**Facile synthesis of Si-C nanocomposites with yolk-shell structure as an anode for
lithium-ion batteries**

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Abstract

A yolk-shell structured Si-based anode is synthesized by depositing MgO, instead of SiO₂, as sacrifice layer and CVD process. Thus the HF etching can be substituted by using diluted HCl, which is less toxic and corrosive. The results show the yolk-shell structure is successfully synthesized and has an improved electrochemistry performance. The amount of MgO coating also has been investigated. The proper mass ratio of MgO and Si can be approx. 2 and a reversible charge capacity of 901 mAh g⁻¹ and 88.3% retention was achieved after 100 cycles at 1.0 A g⁻¹. The significant improvements for cycle performance demonstrate the yolk-shell structured Si-C nanocomposite in this work is a promising anode material for lithium-ion batteries.

Keywords: silicon; nanocomposite; yolk-shell structure; anode; lithium-ion battery

1. Introduction

With the development of electric vehicles and consumer electronic devices, lithium ion (Li-ion) batteries are becoming among the most promising energy storage devices for their high energy density, long cycle life and environmental benignity [1, 2]. Silicon has attracted lots of attention from researchers because of its high theoretical specific capacity (3579 mAh g^{-1}) [3, 4], which is ten times higher than that of traditional graphite anode (372 mAh g^{-1}). Its natural abundance and low discharge potential are also advantages for cheap and high power lithium-ion batteries.

However, huge volume change ($\sim 300\%$) during Li^+ lithiation and delithiation process will make the binder and active particles and SEI layer fracture and to disrupt. The fracture of binder and active particles cause the loss of electrical contact and disruption of the SEI layer leads to sustained consuming of lithium ion and increasing resistance, resulting in severe capacity fading [5].

Many efforts have been devoted to alleviate these disadvantages, such as designing nanostructures or encapsulating Si particles with protective coatings [6, 7]. Various silicon nanostructures have been designed to improve electrical performance, such as nanotube [8], nanowires [9, 10], porous [11, 12] and hollow [13-16]. Liu *et al.* [17] showed a result that, particles under diameter of 150 nm are more unlikely to crack during lithiation and delithiation process. Cui *et al.* [13, 14] demonstrated a yolk-shell structure which leaves enough space for expansion and contraction during lithiation and delithiation. This structure protected the electrode from pulverization and kept a reversible capacity of 1000 mAh g^{-1} after 1000 cycles. However, removing the SiO_2

shell using HF acid is difficult to realize commercial production because of its toxic and environmental problems. Ru *et al.* [18] made void space by etching SiO₂ with NaOH solution, and then reduced the remained SiO₂ by in situ magnesiothermic reduction. The reversible special capacity reached 790 mAh g⁻¹ for the second cycle at a current density of 200 mA g⁻¹. Pan *et al.* [15] etched the Si nanoparticles directly by NaOH solution to build a yolk-shell structure, get a stabilized capacity about 928 mAh g⁻¹ at 1000 mA g⁻¹.

In the work reported here, Si-C nanocomposites with yolk-shell structure have been synthesized using a facile route by replacing the SiO₂ layer by MgO. Therefore we can make void space by diluted HCl rather than HF. As shown in Fig. 1, to make the silicon powder hydrophilic, aqueous ammonia was used to get the silicon powder surface oxidized [19]. Then MgSO₄ solution and Na₂CO₃ solution were used to obtain a Si@SiO₂@MgCO₃ precursor by precipitation. Followed by calcination and CVD process, the SiO₂@MgCO₃ shell was turned into Mg₂SiO₄@MgO shell and covered by carbon layer. Finally to make the void space, we remove the MgO layer by magnesiothermic reduction and diluted HCl.

2. Experiment

2.1. Materials preparation

2.1.1. Preparation of the surface oxidized Si particles

For the preparation of Si@SiO₂ nanoparticles, 0.8 g Si nanoparticles (SiNPs, 60~120 nm, 99%, Shanghai Chaowei Nanotechnology Co., Ltd, China) were firstly

dispersed into 240 mL of ethanol by sonication for 1 h. Subsequently, 4 mL of the concentrated ammonia solution (28 wt. %) and 20 mL of water was added into the dispersion simultaneously. The reactions were carried out under magnetic stirring for 30 minutes. Then the solid products were filtered and washed to neutral using ethanol, and dried at 45 °C.

