

CAPACITANCE BEHAVIORS OF ACETYLENE BLACK SERIES WITH CHANGES OF GRAPHITIZATION DEGREE

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Abstract

Morphological and electrochemical properties of 4 different acetylene blacks were traced. The studied acetylene blacks were different from each other in primary structural unit size and degree of oxidation. Two special acetylene blacks with very small structural unit (small acetylene black/oxidized small acetylene black) and two general acetylene blacks (large acetylene black/oxidized large acetylene black) have been used in the study for the examination of electrochemical properties.

Electrochemical characteristics of acetylene black series were examined by cyclic voltammetry to estimate the effect of morphological changes by the heat treatments at 1000, 1200, 1400, 1600, 2200 and 2800 °C. To elucidate the capacitance changes of resultant acetylene blacks, the capacitances weigh the related changes of crystalline property, surface structure, surface area, pore size and degree of oxidation by graphitization. Morphological changes of resultant acetylene blacks were observed by TEM and SEM. Crystalline properties were measured using XRD and Raman spectroscopy. Chemical compositions were characterized using elemental analysis. Surface areas and the pore size distributions were evaluated by N₂-BET and NL-DFT method.

Introduction

Carbon has been considering one of the important materials for electrodes of electrochemical double layer capacitors [Nishino, A., 1996]. The focus projected on carbon materials is due to structural diversity, chemical stability, manageability, and abundance [Marsh, H., 2000, Mochida, I., 2006]. The structural diversity, however, casts inversely many difficulties in understanding the factors governing the capacitive behavior of carbon materials [Mochida, I., 2004]. In an effort to resolve the complications associated with the correlations between various properties of carbon materials and electrochemical double layer capacitances, we have tried to differentiate the effectiveness of edge surface and basal plane surface of graphite [Kim, T., 2006]. Using well-defined carbon nanofibers (CNFs) and surface-modified platelet CNFs, it has been found that the edge surfaces of CNFs were more effective roughly 3-5 times in capacitive charging than the basal-plane surfaces. The effectiveness of the edge surfaces was ascribed to

building up a higher electrical charge in the directions perpendicular to the c-axis of graphite under an electrochemical polarization, which is consistent with the smaller screening length of the electric field on edge surface as proposed by Kötzt's group [Hahn, M., 2004].

In this work, we present variations of electrochemical double layer capacitances of various acetylene blacks with their several properties. The studied acetylene blacks were chosen as basis of a reasonably well-defined set for a comparative study; they were manufactured in an identical process but modified in systematic ways, so that any complication coming from structural diversities of carbon materials produced from different processes (e.g. tremendous differences in pore-related properties) is negligible. Therefore, the chosen acetylene blacks are proper to investigate the effects of the graphitic properties except pore. The acetylene blacks of interest are different from each other in primary structural unit size and degree of oxidation, to enhance the effects of surface properties such as surface area and morphology. Furthermore, a systematic heat treatment of the studied acetylene blacks will lead to modified surfaces to understand an influence of surface morphology. From this particular point of view, the acetylene blacks under investigation provide exclusively a reasonably well-defined set of model compounds to disclose the various properties affecting electrochemical double layer capacitance of carbon materials, such as structural units, degree of oxidation and graphitization, excluding pore-related properties.

Experimental

Materials. Four acetylene blacks (supplied by Denki Kagaku Co., Japan) were used in this work: large acetylene black (LAB), small acetylene black (SAB), oxidized large acetylene black (OLAB) and oxidized small acetylene black (OSAB). The plain LAB and SAB were oxidized under the air atmosphere at 500°C for 1 h. Figure 1 shows SEM images of the four acetylene blacks. Clearly distinguishable were the primary structural units of LAB and SAB, the mean diameters of which were 35 nm and 12 nm, respectively. Also, the air oxidation process did not change the sizes of the structural units. The four acetylene blacks manufactured by the company were used as received without any treatment such as purification.

