Electronic supporting Information for

Towards flexible binderless anodes: silicon/carbon fabrics via double-nozzle electrospinning

Changling Li, Chueh Liu, Wei Wang, Jeffery Bell, Zafer Mutlu, Kazi Ahmed, Rachel Ye, Mihrimah Ozkan and Cengiz S. Ozkan*

Calculation of packaged battery full-cell:

\[ \frac{1}{\frac{1}{C_{\text{cathode}}} + \frac{1}{C_{\text{anode}}}} \]

The total capacity of full-cell is calculated: \( C_{\text{total}} = C_{\text{cathode}} + C_{\text{anode}} \) (\( C_{\text{total}} \): the total capacity of the full-cell, \( C_{\text{cathode}} \): the capacity of cathode, \( C_{\text{anode}} \): the capacity of anode\(^1,2\).

**Table.** Capacities of full-cells.

<table>
<thead>
<tr>
<th>Anode materials</th>
<th>( C_{\text{anode}} ) (mAh g(^{-1}))</th>
<th>( C_{\text{cathode}} ) (LiCoO(_2), mAh g(^{-1}))</th>
<th>( C_{\text{total}} ) (mAh g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite</td>
<td>372(^3)</td>
<td>274</td>
<td>157</td>
</tr>
<tr>
<td>Si</td>
<td>3572(^4)</td>
<td>274</td>
<td>254</td>
</tr>
</tbody>
</table>

Theoretical \( C_{\text{total}} \) increase (Si to graphite) (%) = \( [(254 – 157)/157] \times 100\% = 61\%.

Practical \( C_{\text{total}} \) increase (Si to graphite) (%) = \( [(139 – 104)/104] \times 100\% = 34\%.

Experimental

*Experimental preparation of self-supported fabrics.*

(a) Polymer fabrics. (1) PAN fabric: 7 wt.% PAN (M_w of PAN = 150,000 g/mol) was dissolved in DMF and stirred at 40 °C for 12 hours. 0.01 wt.% BYK 307 surfactant (ALTANA, USA) was then added to the solution to reduce its surface tension. (2) PVP fabric: 70 mg ml\(^{-1}\) PVP was dissolved in ethanol and stirred for 6 hours. For single-nozzle electrospinning, the feed rates of PAN and PVP solutions were 0.4 mL h\(^{-1}\) and 0.5 mL h\(^{-1}\) driven at a same voltage of 7 kV. (3) PAN/PVP fabric: To achieve a stable and continuous jet during double-nozzle electrospinning, the voltage used for producing PAN/PVP composite fabric increased to 11 kV for the support of the stable Taylor cones of two nozzles, which was due to the insufficient power generated from one power supply. The feed rates of PAN and PVP kept 0.4 mL h\(^{-1}\) and 0.5 mL h\(^{-1}\) driven by two separate syringe pumps. The tip-to-rotating drum distances of PAN and PVP were both 15 cm.

(b) Si/polymer fabrics. (1) Si/PAN fabric: 100 mg ml\(^{-1}\) Si nanoparticles (Diameter: 50-70 nm, Nanostructured & Amorphous Materials, Inc.) was dispersed in 7 wt.% PAN/DMF solution for 1 hour, followed by vigorous stirring overnight. 0.01 wt.% BYK 307 surfactant (ALTANA, USA) was then incorporated to the well-mixed solution to adjust its surface tension. (2) Si/PVP fabric: 65 mg ml\(^{-1}\) Si were dispersed in ethanol containing 70 mg ml\(^{-1}\) PVP, and stirred overnight at room temperature. The electrospinning voltages of both fabrics were 7 kV. The feed rates of Si/PAN and Si/PVP were 0.6 mL h\(^{-1}\) and 0.7 mL h\(^{-1}\). The tip-to-rotating drum distances were both 10 cm.

