One-Step Electrodeposition of Layer by Layer Architectural Si-Graphene Nanocomposite Anode of Lithium Ion Battery with Enhanced Cycle Performance

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Lithium ion battery has attracted more and more attention as one of the most promising power sources in the electric vehicles and portable electronic devices.1 Silicon, with a much larger theoretical specific capacity of 4200 mAh·g−1 and superior safety characteristics,3,4 compared to the current graphite anode, has been regarded as the most promising next generation anode for lithium ion batteries.5 However, some inherent drawbacks of Si anode such as low electronic conductivity (∼10−4 S m−1) and a large volumetric change2,7,8 during charging and discharging processes, have limited the electrochemical performances and the practical application of Si anodes in lithium ion battery.

Extensive investigations show that nano-structured Si such as Si nanotubes6–12 and nanowires13–17 can improve the electrochemical performances of Si anodes. The Si nanotubes by reductive decomposition of silicon precursors in an alumina template followed by etching according to Cui14 maintain 2878 mAh·g−1 at a 5C rate after 200 cycles. However, Si-based anodes are still needed to further enhance the cyclability and rate performances.

Graphene (G), as reported, not only can increase the conductivity of Si anode,1,15,19 but also can accommodate the large volumetric change of Si anode during cycling2,6,21 due to its excellent electrical conductivity and exceptionally large specific surface area.20 Yi and Ran16 use H2 to reduce SiO2 and graphene oxide mixture at 950°C to prepare G/Si–C composite, and the capacity of this composite is about 1314 mAh·g−1 at a rate of 0.4 A·g−1. And the charge transfer resistance of G/Si–C is reduced from 59.98 Ω to 9.14 Ω as the addition of graphene.

Compared with the above methods, electrodeposition can simplify the production of SiG composite and the use of IL can make it possible to output the composite at room temperature. Moreover, the electrodeposited SiG composite on copper substrate can be directly served as the anode without the conventional anode manufacture process. So direct electrodeposition of SiG composite has shown more advantages than the above methods. According to Abedin et al and Park et al.,22,23 silicon thin films are obtained by the electrochemical deposition from 1-butyl-1-methylpyrrolidinium bis(trifluoromethysulfonyl)imide ([BMP][Tf2N]) with SiCl4 as a Si source at room temperature. The above work encourages us to prepare Si-Graphene composites with alternate Si and graphene layer structure by electrodeposition from the liquidic with SiCl4 and graphene as precursors.

Here we present Si-Graphene (SiG) composites with alternate Si and graphene layer structure by one step electrochemical deposition from SiCl4-[BMP][Tf2N] ionic liquid containing dispersive graphene, which have exhibited a high specific capacity after 400 cycles. This method is relatively simple and easy to control the properties of Si-Graphene (SiG) composites.

Materials and Methods

The raw materials including SiCl4 (Alfa Aesar, 98%), 1-butyl-1-methylpyrrolidinium bis(trifluoromethysulfonyl)imide ([BMP][Tf2N]) (Alfa Aesar, 98%) and graphene (G) (Alfa Aesar, 98%) were directly used without any treatment. The ILs SiCl4-[BMP][Tf2N] and G-SiCl4-[BMP][Tf2N] were prepared by adding SiCl4 into [BMP][Tf2N]22,23 with or without graphene in a screw bottle, followed by well dispersion by ultrasonic method24 at room temperature. The suspension can maintain stable for at least 5 hours. After 5 hours, precipitation of graphene can be seen at the bottom of the cell.

Electrochemical measurements and electrodeposition were carried out in a three-electrode cell consisting of a PAR-STAT2273 (PAR-Stat ElectroChem, Ltd) in an argon-filled glove box (O2 and H2O < 1 ppm) under nonconvection conditions at room temperature. Cu sheet (99.9%) and a graphite rod were used as working electrode and counter electrode in the electrodeposition, respectively, while a Pt (99.99%) wire instead of Cu sheet was served as working electrode in the electrochemical measurements. A W (99.9%) wire in a fritted glass tube with [BMP][Tf2N] ionic liquid was used as a reference electrode. All the electrodes were cleaned as follows. Firstly, they were polished with emery papers, then distilled by ethanol, dipped in dilute sulfuric acid for 15 min and cleaned by acetone and finally dried in air. After each electrodeposition, Cu sheet covered with Si-Graphene (SiG) composites was quickly moved into acetonitrile for rinse three times. As the graphene concentration in ionic liquid is increased from 0.0926 mol·l−1 to 0.1296 mol·l−1 and 0.1852 mol·l−1, the obtained Si-Graphene (SiG) composites are referred as sample SiG1, SiG2 and SiG3, respectively. And then, the as-prepared Si-Graphene (SiG) composites were directly assembled into a coin-type cell with lithium plate (Φ 16 mm × 1.5 mm, China Energy Lithium Co., Ltd.) in a 1 M LiPF6 in ethylene carbonate (EC), dimethyl carbonate (DMC) and ethyl methyl carbonate (EMC) (1:1:1 in volume) electrolyte.
Results and Discussion

