

Electrochemical performance of amorphous carbon coated α -Fe₂O₃/expanded natural graphite composites as anode active materials for lithium ion batteries

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An amorphous carbon-coated α -Fe₂O₃/expanded natural graphite (ENG) composite as an anode active material for lithium-ion batteries was successfully synthesized by a simple hydrothermal method. The ENG anode material used as a matrix showed better cycling performance but a larger irreversible capacity than pristine NG anode material due to the large amount of solid electrolyte interface film. The reversible capacity of the ENG anode material increased by approximately 26% through impregnation of α -Fe₂O₃ nanoparticles. Nevertheless, the capacity retention significantly decreased from 98.9 to 74.9% after 63 cycles due to volume expansion and microstructural change caused by aggregation of Fe and Li₂O during the charge-discharge process. This degradation of cycling performance was overcome by the surface coating of amorphous carbons. The reversible capacity of an amorphous carbon-coated α -Fe₂O₃/ENG composite increased with cycling and reached 576 mAh/g at the 95th cycle and 524 mAh/g at the 350th cycle, showing 99% capacity retention. The favorable cycling performance was attributed to suppression of nanoparticle aggregation, a fast charge transfer, and lowering of the contact resistance by the conductive amorphous carbon coating.

Key words: Lithium ion batteries, Natural graphite, Fe₂O₃, Expanded graphite, Anode active materials.

Introduction

Various kinds of secondary batteries, including lead-acid, nickel-cadmium, nickel-hydrogen, and lithium ion batteries, have been widely used for electronic devices [1-3]. In recent years, as the use of portable electronic devices requiring high performance has increased, lithium ion batteries have attracted considerable attention owing to their high energy density, long cycle life, low self-discharge rate, and high operating voltage [4]. The application range of lithium ion batteries extends not only to power supplies for small electronic devices, but also to electric vehicles and energy storage systems. Therefore, there is a great demand for development of high-performance, high-capacity, and low-cost lithium ion batteries.

Graphite has been used as a typical anode active material of lithium ion batteries and can be divided into synthetic and natural graphite (NG). While synthetic graphite is very expensive due to the high-temperature heat treatment above 2,400 °C required to form the lamellar structure, NG is very inexpensive and abundant. Thus, with its low-cost advantage, NG is compelling as an anode active material for lithium-ion batteries. However, pristine NG contains various impurities, such

as Al, Fe, and Si. For commercial use, the impurity level should be controlled because they have a negative effect on both the electrolytes and electrodes of lithium-ion batteries. Various endeavors, such as amorphous carbon coating [5, 6], surface modification [7-9], and complexing with metal alloy or metal oxide [10-12], have been undertaken to improve the performance of graphite as an anode active material.

Crystalline graphite with a layered structure has a theoretical capacity of 372 mAh/g with the formation of LiC₆ by intercalating lithium ions between the layers. On the other hand, nanostructured transition metal oxide (M_xO_y, M = Co, Ni, Fe) reacts with lithium ions and forms a lithium oxide exhibiting a capacity of approximately 1,000 mAh/g. For example, α -Fe₂O₃ with a rhombohedral structure is not only non-toxic and inexpensive, but also has a theoretical capacity of 1,007 mAh/g. However, despite having a very high capacity, the transition metal oxide as an anode active material has the following problems. (1) The formation of lithium oxide after the charging process engenders a large irreversible capacity owing to its low electrical conductivity. (2) The reversible capacity is reduced because of the agglomeration of metal particles and lithium oxide particles during the reaction with lithium ions. (3) The active material and the current collector may separate from each other owing to a large volume change accompanied by the charge-discharge process. For these reasons, the transition metal oxide is mainly mixed with a carbonaceous material, such as amorphous

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carbon, graphite, carbon nanotube (CNT), and graphene [13–18]. By mixing with a carbon-based material, the electrical conductivity is improved and the volume change is suppressed.

Given the above considerations, we performed a rational composition design of anode-active material while accounting for low-cost, high-capacity, and high-performance requirements. First, low-purity NG was selected as the matrix material under the low-cost consideration. α -Fe₂O₃ was added to the matrix to increase the capacity. Prior to mixing α -Fe₂O₃ and NG, the NG was chemically expanded. The α -Fe₂O₃ nanoparticles were impregnated into the expanded NG (ENG) by a hydrothermal method to suppress the aggregation of Fe and Li₂O which are the products of the reduction reaction and to buffer the volume expansion. Finally, amorphous carbon was applied as a coating to improve the cyclability. In this study, the properties of the as-synthesized amorphous carbon-coated α -Fe₂O₃/ENG composites were investigated, and their electrochemical performances as anode active materials for lithium ion batteries were evaluated.

