

Effect of amorphous carbon coating on low-purity natural graphite as an anode active material for lithium-ion batteries

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Anode active materials that are low cost and have excellent capacity retention are suitable for large secondary battery systems such as energy saving systems (ESSs). In this study, inexpensive low-purity natural graphite was used as a matrix. This matrix was coated with amorphous carbon to improve the cycle characteristics and inhibit dissolution of impurities. The natural graphite coated with amorphous carbon was prepared by the pyrolysis of sucrose during heat treatment. The shape and crystal structure of the natural graphite powder were maintained even after a coating process that included heat treatment. The thickness of the amorphous carbon layer measured by TEM was less 10 nm. After amorphous carbon coating, the coulombic efficiency during the first cycle decreased from 91.3 to 87.9%. On the other hand, the capacity retention rate during 50 cycles increased from 90.9 to 94.7%. Interestingly, impurities in the natural graphite such as Al, Fe, and Zn did not affect the stability of the electrolyte.

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

Introduction

Carbonaceous materials have been used widely as anode active materials for lithium ion batteries since they can easily insert lithium ions into the interior of the anode. In addition, carbonaceous materials are capable of continuous and repetitive oxidation-reduction reactions because the electrochemical reaction potential of such carbonaceous materials with lithium ions is very close to that of lithium metal, and the crystal structure change during the lithium ion insertion/de-insertion process is very small. These carbonaceous materials can be classified into crystalline graphite and amorphous carbon materials, such as soft carbon and hard carbon [1-3].

Crystalline graphite with a layered structure has a high theoretical energy density of 372 mAh/g because LiC_6 is formed by ideally intercalating lithium ions between the layers. However, the insertion rate of lithium ions is slow and the performance at a high C-rate is not acceptable. This is because graphite has a very short interlayer distance of 0.335 nm and a long diffusion distance between the basal plane and reaction site due to its flake-like structure. Moreover, exfoliation phenomena may occur due to intercalation of the electrolyte molecules. Generally, crystalline graphite can be divided into synthetic and natural graphite. Natural

graphite is cheaper than synthetic graphite, but it has the disadvantage of poor cycle characteristics. In this regard, various suggestions have been proposed for the development of graphite-based anode active materials that have large capacity, high rate and long life including: (1) surface modification with amorphous carbon materials [4-6], (2) mild oxidation by chemical treatment or heat treatment in an air atmosphere [4, 5], and (3) polymer or silicon coatings [6-8].

Meanwhile, amorphous carbon materials have a longer interlayer distance than that of crystalline graphite, and the insertion rate of lithium ions is larger [9-11]. Therefore, surface coating of graphite with amorphous carbon may improve the cycle performance of natural graphite. Therefore, low-purity natural graphite was coated with amorphous carbon by the decomposition of sucrose in this study. The effect of amorphous carbon coatings on the electrochemical performance of low-purity natural graphite and dissolution of impurities has been investigated.

Experimental Procedure

Powder preparation

Spherical natural graphite with an average particle size of 18 μm and a purity of 95% was used as a matrix powder. The natural graphite was coated with amorphous carbon by decomposing sucrose (99%, Alfa Aesar) via heat-treatment. Amorphous carbon-coated natural graphite was synthesized by the following procedure [13,14]. Sucrose (1.2 g or 2.4 g) was dissolved in 100 g of D.I. water. Then, 9.0 g or 9.5 g of natural graphite were

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immersed in each solution, and the solutions were stirred for 1 hr after being dried at 90 °C for 24 hrs. The residual mixtures were heated at 700 °C for 3 hrs in a N₂ atmosphere. The prepared samples were dubbed LSNG (pristine natural graphite), 2-LSNG (amorphous carbon coated natural graphite with 1.2 g sucrose), and 4-LSNG (amorphous carbon coated natural graphite with 2.4 g sucrose) according to the amount of sucrose used.

