Pomegranate-type Si/C anode with SiC taped, well-dispersed tiny Si particles for lithium-ion batteries

Pengfei WU^{a,b,†}, Benyang SHI^{a,†}, Huibin TU^a, Changqing GUO^a,
Anhua LIU^{a,b,*}, Guan YAN^{c,*}, Zhaoju YU^{a,*}

^aKey Laboratory of High-Performance Ceramic Fibers of Ministry of Education,
College of Materials, Xiamen University, Xiamen 361005, China

^bShenzhen Research Institute of Xiamen University, Shenzhen 518000, China

^cCollege of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

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Abstract: Severe volume expansion and inherently poor lithium ion transmission are two major problems of silicon anodes. To address these issues, we proposed a pomegranate-type Si/C composite anode with highly dispersed tiny silicon particles as the core assisted by small amount of SiC. Skillfully exploiting the high heat from magnesiothermic reduction, SiC can assist the good dispersion of silicon and provide good interface compatibility and chemical stability. The silicon anchored to the carbon shell provides multipoint contact mode, that together with the carbon shell frame, significantly promoting the transfer of dual charge. Besides, the pomegranate-type microcluster structure also improves the tap density of the electrode, reduces the direct contact area between active material and electrolyte, and enhances the electrochemical performance.

Keywords: Si/C anode; anchored Si; SiC tape; magnesiothermic reduction; pomegranate like

1 Introduction

The rapid development of new energy industries forces the exploration of lithium ion batteries (LIBs) into the higher, faster, and safer area. The widely used graphite anodes gradually show a sign of dissatisfactory, while many alloying anodes exude a strong competitive edge [1,2]. Silicon is considered to be the most exciting candidate material for LIBs' anode due to its high special

capacity, suitable discharge potential, and abundant reserves. However, full industrialization of silicon anodes still faces two fatal obstacles [3,4], as follows:

1) One is huge volume expansion caused by the steady alloying phase change and excess Li⁺ insertion, following with the pulverization of Si, uncontrollable interfacial reaction, and unstable formation of solid electrolyte interface layers (SEI);

2) The other is the high cost of nano-silicon from an efficiency, safe, and scalable approach.

In order to avoid the limitation influence of the first disadvantage, carbon coating and nano-scaled silicon materials are adopted to form core@shell structure, yolk@shell structure, or other ingenious framework [5,6]. Yolk@shell structure contains a tailorable hollow void

† Pengfei Wu and Benyang Shi contributed equally to this work.

* Corresponding authors.

E-mail: A. Liu, ahliu@xmu.edu.cn;

G. Yan, 0006177260@pku.edu.cn;

Z. Yu, zhaojuyu@xmu.edu.cn

for the free expansion of Si and an armour liked shell to protect the inner active material from the direct-contact of electrolyte, guaranteeing the structure integrity and long-life cycle. Recently, various methods have been involved in preparation of yolk@shell structure, and achieved excellent results [7–9]. However, the high specific surface area increases the interfacial reaction between electrode material and electrolyte, leading to an increase in irreversible Li^+ loss, a decrease in coulombic efficiency (CE) and tap density. Liu *et al.* [10] designed a pomegranate-inspired Si/C anode by gathering a number of yolk@shell nano particles to form a micro-sized particle. This novel nano–micro secondary structure delivers high areal capacity and ultralong cycling life.

Magnesiothermic reduction (MR) can be used to fabricate Si from very cheap silica, so it is treated as a method for scale-up Si fabrication [11]. The porosity and structure of Si can be easily controlled by changing the thermal process [12,13]. Not only the porous silicon [14], but also the tiny Si nanodots or nanoparticles were prepared by MR [15]. Unfortunately, chemically inert SiC is always accompanied, when the previously carbon coated silica is used as the reactant because of the local superhigh temperature. To avert the unexpected side reaction, salts with suitable melting point are often employed as the heat-absorbing medium to supply a mild reaction environment [16]. However, in some works, thin or porous SiC layer can also protect the inner Si core and provide satisfying ion transfer efficiency [17,18]. Therefore, the limitation of the amount of SiC formed during MR reaction to an acceptable level can be a proper way to stabilize the Si anode capacity [19,20].

