High-energy-density activated carbon electrode for organic electric-double-layer-capacitor using carbonized petroleum pitch

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Abstract
Activated carbons (ACs) have been used as electrode materials of electric double-layer capacitors (EDLC) due to their high specific surface areas (SSA), stability, and ecological advantages. In order to make high-energy-density ACs for EDLC, petroleum pitch (PP) pre-carbonized at 500–1000°C in N₂ gas for 1 h was used as the electrode material of the EDLC after KOH activation. As the pre-carbonization temperature increased, the SSA, pore volume and gravimetric capacitance tended to decrease, but the crystallinity and electrode density tended to increase, showing a maximum volumetric capacitance at a medium carbonization temperature. Therefore, it was possible to control the crystalline structure, SSA, and pore structure of AC by changing the pre-carbonization temperature. Because the electrode density increased with increasing of the pre-carbonization temperature, the highest volumetric capacitance of 28.4 F/cc was obtained from the PP pre-carbonized at 700°C, exhibiting a value over 150% of that of a commercial AC (MSP-20) for EDLC. Electrochemical activation was observed from the electrodes of PP as they were pre-carbonized at high temperatures above 700°C and then activated by KOH. This process was found to have a significant effect on the specific capacitance and it was demonstrated that the higher charging voltage of EDLC was, the greater the electrochemical activation effect was.

Key words: activated carbon, petroleum pitch, EDLC, electrochemical activation, volumetric capacitance

1. Introduction

Electric double-layer capacitors (EDLCs) are used as auxiliary power sources for hybrid electric vehicle or energy storage system because they have faster charge-discharge rates, higher power density, and longer life cycles than those aspects of secondary batteries. However, since EDLCs have energy density lower than that of secondary batteries, studies are being conducted to increase the energy density of EDLCs [1-4]. The energy density of EDLCs is generally expressed in terms of gravimetric capacitance (F/g), which is independent of the density of the electrodes. However, a high-density electrode is essential because the volumetric capacitance (F/cc) is more important than the gravimetric capacitance in order to reduce the size of EDLC [5,6].

Petroleum pitch (PP) is cheap and abundant as a residue obtained from the distillation of petroleum oil. In addition, since it has wider molecular weight and lower aromatic content than those aspects of coal tar pitch (CTP), it is suitable for producing activated carbon (AC) [7-10]. Also, PP, one of the soft carbons, can be made into a high-density electrode by increasing the crystallinity through the heat treatment process [6]. To make ACs, there are physical and chemical activation methods. Physical activation is an inexpensive and simplified process, but the ACs produced generally have low specific surface areas (SSA),
resulting in low capacitances. Meanwhile, chemical activation is an expensive process, but it is widely used to make electrode materials for EDLC because of their high capacitances. Chemicals such as KOH, NaOH, H3PO4, and ZnCl are mainly used as activation agents; KOH is most widely used because, generally, the highest SSA can be obtained by KOH activation [11-15].

In this study, various ACs for EDLC electrode materials were prepared by the KOH activation of pre-carbonized PPs. In order to obtain a high-density electrode, the effects of increased crystallinity with increasing of the pre-carbonization temperature on the structural and electrochemical properties of the ACs were investigated. The properties of ACs prepared from pre-carbonized PPs were compared with those of ACs prepared from pre-carbonized CTPs under similar conditions.

2. Experimental

2.1. Materials

A PP having a softening point of 205°C, provided by GS Caltex Co. (Korea), was used as a precursor for AC. Potassium hydroxide (KOH, 85%; Daejung Chem. & Metals Co., Ltd, Korea) was used as the activation agent. N2 gas (JC gas Ltd., 99.99%) was flowed during carbonization and KOH activation of PP. The electrodes were prepared by mixing AC, Super-P, and polyvinylidene fluoride (PVDF, power; Aldrich, USA) dissolved in 1-Methyl-2-pyrrolidone (NMP, 99.5%; Sam Chun Pure Chem. Co., Ltd., Korea). Coin type EDLC cells were assembled using poly propylene as a separator and 1 M tetraethylammonium tetrafluoroborate in acetonitrile (TEABF4/AN) as an electrolyte.

