

Facile Synthesis of Free-Standing Silicon Membranes with Three-Dimensional Nanoarchitecture for Anodes of Lithium Ion Batteries

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Supporting Information

ABSTRACT: We propose a facile method for synthesizing a novel Si membrane structure with good mechanical strength and three-dimensional (3D) configuration that is capable of accommodating the large volume changes associated with lithiation in lithium ion battery applications. The membrane electrodes demonstrated a reversible charge capacity as high as 2414 mAh/g after 100 cycles at current density of 0.1 C, maintaining 82.3% of the initial charge capacity. Moreover, the membrane electrodes showed superiority in function at high



current density, indicating a charge capacity >1220 mAh/g even at 8 C. The high performance of the Si membrane anode is assigned to their characteristic 3D features, which is further supported by mechanical simulation that revealed the evolution of strain distribution in the membrane during lithiation reaction. This study could provide a model system for rational and precise design of the structure and dimensions of Si membrane structures for use in high-performance lithium ion batteries.

KEYWORDS: Silicon, lithium ion batteries, 3D membrane, volume expansion

T he demand for high-power and high-energy-density lithium ion batteries (LIBs) has been increasing to meet the ever-growing requirement for use in portable electronics and electric vehicles.¹⁻⁴ In principle, the energy storage capacity of LIBs can be improved by replacing current electrode materials with ones of higher specific capacity.⁵⁻⁹ Compared with conventional graphite anodes, silicon (Si) has a 10 times higher theoretical specific capacity (4200 mAh/g for $Li_{22}Si_5$ and 3579 for $Li_{15}Si_4$),¹⁰⁻¹² which makes it the most promising candidate for high-performance LIB electrodes. However, the implementation of Si in practical LIB electrodes has been hindered due to its large volume expansion up to ~300-400% upon full lithiation (lithium insertion into Si) that causes a mechanical fracture and poor capacity retention during cycling.^{8,13}

A variety of nanostructured Si materials, including nanoparticles,^{14–17} nanowires,^{8,18–21} nanotubes,^{22–25} and hollow nanospheres,^{26,27} have recently emerged as promising alternatives capable of overcoming the critical issues associated with the large volume change. The introduction of high-aspect ratio Si nanowires (NWs) demonstrates significant improvement in initial capacity and cycling capability. This enhancement was postulated to be due to their sufficient wire-to-wire space, which accommodates large volume expansion, and a large

specific surface area, which allows efficient transport and incorporation/extraction of Li ions. However, the repeated outward expansion and shrinkage of Si NWs that accompanies repeated charge/discharge cycles may cause a pile-up of solidelectrolyte interphase (SEI) layers on the NW surface. The development of thicker SEI layers on the Si surface degrades ionic/electronic transport as well as mechanical integrity of the Si anode, and eventually results in capacity fading as cycle number increases.⁸ An upgraded electrode layout has been designed to further improve the cycle performance of Si NW electrodes by utilizing sealed hollow structures, including nanotubes,^{22,23} porous nanospheres,^{14,28} and inverse opals.^{26,29–31} Compared with their solid counterparts, the interior voids not only possess higher resistance to mechanical failure, but also effectively release the strain/stress within Si anodes during lithiation, which decelerates the capacity fading associated with excessive SEI growth. Despite these advancements, most research interests have involved the design of individual units of nanomaterials, although these units are tightly interconnected with each other and/or current

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Figure 1. (a,b) Schematic illustrating preparation of well-ordered ZnO nanopillar template (a) and CVD coating of Si layer (b). (c,d) Corresponding SEM images of ZnO nanopillars (c) and ZnO/Si core–shell nanopillars (d) in side view and top view (insets). Scale bars: 1 μ m.

collectors to constitute whole electrodes. In these configurations, the interrelations of each unit, such as interdistance, spacing, and arrangement, may play an important role in determining overall performance. Moreover, the pulverization of Si anodes is more severe near the Si/current collector interface, which causes fast capacity fading. Accordingly, engineering the interface is additionally important to optimize the cyclic performance of anodes.

