

Evaluation of low-purity natural graphite as a cost-effective anode active material for lithium ion batteries

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Low-purity natural graphite as an anode active material for lithium ion batteries was studied in order to reduce the cost of lithium ion batteries. The electrochemical performance of low-purity natural graphite was compared to that of high-purity commercial grade graphite. No significant differences of the morphology or crystal structure were observed in the SEM, XRD, and Raman measurements. Based on the EDX and ICP-AES results, relatively larger amounts of Al and Fe than other impurities were found in the low-purity natural graphite powders. Although the LP18-99 sample contained various impurities, it showed good performance in comparison with the NG-R sample.

Key words: Lithium ion batteries, Natural graphite, Impurity, Crystal disorder.

Introduction

A lithium ion battery is a high energy density battery that is widely used in portable electronic devices. In recent years, to meet the demand for batteries to possess a higher energy density and improved cycle properties, new attempts have been made to develop alternative electrode materials or to design new structures of electrode materials [1-5]. Meanwhile, the cost of materials and manufacturing processing is one of the main issues for mobile electronic device and electric vehicle applications [6-9].

Graphite, which is a carbonaceous material, has shown high capacity and good cycling performance when used as a lithium intercalation compound. Graphite can be divided into synthetic and natural graphite. Most synthetic graphite must be heated above 2400 °C to form a lamellar structure. The graphitization process is very expensive, which reduces its commercial competitiveness. On the contrary, natural graphite is very cheap and abundant. Due to its low-cost advantage, natural graphite is highly attractive as an anode active material for lithium ion batteries. However, the material cost should be reduced further in order to be used for electric vehicles and energy saving systems. The purity grade of natural graphite can be classified based on the purification process. As the purity requirement increases, more purification steps are needed, resulting in increased costs. Therefore, the main issue for the application of natural graphite as an anode active material is to use

low-purity natural graphite without encountering critical problems.

In this study, the phase, structure, morphology, and particle size distribution of low-purity natural graphite were investigated. Inductively coupled plasma mass spectroscopy (ICP-MS) was used to confirm the dissolved impurities in the electrolyte after charge-discharge testing. Finally, the electro-chemical properties of the low-purity natural graphite as an active material for lithium ion batteries were evaluated.

Experimental

Low-purity natural graphite (LP18-95, 95% and LP18-99, 99%, China) was used as the starting material. For comparison, commercial grade natural graphite (NG-R, 99%, Posco Chemtech, Korea) was used as a reference material. The morphology of the natural graphite powders was observed by scanning electron microscopy (SEM, JSM-5900, JEOL, Japan). The particle size of each powder was measured by a dynamic light scattering method (ELS 6000 zeta potential and particle size analyzer, Otsuka Electronics, Japan). Powder X-ray diffraction (XRD, MAX-2500, RIGAKU) analysis was conducted using Cu K α radiation with a wavelength $\lambda = 1.5406 \text{ \AA}$. The crystallite sizes (L_a and L_c) were calculated on the basis of the d002 XRD lines by application of the Scherrer equation. The crystallinity of the graphite powders was investigated by Raman spectroscopy (LabRAM, Horiba Jobin-Yvon). The concentrations of impurities in the natural graphite were determined by using an inductively coupled plasma atomic emission spectrophotometer (ICP-AES).

A working electrode paste was fabricated from a mixture of natural graphite with a binder consisting of

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carboxymethylcellulose (CMC)/styrene-butadiene rubber (SBR) dissolved in D.I. water. The weight ratio of graphite to binder (CMC : SBR = 1 : 1) was 96 : 4. The prepared paste was coated onto 10 μm Cu foil by using a doctor blade and then dried under vacuum at 120 $^{\circ}\text{C}$ for 12 h. Electrochemical characterizations were conducted using CR2032 coin-type cells with a Cellgard 2300 porous membrane separator with a thickness of 20 and 1 M $\text{LiPF}_6\text{-EC/DMC}$ (1 : 1 in volume ratio) electrolyte. Lithium metal foil was used as the counter electrode.

