

Silicon Thin Films as Anodes for High-Performance Lithium-Ion Batteries with Effective Stress Relaxation

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There is a great deal of interest in developing next-generation lithium ion (Li-ion) batteries with higher energy capacity and longer cycle life for a diverse range of applications such as portable electronic devices, satellites, and next-generation electric vehicles. Silicon (Si) is an attractive anode material that is being closely scrutinized for use in Li-ion batteries because of its highest-known theoretical charge capacity of 4200 mAh g⁻¹.^[1] The development of Si-anode Li-ion batteries has been hindered, however, mostly because of the large volumetric changes (up to 400%) that occur upon insertion and extraction of Li ions, and in turn the large electrochemically related stress, which results in electrode pulverization, loss of electrical contact, and early capacity fading of battery cells.^[2–5] Despite this challenge, the extraordinarily high energy capacity of Si in its own right has motivated researchers to develop new techniques that reduce the limitations of Si as a practical anode material. Ultrathin Si films down to 50 nm in thickness have been reported for successful antipulverization and capacity nondegradation over two thousand charge/discharge cycles on roughened current collectors.^[6] This result, together with a surge of work on improving the capacity retention of Si anodes such as nanoparticles^[7,8] and/or composites,^[9–12] nanowires,^[13–15] or nanotubes^[16,17] have shown improved performances, where the nanoforms of materials can offer expansion spaces during lithium insertion/extraction (Figure 1A). However, some degree of capacity fading still exists due to the limited space for accommodating the facile strain expansion as well as decreased accessibility of the electrolyte to the solid–electrolyte interphase (SEI) between the silicon nanostructures and electrolyte. Here, we present a new strategy of stress relaxation for Si films using an elastomeric substrate that will establish an alternative route for new electrode design. In addition, the design of the anodes offers more efficient ion and electron transport than the reported work that uses nanoparticles, nanowires, or nanotubes.

The general concept of stress relaxation can be understood using an eigen strain analogy. It is well-known that the eigen deformation of a free-standing material does not lead to mechanical stress, but only to self-compatible deformations, and eigen-strain-induced stresses are generated when the eigen strain is constrained. Consequently, the stress can be released by removing these constraints (e.g., stainless steel^[13] and rough substrates^[6]). Herein, we report an approach in which the rigid substrates (e.g., current collectors) that constrain the “free” expansion/contraction of the Si anodes during charge/discharge are replaced by soft substrates. The mechanism for stress relaxation is that the volumetric strain in Si that is induced by charge/discharge cycling can buckle the flat Si thin films when they are on soft substrates (Figure 1B), which in turn releases the stress in the Si films by balancing the electrochemically induced axial component and buckling induced bending component of the stress. A similar mechanism has been extensively studied for the compression of stiff thin films on elastomeric substrates^[18,19] and was successfully utilized to develop stretchable electronics,^[20,21] though the mechanism presented here is different from those in existing studies. We present experimental studies that demonstrate a proof-of-concept and exhibit superb performances of Si film anode based Li-ion batteries resulting from successful stress relaxation. Theoretical examinations including continuum analysis and first-principle calculations provide qualitative understanding of such an electrochemically–mechanically coupled system.

The realization of Si anodes involves the fabrication of Si thin films from bulk Si wafer, then separation of these two by undercutting the intermedia layer, and finally transfer-printing Si thin films as anodes onto soft substrates. Figure 2A illustrates this procedure. The Si anodes are derived from the device layer of silicon-on-insulator (SOI) wafers (Soitec Inc.), whereas low-cost Si materials from chemical vapor deposition (CVD) are adoptable without adding any complexity, by following the procedures below with large-scale capabilities. Poly(dimethylsiloxane) (PDMS) was used as the soft substrate and its stability in the electrolyte (1 M LiPF₆ + EC + DEC 1:1:1 by volume) was carefully examined at room temperature under ambient argon pressure, and no mechanical or chemical degradation was found. The fabrication started by patterning the top Si (100–400 nm) of SOI wafers into ribbons and removing the buried SiO₂ layer (400 nm). Thin layers of chromium (5 nm), gold (100 nm), and chromium (5 nm) were then deposited in sequence on top of the Si ribbons, followed by oxidization of the top Cr layer. A flat PDMS substrate (300–500 μm thick) was brought into contact with the multilayer structure (Cr₂O₃/Au/Cr/Si). Prior to the contact, the PDMS surface was treated

