

A comparative study on low-purity natural graphite with various metal oxide impurities as an anode active material for lithium ion batteries

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Low-purity natural graphite, which is used as an anode active material for lithium-ion batteries, contains various impurities. To investigate the effects of these impurities on the lithium ion battery system, various metal oxides such as Fe₂O₃, Al₂O₃, and SiO₂ were mixed with high-purity natural graphite using a glycine nitrate process (GNP) or hydrothermal method. While there are no significant changes in the physical or chemical structure due to the addition of metal oxide impurities, the electrochemical performance was considerably improved. Both Fe₂O₃- and SiO₂-natural graphite composites showed a larger first charge capacity and better capacity retention compared to the high-purity natural graphite (NG-R) due to the conversion reaction and formation of the solid electrolyte interface (SEI) film, respectively. Specifically, the 05-Fe sample showed a charge capacity of 421.8 mAh/g at the first cycle, but a high irreversible capacity of 50.4 mAh/g due to the irreversible conversion reaction. Nevertheless, the 05-Fe sample exhibited a significantly higher capacity retention (95.9%) than NG-R (84.9%).

Key words: lithium-ion batteries, natural graphite, impurity, low-purity, anode materials.

Introduction

The use of carbonaceous materials such (e.g., graphite) as a lithium intercalation compound has shown a high capacity and good cycling performance [1-5]. Graphite materials can be divided into synthetic and natural graphite. However, the use of synthetic graphite in lithium ion batteries for electric vehicles and energy storage system (ESS) is limited due to its relatively high costs. In this regard, relatively inexpensive natural graphite is a suitable alternative for synthetic graphite [6].

Natural graphite (NG) has been attractive as a promising anode material for lithium ion batteries due to its appropriate charge/discharge profile, high reversible capacity, and low cost. However, pristine natural graphite contains various impurities, such as Al, Fe, and Si. For commercial use, pristine natural graphite should be refined because such impurities have negative effects on both the electrolytes and electrodes of lithium ion batteries. The purity grade of natural graphite can be classified based on the purification process [7]. As the purity requirement increases, more purification steps are needed, resulting in high costs. Therefore, the main goal for the application of natural graphite as an anode active material is to use low-purity natural graphite with a minimal purification process. Since most impurities in low-purity natural graphite are Fe₂O₃,

Al₂O₃, and SiO₂ [8, 9], these metal oxides were introduced to high-purity natural graphite using a glycine nitrate process (GNP) or hydrothermal method in this study in order to achieve a precise understanding of the effects of these impurities on the structure, stability, and electrochemical performance.

Experimental Procedure

Spherical natural graphite (Poscochemtech, Korea) with an average particle size of 18 μm and a purity of 99.98% was used as the matrix powder, which is called NG-R. Fe(NO₃)₃·9H₂O (98+%, metals basis, Alfa Aesar, UK), Al(NO₃)₃·9H₂O (98+%, ACS reagent Alfa Aesar, UK), and tetraethyl orthosilicate (TEOS, Sigma-Aldrich, Germany) were used as precursors for the metal oxide impurities. The Fe₂O₃- or Al₂O₃-natural graphite composite powders were prepared by a glycine nitrate process (GNP) [10, 11]. Appropriate amounts of metal nitrates (Fe or Al), glycine (99%, Alfa Aesar, UK) and natural graphite were dissolved into deionized water (D.I.) water. After stirring for 2 h, the mixed solution was heated at 250 °C until combustion occurred. The residue formed by the combustion was calcined at 500 °C in an air atmosphere. The SiO₂-natural graphite composite powder was synthesized by a hydrothermal method [12-14]. The precursor solution was prepared with TEOS and natural graphite in ethanol. Then, HNO₃ and D.I. water were added to accelerate the hydrothermal reaction. After 12 hrs of hydrothermal treatment at 160 °C, the residue was dried for 24 hrs at 60 °C. The dried powder was calcined at 500 °C for

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2 hrs in an air atmosphere. As-synthesized metal oxide-natural graphite composite powders were also named 05- or 10- according to the amount of impurities added. The prefixes of 05- and 10- represent 5 and 10 wt% of impurity as a designed amount, respectively.

X-ray diffraction (XRD, MAX-2500, Rigaku, Japan) and Raman spectroscopy (LabRAM, Horiba Jobin-Yvon, Japan) were used to verify the structural changes before and after the synthesis process. Morphology and compositional characteristics of the metal oxide-natural graphite composite powders have been studied by using field emission scanning electron microscopy (FE-SEM, SUPRA 40VP, Carl Zeiss, Germany) with an energy dispersive spectrometer (EDS). The impurities in the powders were confirmed by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Ultima2, Horiba Jobin-Yvon, Japan) and X-ray photoelectron spectroscopy (XPS, AXIS Ultra DLD Kratos, UK).

