An Integrated SiO@GC/Cu Foil Composite Anode Prepared by One-Step Carbonization Method for High-Performance Lithium-Ion Battery

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Abstract: Silicon-based anodes, for lithium-ion batteries (LIBs), have received extensive attention recently as they possess high theoretical capacity. However, the short cycling life, poor rate performance and low coulomb efficiency have limited their practical application. In order to address these problems, carbon coating has been proved to be an effect strategy. For that matter, the ability to tailor the thickness, homogeneity and graphitization degree of carbon-coating layers is of great importance for improving the electrochemical performances. Moreover, the adhesion among the particles of active material and the stickiness between the active material particles and the current collector could not be well achieved by using the conventional slurry coating of carbon-coated active materials on Cu foil. In this research, an integrated SiO@GC/Cu foil composite anode was successfully prepared by one-step carbonization method from a ball-milled SiO powder, thus gelatin and polyvinyl pyrrolidone (PVP) were used as raw materials. Superior electrochemical performance was achieved due to the special structure of this integrated composite anode. At a current density of 0.2 A g⁻¹, the discharge capacity for the integrated SiO@GC/Cu foil composite anode was 1270 mAh g⁻¹ after 50 cycles. It also exhibited a preferable rate performance (640 mAh g⁻¹ at 1.5 A g⁻¹). Compared with the pristine ball-milled SiO anode prepared by conventional slurry coating, the performance improvement can be analyzed with the suppressed volume change and improved electrical conductivity. The facile preparation and superior performance render the integrated SiO@GC/Cu foil composite anode a very promising variable for LIBs.

Keywords: Silicon monoxide, Composite, Integrated anode, Lithium-ion battery, Electrochemical performance.

INTRODUCTION

Lithium-ion batteries (LIBs) are widely used in portable electronic equipments and electric vehicles. Hence they are observed to be the most promising electrochemical device for energy storage and conversion. With industrial development and improvement in the living standard of people, there has been an ever increasing demand of electric vehicles and smart grids. Consequently the need for high-capacity and life-long LIBs is growing rapidly.

For that matter, high performance anode material can be used as an important component to directly affect the cycling life, capacity, safety and other properties of LIBs. Graphites are the most commonly used anode materials with the theoretical capacity of only 372 mAh g⁻¹, which cannot meet the ever-growing demand [1]. In order to satisfy the needs of high-energy density LIBs [2,3], it is of great pertinence to find alternative anode materials with high capacity, good cycle stability [4], low cost [5], wide applicability and nontoxicity [6,7]. In the same group of IVA in Periodic Table, silicon and carbon have similar electronic structure and chemical properties. Both of them are abundant as crustal elements, have low cost and are environmentally friendly. Unlike carbon, silicon can be alloyed with lithium at room temperature to form Li₁₅Si₄ phase, which makes it a very high theoretical specific capacity of 4200 mAh g⁻¹, much higher than that of commercial graphite. Moreover, the discharge/charge voltage platform of silicon is relatively low (~ 0.5 V vs. Li⁰/Li⁻) [1,3,6,8-10]. However, because of the low conductivity of silicon (4.0 × 10⁻⁴ S·m⁻¹) and volume expansion (300-400%) during charge-discharge cycle [11-14], the commercial application of the silicon anode is thus limited. Among Si-based anode materials, SiO has gained great attention due to low cost and relatively small volume change, thus exhibiting better cycle stability and application prospects relative to Si [15-17].

The effective combination of constructing carbon coatings and designing porous structures has been recognized as one of the most promising approaches to address the inherent shortcomings of SiO anodes [18-25]. However, due to the performance and production costs, the practical application of SiO anodes remains a serious challenge. In recent years, many methods have been discovered and taken in consideration to suppress the volume expansion of SiO...
with carbon shell through a one-step carbonization method. During preparation, gelatin as binder can be evenly coated on SiO particles due to its good film-forming property and also stick the SiO particles on Cu foil current collector. As a low-cost and sustainable biomass with rich carboxyl (-COOH) and amino-group (-NH₂), there is a strong interaction (hydrogen bonds, chemical bonds or ion-dipole interactions) between the polymer (gelatin) and the active material. Good water solubility enables gelatin to be thoroughly mixed with SiO particles in deionized water. After removing deionized water, gelatin can be evenly coated on SiO particles due to its good film-forming properties. In addition, gelatin acts as a binder and can simultaneously adhere SiO particles to the current collector. Thus a uniform carbon layer on SiO particles and a favorable connection between Cu foil and active material could be achieved. The carbon coating resulting from carbonization can not only buffer large volume changes of SiO but also provide electron and ion diffusion paths to enhance conductivity and charge transfer. Furthermore, the thickness, homogeneity and graphitization degree of carbon layer can be controlled by adjusting the amount of gelatin and/or carbonization temperatures. The as-prepared carbon coating layer could effectively address the shortcomings of SiO-based anodes in high-performance LIBs, particularly in stabilizing the formation of SEI layers, maintaining the structural integrity of the electrode and improving the conductivity. Therefore, the obtained integrated SiO@GC/Cu foil composite anode has superior cycle stability, high reversible capacity and excellent rate performance even at high current densities.

