

Electrochemical properties of low-purity natural graphite as an anode active material for lithium-ion batteries

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The possibility of using low-purity natural graphite as an anode active material for lithium-ion batteries has been investigated. Pristine and modified natural graphites showed different degrees of crystallinity based on XRD and Raman measurements. Whereas the reversible capacities of pristine and modified natural graphites were similar, the latter had better cycle performance. The dissolution of impurities from the natural graphite into the electrolyte was found to be negligible based on ICP-MS analysis.

Key words: Lithium-ion batteries, Natural graphite, Soft carbon, Impurity, Dissolution.

Introduction

Presently, lithium-ion rechargeable batteries are extensively used in popular portable devices such as cell phones, laptop computers, and camcorders. There is also a strong interest in using lithium-ion rechargeable batteries for electric vehicles. However, the use of lithium-ion rechargeable batteries for these applications is confronted with the barriers of high price and poor cycle life. To reduce the high manufacturing cost of lithium-ion rechargeable batteries, natural graphite is a highly useful alternative material to high-cost synthetic graphite; natural graphite has abundant reserves and is inexpensive. However, flake-type natural graphite is likely to generate side reactions and to undergo exfoliation. Moreover, purification of natural graphite is necessary prior to its use. Both surface modification and coating approaches have been researched to address these problems of natural graphite. Surface modification is carried out by means of mild oxidation using oxidation catalysts such as H_2O_2 or $\text{Ce}(\text{SO}_4)_2$ [1-5]; surface coating is typically carried out by means of mechanical milling followed by coating with epoxy resin or ionic conductive copolymer [6-8]. Although these efforts can mitigate the disadvantages of natural graphite, they also increase the manufacturing cost.

A major reduction in manufacturing cost could be realized if it were possible to use unrefined natural graphite as an anode active material for lithium-ion rechargeable batteries, without introducing critical problems. This possibility was investigated in the present work.

Experimental Procedure

Powder preparation

Pristine natural graphite obtained from China was used as a starting material. The pristine natural graphite sample was classified by sieving with a 325-mesh sieve, and this material is termed original natural graphite (O-NG) hereafter. To prepare 5 wt% soft carbon-coated spherical natural graphite (SS-NG), simultaneous coating and sphericalization was carried out. A mixture of O-NG and pitch was crushed by using a ball milling machine, during which process the broken particles became rounded out owing to their unstable surface energy. Finally, the resulting powdered mixture was fired at 1300 °C for 1 h, which yielded the 5 wt% SS-NG.

Characterization

A working electrode paste was fabricated from a mixture of natural graphite with a binder of carboxymethylcellulose (CMC)/styrene-butadiene rubber (SBR) dissolved in water; the weight ratio of graphite to binder was 97/3. The prepared paste was coated onto 10 μm Cu foil by using a doctor blade, and then was dried under vacuum at 120 °C for 12 h. Electrochemical characterizations were conducted using both CR2032 coin-type cells and beaker cells of 50 mL capacity. In each cell, a Cellgard 2300 porous membrane with 20 thickness and 1 M LiPF_6 -EC/DMC (1 : 1 in volume ratio) was used as the separator and the electrolyte, respectively. Lithium metal foil was used as the counter electrode.

Powder morphology was observed by scanning electron microscopy (SEM, JSM-5900, JEOL). Powder X-ray diffraction (XRD, MAX-2500, RIGAKU) measurement was conducted by using Cu K_α radiation of wavelength $\lambda = 1.5406 \text{ \AA}$. Crystallite sizes (L_a and L_c) were calculated on the basis of the d_{002} and d_{101}

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XRD lines by using the Scherrer equation. Crystallinity of the powders was also investigated by Raman spectroscopy (LabRAM, Horiba Jobin-Yvon). The concentrations of impurities in graphite were determined by means of inductively coupled plasma mass spectrometry (ICP-MS, X series, Thermo Electron Co.).