2.2. Preparation of AC

In order to change the degree of crystallinity of the precursors before the KOH activation process, the PPs were ground and pre-carbonized for 1 h at a temperature range of 500°C–1000°C under N2 flow in an electric tube furnace. The sample pre-carbonized at 500°C was denoted as P5, and so on. Various ACs were prepared by KOH activation of the pre-carbonized PPs (P5–P10). The pre-carbonized PPs were mixed with KOH powders at a PP/KOH mass ratio of 1:4 and the mixtures were activated at 900°C for 3 h. The obtained ACs were thoroughly washed with distilled water three times and dried at 110°C in an oven for 1 day. The ACs activated from P5–P10 were denoted as P5AC–P10AC, respectively. For comparison, ACs were also prepared from a CTP precursor having a softening point of 292°C, provided by OCI Co. (Korea), using the same carbonization and activation procedures.

2.3. Characterization and electrochemical properties of AC

Pore structures of the obtained ACs were characterized by N2 adsorption/desorption measurements using an ASAP 2010 (Micromeritics, USA) instrument. SSAs of ACs were calculated by the Brunauer-Emmett-Teller (BET) method. Nitrogen absorption/desorption isotherm, micro-pore analysis method, Barrett-Joyner-Halenda, and non-local density functional theory (NLDFT) analyses were used to obtain the pore volume, pore diameter, and pore size distribution (PSD) of the ACs. Crystalinity of pristine PP, carbonized PPs, and activated PPs was determined by X-ray diffraction (XRD) measurement (XRD-7000; Shimadzu, Japan) using Cu-Kα radiation (λ=1.54056 Å) operated at 40 kV and 30 mA. The interlayer spacings (d002 and di00) were calculated using the Bragg equation (1).

$$\lambda = 2d \sin(\varphi)$$  \hspace{1cm} (1)

where $\varphi$ is the Bragg angle for the reflection concerned and $\lambda$ is the wavelength of the radiation. The in-plane crystallite size ($L_a$) and the stacking height of the crystallite ($L_c$) were determined from the (101) peak at ~43° and the (002) peak at ~26°, respectively, using the following Scherrer equations [16-19].

$$L_a = 1.84\lambda / B_\alpha \cos(\varphi_\alpha)$$  \hspace{1cm} (2)

$$L_c = 0.89\lambda / B_\alpha \cos(\varphi_\alpha)$$  \hspace{1cm} (3)

where $\lambda$ is the wavelength of the radiation used, $B_\alpha$ and $B_\beta$ are the width of the (101) and (002) peaks, respectively, at 50% height, and $\varphi_\alpha$ and $\varphi_\beta$ are the corresponding scattering angles. Electrodes were prepared by mixing AC, Super-P, and PVDF at a mass ratio of 8:1:1. PVDF and Super-P were used as a binder and a conductive additive, respectively. The mixture was homogenized in a sufficient quantity of NMP solvent to make a homogeneous slurry. On etched aluminum foil used as a current collector, the mixed slurry was coated by doctor blade apparatus and dried in an oven at 70°C for 24 h. The dried electrode was then pressed using a roll press at 80°C and dried in a vacuum oven at 70°C for 24 h.

Coin-type EDLC cells of CR2032 size were fabricated using two symmetrical carbon electrodes, a separator, and a spacer. The electrodes were punched into small disks with 18 mm diameter; these were placed in a glass vial containing 1 M TEABF4/AN electrolyte after measuring the mass and thickness. The bulk density of the AC electrodes was measured by dividing the mass of the dried carbon electrodes without the current collector by the volume, which was obtained by multiplying the area and the thickness of carbon electrodes. The immersion was maintained for 24 h so that the electrolyte could sufficiently permeate the electrode materials. The 19-mm diameter separator, soaked with the electrolyte solution, was placed between the electrodes. Finally, the coin cell was sealed using a coin cell crimper (Wellcos Co.). All processes for assembling the coin-type EDLC cell were carried out in a glove box filled with N2 gas.

The electrochemical performance of the assembled coin-type EDLC cells was measured by cyclic voltammetry (CV; Potentiostat/Galvanostat Model 273 A, EG&G, USA) and galvanostatic charge/discharge (C/D; WBCS-3000, WonA Tech Co., Ltd., USA). The CV measurement was conducted at potential scan rates of 10 and 100 mV/s in the voltage range of 0–2.7 V. Constant current loads (1, 3, and, 5 A/g) were applied to the C/D measurement in the voltage range of 0–2.7 V. Gravimetric capacitance (F/g) was calculated by CV using the following equation; volumetric capacitance (F/cc) was cal-

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culated by multiplying the electrode density (g/cc) by the gravimetric capacitance.

\[ C = \frac{\int I \, dV}{2m \cdot v \cdot \Delta V} \]  

(4)

where \( I \) is current, \( v \) is the scan rate, \( m \) is the mass of the electrode materials, and \( \Delta V \) is the measured voltage range (0–2.7 V). Capacitance (F/g) was also calculated by charge/discharge test using the following equation.

\[ C = \frac{I \times \Delta t}{\Delta V} \]  

(5)

where \( I \) is the current density (A/g), \( \Delta t \) is the discharge time, and \( \Delta V \) is the measured voltage range (0–2.7 V).

