Mechanochemical Processing of Natural Graphite under Different Atmospheres for Fabricating Electrodes Used in Electric Double-layer Capacitors

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ABSTRACT

This study focused on the mechanochemical processing of natural graphite using a planetary ball mill under different atmospheres and analyzing their influence on the electrochemical behaviors of the processed graphite materials in electric double-layer capacitors (EDLCs). Oxygen and/or nitrogen were incorporated in the carbon framework from the atmosphere used during milling. Specific surface areas of the pulverized graphite did not significantly depend on the employed atmosphere. These pulverized graphites processed under different atmospheres were evaluated as electrode materials for application in EDLCs with an organic electrolyte. All the pulverized graphites showed comparable capacitances independently of the used atmospheres. Considering the effect of post-thermal treatment of the pulverized graphite to remove oxygen surface functionalities, changes in the surface functionalities of pulverized graphites caused by ball milling did not significantly influence their applications as electrode materials in EDLCs.

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Keywords : Electric Double-layer Capacitor, Pulverized Graphite Electrodes, Mechanochemical Processing, Surface Functionalities

Article

1. Introduction

Carbon materials with high specific surface areas, typically microporous activated carbons, are employed as electrode materials in electric double-layer capacitors (EDLCs).1–4 Recently, we developed electrodes using pulverized graphite for EDLCs, prepared by ball milling of natural graphite under air.5 This pulverized graphite had a maximum specific surface area of approximately 800 m² g⁻¹ and showed high volumetric capacitance of 16 F cm⁻³ (based on the total volume of two electrodes) as well as excellent rate performance, compared to commercial microporous activated carbon. These results were ascribed to the high density of the pulverized graphite electrodes, high electrical conductivity of these materials, and their mesoporous-rich structures. In addition, we revealed that pulverized graphite was as durable as commercial microporous activated carbon. Furthermore, ball milling of graphite under air introduced oxygen and nitrogen into the carbon framework. Several researchers have investigated mechanochemical exfoliation of graphite with milling under different atmospheres.6–13 Ong et al. reported that milling of graphite under N₂ and Ar atmosphere provided a higher surface area than that under O₂ atmosphere.9 Similarly, Chevallier et al. concluded that milling under O₂ atmosphere increased oxygen functionalities of carbons and resulted in decreased surface areas owing to easy aggregation of oxygen-terminated carbon particles.7 Thus, the atmosphere employed during ball milling of graphite has a strong influence on its surface area and surface functionalities. However, the influence of the surface functionalities of pulverized graphites on their electrochemical behaviors has not been investigated. Surface functionalities, particularly oxygen-containing groups, have a strong influence on the capacitive properties such as rate characteristics and stability.14–17 Therefore, it is essential to investigate the influence of the employed atmospheres on the capacitive performance of pulverized graphite. Hence, in the present study, we performed mechanochemical processing of graphite through ball milling under various atmospheres and investigated the influence of these atmospheres on the surface functionalities as well as the capacitive behaviors of the obtained pulverized graphites in organic electrolytes.

2. Experiments

2.1 Preparation and characterization of pulverized graphite

Approximately 2 g of high-purity natural graphite powder (SN-100, >98%, Median diameter: 100 µm, provided by SEC Carbon, Ltd.) and 75 g of 1 mm (ø) zirconia balls were placed in a 45 cm³ zirconia vessel under an air atmosphere. The ball milling procedure was then performed at 700 rpm for 150 min using a planetary ball mill (PLP-7, Fritsch GmbH). The milling was paused for 3 min every 15 min to avoid an increase in temperature during the ball-milling process. For milling under O₂ and N₂ atmospheres, air was evacuated after the vessel was sealed, and then the vessel was filled with each gas. To perform milling under an Ar atmosphere, the vessel was sealed in a glove box filled with purified Ar gas. After milling under N₂ and Ar atmospheres, the acquired pulverized graphites were stored in the glove box. In addition, post-thermal treatments at 1000 and 1500°C were performed in a N₂ gas stream using an electric furnace for the graphite milled under air to evaluate the effects of the reduced oxygen functionalities on the capacitive behavior.

