

Silicon-based nanomaterials for lithium-ion batteries

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Silicon-based nanomaterials have been of scientific and commercial interest in lithium-ion batteries due to the low cost, low toxicity, and high specific capacity with an order of magnitude beyond that of conventional graphite. The poor capacity retention, caused by pulverization of Si during cycling, triggers researchers and engineers to explore better battery materials. This review summarizes recent work in improving Si-based anode materials via different approaches from diverse Si nanostructures, Si/metal nanocomposites, to Si/C nanocomposites, and also offers perspectives of the Si-based anode materials.

silicon, high energy density, nanomaterials, anode, lithium-ion batteries

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Lithium ion batteries (LIBs) as attractive energy storage devices have become ubiquitous power sources for mobile electronics. Increasing power and energy requirements for applications such as electric and hybrid electric vehicles, have spurred intense interest in developing high capacity electrode materials to surpass the capacities of electrode materials used in current LIBs [1–7]. To achieve the requirements, much research work has been performed on new anode materials with high specific capacities.

Silicon has attracted increasing attention as a potential high-capacity anode material because of numerous appealing features such as high theoretical specific capacity of 4212 mAh g⁻¹, higher safety and stability than graphite (lithiated silicon is more stable in typical electrolytes than lithiated graphite). Si anode materials, however, suffer from some drawbacks involving the drastic volume change (larger than 300%) during the alloying/de-alloying reactions with Li [8], the intrinsic low electrical conductivity, and the unstable solid electrolyte interphase (SEI) formed in the common electrolyte of LiPF₆. These limitations still challenge the investigation and development on identification of higher capacity for the next generation LIBs. Various ad-

vances in Si morphology have been achieved in the past years, demonstrating that nanostructured Si-based materials particularly offer superior properties in LIBs.

In this review, we address the recent developments in optimizing Si-based materials via diverse Si nanostructures, Si/metal nanocomposites, and Si/C nanocomposites. In addition, we offer some perspectives for the design of better Si nanomaterials.

1 Si nanostructures

In principle, Si-based bulk materials exhibited a marked loss of capacity in a few cycles. To alleviate the absolute volume variation during cycling, diverse Si nanostructures have been developed. It has been demonstrated that Si nano-powder (78 nm) could exhibit a better capacity retention than the commercial Si powder (250 mesh) [9]. The improvement was assigned to the shortening of lithium ion diffusion distance and enhancing the electroactivity toward Li uptake/release.

Controlling the nanoparticle shape as well as size can offer advantages, which is illustrated by recent results on different morphologies of Si. Zero-dimensional (0D) Si nano-

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spheres were constructed with enhanced electrochemical performances due to preventing Si particles' aggregation on the nanometer scale. Nest-like Si nanospheres prepared by a modified solvothermal method exhibited a large specific capacity of 3052 mAh g^{-1} under a current density of 2000 mA g^{-1} (ca. 0.5 C) in the electrolyte of 1 mol/L LiPF_6 dissolved in a 3:1:1 mixture of ethylene carbonate (EC), propylene carbonate (PC) and diethyl carbonate (DEC) [10]. After cycling of up to 48 cycles under 2000 mA g^{-1} , the electrode modified by the nest-like Si nanospheres still showed a specific capacity of 1095 mAh g^{-1} . Additionally, an excellent capacity retention was noted for the interconnected Si hollow nanospheres electrode (Figure 1) [11], synthesized via chemical vapor deposition (CVD) of Si on silica particles and then etching SiO_2 by HF. The as-prepared hollow spherical structure was capable of delivering a high initial discharge capacity of 2725 mAh g^{-1} at a rate of 0.1 C in the electrolyte of 1 mol/L LiPF_6 in a 1:1 (w/w) EC/DEC mixture. Even after 700 cycles, the Si hollow sphere electrode still retained 1420 mAh g^{-1} at a rate of 0.5 C .