Characterization

Powder morphology was characterized by field emission scanning electron microscopy (FE-SEM, SUPRA 40VP, Carl Zeiss, Germany) and high-resolution transmission electron microscopy (HR-TEM, JEM-2010, JEOL, Japan). The impurities in the powders and electrolyte after electrochemical reaction were confirmed by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Ultima2, Horiba Jobin-Yvon, Japan). X-ray diffraction (XRD, MAX-2500, Rigaku, Japan) and Raman spectroscopy (LabRAM, Horiba Jobin-Yvon, Japan) were used to verify the structural changes after the coating process. Thermal analysis equipment, including a thermal gravimetric analyzer, a differential temperature analyzer (TGA-DTA, TG-8121, Rigaku, Japan) and a differential scanning calorimeter (DSC, Q20, TA instrument Ltd., USA), were used to measure the amount of coated amorphous carbon and to analyze the amount of solid electrolyte interface (SEI) film formed by the electrochemical reaction. To investigate the stability of the electrolyte in the presence of impurities, linear sweep voltammetry (LSV, Parstat 4000A, Ametek, USA) was performed at 25 °C at a scan rate of 10 mV/s by a three-electrode method using a Pt rod, Pt wire, and Li metal as a working electrode, counter electrode, and reference electrode, respectively. Samples of electrolytes into which electrodes were dipped for 14 days were analyzed for comparison.

Coin cells (CR2032) for the electrochemical measurements consisted of a working electrode (LSNG, 2-LSNG, or 4-LSNG), a counter electrode (Li metal), and a separator (Celgard 2300). A mixture of 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 components was 95/2/2/1. The prepared slurry was coated onto a 10 µm Cu foil by using a doctor blade, and was then dried under vacuum at 120 °C for 12 hrs. Beaker cells were specially designed to confirm the dissolution of impurities from the natural graphite into the electrolyte.

A battery tester (WBCS-3000, Wonatech, Korea) was used for electrochemical characterization. The initial 3 cycles were charged to 5 mV at 0.1 C-rate using a constant current (CC) method, and they were

then charged to a constant voltage (CV) 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 10 cycles at a 0.2 C-rate and then 37 cycles at a 0.5 C-rate.

Results and Discussion

The morphology of low-purity natural graphite before and after the coating process was observed via FE-SEM, as shown in Fig. 1. The samples are shown as uniform spherical particles of about 10–20 µm, and no noticeable change was observed even after coating with amorphous carbon. It is difficult to obtain a thin and uniform electrode during the electrode manufacturing process when using non-spherical natural graphite. Thus, the electrode was arranged parallel to the direction of the current collectors so that the lithium ions cannot be easily inserted and removed. On the other hand, since the spherical shape of natural graphite can reduce the surface area, spherical natural graphite exhibits a low irreversible capacity caused by side reactions with electrolyte as compared to non-spherical natural graphite [15].

XRD measurements were performed to confirm the change in crystal structure before and after the coating process. Fig. 2 shows the XRD patterns of the LSNG, 2-LSNG, and 4-LSNG powders. The XRD patterns of all samples indicated hexagonal (2H) and rhombohedral (3R) structure peaks, which are characteristic of typical

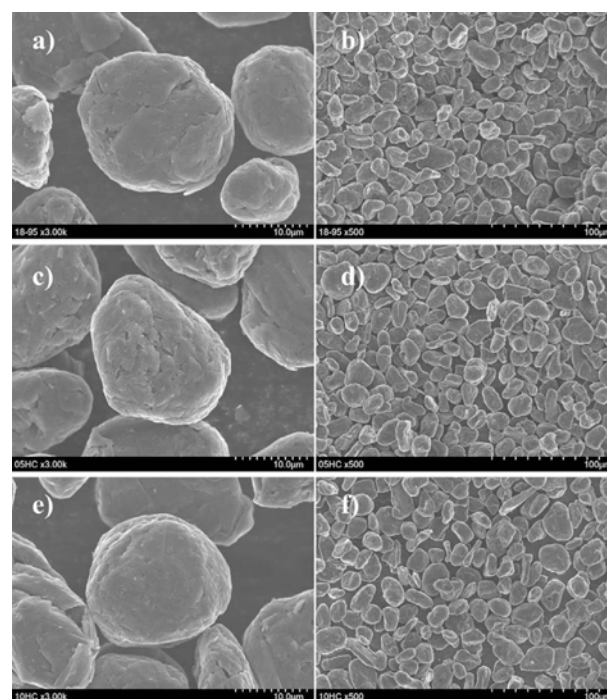


Fig. 1. FE-SEM images of the modified natural graphite by amorphous carbon coating: (a, b) LSNG, (c, d) 2-LSNG, (e, f) 4-LSNG.