Results and Discussion

Fig. 1 shows SEM images of the LP18-95, LP18-99, and NG-R powders. The morphology of the particles reveals a spherical shape. Generally, natural graphite has flake shapes with sharp edges. However, the original natural graphite was milled in order to increase the tapped density of the electrode. The crushed particles agglomerated and became rounded due to the

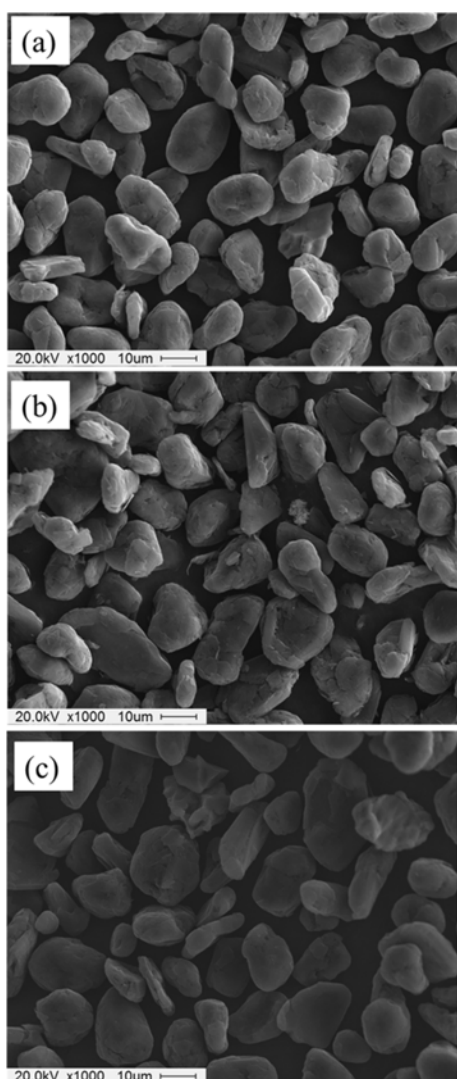


Fig. 1. SEM images of natural graphite powders: (a) LP18-95, (b) LP18-99, and (c) NG-R.

Table 1. ICP-AES analysis results for the natural graphite powders.

Sample	Element concentration (ppm)				
	Al	Fe	Zn	Cr	S
LP18-95	3031	5173	7	5	49
LP18-99	610	2678	0	0	0
NG-R	0	8	1	1	0

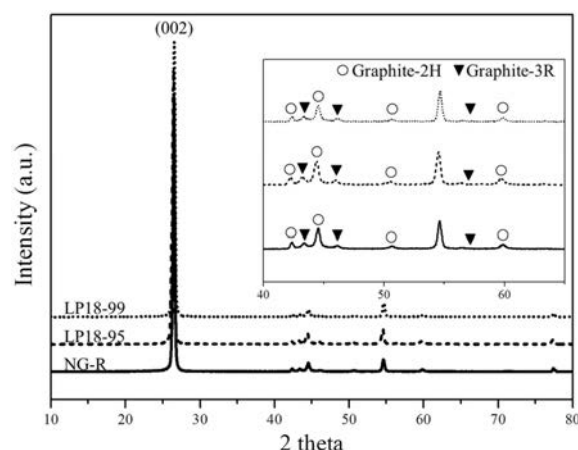


Fig. 2. XRD patterns of natural graphite powders.

unstable surface energy during ball milling, a process which is referred to as sphericalization. All of the samples studied in this work were treated by sphericalization. According to the particle size analysis, the mean diameters of the LP series and NG-R powders were 18 and 16 μm , respectively.

The carbon contents of LP18-95, LP18-99, and NG-R in the reported certifications are 95, 99, and 99.98%, respectively. ICP-AES analysis was carried out in order to confirm the other elements except for carbon in the natural graphite samples and the results are shown in Table 1. While commercial grade NG-R powder has a negligible amount of impurities, unrefined natural graphite such as the LP18-95 and LP18-99 samples contain a large amount of impurities. The LP18-95 powder has a much larger amount of impurities than the LP18-99 powder. Certain impurities such as metal ions or oxides may lead to side reactions and interrupt Li-ion insertion/de-insertion. In this regard, if the low-purity natural graphite does not cause critical problems due to impurities, it may be possible to use unrefined natural graphite as an anode active material for lithium-ion rechargeable batteries.

