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Total number of authors:
14

Published in:
Diamond and Related Materials

Link to article, DOI:
[10.1016/j.diamond.2018.06.023](https://doi.org/10.1016/j.diamond.2018.06.023)

Publication date:
2018

Document Version
Peer reviewed version

[Link back to DTU Orbit](#)

Citation (APA):

Ai, Q., Zhou, P., Zhai, W., Ma, X., Hou, G., Xu, X., Chen, L., Li, D., Chen, L., Zhang, L., Si, P., Feng, J., Chi, Q., & Ci, L. (2018). Synergistic double-shell coating of graphene and Li₄SiO₄ on silicon for high performance lithium-ion battery application. *Diamond and Related Materials*, 88, 60-66.
<https://doi.org/10.1016/j.diamond.2018.06.023>

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Accepted Manuscript

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PII: S0925-9635(18)30167-5
DOI: doi:[10.1016/j.diamond.2018.06.023](https://doi.org/10.1016/j.diamond.2018.06.023)
Reference: DIAMAT 7146
To appear in: *Diamond & Related Materials*
Received date: 13 March 2018
Revised date: 2 June 2018
Accepted date: 22 June 2018

Please cite this article as: Qing Ai, Peng Zhou, Wei Zhai, Xiaoxin Ma, Guangmei Hou, Xiaoyan Xu, Lina Chen, Deping Li, Long Chen, Lin Zhang, Pengchao Si, Jinkui Feng, Qijin Chi, Lijie Ci , Synergistic double-shell coating of graphene and Li₄SiO₄ on silicon for high performance lithium-ion battery application. *Diamat* (2018), doi:[10.1016/j.diamond.2018.06.023](https://doi.org/10.1016/j.diamond.2018.06.023)

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Synergistic Double-shell Coating of Graphene and Li_4SiO_4 on Silicon for High Performance Lithium-Ion Battery Application

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ABSTRACT

We demonstrate that the double-shell coating of graphene and Li_4SiO_4 on commercial Si nanoparticles as an effective strategy for improving the anode of lithium ion batteries to overcome the two critical concerns, i.e. rapid capacity decay and inferior coulombic efficiency caused by the large-volume changes. It is proven that the double-shell coating enables the formation of a stable hybrid solid electrolyte interphase, leading to much higher coulombic efficiency and longer cycling stability of the Si anodes. Furthermore, the rate performance of Si is significantly enhanced by the outstanding electrical conductivity of inner graphene layers and the excellent ionic conductivity of Li_4SiO_4 out-shell. The overall results suggest that this new strategy holds promising perspectives in optimizing electrochemical performances of Si anodes, which should promote their practical applications for next-generation lithium ion batteries with increasingly demanded energy density.

1. Introduction

The emerging markets of portable electronic devices and electric vehicles have generated a tremendous demand for lithium-ion batteries (LIBs) with higher energy and power density and longer cycling life.^[1-4] Silicon (Si) has been regarded as one of the most promising alternative to the current used graphite anode materials for LIBs due to its natural abundance, low discharge potential and high theoretical capacity (4200 mAh/g if $\text{Li}_{4.4}\text{Si}$).^[5] However, silicon suffers from extreme volume change (up to 300%) and unstable solid-electrolyte interphase (SEI) during charge-discharge cycling which causes structure degradation, rapid capacity decay and inferior coulombic efficiency. Besides, the intrinsic low electrical conductivity of Si also leads to poor rate capability.

Researchers have attempted a number of approaches to address the large-volume variation problems. For example, designing various Si nanostructures such as nanowires, nanotubes, porous materials, and Si/C composites to reduce the problems.^[5-11] Typically, electrolyte decomposition occurs on the surface of Si due to its low potential (< 0.5 V versus Li/Li^+), resulting in formation of electronic insulating solid electrolyte interphase (SEI) film. SEI protects