(c) Polymer-Si/polymer fabrics. (1) PAN-Si/PAN fabric: 7 wt.% PAN in DMF and 100 mg ml\(^{-1}\) Si in 7 wt.% PAN/DMF solutions were prepared separately. A voltage of 11 kV was applied on both solutions from the same power supply. The feed rates of PAN and Si/PAN were 0.4 mL h\(^{-1}\) and 0.6 mL h\(^{-1}\). The tip-to-rotating drum distances were 15 cm and 10 cm for PAN and Si/PAN. (2) PAN-Si/PVP fabric: 7 wt.% PAN in DMF and 65 mg ml\(^{-1}\) Si in 70 mg ml\(^{-1}\) PVP/ethanol solutions were well-mixed separately. 11 kV was used as the common voltage for both solutions.
0.4 mL h\(^{-1}\) and 0.7 mL h\(^{-1}\) were the feed rates for PAN and Si/PVP solutions. The tip-to-rotating drum distances for PAN and Si/PVP were 15 cm and 10 cm, respectively. (3) PVP-Si/PAN fabric: 70 mg ml\(^{-1}\) PVP in ethanol and 100 mg ml\(^{-1}\) Si in 7 wt.% PAN/DMF solutions were prepared separately. The power supply produced 11 kV to electrospin these two solutions. Feed rates with 0.5 mL h\(^{-1}\) and 0.6 mL h\(^{-1}\) were driven for PVP and Si/PAN solutions. The tip-to-rotating drum distances were 15 cm and 10 cm for PVP and Si/PAN solutions. (4) PVP-Si/PVP. 70 mg ml\(^{-1}\) PVP in ethanol and 65 mg ml\(^{-1}\) Si in 70 mg ml\(^{-1}\) PVP/ethanol were well-stirred separately. The common electrospinning voltage for both solutions was 11 kV with feed rates of 0.5 mL h\(^{-1}\) and 0.7 mL h\(^{-1}\) for PVP and Si/PVP solutions, respectively. 15 cm and 10 cm were the tip-to-rotating drum distances for PVP and Si/PVP, respectively.

(d) Carbonization of C, Si/C and C-Si/C fabrics. The above fabrics were collected on a rotating drum with a constant rotation speed of 400 rpm. All as-spun fabrics were first stabilized at 270 °C for 4 hours with a heating rate of 5 °C min\(^{-1}\). Then the fabrics were carbonized at 700 °C for 3 hours with a heating rate of 5 °C min\(^{-1}\) in Argon atmosphere.

(e) Control of the mass densities of flexible fabrics. PAN fibers show high carbon residual weight than that of PVP fibers (47.8 wt.% > 25.4 wt.%) at 700 °C. To balance the different degrees of carbonization of PAN and PVP fibers and achieve a small Si-to-C ratio range for electrochemical comparison, less Si concentration (65 mg ml\(^{-1}\)) is prepared in PVP/ethanol compared with a higher Si content (100 mg ml\(^{-1}\)) dispersed in PAN/DMF. Furthermore, the feed rates of PVP and Si/PVP solutions are adjusted to be higher than those of PAN contained solutions during double-nozzle electrospinning as mentioned above, which assist in compensating the low carbon residue weight of PVP after carbonization and narrowing the differences of Si-to-C ratios among all the carbonized fabrics. The electrospinning time varies from 6 to 8 hours with a feed rate range of 0.4-0.7 mL h\(^{-1}\). Finally, the free-standing C, Si/C and C-Si/C fabrics are cut into approximate 4 mm x 4 mm pieces with a close mass loading range of 0.8-1.1 mg cm\(^{-2}\) for the electrochemical measurements.

Materials Characterization
Surface structure and elemental analysis were characterized by SEM (FEI NovaNanoSEM 450) with energy dispersive X-ray spectroscopic (EDS) detector. Crystal phase of C-Si/C and Si/C fabrics were conducted by X-ray diffraction (XRD, PANalytical Empyrean) with Cu-Kα radiation at a scan rate of 3.5° min⁻¹. Raman spectroscopy system with a 532 nm laser source (8 mW excitation power, 100x objective lens, Renishaw DXR) was used to verify the carbon fiber structures. TGA measurements were performed in air to estimate the Si/C compositions with heating rate of 5°C min⁻¹. Surface tension of solutions were measured by Tensiometer (Scientific*Gear, VA).