**EXPERIMENTAL SECTION**

**Preparation of an Integrated SiO@GC/Cu Foil Composite Anode**

Silicon monoxide (Aldrich Chemical Company, >200 mesh, 99%) was ball milled in a QM-3SP04 planetary ball mill using a 100 mL stainless steel milling jar at a speed of 400 rpm for 6 h. The ball-to-powder ratio was 15:1 in weight. The ball-milled silicon monoxide was used for the synthesis of the integrated SiO@GC/Cu foil composite anode (represented as SiO@GC/Cu hereafter). Typically, 0.4 g of ball-milled SiO, 1 g of gelatin, 0.2 g of polyvinyl pyrrolidone (PVP) and 10 mL of deionized water were dissolved in a water bath at 50 °C and stirred for 2 h. The slurry was coated on a Cu foil, and then the coated Cu foil was placed in a vacuum oven at 70 °C for 12 h. Finally, the SiO@GC/Cu composite electrode was obtained by
carbonization at 450 °C or 550 °C for 1.5 h at a heating rate of 3 °C min⁻¹, which are represented as SiO@GC/Cu-450 and SiO@GC/Cu-550, respectively.

Characterization

Thermal gravimetric (TG) were carried out from room temperature to 900 °C on a thermal analyzer (SDT-Q600, TA, USA) under air at a heating rate of 10 °C min⁻¹. X-ray diffraction (XRD) patterns of samples were obtained by using a Bruker D8 Advance diffractometer with Cu Kα radiation at a voltage of 40 kV and a current of 40 mA. The morphology of SiO@GC/Cu was characterized by scanning electron microscopy (SEM, JSM-6360LV, JEOL Ltd) and transmission electron microscopy (TEM, Hitachi JEM-1200EX, JEOL Ltd). The corresponding elemental mapping was obtained by using an energy dispersive spectrometer (EDS). Raman spectra were collected using a LabRAM HR Evolution spectrometer (Horiba JY). In order to characterize chemical composition and surface functionalities of SiO@GC/Cu, X-ray photoelectron spectroscopy (XPS, Thermo Scientific Escalab 250Xi) was performed.

Electrochemical Measurements

Electrochemical characterization was carried out by using 2025 type-coin half-cells with the lithium metal as counter and reference electrodes. As-prepared SiO@GC/Cu composite was used as both anode and current collector. The electrolyte was LiPF₆ (1 M) in a mixed solution of dimethyl carbonate (DC), ethylene methyl carbonate (EMC) and ethylene carbonate (EC) (1:1:1, vol.). After pressing and punching, the working electrodes in 12 mm diameter were fabricated and assembled into coin-type cells in an Ar-filled glovebox. The galvanostatic charging/discharging (GCD) tests were conducted on a LAND CT2001A battery testing system within a voltage range of 0.01–1.5 V at various current densities. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were carried out on a CHI660D electrochemical workstation. CV was conducted at a scan rate of 0.1 mV s⁻¹ in a potential range of 0.01–1.5 V and EIS was performed over the frequency range of 100 kHz–10 mHz.

RESULTS AND DISCUSSION

Carbon black was agglomerated in large amount and the insulator binder separated the active material from the conductive agent, hindering the transfer of electrons and lithium ions. This was done for the preparation of anode by the conventional slurry coating method (Figure 1).