Si particles against further electrolyte decomposition, and the stability of the SEI film is thus critical for the cycling performance of the Si particles. Thin SEI film can transport lithium ions, while a thick SEI would retard the charge transfer. The pulverization of Si particles due to the large volume change during lithiation/delithiation leads to a continuous growth of SEI film, which would cause degradation of their electrochemical performance (Figure 1a). Approaches to achieve stable SEI by designing core-shell and yolk-shell structures have been investigated.^[12-15] Carbon materials are widely used as coating layers for Si electrode.^[16-18] Graphene coated Si nanoparticles (Si-NPs) were prepared by a chemical vapor deposition (CVD) process. Multi-layer graphene coating on Si surface accommodates the volume expansion of silicon via a sliding process between adjacent graphene layers.^[19] The graphene coated Si-NPs demonstrate good rate performance and cycling life even up to 200 cycles. Graphene coating may prevent the pulverization of Si-NPs. However, the large volume change still easily causes the thickening of SEI film formed on the surface of graphene layer. Moreover, inevitable cracks of graphene shell during cycling still cause the pulverization of Si-NPs (Figure 1b). Stable artificial SEI film formed by coating LiPON, TiO₂, and Al₂O₃ on Si was attempted to improve the electrochemical performance of silicon electrodes by enhancing its ion conductivity.^[20, 21] Amorphous TiO₂ shell on Si-NPs could greatly increase their initial coulombic efficiency, reversible capacity and cycling stability.^[22] Although individual carbon or artificial SEI films coating^[22-25] have been developed to improving electrochemical performance of Si anode, the challenging issues caused by the huge volume change of Si remain.

Herein, we have designed and synthesized a new Si-NPs structure with double-shell coating of Li₄SiO₄ and graphene (Si@graphene@Li₄SiO₄) (Fig. 1c). According to some reports^[26, 27], Li₄SiO₄ is not only a good Li⁺ conductor, but also can prevent fracture of Si particles for its good mechanical properties. As artificial SEI film, Li₄SiO₄ layer on the surface of Si-NPs would be beneficial to the electrochemical performance of Si electrodes. The inner graphene shell can buffer the volume change thanks to its flexible multi-layer structure and improve the rate capability due to its high electrical conductivity, while the outer shell Li₄SiO₄ coating helps to build and maintain stable SEI layer with a higher ion conductivity. Thanks to the synergistic effect of the double coating layers on Si, when working as the anode material for LIBs, the electrodes can offer a specific capacity of 2525 mAh/g at a current density of 0.05 C, 1370 mAh/g at a current density of 0.5 C and have a capacity retention of more than 80% after 200

cycles. We believe that the double-shell coating is a very promising strategy for designing high performance Si-based LIBs.

2. Materials and methods

2.1 Preparation of Si@graphene

The 0.15 g Si-NPs were first placed in quartz boat, then the quartz boat was transferred into a furnace tube. After that, argon gas of 200 s.c.cm was introduced into the tube and maintained for 15 min to empty the air in the tube. Then the system was heated to 1000°C at a ramping rate of 25 °C/min in the argon atmosphere. The mixed gas consisting of 25 s.c.c.m CH₄ and 25 s.c.cm CO₂ was introduced into the tube furnace after the temperature reached 1000°C, argon was turned off at the same time. After 5 min of graphene growth, the tube furnace was cooled down to room temperature with an argon flow.

2.2 Preparation of Si@graphene@Li₄SiO₄

As prepared Si@graphene particles were used as precursor of Si@graphene@Li₄SiO₄. 0.15 g Si@graphene nanoparticles were first dispersed in a mixture of 240 mL ethanol and 60 mL DI water by ultrasonication, followed by the addition of concentrated ammonium hydroxide (3.0 mL). Under vigorous stirring, 0.6 g tetraethoxysilane (TEOS) was added dropwise into the dispersion and the reaction was left at room temperature under stirring for 12 hours. Si@graphene powders were collected by centrifugation, and washed three times using DI water. Then as-obtained Si@graphene@SiO₂ nanoparticles were dried in vacuum oven at 80°C. Then the dried powders were mixed with sufficient lithium hydroxide monohydrate (LiOH·H₂O) in a mortar and then heated to 550°C for 3 hour in an argon atmosphere. After washing by ethanol for three times and drying in vacuum oven at 80°C, Si@graphene@Li₄SiO₄ powders were obtained.

