Supplementary Information

Electrospun core-shell silicon/carbon fibers with internal honeycomb-like conductive carbon framework as anode for lithium ion batteries

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The Calculation Method of Volumetric Properties for Si/po-C@C Electrode:

In order to better estimate the benefit of the obtained Si/po-C@C composite fibers, the volumetric properties of the material (mAh cm^{-3}) and Wh L^{-1} in a full cell model were calculated according to the recently published cell model in the reference [45].

Firstly, for the only bare Si/po-C@C composite, considering the volume expansion, the volumetric capacity was calculated to be 1742 mAh cm^{-3} for the largest volume after the first full lithiation, and the corresponding reversible volumetric capacity is calculated to be 1133 mAh cm^{-3}. The total expansion of Si/po-C@C was determined to be 23 % based on the following method. The Si/po-C@C composite can be considered to be composed by three parts: compact amorphous carbon (2.24 g m^{-3}), silicon (2.33 g cm^{-3}) and pores (0.178 cm^3 g^{-1}). For the compact carbon, we assumed that the volume expansion is proportional to the lithium ion insertion. According to the report in the reference [45], the gravimetric

capacity of 1115 mAh g^{-1} corresponds to a volume expansion of 31%. Thus, in this work, the volume expansion of compact carbon matrix can be calculated to be 23 % based on its specific capacity of 827 mAh g^{-1}. For silicon component, the complete lithiation of Si causes an expansion of about 280%. The Si content in Si/C composite is 21.8 wt%. The volumes of Si and carbon matrix in Si/C composite are 0.218/2.33=0.094 and 0.782/2.24=0.349 cm^3 g^{-1}, respectively. Thus, the overall volume of Si/po-C@C including internal space is 0.094+0.349+0.178=0.715 cm^3 g^{-1}. After complete lithiation, the total expansion of silicon component and carbon matrix is 0.094*2.8+0.349*0.23=0.343 cm^3 g^{-1}. However, the pore volume in Si/po-C@C is only 0.178 cm^3 g^{-1}, it is hard to buffer all the volume expansion of 0.343 cm^3 g^{-1}. An additionally overall volume expansion of 0.343-0.178=0.165 cm^3 g^{-1} (0.165/0.715=23%) was generated for the neat Si/po-C@C during the first complete lithiation. Thus, according to the new method for evaluating the volumetric properties provided in literatures [42,45], the volumetric capacity of active Si/po-C@C composite can be calculated to be 1533 mAh g^{-1}/(0.715+0.165) cm^3 g^{-1} =1742 mAh cm^{-3}. Correspondingly, the reversible volumetric capacity is determined to be 997/0.88=1133 mAh cm^{-3}.

The full cell model demonstrated in the reference [1] is used to evaluate the impact of using anodes that comprise elements that alloy with lithium on the cell energy. The anode is assumed to be comprised entirely of the active element with zero porosity. In the case of the applied cell model, a simple equation (eq 1) can be used to estimate the cell stack energy density of an anode $\tilde{q}_{\bar{R}}$ (in Wh L^{-1}) with a reversible coating volumetric capacity (in Ah L^{-1}) and average voltage $V_{\bar{avg}}$ (in volts):

$$\breve{U}_R = \frac{(58327.5\ Ah/L)}{70\ +\ (110)\left[1\ +\ \frac{(583.275\ Ah/L)}{\tilde{q}_{\bar{R}}}\right]}[(3.9\ V)\ -\ V_{\bar{avg}}] \quad (1)$$

In this study, a Si/po-C@C thin film electrode with no porosity has a reversible volumetric capacity of 1133 Ah L^{-1} and an average voltage of 0.4 V. Substituting these values into eq 1 as $\tilde{q}_{\bar{R}}$ and $V_{\bar{avg}}$, respectively, results in a stack energy density of $\mathcal{U}_R$=863 Wh L^{-1}. This indicates a 19 % increase in volumetric energy as compared to the baseline $LiCoO_2$/graphite cell of 726 Wh L^{-1}, described in the reference [45].

