Supplementary Information

Soft silicon anodes for lithium ion batteries

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Experimental Section

Polyvinylidene fluoride (PVDF) was dissolved into a mixture of acetone and DMF (30:70 vol%) under constant stirring for 2h at 30 °C. Nanofibers were electrospun from the PVDF solution with a feeding rate of approximately 0.5 mL/h through a stainless steel sypringe pipette needle under a potential of 26 kV. Nanofibers were collected on a sheet of aluminium foil placed 12 cm below the springe tip, the thickness of the nanofiber membrane could been controlled by electrospinning time. The resulting nanofiber membrane was then dried at 50 °C for 10 h in low vacuum.

Prior to coating nickel, PVDF nanofiber membrane was cut into a piece of 3 cm × 2 cm (see Figure 3a). The nanofiber membranes were activated by introducing palladium seeds on the nanofiber surface. During the seeding process, the nanofiber membrane was first immersed in 3.0 mM $SnCl_2$ aqueous solution for 30min and then in 3.0 mM $PdCl_2$ solution for 10 min. The surface activated nanofiber membrane was then immersed in the 0.01 M Ni $(NO_3)_2$ aqueous solution for Ni electroless plating at 50 °C for about 15 min. The Ni coated nanofiber membrane was rinsed with distilled water and dried in vacuum. The plating time can be adjusted to control the thickness of coated nickel shell. The d.c. electrical conductivity was measured using a four-point probe station. Amorphous silicon was coated onto the Ni/PVDF coaxial nanofibers using a RF magnetron sputtering system (ELITE RF/ DC magnetron sputtering), where a pure silicon target (99.999%, Super

Conductor Materials, Inc.) was RF sputtered at 200 W under pure Ar atmosphere. The total a-Si mass was calculated by weighing the Ni/PVDF membrance before and after a-Si coating using an analytical balance (Mettler Toledo XP 26, 0.001 mg). It is found that 100 µm thick membrane yielded non-uniform silicon coating due to strong shadowing effect. If the membrane thickness is reduced to 10 µm, the a-Si could be uniformlly coated onto Ni/PVDF fibers. The mass ratio between the Si shell and Ni/PVDF core is therfore calculated according to their diameter ratio. As shown in the TEM image (Figure 2), the thickness of the adverge diameter is about 400 nm, the thickness of Ni shell is about 100 nm, and the thickness of outer shell Si is about 80 nm. Given that the density of the PVDF and Ni is 1.17 and 8.9 g cm^{-3}, respectively and the density of the amorphous Si prepared with our recipe is 2 g cm^{-3}, the mass ratio should be m_{si}:$m_{(Ni+PVDF)}$=18.1:81.9, calculated using the formula:

$$m_{\mathrm{Si}} : m_{(\mathrm{Ni+PVDF})} = \rho_{\mathrm{Si}}(\pi \mathrm{r}_3^{\ 2} - \pi \mathrm{r}_2^{\ 2}) / \left((\rho_{\mathrm{Ni}}(\pi \mathrm{r}_2^{\ 2} - \pi \mathrm{r}_1^{\ 2}) + \rho_{\mathrm{PVDF}} \pi \mathrm{r}_1^{\ 2}\right),$$

where r_1, r_2 and r_3 are the radius of the PVDF, the Ni/PVDF, and the Si/Ni/PVDF, respectively. ρ_{Si}, ρ_{Ni} and ρ_{PVDF} represent the densities of amorphous Si , Ni metal, and PVDF, respectively.

The testing electrode was made by laminating a flexible freestanding Si/Ni/PVDF coaxial membrane on a coin cell shell. Loading a-Si mass was 0.08 mg/cm and no conducting carbon were used. To test the performance of the Si/Ni/PVDF coaxial membrane in batteries, the coin cells were made using freestanding Si/Ni/PVDF coaxial membrane as the working electrode, Celgard 2250 as the separator, and Li metal foil as the counter electrode. 1.0 M $LiPF_6$ in 1:1 w/w ethylene carbonate/diethyl carbonate was employed as the electrolyte. The cells were assembled into CR 2032 type half cells inside a glove box filled with Ar. Galvanostatic measurements were made using the NEWARE BTS-5V multichannel system (Neware Technology Co., Ltd.). The cells were cycled between 1.2 V and 0.05 V at different rates. The Cyclic voltammogram (CV) was performed using a multi-channel electrochemical station (Autolab, M 101). Soft packing cells were made from a heat sealable aluminium laminated film (D-EL40H, DNP Japan). The 100 µm thick Si/Ni/PVDF coaxial membrane was cut into 1 cm × 2 cm, and the top edge of the membrane was attached to a Ni metal tab. The anode was 1 cm ×

2 cm and 0.5 mm thick lithium metal pressed onto a copper foil current collector with attached Ni metal tabs. Electrodes were assembled into aluminium laminated pouch cells with Celgard separator (2250) and 1.0 M $LiPF_6$ in 1:1 w/w ethylene carbonate/diethyl carbonate.