Experimental

Preparation of materials

The spherical NG (average particle size of 20 μ m, purity of 95%, China) was used as the starting material. Expanded NG (ENG) was prepared by chemical intercalation with H₂SO₄ (60%, Samchun, Korea) and HNO₃ (97%, Samchun, Korea). After reacting at 40 °C for 1 h, the as-prepared ENG was washed with distilled water and dried at 60 °C for 24 h. It was then heated at 900 °C for 6 h in an Ar atmosphere [19].

The α -Fe₂O₃/ENG composites were prepared via a simple hydrothermal method in which 2.02 g of Fe(NO₃)₃·9H₂O (98+%, metals basis, Alfa Aesar, United Kingdom) and 1.5 g of ENG powder were stirred for 1 h with 50 and 100 ml of distilled water, respectively. Fe(NO₃)₃·9H₂O solution and ENG suspension were mixed and ultrasonicated for 30 min due to homogeneous dispersion. Then, the mixture solution was transferred to a Teflon-lined stainless steel autoclave and maintained at 160 °C for 18 h. The resulting dark-red residue was collected by filtration, washed with ethanol and distilled water each for several times, and dried at 60 °C for 24 h. The as-synthesized α -Fe₂O₃/ENG composite (ENG-Fe) powder was heated at 500 °C for 2 h to remove residues.

The ENG-Fe powder was coated with the amorphous carbon by a hydrothermal method in which 1.5 g of glucose (Alfa Aesar, United Kingdom) was dissolved in 150 ml of distilled water. Then, 1.5 g of ENG-Fe powder was added to the glucose solution, and 1 g of poly(vinylpyrrolidone) (PVP, molecular weight = 360,000, Alfa Aesar, United Kingdom) was also added as a competitive molecule to form a thin carbon film

[20, 21]. After stirring for 1 h and ultrasonication for 2 h, the mixed suspension was transferred into a Teflon-lined stainless steel autoclave and maintained at 160 °C for 24 h, followed by filtration and washing several times. The residual mixtures after filtration and washing were heated at 900 °C for 6 h in an Ar atmosphere to obtain the final amorphous carbon-coated α -Fe₂O₃/ENG composite (ENG-Fe-C) powder.

Material characterization and electrochemical performance test

X-ray diffraction (XRD, MAX-2500, Rigaku, Japan) using Cu K α radiation (λ = 0.15406 nm) was employed to identify the crystalline phase of the prepared materials. Raman spectroscopy (Nanofinder 30, TII Ltd., Japan) with a 532-nm wavelength laser light was used to verify the structural changes after the synthesis process. The morphologies of the as-synthesized powders were observed by a scanning electron microscope (SEM, JSM-5900, JEOL, Japan), field-emission scanning electron microscope (FE-SEM, SU8230, Hitachi, Japan), and high-resolution transmission electron microscope (HR-TEM, JEM-2200FS, JEOL, Japan). The Brunauer-Emmett-Teller (BET) surface areas were measured with a surface area and pore-size analyzer (ASAP2010, Micromeritics, USA).

The electrochemical performances of all the prepared samples were evaluated using CR2016 coin-type cells with Li metal as a counter-electrode, a Celgard-2300 separator, and a solution of 1 M LiPF₆ in EC/DMC (1 : 1 volume ratio) as an electrolyte. The working electrode slurry was fabricated from a mixture of 85 wt.% active material, 10 wt.% PVDF binder, and 5 wt.% Super P as a conductive agent with an appropriate amount of N-methyl pyrrolidinone (NMP). The prepared slurry was coated onto a 10- μ m Cu foil using a doctor blade and was then dried under vacuum at 120 °C for 24 h.

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 method and then charged to a constant voltage until decreasing to 1/20 of the initial current rate. The discharge process was conducted up to 1.5 V or 3 V at a 0.1 C rate for three cycles by the constant current method. Subsequently, the charge-discharge characteristics were evaluated in the same manner from the 4th to the 13th cycles at a 0.2 C rate and then from the 14th to the 63rd cycle at a 0.5 C rate. Cyclic voltammetry (CV) measurements were performed using a beaker cell with a three-electrode method, whereby 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 change in morphology during the process of

