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Silicon Nanofibrils on a Flexible Current Collector for Bendable Lithium-Ion Battery Anodes

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A high-energy-capacity, flexible lithium-ion battery is fabricated using a new nanofibril-structured silicon anode on a flexible current collector. Silicon is known to be the highest capacity anode material. However, its huge volume changes during the lithium insertion and extraction results in pulverization, which is the cause of the rapid capacity fade that occurs as the charge-discharge cycles progress. Nanostructured silicon can overcome this pulverization problem. A flexible current collector with high electric conductivity is prepared by a RF-magnetron sputtering of a thin copper layer (<1 μm) onto a porous polymeric membrane. This provides not only flexibility of the electrode but also a template for simple fabrication of nanostructured silicon. Cells using the new, flexible current collector and corresponding silicon nanofibril-structured anode exhibit energy capacities over 2000 mAh g^{-1} during 30 charge-discharge cycles at C/2. In addition, the coulombic efficiency remains over 99% after the third cycle. These results demonstrate the potential of the new anode for use in commercial high-capacity, flexible lithium-ion batteries.

1. Introduction

Lithium-ion batteries,[1] the most widely used energy source for portable devices, are attracting much interest as bendable or flexible batteries that can be integrated into soft electronic equipment such as rollup displays,[2,3] wearable devices, active RF identification tags, and integrated circuit smart cards. A flexible lithium-ion battery should simultaneously provide the flexibility and high energy capacity demanded by these rapidly developing soft mobile applications.

Two effective strategies to obtain a high energy capacity are to utilize superior electrode materials and to reduce the weight of the inactive components in the electrochemical cell. Silicon is one of the most promising candidates as an anode material for high-energy-capacity lithium-ion batteries owing to its abundance in nature, relatively low working potential, and highest known theoretical charge capacity of 4200 mAh g^{-1}, which is 11 times higher than that of commercial graphite.[4] However, the large volumetric changes (up to 400%) that occur upon insertion and extraction of Li ions result in electrode pulverization, loss of electrical contact, and early capacity fade of the battery cells.[5,6] Silicon nanostructures have emerged as an appropriate alternative for accommodating these severe volume changes,[7–11] and various approaches have been suggested including the preparation of Si nanostructures, such as porous Si nanoparticles,[12,13] nanocomposites,[14,15] nanotubes,[16] nanowires,[17,18] core-shell nanoparticles,[10,19] and porous nanostructures.[20] In addition, continuous efforts are being made to improve the cycle performance of these nanostructured silicon anodes.

Interestingly, the actual improvement in the energy capacity in current commercial lithium-ion batteries has resulted from reductions in the amount of inactive material involved in providing the energy capacity, such as the binder and conducting particles, and optimization of the cell design performed by industrial companies. In a commercial lithium-ion cell, the anode material is usually coated on a copper foil current collector to form a thin-sheet anode. The metal current collector on the anode side is usually a 12-μm-thick copper sheet with an areal density of ≈8.93 mg/cm^3. This copper sheet is a relatively heavy component in a lithium ion cell; it is comparable in weight to the anode active material and accounts for ≈10% of the total weight.[21,22] Although the current collector contributes a considerable weight to the battery cell, fewer efforts have been made to reduce the weight of the current collector as compared to other inactive components owing to the high electric conductivity of the copper foil.

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A flexible current collector made of a conductive material with a lower density can both help endow flexibility and reduce the weight. For this purpose electrodes using carbon or conducting polymers in the form of paper or free-standing films have been studied as potential material providing flexibility in lithium secondary batteries.[23,24] Cui et al. reported on a light-weight current collectors made from a stainless-mesh-supported carbon nanotube (CNT)-silicon composite or a free-standing carbon nanotube-silicon composite.[22] The surface resistance of the CNT films was ≈5 Ω/sq.

