Controlled synthesis of nanosized Si by magnesiothermic reduction from diatomite as anode material for Li-ion batteries

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Abstract: Li-ion batteries (LIBs) have demonstrated great promise in electric vehicles and hybrid electric vehicles. However, commercial graphite materials, the current predominant anodes in LIBs, have a low theoretical capacity of only 372 mAh·g\(^{-1}\), which cannot meet the ever-increasing demand of LIBs for high energy density. Nanoscale Si is considered an ideal form of Si for the fabrication of LIB anodes as Si–C composites. Synthesis of nanoscale Si in a facile, cost-effective way, however, still poses a great challenge. In this work, nanoscale Si was prepared by a controlled magnesiothermic reaction using diatomite as the Si source. It was found that the nanoscale Si prepared under optimized conditions (800°C, 10 h) can deliver a high initial specific capacity (3053 mAh·g\(^{-1}\) on discharge, 2519 mAh·g\(^{-1}\) on charge) with a high first coulombic efficiency (82.5%). When using sand-milled diatomite as a precursor, the obtained nanoscale Si exhibited a well-dispersed morphology and had a higher first coulombic efficiency (85.6%). The Si–C (Si:graphite = 1:7 in weight) composite using Si from the sand-milled diatomite demonstrated a high specific capacity (over 700 mAh·g\(^{-1}\) at 100 mA·g\(^{-1}\)), good rate capability (587 mAh·g\(^{-1}\) at 500 mA·g\(^{-1}\)), and a long life cycle (480 mAh·g\(^{-1}\) after 200 cycles at 500 mA·g\(^{-1}\)). This work gives a facile method to synthesize nanoscale Si with both high capacity and high first coulombic efficiency.

Keywords: silicon anode; magnesiothermic reduction; diatomite; Li-ion batteries

1. Introduction

Recently, Li-ion batteries (LIBs) have shown a promising application in electric vehicles and hybrid electric vehicles due to their high energy density and long cycle life [1–6]. However, commercial graphite materials, the current predominant anodes in LIBs, have a low theoretical capacity of only 372 mAh·g\(^{-1}\), which cannot meet the ever-increasing demand of LIBs for high energy density. Silicon materials have been considered as promising anodes because of their high theoretical specific capacity (4200 mAh·g\(^{-1}\)), which is significantly higher than that of graphite [7–11]. Also, Si is cost-effective as it is the second richest element in the crust of the earth. Importantly, Si has a moderate working voltage of ~0.4 V (vs. Li/Li\(^+\)) [12–15]. The main disadvantage of a Si anode is the large volumetric change upon the lithium insertion/removal process, which gives rise to particle fracture, pulverization, and damage of the solid electrolyte interface (SEI). Therefore, a Si anode suffers from a limited cycle life. Moreover, Si shows a low electronic conductivity and sluggish Li-ion transport rate, and thereby, a poor rate capability [16–23]. To solve these issues, many measures have been taken in recent years. Using nanoscale Si with different structures such as nanotubes, nanowires, and nanorings provides a practical method to relieve volume change and improve cycle life [24–30]. For example, the milled flake graphite/plasma nano-silicon-carbon (MFG/PNSi–C) void sandwich structure was synthesized by assembling thin MFG sheet loadings with carbon-coated PNSi via a facile method. The obtained composite exhibits excellent electrochemical performance with a high reversible capacity of 1141 mAh·g\(^{-1}\), a high initial coulombic efficiency of 84.4%, and a
high capacity retention of 84.1% after 200 cycles at 0.1 A·g⁻¹ because the void sandwich structure can dramatically shorten the Li-ion diffusion path and the carbon shell can buffer huge volume expansions [31]. However, it remains a challenge to produce nanoscale silicon at a high yield with low cost [32–34].