Coin cells (CR2032) for the electrochemical measurements consisted of a working electrode (metal oxide-graphite composite powders), a counter electrode (Li metal), and a separator (Celgard 2300). 1 M LiPF₆ in EC:DMC (1:1, volume ratio) was used as an electrolyte. The working electrode slurry was fabricated from a mixture of natural graphite with a binder of carboxymethylcellulose (CMC)/styrene-butadiene rubber (SBR) and a conductive agent of super-p dissolved in water; the weight ratio of graphite to binder was 95/2/2/1. The prepared slurry was coated onto 10 μ m Cu foil using a doctor blade, and was then dried under vacuum at 120 °C for 12 hrs.

A battery tester (WBCS-3000, Wonatech, Korea) was used for electrochemical characterization. The initial three cycles were charged to 5 mV at a 0.1 C-rate using a constant current (CC) method, and then charged to a constant voltage until it decreased to 1/50 of the initial current rate. The discharge process was conducted up to 2 V at a 0.1 C-rate by the CC method. Subsequently, the charge-discharge characteristics were evaluated in the same manner for ten cycles at the 0.2 C-rate, and then 50 cycles at the 0.5 C-rate. Cyclic voltammetry (CV) measurements were performed using a beaker cell with three-electrode method, wherein Li metal was employed as a reference electrode. CV analysis was conducted in a voltage range of 0 to 3 V at a scan rate of 0.1 mV/s.

Results and Discussion

The XRD analysis was performed to confirm the phases of the metal oxide-natural graphite composite powders. No secondary phase, except for the as-designed metal oxide and natural graphite matrix, was found in all the composite powders, as shown in Fig. 1. Higher amounts of impurity yielded greater metal oxide intensities. While hematite (#33-0664) with a rhombohedral structure was found in the 05-Fe and 10-Fe samples, corundum (#46-1212) with a rhombohedral structure was found in the 05-Al and 10-Al samples. The 05-Si and 10-Si samples have no distinct peaks with a broad peak around 20-30 degrees, which indicates SiO₂ may exist as an amorphous phase. The

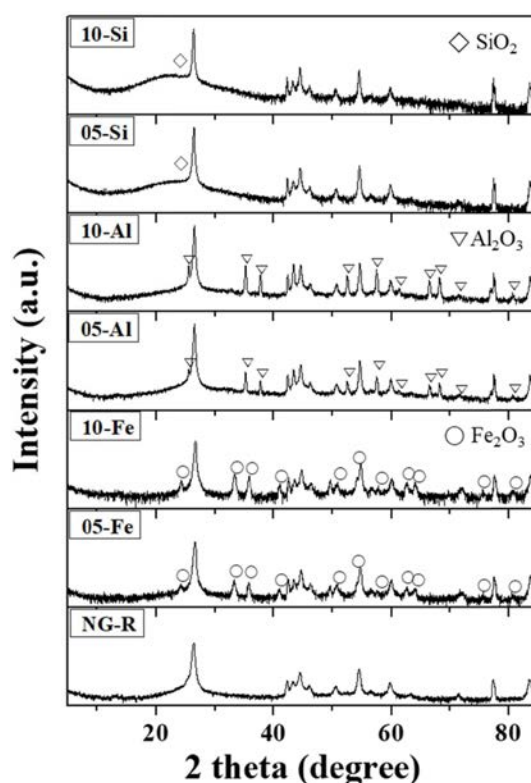


Fig. 1. XRD patterns of the high-purity natural graphite (NG-R) and metal oxide-natural graphite composite powders.

Table 1. EDS and XPS analysis results for the NG-R and metal oxide-natural graphite composite powders.

Sample	Element concentration analyzed by EDS (wt%)			Element concentration analyzed by XPS (wt%)		
	Carbon	Oxygen	Metal	Carbon	Oxygen	Metal
NG-R	94.85	5.15	0	92.72	7.28	0
05-Fe	93.36	4.82	1.82	82.29	13.65	4.06
10-Fe	86.58	6.46	6.96	75.17	17.45	7.38
05-Al	91.62	6.30	2.08	84.37	10.89	4.74
10-Al	89.15	7.56	3.30	78.57	13.03	8.39
05-Si	91.40	7.07	1.53	69.78	18.70	11.53
10-Si	88.34	9.73	1.94	58.15	24.45	17.40

