Implementing an in-situ carbon network in Si/reduced graphene oxide for high performance lithium-ion battery anodes

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Abstract: Despite the intensive studies of combining silicon (Si) and reduced graphene oxide (rGO), the architecture of Si-rGO composites still needs to be improved to maintain better electrode structure integrity and stable solid electrolyte interphase (SEI) upon extensive cycling. Herein, a conductive and protective network with rGO and CVD-implemented carbon is constructed with silicon nanoparticles (Si NPs) embedded inside for the first time. Compared with the regular Si-rGO composite with only Si NPs wrapped by rGO, Si-rGO-C composite successfully improves the electrical conductivity and structure stability. In addition to the wrapping of rGO on Si NPs, the additional carbon layer on the partially exposed Si NPs provides extra protection from fracture during volume change and helps form a stable SEI layer. Carbon rods between rGO flakes function as conductive bridges, creating an effective conductive network on a macroscopic scale. The initial capacity of Si-rGO-C composite reaches 1139 mAh g⁻¹ and 894 mAh g⁻¹ at 0.1 A g⁻¹ and 1C respectively, and retains 94% of its initial capacity after 300 cycles at 1C. The electrode is stabilized at 770 mAh g⁻¹ at 2C during rate performance testing.

Key words: Lithium ion battery, anode material, silicon, reduced graphene oxide, carbon network.

Introduction:

The ever soaring market of portable electronic devices has triggered significant demand and unprecedented research interests for high performance batteries. Lithium ion batteries (LIBs) have been dominating the market for electronic devices due to its relatively higher working potential, higher specific power and energy densities, and better environmentally friendliness compared to previous battery technologies such as lead acid, nickel cadmium, and nickel metal hydride batteries.[1, 2] However, the development of LIB technology has fallen far behind the pace of the advancement of

electronic devices, which roughly follows Moore's Law.[3] Electric vehicles have emerged as a potential replacement of traditional vehicles due to the limited supply of fossil fuels, long-term increasing oil prices, and the environmental benignity and sustainability of electricity generated from green energy technologies. To meet the demands of increasingly sophisticated electronic devices and competitive electric vehicles, which require both high energy density and power density, tremendous efforts have been devoted to developing high-performance electrode materials in LIBs.[4, 5] An increase of specific electrode capacity can greatly reduce a battery's mass and volume.

Silicon (Si) has been regarded as a promising candidate anode material for next-generation LIBs due to its outstanding properties. The theoretical gravimetric capacity of Si is approximately 4200 mAh g^{-1} – more than ten times that of the commercial graphite (372 mAh g^{-1}). [6] In addition, Si's high natural abundance, environmental compatibility, low working potential (0-0.4 V vs. Li/Li^+), and maturity in the Si semiconductor industry all make it highly desirable as an anode material for LIBs.[7-9] However, several intrinsic drawbacks of Si have prevented it from being widely commercialized as LIB anodes. One of the critical challenges is that the large volume expansion of Si upon lithiation (up to 400% of its original volume) can cause it to crack and pulverize, resulting in the loss of contact points between the active material and the current collector.[10-12] This large volume change also leads to the continuous formation of an unstable solid electrolyte interphase (SEI) which consumes a considerable amount of electrolyte and lithium in a battery.[13] Columbic efficiency and electrode capacity are hence lowered due to these continuous side reactions. Furthermore, the repetitive growth of the SEI may severely block the conductive pathway of electrons between Si and the current collector. These phenomena significantly decrease the electrode's integrity and electron conductivity and, ultimately, the battery's rate performance.[14] Although the pulverization of Si can be prevented by engineering nano-sized structures, the severe volume variation can still lead to the displacement and the detachment of Si from the electrode's original conductive network during cycling.[15] The above disadvantages consequently result in poor cycling and rate performance of Si electrodes. To circumvent the aforementioned problems with Si electrodes, several strategies have been proposed by researchers. One of the potential solutions is to design various nano-structured Si electrodes. Nano-sized Si can better accommodate mechanical strain during lithiation and delithiation processes, and avoid cracking and fragmentation.[16] Improved cycling stability has been demonstrated with mechanically-milled nanostructured particles,[17] and chemically synthesized nanostructures including nanowires,[18] nanotubes,[19] nanoporous structures,[20] and core-shell nanostructures.[21] Another effective strategy to improve Si's performance in batteries is to build an efficient conductive network for Si. Si/C,[22] Si/Graphene,[23] Si/CNT[24] and Si/conductive polymers[25] have been reported to exhibit enhanced performance compared to bare Si. Recent reports of novel binding materials in electrode fabrication have also shown significant improvement in Si