Herein, we combined the nano–micro secondary structure and MR to design a small amount SiC containing, tiny Si well dispersing, and pomegranate-shape-like Si/C composite anode (PSi/C). The small amount SiC, gained from the local high temperature of MR by controlling NaCl, can play a role like double side tape to anchor the Si particles on the C shell with a good dispersion. This design of tape-SiC exhibits three kinds of excellent peculiarities, as follows:

- 1) Intrinsic chemical inert can protect Si from the corrosion of the permeable electrolyte.
- 2) C–SiC–Si interface provides better interface compatibility than C–Si.
- 3) Random anchored Si tiny particles on C shell supply a multipoint contact mode [21], facilitating effective Li^+/e^- transfer pathway and decreasing the diffusion length of Li^+ instead of various disadvantages of nanoparticles' aggregation (Figs. 1(a) and 1(b)).

What is more, the pomegranate-shape-like structure armed with carbon shell can:

- 1) limit the direct contact of electrolyte and silicon;
- 2) improve the electronic conductivity of Si nanoparticles;
- 3) provide hollow void for the free volume expansion of silicon.

2 Experimental section

2.1 Synthesis of active materials

2.1.1 Synthesis of SiO_2 particles

First, 90 mL of ethanol (analytically pure, XILONG

Fig. 1 Schematic illustration of lithium ion transfer pathways and the morphology evolutions of Si particles. (a) Yolk@shell structure with aggregated silicon core; (b) yolk@shell structure with anchored silicon core; (c) schematic preparation procedure of PSi/C nanocomposites.

Scientific, China) and 9 mL of deionized water was added to the flask and mixed well, and then 3 mL of ethyl orthosilicate (analytically pure, XILONG Scientific, China) was added and heated slowly to 50 °C in an oil bath. Then, 7.5 mL of ammonia water (analytically pure, XILONG Scientific) was quickly added to adjust the pH of the solution, continuing to stir for 2 h, and then ethanol was used for centrifugal purification three times. Finally, it was placed in a vacuum oven at 50 °C for 5 h to obtain SiO₂ particles [22]. After the nano-scale SiO₂ particles were obtained, the porous Si/C composite materials were synthesized through the following steps.

2.1.2 Synthesis of SiO₂ micron clusters

0.36 g of SiO₂ nanoparticles were uniformly dispersed into 9 mL of deionized water by ultrasonic dispersion, and then mixed with 72 mL of 1-octadecene (analytically pure, XILONG Scientific, China) solution containing 0.4% emulsifier (Hypermer 2524-NV-LQ-(AP), Croda). The mixed solution was dispersed at a high speed at 12,000 rpm for 10 min, and then heated in an oil bath at 96–98 °C for 8 h to evaporate the deionized water. The obtained sample was centrifuged and cleaned with *n*-hexane for three times and then calcined in the air at 550 °C for 1 h to remove the organic emulsifier and obtain SiO₂ micron clusters.

2.1.3 Coating of carbon layer on the surface of SiO₂ micron clusters

0.3 g of SiO₂ micron clusters were dispersed in 90 mL of deionized water, and then 3 mL of CTAB (analytically pure, SINOPHARM, China) and 0.3 mL of ammonia were added, and then stirred for 30 min to mix well. Next, 0.12 g of resorcinol and 168 µL of formaldehyde solution (analytically pure, XILONG Scientific, China) were introduced, and stirred at room temperature for 16 h. The phenolic resin-coated SiO₂ micron clusters were collected by centrifugation and washed with ethanol three times. Then the powder was heated to 850 °C at a heating rate of 5 °C·min⁻¹ in an argon atmosphere and kept for 2 h. The final sample was named SiO₂/C micron clusters.

