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Synthesis of silicon–carbon black composite as anode material for lithium ion battery

Hanvin Kim¹, Yongsub Yun², Young-Chan Lee³, Myeong-Hoon Lee¹, Nagahiro Saito⁴, and Jun Kang¹*

¹Division of Marine Engineering, Korea Maritime and Ocean University, Busan 49112, Korea
²Division of Marine System Engineering, Korea Maritime and Ocean University, Busan 49112, Korea
³Division of Marine Information Technology, Korea Maritime and Ocean University, Busan 49112, Korea
⁴Graduate School of Engineering, Nagoya University, Nagoya 464-8603, Japan

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1. Introduction
Because of their stable lifetime characteristics and high efficiency, lithium-ion batteries (LIB) have been increasingly used in high-capacity storage devices such as electric vehicles and energy storage devices (ESS), as well as in mobile devices.¹⁻⁴⁻⁰

The following strategies can be adopted to improve the energy density (Wh/kg) of LIBs: 1) varying the electrode material 2) improving the coating technique 3) improving the packing of materials within the anode and cathode and 4) increasing the Li absorption rate of the cathode. However, methods 2–4 are typically limited by the optimization of internal space and design, and thus, studies on the synthesis of new electrode materials are actively pursued.

Currently, the most representative material used for the cathode in LIBs is graphite. It exhibits a highly reversible charging/discharging behavior due to the uniaxial orientation of the graphene layer, and consequently, has a long cycle life. In addition, when graphite is fully charged, i.e., has lithium ions residing between the layers, the electrode potential is 0 V vs Li/Li⁺. This indicates that graphite can exhibit a potential similar to that of pure Li metal, and thus, a higher energy can be obtained by assembling a cell with a graphite cathode and an oxide-based anode.

However, the low theoretical capacity of graphite (372 mAh/g, 837 mAh/cm³) is a crucial obstacle to the continuous use of graphite as an anode material, given the current demand for high-capacity batteries. Therefore, in order to develop a high-capacity and high-performance lithium secondary battery, the development of a noncarbonaceous anode material is essential.

Among these noncarbonaceous materials, Si is known to be the most suitable because it has a high discharge capacity of 4,200 mAh/g and a lithium reaction potential of 0.4 V (vs Li/Li⁺). However, Si suffers from a critical problem, namely, severe volume change during charging/discharging, which results in poor reversibility and rapid capacity decay.⁵⁻¹⁰

Numerous methods have been proposed to mitigate volume expansion, such as nanosizing of the metal particles reacting with lithium, the synthesis of a multiphase alloy that reacts with lithium, and the synthesis of an active/inactive metal complex and a lithium alloy/carbon composite.¹¹⁻¹⁵

In this study, we have tried to solve the problem of volume expansion in silicon by synthesizing a silicon–carbon black (Si–CB) composite. The CB structure is formed by the aggregation of the primary particles in different directions to form networks in various directions and space created inside a CB aggregate due to random growth.¹⁶⁻¹⁹ Therefore, these spaces will serve as a buffer to accommodate silicon in the event of volume expansion.

2. Experimental methods
We attempted to synthesize Si–CB composites using the solution plasma processing (SPP) method. Previous studies have shown that SPP is an excellent method for synthesizing CB with a meso-macro hierarchical pore structure and a high pore volume.²⁰⁻²² In those studies, only organic solvents such as benzene were used to synthesize CB. However, in this study, we attempted to synthesize composites by dispersing the synthesized silicon nanoparticles in an organic solvent prior to plasma discharge.

The experiments were carried out at room temperature under atmospheric pressure. A pair of mechanical pencil leads was used as an electrode for plasma generation because most metal wires were sputtered or vaporized by plasma, and could be included as impurities in the synthesized material. Each electrode was covered with a ceramic tube that was inserted in a silicone stopper. A pair of electrodes was enclosed in a ceramic tube and fitted in a silicon plug stopper; this assembly was then placed in a beaker 50 mm in diameter and 100 mm in height (Fig. 1). The distance between the electrodes was maintained at 1 mm. The pure xylene (reagent grade, Sigma-Aldrich) was applied as the carbon precursor and silicon nanopowder (average size = 100 nm, Alfa Aesar) was mixed with xylenes. A bipolar pulsed power generator was applied to generate the discharge. The frequency and pulse width of the power supply were adjusted to 25 kHz and 0.5 µs, respectively. After the discharge, the discharged solution was filtered through glass fiber paper to obtain any solid compounds present in the solution. These were filtered and then dried at 80 °C, leaving a powdery material.
after the evaporation of xylene. To improve the electrical conductivity, the obtained powder was subjected to heat treatment at 700 °C for 1 h, in an electric furnace under N2 gas atmosphere.