electrode's performance.[26-28] Although these results have shown some promise, there are some significant issues regarding their synthesis. Many of these procedures are highly complex and expensive. For example, the synthesis of Si nanowires (Si NWs) usually requires complex procedures and dangerous precursors such as silane gas. Template growth of Si usually involves multi-step template synthesis and removal steps, adding to the cost of the final Si product. All these factors make it merely impossible for these materials to be widely commercialized.[29]

rGO has been intensively studied in the electrochemical field because of its unique structure and superior physical properties including conductivity, mechanical strength and flexibility. It has recently been combined with Si to form composite anode materials in LIBs.[30] Wrapping rGO around Si NPs significantly improves the electrochemical performance of Si NPs in terms of both cycle and rate performance. However, despite the good contact between rGO and Si, the composite still fails to maintain long-term stability. Reported Si-rGO composites generally suffered considerable degradation after certain cycles.[31, 32] The degradation of the above Si-rGO anode can be explained by the fact that many of these composites are synthesized using physical mixing, which does not lead to strong chemical bonding between Si and rGO. In addition, the size of rGO sheets is usually much larger than that of Si NPs. These make it difficult to homogeneously wrap Si NPs with rGO. Poor wrapping of Si with rGO and migration of Si NPs from rGO during cycling result in most of the reported unsatisfactory performances.

Herein, we present a highly efficient Si reduced graphene oxide carbon (Si-rGO-C) composite with good Si wrapping and thus improved electrochemical performance compared to commercial Si NPs and regular Si-rGO composite. In order to take advantage of both carbon coating and rGO wrapping, a facile freeze-drying method and a subsequent chemical vapor deposition (CVD) process were conducted using commercially available Si NPs. Si NPs were well embedded onto the GO layers, and the sponge-like composite served as the precursor of the next step carbon incorporation. The following advantages of the obtained Si-rGO-C composite were first proposed and proved based on the electrochemical performances presented in the context. First, a layer of carbon on exposed Si NPs provides enhanced electron conductivity between particles and other rGO flakes with wrapped Si NPs. Second, the carbon rods between the rGO flakes create an effective conductive network in the whole electrode, helping electrons transfer from one rGO sheet to another and eventually to the current collector. Moreover, the flexibility of rGO and the carbon network can also help restrain the electrode morphology change during cycling, avoiding significant detachment of the active material from the conductive network and helping to maintain contact between the electrode material and the current collector. Various physical and electrochemical measurement techniques were adopted to characterize the samples.

Experimental:

Material synthesis:

Experimental procedures constructing the Si-rGO composite resemble our previous work.[23] The schematic illustration of the synthesis procedure of Si-rGO-C composite is shown in Figure 1. Si NPs (Nanostructured & Amorphous Materials Inc, USA. Average diameter 70 nm) and GO (Prepared using a modified Hummer's Method) were separately dispersed in distilled de-ionized water (DDI 18 M MΩ·cm) in a sonicator bath (Fisher Scientific FS220, USA) for 5 hours. The mass ratio of Si NPs to GO was 2:1. Two dispersions were subsequently mixed together and sonicated for another 5 hours to achieve a homogeneous solution. The final mixture was rapidly frozen with liquid nitrogen and placed in a freeze-dryer (Labconco Freezone 1, USA). The sponge-like Si-GO composite was then transferred into a quartz tube in a CVD system (Thermal Product Solutions, Lindberg Blue M 1200°C Small Tube Furnace, USA). 10% hydrogen (H₂) in argon (Ar) gas was used to purge the system at a rate of 140 cm³ min⁻¹ for 20 minutes. The rate of the gas was subsequently adjusted to 70 cm³ min⁻¹ for the reaction until the furnace cooled down to room temperature. The furnace was set to ramp from room temperature to 900 °C in 15 h and held at this temperature for 3 h. Toluene was used as the carbon source in the CVD reaction. After 2.5 h at 900 °C, toluene was injected with a syringe pump at a rate of 0.05 mL min⁻¹ for 10 minutes for the carbon growth. The furnace was shut down immediately and cooled down naturally to room temperature. Si-rGO composite without carbon coating was synthesized using the same method but without the CVD step.