2.1.4 Synthesis of pomegranate-type Si/C composite

0.3 g of SiO₂/C powder and 0.3 g of magnesium powder (analytically pure, Aladdin, China) were mixed and grounded in a mortar, and then 3 g of sodium chloride powder (analytically pure, XILONG Scientific, China) was added and mixed uniformly. The obtained mixture

was placed in a closed crucible, and heated to 660 °C at a heating rate of 5 °C·min⁻¹ in a tube furnace filled with argon and keep it for 4 h [23]. The sample powder was transferred into a 1 mol·L⁻¹ dilute hydrochloric acid (analytically pure, XILONG Scientific, China) solution and stirred for 4 h to remove unreacted magnesium powder and by-products MgO and Mg₂SiO₄, while dissolving and removing NaCl acting as an endothermic. Finally, the product was cleaned in a 5 wt% HF dilute solution (analytically pure, XILONG Scientific, China) for 5 min to remove unreacted SiO₂ in the composite material. The porous Si/C composite material was collected by centrifugation and placed in a vacuum oven at 50 °C for 5 h to obtain a three-dimensional continuous porous silicon–carbon composite material PSi/C (yield is 58%).

2.2 Characterization

The morphology of the samples was characterized by scanning electron microscope (SEM, Hitachi SU-70, Japan) and transmission electron microscope (TEM, JEM-2100, Japan). The crystal structure of the products was determined using X-ray diffraction (XRD, Bruker-axs, Cu Kα radiation, 40 kV, 40 mA). Raman spectra were obtained on HORIBA and CCD spectroscopy systems with an excitation wavelength of 532 nm. The N₂ adsorption/desorption measurement (BET, Micromeritics Tristar II 3020 static volumetric analyzer, USA) was used to identify the surface area and pore size distribution of the sample.

2.3 Electrochemical measurements

The electrochemical measurements were conducted by assembling 2025 coin-type half-cells in an argon-filled glove box (MBRAUN, H₂O < 0.1 ppm, O₂ < 0.1 ppm) with lithium metal (analytically pure, Canrd, China) as the counter/reference electrode and Celgard 2400 (analytically pure, DoDoChem, China) as the separator. The anode was prepared by using deionized water as a solvent and using active materials, conducting agent (Super C, analytically pure, DoDoChem, China), and sodium carboxymethyl cellulose (CMC, analytically pure, DoDoChem, China) at a mass ratio of 6 : 2 : 2. The electrodes were prepared by coating the slurry on copper foil at a thickness of 100 µm, which was then dried at 50 °C for 5 h and subsequent 80 °C for 12 h in a vacuum oven. The electrolyte (analytically pure, DoDoChem, China) was 1.0 M LiPF₆ in 1 : 1 (weight

ratio) ethylene carbonate (EC)/diethylene carbonate (DEC), with 10 wt% fluoroethylene carbonate (FEC) additive. All batteries were tested between 2.0 and 0.01 V using the Neware battery test system. Electrochemical impedance curve (EIS) was obtained in the frequency range of 100 kHz to 0.01 Hz, and cyclic voltammetry (CV) measurements were performed at a scan rate of $0.05 \text{ mV}\cdot\text{s}^{-1}$ at a voltage range of 0.01–2 V.

3 Results and discussion

The SiO_2 nano-particles synthesized from the hydrolyzation of tetraethyl orthosilicate (TEOS) present regular sphere shape with smooth surface and uniform size ($\sim 180 \text{ nm}$) (Fig. S1 in the Electronic Supplementary Material (ESM)). In order to gain the micro-sized cluster particles, aqueous dispersion of silica particles is dropped into 1-octadecene containing 0.04 wt% Hypermer as emulgator under highspeed stirring. Carbon layer is formed from the normal coating and carbonization of resorcinol formaldehyde (RF) resin. After MR procedure and etching of side products, the final PSi/C particles are prepared. The intuitive steps are shown in Fig. 1(c).

Figure 2 shows the SEM images of SiO_2 microclusters, SiO_2/C and PSi/C composite materials. It can be seen from Fig. 2(a) that the size of the SiO_2 micron clusters synthesized by the microemulsion method is in the range of 1–4 μm , and the micro-sized electrode material can greatly increase the tap density and volume capacity of the battery, effectively avoiding the defects caused

by nanoelectrodes [24]. It can be seen from the SEM image of SiO_2 micron cluster (Fig. 2(b)) that the SiO_2 particles are densely arranged. This structure is conducive to the formation of three-dimensional interconnected carbon materials inside the composite, thereby effectively improving the conductivity of Si and promoting the transmission of lithium ions. The SiO_2/C composite material was synthesized by coating the SiO_2 micron cluster with RF resin and the subsequent carbonization process, as shown in Fig. 2(c). The SiO_2 micron clusters coated by the carbon layer can still maintain a relatively regular spherical shape, and the size does not change obviously, which indicates that the structure of the composite material is relatively stable. Compared with SiO_2 micron clusters, the surface of the SiO_2/C composite material coated with a carbon layer is smoother.