2.3 Materials characterization

The morphology of as-prepared Si and Si composites were characterized by field-emission scanning electron microscope, high resolution transmission electron microscope. The X-ray diffraction (XRD) patterns of composites and raw materials were characterized on an X-ray-diffractometer (Rigaku) with Ni filtered Cu K_α radiation, scanning rate of 10°/min. Raman spectrums of Si at different steps of process were recorded by Raman spectrometer (Renishaw) with 632 nm laser excitation wavelength at laser power of 1%. Weight loss curves were collected

on Mettler-Toledo TGA2 Thermo Analyzer. The Si@graphene weight loss curves was collected by heating the sample from 30°C to 1000°C at rate of 10°C/min using simulated air atmosphere (20% O₂+80% Ar), which measure the mass percentage of graphene in Si@graphene composite. To characterize the electrode after cycling, the Si@graphene@Li₄SiO₄ electrodes were washed in acetonitrile in glove box with argon-filled to remove the electrolyte with keeping the SEI.

2.4 Anode fabrication and electrochemical measurements

The mixture of active material powder (80wt.%), conductive agent (Super-P, 10wt.%) and Polyvinylidene Fluoride binder (PVDF, 10wt.%) were dissolved in N-Methyl pyrrolidone (NMP). After vigorous stirring for overnight, the electrodes were prepared by casting the solution on the Cu-foil with a mass loading of about 1.3 mg/cm² and drying in vacuum oven for 10h at 80°C. CR2016 cells were assembled in an argon-filled glove box using Li metal foil as the counter electrode. The specific capacity of the active materials was calculated based on the total mass of Si composite. The electrochemical impedance spectroscopy (EIS) was carried out on Metrohm-Autolab with an AC amplitude of 10 mV in frequency range of 0.1 Hz-1 MHz.

3. Results and discussion

The synthesis process of Si@graphene@Li₄SiO₄ composite is schematically summarized in Figure 2a. We used a CVD process to get graphene coated Si (Si@graphene) by using CO₂, a mild oxidant, along with methane (CH₄) during CVD process.^[19, 28] By controlling the CVD temperature, time and ratio of CO₂/CH₄, the thickness of graphene coating layer could be steadily controlled. A Two-step procedure was used to coat Li₄SiO₄ on the surface of graphene encapsulated Si-NPs. First, we used a stober method to coat amorphous SiO₂ onto the Si@graphene particles.^[23, 29] The thickness of the SiO₂ coating was adjusted by controlling the TEOS concentration, pH, and coating time.^[22] Second, a solid-state reaction between SiO₂ and LiOH·H₂O was performed at 550°C in a tube furnace for 3 hours with argon protection to form Li₄SiO₄ coating.^[30]

Scanning electron microscope (SEM) image (Figure 2b) indicates that the as-prepared Si@graphene@Li₄SiO₄ particles have a predominant size of ≈50 nm. The morphological evolution of Si-NPs was investigated by transmission electron microscope (TEM) as shown in Figure 2c. The as-prepared Si@graphene and Si@graphene@Li₄SiO₄ nanoparticles inherit the spherical morphology of Si-NPs cores, forming a typical core-shell structure. As shown in Figure

2d, the surface of Si-NPs are uniformly wrapped with a multi-layer graphene film on. Figure 2d also shows the Li_4SiO_4 coated on the surface of graphene. The crystalline structure of products obtained at different preparing steps was characterized by X-ray diffraction (XRD) (Figure 2e). The silicon nanoparticles show typical silicon patterns. After coating with graphene by the CVD process, the XRD pattern of resultant Si@graphene composite shows a broad bump between 20 and 25 degrees which is assigned to graphene. Weak signal of Li_4SiO_4 appears in the XRD pattern, indicating SiO_x coating is transformed into Li_4SiO_4 .^[30, 31] Raman spectroscopy (Figure 2f) shows the characteristic peaks of graphene at 1320, 1595 and 2615 cm^{-1} , assigned to the D band, G band and 2D band of graphene, respectively.^[32, 33] D-band is related to disorder and defects of carbon, which can be attributed to the defects of the graphene layers. Those defects on graphene could provide diffusion channels for Li^+ , which are beneficial for Li^+ transporting through the graphene shell.^[34] The peaks located at 510 and 935 cm^{-1} are assigned to silicon nanoparticles. The mass percentage of graphene in Si@graphene composite was estimated by TGA to be 8% (Figure S1).