The morphology of the prepared samples was observed using scanning electron microscopy (SEM, LEO 1550 Gemini). After 200 cycles, delithiated Si/Ni/PVDF coaxial membrane electrodes were taken out of the cell inside a glove box, washed with propylene carbonate to remove residual electrolyte and lithium salts and dried at room temperature prior to SEM examinations. The Raman spectra were obtained using a WITec Raman system with a laser line at λ= 532 nm. The X-ray diffraction (Siemens D5005 X-ray diffractometer) with Cu Kα of 1.540A was used to characterize the structures of samples. The bend and stretch tests were carried out with a two point bending device and a high precision mechanical system with Zwick 20TN2S apparatus.

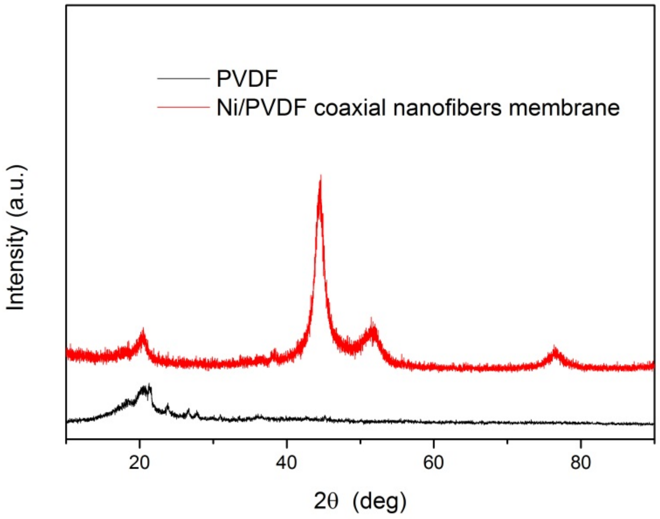

Figure S1. The X-Ray Diffraction spectra of PVDF and Ni/PVDF, respectively.

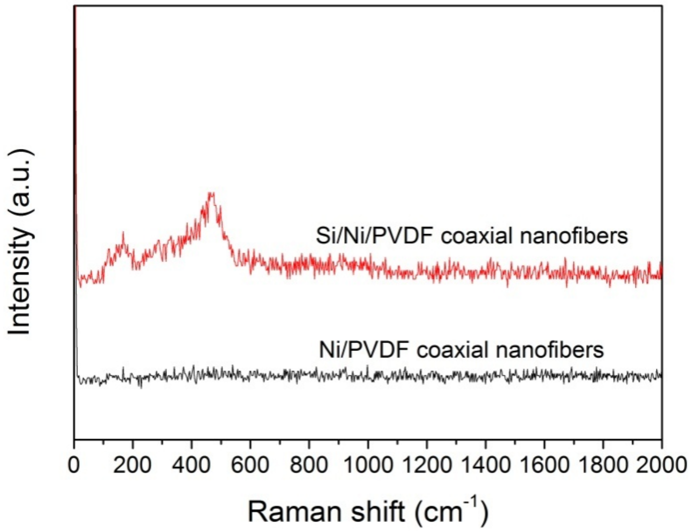

Figure S2 The raman spectra of Ni/PVDF and Si/Ni/PVDF, respectively.

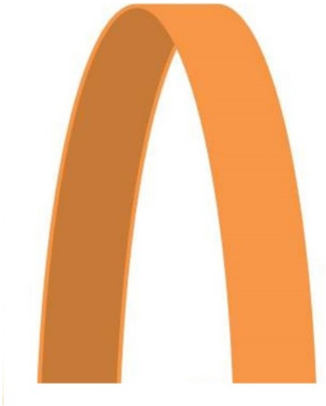

Figure S3 Schematic of flexible coaxial nanofiber membrane anode bent inwards at 180^o