One-dimensional (1D) nanowires or nanotubes are also intriguing structures with good cycle stability. For example, Si nanowire electrode without binder, synthesized via the vapour-liquid-solid process on stainless steel substrates using Au catalyst, exhibited a reversible capacity of 3193

mAh g^{-1} over 10 cycles at a $\text{C}/20$ rate in the electrolyte of 1 mol/L LiPF_6 in a 1:1 (w/w) EC/DEC mixture [12]. Array of sealed Si nanotubes (Si NT), prepared by CVD of Si onto ZnO nanorods and selective removal of ZnO (Figure 2), showed 3360 and 1490 mAh g^{-1} of charge capacity at rates of 0.05 and 0.2 C respectively in the electrolyte of 1.3 mol/L LiPF_6 in EC/DEC (3:7 in volume). The capacity retentions after 50 cycles are about 81% and 82% at 0.05 and 0.2 C , respectively [13]. Possibly, 1D nanostructures might undergo facile strain relaxation and expand freely to accommodate the volume change during cycles.

Two-dimensional (2D) Si thin film is another promising nanostructure with improved cycle stability and rate capabilities. Basically, nanosized thin film can minimize the volume variation and retain structural integrity. The cycling stability and the Li accommodation capacity mainly depend on the film thickness as thinner films deliver larger accommodation capacity. A 50 nm -thick Si film prepared from n -type Si was found to deliver a charge capacity over 3500 mAh g^{-1} and maintained during 200 cycles at a rate of 2 C , while a 150 nm -thick film showed around 2200 mAh g^{-1} during 200 cycles at 1 C in the electrolyte of 1 mol/L LiClO_4 in PC [14]. Although Si thin films offer high specific capacity, good capacity retention and fast charge/discharge rate, the practical application is hampered because of their

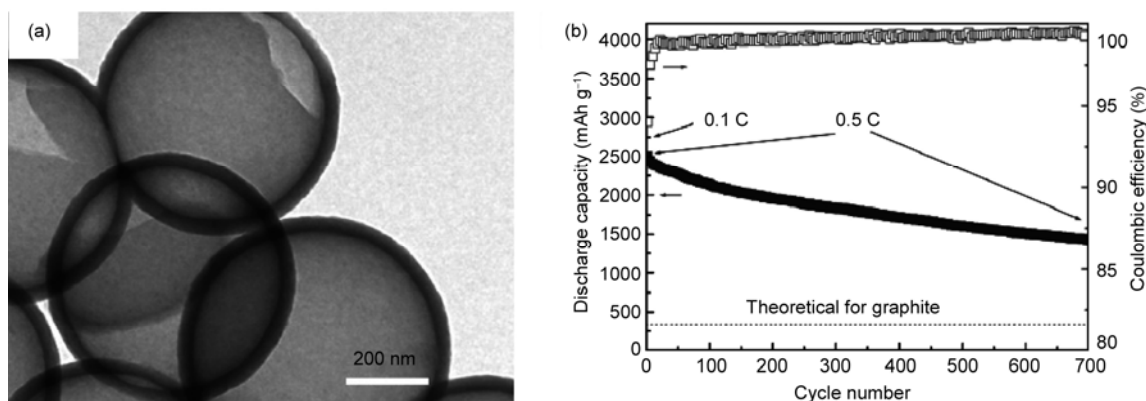


Figure 1 (a) TEM image and (b) reversible Li discharge capacity and Coulombic efficiency versus cycle number of interconnected hollow Si spheres. Reprinted with permission from [11]. Copyright (2011) American Chemical Society.

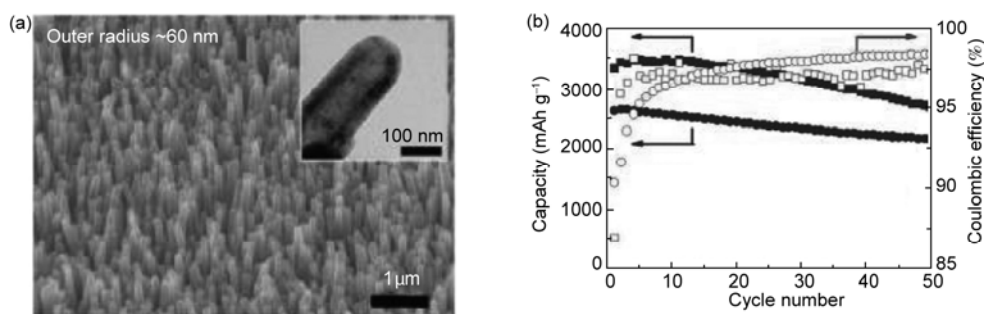


Figure 2 (a) SEM image (insets showing high magnification TEM images of the sealed tip of a Si NT) and (b) cycle performances at a rate of 0.05 and 0.2 C (square: 0.05 C , circle: 0.2 C) of a vertically aligned Si NT array. Reprinted with permission from [13]. Copyright (2010) American Chemical Society.

prohibitively high synthesis costs for industry and low active material content.

