Capacitor Properties of Carbon Electrodes Derived from α-Cyclodextrin
Masahiro TOKITA, Minato EGASHIRA, Nobuko YOSHIMOTO, and Masayuki MORITA

Abstract
Capacitor performances and degradation behavior of porous carbon electrodes derived from α-cyclodextrin precursor have been investigated. Porous carbons with different pore size distribution have successfully been prepared from α-cyclodextrin by changing the heating rate of carbonization. The carbonaceous materials obtained by the heating rates of 10 and 50 K min⁻¹ exhibited similar crystalline structures and elemental compositions. However, the cells with different electrodes showed different capacitance degradation modes under high temperature and high voltage conditions. The α-cyclodextrin-derived carbon having a higher ratio of mesopore volume lost its capacitance significantly at initial cycles by the passivation of electrode.

Keywords: Electric Double Layer Capacitor, Porous Carbon, Electrode Performance, Biomass-derived Carbon

1. Introduction
Electric double layer capacitors (EDLCs) are rechargeable energy storage devices based on the capacitance of electric double layer at electrode/electrolyte interface without charge transfer reaction. Porous carbon electrodes such as activated carbons (ACs) have been utilized for EDLC devices. Many kinds of porous carbons derived from various precursors, with different activation processes utilizing oxidizing agents in solid, liquid and gas phases, have so far been proposed. Recently, some porous carbons with ordered micro-structures have been prepared by so-called soft- and hard-template methods and their capacitor performances examined. The EDLC performances are generally dependent on the characteristics of the porous carbon electrodes, in particular crystalline structure, pore structure and surface functional groups.

Besides the charge-discharge performances, long-term stability should be taken into consideration for designing EDLC electrodes. While EDLC is, in principle, expected to have much longer cycle life than that of a conventional battery, due to its charge storage mechanism, practical EDLC devices show severe capacitance degradation at shorter time than expected. Thus, many attempts have been made to understand the degradation mechanism of EDLCs. Parasitic reactions such as decomposition of electrolyte and/or deformation of electrode have been proposed as the main cause of the degradation. However, details in the influences of pore structure on such parasitic reactions remain still unclear.

More recently, nano-structured carbon materials including carbon nano-rods with high specific surface area (~800 m² g⁻¹) have been prepared by simple carbonization of α-cyclodextrin acquirable from biomass with varying the heating rate. These carbons are expected as alternative porous carbons because of low-cost production processes (without additional activation processes) and interesting nano-structures with uniform pore-size distribution. In the present study, the reproducibility of porous carbons with various nano-structures from α-cyclodextrin has been assessed under different heating rates, and their electrode properties have been compared with each other. Especially, influences of the porous structure on the aging behavior of EDLCs have been focused as well as on the capacitance and rate capability.

2. Experimental
2.1 Preparation of porous carbons having different pore structures
Porous carbons were prepared by the carbonization of α-cyclodextrin (Kanto Chemical) precursor up to 1273 K with different heating rates of 10 and 50 K min⁻¹, followed by continuous heating at 1273 K for 20h. The products obtained by the former and the latter heating rates are denoted as CyDC10 and CyDC50, respectively. The microscopic structures of the obtained carbons were observed by a transmission electron microscope (TEM; JEM-6320F; JEOL, Japan), and their crystalline structures were confirmed by X-ray diffraction (XRD; Ultima IV Proteus, Rigaku, Japan). The contents of surface functional groups were estimated by elemental analysis. Specific surface area and pore-size distribution of CyDCs were respectively estimated by BET analyses and BJH method from nitrogen adsorption isotherms (NOVA2000, Quantachrome).