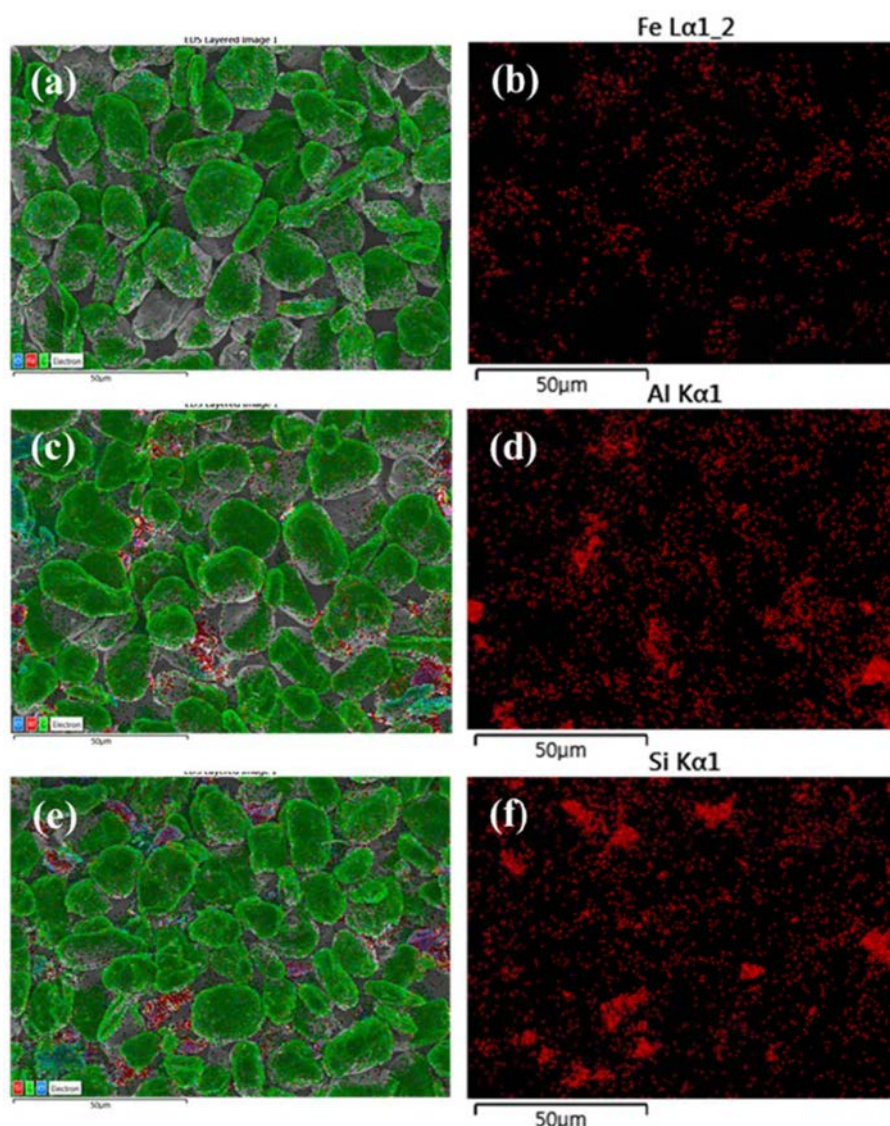


Fig. 2. SEM images and EDS data of the metal oxide-natural graphite composite powders: (a, b) 10-Fe, (c, d) 10-Al, and (e, f) 10-Si.

high-purity natural graphite (NG-R) used as the matrix had both hexagonal and rhombohedral structures.

The morphology of the metal oxide-natural graphite composite powders was observed via FE-SEM with EDS, as shown in Fig. 2. Fine metal oxide particles were evenly distributed in all the samples. However, some Al_2O_3 and SiO_2 particles were found to be agglomerated. The metal oxide particles are mainly formed on the edge surface of the graphite.

EDS and XPS analyses were carried out to determine the relative amount of impurity in the composite powder and the results are shown in Table 1. There is a slight difference between the measured value and the designed content, which may be a problem with the sampling method used. Meanwhile, the amount of metal oxide detected by XPS is larger than that detected by EDS. While EDS mapping mainly analyzes the components to depths of tens of micrometers, XPS mainly analyzes the surface to several nanometers.

Since metal oxide is added to natural graphite, which has already been finished via a sphericalization process, most of the added metal oxide is placed onto the surface of the natural graphite. Therefore, it seems that a higher amount of metal oxide was detected by XPS than EDS.

Raman spectra were used to analyze the degree of structural disorder as shown in Fig. 3. While distinct peaks of Fe_2O_3 were found at 210 and 278 cm^{-1} , a very strong peak of Al_2O_3 at $4,390\text{ cm}^{-1}$ was detected. In the case of the SiO_2 -natural graphite composite powder, the SiO_2 peaks were not detected because the fluorescence reaction was so severe that no distinct peaks could be identified. Meanwhile, crystalline graphite showed distinct peaks at $1,350$ and $1,580\text{ cm}^{-1}$, which are the D band peak and G band peak, respectively. The intensity ratio of the D band to G band (I_D/I_G) was calculated to confirm the degree of structural disorder in the natural graphite. The greater the amount of Fe_2O_3 added, the larger the resulting