Physical Characterization:

The weight ratio of total carbon content was examined by thermal gravimetric analysis (TGA) (TA Instrument Q500, USA). A 5 mg sample was used in the analysis. The sample was heated up to 850 °C at a ramping rate of 10 °C min⁻¹, and the test was conducted in air atmosphere. X-ray diffraction (XRD) (monochromatic Cu K X-rays, 0.154 nm wavelength, Inel XRG 3000 Diffractometer, France) was used to examine the crystallinity of Si after the high-temperature reduction of rGO and the CVD carbon coating process. X-ray photoelectron spectroscopy (XPS) (Thermo Scientific K-Alpha, USA) was conducted with Si-GO, Si-rGO, and Si-rGO-C samples to study the change of GO and the growth of carbon. The morphology of the composite was studied by field emission scanning electron microscopy (FESEM) (Zeiss Ultra Plus, UK) and transmission electron microscopy (TEM) (FEI Philips CM300, USA).

Electrochemical characterizations (Electrochemistry):

A slurry for the electrode was prepared with 80 wt% as-synthesized active material and 20 wt% sodium carboxymethyl cellulose (NaCMC) binder. Traditional conductive additives such as super-P were eliminated to increase the ratio of active material in electrodes. NaCMC was first dissolved in water to form a 2 wt% solution. The slurry was cast onto a thin and flat copper foil with a doctor blade. The foil was subsequently placed in a regular oven at 80 °C for 2 hours and then transferred to a vacuum oven overnight to evaporate the solvent from the slurry and foil. Electrodes were punched from the foil and pressed. The average loading of the Si-rGO-C

composite on copper foil was 1.1 mg cm^{-2} . CR 2032 coin cells were fabricated inside an argon-filled dry glovebox (Labstar 10, Mbraun, USA) where both oxygen and water content were maintained below 0.5 ppm. The electrolyte consisted of lithium hexafluorophosphate (LiPF_6) dissolved in a solvent containing 45% dimethyl carbonate (DMC), 45% ethylene carbonate (EC), and 10% fluorinated ethylene carbonate (FEC). Lithium metal was used as both a counter electrode and a reference electrode. A polypropylene membrane (PP2075, high porosity, $20 \text{ }\mu\text{m}$ micro porous, Celgard, USA) was used as the separator. Cycling tests and rate capability tests were conducted using a battery testing system (BTS 3000, Neware, China). Cyclic voltammetry (CV) was performed using an electrochemical work station (Versa Stat MC, Princeton Applied Research, USA). The battery was scanned between 0.05V to 1.5V using a scan rate of 0.1 mV s^{-1} . Batteries of the control group (Si-rGO) were also fabricated and tested using same testing procedures. All electrochemical tests were conducted at room temperature. All measurements were based on the gravimetric mass of entire composite (Si-rGO, Si-rGO-C). A five-cycle activation/aging process at 100 mA g^{-1} was applied to all cells except for cells fabricated for CV tests.

Results and discussion:

A versatile freeze-drying method was used to obtain a well-aligned structure of GO with Si NPs. Ice as a template not only forms in-situ inside the composite, but also fills the microchannels and helps keep aligned/ordered porous structures. In addition, ice can be easily removed by a low temperature sublimation process. Its low cost and environmental friendliness make it a suitable template reagent for large scale production of the Si-GO composite.[33] Figure 2(a) shows that the dried Si-GO composite is a low-density sponge-like material with a well-maintained size and shape. The sponge-like structure is also well maintained after the carbon coating process, while the color of the composite turns to black after the reduction of GO to rGO and the growth of additional carbon.

TGA analyzes the total amount of carbon content in the final product, including both rGO and added carbon. It is shown in Figure 2(b) that the total carbon content in Si-rGO-C is 26.1%. Without the CVD carbon coating process, the Si-rGO composite contains 21.3% carbon, which is attributed purely to rGO. The overall added carbon by CVD in the Si-rGO-C is calculated to be 5.7%. The characteristic peaks of crystalline Si from XRD in Figure 2(c) corresponds to cubic Si (JCPDS 27-1402) and confirms that Si NPs maintain their crystallinity after vigorous mixing in aqueous solution and treatment at high temperatures, verifying there is no side reaction during the synthesis procedure. A broad peak at around 26° confirms that GO is successfully reduced to rGO. No other peaks can be observed from the XRD result, suggesting that no side product such as silicon carbide is formed during the process.

