Oxygen group-containing activated carbon aerogel as an electrode material for supercapacitor

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ABSTRACT

Carbon aerogel was prepared by a sol–gel polymerization of resorcinol–formaldehyde (RF) method, and it was activated with CO2 to obtain activated carbon aerogel (ACA). A series of modified activated carbon aerogels (MACA-X, X = 3, 6, 9, and 12 h) were then prepared by HNO3 oxidation of ACA with a variation of oxidation time (X) in order to investigate the effect of surface oxygen group on their electrochemical performance as supercapacitor electrode material. Electrochemical properties of ACA and MACA-X were measured by cyclic voltammetry, galvanostatic charge/discharge, and EIS (electrochemical impedance spectroscopy) measurements. Among the samples, MACA-6 h showed the best rate capability and the highest specific capacitance. Thus, an optimal HNO3 oxidation condition was required for the highest supercapacitive electrochemical performance of modified activated carbon aerogel.

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1. Introduction

During a few decades, supercapacitors have attracted much attention as an electrochemical energy storage device due to their unique properties such as long life cycle, rapid storage, and lossless release of energy [1,2]. Generally, supercapacitors can be classified into two categories according to the energy storage mechanism; electrochemical double-layer capacitors (EDLCs) and pseudocapacitors. In case of electrochemical double-layer capacitors, electronic and ionic charges are accumulated at the interface between electrode material and electrolyte [3,4]. In pseudocapacitors, on the other hand, electric energy is generated by fast and reversible faradaic redox reactions induced by electro-active species on the surface of the electrode [5,6]. Therefore, various materials ranging from porous carbons for EDLCs to oxygen- and nitrogen-containing surface functional groups, metal oxides, and conducting polymers for pseudocapacitors have been investigated as electrode materials for supercapacitors [7–10].

Carbon aerogels have been recognized as promising electrode materials because of their outstanding electrical conductivity and textural property [11]. These excellent properties of carbon aerogels are due to three-dimensional mesoporous network of carbon nanoparticles [12,13]. However, carbon aerogels not only have lower surface area for EDL than activated carbon but also show limited power density and energy capacity. To overcome these problems, various activation methods of carbon aerogels have been investigated. Activation of carbon aerogel with KOH and CO2 increases surface area and micropore volume [14,15]. However, the large amount of micropores in activated carbon causes high internal resistance. In addition, hydrophobic property of activated carbon also decreases wettability of electrode in aqueous electrolyte solution, resulting in suppressed electrolyte accessibility and high internal resistance [16,17]. To overcome these drawbacks, various modification methods of activated carbon surface chemistry have been investigated [18,19]. It is known that the existence of surface oxygen group on carbon surface not only provides pseudocapacitive reactions for specific capacitance but also improves affinity of carbon electrode to aqueous electrolyte for rate capability [20,21].

In this work, a series of modified activated carbon aerogels were prepared to improve electrochemical performance of activated carbon aerogel (ACA). For this purpose, carbon aerogel I was prepared by a sol–gel polymerization of RF (resorcinol–formaldehyde) and it was activated with CO2. A series of modified activated carbon aerogels (MACA-X, X = 3, 6, 9, and 12 h) were then prepared by HNO3 oxidation of activated carbon aerogel (ACA)
with a variation of oxidation time \((X)\). For comparison, activated carbon aerogel (ACA) without \(\text{HNO}_3\) oxidation was also examined. Through this work, we have demonstrated that surface oxygen group played an important role in determining supercapacitive electrochemical performance of modified activated carbon aerogel. We have also found that an optimal \(\text{HNO}_3\) oxidation condition was required for the best electrochemical performance of modified activated carbon aerogel.

2. Experimental

2.1. Preparation of activated carbon aerogel (ACA)

Carbon aerogel (CA) was prepared by a sol–gel polymerization of resorcinol and formaldehyde according to the method in our previous work [22]. Activated carbon aerogel was then prepared by \(\text{CO}_2\) activation. In short, RF (resorcinol–formaldehyde) aerogel (4 g) was carbonized at 950 °C for 1 h under \(\text{N}_2\) stream (30 ml/min) to obtain carbon aerogel. The carbon aerogel (2 g) was then activated at 950 °C for 1 h using \(\text{CO}_2\) stream (30 ml/min). The prepared activated carbon aerogel was denoted as ACA.