However, the surface resistance of this flexible current collector is considerably high compared to that of copper metallic foil (1.4 mΩ/sq calculated using the resistivity of pure copper with 12-μm thickness). It was reported that the lithiation is limited by the electron conductivity rather than the lithium diffusion step in Si nanowires.[25] Therefore, nanostructured silicon anodes prepared using copper foil current collectors were examined and found to exhibit high energy capacity (>1500 mAh g^{-1} for 30 charge-discharge cycles) as well as a high coulombic efficiency (>98%).[26–28] This clearly indicates that the current collector should provide high electric conductivity to make the most of the Si anode.

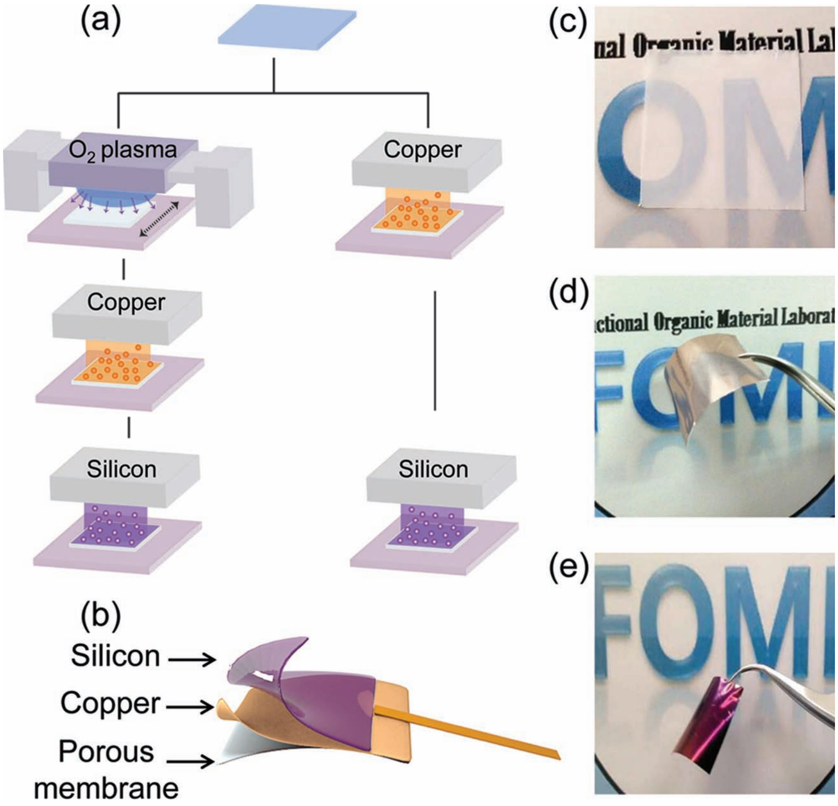

Figure 1. a) Schematic of the fabrication process for the flexible current collector and electrode. b) Illustration of the anode electrode. c) Photograph of the porous separator. d) Copper sputtered onto the separator. e) Silicon sputtered onto the copper layer.

Utilization of a flexible plastic substrate is one promising approach to obtaining flexible components. We recently reported on a flexible current collector made from a thin copper layer on a dense, transparent plastic film and found that the selection of the films should be based on their structural stability in the electrolyte solution. We also showed that a high conductivity is required to obtain capacities comparable to those obtained using graphite anodes.[29]

In this study, we demonstrate for the first time a flexible current collector made from a porous membrane that also provides a template for the facile fabrication of a nanofibril-structured Si anode for a high-capacity flexible battery.

2. Results and Discussion

A schematic illustration of the fabrication of the flexible current collector and subsequent formation of the nanofibril silicon anode on the flexible current collector is given in **Figure 1**.

As a porous polymeric membrane for the flexible substrate, we selected a polyolefin separator. Generally, a commercially available porous polyolefin separator is placed between the cathode and anode to prevent electrical short circuits while providing a path for ionic conduction through the porous structure.[30,31] Thus, utilization of a separator as a substrate is advantageous because of its thin, flexible character and mechanical stability under battery operation.

