EDLC Performances of the Electrodes from Electrospun Pitch-based ACFs

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Abstract

Isotropic pitch solution was electrospun to be ultra-fine fibers. The fibers were activated in two processes i.e., activated after stabilization (SAF) and activated after carbonization (CAF). The activation processes affected to the activation behaviors and electrochemical properties of the electrodes formed. The specific surface area and the electrical conductivity were larger for CAF than for SAF. The highest specific capacitance among the experimental range was 123 F/g and the value was almost sustained at high current of 1000 mA/g. The results represented a rapid dissipation and rapid build-up of the charges in the highly conductive electrodes in comparison with electrodes of low conductivity.

1. Introduction

The electrospinning technology produces non-woven web consisting of polymeric fibers with diameters down to hundreds nanometers. Therefore, the ACF webs from the fibers have advantages for easier handling, the enhancement in the specific density in adsorption due to the high density of the contact points, and the low cost in applications to electrodes [1-3].

In this work, EDLC performances were tested on the basis of the electrodes prepared from pitch-based ACF webs activated at various temperatures.
2. Experimental

2.1 Preparation of ACFs

After the dimethylformamide (DMF) soluble fractions cut off from the isotropic pitch precursor (Hanwha Chemical Co., Korea), the 40 wt.% DMF insoluble pitch solution in tetrahydrofuran (THF) was electrospun into web using an electrospinning apparatus equipped with power supply (10–25 kV DC, HYP-303D, Hanyoung Co., Korea). The electrospun fiber webs were oxidatively stabilized. The stabilized pitch fiber webs were carbonized by heating up to 1000°C. The carbonized fiber and stabilized fiber webs were activated by 40 vol.% steam in carrier gas of N₂ at 700, 800, and 900°C. ACFs prepared from carbonized and stabilized fibers indicated CAF and SAF, respectively.

2.2 Unit cell capacitance and AC impedance

The charge/discharge profile of the unit cell was monitored by using a Potentiostat/Galvanostat (WBCS 3000, Won A Tech Co., Korea). The unit cell was first charged up to 0.9 V at 10 mA/g and sustained for 10 min as a rest period and then discharged down to 0.001 V at 10–1000 mA/g. Cyclic voltametry was performed in the potential range of 0 to 0.9 V at a scan rate of 10 mV/sec. The impedance measurement was performed in range of 1 mHz to 1 MHz frequency with an amplitude of 20 mV by means of an AC impedance analyzer (IM6e, Zahner Elektrik, Germany).

3. Results and Discussion

The electrical conductivity of the CAF, which was carbonized at 1000°C first and then activated at the respective temperatures, decreases with increasing activation temperature. On the other hand, the SAF, ACF prepared directly from stabilized fiber web, shows increasing trend with an increase in activation temperature. Hence, the enhancement of electrical conductivity is strongly related to morphology.
Table 1 Properties of electrospun ACFsat various activation temperature.

<table>
<thead>
<tr>
<th>Activation temperature (°C)</th>
<th>Burn-off (%)</th>
<th>BET surface area (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Average pore diameter (Å)</th>
<th>Pore volume fraction (%)</th>
<th>Micro</th>
<th>Meso</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>CAF  25</td>
<td>2222</td>
<td>0.899</td>
<td>16.2</td>
<td>99.7</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SAF  30</td>
<td>1022</td>
<td>0.404</td>
<td>15.8</td>
<td>99.7</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>800</td>
<td>CAF  40</td>
<td>2056</td>
<td>0.924</td>
<td>17.9</td>
<td>99.0</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SAF  47</td>
<td>1187</td>
<td>0.482</td>
<td>16.2</td>
<td>99.8</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>900</td>
<td>CAF  49</td>
<td>2025</td>
<td>1.109</td>
<td>21.0</td>
<td>92.2</td>
<td>7.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SAF  60</td>
<td>2191</td>
<td>0.915</td>
<td>16.7</td>
<td>99.3</td>
<td>0.7</td>
<td></td>
</tr>
</tbody>
</table>

The BET characteristics of the CAF and SAF were summarized in Table 1. In general, the CAF exhibited larger specific surface area than SAF from lower burn-off %. The 2,222 m²/g for CAF 700 at 25% burn-off is unique and large specific surface area. The specific surface area of CAF decreased with increasing activation temperature, representing unifications of the smaller pores to be larger pores as indicated by the enlargement of pore sizes. The SAF showed opposite trend in surface area, but same trend in pore size with CAF. Though the pore size increased with increasing activation temperature, they still remained in the range of micro-pores.

The specific capacitance was enhanced with increasing current density as shown in Fig. 1. The maximum capacitance of each sample was shifted to higher current density with increasing electrical conductivity. The highest capacitance was as large as 123 F/g from CAF 800. The lower conductive electrode such as SAF showed higher specific capacitance at the range of low current of about 10 to 50 mA/g, whereas the higher conductive electrodes such as CAF 900 showed the opposite behaviors. The capacitance would be determined by the amount of the charges accumulated on the double layers summed from applied current and dissipated charges into the electrode. The higher conductive electrode such as CAF may dissipate charges along the electrode exhibiting higher specific capacitance at
the range of higher current of about 100 to 1000 mA/g.

Fig. 1. Specific capacitance dependencies on the discharge current.

4. Conclusions

The highest specific capacitance was obtained from the electrode with 23 S/cm of electrical conductivity, 2056 m²/g of specific surface area and 17.9 Å of average pore diameter. The highest specific capacitance among the experimental range was 123 F/g and the value was almost sustained at high current of 1000 mA/g. Consequently, the higher the electrical conductivity with proper surface area of electrode, the lower impedance of a unit cell will be expected.

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6. 참고문헌