The XRD patterns of the low-purity natural graphite powders and commercial grade NG-R powder are shown in Fig. 2. All samples have both hexagonal and rhombohedral phases. While the diffraction peaks for the (002) and (004) planes correspond to a hexagonal structure, the diffraction peaks for the (102) and (012) planes correspond to a rhombohedral structure [10]. Based on the XRD measurements, the crystallite size of the natural graphite powders was calculated by the Scherrer equation [11] and the results are listed in

Table 2. d(002) spacing and crystallite size of natural graphite powders based on XRD data.

Sample	$d_{(002)}$ (Å)	Crystallite size (μm)	
		L_c	L_a
LP18-95	3.3683	26.2	53.5
LP18-99	3.3533	26.9	55.1
NG-R	3.3488	27.8	56.8

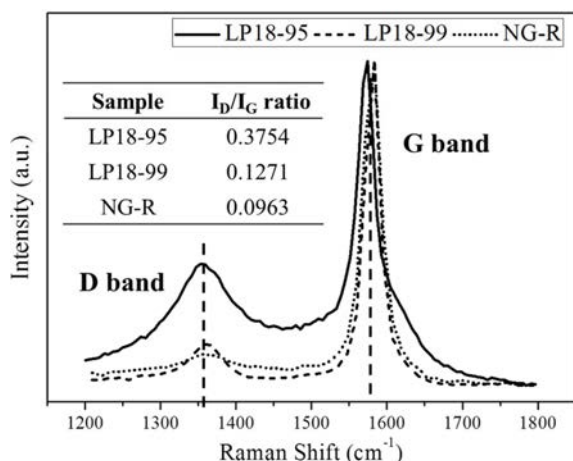
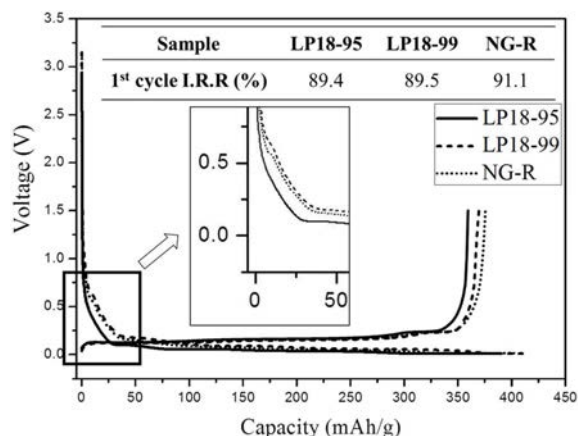
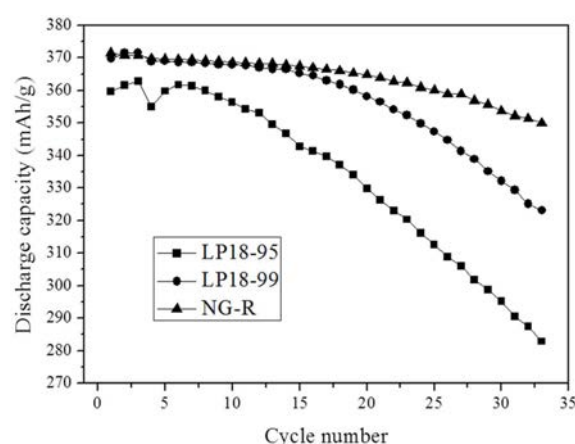
**Fig. 3.** Raman spectra of natural graphite powders.**Fig. 4.** Voltage versus capacity curves and irreversible retention rate (I.R.R.) of natural graphite anode materials at the 1st cycle.

Table 2. The crystallite size of the LP18-95 powder is the lowest (26.2 nm) while its d002 spacing is the highest (3.3683 Å). However, there are no significant differences of the crystal structures due to impurities.

