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Seung Ho Choi and Yun Chan Kang (✉)

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Enhanced Li⁺ Storage Properties of Few-Layered MoS₂–Carbon Composite Microspheres Embedded with Si Nanopowders
Seung Ho Choi, Yun Chan Kang

Department of Materials Science and Engineering, Korea University, Republic of Korea.

Few-layered MoS₂-carbon composite with high capacities and good cycling performance is successfully applied as a protective matrix of silicon nanopowders. The MoS₂–C composite material accommodates the large volume expansion of the Si nanopowders, but it also prevents the formation and propagation of a SEI layer on the Si surface during repeated cycling. The MoS₂-C composite microspheres embedded with 30 wt% Si nanopowders with enhanced Li⁺ storage properties are evaluated as a novel anode material with superior electrochemical properties for lithium-ion batteries.
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Seung Ho Choi and Yun Chan Kang

Department of Materials Science and Engineering, Korea University, Anam-Dong, Seongbuk-Gu, Seoul 136-713, Republic of Korea.

ABSTRACT

Few-layered MoS₂–carbon composite material is studied as a supporting material of silicon nanopowders. Microspheres of few-layered MoS₂–C composite embedded with 30 wt% Si nanopowders are prepared by one-pot spray pyrolysis. The Si nanopowders with high capacity are perfectly surrounded by the few-layered MoS₂–C composite matrix. The discharge capacities of the MoS₂–C composite microspheres with and without 30 wt% Si nanopowders after 100 cycles are 1020 and 718 mA h g⁻¹ at a current density of 1000 mA g⁻¹, respectively. The spherical morphology of the MoS₂–C composite microspheres embedded with Si nanopowders is preserved even after 100 cycles because of their high structural stability during cycling. The MoS₂–C composite layer prevents the formation of unstable solid–electrolyte interface (SEI) layers on the Si nanopowders. Furthermore, as the MoS₂–C composite matrix exhibits high capacities and excellent cycling performance, these characteristics are also reflected in the MoS₂–C composite microspheres embedded with 30 wt% Si nanopowders.

1. Introduction

As the technologies for electric vehicles and portable electronic devices develop, silicon is considered an extremely promising anode material for lithium-ion batteries (LIBs) with high capacity and fast charging–discharging properties [1-11]. Available in abundance, Si is an outstanding LIB anode material owing to its low discharge potential (< 0.5 V vs. Li/Li⁺) and the highest theoretical reversible capacity of approximately 4200 mA h g⁻¹, which is ten times more than the value for commercial graphite anodes (372 mA h g⁻¹) [1-11]. However, silicon experiences a large volume expansion (300%) during the Li⁺ insertion–extraction process, resulting in poor cycle properties because of pulverization of materials and loss of electrical contact between the electronic materials and the current collector [1-11]. Nanostructured materials and carbon-based composite materials have been developed to control the volume expansion of the Si electrode [12-36]. Various types of Si-based nanostructured materials, such as hollow nanospheres, cubic nanocrystals,
nanowires, and nanotubes, have improved Li\(^+\) storage properties beyond those of bulk materials [12-21]. Although these Si-based nanostructures can tolerate the large change in volume, the formation of an unstable layer at the solid–electrolyte interface (SEI) between the Si surface and the organic electrolyte leads to low Coulombic efficiency and a decrease in capacity during cycling [8-10,12,21]. Carbon-based silicon composite materials have attracted much attention as promising anode materials with stable and excellent Li\(^+\) storage properties because of their high electrical conductivity and the stress-buffer layer of carbonaceous materials [22-36]. Carbon-based silicon composite materials such as Si–graphite, Si–amorphous carbon, Si–C nanotubes, and Si–graphene have long cycle life when the silicon content in the composite materials was low [22-35]. As the Si content in a Si–C composite was increased, the Li\(^+\) storage properties deteriorated. However, high content of carbon material resulted in increases in the initial irreversible capacity and decreases in the reversible capacity [22-31]. Thus, the search for new replacement carbonaceous supporting material for the Si anode remains a great challenge.

