



# Carbon-shell-constrained silicon cluster derived from Al-Si alloy as long-cycling life lithium ion batteries anode



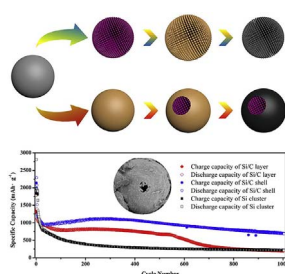
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## HIGHLIGHTS

- A novel nanostructure — carbon-shell-constrained Si cluster (Si/C shell).
- The structure provide enough void space and electrical contact sites.
- The Si/C shell delivers 0.03% capacity loss from in each cycles.
- The structure of Si anode guarantees the stability of electrodes.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

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## ABSTRACT

Although silicon is the most promising anode material for Li-ion batteries, large volume expansion during lithiation and delithiation is the main obstacle limiting the commercial application of silicon anodes. There are two ways to alleviate volume expansion and prevent further pulverization of a Si anode: fabrication of a rational nanostructure possessing void spaces and uniform distribution of the conducting sites, without a good balance effect in mitigating the limiting factors and enhancing battery performance. In this paper, we propose a novel nanostructure — a carbon-shell-constrained Si cluster (Si/C shell) with both adequate void space and good distribution of electrical contact sites to guarantee homogeneous lithiation in the initial cycle. Benefiting from the ability to maintain electrical conductivity of the outer carbon shell, even after cluster fragmentation, the Si/C shell synthesized from low-cost commercial Al-Si alloy spheres can deliver 0.03% capacity loss from 100<sup>th</sup> to 1000<sup>th</sup> cycles at a current density of 1 A g<sup>-1</sup>. The Si/C shell sample with the dual functional structure mentioned above can also maintain its own nanostructure during cycling and deliver excellent rate performance. It is a concise and scalable strategy which can simplify the preparation of other alloy anode materials for Li-ion batteries.

## 1. Introduction

In light of today's fossil energy shortages, the burgeoning portable electronics and electric vehicle industries have created an urgent demand for high-energy lithium-ion batteries (LIBs) with prolonged cycling performance for its higher energy density, longer cycling life [1–6]. To further enhance the power density of LIBs, high performance

anode materials are required for large-scale application. Among all alloy anode materials have been studied, such as Si, Ge, Sn, and metallic oxide, Si is the most promising substitute for current commercial graphite anodes (theoretical capacity 372 mAh g<sup>-1</sup>) due to its high theoretical specific capacity (~4200 mAh g<sup>-1</sup>), low voltage (< 0.5 V versus Li/Li<sup>+</sup>), environmentally friendly properties, and elemental abundance [7–10]. Beyond those merits, pulverization of Si particles resulting from

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large volume changes ( $\sim 300\%$ ) during lithiation and delithiation processes harms the stability of anode electrodes, which inevitably leads to loss of electrical contact and diminished capacity and further restricts its application in mass energy storage LIBs [11–14]. To overcome this drawback, many nanostructures of silicon anode with a reasonable distribution of void space to absorb volume stress have been proposed, such as porous [15–18], three-dimensional networks [19–22], hollow spheres [23,24], yolk shells [24–27], graphene sandwich [28–30], and free-standing conductive paper [31,32], but all of which require high cost, complicated synthesis and post-processing.

The uniformity of the first lithiation of silicon anode is vital to the long cycling performance of LIBs. As had been proved in many papers, silicon with better electrical conductivity has kinetic advantage of lithiation, so the average distribution of conductive sites is an important factor in electrochemical performance [33–36]. Therefore, in addition to providing void space, the average distribution of conductive sites on the surface of silicon should also be taken into account in the design of material nanostructure, which benefits the uniformity of lithiation in the first cycle and stability of both anode materials and electrodes [21,35,36]. The synergistic effect provided by these two aspects is the key to guarantee the life cycle of silicon anode.

In this work, we demonstrate a low-cost and scalable method of constructing a reasonable structure, carbon-shell-constrained silicon clusters (Si/C shell), from commercial Al-Si alloy spheres. This material possessing both adequate void space and conductive sites exhibits excellent cycling performance for 1000 cycles at  $1 \text{ A g}^{-1}$  and delivers 0.03% capacity after from 100<sup>th</sup> cycles. In addition, the sample of Si/C shell could keep its structural stability of electrodes after cycles, but Si clusters coated with carbon layer (Si/C layer) do not.

## 2. Materials and methods

### 2.1. Synthesis of Si/C shell and Si/C layer

In a typical process to coat phenolic resin on Al-Si alloy spheres, 2.5 g AlSi alloy spheres (Al:Si = 80:20 wt%, Jiweixin Co., China), 0.04 g hexadecyl trimethyl ammonium bromide, and 1 mL ammonium hydroxide (25%  $\text{NH}_3\text{H}_2\text{O}$  aqueous solution) were put into a mixed solution (200 mL ethanol and 100 mL deionized water) followed by ultrasonic dispersion for 30 min to obtain a homogeneous suspension. After stirring for 100 min at room temperature, 0.3 g resorcinol was added to the suspension and stirring maintained for an additional 2 h. Then, 0.4 mL formaldehyde (38% aqueous solution) was added to the suspension followed by stirring for 12 h. The obtained Al-Si/RF spheres were centrifuged and washed with deionized water and ethanol three times and dried in an oven at  $80^\circ\text{C}$ . To eliminate the Al component in the Al-Si alloy, the obtained Al-Si/RF spheres were etched in a 2 M HCl aqueous solution with gentle stirring for 12 h, followed by filtering and washing three times with deionized water, and drying at  $80^\circ\text{C}$  so that the Si cluster packaged in the RF shell (Si/RF shell) was obtained. Finally, the Si/RF shell was transferred to a tube furnace and heated at  $800^\circ\text{C}$  for 5 h and converted to Si/C shell. The only difference in the synthesis procedure of the Si/C layer to Si/C shell is the Al-Si alloy spheres were RF coated after etching step.