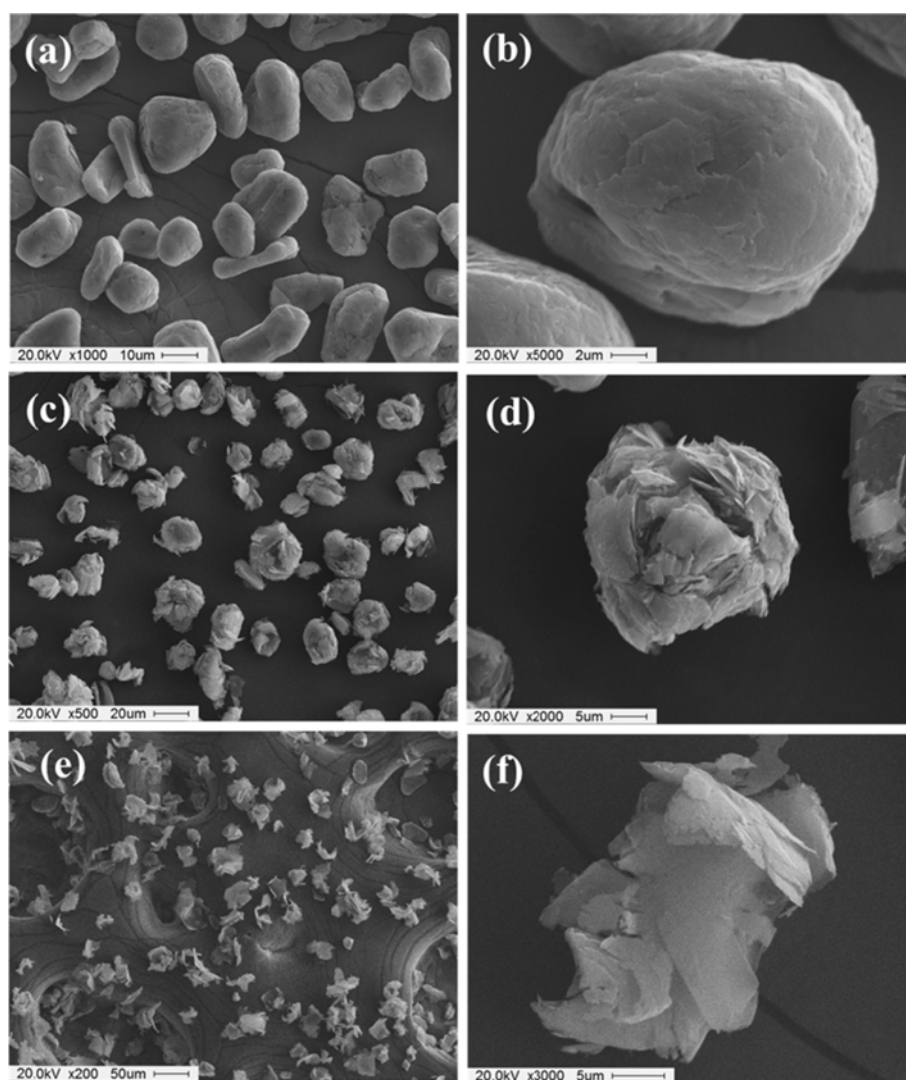


Fig. 1 SEM images of (a, b) NG base material powder, (c, d) ENG power immediately after chemical intercalation, and (e, f) ENG powder after heat-treatment at 900 °C for 6 h in Ar.

ENG synthesis is shown in Fig. 1. Generally, NG has flake shapes with sharp edges. However, to increase the tapped density of the electrode, the original NG is crushed, agglomerated, and rounded by ball milling, which is referred to as sphericalization. Therefore, NG as a starting material has a spherical shape and smooth surface, as shown in Figs. 1(a) and (b). During the chemical intercalation, ions such as SO_x^- and NO_x^- were intercalated between the graphene layers in the graphite and accompanied by interlayer widening. Then, the graphene layers were delaminated during the desorption process by electromagnetic waves or thermal energy [19]. When the inserted ions were desorbed, the degree of expansion varied depending on the temperature, energy, and amount of inserted ions. As shown in Figs. 1(c) and (d), the aggregated NG particles, having spherical shapes and smooth surfaces, were loosened, and gaps that opened between the layers were observed after the intercalation process.

After the heat treatment, the NG no longer had a spherical shape but was instead a plate shape. The graphene layers were delaminated and the NG edges were expanded (Figs. 1(e) and (f)).

Based on the matrix material of ENG, α -Fe₂O₃ was impregnated, and amorphous carbon was applied as a coating. The morphologies of the as-synthesized powders of ENG, α -Fe₂O₃/ENG composites (ENG-Fe), and amorphous carbon-coated α -Fe₂O₃/ENG composites (ENG-Fe-C) are shown in Fig. 2. The ENG powder shows a clear delamination of the graphene layers (Fig. 2(a)). In the case of the ENG-Fe powder (Fig. 2(b)), α -Fe₂O₃ nanoparticles were impregnated by the hydrothermal method at 500 °C and were mainly formed on the edge surface as well as on the delaminated graphene surface in the ENG powder. Generally, when large amounts of α -Fe₂O₃ nanoparticles are formed in graphite inter-layers, the effect of suppressing the volume change of α -Fe₂O₃ during the charge-discharge process can be maximized.

