This study demonstrates the applications of Si/C composite fibers as anode materials for all-solid-state lithium-ion batteries. Using polycrylonitrile as the carbon precursor, Si/C fibers were prepared through electrospinning and subsequent heat-treating processes. To investigate the correlation between fiber diameter and electrochemical performance, we prepared three electrodes (A, B, C), containing Si/C fibers with ~2 μm, ~1 μm and ~0.1 μm diameters, respectively. Our results revealed that although the composition of all three electrodes was nearly the same, the Si/C fiber based electrodes exhibited better capacity retention when their fiber diameters were smaller. Normalized to the total mass of electrode composite, the solid-state half-cell prepared with the smallest diameter (~0.1 μm) Si/C fibers achieved a reversible specific capacity of ~700 mAh g⁻¹ (normalized to electrode mass) over 70 cycles. We believe that this report can serve as an informative approach toward the utilization of electrospun Si/C fibers as anode materials for all-solid-state lithium-ion batteries.

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were all set at 2.5:1. These suspensions were then kept on the magnetic stirring system for another 24 hours in order to disperse the Si powders evenly in the PAN+DMF solutions. After mixing, the suspensions were loaded into the 10 mL syringe included with the electrospinning system. Electrospinning was then performed with a 0.7 ml h\(^{-1}\) feed rate onto a Cu foil collector at 27 kV. When the electrospinning process was completed, the Si/PAN fiber mat was removed from the Cu collector and dried in air for two hours at 60°C in order to remove all residual DMF solvent. Next, the PAN was stabilized in air at 300°C for two hours, forming infusible ladders in the PAN’s polymer structure.\(^{12,43,44}\) This stabilization of the PAN fibers is important in maintaining their shape during the following pyrolysis process, which occurs at temperatures well above PAN’s melting point (322°C).\(^{45,46}\) The pyrolysis of the Si/PAN fiber mat, in which the stabilized PAN is decomposed to turbostratic carbon, was completed after three hours at 900°C in an argon atmosphere.\(^{46,47}\) Lastly, the Si/pyrolyzed PAN (p-PAN) fibers were gently hand-ground with the ball-milled Li\(_2\)S-P\(_2\)S\(_5\) SSE powders at a 7:3 weight ratio. After mixing, 2 mg of this composite was collected for use as the working electrode in our SLIB half-cells.

For the counter electrode, 100 mg of InLi\(_{0.8}\) powers were used. We chose to use InLi\(_{0.8}\) as a source of mobile Li-ions because it does not develop troublesome dendrites as readily as pure Li powders/foil.\(^{58}\)

These working and counter electrode materials were then pressed onto opposing sides of the SSE separator layer for five minutes at five metric tons force. This ensured that a high degree of interfacial contact was developed between the three layers of the pellet.\(^{59}\) After the completion of this final pressing, the tri-layered pellets were clamped between two Ti-plunger current collectors within the PEEK-lined Ti cell die. Detailed illustrations of our SLIB test-cell dies were exhibited in our previous reports.\(^{9,50}\) These half-cells were then cycled under a small, externally applied compressive clamping stress (20 MPa). We chose to do this because our previous study confirmed that a consistently applied compressive stress is effective in improving the capacity retention of Si-based anodes in all-solid-state cells.\(^9\)

All cycling tests were carried out inside an Ar-filled glove box at 60°C using an Arbin BT2000 Battery tester with a 0.1 C-rate. The voltage range for these tests was 0.005 to 1.5 V versus Li/Li\(^+\). We employed a Constant Current-Constant Voltage (CC-CV) protocol in which constant voltage modes follow every constant current mode, so as to improve the reversibility of not only the p-PAN (carbon) but also Si active materials.\(^{57}\) The length of the CV modes for the discharging and charging processes were set to 1.5 h and 2.5 h, respectively. One discharge-charge cycle thus consisted of a \(<10\)-hour CC-CV discharge and a \(<10\)-hour CC-CV charge. At the end of each CC-CV charge cycle, an in-situ Internal Resistance (IR) measurement was carried out at 0.1 mA current for three seconds. This allowed us to track the electrodes’ increasing IR values during the cycling test. SEM observations were carried out using a FEI NOVA200 dual beam system.