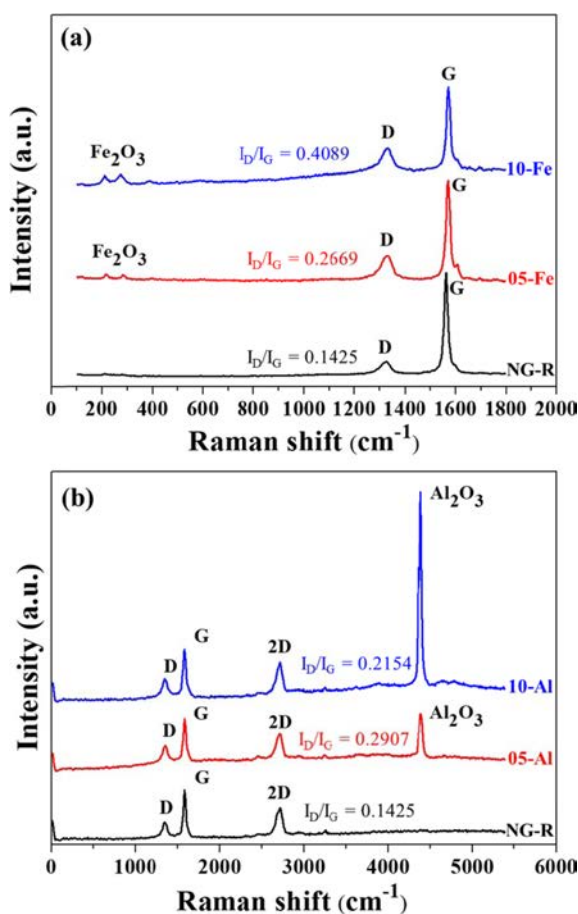
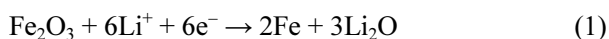


Fig. 3. Raman spectra of the (a) Fe_2O_3 - and (b) Al_2O_3 -natural graphite composite powders.

I_D/I_G ratio, which indicates that the degree of structural disorder increases. This phenomenon is attributed to the Fe_2O_3 adsorbed on the natural graphite surface, as well as functional groups generated during the calcination process. On the other hand, the I_D/I_G ratio of the Al_2O_3 -natural graphite composite powder decreases with increasing amounts of Al_2O_3 .

The charge-discharge profiles of the Fe_2O_3 -natural graphite composite sample at the first cycle with a C-rate of 0.1 C are presented in Fig. 4(a). The discharge curve of the first cycle can be divided into two regions, marked with circles. Region I with a plateau around 0.7 V corresponds to the processes of lithium conversion on the Fe_2O_3 nanoparticles, accompanied by the reduction reaction from Fe^{3+} to Fe^{2+} and from Fe^{2+} to Fe^0 , described as follows:



Additionally, the formation of a solid electrolyte interface (SEI) film on the surface of natural graphite particle occurs in this region. Region II corresponds to the lithium ion staging, where lithium ions are inserted into the graphite layer. Natural graphite has both a hexagonal structure and rhombohedral structure, as

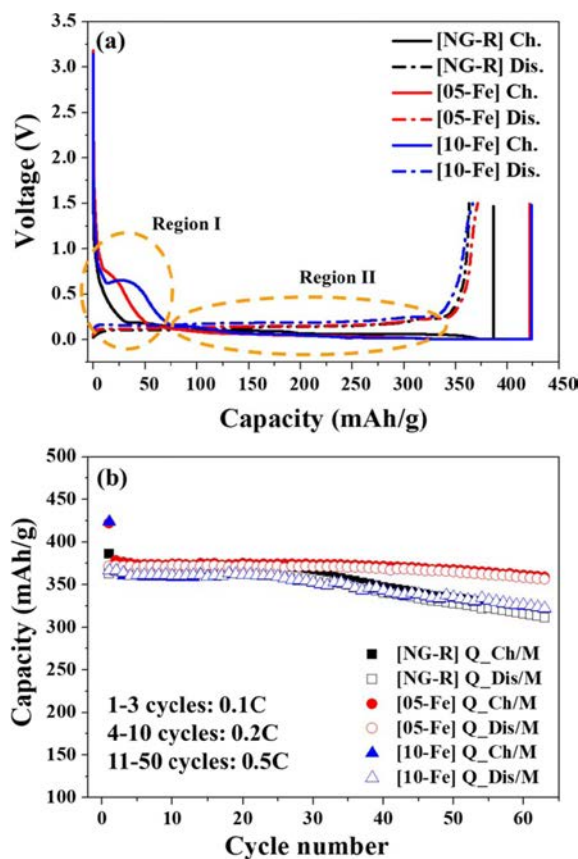


Fig. 4. (a) Charge-discharge curves and (b) capacity retentions of NG-R, 05-Fe, and 10-Fe anode materials.

Table 2. Charge-discharge characteristics of the NG-R and metal oxide-natural graphite composite powders.