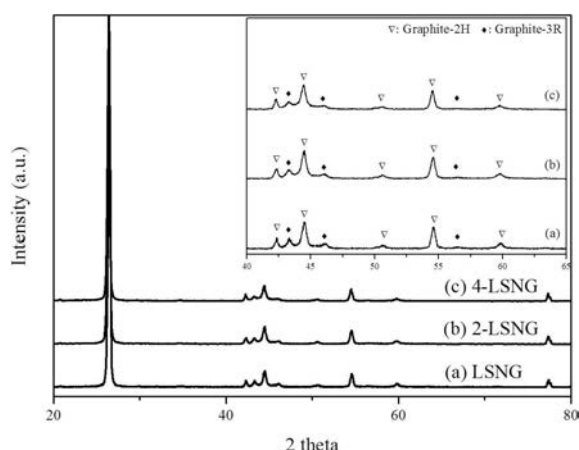


Fig. 2. XRD patterns of the LSNG, 2-LSNG, and 4-LSNG powders.

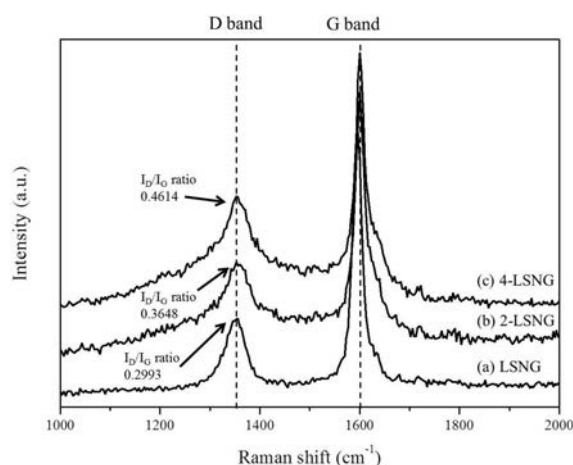


Fig. 3. Raman spectra of the LSNG, 2-LSNG, and 4-LSNG powders.

natural graphite. The relative proportions of the two structures were calculated by comparing the intensities of the (101) planes located at 44.5 and 43.2 degrees [16], respectively, and there was no structural change before and after coating. The only factor that can change the structure of graphite during the coating process is the heat energy involved in the heat treatment process. However, since the structural change from the 3R structure to the 2H structure occurs above 1300 °C [17, 18], the structural change caused by the coating process at 700 °C is negligible. On the other hand, when the 2H structure and the 3R structure coexist, the structural defects increase more than when they do not coexist.

Raman spectroscopy measurements were performed to identify the structural defects. Raman spectroscopy is mainly used for structural analysis of carbon materials and is particularly suitable for discriminating carbon allotropy and analyzing the crystallinity of graphite. Crystalline graphite has distinct peaks at 1355 and 1582 cm^{-1} , which are the D band peak and G band peak, respectively [19, 20]. The G band peak is related

to sp^2 binding in graphite, and the D band peak 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 band intensity (I_D) to the G band intensity (I_G). Fig. 3 shows the Raman spectra of LSNG, 2-LSNG and 4-LSNG. Although LSNG is not coated with amorphous carbon, it shows a D band peak. The I_D/I_G ratio increased with amorphous carbon coating. 4-LSNG, which had a large amount of amorphous carbon in the coating, showed the highest I_D/I_G ratio value of 0.4614.

Since crystalline graphite and amorphous carbon have different binding energies, they show different oxidation temperatures [21, 22]. Based on this, we determined the fraction of coated amorphous carbon by thermal analysis. Fig. 4 shows the TGA/DTA results obtained by heating the samples in an oxidizing atmosphere at a rate of 10 °C/min from room temperature to 1000 °C. The LSNG samples without amorphous carbon