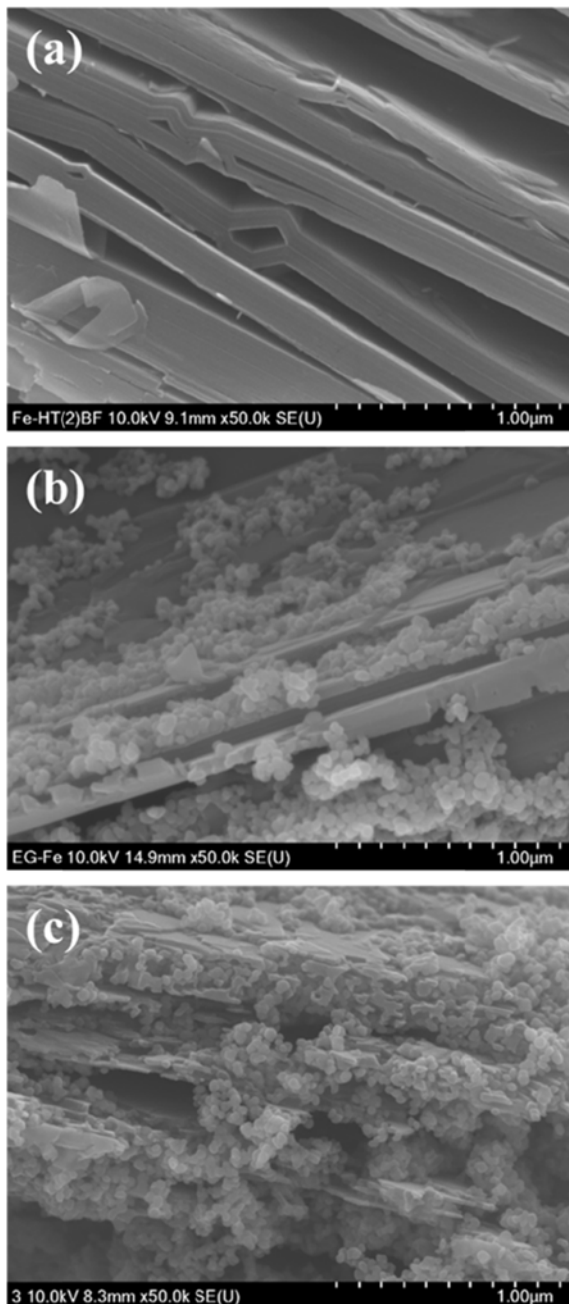


Fig. 2 FE-SEM images of the as-synthesized (a) ENG, (b) ENG-Fe, and (c) ENG-Fe-C powders.

Unfortunately, in this study, it was difficult to control the ratio of α -Fe₂O₃ impregnated on the edge surface to that on the graphite inter-layers. Meanwhile, no significant differences were identified in the morphology of ENG-Fe and ENG-Fe-C powders (Fig. 2(c)). Therefore, HR-TEM observation was conducted to identify a more detailed morphology of the ENG-Fe-C powder.

It is clearly shown in Fig. 3(a) that α -Fe₂O₃ nanoparticles with a size of approximately 50 nm are located between the cracked graphite layers. Dominant lattice fringes are clearly observed in Fig. 3(b); the

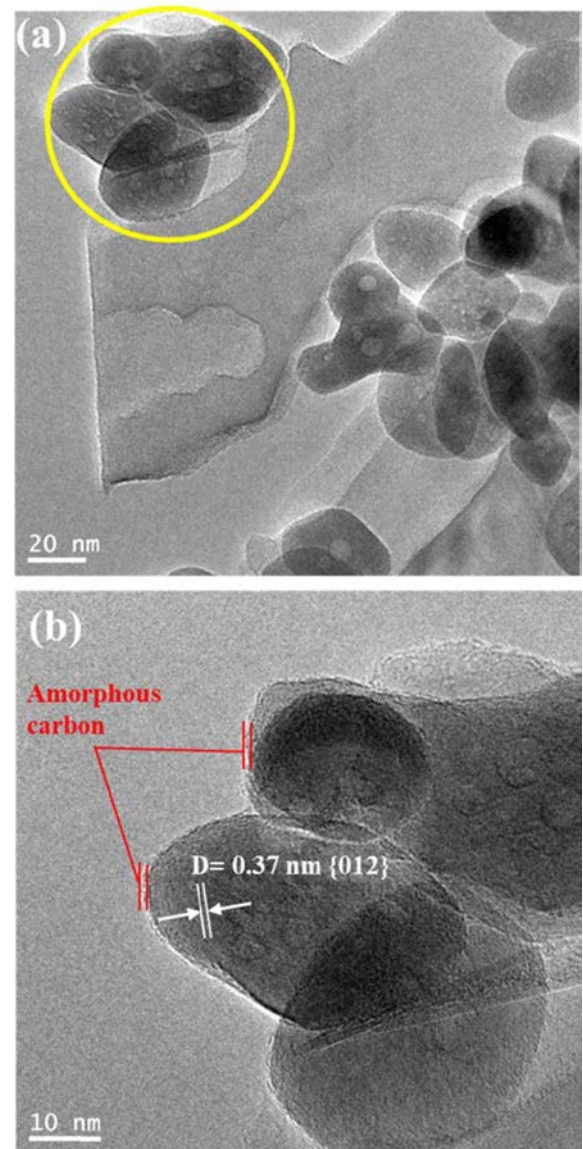


Fig. 3 HR-TEM images of (a) ENG-Fe-C powder and (b) an enlarged view of the circled area.