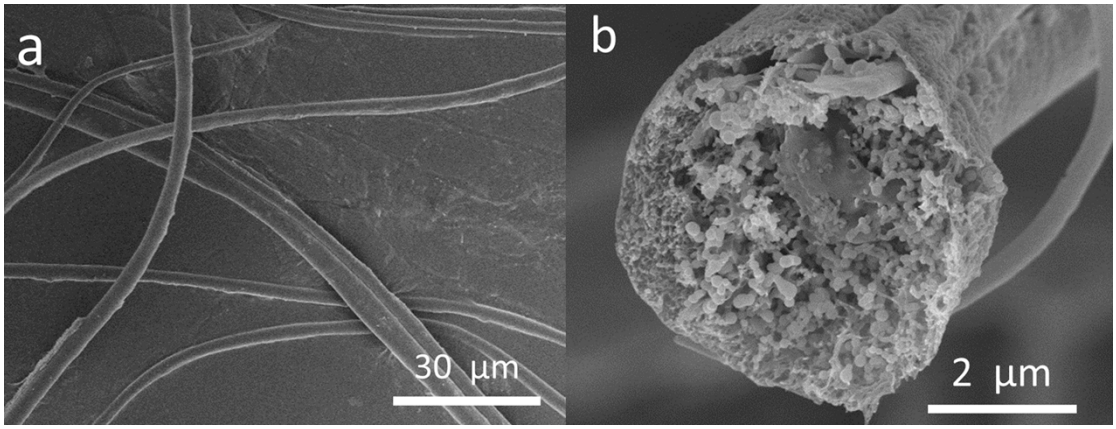

Figure S1. SEM images of (a) Si/PAN/PS@PAN precursor fibers and (b) cross-section with a core-shell structure. Si NPs are encapsulated in the core section.

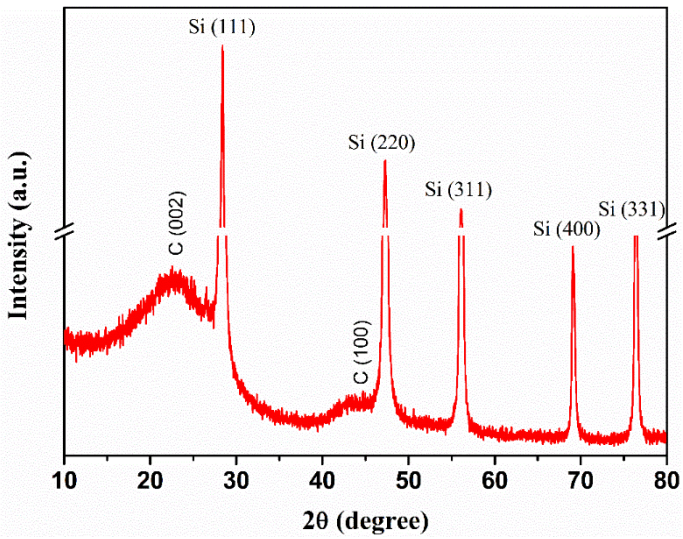

Figure S2. XRD patterns of Si/po-C@C.

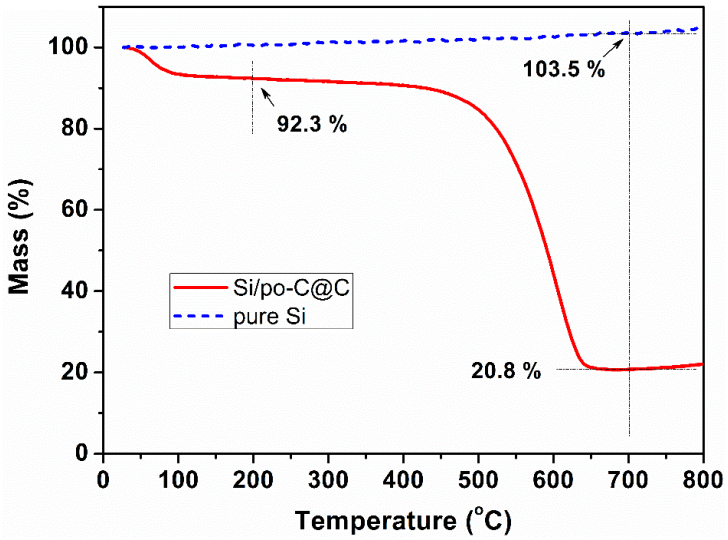

Figure S3. TGA of pure Si and Si/po-C@C in air with a heating rate of 5 °C/min.