Raman spectra were used to analyze the degree of structural disorder in the natural graphite powders (Fig. 3). While the G band at $1,600\text{ cm}^{-1}$ corresponds to E2g vibrational modes in the graphitic region of carbon material, the D band around $1,350\text{ cm}^{-1}$ corresponds to the A1g mode in the disordered region of carbon materials or edge plane of powdery carbon [12]. The degree of structural disorder can be quantified by the ratio of the D band intensity (I_D) to the G band intensity (I_G). The I_D/I_G values of LP18-95, LP18-99, and NG-R were 0.3754, 0.1271, and 0.0963, respectively. This

**Fig. 5.** Discharge capacities of the natural graphite anode materials as a function of the cycle number.

indicates that the LP18-95 sample is less crystalline than the other samples due to both its low purity and small crystallite size. A disordered structure allows lithium ions to be inserted into free space more easily than an ordered structure. However, it is very difficult to de-insert lithium ions in an irregular structure. In the case of the LP18-95 samples, the diffusion of lithium ions may be disturbed by the impurities and trapped by the disordered structure.

Fig. 4 shows the charge-discharge curve of the natural graphite anodes at the 1st cycle and the irreversible capacity was calculated based on the curve. It is clear that all of the discharge curves have quite similar shapes. This indicates that there are no significant differences of the Li-ion insertion/de-insertion structure and mechanism between the low-purity natural graphite and refined natural graphite [13]. The irreversible capacity for the 1st cycle is generally known to be due to the formation of a solid electrolyte interface (SEI) film and decomposition of electrolyte. During the first cycle, an initial dramatic decrease from the open circuit voltage to around 0.7 V occurs and then, a single plateau is formed. This is associated with the formation of a SEI film between the graphite electrode and electrolyte. Unlike the LP18-95 sample, both the LP18-99 and NG-R samples showed a plateau region from 0.5 to 0.7 V. This result demonstrates that the LP18-95 sample does not form a SEI film. Nevertheless, the LP18-95 sample exhibits a higher irreversible capacity than the other samples. This may be attributed to the crystal disorder. As shown in Fig. 3, the I_D/I_G ratio of LP18-95 is much higher than that of the other samples due to both its low purity and small crystallite size. This indicates that the LP18-95 sample has many less-crystalline phases. The higher amount of less-crystalline phases leads to an increase of the irreversible capacity during the charge-discharge reactions where the 1st cycle I.R.R. of LP18-95 is the lowest (89.4%) due to its high irreversible capacity.

Fig. 5 shows the discharge capacity retentions over 33 cycles. The first discharge capacities of LP18-95,

LP18-99, and NG-R were 359.7, 369.7, and 371.5 mAh/g, respectively, which are comparable to that of synthetic graphite. The NG-R sample exhibited the best performance with a capacity retention of 94.2% (33th/1st cycle). In the case of the low-purity natural graphites, the LP18-95 and LP18-99 samples showed capacity retentions of 78.7 and 87.4%, respectively. Although the first discharge capacities of LP18-95, LP18-99, and NG-R are comparable, the cycle retention of the LP18-95 sample decreased more rapidly than that of the LP18-99 and NG-R samples over 33 cycles. However, the LP18-99 sample can be used as a potential anode active material for lithium ion batteries considering its initial capacity and performance over 15 cycles.

Conclusions

The morphology, structure, impurities, and electrochemical performance of low-purity natural graphite were investigated for use as a cost-effective anode active material for lithium ion batteries. There were no significant differences of the morphology or crystal structure as a result of the purity. Al and Fe were found as major impurities in the low-purity natural graphite powder. Although the overall electrochemical performances of the low-purity natural graphites are insufficient compared to that of the commercial grade sample, the cycle retention of the LP18-99 sample is comparable to that of the commercial sample. By means of further treatment such as chemical or thermal oxidation, carbon coating, and mechanical milling, the low-purity natural graphite could be used as an anode active material for lithium ion batteries.

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