Electrochemical measurements.—In order to maximize the electrodeposition speed of Si, we choose the 1 mol·l⁻¹ SiCl₄·[BMP]Tf₂N ionic liquid for electrodeposition Si. Fig. 1 compares cyclic voltammograms (CVs) recorded on W electrodes in various G-SiCl₄·[BMP]Tf₂N ILs. In pure [BMP]Tf₂N ionic liquid without SiCl₄, a reduction peak A at −2.40 V in curve 1 is related to cation ions decomposition of [BMP]Tf₂N. While in 1 mol·l⁻¹ SiCl₄·[BMP]Tf₂N ionic liquid, a reduction peak B at −2.25 V and reduction peak C at −2.50 V in curve 2 are attributed to reduction of Si⁴⁺ and the cation ions decomposition of [BMP]Tf₂N, respectively. Compared with curve 1, reduction peak C at −2.50 V in curve 2 is a slightly positive than peak A in curve 1 due to Si reduction. The CV profile in curve 3 obtained from G-SiCl₄·[BMP]Tf₂N ILs, where graphene is 0.1852 mol·l⁻¹ and SiCl₄ is 1 mol·l⁻¹, has no obvious difference from curve 2, which means that there’s no strong bond between graphene and IL, but the reduction current for peak B is larger than the one in curve 2, maybe due to smaller electron transfer resistance of Si reduction on the adsorbed graphene as explained below.

Some electrochemical measurements were carried out to describe the effects of graphene in ILs. Electrochemical impedance spectrum (EIS) test reveals that the IL with graphene has a smaller electrochemical charge transfer resistance. The contact resistance is 120.6 ohms for IL without graphene and 6.3 ohms for IL with graphene. And the electron transfer resistance is about 282.2 ohms and 225.3 ohms relatively, as shown in Fig. 1d. Before electrodeposition, chronoamperometric curves at −0.5 V, −1.0 V and −1.5 V in Fig. 1b show that the addition of graphene can significantly improve the reduction current, especially as the potential increases to −1.5 V due to smaller electron transfer resistance of Si reduction on the adsorbed graphene.

As for the period of electrodeposition, chronoamperometric curves at −2.0 V in Fig. 1c indicate that the participation of graphene can raise Si reduction current, about 2 times as the one without graphene. There is a very interesting phenomenon that the graphene in the IL can also make the reduction current density regularly fluctuating between about 0 mA·cm⁻² and about 0.8 mA·cm⁻². This is caused by an alternate process between Si reduction (including Si nucleation and growth) and graphene adsorption. During electrodeposition, Si gradual growth decreases the Si reduction current due to a worse conductivity of Si. As Si particles grow to a certain size, the Si reduction current decreases to nearly zero, at this time the graphene is adsorbed on the surface of Si particles, the lower electron transfer resistance of the graphene induces Si to reduce on the adsorbed graphene again followed by Si nucleation and growth. The above processes including the alternate process of Si reduction, nucleation and growth, and graphene adsorption, remain repeating throughout the electrodeposition processes and result in the current density regularly fluctuating as seen in Fig. 1c. Nucleation and growth of Si occurred on the surface of the adsorbed graphene, has been proved by the SEM graphs in Fig. 2.

It has also found that Si growth has shown a smaller current than Si nucleation on graphene. Furthermore, the amplitude of current fluctuation gradually reduces as electrodeposition time prolongs, since the
Electrodeposition of SiG composites.—Firstly, electrodeposition of SiG is carried out from different concentration of G-SiCl$_4$-[BMP]Tf$_2$N ILs. As the graphene concentration in ionic liquid is increased from 0.0926 mol·l$^{-1}$ to 0.1296 mol·l$^{-1}$ and 0.1852 mol·l$^{-1}$, the obtained Si-Graphene (SiG) composites are referred as sample SiG1 (Fig. 2a), SiG2 (Fig. 2b) and SiG3 (Fig. 2d), respectively. The Si particle morphology changes from flocculent to nanoparticles and the average particle size of Si is decreased from 193.6 nm to 87.6 nm as the graphene concentration increases 0.1296 mol·l$^{-1}$ to 0.1852 mol·l$^{-1}$ in the ionic liquid, as shown in Fig. 2c.