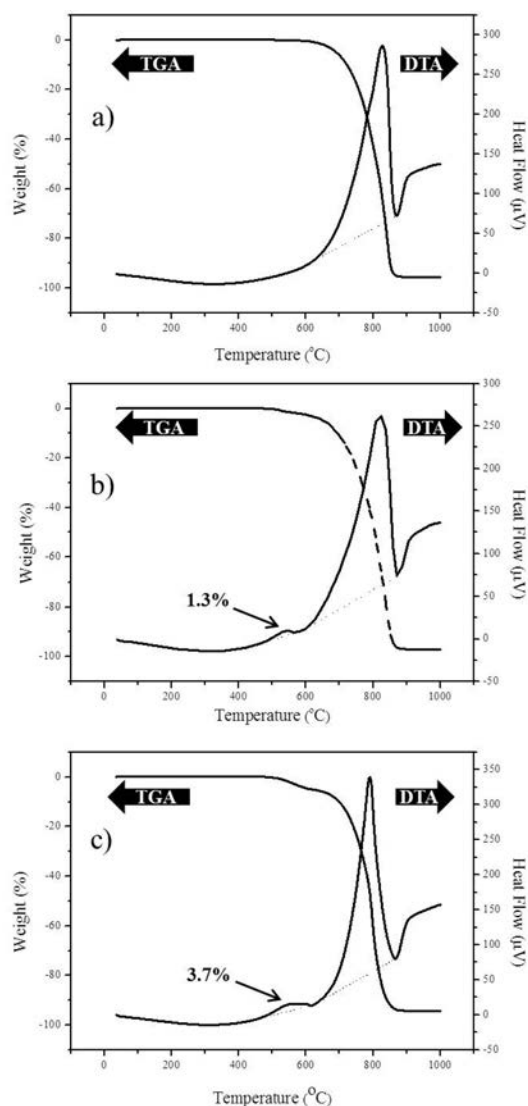


Fig. 4. TGA and DTA curves of the (a) LSNG, (b) 2-LSNG, and (c) 4-LSNG powders.

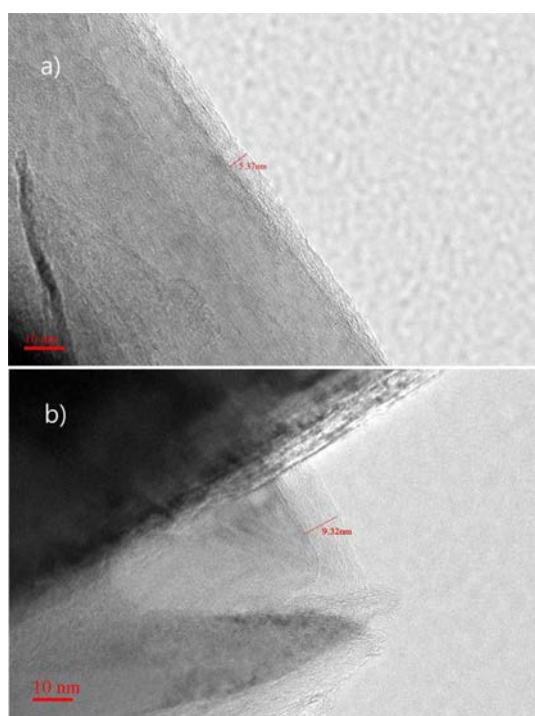


Fig. 5. HR-TEM images of the (a) 2-LSNG and (b) 4-LSNG powders.

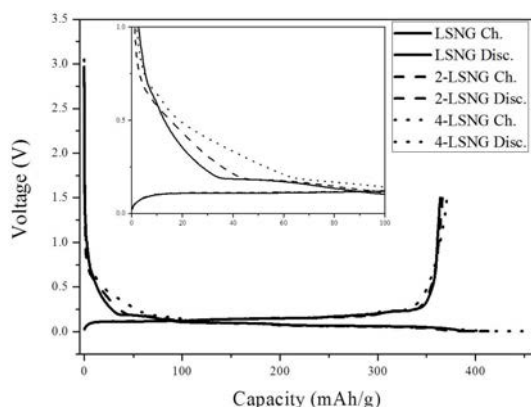


Fig. 6. Charge-discharge curves of the LSNG, 2-LSNG, and 4-LSNG anode materials in the first cycle with a 0.1 C-rate.

coating showed only one peak at 827 °C, indicating the oxidation of graphite. In contrast, the amorphous carbon-coated 2-LSNG and 4-LSNG samples showed additional peaks at 535 and 548 °C, respectively, indicating oxidation of the coated amorphous carbon. The amount of coated amorphous carbon was calculated to be 1.3 wt% for 2-LSNG and 3.7 wt% for 4-LSNG. TEM measurements were carried out to directly determine the thickness of the coated amorphous carbon layer. As shown in Fig. 5, the thicknesses of the amorphous carbon layer in 2-LSNG and 4-LSNG were about 5 and 9 nm, respectively.

Fig. 6 shows the charge-discharge curve of the natural graphite anodes for the first cycle at 0.1 C, and the calculated capacity data and coulombic efficiency are

Table 1. Capacity data and coulombic efficiency for the LSNG, 2-LSNG, and 4-LSNG samples during the first cycle.

