Binder-Free Carbon-Coated Silicon–Reduced Graphene Oxide Nanocomposite Electrode Prepared by Electrophoretic Deposition as a High-Performance Anode for Lithium-Ion Batteries

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A simple yet versatile binder-free electrophoretic deposition method is developed to fabricate a carbon-coated Si/reduced graphene oxide (Si@C/rGO) nanocomposite as a high-performance anode for lithium-ion batteries. In this nanostructure, high specific capacity Si nanoparticles are uniformly coated with the carbon layer and embedded in graphene sheets to form an integrated, robust and conductive framework. Electrochemical studies show that this nanostructured Si@C/rGO electrode exhibits a high reversible specific capability (1165 mAhg⁻¹ at 0.1 Ag⁻¹, three times of that of graphite) and excellent cycling stability (capacity retention of 96.8% at 1 Ag⁻¹, and 95.4% at 2 Ag⁻¹ after 100 cycles).

1. Introduction

Rechargeable lithium-ion batteries (LIBs) are key components in consumer electronic devices and are of great potential for applications in electrical vehicles and for renewable energy storage.^[1] However, current LIB technology cannot meet the high energy demands from electrical vehicles because both the cathode and anode materials reach their maximum specific capacities. Among the high-energy density anode materials investigated, silicon (Si) is the most likely material to be used in the next generation of anodes. Compared with the state-of-art anode material used in LIBs, graphite, the theoretical capacity of Si (4200 mAhg⁻¹) is approximately ten times higher than graphite $(372 \text{ mAhg}^{-1} \text{ for LiC}_6)$.^[2] However, the use of Si as an anode material in LIB manufacture has been seriously hindered by its huge volume change (up to about 300%) during the lithiation/delithiation process, which results in: 1) physical deformation of the electrode and the cell; 2) pulverization of the silicon particles to cause the loss of electrical contact,^[3] and 3) the rupture and reformation of the (unstable) solid-electrolyte interface (SEI) at the Si surface, which causes a continuous consumption of the electrolyte.^[4] Therefore, it is challenging to achieve stable electrochemical cycling with an Si anode.

It has been demonstrated that an Si nanoparticle with a critical size can sustain its morphology even after the huge

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volume expansion and shrinkage during lithiation/delithiation,^[5] thus many exotic nanostructured Si materials of various morphologies, such as thin films,^[6] nanoparticles,^[7] nanowires,^[8] and nanotubes,^[9] have been tested as stable high-energy LIB anodes. These Si nanostructures are effective for the accommodation of large volume changes during lithiation/delithiation, but they are unable to sustain a stable SEI at the Si particle surface, which is detrimental to cell-cycling life.^[10] One method widely applied to stabilize the SEI is to coat a layer of carbon onto the nanostructured Si surface, so that the SEI is formed at the carbon surface instead of Si.^[4, 11] Carbon coating not only favors the formation of a stable SEI on the surface of the carbon shell, it also enhances the electrical conductivity.^[12]

In order to generate voids between carbon shells to further accommodate the volume change and have better electrical conductivity, the highly conductive and flexible graphene has been incorporated into Si/carbon composites. Zhou et al.[13] synthesized graphene/carbon-coated Si hybrids using an ionic liquid as the carbon precursor, after the Si nanoparticles were dispersed on a graphene surface by electrostatic assembly. Lin et al.^[14] fabricated carbon-coated Si (Si@C)/reduced graphene oxide (rGO) composites assisted by polyaniline. Wu et al.^[15] prepared a multilayered Si-embedded porous carbon/graphene hybrid film through electrostatic spray deposition technology. All of these studies indicated that introduction of a graphene layer and a carbon coating to the nanostructured Si can promote effectively the formation of a stable SEI and provide a buffer to accommodate the huge volume change of the Si during cycling. However, it is still a challenge to fabricate Si/ carbon/rGO composites for practical LIB applications in a facile and scalable manner.

The electrophoretic deposition (EPD) method is a binderfree coating technique that has the advantage of short formation times and it is inexpensive and suitable for mass produc-

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tion.^[16] We previously demonstrated that the EPD method can be used to assemble Si nanoparticle electrodes.^[17] In this study, we modified the EPD method that we developed previously to fabricate a binder-free Si@C/rGO nanocomposite electrode in which Si NPs were embedded in an interconnected graphene framework and coated with an uniform carbon layer by pyrolysis of polyethylene glycol (PEG; Figure 1). In this composite, Si



Figure 1. Fabrication of the Si@C/rGO composite electrode.