Sample	Charge capacity at 1 st cycle (mAh/g)	Irreversible capacity at 1 st cycle (mAh/g)	Discharge capacity (mAh/g)		Capacity retention, 63 rd /4 th (%)
			4 th	63 rd	
NG-R	386.1	23.1	367.0	311.6	84.9
05-Fe	421.8	50.4	371.3	356.2	95.9
10-Fe	423.7	56.8	360.5	322.0	89.3
05-Al	374.6	24.7	353.7	317.2	89.7
10-Al	367.0	33.7	334.6	309.3	92.4
05-Si	400.9	44.1	356.8	323.8	90.8
10-Si	396.6	59.4	337.2	305.0	90.5

shown in Fig. 1. The plateau of natural graphite around 0 V is flatter than that of artificial graphite, because the lithium ion staging process depends on the interface and the ratio of the two phases. Since lithium ions can be intercalated into Fe_2O_3 nanoparticles, Fe_2O_3 as an impurity can be also used as an active material in a lithium ion secondary battery; the theoretical capacity of Fe_2O_3 is 1,007 mAh/g, which is about three times higher than that of graphite. Therefore, Fe_2O_3 is more likely to be used as an additive rather than an impurity. The cyclability of the Fe_2O_3 -natural graphite composite

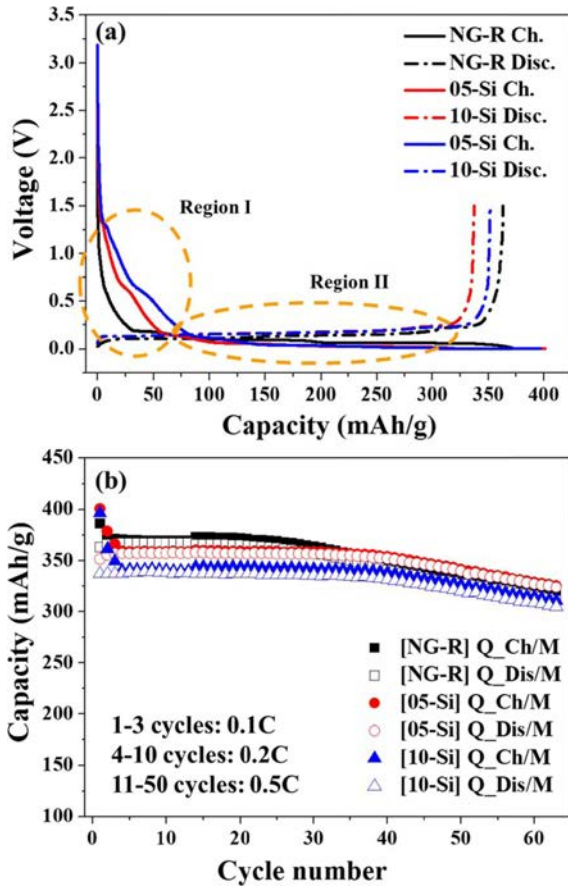


Fig. 5. (a) Charge-discharge curves and (b) capacity retentions of the NG-R, 05-Si, and 10-Si anode materials.

samples at various C-rates is shown in Fig. 4(b). The calculated capacity and capacity retention are also shown in Table 2. The Fe_2O_3 -natural graphite composite samples show better capacity retention than NG-R. The capacity retention values of 05-Fe, 10-Fe, and NG-R are 84.9, 95.9, and 89.3%, respectively. However, the irreversible capacity of the Fe_2O_3 -natural graphite composite has increased significantly, as shown in Table 2. This irreversible capacity includes not only the lithium conversion on Fe_2O_3 , but also the SEI film formation. Although the reversible capacity decreased due to the formation of a SEI film, the SEI film inhibits degradation of the anode active material, which consequently improves the cycle characteristics.

The charge-discharge profiles of SiO_2 -natural graphite composite sample at the first cycle with a C-rate of 0.1 C are presented in Fig. 5(a). Similar to the Fe_2O_3 -natural graphite composite sample, the SiO_2 -natural graphite composite sample exhibits a plateau from 0.7 to 1.4 V (Region I) corresponding to the lithium conversion on the SiO_2 nanoparticles and SEI film formation. Region II corresponds to the lithium ion staging for the graphite layer. Meanwhile, the lithium conversion on the SiO_2 can be described by the following three reactions.

