High-Performance Li-Ion Battery Anodes Based on Silicon-Graphene Self-Assemblies

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A series of Si/graphene sheet/carbon (Si/GC/C) composites was prepared by electrostatic self-assembly between amine-grafted silicon nanoparticles (SiNPs) and graphene oxide (GO). The Si/GC derived from carbonization of Si/GO composite showed limited cycling stability owing to loose cohesion between SiNPs and graphene, and increased impedances during cycling. To counteract the cycling instability of Si/GC, an additional carbon-gel coating was applied to the Si/GC assemblies in situ in solution followed by carbonization to yield dense three-dimensional particulate Si/GS/C composite with many internal voids. The obtained Si/GC/C composites showed much better electrochemical performances than the Si/GC owing to enhanced cohesion between the SiNPs and the carbon structures, which reduced the impedance buildup and protected the SiNPs from direct exposure to the electrolyte. A strategy for practical use of a high-capacity Si/GS/C composite was also demonstrated using a hybrid composite prepared by mixing it with commercial graphite. The hybrid composite electrode showed specific and volumetric capacities that were 200% and 12% larger, respectively, than those of graphite, excellent cycling stability, and CEs (>99.7%) exceeding those of graphite. Hence, electrostatic self-assembly of SiNPs and GO followed by in situ carbon coating can produce reliable, high-performance anodes for high-energy LIBs.

Energy storage via rechargeable batteries will play an increasingly important role in the future not only to power advanced mobile electronic devices, power tools, sensors for internet-of-things devices, medical implants, military and aerospace devices, drones, e-bikes, many electrified vehicles, and so on, but also to store energy from intermittent renewable resources (solar and wind power) and for backup energy supplies for smart electric grids. Among many rechargeable batteries, lithium-ion batteries (LIBs) offer the highest energy density to date and reasonably long cycle life and power capability. Nevertheless, the demands for high-energy LIBs are increasing, especially the demand for electric vehicles to carry sufficient energy comparable to that of internal combustion vehicles.

To further enhance the energy content of an LIB, electrode materials capable of delivering high capacity at a high working voltage (a higher-potential cathode coupled with a lower-potential anode vs. Li/Li+) have to be incorporated, and the cell design has to be optimized to maximize the packing density. Noticeable progress has been made on the cathode side recently by optimizing the composition and structure of Ni-rich LiNi1−xMnxO2 (0 ≤ x ≤ 0.1),11,12 Li-rich layered oxide Li1+yTi1−xAlxO2 (0 ≤ x ≤ 1),13 and Li-rich layered oxide cathodes, which has resulted in LIBs with a much higher energy content. On the other hand, all LIB anodes are still made of graphite, whose theoretical capacity (372 mAh g−1) has been achieved since its first introduction in 1991. Therefore, a breakthrough in terms of the energy density of LIBs would require adoption of new anodes having a much higher capacity than graphite. Among many candidates to replace graphite, silicon is the most promising because of its high theoretical specific capacity of 3579 mAh g−1 (in the form of Li1+xSi1−x at room temperature)14−16 and relatively low discharge (delithiation) potential (≈0.5 V vs. Li/Li+). However, the electrochemical reaction between nonconducting silicon and lithium ions is accompanied by a huge net volume expansion (≈300%) localized around the electrode contact, growth of a newly formed unstable solid–electrolyte interface (SEI),19,20 electrolyte depletion, and so on. To address these issues associated with silicon, tremendous research efforts have been devoted to rational designs of silicon-based composites in which the huge volume variation is effectively accommodated and thus the electrical network is well preserved to secure a long cycle life.

