Porous silicon from the magnesiothermic reaction as a high-performance anode material for lithium ion battery applications

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Graphical abstract

A carbon layer was successfully wrapped porous silicon from magnesiothermic reaction of SiO to form carbon wrapped porous silicon, which exhibited superior electrochemical performance than naked or infiltrated-carbon coated porous silicon due to its better accommodation of volume change during the cycling.

Abstract: Porous silicon (PSi) is one of the most promising anode materials for next generation lithium ion batteries. Additionally, good cycling stability and rate capability are expected for PSi-based anode because of its possible accommodation of volume change during the charge/discharge process. In this work, we have demonstrated that PSi with tunable pore diameters and specific surface areas up to 303.2 m² g⁻¹ can be synthesized with a magnesiothermic reaction of silicon monoxide. The result indicates that pore structure can be largely controlled by the reaction temperature while the electrochemical performance of PSi is found to be closely related with their pore structure. The anode based on PSi with the optimized pore structure exhibits a reversible specific capacity of 1045.6 mA h g⁻¹ at a specific current of 1000 mA g⁻¹. To further demonstrate the potential of PSi from magnesiothermic reaction as high-performance anode material, a conductive carbon layer has been wrapped around the periphery of PSi particles. At a specific current of 1000 mA g⁻¹, carbon wrapped PSi retains a reversible capacity of 1639.0 mA h g⁻¹, 84.5% of the initial capacity after 200 cycles. The performance is much better than those of naked PSi or infiltrated carbon coated PSi due to its effective accommodation of the volume change during the charge /discharge process.

Keywords: Porous silicon, Pore structure, Carbon wrapping, Lithium-ion batteries

1. Introduction

Silicon is regarded as one of the most promising anode materials for lithium ion batteries (LIB) due to its high theoretical capacity ($\sim 4200 \text{ mAh g}^{-1}$). [1-5] However, it suffers from the large volume change ($>300\%$) during lithiation/delithiation, causing pulverization of silicon anodes and finally leading to capacity fading. [6-10] To overcome degradation of silicon anode during cycling, researchers have designed and utilized its porous form, porous silicon (PSi). [11-21] Pores in its microstructure are expected to accommodate the volume change and improve the cycling stability of silicon anodes. Additionally, the wall thickness of some PSi is in a range of several to tens of nanometers and keeps the diffusion path of lithium ions short, which can improve the rate capabilities of the electrodes. So far, a lot of work has demonstrated that PSi has improved electrochemical performance compared with its solid counterparts. [2,12,22,23] However, the influence of pore structure of PSi on its electrochemical performance has not been studied in detail due to unfeasible control of pore structure of PSi. Traditionally, PSi can be fabricated by anodization, stain etching or metal-assisted etching of silicon wafer or powder in the concentrated hydrofluoric acid solutions. [8,24,25] However, the control of pore structure of PSi by the aforementioned methods has not been widely reported. [26] Recently, it has been demonstrated that PSi can also be synthesized through the reduction of silicon oxide by a magnesiothermic reaction [27-30]:

where SiO_x can be either silicon dioxide ($x=2$) or silicon monoxide ($x=1$). The aim of this work is to demonstrate the feasibility of tuning the pore structure of PSi by controlling the parameters (*e.g.*, temperature, time) of the magnesiothermic reaction and study the influence of microstructure on the electrochemical performance (*e.g.*, cycling stability and rate capability). Moreover, a conductive carbon layer is designed to wrap around the periphery of PSi particle to improve the electrochemical performance of PSi.[18] The carbon wrapped porous silicon (CWPSi) exhibits capacities of 2281.8, 1892.2, 1492.3 and 1074.1 mAh g⁻¹ at 500, 1000, 2000, 4000 mA g⁻¹, respectively and retains a capacity of 1639.0 mA h g⁻¹, 84.5% of the initial capacity, at 1000 mA g⁻¹ after 200 lithiation/ delithiation cycles. The above performance of CWPSi is far better than naked PSi or infiltrated carbon coated PSi (CCPSi) due to its better accommodation of the volume change during cycling.