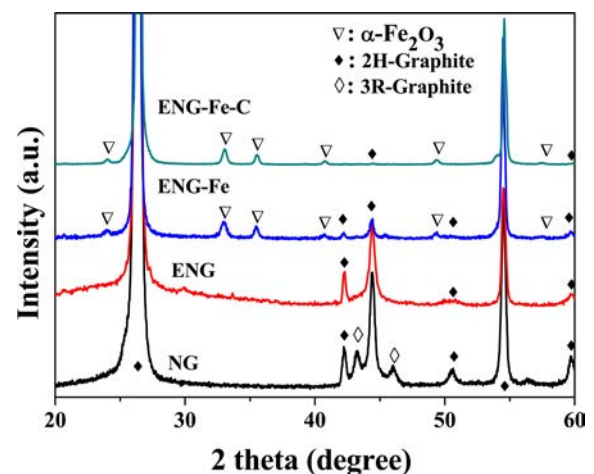


Fig. 4 XRD patterns of the as-synthesized NG, ENG, ENG-Fe, and ENG-Fe-C powders.

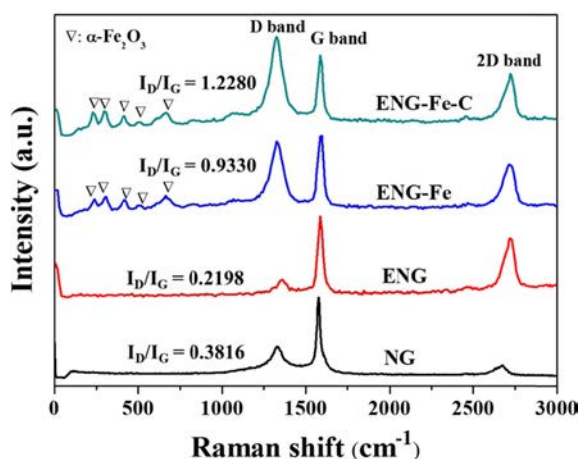


Fig. 5 Raman spectra of the as-synthesized NG, ENG, ENG-Fe, and ENG-Fe-C powders.

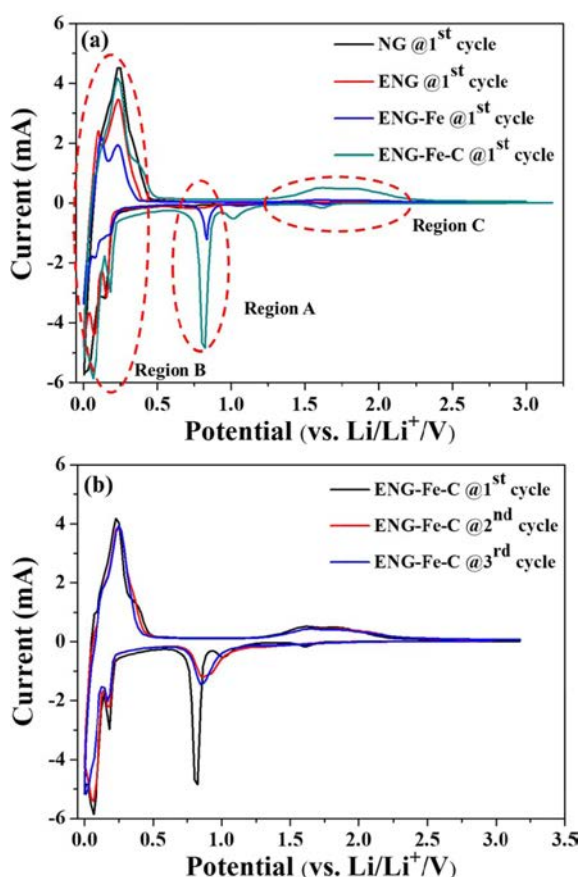


Fig. 6 Cyclic voltammogram of (a) the NG, ENG, ENG-Fe, and ENG-Fe-C anode materials at the first cycle and (b) the ENG-Fe-C anode material for 3 cycles.

distance between parallel fringes is equal to the d-spacings of the $\{012\}$ planes in the α -Fe₂O₃. It is also confirmed that amorphous carbon without lattice fringes is coated on the surface of α -Fe₂O₃ with a thickness of a few nanometers. Although the amorphous carbon coating layers are not completely uniform, it can be expected that the amorphous carbon coating may

inhibit the aggregation of Fe and Li₂O particles during the charge-discharge process.

