Three-Dimensional Metal Scaffold Supported Bicontinuous Silicon Battery Anodes

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Supporting Information

ABSTRACT: Silicon-based lithium ion battery anodes are attracting significant attention because of silicon’s exceptionally high lithium capacity. However, silicon’s large volume change during cycling generally leads to anode pulverization unless the silicon is dispersed throughout a matrix in nanoparticulate form. Because pulverization results in a loss of electric connectivity, the reversible capacity of most silicon anodes dramatically decays within a few cycles. Here we report a three-dimensional (3D) bicontinuous silicon anode formed by depositing a layer of silicon on the surface of a colloidal crystal templated porous nickel metal scaffold, which maintains electrical connectivity during cycling due to the scaffold. The porous metal framework serves to both impart electrical conductivity to the anode and accommodate the large volume change of silicon upon lithiation and delithiation. The initial capacity of the bicontinuous silicon anode is 3568 (silicon basis) and 1450 mAh g−1 (including the metal framework) at 0.05C. After 100 cycles at 0.3C, 85% of the capacity remains. Compared to a foil-supported silicon film, the 3D bicontinuous silicon anode exhibits significantly improved mechanical stability and cyclability.

KEYWORDS: Silicon anode, 3D porous metal, current collector, scaffold, rechargeable battery

The development of high energy density lithium ion (Li-ion) cells has been a long-standing goal.1,2 Two important factors defining the maximum energy density of a Li-ion cell are the cell voltage and the specific capacity of anode and cathode. Given the challenges of developing electrolytes that can support significantly increased voltages, increasing the capacity of the electrode materials is very important for increasing the energy density of Li-ion cells. Here we focus on the anode. Silicon has the highest specific capacity (4200 mAh g−1) of known Li-ion anode materials. However, the large volume change (up to 400%)3 of a silicon anode during lithium insertion and extraction leads to electrode pulverization and a resultant loss of electric contact between Si and the current collector (illustrated in Figure 1a). Once this happens, the capacity rapidly fades.4

There have been a number of recent reports describing possible approaches to circumvent the issues posed by the volume change of silicon.4–11 Electrodes comprised of nanosized silicon particles dispersed in a matrix could exhibit improved cycleability, however, at the expense of the overall energy density. Moreover, the matrix must be both mechanically compliant to absorb the silicon volume change and electrically conductive.12 Results obtained by dispersing silicon nanoparticles in a graphite anode appear promising, however, the energy density of this composite remains well below that of pure silicon.3,13 Rather than dispersing silicon nanoparticles in a second phase, several reports have shown the potential of microstructural engineering of porous Si anodes.1,2,14–24 At least in principle, engineering porosity inside a Si anode enables accommodation of the large volume changes during cycling and thus avoids pulverization and loss of electrical contact. The pioneering work of Stein,25–27 Ozin,5 and Cui28 in developing macroporous or nanoporous carbon scaffolds for silicon Li-ion battery anodes is particularly promising. However, to maximize both mechanical stability and electronic conductivity, it would be preferable that the silicon be supported by an electrolytically inactive metal. Ni, Cu, Ti, Mo, Nb, Cr, and W are all possible candidates, as they do not alloy with lithium.29,30 Taking into account various fabrication issues, cost, and safety, Ni, Cu, and W are in particular very good candidates. Previous studies reported that an electrode consisting of a very thin (50 nm thick) Si film on a Ni foil could be cycled over 3000 times because of the good adhesion between the Si film and the Ni current collector.3,31 Recently, a Ni nanocone array (∼400 nm height) was used to support a thin film silicon anode.32 For both these systems, the Ni support is electrolytically inactive and provides mechanical support and good electrical conductivity. The intrinsic mechanical stability of thin films relative to their bulk equivalent, and the electronic and mechanical properties of

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the Ni substrate prevent pulverization of the silicon and result in an improved cycle life.31,33−35 The nanocone architecture also modestly increases the effective surface area and thus overall energy density. Recently, both theory and experiment have shown that there is a critical silicon film thickness or particle size below which cracking does not occur.4,36 Although different values have been suggested, it is generally agreed that the critical size is on the scale of 150 nm.36 As we show here, by effectively folding a Si thin film with a thickness below the critical value into a 3D electrically connected structure, it is possible to create an anode with good cycling capability and, due to the combination of a high Si volume fraction and surface area, a high energy density and reasonable power density.