In recent years, transition-metal oxides and metal sulfides have been widely studied as anode materials for LIBs because they have higher theoretical capacities than commercial carbonaceous materials [37-43]. Two-dimensional (2D) layered MoS\(_2\) is especially attractive because of its high reversible capacity and good cycling performance. Controlled MoS\(_2\) materials consisting of single layer or few layers facilitate a fast Li\(^+\) charging–discharging process, which allows the interlayer distance to relax the strain and lower the barrier for Li intercalation [44-47]. Because the graphene-like layered MoS\(_2\) can be very uniformly mixed with carbonaceous materials, the combination of the two materials has been regarded as a fundamental strategy to enhance the electrochemical properties of a LIB anode. For example, Zhu et al. reported that a single-layered MoS\(_2\)–carbon fiber composite exhibits high capacity and long cycle stability for LIBs [45]. However, the MoS\(_2\)-based materials had lower reversible capacities than those of the Si-based materials. The layered MoS\(_2\)-carbon composite material with high structural stability during repeated Li insertion and desertion processes could be efficient as the supporting material for the Si materials with high Li ion storage capacities. To the best of our knowledge, metal sulfide–Si composite materials have not been reported as anode materials for LIBs applications.

In this study, the few-layered MoS\(_2\)–C composite microspheres embedded with Si nanopowders were prepared by one-pot spray pyrolysis, using ammonium tetrathiomolybdate, polyvinylpyrrolidone (PVP), and Si nanopowders. Few-layered MoS\(_2\) nanosheets embedded in carbon spheres served as a protective matrix of silicon nanopowders. In addition to accommodating the large volume expansion of the Si nanopowders, the MoS\(_2\)–C composite material prevented the formation and propagation of the SEI layer on the Si surface during repeated cycling. The electrochemical properties of the microspheres were compared with those of microspheres without the embedded Si nanopowders.

2. Experimental section

2.1 Synthesis of few-layered MoS\(_2\)–C composite microspheres embedded with Si nanopowders. MoS\(_2\)–C composite microspheres embedded with Si nanopowders were directly prepared by ultrasonic spray pyrolysis at 800°C; a schematic of the apparatus is shown in Figure S1. A quartz reactor measuring 1200 mm in length and 50 mm in diameter was used; the nitrogen flow rate (carrier gas) was 10 L min\(^{-1}\). A 500-mL volume of distilled water was added to 1.8 g of ammonium tetrathiomolybdate and 5.0 g of polyvinylpyrrolidone (PVP) to form the spray
solution. The silicon nanopowders (85 nm) were dispersed in the spray solution with ammonium tetrathiomolybdate and PVP.

2.2 Characterization.

The crystal structure of the MoS_{2}–C composite microspheres embedded with Si nanopowders was investigated by X-ray diffractometry (XRD; X’pert PRO MPD, PANalytical, The Netherlands), using Cu Kα radiation (\( \lambda = 1.5418 \) Å). The morphological features were investigated using field-emission scanning electron microscopy (FE-SEM; S-4800, Hitachi, Japan) and high-resolution transmission electron microscopy (HR-TEM; JEM-2100F, JEOL, Japan) at a working voltage of 200 kV. The specific surface areas of the composite microspheres were calculated from a Brunauer–Emmett–Teller (BET) analysis of nitrogen adsorption isotherms (TriStar 3000 gas adsorption analyzer, Micromeritics, USA). The composite microspheres were also investigated using X-ray photoelectron spectroscopy (XPS; ESCALAB 210, VG Scientific, now Thermo Scientific, USA) with Al Kα radiation (1486.6 eV).

2.3 Electrochemical measurements.

The capacities and cycling properties of the composite microspheres were determined using a 2032-type coin cell. The electrode was prepared from a mixture containing 70 wt% of the active material, 15 wt% of Super P (conductive carbon black), and 15 wt% of sodium carboxymethyl cellulose (CMC) as the binder. Lithium metal and a microporous polypropylene film were used as the counter electrode and separator, respectively. The electrolyte was 1 M LiPF₆ in a 1:1 (v/v) mixture of ethylene carbonate and dimethyl carbonate (EC–DMC) with 5% fluoroethylene carbonate. The charging–discharging characteristics of the samples were determined through cycling in the potential range of 0.001–3.0 V at various fixed current densities. The cyclic voltammetry (CV) measurements were carried out at a scan rate of 0.1 mV s⁻¹. Dimensions of the negative electrode were 1 cm × 1 cm and mass loading was approximately 1.2 mg cm⁻².