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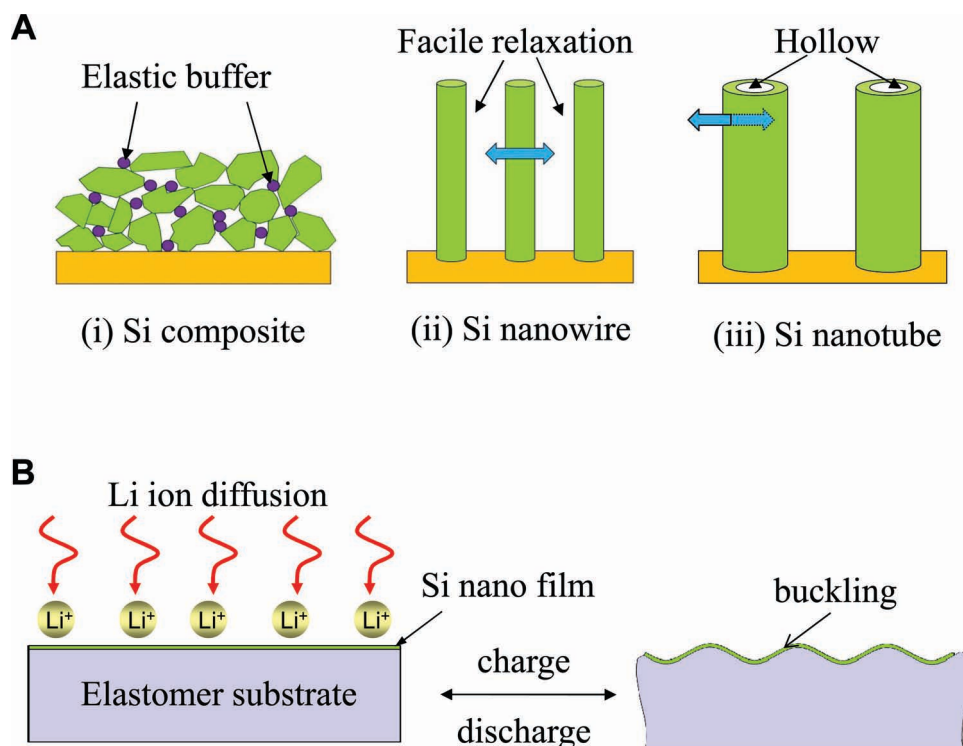


Figure 1. Different approaches to achieve longer cyclic lifetimes for Si-based anodes of lithium ion batteries. A) Various nanostructured Si as anodes in Li-ion batteries. i) Si nanocomposites using an elastic matrix to act as a buffer for strain release; ii) Si nanowires, and iii) Si nanotubes utilizing the lateral free surface to accommodate volume expansion. B) The approach using soft substrates to release the lithiation-induced stress in a Si thin film during cyclic charge/discharge. The compressive stress is released by generating out-of-plane deformation, i.e., buckling.

with ultraviolet/ozone (UVO) light, which changes the surface properties of the PDMS^[22–23] and helps to form strong chemical bonds via condensation reactions with various other surfaces that contain –OH groups, such as covalent bonds (–Si–O–Cr) between PDMS and Cr₂O₃. Peeling the PDMS away resulted in the transferral of multilayers onto the PDMS to give the Si anodes on the soft PDMS substrate with an underneath Au current collector; this collector takes advantage of short diffusion distance along the Si thickness direction, which allows more efficient ion and electron transport than in reported work that uses nanoparticles, nanowires, or nanotubes, and therefore beneficially increases the power density. Finally, thin layers of Cr (10 nm) and Au (100 nm) were deposited on top of the two ends of the Si ribbons through a shadow mask as a means of wiring out. For additional details, see the Experimental Section.