2.2. Preparation of modified activated carbon aerogels (MACA)

Modified activated carbon aerogels were prepared by chemical oxidation of ACA with \(\text{HNO}_3\) solution. Fig. 1 shows the preparation procedures for modified activated carbon aerogel. The activated carbon aerogel (ACA) powder (0.5 g) was stirred in 100 ml of concentrated \(5 \text{ M HNO}_3\) solution and refluxed at 90 °C with a variation of oxidation time. After oxidation, it was filtered and washed with deionized water to remove residual \(\text{HNO}_3\) from the sample. The resulting material was then dried at 100 °C for 12 h. The modified activated carbon aerogels were denoted as MACA-\(X\) (\(X = 3, 6, 9,\) and 12 h), where \(X\) represented \(\text{HNO}_3\) oxidation time.

2.3. Preparation of ACA and MACA-X electrodes

MACA-X was casted using Super PTM conductive carbon (Timcal) and polytetrafluoroethylene (PTFE) as a conductive additive and a binder, respectively. A mixture of modified activated carbon aerogel, conductive additive, and binder with weight ratio of 8:1:1 was dispersed in 2-propanol. The resultant was mixed with mortar and pestle, and then it was rolled to be 8–10 μm thickness. The active material was cut into 1 cm × 1 cm and pressed onto nickel foam, which was used as an electrode. Weight of the electrode was ca. 2.5 mg. For comparison, activated carbon aerogel (ACA) electrode was also prepared by the same method described above.

2.4. Measurement of electrochemical properties of ACA and MACA-X electrodes

Electrochemical properties of ACA and MACA-X were measured with a two-electrode cell system in 6 M KOH aqueous electrolyte. Cyclic voltammetry, galvanostatic charge/discharge, and electrochemical impedance spectroscopy measurements were carried out to investigate the electrochemical properties of the samples. The cyclic voltammetry measurements were carried out within potential range of \(-1.0\) to \(-0.2\) V by varying scan rate from 10 to 200 mV/s. Galvanostatic charge/discharge measurements were carried out at constant current of 1 A/g and 5 A/g within potential range of \(-1.0\) to 0 V. EIS (electrochemical impedance spectroscopy) measurements were also carried out within frequency range from 100 kHz to 0.01 Hz at open circuit potential with an ac perturbation of 5 mV.

2.5. Characterization

\(\text{N}_2\) adsorption–desorption isotherms were measured with an ASAP 2010 (Micromeritics) instrument and surface areas were derived from Brunauer–Emmett–Teller (BET) method [23]. Pore volume was determined by the Barrett–Joyner–Halenda (BJH) method applied to the desorption branch of the \(\text{N}_2\) isotherm [24]. Surface morphologies of ACA and MACA-X were examined by transmission electron microscopy (TEM) (Jeol, JEM-2100). FT-IR analyses ( Nicolet, Nicolet 6700) of ACA and MACA-X were performed to analyze oxygen-containing functional group. Oxygen contents of ACA and MACA-X were quantitatively determined by CHN elemental analyses (CHN 932, Leco).

2.6. Calculation

At cyclic voltammetry measurements, specific capacitances of the electrodes were calculated according to the following equation. Where \(I_s\) and \(I_c\) represent anodic current and cathodic current, respectively. \(W\) is weight of electrode material and \(dV/dt\) represents scan rate.

\[
\text{Specific capacitance} = \frac{C \times W \times \Delta V}{I_c \times \Delta t}
\]
Table 1

<table>
<thead>
<tr>
<th></th>
<th>( S_{\text{BET}} ) (m(^2)/g)</th>
<th>( S_{\text{micro}} ) (m(^2)/g)</th>
<th>( S_{\text{meso}} ) (m(^2)/g)</th>
<th>( V_{\text{meso}} ) (cm(^3)/g)</th>
<th>( V_{\text{pore}} ) (cm(^3)/g)</th>
</tr>
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<tbody>
<tr>
<td>ACA</td>
<td>1268</td>
<td>566</td>
<td>702</td>
<td>0.95</td>
<td>1.43</td>
</tr>
<tr>
<td>MACA-3 h</td>
<td>1016</td>
<td>329</td>
<td>687</td>
<td>0.93</td>
<td>1.34</td>
</tr>
<tr>
<td>MACA-6 h</td>
<td>976</td>
<td>317</td>
<td>659</td>
<td>0.92</td>
<td>1.30</td>
</tr>
<tr>
<td>MACA-9 h</td>
<td>779</td>
<td>302</td>
<td>477</td>
<td>0.71</td>
<td>1.06</td>
</tr>
<tr>
<td>MACA-12 h</td>
<td>508</td>
<td>247</td>
<td>261</td>
<td>0.49</td>
<td>0.95</td>
</tr>
</tbody>
</table>

\[ C = \frac{I_0 + |I_c|}{2W(dV/dr)} \]