Excellent electrochemical performance is expected for the Si@graphene@ Li_4SiO_4 composite due to the synergistic effect of graphene and Li_4SiO_4 coating layers. Their electrochemical performance was characterized by galvanostatic charge/discharge in a coin-cell configuration. With the coating of only Li_4SiO_4 shell, Si@ Li_4SiO_4 composite demonstrates a better electrochemical performance compared to the pure Si-NPs both at high and low current density as shown in Figure 3a and 3b. The pristine Si electrodes deliver initial discharge and charge capacities of 3245 and 1893 mAh/g, respectively, giving a low initial coulombic efficiency (ICE) of only 58.3%. The ICE increases from 58.3% to 66.4% after coating Li_4SiO_4 on the surface of Si-NPs (Figure 3c), the improved coulombic efficiency (CE) of following cycles also indicate that Li_4SiO_4 helps to build a stable SEI. However, the obvious Li^+ consumption for Si@ Li_4SiO_4 anode indicates that there still exists SEI formation on the exposed area due to the crack of Li_4SiO_4 coating induced by the volume change of Si-NPs. The ICE of double-shell coated Si (Si@graphene@ Li_4SiO_4) can be further improved to 75.4% with an initial discharge and charge capacities of 2525 and 1905 mAh/g. The improved ICE is attributed to the stable SEI since the co-existence of Li_4SiO_4 and graphene films can facilitate forming a very stable hybrid SEI film, which leads to much less irreversible consumption of Li^+ by reducing side reaction between silicon and electrolyte.

Combining the Li_4SiO_4 and graphene together as coating layers brings great improvements in cycling performance of silicon anodes as shown in Figure 3a and 3b. Without coating of graphene or Li_4SiO_4 , the capacity of pristine Si-NPs anodes declines rapidly both at the low current density of 0.05 C (Figure 3a) and the high current density of 0.5 C (Figure 3b). As shown in Figure 3a, the initial capacity fading of pristine Si-NPs, $\text{Si@Li}_4\text{SiO}_4$, Si@graphene and $\text{Si@graphene@Li}_4\text{SiO}_4$ are 43%, 27%, 32% and 20%, respectively. $\text{Si@Li}_4\text{SiO}_4$, Si@graphene and $\text{Si@graphene@Li}_4\text{SiO}_4$ display the enhanced cycling stability (Figure 3a and 3b), resulting from the improved conductivity, more stable SEI forming and better toleration for volume change due to the synergistic effect of double shells of graphene and Li_4SiO_4 . The graphene coating can maintain its continual structure via a layer sliding process with expanded volume change during lithiation,^[19, 28] thus buffer the expansion of Si-NPs due to its flexible structure and superior mechanical properties. Besides, graphene layers can also supply electron-transfer highway which would be beneficial to the rate performance. Li_4SiO_4 is a good ion conductor, and it can be used as the artificial SEI film.^[26, 35] The continual coating of Li_4SiO_4 on Si@graphene particles could prevent further SEI forming reaction between the electrolyte and the particles, thus reducing the consumption of Li ions and improving the ICE. $\text{Si@graphene@Li}_4\text{SiO}_4$ composite has a higher specific capacity than the $\text{Si@Li}_4\text{SiO}_4$ (Figure 3a, b), indicating the contribution of graphene coating through its improving the CE of the anode. However, only graphene coating is not enough to enhance the electrochemical performance. Our cycling data indicates the $\text{Si@graphene@Li}_4\text{SiO}_4$ composite has the much higher specific capacity than the Si@graphene composite with the similar cycling performance (Figure 3a, b). The cyclic voltammetry (CV) curves of the $\text{Si@graphene@Li}_4\text{SiO}_4$ composite is shown in Figure S2. The reduction peak below 0.2 V are assigned to lithiation of Si and oxidization peak around 0.5 V is attributed to lithium extraction from Li-Si alloy.