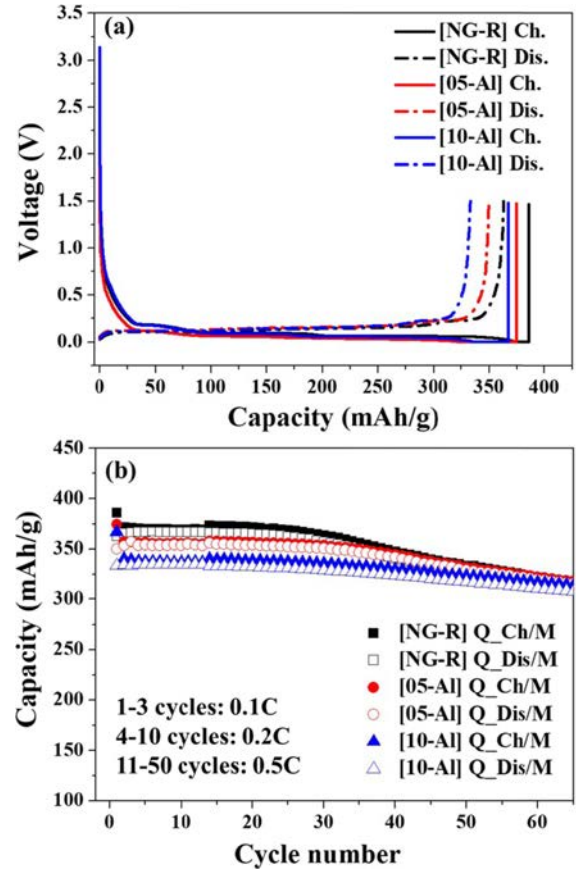
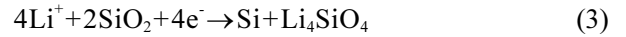
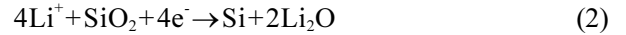


Fig. 6. (a) Charge-discharge curves and (b) capacity retentions of the NG-R, 05-Si, and 10-Si anode materials.



Generally, the formations of Li_2O or Li_4SiO_4 in reactions (2) and (3), respectively, are known as irreversible reactions [15, 16]. These compounds with their thermodynamic stability and electrochemically inactive properties result in a low capacity retention at the first cycle [17]. On the other hand, reaction (4) is reversible at room temperature [18]. The large irreversible capacity of the SiO_2 -natural graphite composite at the first cycle is due to the formation of Li_2O or Li_4SiO_4 , as well as the formation of SEI film, as shown in Table 2. However, the lithium oxide and SEI film formed in the reduction reaction contributed to the improved capacity retention compared to NG-R, as shown in Fig. 5(b).

The charge-discharge profiles of the Al_2O_3 -natural graphite composite sample at the first cycle with a C-rate of 0.1 C are presented in Fig. 6(a). Since Al_2O_3 does not react with lithium ions, the reversible capacity corresponds only to the lithium ions inserted into the graphite layer. Therefore, the Al_2O_3 -natural graphite composite sample shows both the lowest charge capacity