Therefore, facile and cost-effective methods are needed to realize large-scale production of nanoscale Si. Many routes such as chemical vapor deposition [35–36], ball milling [37], and magnesiothermic reaction [38‒40] have been adopted to produce nanoscale silicon. Similarly, borothermal reduction has been used to synthesize ZrB₂ [41]. Among these methods, magnesiothermic reduction, where silica is reduced in the presence of magnesium vapor, is considered one of the practical routes to prepare silicon in nanoscale via a simple, cost-effective process. On account of low cost and easy availability, rice husk, sand, and diatomite are considered ideal silicon sources. Diatomite, whose main chemical composition is SiO₂, usually has a porous structure, and the porous SiO₂ can be easily converted into nanoscale Si after magnesiothermic reaction and subsequent MgO etching. At the same time, diatomite is abundant on earth, making it an ideal raw material for synthesizing nanoscale silicon [42‒43].

In this paper, we will report a controlled, cost-effective route to prepare nanoscale Si by magnesiothermic reduction using diatomite as the silicon source. Nanoscale Si with a high capacity and a high first coulombic efficiency (82.5%) can be obtained by optimizing temperature (800°C) and time (10 h) of the magnesiothermic reduction. Well-dispersed nanoscale Si with a higher first coulombic efficiency (85.6%) was obtained by sand milling the diatomite before the magnesiothermic reaction. The obtained nanoscale Si was used to prepare Si–C composites constructed by Si nanoparticles, artificial graphite, and amorphous carbon pyrolyzed from glucose and polyvinylpyrrolidone (PVP). In Si–C, the amorphous carbon covers the silicon particles and connects with the graphite plates, providing combined conducting, binding, and buffering effects for Si particles. Si–C shows a high specific capacity, a long cycling life, and a good rate capability. This work will shed light on the synthesis of nanoscale Si and Si–C composites through a facile, controlled, and cost-effective method.

2. Experimental

2.1. Synthesis of nanoscale Si

Diatomite (Alfa Aesar) was fired for 2 h at 800°C in air to eliminate the organics. The fired diatomite was further purified by stirring in 4 mol·L⁻¹ HCl overnight to etch the oxide impurities. The silicon was synthesized by a magnesiothermic reaction using the purified diatomite as a precursor and Mg powder as the reducing agent. First, the purified diatomite (2 g), Mg powder (1.6 g, 99.5% purity, Aladdin), and NaCl (20 g, 99.5% purity, Sinopharm Chemical Reagent Co., Ltd.) were uniformly mixed. Second, the obtained mixture was put in a stainless steel apparatus in an Ar-filled glove box. Third, the stainless steel apparatus was placed in a furnace that was heated at 700–850°C for 2–14 h in flowing Ar, and then naturally cooled to room temperature. Fourth, the reaction product was rinsed with 1 mol·L⁻¹ HCl overnight to remove NaCl, residual Mg, and other byproducts such as MgSi and MgO. Finally, Si was obtained by washing with deionized (DI) water followed by drying at 80°C overnight under a vacuum. For comparison, the purified diatomite was sand milled before the magnesiothermic reaction with other procedures unchanged.

2.2. Preparation of silicon–carbon (Si–C) composite

To prepare the Si–C composite, the nanoscale Si from sand-milled diatomite was first mixed with the artificial graphite (Jiangxi Zichen, Si:graphite = 1 : 7 in weight) by dry ball milling for 10 h at 350 r·min⁻¹. Then, the ball-milled product, PVP, and glucose were mixed in DI water (Si + graphite:glucose:PVP = 8 : 1 : 2 in weight) followed by wet ball milling at 350 r·min⁻¹ for 5 h. The ball-milled product was spray dried with an inlet temperature of 230°C and an outlet temperature of 110°C to prepare the precursor for Si–C. The precursor was put in an Al₂O₃ boat and fired at 600°C for 3 h under Ar flow in the tubular furnace to get the Si–C composite.