The flexible current collector was fabricated by forming a thin copper layer on the porous membrane using RF-magnetron sputtering. When the porous membrane was additionally treated with O_2 plasma (1 min) before the copper sputtering, the roughness was enhanced and a fibril-like surface morphology was formed from interconnections of the nanopores (**Figure 2**). The roughness of the porous membrane increased from 40.4 nm to 88.9 nm after 1 min of O_2 plasma treatment. This indicates that the plasma treatment increased the contact area of the porous membrane, which can improve the coating of the copper layer and the active material. The short plasma treatment also improved the adhesion of the sputtered copper layer and improved the resistance to detachment of copper layer during storage in the electrolyte solution (Figure S1 in the Supporting Information). Here, we call the flexible current collectors based on the porous membrane and plasma-treated membrane the FCC and P-FCC, respectively.

The electric conductivity of the flexible current collector was evaluated by measuring the surface resistance for different thicknesses of the copper layer on the flexible porous matrix (**Figure 3**). The thickness of the copper layer was estimated by measuring the thickness of the layer on a silicon wafer after different sputtering times. The surface resistance of the copper layer was inversely proportional to the layer thickness. When the copper layer thickness exceeded 230 nm, the surface resistance reached below 1 Ω/sq, which cannot be obtained using a conductive polymer or carbon nanotubes. The resulting flexible current collector was highly flexible, and the opposite side of the copper layer exhibited an electrical insulating property (see the movie in the Supporting Information). The surface resistance values of P-FCC were slightly lower than those of FCC.