We fabricated and characterized a bicontinuous anode consisting of a thin layer of silicon on a porous 3D nickel metal support (Figure 1c). The bicontinuous electrode shows an initial capacity of 3568 (silicon basis) and 1450 mAh g−1 (including the metal support but not any underlying current collector) and high capacity retention during cycling. The fabrication procedure is outlined in Figure 1d. First, an ∼10 μm thick opal template is prepared by vertical deposition of 500 nm diameter polystyrene (PS) spheres on a tungsten foil. After a heat treatment at 95 °C (near Tg of PS) to enhance the connection strength between PS spheres, Ni is electrodeposited into the void space of the opal template. Removal of the PS template with solvent (tetrahydrofuran) results in a Ni inverse opal with narrow interconnects between two adjacent spherical voids (Figure 2a). The window size is enlarged by pulsed electrochemical etching to form the highly porous Ni scaffold shown in Figure 2b,c following our previously published procedure.37,38 Figure 1 in the Supporting Information shows scanning electron microscopy (SEM) images of the Ni inverse opal during stages of the etching. By adjusting the number of etching pulses, the porosity can be controlled between 74% (ideal inverse face-centered cubic structure) and 96 vol% (the point where the structure looses mechanical integrity) (Supporting Information Figure 2). Finally, a thin film of silicon is deposited onto the nickel scaffold by chemical vapor deposition (CVD) from disilane (Figure 2d). Details on the nickel inverse opal fabrication and Si CVD can be found in the SI and our previous publications.37−39

In the example shown in Figure 2d, about 35 nm of silicon was conformally grown onto the nickel scaffold by CVD.39 As the following calculation shows, upon lithiation, this 35 nm silicon layer expands to almost fill the voids in the porous nickel scaffold; if a thicker silicon layer was grown, the voids would become completely filled, and Li+ transport would be substantially reduced. Starting with a nickel inverse opal scaffold derived from a template with a colloid diameter of 500 nm and electropolished to 92% porosity, a conformal silicon film of 40 nm thickness occupies 23% of the inverse opal volume. After full lithiation, the volume of this silicon layer expands about 3-fold and would completely fill the 92% empty volume present in the initial electropolished Ni inverse opal. Starting with 35 nm of silicon is thus appropriate, as this would leave a small volume fraction of pores upon lithiation. Figure 3a presents a focus ion beam (FIB) prepared cross-section image of a lithiated silicon anode. As expected, in the lithiated state the 3D structure of the scaffold can barely be observed as the void volume is quite small. After delithiation, the silicon layer contracted (Figure 3b). During the contraction, the silicon does not remain in complete contact with the nickel scaffold, and some voids appear between the scaffold and the silicon. The
silicon appears to maintain sufficient electrical contact despite the void formation, as the capacity remains high after many cycles. Even in the SEM, it can be noted that the voids between the silicon and nickel do not extend entirely around the silicon, which is probably the reason good electrical contact remains between the two materials. Finally, it appears the nickel scaffold is mechanically robust enough to support and accommodate the silicon volume change without being destroyed.

Silicon has a very low electronic conductivity ($\sim 10^{-3}$ S m$^{-1}$) and alloying reactions normally have sluggish kinetics as compared to intercalation reactions.$^{40}$ Thus, for a given thickness Si has to be cycled at much lower C-rates than a carbonaceous anode. It should be kept in mind, however, that the much higher capacity of silicon relative to graphite means that even low C-rates deliver significant powers. We cycled the Si anode between 0.01 and 2.0 V at 0.05C rate. The potential during cycling is shown in Figure 4a. The first cycle charge capacity is 3568 mAh g$^{-1}$ (Si basis). Except for an $\sim 5\%$ decay in the first few cycles, the reversible capacity fades little during the prolonged cycling. In comparison, we deposited an $\sim 3$ μm thick layer of silicon on a nickel foil by e-beam evaporation. Its cycling behavior is also shown in Figure 4b. Because of the high resistance, the initial capacity of flat film on nickel foil is lower than that of the thin-film silicon in nickel scaffold. After 10 cycles, only 10% capacity remained, because the silicon pulverized and lost electronic contact with the substrate during the cycling process (partial detachment of active material can be seen after disassembling the cell). In contrast with the flat film, each spherical pore in the nickel scaffold provides a nanoscale reaction space for the Si–Li alloying/dealloying process and confines the volume change so as to avoid the loss of electronic contact during cycling while maintaining good electrical contact.

The distinct peaks in the capacity differential curves in Figure 4c correspond to specific lithiation or delithiation steps. The peaks around 0.2 and 0.07 V versus Li/Li$^+$ in the cathodic branch corresponded to Li$_{1.71}$→2.33Si or Li$_{2.33}$→3.25Si and Li$_{3.25}$→4.2Si.$^{41}$ The initial capacity of 3568 mAh g$^{-1}$ (0.05C) indicates the final structure contains between 3.25 and 4.2 lithium atoms per silicon atom. In Figure 4d, the bicontinuous electrode is cycled at 0.3C and shows the maximum capacity of 3116 mAh g$^{-1}$. After 100 cycles, it retains a capacity of 2660 mAh g$^{-1}$. The initial Coulombic efficiency is low but gradually increases to 99.3%. One possible reason for the nonideal
behavior may be because alloying and de-alloying reactions potentially fracture the solid electrolyte interface (SEI) film due to the large volume change of Si anodes. This agrees with the previous reports of Si anodes and other alloy anodes such as Ni–Sn, Cu–Sb, and so forth. The second reason is that the low voltage limit during cycling (0.01 V vs Li) may be too low. It has been reported that the Coulombic efficiency could be significantly improved by a combination of setting the low potential limit to 0.23 V and coating the Si with an inert layer. The purity of electrolyte may also contribute to the low Coulombic efficiency. As the Coulombic efficiency increases (Figure 4d), one possibility is that the SEI is becoming more stable.