2.3. Materials characterization

The X-ray diffraction (XRD) patterns were obtained using a powder diffractometer (Rigaku D/MAX-2550pc) with Cu Kα radiation (λ = 0.1542 nm). The morphologies of the materials were observed by scanning electron microscopy (SEM) using a field-emission scanning electron microscope (S-4800, Hitachi). The microstructure of the samples was characterized by transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) using a high-resolution transmission electron microscope (FEI Tecnai G2 F20 S-TWIN) at an acceleration voltage of 200 kV. Thermogravimetric (TG) analysis was conducted from 50 to 900°C at a heating rate of 10°C·min⁻¹ in air on a TGA 5500 instrument.

2.4. Electrochemical measurements
The performance of the obtained products was tested using CR2025 coin-type cells at room temperature. The electrodes were made by blending active material (Si or Si–C composite), acetylene black, and polyacrylic acid (PAA) (8 : 1 : 1 in weight) in N-methylpyrrolidone (NMP) followed by a coating slurry on the Cu foils and drying first at 80°C for 3 h in air and then at 60°C overnight under a vacuum. The half cells were fabricated using Li foils as the counter electrodes and Celgard 2300 membranes as the separators in the Ar-filled glove box. The electrolyte was 1 mol·L\(^{-1}\) LiPF\(_6\) dissolved in a mixed solvent of ethylene carbonate (EC)/dimethyl carbonate (DMC)/methyl ethyl carbonate (EMC) (1 : 1 : 1 in volume) with a fluoroethylene carbonate (FEC, 5vol%) additive. Galvanostatic cycling was carried out using a battery cycler (Neware, Shenzhen). The current density and capacity were calculated normalized to the weight of the active material (Si or Si–C composite). Cyclic voltammetry (CV) measurements were performed using an electrochemistry workstation (Versa-STAT3, Princeton Applied Research) at 0.1 mV·s\(^{-1}\) between 0.01–1.5 V (vs. Li/Li\(^+\)).

### 3. Results and discussion

Fig. 1(a) shows the XRD patterns of the purified diatomite. The main peaks of the diatomite agreed well with the SiO\(_2\) in an amorphous state suggesting that diatomite can be used as a precursor to produce Si. As seen in Fig. 1(b), the diatomite had various morphologies such as rods, irregular particles, and regular plates with an ordered arrangement of holes. Fig. 2 exhibits XRD patterns of the products after the magnesiothermic reduction at different temperatures for 6 h. For all the products, the formation of Si was evident, indicating the occurrence of the magnesiothermic reduction SiO\(_2\)(s) + 2Mg(g) = Si(s) + 2MgO(s). The sharp Si peaks indicated its good crystallization. Note that with an increasing reaction temperature, the SiO\(_2\) peak intensity at approximately 20°–25° (2\(\theta\)) was on the decrease. At a temperature below 750°C, residual SiO\(_2\) was still observed. Nearly phase-pure Si was obtained at 800 and 850°C, which indicated that increases in temperature could promote the reaction during the magnesiothermic reduction.

Fig. 3 gives the first-cycle galvanostatic plots of silicon at 100 mA·g\(^{-1}\). During the initial stage of discharge, the curve exhibited a sloping feature, which was associated with the formation of the SEI film on the silicon particles. The long plateau during the subsequent discharge indicated the transition from silicon to Li\(_x\)Si with the reaction Si + \(x\)Li\(^+\) + \(x\)e\(^-\) \(\rightarrow\) Li\(_x\)Si. The electrochemical data of the Si in the first cycle are listed in Table 1. In the four Si samples, the sample prepared at 800°C delivered the highest discharge capacity (2036 mAh·g\(^{-1}\)) and the highest charge capacity (1295 mAh·g\(^{-1}\)). However, the capacities were far lesser than the theoretical value of the Si material when lithiated to Li\(_{4.4}\)Si. In addition, all the samples exhibited a low first coulombic efficiency. The low yieldable capacity and the first coulombic efficiency were ascribed to the reactive SiO\(_x\) layer, which not only inhibited the reaction of Si with Li but also contributed to the irreversible capacity by forming LiO, Li\(_2\)SiO\(_4\), etc.
The 800°C Si sample showed a less sloping feature in its discharge curve than the other samples, which meant that it had the thinnest SiO\textsubscript{x} layer on the Si. Therefore, 800°C was considered as a suitable temperature for the magnesiothermic reaction.