The cross-section SEM morphologies of the SiG3 composites in Fig. 2e and Fig. 2f show the alternate layer structure of silicon and graphene. Each layer is about 120 nm thickness, and the whole SiG3 composites is about 12µm thick. The TEM image in Fig. 3 exhibits the single layer of SiG3 structure, in which the Si particle size is about 80–110 nm on graphene and each layer contains 4–5 layers of graphene as shown in Fig. 3a.

The graphene used in our experiments is several micrometers large with an irregular shape rather than a large complete sheet. Therefore, these graphene sheets are linked and covered by each other and may form unevenly surface during electrodeposition, which may result in uneven Si electrodeposition and distribution. However, in fact, from the SEM graphs, we can see that Si nanoparticles have a quite uniform distribution, with a particle size range in the 80–110 nm, as shown in Fig. 2c.

EDS analysis in a large area reveals that the SiG composites consist of Si, C and a small amount of O. The molar ratio of Si and C in the three samples SiG1, SiG2 and SiG3 is 6.24:1, 5.06:1 and 4.57:1, relatively. From the XPS graph (Fig. 4), we can see that most of the graphene in SiG3 hasn’t been oxidized because the C-C peak (284.7) is much more obvious than the one of C-O (286.1).

The Si particle diameter and morphology are controlled by nucleation rate and growth rate during electrodeposition. The formation mechanism of SiG can be explained through Fig. 5. As a reduction potential more negative than −2.00 V is imposed on the working electrode at 25°C, the double layer is firstly charged, then Si$^{4+}$ ions are reduced onto the Cu substrate followed by Si nucleation and then continuous growth. As Si particles grow to a certain size, the Si reduction resistance increases and the current decreases close to zero because of the worse conductivity of Si, at this time the graphene

Figure 2. Typical surface SEM images of (a) SiG1, (b) SiG2 and (c) particles size of SiG2 and SiG3, (d) SiG3, (e)cross-sectional SEM image of SiG3, (f) cross-sectional SEM image of SiG3.

Figure 3. TEM images of SiG3.
is adsorbed on the surface of Si particles, the lower electron transfer resistance of the graphene induces Si to reduce on the adsorbed graphene again followed by Si nucleation and growth. The whole electrodeposition processes involve the alternate process of Si reduction, nucleation and growth, and graphene adsorption. The above processes repeat over and over, resulting formation of the alternate layer-structure of Si and graphene. The processes have already proved by the pulsation of chronoamperometric curve in Fig. 1c. Therefore, the addition of graphene in the ionic liquid causes the adsorption of graphene on the deposits that facilitates to reduce Si particle size and form a layer by layer structure of Si and graphene, which can improve the conductivity and electrochemical performances of SiG anode.

**Cycling performances.**—Fig. 6b displays the cycling performances of as-prepared Si and SiG composites measured at 1.6 A·g⁻¹ for 200 cycles. Pure Si electrode delivers a relatively low capacity of 970 mAh·g⁻¹ at the end of 200th cycle. As the graphene concentration increases from 0.0926 mol·l⁻¹ to 0.1852 mol·l⁻¹ in SiCl₄-[BMP]Tf₂N-G ILs, the obtained SiG composite shows the alternate layer structure of silicon and graphene, the specific capacity of SiG composite is enhanced from 1162 mAh·g⁻¹ to 1541 mAh·g⁻¹ according to the total mass of the SiG composites. Introducing graphene to the Si can significantly improve the capacity and cycling ability. Particularly, SiG3 electrode shows an initial discharge capacity as high as 1720 mAh·g⁻¹, the capacity still maintains 1541 mAh·g⁻¹ (retention of 89%) after 200 cycles, showing good cycling performances, which is also shown in the charge and discharge curves in Fig. 6a. According to literature, the capacity fading during the initial few cycles is mainly caused by the formation of a surface oxide layer composed of Li₂O.

