1. INTRODUCTION

The electric double layer capacitor (EDLC) has been widely used as energy storage devices for memory back-up systems and are receiving considerable attention as a promising high power energy source for electric devices and hybrid electric vehicles. The energy storage mechanism of EDLCs is based on the phenomenon that an electric double-layer is formed at the boundary between the electrode and an electrolyte. In electronic devices requiring higher energy density with smaller size, the higher specific volume capacitances of EDLCs is important factor. However, conventional physically/chemically activated carbons possess micro-porous structure with moderately high specific surface area, which has limited the specific volume capacitance less than 20 F/ml, due to low electrode density, in the two electrode system.

In recent years, an alkali-activation procedure has been investigated to introduce the larger specific volume capacitance for the graphitizable carbons. The graphitizable carbons, activated with alkaline solutions such as KOH, NaOH, K₂CO₃ etc. at 700 - 900°C, exhibited larger specific volume capacitance of 20 - 30 F/ml. It is reported that the first cycle, that is, the electric field activation makes the electrolyte ions to intercalate into the graphene layer of carbons, which introduce small pore structure of the electrode. Such structural changes during the first cycle shows irreversible, providing larger specific volume capacitance and charge/discharge profile in successive runs. However, it has been also reported to have many problems such as a high activation cost, the corrosion of the activation vessel and the rapid degradation of the capacitance in charge-discharge cycle life etc. This bad electrochemical performance may be associated with high diffusion resistivity of the electrolyte ions to penetrate the graphene units.

In general, the activated carbons that have been developed up to now have a pore structure generated by partial etching at the internal of carbon material. They have different electrochemical characteristics according to the micro structure of pore adjusted by diverse methods.

As a manufacturing method of micro pore, this study suggests the oxidation method at the room temperature in stead of high temperature activation of carbon material. The oxidation and heat treatment of the graphitizable carbon with a dilute nitric acid and sodium chlorate (NaClO₃) was attempted to achieve a electrochemically stable active material with a large capacitance. The electrochemical
performance and the structural feature of oxidized carbon were examined in terms of the weight ratio of NaClO₃/coke, and compared with KOH-activated carbon.

2. EXPERIMENTAL

2.1 Oxidation condition of needle coke

Needle cokes derived from coal tar pitch and calcinated at 1100°C were supplied by Nippon Steel Chemical Co. Ltd. For the oxidation of needle cokes, needle cokes (5g) and sodium chlorate with the range 12.5 to 50g were put in dilute nitric acid (150ml), and then stirred at room temperature during 24h. As a comparison, activation of the same coke was carried out with KOH (KOH/coke = 4/1 by weight) at 700°C for 2h under an Ar atmosphere. After oxidation or activation, needle cokes were thoroughly washed with distilled water and heated under vacuum at 100°C, and 200°C. The increase rate of the temperature was 3°C/min.

2.2 Preparation of electrode and cell capacitor

The electrodes were composed of the oxidized coke, carbon black as an electric conductor and polytetrafluoroethylene (PTFE). A mixture containing the oxidized coke, carbon black with 10 wt.% and PTFE with 10 wt.% was mixed with water. A paste obtained by drying the mixture was repeatedly roll-pressed for the modification of the sheet type electrode. The cell capacitors were constructed with an electrolyte impregnated the separator sandwiched between the electrodes, whose size was 2×2 cm². These assembles were housed in Al-laminated film cells. After an organic electrolyte solution of 1.2M Et₄NBF₄ in AcN. solution was poured, the cell capacitors were sealed taking out the leads.