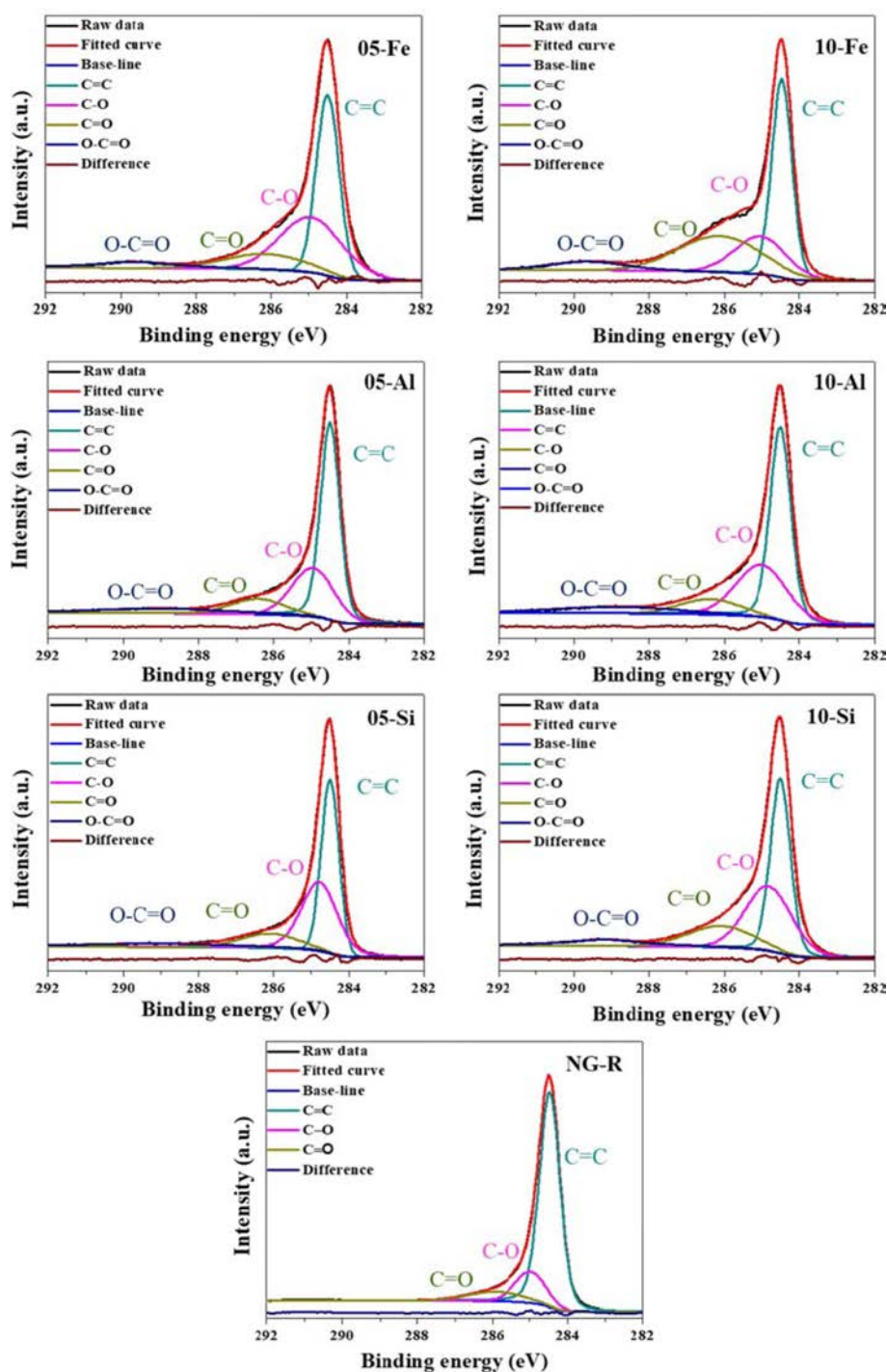


Fig. 7. Carbon 1s XPS spectra of the NG-R and metal oxide-natural graphite composite powders.

(334.6 mAh/g) and irreversible capacity (33.7 mAh/g) at the first cycle compared to the Fe_2O_3 - and SiO_2 -natural graphite composite samples.

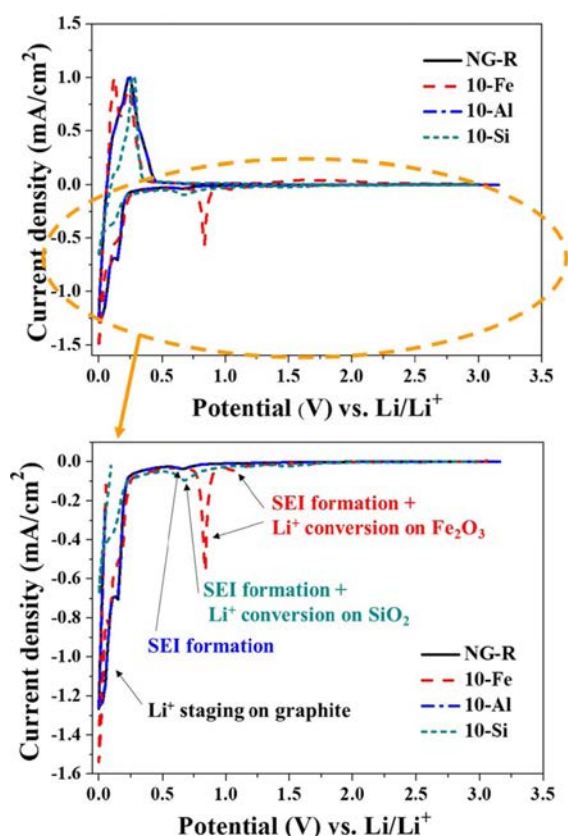
The capacity retention of metal oxide-natural graphite composites has been improved significantly compared to the NG-R sample, as shown in Figs. 4-6, and Table 2. Since the cyclic characteristics of graphite as the anode active material depend on the characteristics of the SEI film, the improved cyclability of natural graphite

through the addition of metal oxides may be due to two reasons: (1) an increase in functional groups via oxidation of the graphite surface during the heat treatment process and (2) an increase in the specific surface area by the addition of metal oxide particles.

In order to confirm the functional groups on the surface of the anode materials, XPS analysis was carried out and the results are shown in Fig. 7 and Table 3. The C 1s spectrum of all the samples showed three components

Table 3. Calculated peak proportion for the C 1s components by curve fitting from the XPS data.

Sample	Peak proportion (%)			
	C=C	C-O	C=O	O-C=O
NG-R	76.7	15.2	8.2	0
05-Fe	42.9	36.2	13.3	7.6
10-Fe	41.8	20.3	30.5	7.3
05-Al	53.5	26.5	10.6	9.4
10-Al	50.3	31.0	10.3	8.4
05-Si	42.0	36.6	11.5	9.9
10-Si	41.0	34.6	15.8	8.6

**Fig. 8.** Cyclic voltammogram of the NG-R, 10-Fe, 10-Al, and 10-Si anode materials at the first cycle.

corresponding to carbon atoms in different functional groups: aromatic carbon (C=C), carbon with C-O bonds of epoxy and alkoxy, and carbonyl carbon (C=O). Meanwhile, metal oxide-natural graphite composites showed a specific peak for carboxylate carbon (O-C=O) [19, 20]. The ratio of these functional groups has an important effect on the formation of SEI film, as well as the decomposition reaction of the electrolyte. As shown in Table 3, while the amount of the aromatic carbon (C=C) decreased, the amount of carbon with C-O bonds of epoxy and alkoxy, as well as the carbonyl carbon (C=O), increased significantly with the addition of metal oxide. This trend corresponds to the improvement of the cycle characteristics as shown

in Figs. 4-6, and Table 2. Since it is well known that the formation of SEI film improves the cyclability of the active materials, the improved cycle characteristics by the addition of metal oxides may result from formation of the SEI film.