3. Results and discussion

Scheme 1 shows the formation mechanism of the few-layered MoS_{2}–C composite microspheres embedded with Si nanopowders via the one-step and continuous spray-pyrolysis process. Droplets were formed from the colloidal spray solution consisting of Si nanopowders dispersed in an aqueous solution of ammonium tetrathiomolybdate and PVP. In this study, PVP acted as a stabilizer for
the Si nanopowders and the source material for amorphous carbon, thus preventing the stacking of MoS$_2$ layers [45,48]. In the precursor solution, the surface of the Si nanopowder was functionalized with water-soluble PVP. The drying of each droplet produced a composite microsphere of Si–ammonium-tetrathiomolybdate–PVP in the front part of the reactor that was maintained at 800°C. Thermal decomposition of ammonium tetrathiomolybdate into MoS$_2$ and carbonization of PVP under the nitrogen atmosphere resulted in a Si–MoS$_2$–C composite microsphere at the rear part of the reactor. In other words, one MoS$_2$–C composite microsphere embedded with Si nanopowders was formed by drying and decomposition of one droplet, and few-layered ultra-small nanoplates of MoS$_2$ were embedded within the MoS$_2$–C composite microsphere. The MoS$_2$–C composite layers with an elastic two-dimensional structure completely covered the individual Si nanopowders. The content of Si nanopowders in the composite microsphere could be controlled by changing the amount of Si nanopowders dispersed in the spray solution.

The morphologies of the MoS$_2$–C composite microspheres containing a small amount of enclosed Si nanopowders are shown in Figure 1. The designed Si content in the composite microspheres shown in Figure 1 was 30 wt% based on MoS$_2$. The morphology of the commercial Si nanopowders used in this study is shown in Figure S2; the nanopowder had a mean size of 85 nm and a slightly aggregated structure. The FE-SEM and low resolution TEM images revealed that the composite microspheres had a spherical shape and did not show any tendency to aggregate. The surface of the composite powder, as shown in Figure 1, had an embossed structure owing to the Si nanopowders enclosed within the composite microsphere. The TEM images (Figures 1d and e) show the Si nanopowders dispersed within the MoS$_2$–C matrix. Figures 1e and 1f show the amorphous-fluid-like structure of the MoS$_2$–C matrix, in which few-layered MoS$_2$ nanosheets were uniformly distributed within the amorphous carbon matrix; the Si nanopowder, which formed an embossed structure, was fully covered by MoS$_2$–C layers, as shown by the arrows. The enlarged TEM image in the inset of Figure 1f reveals clear lattice fringes separated by distance of 0.31 nm, which corresponds to the interplanar distance between the (111) planes of a Si nanoparticle [19]. The elemental mapping images in Figure 1g show the distributions of MoS$_2$, C, and Si nanopowders. The necking between the Si nanopowders resulted in some segregation of Si component in the low resolution elemental mapping images as shown in Figure S3. MoS$_2$ and the carbon material were uniformly distributed all over the composite microspheres. The Si nanopowders were also well dispersed within the MoS$_2$–C composite matrix. The dozens of the Si nanopowders were dispersed in
one composite microsphere as shown in Figure 1g. Considering that MoS$_2$ was converted into MoO$_3$ when heated in air, the carbon content in the composite microspheres was estimated as 23 wt%, as measured by thermogravimetric analysis (see Figure S5).

Figure 2. Morphologies of the MoS$_2$–C composite microspheres embedded with 60 wt% Si nanopowders: a,b) FE-SEM images, c-f) TEM images, and g) elemental mapping images of Mo, S, Si, and C components.