3. Results and Discussion

3.1. Physical properties of carbonized pitch and AC

Fig. 1 shows the Fourier-transform infrared spectroscopy (FT-IR) spectra of PP, CTP, and their pre-carbonized samples. As described in the previous study [6], the pristine pitch samples exhibited noticeable IR bands below 1700 cm\(^{-1}\) and around 3000 cm\(^{-1}\). Some functional groups were observed to be aromatic (3050, 1161, 1505, 1052, 872, 811, 750, and 438 cm\(^{-1}\)) and aliphatic (2955, 2920, 2855, and 1450 cm\(^{-1}\)) groups. As the carbonization temperature was increased, these IR band intensities gradually dropped. Unlike CTP, PP had relatively large IR band intensities between 2800–3000 cm\(^{-1}\), indicating the relatively high content of aliphatic compounds. However, the low-temperature carbonization at around 500–600°C significantly reduced the large IR band intensities between 2800–3000 cm\(^{-1}\); however, the aromatics peak at 3050 cm\(^{-1}\) was reduced only slightly, showing high aromatic compounds like CTP. These aromatic compounds also disappeared for carbonization temperatures above 700°C. Therefore, the FT-IR spectra of the carbonized PPs and CTPs exhibited very similar shapes for carbonization temperatures above 600°C, although the peak intensities representing various functional groups for CTP were slightly higher than those for PP.

The XRD patterns of the carbonized PPs (P5–P10) and their corresponding ACs (P5AC–P10AC) are presented in Fig. 2. There were two broad diffraction peaks at around 2θ = 26° and 43° in each spectrum, corresponding to the diffraction of the (002) and (100) planes, respectively. The (10ℓ) peak around 43° presented an overlap with the (100) peak at 42.375° and with the (100) peak at 44.571°. In order to correct a background effect, the (10ℓ) peaks were analyzed by using a deconvolution method to curve-fit the two Gaussian peaks [19,20] around 43° and 50°, as shown in Fig. 2a and b. Here, the peak at around 50° implied the background. Although the (10ℓ) peak could not be deconvoluted into a (100) peak at 42.375° and a (100) peak at 44.571°. In order to correct a background effect, the (10ℓ) peaks were analyzed by using a deconvolution method to curve-fit the two Gaussian peaks [19,20] around 43° and 50°, as shown in Fig. 2a and b. Here, the peak at around 50° implied the background. Although the (10ℓ) peak could not be deconvoluted into a (100) peak at 42.375° and a (100) peak at 44.571°, the merged (10ℓ) peak was used for the estimation of the in-plane crystallite size of turbostratic carbon materials [16,21,22].

It is expected that increasing the carbonization temperature will accelerate the growth of graphitic crystallinity and sharpen the XRD peaks. The sharpness and intensity of the (10ℓ) peaks increased gradually with the increase of the carbonization temperature from 500 to 1000°C. However, the intensity and sharpness of the (002) peak decreased with the increase of the carbonization temperature up to 800°C (P8); then, the (002) peak sharpened with further increase of carbonization temperature (P8–P10). The (002) peaks of the activated PPs did not appear for pre-carbonization temperatures below 700°C, but the peaks began to appear at the pre-carbonization temperature of 700°C and gradually increased with the further increase of the carbonization temperature (P8AC–P10AC).

In order to have a closer examination of the XRD patterns, the micro-crystalline parameters of PPs pre-carbonized at 500–1000°C are presented in Fig. 3. The stacking height of the crys-

![Fig. 1. Fourier-transform infrared spectroscopy spectra of petroleum pitch (PP) (a) and coal tar pitch (CTP) (b) with their carbonized samples at different temperatures.](http://dx.doi.org/10.5714/CL.2017.22.070)
Fig. 2. X-ray diffraction patterns of pre-carbonized (a) and activated petroleum pitch (b) at different temperatures.