Figure 2B,C show the scanning electron microscope (SEM) image and optical images of a fabricated Si anode on a PDMS substrate. Figure 2D illustrates a schematic of an assembled testing cell with a fabricated Si anode and lithium metal as reference as well as counter electrode. The mass of Si anodes can be precisely determined by the well-defined geometries of the Si ribbons by photolithography and the well-accepted density of Si.^[24] The typical mass of Si anodes used in this study varied from 5.8–16.3 mg for different Si patterns and Si thicknesses.

Electrochemical characterizations were conducted on the assembled HS-test cells (Hohsen Corp.). Here the surface of the Si anodes was not particularly modified so that the SEI was similar to that in other reported work. Figure 3A shows a

striking example of the long cyclic stability of a half-cell battery up to 500 cycles with nearly 85% capacity retention. The cell was galvanostatically charged and discharged within a voltage window of 0.005–3.000 V (vs. Li/Li⁺) at C/4 rate (the charge/discharge rate was calculated based on the theoretical capacity of 4200 mAh g^{–1} for Si and the C/4 rate corresponds to a current density that allows a full discharge in 4 h). It is noted that the first cycle was not counted because of a varying C rate (0.1 C) and formation of the SEI layer. Compared to specific capacities reported for silicon-based lithium ion batteries,^[5] the battery from the Si thin film on PDMS substrate features an extremely low fading rate (15.4% over 500 cycles, equivalent to 0.033% degradation per cycle at C/4 rate) and a high specific capacity (up to 4137 mAh g^{–1} at the beginning and at 3498 mAh g^{–1} at the 500th cycle); these values indicate much improved cycling stability compared to conventional Si electrodes, which usually fade quickly after tens of cycles due to the well-known volumetric change during Li-ion insertion and extraction (for instance, a pure Si anode degraded from ca. 3200–300 mAh g^{–1} after 20 cycles, equivalent to 4.5% degradation per cycle^[25]). It should also be noted that the strategy of stress relaxation provides significant tolerance to Si thickness (up to 400 nm for the present study though this has not been optimized) compared to the previous study, where the thickness of the Si anode was limited to 50 nm and the surface of the current collector needed to be roughened.^[6] Although theoretical studies^[26–29] predict that ultrathin films or tiny particles, together with plastic deformation and slow charging rate, would somehow avoid fracture, this