2. Experimental

2.1 Preparation of PSi from SiO.

Magnesium powder (200 mesh) was mixed with SiO powder (6000 mesh) thoroughly. The mixture was heated in a tube furnace at 2 °C min⁻¹ to 300 °C, and then held at that temperature for 3 h. Thereafter, it was heated to 500 °C at a ramping rate of 2 °C min⁻¹ and kept at 500 °C for 12 h (600 °C for 4 h or 750 °C for 4 h) in an Ar (95 vol%)/H₂ (5 vol%) flow. The mixture was then cooled down with furnace to room temperature and taken out. The obtained powder was immersed in 1 M HCl

1 solution for 6 h to remove Mg-bearing products, followed by immersion in HF (5
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3 wt%) solution for 5 min to ensure that the newly formed SiO₂ was removed. Finally,
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5 the resulting powder was washed with distilled water and ethanol, and then
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7 vacuum-dried at 80 °C for 10 h. The above samples were denoted as 500°C/12h,
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9 600°C/4h and 750°C/4h PSi samples, respectively.
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13 14 2.2 Preparation of CWPSi. 15

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17 The mixture (200 mg) obtained by magnesiothermic reduction of SiO at 600 °C for
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19 4 h was dispersed in 75 mL Tris-buffer solution (10 mM, PH 8.5) with magnetic
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21 stirring for 30 min. Next, 150 mg dopamine was added and stirred in air overnight to
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23 coat the mixture with polydopamine (pDA). pDA coated powders was collected by
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25 filtration, washed with water several times and dried in vacuum at 60 °C. The
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27 collected powders was then immersed in 3M HCl aqueous solution stirring overnight
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29 to remove the Mg-bearing parts for forming void space, followed by filtration and
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31 water washing three times. The final pDA shell was carbonized in a tube furnace
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33 under Ar at 800 °C for 2 h with a heating rate of 5 °C min⁻¹.
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42 2.3 Preparation of CCPSi. 43

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45 CCPSi sample was synthesized by switching order of acid washing with pDA
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47 coating in the aforementioned synthesis procedure of CWPSi, and then followed by a
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49 carbonization process.
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53 2.4 Material Characterization. 54

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56 X-ray diffraction (XRD) patterns were collected on a Rigaku D/Max-RB
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58 diffractometer with Cu K α radiation (40 kV, 40 mA). Scanning electron microscopy
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(SEM) images were obtained with a Philips XL30 FEG operated at 10 keV. A JEOL JEM-2010 electron microscope operated at 200 keV was used to conduct transmission electron microscopy (TEM) analyses. The element mapping of CWPSi was recorded with JEOL-2100F. The nitrogen adsorption and desorption isotherms were obtained using the Brunauer-Emmett-Teller (BET) method at 77 K after degassing the samples at 200 °C for 4 h by an analyzer (Micrometrics; ASAP 2010). The Barrett-Joyner-Halenda (BJH) method was applied to adsorption branches of isotherms to obtain pore diameter distributions. Raman spectrum was carried out by Raman spectroscopy (632.8 nm excitation laser, Renishaw Raman spectrometer).

2.5 Electrochemical Measurements.

The electrode slurries were composed of 60 wt% of active material, 20 wt% of Super P carbon black and 20 wt% of sodium alginate as binder. The slurries were cast onto a copper current collector with a thickness of 6-7 μm . The cast electrodes were dried at 75 °C for 12 h and punched into disks with a diameter of 1.2 cm. The active mass is 0.4mg cm^{-2} . Lithium hexafluorophosphate (LiPF_6) solution (1 M) in a mixture of ethylene carbonate (EC), diethyl carbonate (DEC) and dimethyl carbonate (DMC) (volume ratio of EC:DEC:DMC=1:1:1) containing 1 vol% vinylene carbonate (VC) (Novolyte Technologies Inc. Suzhou, China) was used as the electrolyte. To test the electrochemical properties, CR2016 cells were assembled in an argon-filled glove box. Pure Li foils were used as the counter electrode. The cells were electrochemically cycled between 0.005 to 1.0 V vs. Li/Li^+ for both charge and discharge galvanostatically on a LAND battery test system (Wuhan Kingnuo Electronics Co.,

Ltd., China) at 25 °C.