Among many conducting carbonaceous platforms for the formation of silicon-based composites, graphene has been effectively incorporated in a variety of formats to enhance the cycling stability of silicon:11,21−38 a self-supporting silicon nanoparticle (SiNP)−graphene paper composite prepared by simple membrane filtering of a homogeneous aqueous mixture of SiNPs or silicon nanowires and graphene oxide (GO),39,40 crumpled-graphene-encapsulated SiNPs prepared by an aerosol-assisted capillary assembly method,41 graphene granules or a graphene hybrid coated with nanosilicon by chemical vapor deposition,30,31 Si/C composites internally wired with dispersed graphene networks prepared by a solution-based sol−gel process,11,39 Si–graphene composites prepared by an electrostatic self-assembly method25,27,29,31,40 and conformal growth of graphene cages on the surface of silicon particles by a Ni-catalyzed dissolution−precipitation mechanism.44

Electrostatic self-assembly is an attractive strategy, among the many applied to prepare Si–graphene composites, and yields a uniform dispersion of SiNPs throughout the composites. Moreover, the cost of raw materials such as SiNPs and GO are decreasing every year. For practical application of Si–graphene assemblies in LIB anodes, however, many issues remain unresolved. For example, most self-assembled Si–graphene composites showed unsatisfactory cycling stability even when operated in a shallow voltage range,25 and low first-cycle Coulombic efficiencies (CEs) (48%−73%),25,27,29,31 Even after the initial cycles, CEs above 99.5%, which is essential for a long cycle life, have seldom been reported for self-assembled Si–graphene composites. Furthermore, key information such as the material or electrode density and volumetric capacity in comparison with those of the state-of-the-art graphite anode is not provided. These previous studies suggest that self-assembled Si–graphene composites need to be further optimized with respect to these issues.

In this study, we prepared a series of Si/graphene sheet/carbon (Si/GS/C) composites using the electrostatic self-assembly method. To counteract the above issues associated with self-assembled...
Si–graphene composites, additional carbon coating was attempted in ways that preserve the close cohesion between SiNPs and graphene provided by electrostatic self-assembly as much as possible. When an additional carbon-gel coating is applied to the Si/GO assemblies in situ in solution or to the Si/GS derived from thermal reduction of Si/GO assemblies ex situ, followed by carbonization, dense three-dimensional (3D) particulate Si/GS/C composites, Si/GS/C-S or Si/GS/C-P, respectively, were formed with many internal voids. Thus, the obtained Si/GS/C composites showed much better electrochemical performance than the Si/GS assemblies owing to enhanced cohesion between the SiNPs and the carbon structures, including graphene, which reduced the impedance buildup and protected the SiNPs from direct exposure to the electrolyte. The Si/GS/C composites exhibited high capacity (>1300 mAh g$^{-1}$ at 100 mA g$^{-1}$) with good cycling stability and high CE (>99.7%). Finally, a strategy for practical use of a high-capacity Si/GS/C composite was demonstrated using a hybrid composite prepared by mixing it with commercial graphite. The three-dimensional (3D) particulate Si/GS/C composites, Si/GS/C-S or Si/GS/C-P, respectively, were formed with many internal voids. Thus, the obtained Si/GS/C composites showed much better electrochemical performance than the Si/GS assemblies owing to enhanced cohesion between the SiNPs and the carbon structures, including graphene, which reduced the impedance buildup and protected the SiNPs from direct exposure to the electrolyte. The Si/GS/C composites exhibited high capacity (>1300 mAh g$^{-1}$ at 100 mA g$^{-1}$) with good cycling stability and high CE (>99.7%). Finally, a strategy for practical use of a high-capacity Si/GS/C composite was demonstrated using a hybrid composite prepared by mixing it with commercial graphite. The three-dimensional (3D) particulate Si/GS/C composites, Si/GS/C-S or Si/GS/C-P, respectively, were formed with many internal voids. Thus, the obtained Si/GS/C composites showed much better electrochemical performance than the Si/GS assemblies owing to enhanced cohesion between the SiNPs and the carbon structures, including graphene, which reduced the impedance buildup and protected the SiNPs from direct exposure to the electrolyte. The Si/GS/C composites exhibited high capacity (>1300 mAh g$^{-1}$ at 100 mA g$^{-1}$) with good cycling stability and high CE (>99.7%). Finally, a strategy for practical use of a high-capacity Si/GS/C composite was demonstrated using a hybrid composite prepared by mixing it with commercial graphite. The hybrid composite electrode showed specific and volumetric capacities that were 200% and 12% larger, respectively, than those of graphite, excellent cycling stability up to 200 cycles, and CEs (>99.7%) exceeding those of graphite.