NPs are the active material with high specific capacity, the interconnected graphene sheets serve as electrical conducting media, the voids between the graphene sheets are buffer zones for silicon volume change during lithiation/delithiation, and the surface layer of carbon provides structural reinforcement and a locale for a stable SEI to form. Thus, the resultant Si@C/rGO nanocomposite electrode exhibited enhanced cycling stability and rate capability. The EPD fabrication of the Si@C/rGO nanocomposite electrode is scalable, binder-free, inexpensive, and offers a new avenue for the application of high-capacity Si-based materials in LIBs.

2. Results and Discussion

In EPD processes, charged particles in a suspension are deposited onto an electrode under the influence of the applied electric field. The particles with positive surface charges are deposited onto the cathode, whereas those with negative charges are deposited onto the anode. Therefore, it is critical to ensure that each component in the suspension has the same type of surface charge during multicomponent EPD, so that they can be deposited onto the same electrode.^[18] The surface charges of Si NPs in acetone (sample 1, Table 1) are negative, whereas the surface charges of GO (sample 3, Table 1) are positive, thus it is impossible to assemble two components onto the same electrode directly. To alter their surface charge to be the same

Table 1. acetone	I. Zeta potential of Si and GO particles suspended in acetone and $e+l_2.$					
Sample	Concentratio Si	on in suspensio GO	n [mgmL ⁻¹] I ₂	Zeta potential [mV]		
1	0.1	0	0	-3.05		
2	0.1	0	2	5.86		
3	0	0.05	0	2.15		
4	0	0.05	0.02	5.15		

type, I_2 is added to the suspension. Protons are formed by the reaction between acetone and I_2 , as shown in Equation (1):^[16b]

$$CH_3 - CO - CH_3 + 2I_2 \rightleftharpoons ICH_2 - CO - CH_2I + 2H^+ + 2I^-$$
(1)

Through a steric stabilization mechanism,^[19] the protons formed are adsorbed onto the surface of Si NPs (sample 2, Table 1) and GO particles (sample 4, Table 1) to render both components positively charged. The positively charged particles repel others to form a well-stabilized suspension for cathodic EPD.^[20] If a dc field is applied to the EPD suspension, Si and GO particles are deposited on the cathode simultaneously. After drying, PEG remains on the surface of Si to form a Si@C/ rGO hybrid structure, and the remaining I_2 on the electrode sublimes.

The coating of PEG on the Si NPs was confirmed by FTIR spectroscopy (Figure 2a). In the spectra of Si@PEG/GO, the bands centered at 2867 and 950 cm⁻¹ correspond to CH₂ stretching vibrations and CH out-of-plane bending vibrations of PEG molecules, respectively.^[21] The strong peak at 1104 cm⁻¹ is attributed to the C–O–C ether stretch vibration. The Si–O–Si bending mode was also observed at 1148 cm⁻¹.^[22]

The Raman spectra of the Si@PEG/GO and Si@C/rGO electrodes are shown in Figure 2 b. Four peaks were observed at 519, 960, 1357, and 1601 cm⁻¹ in both samples. The peaks at 519 and 960 cm⁻¹ correspond to the first-order optical phonons and 2TO modes of crystalline Si, respectively,^[23] the corresponding peaks are also observed in the Raman spectra of the



Figure 2. a) FTIR spectra of pristine Si, pristine PEG and Si@PEG/GO electrode. b) Raman spectra of Si@PEG/GO and Si@C/rGO electrodes.



reference material of crystalline Si (Figure S1 in the Supporting Information). The D band is attributed to the defects or imperfections of the graphene, and the G band to the ordered graphitized structure.^[24] After annealing, the ratio of their intensities, I_D/I_G , increases from 0.87 to 1.02, suggesting that more defects are introduced to the Si@C/rGO with the reduction of GO.^[25] The reduction of GO to rGO can drastically enhance the electron conductivity.^[26]

The XRD analysis of the Si@C/rGO electrode is shown in Figure 3. The peaks of both the Si@C/rGO electrode (Figure 3 a) and Si NPs (Figure 3 b) at 28.4°, 47.3°, 56.1°, 69.1°, 76.4°, and 88.0° correspond to (111), (220), (311), (400), (331), and (422) diffractions of crystalline Si (JCPDS No. 27-1402). The high-intensity peaks marked with stars are assigned to the Cu substrate. These results indicate that Si NPs in the Si@C/rGO electrode retain their crystalline structure during the EPD and annealing processes.

b) 50 μm 50 μ

Figure 4. SEM images of Si@C/rGO electrode at the surface (a and b) and in cross-section (c and d).