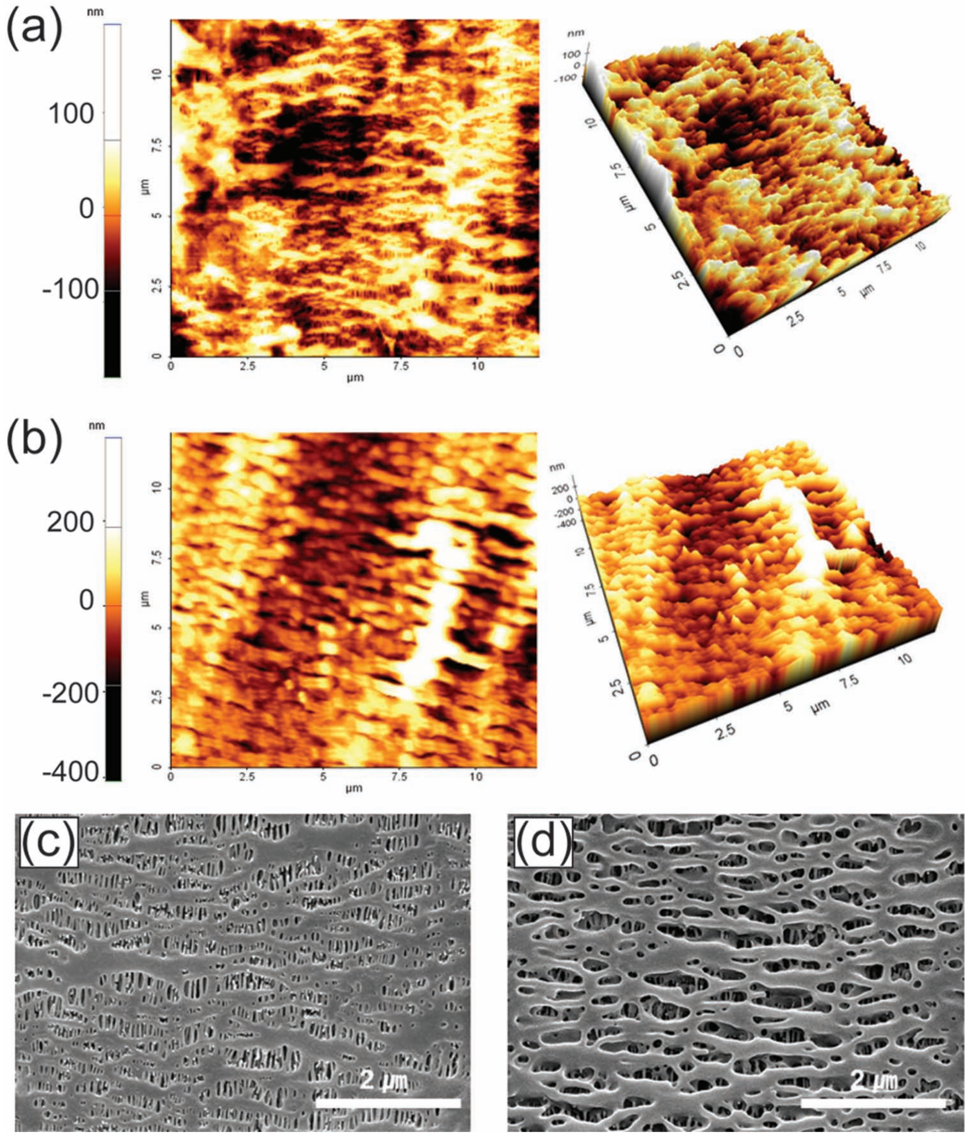

Figure 2. 2D (left) and 3D (right) atomic force microscopy (AFM) images of a) the porous separator and b) the O_2-plasma-treated porous separator. Scanning electron microscopy (SEM) images of c) the porous separator and d) the O_2-plasma-treated porous separator.

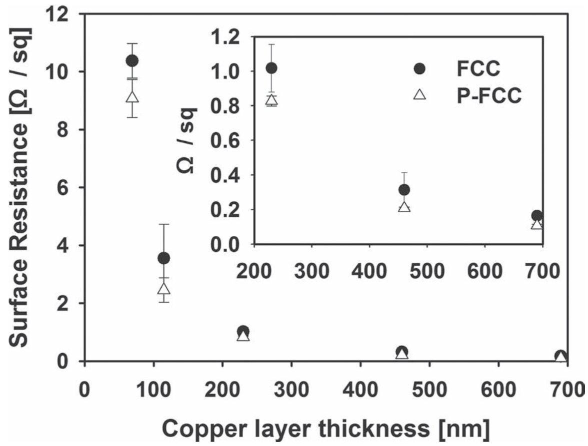

Figure 3. Surface resistance of the flexible current collector for different thicknesses of the copper layer.

The mechanical properties of the flexible current collector with the thin copper layer were compared with those of a commercial copper foil current collector (12 µm) using a nano-indentation test (**Figure 4**). It should be noted that the copper foil and fabricated flexible current collector yield different load-displacement indentation curves. The copper foil exhibits a smaller indentation displacement owing to its rigid characteristics, while the flexible current collector exhibits a larger indentation displacement. The residual indentation depth of the flexible current collector was twice that of the copper foil. The unloading curve of the fabricated flexible current collector indicated partial elastic recovery of the substrate.[32] Finally, the hardness and elastic modulus of flexible current collector were calculated as 3.225 and 0.211 GPa, respectively (Figure S2 in the Supporting Information) from the load-displacement data obtained from the nanoindentation test using the Oliver–Pharr

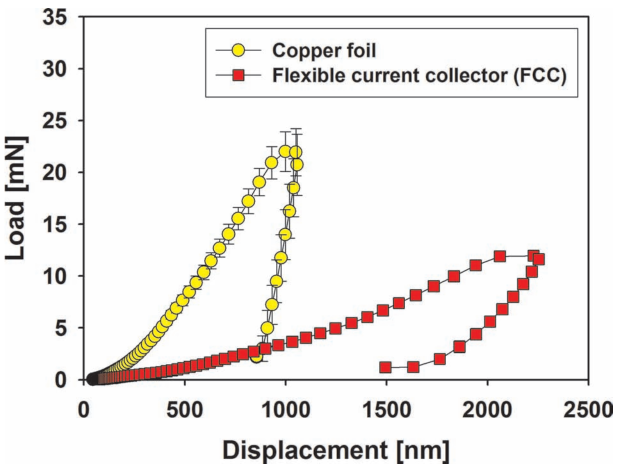

Figure 4. Load-displacement nanoindentation curves for copper foil and fabricated current collector (copper layer thickness: 690 nm; copper foil thickness: 12 μm).

method.[33] It can be expected that the porous polymeric substrate will play a beneficial role in the electrode while allowing it to expand and contract reversibly during the repeated lithiation and delithiation processes.