Moreover, the connectivity between SiO@GC and Cu foil was very poor. The integrated SiO@GC/Cu composite anode was prepared according to the procedure shown in Figure 1. The slurry mixture of SiO powder, gelatin and polyvinyl pyrrolidone (PVP) was first coated on Cu foil. The subsequent carbonization gave rise to a uniform carbon coating on SiO surface, which could improve the electronic conductivity and promote the transport of lithium ions. Furthermore, during the cycles of charge and discharge, this carbon layer suppressed the volume expansion of SiO and thus formed a stable solid electrolyte interphase (SEI). Moreover, the strong interfacial bonding between the carbon coating and the Cu foil can enhance the transfer of electrons between them. Consequently, the peel off of SiO@GC from the Cu foil was effectively prevented during the charging/discharging cycles. Due to the unique integrated structure of SiO@GC/Cu composite anode, it will exhibit excellent lithium ion storage performance. It is worth noting that the synthesis of the SiO@GC/Cu composite anode is feasible and easy to mass produce.

Figure 1: Schematic procedures to prepare SiO@GC/Cu composite anode.
monoxide [47,48]. In addition, for SiO@GC/Cu, no characteristic peaks of silicon were found except for three peaks at 43.3°, 50.4° and 74.1° from the current collector of Cu foil [17,32,43], indicating that no disproportionation occurred during carbonization at 450 °C and 550 °C. Moreover, no characteristic peaks of carbon were observed from the SiO@GC/Cu, indicating that an amorphous carbon was formed on the SiO surface [44,46]. Besides, the Cu foil was not oxidized during carbonization under a nitrogen atmosphere because there were no XRD peaks coinciding with copper oxide or other copper-based compounds [17,31,32]. Figure 2b shows the Raman spectra of the SiO@GC/Cu composite anodes. A broad peak at 466 cm⁻¹ could be attributed to the SiO matrix [48]. In addition, the Raman spectra of the SiO@GC/Cu-450 and SiO@GC/Cu-550 composite anodes exhibited two characteristic peaks at 1370 cm⁻¹ and 1582 cm⁻¹ could be attributed to D band and G band of carbon, respectively [15,18,21]. This again indicated that the surface of the SiO particles was successfully coated with carbon layer. The ratio (I_D/I_G) represents the degree of graphitization and also indicates the electrical conductivity of carbon material [18,45,46]. This ratio of SiO@GC/Cu-450 (I_D/I_G = 0.8) is slightly lower than that of SiO@GC/Cu-550 (I_D/I_G = 0.86), indicating that lower carbonization temperature resulted in an improved electrical conductivity of the SiO@GC/Cu composite anode. Hence it will exhibit superior electrochemical properties [22,43].

In this study, the commercial SiO particles (>200 mesh) were first ball milled and then used for the preparation of composite anodes. The content of SiO in both composite anodes was moderated to be lower than 70 wt% in order to obtain an improved cyclic stability with low costs. In the SiO@GC/Cu composite anodes, the reduction of SiO particle size by high-energy ball-milling and the further utilization of gelatin and PVP as a coating precursor can realize the granulation of the final products. The electrical conductivity of the integrated composite anodes can be ensured by carbon coating, which could also buffer the volume expansion of SiO. The as-prepared SiO@GC/Cu composite anodes are black in appearance, indicating that the brown SiO particles have been coated by a carbon layer. Figure 3 shows the morphology and microstructure of the SiO@GC/Cu composite anodes. SEM images of SiO@GC/Cu-450 shown in Figure 3a and b exhibited dense particles with a maximum diameter of about 5 µm [30,40,42,43,48,49]. For the case of SiO@GC/Cu-550 (Figure 3c), the particle size was slightly increased to be about 5-7 µm. TEM image (Figure 3d) further indicated that SiO is uniformly covered by the nanocarbon layer. The microstructure of SiO@GC/Cu-450 was further characterized by high-resolution transmission electron microscopy (HRTEM), which are shown in Figure 3e and f. The boundary between SiO and carbon can be clearly observed and the SiO particles are covered by a layer of carbon with a thickness of about 4.5 nm (Figure 3f) [6,7,44,46-48]. The aforementioned figures showed an irregular morphology of the SiO@GC/Cu composite anodes, which is resulting from the ball milling treatment and the following carbonization of PVP and gelatin as carbon precursors. The morphological image in Figure 3 shows that there are gullies on the smooth surface of the SiO@GC/Cu composite anodes [15,18,30,43]. Thus more active sites are provided, which is conducive to the transmission of electrons. To further illustrate the structure of the composite, elemental mapping analysis was performed to investigate the elemental distribution in SiO@GC/Cu-450. Figure 3g-j demonstrates that SiO is encapsulated by carbon layer.
Furthermore, the other elements of N and O are evenly distributed in the as-prepared integrated composite anode [44].