Cyclic voltammetry was carried out in order to verify the electrochemical reactions during the charge-discharge process and the results are shown in Fig. 8. The peak below 0.25 V in the reduction region at a negative current density corresponds to the lithium ion staging into the graphite layers, known as lithiation. The peak below 0.4 V in the oxidation region at positive current density are attributed to the de-staging step (de-lithiation). Meanwhile, all the samples show specific peaks from 0.6 to 1.0 V in the reduction region, which correspond to formation of the SEI film. The peaks of the 10-Fe and 10-Si samples from 0.6 to 1.0 V are sharper and larger than those of the NG-R and 10-Al samples because the 10-Fe and 10-Si samples include a conversion reaction, as shown in Figs. 4 and 5, respectively. No other specific peaks were observed, which indicates that no side reaction occurs.

Conclusions

The effects of metal oxides such as Fe₂O₃, Al₂O₃, and SiO₂ on structure, stability, and electrochemical performance of natural graphite have been investigated. The added metal oxides play a role corresponding to the impurities contained in the low-purity natural graphite. Although the structure and chemical stability of the natural graphite were not affected by the addition of the metal oxide, the electrochemical performance was improved significantly due to the change of functional groups during the synthesis process. Specifically, both Fe₂O₃- and SiO₂-natural graphite composites showed better capacity retention and higher charge capacity than the high-purity natural graphite due to conversion reaction. This suggests that low-purity natural graphite including impurities such as Fe₂O₃ or SiO₂ can be sufficiently used as an anode active material in a lithium ion secondary battery.

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References

1. Y.P. Wu, E. Rahm, R. Holze, J. Power Sources 114 (2003) 228-236.

2. Y.P. Wu, C. Jiang, C. Wan, R. Holze, *Solid State Ionics* 156 (2003) 283-290.
3. F. Cao, I.V. Barsukov, H.J. Bang, P. Zaleski, J. Prakash, *J. Electrochem. Soc.* 147 (2000) 3579-3583.
4. H. Zhao, J. Ren, X. He, J. Li, C. Jiang, C. Wan, *Solid State Sci.* 10 (2008) 612-617.
5. L. Zou, F. Kang, X. Li, Y.P. Zheng, W. Shen, J. Zhang, *J. Phys. Chem. Solids* 69 (2008) 1265-1271.
6. H. Shi, J. Barker, M.Y. Saidi, R. Koksang, *J. Electrochem. Soc.* 143 (1996) 3466-3472.
7. K. Zaghib, X. Song, A. Guerfi, R. Rioux, K. Kinoshita, *J. Power Sources* 119-121 (2003) 8-15.
8. Y.T. Park, K.T. Lee, *J. Ceram. Process. Res.* 17 (2016) 1-4.
9. Y.T. Park, K.T. Lee, *J. Ceram. Process. Res.* 17 (2016) 348-351.
10. J. Toniolo, A.S. Takimi, M.J. Andrade, R. Bonadiman, C.P. Bergmann, *J. Mater. Sci.* 42 (2007) 4785-4791.
11. F. He, H. Wang, Y. Dai, *J. Nat. Gas Chem.* 16 (2007) 155-161.
12. Y. Fan, C. Ma, W. Li, Y. Yin, *Mat. Sci. Semicon. Proc.* 15 (2012) 582-585.
13. J. Wang, H. Zhao, J. He, C. Wang, J. Wang, *J. Power Sources* 196 (2011) 4811-4815.
14. B. Guo, J. Shu, Z. Wang, H. Yang, L. Shi, Y. Liu, L. Chen, *Electrochem. Commun.* 10 (2008) 1876-1878.
15. K.S. Song, S.Y. Yoo, K.B. Kang, H.S. Heo, Y.M. Kang, M.H. Jo, *J. Power Sources* 229 (2013) 229-233.
16. N. Yan, F. Wang, H. Zhong, Y. Li, Y. Wang, L. Hu, Q. Chen, *Sci. Rep.* 3 (2013) 1568-1573.
17. T.A. Kim, S.J. Park, S.M. Oh, *J. Electrochem. Soc.* 154 (2007) A1112-A1117.
18. X.H. Liu, L. Zhong, S. Huang, J.Y. Huang, *ACS Nano* 6 (2012) 1522-1531.
19. Q. Zhou, Z. Zhao, Y. Zhang, B. Meng, A. Zhou, J. Qiu, *Energy Fuels* 26 (2012) 5186-5192.
20. S.V. Harb, B.M. Cerrutti, S.H. Pulcinelli, C.V. Santilli, P. Hammer, *Surf. Coat. Tech.* 275 (2015) 9-16.