Sample	Charge capacity (mAh/g)	Discharge capacity (mAh/g)	Irreversible capacity (mAh/g)	Coulombic efficiency (%)
LSNG	398.4	363.8	34.6	91.3
2-LSNG	413.4	366.6	46.8	88.7
4-LSNG	421.9	370.9	51.0	87.9

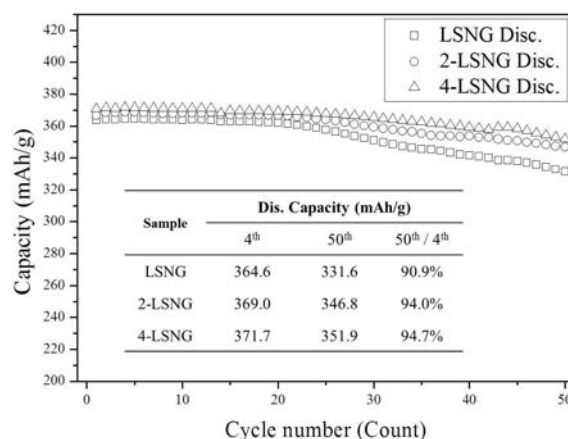


Fig. 7. Discharge capacities of LSNG, 2-LSNG, and 4-LSNG as a function of the cycle number.

shown in Table 1. Typical graphite electrodes exhibit a plateau from 0.7 to 0.8 V due to the SEI film formation during the first cycle of charging. Both the charging and discharging capacities of all samples increased as the amount of coated amorphous carbon increased. However, the irreversible capacity increased as well. In the case of the sample coated with amorphous carbon, the lithium ion inserted into the amorphous carbon was trapped and cannot be reinserted during the discharge step, thus appearing as irreversible capacity. Therefore, while LSNG showed the highest coulombic efficiency of 91.3% for the first cycle charge-discharge capacity, 4-LSNG showed the lowest coulombic efficiency of 87.9%.

To evaluate the cycle characteristics, the charge-discharge test was performed by varying the C-rate for a total of 50 cycles, and the discharge capacity retention results are shown in Fig. 7. The discharge capacity of LSNG decreased significantly after the 20th cycle compared with 2-LSNG and 4-LSNG. While 4-LSNG showed the lowest coulomb efficiency during the first cycle (Table 1), it exhibited the best overall performance with a capacity retention of 94.7% (50th/4th cycle). Generally, the SEI film formation causes irreversible capacity loss, but the SEI film inhibits the deterioration of the anode active material, which consequently improves cycle characteristics. Therefore, 4-LSNG, which has the highest irreversible capacity, may have a thicker SEI film than LSNG without amorphous carbon.

DSC measurements were performed to quantitatively

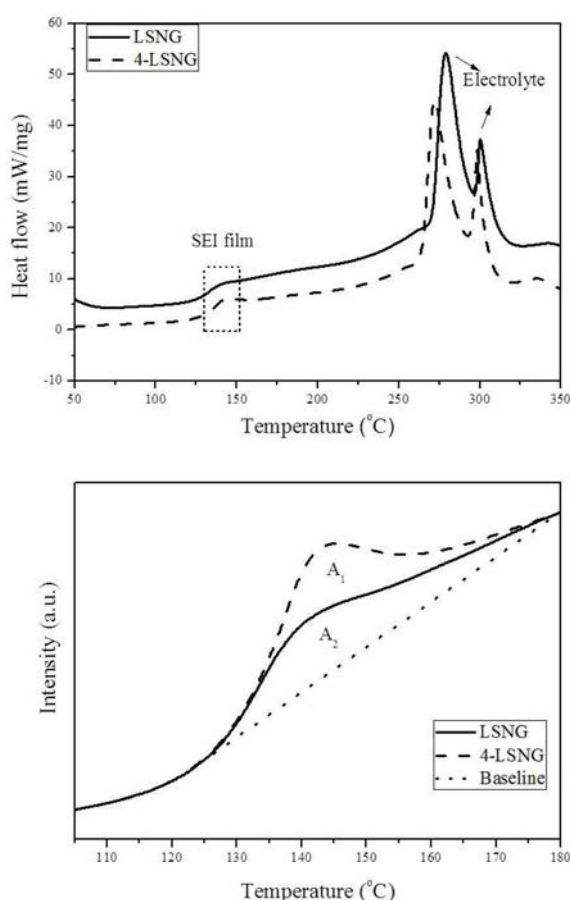


Fig. 8. DSC data of the LSN and 4-LSNG powders after the charge-discharge test for 3 cycles.

