Rapid Communication

Dual conductive network-enabled graphene/Si-C composite anode with high areal capacity for lithium-ion batteries

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Abstract
Silicon has been regarded as one of the most promising alternatives to the current commercial graphite anode for Li-ion batteries due to its high theoretical capacity and abundance. Although high gravimetric capacity (mAh/g) of Si-based materials can be achieved, areal capacity (mAh/cm²), an indication of the energy stored at the electrode level, has rarely been discussed. Herein, a novel micro-sized graphene/Si-C composite (G/Si-C) is reported, in which micro-sized Si-C particles are wrapped by graphene sheets. Owing to dual conductive networks both within single particles formed by carbon and between different particles formed by graphene, low electrical resistance can be maintained at high mass loading, which enables a high degree of material utilization. Areal capacity thus increases almost linearly with mass loading. As a result, G/Si-C exhibits a high areal capacity of 3.2 mAh/cm² after 100 cycles with high coulombic efficiency (average 99.51% from 2nd to 100th cycle), comparable to that of commercial anodes. The current findings demonstrate the importance of building a conductive network at the electrode level to ensure high material utilization at high mass loading and may shed light on future designs of Si-based anodes with high areal capacity.

Introduction
Lithium-ion batteries (LIBs) have been intensively studied because of their relatively high energy density, which makes them attractive for use in many electronic devices [1]. Recently, the emerging market for electric vehicles requires
LIBs with higher energy density [2, 3]. Developing new anode materials with high specific capacity is an effective way to increase the energy density of LIBs. Due to its high theoretical capacity (3579 mAh/g) and abundance, silicon has been regarded as one of the most promising alternatives to the currently-used graphite anode, which has a low theoretical capacity of 372 mAh/g [4, 5]. However, there is a major barrier to the practical application of Si: its large volume change during charge/discharge causes to severe pulverization of Si particles and degradation of Si electrodes, leading to poor cycling stability [6]. Extensive efforts have been devoted to improving the cyclability of Si-based anodes with encouraging results, including development of various Si nanostructures/nanocomposites, novel binders and electrolyte additives [7-16].

However, most of the advances in Si-based materials to date were reported in the form of gravimetric capacity (mAh/g), while areal capacity (mAh/cm²) has rarely been discussed. Gravimetric capacity describes the capacity that a material can deliver. However, in practical applications the performance of anodes is evaluated at the electrode level, and areal capacity is an indication of the energy that an electrode can store. Although high gravimetric capacity of Si-based materials can be achieved, it usually comes with very low mass loading, which in turn leads to electrodes with limited areal capacity [11, 13]. In the few reports involving high mass loading, higher areal capacity was demonstrated with: (1) limited cycle numbers; (2) fixed gravimetric capacity/reduced voltage range; (3) low coulombic efficiency; or (4) electrodes fabricated by special techniques which are not compatible with industrial slurry coating approaches, such as binder-free electrodes [17-21].

We previously demonstrated a micro-sized Si-C composite composed of interconnected Si nanoscale building blocks and carbon conductive network [22-24]. However, the conductive network is only within the micro-sized particles and no such a network exists between particles, potentially leading to large interparticle contact resistance. Due to its extraordinary electronic conductivity and two-dimensional morphology [25, 26], graphene has been identified as an excellent conductive additive in various composites to enhance the electrochemical performance of electrode materials by improving electron transport and maintaining electrical contact in electrodes [27-31]. However, graphene has majorly been incorporated with nanomaterials to form nanocomposites and graphene-containing micro-sized composites have been less reported.

Herein, we report a novel micro-sized graphene/Si-C composite (G/Si-C), in which micro-sized Si-C particles are wrapped by graphene sheets. The two-dimensional conductive graphene sheets act as a conductive network between particles and thus decrease the contact resistance of the whole electrode. Thanks to it having conductive networks both within single particles and between different particles, G/Si-C shows a higher degree of material utilization at high mass loading compared to the raw micro-sized Si-C composite (Si-C). An areal capacity of 3.2 mAh/cm² after 100 cycles and high coulombic efficiency (average 99.51% from 2nd to 100th cycle) are achieved by G/Si-C, comparable to that of commercial LIBs [32], making it a promising anode material for practical applications in LIBs.