The morphologies of the MoS$_2$–C composite microspheres embedded with a high amount of Si nanopowders are shown in Figure 2. The designed Si content in the composite microspheres was 60 wt% based on MoS$_2$. The composite microsphere shown in Figure 2 had a more embossed structure than that of the microspheres shown in Figure 1 because of the high Si nanopowder content. The Si nanopowders were well dispersed within the composite microspheres, as shown by arrows in Figures 2d and 2e. The Si nanopowders located near the surface of the composite microsphere, as shown in Figure 2f, had a uniform MoS$_2$–C composite coating. The elemental mapping images in Figure 2g also show uniform distributions of MoS$_2$, C, and Si nanopowders within the composite microsphere. The morphologies of the MoS$_2$–C composite microspheres are shown in Figure S5. The composite microspheres had completely spherical shape and showed no tendency to aggregate. The HR-TEM image in Figure S4d shows the uniform distribution of MoS$_2$ nanosheets over the entire carbon matrix formed from the carbonization process that restricted the of MoS$_2$ layers.

Figure 3. Properties of the MoS$_2$–C composite microspheres embedded with 30 wt% and 60 wt% Si nanopowders. a) XRD patterns, b) XPS C1s spectrum of the MoS$_2$–C composite microspheres embedded with 30 wt%, c) XPS Mo3d spectrum, d) XPS S2p spectrum.

The structural characteristics of the MoS$_2$–C composite microspheres embedded with Si nanopowders are shown in Figure 3. The XRD patterns of the composite microspheres with low and high amounts of Si nanopowders had broad peaks corresponding to a hexagonal MoS$_2$ structure and sharp peaks of the Si phase. Broad peaks of MoS$_2$ layers were observed at 2θ of approximately 33° and 59°. However, the (002) reflections of the stacked MoS$_2$ layers at 2θ ~ 16° were not observed, indicating the presence of only few-layered MoS$_2$ [45-47]. Therefore, the results of the XRD patterns confirm the formation of few-layered MoS$_2$ nanosheets in the MoS$_2$–C composite microspheres embedded with Si nanopowders. Figures 3b-d
shows the XPS peaks of the MoS$_2$–C composite microspheres embedded with 30 wt% Si nanopowders. The C1s XPS peak centered at 284.6 eV in Figure 3b, which corresponds to the binding energy of the sp$^2$ C–C bond, confirms the formation of amorphous carbon by the carbonization process of PVP [49]. Two strong Mo3d XPS peaks at around 229.4 and 232.5 eV in Figure 3c, which can be attributed to Mo3d$_{5/2}$ and Mo3d$_{3/2}$ binding energies of MoS$_2$, respectively, confirm the formation of MoS$_2$ by decomposition of ammonium tetrathiomolybdate [50,51]. The negligibly weak peak intensities of Si2p in Figure S6 confirm that the Si nanopowder particles were completely covered by MoS$_2$–C composite layers. The BET surface areas of the MoS$_2$–C composite microspheres with 0 and 30 wt% Si nanopowders were 17.0 and 64.3 m$^2$ g$^{-1}$, respectively. The addition of Si nanopowders increased the porosity of the MoS$_2$–C composite microspheres as shown in Figure S7.

The electrochemical properties of the MoS$_2$–C composite microspheres with and without embedded Si nanopowders are presented in Figure 4. Figure 4a shows the cyclic voltammogram (CV) curves of the composite microspheres with 30 wt% Si during the first four cycles at a scan rate of 0.1 mV s$^{-1}$ in the voltage range of 0.001–3 V. Three reduction peaks resulting from lithium insertion into MoS$_2$ and Si were observed in the first cathodic scan. The first reduction peak located at 1.4 V is attributed to the intercalation of Li ions into the hexagonal MoS$_2$ lattice, followed by phase transformation to octahedral Li$_x$MoS$_2$ [44-47,52-56]. The peak at around 0.6 V corresponds to the conversion reaction, in which Li$_x$MoS$_2$ was decomposed into metallic Mo nanocrystals embedded in a Li$_2$S matrix, and formation of a SEI layer on the MoS$_2$–C surface, which resulted from electrochemically driven electrolyte degradation [44-47,52-54]. The third reduction peak located at 0.05 V is attributed to the reaction to form Li–Si alloys [12-21]. In the first anodic scan, three oxidation peaks attributed to metallic Mo nanocrystals and Li–Si alloys were observed. The first two anodic peaks observed at voltages of 0.3 and 0.55 V are attributed to the de-alloying reactions of Li–Si alloys [12-21]. The third anodic peak was observed at a voltage of 2.3 V, which corresponds to the conversion reaction of metallic Mo and Li$_2$S to MoS$_2$ [52-56]. From the second cycle onward, the reduction and oxidation peaks overlapped considerably, indicating the superior reversible cycling performance of the MoS$_2$–C composite microspheres with 30 wt% Si. Figure 4b shows the initial discharge and charge.