Results and Discussion

The morphology of the natural graphite before and

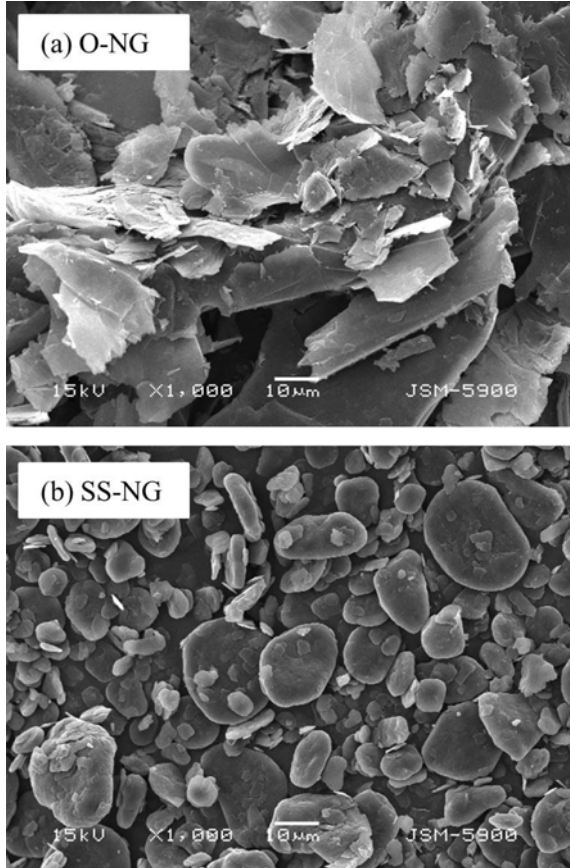


Fig. 1. SEM images of graphite powders: (a) O-NG, (b) SS-NG powders.

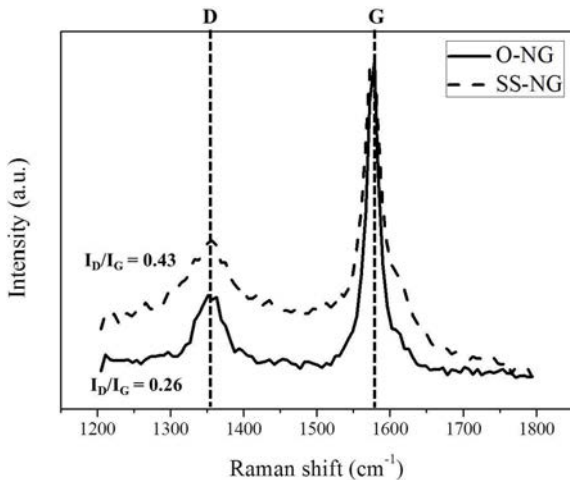


Fig. 2. Raman spectra of O-NG and SS-NG.

after treatment is shown in Fig. 1. The O-NG particles ranged in size from 45 μm to 200 μm and had sharp edges and extremely irregular morphology. The particle size of SS-NG was smaller than that of O-NG due to the ball milling treatment. The crushed particles agglomerated and became rounded owing to their unstable surface energy; this process is called sphericalization. Even though the SS-NG particles were spherically shaped, their surface morphology was inhomogeneous (Fig. 1b). The tapped density of electrode paste prepared from O-NG was less than that of SS-NG, owing to O-NG's morphology of irregular flakes.

Raman spectra were used to analyze the degree of structural disorder in the O-NG and SS-NG (Fig. 2). Both O-NG and SS-NG had G bands at 1580 cm^{-1} , corresponding to the typical graphite structure (sp^2). The carbon or diamond (sp^3) characteristic peak of the D band was detected around 1360 cm^{-1} [9]. The degree of structural disorder was quantified by using the R-value, which is the ratio of the D band intensity to the G band intensity. The O-NG was more crystalline than the SS-NG, with R-values of 0.26 and 0.43, respectively; that is to say, the soft carbon coating and mechanical milling process used to transform O-NG into SS-NG reduced the material's crystallinity.

