Porous Si anode materials for lithium rechargeable batteries

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Si anode materials for lithium rechargeable batteries have received much attention due to their high capacity. The Si itself can alloy with lithium up to Li$_{4.4}$Si, corresponding to 4212 mAh/g (4.4Li $\leftrightarrow$ Li$_{4.4}$Si). However, the large volume expansion of over 300% due to the formation of various Li$_x$Si$_y$ phases generates enormous mechanical stress within the ionic character material, which becomes pulverized during the first few cycles and loses electrical integrity. Although such a drastic volume change cannot be removed completely, the degree of the volume change can be effectively reduced to utilize its application in anode materials. In this regard, when porous particles contain ordered pores, these pores act as a buffer layer for volume changes, demonstrating another means of controlling the volume expansion/contraction. In this review, recent developments in porous Si anodes, such as mesoporous nanowires, 3D porous particles, and nanotubes have been highlighted.

In order to improve both the capacity and cycle life of the Si anodes, researchers have investigated the encapsulation of a particle in a matrix involving Li$^+$/electron transport. This approach is of interest as it possesses mechanical flexibility. However, when using aggregated particles coated with carbon, it eventually leads to segregation of pulverized Si and carbon particles. For instance, Fig. 1a shows a TEM (transmission electron microscopy) image of Si nanocrystals (n-Si) which are commercially available (Nanstructured Materials Inc.). The average particle size is 30 nm and the particles are severely aggregated. Although its charge capacity (after lithium removal) is 3311 mAh/g, the capacity retention after just 5 cycles is below 200 mAh/g, showing only 5%. The result indicates that non-uniform n-Si with aggregation cannot avoid electrical disconnection of the n-Si from the Cu current collector. Accordingly, the minimization of the particle size is crucial, and each particle should be coated with a lithium ion conducting active phase to prevent particle aggregation during cycling.

On the other hand, it can be considered that when bulk or nanowires have an ordered separation distance, the ordered pores can act as a buffer layer for the uniform volume changes. One such example is mesoporous SnO$_2$ and mesoporous tin phosphates prepared by hard or soft templates, which showed excellent capacity retention compared to the nano-sized counterpart, thus demonstrating the role of mesopores. The most efficient way to synthesize the Si nanowires or bulk particles with ordered pores is to use templates. One method is to use ordered mesoporous silica or Al$_2$O$_3$

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Fig. 1 (a) A TEM image of commercially available Si nanoparticles and (b) voltage profiles of the particles in coin-type half cells between 0 and 1.5V at a rate of 0.2C. The inserted figure is a plot of the charge capacity (lithium dealloy) vs. cycle number. Adapted with permission from ref. 14. Copyright 2008, Elsevier.
membrane templates (Fig. 2). A hexagonal SBA-15 silica with \( p6mm \) symmetry, which contains two dimensional parallel cylindrical pores arranged with hexagonal symmetry, and \( \text{Al}_2\text{O}_3 \) templates were used for the nanowire and nanotube syntheses.\(^{24-26} \) After impregnation and annealing of the precursors in the templates, these parent templates should be selectively removed in relatively concentrated \( \text{NaOH} \) or \( \text{HF} \) for silica.

In this highlight, porous Si anodes with different morphologies, such as mesoporous nanowires, 3D porous bulk particles, and nanotubes and their electrochemical performances are reviewed.

**3D-porous Si particles**

Deposition of metals on porous biomimineral templates (diatoms with porous silica frustules with a 3D structure) to acquire 3D porous metals has been reported.\(^{27} \) Another approach to 3D porous metal or metal oxides has been widely used in photonic devices, and this method involves the infiltration of a silica template within the void spaces of a face-centered cubic colloidal crystal mode of micro-spheres (opal).\(^{28-30} \) Depending on the weight ratio of \( \text{SiO}_2 \) template\(^{31} \) and metal precursor, 0D hollow and 3D porous nanoparticle assemblies could be prepared. Normally, with increasing the weight fraction of precursor gels relative to \( \text{SiO}_2 \), 0D hollow nanoparticles were converted to 3D porous nanoparticle assemblies (Fig. 3).

However, we should be cautious when using \( \text{SiO}_2 \) templates without terminating the Si precursors, as during the annealing process, the \( \text{SiO}_2 \) and precursor composite react with each other, resulting in formation of \( \text{SiO}_2 \) on the Si particles. In this regard, the best way to block such \( \text{SiO}_2 \) formation is to use carbon precursors terminated on the Si precursor. To prevent such \( \text{SiO}_2 \) formation, termination with the carbon is necessary,\(^{32,33} \) and a basic synthetic method for the Si precursors is described below. The reaction of \( \text{SiCl}_4 \) was performed under a Schlenk line in an Ar atmosphere. This reaction produces nanometre-sized Si–Cl crystallites with a chloride-passivated surface (Fig. 4). The reaction was allowed to reflux for 12 h. Further reaction with alkyllithium (RLi) provided a stable surface terminated with an alkyl (Si–R) (Fig. 4). \( \text{SiCl}_4 \) was mixed into glyme, and the previously prepared sodium naphthalenide solution was added to this solution, stirring followed for 1 h at room temperature. Here, n-alkyllithium was added and stirred overnight to terminate the surface from Si-chloride to Si-butyllithium. After termination with the alkyl groups, the solvent and naphthalene were removed in a vacuum at 100 °C for 48 h. The resulting viscous yellow gels were rinsed with water and hexane several times, and finally alkyl-capped Si gels could be obtained.