Heat treatment of acetylene blacks. Heat treatment of the acetylene blacks was carried out under a vacuum (1000°C-1600°C) or an argon atmosphere (2400°C-2800°C) for 10 min with a heating rate of 20 °C/min using a high temperature furnace (Kurada Kiken, Japan).

Surface area measurement. Multi-point Brunauer, Emmett, and Teller (BET) surface areas of the acetylene blacks were measured (Nippon Bell, Japan) after degassing at 300°C for 8 h.

Crystallographic analysis. The crystallographic analysis was performed according to the JSPS method [JSPS, 1963] with an X-ray diffractometer (Rigaku Ultima I, Japan, CuK α target).

Microscopic analysis. The external appearances of the acetylene blacks were examined using a scanning electron microscope (SEM, JSM-6700F, JEOL, Japan), and their morphologies in nanometer scale were

observed with a transmission electron microscope (TEM, JEM-2100F, JEOL, Japan).

Crystalline property analysis. Raman spectroscopic measurements (NRS-2000B, JASCO, Japan) were carried out to estimate the edge-to-basal plane ratios, expressed with the intensity ratios of the peaks at 1350 cm^{-1} (I_D) and at 1580 cm^{-1} (I_G) [Katagiri, G., 1988, Chieu, T. C., 1982].

Elemental analysis. Chemical compositions of the acetylene blacks were characterized using elemental analysis (Yanaco CHN-coder MT-5, Yanagimoto, Japan).

Electrochemical measurements. The capacitance was measured with cyclic voltammetry using a conventional three-electrode system. For preparation of an acetylene black electrode, a slurry of each acetylene black was made by mixing proper amounts of the acetylene black, 5% Nafion solution (Wako, Japan) and water. On the Au disk, the slurry was spread uniformly and dried under an IR lamp. To evaluate the capacitances, cyclic voltammetry was performed in 0.5 M H_2SO_4 solution (Johnson Matthey, ACS grade, USA) as in ref 5. The reported potentials in this work were measured against a home-made Ag/AgCl reference electrode.

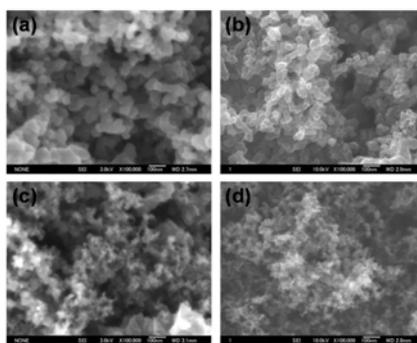


Figure 1. SEM images of the as-received acetylene blacks: (a) LAB, (b) OLAB, (c) SAB, and (d) OSAB.

Results and discussion

Comparison of capacitances of as-received acetylene blacks and fully graphitized acetylene blacks.

Figure 2 shows typical cyclic voltammograms of the as-received acetylene blacks (solid line) and the heat-treated acetylene blacks at 2800°C (dashed line). The general shapes of the cyclic voltammograms are rectangular, being typical to electrochemical capacitive charging. From the voltammograms of the as-received acetylene blacks, two important observations could be extracted: the acetylene blacks of small primary structural unit are more effective (e.g. LAB vs. SAB), and the oxidized acetylene blacks are more efficient (e.g. SAB vs. OSAB). Also, it is notable that in the case of the oxidized acetylene blacks, a pseudocapacitance of O-containing functional groups around 0.3 V, although not significant, is superimposed on the rectangular component. On the other hand, the capacitance values of the heat-treated acetylene blacks are much smaller than those of the as-received ones, and are similar to each other, regardless of structural unit sizes. Thus, it is demonstrated clearly that the capacitance of acetylene black truly depends on primary structural unit size, degree of oxidation, and heat treatment.