Raman spectroscopy is capable of investigating crystal structures of carbonaceous materials. D and G bands ($\sim 1350 \text{ cm}^{-1}$ and $\sim 1580 \text{ cm}^{-1}$, respectively) are well-known characteristic peaks for carbonaceous materials; they represent the defects/disorder

and graphitized structure of carbon, respectively.[34] I_D/I_G ratio is a value commonly used to estimate the relative amount of defects in a carbonaceous sample. This is because the G-band is associated with E_{2g} breathing mode of sp² carbon atoms in the conjugated structure, while the D-band is associated the A_{1g} breathing mode at domain boundaries (specifically from armchair edge defects). As shown in Figure 2(d), the ratio of I_D/I_G increases from 0.714 to 1.073 after the high temperature treatment, which means the defects/disorder in the carbon material increase with the reduction of GO and the implementation of additional carbon. This indicates that the rGO-carbon matrix contains a significant amount of disordered sp² carbon, which may be due to the GO reduction process that can partially break the sheets and increase the amount of edge defects. The reduction of GO to rGO can therefore lead to a higher electron conductivity, and higher porosity lithium diffusion, which can improve the overall rate capability and stability of the electrode.[35]

The morphology of Si-rGO composite with and without CVD carbon coating was obtained with SEM and is shown in Figure 3. Figure 3(a) shows that the size of a typical rGO sheet wrapping the Si NPs is between 1 and 10 μm . The sheet with Si NPs is interconnected with other sheets by both overlapping sheets and carbon branches. These additional electron pathways provide the composite with enhanced conductivity on a macroscopic level. Figure 3(b) shows the carbon branches with an average length of several hundred nanometers, and a diameter of 30-40 nm. Most of the carbon branches are closely embedded onto the rGO sheets and some also intertwine with Si NPs. The branches at the edge of the rGO sheets successfully bridge the gaps between these sheets, which may provide better electron conductivity in the composite. In comparison, Si-rGO composite without carbon coating in Figure 3(c) has no carbon branches in between rGO sheets or Si NPs. Si NPs on the rGO sheets appear to be more dissociative from the rGO sheets, while Si NPs in the Si-rGO-C composite are tightly implanted onto the rGO sheets and added carbon. Figure 3(d) is a typical view of Si-rGO composite with the initial Si:GO ratio of 2:1. It can be observed that the Si NPs aggregate on the rGO sheets, with no additional carbon shown.

A typical part of the Si-rGO-C sample was shown in the low-magnification TEM image in Figure 4(a), the area with Si NPs appears darker compared to the area with only flattened rGO layer. Figure 4(b) clearly shows the existence of created carbon branches and stuffed carbon on the rGO sheet and in between the Si NPs. Figure 4(c) shows an area of Si-rGO-C composite with only a few particles in view, from which EDX element mapping of Si and carbon is revealed in Figure 4(d) and Figure 4(e), respectively. Stronger signals from Si come from areas where particles overlap. Element mapping of carbon in Figure 4(e) provides a clear distinction between areas of different carbon densities. The relatively brighter signal from the edges of Si NPs demonstrates that carbon and rGO enclose Si along the arc of spheres, further confirming good contact and wrapping of both rGO and carbon on Si NPs. Figure 4(f) is the high resolution TEM (HRTEM) image of the Si-rGO-C composite. The

d-spacing of the (111) plane is 0.31 nm, and the fast Fourier transform (FFT) from the inset confirms that the crystallinity of the Si NPs is mostly retained. A thin layer of amorphous SiO_x (around 4 nm) can be observed from the HRTEM image as well. rGO is closely attached to the SiO_x shell, with amorphous carbon deposited on the surface of the composite.