2.1.2. Preparation of the Si@SiO₂@MgCO₃ particles

A certain amount of MgSO₄ (0.01 and 0.02 mol) were dissolved in 100 mL of water and then mixed with 200 mL of ethanol. Then 400 mg as-prepared Si@SiO₂ nanoparticles were dispersed in the MgSO₄ solution by sonication. Under vigorous stirring, 100 mL Na₂CO₃ solution (change the concentration to make $n_{\text{Mg}}:n_{\text{CO}_3} = 1$) was added into the dispersion in 30 min, the reaction was left at room temperature under stirring overnight, and then kept 50 °C for 1 h to make all MgCO₃ precipitate. Finally, Si@SiO₂@MgCO₃ particles were collected by filtration and washed with water, and dried at 45 °C.

2.1.3. Calcination and carbon coating

The Si@SiO₂@MgCO₃ particles were first loaded in a ceramic boat and placed at the center of the quartz tube furnace. To turn MgCO₃ into MgO, the tube was first heated to 360 °C and kept for 3 h under argon atmosphere. Subsequently, the temperature was increased to 800 °C and argon flow at a rate of 60 mL min⁻¹ was introduced into a gas bottle containing 100 mL toluene to bring the reactant gases into the tube. After 1 hour, the gas flow was switched to pure argon again and kept for 1 h

to remove the unreacted toluene. Then the tube was cooled to room temperature in argon flow. Finally Si@Mg₂SiO₄@MgO@C particles were obtained.

2.1.4. MgO layer etching

Si@Mg₂SiO₄@MgO@C particles were immersed in diluted HCl for 2 h and washed with water to remove the MgO layer. Then 500 mg Si@Mg₂SiO₄@void@C particles were well mixed with 80 mg Mg powder and and annealed in a tube furnace at 650 °C for 3 h under argon atmosphere to reduce Mg₂SiO₄ to MgO. The product was washed again using diluted HCl and water to get the Si@void@C nanocomposites (denoted as SiVC). The final products were denoted as SiVC-1 and SiVC-2 with the respective MgSO₄ amount of 0.01 mol and 0.02 mol.

2.2. Materials characterizations

In order to characterize the composition of the composites, X-ray diffraction (XRD) patterns using Cu-K α radiation were obtained (Shimadzu XRD-6100) at a step scanning of 4° min⁻¹. The weight percentage of carbon in Si-C nanocomposite was measured under air atmosphere on a TG/DTA instrument with a heating rate of 10 °C min⁻¹. The surface morphologies and elemental distribution were characterized via the scanning electron microscope (SEM, JEOL JSM-6510) with an energy dispersive X-ray spectroscopy (EDAX) attachment. High resolution transmission electron microscopy (TEM, tecnaiG2 F20) was used to determine the nanostructure of different samples.

2.3. Electrochemical measurements

The anode electrodes consist of active material (60 wt. %), super P (20 wt. %) as the conductive agent, and sodium alginate (20 wt. %) as the binder. The slurry was coated on a copper foil and dried for 12 h at 80 °C in air. The average mass loading of electrode was measured $\sim 1.78 \text{ mg cm}^{-2}$, the loading of active material was 1.07 mg cm^{-2} . 1 M LiPF_6 was added to the electrolyte which consisted of a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (1: 1 in volume) (Dongguan Shanshan Battery Material Co., Ltd, China) with an additive of 10 wt. % fluorinated ethylene carbonate (FEC). The anode and cathode were separated by a Celgard 2300 separator (Celgard Inc., USA), and metallic lithium foil was used as counter electrode. The CR2032-type coin cell was assembled in argon gas filled glove box. The cycle performance was performed on a NEWARE CT-3008 system (accuracy: 0.1 %) at room temperature with the voltage range from 0.01 to 1.5 V. Cyclic voltammetry (CV) was performed on CHI1000C electrochemical workstation (CH instrument, Shanghai) with a scan rate of 0.1 mV s^{-1} . Electrochemical impedance spectroscopy (EIS) was obtained using a PCI4/750 Potentiostat (Gamry Instruments, USA) in the frequency range of 10 kHz-0.01 Hz.