Based on the TGA results, the weight loss of 7.7 % for Si/po-C@C below 200 °C can be attributed to water evaporation. At 700 °C, the carbon matrix is burnt-out, and the mass residual of 20.8 % is composed of Si and SiOx. Based on the curve for pure Si, the weight of Si increases by 3.5 % at 700 °C, because a certain amount of SiOx is formed during oxidation. Thus, the Si content in Si/po-C@C composite can be determined by the following Equation : $\frac{0.208 \div 1.035}{1 - 0.077} \times 100\% = 21.8\ \%$

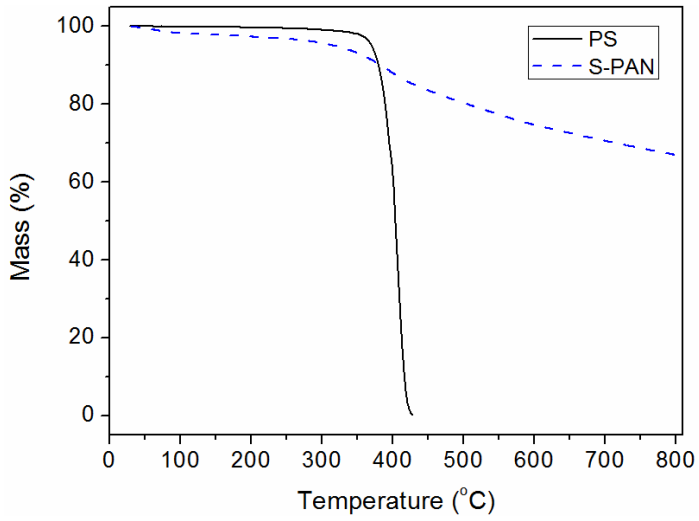

Figure S4. TGA curves of PS and S-PAN (PAN was stabilized in air at 250 °C for 2 h). The testings were performed in argon with a heating rate of 10 °C/min.

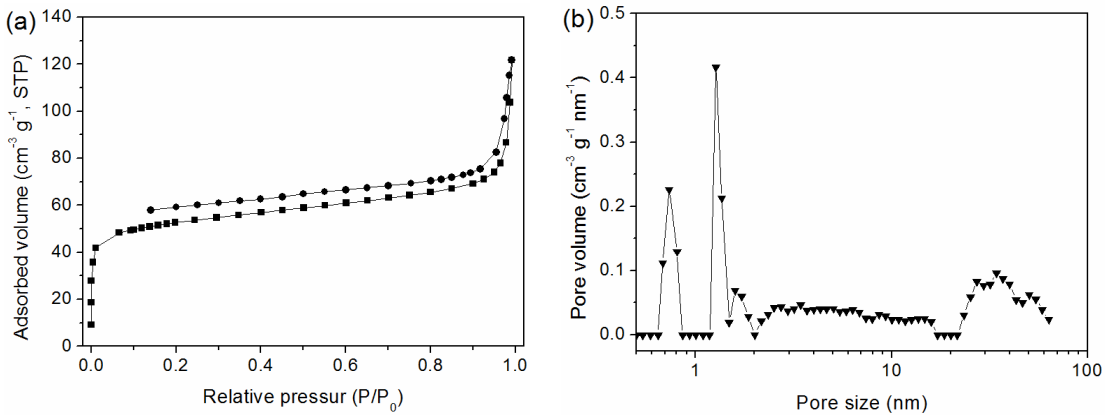

Figure S5. (a) Nitrogen adsorption/desorption isotherm and (b) pore size distribution of Si/po-C@C composite fibers.

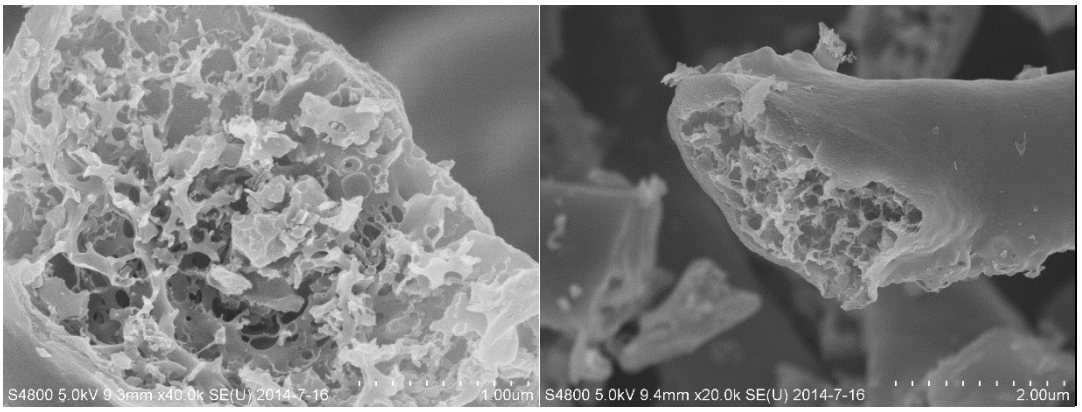

Figure S6. The internal honeycomb-like structure of po-C@C fibers.