To further investigate the change of GO during the high temperature process and confirm the successful implantation of carbon into Si-rGO composite, X-ray photoelectron spectroscopy (XPS) was conducted with Si-GO, Si-rGO, and Si-rGO-C samples. Gaussian-Lorentzian fitting and Shirley background correction were adopted for all spectra except for Si-rGO-C, where no obvious Si signal was detected. As shown in Figure 5 (a), the C 1s peak at 284.7 eV and C 1s peak at 286.7 eV represent the chemical state of sp²/sp³ C-C bonding and C-O bonding respectively.[36] C=O peak is observed at around 288.5 eV. The intensity ratio of C-C bonding over C-O bonding increases dramatically upon the high temperature reduction process (Figure 5 (b) and (c)). As shown in Figure 5 (d), both elemental Si peaks of Si 2p_{1/2} and 2p_{3/2} and Si-O peaks can be easily found in Si-GO composite. Only one Si-O peak can be observed in the spectra of Si-G (Figure (e)), while no obvious Si signals are shown in Si-rGO-C spectra (Figure 5 (f)). This could be explained by the partial oxidation of Si NPs and thus the increase of SiO_x layer during the reduction of GO. The diminished Si signal in Si-rGO-C spectra is attributed to the thickness increase of carbon shell on Si NPs as the XPS adopted can only detect a few nanometers from the surface of the sample. This also confirms the good wrappability of carbon on the surface of Si NPs. The carbon shell around Si NPs can help form a stable SEI and protect the material from severe structure deterioration during cycling and result in the improved performance of Si-rGO-C over Si-rGO.

Charge and discharge profiles of the Si-rGO-C composite are shown in Figure 6(a). The gravimetric capacity of Si-rGO-C increases to 1352 mAh g⁻¹ from its initial value of 1139 mAh g⁻¹. Here the Si-rGO-C electrode material contains 80% of active material (80% active material, 20% binder), while the reference Si-rGO electrode only contains 70% of Si-rGO (20% binder, 10% carbon black). Thus the specific capacity of Si-rGO-C electrode based on the whole electrode material is calculated to be 911.2 mAh g⁻¹ for the first discharge and 1081.6 mAh g⁻¹ in the third cycle. All other values of gravimetric capacity were calculated based on the mass of Si-rGO-C, Si-rGO, or bare Si for direct comparison among active materials. The capacity increase of Si-rGO-C cell continued for more than 30 cycles, and the phenomenon is detailed in the discussion of cycling performance below. The discharge profile changes from a very flat plateau at around 0.1V to a slowly descending curve from 0.3V to the low cut-off voltage. This is due to the transformation of the crystalline Si to the amorphous Si after Li insertion and extraction process.[37] Figure 6(b) shows the charge and discharge profiles of Si-rGO without additional carbon. During the first three cycles, the charge capacity of the Si-rGO electrode is almost stabilized at 1630 mAh g⁻¹, with no observable increase in capacity. The capacity difference

between the first discharge and charge is 344.1 mAh g^{-1} , (23.2%) for Si-rGO-C, and 724.7 mAh g^{-1} (30.7%) for Si-rGO. These results show that the Si-rGO-C electrode has a higher coulombic efficiency than Si-rGO in first cycle, providing a higher lithium utilization rate.

The charge and discharge behavior of the Si-rGO-C electrode was further investigated using a CV test, shown in Figure 7(a). The first broad cathodic peak at around 0.22 V corresponds to the lithiation of crystalline Si and the formation of amorphous Li_xSi . [37] In the anodic scan, the two peaks at 0.31 V and 0.5 V are due to the reversible delithiation of the active material. From the second cycle, the positions of both anodic and cathodic peaks remain almost unchanged, indicating that the lithiation and delithiation processes are high reversible. The strengthening peaks in the following cycles are in agreement with the charge and discharge profiles and the cycling data that show a capacity increase during the initial cycles. This phenomenon is attributed to the gradual kinetic activation of Si upon Li alloying/dealloying.

The cycling data of the Si-rGO-C and Si-rGO composites are shown in Figure 7(b) and 7(c). It is noted that the batteries are tested 5 cycles at 100 mA g^{-1} for initial stabilization procedure of each composite. According to the capacities of batteries after activation/aging process, the 1C rates of Si-rGO-C and Si-rGO are determined to be 1400 mA g^{-1} and 1600 mA g^{-1} , respectively.

Cycling tests were conducted to obtain the cycling and rate performance of Si electrodes. As shown in Figure 7(b), it should be noted that the capacity of Si-rGO-C increases in the initial 25 cycles from its initial value of 1139 mAh g^{-1} to a maximum of 1570 mAh g^{-1} (a 38% increase). After 100 cycles, the capacity of the Si-rGO-C composite remains at 1445 mAh g^{-1} , which is much higher than its initial capacity. Si-rGO shows a higher capacity than Si-rGO-C in the first few cycles. However, Si-rGO is quickly surpassed by Si-rGO-C due to its dramatic degradation after only five cycles. A cell made from commercial Si NPs is maintained at 100 mA g^{-1} throughout the test. Although the initial discharge capacity of bare Si NPs reaches around 3500 mAh g^{-1} , the stability is much worse than the other two materials.