![Figure 4. Electrochemical properties of the MoS$_2$–C without Si nanopowders and MoS$_2$–C composite microspheres embedded with 30 wt% and 60 wt% Si nanopowders. a) CV curves of MoS$_2$–C composite microspheres embedded with 30 wt% Si, b) initial charge/discharge curves at a current density of 1 A g$^{-1}$, c) cycling performances at a current density of 1 A g$^{-1}$, d) rate high performance.](image-url)
curves of the MoS₂–C composite microspheres with and without embedded Si nanopowders at a current density of 1000 mA g⁻¹. The initial discharge curves of the composite microspheres with embedded Si nanopowders had clear plateaus at around 0.1 V owing to the reaction of Li with Si to form Li–Si alloys. However, the obvious plateaus corresponding to the formation of Li₄MoS₄ and Mo nanocrystals embedded in a Li₂S matrix were not observed in the initial discharge curves of the three samples because of the amorphous-fluid-like structure of the MoS₂–C composite. The initial discharge capacities of the MoS₂–C composite microspheres with 0, 30, and 60 wt% Si nanopowders were 1100, 1448, and 1746 mA h g⁻¹, respectively, and their initial Coulombic efficiencies were 69.5, 65.3, and 67.8%, respectively.

The cycling performances of the three samples at a current density of 1000 mA g⁻¹ are shown in Figure 4c. The MoS₂–C composite microspheres without Si nanopowders had discharge capacities of 740 and 718 mA h g⁻¹ for the 2nd and 100th cycles, respectively. The capacity retention of the MoS₂–C composite microspheres without Si nanopowders measured from the 2nd cycle was 97%, indicating that the few-layered MoS₂–C composite microspheres had excellent cycling performance even at a high current density of 1000 mA g⁻¹. The discharge capacities of the MoS₂–C composite microspheres with embedded Si nanopowders increased during cycling for the first 20 cycles. The gradual activation of highly crystalline Si nanopowders with a mean size of 85 nm during the first 20 cycles increased the capacities of the composite microspheres with increasing cycle number [28,57]. The increase in the oxidation peak intensity in the CV curves in Figure 3a, related to the de-alloying reaction of Li–Si alloys during cycling, also indicates gradual activation of the Si nanopowders. After achieving the maximum value of 1390 mA h g⁻¹, the discharge capacity of the composite microspheres with 60 wt% Si nanopowders decreased steadily to 1129 mA h g⁻¹ for the 100th cycle. However, the composite microspheres with 30 wt% Si nanopowders showed stable discharge capacities during further cycling after achieving the maximum capacity at the 20th cycle, and had a value of 1020 mA h g⁻¹ at the 100th cycle. The embedded Si nanopowders increased the capacities of the MoS₂–C composite microspheres. The Coulombic efficiencies of the composite microspheres embedded with 30 wt% Si nanopowders (Figure 4c) had high values above 99.5% from the 2nd cycle. The Li ion storage properties of the MoS₂–C composite microspheres were compared with those of the MoS₂ powders prepared by the spray pyrolysis process reported in the previous literature [52]. The bare MoS₂ powders with filled and yolk-shell structures had discharge capacities of 362 and 687 mA h g⁻¹ for 100th cycle at a current density of 1 A g⁻¹, respectively. Embedding of Si nanopowders with high capacities improved the Li ion storage properties of the MoS₂ material.