To address this challenge, we report an LIB anode based on transferable Si membranes with well-organized, three-dimensional (3D) nanoarchitecture. As shown in Figure 1, the Si membrane was synthesized by conformal coating of Si layers on a template of an array of ZnO hexagonal pillars in hexagonal, closed-packed arrangement.³² The resulting structure consisted of a capped hexagonal wall array interconnected with an underlying thin layer. Distinguished from the previous works based on randomly distributed nanostructures, the use of welldefined dimensions and structure enables us to explore the potential limits of Si electrodes. In particular, structural evolution of the Si membranes following lithiation and delithiation processes could be systematically analyzed by direct transmission electron microscopy (TEM) observation. These results, combined with mechanical analysis based on theoretical modeling, represent a crucial step toward rational and precise design of the Si membrane anode structures for high performance LIBs.

The key steps of 3D Si membrane synthesis involve (i) hydrothermal growth of hexagonal array of ZnO nanopillar templates through nanosphere lithography, (ii) a thin Si layer coating on the ZnO template by chemical vapor deposition (CVD), and (iii) transfer of Si membranes to target substrates, including current collectors for LIBs (Figures 1 and 2). A more

detailed description of the procedures is given in the Methods (Supporting Information). Scanning electron microscopy (SEM) images taken before and after Si coating on ZnO templates (Figure 1c,d) illustrate the morphology and size change. Pristine ZnO templates are composed of single-crystal ZnO columns with well-defined hexagonal facets. Individual ZnO pillars have an average diameter (i.e., longest diagonal of the hexagon) of ~300 nm and center-to-center distance of \sim 500 nm, as shown in Figure 1c. After Si coating, the diameter increased by 100 to 400 nm, indicating that in this case, the 50 nm thick Si layer was conformally coated on the ZnO nanopillar template. The thickness can be easily controlled by Si coating time while overall lattice spacing and the size of individual ZnO nanopillars within the pattern can be controlled by a combination of the fabricating parameters (Figure S1, Supporting Information), providing much room for precise design of the structure and dimension of resulting nanostructures. Notably, this nanofabrication involves self-assembly of silica spheres in the generation of monolayer crystal masks (which can be replaced with many other unconventional techniques for more cost-effective production) and lowtemperature hydrothermal process. Accordingly, this approach can be easy to scale up to commercial-scale manufacturing and thus useful for practical battery application.

Conformal coating of Si layers constructs a continuous form of 3D Si membranes that can be separated from the growth substrates by selective etching of ZnO in a hydorfludic (HF) solution. To minimize mechanical fractures during the transfer, Si membranes were generally coated with poly(methyl methacrylate) (PMMA) layers. In HF solution, the intermediate ZnO layer and pillars were selectively etched, and the PMMA/Si membrane could be separated from the substrate.



Figure 2. Synthesis, transfer, and characterization of free-standing Si membrane electrode. (a) Detachment of Si membrane from substrate by etching ZnO nanopillar template in HF solution. Scale bar: 1 cm. (b) Si membrane transferred to stainless steel foil. Scale bar: 1 cm. (c) SEM images of Si membrane. Scale bar: 1 μ m (scale bar in inset: 300 nm). (d) Low-magnification TEM of Si membrane fragment deposited on TEM grid. Scale bar: 1 μ m. (e-g) Top view (e) and side view TEM images of single hexagonal walls and proposed schematic based on analysis (g). Scale bar: 300 nm. (h) High-magnification TEM images of Si membrane and corresponding SAED pattern (inset). Scale bar: 5 nm. (i) EDS spectrum of Si membrane.

The photographs of the Si membrane/PMMA sheets partially exfoliated from substrates and transferred to stainless steel (SUS) foil were shown in Figure 2a and Figure 2b, respectively. The freestanding Si membrane was mechanically robust so that it could be transferred to other substrates, readily creating a large area of 3D structure (Figure 2c). Moreover, its fragments that were delaminated through ultrasonication to prepare a TEM specimen maintained their original form. The resulting TEM images shown in Figure 2d-f revealed the membrane structure with nice geometry; the membrane is consisting of hexagonal walls with uniform thickness and an underlying 2D clamping layer. Both the inner and outer surfaces of the walls were very flat and smooth, illustrating the conformal coating of the Si layer and complete removal of the core ZnO template. Side view images confirmed that the hexagonal walls were sealed at the top by a thin cap layer, while they were open at the bottom and interconnected with an underlying 2D clamping layer (Figure 2e,f). By correlating the top view and side view images, the thicknesses of the top caps and underlying layers were substantially confirmed to be identical to that of the side