2 Si/metal composites

In comparison with bulk Si materials, the pristine nanostructures of Si have shown improved capacity retention. However, the greatest disadvantage of the pristine nanostructures with high surface areas may lead to the risk of excessive side-reactions with the electrolyte [6]. Furthermore, the pristine nanosized Si anode materials are still plagued with the intrinsic low electrical conductivity of Si. Various studies have demonstrated that utilization of Si-based nanocomposites can circumvent the limitations of pure Si nanomaterials. In this context, metal with good electronic conductivity is one appealing candidate to cooperate with Si for improving lithium storage properties, especially rate capabilities.

Ag-coated three-dimensional (3D) macroporous Si has been constructed, in which Ag nanoparticles formed an interconnected conductive network, providing electron path-

ways from the current collector to the whole surface area of the 3D porous Si particles. The Ag-coated 3D macroporous Si delivered not only a reversible capacity of 1163 mAh g^{-1} at a rate of 0.2 C after 100 cycles (Figure 3), but an enhanced rate capability of 1930 mAh g^{-1} at a rate of 1 C in the electrolyte of 1 mol/L LiPF_6 in dimethyl carbonate (DMC)/EC (1:1 in volume) containing 2 wt\% vinylene carbonate (VC) [15].

In addition to the electrochemical active silver toward lithium storage, electrochemical inactive metal silicides with good conductivity also favor the effective charge transport. Si/TiSi₂ heterostructures (Figure 4), consisting of TiSi₂ nanonets coated with Si nanoparticles, displayed above 99% capacity retention per cycle at the level of $>1000 \text{ mAh g}^{-1}$ over 100 cycles under a charging current density of 8400 mA g^{-1} in the electrolyte of 1 mol/L LiPF_6 in EC/DEC (1:1 in volume) [16]. The excellent performance was attributed to the highly conductive TiSi₂ nanonets used as the structural support. Another typical metal silicide, Cu₃Si, as reported recently by our laboratory, was *in situ* formed on the surface of Si nanoparticles by annealing Si/copper alginate microspheres in an inert atmosphere. The

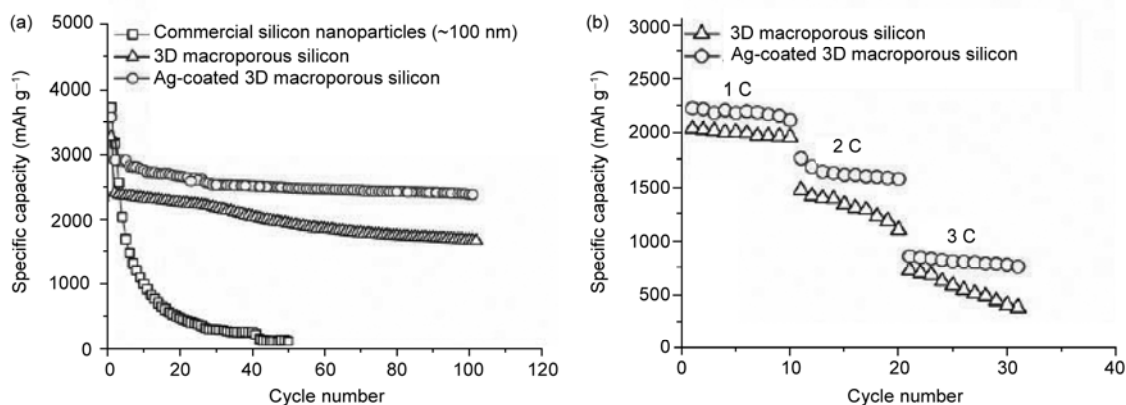


Figure 3 (a) Cyclability of 3D macroporous Si, Ag-coated 3D macroporous Si, and commercial Si nanoparticles; (b) rate capabilities of 3D macroporous Si and a Ag coated 3D macroporous Si electrode. The current densities are indicated in (b). All of them were tested at a rate of 0.2 C in a voltage range of 5 mV – 1.0 V . Reprinted with permission from [15].