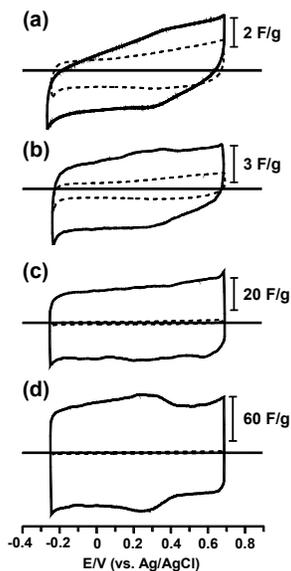


Figure 2. Cyclic voltammograms of the as-received and heat-treated acetylene blacks: (a) LAB, (b) OLAB, (c) SAB, and (d) OSAB in 0.5 M H₂SO₄ solution. The solid and dashed lines stand for the as-received acetylene blacks and heat-treated acetylene blacks, respectively. The heat treatment temperature was 2800°C. Scan rate: 10 mV/sec.

Comparison of morphologies of as-received acetylene blacks and fully graphitized acetylene blacks.

Typical TEM images of the as-received acetylene blacks and the heat-treated acetylene blacks at 2800°C are displayed in Figure 3 and Figure 4, respectively. As presented in Figure 3, the TEM features of the as-received acetylene blacks vary from image to image. The surfaces of LAB and OLAB are smooth to expose mainly graphitic layers (Figure 3 (a) and (b)), while those of SAB and OSAB are irregular to show features like spreading, sometimes folded, sheets (indicated with arrows in Figure 3 (c) and (d)). We refer these features to protruding graphene sheets, hereafter. These particular features of SAB and OSAB can be ascribed to high curvatures of the small primary structural units, which may cause high surface tensions to be relaxed somehow by bursting off the curved uppermost graphitic layers into the graphene sheets protruding from the surfaces of the primary units, otherwise smooth. On the other hand, respective comparisons of the images of OLAB and OSAB (Figure 3 (b) and (d)) with those of the un-oxidized LAB and SAB (Figure 3 (a) and (c)) reveal that the number of protruding graphene sheets increases after oxidation, supporting that the oxidation facilitates the formation of protruding graphene sheets. Furthermore, the number of protruding graphene sheets of OSAB (Figure 3 (d)) is higher than that of OLAB (Figure 3 (b)), certainly due to the higher curvature of structural unit and thinner graphitic layers of SAB than those of LAB. Thus, it appears that there is a correlation between the protruding graphene sheet and the capacitance: more protruding graphene sheets, more effective in capacitive charging. Also, it is evident that the primary structural unit size and degree of oxidation influence the

number of protruding graphene sheets, thereby the capacitive behavior of the acetylene blacks.

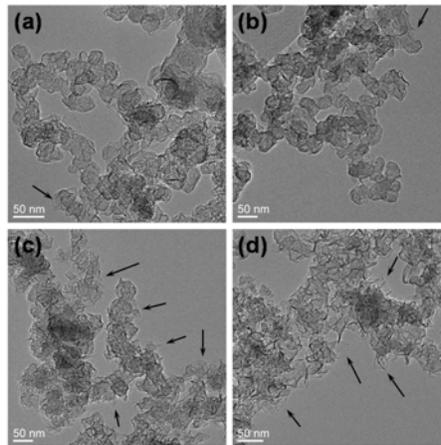


Figure 3. Typical TEM images of the as-received acetylene blacks: (a) LAB, (b) OLAB, (c) SAB, and (d) OSAB. The arrows indicate protruding graphene sheets detailed in the text.

Figure 4 shows typical TEM images of the acetylene blacks after graphitization at 2800°C. As shown in the left panel of Figure 4, a heat treatment at 2800°C brought tremendous changes in the morphologies of the acetylene blacks (compare with the images in Figure 3, also).