Fig. 5a and b show SEM (scanning electron microscopy) images of the 3D porous Si obtained from etching \( \text{SiO}_2/c\text{-Si} \) composites consisted of 30 : 70 wt% \( (\text{SiO}_2 : \text{Si} \, \text{gel}) \).\(^{34} \) The Si particles have many voids, like an “octopus foot.” Because the porous Si particles were terminated with carbon, Si dissolution into the HF solution was unlikely to occur. Cross-sectioned c-Si particles (Fig. 5c) show the 200nm interconnected pores with a pore-wall thickness of ≈40nm. The TEM image of the cross-section of the porous 3D c-Si particle (Fig. 5d) shows an amorphous carbon layer with a thickness <10 nm. The lattice fringes of the /spacing value (3.1 Å) correspond to the (111) plane of the Si diamond cubic structure. The electron diffraction pattern of the sample shows the presence of the spotty pattern only, indicating the presence of single crystalline Si.

In contrast to Si nanoparticles (Fig. 1a), the capacity retention at a rate of 0.2C is 99% (2820 to 2780 mAh g\(^{-1} \)) after 100 cycles, while at a rate of 1C it is 90% (2668 to 2434 mAh g\(^{-1} \)) (Fig. 6a). Further more, coulombic efficiencies of the porous c-Si particles at both 0.2C and 1C rates were >98%.\(^{34} \) Capacity retentions of the 3D-porous Si are far superior to previous nano-sized Si/carbon composites or Si nanoparticles.\(^{1-12} \) A SEM image (Fig. 6b) shows the preservation of the pristine morphology even after cycling (Fig. 6b). HRTEM (high
resolution transmission electron microscopy (TEM) images of the cross-sectioned particle (Fig. 6c) show that crystalline Si nanoparticles <5nm in diameter are distributed throughout the amorphous Si matrix. Once this amorphous Si matrix is formed, it also serves as a buffer layer for the volume changes. The crystallite size in the cycled sample decreased from 100 nm to 2–5 nm. This result indicates that the pristine Si crystalline phase is not fully transformed into the amorphous phase even after extensive cycling. This porous structure provides empty space to accommodate Si volume changes and allow for facile strain relaxation without mechanical fracture upon lithium insertion. In addition, although there was nucleation of Si nanocrystals after long term cycles, major parts of the materials are amorphous, which led to very isotropic volume changes.

Mesoporous Si nanowires

Mesoporous Si nanowires could be obtained after the fourth impregnation into the SBA1-5 templates and fully-grown nanowires are observed (Fig. 7a). The light lines in Fig. 7a are considered projections of the mesopore channels, whereas the dark lines are the Si walls. In addition, a very thin amorphous carbon layer is observed (Fig. 7b) and CHS analysis confirmed that the carbon content was 6 wt%. The ordering of the carbon layer was examined by surface enhanced Raman spectral analysis (Fig. 7c). The mode at 1582 cm\(^{-1}\), referred to as the G mode, was assigned to the ‘in plane’ displacement of carbons strongly coupled in the hexagonal sheets. When disorder was introduced into the graphite structure, the bands broadened. Furthermore, the band near 1357 cm\(^{-1}\) is typically called the ‘disorder-induced’ or D mode, and the integrated intensity ratio \(I_D/I_G\) is indicative of the degree of carbonization. A smaller intensity ratio indicates a higher degree of carbonization. The value was 0.09 for ordered synthetic graphite, but that value of the Si nanowires was 1.45, indicating the formation of a disordered carbon layer.