Fig. 3. X-ray diffraction parameters calculated from Fig. 2.
tallite (Lc) for the pre-carbonized PPs decreased significantly with the increase of the carbonization temperature to 800°C; it then increased gradually with further increase of the carbonization temperature. The in-plane crystallite size (La) increased gradually until the carbonization temperature reached 800°C; it then increased sharply at the higher carbonization temperatures. The interlayer spacing d002 did not change significantly with the carbonization temperature, showing a minimum value at 700°C. The sharp decrease of Lc at the low carbonization temperatures below 800°C could be explained by the gas evolution [19,23]; the gradual increase at high carbonization temperatures above 800°C was due to the development of structural order [24]. Meanwhile, the La value increased monotonously with the increase of the carbonization temperature from 500 to 1000°C, indicating that the gas evolution did not interfere with the in-plane order formation.

In the case of activated PPs, the (002) peaks disappeared for the ACs from the PPs pre-carbonized at low temperatures of 500–600°C and the (002) peaks became progressively sharp with increasing of the pre-carbonization temperature, as shown in Fig. 2b. The intensity of the (10ℓ) peaks did not change significantly but tended to increase at high carbonization temperatures over 800°C. In Fig. 3b, it can be seen that the stacking heights of the crystallite (Lc) of activated PPs were lower than those of the pre-carbonized PPs and increased with the increase of the pre-carbonization temperature. As a result, the difference of Lc between the pre-carbonized PPs and the corresponding ACs decreased steadily. These results indicate that pitch precursors pre-carbonized at high temperatures are more difficult to activate with KOH than are those pre-carbonized at low temperatures. On the other hand, the in-plane crystallite sizes (La) were higher than those of the pre-carbonized PPs, and almost constant until the carbonization temperature reached 800°C; these sizes then increased slightly at the higher carbonization temperatures. Thus, crossover occurred at a carbonization temperature around 1000°C. These results demonstrate that the in-plane crystallinity was not destroyed by KOH activation because there are very few active sites on the basal plane of the carbon structure. Instead, the in-plane crystallinity increased during the KOH activation reaction due to the thermal effect of a high activation temperature of 900°C. The PPs pre-carbonized above 900°C would have not been affected by the activation temperature of 900°C. In Fig. 3a, the interlayer spacings d002 of the ACs are larger than those of the pre-carbonized PPs; these values decreased sharply with the increase of the pre-carbonization temperature. It was concluded that the ACs prepared from PP exhibited typical parameters of highly disordered solid carbon; it was possible to control their order using the variation of the pre-carbonization temperature.

The porous texture of the various ACs was determined by N2 adsorption at 77 K; the adsorption-desorption isotherms of P5AC–P9AC are presented in Fig. 4. These isotherms and the PSDs by NLDFT plot, shown in Fig. 5, indicate a well-developed micro- and meso-porous character for these AC samples at the pre-carbonization temperatures below 700°C. The N2 adsorption capacity of the obtained ACs decreased significantly with the increase of the pre-carbonization temperature. The effects of the pre-carbonization temperature on the PSD of the ACs from PP and CTP are compared in Fig. 5; detailed pore characteristics of the ACs from PP are presented in Table 1.

It can be seen that the PSDs of the ACs from PP and CTP exhibited bimodal or trimodal curves with a dominant pore size of around 0.7 nm; the other dominant pore sizes were around 1–5 nm. As the pre-carbonization temperature increased, the former pore size increased slightly, but the latter decreased, resulting...
in an effect in which both peaks approached each other. It was interesting to note that the trimodal curves were observed with both pre-carbonized pitch precursors at 600°C only. In Fig. 5, the PSDs of the ACs from PP can be seen to be larger than those from CTP, especially for the pore sizes of around 1–5 nm. Since PP generally has larger aliphatic compounds and broader molecular weight distribution than CTP [10], PP may be advantageous for the formation of pores during KOH activation by providing more active sites and disorganized carbons. Comparing the porous characteristics of PP derived ACs to those of commercial AC (MSP-20) for EDLC electrodes, the ACs from the PP pre-carbonized below 700°C have larger micro-pore volumes (about 1–3 times larger), larger meso-pore volumes (about 4–17 times larger), and larger SSAs and pore diameters than those of MSP-20 (Table 1). The SSAs of P5AC and P6AC were exceptionally large, showing hysteresis loops at a relative pressure of around 0.4–0.7. For meso-porous materials exhibiting pore diameters between 2 and 4 nm, pore filling is observed at pressures close to the pressure range in which mono-multilayer formation on the pore wall occurs [25]. It would be difficult to separate mono-multilayer adsorption from pore filling. Although the BET isotherms had adequate C values of around 100, with good linearity, this pore filling might occur with P5AC and P6AC, resulting in an over estimation of the monolayer capacity in the BET analysis.