walls (~50 nm), as schematically illustrated in Figure 2g. A high-resolution TEM (HRTEM) image taken at the surface of the hexagonal wall and a selected area electron diffraction pattern indicate the dominant presence of an amorphous Si (α -Si) phase (Figure 2h). Energy dispersive X-ray spectroscopy (EDS), shown in Figure 2i, demonstrates that Si was the main component of the membranes, and weak O and Cu peaks originated from the native oxide on the membrane wall surface and TEM grid, respectively. Analysis of cross-sectional elemental mapping data also confirms higher O contents within ~5–10 nm outer surface of the walls (Figure S2, Supporting Information), representing the formation of SiO_x shells presumably during the Si CVD coating and thermal annealing processes.

To investigate the electrochemical performance of Simembranes, two-electrode 2032 coin cells were prepared with Si-membrane anodes and lithium metal foil as the counter/ reference electrodes. Figure 3 shows the galvanostatic charge– discharge characteristics of a typical Si-membrane anode with voltage cutoff of 0.01 and 1.5 V versus Li/Li⁺. In the first cycle



Figure 3. Electrochemical performance of Si membrane electrode. (a) Galvanostatic charge–discharge characteristics for first cycle at rate of 0.1 C. (b) Charge/discharge capacity (black squares/red circles) and Coulombic Efficiency (blue stars) at rate of 0.1 C for 100 cycles. (c) Charge/discharge capacity (black squares/red circles) cycled at 0.1, 0.2, 0.5, 1, 2, 4, and 8 C. (d) Cell impedance of Si membrane before and after 50 and 100 cycles.

with a rate of 0.1 C (current density of 300 mA/g), the discharge and charge capacities of the Si membrane were estimated to be 3644 and 3124 mAh/g, respectively, demonstrating Columbic efficiency of ~86% (Figure 3a). By using the density and theoretical capacity values of SiO and SiO₂, theoretical capacity for Si/SiO and Si/SiO₂ membranes with abrupt heterointerface of inner 40 nm thick Si and outer 10 nm thick SiO_x (x = 1 or 2) are calculated to be 3951 and 3631 mAh/g, respectively (see Supporting Information, Table S1). Our measured value for first discharge capacity (3644 mAh/g) is larger than theoretical capacity of Si/SiO₂ membrane but much lower than that of Si/SiO membrane. This result is reasonable considering the graded heterointerface of Si/SiO_x as confirmed from the cross-sectional elemental mapping data (Supporting Information Figure S2). The volume capacity could be 0.50 Ah/cm³ concerning the total height of membrane is 1.2 μ m. Flat plateaus appeared at ~0.2 V for the discharge cycle and 0.44 V for the charge cycle. These are characteristic features of the reaction of lithium with α -Si,^{18,33,34} whose phase was confirmed by HRTEM, as shown in Figure 2h. The cycleability and corresponding Columbic efficiency of this Si membrane cycled at 0.1 C (300 mA/g) for 100 cycles are plotted as a function of cycle number in Figure 3b. Compared to previous results, such as Si nanowires⁸ with ~60% capacity retention after 50 cycles and Si nanoparticles¹⁷ with 81% capacity retention after 40 cycles, the current membrane electrode showed excellent stability with capacity retention of 82.3% after 100 cycles. In particular, capacity decay became smaller with charge capacity decrease less than 8% from the 25th cycle to the 100th cycle. On the other hand, the initial Columbic efficiency of 86% is relatively low, and it is associated with the initial formation of SEI and some indecomposable LiSi alloys. However, Columbic efficiency increased to \sim 99% after five cycles and stabilized within the subsequent cycles.