Results

Figures 1a–1c compare the sizes of the Si/p-PAN fibers in Electrodes A–C. It is clear that the diameter of the electrospun Si/p-PAN fibers were smaller when the PAN concentration in the precursor slurry was lower. When the slurry had a PAN concentration of 17.6 wt% (Electrode A), the mean diameter of the Si/p-PAN fibers was measured to be 2,171 nm. On the other hand, the fibers prepared with slurries containing 14.6 and 11.7 wt% PAN (Electrodes B and C) had diameters of 1,088 nm and 117 nm, respectively. We summarized the properties of Electrodes A–C in Table I. Notice that even though Electrodes A–C contain fibers with different diameters, their final composite compositions are nearly identical.

Figure 2 displays the discharge/charge capacities and coulombic efficiencies (CEs) of Electrodes A–C, along with a p-PAN-based electrode, over 50 cycles. The p-PAN-based electrode was prepared by hand-mixing pure p-PAN fibers with the ball-milled Li\(_2\)S-P\(_2\)S\(_5\) SSE powders at a 7:3 (p-PAN:SSE) weight ratio. This cell was made in order to analyze the electrochemical performance of just the p-PAN material when cycled in our Li\(_2\)S-P\(_2\)S\(_5\) electrolyte-based solid-state half-cell. Figure 2 shows that the p-PAN-based electrode had a somewhat irreversible capacity for the initial number of cycles, but thereafter maintained a reversible capacity of \(\sim 320\) mAh g\(^{-1}\) with CEs >99.9% over 50 cycles. The initial irreversible capacity and subsequent reversible capacity of the p-PAN-based electrode confirmed that

![Figure 1. SEM images of pyrolyzed-PAN/Si fibers in Electrodes (a) A, (b) B and (c) C.](image)

| Table I. Specifications of Electrodes A–C. |
|------------------------------------------|
| Electrode | PAN concentration in DMF solvent (wt%) | Si/p-PAN fiber diameter (nm) | Composition (p-PAN:SSE, wt%) |
| A | 17.6 | 2,171 | 40.6:29.4:30.0 |
| B | 14.6 | 1,088 | 39.9:30.1:30.0 |
| C | 11.7 | 117 | 38.5:31.5:30.0 |
the stabilized PAN fibers successfully decomposed into Li active turbostratic carbon during the 900°C pyrolysis reaction. As confirmed in the literatures, the initial irreversible capacity of our p-PAN-based electrodes is believed to be due to side reactions occurring at wide specific surface areas of the turbostratic carbon fibers, or the fibers’ insufficient carbonization microstructures.46,47 Accordingly, the specific surface areas of the turbostratic carbon fibers, or the fibers’ capacities, Electrode A–C are expected to contribute to the overall capacity of each electrode.

Figure 2 clearly shows that the electrochemical performance of the p-PAN/Si fiber based electrodes is dependent on the diameter of their electrospun fibers. Electrode A, which consisted of relatively large p-PAN/Si fibers (~2,171 nm diameter), achieved the highest 1st cycle discharge/charge capacities of any cell in Figure 2, but its capacity quickly decreased due to unstable CEs lower than 98.1% in the subsequent cycles. Consequently, the charge capacity for Electrode A at its 50th cycle was only 55.7% of that at its 5th cycle. We set the 5th cycle charge capacity as the standard value when calculating the capacity retention (CR) of Electrodes A–C in order to exclude the above-mentioned irreversible capacities of the p-PAN material up to 5th cycle. Utilizing this method, we calculated CRs of 71.5% and 84.2% for Electrodes B and C, respectively. Therefore, even though Electrode A displayed the highest first cycle discharge/charge capacities, Electrode C retained more of its initial capacity throughout 50 cycles. The clear difference in the IRs of Electrode A and C indicates that residual Li, which was not delithiated after every CC-CV charge process, gradually accumulated in the core of Electrode A. This can be attributed to the fact that due to stable high CEs, Electrode C is effective in suppressing the growth of Li concentration gradients in each fiber, which is expressed by the equation below:53

\[ i_{\text{diffusion}} \propto D_{Li} \frac{dC_{Li}(x, t)}{dx} \bigg|_{x=0} \]