The SSA, micro-pore volume, and meso-pore volume decreased dramatically with increasing pre-carbonization temperature due to the increased order, resulting in the mitigation of KOH activation. However, the bulk density of the AC electrode increased with the increase of the pre-carbonization temperature, showing higher densities than that of MSP-20 with the PP pre-carbonized above 700°C. This increased bulk density would contribute to enhancing the energy density of EDLC.

### 3.2. Electrochemical properties as EDLC electrode material

The capacitances per mass and volume of P5AC–P10AC are summarized in Table 1. The capacitances were measured by CV at a scan rate of 10 mV/s. It is usually anticipated that the capacitance of porous carbon will be proportional to its available surface area, assuming that the BET surface area accessed by nitrogen is similar to the surface area accessed by the electrolyte. However, the electrolyte (especially the larger organic electrolyte) accessibility into fine micro-pores will be restricted due to the ion sieving effect. Considering the sizes of the electrolyte ions, narrow micro-pores (up to 0.7 nm) would not contribute to the capacitance of porous carbon even if their contribution to SSA is important. The gravimetric capacitance as well as the volumetric capacitance increased and then decreased with increasing of the pre-carbonization temperature, showing a maximum gravimetric capacitance with P6AC and a maximum volumetric capacitance with P7AC. The highest volumetric capacitance of 28.4 F/cc, achieved for P7AC, was more than 150% of that for MSP-20 (18.5 F/cc). It was noticeable that the larger capacitances were obtained for P6AC–P7AC, although the micro-pore volumes, meso-pore volumes, and SSAs of these ACs were much lower than those of P5AC. The reason that the highest capacitances were obtained at medium pre-carbonization temperatures of 600–700°C could be that the optimum PSD for the given electrolyte is obtained from a precursor with a suitable pore structure. Such a pore structure might be prepared by KOH activation of the pre-carbonized PP at a medium temperature. As the pre-carbonization temperature increased, both the micro-pore volume and the meso-pore volume decreased sharply, together with a slight increase of the micro-pore sizes and a decrease of the meso-pore size (Fig. 5). These decreases of both pore volumes were further accelerated when the pre-carbonization temperatures were over 800°C, exhibiting very small values, as shown Table 1. As the result, the PSDs approached each other, exhibiting a relatively high intermediate PSD near 1 nm of width with the PP pre-carbonized at a medium temperature. This medium temperature was higher for the volumetric capacitance because the bulk density of the AC electrode increased with the increase of the pre-carbonization temperature. P6AC and P7AC had pore characteristics of more developed PSD near 1 nm than did the other samples. It has been reported that pore sizes around 1 nm are important to attain high specific capacitance of EDLC electrodes [26]. The electrolyte was 1 M TEABF₄ in AN. Although the sizes of both the anion and the cation associated with the solvent molecules were available surface area, assuming that the BET surface area accessed by nitrogen is similar to the surface area accessed by the electrolyte. However, the electrolyte (especially the larger organic electrolyte) accessibility into fine micro-pores will be restricted due to the ion sieving effect. Considering the sizes of the electrolyte ions, narrow micro-pores (up to 0.7 nm) would not contribute to the capacitance of porous carbon even if their contribution to SSA is important. The gravimetric capacitance as well as the volumetric capacitance increased and then decreased with increasing of the pre-carbonization temperature, showing a maximum gravimetric capacitance with P6AC and a maximum volumetric capacitance with P7AC. The highest volumetric capacitance of 28.4 F/cc, achieved for P7AC, was more than 150% of that for MSP-20 (18.5 F/cc). 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### Table 1. Properties of AC prepared from PPs pre-carbonized at different temperatures