3. Results and discussions

3.1. Material characterizations

The XRD profiles of the (a) Si, (b) Si@SiO_2 and (c) $\text{Si@Mg}_2\text{SiO}_4\text{@MgO}$ and (d) Si@void@C nanoparticles are shown in Fig. 2. The intensity of the main peak of Si at 28.50° was set to the same value. The XRD pattern of (b) Si@SiO_2 (red) demonstrates

a wide peak from 20° to 25° which is slightly higher than (a) Si (green). This means the Si particles were partial oxidized after treated by ammonia [20]. (c) Si@Mg₂SiO₄@MgO is the sample described in section 2.1.3 but without carbon coating. The pattern demonstrates the existence of MgO (JCPDS #74-1225) and Mg₂SiO₄ (JCPDS #85-1364). MgO was derived from the decomposition of MgCO₃, and then Mg₂SiO₄ was formed by MgO and SiO₂ during the calcination. (d) Si@void@C is the final product in section 2.1.4. As seen from the XRD pattern, there is a wide low intensity peak centered ~25°, which is assigned to amorphous carbon by CVD process. We can also find that Mg₂SiO₄ in Si@Mg₂SiO₄@MgO has been completely reduced:

Moreover, there is no apparent peak except Si (2 θ = 28.44, 47.30, 56.12, 69.13, 76.38), indicating that the method can remove all the sacrifice layers we added in section 2.1.1 and 2.1.2.

For comparison between the Si@C and SiVC particles, the morphologies were examined by SEM and the results are showed in Fig. 3. From Fig. 3a, it can be seen that the Si particles after CVD have the size range of 60~130 nm. This indicates that the size and morphology of the Si nanoparticles are almost unchanged after the CVD process (compared to Supplementary Materials Fig. S1). As displayed in Fig. 3c and 3d, because of the void space left by the MgO sacrifice layer, the SiVC particles have obviously larger size than the Si@C particles. Besides, we can see the SiVC particles have slight agglomeration, caused by the growth of MgCO₃ in the precipitation. EDS

mappings of SiVC (Fig. S2 (a, b) in supplementary data) showed that the carbon layer was uniformly coated on the outer surface of silicon.

The structure of a single particle can be seen in the TEM results. Fig. 4b and 4c evidently show the void space of SiVC-1 and SiVC-2, compared to the Si@C in Fig. 4a. SiVC-1 displays a void space with width less than 10 nm, while SiVC-2 has obviously larger void space. The crystal structure of SiVC is revealed clearly in Fig. 4d, which shows the lattice fringes of silicon and carbon. The lattice fringes on the edge of silicon particle are measured as 0.314 nm, which corresponds to the (111) crystal plane of silicon (JCPDS #75-0590). No lattice fringes of Mg_2SiO_4 can be found inside the particle, confirms that sacrifice layer has mostly been removed. The carbon shell is about 5 nm thick, showed in Fig. 4d. The lattices of carbon are disordered and measured as ~ 0.34 nm, which is a little larger than the (002) crystal plane of graphite (JCPDS #75-1621), this is also confirmed by the broad peak around $2\theta = 25^\circ$ in Fig. 2. Fig. 4e showed the SiVC-2 structure after cycling. Although the inner structure was sheltered by the residual Super P and binder, it can be observed that the carbon shell of SiVC-2 was kept perfectly through the volume change during cycling process. This shows that the yolk-shell structure can provide buffer space for the silicon [21].

The nitrogen adsorption-desorption measurements are employed to investigate the porous structure and the specific surface areas of SiVC and Si@C particles. It can be observed from Fig. 5a that the specific surface area is becoming larger with the increasing amount of MgO. Fig. 5b shows the BJH pore size distributions extracted

from the adsorption branches. Compared to Si@C, it can be mentioned that SiVC-1 and SiVC-2 exhibited two new sized pores around 10 nm and 20-30 nm respectively, which probably originated from the void space left from the MgO layer [22-25]. From the difference of the pore size distribution, we can make further inference that SiVC-2 has a larger void space.

The results from thermo gravimetric (TG) analysis are given in Fig. S3, which show the Si@void@C nanocomposite has a weight loss of between 100 and 700 °C. The 1.7 wt. % weight loss around 100 °C is caused by the removal of absorbed water. The main loss of weight between 600 to 700 °C is about 51.8 wt. %, corresponding to combustion of the carbon layer on the Si@void@C nanocomposite. The weight increment about 3.9 wt. % after 700 °C is due to the oxidation of silicon in air. The carbon amount is calculated as 54.0 wt. %.