XRD analysis was performed to confirm the phases and crystal structure of the composite powders. As shown in Fig. 4, the NG powder shows typical patterns of natural graphite with a mixture of hexagonal and rhombohedral structures [22, 23]. However, the ENG powder shows a single phase of a hexagonal structure. Since ABC-stacking layers form one unit cell in the rhombohedral structure, if the graphene layer is peeled off in the C-axis direction, destruction of the rhombohedral structure is likely to occur. Therefore, the ENG powder shows only a hexagonal graphite phase. Additionally, since the graphene layer was peeled off by the Lorentz force generated as the ions in the graphite intercalation compounds (GIC) were rapidly released, the graphene layers rapidly expanded in the C-axis direction, and the d-spacings of the $\{002\}$ planes in the hexagonal phase increased. The calculated d-spacing values of the $\{002\}$ planes in the hexagonal phase for NG and ENG powders were 0.3361 and 0.3556 nm, respectively. Meanwhile, the α -Fe₂O₃ phase was clearly identified in the XRD patterns of ENG-Fe and ENG-Fe-C powders, and no secondary phases were found in any composite powders.

Raman spectra were used to analyze the degree of structural disorder, as shown in Fig. 5. Detachment of the graphene layers can be confirmed by comparing the intensities of the G peak (I_G) and the 2D peak (I_{2D}) from the Raman spectra [24]. The G peak, called a graphite peak, is due to the doubly degenerated zone center E_{2g} mode. The 2D peak is caused by a double-resonance phenomenon and appears to be sharper in the single layer graphene than in the graphite. The ENG sample shows a significant increase in the I_{2D}/I_G ratio compared to the pristine NG sample. In the ENG-Fe and ENG-Fe-C samples, peaks from 250 to 750 cm^{-1} are indexed as α -Fe₂O₃ peaks [25]. The D peak intensity increases as the α -Fe₂O₃ nanoparticles are impregnated. The D peak is called a diamond or disordered peak, which is related to disordered structures such as diamond-like or amorphous carbon materials. Therefore, the degree of structural disorder can be quantified by the ratio of the D peak intensity (I_D) to the G peak intensity (I_G). The addition of α -Fe₂O₃ nanoparticles significantly increases the I_D/I_G ratio due to bonds of α -Fe₂O₃ and other functional groups on the graphite layer [26]. The I_D/I_G ratio also increases in accordance with the amorphous carbon coating.

Cyclic voltammetry was conducted to verify the electrochemical reactions during the charge-discharge process. The results are shown in Fig. 6. As shown in Fig. 6(a), all the samples show specific peaks around 0.75 V in the reduction region at a negative current density (Region A), which corresponds to formation of the solid electrolyte interface (SEI) film. The ENG-Fe and ENG-Fe-C samples show sharper and larger peaks

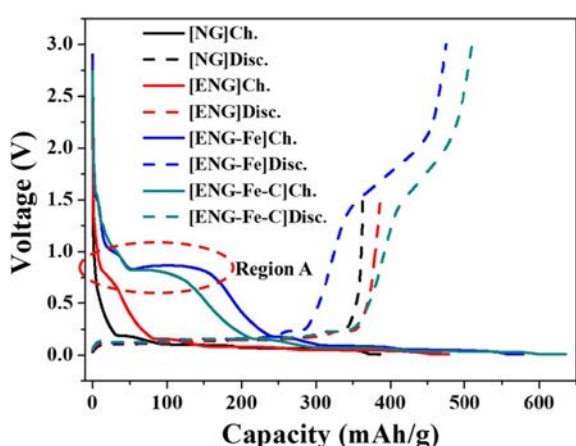
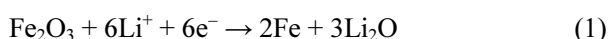


Fig. 7 Charge-discharge curves of the NG, ENG, ENG-Fe, and ENG-Fe-C anode materials at the first cycle.

in Region A than the NG and ENG samples due to the reduction reaction of $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles as well as the formation of the SEI film [27].