The areal capacity of the Si-rGO-C electrode is around 1.6 mAh cm^{-2} , based on the specific gravimetric capacity after 100 cycles at 0.2C and the areal mass loading of active material on the substrate. The electrode density was measured to be 0.92 g cm^{-3} from the mass, area, and thickness of the electrode. And the volumetric specific capacity was calculated to be 1373 mAh cm^{-3} based the electrode density and the areal capacity. Although the electrode density is lower than that of commercial graphite electrode (1.4 g cm^{-3}), the volumetric specific capacity of Si-rGO-C electrode is much higher than that of graphite electrode (490 mAh cm^{-3}). [38] This can lead to a significant advantage in volumetric energy density for Si-rGO-C electrode considering the similar operating potentials of silicon full cells and graphite full cells.

Figure 7(c) reveals the rate capability of the Si-rGO-C and Si-rGO composites. After initial activation at 100 mA g^{-1} for 5 cycles, the electrodes are tested at 0.2C, 0.5C, 1C, 1.5C, 2C, and then 0.2C again. The capacity of the Si-rGO-C electrode continues increasing until it is stabilized at 0.2C with a capacity of 1290 mAh g^{-1} . Gradual decline of the cell's capacity can be observed with the increase of charge and discharge rates. However, Si-rGO-C stabilizes at higher rates (e.g. 1.5C and 2C). At 2C (2.8 A g^{-1}), the electrode presents a capacity of 770 mAh g^{-1} . When the cell is tested at a lower rate of 0.2C, it recovers its capacity of 1380 mAh g^{-1} and remains highly stable. In comparison, the Si-rGO composite degrades quickly even at low rates of 100 mA g^{-1} and 0.2C. The capacity of Si-rGO falls below that of Si-rGO-C when the charge and discharge rate is raised to 0.5C. The difference in capacity between the two composites continues to increase at higher C rates. When the rate is set back to 0.2C, the capacity of Si-rGO (691 mAh g^{-1}) is approximately half that of the Si-rGO-C composite. At this point, Si-rGO-C still performs stable cycling while Si-rGO continues to decay at 0.2C. Figure 7(d) illustrates the long term cycling performance of the Si-rGO-C electrode at 1C after initial activation at 100 mA g^{-1} . Phenomena similar to that of the cell at 0.2C are observed. After 300 cycles, the cell still retains a capacity of 840 mAh g^{-1} , which corresponds to 79% retention compared to its peak capacity and 94% retention compared to its original capacity at a rate of 1C.

The coulombic efficiencies for Si-rGO-C cells increase from around 75% in first cycle to more than 99.5% for both cycling tests and 99% for rate test, while batteries from bare silicon and Si-rGO present much lower coulombic efficiencies. The high and stable coulombic efficiency of Si-rGO-C cells can be attributed to the stable structure of the electrodes and minimized side reactions during cycling. But it is interesting to notice that the initial coulombic efficiency for bare silicon electrode is higher than that of Si-rGO-C. The relatively low initial irreversible capacity of bare silicon electrode can be explained by the fact that bare silicon electrode contains a lower ratio of carbon, which contributes to much of the irreversible capacity in first cycle."

To further understand the effect of additional carbon on the electrochemical performance of Si-rGO-C composite in LIBs, electrochemical impedance spectroscopy (EIS) measurements were conducted after 1st and 100th discharges of both Si-rGO-C and Si-rGO composites at 0.2C (Figure 8 (a)). The equivalent circuit model is shown in Figure 8 (b). The high frequency x -intercept corresponds to the equivalent series resistance, R_s . The value represents Ohmic resistance, with contributions from electrical contact resistance in the outer circuit, current collectors, electronic conductivity of electrodes, and ionic conductivity of bulky electrolyte. The semi-circle corresponds to the combined SEI resistance (R_{SEI}) and charge transfer resistance (R_{CT}). R_{SEI} measures the ionic diffusion resistance of Li^+ in the SEI layer and is the main parameter of interest. R_{CT} represents the charge transfer resistance of electrode/electrolyte interphase. CPE_1 and CPE_2 represent the capacitance of the SEI

