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Graphene-based materials produced by ball milling of graphite for electric double layer capacitors

Graphene-based materials have been attracting great interest for electric double layer capacitors because of their high conductivity and high specific surface area (surface area of an ideal monolayer graphene: 2630 m^2 g^{-1}) [1]. The most widely used production methods of them are mechanical exfoliation with adhesive tapes, epitaxial growth by chemical vapor deposition (CVD) on metal substrates, liquid-phase exfoliation, and reduction of graphite oxide (GO). Methods for the large-scale and economical production of high-quality graphene-based materials are essential. High-energy ball milling of natural graphite has potential for the scalable and cost-effective production of graphene-based materials. Mechanochemical exfoliation of graphite with ball milling has been already investigated by several researchers [2–5]. Long time milling of graphite (2–112 h) at rotational speeds of 200–400 rpm has yielded carbons with maximum specific surface area of 580 m^2 g^{-1}. In the present study, we investigated the capacitive behaviors of carbons produced by high-energy ball milling of graphite at higher rotational speeds than 500 rpm.

For preparation of graphene-based materials, graphite powders and 1 mm-diameter balls (zirconia) were set into a zirconia vessel under air. The ball milling of graphite was conducted for 1–750 min at 500–900 rpm using a planetary ball mill (P-7 Premium Line, Fritsch). Based on the N_2 adsorption isotherm, the total pore volume and BET surface area of the carbons produced by ball milling of graphite for 150 min at 700 rpm were 0.70 cm^3 g^{-1} (P/P_0 = 0.99) and 770 m^2 g^{-1}, respectively. The carbons exhibited a predominantly mesoporous nature with a peak pore size of 8 nm. The crystal structure of the carbons was analyzed by X-ray diffractometer. The average number of stacked graphene layers in the 700 rpm-milled carbon was estimated to be 2.7 based on the Hirsch theory [6]. TEM analysis indicated that the obtained carbons mainly consisted of few-layer graphenes but relatively large crystallites partially remained, particularly in the case of a low rotational speed milling (Fig.1). In addition, the XPS measurement indicated that oxygen and nitrogen functional groups were introduced in the carbon frameworks by milling under air. For preparing the electrodes, the active materials were mixed with carbon black, CMC, and SBR in the weight ratio of 85:5:5:5, and the obtained slurry was placed on an aluminum current collector by doctor blading. Finally, the carbon film electrodes having a thickness of 40 μm were punched with a 10 mm-diameter disk cutter. Coin-type cells in a two-electrode configuration were assembled. The electrolyte was propylene carbonate containing 1 M tetraethylammonium tetrafluoroborate ($TEABF_4$/PC). Figure 2a shows a cyclic voltammogram at the scan rate of 10 mV s^{-1} and an almost rectangular shape was observed, indicating capacitive behavior. Similarly, Fig.2b shows the nearly linear voltage profile in the charge-discharge process. The gravimetric capacitance was 12.5 F g^{-1} at 0.1 A g^{-1}. Compared to the result of a commercial activated carbon, the 700 rpm-milled carbons in this work showed a lower capacitance at low current densities but exhibited a superior rate performance. In addition, the floating stability test showed an enhanced durability of the proposed materials. To further improve the capacitance, the milling conditions should be optimized in the future work.

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References

[1] A. Lemine, M. Zagho, T. Altahtamouni, N. Bensalah, International Journal of Energy Research, 42 (2018) 4284–4300
[2] T.S. Ong, H. Yang, Carbon, 38 (2000) 2077–2085.
[3] E. Gomibuchi, T. Ichikawa, K. Kimura, S. Isobe, K. Nabeta, H. Fujii, Carbon, 44 (2006) 983–988.
[4] H. Lyu, B. Gao, F. He, C. Ding, J. Tang, J.C. Crittenden, ACS Sustainable Chemistry & Engineering, 5 (2017) 9568–9585.
[5] I. Jeon, S. Bae, J. Seo, J. Baek, Advanced Functional Materials, 25 (2015) 6961–6975.
[6] P. B. Hirsch, Proceedings of the Royal Society A, 226 (1954) 143.

Figures

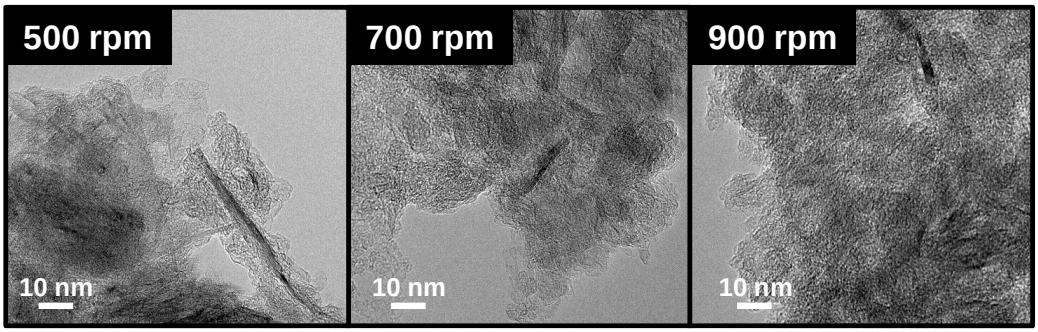

Figure 1: TEM image of the graphene-based materials produced by ball milling of graphite at the rotational speed of 500, 700, and 900 rpm.

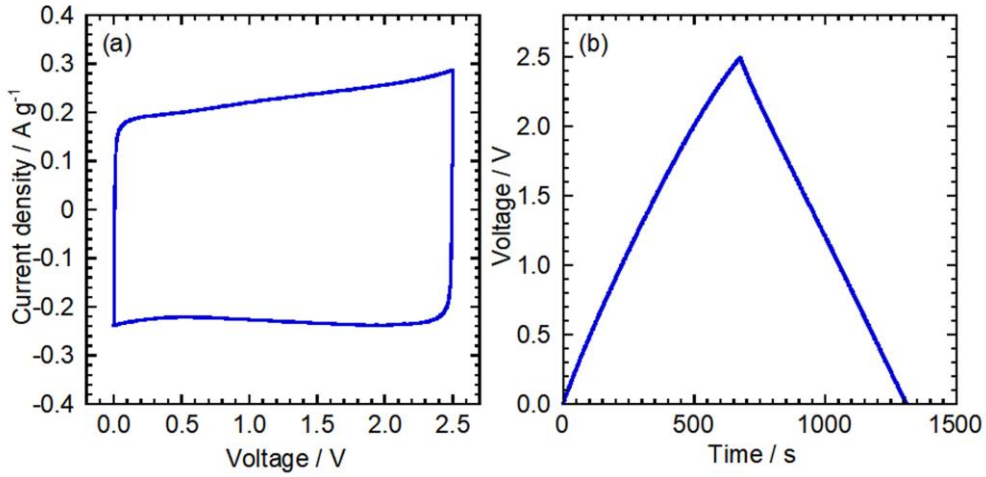

Figure 2: (a) Cyclic voltammogram (Scan rate: 10 mV s^{-1}) and (b) charge/discharge curve (Current density: 0.1 A g^{-1}) of the carbon produced by ball milling of graphite for 150 min at 700 rpm.