**Preparation of Si–graphene composite anodes.—**A series of Si–graphene sheet–carbon (Si/GS/C) composites was prepared according to Scheme 1. To prepare the Si/GS sample, the Si/GO assemblies were collected by centrifugation and dried at 80°C overnight. The dried Si/GO assemblies were thermally reduced at 850°C for 2 h under Ar flow to yield the Si/GS sample. Two Si/GS/C composites were prepared by carbon-gel coating on the Si/GS ex situ or on the Si/GO assemblies in situ in solution, followed by carbonization at high temperature in Ar flow. For the Si/GS/C-P sample, the thermally reduced Si/GS particles (0.12 g) were dispersed in acetone, and polyvinylidene fluoride (PVdF) (5.0 wt%, Solvay) dissolved in acetone was added to the Si/GS solution under stirring. After 30 min, the acetone was evaporated at 50°C, and the thoroughly dried sample was carbonized at 850°C for 2 h under Ar flow in a tube furnace to obtain the Si/GS/C-P composite. To prepare the Si/GS/C-S sample, the solvent of Si/GO after the electrostatic self-assembly process was replaced with an acidic solution containing sulfuric acid to maintain electrostatic attraction in the assemblies. Then, sucrose (0.67 g, 99.5%, Sigma-Aldrich) dissolved in DI water was added dropwise to the mixture through a micro-syringe pump for 2 h to produce an in situ carbon-gel coating around the Si/GO assemblies. After further stirring at room temperature for 1 h, the solution was kept at 100°C under stirring until the sample was dry. The dried dark brown sample was further reacted at 160°C in air for 5 h followed by carbonization at 850°C for 2 h under Ar flow in a tube furnace. The sample thus obtained was denoted as Si/GS/C-S.

**Characterizations.—**Fourier-transform infrared (FTIR) spectra were obtained on a Thermo Scientific Nicolet 380 spectrometer using KBr pellet methods. The amount of APTMS in Si–APTMS was quantified by elemental analysis and thermal gravimetric analysis (TGA). The particle sizes of SiNPs and Si–APTMS were measured by dynamic light scattering (DLS), X-ray diffraction (XRD) patterns of the samples were recorded on a Rigaku model Miniflex 600 X-ray diffractometer (40 kV, 15 mA, Cu–K$_\lambda$ radiation, $\lambda = 1.5418$ Å). Raman spectra were obtained using a WITec alpha 300R spectrometer equipped with a 532 nm laser. The structure and morphology of the samples were investigated using field-emission scanning electron microscopy (FE-SEM, JEOL JSM-35CF operated at 10 kV) and transmission electron microscopy (TEM, JEOL JEM-2010 operated at 200 kV). To investigate the microstructure of cross sections of sample particles, a sample was mounted in epoxy resin and cut into thin slices...
Functional groups such as –C=O, –O–H, and –C–O in the carboxylic, phenolic ether, and alcoholic groups on GO are identified in the FTIR spectrum in Figure 1a. The FTIR spectra of the parent boxylic, phenylic ether, and alcoholic groups on GO are identified with an Ar ion beam. The particle cross section was examined by SEM and energy-dispersive X-ray spectroscopy (EDS) element mapping. The Si and C contents of composite samples were determined by TGA run to 800°C at a ramp rate of 10°C min⁻¹ under air flow.