Fig. 4 gives the XRD patterns of the products of magnesiothermic reduction at 800°C for different reaction times. Note that the most phase-pure Si was obtained when the reaction time was set at 10 h. The charge–discharge cycling on the four Si samples was performed to study the effect of reaction time on electrochemical performance as seen in Fig. 5. Table 2 summarizes the electrochemical data of the four Si samples in the first cycle. The Si prepared for 10 h yielded a highest first discharge capacity of 3053 mAh·g\textsuperscript{−1} and the highest first charge capacity of 2519 mAh·g\textsuperscript{−1}. Moreover, the 10 h sample also demonstrated the highest first coulombic efficiency of 82.5%. This suggested that the 10 h sample had the thinnest SiO\textsubscript{x} layer, which enabled both low irreversible capacity and high reversible capacity. From the above results, it seemed that the reaction conditions of 800°C and 10 h were the most suitable for the magnesiothermic reduction. Thus, in the following experiments, the reaction conditions were set at 800°C and 10 h.

Fig. 3. First discharge–charge curves at 100 mA·g\textsuperscript{−1} between 0.002 and 2.5 V of the Si prepared by magnesiothermic reduction for 6 h at (a) 700°C, (b) 750°C, (c) 800°C, and (d) 850°C.

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Fig. 4. XRD patterns of the Si prepared by magnesiothermic reduction at 800°C for different times.

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Fig. 7(a) shows the SEM image of the Si prepared by magnesiothermic reduction at 800°C for 10 h. During the magnesiothermic reduction and subsequent rinsing, the large-sized diatomite was converted into small-sized Si particles with a size below 200 nm. However, it should be noted that
the small Si particles tend to form large aggregates due to easy adhesion among the small Si particles with large specific surfaces at high temperature. The TEM image in Fig. 7(b) confirms the aggregation of the silicon particles after the reaction. The particle aggregation was unfavorable for the homogeneous dispersion of Si particles in the carbon materials for the Si–C composites.

To relieve the aggregation of the silicon particles, the diatomite was first sand milled to reduce its size to nanoscale. As seen in Fig. 8(a), the size of the microscaled diatomite particles was reduced to nanoscale after sand milling. Fig. 8(b) shows the SEM images of Si produced by the magnoothermic reaction at 800°C for 10 h using the sand-milled diatomite as the precursor. The Si had an average particle size of approximately 100 nm with clearly alleviated particle aggregations compared with that using the pristine diatomite.

![Fig. 5. First discharge–charge curves at 100 mA·g⁻¹ between 0.002 and 2.5 V of the Si prepared by magnoothermic reduction at 800°C for (a) 2 h, (b) 6 h, (c) 10 h, and (d) 14 h.](image)

Table 1. Electrochemical data in the first cycle of the Si prepared by magnoothermic reduction at different temperatures for 6 h

<table>
<thead>
<tr>
<th>Temperature / °C</th>
<th>Discharge capacity / (mAh·g⁻¹)</th>
<th>Charge capacity / (mAh·g⁻¹)</th>
<th>Coulombic efficiency / %</th>
</tr>
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<tr>
<td>700</td>
<td>873</td>
<td>485</td>
<td>55.6</td>
</tr>
<tr>
<td>750</td>
<td>1093</td>
<td>714</td>
<td>65.3</td>
</tr>
<tr>
<td>800</td>
<td>2036</td>
<td>1295</td>
<td>63.7</td>
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<tr>
<td>850</td>
<td>1348</td>
<td>814</td>
<td>60.4</td>
</tr>
</tbody>
</table>