where \( D_{Li} \), \( C_{Li} \), x and t represent Li diffusion coefficient, Li concentration gradient, location in the fiber and time, respectively. And \( x = 0 \) means the electrode surface. Interestingly, the final currents of Electrodes A–C were not the same. While the currents of Electrode A stabilized to ~20 μA after consistently increasing over the first 20 cycles, the currents of Electrodes B and C saturated after only a few cycles to 13.3 μA and 11.0 μA, respectively. The increasing currents of Electrode A indicate that residual Li, which was not delithiated after every CC-CV charge process, gradually accumulated in the core of the relatively large p-PAN fibers due to the long distance for Li diffusion. Accordingly, the use of small diameter p-PAN/Si fibers, like those in Electrode C, is effective in suppressing the growth of Li concentration gradients in each fiber. This can be attributed to the shorter Li diffusion distance in these smaller fibers, a phenomenon previously reported for other nano-structured LIB materials.54

During our analysis, we noticed that Electrodes A–C had different Internal Resistances (IRs) at the end of each CC-CV charge cycle. Figure 3a compares the increasing IRs of Electrodes A–C over 50 cycles. Our data shows that the increase of IRs during cycling was better suppressed when the electrodes contained smaller diameter fibers. In the case of Electrode A, which experienced rapid capacity fading (Figure 2), the IRs drastically increased from 114 to 344 μΩ after consistently increasing over the first 20 cycles. On the other hand, the IRs of Electrode B, with ~1,088 nm diameter fibers, were just about one-third of those of Electrode A (118 Ω after 50th cycle). Furthermore, the IRs of Electrode C, having ~0.1 μm diameter p-PAN/Si fibers, stayed below 100 Ω throughout the 50 cycles. The clear difference in the IRs of Electrodes A and C implies that the large diameter fibers in Electrode A underwent a substantial change in morphology with cycling, resulting in its relatively drastic capacity decay.

Figure 3b compares the currents of Electrodes A–C over 50 cycles. These currents, which were measured immediately after the completion of each CV charging step, represent the driving force for Li diffusion toward a dynamic equilibrium state within the p-PAN/Si fibers. Analysis of these measurements gives a glimpse into how evenly the lithium was dispersed throughout the p-PAN/Si fibers in Electrodes A–C. This is due to the fact that these currents are proportional to the Li concentration gradient in each fiber, which is expressed by the equation below:53

\[ i_{\text{diffusion}} \propto D_{Li} \frac{dC_{Li}(x, t)}{dx} \bigg|_{x=0} \]
The dQ/dV plots of Electrodes A-C are presented in Figures 4a–4c, respectively. Electrodes A-C all developed sharp peaks at ~0.4 V during charging, however, the cycles in which these sharp peaks were first detected and subsequently disappeared were not the same. In Figures 4a and 4b, the peaks were observed during the 1st and 2nd charge, respectively. These peaks broadened and weakened in the following cycles, disappearing completely after the 30th charge. On the other hand, Electrode C consistently displayed a sharp delithiation peak up to its 50th cycle. Considering that no peaks were detected at ~0.4 V during the delithiation of the p-PAN-based electrode (Figure S1), the presence of the sharp peaks in Figures 4a–4c indicate the co-existence of amorphous and crystalline Li$_x$Si phases (hereafter referred to as c-Li$_x$Si and a-Li$_x$Si, respectively). Since it is believed that the c-Li$_x$Si phase can alloy with more Li-ions than the a-Li$_x$Si phase, we speculate that the c-Li$_x$Si phase consistently formed up to 50th cycle in Figure 4c, contributing to Electrode C achieving the highest capacity retention of any anode in this study (Figure 2).

The use of small diameter p-PAN/Si fibers was also effective in suppressing the overpotential phenomenon during cycling. In Figure 4a, the sharp peak corresponding to the co-existence of the a-Li$_x$Si and c-Li$_x$Si phases was first detected at 0.419 V during 1st cycle in Electrode A. However, this peak then shifted by 0.031 V after only 20 cycles, as indicated by η. The magnitude of this overpotential effect was noticeably reduced when the fiber diameter in the electrodes decreased. For example, the position of the two-phase delithiation peak in Figure 4b shifted by only 0.009 V over 19 cycles. Furthermore, this peak shifted by only 0.004 V in Figure 4c, despite the fact that Electrode C consistently displayed a sharp peak up to its 50th cycle. We believe that the variation in the extent to which the overpotential phenomena was observed in Figures 4a–4c can be attributed to the difference in which the IRs of these cells increased during cycling (Figure 3a).