Electrochemical measurements.—The electrochemical properties of the prepared samples were measured using CR2032 coin-type half-cells assembled in an argon-filled glove box with Li foil as the counter electrode. A homogeneous slurry comprised of active material:carbon black (Super P Li, Timcal Ltd.):polyvinyl alcohol binder (5 wt%, dissolved in dimethyl sulfoxide) at a mass ratio of 8:1:1 was uniformly coated onto a copper foil using a Meyer-bar coating device (Kipae E&T, Korea). As a hybrid active material, Si/GS/C-S@Gr was prepared by mixing Si/GS/C-S and commercial graphite at a mass ratio of 4:6. For the working electrode of commercial graphite, PVdF (5 wt%, Solef 5130, Solvay, dissolved in N-methyl-2-pyrrolidone) was used as the binder. The coated electrodes were dried at room temperature in air for 2 h and then dried at 80°C in air for 2 h. Then, the electrodes were roll-pressed several times and further dried under vacuum at 80°C for 2 h. A microporous polypropylene membrane (Celgard 2400) was used as the separator. The electrolyte was 1 M LiPF₆ in a mixture of ethylene carbonate, ethyl methyl carbonate, and dimethyl carbonate (3:4:3 vol. ratio) containing 10 vol% of fluoroethylene carbonate (FEC) (Panax Etech Co., Ltd., Korea). For the graphite anode, the above electrolyte without FEC was used. Electrochemical cycling and rate tests were performed in the cutoff voltage range of 0.02–1.5 V vs. Li/Li⁺, and cyclic voltammetry (CV) tests were conducted at a scanning rate of 0.1 mV sec⁻¹ on a galvanostat/potentiostat system (WonATech Co., Ltd., Korea). Electrochemical impedance spectroscopy (EIS) measurements were conducted in a frequency range of 100 kHz to 0.01 Hz with an AC amplitude of 10 mV on a ZIVE SP2 (WonATech Co., Ltd., Korea) analyzer.

Results and Discussion

As described in Scheme 1, the Si/GO assemblies were thermally reduced to obtain Si/GS. The reduced Si/GS particles were further charge-stabilized via APTMS grafting. Figure 2a shows photographs of the GO and Si-APTMS dispersions in water and in ethanol, respectively, which present stable colloids of the dispersions. In an acidic solution, APTMS grafting makes the surface of the SiNPs positively charged owing to protonation of the amine groups of APTMS, whereas the surfaces of the GO sheets become negatively charged owing to ionization of the carboxylic and phenolic hydroxyl groups in GO. As soon as the Si-APTMS solution was added to the aqueous GO solution at a pH of around 2 under stirring, the two oppositely charged species assembled to form aggregates by electrostatic attraction. The Si/GO aggregates thus precipitated to leave a clear aqueous solution, as shown in Figure 2a. The TEM image of Si/GO assemblies in Figure 2b and its inset indicate that all the SiNPs are located on the surfaces of the GO sheets owing to electrostatic interaction. A SEM image of the Si/GO assemblies shows their two-dimensional (2D) planar structures (Figure 2c), and a SEM image at high magnification reveals that most of the SiNPs are removed from GO sheets, although some fraction of the SiNPs is loosely bound on GO sheets and open to the particle surface, as seen in the inset of Figure 2d.

Figure 1. FTIR spectra of (a) GO and (b) SiNPs and Si-APTMS, (c) TGA profile and EA result (in the inset) of Si-APTMS, and (d) DLS results of SiNPs and Si-APTMS.
coated with carbon using PVdF as the carbon precursor to prepare Si/GS/C-P. The Si/GS/C-S composite was prepared by additional carbon-gel coating in situ on Si/GO assemblies using sucrose as the carbon precursor, followed by thermal reduction. Figure 3a shows the XRD patterns of the parent SiNPs and composite samples derived from the Si/GO assemblies. Diffraction peaks assignable only to crystalline silicon phases were observed with small humps at 20 = 17.27° due to graphene and amorphous carbons. The graphitic carbon phase at around 20 = 26.4° was absent in the Si/GS, Si/GS/C-P, and Si/GS/C-S composites. This indicates that graphene sheets (GSs) are highly dispersed in the composites and they do not reconstitute to form the thick crystalline graphitic phase that was commonly observed in Si–graphene composites prepared by physical mixing of GO and SiNPs followed by thermal reduction at high temperature.

From the mass losses in the TGA profiles in Figure 3b, the Si contents of Si/GS, Si/GS/C-P, and Si/GS/C-S were estimated to be 82.9, 61.9, and 51.4 wt%, respectively. Raman spectra of composite samples in Figure 3c showed sharp peaks centered at around 520 cm\(^{-1}\) and 51.4 wt%, respectively. The Raman spectra of composite samples increased compared to those for Si/GS. However, the relative intensity ratios (ID/IG) for Si/GS, Si/GS/C-P and Si/GS/C-S were 0.35, 0.99, 0.99 and 0.96, respectively, which are much higher than that of crystalline graphite (ID/IG = 0.35). The relatively high ID/IG ratio of samples indicates large portion of disordered carbon in the composites and additional carbon coating with sucrose induces slight increase of the ID/IG ratio.