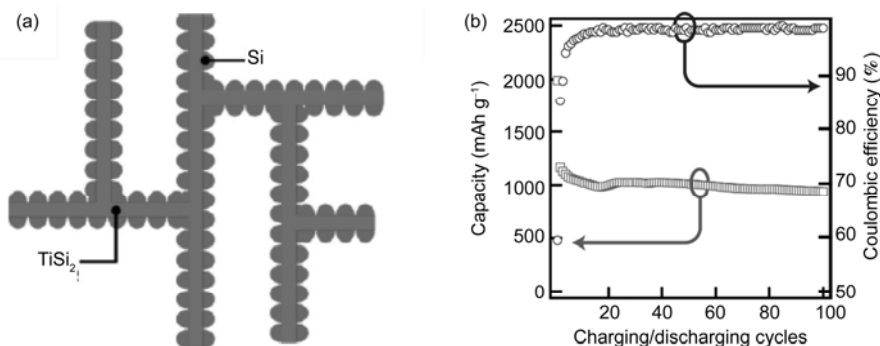


Figure 4 (a) Schematic and (b) charge capacity and Coulombic efficiency under a current density of 8400 mA g^{-1} between 0.15 – 3.00 V of the Si/TiSi₂ heterostructure. Reprinted with permission from [16]. Copyright (2010) American Chemical Society.

utilization of Cu_3Si endowed the resulting Si/C nanoporous microspheres with enhanced cycling performance and rate performance compared with Si nanoparticles [17]. Aside from the improvement of conductivity for Si/metal nanocomposites, inactive metal oxides coating was utilized to form stable SEI on the surface of electrode materials in the common electrolyte of LiPF_6 . An elegant Cu-Si nanocable array (Figure 5) was prepared firstly from the growth of CuO nanowire arrays by heating a copper current collectors in oxygen atmosphere. Then the CuO nanowire arrays were coated with Si and Al_2O_3 step by step, and subsequently annealed in reduced atmosphere [18]. The Cu-Si- Al_2O_3 nanocables exhibited a specific capacity of about 1560 mAh g^{-1} after 100 cycles under a current density of 1400 mA g^{-1} in the electrolyte of 1 mol/L LiPF_6 in a mixture of EC/DMC/DEC (1:1:1 wt%) plus 2 wt% VC. Furthermore, the nanocables displayed a specific capacity of 1490 and 1140 mAh g^{-1} as increasing the current density to 2800 and 7000 mA g^{-1} , respectively. The remarkably high rate capability mainly benefits from the unique configuration of nanocables with excellent ionic-electronic conductivity [19–21]. The attractive structure of Cu-Si- Al_2O_3 nanocables enabled lithium ion to diffuse readily into Si nanolayer from the outside liquid electrolyte. The copper core inside acts as the continuous electron diffusion pathway and thereby allows for fast electron transport in the electrode. In addition,

the Al_2O_3 coating layer on Si surface serves as a thin and stable surface and thereby facilitates the formation of stable SEI layer in the common electrolyte of LiPF_6 upon cycling.

3 Si/C composites

Concerning graphite, the commercial anode material, tremendous studies have focused on carbonaceous materials, owing to their unique characteristics (relative softness, small volume change during Li insertion/extraction, good electronic conductivity, and the moderate SEI formation). Incorporation of Si/C nanocomposites represents one attractive route to conquer the intrinsic drawbacks of Si.

Highly conductive carbon (such as graphite) was utilized to load Si nanoparticles by ball milling and subsequently coated with amorphous carbon, in which Si nanoparticles were embedded into a relatively dense carbon matrix [22–25]. The as-prepared Si/C nanocomposites only showed limited enhancements of cycle stability and capacity because the dense carbon matrix could accommodate the volume changes only to a limited degree.

Carbon nanotubes (CNTs) and graphene nanosheets have been widely investigated as conductive substrates to facilitate charge transport, flexibility and mechanical strength to