3. Results and discussion

[Figure 1]

Commercially available silicon monoxide was reacted with magnesium powder at 500 °C, 600 °C and 750 °C, respectively. X-ray diffraction (XRD) patterns (Figure 1a and b) of products obtained by the magnesiothermic reaction of SiO at 500 °C and 600 °C indicated the formation of Mg₂Si, in addition to expected MgO and Si phases. Prior work revealed that Mg₂Si was an intermediate phase via reaction (2), and then reacted with left SiO to yield more MgO and Si via reaction (3)[30,31]:

However, the product obtained at 750 °C for 4 h contained no intermediate phase of Mg₂Si, which was due to the faster reaction rate of Mg₂Si and SiO at the elevated temperature. After the products were selectively etched in a HCl and then a HF solution, MgO and Mg₂Si were successfully removed and only silicon was left, as indicated in XRD patterns (Figure 1d, e and f). Based on Scherrer analysis of XRD patterns, average crystallite diameters of silicon were calculated to be 10, 11 and 12 nm for the products generated by the magnesiothermic reduction of SiO at 500 °C for 12 h, 600 °C for 4 h and 750 °C for 4 h, respectively.

[Figure 2]

TEM images (Figure 2a, b and c and Figure S1 in Supporting Information) in the bright fields confirmed that mesoporous structures (with pore size <50 nm) existed in the final Si products though they were not obvious in the secondary electron microscopy (SEM) images (see Figure S2 in the Supporting Information). The appearance of Si nanocrystals in the products was confirmed by the high-resolution transmission electron microscopy (HRTEM) images (Figure 2d). The pore sizes and wall-thicknesses of silicon products obtained by the magnesiothermic reduction of SiO at 750 °C were larger than that of silicon product obtained at 500 °C and 600 °C due to the coarsening of Mg-bearing and silicon phases in the magnesiothermic reaction process, as confirmed by the yellow circle region in Fig 2c.

[Figure 3]

The appearance of mesoporosity was confirmed by nitrogen adsorption-desorption analyses. The isotherms of all the three silicon products (Figure 3a, b and c) were type IV curves with distinct hysteresis loops at the high relative pressures (P/P_0), indicating that all products were mesoporous materials. Brunauer-Emmett-Teller (BET) analyses yielded specific surface areas (SSAs) of 218.4, 303.2 and 86.4 m² g⁻¹ for 500°C/12h, 600°C/4h and 750°C/4h silicon samples, respectively. The most probable diameters in Barrett-Joyner-Halenda (BJH) pore diameter distributions (insets in Figure 3) were 4.6, 4.6, and 21.2 nm for the above three silicon samples, respectively.

[Table 1]

To study the influence of the reaction time on the pore structure of silicon samples, the reaction time was doubled at 500, 600 and 750 °C. The parameters of porous structure in mesoporous silicon were summarized in Table 1 together with the average crystallite diameters of Mg-bearing phases. The average pore diameters listed in the Table 1 were found to be similar with the average diameters of MgO crystallites, which were calculated from the XRD patterns and TEM images shown in Figure S3 and Figure S4, respectively. The result indicated that the mesoporosity of porous silicon samples was largely produced by the removal of MgO nanocrystallite formed in the magnesiothermic reaction. Although the reaction time was doubled at each temperature, the equivalent pore diameters of silicon samples varied within 18.8%. Even in the two 600 °C or 750 °C silicon samples, their BET SSAs and porosities only varied a little. The big difference of BET SSA and porosity in the two 500 °C samples could be ascribed to the influence of Mg₂Si. However, equivalent pore diameters in 500°C/12h and 750 °C/8h were 5.3 nm and 22.7 nm, respectively and the value changed 328.3%. The big difference for BET SSA between 500°C and 750 °C samples originated from different MgO sizes at each temperature. The smaller MgO particle formed at 500 °C due to the slow reaction kinetics and coarsening rate. When we removed the smaller MgO particles, the higher surface area could be obtained. While for 750 °C, the rates were high, some MgO nanocrystals even merged together, as confirmed by TEM image in Figure 2. At each temperature formed MgO nanocrystals also grew with increasing reaction time though it was slow. Thus bigger