20 µm



Figure 3. XRD patterns of a) pristine Si and b) the Si@C/rGO electrode.

SEM images of the Si@C/rGO electrode are shown in Figure 4. The graphene sheets are indicated by blue arrows and Si NPs by brown arrows. The Si NPs and graphene layers are interconnected to form a porous matrix with many voids in the composite structure (these can be more clearly seen in Figure S3). This porous structure provides buffer space to accommodate the volume change occurring during lithiation/delithiation, easy access of the electrolyte as well as high electrical conductivity for high-rate capability.^[27] The co-deposited film is approximately 14 μ m thick, and is tightly adhered to the Cu substrate (Figure 4c). The Si NPs are loaded between the graphene sheets, as seen in the cross-sectional image (Figure 4d). EDX mapping images (Figure 5) show that Si and carbon elements are homogenously distributed in the composite structure.

TEM images of the Si@C/rGO nanocomposite are shown in Figure 6. In Figure 6a, it is apparent that Si NPs are 50–100 nm in size and are well spread over the graphene sheets. Notably, the bonding between Si NPs and graphene is so strong that the composite survives the ultrasonic process used to detach the composite film from the Cu foil prior to TEM characteriza-



Figure 5. EDX mapping images of the Si@C/rGO electrode on the surface.

tion. A uniformly coated carbon layer approximately 14 nm thick is observed on the Si NPs (Figure 6). The corresponding selected electron diffraction (SAED; Figure 6c) of the Si@C/rGO nanocomposite only shows the diffraction rings of Si NPs; these rings can be assigned as (111), (220) and (311), in good agreement with crystalline Si.^[4] As shown in the high-resolution transmission electron microscopy (HRTEM) image (Figure 6d), it is evident that the Si NPs are coated with a layer of carbon. The interplanar distance of the Si NPs was measured to be approximately 0.32 nm, which is a good match to the (111) planes of crystalline Si. The total carbon content of the Si@C/rGO electrode was measured to be 37.2% by elemental analysis.

The Si@C/rGO nanocomposite prepared by EPD has the unique structural features required for improved electrochemical performance as a high-energy anode because: 1) the voids between graphene sheets can accommodate the huge volume

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Figure 6. a, b) TEM, c) SAED, and d) HRTEM images of the Si@C/rGO nanocomposite.

change of Si NPs during lithiation/delithiation, and the carbon coating can preserve its structure; 2) the highly electrically conductive graphene, along with the carbon coating, can facilitate fast electron transfer through an interconnected network and with good contacts between carbon and Si NPs; and 3) a stable SEI is likely formed on the carbon surface coating instead of the surface of the Si NPs.

The electrochemical performance of the Si@C/rGO nanocomposite electrode is shown in Figure 7. Figure 7a shows the voltage profile of the Si@C/rGO electrode. The first discharge and charge capacities are 1609 and 1179 mA hg⁻¹, respectively, corresponding to a coulombic efficiency (CE) of 73%. The irreversible loss of capacity during the first cycle is likely due to the formation of an SEI on the carbon surface and graphene layers.^[28]

Figure 7 b shows the cycling performance of the Si@C/G nanocomposite in comparison with the bare Si electrode. The Si@C/rGO nanocomposite electrode clearly exhibits improved cycling stability over bare Si electrodes. After 100 cycles, the capacity of the Si@C/G nanocomposite electrode was maintained at 1165 mAhg⁻¹, which corresponds to 98.8% retention of the original reversible capacity. The CE was above 97% after the eighth cycle and stabilized thereafter. On the contrary, the cell with bare Si nanoparticles exhibited a much lower capacity of 574 mAhg⁻¹ with a retention of 23% after 100 cycles. The Si@C/rGO nanocomposite electrode fabricated by the EPD method also exhibited higher stability compared with some previous graphene/carbon-coated Si hybrids.[13,14] This is likely due to the similar zeta potentials of the Si NPs and GO in the EPD suspension, which allows for each component to be deposited on the substrate at the same rate to ensure a uniform mixing state.

The rate performance of the Si@C/rGO nanocomposite electrode was further investigated by cycling at various current densities ranging from 0.1 to 5 Ag^{-1} (Figure 7 c). An activation process occurs over the first few cycles, which can be attributed to delayed electrolyte wetting of the 3D porous structure of the composite electrode.^[29] As the applied current was increased, the capacity slightly decreased. Stable capacities were observed at around 1240, 1227, 1181, 1106, 978, and 683 mAhg⁻¹ at rates of 0.1, 0.2, 0.5, 1.0, 2.0 and 5 Ag^{-1} , respectively. In addition, the capacity of approximately 1267 mAhg⁻¹ can be remarkably recovered after the discharging and charging rate is decreased to 0.1 Ag⁻¹, again this suggests an outstanding rate performance.