As in the coating process of RF, resorcinol and formaldehyde can penetrate into the gaps inside the material, so the surface of each SiO_2 nanoparticle is coated with a layer of RF resin, which forms a three-dimensional interconnection carbon framework after carbonization. After the partial MR and subsequent HCl etching, the PSi/C particles can maintain the original shape (Fig. 2(d)), which shows that the MR process does not affect the structure of the material. This structure is similar to a pomegranate. The outer carbon shell is similar to the skin of a pomegranate and covers the inner material. Each egg yolk shell structure is like a pomegranate seed, and silicon nanoparticles are like pomegranate seeds. Such a structure can endow silicon active material good structural stability and double charge

Fig. 2 Morphological characterization by SEM. (a) Micro-sized SiO_2 cluster particles. (b) Single micro-sized SiO_2 cluster particle. (c) Micro-sized SiO_2/C cluster particles. (d) Pomegranate-shape-like PSi/C nanocomposites.

transfer ability. No SiO_2 is observed in the SEM image of the PSi/C composite, and the outer carbon shell can maintain a perfect spherical shape. The three-dimensional interconnected carbon shell can effectively isolate the direct contact between silicon and electrolyte, thereby reducing the formation of SEI film and inhibiting the continuous consumption of electrolyte, which can greatly improve the coulombic efficiency of the battery.

In order to more intuitively observe the composition and structure changes of these composite materials during the entire preparation process, we performed SEM–EDS mapping analysis on SiO_2 microclusters, SiO_2/C and PSi/C composite materials, shown in Fig. S2 in the ESM. As can be seen from Fig. S2(a) in the ESM, only Si (red) and O (yellow) are two elements in the SiO_2 micron clusters before coating the amorphous carbon layer, and they are evenly distributed. The Si, C (blue), and O elements in the SiO_2/C composite material are evenly distributed, indicating the presence of SiO_2 and amorphous carbon in the material (Fig. S2(b) in the ESM). After MR and etching, the content of O element in PSi/C composites is greatly reduced. While the Si and C elements can still be evenly distributed in the sample. This shows that MR process causes SiO_2 to be partially reduced to elemental Si, which is also the same as observed in the above SEM images. The silicon produced by this inexpensive method has a tiny size which limits the damage caused by the volume expansion of silicon

during the cycle [25,26].

The internal structure and morphology of the PSi/C composite were further characterized by TEM, and the results are shown in Fig. 3. After the MR step and acid etching, unreacted Mg and undesirable products MgO are removed, leaving well dispersed tiny sized Si nanoparticles within 10 nm (Figs. 3(a) and 3(b)). As seen in the SEM image, the PSi/C composite presents a relatively regular spherical shape with a size of about 4 μm , and a large number of amorphous carbon shells and pores can be observed. It can be seen from the enlarged view in Fig. 3(b) that the size of the spherical carbon shell is consistent with the size of SiO_2 synthesized by the sol–gel method (about 180 nm), which indicates that the thin amorphous carbon layer is successfully coated on the SiO_2 nanoparticles' surface. The carbon layer (thickness of about 8 nm) can not only isolate the direct contact between the internal silicon particles and the electrolyte, but also provide with better mechanical stability, cushion the silicon volume expansion in the process of charge and discharge, and improve the cycling stability of the electrode material [27].