The $\text{Si@graphene@Li}_4\text{SiO}_4$ composite also demonstrates excellent rate capability comparing to the pristine Si-NPs due to the improved electron and ion conductivity. As shown in Figure 3d, the specific capacities of 1450, 998, 566 mA h/g can be reached at the high current densities of 0.5 C, 1 C, 2 C, respectively. The specific capacity of $\text{Si@graphene@Li}_4\text{SiO}_4$ recovers to 1730 mAh/g after restoring the current density to 0.05 C, showing the excellent electrochemical reversibility of Si composite. A specific capacity retention of more than 1100 mAh/g after 200

cycles at the higher current density of 0.5 C can be achieved, with the first three cycles activated at 0.05 C (Figure 3f).

In order to further reveal the changes of inner electrochemical resistances and interfacial properties, the electrochemical impedance spectroscopy (EIS) of pristine Si-NPs, Si@graphene, Si@Li₄SiO₄ and Si@graphene@Li₄SiO₄ electrodes were investigated (Figure 3e). All the Nyquist plots show a depressed semicircle in the high frequency region and an inclined line in the low frequency domain, which are related to the charge-transfer process and lithium ionic transfer, respectively. The radius of semicircle of Si@graphene@Li₄SiO₄ electrode is much smaller than that of pristine Si-NPs, Si@Li₄SiO₄ and Si@graphene electrodes, indicating that the synergistic double shell coating of graphene and Li₄SiO₄ efficiently improves the electron/ion transfer kinetics during the lithiation/delithiation process. The almost vertical line of Si@graphene@Li₄SiO₄ also indicates that the double-shell coating can greatly improve the diffusion rate of lithium ion.

Ex-situ HR-TEM measurements has been applied to analyze the morphology evolution of the Si@graphene@Li₄SiO₄ particles after cycling in order to better understand the mechanisms for such superior cycling stability and rate capability. After 1st cycle, the double-shell remains on the Si-NPs (two inserts in Figure 4a), which indicate double-coating is robust and able to protect particle from structural rupture. With the space created by layer sliding of graphene, inner-shell graphene layers help to retain the core-shell structure during the initial lithiation process. In the meanwhile, out-shell helps with building a stable hybrid SEI mainly consisting of Li₄SiO₄ and substances formed from the decomposition of the electrolyte on the exposed surface area of graphene as shown in inset images in Figure 4b. The structure evolution of Si composites in first cycle is investigated, distortion of Si cores is observed comparing with the original Si@graphene@Li₄SiO₄ as shown in Figure S3. It should be also noted that voids are left after lithiation process (Figure S3). These voids can be used as the exact space for the cycling volume expansion in the following charge/discharge process. The particles of de-lithiation of Si@graphene@Li₄SiO₄ basically maintain as the similar size compared to lithiation status. The Li₄SiO₄ and graphene layers remains on the surface of Si particles (Figure 4a), showing a good mechanical properties of the double shell.

After cycling for 200 times the thin double-shell structure on the surface of Si nanoparticles well retained (Figure 4b), an indication that the hybrid SEI coating constructed in the initial lithiation process can tolerate large cycling volume change of Si-NPs and no additional thick SEI is formed around the Si particles in following cycles (the inset in Figure 4b). On the contrary, the raw Si-NPs (Figure 4c) are totally pulverized and covered by thick SEI layer after 200 cycles. Even only coated by graphene layers, the morphology of Si@graphene is changed a lot after 200 cycles and thick SEI are formed as shown in Figure 4d. TEM images (Figure 4e) of the Si@graphene@Li₄SiO₄ after 200 cycles indicate that the spherical shape of Si nanoparticles is well maintained, and the double-shell structure can be well identified.

4. Conclusion

In summary, we have introduced the “double-shell” coating concept for Si particles using graphene and Li₄SiO₄. This composite structure as LIBs anodes has shown positive synergistic effects of two coating materials and demonstrated several advantages. First, the Li₄SiO₄ together with graphene coating can help form a stable hybrid SEI film, so that the coulombic efficiency and cycling performance of the battery are much improved. Second, the hybrid coating improves the rate performance of the Si anode by improving the ion conductivity and electrical conductivity simultaneously. Compared to the unmodified Si-NPs, double-shell coated ones delivered a high rechargeable specific capacity of 1370 mAh/g at a current rate of 0.5 C, good rate capability and high capacity retention of 1105 mAh/g after 200 cycles. The synthesis method is low-cost and easy to scale up, and thus holds great potential for practical production and LIB application of this new type of Si materials.

