazolium

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![Figure 1. Temperature and atmospheric conditions for carbonization of sawdust.](image1)

![Figure 2. Schematic diagram of construction of two electrode for measuring electrochemical properties.](image2)
distributions of these carbon materials are shown in Fig. 4. The curve of the cumulative pore volume for A0, which is not activated by CO$_2$, shows that A0 is microporous carbon. The cumulative pore volume curve for A1 shows an increase in the pore volume in the mesoporous region. The difference in the pore volume between A0 and A1 arises from the mesopore region. The cumulative pore volume curve for A5 shows that the mesopores are further developed. In A30, the development of mostly mesopores is indicated, and the development of mesopores with diameters of more than 10 nanometers is particularly significant. In A60, the development of pores with diameters of more than 20 nm is remarkable, and conversely, there is only a slight development of micropores. In A90, it is suggested that most of the pores are mesopores 2 nm or more in diameter. This drastic change in pore structure was observed within 30 min activation time and suggested that the initial activation process was important for controlling the mesopore structure.

### 3.2 Charge and discharge properties

The effect of the pore structure on the charge and discharge characteristics of a capacitor was investigated. EDLC can be considered that two different condensers are connected in series. Capacitance and charge and discharge characteristics of EDLC are strongly affected by smaller capacitance of the two electrode. Ion diameter of BF$_4^-$, EMI$^+$ and OMI$^+$ is 0.45 nm, 0.61 nm, 0.75 nm, respectively. Therefore, the negative electrode where the larger ion OMI$^+$ and EMI$^+$ diffuse in the pore of carbon dominates the capacitive performance of EDLC. In this study, the effect of pore structure and size of electrolyte ion on the capacitive performance were briefly investigated by the two electrode cell system.

Three representative carbonaceous materials, A0, A5 and A30, were examined. The cyclic voltammograms for A0, A5 and A30 are shown in Fig. 5. EMIBF$_4$ is used as the electrolyte. The scan rate is 50 mA/s at 303 K.

![Figure 3](image-url) (Color online) Microscope image of carbonized material for electrode (sample A60).

![Figure 4](image-url) Cumulative pore volume of carbonaceous materials prepared at various activation times. An: n indicates activation time in minutes.

![Figure 5](image-url) Effect of different activation times on cyclic voltammograms. Electrolyte: 0.1 M EMIBF$_4$ propylene carbonate solution; Scan rate: 50 mA/s at 303 K.

### Table 2. The parameters of pore structures of carbonaceous materials.

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Activation time [min]</th>
<th>$S_{BET}$, BET surface area [m$^2$/g]</th>
<th>Average $d_p$, pore diameter [nm]</th>
<th>$V_{meso}$, Volume of mesopore [mm$^3$/g]</th>
<th>$V_{total}$, Volume of total pore [mm$^3$/g]</th>
<th>$V_{meso}/V_{total}$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A0</td>
<td>0</td>
<td>420</td>
<td>2.6</td>
<td>150</td>
<td>270</td>
<td>55.4</td>
</tr>
<tr>
<td>A1</td>
<td>1</td>
<td>460</td>
<td>3.8</td>
<td>320</td>
<td>440</td>
<td>74.1</td>
</tr>
<tr>
<td>A5</td>
<td>5</td>
<td>500</td>
<td>7.4</td>
<td>830</td>
<td>922</td>
<td>90.0</td>
</tr>
<tr>
<td>A30</td>
<td>30</td>
<td>610</td>
<td>8.6</td>
<td>1220</td>
<td>1320</td>
<td>92.2</td>
</tr>
<tr>
<td>A60</td>
<td>60</td>
<td>660</td>
<td>9.4</td>
<td>1450</td>
<td>1540</td>
<td>94.1</td>
</tr>
<tr>
<td>A90</td>
<td>90</td>
<td>804</td>
<td>10</td>
<td>1890</td>
<td>2010</td>
<td>94.2</td>
</tr>
</tbody>
</table>
that reduce the diffusion resistance of the electrolyte ions in the pores of the carbon electrode. The cyclic voltammograms for A0, A5 and A30 when OMIBF4 is used as the electrolyte are shown in Fig. 6. The tendency of the cyclic voltammograms was almost the same as in Fig. 5. The shapes of the cyclic voltammograms of A0 and A5 are parallelograms. However, the shape of the cyclic voltammogram of A30 resembles a butter\[.\]

These results suggested that larger electrolytes were sensitively affected by the pore structure. Compared with Fig. 5, the capacitance of A0 and A5 is smaller, while that of A30 is almost the same. The diffusion resistance for OMI ions is small in pores with diameters of 10 nm or more. These results imply that (1) the diffusion resistance for OMIBF4 (larger molecule) is greater than that for EMIBF4 (smaller molecule) in the A0 and A5 porous carbons, and (2) fully developed mesopores in A30 do not give rise to diffusion resistance for OMIBF4.