The pore structures of the pulverized graphite were evaluated with N₂ adsorption isotherms obtained at 77 K using a surface area
and porosity analyzer (ASAP 2020, Micromeritics instrument Co.). The Brunauer–Emmett–Teller (BET) surface areas ($S_{\text{BET}}$) were determined from the adsorption isotherms in the $P/P_0$ range of 0.01–0.05 to avoid overestimating the microporous characteristics of the pulverized graphite. The total pore volume ($V_{\text{total}}$) was determined from the amount of N2 adsorbed at a relative pressure ($P/P_0$) of 0.99. The micropore volume ($V_{\text{micro}}$) was estimated based on the quenched solid density functional theory (QSDFT) using the VersaWin software package (Quantachrome Instruments Japan G. K.), and the pore volume related to mesopores and macropores ($V_{\text{meso} + \text{macro}}$) was determined based on the balance between $V_{\text{total}}$ and $V_{\text{micro}}$. The pore size distributions were estimated based on the Barrett–Joyner–Halenda (BJH) method. The surface chemistry of the pulverized graphites was analyzed using x-ray photoelectron spectroscopy (XPS, ESCALAB250, Thermo Fisher Scientific Inc.) with Al Kα radiation. Elemental analysis was performed using a model JM11 elemental analyzer (J-SCIENCE LAB CO., Ltd). The carbon, hydrogen, and nitrogen contents were determined directly while the oxygen content was calculated by difference assuming only these elements were contained.

2.2 Electrochemical measurements
The pulverized graphites were mixed with acetylene black (DENKA BLACK, Denka Company Ltd., Japan), BM-400B styrene-butadiene rubber (SBR, Zeon, Japan), and D2200 carboxymethyl cellulose (CMC, Daicel FineChem Ltd., Japan) with a weight ratio of 85:5:5:5 in distilled water using a mortar and pestle. The slurry was placed on an aluminum current collector through doctor blading. The pulverized graphite films were pressed to a thickness of ~50 µm under 250 MPa and punched with a 10-mm-diameter disk cutter. The disk electrodes were dried overnight under vacuum at 120°C before cell assembly.

A propylene carbonate solution containing 1 M tetraethylammonium tetrafluoroborate (TEABF4/PC) was purchased from Kishida Chemical Co., Ltd and used as the electrolyte without further purification. The electrodes and cellulose based separators (TF40-50, Nippon Kodoshi Co.) were immersed in the electrolyte for 30 min under reduced pressure, and coin-type cells were assembled in a two-electrode configuration. Electrochemical measurements were performed using a VMP2 multichannel galvanostat-potentiostat (BioLogic, Cary, NC). Cyclic voltammetry and charge/discharge measurements were conducted in the voltage range of 0–2.5 V to avoid Faradaic reactions involving electrochemical decomposition of the electrolytes. The cell capacitance ($C_G$) was calculated as $C_G = i \Delta t / \Delta V m_{\text{total}}$, where $i$ is the current, $\Delta t$ is the discharge time, $\Delta V$ is the voltage change, and $m_{\text{total}}$ is the total weight of the two electrodes including acetylene black and binders. Accelerated durability tests at 70°C were performed by charging to 3.2 V with a current density of 0.1 A g$^{-1}$ and then by holding at the same voltage for 100 h.

3. Results and Discussion
Figure 1 shows the N2 adsorption/desorption isotherms obtained after ball milling of graphite under air, O2, N2, and Ar atmospheres. All these isotherms showed an increase in the amount of N2 adsorption under a wide range of pressures. The inset is the pore size distribution determined using the BJH method. Broad distributions were observed, and the peak pore size was 20–30 nm (classified as mesopores). The BET surface areas and pore volumes
pyrrolic and pyridinic nitrogen atoms as nitrogen species. A similar tendency was observed in the elemental analysis results. According to air when XPS measurements and elemental analysis were conducted. It is also likely that ZrO₂ partially oxidized the graphites during high-power milling. The oxygen content determined from the XPS measurements was larger than that estimated via elemental analysis, indicating that oxygen species existed predominantly on the surfaces of pulverized graphites. Thus, although the nitrogen content clearly increased when the graphites were milled under an air or N₂ atmosphere, no significant difference in the oxygen content was observed when the graphites were milled under different atmospheres. These pulverized graphites were evaluated as electrode materials for EDLCs using an organic electrolyte. Figure 3a shows the cyclic voltammograms of the pulverized graphites obtained by ball milling at 700 rpm for 150 min under different atmospheres acquired at a scan rate of 10 mV s⁻¹. The shapes are almost rectangular without clear Faradaic reactions. In addition, almost nearly linear voltage profiles were observed in the charge/discharge measurements in the range of 0–2.5 V (Fig. 3b). These results indicate capacitive behaviors of the pulverized graphites. No significant difference was observed for the graphites milled under different atmospheres. The gravimetric capacitance at different current densities was estimated based on the charge/discharge measurements (Fig. 4). The graphites milled under O₂ and Ar atmospheres showed slightly higher capacitance than others, which corresponds to the tendency of the BET surface area (Table 1). Furthermore, all the pulverized graphites showed similar levels of durability (Fig. 5). This result is supported by the very analogous time transient of current in the floating test, considering that the faradaic reaction causes degradation of EDLCs (Fig. 6). These capacitance retentions after the durability test are comparable to that of a commercial activated carbon. Thus, the graphites milled under different atmospheres exhibited very similar electrochemical behaviors; moreover, the increased oxygen and nitrogen contents had no significant influence on their capacitive performance.