The addition of graphene has positive effects on the initial cycle performances of the three SiG composites. But SiG1 has behaved a faster capacity decay than the pure Si because insufficient amount of graphene only can form an inferior layer structure, as shown in the SEM graphs in Fig. 2a, which lead to a worse performance in the subsequent cycles than pure Si.

The SEM image of SiG3 after 400 cycles is given in Fig. 7, from which it can be seen that the original alternate layer structure maintains very well with no crack or detachment despite of the volume expansion of Si after 400 cycles. This explains the high cyclic stability of SiG3, and also indicates that the SiG composites electrode obtained by electrodeposition has a strong binding force between Si and graphene and the layer-structure of Si and graphene helps to relieve destruction caused by volume expansion during cycling test. Fig. 6c depicts the cycling performance of SiG3 electrode measured at 4 A·g⁻¹ for 400 cycles. SiG3 electrode displays a specific capacity as high as 1378 mAh·g⁻¹ at the initial cycle, and 1083 mAh·g⁻¹ at the end of 400 cycle (retention of 78%), showing a good cycle ability at a relatively high rate.

The SiG3 electrode also shows an excellent rate ability, as shown in Fig. 6d. As the current density increases from 0.4 to 0.8, 2, 4, 8, 16, and 42 A·g⁻¹, the SiG3 electrode exhibits steady and reversible specific capacities of 1520, 1473, 1322, 1207, 988, 542, 184 mAh·g⁻¹ and goes up to 1378 mAh·g⁻¹ when the current density goes back to 2 A·g⁻¹. SiG composites can effectively improve the specific capacity and cycling performances compared with pure Si. However, the rate performance of SiG electrode at high current density is not relatively good. This may be attributed to following reasons, (1) the space between two layers of SiG is still insufficient, these layers seem to be stuck to each other which impedes the transportation of electrons and Li ions among layers. (2) Some Si particles aggregate together, which also hinders the transportation of electrons and Li ions and causes larger volume expansion.

Though this SiG composites structure has not given a better rate performance, the structure provides a basic understanding of layer by layer through electrodeposition, as shown in Fig. 7. A more reasonable structure of the SiG composites is underway by electrodeposition from ionic liquid with addition of other elements. The research has proved a feasibility for electrodeposition preparation of layer-structured composite.
Figure 6. Electrochemical performance of Si and SiG electrodes, (a) Charge and discharge curves of SiG3 at 1.6 A·g⁻¹, (b) Cycling performance of four different electrodes Si(black), SiG1(red), SiG2(blue), SiG3(purple) at a current rate of 1.6 A·g⁻¹ for 200 cycles, (c) Cycling performance of SiG3 electrode at a current rate of 4 A·g⁻¹ for 400 cycles, (d) Rate performance demonstration of SiG3 electrode at 0.4, 0.8, 2, 4, 8, 16, and 42 A·g⁻¹ rates.

Figure 7. SEM graphs of SiG3 (a) initial, (b) after 400 cycles.

Conclusions

One step electrodeposition method is applied to prepare SiG composites from Graphene(G)-SiCl₄-[BMP]I₂N ionic liquid. SiG composites have shown an alternate layer-structure of Si and graphene. The average particle size of Si is decreased from 193.6 nm to 87.6 nm corresponding to the molar ratio of Si and C decrease from 6.24:1 to 4.57:1 as the graphene concentration increases from 0.0926 mol·l⁻¹ to 0.1852 mol·l⁻¹ in the ionic liquid. The single layer of SiG composites is composed of about 90–110 nm Si closely stick on the 4–5 layers of graphene. SiG anode displays a specific capacity as high as 1378 mAh·g⁻¹ at the initial cycle, and 1083 mAh·g⁻¹ at the end of 400 cycle (retention of 78%) at 4 A·g⁻¹, showing a good cycle ability at a relatively high rate. SiG composites also present a good rate performance, such as 988 mAh·g⁻¹ at current density of 8 A·g⁻¹. The regular current pulsation in the chronoamperometric curves indicates the addition of graphene causes an alternate process of Si reduction and graphene adsorption. The layer-structured SiG anode significantly improve the conductivity and electrochemical performances of Si materials, especially for semiconductor-based alloys, graphene-based alloys in large-scale.
anode. And the electrodeposition method can simplify the production processes of Si anode. The research has proved a feasibility for electrodeposition preparation of layer-structured materials, especially for semiconductor-based alloys, graphene-based alloys in large-scale.

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