Specific capacitances of the electrodes in galvanostatic charge/discharge measurements were calculated according to the following equation. Here \( I \) represents discharge current and \( \Delta t \) is discharge time. \( m \) is mass of an active material and \( \Delta V \) is potential change during discharging process.

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

3. Results and discussion

3.1. Physicochemical properties of ACA and MACA-X

Nitrogen adsorption–desorption isotherms measurements were carried out in order to investigate the effect of HNO\(_3\) oxidation on the textural properties. Fig. 2 shows the N\(_2\) adsorption–desorption isotherms of ACA and MACA-X (\( X = 3, 6, 9, \) and \( 12 \) h). According to classification of IUPAC [25], ACA exhibited type-IV isotherm indicative of the existence of well-developed porous structure. After HNO\(_3\) oxidation, however, hysteresis loop was diminished with increasing HNO\(_3\) oxidation time. In case of MACA-12 h, isotherm was transformed from type-IV isotherm to type-I isotherm. These results indicate that HNO\(_3\) oxidation caused degradation of porous structure and decrease of textural properties, in good agreement with the previous results [26,27].

Detailed textural properties (BET surface area, micropore surface area \( (S_{\text{micro}}) \), mesopore surface area \( (S_{\text{meso}}) \), mesopore volume \( (V_{\text{meso}}) \), and total pore volume \( (V_{\text{pore}}) \)) of ACA and MACA-X \( (X = 3, 6, 9, \) and \( 12 \) h) are listed in Table 1. It was found that all the textural properties of the samples decreased with increasing HNO\(_3\) oxidation time due to dissolution of carbon pore walls by oxidant treatment [28]. Interestingly, BET surface area, mesopore surface area \( (S_{\text{meso}}) \), and mesopore volume \( (V_{\text{meso}}) \) gradually decreased at HNO\(_3\) oxidation time up to 6 h, but sharply decreased at HNO\(_3\) oxidation time longer than 9 h. It is reported that specific capacitance depends on BET surface area and significant loss of mesopores results in lower rate capability [29–31]. Therefore, it is inferred that an optimal HNO\(_3\) oxidation condition would be required for the best electrochemical performance.

Fig. 3 shows the TEM images of ACA and MACA-X \( (X = 3, 6, 9, \) and \( 12 \) h). After HNO\(_3\) oxidation, morphology of ACA was clearly changed. In the TEM image of ACA, carbon nanoparticles formed an interconnecting network structure with uniform textural porosity. In case of MACA-3 h and MACA-6 h, this network structure was gradually etched by nitric acid. Nonetheless, these two samples (MACA-3 h and MACA-6 h) still maintained a three-dimensional structure of primary carbon particles. On the other hand, formation of many hollow parts was observed in the MACA-9 h and MACA-12 h. This was attributed to dissolution of carbon layer by excessive oxidation, resulting in the formation of hollow cell and the collapse of mesoporous structure [28].

In order to confirm the formation of surface oxygen group on MACA-X \( (X = 3, 6, 9, \) and \( 12 \) h), FT-IR measurements were carried out. Fig. 4 shows the FT-IR spectra of ACA and MACA-X \( (X = 3, 6, 9, \) and \( 12 \) h). No characteristic IR bands were observed for ACA due to its hydrophobic property. However, formation of oxygen-containing functional groups on the MACA-X could be identified by IR bands appearing in the range of 1000–2000 cm\(^{-1}\). It was observed that two types of oxygen-containing species (C=O and C–O) were formed after HNO\(_3\) oxidation of ACA [32]. IR peaks appearing at 1750 and 1600 cm\(^{-1}\) were associated with C=O stretching vibration derived from various functional groups such as lactone, carboxyl acid and carbonyl groups [33,34]. IR peak appearing at
1250 cm\(^{-1}\) was attributed to C—O stretching in ether, phenol, and carboxylic anhydride groups [33,34]. These IR peak intensities increased with increasing HNO\(_3\) oxidation time. This result indicates that the amount of surface oxygen group on carbon surface increased with increasing HNO\(_3\) oxidation time.