<table>
<thead>
<tr>
<th>Sample</th>
<th>Carbonization temp (°C)</th>
<th>Activation yield (%)</th>
<th>SSA (m²/g)</th>
<th>Vₘicro (cm³/g)</th>
<th>Vₘeso (cm³/g)</th>
<th>dₘicro (nm)</th>
<th>F/g</th>
<th>F/cc</th>
<th>Density (g/cm³)</th>
<th>dₑlectric (μF/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P5AC</td>
<td>500</td>
<td>17.2</td>
<td>4053</td>
<td>2.71</td>
<td>1.90</td>
<td>2.67</td>
<td>28.8</td>
<td>16.4</td>
<td>0.57</td>
<td>0.71</td>
</tr>
<tr>
<td>P6AC</td>
<td>600</td>
<td>22.4</td>
<td>3238</td>
<td>1.74</td>
<td>1.10</td>
<td>2.38</td>
<td>30.2</td>
<td>20.2</td>
<td>0.67</td>
<td>0.93</td>
</tr>
<tr>
<td>P7AC</td>
<td>700</td>
<td>26.6</td>
<td>1670</td>
<td>0.84</td>
<td>0.39</td>
<td>2.21</td>
<td>29.9</td>
<td>28.4</td>
<td>0.95</td>
<td>1.79</td>
</tr>
<tr>
<td>P8AC</td>
<td>800</td>
<td>35.4</td>
<td>192</td>
<td>0.09</td>
<td>0.12</td>
<td>3.64</td>
<td>22.0</td>
<td>24.6</td>
<td>1.12</td>
<td>11.5</td>
</tr>
<tr>
<td>P9AC</td>
<td>900</td>
<td>45.0</td>
<td>23</td>
<td>0.01</td>
<td>0.04</td>
<td>7.50</td>
<td>16.7</td>
<td>21.0</td>
<td>1.26</td>
<td>72.6</td>
</tr>
<tr>
<td>P10AC</td>
<td>1000</td>
<td>52.4</td>
<td>14</td>
<td>0.003</td>
<td>0.05</td>
<td>14.9</td>
<td>14.5</td>
<td>18.6</td>
<td>1.28</td>
<td>104</td>
</tr>
<tr>
<td>MSP-20</td>
<td>-</td>
<td>-</td>
<td>2277</td>
<td>0.85</td>
<td>0.11</td>
<td>1.76</td>
<td>25.0</td>
<td>18.5</td>
<td>0.74</td>
<td>1.10</td>
</tr>
<tr>
<td>C7AC</td>
<td>700</td>
<td>51.0</td>
<td>1157</td>
<td>0.40</td>
<td>0.20</td>
<td>2.03</td>
<td>27.2</td>
<td>23.9</td>
<td>0.88</td>
<td>2.35</td>
</tr>
</tbody>
</table>

AC, activated carbon; PP, petroleum pitch; temp, temperature; SSA, specific surface areas.
larger than 1 nm, the ions were able to enter into the pores below 1 nm, either bare or with partial solvent shells. Chmiola et al. [27,28] reported on this phenomenon in detail. They explained the anomalous increase in specific capacitance at pore sizes less than 1 nm as the result of the potential removal of solvent shells around the electrolyte ions; thus, the average distance between the pore wall and the center of the ions was reduced.

The surface normalized specific capacitances (μF/cm²) are also shown in Table 1. These values increased continuously with the increase of the pre-carbonization temperature and rose dramatically in the temperature range of 800–1000°C. The SSAs and pore volumes of P9AC–P10AC were extremely low (almost non-porous) compared to those of P5AC–P6AC. However, their gravimetric capacitances (F/g) were about half of the values for P5AC–P6AC; their volumetric capacitances (F/mL) were about the same. This unusually high capacitance has been reported for soft carbon electrodes in organic electrolytes and can be explained by further activation in an electric field [2,4-6,14,15,24-26,29], so-called electrochemical activation. This phenomenon has been observed for low SSA AC electrodes, which are made of soft carbon with mild chemical activation performed using either high crystalline precursors [4-6,26,29-31] or mild activation agents [20,32]. The storage mechanism of electrolyte ions with a non-porous AC electrode has been proposed to be that of insertion or intercalation of ions into the narrow space inside of the carbon materials, which would occur at the first electrochemical polarization, providing additional active sites for the ion adsorption to achieve the high capacitance.

Cyclic voltammograms of the P5AC–P10AC electrodes at different scan rates of 10 and 100 mV/s are presented in Fig. 6. As shown in Fig. 6a and b, the CV curves of C5AC–P7AC showed a rectangular, symmetric, and reversible shape in the voltage range of 0–2.7 V at both scan rates, indicating the excellent electrochemical properties of the carbon electrode. In the cases of P9AC–P10AC, although rectangular shapes of the CV curves were obtained at a scan rate of 10 mV/s, curves were distorted severely at a scan rate of 100 mV/s, showing tapered shapes at low potentials below 1.0 V. It was demonstrated that at the low scan rate the mobility of electrolyte ions was limited through the narrow active sites formed by the electrochemical activation, but it would suffer resistance at the high scan rate, especially at low potentials below 1.0 V. This resistance was relieved at the high charging potentials above 2.0 V. Similar results were obtained in charge/discharge tests at various current densities, with results shown Fig. 7. As expected, a gradual decrease in the capacitance with the increasing current density was observed; this decrease rate with current density increased as the carbonization temperature increased. Similar to the results shown in Fig. 6, the specific capacitance of P5AC was slightly affected by the current density; however, the specific capacitance of P9AC dropped by half with the rise of the current density from 1 to 5 A/g. The narrow active sites formed by the electrochemical activation seemed to limit the easy movement of electrolyte ions at high current density.