To further evaluate the potential of Si-membrane anodes, charge/discharge cycling tests were performed under various rates of 0.1, 0.2, 0.5, 1, 2, 4, and 8 C. The results are plotted in Figure 3c. The charge capacities at these rates were measured to be $3140 \pm 50, 2950 \pm 20, 2720 \pm 10, 2270 \pm 40, 1850 \pm 60,$ 1530 ± 30 , and 1220 ± 30 mAh/g, respectively; even when charging rate increased 10-fold from 0.1 to 1 C, the Simembrane anode maintained ~75% of its initial capacity; even at 8 C, it preserved ~40% of its initial capacity, which is still \sim 3.3 times greater than the theoretical capacity of a graphite anode (372 mAh/g). Moreover, the Si membrane anode showed superior rate capability with a higher capacity than the previously reported values (Si nanowire⁸ anode of \sim 2100 mAh/g at 1 C; sealed Si nanotube²³ anode of \sim 1900 mAh/g at 1 C). Given that the fierce lithiation reactions involve essentially the flow of high-density electrons and lithium ions, enhanced electrochemical performance may represent the good electrical conductance and stability of Si membrane anodes. This is further verified by measuring cell impedance before and after 100 cycles. As shown in Figure 3d, the cell impedance spectra measured before and after 100 cycles exhibited similar semicircle radii and real impedance values that indicates no significant change in the impedance of Si electrodes and their interfaces with both electrolyte and current collectors. In particular, the semicircle radius that corresponded to impedance at the electrolyte/electrode interface changed by only ~11%, indicating no significant SEI growth during cycling.^{5,35} The considerable inner space of the wall would ease the pile-up of SEI caused by compensation for the outward



Figure 4. Structural evolution of Si membrane electrode following lithiation (a-d) and delithiation (e-h) reactions. (a,b) SEM (a) and TEM (b) images of fully lithiated Si membrane electrode. Scale bars: 400 nm. (c,d) Top-view (c) and side-view (d) TEM images of individual lithiated wall. Scale bars: 200 nm. (e,f) SEM (e) and TEM (f) images of delithiated Si membrane electrode. Scale bars: 400 nm. (g,h) Top-view (c) and side-view (d) TEM images of individual lithiated wall. Scale bars: 200 nm. (e,f) SEM (e) and TEM (f) images of delithiated Si membrane electrode. Scale bars: 400 nm. (g,h) Top-view (c) and side-view (d) TEM images of individual delithiated wall. Scale bar: 200 nm.

expansion toward the electrolyte, thus facilitate the exchange of Li^+ ions on the interface of the Si electrode and electrolyte.

To increase our understanding of the electrochemical alloying reaction of Si membranes, we explored the structural evolution of Si membranes following lithiation and delithiation reactions. When fully lithiated, the inner radius R_{in} decreased from ~150 to ~50 \pm 20 nm while the outer radius R_{out} increased from ~200 to ~225 nm, indicating that wall thickness increased from \sim 50 to \sim 175 nm (Figure 4a–d). This gave rise to volume expansion of ~275% if expansion along vertical direction was ignored. When fully delithiated, R_{in} increased to ~115 nm and R_{out} decreased to ~200 nm while wall thickness decreased to ~85 nm (Figure 4e-h). Interestingly, after complete lithiation and delithiation, the membrane regained its initial geometry with a sealed hexagonal shaped wall but still remains ~153% volume expansion in comparison to the original membrane. Note that the first Coulombic Efficiency was as low as 86%, and the \sim 14% irreversible capacity loss is usually associated with Li⁺ ions that are still captured in the anode in an indecomposable Li-Si alloy form.^{12,36} By simply assuming that volume expansion is directly proportional to the degree of Li⁺ ion insertion, a volume increase of $\sim 30\%$ is expected after the first cycle. The deviation between expected and measured volumes (30% versus 53%) may originate from the formation of an SEI layer on the outer Si surface as well as from nanopores and defects generated within the Si electrode upon delithiation.^{12,37,38}

In essence, the high performance of Si membrane anodes owes to their characteristic 3D features. First, in Si membranes, the interior spaces within capped hexagonal nanowalls and the exterior spaces between them can effectively accommodate reversible volume change, which promotes cycleability. SEM images of Si membranes taken after 100 cycles (Figure S3, Supporting Information) show that the 3D feature of hexagonal-shaped walls was still intact, and no severe fracture had occurred. Second, the 3D architectures enabled the "electrolyte river" to adequately irrigate the anode material, therefore Li⁺ ions easily infiltrated into or escaped from the anode for lithiation–delithiation reactions and thus rate capability was markedly improved. Third, the role of the underlying layer that is not only interconnecting individual hexagonal walls but also interfacing with the current collector is crucial.³⁹ Since it is very thin and does not fully cover the current collector, the underlying layer can effectively clamp one end of the hexagonal walls to the current collector surface, ensuring robust electrical and mechanical connection during cycling (Figure S4, Supporting Information).