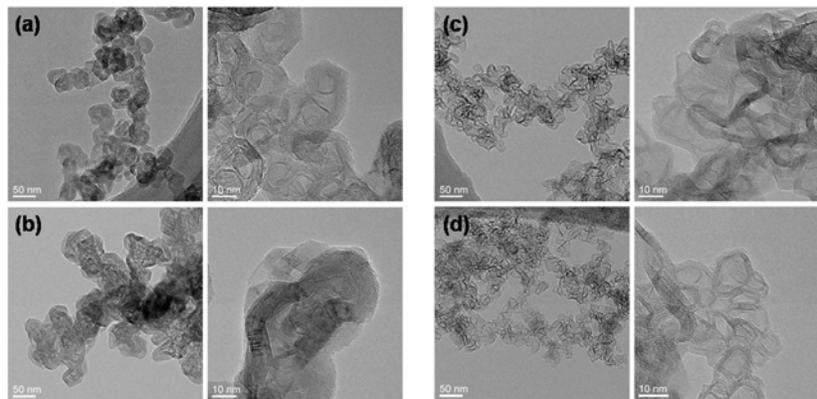


Figure 4. TEM images of the acetylene blacks treated at 2800°C: (a) LAB, (b) OLAB, (c) SAB, and (d) OSAB. The right panel represents the images of higher magnification of (e) LAB, (f) OLAB, (g) SAB, and (h) OSAB.

The acetylene blacks become aggregates of thicker graphitic layers after heat treatment, as detailed in the right panel of Figure 4. The graphitic layers are connected with each other in an angle of 120° to yield sp^2 hybridization of carbon atoms in graphite. In addition, the thickness of SAB and OSAB (15 graphene layers in average) is less than that of LAB and OLAB (20 graphene layers in average). Here, it is critical to notice that the surfaces of the acetylene blacks treated at 2800°C are covered with the basal

planes of graphite, and that most of the protruding graphene sheets are not discernible any longer. Because the capacitances of the heat-treated acetylene blacks are extremely low (Figure 2), it is confirmed again that the capacitance of acetylene black is relevant to the existence of protruding graphene sheets as mentioned previously.

The changes in the morphologies and properties of the acetylene blacks during heat treatments.

Figure 5 demonstrates a structural variation of OSAB along with heat treatment. Figure 5 (a) indicates that the as-received OSAB has numerous thin graphene sheets. In the image obtained after heat treatment at 1400°C, Figure 5 (b), some graphitic layers (imaged as thick dark fringes) appear at the rims of the protruding graphene sheets, simultaneously with a decrease in the number of graphene sheets.

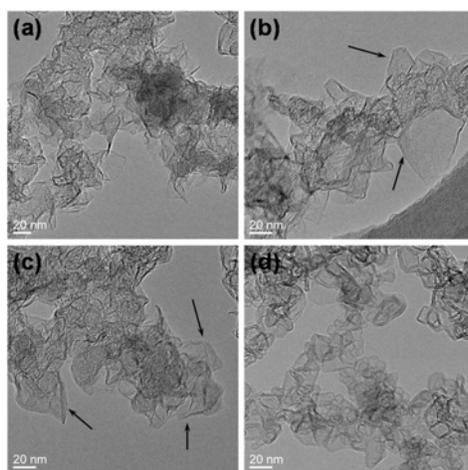


Figure 5. Variation in the TEM images of OSAB along with heat treatment: (a) not treated, and treated at (b) 1400°C, (b) 1600°C, and (d) 2800°C, respectively. The arrows indicate thin graphitic layers at the rims of protruding graphene sheets detailed in the text.

The OSAB treated at 1600°C has only graphene sheets completely enclosed with graphitic fringes as shown in Figure 5 (c). Heat treatments at temperatures higher than 1600°C lead to a totally different TEM image. In Figure 5 (d), the protruding graphene sheets almost disappear, and the graphitic layers interconnect with each other. It should be underlined that the graphitic layers obtained after the heat treatment at 2800°C become thicker than those in Figure 5 (c). Similar variations in the TEM images of the other acetylene blacks were observed during heat treatment in the temperature range from 1000°C to 2800°C.

Figure 6 shows the changes in the various graphitic properties of the heat-treated acetylene blacks as a function of temperature. The general trend observed in the variations of the graphitic properties is that they remain fairly constant below 1600°C and change significantly above 1600°C. Again, the properties show strong correlations with the sizes of primary structural units.