Table 2. ICP-AES analysis results for the pristine LSN powder and 4-LSNG powder after charge-discharge testing, and raw electrolyte.

(Units: ppm)						
Element	Al	Fe	Zn	Cr	S	Ni
LSN (powder)	3039	2743	21.1	0.1	—	0.1
Raw electrolyte	897.5	14.5	<1	<1	<1	<1
Electrolyte after test with 4-LSNG	944.3	59.1	2.323	<1	<1	<1
Total amount of dissolution	46.8	44.6	1.3	—	—	—

analyze the SEI film layer. After the coin cells were subjected to a charge-discharge process in a formation cycle, they were disassembled in a glove box, and electrode powders were collected. Fig. 8 shows the DSC results measured in the temperature range of 50 to 350 °C at a heating rate of 10 °C/min. Pyrolysis peaks of the SEI film and electrolyte appeared at about 140 and 250 °C, respectively. The separation of the two peaks in the electrolyte indicates that two organic solvents were used. The amounts of SEI film can be compared by comparing the areas of the pyrolysis peaks. The amount of SEI film in LSN and 4-LSNG correspond to A2 and A1 + A2, respectively, and 4-

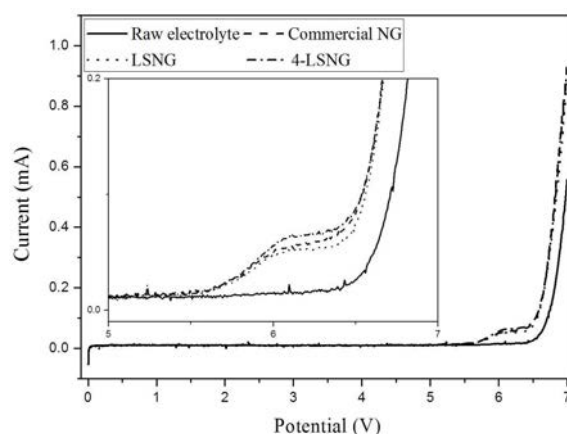


Fig. 9. LSV curves of the raw electrolyte and electrolyte samples into which electrodes were dipped for 14 days.

LSNG has 63% more SEI film than LSN.

Low-purity natural graphite contains a number of impurities that may influence stability. To investigate the influence of these impurities, electrolyte samples collected after charge-discharge testing and pristine natural graphite powder were analyzed using ICP-AES. Table 2 lists the ICP-AES analysis results, including impurity compositions of the pristine LSN powder as well as those of electrolyte samples after charge-discharge testing. Large amounts of Al and Fe and various other impurities were detected in the pristine LSN powder. The amount of impurities contained in the electrolyte after the charge-discharge test for 300 cycles increased to 92.7 ppm. This amount corresponds to about 1.6% of the impurities contained in the LSN powder. This indicates that a very small amount of impurities from the natural graphite dissolved into the electrolyte.

Trace amounts of impurities dissolved into the electrolyte, potentially affecting the stability of the electrolyte solution. Therefore, the LSV measurement was carried out to confirm the stability of the electrolyte. As shown in Fig. 9, the decomposition voltage of the raw electrolyte was about 6.5 V. Although the shoulder peaks appear at about 5.5 V for the electrolyte samples into which electrodes were dipped for 14 days, there is no significant change in the main decomposition peak at 6.5 V compared to the raw electrolyte. This indicates that the electrochemical stability of the electrolyte solution is not affected by the amorphous carbon or the impurities contained in the amorphous carbon-coated low-purity natural graphite powder.

Conclusions

Surface modification of low-purity natural graphite by means of an amorphous carbon coating led to an increase in the I_D/I_G ratio and irreversible capacity. However, the amorphous carbon-coated sample with a thicker SEI film showed better capacity retention than

pristine natural graphite over 50 cycles. Although the low-purity natural graphite sample had large amounts of impurities such as Al, Fe, and Zn, only trace amounts of these impurities dissolved into the electrolyte during electrochemical cycling. Moreover, no change in the stability of electrolyte was observed after the dissolution of the impurities. Thus, the amorphous carbon-coated low-purity natural graphite was used as an anode material for lithium-ion batteries.

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