Electrodes A-C also exhibited different voltage relaxation phenomena in their voltage profiles. Highlighted by dotted squares in Figures 5a–5c, the voltages of Electrodes A-C were instantly relaxed after every CC charging. The voltage values to which Electrodes A-C relaxed were, however, not the same. Shown in the inset of Figure 5a, the magnitude of the voltage relaxations in Electrode A gradually increased over 50 cycles, with the relaxed voltage value after the 50th charge being 1.21 V. This is significantly different from the expected value of 1.52 V. On the other hand, the relaxed voltages of Electrodes B and C after their 50th charge (Figures 5b and 5c) were both 1.45 V. This result indicates that the voltage relaxation phenomenon can be more greatly mitigated when the p-PAN/Si fiber diameter is small. We believe that this voltage relaxation phenomenon, observed to varying degrees in Figures 5a–5c, is related to the different Li concentration gradients shown in Figure 3b, and that the alleviated voltage drop of Electrode C contributed to its highly reversible capacities during cycling (Figure 2).

It is interesting that even though Electrodes A-C all contained the same Si nano-particles and had nearly identical electrode compositions (Table I), the three electrodes performed remarkably different over 50 charge/discharge cycles. We believe that the variable cycling performances of these electrodes can be attributed to the agglomeration of 50 nm Si particles embedded in their p-PAN fibers. The unexpected dQ/dV delithiation peaks ~0.4 V in Figures 4a–4c support this hypothesis. These peaks, which indicate the existence of c-Li$_x$Si phases, are rarely observed in electrodes containing nanoscale Si particles. This is because it is believed to be unfavorable for the c-Li$_x$Si phases to nucleate within such small domains. The presence of these delithiation peaks (Figures 4a–4c) therefore suggests that the Si nano-particles in these electrodes had agglomerated into aggregates large enough to favorably form the c-Li$_x$Si phases. While these sharp delithiation peaks were observed in all three electrodes, it should be noted that the cycle in which the peaks, and thus the large silicon agglomerates, appeared/disappeared varied with the diameter of the electrospun fibers. For example, a sharp delithiation peak ~0.4 V can clearly be seen in Figure 4a after only the first charging process. On the other hand, the same peaks were not detected in Electrodes B or C until after the second cycle (Figures 4b and 4c). This suggests that the diameter of the electrospun PAN fibers influences both the initial size of Si nano-particle agglomerates as well as their subsequent growth with cycling. We believe that the small fiber diameters in Electrodes B and C prevented Si aggregates from forming during the electrospinning process. While these Si nanoparticles remained mostly isolated in the pristine fibers, they seem to have quickly

Figure 4. dQ/dV plots of Electrodes (a) A, (b) B and (c) C during 50 cycles.
agglomerated with neighboring particles as a result of their substantial volumetric expansion upon lithiation. This process appears to have led to the formation of aggregates large enough to nucleate the c-LixSi phases after the electrodes’ first discharge-charge cycle. The poor electrochemical performances of Electrodes A and B (high internal resistances and low capacity retention) were likely attributed to the continuous agglomeration of Si particles into large, unstable aggregates. A previous study has reported that the critical size, over which Si particles typically experience mechanical fracture during lithiation, is 150 nm. Therefore, we believe that the 2,171 nm and 1,088 nm diameter fibers in Electrodes A and B allowed Si particles to agglomerate into aggregates, >150 nm in size, despite being encapsulated in the p-PAN fiber matrix. The continued fracturing of these large aggregates accounts for the capacity fading observed in these electrodes with cycling. As the aggregates crack and break apart, active Si particles become electrochemically isolated. This results in irreversible capacity losses, as well as the voltage shift and eventual disappearance of the sharp delithiation peak originally observed ~0.4 V, after the 30th cycle. On the other hand, we suspect that the ~0.1 μm p-PAN fibers in Electrode C effectively limited the size of Si aggregates to <150 nm. This constraining of the silicon particle aggregates to <150 nm resulted in minimal active material fracture or isolation up to the 50th cycle, enabling Electrode C to achieve the best cycling performance of any cell tested in this study (Figure 2).