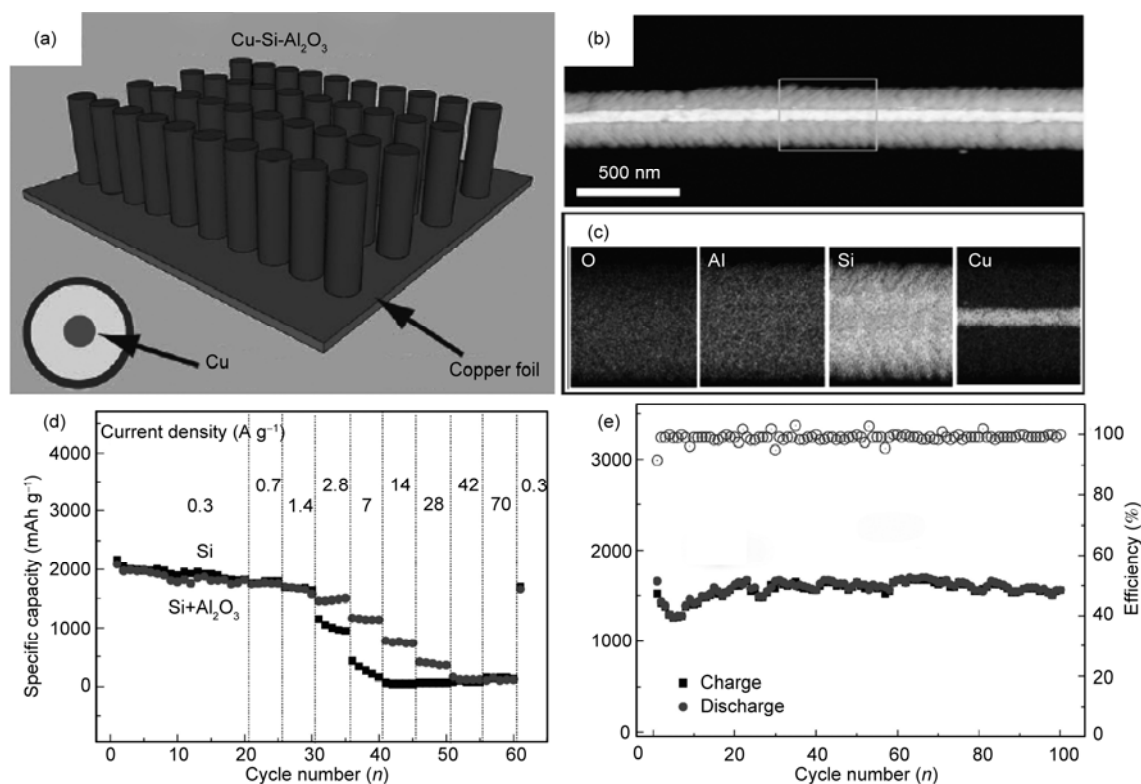


Figure 5 (a) Schematic; (b) annual dark-field TEM image and (c) corresponding EDX elemental mappings of O, Al, Si, and Cu for the Cu-Si- Al_2O_3 nanocables; (d) comparison of the rate capabilities of Cu-Si- Al_2O_3 nanocables and Cu-Si cycled under different current densities; (e) cycling behavior under a current density of 1400 mA g^{-1} of Cu-Si- Al_2O_3 nanocables. Voltage limits are between 0 and 2 V (vs. Li^+/Li). Reprinted with permission from [18].

accommodate the volume change of active electrode materials during cycles. The resulted Si/CNTs and Si/graphene nanocomposites could exhibit good cycle stability and rate performances. In this aspect, Si/CNT nanocomposites with enhanced properties were prepared either via depositing Si nanoparticles on the surface of CNTs [26] or CNTs' film [27–29], or via growing CNTs directly on the surface of Si nanoparticles [30]. Additionally, Si/graphene composite [31,32], including Si nanoparticles highly dispersed between graphene nanosheets via freeze-drying [32], showed a reversible specific capacity above 1153 mA h g^{-1} after 100 cycles in the electrolyte of 1 mol/L LiPF_6 in a mixture of EC/DMC/DEC (1:1:1 wt%) containing 2 wt% VC. Note that it is vital to uniformly disperse Si nanoparticles in CNTs or graphene nanosheets to sustain good cycle stability. The well-dispersed Si nanoparticles were actually prevented from agglomeration into even larger particles, which are considered to be more vulnerable to fracture and pulverization during cycling.

In addition to the utilization of conductive carbonaceous materials to combine with Si, core/shell structure with Si core were utilized for the formation of stable SEI via pyrolysis of organic precursors [33–36]. For example, Si nanoparticles were coated with carbon by the hydrothermal carbonization of glucose to obtain Si@SiO_x/C nanocomposite [34]. The reversible capacity of Si@SiO_x/C nanocomposite was as high as 1100 mA h g^{-1} under a current density of 150 mA g^{-1} with no further decay of capacity even after 60 cycles in the electrolyte of 1 mol/L LiPF_6 in EC/DMC (1:1, v/v) containing 2 wt% VC.