The charge and discharge of an electrode involves multiple coupled physiochemical processes. The slow charge/discharge kinetics of Si anodes may result from multiple factors. To determine the major factors driving the slow kinetics (the various resistances and the influence of structural change), the total internal resistance was determined by the galvanostatic intermittent titration technique (GITT). The internal resistance includes the combined influence of the interface electron transfer, electronic conduction, and Li-ion transport. By measuring the quasi-equilibrium potential change before and after a galvanostatic pulse, the internal resistance is evaluated by the potential difference divided by the current. At high potential, the active material contracts due to de-alloying and thus opens up liquid channels that provide for better Li-ion transport. However, Figure 5a shows that the internal resistance increases ~20 times when the electrode potential changes from 0.1 to 1.0 V. This is primarily because silicon electronic resistance increases markedly with delithiation. Electrochemical impedance spectroscopy (EIS) in Figure 5b shows the semicircle diameter increases significantly when the electrode is charged to 1.0 V, indicating an increase in electron transfer resistance.

The expansion of active material during lithiation decreases the liquid volume fraction inside pores and probably slows down Li-ion transport through the electrode. To investigate the transport process, the silicon layer with the same thickness (~40 nm) is deposited onto two nickel scaffolds that are derived from 500 nm (sample A) and 1.8 μm (sample B) colloid diameter templates (Figure 6a,b). The rate performance at various C-rates is shown in Figure 6c. The capacity retention of both samples falls significantly with increasing C-rates. At a...
very low C-rate (~0.05C) both samples deliver almost the same specific capacity. For sample A, the capacity falls to 36% of its low-rate (0.05C) capacity when the charging rate increases to 2.2C (upon full lithiation, the pores in Sample A are essentially filled). Sample B shows better rate performance. Even at 9.5C, it delivers 48% of its low-rate capacity. We believe this is because the liquid-phase channels remain open even after lithiation and the Li-ion transport resistance is low. It should be noted that although these C-rates may not appear impressive, because of the ~10 times capacity of a silicon anode relative to a conventional carbonaceous electrode, a low C-rate silicon anode still delivers more power than a much higher C-rate conventional electrode.

The effective Li-ion chemical diffusion coefficients as determined by GITT and EIS are shown in Figure 6d. It is understandable that lithium ions transport much more quickly in sample B than A because large pores provide liquid channels thus minimizing the Li-ion transport resistance. When charged to 0.1 V, silicon volume expansion in sample A should have thus minimizing the Li-ion transport resistance. When charged to 0.1 V, silicon volume expansion in sample A should have increased Li-ion diffusion coefficient upon charging. Because the Li-ion chemical diffusion coefficient ($\bar{D}$) in the solid electrode is determined by the self-component diffusivity ($D_e$), the electron transference number ($t_e$), and the Li-ion activity coefficient ($\gamma$) $\bar{D} = D_e(1 + (\partial \ln(\gamma))/\partial \ln(c))$, the enhancement can be attributed to the influence of the Li-ion activity coefficient and the improvement of the Si electronic conductivity with charging that serves to accelerate the ion diffusion. The key point is that within a range, the rate performance and energy density can be engineered through pore size control and Si thickness control. Thus, the rate and cycling properties that can only be obtained in the thin film could be realized in the effectively 3D nickel scaffold supported structures.

Here, we report the fabrication and characterization of a nanoscale Ni metal scaffold supported bicontinuous 3D silicon anode with potential for high energy Li-ion batteries. Because of the well-controlled nanoscale pore structure, good mechanical stability, and conductive pathway provided by the metal scaffold, the 3D bulk electrode shows high specific capacity and capacity retention during cycling. This approach may also be applicable for many other high energy electrode materials such as nickel–tin alloys and sulfur, where large volume changes and the resultant capacity fade have hindered the practical applications. Although the 3D porous scaffold could eliminate the usage of the current collector foil and decrease the total mass of inactive parts, Ni is a relatively dense metal and additional research on lightweight electrochemically stable conductive 3D scaffolds may further advance this concept. In this report, we use an ordered template and electrodeposition-based materials growth strategies. Scaleup will likely require faster template fabrication processes that will likely require use of a randomly packed template (formation of colloidal glasses is very fast relative to colloidal crystallization) and fast, for example, CVD-based, metallization strategies. Studies along these directions are ongoing. In summary, here we demonstrate that a colloidal crystal-templated porous nickel scaffold can accommodate silicon’s significant volume changes during cycling while maintaining good electrical conductivity and electrode integrity.

**REFERENCES**