pore formed in samples with longer reaction time. It clearly revealed that the temperature was more influential than reaction time although the two factors could both influence the pore structure of silicon samples. The above results indicated that the average diameter of formed MgO nanocrystals could be controlled by the temperature and time in the magnesiothermic reaction while pores in silicon samples could be formed by the removal of MgO nanocrystallites. Thus, the pore structure of mesoporous silicon could be tailored with different preparation conditions, especially with temperature.

[Figure 4]

The electrochemical performance of PSi products obtained at different temperatures was further evaluated. Figure 4a showed the plots of the differential capacity *versus* voltage for the initial cycle. For 750°C/4h PSi sample, there was only one lithiation peak near 0.10 V, which corresponded to lithiation of crystalline silicon.[32] While for 500°C/12h and 600°C/4h silicon samples, there were additional lithiation peaks at 0.21 V and 0.19 V other than the peak at ~0.10 V, respectively. We speculated the appearance of the amorphous silicon in the latter two samples was due to low synthesis temperature. The appearance of amorphous silicon in 500 °C/12h and 600 °C/4h was confirmed by Raman analyses (Figure S5). The peaks of 500 °C/12h and 600 °C/4h porous silicon samples located at 502.8 and 506.8 cm⁻¹ respectively. There were 8.6 and 4.6 cm⁻¹ shift compared with peak location of 750 °C/4h samples. The shift was due to presence of amorphous silicon, with peak located at 480 cm⁻¹.[33] We believed the different behavior in differential capacity versus voltage (dQ/dV)

curves of 750°C /4h and 500°C /12h samples was due to the appearance of amorphous silicon in the latter one. For the 500 °C and 600 °C samples, two lithiation peaks at ~0.1V and ~0.21V appeared, which was similar to the discharge behavior of amorphous silicon [34, 35]. To further prove the appearance of amorphous silicon, dQ/dV curves of the 2nd cycle for the 500°C/12h and 750°C/4h electrodes were obtained in Figure S6. Because there was amorphous silicon formed after initial charge, the differential capacity peak could be an indicator of amorphous silicon if the phase was then lithiated. The above plot showed the typical differential capacity versus voltage plots of amorphous silicon. However, a peak at 0.25 V, resulting from the formation of Li_4SiO_4 and Li_2O from SiO [36] was not observed, which was consistent with the absence of SiO after the magnesiothermic reduction. Although there was no apparent SEI formation peak in dQ/dV versus voltage curve. There was a broader cathodic peak at ~0.78V[37] observed in the cycle voltammogram (CV) curves (Figure S7) of 500 °C/12h sample. It indicated that the solid-electrolyte interphase (SEI) film began to form in the first discharge process. The delithiation peaks at 0.29 V and 0.44 V were ascribed to the phase transition between amorphous Li_xSi and amorphous Si.[38-41] The corresponding discharge/charge curves in the first cycle for 500°C/12h, 600°C/4h and 750°C/4h silicon samples were shown in Figure 4b. Though the first discharge capacities for the 500 °C and 600 °C samples were much higher than that of 750 °C, Coulombic efficiencies (CEs) of the formers were 61.6% and 68.2%, lower than that (73.9%) of the latter. The high surface area and presence of amorphous silicon phase in the 500 °C and 600 °C samples increased