Silicon nanostructures can be fabricated using either complex procedures[34] or a simple procedure in which the current collector act as a template for a complex structured electrode that will reflect the surface morphology of the current collector.[35–37] Here, a silicon anode with a nanofibril structure was fabricated simply by sputtering silicon onto the prepared flexible current collector. As a result, the Si layer formed a nanofibril (or wave-like nanosheet) structure (**Figure 5**). This structure was more evident on the anode prepared from the plasma-treated porous membrane substrate. It is generally acknowledged that 2D configurations have more active sites than 0D or 1D structures and are thus more effective as electrodes than other structures.[38] Moreover, 2D structures have other superior properties, including low weight, a large surface area, and a regular distribution, which correspond exactly to the requirement for lithium storage. Because of their unique properties, the nanopores can accommodate the volume swell and make the materials more stable.[38]

The electrochemical properties of the cell prepared using the newly fabricated anode and lithium metal as a counter electrode were measured (**Figure 6**). The initial discharge capacity after the first cycle shows that a capacity of about 2800 mAh g^{-1} can be obtained using the Si nanofibril anode on P-FCC. The discharge capacity as a function of the number of cycles is shown in Figure 6a. All the cells exhibited energy capacities above 2000 mAh g^{-1} after 30 cycles at C/2. The cells fabricated using the flexible current collectors appeared to have higher capacities with improved capacity retention than those prepared using copper foil. In addition, the Si anodes prepared from P-FCC appeared to yield higher capacities than those prepared from FCC.

This suggests that it was easier for the fabricated flexible current collectors to relax stress than the copper foil, since the capacity retention is related to the film stress during cycling.[39] A plot of the coulombic efficiency as a function of cycle number is provided in Figure 6b. A stabilized coulombic efficiency after the first few cycles is crucial for commercialization.[40] The half-cells from FCC and P-FCC exhibited excellent coulombic efficiencies of over 99% beyond the second cycle.

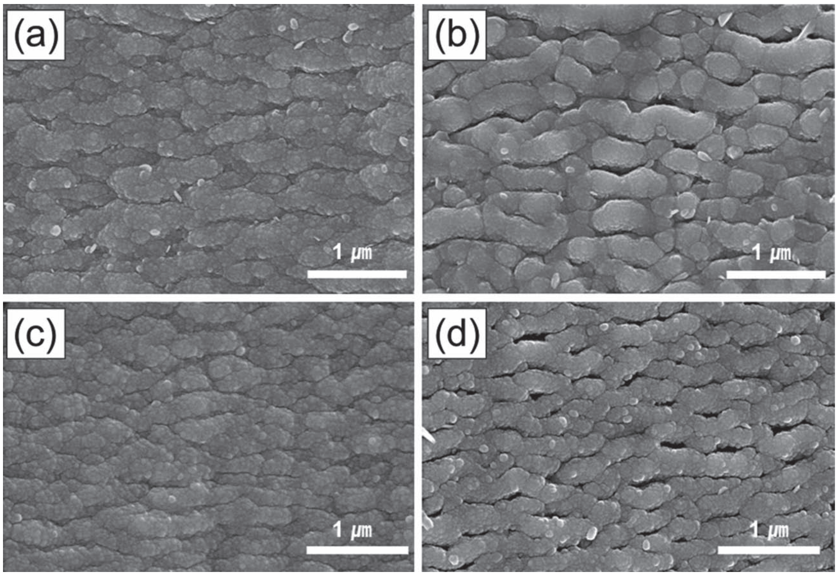

Figure 5. SEM images of the flexible current collectors and silicon anodes based on a,c) a pristine porous membrane and b,d) an O_2-plasma-treated porous membrane.