2.2 Electrochemical properties of CyDCs
CyDC powder was molded with 10 wt% of poly(tetrafluoroethylene) (PTFE; Mitsui Fluorochemical, Japan) binder, and the resulting sheet was cut into a disk with 7 or 12 mm in diameter. The thickness of the electrode disk was set to 0.30 mm and the loading mass was about 18 mg cm⁻² for CyDC10 and about 20 mg cm⁻² for CyDC50. A PTFE disk as the working, a platinum plate as the counter and silver wire as the quasi-reference electrode was used for cyclic voltammetry (CV). For constant-current charge-discharge tests, 2-electrode configuration with two parallel carbon/PTFE disks and a glass-filter separator was utilized. The accelerated aging tests and AC impedance measurements were also conducted using the 2-electrode cell. The solution of 1 mol dm⁻³ tetraethylammonium tetrifuoroborate (TEABF₄; Kishida Chemicals, Japan) in propylene carbonate (PC; Kishida Chemicals, Japan) was used as the electrolyte. Each cell was assembled in a glove box filled with dry argon, and placed in a sealed vessel for the measurements outside of the glove box. The electrochemical measurements including the rate capability estimation of the EDLC cell were conducted using a potentiostat (VersaStat4, Princeton Applied Research) with a potential...
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range between −1.0 and 1.0 V at prescribed scan rates. The constant-current charge-discharge experiments were carried out under such conditions as the cut-off voltage of 0 to 2 V, at the prescribed current density, using a charge-discharge cycler (BT-S2004 Nagano, Japan).

The accelerated aging behavior of each electrode was monitored by the following procedure. Constant cell voltage of 3.5 V was applied for 5 h under constant temperature of 333 K (60°C), controlled by a constant-temperature chamber (SU-241, Espec, Japan), and then discharged under constant-current of 1.0 mA per unit geometric area of the electrode to 0 V. This procedure was repeated for 20 cycles by using the same cell cycler as described above. The cell resistance after this accelerated aging process was estimated by AC impedance methods using a frequency response analyzer (Versastat 4) with a frequency range from 10⁸ to 10⁻² Hz.

3. Results and Discussion

3.1 Characterization of CyDCs

Typical TEM images of CyDCs are shown in Fig. 1, where dotted white lines are added as the outlines of the particles for visualization. It is not so clear but we found that CyDC10 has larger visualization. CyDC50 has different particle size, specifically CyDC10 has larger visualization. CyDC50. Dotted white lines indicate the outlines of the particles for visualization.

![Figure 1](image)

Figure 1. (Color online) TEM images of CyDCs. (a) CyDC10, (b) CyDC50. Dotted white lines indicate the outlines of the particles for visualization.

![Figure 2](image)

Figure 2. Pore size distribution of CyDCs. CyDC10: black line, CyDC50: gray line.

3.2 Electrode properties of CyDCs

Cyclic voltammograms of CyDCs under a scan rate of 2 mV s⁻¹ are shown in Fig. 3. Both CyDC electrodes gave typical rectangular shapes of double-layer charging without any redox currents. The specific capacitance values calculated from the voltammograms were 40 and 19 F g⁻¹ for CyDC10 and CyDC50, respectively. This trend in the specific capacitance is consistent with the specific surface area obtained by BET method. Here, the capacitance per unit real surface areas is calculated to be 5.3 mF m⁻² for CyDC10 and 5.2 mF m⁻² for CyDC50. Both of the specific capacitance (F g⁻¹) and the capacitance per unit surface area (F m⁻²) are much smaller than those of activated carbon electrodes used in conventional EDLCs, which is probably due to insufficient utilization of the micropores, and to insufficient wettability toward the organic electrolyte. From a practical viewpoint, the utilization of the surface area and the wettability of the electrode should be improved by an adequate ‘activation’ process. Figure 4 shows the dependence of the specific capacitance on the scan rate in the CV experiments. Both electrodes exhibit capacitance decrease by the increase in the scan rate.

![Figure 3](image)

Figure 3. Cyclic voltammograms of CyDCs in 1 mol dm⁻³ TEABF₄/PC. Scan rate: 2 mV s⁻¹.