CHN elemental analyses were conducted to determine the oxygen content of ACA and MACA-X (X = 3, 6, 9, and 12 h) as listed in Table 2. As expected, oxygen content of MACA-X increased with increasing HNO\(_3\) oxidation time. This result was well consistent with FT-IR results.

### Table 2

<table>
<thead>
<tr>
<th></th>
<th>C (wt%)</th>
<th>H (wt%)</th>
<th>N (wt%)</th>
<th>O* (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACA</td>
<td>89.2</td>
<td>–</td>
<td>0.4</td>
<td>10.4</td>
</tr>
<tr>
<td>MACA-3 h</td>
<td>72.3</td>
<td>–</td>
<td>0.7</td>
<td>27.0</td>
</tr>
<tr>
<td>MACA-6 h</td>
<td>70.8</td>
<td>–</td>
<td>0.8</td>
<td>28.4</td>
</tr>
<tr>
<td>MACA-9 h</td>
<td>64.7</td>
<td>0.9</td>
<td>0.9</td>
<td>33.5</td>
</tr>
<tr>
<td>MACA-12 h</td>
<td>61.2</td>
<td>2.7</td>
<td>1.1</td>
<td>35.0</td>
</tr>
</tbody>
</table>

*Oxygen content was calculated as a difference between 100% and the sum of C + H + N.

#### 3.2. Electrochemical properties of ACA and MACA-X electrodes

Cyclic voltammetry (CV) measurements were carried out to examine the electrochemical properties of ACA and MACA-X (X = 3, 6, 9, and 12 h). Fig. 5(a) and (b) shows the cyclic voltammograms of ACA and MACA-X obtained at different scan rate, and the calculated specific capacitance is summarized in Table 3. At a scan rate of 10 mV/s (Fig. 5(a)), CV curves of ACA and MACA-X exhibited a roughly rectangular-like shape within the range of —1.0 to —0.2 V, indicating that the samples showed a general electric double-layer capacitance behavior of carbon material. It is noticeable that the redox peak at 0.7 V was observed in the MACA-X, which might be attributed to the redox reactions of surface oxygen group. Specific capacitance (calculated from Fig. 5(a)) showed a volcano-shaped trend with respect to HNO\(_3\) oxidation time. Among the samples, MACA-6 h exhibited the highest capacitance (120 F/g). At a scan rate of 100 mV/s (Fig. 5(b)), obvious distortion in the cyclic voltammogram was observed in the MACA-12 h compared to the other samples. It has been reported that narrow cyclic voltammogram with large oblique angle is a typical feature of highly resistive electrode [35]. Therefore, it can be inferred that MACA-12 h showed the highest electrode resistance.

Fig. 6 shows the specific capacitances of ACA and MACA-X (X = 3, 6, 9, and 12 h) plotted as a function of scan rate. Among the samples, specific capacitance of MACA-6 h showed the smallest decrease at a fast scan rate region. In other words, specific capacitance of MACA-6 h was maintained at 73% of the initial value. This value decreased in the order of MACA-6 h (73%) > MACA-3 h (67%) > MACA-9 h (53%) > ACA (45%) > MACA-12 h (36%). Thus, MACA-6 h exhibited the best rate capability.

Fig. 7(a) and (b) shows the charge/discharge profiles of ACA and MACA-X (X = 3, 6, 9, and 12 h). The specific capacitance of ACA and
MACA-X (X = 3, 6, 9, and 12 h) measured from charge/discharge measurements is summarized in Table 4. At a low current density (Fig. 7(a)), the curves of ACA and MACA-X showed a virtually linear shape and triangular distribution. It should be noted that MACA-6 h showed the longest charge/discharge time. This indicates that MACA-6 h showed the highest specific capacitance (128 F/g), in good agreement with the results of cyclic voltammetry measurements. At a high current density (Fig. 7(b)), the specific capacitance of ACA and MACA-X showed the same trend as that obtained at a low current density. Interestingly, IR drop was obviously observed in the MACA-12 h. This drop was attributed to inner resistance of ion diffusion in carbon pores [36,37].