The cells also exhibited a high rate capacity (Figure 6c), suggesting that the combination of the high electric conductivity of the flexible current collector and the nanofibril structure of the Si anode positively influenced the electrochemical performance. The total resistance of the unit cell was compared after precycling and after 30 cycles (Figure 6d) for cells made from copper metal foil and from a flexible current collector (O_2-plasma-treated matrix). The interfacial resistance of the cells with flexible current collectors is found to be slightly less than twice that of the cells with copper metal foil. This indicates that the solid electrolyte interface (SEI) layer has been modified during precycling. The higher interfacial resistance after precycling is considered to be related to the stable structure of the SEI layer formed in this stage.[41] The interfacial resistance is observed to decrease after 30 cycles in both cases. However, the severe reduction in interfacial resistance of the cells with copper metal foil is attributed to pulverization of the Si surface and a subsequent increase in the surface area[41] that reduces the interfacial resistance. The mitigation of this effect is another evidence for the enhanced electrochemical performance of Si nanofibril anodes on flexible current collector. The surface morphologies of the Si electrodes removed from the cells after 30 cycles were compared (**Figure 7**). Although nano-scale thin Si film are known to show enhanced stability,[42] Si thin films on copper metal foil form severe cracks after cycling.[43] The formation of large cracks on

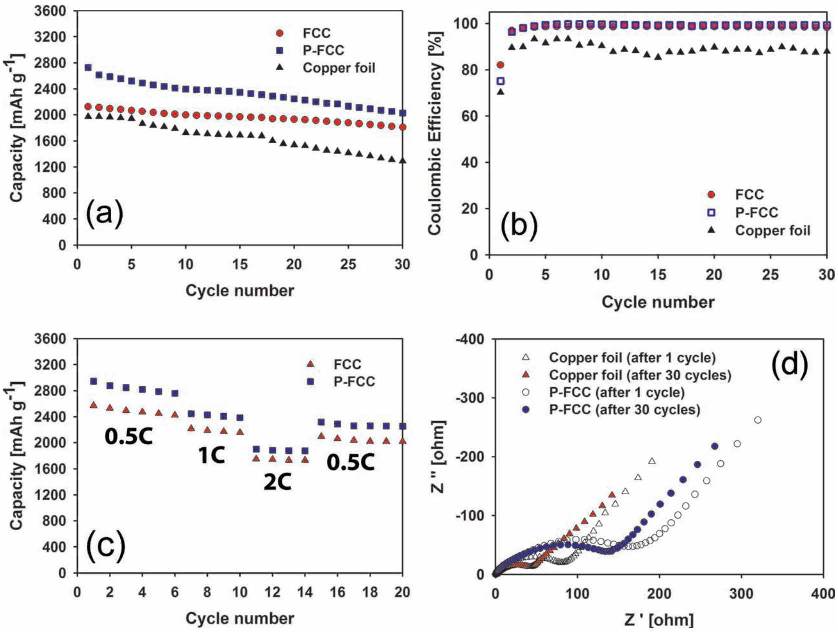

Figure 6. Comparison of cycling performance of batteries with Si anode on a current collector from a porous membrane (FCC), an O_2-plasma-treated porous membrane (P-FCC), and copper foil in terms of a) capacity, b) coulombic efficiency, and c) rate capability. d) Comparison of impedance spectra of unit cells measured after 1 and 30 cycles.

the surface of the Si thin films is due to the repeated aggregation, pulverization, and large volume expansions/contractions. We also observed the same situation for the silicon thin film anode deposited onto commercial copper foil (Figure 7b).

Although the surface morphology of the Si nanofibril-structured anode was different after 30 cycles, no micrometer-scale cracks were observed and the surface still appeared rather smooth. This implies that the superior electrochemical performance originates from the Si nanofibril structure that buffers the severe volume change during cycling.