![Table 1](image)

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<th>SSA (m² g⁻¹)</th>
<th>(V_{\text{total}}) (×10⁻² cc g⁻¹)</th>
<th>(V_{\text{micro}}) (×10⁻² cc g⁻¹)</th>
<th>(V_{\text{meso}}/V_{\text{micro}})</th>
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<tr>
<td>CyDC10</td>
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<tr>
<td>CyDC50</td>
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<th>(%) (diff. %) (×10¹⁰ mol m⁻²) (×10¹⁰ mol m⁻²)</th>
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<td>CyDC50</td>
<td>95</td>
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![Table 2](image)

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Table 1. \(N_2\) sorption data of CyDCs prepared from \(\alpha\)-cyclodextrin.

Table 2. Elemental analyses of \(\alpha\)-cyclodextrin derived carbons.
However, CyDC50 shows better rate capability than CyDC10, which is probably related with higher amounts of mesopore at the surface of CyDC50.

3.3 Accelerated aging behavior of CyDCs

Variations in the cell capacitance with the cycle number during the accelerated degradation test are plotted in Fig. 5(a), and the normalized capacitance by the first cycle is also shown in Fig. 5(b) as a function of the cycle number. The capacitance of the CyDC10 and the CyDC50 cells at the first cycle was 14 and 6 F g⁻¹, respectively. The cell capacitance decreased with the increase in the cycle number regardless of the electrode. The cell capacitance at 20th cycle was down to about 40% of the initial cycle for CyDC10, while it decreased to about 16% for CyDC50. That is, the capacitance decrease in the CyDC50 was much severer than the CyDC10 cell. As the states of the crystalline structure and surface functional groups were almost the same for both carbons, the differences in the ratio of mesopore volume and the nano-structure would be responsible for the difference in the accelerated aging behavior. That is, CyDC50 has a larger ratio of mesopore on its surface than that of CyDC10, whose difference will influence the aging behavior significantly.

Nyquist plots of AC impedance measured for the fresh CyDCs cells and for the cells after aging are shown in Figs. 6(a) and 6(b), respectively. The plots of the fresh cells showed semicircles at higher frequency regions, assigned to charge-transfer (interfacial) resistance, and linear parts with about 45° slope in lower frequency regions which are assigned to diffusion-limited processes. After the accelerated aging, the semicircle and 45° slope line regions of the cell consisting of CyDC10 become slightly extended with an increase in Z' intercept at the high frequency region, namely a series-resistance component increased. In contrast to this, the cell consisting of CyDC50 showed a two-semicircle resistance after the aging. This behavior indicates that charge-transfer resistance increased significantly with the cycle repeated. In the authors’ previous work, decomposition product of the electrolyte was observed at nano-fiber electrode after the accelerated aging.17 Thus, it is suggested that the deposition of the decomposition products would occur more significantly at CyDC50 than at CyDC10.

For the porous carbon having micropores with more extents, like CyDC10, the decomposition product derived from the electrolyte will deposit mainly at the “entrance” of the pores because of the limited ion diffusion rate in the micropores, which does not accompany the blocking of the pore structure. On the other hand, for the porous carbon having larger ratio of mesopore against total surface area, like CyDC50, the deposition of the decomposition products can initially occur inside the pores because of the relatively fast mass-transport in the mesopore structures. The coverage of the pores by the decomposition product inside the pores would reduce the capacitance significantly, especially at initial cycles.

4. Conclusion

Carbons having different nano-structures were obtained by simple carbonization of α-cyclodextrin with different heating conditions: CyDC10 has larger particle size with significant
micropores and CyDC50 has smaller particle size with higher ratio of mesopore volume. The rate capability of the double-layer capacitance depended on the nano-structures of the α-cyclodextrin-derived carbons (CyDCs). The accelerated aging tests using server cycling conditions (constant-voltage charging at 3.5 V for 5 h at 333 K) showed that CyDC50 having higher ratio of mesopore volume leads to the degradation of the cell capacitance significantly, compared with that of CyDC10. The AC impedance results after the accelerated aging tests suggest that the differences in the decomposition process of the electrolyte component are responsible for such degradation process.

References