the side reactions with the electrolyte and created the irreversible site for lithium ion adsorption. Figure 4c showed the curves of discharge capacity and CE *versus* cycle number for 500°C/12h, 600°C/4h and 750°C/4h PSi samples at a discharge rate of 1000 mA g⁻¹. After just 3 cycles, CEs of mesoporous silicon electrodes reached 98%. It was found that the electrode fabricated from PSi sample obtained at 750 °C for 4 h exhibited a lower discharge capacity of 451.1 mA h g⁻¹ after 200 cycles. In contrast, PSi obtained at 500 °C for 12 h and 600 °C for 4 h had higher capacities, 783.6 and 697.7 mA h g⁻¹, respectively. Since 1000 mA g⁻¹ was a relatively large specific current, the variation in the reversible capacities of different PSi products was related with their rate capability. Figure 4d further showed the rate capability of the silicon products at different specific currents. 600°C/4h PSi sample delivered reversible capacities of about 1449.3, 1045.6, 808.4 and 626.5 mA h g⁻¹ at the discharge currents of 500, 1000, 2000 and 4000 mA g⁻¹, respectively. However, the silicon product obtained at 750 °C for 4 h only had capacities of 840.8, 754.8, 538.9 and 245.5 mA h g⁻¹ at the same discharge currents, respectively, which were also inferior to the capacities of the silicon product obtained at 500 °C for 12 h. The improvement of rate capability of mesoporous silicon products obtained at 500 °C and 600 °C could be attributed to their high specific surface area and thin wall. Since the specific surface area was large, the local current density decreased and the rate capability could be enhanced. At the same time, because the wall thickness was thin, it allowed for a short path for diffusion of lithium ions and improved the rate capability further.[42] The above results indicated that the electrochemical properties of PSi closely depended on

1 their porous structure, which could be adjusted by parameters such as temperature and
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3 time in the reaction process.
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6 [Figure 5]

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8 To further improve the electrochemical performance of porous silicon, it was
9 wrapped with a carbon layer to form CWPSi. In briefly, pDA coating was coated on
10 the composite (mixture of magnesium bearing phase and silicon) obtained from
11 magnesiothermic reaction of SiO at 600 °C for 4h. After the Mg bearing phases were
12 etched away, the pDA layer was carbonized to obtain CWPSi. As comparison, 600
13 °C/4h PSi was directly immersed in dopamine solution to coat pDA layer. Then pDA
14 layer was carbonized to form a carbon coating on PSi to obtain CCPSi. Figure 5a, b
15 and 5c, d show TEM images of CWPSi and CCPSi, respectively. It exhibited a clear
16 continuous boundary between the carbon layer and PSi particle in CWPSi. The
17 thickness of the carbon layer of CWPSi was estimated to be ~25 nm. However, the
18 boundary in CCPSi image was blurred. It indicated that carbon might be coated on
19 both the inner and outer surfaces of PSi in CCPSi. Raman spectroscopy of carbon
20 coated porous silicon (CCPSi) in Figure S8 showed the silicon peak at 506 and carbon
21 bands at 1342 and 1583cm⁻¹, demonstrating the coexistence of Si and carbon.[18]
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23 STEM image of CWPSi and its mapping of related elements (carbon, nitrogen and
24 silicon) are shown in Figure 5e. Among them, the nitrogen and carbon signals were
25 from carbon coating inherited from pDA. Those signals much stronger on the edge
26 than in the center of PSi particle indicating little carbon enter the pores of PSi. The
27 above results indicated that a carbon layer was successfully wrapped around the
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periphery of PSi in CWPSi. Figure S9 showed the plots of the differential capacity versus voltage of CWPSi and CCPSi. The disappearance of the lithiation peaks at 0.20 V indicated that the amorphous silicon became crystallized after high-temperature treatment during the formation of the carbon layer.