Figure 4 shows SEM images of the Si/GS/C-P and Si/GS/C-S composites. Compared to the 2D planar Si/GS/C-P and Si/GS/C-S composites in Figure 3c, the Si/GS/C-S composites show a 3D particulate morphology due to the additional carbon coating with PVdF and sucrose, respectively. The particles of Si/GS/C-S (Figure 4d) have a densely packed surface structure, whereas the surfaces of the Si/GS/C-P particles exhibit rather open structures, as reported in the literature when PVdF was employed as a carbon source. Figures 5a and 5b show the structures of the Si/GS/C-P and Si/GS/C-S composites, respectively, in more detail as examined by TEM. In both samples, SiNPs and carbon-coated SiNPs (Si/C particles) are either encapsulated in or in close contact with transparent and wrinkled GSs. Some amorphous carbons derived from the additional carbon coating also appear around the particles. The SiNPs and Si/C particles are clearly well dispersed through the composites, and they are all connected by GSs. The flexible and conducting GS also forms sufficient voids between SiNPs and Si/C particles, which are beneficial in damping the mechanical stresses associated with huge volume changes during the electrochemical alloying and de-alloying cycles of silicon with lithium. The microstructure of the particle cross section of Si/GS/C-S was further investigated by SEM and element mapping, as shown in Figure 6.

As seen in the high-magnification SEM image (Figure 6b) of a selected area in Figure 6a, spherical SiNPs or Si/C particles are distributed between randomly oriented graphene layers. In accordance with the TEM observation in Figure 5, many empty spaces were generated inside Si/GS/C-S particles, mainly because of the inherent wrinkled nature of GSs. The EDS maps of C (in red) and Si (in yellow) in Figures 6c and 6d, respectively, support homogeneous distributions of C and Si in the 20 \(\times\) 30 \(\mu\)m\(^2\) particle cross section, and there is a rather low concentration of Si along the particle edges.

The electrochemical properties of Si/GS, Si/GS/C-P, and Si/GS/C-S in use as anodes for LIBs were compared to those of commercial graphite. The galvanostatic discharge (lithiation)/charge voltage profiles for the first cycle of Si/GS, Si/GS/C-P, and Si/GS/C-S samples are compared in Figure 7a. Si/GS, Si/GS/C-P, and Si/GS/C-S delivered initial discharge/charge capacities of 2948/2365, 2246/1511, and 2059/1582 mAh g\(^{-1}\), yielding first-cycle CEs of 80.2%, 67.3%, and 76.8%, respectively. In the first discharge, voltage slopes between 1.6 and 0.2 V commonly appeared for the composites owing to the formation of an irreversible SEI layer, which accounted for the fact that Si/GS/C-P had the largest area and thus the lowest CE, possibly due to graphene and amorphous carbons. The graphitic carbon phase at around 20 = 26.4° was absent in the Si/GS, Si/GS/C-P, and Si/GS/C-S composites. This indicates that graphene sheets (GSs) are highly dispersed in the composites and they do not reconstitute to form the thick crystalline graphitic phase that was commonly observed in Si–graphene composites prepared by physical mixing of GO and SiNPs followed by thermal reduction at high temperature.

At a high current of 1.6 A g\(^{-1}\), the specific capacities of Si/GS, Si/GS/C-P, and Si/GS/C-S were 1325, 1737, and 1808 mAh g\(^{-1}\), respectively. The discharging capacities for the three samples are compared in Figure 7b. Si/GS/C-P delivered reversible discharge capacities of more than 2150 mAh g\(^{-1}\) at a current of 100 mA g\(^{-1}\). At a high current of...
Figure 3. (a) XRD patterns, (b) TGA profiles and (c) Raman spectra of samples.