2.3 Structure and Electrochemical analyses

The structure changes of needle cokes were measured by X-ray diffraction using Cu K radiation. The cross sectional morphologies of polished needle cokes were observed with a field emission SEM. Surface area and pore volume of the needle cokes were measured according to the BET method by physical adsorption of N₂ at 77K, using an automatic adsorption system. The crystal structure analysis was obtained by Raman Spectroscopy. The cell capacitors were charged and discharged at a constant current of 2mA/cm² between 0 − 2.5V with a Maccor test system. The capacitance was calculated from:

\[ C = \frac{it}{V} \]

where t is the time period, V, voltage change, I, a constant discharge current.
3. RESULTS AND DISCUSSION

3.1 Structure of needle cokes activated with NaClO₃+HNO₃ and KOH

Table 1 shows the preparation conditions and the properties of needle cokes oxidized with dilute nitric acid and sodium chlorate and activated with KOH. The values of O/C for N-sample after 100°C-heating increased with the increase of the ratio of NaClO₃/coke, and the smaller values of H/C and O/C in the N-sample after 200°C-heating were obtained. Whereas the H/C and O/C for K1 sample have a far fewer values and were not affected by the drying condition. The surface areas of N3 and K1 sample has exhibited 14 and 4.3 m²/g, respectively.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Chemical</th>
<th>Reagent/coke</th>
<th>Reaction condition</th>
<th>Sp (m²/g⁻¹)</th>
<th>Smicro/Sp</th>
<th>Vmicro/Vpore</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1</td>
<td>NaClO₃+HNO₃</td>
<td>2.5/1</td>
<td>24 h at 25°C</td>
<td>0.16</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>N2</td>
<td>NaClO₃+HNO₃</td>
<td>5.0/1</td>
<td>24 h at 25°C</td>
<td>0.09</td>
<td>0.16</td>
<td></td>
</tr>
<tr>
<td>N3</td>
<td>NaClO₃+HNO₃</td>
<td>7.5/1</td>
<td>24 h at 25°C</td>
<td>0.10</td>
<td>0.30</td>
<td>0.42</td>
</tr>
<tr>
<td>N4</td>
<td>NaClO₃+HNO₃</td>
<td>10/1</td>
<td>24 h at 25°C</td>
<td>0.11</td>
<td>0.40</td>
<td></td>
</tr>
<tr>
<td>K1</td>
<td>KOH</td>
<td>4/1</td>
<td>2 h at 700°C</td>
<td>0.02</td>
<td>0.2×10⁻⁵</td>
<td>0.3×10⁻⁵</td>
</tr>
</tbody>
</table>

Table 1. Preparation conditions and properties of needle cokes oxidized with NaClO₃+HNO₃ and activated with KOH.

Figure 1 shows X-ray diffraction patterns of raw needle cokes, and needle cokes (N1 N4) oxidized and heated at 100°C, and KOH-activated needle cokes (K1). From a typical graphite structure with (002) diffraction peak shown in raw needle cokes, another diffraction peak at around 12° (by Cu K) was observed for needle cokes oxidized with acidic solution. This diffraction peak must be estimated to the graphite oxide, as reported previously [5, 6], and the inter-layer distance of the oxidized needle coke was calculated to 0.7nm. The diffraction peak of graphite oxide was predominant in the X-ray diffraction pattern for the needle cokes oxidized with acidic solution having the composition ratio, NaClO₃/coke, of above 7.5. It can be assumed from the figure that, as the amount of NaClO₃ added to the acidic solution increases, the coke is more strongly oxidized and the formation of graphite oxide is further facilitated. However, KOH-activated needle coke reduced the intensity and broadened the line width of the (002) diffraction peak without shifting.
Figure 1. X-ray diffraction patterns of raw needle coke, needle cokes (N1-N4) oxidized and heated at 100°C, and KOH-activated needle coke (K1).

