Thermal Pore Stability of Activated Carbon Materials to Heat Treatment above 1000°C and Lithium-ion Capacitors Using Heated Silicon-carbide-derived Carbon

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ABSTRACT
Thermal pore stability of activated carbon materials and float charging durability of Li-ion capacitors (LICs) using heated activated carbons were evaluated. Silicon-carbide-derived carbon (SiC-CDC) was prepared via a chlorination/steam activation process, and its properties were compared to commercial activated carbon. After heat-treating both samples at 1400°C, the surface area of SiC-CDC decreased by only 10%, whereas that of the commercial activated carbon declined by 20%. The heat-treated SiC-CDC exhibited excellent durability as an LIC positive electrode. These results provide insights into the effect of preparation methods on the thermal stability and durability of carbon-based electrodes as LIC positive electrode.

Keywords : Silicon-carbide-derived Carbon, Li-ion Capacitor, Thermal Pore Stability

1. Introduction
Li-ion capacitors (LICs) are constituted of the negative electrode for Li-ion batteries (LIBs) and the positive electrode for electric double layer capacitors (EDLCs). The LICs exhibit the excellent energy density derived from the LIBs and achieve the high power density and durability of EDLCs.1–3 The energy density of the LIC depends on the capacitance of its activated carbon electrode and its maximum applied voltage. The surface modification of activated carbon materials via heat treatment is known as a simple and effective way to increase the maximum applied voltage of capacitors.4 Heat-treatments above 1000°C have been shown to be effective in removing acidic surface functional groups and improving the carbon crystallinity of the carbon wall of micropore. Despite these advantages, simultaneous pore shrinkage during heat-treatments has caused a significant decrease in capacitance for carbon-based electrodes.

Recently, the authors investigated the pore structures of carbide-derived carbons (CDCs), which are one of the porous carbons obtained by the chlorination of carbides,5–7 carbonized via chlorination at temperatures above 1000°C.5 The porosity of silicon-carbide-derived carbons (SiC-CDCs) remained stable from 1000°C to 1400°C, whereas the micropores of titanium-carbide-derived carbons (TiC-CDCs) gradually shrunk at these temperatures, indicating a greater stability of SiC-CDCs at high temperatures. The authors also subjected the SiC-CDCs to steam activation treatments, which increased their Brunauer–Emmett–Teller (BET) surface area by up to ~2000 m² g⁻¹.8

As an extension of the previous research efforts, in the present research, the authors focus on the pore thermal stability of the post-activated SiC-CDCs to the heat treatment at temperatures above 1000°C and compared with the stability of commercial activated carbon. In this paper, the authors report the electrochemical durability of the SiC-CDCs as LIC positive electrode, demonstrating the potential of these modified SiC-CDCs as high-performance materials in energy-related applications.

2. Experimental
The activated SiC-CDCs were prepared by chlorination of α-SiC in a nitrogen atmosphere at 1100°C and subsequent steam activation at 900°C for 2.5 h under continuous nitrogen flow. Then, the heat treatment was conducted at between 1000°C and 1400°C for 3 h under nitrogen gas. For comparison, commercial steam activated carbon (YP50F, Kuraray Chemical) for the EDLC was also subjected to heat treatment under the same conditions. The pore structures of these specimens were characterized by nitrogen adsorption measurements. The crystalline structures were elucidated by powder X-ray diffraction measurements and Raman spectroscopy. The acidic surface functional groups were measured by the Boehm titration method. The LIC test cells with lithium metal reference electrode were fabricated with the positive electrode using the activated carbons and pre-lithiated negative electrode using a hard carbon in a 1.0 M LiPF₆ dissolved in EC/EMC (3:7). The durability against high voltage charge for these LICs were measured by carrying out floating tests at 60°C with a cell voltage of 4.0 V for 1000h. The floating test was ceased every 250h, and the capacitance and internal resistance were measured by the constant-current charge/discharge tests in a cell voltage range of 2–4 V at a current density of 40 mA g⁻¹ and current rest method9 at a current density of 120 mA g⁻¹. The details of fabrication and characterization of the materials and test cells are described in the Supporting Information.
3. Results and Discussion

Figure 1 shows the retentions of the BET surface areas of the activated SiC-CDCs and YP50F as a function of heat-treatment temperature, Fig. S1 shows the pore size distributions of the samples, and Table S1 summarizes the detailed characterizations of their pore structures. For the heat-treatment temperature of 1000°C, the BET surface area of the SiC-CDCs was not affected by the heat treatment, whereas that of YP50F decreased by 10%. Following the 1400°C heat treatment, the pores of the SiC-CDCs slightly shrunk, with a 10% decrease in its surface area. In contrast, the surface area of the YP50F pores decreased by 20%, indicating that the SiC-CDCs have greater pore stability than YP50F. Changes in the micro- and meso-pore volumes of the samples indicated the same trend. This difference in pore stability was attributed to the corresponding carbonization temperatures of the materials. The SiC-CDC was carbonized at 1100°C by a chlorination process. In contrast, YP50F was prepared as a coconut shell-based steam activated carbon material from a previously reported procedure, involving carbonization and steam activation processes at temperatures between 500°C and 700°C and 700°C and 950°C, respectively. Considering that the pore structure of the activated SiC-CDC was unchanged by the heat-treatment at 1000°C, the activation temperature (900°C) of the SiC-CDC less than that of the chlorination (1100°C) appeared not to affect its pore stability during the post heat-treatment.