For more detailed investigation of the electrochemical activation, the 1st and the 2nd cycles of P5AC and P9AC are presented in Fig. 8. The CV curves of C5AC did not change significantly between the 1st and the 2nd cycle, though there was a slight increment of the current in the 1st cycle in the voltage range of 1.5–2.7 V. In contrast, the CV curves of P9AC exhibited a significant change between the 1st and the 2nd cycle, generating electrochemical activation. When the charging potential was low, the current was stable in the 1st cycle. However, the current started to increase suddenly at a charging potential around
High-energy-density activated carbon electrode using petroleum pitch

Fig. 8. Cyclic voltammograms of P5AC (a) and P9AC (b) electrodes at a scan rate of 100 mV/s. AC, activated carbon.

Fig. 9. Charge-discharge profiles of selected carbon electrodes at a constant current of 1 A/g: 1st cycle of P5AC, P7AC, and P9AC (a), and 1st–5th cycles of P5AC, and P9AC (b). AC, activated carbon.

2.0 V, reaching a peak current at 2.7 V. The 2nd cycle and the next cycles followed the same loop, generating stable profiles. This result indicates that the increased capacitance during the 1st charging was maintained in the repeated runs and that the structural change of the P9AC electrode resulting from the electrochemical activation appears to be irreversible.

The charge/discharge profiles of the P5AC, P7AC, and P9AC electrodes are presented Fig. 9. In the 1st cycle of charge (Fig. 9a), the voltage increased in proportion to the charging time for sample of 5AC. With the increase of the pre-carbonization temperature, the proportionality was disfigured. The voltage shot up rapidly to near 2.0 V and then increased gradually to 2.7 V for sample P9AC. Such a gradual increase demonstrates a structural change in the pore texture of the P9AC sample at charging potentials above 2.0 V [6,24,32]. The charge/discharge profiles from 1st to 5th cycles for the P5AC and P9AC electrodes are also presented in Fig. 9b. The increase of the voltage for C9AC became proportional to the charging time in the 2nd cycle; the profile was stable after the 2nd cycle. The electrochemical activation would be taken place during the 1st charge above 2.0 V.

In order to investigate the structural change due to electrochemical activation, XRD analyses of the C9AC electrodes be-

Fig. 10. X-ray diffraction patterns of P9AC before and after the electrochemical activation in 1 M TEABF₄/acetonitrile.
C9AC electrodes, some XRD peaks from those additives were observed even after the vacuum drying at 70°C for 24 h. After removing a part of those peaks from the additives near 2θ=25°, the interlayer spacing d_{002} and the stacking heights of the crystallite (L_c) for both C9AC electrodes were calculated. After the potential scanning, the value of d_{002} increased from 0.369 nm to 0.377 nm and the value of L_c decreased from 1.061 to 0.766 nm. These observations could be explained by the possible insertion of ionic species inside the carbon electrode, which would cause expansion of the graphite structure of C9AC and might be evidence of electrochemical activation [2,14,30,31].

In order to investigate the effect of the charging voltage on the electrochemical activation, various CV curves for the P5AC–P10AC electrodes, measured at a scan rate of 100 mV/s, are compared in Fig. 11 and Table 2. In the case of the P5AC electrode, the specific capacitance did not change significantly with the increase of the charging voltage from 1 to 2.7 V. However, the effect of the charging voltage on the specific capacitance could gradually be distinguished with the increase of the pre-carbonization temperature. The capacitance of the P9AC electrode increased dramatically from 1.3 to 11.3 F/g (an increase of 8.7 times) with the increase of the charging voltage from 1 to 2.7 V, indicating the occurrence of electrochemical activation at charging voltages of 2.0 and 2.7 V. It was concluded that the electrochemical activation had a great influence on the specific capacitance and that a high voltage, beyond a certain threshold depending on the given electrode system, was required for electrochemical activation. It was also demonstrated that the higher the charging voltage of EDLC was, the greater the effect of the electrochemical activation was, exhibiting the higher specific capacitance. Therefore, to enhance the electrochemical activation, the charging voltage in the 1st cycle was further increased to 3.5 V; this value was then reduced to the working voltage of 2.7 V in the 2nd cycle. The effect of the pre-charging voltage being higher than the working voltage is presented in Table 3.