[Figure 6]

The rate performance of CWPSi and CCPSi was shown in Figure 6a. Its initial specific capacity and initial CE of CWPSi were 4224 mAh g⁻¹ and 66.8%, respectively. The high initial discharge capacity of the CWPSi electrode could be due to the electrolyte decomposition and the irreversible lithium insertion into the carbon shell, suggested by other reports.[43, 44] While the corresponding value of CCPSi are 3367.1 mAh g⁻¹ and 63.1%, respectively. The high CE for CWPSi was due to its lower carbon content since carbon layer wrapped the entire PSi particle and little carbon entered its inner pore of PSi, reducing the irreversible sites of Li ions. CWPSi sample delivered reversible capacities of 2281.8, 1892.2, 1492.3 and 1074.1 mA h g⁻¹ at the discharge currents of 500, 1000, 2000 and 4000 mA g⁻¹, respectively. The corresponding values for CCPSi were only 1899.7, 1497.3, 1058.9, 708.9 mA h g⁻¹, respectively. The cycling performance of CCPSi and CWPSi was shown in Figure 6b. After 200 cycles with a specific current of 1000 mA g⁻¹, the capacity of CWPSi was kept at 1639 mA h g⁻¹, 84.5% of the initial capacity, compared with the CCPSi's 743.6 mAh g⁻¹, 50.9% of initial capacity. It should be stated that the capacity appeared a slight increase during the first several cycles (Figure 6b) for CCPSi, because the silicon gradually participated in the electrochemical reactions, which was also

observed in other Si/C electrode.[18,42] The electrochemical performance of CWPSi sample was also comparable to other PSi samples which were summarized in Table S1. During first 100 cycles, CEs of CCPSi decreased with cycles and were lower than CWPSi, implying the formed solid electrolyte interface (SEI) was less stable.[45] The infiltrated carbon coating might be unable to bear the stress due to the lack of free volume for expansion. As a result, new fracture surface in CCPSi could be formed during the charge/discharge process. While for CWPSi electrode, the porosity (57.1%) was wrapped by the conductive carbon layer, which partially provided the free volume for its expansion. It was consistent with observation of cross section images (Figure S10) of the electrodes before and after 50 charge/discharge cycles. The thickness of the electrode of CWPSi increased from 6.76 μm to 7.35 μm after 50 cycles, about 8.7% increase while the value for the electrode of CCPSi was 23.8%. The smaller volume change in the CWPSi electrode indicated that less stress was built up in the electrode and there was more chance to keep the electrode integrated, which made the excellent cyclability possible.

[Figure 7]

Above results were also consistent with the impedance analyses. The Nyquist plots (Figure 7) of these two electrodes displayed two semicircles in the high-medium frequency region which represents the charge transfer between the electrolyte and SEI, and the contribution between SEI and the silicon, respectively. The sloped line in the low frequency region was related to the mass transfer of the lithium ions.[46,47] Unlike the CCPSi electrode, the impedance variance of the CWPSi sample was much

1 smaller between 5th and 50th cycles, which indicated a more stable interphase formed
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3 on the surface of CWPSi. The high impedance of CCPSi after 50th could be ascribed
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5 to the deterioration of electrode, including electrode pulverization and breakdown of
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7 the conductive carbon layer. Overall, the carbon covered on PSi in carbon/PSi
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9 composites could enhance the electronic contact and improve the rate capability of
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11 PSi. Meanwhile, the void wrapped in CWPSi could better accommodate the volume
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13 change in cycling and improve the cyclability.
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20 **4. Conclusions**

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22 In this work, we demonstrated that PSi with tunable pore diameters and specific
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24 surface areas up to $303.2\text{m}^2\text{g}^{-1}$ was synthesized through the magnesiothermic
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26 reduction. The pore diameter of porous silicon was mainly controlled by the
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28 reduction temperature. The synthesized mesoporous silicon as an anode
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30 material exhibited a reversible capacity of up to 1045.6mAh g^{-1} at a specific
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32 current of 1000mA g^{-1} . Carbon layer was also successfully wrapped on PSi,
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34 which further improved the rate and cycling capability of porous silicon.
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36 CWPSi sample could retain a specific capacity of 1639.0mA h g^{-1} , 84.5% of
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38 the initial capacity. Such improvement could be ascribed to better accommodate
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40 volume change with the structure of CWPSi during the lithiation/delithiation
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42 process. Magnesiothermic reduction of silicon oxide combining with carbon
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44 wrapping could be a new strategy to obtain the high-performance anode
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46 material for LIB applications.
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Tables and Figure captions