From the HRTEM images in Figs. 3(c) and 3(d), a lattice fringe of 0.31 nm can be observed (white areas), corresponding to the (111) plane of crystalline silicon, which also proves that SiO_2 is transformed into crystalline Si after the MR procedure. Because every Si tiny particle is isolated with each other, the obtained silicon is not

Fig. 3 Morphological and structural characterization of PSi/C composite by TEM. (a) Single PSi/C particle; (b) enlarge area vision; (c) and (d) HRTEM images of different areas in one particle. The white area is Si and the red area is SiC.

the connected porous Si material but the well dispersed tiny Si nanoparticles which is different from the most MR related works. Importantly, the reason that these Si nanoparticles can be well dispersed or anchored on the carbon inner wall after such harsh thermal reaction is unsettled, although Chen *et al.* [28] also proposed a yolk@shell structure with tiny Si dispersed inside by MR method. The results show that the material with different length (0.25 nm) lattice fringe adjacent to these Si particles is SiC [29]. It is well known that the temperature of the direct reaction between Si and C will only occur when the temperature exceeds 1100 °C, which is much higher than the temperature used for the MR reduction. In this study, NaCl cannot fully absorb the large amount of heat released by the thermal reaction, heating the surrounding atmosphere to the temperature required for the reaction between Si and C, thereby forming SiC nanodots [30]. However, the heat formed from MR reaction is hardly controlled, so the size of SiC and the size ratio of SiC with Si in one particle are irregular. The adjacent relationship between SiC and Si endows SiC an interesting role as double side tape to anchor the Si particles onto the C inner wall, providing a good compatible interface. Compared with amorphous carbon materials, it has better mechanical stability, so a small amount of SiC can increase the structural stability

of electrode materials [31–33].

From the selected area electron diffraction pattern of the composite material, it can also be seen that there is a crystal structure (Fig. S3(a) in the ESM), which also corresponds to the above-mentioned Si and SiC crystals. Figure S3(b) in the ESM shows the carbon skeleton after Si is etched away with a dilute NaOH solution. The existence of three-dimensional interconnected amorphous carbon shells can be undoubtedly seen and they all show a relatively regular spherical shape, which indicates that resorcinol and formaldehyde have penetrated into the material and covered the surface of each SiO₂. The carbon shell can still remain intact during the subsequent MR process.

The X-ray diffraction (XRD) pattern of the PSi/C composite material can reflect the composition and phase structure of the material, as shown in Fig. 4(a). It can be detected that the characteristic peaks of 2θ at 28.4°, 47.3°, 56.1°, 69.1°, and 76.4° correspond to the (111), (220), (311), (440), and (331) planes of Si (JPCDS No. 27-1402), respectively, which shows that SiO₂ reacts with magnesium vapor to form Si during the thermal reduction [33]. The characteristic peak of 2θ at 35.6° corresponds to the (111) plane of SiC (JPCDS No. 74-2307), which means that the local heat generated during MR causes the formation of SiC due to the direct

Fig. 4 Characterization of PSi/C composite. (a) XRD pattern; (b) Raman spectra; (c) N₂ adsorption–desorption curve; (d) pore size distribution curve.

react of Si and amorphous carbon [20]. The broad peak around 22° can be attributed to the presence of the amorphous carbon layer, except that no other impurity peaks were found. These results are consistent with those observed in the above TEM images.

The Raman curve of the PSi/C powder in Fig. 4(b) shows two characteristic peaks of carbon at 1337.8 and 1598.6 cm^{-1} , corresponding to the disordered D band and graphite G band ($I_D/I_G = 1.09$). The strong D peak indicates that the carbon material in the composite material is in the state of amorphous carbon, which is consistent with the above XRD pattern. The two peaks centered at 516 and 948 cm^{-1} correspond to the characteristic peaks of crystalline silicon. The wavelength of 516 cm^{-1} is lower than that of bulk silicon (520 cm^{-1}), which means its tiny nano-sized morphology [34,35]. The Raman result is consistent with the observation in HRTEM.

The porous properties of PSi/C composites were measured by N_2 adsorption–desorption isotherm. Figure 4(c) shows a typical type IV adsorption–desorption isotherm, which proves the porous characteristics of the sample [36,37], and the BET specific surface area (SSA) is $304.81\text{ m}^2\cdot\text{g}^{-1}$. The reason of high SSA is mainly attributed to the amorphous carbon layer, the internal unoccupied inner hollow space, and the voids/channels formed during MR. Barrete–Joynere–Halenda (BJH) method is used to calculate the pore size distribution of the sample (Fig. 4(d)). The results show that the pore structure of the sample covers the micro- and meso-pores. The smaller pores are left by the removal of surfactants Hypermer and CTAB, while the larger pores are formed from MR and acid washing process, or the space gap between different Si nanoparticles. These pores provide a buffer space for the volume expansion in the lithium

process and give the sample a good cycling stability.