Fig. 7d exhibits a low and high angle X-ray diffraction (XRD) pattern of the synthesized nanowires after removing the templates. The well-resolved intense (100) peak indicated excellent replication of SBA-15\(^{19,37,38}\) into a highly ordered 2D hexagonal mesoporous structure with a space group of \(p6mm\). The nitrogen adsorption-desorption isotherms of mesoporous Si nanowires gave a typical type IV isotherm with clear H1-type hysteresis loop, which was characteristic for mesoporous materials. Overall, reports in the literature and previous studies from our group have suggested that successful replication of mesoporous Si nanowires from calcined SBA-15 is possible. The crystal size of the sample, calculated using the Scherrer formula, was estimated to be approximately 6.5 nm (inset of Fig. 7d).
Mesoporous Si nanowires have an initial charge (lithium dealloy) of 3163 mAhg$^{-1}$, respectively, with an initial coulombic efficiency of 86% (Fig. 8a). The capacity after 80 cycles was 2738 mAhg$^{-1}$, which corresponds to 87% capacity retention. Fig. 8b shows the TEM images of the nanowires after 80 cycles, and compared to the image of the pristine sample, some mesoporous Si nanowires were demolished. The formation of the aggregated nanoparticles may be due to the non-uniform volume changes among nanowires. On the other hand, Si nanowires with a diameter <50 nm were prepared by vapor-liquid-solid (VLS) template-free growth by Cui et al.$^{39-41}$ and by metal-induced chemical etching by Lee and coworkers.$^{42}$ It is especially notable that Si nanowires prepared by VLS demonstrated a reversible capacity of ~2000 mAhg$^{-1}$ and good capacity retention >80%.

**Si nanotubes**

Porous Si nanowires and 3D porous Si particles have been demonstrated to exhibit good cycling performance as anode materials since both types of structures provide empty space to accommodate Si volume changes and allow for facile strain relaxation without mechanical fracture upon lithium
insertion. However, these materials exhibited increased polarization at higher current rates and some degree of capacity fading over many cycles. This could possibly be due to the limited surface area accessible to the electrolyte and the continuous growth of solid electrolyte interphase (SEI) at the interface between the silicon and electrolyte.\textsuperscript{41}

Fig. 9 shows SEM and TEM images of the Si nanotubes after the removal of the alumina template by treatment with NaOH. The carbon coating protects the Si nanotubes from being etched away by NaOH. The assemblies of uniform Si nanotubes with outer diameters of \(\sim\)200–250 nm were recovered and their wall thickness was measured to be \(\sim\)40 nm.\textsuperscript{43} Fig. 9b shows a HRTEM image of the surface of the outer wall of a nanotube, which indicates that the outermost layer is covered with nanometre thick amorphous carbon, although weak lattice fringes with a \(d\)-spacing of 1.93 Å can also be observed, corresponding to the Si (220) plane. Fig. 9c shows the Raman spectrum of the Si nanotubes. The sharp peak at \(\sim\)516 cm\(^{-1}\) is related to the Si–Si stretching mode, which is identical to that of the reference Si wafer. A small peak at \(\sim\)957 cm\(^{-1}\) is due to the stretching mode of amorphous Si–Si, which is also observed in the Si wafer. The two other peaks at \(\sim\)1360 and \(\sim\)1580 cm\(^{-1}\) are assigned to the D band (disordered band) and G band (graphene band) of carbon, respectively.

Rate capability and cycle life to 200 cycles were also tested by using a Li-ion full cell consisting of a LiCoO\(_2\)-based cathode and a Si nanotube-based anode (Fig. 10a and b). Excitingly, the initial capacity at rates of both 3C and 5C is above 3000 mAhg\(^{-1}\), and capacity retention after 200 cycles is 89\% at a rate of 1C. These results are comparable to a cell made with commercial graphite. In order to determine whether the Si nanotube morphology was changed after 200 cycles, the cells were disassembled and the anode was further characterized. Fig. 10c shows an SEM image of the electrode after 200 cycles; its original morphology is apparently retained. HRTEM revealed the presence of Si nanocrystals with sizes smaller than 5nm. In nanomaterials, the energy barrier for nucleation should be smaller because a large fraction of the Si surface is highly metastable. Accordingly, due to its highly disordered nature, the amorphous Si matrix has many defects, which could act as preferred nucleation sites for the formation of Si nanoclusters after long-term cycling.

**Conclusion**

Unlike the porosity that exists between nanoparticles coated with carbon in an electrode, the size of which is random and highly distributed, the uniformity of pore size and regularity in the arrangement of the pores (ordered porosity) in mesoporous nanowires and 3D porous bulk particles, and Si nanotubes ensured an even distribution of electrolyte in contact with the electrode surface. The thin walls, of uniform dimensions throughout, ensured short diffusion paths for lithium ions on alloy/dealloy and electrons, and hence equal, high rates of transport throughout the material. In addition, due to the nature of the carbon coating layers, direct contact among the porous Si anodes could be minimized, and less aggregation was expected. Electrochemical results of Si nanotubes supported previous findings that showed increased fracture toughness of nanowires with diameters less than 100 nm. This effect could be because the surface area to volume ratio increases dramatically when size decreases to the nanometre range, and any dislocations may be quickly drawn to the surface. Considering the volumetric energy density of the anode, bulk Si with tailored porosity may be the best candidate, and correlation between the porosity, pore sizes and electrochemical properties needs to be further investigated.

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