In Region B, the reaction of reversible lithium intercalation/de-intercalation into the NG layer occurs [28,29]. The peaks below 0.25 V in the reduction region at a negative current density correspond to lithiation. The peaks below 0.4 V in the oxidation region at a positive current density are attributed to delithiation. As mentioned above, the ENG-Fe and ENG-Fe-C anode materials undergo the lithium-conversion reaction by $\alpha\text{-Fe}_2\text{O}_3$ (Region A) as well as the reversible lithium intercalation/de-intercalation reaction into the NG layer. The lithium conversion reaction on the $\alpha\text{-Fe}_2\text{O}_3$ corresponds to Region A along with the reduction reaction from Fe^{3+} to Fe^{2+} and from Fe^{2+} to Fe^0 , described as follows:



Actually, it is very difficult to distinguish the lithium conversion reaction on the $\alpha\text{-Fe}_2\text{O}_3$ from the SEI film formation reaction because both peaks appear near 0.7 V. In addition to the lithium-conversion reaction and the SEI film formation reaction, the peaks at 1.0 and 1.6 V in the reduction region (Region C) for the samples with $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles correspond to lithium-ion intercalation into the $\alpha\text{-Fe}_2\text{O}_3$ lattice, which is known to be an irreversible reaction [15]. Meanwhile,

Fig. 6(b) shows cyclic voltammogram of the ENG-Fe-C anode material for three cycles. Specific peaks around 0.75 V in the reduction region at a negative current density (Region A) significantly decrease, and peaks at 1.0 and 1.6 V (Region C) in the reduction region at a negative current density disappear after the first cycle. This finding indicates that SEI film formation and the reduction reaction of $\alpha\text{-Fe}_2\text{O}_3$, as well as the irreversible lithium-ion intercalation into the $\alpha\text{-Fe}_2\text{O}_3$ lattice, may lead to a large irreversible capacity. Details of the irreversible capacity are discussed in the next section.

The charge-discharge profiles of the NG, ENG, ENG-Fe, and ENG-Fe-C anode materials at the first cycle with a C-rate of 0.1 C are shown in Fig. 7. The ENG-Fe and ENG-Fe-C samples show stronger intensities than the NG and ENG samples in Region A, with a plateau around 0.7 V corresponding to the processes of lithium conversion on the $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles as well as the SEI film formation. The characteristic values for the charge-discharge process, as well as the BET surface areas of the NG, ENG, ENG-Fe, and ENG-Fe-C anode materials, are listed in Table 1. The charge capacity of the ENG sample at the first cycle is larger than that of the NG sample owing to an increase in the specific surface area. The addition of $\alpha\text{-Fe}_2\text{O}_3$ leads to a further increase in the charge capacity due to the lithium conversion reaction by $\alpha\text{-Fe}_2\text{O}_3$, which is described as equation (1), and the lithium ion intercalation into the $\alpha\text{-Fe}_2\text{O}_3$ lattice.

Similarly, the ENG-Fe-C sample exhibits the largest charge capacity because lithium ions can be intercalated into the amorphous carbon. However, the irreversible capacity also increases in a similar manner. An increase in the specific surface area of the active material is one of the factors that increase the SEI film formation reaction, which hence increases the irreversible capacity at the first cycle. Therefore, the ENG sample with a larger specific surface area has a much larger irreversible capacity than the NG sample. Moreover, the addition of $\alpha\text{-Fe}_2\text{O}_3$ increases the irreversible capacity due to the lithium conversion reaction and the irreversible lithium-ion intercalation by $\alpha\text{-Fe}_2\text{O}_3$ as well as the SEI film formation reaction, as shown in Figs. 6 and 7. In the case of the ENG-Fe-C sample coated with amorphous carbon, since the lithium ions inserted into the amorphous carbon might be trapped and cannot be re-inserted at the next discharge step, it shows a much

Table 1 Charge-discharge characteristics and BET surface area of the NG, ENG, ENG-Fe, and ENG-Fe-C anode materials.

Sample	Charge capacity at the 1 st cycle (mAh/g)	Irreversible capacity at the 1 st cycle (mAh/g)	Discharge capacity (mAh/g)		Capacity retention, 63 rd /4 th (%)	Coulombic efficiency (%)	BET surface area (m ² /g)
			4 th	63 rd			
NG	398.4	34.6	364.6	314.1	86.2	91.3	4.39
ENG	478.5	92.4	385.7	381.5	98.9	80.7	7.46
ENG-Fe	578.0	103.3	462.9	346.9	74.9	82.2	10.72
ENG-Fe-C	636.9	116.3	518.0	558.4	120.6	81.8	10.54

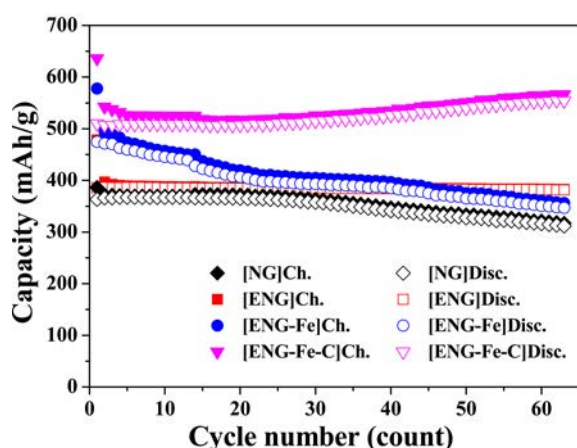


Fig. 8 Variation of capacities of the NG, ENG, ENG-Fe, and ENG-Fe-C anode materials through 63 cycles.