Material and methods

Synthesis of G/Si-C

Graphite oxide (GO) was firstly prepared from natural graphite powder (300 mesh, Alfa Aesar) by a modified Hummers method [33, 34]. In a typical process, 1 g of SiO (2 μm) was dispersed in 150 mL water under stirring for 30 min. Then 3 g of PDDA (Sigma-Aldrich) was added and the mixture was stirred for another 30 min. Afterwards, as-prepared GO solution was added dropwise to the PDDA-SiO suspension with a mass ratio of 28:1 between SiO and GO. After 2 h stirring, the GO/PDDA-SiO was obtained by vacuum filtration followed by washing sequentially with water and ethanol, and finally drying in vacuum oven at 80 °C overnight. The GO/PDDA-SiO was then transferred to a horizontal quartz tube. Ar/H₂ (95:5 v/v) was introduced at a flow rate of 1500 sccm for 20 min to purge the system. Afterwards the flow rate was reduced to 100 sccm and the tube was heated to 950 °C with a ramping rate of 10 °C/min and kept for 5 h. The samples were taken out of the tube at temperatures below 40 °C and immersed in 20 wt% HF solution (H₂O:ethanol = 5:1 by volume) at room temperature for 3 h to remove SiO₂. The obtained porous Si was collected by filtration and washed with distilled water and ethanol in sequence several times. The final product was dried in a vacuum oven at 60 °C for 4 h. Carbon coating of G/Si was done by thermal decomposition of acetylene gas at 800 °C for 10 min in a quartz furnace. The mixture of acetylene and high-purity argon (argon:acetylene = 9:1 by volume) is introduced at a flow rate of 100 sccm. Si-C was prepared similarly without the addition of GO.

Characterization

The obtained samples were characterized on a Rigaku Dmax-2000 X-ray powder diffractometer (XRD) with Cu Kα radiation (λ=1.5418 Å). The operating voltage and current were kept at 40 kV and 30 mA, respectively. The size and morphology of the as-synthesized products were determined by a JEOL-1200 transmission electron microscope (TEM), FEI Nova NanoSEM 630 scanning electron microscope (SEM). Raman spectroscopy was conducted with a Witec CMR200 confocal Raman instrument.

Electrochemical measurements

Electrochemical experiments were performed using 2016-type coin cells, which were assembled in an argon-filled dry glovebox (MBraun, Inc.) with the G/Si-C and Si-C electrodes as the working electrode and the Li metal as the counter electrode. The working electrodes were prepared by casting the slurry consisting of 80 wt% of active material and 20 wt% of poly(acrylic acid) (PAA) binder. Six different electrode types with different mass loadings of active materials (around 1.2, 2.0 and 3.2 mg/cm²; see Table S1 in Supporting Information for details) were fabricated using G/Si-C and Si-C. 1 mol/L LiPF₆ in a mixture of ethylene carbonate, diethyl carbonate and dimethyl carbonate (EC:DEC:DMC, 2:1:2 by vol %) and 10 wt% fluoroethylene carbonate (FEC) was used as the electrolyte (Novolyte Technologies, Independence, OH). The
electrochemical performance was evaluated by galvanostatic charge/discharge cycling on an Arbin BT-2000 battery tester at room temperature under different current densities in the voltage range between 1 and 0.01 V versus Li$^+$/Li. The current density and specific capacity are calculated based on the mass of the composites.

**Results and discussion**

**Figure 1** shows the preparation process of the G/Si-C composite. According to the previous report [35], poly(diallyldimethylammonium chloride) (PDDA) is employed to make a GO/PDDA-SiO assembly, with PDDA acting as a positively charged medium to attract (graphite oxide) GO and SiO, both of which are negatively charged (see Figure S1 in Supporting Information for more on the influence of PDDA) [35, 36]. The GO/PDDA-SiO assembly is then heated in an H$_2$/Ar atmosphere. During this process, GO is reduced to graphene and at the same time SiO is disproportionated to Si and SiO$_2$. After removal of SiO$_2$ by HF treatment, G/Si is obtained. Finally, carbon filling by decomposition of gaseous carbon precursor leads to formation of G/Si-C, in which both of graphene sheets and porous Si are coated by carbon.