For the electrochemical evaluation of the Si–CB composite, the anodes were prepared by coating a slurry comprising the Si–CB composite (80 wt %) as the active material, CB (10 wt %; Super P) as the conducting agent, and poly(acrylic acid) (PAA; 10 wt %) in distilled water as a binder onto Cu-foil substrates and drying these in a vacuum oven at 50 °C for 12 h. CR2032 coin-type cells were assembled in an Ar-filled glove box using Celgard 2400 as the separator, Li foil as the counter and reference electrodes, and 1 M LiPF6 in ethylene carbonate/diethyl carbonate (EC/DEC) (1:1 by volume) containing 10 wt % fluoroethylene carbonate (FEC) as the electrolyte. All the cells were tested galvanostatically between 0.05 and 3 V (vs Li/Li+) at a current density of 1 C \[372 \text{ mAh/g; one Li per six formula units (LiC}_6\text{) in 1 h}\] using a Biologic BCS 805 battery test system for both charge (Li extraction) and discharge (Li insertion) at room temperature.

3. Results and discussion

Figure 2 shows the X-ray diffraction (XRD) pattern of the Si–CB composite. A very strong and unshifted Si peak was detected, confirming the presence of Si in the composite material.

The BET plots for the Si–CB composite and pure CB are shown in Fig. 3. The curve for the Si–CB composite appears above the CB curve because of the large increase in the amount of nitrogen adsorbed by the silicon nanoparticles contained within the CB structure. The specific surface area, as calculated by BET, also increased in the Si–CB composite owing to the increased overall adsorption, with the calculated values for CB and Si–CB being 202 and 220 m²/g, respectively. However, the pore volumes calculated from the adsorption curve were 0.0035 and 0.0012 cm³/g for CB and Si–CB, respectively, indicating that the total pore volume is reduced by the silicon nanoparticles. Therefore, it can be assumed that the silicon nanoparticles are present in the spaces formed between the agglomerates of CB.

Figure 4 shows a bright-field scanning transmission electron microscopy (BF-TEM) image of the as-prepared Si–CB composite. It can be seen that primary carbon particles of 20 to 30 nm form agglomerates with a chainlike shape. This image also shows the void space between the agglomerates and the existence of 50 to 200 nm silicon nanoparticles in these voids. Therefore, Si nanoparticles were dispersed on the surface and trapped in the void space of CB. These observations further support the conclusions obtained from the nitrogen adsorption/desorption isotherms. Importantly, CB shows a large network formed by the connection between
small agglomerates. Therefore, if volume expansion occurs, silicon can remain in the structure because of the tortuous nature of the CB network.

The effect of the void spaces in CB on the electrochemical performance of the Si–CB composite electrodes was investigated by a series of galvanostatic charge/discharge experiments. Figure 5(a) shows the charge/discharge curves of Si–CB for the first three cycles at rates of C/5, C/2, and C with the calculated irreversible capacities of 1005, 801, and 553 mAh/g, respectively. Although the discharge current increased with the Crane, the discharge capacity did not decrease significantly. This is considered to be due to the fact that the diffusion of lithium ions inside the active material was facilitated by a large specific surface area. However, as the large specific surface area facilitated the formation of an SEI layer, the irreversible capacity in the first cycle was about 1000 mAh/g; as such, the calculated coulombic efficiency (CE) was about 55%. This large irreversible capacity is inevitable in a nanoscale active material. However, it can be sufficiently reduced through a prelithiation process. Figure 5(b) shows the long-term cycling performance of Si–CB over 50 cycles at a rate of 1 C [Fig. 5(b)]. The CE for each charge–discharge process was calculated to be more than 95% on average, which indicates that a stable SEI layer is formed on the surface of the material. On the other hand, the discharge capacity decreased gradually with increasing number of cycles to 260 mAh/g after 50 cycles. Although the discharge capacity of Si–CB is continuously reduced by cycling, this can be prevented by optimizing the slurry coating process elements (e.g., binder type, binder amount and drying speed). In addition, if smaller Si nanoparticles with a uniform size (10 nm or less) are used, the cycling performance is expected to further improved because it is suggested that the stored strain energy from electrochemical reactions is insufficient to drive crack propagation in Si nanoparticles if the particle diameter is <150 nm.23)

