ELECTROCHEMICAL CAPACITIVE PERFORMANCES OF BORON/CARBON MATERIALS

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Abstract

Carbonaceous materials containing boron (B/C materials) were prepared by solid-gas reaction of cellulose with boron trichloride. The reaction began at around 360K, while the pyrolysis of cellulose began by itself at 470K in appearance. A material prepared at 1070K showed a non-crystalline carbonaceous structure. Electrochemical capacitive performances were measured by 3 electrodes method in various aqueous solutions. The material prepared at 1070K showed a capacitance of 100F/g in 1M-H_2SO_4, which was larger than that (2F/g) of carbon prepared by a pyrolysis of cellulose at 1070K. The results suggest that the reaction of cellulose with BCl_3 proceeded in a manner similar to the chemical activation process by using KOH or $ZnCl_2$ as a reagent and introduced meso-pores in the non-crystalline structure. The meso-pores made by the activation in the structure could increase the capacity.

Introduction

Activated carbon is generally used for electrode materials of electric double layer capacitor (EDLC) because the large specific surface area generates the large capacitance. Recently, carbonaceous materials containing hetero atoms were prepared and applied for electrochemical capacitor. In this study, carbonaceous materials containing boron (B/C materials) were prepared by the reaction of cellulose with boron trichloride. Electrochemical capacitive performances were measured in various kinds of aqueous electrolytes.

Experimental

Preparation of B/C materials

B/C materials were prepared by solid-gas reaction of cellulose ($[C_6H_{10}O_5]_n$) with boron trichloride (BCl_3). Cellulose powders were set on a quartz boat and were heated at 1070K for 1 hour under BCl_3 atmosphere. Non-crystalline carbon as a reference was prepared by the heat treatment of cellulose at 1070K under N_2 atmosphere.

Electrochemical measurements

The obtained B/C materials were pulverized into fine powders with diameters under 45μm. The B/C powders, acetylene black powders and styrene-butadiene elastomer were mixed at a weight ratio of 8:1:0.4. The mixed powders were pasted on two of Pt plates (WE and CE) for the capacitor. The electrochemical measurements were performed by 3 electrode cell with an Ag/AgCl electrode as a reference in 1M-H_2SO_4, 2M-HCl, 1M-NaCl, or 1M-NaOH aqueous solution. The specific capacitances of the materials were calculated from the chage/discharge curves at a current density of 10mA/cm^2 by galvanostatic method. Cyclic voltammograms were also measured.

Results and discussion

B/C materials

The reaction of cellulose with BCl_3 began at around 360K, while the pyrolysis of cellulose began by itself at 470K in appearance. X-ray diffraction pattern indicated that the B/C material had the layered structure similar to non-crystalline carbon. The composition of the B/C material was B:C = 0.23:1.0, which was estimated by ESCA. However, most of the boron could not be in the carbon network but existed on the surface of the material, because most of them could be removed by a treatment with hot water. The B/C material had a specific surface area of 11m^2/g with a peak diameter of 4.8nm in the pore size distribution. On the other hand, the reference carbon had a 443m^2/g with a peak diameter of less than 1.7nm in the pore size distribution.

Specific capacitances in various electrolytes

Figure 1 shows galvanostatic charge/discharge curves of B/C material in 1M-H_2SO_4 aqueous solution. The capacitance of 100F/g (per single electrode of capacitor) was observed in the 1M-H_2SO_4. On the other hand, the reference carbon had a capacitance of 2F/g in 1M-H_2SO_4. The large capacitance observed for the B/C material could be due to the existence of meso-pore, which could introduce ions more effectively. Specific capacitances in the various electrolytes were calculated from these curves to be indicated in Table 1. The capacitance of 170F/g was observed in the 2M-HCl. On the one hand, the

reference carbon had a capacitance of 150F/g in 2M-HCl. The larger capacitances in 2M-HCl could be due to ion sizes smaller than those in 1M-H_2SO_4.

These results suggest that the reaction of cellulose with BCl_3 proceeded in a manner similar to the chemical activation process by using KOH or $ZnCl_2$ as a reagent and introduced meso-pores in the non-crystalline structure. The meso-pores made by the activation in the structure could increase the capacity. And there is a possibility of pseudo-capacitance in the case of using B/C materials as electrodes because the CV curves was not a typical rectangler-shape of EDLC but an asymmetric shape.

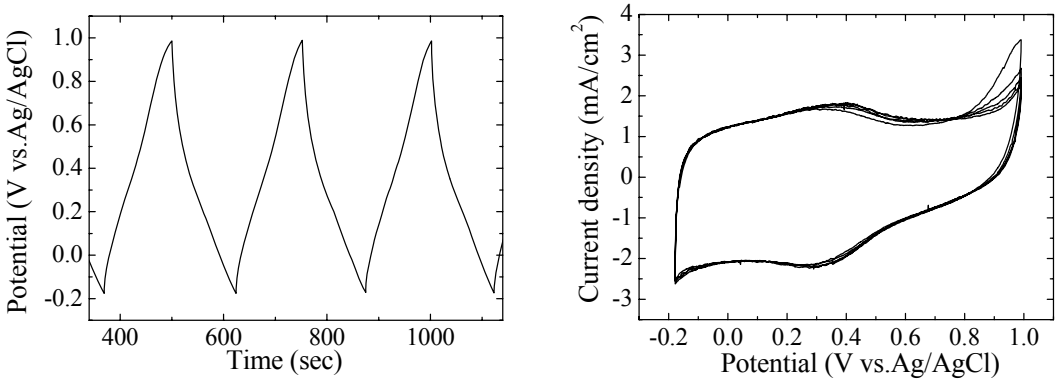

Figure 1. Galvanostatic charge/discharge curves (left) and cyclic voltammograms (right) of B/C material prepared by the reaction of cellulose and BCl_3. Electrolyte : 1M-H_2SO_4 aq.

Table 1. Capacities in various electrolytes for B/C material prepared by the reaction of cellulose and BCl_3, compared with those of carbon prepared from cellulose.

Electrolyte	B/C material Capacitance (F/g)	Carbon Capacitance (F/g)
2M-HCl	170	150
1M-H_2SO_4	100	2
1M-NaCl	60	20
1M-NaOH	70	30

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