XRD patterns of both the pristine and surface-modified natural graphite powders are shown in Fig. 3. Although the natural graphite contained various impurities, they were not detected by XRD. Both the pristine and surface-modified natural graphite had main diffraction peaks for the (002) and (004) planes corresponding to the hexagonal structure. However, (101) and (012) peaks corresponding to the rhombohedral structure became visible after the sphericalization process. The d_{002} spacings of O-NG, spherical natural graphite without soft carbon coating (S-NG), and SS-NG were 0.3358, 0.3353, and 0.3350 nm, respectively. These decreases in the d_{002} spacing values are likely to have arisen from the heat treatment used during the sphericalization process, which entailed heating at $1300\text{ }^\circ\text{C}$ for 1 h; these

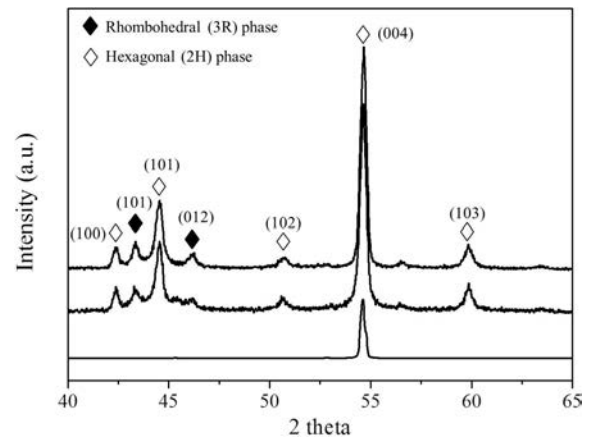


Fig. 3. XRD patterns of O-NG, SS-NG, and S-NG.

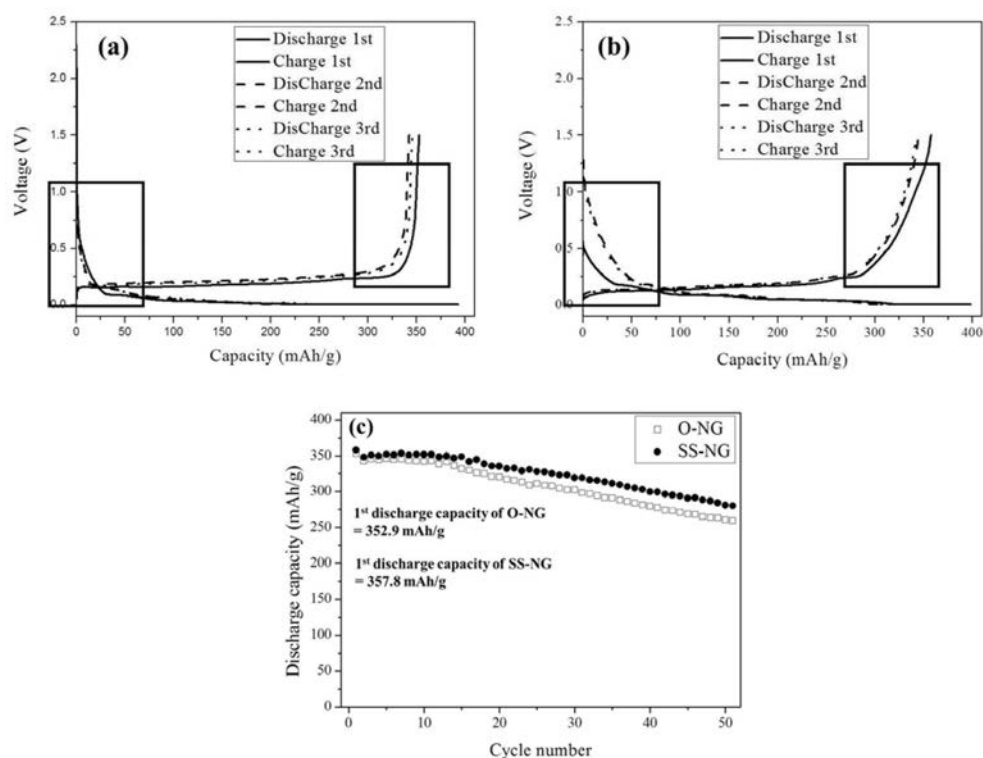


Fig. 4. (a, b) Voltage versus capacity during 3 charge-discharge cycles of (a) O-NG and (b) SS-NG; (c) discharge capacity versus cycle number.

Table 1. ICP-MS analysis results for O-NG powder and electrolytes.