The phase and crystallinity of G/Si-C were investigated by XRD. As shown in Figure 2a, the peaks of the pattern can be indexed to those of crystalline face-centered cubic Si (JCPDS Card no. 27-1402). Figure 2b shows the Raman spectrum of G/Si-C, with peaks at 1333 and 1614 cm$^{-1}$, corresponding to the D (disordered) band and the G (graphitic) band of carbon, respectively [37]. These two peaks confirm the presence of carbon in the composite. The carbon content was determined by elemental analysis before and after carbon coating to distinguish graphene and carbon from acetylene decomposition. The carbon content is around 30 wt% in total, with 6 wt% and 24 wt% in the form of graphene and carbon from acetylene decomposition, respectively. The intensity of the D band is comparable to that of G band, indicating an overall amorphous carbon structure derived from the majority of the carbon formed by acetylene decomposition.

The morphology, size, and structure of the composite have been investigated by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). Figure 2c shows a typical TEM image of GO/PDDA-SiO. It is clear that SiO particles are covered by graphene sheets (the edge is marked by white arrows). TEM images of products obtained at different steps are available in Figure S2 (see Supporting Information). Similar morphology to these is observed in G/Si-C (Figure 2d), which indicates that the assembled graphene/Si structure is preserved during the HF etching and carbon coating processes. The high-magnification TEM image in Figure 2e shows micro-sized particles composed of interconnected nanoparticles with a size of about 10-15 nm. In addition, wrinkles, a characteristic feature of graphene sheets [28, 31, 38, 39], can also be clearly seen (marked by white arrows). Figure 2f shows an SEM image of G/Si-C, in which micro-sized particles wrapped by graphene sheets are found, consistent with the TEM observations.

**Electrochemical studies of G/Si-C and Si-C**

Galvanostatic charge-discharge tests were carried out to evaluate the electrochemical performance. To determine the influence of the incorporation of graphene, Si-C composite with similar carbon content (30 wt%) was also prepared and tested as the control sample. Electrodes with three different active material mass loadings (around 1.2, 2.0 and 3.2 mg/cm$^2$) were fabricated for each composite, and were designated G/Si-C@low, G/Si-C@medium, G/Si-C@high. G/Si-C@low, Si-C@low, Si-C@medium and Si-C@high, where low, medium, and high referred to mass loading. Note that all electrodes were prepared without any external carbon additives (electrodes used only composites and binder in an 8:2 ratio). Considering the potential increase in electrode resistance with increasing mass loading, lower activation current densities were used for electrodes with medium and high mass loading (see Table S1 in Supporting Information for details).

Figure 3a-d shows cycling performance of G/Si-C and Si-C electrodes with different mass loadings in both gravimetric and areal forms. It is clear that increasing mass loading has no obvious effect on gravimetric capacity of G/Si-C for the initial cycles. All three G/Si-C electrodes exhibit similar gravimetric capacities of about 1100 mAh/g (Figure 3a), indicating a similar degree of material utilization. Areal capacity thus increases almost linearly with mass loading. As shown in Figure 3b, G/Si-C@low and G/Si-C@medium exhibits about 1.3 and 2.1 mAh/cm$^2$, respectively, while G/Si-C@high can deliver an areal capacity of 3.2 mAh/cm$^2$ after 100 cycles, comparable to that of commercial LIBs [32]. By contrast, the gravimetric capacity of Si-C is sharply decreased by high mass loading. Although Si-C@low has a similar gravimetric capacity to that of G/Si-C@low, the increase in mass loading dramatically decreases the gravimetric capacity. Si-C@medium shows a low gravimetric capacity of about 740 mAh/g after the initial two cycles, only about 65% of that of Si-C@low. As a result, the areal capacity of Si-C@medium is close to that of Si-C@low. Further increase in mass loading leads to even lower gravimetric capacity. Si-C@high delivers only 580 mAh/g, barely above half that of Si-C@low. This gravimetric capacity drop means that only a slight increase in areal capacity of Si-C, from 1.3 to 1.8 mAh/cm$^2$, was achieved when the mass loading was almost tripled. It is also clear that Si-C@high showed capacity fading. We ascribe this to high mass loading and high degree of material utilization. Higher mass loading, generally accompanied by larger volume, results in slow relaxation of stress. Added to this, higher
degree of material utilization is directly related to larger volume change, which generates more stress. These two factors together lead to larger stress in the electrode. Further material and electrode optimization such as introducing built-in void into materials and developing new binders may help to stabilize the cyclability.