Figure 2 shows the X-ray diffraction patterns of raw needle cokes, N3 samples after 100°C and 200°C. It can be seen that the graphite oxide peak of N3 sample shifted to 2θ with more broadened line width after heating at 200°C. This reduction to the graphite structure is associated with the thermal decomposition of graphite oxide. As well known that thermal decomposition usually occurs between 150 and 200°C, heating at 200°C causes simultaneous loss of oxygen from each layer plane resulting in a gradual decrease of the layer spacing. In generally, thermal decomposition, if the temperature is not increased very slowly, may also occur with nearly explosive violence. During heating the oxygen atoms between the layer planes probably tend to migrate to peripheral surfaces where they react to form mostly CO or CO₂. The mechanical action by releasing these gases or the carbon depleting from the layer plane may partially fractures the graphite structure as shown in X-ray diffraction to be graphite of small and imperfect crystallites.
3.2 Electrochemical performance of activated needle cokes

The electrochemical performances of the needle cokes of N3 and KOH-activated needle cokes of K1 as the electrode for EDLC were examined. Figure 3 shows first (a) and second (b) charge-discharge curves of cells with needle coke of N3 after 200°C-heating and K1 after 200°C-heating. In the KOH-activated needle cokes, K1-cell was charged up to 3.5V at 1st charge-discharge, because K1-cell charged up to 2.5V exhibited very small capacitance. We can see from the figure that after the linear increase of capacitance in proportion to voltage in the 1st charge, it showed redox reaction that deviates from the linear line. However, since the 2nd charge/discharge, the cell makes linear behavior against the voltage regardless of the charge/discharge number of times. These behaviors, as reported previously, is associated with the electric field activation at the 1st charge, and since 2nd charge/discharge the capacitance is generated in the pores formed between inter-layer by 1st charge. That is, the needle coke makes negligibly small electric double layer when it is dipped into an electrolyte solution in the beginning. During the initial charging process, however, the intercalation of ions builds double layers between inter-layer, and during the discharging process, the electrolyte ions go out. After that, the electrodes behave like conventional activated porous carbon electrodes with a high capacitance. In the 1st charge, the onset point represented by an arrow can be regulated as intercalation starting voltage (ISV), and N3 and K1 indicate about 1.0V and 2.8V respectively. In KOH activation, as it can be estimated that the inter-layer structure of needle coke receives almost no influence in the activation process, the intercalation of electrolytes ion into the interlayer of carbon seems to depend on the high voltage. On the other side, the reason that the ISV of N3-cell is lower than that of the cell made of KOH activation powder is considered
that the electrolyte ions can intercalate easily into the inter-layer which have a lot of structure defect generated during the inter-layer expansion and shrinkage. Larger capacitance of N3 may be associated with much more pore site generated during 1st charge.

![Graph showing charge-discharge curves](image)

**Figure 3.** First (a) and second (b) charge-discharge curves of cells with needle coke of N3 after 200°C-heating and K1 after 200°C-heating.

The oxidation conditions and the specific capacitance of the oxidized cokes are summarized in Table 1. The specific capacitance per weight of the oxidized coke and the volume of electrode in the two electrode system increased with increasing the ratio of NaClO₃/coke, and the maximum values in N3 sample exhibited 30.3 F/g and 26.9 F/ml, respectively. For N4 sample, the specific capacitance per volume indicated the lower value than that of N3 sample due to the lower density of electrode.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Oxidant</th>
<th>NaClO₃/Coke</th>
<th>Density of Electrode (g/ml)</th>
<th>Capacitance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>F/g</td>
</tr>
<tr>
<td>N1</td>
<td>NaClO₃+HNO₃</td>
<td>2.5/1</td>
<td>1.14</td>
<td>20.5</td>
</tr>
<tr>
<td>N2</td>
<td>NaClO₃+HNO₃</td>
<td>5/1</td>
<td>1.11</td>
<td>25.8</td>
</tr>
<tr>
<td>N3</td>
<td>NaClO₃+HNO₃</td>
<td>7.5/1</td>
<td>1.11</td>
<td>30.3</td>
</tr>
<tr>
<td>N4</td>
<td>NaClO₃+HNO₃</td>
<td>10/1</td>
<td>0.87</td>
<td>30.4</td>
</tr>
</tbody>
</table>

**Table 2.** Oxidation conditions and electrochemical performances of pyrolyzed needle cokes.

**REFERENCE**