FIGURES

Figure 1. Schematic illustration of the structure evolution during cycling of pristine Si, Si@graphene@ Si@graphene@ Li_4SiO_4 (a) Bare Si particles experience huge volume expansion with thin SEI after 1st lithiation. During de-lithiation, Si structure rupture and leave cracks on both Si particles and SEI layers, exposing fresh interphase of Si particles to electrolyte. In the following cycles, SEI layers continuously grow until Si particles are fully pulverized. (b) The graphene coated Si particles experienced similar volume changes during cycling, but graphene shell can buffer the volume change and fewer cracks were formed. However, after many cycles, graphene shell cannot maintain its structure and a stable SEI on Si particles. This structure ends up with better cycling stability comparing to the Bare Si. (c) The double-shell coated Si particles resisted the huge volume change and maintain thin SEI layer by synergistic effect of graphene and Li_4SiO_4 .

Figure 2. (a) Schematic preparation procedure of Si@graphene@Li₄SiO₄ composites. (b) SEM image of as prepared Si@graphene@Li₄SiO₄. (c) TEM images of pristine Si-NPs, Si@graphene and Si@graphene@Li₄SiO₄, showing the morphology evolution of Si-NPs during the double coating procedure. (d) HR-TEM images of as prepared Si@graphene@Li₄SiO₄, demonstrate double-shell coating structure with graphene as the inner-shell and Li₄SiO₄ as the out-shell. (e) XRD patterns of pristine Si-NPs, Si@graphene and Si@graphene@Li₄SiO₄. (f) Raman spectra of Si@graphene@Li₄SiO₄.

Figure 3. Electrochemical performance of Si@graphene@Li₄SiO₄ composites. (a) Cycling performance of the pristine Si-NPs, Si@Li₄SiO₄, Si@graphene and Si@graphene@Li₄SiO₄ electrodes at a current density of 0.05 C. (b) Cycling performance of the pristine Si-NPs, Si@Li₄SiO₄, Si@graphene and Si@graphene@Li₄SiO₄ electrodes at a current density of 0.5 C (first activated with three cycles at 0.05 C). (c) Coulombic efficiency of pristine Si-NPs,

Si@Li₄SiO₄, Si@graphene and Si@graphene@Li₄SiO₄ electrodes for the first 10 cycles. (d) Rate performance of Si@graphene@Li₄SiO₄. (e) Nyquist plots from the electrochemical impedance spectroscopy (EIS) measurements of Si-NPs, Si@graphene, Si@Li₄SiO₄ and Si@graphene@Li₄SiO₄ electrodes. (f) Long cycling performance Si@graphene@Li₄SiO₄ electrode at a current density of 0.5 C (first activated with three cycles at 0.05 C).

Figure 4. (a) TEM images of Si@graphene@Li₄SiO₄ after 1st cycle. (b) TEM images of Si@graphene@Li₄SiO₄ after 200th cycle. (c), (d) & (e) Low and high magnification TEM images display the morphology difference of pristine Si, Si@graphene and Si@graphene@Li₄SiO₄ after 200th cycle at 0.5 C.

ACKNOWLEDGMENTS

This work was supported by Startup Funding of Distinguished Professorship of “1000 Talents Program” (31370086963030), Shandong Provincial Science and Technology Major Project (2016GGX104001, 2017CXGC1010), the Fundamental Research Funds (2016JC005) and (2015JC033) at Shandong University, and the National Science Foundation of Shandong Province (ZR2017BEM049).

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Graphical Abstract

Highlights

- [1] The ultra-thin graphene and Li_4SiO_4 double-shell structures were successfully designed and prepared.
- [2] The double coating layer of electron and ion conductor is firstly designed to address the issues of rapid capacity decay and inferior coulombic efficiency caused by the large volume change of Si anode materials.
- [3] The optimized coatings benefit lithium ion transfer and prevent the anode from reacting with the electrolyte.
- [4] This double-shell coating structure has been demonstrated to promote the formation of a stable hybrid solid electrolyte interphase thus improve the cycling stability, as well as enhance the rate performance for its excellent conductivity.