Fabrication and testing of lithium ion battery

The electrodes were directly prepared by cutting into a square piece of C-Si/C or Si/C fabrics with a pre-mass loading of 0.8-1.1 mg cm⁻². Electrochemical characterizations were measured with CR 2032 button-type two-electrode half-cell configuration. Cells were assembled in Argon filled VAC Omni-lab glovebox (O₂ < 0.5 ppm, H₂O < 1 ppm). Lithium metal chip was used as counter electrode. A porous membrane (Celgard 3501) was used as separator. The electrolyte comprised 1M LiPF₆ in a mixture of fluoroethylene carbonate/dimethyl carbonate (FEC/DMC) in a volume ratio of 1 : 1. Galvanostatic charge-discharge and cycling performance were tested using Arbin BT300 with a voltage window of 0.01-1 V (vs. Li⁺/Li). Capacity and current density were calculated based on the total mass of the free-standing fabrics (1C = 3.6 A g⁻¹). Electrochemical impedance spectroscopy analysis was conducted on Biologic VMPs with a frequency ranging from 0.01 Hz and 1 MHz.
**Fig. S1.** (a) Structure of BYK 307 (b) BYK concentration effect on the surface tension of precursors.

**Fig. S2.** EDX elemental mapping of C\textsubscript{PAN}-Si/C\textsubscript{PAN} fabric electrode: (a) Electron image with superposed elemental maps. Elemental maps of (b) C, (c) Si, (d) O, (e) N and (d) Elements weight percentages (wt.%).
Fig. S3. SEM images of (a-b) C\textsubscript{PAN}-Si/C\textsubscript{PVP}, (c-d) C\textsubscript{PVP}-Si/C\textsubscript{PAN}, (e-f) C\textsubscript{PVP}-Si/C\textsubscript{PVP}, (g-h) Si/C\textsubscript{PAN} and (i-j) Si/C\textsubscript{PVP} with low and high magnifications, respectively.
For Si/C composites via single-nozzle electrospinning, a voltage of 7 kV is applied to both Si/C\textsubscript{PAN} and Si/C\textsubscript{PVP} solutions to achieve stable Taylor cones for continuous electrospinning. If the applied voltage is lower than 7 kV, droplets occur on the tip of the nozzle rather than form steady stream. This phenomenon results from the insufficient electrostatic force to overcome the surface tension of the solution; if the voltage is higher than 7 kV, the Taylor cones start shaking and lead to non-uniform deposition of fiber mats, which is due to the over-charged repulsive interaction. For C-Si/C composites via double-nozzle electrospinning, one power supply of the electrospinning set-up is unable to provide enough power for two simultaneous spinning at 7 kV, which is due to the existence of droplets on the tip of the two nozzles. To guarantee the stable spinning process and the uniformity of the resulting interwoven mats, the voltage is increased to 11 kV for continuous electrospinning the C-Si/C fabrics. The higher voltage applied on C-Si/C fabrics narrows their fiber sizes compared with Si/C fibers electrospun at a lower voltage, which is attributed to the increased degree of stretching the polymer precursor at a higher voltage in correlation with the increased charge repulsion within the polymer jet.\textsuperscript{6,7}
Similarly, it is worth noting that PAN and PVP fibers are electrospun at 7 kV, however, PAN/PVP composite is produced at a higher voltage of 11 kV. The insufficient power generated by one power supply is unable to form a stable and simultaneous double-nozzle jetting at 7 kV, thus, the increased voltage to 11 kV further stretches the PAN/PVP fibers to smaller diameter compared with individual PAN and PVP fibers.
Fig. S5. (a) TGA of non-dried and dried PVP nanofibers. (b) Carbonization of C-Si/C and Si/C composites under argon. (c) TGA curves of all C-Si/C and Si/C fabrics under air atmosphere with a heating rate of 5 °C min⁻¹.

In Fig. S5c, the gradual decrease in mass retention as the temperature increases to around 680 °C is related to the removal of carbon by air flow, and the subsequent growth in mass percentage is owing to the oxidation of silicon particles in air. Thus, the lowest mass retention of each curve is used to signify the Si contents in Si/C and C-Si/C composites. The TGA curve of $C_{\text{PAN}}$-Si/$C_{\text{PAN}}$ shows its lowest Si content of 47.2 wt.% among all fabrics.
**Fig. S6.** Selective charge/discharge profiles of (a) Si/C\textsubscript{PVP}, (b) Si/C\textsubscript{PAN}, (c) C\textsubscript{PVP}-Si/C\textsubscript{PVP}, (d) C\textsubscript{PVP}-Si/C\textsubscript{PAN}, (e) C\textsubscript{PAN}-Si/C\textsubscript{PVP} and (f) C\textsubscript{PAN}-Si/C\textsubscript{PAN}.