Table 2. Electrochemical data in the first cycle of the Si prepared by magnoothermic reduction for different times at 800°C

<table>
<thead>
<tr>
<th>Time/ h</th>
<th>Discharge capacity / (mAh·g⁻¹)</th>
<th>Charge capacity / (mAh·g⁻¹)</th>
<th>Coulombic efficiency / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1982</td>
<td>1443</td>
<td>72.9</td>
</tr>
<tr>
<td>6</td>
<td>2036</td>
<td>1295</td>
<td>63.7</td>
</tr>
<tr>
<td>10</td>
<td>3053</td>
<td>2519</td>
<td>82.5</td>
</tr>
<tr>
<td>14</td>
<td>1544</td>
<td>1057</td>
<td>68.6</td>
</tr>
</tbody>
</table>
The TEM image in Fig. 8(c) also verifies that using the sand-milled precursor was useful in relieving aggregation of the product of the magnesiothermic reduction. The XRD patterns in Fig. 8(d) confirm the conversion of the SiO$_2$ to Si after the magnesiothermic reaction. Note that compared with that using the pristine diatomite, the Si using sand-milled diatomite delivered a smaller first capacity possibly because of the introduction of the SiO$_x$ layer on the Si during sand milling (Fig. 9(a)). However, the first coulombic efficiency of the Si increased to 85.6% using the sand-milled precursor. This was favorable for practical applications of the silicon anodes. Moreover, the Si from the sand-milled precursor exhibited improved cycling stability as seen in Fig. 9(b).

The nanoscale Si from sand-milled diatomite was used to prepare the Si–C composite. As seen in Fig. 10(a), the composite had a similar morphology to the pristine artificial graphite. The TEM image in Fig. 10(b) reveals that small-sized Si particles were attached on the large-sized graphite plates. The HRTEM image in Fig. 10(c) reveals that the surface of the silicon particles was covered by an amorphous carbon layer that was also connected with the graphite plate. The amorphous carbon layer pyrolyzed from PVP and glucose not only bound silicon particles on the graphite plate but also provided electronically-conducting channels for Si and graphite. In Fig. 10(c), the lattice fringes with a spacing of 0.31 nm correspond to the (111) planes of Si. This structure is considered to be beneficial in the cycling stability of the Si–C composite. In Fig. 10(d), as expected, the composite exhibited both Si and graphite diffraction peaks, thereby confirming the formation of the Si–C composite. As seen in Fig. 10(e), a TG test was performed to calculate the Si content of Si–C. There were two distinct weight loss processes in the temperature range of 400–510°C and 510–830°C corresponding to the burning of amorphous carbon and graphite, respectively. The residual mass was regarded as the content of Si in the Si–C composite, which was approximately 17wt%.
The first three and the 31st discharge–charge plots of the Si–C composites at 0.1 A·g\(^{-1}\) are shown in Fig. 11(a). The Si–C composite delivered a discharge capacity of 849 mAh·g\(^{-1}\) and a charge capacity of 562 mAh·g\(^{-1}\) in the first cycle. The charge capacity showed a gradual increase upon cycling and reached 769 mAh·g\(^{-1}\) in the 31st cycle. The low first charge capacity and the gradual capacity increase were possibly related to the large cell internal resistance where the electrode may have undergone an activation process. Fig. 11(b) shows the CV plots in the initial three cycles at 0.1 mV·s\(^{-1}\). Note that in the first discharge, a broad but weak reduction peak between 0.4 and 0.8 V appears, but it disappears in the subsequent scanning, which was associated with the formation of the SEI layer. In the following cycles, cathodic peaks corresponded to the lithiation of silicon and graphite to form Li\(_x\)Si and Li\(_x\)C\(_6\), and the anodic peaks were
Fig. 10. SEM image (a), TEM image (b), HRTEM image (c), XRD patterns (d), and TG curves (e) of the Si–C composite.

