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# Si-based anode materials for lithium rechargeable batteries

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Silicon is a very promising candidate to replace graphite as the anode in Li-ion batteries because of its very high theoretical capacity, relatively low cost and low toxicity. However, it has not yet made its way into commercial cells. This review highlights recent progress on Si-based anode materials for lithium rechargeable batteries.

Huge investments are being made worldwide in the development of silicon-based anodes for Li-ion batteries. On 17 February 2009, the Green Car Congress<sup>1</sup> reported that Nexeon Limited, a spin-off from Imperial College London, would receive additional funding of £10 million (US\$14 million) for its Silicon-Based Anode Start-up project. Although Si has a much higher theoretical specific capacity (4200 mAh/g, corresponding to a fully lithiated state of  $\text{Li}_{22}\text{Si}_5$ ) than graphite (the commercial anode material), it is still not suitable for commercial use. The reason is that silicon swells by up to 300 per cent when the alloy forms, and then shrinks when the lithium ions are released. After a few cycles of discharging and recharging, the structure of the silicon begins to crumble away and can no longer hold  $\text{Li}^+$  ions effectively, so bulk silicon breaks and loses capacity too quickly.

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Thus most work on silicon-based anode materials has been focused on the issues of volume and particle morphology changes during charge–discharge cycling.

## Nanostructured Si-based anode materials

For solving the volume change problem, researchers have developed synthetic strategies using nanostructured Si-based anode materials to release the structural stress. When employed in batteries, nanostructured active materials may also outperform the corresponding bulk form because they facilitate more efficient electronic/ionic diffusion, provide more active sites, enhance structural flexibility, and allow new reaction mechanisms.<sup>2,3</sup>

A first principles model of amorphous silicon lithiation to simulate the lithiation of amorphous Li alloys at room temperature<sup>4</sup> has yielded a potential–composition curve comparable to what is seen experimentally, as well as insight into the structural changes occurring during lithiation.

Kim *et al.* at Hanyang University in South Korea believe that they have solved the problem by a clever approach to produce 3D porous bulk Si particles that can accommodate the expansion and contraction.<sup>5</sup> The particles they made facilitate faster transport and better intercalation kinetics of lithium ions, and a rapid charge–discharge process resulted in a high specific capacity, even with a high charge–discharge current. The porous bulk Si particles with thin Si pore walls (approximately 40 nm in thickness) maintained a charge capacity of greater than 2800 mAh/g at a rate of 1 C (= 2000 mAh/g) after expanding and contracting over 100 recharge cycles.

Si nanotubes,<sup>6</sup> which were prepared by reductive decomposition of a silicon precursor in alumina template with subsequent etching, have shown impressive results. The nanotube electrodes have ultra-high reversible charge capacities of ~3200 mAh/g, and they have outstanding capacity retention of 89% after 200 cycles at the rate of 1 C in practical Li-ion cells.

The above developments are encouraging for industrial commercialisation of nanostructured Si anode material.

## Si–carbon composite anode materials

Another possible solution to overcome the volume change during cycling is to form a composite material including a matrix and an active material. The matrix can accommodate the mechanical stresses/strains of the active phase during the alloying/de-alloying processes.

L. Cui *et al.* made carbon-silicon core-shell nanowires,<sup>7</sup> which showed a high charge storage capacity of 2000 mAh/g at

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0.2 C over 30 cycles and a storage capacity of 800 mAh/g at 1 C. The material had a high coulombic efficiency of 90% for the first cycle and 98–99.6% for the following cycles, with the capacity retained at the 90% level over 100 charge-discharge cycles. The core-shell nanowire design enables a very fast cycle, about seven minutes, and can provide a very large amount of power. These results are good as those for nest-like Si nanospheres made by a modified solvothermal method,<sup>8</sup> which exhibited large specific capacity of 3628, 3291, and 3052 mAh/g at the current density of 400 (0.1 C), 800 (0.2 C) and 2000 mA/g (0.5 C), respectively. After cycling for up to 48 cycles at 2000 mA/g, the electrode made of the nest-like Si nanospheres retained 1095 mAh/g. Ma *et al.* believe the beneficial effects on the high-rate capability and cycling performance exist because the nest-like Si nanospheres prevent nano-Si aggregation and increase the density of active sites for reversible electrochemical Li storage, leading to high coulombic efficiency of nearly 100%.

Yen *et al.* reported that coating Si particles with a graphitized carbon layer has significant effects on the solid electrolyte interphase (SEI) formation. It helps to keep the Si particles intact after cycling, resulting in a smooth superficial SEI layer.<sup>9</sup>

Apart from amorphous carbon, graphite, carbon nanotubes, and mesoporous carbon as carbon matrix, as well as nanosize silicon/graphene composites,

**Table 1** The specific discharge capacities of the silicon based anodes obtained at different current densities and room temperature