3.2. Electrochemical properties

Fig. 6a shows the cyclic voltammetry (CV) characterization of SiVC anode. From the first cathodic sweep, we can see two broad peaks around 1.3 V and 0.7 V vs. Li/Li⁺. The peak around 1.3 V is attributed to the reduction or decomposition of FEC [26, 27], and the broad one around 0.7 V represents the further formation of SEI film by decomposition of solvent [28, 29]. When the potential goes lower to ~0.1 V, a sharp reduction peak can be observed. This peak corresponds to the formation of amorphous Li-Si phase shown by equation (2) and crystallization of a-Li_ySi to Li₁₅Si₄ at about 0.06 V [4, 30].

The extraction of Li^+ occurs at 0.34 V and 0.52 V. The peaks become higher with the increase of active Si and finally get stable. The broad peak at 0.7 V disappears in the following cycles, indicating a stable SEI layer has formed. A new peak appears around 0.14 V at second cycle, which corresponds to the reduction of amorphous Si formed in anodic process [4, 31].

Fig. 6b shows the discharge-charge profiles of the SiVC-2 after various cycles. The test was taken at rate of 300 mA g^{-1} . Two discharge plateaus appear in the first cycle, the short plateau at 1.25 V corresponds to the peak around 1.3 V in Fig. 6a, reflects the formation of SEI film that caused by the reduction of FEC. The plateau below 0.1 V represents the insertion of lithium ion into the crystalline silicon. In the first cycle, the nanocomposite give capacities of 1782 mAh g^{-1} and 1114 mAh g^{-1} for discharge and charge process, respectively. The initial Columbic efficiency is calculated as 62.5%. The low Columbic efficiency is caused by the large specific surface area, which increases the side reaction with the electrolyte [14, 32]. In next few cycles, the reversible capacity increases from 1114 mAh g^{-1} to 1190 mAh g^{-1} at the 10th cycle, and the Columbic efficiency increases to 98%, indicating an activation process has happened in the first 10 cycles. The activation process is considered due to the thick carbon layer, which will hinder the penetration of the electrolyte.

The cycling performances for the Si@C and SiVC electrodes are displayed in Fig. 7. The rate was 100 mA g^{-1} for the first cycle and 1000 mA g^{-1} for later cycles. The SiVC-1, SiVC-2 and Si@C anodes give a discharge capacity of 1923, 2122 and 1511 mAh g^{-1} in the first cycle, respectively. The lower capacity of SiVC-1 and Si@C

electrodes are caused by the carbon shell directly covered on the particle surface, which limits the volume expansion of the silicon [33]. In the beginning few cycles, the SiVC-1 has a faster activation and exceeds SiVC-2, then has a severe decay after about 10 cycles. This phenomenon can be explained by the crush of carbon shell caused by the insufficient buffer voids in SiVC-1 anode, while SiVC-2 anode has void space large enough to buff the volume change [34]. After 100 cycles, the capacity of Si@C anode decreases from 727 mAh g⁻¹ (the 2nd cycle) to 404 mAh g⁻¹ showing capacity retention of 55.6%, SiVC-1 shows a retention of 48.5% (from 905 mAh g⁻¹ to 439 mAh g⁻¹). In contrast, SiVC-2 anode shows better capacity retention of 88.3%, decrease from 901 mAh g⁻¹ to 796 mAh g⁻¹, much higher than the Si@C and SiVC-1 anodes. Fig. 8 shows the long term cycling performance of SiVC-2. The capacity retention after 200 cycles is 657 mAh g⁻¹ (73.7% of the 2nd cycle). From the summaries of Table 1, we can see SiVC-2 has better percentage retention than most yolk-shell Si-C composites in previous reports. The SiVC-2 anode can deliver promising capacity retention at a relatively large current density (1000 mA g⁻¹).

In addition, the rate capacity of the SiVC-2 was tested and the result is shown in Fig. 9. The current density was 0.3 A g⁻¹ in the beginning 10 cycles, and the capacity is considered to be 1243 mAh g⁻¹. The current density was then rose to 0.5 A g⁻¹ and 1.0 A g⁻¹ every ten cycles, while the reversible capacity showed slightly decrease to 1125 mAh g⁻¹ and 956 mAh g⁻¹, respectively. As a higher current density was applied, the Si@void@C anode could still have capacity of 742 mAh g⁻¹ at 2.0 A g⁻¹ and 350

mAh g⁻¹ at 5.0 A g⁻¹. The good rate capacity is considered owe to the improvement of electronic conductivity by carbon coating.