Figure 4a shows the XPS survey spectrum of SiO@GC/Cu-450, which further confirms the presence of silicon, carbon, nitrogen and oxygen in the sample, consistent with the EDS mapping results. The high-resolution spectrum of Si 2p (Figure 4b) shows that the two peaks are located at 103.1 and 103.8 eV, respectively, corresponding to the species of silicon oxides (SiO$_x$, x < 2; and SiO$_2$) [22,23,43]. Note that, no peak of Si$^0$ was detected, which is consistent with the XRD results [43]. C 1s spectrum (Figure 4c) can be fitted to three peaks at 284.5, 285.2 and 286.5 eV, which can be related to C-C, C-N and C-O bonds, respectively [36]. This also confirms the formation of strong covalent bond between C and N. And the introduction of N element could enhance the combination of SiO particles and carbon coating, which is beneficial to improve the affinity of the carbon layer on the SiO particles during the cycles and thus maintain the structural integrity [43]. The N in SiO@GC/Cu-450 consists mainly of pyridine N and pyrrole N at 398.5 and 400.2 eV (Figure 4d) [36,50]. Doping N is also beneficial to improve the electrical conductivity of the integrated composite anode [36,51]. A single highly symmetrical peak centered at 532.7 eV (Figure 4e) from the SiO component can be observed in the spectrum of the O 1s region [45]. In order to determine the carbon content in the SiO@GC/Cu composites, TG analysis was performed and shown in Figure 4f. The weight loss of SiO@GC/Cu-450 and SiO@GC/Cu-550 is about 28.25% and 47.55% from 50 to 500 °C, which can be considered as the mass fraction of carbon derived from the precursors of gelatin and PVP [6,15,36,42,44,45].

The electrochemical reaction of the active material was shown in Figure 5. CV curves of SiO@GC/Cu-450 at a scan rate of 0.1 mV s$^{-1}$ (Figure 5a) showed that a cathode peak at about 0.5 V was observed in three
cycles due to the formation of SEI layer [19]. The peak at 0.01 V is corresponded to the lithiation alloying reaction of Si. These CV curves are almost coincided for the initial three cycles, which means that SiO@GC/Cu-450 has stable cycle performance (Figure 5a). And SiO@GC/Cu-550 showed similar CV results (Figure 5b). However, the coincidence of CV curves for SiO@GC/Cu-550 is not good as SiO@GC/Cu-450. The cathode peak near 0.19 V is attributed to the lithiation of SiO@GC/Cu-45 [52,53]. Two anodic peaks at about 0.31 and 0.42 V can be related to the delithiation of Li,Si alloy [9,10,25-27,30,52,53]. From the CV curves of SiO@GC/Cu-450 at different scan rates (Figure 5c), a linear relationship between the square root of the scanning rate ($v^{1/2}$) and the peak current ($i_p$) can be determined (Figure 5d). The Li-ion diffusion coefficients of various electrodes can be calculated through the following formula (1) [54].

$$i_p = 2.69 \times 105 \times n^{3/2} \times A \times c \times D^{1/2} \times v^{1/2}$$ (1)
where $n$ stood for the number of electrons per reaction ($n = 1$), $A$ represented the surface area of the electrode ($A = 1.1 \text{ cm}^2$ in our case) and $C$ is the surface concentration of the Li ion (1 M) [20,27,55,56]. The lithium ion diffusion coefficient ($D_{Li^+}$) of SiO@GC/Cu-450 was calculated to be $1.79 \times 10^{-9} \text{ cm}^2 \text{s}^{-1}$.

The carbon coating on the SiO surface and the incorporation of nitrogen are two important factors for improving the electrical conductivity. The electrochemical performance of SiO@GC/Cu-450 was evaluated by using CR2025 coin cells in a voltage range of 0.01–1.5 V vs Li$^+$/Li [30,42,46,57]. Figure 6a shows the charge and discharge curves for the different cycles at a current density of 0.2 A g$^{-1}$. A long slope instead of a flat plateau appears between 0.3 and 0.0 V in the first discharge profiles, which is typical characteristics of SiO [42,58]. The initial discharge capacity of SiO@GC/Cu-450 is 1935.8 mAh g$^{-1}$ with the initial coulombic efficiency of 64%. Figure 6b shows the cycle performance curve of SiO@GC/Cu at 0.2 A g$^{-1}$. For comparison, the ball-milled SiO was also included. It can be seen that SiO@GC/Cu exhibited better cycle stability and capacity retention than pristine ball-milled SiO, indicating the effectiveness of carbon coating. The SiO@GC/Cu-450 and SiO@GC/Cu-550 showed a specific capacity of 1935.8 mAh g$^{-1}$ and 1521.1 mAh g$^{-1}$ at the 1$^{st}$ cycle. After 50 cycles, the reversible capacity of SiO@GC/Cu-450 was ~1090 mAh g$^{-1}$ with capacity retention of ~60%. For SiO@GC/Cu-550, the reversible capacity is ~910 mAh g$^{-1}$ with capacity retention of ~59%. That is to say, by introducing a carbon coating, the cycle stability of SiO-based anodes is effectively improved. As the carbonization temperature during synthesizing process is increased, the cycle performance and reversible capacity are slightly decreased, which suggests that SiO@GC/Cu-450 can better adapt to the strain caused by volume change [21,30,36,43,53]. However, in LIBs, low CE of anodes lead to a continuous consume of lithium ions from the cathode and electrolyte, resulting in severe capacity degradation.