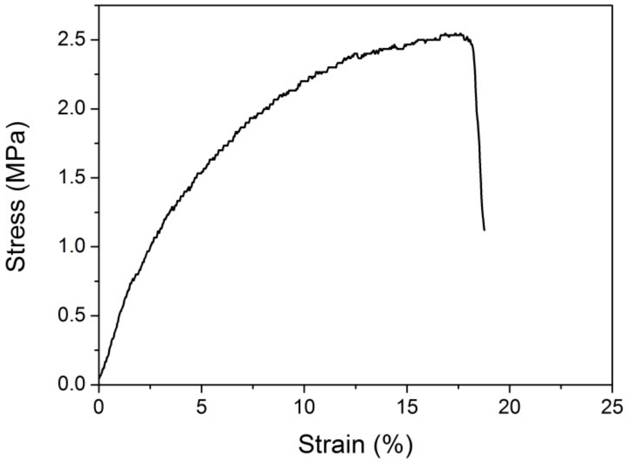

Figure S4 Typical Stress-strain curve of Si/Ni/PVDF coaxial nanofiber membrane

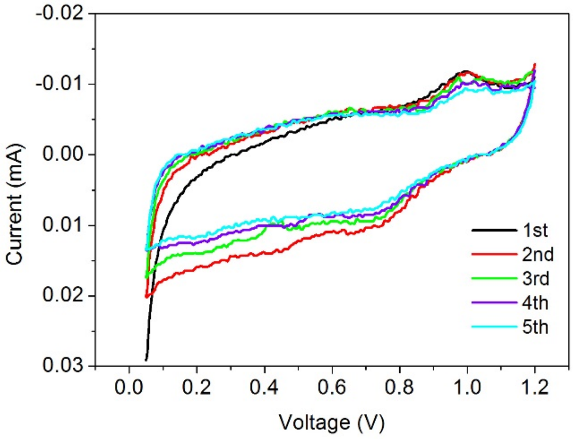

Figure S5 Cyclic voltammogram of the flexible Ni/PVDF coaxial nanofiber membrane using Li metal foil as the counter electrode

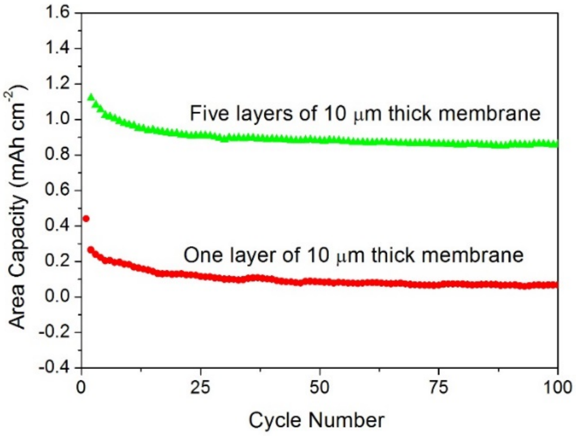

Figure S6 Areal capacities of the Si/Ni/PVDF coaxial nanofiber membrane anode with the multilayer 10 μm thick membranes at 2 C

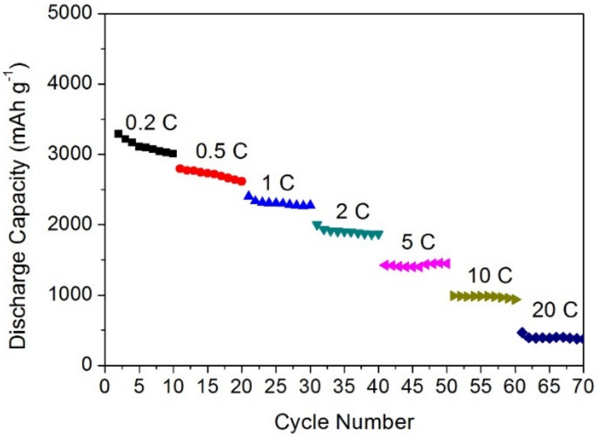

Figure S7 The rate capability of the five layers of 10 μm thick Si/Ni/PVDF coaxial nanofiber membrane anode