layer and the electrode/electrolyte interphase, respectively. The low frequency tail is associated with the Warburg diffusion impedance (Z_w) from the lithium-diffusion process.[39] The fitted impedance data can be seen in Table 1. R_s values for all electrodes are similar because the same fabrication procedure and battery components were used. R_{SEI} of the Si-rGO-C composite after 1st discharge is 37.1 Ω , and the value slightly increases to 49.58 Ω after 100 cycles. R_{SEI} of Si-rGO electrode increases from 59.95 Ω to 116.1 Ω from 1st discharge to 100th discharge. These results show that the Si-rGO-C electrode maintains a much more stable SEI layer than Si-rGO upon cycling. The final value of R_{CT} for Si-rGO-C is smaller than that of Si-rGO, and the change of Si-rGO-C's R_{CT} upon cycling is much smaller than that of Si-rGO, indicating that the incorporation of additional carbon can help maintain the electrode's structure and ensure the rapid electron transfer during the electrochemical lithium insertion/extraction process. These results reveal that the addition of carbon into Si-rGO successfully provides efficient and stable electron and ion conductive pathways.

Conclusions:

In summary, a Si-rGO-C composite was designed with Si NPs well wrapped by an rGO/carbon hybrid. The Si-rGO-C composite successfully resolved the problem by facilitating the wrapping of Si NPs and interconnecting rGO flakes by CVD carbon implantation. CVD carbon coating enhances battery performance by forming carbon branches on rGO and Si, which facilitates electron transport in the electrode. The additional carbon also provides structure integrity to the composite, and helps form a stable SEI layer over repeated lithiation/delithiation processes. The composite successfully delivered improved cycling performance compared to Si-rGO composite. The Si-rGO-C obtained a capacity of 840 mAh g⁻¹ (94% retention) after 300 cycles at 1C. Rate capability testing further presented a capacity of 770 mAh g⁻¹ at 2C. These results bring high energy and power density Si anodes one step closer to wider applications in commercial LIBs.

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Figure 1. Schematic illustration of the synthesis procedure of Si-rGO-C composite.

Figure 2. (a) Optical images of Si-GO mixture before (left) and after (right) freeze-drying process. (b) TGA curves of Si-rGO composite with and without additional carbon coating. (c) XRD data of the as-obtained Si-rGO-C composite. (d) Raman spectra of D bands and G bands from Si-GO and Si-rGO-C composites.

Figure 3. SEM images of a typical site of Si-rGO-C composite with a whole piece of rGO flake (a), a close view of Si-rGO-C composite including branched carbon with Si NPs wrapped with rGO sheets (b), a typical site of Si-rGO composite (c), and Si-rGO composite with higher magnification (d).

Figure 4. (a) TEM image of Si-rGO-C composite at low magnification with the grid of TEM holder in view. (b) A zoomed-in TEM image of (a) with detailed features of Si-rGO-C. (c) Dark field TEM image of Si-rGO-C composite with higher resolution, (d) EDX mapping of element Si for the area marked in (c), (e) EDX mapping of element C for the area marked in (c), and (f) HRTEM image of Si-rGO-C composite with insets of increased magnification TEM image and FFT pattern of the selected area.

Figure 5. XPS spectra of C (a, b, and c) and Si (d, e, and f) for Si-GO (a and d), Si-rGO (b and e), and Si-rGO-C (c and f) composites.

Figure 6. Charge and discharge profiles of Si-rGO-C (a) and Si-rGO (b) of first three cycles.

Figure 7. (a) CV test of the Si-rGO-C composite with 1st, 3rd, 6th and 8th cycles shown. (b) Cycling performance of Si-rGO-C, Si-rGO composites, and bare Si at 0.2C following activation. (c) Rate capability tests for Si-rGO-C and Si-rGO composites. (d) Long-term cycling performance of Si-rGO-C composite at 1C following activation.

Figure 8. (a) Impedance measurements for Si-rGO-C and Si-rGO composites after 1st and 100th discharges, (b) The equivalent circuit model.

Table 1: Impedance parameters for Si-rGO-C and Si-rGO electrodes after 1st and 100th cycles.

Electrode	R_s/Ω	R_{SEI}/Ω	R_{CT}/Ω
Si-rGO-C 1 st discharge	7.291	37.1	3.623
Si-rGO-C 100 th discharge	4.454	49.58	18.5
Si-rGO 1 st discharge	7.911	59.95	1.013
Si-rGO 100 th discharge	7.695	116.1	64.98

Graphical Abstract