Due to the small diameters of its p-PAN fibers, Electrode C reversibly maintained 80% of its 5th charge capacity after its 70th cycle. Figure 6 displays the discharge/charge capacities, coulombic efficiencies and projected number of moles of Li alloying with each Si particle in Electrode C over 70 discharge-charge cycles. Note that the capacities in Figure 6 were normalized to the total mass of electrode composite (2 mg) for a more practical view of electrode’s energy density. On the 70th cycle, the discharge and charge capacities for this cell were measured to be 714 and 709 mAh g\(^{-1}\) (respectively) with a Coulombic efficiency of 99.2%. To the best of our knowledge, this is the first report demonstrating a Si-based anode capable of achieving a reversible capacity >700 mAh g\(^{-1}\) after 70 cycles in a Li\(_2\)S-P\(_2\)S\(_5\) electrolyte-based SLIB. While previous studies have presented SLIB electrodes with specific capacities >700 mAh g\(^{-1}\), these capacities were normalized to the mass of Li active materials, not the total electrode mass, like in this report.

Although Electrode C achieved a large specific capacity, it unfortunately experienced a sluggish capacity degradation up through its 70th cycle. This consistent capacity decline can be attributed to the electrode’s Si particles alloying with progressively less Li with each cycle. On the (right) Y-axis of Figure 6, we verify that the projected x value in Li\(_x\)Si gradually decreased from 2.45 to 1.95 over 70 cycles. A previous study suggests that Si/C composite anode materials have optimal cycling performances when their Si:C weight ratio is close to 30:70. This led us to believe that the capacity degradation in Electrode C may be due to its large mass loading of Si (the Si:C ratio of Electrode C was approximately 63:77). In order to test this hypothesis, we prepared another electrode (Electrode D) which contained a Si:C mass ratio of 30:70. The electrochemical performance of Electrode D is shown in Figure S2. While the Si content of Electrode D was greatly reduced in comparison to Electrode A, C, the projected x value in Li\(_x\)Si gradually decreased from 2.45 to 1.95 over 70 cycles. A previous study suggests that Si/C composite anode materials have optimal cycling performances when their Si:C weight ratio is close to 30:70. This led us to believe that the capacity degredation in Electrode C may be due to its large mass loading of Si (the Si:C ratio of Electrode C was approximately 63:77). In order to test this hypothesis, we prepared another electrode (Electrode D) which contained a Si:C mass ratio of 30:70. The electrochemical performance of Electrode D is shown in Figure S2. While the Si content of Electrode D was greatly reduced in comparison to Electrode A, C,
Electrode D achieved a CR (ratio of the 50th charge capacity to the 5th charge capacity) of only 78.1%. This result suggests that, in the case of our electrospun Si/C composite fibers, reducing the mass loading of Si to ~30 mass-percent does not have a large positive impact on the electrode’s capacity retention with cycling. The gradual capacity degradation of Electrode C in Figure 6 is likely to be related with the microstructure of Si changed during the 70 cycles. It is because that 50 nm Si particles were well dispersed in each carbon fiber in the as-prepared state (Figure S3) but they were identified as long chain networks of >500 nm in length after 70 cycles. (Figure S4) Therefore, we will conduct a systematic microstructure analysis study to confirm the microstructural evolution process of Si. We hope that this investigation will allow us to minimize the irreversible capacity losses observed in these electrodes in future tests.

Conclusions

In this study, we demonstrated the use of Si/C fibers as anode materials for solid-state lithium-ion batteries. We prepared various fibers, with different diameters, in order to study the correlation between fiber size and electrochemical performance. Compared with Electrodes A and B, which contained ~2 and ~1 μm diameter Si/C fibers (respectively), Electrode C, composed of ~0.1 μm diameter fibers, exhibited significantly enhanced capacity retention over 70 cycles. Normalized to the total mass of electrode materials, Electrode C achieved a reversible capacity of ~700 mA h g⁻¹ with coulombic efficiencies reaching 99.2%. Si/C fibers with the diameter of ~0.1 μm and with Si particle size of ~50nm have been found to be most effective in terms of mitigating the increase of the internal resistance and the formation of lithium concentration imbalance in each fiber during the subsequent cycling test. This finding demonstrates the importance of Si/C fiber diameter and Si particle size for achieving improved reversible gravimetric capacity in the all-solid-state Li ion battery system.

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