According to the XPS survey vision of the PSi/C composite, there are three elements (O, C, and Si) in the as-characterized sample without any other heteroatoms (Fig. S4(a) in the ESM). After fitting the high resolution vision of Si 2p (Fig. S4(b) in the ESM), two peaks representing Si–O and Si–C bonds can be recognized at 103.7 and 104.5 eV , respectively. The former Si–O band should be introduced by the absorption of water or oxygen on the surface of nano-Si particles because of the high surface energy of nano-scaled Si materials [38]. And the peak appearing at $99\text{--}103\text{ eV}$ is assigned to Si nanoparticles. However, XPS is a method to analyze the elements on the surface of the sample, so the ratio can not reflect the real value effectively. In order to determine the correct proportions of free carbon, SiC, and Si in this composite, we resort to TGA and C/S analyzer and the results are shown in Fig. S5 and Table S1 in the ESM. The content of free carbon can be easily gained from TGA (18.6%), and the total C element in the sample is 25.9% from C/S analyzer. Finally, the proportions of different components are calculated as 18.6%, 24.3%, and 57.1% of free carbon, SiC, and Si, respectively.

PSi/C was coated on the Cu foil cooperated with binder and conductive agent as the anode (surface density is $3.49\text{ mg}\cdot\text{cm}^{-3}$), and its electrochemical properties were tested in a half cell. In order to better analyze the redox reaction of the anode material during the cycle, the CV curve of the PSi/C composite material was tested at a scan rate of $0.5\text{ mV}\cdot\text{s}^{-1}$ in the voltage range of $0.01\text{--}2.0\text{ V}$, shown in Fig. 5(a). In the first cathodic scan, there was a cathode peak at about 0.40 V , which was mainly due to the formation of SEI film on the surface of carbon materials and the irreversible consumption of lithium

Fig. 5 Electrochemical performance of the PSi/C anode for the first 3 cycles. (a) Cyclic voltammetry curve, where the scan rate is $0.5\text{ mV}\cdot\text{s}^{-1}$ tested in the voltage range of $0.01\text{--}2.0\text{ V}$; (b) discharge/charge curves under a current density of $0.2\text{ A}\cdot\text{g}^{-1}$.

ions in the first lithiation process. However, the cathode peak disappeared during the subsequent cycles, and a new cathode peak appeared near 0.19 V, which corresponds to the phase transition from amorphous a-Si to amorphous a-Li_xSi [39]. In the anode scan, due to the delithiation reaction of the a-Li_xSi alloy phase and the formation of amorphous silicon, the electrode material has two anode peaks near 0.32 and 0.53 V. By comparing the scans of the first 3 cycles, it can be found that both the cathode peak and the anode peak increase a lot, which is mainly due to the continuous activation of the active material during the previous cycles [40].

Figure 5(b) depicts the first 3 charge and discharge characteristics of the PSi/C anode at a current density of 0.2 A·g⁻¹ in the voltage range of 0.01–2.0 V. During the first discharge, the longer sloping potential plateau from about 0.4 V is due to the irreversible formation of the SEI film, which is consistent with the results observed in the CV curve. During the first charge and discharge, the charge and discharge capacities of the PSi/C anode are 1825.8 mAh·g⁻¹ (energy density is 155.2 Wh·kg⁻¹) and 1313.3 mAh·g⁻¹, respectively, and the initial coulombic efficiency reaches 72%. The initial irreversible capacity loss (28%) was mainly attributed to the formation

of the SEI film or the irreversible trap of Li⁺ on the surface of the amorphous carbon layer [41]. In the first four deep cycles, the composites are gradually activated to form stable SEI and develop proper structural network [42]. After activation, coulombic efficiency can achieve to 97% and be stable at 99% in the future cycling (Fig. 6(b)).

In order to explore the lithium ion and charge transfer resistance of the electrode material, an EIS test was performed on the PSi/C anode in the frequency range of 0.01–100 Hz, and the results are shown in Figs. 6(a) and S6 in the ESM. It can be seen that the charge transfer resistance in the high-frequency region is small (about 44.57 Ω), while the slope is large in the low-frequency region, indicating that the diffusion rate of lithium ions inside the material is high. For comparison, EIS spectrum of bare Si nanoparticles was also detected, showing a larger charge transfer resistance. The results indicate the multipoint contact mode nature between Si and C shell of the PSi/C anode material diffusion.