### 2.2. Material characterizations

XRD measurements were carried out using a D8-Advance x-ray diffractometer (Cu  $K\alpha$ ,  $\lambda = 1.5406 \text{ \AA}$ ) at 40 kV and 40 mA. The morphologies and structures of the two samples were characterized by FESEM (S-4800, Hitachi Ltd., Japan) and FRTEM (JEM-2100F, JEOL Ltd., Japan). The carbon content of samples were measured with TG analysis (209 F1 NETZSCH at oxygen airflow (20 mL/min)). Surface area analysis was carried by Micromeritics Tristar 3000. Cyclic voltammetry (CV) measurements were performed on a CHI 660C electrochemical workstation (CH Instruments, Inc., U.S.A.) at a sweep rate of

$0.1 \text{ mV s}^{-1}$ . The galvanostatic discharge/charge performance was measured on a Land CT2001A battery test system (Wuhan Jinnuo Electronics Co., Ltd., China).

### 2.3. Electrochemical testing

The two samples obtained were mixed with carbon conductive agents (Super P) and binder (sodium alginate) at a weight ratio of 6:2:2 to make a homogeneous slurry, and followed by casting on a copper foil, drying in a vacuum oven at  $80^\circ\text{C}$  for 12 h and cutting into 12 mm-diameter discs. The average load of active material in each electrode was approximately  $1 \text{ mg cm}^{-2}$ . Coin-type cells (CR2016) were assembled in an Ar-filled glove box (Superstar 1220/750/900 Mikrouna, China) using metallic lithium foil as a counter electrode. The electrolyte employed was 1.0 M  $\text{LiPF}_6$  in 1:1 vol/vol ethylene carbonate/dimethyl carbonate with 10 vol % fluoroethylene carbonate and 2 vol % vinylene carbonate additives. The cycling performance of cells at different currents was tested in the voltage range from 0.01 to 1.2 V (versus  $\text{Li/Li}^+$ ) at  $25^\circ\text{C}$ . Unless otherwise specified, the specific capacity referred in this paper was calculated based on the total weight of the samples.

## 3. Results and discussion

A scheme of three steps required to synthesize such a structure is shown in Fig. 1a (details in Method). A silicon cluster coated by a carbon layer (Si/C layer) is also synthesized for comparison. As shown in Fig. 1b, x-ray powder diffraction (XRD) patterns of all samples (include intermediate products) are assigned to two components, aluminum and silicon, and the aluminum is completely removed after an etching step.

The sizes of samples are determined by the commercial raw material as acquired, and the morphology of all samples are shown in Fig. 2. As shown in Fig. 2a, the diameter of the Al-Si alloy spheres ranges from 0.2 to  $2 \mu\text{m}$ , and the silicon component exists in the Al-Si alloy spheres in the shape of the cluster consisting of silicon nanorods (Fig. 2b). Fig. 2d is an image of the Si/C layer converted from the Si cluster coated by a phenolic resin layer (Si/RF layer, Fig. 2c). The aluminum component in Al-Si spheres coated with a phenolic resin layer (Al-Si/RF) (Fig. 2e) has been removed completely by an acid etching step, in which hydrogen generated from the reaction of aluminum and hydrochloric acid breaks through and creates holes in the RF shell, so that a Si cluster packaged in a RF shell (Si/RF shell, Fig. 2f) forms. After carbonization of the RF shell in argon atmosphere, a Si/C shell (Fig. 2g and h) is generated. As shown in Fig. 3a, the carbon content of the Si/C layer and Si/C shell is 25% and 20%, respectively. Raman spectrum (Fig. 3b) suggests that the peak area ratio of D and G bands and the carbon type in the two samples are the same, because they are both carbonized from the same phenolic resin, and the distribution and shape have no effect on the phenolic resin. The specific surface area of the Si/C layer and Si/C shell is 200 and  $258 \text{ m}^2 \text{ g}^{-1}$ , respectively (nitrogen adsorption-desorption isotherm linear plot and are shown in Fig. 3c). The two samples are deliver the similar adsorption and desorption isotherms (type II), but Si/C shell could provide an additional area for the presence inside and outside surface of C shell. And as shown in nonlocal density functional theory (NLDFT) pore size distribution curves (Fig. 3d), the two samples have the same pore size distribution.

To further investigate the inner structure of the Si cluster, Si/C layer and Si/C shell, transmission electron microscopy (TEM) images were generated, and are shown in Fig. 4. The Si cluster consists of Si nanorods connected at the center of the Al-Si sphere (Fig. 4a). Because of the swelling stress coming from lithiation of one-dimensional Si nanorods mainly releases in the radial direction [37,38], and because the void space among nanorods occupied by the aluminum component before acid etching can absorb the swelling stress, the Si/C shell possesses excellent structural stability. It is worth noting the existence of an amorphous silica layer ( $\sim 2 \text{ nm}$ ) on the surface of the Si nanorods

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