The cycling performance of the Si@C/rGO nanocomposite electrode at high current densities was also investigated (Figure 7d). The cells were galvanically charged–discharged at a rate of 0.1 Ag⁻¹ for the first five cycles and then cycled at high rates (1.0 and 2.0 Ag⁻¹) for all subsequent cycles. The reversible capacity of 1090 mAhg⁻¹ was retained after 100 cycles at a current density of 1 Ag^{-1} . Even at a high current density of 2 Ag^{-1} , the specific capacity was 915 mAhg⁻¹, a value much higher than the theoretical capacity of graphite (\approx 372 mAhg⁻¹). The capacity retention of the Si@C/rGO nanocomposite electrode was 96.8% and 95.4%, respectively, from the sixth to the 105th cycle at 1.0 and 2.0 Ag⁻¹, indicating the excellent cycling stability at high current density.

Figure 7 e shows the cyclic voltammogram of Si@C/rGO nanocomposite electrode. After the first sweep to 0.02 V, the broad peak at 0.7 V disappears in subsequent cycles, indicating an irreversible electrode reaction such as that to form an SEI layer.^[30] The sharp peak located below 0.1 V represents the lithiation process of the crystalline Si.[31] During the following scans, two cathodic peaks appear at 0.22 and 0.03 V, suggesting a two-step phase transition of α -Si into α -Li_xSi.^[32] The two peaks at 0.32 and 0.47 V that appear during the first sweep from 0.02 to 1.5 V are related to the de-alloying of $\text{Li}_x\text{Si.}^{[33]}$ The broad cathodic peak at 0.22 V and the anodic peaks at 0.32 and 0.47 V gradually increase over subsequent charge-discharge cycles, which is a typical characteristic of the transition from crystalline silicon to amorphous silicon.[34] The increase of peak current in the cyclic voltammogram may be attributed to the gradual activation of the Si@C/G nanocomposite electrode, enabling more Li to react with Si, which has been reported from other studies.[15,35]

Figure 7 f shows the Nyquist plots of the Si@C/rGO nanocomposite and bare Si electrodes after 20 cycles at a delithiated state as well as the fitting results using the equivalent circuit. The impedance curves show one compressed semicircle in the medium-frequency region, which is assigned to the chargetransfer resistance (R_{ct}), and an inclined line in the low-frequency range, which is considered to be Warburg impedance.^[36] The R_{ct} value of the Si@C/rGO nanocomposite electrode is 22.91 Ω , much lower than that of the bare Si electrode (121.6 Ω ; Table 2). This indicates that the carbon layer and rGO work together to facilitate electron/ion transfer.

Photographs of the Si@C/rGO electrode before and after 100 cycles are shown in Figure S2. No cracks in the films were





Figure 7. a) Galvanostatic charge–discharge profiles of the Si@C/rGO nanocomposite electrode at a current density of 0.1 A g^{-1} . b) Charge–discharge cycling test of Si@C/rGO and bare Si electrodes at a current densities of 0.1 and 0.3 A g^{-1} , respectively. c) Specific capacity of the Si@C/rGO electrode at various current densities: 0.1, 0.5, 1.0, 2.0, and 5.0 A g^{-1} . d) Cycling performance of the Si@C/rGO electrode at 1.0 and 2.0 A g^{-1} for 100 cycles. e) Cyclic voltammograms of the Si@C/rGO electrode. f) Nyquist plots of the Si@C/rGO and bare Si electrodes. The capacity values were calculated based on the total mass of the Si@C/rGO anaccemposite.

Table 2. Impedance parameters of Si@C/rGO nanocomposite and bare Si electrodes. R_s is a component in the fitting process.							
Sample	$R_{\rm s} \left[\Omega\right]$	Error [%]	$R_{\rm ct} \left[\Omega \right]$	Error [%]			
Si@C/rGO Si NPs	2.556 2.801	1.26 1.74	22.91 121.6	0.71 0.79			

noticeable, which demonstrates that even without binder, high mechanical strength can be obtained by using EPD. The morphology of the Si@C/rGO nanocomposite electrode was also evaluated after 100 cycles in the delithiated state (Figure 8). The SEM image of the Si@C/rGO electrode after 100 cycles shows a porous structure with many voids, except that a thin SEI layer is coated on the Si NPs and rGO. This demonstrates

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Figure 8. SEM images of Si@C/rGO electrode after 100 cycles. a) The surface and b) a cross-section.

that the unique structure of the Si@C/rGO nanocomposite electrode can well accommodate volume expansion of Si, contributing to excellent structure stability.