For Si/C composite fabrics in Fig. S6a-b, Si/C\textsubscript{PAN} electrode shows less capacity fading with a higher capacity retention of 70.7 % over that of Si/C\textsubscript{PVP} electrode (capacity retention: 51.8 %) for the initial 20 cycles at 500 mA g\textsuperscript{-1} (excluding the 1\textsuperscript{st} and 2\textsuperscript{nd} cycles for the activation of active materials at low
current densities). The fast capacity fading is mainly owing to the fracture of Si/C fibers caused by Si expansion during alloying. To strengthen Si/C structure and mitigate the expansion, a pure carbon frame is introduced to enclose Si/C fibers and form a C-Si/C network. Compared with Si/C fabrics, all C-Si/C electrodes show more stable charge-discharge behaviors with reduced capacity loss for the initial 20 cycles as verified in Fig. S6c-f. Among the four kinds of C-Si/C composites, C_{pvp-Si/C_{pvp}} fabric has the fastest capacity decay with a capacity retention of 84.5 %. A general trend is observed that the more C_{pvp} of a composite contains, the higher degree of capacity fading it suffers. We attribute this phenomenon to two reasons. (a) The slightly higher Si contents in Si/C_{pvp} and C_{pvp-Si/C_{pvp}} may result in more expansion of Si during lithiation, leading to a higher degree of fiber fracturing. (b) However, due to the close Si-to-C ratio ranges controlled in Si/C and C-Si/C composites (TGA curves in Fig. S5), the primary factor related to capacity fading is the structural difference of the two carbon matrixes. C_{PAN} show stabilized fibrous morphology, which not only effectively encapsulates Si particles, but also acts as a strongly resilient pure C_{PAN} frame to prevent the structure from severe change during Si expansion and contraction. In contrast, C_{PVP} fibers appear to be flat and merged. The integrity of the fibrous structure is not well-preserved, which is not as flexible as C_{PAN} while forming a weakly resilient carbon matrix to trap Si particles.
To characterize and compare the stability performance of Si/C fabric electrodes, the capacity loss per cycle and cumulative irreversible capacity for cycling are displayed in Fig. S8. After the 1st and 2nd cycles, the electrodes exhibited capacity loss of ~379, ~480, ~408, ~493, ~577 and ~592 mAh g\(^{-1}\) for C\(_\text{PAN}\)–Si/C\(_\text{PAN}\), C\(_\text{PAN}\)–Si/C\(_\text{PVP}\), C\(_\text{PVP}\)–Si/C\(_\text{PAN}\), C\(_\text{PVP}\)–Si/C\(_\text{PVP}\), Si/C\(_\text{PAN}\) and Si/C\(_\text{PVP}\), respectively, which were mainly attributed to the irreversible lithium existing in the SEI and the decomposition of electrolyte.\(^8\) In the subsequent cycling at 500 mA g\(^{-1}\) until 100 cycles, the electrodes showed total irreversible capacity loss (including 1st and 2nd cycles) of ~565 mAh g\(^{-1}\), 629 mAh g\(^{-1}\) and 916 mAh g\(^{-1}\) with 0.17, 0.23 and 0.57 % capacity decay per cycle for C\(_\text{PAN}\)–Si/C\(_\text{PAN}\), C\(_\text{PAN}\)–Si/C\(_\text{PVP}\), C\(_\text{PVP}\)–Si/C\(_\text{PAN}\) and C\(_\text{PVP}\)–Si/C\(_\text{PVP}\), respectively, which are lower than those of C\(_\text{PVP}\)–Si/C\(_\text{PVP}\), Si/C\(_\text{PAN}\) and Si/C\(_\text{PVP}\) even tested with shorter cycles. The lowest capacity fading rate demonstrated by C\(_\text{PAN}\)–Si/C\(_\text{PAN}\) compared with other C-Si/C and Si/C electrodes indicates its good reliability for relatively fast charge-discharge process.
Fig. S8. (a) Cycling performance of various carbon fibers (CFs) in a window range of 0.01-1 V. (b) Charge-discharge profiles of the 1st cycle for CFs electrodes. (c) Charge-discharge profiles of the 50th cycle for CFs electrodes. (d) Charge-discharge profiles of the 100th cycle for CFs electrodes.
Discussion

Fig. S9. (a) Equivalent circuit of $C_{\text{PAN}}$-$Si/C_{\text{PAN}}$ fabric electrode used to produce fitted model data. (b) Nyquist plots of Si/C fabric electrode. (c) Characterized resistances for EIS cycles.