500 mA g\(^{-1}\), it delivered a high reversible capacity of 1400–1600 mAh g\(^{-1}\) up to 15 cycles followed by rapid capacity fading. As shown in Figure 7c, the CEs of Si/GS never exceeded 99% until it lost most of its capacity. On the other hand, Si/GS/C-P and Si/GS/C-S exhibited much better cycling performance than Si/GS. Although Si/GS/C-S contained much less silicon than Si/GS/C-P, Si/GS/C-S exhibited a slightly higher reversible capacity and better cycling stability with higher CEs than Si/GS/C-P. Si/GS/C-S delivered reversible capacities of \(>1350\) and \(>900\) mAh g\(^{-1}\) at currents of 100 and 500 mA g\(^{-1}\), respectively, with excellent cycling stability. The CEs of Si/GS/C-S reached 99.6% in 10 cycles at 500 mA g\(^{-1}\). The average reversible discharge capacities of Si/GS, Si/GS/C-P, and Si/GS/C-S at a current of 100 mA g\(^{-1}\) were 2190, 1334, and 1383 mAh g\(^{-1}\), respectively, which correspond to 73.0%, 58.2%, and 71.4% of the theoretical capacities estimated using the Si and C contents determined by TGA (Figure 3b), and the theoretical capacities of Si (3579 mAh g\(^{-1}\)) and carbon (200 mAh g\(^{-1}\), amorphous carbon mixed with graphene).

To boost the energy density of current LIB cells, high-capacity anode materials having a specific capacity in the range of 600–1000 mAh g\(^{-1}\) are demanded given the rather low capacities of current cathode materials (\(\sim 200\) mAh g\(^{-1}\)). It is also desirable for high-capacity anodes to have a volumetric capacity higher than or comparable to that of graphite anodes. To prepare such an anode material, the high-capacity Si/GS/C-S (1383 mAh g\(^{-1}\) at 100 mA g\(^{-1}\)) and commercial graphite were physically mixed at a weight ratio of 4:6. The mixed sample was denoted as Si/GS/C-S@Gr, and its specific capacity is expected to be around 776 mAh g\(^{-1}\) (= 1383 mAh g\(^{-1}\) \(\times 0.4 + 372\) mAh g\(^{-1}\) \(\times 0.6\)). Figure 8a shows the CV profiles of Si/GS/C-S@Gr (dotted green lines) and the weight-averaged CV profiles (red lines), which were obtained by adding the CV profiles of Si/GS/C-S and graphite (see the inset of Figure 8a) corrected by the corresponding weight ratio. The CV profiles of Si/GS/C-S@Gr show an activation process over
the first few cycles, as indicated by an increase in the CV peak intensity due to kinetic enhancement in the electrode.\(^{45,46}\) Cathodic CV peaks due to lithiation of both Si and graphite developed at around 0.15 V, with humps at around 0.1 and 0.2 V, for Si/GS/C-S@Gr, whereas they appeared at around 0.17 V in the weight-averaged CV profiles. Distinct anodic CV peaks due to delithiation of Li\(_2\)Si\(^{15}\) developed at 0.50 V for Si/GS/C-S@Gr, whereas the corresponding peaks appeared at around 0.53 V in the weight-averaged CV profile and in the CV profile of Si/GS/C-S. It is evident that the anodic peak for Si/GS/C-S at 0.53 V, which is high enough that it does not experience interference from the other peaks due to delithiation of Li\(_2\)Si\(^{15}\) and Li2Si (0.25 V) and Li2Si (0.36 V), shifted to a lower voltage (0.50 V) for Si/GS/C-S@Gr. This indicates that the electrochemical overpotential associated with silicon was suppressed in Si/GS/C-S@Gr compared to that in Si/GS/C-S owing to the presence of highly conducting graphite particles. Figure 8b shows the voltage profile of Si/GS/C-S@Gr for the first and second cycles. After initial stabilization in a few cycles, the average discharge/charge potentials of Si/GS/C-S, Si/GS/C-S@Gr, and graphite were 0.49/0.22, 0.41/0.20, and 0.28/0.14, respectively. Thus, the average working potential of Si/GS/C-S@Gr was lower than that of Si/GS/C-S, in agreement with the CV results in Figure 8a. The first discharge/charge capacities were 890/663 mAh g\(^{-1}\) at a current of 100 mA g\(^{-1}\), yielding an initial CE of 74.5%. After the second cycle on, the CEs increased to 99.1% in a few cycles owing to the initial activation process seen in the CV profiles in Figure 8a, and then the CEs increased to over 99.7% in 60 cycles. The reversible discharge capacity gradually increased to 752 mAh g\(^{-1}\) at 100 mA g\(^{-1}\), which is close to the expected capacity of 776 mAh g\(^{-1}\) as estimated above. The cycling stabilities and CEs of Si/GS/C-S@Gr and graphite are compared in Figure 8c. At a current of 200 mA g\(^{-1}\), the discharge capacity of Si/GS/C-S@Gr decreased to around 550 mAh g\(^{-1}\) in the first few cycles and stabilized at around 600–620 mAh g\(^{-1}\) with excellent cycling stability up to 200 cycles. Graphite delivered a reversible discharge capacity of around 340 mAh g\(^{-1}\) at 200 mA g\(^{-1}\) after the initial activation process. Graphite was cycled for 200 cycles without capacity fading, and its CEs increased to over 99.7% in 20 cycles. Note that the CEs of Si/GS/C-S@Gr became larger than those of graphite after 80 cycles on.