3. Conclusions

In conclusion, we successfully applied an EPD method to the fabrication of carbon-coated Si nanoparticles embedded in a graphene framework electrode. The resultant binder-free electrode combines the advantages of both carbon-coated Si NPs and graphene and exhibits enhanced electrochemical properties compared with traditional Si electrodes. The carbon layer, pyrolyzed from PEG, provides high electrical conductivity and restricts the continual rupturing and reformation of the SEI. The graphene sheets prevent Si NPs from aggregating and they serve as effective buffering agents to limit the volume expansion during Li⁺ insertion. Carbon-coated Si NPs and graphene form a porous conducting matrix and an integrated architecture with robust structure stability and electrical conductivity. The resultant Si@C/rGO nanocomposite electrode presents excellent cycling stability with capacity retention of 98.8% at 0.1 A g^{-1} , 96.8% at 1 A g^{-1} , and 95.4% at 2 A g^{-1} after 100 cycles. The binder-free EPD method is inexpensive, easy to scale up, and has potential for realizing the industrial application of Si anodes.

Experimental Section

GO was produced from natural graphite flakes by the modified Hummers method.^[37] In a typical preparation of EPD suspension, Si (50.0 mg, crystalline, average particle size \approx 50 nm, 99%, plasma synthesized, Alfa Aesar), PEG (500 mg, average M_n = 1000, Aladdin) and I₂ (50.0 mg) were added to acetone (40.0 mL). The suspension was dispersed by using a homogenizer (T10 basic, IKA Works GmbH & Co., Staufen, Germany) for 30 min, then a GO suspension (2.0 mg mL⁻¹, 10.0 mL), which was previously ultrasonically agitated for 4 h, was added and dispersed for a further 30 min to obtain the final suspension for EPD.

The Si@C/rGO nanocomposite electrode was fabricated in two steps (Figure 1). A Cu foil of 10 μ m thickness and a Pt plate of 2 mm thickness were used as the substrate (cathode) and counter electrode (anode), respectively. The composite films were cathodically deposited by applying a constant voltage between two electrodes in the suspension. The deposition conditions were as follows: applied voltage: 100 V, deposition time: 10 s to 1 min, distance between the electrodes: 1.5 cm. After deposition, the ob-

tained samples were dried at 80 °C in a vacuum oven overnight, followed by annealing at 700 °C for 4 h under an Ar/H₂ (95:5 v/v) atmosphere with a heating rate of 5 °C min⁻¹ to afford the Si@C/ rGO nanocomposite electrode. Before being assembled into the coin cell, the Si@C/rGO electrode was cut into a disc-like electrode with a diameter of 1.2 cm and weighed using a microbalance accurate to 0.01 mg. The weight of active substance was calculated by subtracting the weight of the Cu foil from the weight of the disc-like electrode.

The zeta potential of particles was characterized by using a Zeta-PALS zeta potential analyzer (Brookhaven Instruments Corporation, Holtsville, NY, USA). FTIR spectra were performed on a Nicolet IS5 FTIR spectrometer (Thermo Scientific). Raman spectra were performed on an Xplora Raman spectrometer (Horiba) with a 532 nm Ar-ion laser. The XRD data was acquired on a Rigaku Miniflex 600 equipped with a CuK α radiation source. The carbon content was measured using a Vario EL III element analysis instrument (Elementar Co., Hanau, Germany). The morphologies of the nanocomposite electrode were characterized by SEM (Hitachi S-4800) and HRTEM (FEI Tecnai G2 F30). Elemental mappings were conducted using an EDX device attached to a Hitachi S-4800 scanning electron microscope.

The electrochemical performance of the electrodes was assessed by using a CR2016-type coin cell. Cells were assembled in a glovebox filled with ultrahigh-purity argon with water and oxygen contents below 1 ppm using Celgard 2400 as the separator. Li foil was used as the counter and reference electrodes. The electrolyte was LiPF₆ (1 M) in a mixture of ethylene carbonate/diethylene carbonate/dimethyl carbonate (1:1:1 v/v/v) containing 5 wt.% of fluoroethylene carbonate as an additive. The coin cells were tested on a battery tester (Neware). Cyclic voltammetry was performed on a CHI440B electrochemical workstation at a scan rate of 0.1 mV s⁻¹. Electrochemical impedance spectra were performed on an electrochemical workstation (Solartron SI 1287) at frequencies from 0.01 Hz to 100 kHz.

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