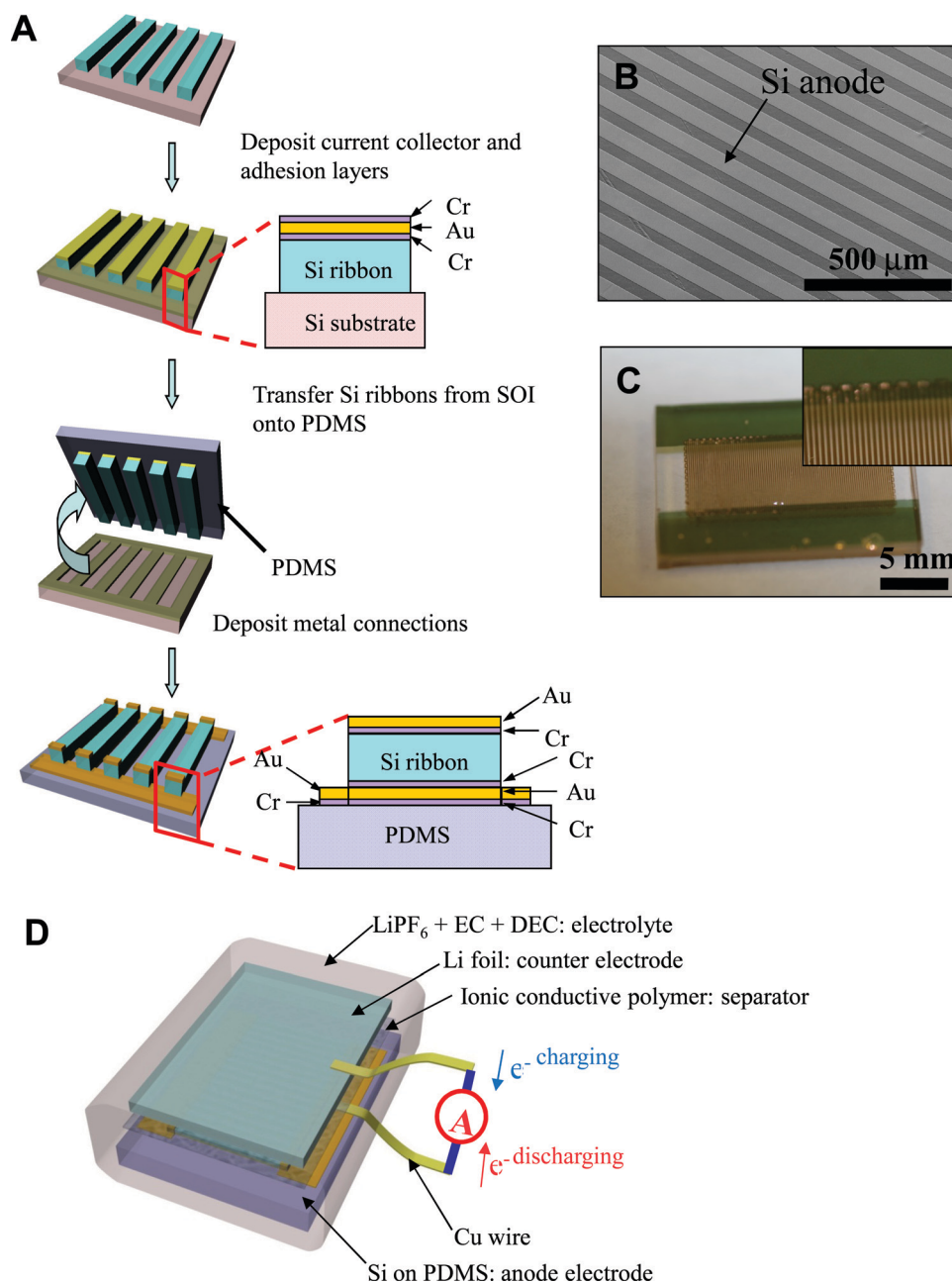


Figure 2. Half-cell lithium ion battery based on Si anodes, produced by microfabrication. A) Schematic steps to fabricate the Si anodes on PDMS substrates. B) An SEM image of Si anode on PDMS, and C) optical images of fabricated anode before assembling. D) An illustration of the battery cell assembly.

alternative solution of stress relaxation would have profound significance in meeting the requirements of current batteries with thicker anodes and/or cathodes.

The superb cycle stability is primarily attributed to the unique combination of the Si ribbons and the soft PDMS substrate, which helps to release the lithiation stress in Si via buckling of the Si ribbons. The evolution of the morphology change of the Si anodes was observed in situ (see Movie S1 in the Supporting Information). Figure 3B shows the SEM images of buckled Si ribbons (400 nm thick) after six cycles charge/discharge at a charge rate of 1 C, which verifies the hypothesis that

the lithiation strain causes the Si thin films to buckle on soft substrates. The buckled structures (Figure 3B), which are similar to springs, accommodate the accumulated stress to avoid cracking and crumbling of the Si electrode, thus maintaining the structural integrity and in turn, contributing to the superior cycling performance. We noticed that some cracking or extreme localized wrinkles exist, which may be caused by the initial cell-assembly process.

Figure 3C demonstrates a significantly stable and high Coulombic efficiency of up to 500 cycles. The Coulombic efficiency, which is defined here as the ratio of the capacity of the charge