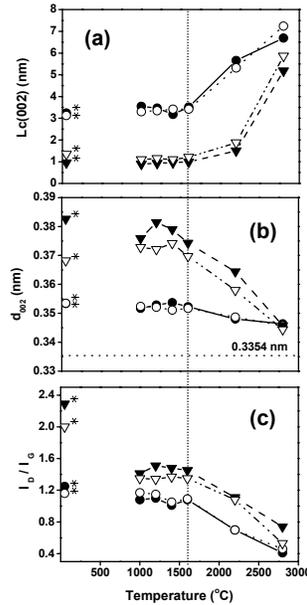


Figure 6. Variations of the graphitic properties of the heat-treated acetylene blacks as a function of temperature: (a) the distance of interlayer spacing (d_{002}), (b) the height of layer stacking ($L_C(002)$), and (c) the ratio of edge-to-basal-plane (I_D/I_G). ●: LAB, ○: OLAB, ▼: SAB, ▽: OSAB.

The variations in the TEM images of the acetylene blacks during heat treatments (Figure 5) are coherent with the changes in the graphitic properties (Figure 6). Specifically, the linear relationships of the graphitic properties in Figure 6 deflect at 1600°C, where the formation of the thin graphitic layers at the rims of the protruding graphene sheets completes in Figure 5. Combining the results in Figure 5 and Figure 6, therefore, provides the details taking place during a heat treatment of the acetylene blacks. Comparing the properties of the as-received acetylene blacks (indicated with asterisks) with those of the acetylene blacks heat-treated at 1000°C (Figure 6) supports the formation of the thin graphitic layers at the rims of the protruding graphene sheets (Figure 5). Further heat treatment up to 1600°C, however, did not induce any significant change of the graphitic properties, indicating that the formation of new graphitic layers, probably not highly ordered, continues at the perimeters of the protruding graphene sheets. As the temperature of heat treatment become higher than 1600°C, the graphitic layers are stacked more closely, and become thicker, and are interconnected with each other. Therefore, we propose that during heat treatment, two steps may take place sequentially: formation of the thin graphitic layers at the rims of the protruding graphene sheets up to 1600°C, and subsequent growth and interconnection of the thin graphitic layers to aggregates of thick graphitic layers above 1600°C.

Figure 7 presents the variations of the BET surface area of the heat-treated acetylene blacks as a function of temperature. As the heat treatment temperature increases, the surface areas of the acetylene blacks monotonously decrease and converge to certain values depending only on the structural unit sizes,

i.e. $\sim 60 \text{ m}^2/\text{g}$ for LAB and OLAB, and $\sim 150 \text{ m}^2/\text{g}$ for SAB and OSAB. The surface area may decrease by reducing the number of protruding graphene sheets during formation of thin graphitic layers below 1600°C , and by reducing the number of pores among small graphitic crystallites during interconnecting them to aggregate of thick graphitic layers above 1600°C .

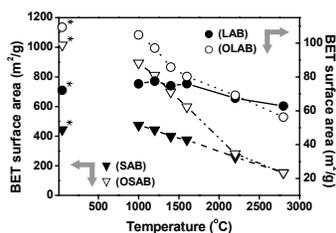


Figure 7. Variations of the BET surface areas of the heat-treated acetylene blacks as a function of heat treatment temperature. ●: LAB, ○: OLAB, ▼: SAB, ▽: OSAB.

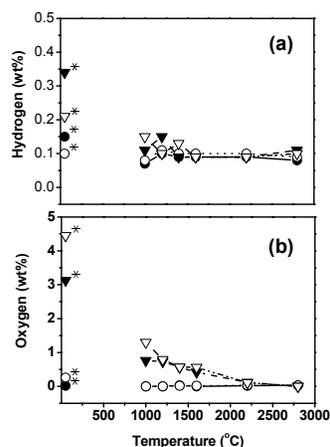


Figure 8. Variations of the chemical compositions of the heat-treated acetylene blacks as a function of temperature: (a) hydrogen, and (b) oxygen. ●: LAB, ○: OLAB, ▼: SAB, ▽: OSAB.