EIS (electrochemical impedance spectroscopy) measurements were carried out to examine the resistance of ACA and MACA-X. Fig. 8 shows the Nyquist plots of ACA and MACA-X (X = 3, 6, 9, and 12 h). According to the literatures [38,39], the Nyquist plot can be divided into high frequency region and low frequency region of the plot. The semi-circle at a high frequency represents internal resistance related to charge transfer between surface of electrode material and electrolyte [38,39]. At a low frequency, on the other hand, vertical line represents the Warburg’s impedance related to diffusive resistance of electrolyte ion in the electrode pores [38,39]. At a high frequency region, ACA and MACA-X showed the semi-circles, which were indicative of a charge transfer resistance. The diameter of semi-circles increased with increasing HNO₃ oxidation time. This result was attributed to surface redox reactions between electrolyte ion and surface oxygen group on carbon surface [30]. Thus, it can be inferred that pseudocapacitance increases with increasing HNO₃ oxidation time. At a low frequency region, the line slope leaned more toward imaginary axis (Z”), indicating low diffusivity resistance. At HNO₃ oxidation time shorter than 6 h, interestingly, line slope increased with increasing HNO₃ oxidation time, indicating that ion diffusion became faster. At HNO₃ oxidation time longer than 6 h, however, line slope decreased with increasing HNO₃ oxidation time, indicating that ion diffusion was impedes. This result of Warburg’s impedance was in good agreement with the rate capability result.

On the basis of experimental results described above, it was found that MACA-6 h showed the best rate capability and the highest specific capacitance. In case of rate capability, it is affected by two factors; wettability and mesopores. It has been reported that wettability improved by surface oxygen group enhances rate capability [20,21], while decrease of mesopore surface area (Smeso) causes low rate capability [40]. However, our experimental data revealed that these two factors showed the opposite trend with respect to HNO₃ oxidation time. Thus, it is inferred that an optimal condition might exist for achieving the best rate capability. In case of energy capacity, two factors affect the specific capacitance; EDL capacitance and pseudocapacitance. It is well known that EDL capacitance depends on BET surface area, while pseudocapacitance depends on the amount of surface oxygen group [30,31]. In this work, we observed that EDL capacitance decreased with increasing HNO₃ oxidation time, whereas pseudocapacitance increased with increasing HNO₃ oxidation time. Hence, it can also be inferred that an optimal condition might exist for achieving the highest specific capacitance. In summary, the best rate capability and the highest

Table 4 Specific capacitance of ACA and MACA-X (X = 3, 6, 9, and 12 h) calculated by charge/discharge measurements.⁴

<table>
<thead>
<tr>
<th></th>
<th>Calculated specific capacitance (F/g)</th>
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<tbody>
<tr>
<td></td>
<td>1 A/g</td>
</tr>
<tr>
<td></td>
<td>5 A/g</td>
</tr>
<tr>
<td>ACA</td>
<td>94</td>
</tr>
<tr>
<td>MACA-3 h</td>
<td>112</td>
</tr>
<tr>
<td>MACA-6 h</td>
<td>128</td>
</tr>
<tr>
<td>MACA-9 h</td>
<td>106</td>
</tr>
<tr>
<td>MACA-12 h</td>
<td>85</td>
</tr>
</tbody>
</table>

⁴ Measured at a constant current of 1 A/g and 5 A/g in an aqueous solution of 6 M KOH.
specific capacitance were observed when the activated carbon aerogel (ACA) was oxidized for 6 h.

4. Conclusions

A series of modified activated carbon aerogels (MACA-XX = 3, 6, 9, and 12 h) were prepared by HNO$_3$ oxidation of activated carbon aerogel (ACA) with a variation of oxidation time (X). For comparison, activated carbon aerogel (ACA) was also examined. Textural properties (BET surface area, micropore surface area ($S_{\text{micro}}$), mesopore surface area ($S_{\text{meso}}$), and pore volume ($V_{\text{pore}}$)) decreased with increasing HNO$_3$ oxidation time, while the amount of surface oxygen group increased. Among the samples, MACA-6 h exhibited the best rate capability and the highest specific capacitance. It is concluded that an optimal HNO$_3$ oxidation condition was required for the highest supercapacitive electrochemical performance of modified activated carbon aerogel.

Acknowledgments

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