Table 2. Specific capacitance (F/g) of P5AC–P10AC electrodes calculated by CV at a scan rate of 100 mV/s with different charging potentials

<table>
<thead>
<tr>
<th>Electrode</th>
<th>1 V</th>
<th>2 V</th>
<th>2.7 V</th>
</tr>
</thead>
<tbody>
<tr>
<td>P5AC</td>
<td>24.3</td>
<td>26.1</td>
<td>27.2</td>
</tr>
<tr>
<td>P6AC</td>
<td>24.8</td>
<td>28.4</td>
<td>30.1</td>
</tr>
<tr>
<td>P7AC</td>
<td>22.1</td>
<td>25.6</td>
<td>28.9</td>
</tr>
<tr>
<td>P8AC</td>
<td>5.8</td>
<td>11.3</td>
<td>19.6</td>
</tr>
<tr>
<td>P9AC</td>
<td>1.3</td>
<td>4.7</td>
<td>11.3</td>
</tr>
<tr>
<td>P10AC</td>
<td>1.1</td>
<td>2.0</td>
<td>10.7</td>
</tr>
</tbody>
</table>

AC, activated carbon; CV, cyclic voltammetry.

Table 3. Specific capacitance (F/g) of P5AC–P10AC electrodes calculated by CV at a scan rate of 10 mV/s using working voltages of 2.7 V and 3.5–2.7 V

<table>
<thead>
<tr>
<th>Electrode</th>
<th>2.7 V</th>
<th>3.5–2.7 V</th>
</tr>
</thead>
<tbody>
<tr>
<td>P5AC</td>
<td>27.9</td>
<td>27.0</td>
</tr>
<tr>
<td>P6AC</td>
<td>29.8</td>
<td>29.1</td>
</tr>
<tr>
<td>P7AC</td>
<td>29.7</td>
<td>30.0</td>
</tr>
<tr>
<td>P8AC</td>
<td>21.4</td>
<td>22.8</td>
</tr>
<tr>
<td>P9AC</td>
<td>16.5</td>
<td>19.3</td>
</tr>
<tr>
<td>P10AC</td>
<td>14.5</td>
<td>15.6</td>
</tr>
</tbody>
</table>

AC, activated carbon; CV, cyclic voltammetry.

4. Conclusions

Various PPs pre-carbonized in the range of 500–1000°C were activated at 900°C by KOH and were used as electrode materials for coin-type EDLCs. After the physical properties of the ACs and the electrochemical characteristics of the coin cells were analyzed, the following conclusions were obtained.

The crystallite sizes, namely both the stacking height (L_c) and the plane crystallite sizes (L_a) of the ACs tended to increase
with increasing of the pre-carbonization temperature. The PSDs of ACs from PPs exhibited a well-developed micro- and mesoporous character with pre-carbonization temperatures below 700°C, showing higher PSDs than those of ACs from CTP. As the pre-carbonization temperature increased, the SSA, micro-pore volume, and meso-pore volume decreased dramatically due to the increased order, but the bulk density of the AC electrode increased, showing a maximum volumetric capacitance at a medium carbonization temperature. The highest volumetric capacitance of 28.4 F/cc was obtained from the PP pre-carbonized at 700°C, which is a value over 150% of that of commercial AC (MSP-20) for EDLC.

The electrochemical activation was observed for AC electrodes prepared from PP pre-carbonized above 700°C. Although the SSAs and pore volumes of P9AC–P10AC were extremely low (almost non-porous) compared to those of P5AC–P6AC, their gravimetric capacitances (F/g) were about half those of P5AC–P6AC; their volumetric capacitances (F/mL) were at about the same level. This unusually high capacitance can be attributed to electrochemical activation. This process was found to have a significant effect on the specific capacitance; it was attributed to electrochemical activation. This process was found to have a significant effect on the specific capacitance; it was demonstrated that the higher the charging voltage of EDLC was, the greater was the effect of the electrochemical activation.

### Conflict of Interest

No potential conflict of interest relevant to this article was reported.

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