(Unit: ppm)										
Elements	Al	Fe	Zn	Cr	S	Ni	Mn	Co	Sr	Cu
O-NG (powder)	4921	3300	24.8	7.78	33.2	6.92	8.70	1.47	2.8	14.5
Raw electrolyte	5.17	0	0.04	0.08	1.31	0	0.01	0	0.03	0
O-NG-D*	0.66	0	0.02	0.05	0.71	0	0	0	0.02	0.08
O-NG-BC**	0.85	0	0.04	0.05	0.89	0	0	0	0.05	0.02
SS-NG-D	0.41	0	0.06	0.05	0.95	0	0	0	0.02	0.03
SS-NG-BC	1.07	1.99	1.20	0.07	1.06	0.72	0.03	0	0.15	0.03

*-D: dipping test.

** -BC: beaker cell test.

conditions are expected to cause crystallization of natural graphite.

Fig. 4 shows charge-discharge capacity curves collected during 3 cycles of the O-NG and SS-NG materials. The first charge-discharge reaction was carried out in order to form a solid electrolyte interface (SEI) layer between the electrolyte and the graphite. During their first cycles, O-NG and SS-NG showed the high irreversible capacities of 39.8 and 40.9 mAh/g, respectively. Figure 4c illustrates the cycle performance of the two materials; the first discharge capacities of O-NG and SS-NG were 352.9 and 357.8 mAh/g, respectively, comparable to that of synthetic graphite. The cycle life of the SS-NG sample was about 5% greater than that of O-NG. The discharge capacities of both O-NG and SS-NG samples started to decrease

after a similar number of cycles.

The first-cycle discharge capacity of O-NG was comparable to that of synthetic graphite. However, it is intuitive to expect that the use of natural graphite without purification in a lithium-ion battery might damage the electrolyte, due to the various impurities present in the natural graphite. But, if this expectation proved false, low-purity natural graphite could be used generally as anode materials for lithium-ion batteries. To investigate the impurities' influence, electrolyte samples collected after charge-discharge testing were analyzed by ICP-MS; for comparison, samples were also analyzed of electrolytes into which electrodes were dipped for 7 days without electrochemical cycling. Table 1 lists the ICP-MS analysis results, including impurity compositions of the O-NG powder as well as those of

electrolyte samples after charge-discharge testing of beaker cells or dipping. Large amounts of Al and Fe, among various other impurities, were detected in the O-NG powder. However, negligible impurities were detected in electrolyte samples subjected either to charge-discharge testing or dipping testing, indicating that no impurities dissolved from the natural graphite into the electrolyte.

Conclusions

The surface modification of natural graphite by means of soft carbon coating and sphericalization produced remarkable changes in crystallite size and in D-band peak intensity. A soft carbon-coated sample showed better capacity retention than pristine natural graphite during 50 cycles. Although the natural graphite sample had large amounts of impurities, including transition metals, these impurities dissolved negligibly into the electrolyte during electrochemical cycling. Thus, natural graphite including various impurities could be used as an anode material for lithium-ion batteries. Furthermore, sphericalization and soft carbon coating treatments can enhance natural graphite's cycle performance regardless of these impurities.

Acknowledgments

This research was financially supported by the Ministry of Trade, Industry and Energy (MOTIE) and Korea Institute for Advancement of Technology (KIAT) through the Promoting Regional Specialized Industry.

References

1. Y. Wu, C. Jiang, C. Wan, E. Tsuchida, *Electrochem. Commun.* 2 (2000) 272.
2. S.G. Oh, R.J. Baker, *J. Catal.* 128 (1991) 137.
3. R.B. Bjorklund, C.U. Odenbrand, G.M. Bundim, A.H. Anderson, B. Lienderberg, *J. Catal.* 119 (1989) 201.
4. Y. Wu, C. Jiang, C. Wan, E. Tsuchida, *Electrochem. Commun.* 11 (2001) 1233.
5. Y. Wu, C. Jiang, C. Wan, R. Holze, E. Tsuchida, *Electrochem. Commun.* 4 (2002) 483.
6. W.H. Qiu, G. Zhang, S.G. Lu, Q.G. Liu, *Solid State Ionics* 121 (1999) 73.
7. Q.M. Pan, K.K. Guo, L.Z. Wang, S.B. Fang, *Solid State Ionics* 149 (2002) 193.
8. H. Wang, T. Ikeda, K. Fukuda, M. Yoshio, *J. Power Sources* 83 (1999) 141.
9. J. Qui, G. Wang, C. Zhao, *J. Nanopart. Res.* 10 (2008) 659.