Porous configuration of Si/C anode materials was confirmed to be a viable solution due to accommodating the large volume changes of Si during cycles, although the volumetric energy density of porous materials was lower than that of dense materials. Porous Si particles with tiny walls were prepared by annealing and etching of physical composites obtained from butyl-capped Si gels and SiO₂ nanoparticles [37]. The porous Si/C composite with a highly porous and interconnected structure, showed a reversible capacity of about 2500 mA h g^{-1} at a 1 C rate after 100 cycles due to its better accommodation of large strains without pulverization during cycles in the electrolyte of 1 mol/L

LiPF_6 in a EC/DEC/ethyl-methyl carbonate (EMC) mixture (30:30:40 vol%) (Figure 6). Furthermore, Coulombic efficiencies of the porous Si/C particles at both 0.2C and 1C rates were higher than 98%. The good rate capability can be attributed to the interconnected 3D porous structure that provides fast lithium-ion mobility, and the improved efficiency may be associated with the carbon coating layer, which decreases the occurrence of side reactions with the electrolyte.

Similar to the role of porous Si framework, Si/C spherical granules with spherical carbon black scaffold was reported with impressive lithium storage properties [38]. Annealed carbon black scaffold were coated with Si nanoparticles and carbon respectively to assemble the porous Si/C granules, which exhibited the specific capacity above 1500 mA h g^{-1} at the fast discharge rate of 1C after 100 cycles in the electrolyte of 1 mol/L LiPF_6 in an EC/DEC/DMC/VC mixture (Figure 7). Highly conductive porous carbon framework provides a mechanical support for Si nanoparticles and an electrical conducting pathway to lithium ion and electrons. Also, the carbon deposited on Si nanoparticles could facilitate the formation of a stable SEI on the surface of Si nanoparticles and prevent the agglomeration of tiny Si nanoparticles.

4 Perspective

In this review, we have focused on the improvements on Si-based anode materials in terms of morphology and structure design, i.e. diverse Si nanostructures, Si/metal nanocomposites, and Si/C nanocomposites. Either designing diverse pristine Si nanostructures, or hybridizing Si/metal and Si/C nanocomposites can significantly improve the lithium storage properties of Si-based materials. As shown from previous studies, fascinating cyclic stability and high rate capabilities could be achieved when the Si-based materials have the following structure features: (1) Nanoporous structure to accommodate the volume variation during cycling; (2) fast electron conducting pathways to improve the poor electrical conductivity of Si; and (3) stable surface coating to form stable and thin SEI layer on the surface of Si.

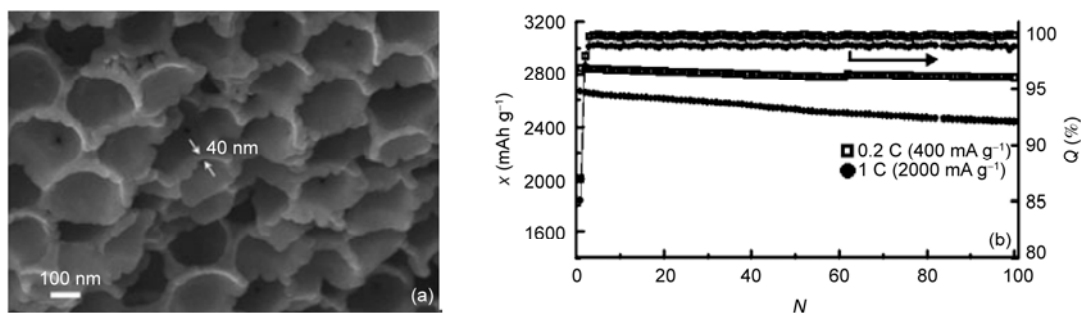


Figure 6 (a) SEM image and (b) plot of charge capacities versus cycle number of the 3D porous Si particles cycled at different rates (0.2 and 1 C) between 0 and 1.5 V. x =charge capacity, N =cycle number, Q =Coulombic efficiency. Reprinted with permission from [37].