To further investigate the influence of the surface functionalities on the capacitive behaviors, post-thermal treatments at 1000 and 1500°C were performed for the graphites milled under air. Thermal treatment of activated carbons can reduce oxygen surface functionalities and improve the durability of EDLCs because oxygen functionalities of carbons are electrochemically active sites for electrochemical decomposition of electrolytes. Table 2 presents the BET surface area, initial capacitance, capacitance retention after durability tests at 3.2 V, and O/C and N/C ratios determined from XPS analysis. Air-1000 and Air-1500 denote the pulverized graphite heated at 1000 and 1500°C, respectively. Clearly, the oxygen and nitrogen contents decreased after the thermal treatment. Thermal treatment at 1500°C significantly improved the durability although the treatment at 1000°C did not have a clear effect despite the decreased oxygen content. This result indicates that the oxygen content of the surface functionalities is the most influential factor on their performance.

### Table 1. BET surface area and pore volume of pulverized graphite obtained through ball milling of graphite under different atmospheres.

| Atmosphere | $S_{\text{BET}}$/m² g⁻¹ | $V_{\text{total}}$/cm³ g⁻¹ | $V_{\text{micr}}$/cm³ g⁻¹ | $V_{\text{meso}}$/cm³ g⁻¹ |
|------------|------------------------|------------------------|------------------------|------------------------|
| Air        | 670                    | 1.02                   | 0.21                   | 0.81                   |
| O₂         | 750                    | 0.98                   | 0.24                   | 0.74                   |
| N₂         | 710                    | 1.05                   | 0.23                   | 0.82                   |
| Ar         | 750                    | 1.12                   | 0.24                   | 0.88                   |

Figure 2. (a) O/C and (b) N/C ratio in at% of pulverized graphites determined by XPS and elemental analysis. Pristine denotes natural graphite used as a precursor.

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content in the pulverized graphite should be decreased to the level observed in the pulverized graphite heated at 1500°C for improving durability, although a slightly enhanced crystal structure would also contribute to improvements in the durability. In this context, it is reasonable to conclude that the atmosphere used during milling of graphite does not have a significant influence on its durability because the oxygen content is relatively high in all the cases, as shown in Fig. 2. Thus, heat treatment can enhance the stability of the pulverized graphites; however, at the same time, it lowers the specific surface area owing to shrinkage of the micropores, resulting in decreased capacitance (Table 2). Accordingly, ball milling of graphite in reductive conditions such as under a hydrogen atmosphere or by employing other reductive additives would be an effective strategy to decrease the oxygen content without destroying its pore structure.

4. Conclusions

In the present study, we produced pulverized graphites with high surface areas through ball milling of natural graphite under different atmospheres. Although the correlation between the heteroatom content and capacitive performance was investigated, no clear tendency was observed. In other words, oxygen uptake by the carbon atoms in the milling process does not have a significant influence on the capacitive behaviors of the pulverized graphites in organic electrolytes. Different results could be obtained in aqueous solutions. Considering the effect of the post-thermal treatment of the pulverized graphites, the capacitance or stability of these materials can likely be further improved through investigations under different milling conditions, particularly under reductive atmospheres. Note, however, that the milling condition should be simple and cost-effective for a practical application. Thus, although the milling condition including pre and/or post treatments has yet to be optimized, this study suggests that mechanochemical processing through ball milling is promising for further developing the carbon-based electrode for EDLCs.

Table 2. BET surface area, initial capacitance at 0.1 A g⁻¹, capacitance retention after the durability test, and O/C as well as N/C ratio determined by XPS analysis. Air-1000 and Air-1500 denote the pulverized graphites annealed at 1000 and 1500°C, respectively, after milling of graphite in air.

|        | \(S_{\text{BET}}\) m² g⁻¹ | Initial capacitance F g⁻¹ | Retention % | O/C   | N/C   |
|--------|-----------------|-----------------|-------------|-------|-------|
| Air    | 670             | 11              | 80          | 0.12  | 0.014 |
| Air-1000 | 700           | 10              | 80          | 0.04  | 0.01  |
| Air-1500 | 550           | 7               | 95          | 0.009 | 0.002 |

Figure 3. (a) Cyclic voltammograms (Scan rate: 10 mV s⁻¹) and (b) charge-discharge curves (Current density: 1.0 A g⁻¹) of pulverized graphites obtained through ball milling of graphite under different atmospheres.

Figure 4. Gravimetric capacitance at different current densities of pulverized graphite obtained through ball milling of graphite under different atmospheres.

Figure 5. Capacitance retention of pulverized graphites after the durability test at 3.2 V.
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Figure 6. Change in the current densities during the durability test at 3.2 V of pulverized graphites obtained through ball milling of graphite under (a) air, (b) O2, (c) N2, and (d) Ar atmospheres.