We further investigated the resistance change during cycling by using EIS measurements. Before testing, the cell was charged to 1.5 V and rested for 1 hour. Fig. 10 shows the Nyquist plot of SiVC-2. The high frequency semicircle appeared after cycling is attributed to the SEI film, while the semicircle in the middle frequency represents the charge transfer resistance [11, 38]. The parameters were calculated by simulation, using the equivalent circuit described as $R(QR)(QR)W$ (see Fig. S4(a, b)). R_1 is the ohmic resistance of electrolyte, R_2 is the resistance of SEI film, R_3 is the charge transfer resistance, Q_2 and Q_3 are constant phase elements for SEI film and active Si (for the fresh cells without SEI film, R_2 and Q_2 don't exist), while W is the Warburg impedance for the solid state diffusion of Li-ion in the electrode. The simulated parameters of resistances are shown in Table 2. From Table 2 we can see the SEI film resistance is stabilized around $\sim 8.8 \Omega$ and rise to 10.8Ω after 50 cycles, correspond to the small capacity decrease in Fig. 6b and 7. The charge transfer resistance is around 17.8Ω , slightly rise to 18.8Ω at the 50th cycle. For Si@C anode in Fig S4 (c), the resistance of SEI film and charge transfer show a huge increase at the 50th cycle, SiVC-1 anode in Fig S4 (d) show a continuous increasing resistance from 3rd to 50th cycle. The results indicate the SiVC-2 has a proper stability during cycling.

4. Conclusions

A yolk-shell structured Si-C nanocomposite was synthesized by using MgO as sacrifice layer and followed by CVD process. The remove of MgO needs only diluted hydrochloric acid, which is more environmentally friendly than using HF to etch SiO₂. After 100 cycles at 1.0 A g⁻¹, the SiVC electrode gave a specific capacity of 796 mA h g⁻¹ with the capacity retention of 88.3%, which was higher than the Si@C produced by directly CVD. Moreover, the Si@void@C nanocomposite anode exhibited good rate capacity, maintained 350 mAh g⁻¹ at current density of 5.0 A g⁻¹. Its superior performance is due to the buffer voids that tolerate the volume change and improve the structural integrity. We consider MgO sacrifice layer is an appropriate option to synthesis yolk-shell structure for silicon anode. It is believed that making the MgO layer fit the shape of silicon better and reducing the amount of carbon will improve the cycle capacity and specific capacity. Further optimization is still under investigation.

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Table 1

Comparison on the synthesis methods and performances of yolk-shell Si-C composites between previous reports and this work.

Ref.	method or sacrifice layer (acid to etch)	Carbon source	Si (wt. %)	Current mA g ⁻¹	Capacity retention mAh g ⁻¹ , % (cycle number)
this work	MgO	toluene	50%	1000	796, 88.3%(100) 657, 73.7%(200)
35	APS (HF)	glucose	78%	400	1249, 75%(100)
15	Si (NaOH)	polydopamine	75%	1000	804, 83%(50)
36	Si (LiOH)	RF resin*	67%	50	628, 42.2%(100)
34	SiO ₂ (HF)	polydopamine	48%	200	1625, 69%(100)
14	SiO ₂ (HF)	RF resin	77%	2100	1160, 96%(1000)
21	SiO ₂ (HF)	toluene	37%	100	767, 98%(100)
37	SiO ₂ (HF)	acetylene		1000	650, 86%(100)
24	magnesiothermic (HCl)	RF resin	56%	400	~900, 73%(50)
22	magnesiothermic (HCl)	citric acid	64%	100	~1200, 88%(150)
18	Si (NaOH)	polydopamine	44%	200	530, 67%(100)

***RF resin:** resorcinol formaldehyde resin.

Table 2

Resistance of SiVC-2 anode after different cycles by EIS simulation

cycle	$R_1(\Omega)$	$R_2(\Omega)$	$R_3(\Omega)$
fresh	5.276		60.95
3rd	3.576	11	15.57
10th	4.074	8.88	17.88
20th	3.394	8.08	16.31
30th	4.201	8.711	17.96
50th	3.97	10.77	18.87

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Fig. 1

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.

Fig. 7.

Fig. 8.

Fig. 9.

Fig. 10.