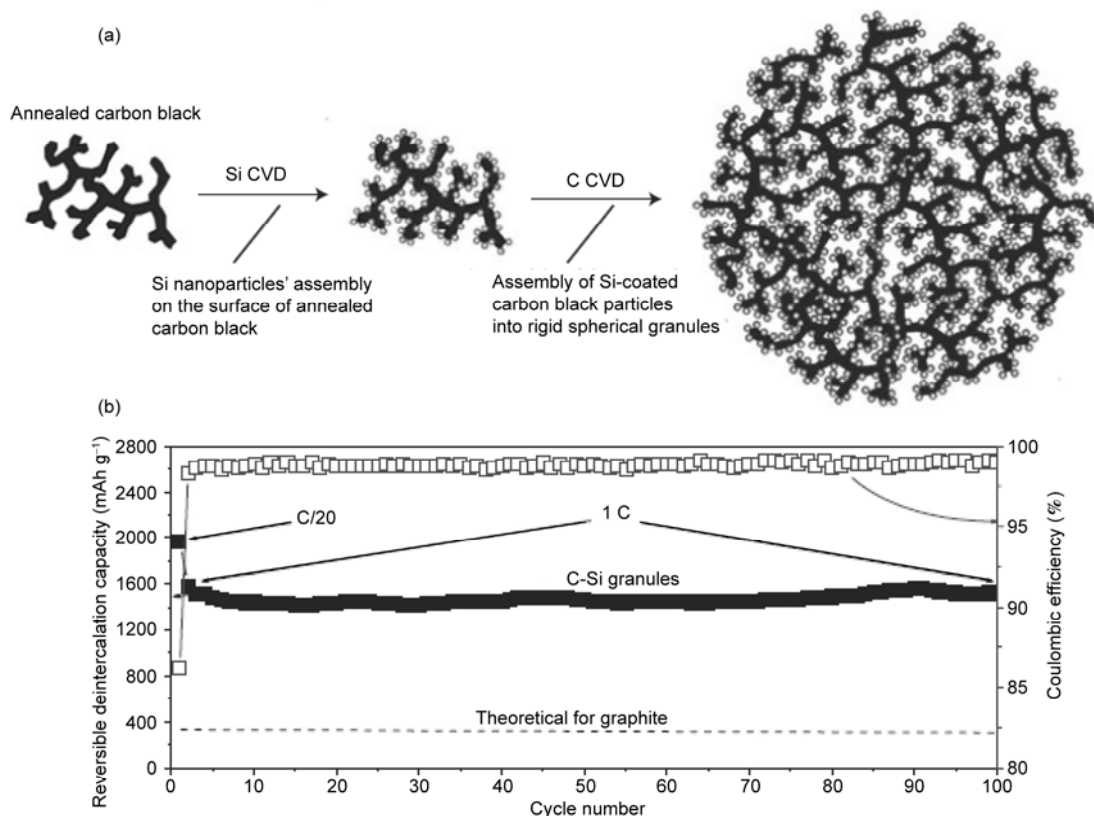


Figure 7 (a) Schematic formation of Si-C nanocomposite granule and (b) reversible Li deintercalation capacity and Coulombic efficiency of the Si-C granule electrode versus cycle number. Reprinted with permission from [38].

Although considerable advances have been achieved in the last decade to design and synthesize Si-based anode materials, some perspectives could focus on electrolytes and binders, greatly influencing the electrochemical performances of Si-based anode materials as mentioned in recent research. For nanostructured Si anode materials, the commonly used LiPF_6 electrolyte decomposes gradually and produces HF, which can etch Si. Additionally, the stable SEI film on the surface of Si is difficult to form owing to repeatedly huge volume change during cycling and the unstable nature of the surface of nanosized Si. As a result, nanostructured Si anode materials exhibited a large irreversible capacity loss (i.e. low Coulombic efficiency) and short cycle life. Except for the stable coating layer on the surface of Si [18,39], the electrolyte containing VC with 1 mol/L LiPF_6 in EC/DMC solution has been recognized to favor the formation of stable SEI [34]. Furthermore, sodium alginate, polyacrylic acid and sodium carboxymethylcellulose with carboxyl groups are potential binders for Si-based electrodes compared with the commonly used poly(vinylidene fluoride) for Si-based electrode materials [40–43]. Particularly, sodium alginate can assist in building a deformable and stable SEI film on the surface of Si, clarifying that it is vital to use a suitable binder to enhance the lithium storage for Si-based anode materials. Achieving

Si-based anode materials with good cycle stability and high specific capacity require the inputs of multiple disciplines, which challenges the design of new structures, reveal more suitable electrolytes and binders to assemble the next generation LIBs with high-energy densities and long cycle life.

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