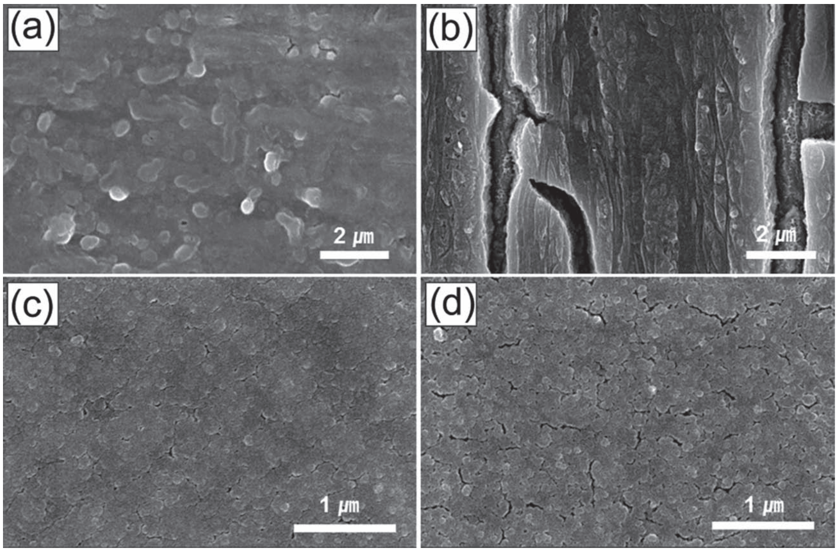

Figure 7. a) SEM image of the initial surface morphology of silicon sputtered onto the copper foil. b–d) Surface morphologies observed after 30 cycles for a Si anode on b) a copper foil, c) a flexible current collector made from a porous membrane (FCC), and d) a flexible current collector made from O_2-plasma-treated porous membrane.

To investigate cycling stability of cells under bending stress, charge-discharge cycling performance of the cells are measured under bending condition (bending radius 1.9 cm) up to 80 cycles (1–5 cycles: 0.5 C, 6–80 cycles: 1 C) using duplicate cells with different current collectors (**Figure 8**). The capacity of the cells showed similar trends as flat cells with cycling. However, increase in the initial capacity was observed for cells using FCC and P-FCC. As from enhanced discharge performance of recently reported flexible alkaline battery under bending condition,[44] this is attributed to better interfacial contact of rough Si anode from flexible current collectors (FCC, P-FCC). Coulombic efficiency of the cells based on flexible current collectors was over 97% whereas a cell from copper foil was 89% under bending condition.

3. Conclusions

We report the successful fabrication of high-capacity, flexible battery made using a nanofibril-structured Si anode on a flexible current collector. The nanofibril-structured Si anode can be fabricated without any complicated procedure. Considerable improvement in the electrochemical performance, including energy capacity is obtained from the new Si anode with the flexible current collector. The new current collector provides the advantages of low weight, high electric conductivity, flexibility, and the ability to provide a template for silicon nanostructure. It is anticipated that the flexible current collector and resulting nanostructured Si anode will contribute to the development of high-energy-capacity, flexible lithium-ion batteries.

4. Experimental Section

Preparation of Electrodes: The flexible current collector was prepared using a microporous polypropylene (PP) separator (Celgard 2400, 25 μm) as a substrate. The surface of the separator was treated with O_2 plasma (MYPL-100, APP Corp. Korea) for 1 min to enhance roughness and adhesion of the copper layer. Copper and silicon were consecutively sputtered onto both the untreated samples and the samples treated with O_2 plasma using RF-magnetron sputtering to fabricate the flexible current collector and flexible silicon anode, respectively. The purity of the target materials used was 99.999%, and the distance between the target and the sample was 10 cm. Prior to the copper and silicon sputtering, the targets were presputtered for 60 min at RF power of 50 W (copper) and 25 W (silicon) to remove the oxidized layer. The working pressure in the stainless steel