Overall, the Si/GS composite derived from direct thermal reduction of the Si/GO self-assemblies delivered high capacity, but it exhibited very poor cycling performance, mainly because of loose cohesion of SiNPs with GSs (Figure 2d). Hence, additional carbon coatings were applied to enhance the cohesion between SiNPs and conducting carbon, including GSs. Si/GS/C-P, which was prepared by carbon coating of Si/GS using PVdF as the carbon source, showed greatly enhanced cycling stability and CEs compared to Si/GS.

Figure 9a compares the specific and volumetric capacities of various samples at the electrode level. Si/GS/C-S delivered specific and volumetric capacities of 1106 mAh g\(^{-1}\) and 948 mAh cm\(^{-3}\), respectively, with an electrode coating density of about 0.86 g cm\(^{-2}\), whereas graphite showed 296 mAh g\(^{-1}\) and 483 mAh cm\(^{-3}\) with an electrode density of 1.63 g cm\(^{-3}\). Therefore, at the electrode
Figure 8. (a) CV profiles of Si/GS/C-S@Gr (dotted green lines), and the weight-averaged CV profiles (red lines) obtained by adding the CV profiles of Si/GS/C-S and graphite in the inset corrected by the corresponding weight ratio, (b) charge/discharge voltage profiles of Si/GS/C-S@Gr at a current density of 100 mA g$^{-1}$, and (c) cycling performances and Coulombic efficiencies of Si/GS/C-S@Gr and graphite.