Figure 3e and f shows the first cycle voltage profiles of the extreme cases - G/Si-C and Si-C electrodes with low and high mass loadings. G/Si-C@low delivered charge (delithiation) and discharge (lithiation) capacities of 1314 and 1939 mAh/g, corresponding to a coulombic efficiency (CE) of 67% (Figure 3e). A similar CE of 64.0% was obtained for G/Si-C@high as 1834 and 2864 mAh/g were achieved (Figure 3e). In comparison, the first cycle CE decreased pronouncedly for Si-C at high mass loading. As shown in Figure 3f, the charge and discharge capacities of Si-C@low are 1320 and 1950 mAh/g, giving a CE of 68%. However, Si-C@high has a lower CE of 57% with charge and discharge capacities of 1423 and 2471 mAh/g, respectively. Aside from the first cycle CE, another noticeable difference between G/Si-C and Si-C is the lithiation plateau at high mass loading. G/Si-C@high has a lithiation plateau of about 0.15 V, higher than 0.11 V of Si-C@high. This is indicative of a lower polarization of the G/Si-C electrode than that of
the Si–C one [31]. Such difference is due to the incorporation of graphene sheets as a conductive network [28, 39], which provides additional electron transport pathways between Si–C particles. It is worth noting that the presence of graphene, unlike in many previous reports [40–43], does not significantly decrease the first CE (only from 68% to 67%), which is probably due to the low content of graphene (6 wt%). G/Si–C@high also has high CE after the initial cycle.

Figure 4a shows the CE from 2nd to 100th cycle, with the red line marking 99.5%. The CE increases above 99.5% in 15 cycles and remains that high afterwards. The average CE from the 2nd to 100th cycle is 99.57%, which is rarely reported for Si-based electrodes with high mass loading.

The difference in electrochemical performance was further studied by electrochemical impedance spectroscopy (EIS) measurements. Figure 4b shows the Nyquist plots of G/Si–C and Si–C electrodes with low and high mass loadings, as two extremes, after five cycles at delithiated state. All spectra consist of a depressed semicircle in the high-to-medium frequency range and a straight line in the low frequency range. The Randles equivalent circuit (upper inset) was employed to analyze the impedance spectra [31]. According to the fitting results (Table S2, Supporting Information), the charge transfer resistance of G/Si–C@low is 10.9 Ω, similar to that of G/Si–C@high (9.14 Ω, middle inset). By contrast, Si–C@high has a much higher charge transfer resistance of 59.98 Ω than Si–C@low (16.83 Ω). The difference in resistance, especially at high mass loading, serves strong evidence of improvement in electronic conductivity through forming conductive network by graphene at both low and high mass loadings.

**Figure 3** (a–d) Cycling performance of G/Si–C and Si–C. First cycle voltage profiles of (e) G/Si–C and (f) Si–C at low and high mass loadings.
To better understand the reason for the high degree of material utilization, post-cycling SEM and TEM investigation was carried out on delithiated Si–C@high electrode after 100 cycles. Acetonitrile and 1 M hydrochloric acid solution were used to remove electrolyte, SEI layer, and binder of the TEM sample. As shown in Figure 5a, the structure of electrode maintains well as only small cracks are present without any active material peeling off, similar to our previous report [23]. TEM observation (Figure 5b) reveals change of the active material at nanoscale level. The micro-sized composite did break into smaller pieces during cycling. However, these pieces were still connected by graphene sheets, similar to the structure before cycling (Figure 2d), which effectively decreased the contact resistance between smaller pieces and thus ensured good material utilization.

Conclusions

In summary, a graphene-wrapped micro-sized Si–C composite has successfully been prepared via a facile approach. The graphene provides additional electron pathways for the whole electrode by forming a conductive network that connects different Si–C particles, giving the G/Si–C conductive networks both within and between particles. As a result, low electrical resistance can be maintained at high mass loading, which enables a high degree of material utilization. Correspondingly, the graphene-wrapped Si–C composite exhibits a high areal capacity of 3.2 mAh/cm² after 100 cycles with high coulombic efficiency. These findings demonstrate the importance of building a conductive network at the electrode level for high material utilization at high mass loading and may shed light on future designs of Si-based anodes with high areal capacity.

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Appendix A. Supporting information

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References

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