As shown in Figure 6c, at a current density of 0.5 A g$^{-1}$, the discharge specific capacity of SiO@GC/Cu-450 was 540 mAh g$^{-1}$ after 150 cycles, which was 1.45 times higher than the theoretical capacity of artificial graphite (372 mAh g$^{-1}$). Figure 6d shows the rate performance of SiO@GC/Cu-450. Even when the current density was increased to 1.5 A g$^{-1}$, it
maintained a high reversible capacity of 640 mAh g\(^{-1}\). Furthermore, after the current density was restored to 0.1 A g\(^{-1}\), the reversible capacity of SiO@GC/Cu-450 was recovered to be 930 mAh g\(^{-1}\), which is very close to the initial discharge capacity (980 mAh g\(^{-1}\)). Excellent rate performance could be ascribed to the improved electrical conductivity and structural integrity of the integrated SiO@GC/Cu-450 composite anode during cycling [12,13,15,43].

When compared to the pristine ball-milled SiO, carbon coating from the carbonized gelatin could give rise to the formation of many voids in the composites, which provides the additional space for volume expansion. At the same time, N-doped carbon could improve the electrical conductivity of SiO [36,49-51]. In order to further investigate the electrochemical reaction during charging and discharge, the electrochemical impedance spectroscopy (EIS) of the samples was measured (Figure 7). All EIS spectra consist of two parts: a semicircle at the high frequency range and a straight line in the low frequency range. The semicircle diameter in the high frequency region represents the interface impedance (R\(_2\)) of charge transfer, while the slope of the line in the low frequency region represents the diffusion impedance (R\(_1\)) of Li-ion in the electrode material [21,30,42,47]. Obviously, the diameter of the semicircle of the integrated SiO@GC/Cu composite anode is much smaller than that of the pristine ball-milled SiO electrode before the cycle, which indicates that the N-doped carbon could significantly improve the electrical conductivity of SiO. EIS was fitted based on the equivalent circuit (the inset in Figure 7) and the fitting parameters are listed in Table 1. The values of R\(_1\) and R\(_2\) were determined to be 3.81 and 89.65 Ω for
SiO@GC/Cu-450, lowest among three samples. Thus it was found to have the best electrochemical properties.

Table 1: EIS Parameters of SiO@GC/Cu-450, SiO@GC/Cu-550 and Pristine Ball-Milled SiO Anodes

<table>
<thead>
<tr>
<th>Composite electrode</th>
<th>$R_1$ (Ω)</th>
<th>$R_2$ (Ω)</th>
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<tbody>
<tr>
<td>SiO@GC-450</td>
<td>3.81</td>
<td>89.65</td>
</tr>
<tr>
<td>SiO@GC-550</td>
<td>6.03</td>
<td>324.2</td>
</tr>
<tr>
<td>SiO</td>
<td>38.99</td>
<td>2096.1</td>
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</table>

CONCLUSIONS

In this work, a simple and low-cost one-step carbonization method was utilized to synthesize the integrated SiO@GC/Cu composite anodes using commercial SiO, PVP and gelatin as starting materials. This can simultaneously achieve both proper carbon coating and strong connectivity between active materials and current collector, which have been confirmed by many structural characterizations. While used in LiBs, the integrated SiO@GC/Cu composite anode has superior cycle stability and rate performance compared to the pristine ball-milled SiO. The enhanced electrochemical performance can be attributed to the stable electrode structure, improved conductivity and preferable diffusion capacity of lithium ion. The simple preparation process and decent electrochemical performance make the integrated SiO@GC/Cu composite anodes to be the potential candidates for high-performance LIBs in future.

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