Figure 9. (a) Comparison of the specific and volumetric capacities of electrodes, (b) capacity retentions of graphite, Si/GS/C-S and Si/GS/C-S@Gr as a function of C-rate, and (c) Nyquist plots of graphite, Si/GS and Si/GS/C-S after 50 cycles, and Si/GS/C-S@Gr after 200 cycles (Inset shows the equivalent circuit).
level, Si/GS/C-S@Gr showed more than twice the specific capacity of graphite, and its volumetric capacity was still higher than that of graphite by about 12%. As shown in Figure 9b, Si/GS/C-S@Gr also showed higher rate responses than graphite and Si/GS/C-S as compared with their capacity retentions as a function of the C-rate. The electrochemical kinetic behavior of the samples was further investigated using EIS measurements, as shown in Figure 9c. The EIS data for graphite, Si/GS and Si/GS/C-S were measured after the 50th cycle, whereas those for Si/GS/C-S@Gr were measured after 200 cycles, on fully delithiated electrodes. In the equivalent circuit in the inset of Figure 9c, $R_s$, $R_{SEI}$, $R_{ct}$, and $R_n$ represent the electrolyte and electrode resistances, SEI resistance, charge-transfer resistance across the electrode–electrolyte interface, and Warburg impedance due to ion diffusion into the active materials, respectively.44,47 CPE1 and CPE2 are constant-phase elements representing the diffusion capacitance for Li-ion diffusion in the SEI film and the electronic double-layer capacitance of the electrode–electrolyte interface, respectively. In the Nyquist plot of the impedance data in Figure 9c, two distinct semicircles are seen in the high- and medium-frequency regions because of the SEI and charge-transfer resistances, respectively, with sloping lines in the low-frequency regions. The impedance data can be well fitted with the equivalent circuit to estimate the various resistances. The $R_{SEI}$ values of the Si/GS, Si/GS/C-S, Si/GS/C-S@Gr and graphite electrodes were estimated to be 70, 25, 5 and 7.4 Ω, respectively. The corresponding $R_s$ values were calculated to be 70, 55, 22 and 14 Ω, respectively. The total resistance and the values of both $R_{SEI}$ and $R_s$ of Si/GS were the largest, suggesting the formation of a thick SEI layer on the electrode and a very poor rate of charge transfer at the electrode–electrolyte interface, leading to poor electrochemical performance of Si/GS. On the other hand, Si/GS/C-S@Gr showed $R_{SEI}$ and $R_s$ values close to those from graphite but much smaller $R_{SEI}$ and $R_s$ values than Si/GS/C-S, indicating a thinner and more stable SEI layer and faster electron transfer. These results help explain why Si/GS/C-S@Gr has better rate responses and cycling efficiencies. Finally, the electrode thicknesses were measured using SEM of cross sections of Si/GS/C-S@Gr electrodes before and after the cycling test. As shown in Figure 10b, the electrode thickness after 200 cycles increased to 36.4–37.9 μm from about 29.0 μm for the pristine electrode, thus giving an electrode thickness increase of only 25.4%–30.7%. This small increase in the electrode thickness could be ascribed to the relatively low Si content (20.6 wt%) and the internal voids (see Figure 6b) generated inside the Si/GS/C-S particles in Si/GS/C-S@Gr, which help maintain electrical networks through the electrode against the large volume expansion of silicon.

Conclusions

Electrostatic self-assembly between Si-APTMS and GO in an acidic aqueous solution was employed to prepare a Si/GS composite, which showed limited electrochemical performance due to loose cohesion between the SiNPs and GOs and direct exposure of some SiNPs to the electrolyte. To counteract the cycling instability of the Si/GS assembly, two methods of adding carbon coating were attempted that preserved the close interactions between SiNPs and GSs resulting from electrostatic self-assembly. The carbon coating turned the 2D planar Si/GS assemblies into dense 3D particulate nanocomposites in which many internal voids were generated that enabled silicon to expand and contract more freely. Si/GS/C-P, which was prepared by carbon coating (using PVdF as the carbon source) of Si/GS obtained by thermal reduction of Si/GO self-assemblies, showed much better cycling stability than Si/GS, but it delivered a very low volumetric capacity owing to its highly open carbon structures. The Si/GS/C-S composite, which was prepared by in situ carbon-gel coating (using sucrose as the carbon source) of the Si/GO self-assemblies in solution followed by carbonization, delivered a high reversible capacity (1338 mAh g⁻¹ at 100 mA g⁻¹) with excellent cycling stability and high CE. The electrode volumetric capacity of Si/GS/C-S was also a factor of two higher than that of a commercial graphite anode.

Finally, a hybrid composite, Si/GS/C-S@Gr, was designed by mixing the high-capacity Si/GS/C-S and graphite at a weight ratio of 4:6 to demonstrate a practical and economical strategy for developing LIB anodes. Si/GS/C-S@Gr still delivered a rather high specific capacity of 750 mAh g⁻¹ with excellent cycling stability up to 200 cycles and high CEs exceeding those of graphite. It was also found to have higher rate responses and to work at a slightly lower potential with much lower impedances than Si/GS/C-S. Moreover, Si/GS/C-S@Gr showed a higher volumetric capacity than graphite with a small increase in electrode thickness (∼30%) after 200 cycles. Hence, electrostatic self-assembly of SiNPs and GO followed by in situ carbon coating can yield reliable, high-performance anodes for high-energy LIBs.

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Figure 10. SEM images of electrode cross-sections of Si/GS/C-S@Gr (a) before and (b) after cycling for 200 cycles.
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