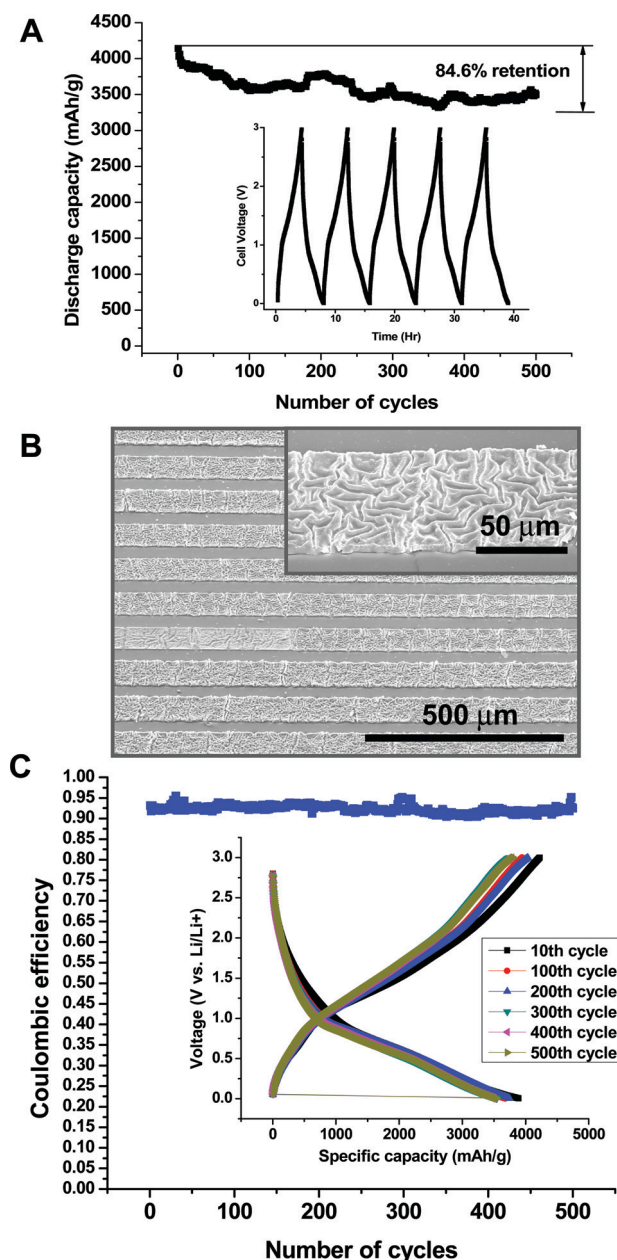


Figure 3. Electrochemical testing of Si anode based lithium ion batteries. A) Long cycle stability of the battery cell up to the 500th cycle with nearly 85% capacity retention. The inset is a typical charge/discharge profile from the 13th cycle to the 18th cycle). B) SEM images show the buckled Si after lithiation, after six cycles charge/discharge under the charge rate of 1 C. The inset is an enlarged image that clearly shows the buckling morphology. Si ribbons buckle on soft substrates due to electrochemical reactions. C) Coulombic efficiency from the 1st cycle to the 500th cycle shows a high value of 99% to nearly 100% efficiency. The inset includes I–V profiles of cycles from the 10th to 500th cycles.

immediately following the previous discharge, is between 92% to 95% throughout the 500 cycles. These data, which are higher than most of the reported values for Si-based lithium batteries which have lower than 90% of the Coulombic efficiency,^[16,30,31] complement the low capacity fading shown in Figure 3A and

indicate that the PDMS substrate plays a tremendously beneficial role in holding the electrode while allowing it to expand and contract reversibly during the repeated lithiation and delithiation processes. The consistent charge/discharge profile (voltage vs. specific capacity) demonstrated in the inset of Figure 3C shows the excellent stability of the dynamic processes during the Li-ion insertion into and extraction out of the Si lattice. Interestingly, the insertion and extraction processes occur across the entire potential window (0–3.0 V), and this Si anode system has an asymmetric reaction window, mostly below 1.0 V for the insertion process and above 1.0 V for the extraction process, which distinguish it from other Si anodes that have a relatively symmetric reaction window, all below 0.5 V.^[32] This unique phenomenon cannot be simply interpreted as a pure Li/Si redox reaction and/or nanostructural effect.^[32] It is plausible that the stress relaxation from the soft substrate may have different effects on the Li-ion insertion and extraction. Since the huge mechanical deformation in Si during electrochemical reactions (e.g., 400% volumetric change), the strain energy (proportional to the square of the deformation) is atypically comparable to the electrochemical energy (hundreds of kJ mol^{−1} as a typical scale). Thus, it is very likely that the mechanical deformation (e.g., the stress relaxation in the present work) affects the battery performance and raises new scientific phenomena, such as the charge/discharge profile in Figure 3C and many others.^[33] Work towards the fundamental understanding of this unique phenomenon is underway.