Figure 8 shows the variations of the H and O contents as a function of heat treatment temperature. The H contents of the as-received SAB and OSAB are higher than those of the as-received LAB and OLAB, which is consistent with Figure 3 in that the as-received SAB and OSAB have more protruding graphene sheets whose perimeters are certainly edges of graphite. Furthermore, the smaller amounts of H found on OSAB and OLAB suggest that the edges of the protruding graphene sheets were oxidized selectively. Regardless of the types of acetylene blacks, however, the H content decreases rapidly to 0.1% until the heat treatment temperature reaches to 1600°C , and maintains the specific level at higher temperatures. The conversion of protruding graphene sheets to thin graphitic layers may remove a significant amount of edges of the protruding graphene sheets. Here again, the variations of the O contents are similar to those of the H contents, indicating a removal of the protruding graphene edges.

Capacitances of the heat-treated acetylene blacks vs. their various properties.

Figure 9 demonstrates the variation of the cyclic voltammograms of OSAB. As the heat treatment temperature increases, the cyclic voltammogram changes to more rectangular shape with smaller double layer charging current. Also, it is notable that the pseudocapacitance disappears even after heat treatment at 1000°C, coincidentally with the removal of H and O in Figure 8. The variations in the cyclic voltammograms of LAB, OLAB and SAB are qualitatively similar to that in Figure 9.

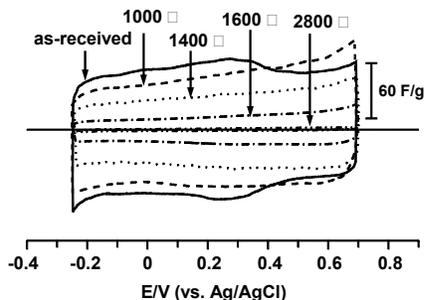


Figure 9. Variation in the cyclic voltammograms of OSAB treated at various temperatures. Scan rate: 10 mV/sec.

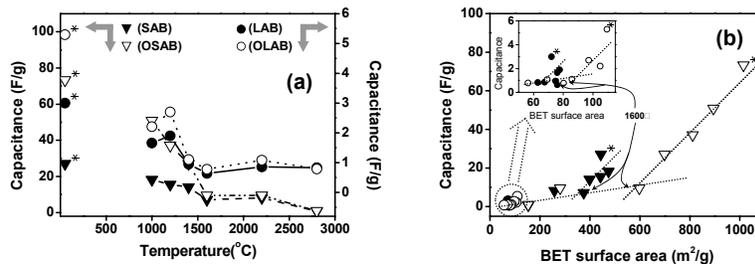


Figure 10. Plots of capacitance vs. the graphitic properties of the heat-treated acetylene blacks: (a) the distance of interlayer spacing (d_{002}), (b) the height of layer stacking ($L_c(002)$), and (c) the ratio of edge-to-basal-plane (I_D/I_G). ●: LAB, ○: OLAB, ▼: SAB, ▽: OSAB.

Figure 10 shows the plots of the capacitances as functions of the graphitic properties. Here again, it is clear that the dependence of the electrochemical capacitance deflects 1600°C. A more important point to be caught is that the capacitance value is independent on the graphitic properties: below 1600°C, the capacitance varies even at fairly constant graphitic properties, while, above 1600°C, the capacitance remains reasonably unchanged even at the wide ranges of graphitic properties. This particular point implies that the capacitance is influenced strongly by the surface properties, not by the bulk properties. In fact, a clear distinction at 1600°C is that the surfaces of the acetylene blacks are covered with the protruding graphene sheets below 1600°C and with the basal planes above 1600°C, respectively.

Conclusion

We have presented the capacitive behavior of various acetylene blacks showing their properties in variety. It is demonstrated that the most crucial factor in determination of capacitance is surface morphology. On the surfaces of a given morphology, the surface area determines the capacitance. The two properties are subjective to primary structural unit size, degrees of oxidation and graphitization. The most effective surface morphology is the surface covered with protruding graphene sheets, which is 2-3 times and 10 times superior to an edge surface and a basal-plane surface, respectively. Thus, a desirable direction to develop a material of acetylene black aimed specifically for electrochemical double layer capacitor would be preparation of an acetylene black on which the number of protruding graphene sheets is maximized.

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