Fig. S9a shows the equivalent circuit used to model the impedance data obtained from a $C_{\text{PAN}}$-$Si/C_{\text{PAN}}$ half-cell after running potentiostatic electrochemical impedance spectroscopy (PEIS). The circuit shown quantizes a number of parameters related to distinct electrochemical phenomenon within a lithium-ion electrode. The model uses combinations of resistors and constant phase elements (CPEs), the latter of which represents spatial and chemical non-uniform distribution of capacitance. $R_s$ is often referred to as the equivalent series resistance (ESR), and it measures the finite ionic conductivity in liquid electrolyte. The first parallel branch characterizes internal impedance within electrode nanostructure, contains an imperfect capacitance and a finitely conductive element and defines the electronic pathway within active material through to the
current collector. The second parallel branch characterizes the solid-electrolyte interphase. The third parallel branch characterizes double-layer impedance, including non-ideal double-layer capacitance and reaction resistance (corresponding to charge transfer during lithiation/delithiation).\(^\text{10}\) Two more CPEs are in series with the aforementioned parallel branches. These two CPEs characterize diffusion in liquid phase (near electrode surface, CPEW2) and in solid phase (within active material, CPEW1) of lithium ions and atoms, respectively.\(^\text{11}\)

We observed stabilizing trends in all resistance values including \(R_s\), \(R_{\text{INT}}\), \(R_{\text{SEI}}\), and \(R_{\text{CT}}\) in Fig. S9b. \(R_s\) remains about the same value throughout the first ten cycles as shown in Fig. 9(c), indicating the low resistance permits Li-ion travel. \(R_{\text{INT}}\) shows a general decreasing trend. This signifies the interface electronic contact resistance between fiber surface and electrolyte decreases, which allows fast electron transport at high current densities. Meanwhile \(R_{\text{SEI}}\) also declines and stabilizes as the cycle increased, which means the formation of the crucial stable SEI. \(R_{\text{CT}}\) also shows a generally decreasing trend. It is concluded that \(\text{CPAN-Si/CPAN}\) electrode was fully activated after the first 7 cycle because the \(R_s\), \(R_{\text{INT}}\), \(R_{\text{SEI}}\), and \(R_{\text{CT}}\) stabilized at certain resistances.
**Fig. S10.** Comparison of Si/C and C-Si/C fabric electrodes during lithium.

We attribute the excellent cycling and C-rates performance of $C_{\text{PAN-Si}}$/Si/$C_{\text{PAN}}$ to several reasons. First, the interwoven $C_{\text{PAN-Si}}$/$C_{\text{PAN}}$ fiber-hybrid framework offers effective electron conduction pathways due to the strong interconnectivity from the same carbon matrix. Meanwhile, the large void spaces existing in the mat not only accommodate the volume change of Si but also offer large accessible area for electrolyte, which facilitates the Li-ion diffusion to the active materials inside. Second, the PAN fibers forms stabilized individual fibers after carbonization. The $C_{\text{PAN}}$ frame traps Si clusters tightly, which prevents the cracking of the electrode during lithiation and delithiation as illustrated in Fig. S9. In addition, the robust Si/C fabric frame is highly flexible and prepared without adding inactive polymer binders, conductive additives and the heaviest metallic current collector, thus the Si and carbon both acting as active materials contribute to the overall capacity. Finally, Wang et al. reported that the surfactant F127 highly enhanced the uniformity of Si nanoparticle distributed in carbon matrix. Thus, the cycling stability of Si/C electrode via single-nozzle electrospinning has been improved due to the alleviated fracturing of Si during lithiation. Surfactants which are able to make homogeneous Si dispersion are expected to further improve the cycling performance of the C-Si/C fabrics in this work.
References