The specific capacitance for A30, A5 and A0 is estimated by the constant current method. The current density was varied in the range of 10–500 mA/g. All discharge curves were straight lines, with their slopes yielding the capacitance. EMIBF4 and OMIBF4 are used as the electrolytes in Figs. 6 and 7, respectively. The capacitance of A0, A5 and A30 increases with activation time. As the current density increases, the capacitance becomes smaller in both cases. The same tendency is observed in Fig. 8. The capacitance of A5 and A0 is smaller than that for A30, and also smaller than in Fig. 7 in which EMIBF4 is the electrolyte. This result suggests that the pores of A0 and A5 are too small for the bulky OMIBF4 to pass through. However, for A30, the diffusion resistance for OMIBF4 due to mesopores is fully developed. These results imply that the pore structure affects the EDLC electrolyte. Viscosity of 1.0 M EMIBF4 and 1.0 M OMIBF4 propylene carbonate solution measured by Ostwald method was 3.0 [mPa·s] and 4.0 [mPa·s], respectively. Electric conductivity of 1.0 M EMIBF4 and 1.0 M OMIBF4 propylene carbonate solution were 14.1 [mS/cm] and 9.36 [mS/cm], respectively. When the alkyl group of the electrolyte are larger, the interactions between the alkyl groups each other and the alkyl group and carbon matrix on pore surface of porous carbon become stronger. Therefore, the diffusion resistance of OMIBF4 were greater than that of EMIBF4.

3.3 Impedance spectrum

AC (alternative current) impedance is measured in order to clarify the movement characteristics of ions in the pores of the carbon electrode. Generally, impedance spectra can be divided into two ranges by frequency,\[.\] that is, the distributed constant-type equivalent circuit range (higher frequency) and the lumped-type equivalent circuit range (lower frequency). The typical Nyquist diagram of EDLC of a porous carbon electrode is shown in Fig. 9. In the very high frequency region, a semi-circular curve is observed. The Warburg resistance (slope = 45°) is observed as a straight line at lower frequency. The slope becomes steeper with decreasing frequency. Finally, the line becomes perpendicular. Itagaki et al.\[.\] reported the theoretical impedance characteristics of porous carbon used as an EDLC electrode. In the Nyquist plot, they describe that the transition region between the Warburg linear region and the vertical line of the lumped-type equivalent circuit range region shifts.
that for (a). The influence of the size of the electrolyte is significant. The transition region for the mesoporous carbons shifts to the left with increasing activation time. The curve for A5 (b, OMI\textsubscript{BF4}) is to the right of the curve for A5 (a, EMIBF\textsubscript{4}). The pores in A5 provide a diffusion path through which EMI\textsuperscript{+} can pass smoothly, but they are too small for OMI\textsuperscript{+}. In contrast, the curves for A30 in (a) and (b) are in almost the same position. This suggests that the pore size in A30 provides large diffusion pathways for both EMI\textsuperscript{+} and OMI\textsuperscript{+}. The diffusion resistance of the electrolyte based on the size of the pores and the development of mesopores can clearly be seen in the Nyquist plot.

4. Conclusion

Mesoporous carbon is prepared by carbonization and short time \(\text{CO}_2\) activation of sawdust that had been immersed in a \(\text{Fe}^{3+}\) ion aqueous solution. Regarding the pore structure and electrochemical properties of the mesoporous carbon, the following results are obtained.

1. The \(\text{CO}_2\) activation time with the Fe catalyst has a significant effect on the resulting pore structure of the carbonaceous materials.
2. The specific capacitances and shapes of the cyclic voltamograms are affected by the activation time due to the generation of mesopores that increase the diffusion rate of the electrolyte in the carbon pores.
3. The capacitance of the bulky electrolyte ion does not decrease with increasing current density to less than that of the electrolyte.
4. The Nyquist diagram shows that the diffusion of ions in the pores is affected by the pore structure and electrolyte. These results imply that the Nyquist diagram is a useful analytical tool for the porous structure of carbon EDLC electrodes.

References