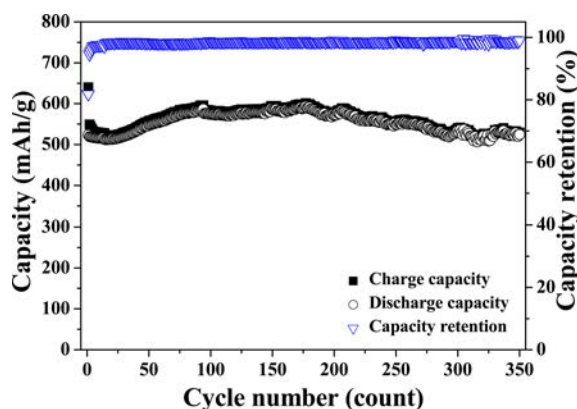


Fig. 9 Variation of capacity and capacity retention of the ENG-Fe-C anode material through 350 cycles.

larger irreversible capacity than the other samples.

Although the SEI film formation reaction may increase the irreversible capacity at the first cycle, it suppresses the performance degradation and thus improves the cycle characteristics as the charge-discharge reaction is repeated [30, 31]. To evaluate the cycle characteristics, the charge-discharge test was performed by varying the C-rate for a total of 63 cycles. The discharge capacity retention results are shown in Fig. 8 and Table 1. Although the ENG sample shows a lower coulombic efficiency (80.7%) due to a larger irreversible capacity than the NG sample (91.3%), the cycle characteristics significantly improve due to the large amount of SEI film. Meanwhile, the addition of α -Fe₂O₃ increases the reversible capacity at the 4th cycle; however, the capacity retention after the 63rd cycle decreases significantly compared to the ENG sample. This is due to the volume expansion and microstructural change caused by aggregation of Fe and Li₂O, which are the products of the reduction reaction during the charge-discharge process.

On the other hand, the amorphous carbon coating on the ENG-Fe leads to a significant improvement in the

cycle characteristics. The ENG-Fe-C sample shows a 120.6% of capacity retention after the 63rd cycle because the amorphous carbon coated on the surface of the α -Fe₂O₃ nanoparticles might suppress the aggregation of Fe and Li₂O as well as provide a large amount of SEI film. Moreover, the amorphous carbon coating on the surface of α -Fe₂O₃ nanoparticles further improves the electrical contact between the α -Fe₂O₃ nanoparticles and the current collector, contributing to fast charge transfer and low contact resistance, which, in turn, lead to a significant improvement in the electrochemical performance. Accordingly, the ENG-Fe-C sample exhibits significantly high capacity retention as well as a high reversible capacity compared with the NG sample.

Fig. 9 shows the variation of capacity and capacity retention of the ENG-Fe-C anode material during 350 cycles. The capacity increases from the 4th cycle (518 mAh/g) to the 95th cycle (576 mAh/g) and is stable until the 200th cycle. It then decreases up to the 350th cycle (524 mAh/g). The increase in capacity relative to the initial capacity up to the 95th cycle might be due to the kinetic activation process of α -Fe₂O₃ nanoparticles relating to the growth of a polymeric gel-like film on the surface of α -Fe₂O₃ nanoparticles or to the charge storage at the interface between Li₂O and α -Fe₂O₃ nanoparticles [32].

Conclusions

An amorphous carbon-coated α -Fe₂O₃/expanded NG (ENG) composite as an anode active material for lithium ion batteries was successfully developed by a facile hydrothermal method. Although the ENG anode material showed a larger irreversible capacity due to a large amount of SEI film relating to an increase in the specific surface area, it showed better capacity retention than the pristine NG anode material. To enhance the reversible capacity of the ENG anode material, α -Fe₂O₃ nanoparticles were impregnated into the ENG matrix by a hydrothermal method. The reversible capacity of α -Fe₂O₃/ENG composites increased by approximately 26% compared to that of the ENG sample. However, the cycling performance was significantly degraded. Interestingly, amorphous carbon coating on the α -Fe₂O₃/ENG composite led to significant improvement in the cycling stability after 350 cycles, which are ascribed to the favorable synergistic effect of the suppression of aggregation of Fe and Li₂O, as well as to the fast charge transfer and low contact resistance caused by conductive amorphous carbons. Consequently, these favorable electrochemical performances demonstrate that the amorphous carbon-coated α -Fe₂O₃/ENG composite might be a promising candidate as an anode-active material for high-performance, high-capacity, and low-cost lithium-ion batteries.

Acknowledgments

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