Figure 3A contains two pieces of exciting information: long cyclic stability and high specific-charge capacity, both of which are related to stress relaxation. The mechanism of relaxation of the stress associated with the electrochemical reaction can be qualitatively understood using continuum analysis. To simplify the problem, we created a two-dimensional model by considering a Si thin film (100-nm thick) bonded to a relatively thick PDMS substrate (500 nm) and ignoring other components, using the finite element analysis package ABAQUS. The Si thin film was modeled as an elastic–plastic material because plastic flow in Si anodes has been experimentally identified;^[34–36] and the PDMS was modeled as an elastic material. The modeling details can be found in the Supporting Information. Because of the buckling, the stress in the Si is nonuniform, i.e., tension and compression on the two sides of a neutral plane. Figure 4 shows the evolution of the maximum Si stress (both tension and compression) with the state of charge (Supporting Information). We notice that the maximum stress at 50% state of charge is only about 500 MPa, which is much smaller than that of the same Si thin films on a rigid substrate; this shows the relaxation of stress by using soft materials.

The current system with soft substrates to release stress has very high specific charge capacity (close to the theoretical value 4200 mAh g^{−1} as shown in Figure 3A). First-principle calculations have been conducted to explain the mechanism of high energy capacity when the stress relaxation is introduced, from the energy point of view. In the calculations, the stress relaxation is simulated by applying a tensile stress to a Li/Si system that originally contained compressive stress (caused by constraints from rigid substrates). For more details, see the Supporting Information. The potential energy *E* is given by Equation (1)

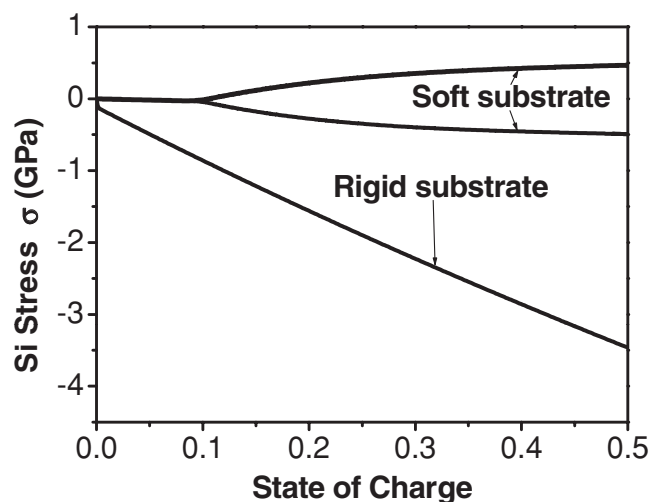


Figure 4. Finite element simulations show that the maximum stresses in Si are released on soft substrates, compared with the high stress developed in Si on rigid substrates.

$$E = E_{\text{pre}} \eta \mu_{\text{Li}} - E_{\text{Li/Si}} \quad (1)$$

where E_{pre} is the energy for a reference (or previously existing) Si system (with or without inserted Li), μ_{Li} is the energy for one Li atom, $E_{\text{Li/Si}}$ is the energy for the integrated Li/Si system after Li insertion, and η is the number of inserted Li atoms. The larger potential energy indicates that the Li insertion into the Si (or Si/Li) is more energetically favorable and thus the Li-inserted Si system is more energetically stable. We calculated the potential energy for inserting 160 Li atoms into a 4×4 repeated Si (111) supercell slab with 192 Si atoms. Without stress relaxation, the potential energy is calculated to be 80.94 eV and the compressive stress due to Li insertion is 10.36 GPa. To be conservative, partial stress relaxation, i.e., a 2.4 GPa tensile stress was applied to the same Li/Si system, which slightly increased E_{pre} from -1149.27 (no stress relaxation) to -1148.03 eV (with stress relaxation). However, $E_{\text{Li/Si}}$ apparently decreased from -1352.89 (no stress relaxation) to -1360.18 eV (with stress relaxation), which increased the potential energy to 89.47 eV. This calculation indicates that the Li/Si system with stress relaxation is more energetically favorable for the accommodation of more Li ions, which qualitatively explains the high specific charge capacity.