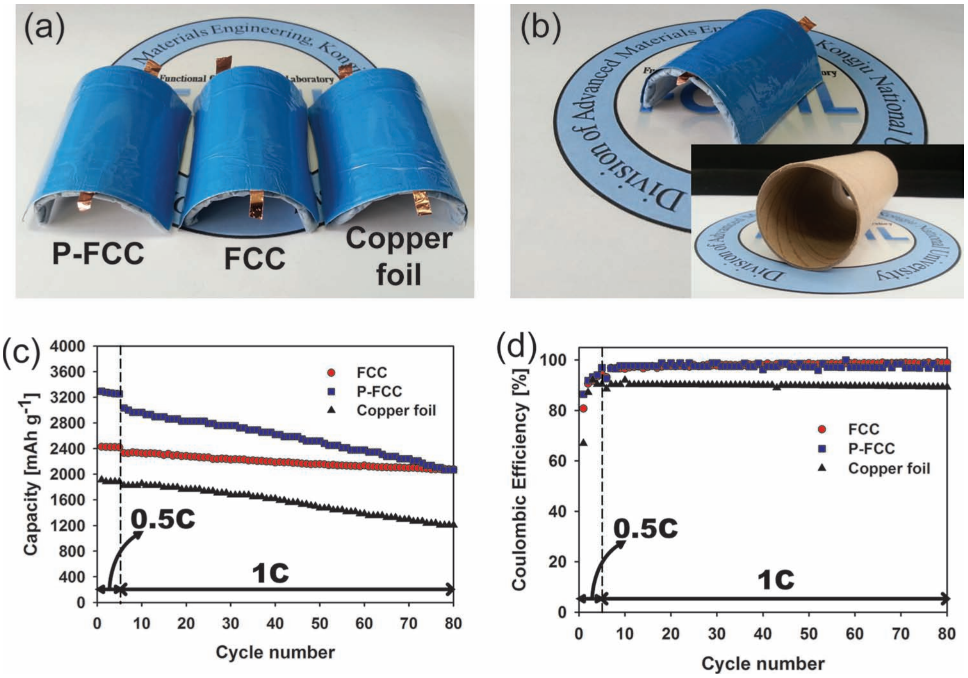

Figure 8. a) Images of cells under bending condition. b) All the cells are bent at the bending radius (R_c) of 1.9 cm using paper core (inset figure) as a support. Comparison of cycling performance of bent batteries with Si anode on a current collector from a porous membrane (FCC), an O_2-plasma-treated porous membrane (P-FCC), and copper foil in terms of c) capacity, and d) coulombic efficiency.

chamber was 7×10^{-3} Torr of argon. Copper and silicon were sputtered for 30 and 10 min, respectively. Amount of silicon anode on current collectors were calculated based on the amount of silicon sputtered on silicon wafer at the same sputtering condition (thickness: 40 nm, area: 2.0 cm x 2.0 cm, and density of Si: 2.3 g cm^{-3})

Cell Fabrication and Testing: A pouch-type cell was prepared using the flexible current collector with the nanostructured silicon anode to investigate its electrochemical performance. Lithium metal was used as a counter electrode. As an electrolyte, 1 M $LiPF_6$ in mixture of 1:1 (v/v) ethylene carbonate (EC) and diethyl carbonate (DEC) was used as received from PANAX Starlyte (Korea). The polyethylene separator (Asahi-Kasei) was soaked in electrolyte for 24 h prior to cell assembly. The cells were assembled inside an Ar-filled glove box and sealed in aluminized polyethylene laminate bags. The charge-discharge cycling properties were measured in the voltage region of 0.005–1.5 V under a constant current condition using a WBCS-3000 instrument (Wonatech, Korea). The electrochemical impedance spectroscopy (EIS) measurements were conducted using a Solartron 1400 frequency response analyzer (FRA) in conjunction with a Solartron 1470E electrochemical interface over a frequency range of 10^6–10^{-1} Hz.

Properties of Electrodes: The surface morphology of the microporous PP separator used to fabricate the flexible current collector was investigated using AFM (XE-100, Park Systems, Korea) and SEM (S-4800, Hitachi, Japan). The surface resistance of the flexible current collector for different sputtering times was measured using four-point probe equipment (CMT-SR1000N, AIT Co. Korea).

Nanoindentation Test: The nanoindentation tests were performed with an MTS Nanoindenter XP system operating in continuous stiffness mode. The nanoindentation system monitors and records the load and displacement of the three-sided pyramidal diamond (Berkovich) indenter during indentation with a force resolution of about 50 nN and a displacement resolution of about 0.01 nm. To achieve a continuous stiffness measurement, the allowable thermal drift rate was limited to 0.15 nm/s. The Poisson's ratio was set to 0.3.[45]

Supporting Information

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

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