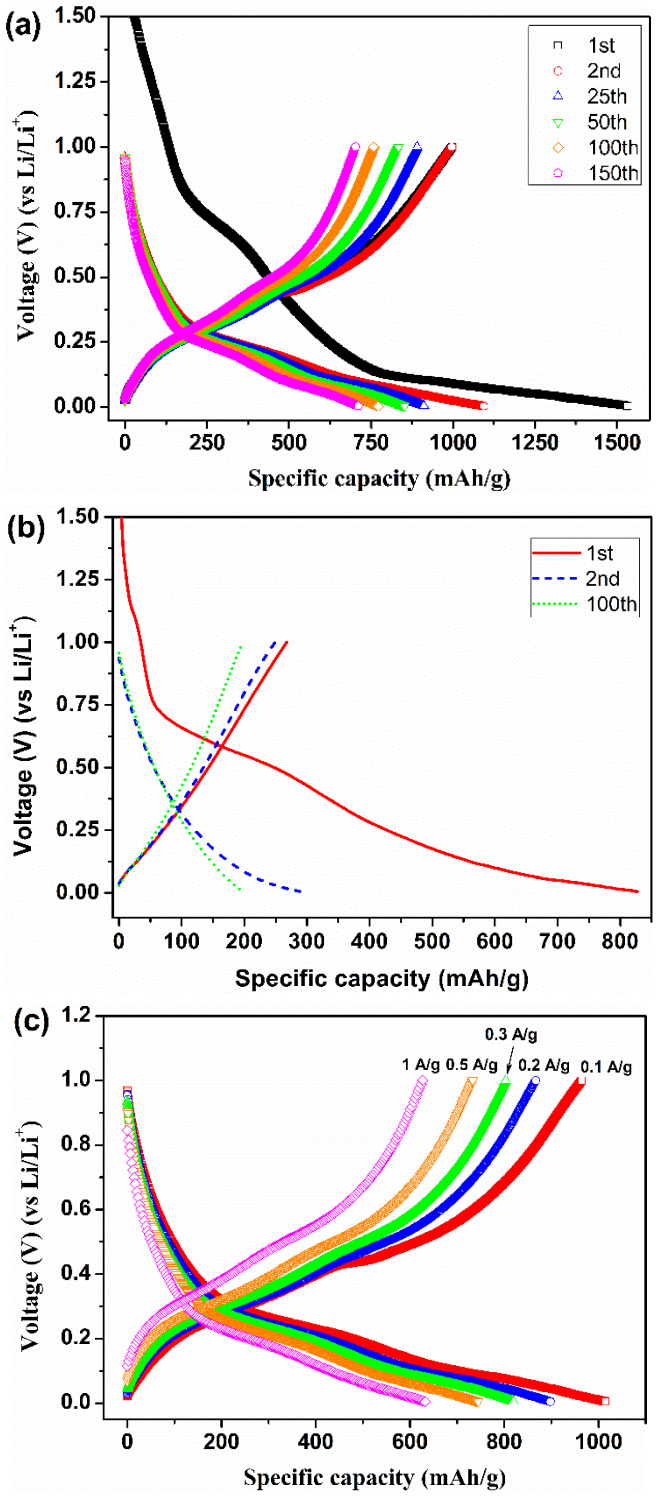

Figure S7. Discharge/charge potential profiles correspond to cycling performance tests of (a) Si/po-C@C and (b) po-C@C at 0.2 A g^{-1}, and (c) rate capability test of Si/po-C@C from 0.1 to 1 A g^{-1}.