Fig. 11. Electrochemical performances of Si–C composites: (a) voltage profiles at 100 mA·g⁻¹ between 0.01 and 1.5 V; (b) CV plots at 0.1 mV·s⁻¹; (c) rate capability; (d) cycling stability at various current densities.
associated with the delithiation of Li$_4$C$_6$ and Li$_4$Si. The gradual increase in peak intensity also indicated the progressive activation of the electrode.

Fig. 11(c) presents the rate capability of Si–C at current densities ranging from 0.1 to 5 A·g$^{-1}$. The charge capacities of the composite were 705, 672, 587, 442, 291, and 115 mAh·g$^{-1}$ at 0.1, 0.2, 0.5, 1.0, 2.0, and 5.0 A·g$^{-1}$, respectively. Moreover, the charge capacity reached 800 mAh·g$^{-1}$ as the current returned to 0.1 A·g$^{-1}$ indicating that the high-current density did not damage the structure of the material. Fig. 11(d) gives the cycling stability of Si–C under various densities with or without the FEC additive in the electrolyte. At 100 mA·g$^{-1}$, the composite using the FEC-free electrolyte demonstrated an initial capacity rise and subsequent stable cycling followed by rapid capacity decay after 30 cycles. The rapid capacity fade was due to the intrinsically large volumetric change of the silicon and the unstable SEI film on the silicon particles. When using the FEC-added electrolyte, an enhanced cycling performance of the Si–C was observed at the same current density. At 200 mA·g$^{-1}$, the composite in the FEC-added electrolyte held a charge capacity of 460 mAh·g$^{-1}$ after 140 cycles. Cycling performance of the composite was also investigated at a high-current density of 500 mA·g$^{-1}$. Before the cycling at 500 mA·g$^{-1}$, the cell was first activated by cycling at 100 mA·g$^{-1}$ for 5 cycles followed by at 200 mA·g$^{-1}$ for 5 cycles. After 200 cycles at 500 mA·g$^{-1}$, a charge capacity of 480 mAh·g$^{-1}$ was held corresponding to a capacity retention of 70.2% indicating a high-current cycling stability. The good rate capability of the composite could be ascribed to the conducting effect of the amorphous carbon and the small size and good dispersion of nanoscale Si. This work can provide a facile and cost-effective route to prepare nanoscale Si for Si–C anodes of Li-ion batteries.

4. Conclusions

(1) In summary, nanoscale silicon was prepared by a controlled magnesiothermic reaction using diatomite as the precursor. Si obtained at 800°C for 10 h delivers a high initial charge capacity of 2519 mAh·g$^{-1}$ and a discharge capacity of 3053 mAh·g$^{-1}$ with a high first coulombic efficiency of 82.5%. Well-dispersed nanoscale Si particles of approximately 100 nm can be obtained when sand-milled diatomite is used. Nanoscale Si from sand-milled diatomite exhibits a higher first coulombic efficiency of 85.6%.

(2) The Si–C composite was prepared by coating Si-loaded artificial graphite with amorphous carbon pyrolyzed from glucose and PVP using Si from sand-milled diatomite. The composite with a 1:7 Si-to-graphite weight ratio can deliver a capacity of over 700 mAh·g$^{-1}$ at 100 mA·g$^{-1}$ and shows good rate capability and cycling stability. At 500 mA·g$^{-1}$, the composite can deliver a capacity of 587 mAh·g$^{-1}$. After 200 cycles at 500 mA·g$^{-1}$, the composite can keep a charge capacity of 480 mAh·g$^{-1}$.

(3) The good rate capability and cycling stability can be ascribed to the combined buffering, binding, and conducting effect of amorphous carbon as well as the small size and good dispersion of nanoscale Si. This work can provide a facile and cost-effective route to prepare nanoscale Si for Si–C anodes of Li-ion batteries.

Acknowledgements

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