Electrochemical impedance spectroscopy (EIS) was conducted to confirm the superior electrochemical properties of the MoS₂–C composite microspheres embedded with 30 wt% Si nanopowders. The impedance measurements were carried out at room temperature before and after 10, 30, 50, and 100 cycles at a current density of 1000 mA g⁻¹. The resulting Nyquist plots, shown in Figure S8, indicate a semicircle in the medium-frequency range, which is assigned to the charge-transfer resistance of the electrodes, and a line inclined at ~45° to the real axis at low frequencies, which corresponds to lithium diffusion within the electrode [58,59]. The charge-transfer resistance of the electrode decreased after the first cycle owing to the transformation of the crystalline structure into an amorphous-fluid-like structure during the first discharge process. The charge-transfer resistance then remained constant through the 100th cycle. The line inclined at ~45° to the real axis at low frequencies was also well

maintained during the first 100 cycles, indicating the good lithium-diffusion properties of the electrode. The morphology of the composite microsphere embedded with 30 wt% Si nanopowders after 100 cycles are shown in Figure S9. The spherical shape of the composite microsphere remained even after 100 cycles because of their high structural stability during cycling as the Si nanopowders with high capacities were completely surrounded by the few-layered MoS$_2$–C composite matrix. The elemental mapping images revealed the uniform distributions of MoS$_2$, C, and Si nanopowders within the composite microsphere even after cycling. The elastic MoS$_2$–C composite matrix accommodated the large volume change of the Si nanopowders during the repeated process of Li$^+$ ion insertion–extraction. As a result, the formation of a stable SEI layer outside the surface during cycling improved the electrochemical properties of the composite microspheres, while the MoS$_2$–C composite layer prevented the formation of unstable SEI layers on the Si nanopowders. Furthermore, the MoS$_2$–C composite matrix exhibited high capacities and excellent cycling performances, which were then shown by the MoS$_2$–C composite microspheres embedded with 30 wt% Si nanopowders. The rate performance of the MoS$_2$–C composite microspheres embedded with 30 wt% Si nanopowders is shown in Figure 4d. The current densities increased stepwise from 0.5 to 7 A g$^{-1}$; for each step, 10 cycles were measured to evaluate the rate performance. The stable reversible discharge capacities of the composite microspheres decreased from 1175 to 677 mA h g$^{-1}$ as the current density increased from 0.5 to 7 A g$^{-1}$. The discharge capacity of the composite microspheres recovered to 1190 mA h g$^{-1}$ as the current density was restored to 0.5 A g$^{-1}$.

**Figure 5.** Shows the long-term cycling performance of the MoS$_2$–C composite microspheres embedded with 30 wt% Si nanopowders at an extremely high current density of 5 A g$^{-1}$. The gradual activation during cycling for the first 100 cycles increased the discharge capacities of the composite microspheres. The composite microspheres attained the maximum discharge capacity of 728 mA g h$^{-1}$ after the first 100 cycles and then steadily maintained this capacity for another 400 cycles. The discharge capacity of the composite microspheres for the 500th cycle was 695 mA h g$^{-1}$, and their capacity retention measured from the 100th cycle was 95.4%.

**4. Conclusions**

In summary, a few-layered MoS$_2$-carbon composite with high capacities and good cycling performance was successfully applied as a protective matrix of silicon nanopowders. Each MoS$_2$–C composite microsphere embedded with Si nanopowders was formed by drying and decomposing one droplet containing ammonium tetrathiomolybdate, PVP, and Si nanopowders. The MoS$_2$–C composite material accommodated the large volume expansion of the Si nanopowders, but it also prevented the formation and propagation of a SEI layer on the Si surface during repeated cycling. The embedded Si nanopowders increased the capacity of the MoS$_2$–C composite microspheres, and its volume fraction in the composite microspheres could be controlled by changing the amount of Si nanopowders dispersed in the spray.
solution. The amount of MoS$_2$ and carbon in the composite microspheres could also be controlled by changing the concentrations of ammonium tetrafluoroborate and PVP that were dissolved in the spray solution. The composite microspheres of MoS$_2$, carbon, and silicon with enhanced Li$^+$ storage properties were evaluated as a novel anode material with superior electrochemical properties for lithium-ion batteries.

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**Electronic Supplementary Material:** Supplementary material (Schematic diagram of one-pot and continuous spray pyrolysis process, FE-SEM image of the Si nanopowders, TG curve of the MoS$_2$-C composite microspheres, Morphologies of the MoS$_2$-C composite microspheres without Si nanopowders, XPS Si 2p spectra of, Nyquist plots, and TEM images after 100 cycles of the MoS$_2$-C composite microspheres embedded with 30 wt% Si nanopowders) is available in the online version of this article at http://dx.doi.org/10.1007/s12274-***-****-** (automatically inserted by the publisher).

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