In summary, the advances reported here using soft elastomeric substrates to release electrochemical-reaction-induced stress in Si anodes offer dramatically improved performances for Li-ion batteries. Although the reported multilayered Si anodes demonstrate the advantages of a half-cell battery, the same approach is fully compatible with cathode designs, which would provide unusual yet huge opportunities in high performance Li-ion batteries, especially using those high energy capacity electrode materials. The fabrication process here is also compatible with standard and mature microfabrication techniques, which makes this method practical for the development of high energy thin-film batteries and bulk batteries by scaling up from multilayer stacking of active materials. In addition to the electrochemical performances from the unique mechanics aspects, this technology also has the immediate potential for

flexible/stretchable and portable high performance Li-ion thin-film batteries based on the presented electrodes design with or without stacked layer-by-layer configurations. Besides its role in stress relaxation, the elastomeric PDMS can also serve as a solid, ion-conductive, and mechanically conformable electrolyte by doping with lithium salt,^[37] where dual functions of PDMS make promising the development of high performance and solid-state thin-film Li-ion batteries that use Si as the anode. We are also aware of the shortcoming of the present design, i.e., the PDMS/Si electrode structure. PDMS releases the stress but also significantly increases the inactive materials, which prevents the practical application of the present method. To remove the PDMS and meanwhile be able to release the stress based on a similar concept (i.e., buckling) is part of our ongoing work.

Experimental Section

Preparation of Si Anodes: The fabrication of thin single-crystal Si anodes followed the reported procedure of transfer-printing inorganic devices for flexible/stretchable electronics.^[18] The procedure includes fabricating thin-film-based configurations from a bulk wafer, then separating these two by undercutting the intermedia layer, and finally picking-up and adhering the thin structures onto soft substrates.

PDMS (Sylgard 184, Dow Corning) was prepared by mixing the base and curing agent (10:1 by weight), debubbling, and curing at 80 °C for 2 hours to polymerize and then cutting to the desired dimensions as substrates. The Si anodes were derived from the top layer Si of SOI wafers (Soitec Inc.). The thickness of the Si layer ranges from 100–400 nm and that of the buried SiO₂ is 400 nm. The thin silicon was doped by implanting boron species (B(11)+) at 20 keV, and followed an annealing process (900 °C in N₂ for 1 min), which changed the resistivity from the initial value of 5–20 Ω cm to 1.5×10^{-3} Ω cm. The top thin silicon layer was patterned to form ribbons ca. 70–200 μm wide, 5 mm long by reactive ion etching (RIE; CF₄, 25 sccm, 25 mTorr, 50 W, Plasmalab) following photolithography (EVG 620, EV Group Inc.) using a photoresist (AZ 4330). The silicon dioxide layer underneath was wet-etched in concentrated (49%) hydrofluoric (HF) acid. Thus the Si ribbons rested on the silicon wafer without any chemical bonding between the two. Three thin layers of chromium (Cr, 5 nm), gold (Au, 100 nm), and then Cr (5 nm) were then deposited in sequence on top of the Si ribbons by thermal evaporation (Edwards). The first Cr layer promotes adhesion between the Si ribbons and the Au layer serves as the current collector. The second layer of Cr was oxidized by oxygen plasma to form Cr₂O₃, which acts as the adhesive layer in the following steps. The anodes was finally completed by transferral from the Si wafer onto UVO (low pressure mercury lamp, BHK Inc.)-treated PDMS and followed wiring out by deposit Cr/Au (5/100 nm) through a shadow mask using thermal evaporation (Edwards Auto 306).

Half-Cell Assembly: The half-cell-based lithium-ion batteries were typically configured by using Si ribbon arrays on PDMS substrates as the anode with lithium metal as reference and counter electrode in a 1 M LiPF₆ + EC + DEC (1:1:1 by volume) electrolyte. The two electrodes were laminated with an ion-permeable polymer (polypropylene/polyethylene/polypropylene from Celgard 2340), which functioned as a separator. All assembly manipulations were performed inside a glove box filled with purified argon. The schematic image is presented as Figure 2D.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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