In addition, a high density of grain boundaries in nanomaterials provides a fast diffusion path for Li ions and acts as additional Li-storage sites.24,25)

4. Conclusions

In this study, a Si–CB composite material was successfully synthesized by SPP. The change in the pore volume of CB in the presence of silicon nanoparticles was observed from N2 gas adsorption curves. From TEM images, it was confirmed that silicon nanoparticles were successfully trapped in the void space of the carbon black network structure. The galvanostatic charge and discharge curves show that the void space of CB could prevent the cycling performance fading caused by the volume expansion of silicon nanoparticles. It is expected that much better results will be obtained if carbon black composite materials are synthesized using smaller silicon nanoparticles (10 nm or less) and a narrower size distribution.

Fig. 5. (Color online) (a) Galvanostatic discharge/charge curves and (b) cycling performance of Si–CB cycled at a rate of 1 C.

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Hanvin Kim is currently a student for a master’s at the Division of Marine Engineering of Korea Maritime and Ocean University and major is Nano-materials in Mechanical Fusion Technology. He has been studying about material science in Korea Maritime and Ocean University since 2010, and he enrolled in master’s in 2016. His research interest is mainly physics, chemistry, electrochemistry, and he focuses on several application fields: lithium-ion battery, fuel cell, seawater battery, corrosions. Especially the latest his research theme is advanced carbon–metal anode materials for lithium-ion battery. He has published several journal papers in the field of carbon materials.

Yongsup Yun is an associate professor in the Division of Marine System Engineering at Korea Maritime and Ocean University. He received his Ph.D. degree in Materials Engineering from Nagoya University in 2007. From 2008 to 2009, he was a research fellow in National Institute of Advanced Industrial Science and Technology (AIST), Japan. His research interest mainly focuses on plasma phenomena in a gas as well as liquid phase, including thin films, molecular dynamics, sterilizations and diamond semiconductors, etc. He has published more than 20 peer-reviewed journal papers in the field of material science, plasma diagnostics, etc.

Young-Chan Lee is currently the Assistant Professor at the Division of Maritime Information and Technology Engineering of the Korea Maritime and Ocean University. Prior to joining the University in the October 2015, he was an Assistant professor of Korea Institute of Maritime and Fisheries Technology. His interest is with respect to electrical and electronic engineering on board ship in application aspect, especially power system quality with intelligent control and power electronics application. He has published more than 10 publications and several books in the field of maritime related matters.

Myeonghoon Lee is currently a professor in the Marine Engineering Department at Korea Maritime and Ocean University. He received his Ph.D. degree from Nagoya University in 1994. His research interest mainly focus on electrochemical application-analysis-evaluation including surface coating and corrosion control, etc. of materials in various environments. He has published more than 80 peer-reviewed journal papers in the field of surface coating and corrosion control, etc.

Nagahiro Saito is currently a full professor at the Department of Chemical Systems Engineering of Graduate School of Engineering in Nagoya University. He is also a director of Institute of Innovation for Future Society Social Innovation Design Center. He received his Ph.D. degree from Waseda University in 2000. He directs the Chemical Reaction and Interface Dynamics (CRID) Laboratory. His research interest mainly focuses on plasma physics in liquid, material science, chemical kinetics, nanomaterials including the catalyst, materials for batteries, thin films technology, etc. He has published more than materials-related 289 publications, book chapters, and has several patents.

Jun Kang is currently an assistant professor at the Division of Marine Engineering, Department of the Korea Maritime and Ocean University. He received Ph.D. degree from Nagoya University in 2013. Then he joined SK Innovation R&D Center as a senior researcher and group leader for developing various kind of nanomaterials. His research is focused on the development of nanomaterials for rechargeable battery technologies, such as lithium ion, lithium oxygen, sodium ion and sea water. He has published more than seven peer-reviewed SCI journal papers in the field of solution plasma. He conceived the idea and designed the experiments.