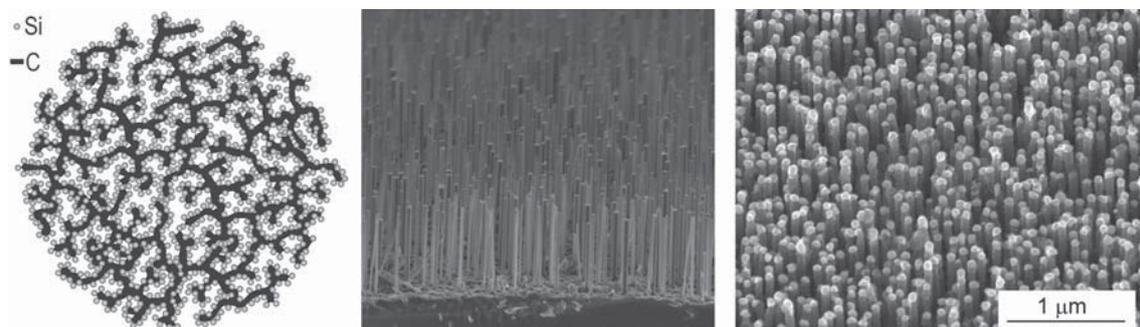
	Current density	Specific discharge capacity (mAh/g)	reference
Porous bulk Si particles with thin Si pore walls	1 C	2800 (100 cycles)	5
Si nanotubes	1 C	3200 (200 cycles)	6
C-Si core-shell nanowires	0.2 C	2000 (30 cycles)	7
Nest-like Si nanospheres	1 C	800 (100 cycles)	8
	0.1 C	3628	
	0.2 C	3291	
	0.5 C	3092	
C-coated Si	0.075 C	2000 (48 cycles)	9
Si/graphene composite	1000 (50 cycles)	10	
	0.025 C		2158
Silicon nanoparticle-graphene paper composite	0.25 C	1168 (30 cycles)	11
		2200 (50 cycles)	
Graphite/Si(15%)	0.1 C	1500 (200 cycles)	12
Si-in-C tubes	0.05 C	512 (10 cycles)	14
		4200 (9% Si)	
		3800 (33% Si)	
		2100 (46% Si)	

can also accommodate the large strains of lithium insertion and de-insertion, and provide good electronic contact, owing to the good mechanical properties and high conductivity provided by graphene. Therefore, the cycling stability can be greatly enhanced.<sup>10, 11</sup> Si/graphene composite maintains a capacity of 1168 mAh g<sup>-1</sup> and an average coulombic efficiency of 93% up to 30 cycles.<sup>10</sup> Silicon nanoparticle-graphene paper composites exhibit high Li ion storage capacities and cycling stability of > 2200 mAh/g after 50 cycles and > 1500 mAh/g after 200 cycles that decreased by < 0.5% per cycle.<sup>11</sup> These work provide a simple and feasible platform for further advances in graphene based composites. Graphite/Si(15%)<sup>12</sup> has

demonstrated an initial capacity 2.7 times greater than that of conventional graphite anodes. However the capacity loss in the initial cycle is still significant. Kang *et al.*<sup>13</sup> reported that a hybrid porous structure consisting of micro-tunnels with nano-structured surface layers appears to provide a viable and practical way to utilize silicon for anode materials in rechargeable microbatteries.

Table 1 gives the specific discharge capacities of the silicon based anodes obtained at different current densities and room temperature.

Further studies on new composite designs for silicon based anodes with improved electrochemical properties are still needed.



**Fig. 1** (a) Schematic structure of ideal Si-coated (in grey) carbon black particles (in black) into rigid spherical granules,<sup>15</sup> A. Magasinski, P. Dixon, B. Hertzberg, A. Kvit, J. Ayala, G. Yushin, High-performance lithium-ion anodes using a hierarchical bottom-up approach, *Nature Materials*, 2010, **9**, 353–358, copyright Nature Publishing Group, produced with permission. (b) SEM pictures of as-synthesized vertical Si Nanowires,<sup>16</sup> G. Yuan, H. Zhao, X. Liu, Z. S. Hasanali, Y. Zou, A. Levine, and D. Wang, Synthesis and Photoelectrochemical Study of Vertically Aligned Silicon Nanowire Arrays, *Angew. Chem. Int. Ed.*, 2009, **48**, 9680–9684, copyright Wiley-vch verlag GMBH & Co. KGaA, produced with permission. (c) Side-view SEM image with 60° tilt of Si nanowires,<sup>17</sup> T. Shimizu, T. Xie, J. Nishikawa, S. Shingubara, S. Senz, U. Gösele, High-performance lithium-ion anodes using a hierarchical bottom-up approach, Synthesis of Vertical High-Density Epitaxial Si(100) Nanowire Arrays on a Si(100) Substrate Using an Anodic Aluminium Oxide Template, *Adv. Mater.*, 2007, **19**, 917–920, copyright Wiley-vch verlag GMBH & Co. KGaA, produced with permission.

## Potential study

Porous Si with a rigid C outer shell<sup>14</sup> shows high capacity, stable performance and provides guidance for the efficient design of building blocks for viable nano-Si anodes. A large-scale hierarchical bottom-up assembly method gives an ideal Si-C structure (Fig. 1(a) containing rigid and robust spheres with irregular channels for lithium ions go in or out.<sup>15</sup> If the anode material could be made as this structure, the volume change problem could be solved. Also aligned Si-nanowires (Fig. 1(b)<sup>16</sup> and Fig. 1(c)<sup>17</sup>) as node materials for Li-ion batteries have not been studied yet, they may show the acceptable performance for industries.

## Summary

Silicon is a very promising candidate to replace graphite as the anode in Li-ion batteries because of its very high theoretical capacity. **Carbon-silicon core-shell nanowires, porous Si with a rigid C outer shell and 3D porous bulk Si particles with thin Si pore walls** have shown outstanding performance among all the Si-based anode materials

investigated for high power and long-life lithium batteries. These results, leading to the development of improved cycle life and greatly increased specific energy in lithium ion batteries, should enable their incorporation into new types of commercial equipment. High energy cells with Si anodes should allow the further development of electric and hybrid electric vehicles, as well as other applications.

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