We tested the rate performance of PSi/C material, and the results are shown in Fig. 6(c). The capacity of PSi/C electrode material is about 1400, 1050, 800, and 500 mAh·g⁻¹ at current densities of 0.2, 0.5, 1, and 2 A·g⁻¹, respectively. When the current density returns to 0.5 A·g⁻¹

Fig. 6 Battery performance of PSi/C anode. (a) EIS curve before cycling; (b) cycling performance at 0.2 A·g⁻¹ current density; (c) rate performance under various current densities; (d) cycle performance under the current density of 1 A·g⁻¹ (the current density of the first 3 cycles is 0.2 A·g⁻¹).

again, the capacity can be restored to $1050 \text{ mAh}\cdot\text{g}^{-1}$ with 100% recover capacity, which shows that the structure can remain stable even at a higher current density. The sufficient void space inside the PSi/C composite material can buffer the expansion of the silicon electrode, and the presence of amorphous carbon [43] and SiC can isolate the direct contact between silicon and the electrolyte and show good structural stability.

Figure 6(b) shows the cycle curve of the PSi/C anode at a current density of $0.2 \text{ A}\cdot\text{g}^{-1}$. It can be seen that the specific capacity after 40 cycles can reach $872.6 \text{ mAh}\cdot\text{g}^{-1}$, which is about 3 times that of the graphite anode. The cycle stability at higher current density also determines an important factor in the industrialization of electrode materials. The cycle performance of the PSi/C anode at a current density of $1 \text{ A}\cdot\text{g}^{-1}$ is shown in Fig. 6(d). The first 3 cycles show the activated cycles at a rate of $0.2 \text{ A}\cdot\text{g}^{-1}$. From the 4th to the 100th cycle, the specific capacity is reduced from 967 to $629 \text{ mAh}\cdot\text{g}^{-1}$, more than 65% of the capacity is retained, and the coulombic efficiency is as high as 99%. Si nanoparticle shows a great decrease within first 30 cycles, and it reaches almost $20 \text{ mAh}\cdot\text{g}^{-1}$ after 40 cycles even at a small current intensity of $0.5 \text{ A}\cdot\text{g}^{-1}$, indicating that the Si/C anode with special structure formed from MR reaction has good cycle stability.

Recent work related to SiC containing Si-based anodes for LIBs was summarized in Table S2 in the ESM to give a comparison. The pomegranate-type Si/C composite in this work can deliver good electrochemical performance and cycling performance, and it has to be considered as an efficient method to prepare potential LIB anodes. Structure stability is the basic of cycling stability. We checked whether the pomegranate-type structure can be maintained after deep cycling by SEM characterization. From Fig. S7 in the ESM, a pomegranate-type framework can be seen clearly, suggesting that the structure can be destroyed by cycling, and the rougher surface compared with SEM image before cycling is due to uniform SEI film formed on the material surface [44]. The intact structure inhibits the continuous electrolyte deposition and ensures the uniform formation of SEI film. These factors ensure its good electrochemical performance.

4 Conclusions

In this work, we used low-cost TEOS as the silicon source, and synthesized a pomegranate-shape-like micron-scale

Si/C composite through the industrially commonly used microemulsion method and magnesiothermic reduction method. In this unique structure, the sufficient void space can buffer the volume expansion of silicon during the cycle, and the well dispersed tiny silicon particles are well covered by the carbon layer to prevent excessive SEI film formation. The multipoint contact mode endowed by tape-role-like SiC and the three-dimensional interconnected carbon shell provide a certain path for the transmission of lithium ions and electrons, which enables the electrode material to have higher coulombic efficiency. The formation of SiC at local irregular high temperature by MR has an important contribution to the structural stability. Therefore, the PSi/C anode shows better cycle stability during the cycling, and more than 65% of the capacity remains after 100 cycles at a current density of $1 \text{ A}\cdot\text{g}^{-1}$.

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Electronic Supplementary Material

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