The crystalline structure of the SiC-CDCs following heat treatment at 1400°C was almost unchanged, suggesting that this process had an insignificant effect on its macro crystalline properties (Figs. S2 and S3).

The amount of acidic surface functional groups in the SiC-CDCs prepared at different heat-treatment temperatures are shown in Fig. 2 and Table S2. Most of the acidic functional groups were phenolic groups because the SiC-CDC was subjected to steam activation at 900°C. The amount of functional groups remaining attached to the surface of the SiC-CDCs decreased with increasing heat-treatment temperatures, and was 0.01 mmol g⁻¹ at 1400°C.

These results indicate that the activated SiC-CDCs maintain the original pore structure or crystal structure and decrease the surface functionalities even after the heat treatment above 1000°C. It is advantageous as an electrode material of electrochemical capacitors from the viewpoint of the capacitance and durability.

The unheated SiC-CDC (u-SiC-CDC) and heat-treated SiC-CDC at 1400°C (SiC-CDC1400) were electrochemically evaluated as the LIC positive electrode through floating tests at 60°C in a cell with a voltage set to 4 V for 1000 h. Figure S4 shows the charge/discharge curves of the SiC-CDCs before the floating test. The initial gravimetric and volumetric capacities (capacitances) of the SiC-

CDC1400 were 52 mAh g⁻¹ (94 F g⁻¹) and 29 mAh cm⁻³ (53 F cm⁻³), respectively, which were approximately 10% less than the u-SiC-CDC values of 60 mAh g⁻¹ (109 F g⁻¹) and 32 mAh cm⁻³ (58 F cm⁻³), respectively. These data are consistent with the corresponding decrease in the BET surface area of SiC-CDC1400.

The internal resistance of the SiC-CDC1400 obtained from a current rest method at the beginning of the discharge was 2.1 Ω and comparable to that of u-SiC-CDC (2.0 Ω).

Figure 3 shows the (a) capacitance retentions and (b) internal resistance during the floating tests.

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potential throughout the duration of the 1000 h floating test. Although the maximum full-cell voltage was kept constant at 4.0 V, the positive electrode potential was increased from 4.05 to 4.30 V vs. Li/Li\(^+\) because of lithium consumption in the negative electrode. Both of the materials’ capacitance retentions slightly decreased, but their trends were distinct. The capacitance of u-SiC-CDC slightly increased after 250 h and then gradually decreased, whereas that of the SiC-CDC1400 linearly decreased over the duration of the floating test. The internal resistance of the u-SiC-CDC significantly increased after 250 h and eventually reached up to 10.4 Ω, whereas the SiC-CDC1400 only reached an internal resistance of 5.8 Ω after 1000 h.

To further investigate the electrochemical performance of these positive electrodes, the authors conducted the floating test for 96 h at a constant positive electrode potential of 4.1 V vs. Li/Li\(^+\) (which was not the cell voltage) using SiC-CDCs as the positive electrode and Li metal as the negative electrode. The amount of leakage current and gas generated during the 96 h floating test was evaluated (see the Supporting Information for full details). During the initial 48 h, the current and volume expansion of the test cell with SiC-CDC1400 was less than the system using u-SiC-CDC as the positive electrode (Table S3). These results suggest a correlation between the suppression of the gas generated during the floating test and the removal of acidic functional groups by the heat treatment.

4. Conclusions

In summary, the authors have investigated the pore thermal stability of activated carbon materials to heat-treatments at temperatures above 1000°C to inform the design of stable LIC positive electrode. Activated SiC-CDCs were prepared via a chlorination process at 1100°C and subsequently subjected to steam activation conditions at 900°C. It was revealed that the BET surface area of the activated SiC-CDCs was unchanged after being processed at 1000°C and only decreased by 10% following heat treatment at 1400°C. In contrast, the coconut shell-based steam activated carbon (YP50F) as commercial EDLC electrode carbon decreased by 20% after being heat-treated at 1400°C. The electrochemical durability of the activated SiC-CDCs (both before and after heat treatment) was then evaluated through floating tests, with the materials serving as LIC positive electrode at a cell voltage of 4.0 V and a temperature of 60°C. After 1000 h, the capacitance retentions of both SiC-CDCs were almost the same; however, the heat-treatment processing proved to play an important role in the internal resistance of the positive electrode. Specifically, the internal resistance of the SiC-CDC following heat treatment at 1400°C increased from 2.1 to 5.8 Ω, whereas that of the unheated SiC-CDC increased from 2.0 to 10.4 Ω. This difference was attributed to the decrease in acidic surface functional groups of the activated SiC-CDC by heat treatment, which suppresses the gas generation. Thus, the present paper demonstrates that SiC-CDC materials exhibit features that make them promising materials for high-performance positive electrodes for capacitors. Moreover, the selection of appropriate chlorination, activation, and heat-treatment conditions is essential when fabricating these carbon-based electrodes.

Supporting Information

The Supporting Information is available on the website at DOI: https://doi.org/10.5796/electrochemistry.19-63062.

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