Figure 1. XRD patterns obtained from products by the magnesiothermic reduction of SiO₂ at 300 °C for 3 h, then at 500 °C for 12 h (a), at 600 °C for 4 h (b), at 750 °C for 4 h (c), respectively. (d), (e) and (f), XRD patterns obtained from the products by etching the samples in (a), (b), and (c) in a HCl and then a HF solution, respectively.

Figure 2. Low resolution TEM images of 500°C/12h porous silicon sample (a), 600°C/4h porous silicon sample (b) and 750°C/4h porous silicon sample (c) obtained by the magnesiothermic reduction of SiO₂ followed by acid dissolution of Mg-bearing product, respectively. (yellow circle exhibited the pore in the samples) (d) High resolution TEM image of 600°C/4h porous silicon sample.

Figure 3. Nitrogen adsorption and desorption isotherms of 500°C/12h(a), 600°C/4h(b) and 750°C/4h(c) silicon samples obtained by the magnesiothermic reduction of SiO followed by acid dissolution of Mg-bearing product, respectively (Insets are corresponding pore diameter distributions).

Figure 4. Plots of the differential capacity *versus* voltage (a), and galvanostatic discharge/charge curves at 100 mA g⁻¹ for the initial cycle of electrodes(b), cycling (c) and rate (d) performance of electrodes based on 500°C/12h, 600°C/4h and 750°C/4h silicon samples obtained by magnesiothermic reduction of SiO followed by acid dissolution of Mg-bearing product, respectively. The charge/discharge current in (c) was 100 mA g⁻¹ for the first cycle and 1000 mA g⁻¹ for the rest cycles.

Figure 5. (a)TEM image of carbon wrapped porous silicon (CWPSi) and (b) magnified image of the yellow rectangle region in (a). (c) TEM image of infiltrated carbon coated porous silicon (CCPSi) and (d) magnified image of the yellow rectangle region in (c). (e) STEM image of CWPSi and its element mapping of silicon, nitrogen and carbon, respectively.

Figure 6. Rate (a) and cycling (b) performance of electrodes based on carbon wrapped porous silicon (CWPSi) and infiltrated carbon coated porous silicon (CCPSi). The charge/discharge current in (b) was 100 mA g⁻¹ for the first cycle and 1000 mA g⁻¹ for the rest cycles.

Figure 7. Nyquist plots of electrodes from electrodes based on carbon wrapped porous silicon (CWPSi) and carbon coated porous silicon (CCPSi) (the inset is magnified plot of rectangular area).

Table 1. Parameters of porous structure of silicon products and average diameter of Mg-bearing phases obtained at different magnesiothermic reaction conditions.

Reaction condition (T/time)	BET SSA (m ² g ⁻¹)	Average diameter ^a (nm)	Porosity (%)	D _{MgO} (nm)/D _{Mg₂Si} (nm) ^b
500 °C /12 h	218.4	5.3	40.4	8.2/13.4
500 °C /24 h	303.2	6.3	52.4	9.4/21.3
600 °C /4 h	303.2	7.9	57.1	9.5/23.4
600 °C /8 h	275.3	8.4	57.2	12.7/21.1
750 °C /4 h	86.4	19.5	50.1	15.7/—
750 °C /8 h	74.8	22.7	49.5	16.7/—

^aAverage pore diameter is calculated as $4V/A$ (V is pore volume and A is BET SSA of porous silicon);

^bD_{MgO} and D_{Mg₂Si} are average crystallite diameters of MgO and Mg₂Si base on the Scherrer analyses of XRD patterns.