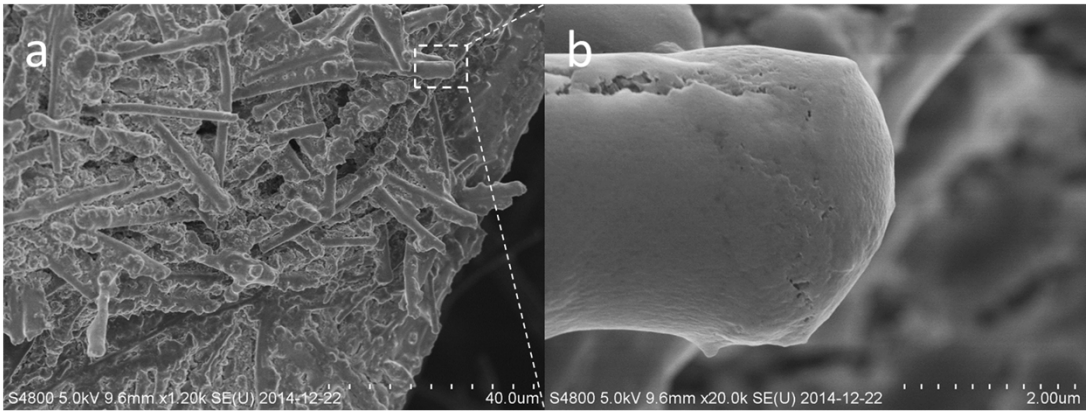

Figure S8. The morphology of SEI film for Si/po-C@C electrode after cycling.

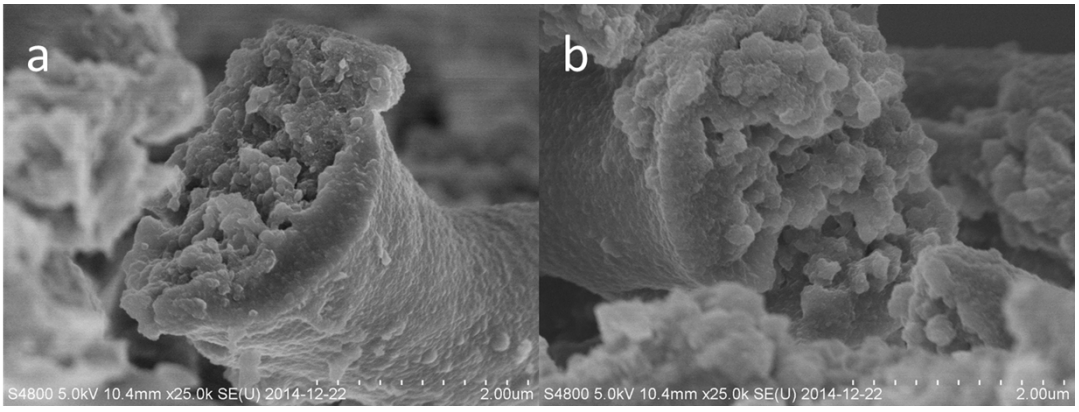

Figure S9. The internal morphology of Si/po-C@C composite after deep cycles.

Table S1. Comparison of capacities of the whole Si/C electrode and accessibility of Si in Si/C composite in this work and in literatures.

Sample style[a)]	Current density [mA g^{-1}] &Voltage range [V]	Si content [wt%]	Initial reversible capacity [mAh g^{-1}]		Cycles	Capacity retention [mAh g^{-1}]		References
			Si/C[b)]	Si[c)]		Si/C[b)]	Si[c)]	
Si/po-C@C	200&0.005-1	21.8	997	3612	150	703	2528	This work
Si@C	240&0.005-1	50	1250	2221	100	1250	2221	[26]
Si@PCNF	200&0.005-1	50.2	1598	2800	100	1104	1900	[27]
SiNP@CT	1000&0.01-1	47	969	1836	200	872	1630	[28]
Si/CNF	50&0.01-3V	26.3	969	2283	50	648	1342	[32]
Si/CNF/G	100&0-1.5	42	905	1892	50	872	1814	[33]
Si/CNT@C	50&0.01-1.5	29	1167	3088	45	850	1995	[35]
Si@C	50&0.01-1.5	29.4	937	2367	45	750	1722	[35]
C@Si@C	50&0.01-1.5	26	1211	3627	100	904	2495	[36]
Si@C	50&0.01-1.5	29.7	1148	3011	100	890	2163	[36]
3D Si/C	500&0.02-1.5	72	1600	2117	100	1200	1562	[37]
Si-G-C	200&0.005-1	78	2379	2996	200	1344	1669	[38]

[a)]All samples were fibrous Si/C composites prepared based on electrospinning; [b)]Specific capacities of the whole Si/C composite electrode calculated based on the total mass of Si and carbon matrix; [c)]Accessibility of Si in the whole Si/C electrode based on the Si content in Si/C composite and the contribution of carbon matrix to the overall capacity.