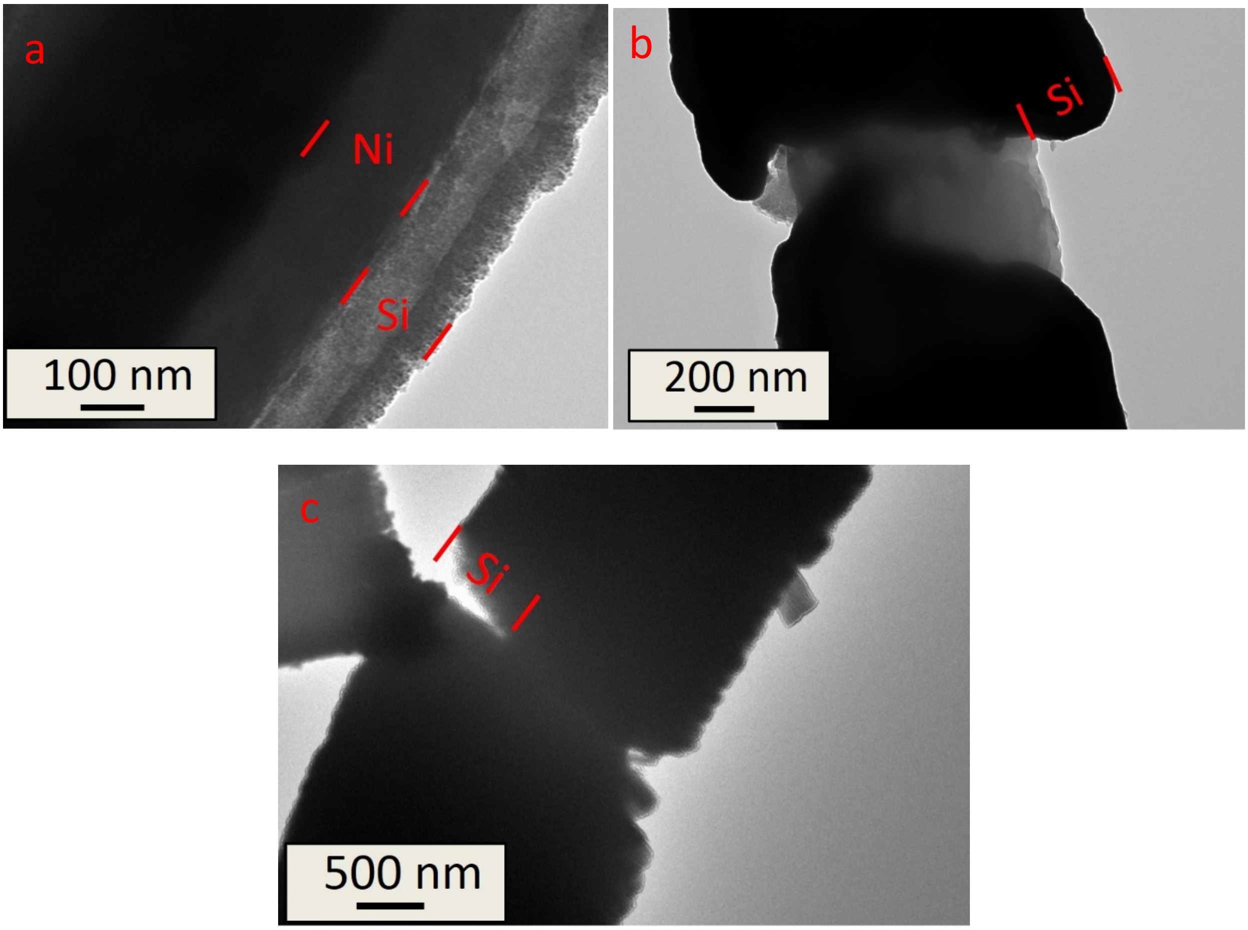

Figure S8 TEM images of Si/Ni/PVDF coaxial nanofiber membrane at deferent thickness of Si

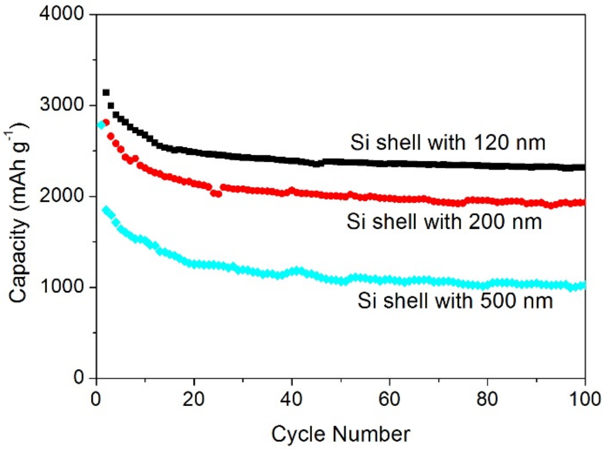

Figure S9 Cycle performance of Si/Ni/PVDF coaxial nanofiber membrane anode with deferent thickness of a-Si coating at 0.2C

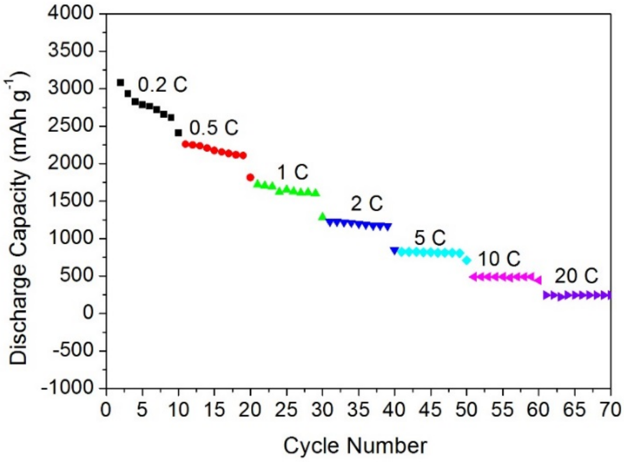

Figure S10 Rate capability of Si/Ni/PVDF coaxial nanofiber membrane anode in the bending battery