In addition, the existence of silicon oxide (SiO_r) layer on the outer surface of Si membrane offers favorable mechanics behavior. Although this SiO_r layer is very thin (less than ~ 10 nm), it would prevent the membrane from outward expansion upon lithiation, because the yield strength of lithiated silicon oxides Li₂Si₂O₅ (2.52 GPa) is ~42 times of that of lithiated silicon $Li_{22}Si_5$ (60 MPa).^{5,24} This characteristic feature is further understood by the finite element analysis (FEA), where the diffusion of lithium ions is modeled by the analogy between heat transfer and diffusion. To simplify the modeling, we assumed that the membrane has abrupt heterointerface of inner Si (40 nm) and outer SiO₂ (10 nm), as shown in Figure 5. The FEA of this structure shows that the inward expansion dominates since the SiO₂ layer imposes restriction on the outward expansion (Figure 5a,b). Specifically, the inner radius reduces from 150 to ~31, ~50, and ~90 nm at places near the cap layer, in the middle, and near bottom underlying thin layer, respectively. This theoretical analysis agrees well with experimental observation (Figure 4a-d), although a larger outward expansion in experiment than expected might be associated with thinner SiO_r layer and/or imperfect (gradient) Si/SiO, heterointerface. Because of the mechanical constraining effect from the outer SiO_x layer, the reduced outward expansion suppresses the formation of additional surfaces for excess SEI growth, thereby facilitating excellent cycling performance and superior rate capability.^{5,40} It is also noted that the strain is larger in the cap and upper part of wall than the others, which suggests that the fracture would initiate preferentially from those parts. The disappearance of the caps in the hexagonal



Figure 5. Finite element analysis of strain distribution in Si membrane. The inward expansion dominates in the case with outer SiO_x layer (a,b), while outward expansion dominates in the case without SiO_x layer (c,d).

walls was also observed experimentally in a harsh cycling condition (after 100 cycles at 8 C), demonstrating the validity of our modeling approach (Supporting Information Figure S5). On the contrary, if there is no SiO_x layer at the outer surface of Si membrane, the inner and outer radii of walls would expand from 150 and 200 nm to 198 and 264 nm, respectively, as similar to a blown balloon (Figure 5c,d). In this case, the walls experience outward expansion and shrinkage during lithiation and delithiation process and the SEI formed on the walls would break apart and become denatured, which eventually results in excess growth of SEI. Moreover, distortion of the membrane in the border between hexagonal wall and underlying layer is more severe in the oxide-free Si membrane. The following strain accumulation would cause fracture and decrepitation. It thus further illustrates additional role of SiO_x layer in reducing the distortion of the membrane in the border between hexagonal wall and underlying layer and improving the electrical and mechanical connection to the current collector during cycling. We believe that these results are very informative not only to find a stress raiser and fatigue crack initiation site but also to avoid (or minimize) these structural irregularities for performance optimization of cyclic property of anode.

In conclusion, freestanding 3D Si membrane anodes with good mechanical strength and well-defined configurations have been synthesized for use in LIBs and their superior electrochemical performance has also been demonstrated. The precise design of structures and dimensions, together with their freestanding forms, allows direct TEM observation for systematic analysis of size and structure changes upon lithiation and delithiation. Overall, this approach elucidates the influences of structure and dimension on the pulverization of Si and thereby suggests optimal parameters for the design of highperformance batteries. Additionally, the transferability and good mechanical deformability of Si membranes enables their latent functions to be exploited in various technological applications.

ASSOCIATED CONTENT

Supporting Information

Experimental details; Figures S1–S5. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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