Continuous-Flow Synthesis of Carbon-Coated Silicon/Iron Silicide Secondary Particles for Li-Ion Batteries

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ABSTRACT: The development of better Li-ion battery (LIB) electrodes requires an orchestrated effort to improve the active materials as well as the electron and ion transport in the electrode. In this paper, iron silicide is studied as an anode material for LIBs because of its higher conductivity and lower volume expansion compared to pure Si particles. In addition, carbon nanotubes (CNTs) can be synthesized from the surface of iron-silicides using a continuous flow coating process where precursors are first spray dried into micrometer-scale secondary particles and are then flown through a chemical vapor deposition (CVD) reactor. Some CNTs are formed inside the secondary particles, which are important for short-range electrical transport and good utilization of the active material. Surface-bound CNTs on the secondary particles may help establish a long-range conductivity. We also observed that these spherical secondary particles allow for better electrode coating quality, cyclability, and rate performance than unstructured materials with the same composition. The developed electrodes retain a gravimetric capacity of 1150 mAh/g over 300 cycles at 1A/g as well as a 43% capacity retention at a rate of 5 C. Further, blended electrodes with graphite delivered a 539 mAh/g with high electrode density (∼1.6 g/cm³) and areal capacity (∼3.5 mAh/cm²) with stable cycling performance.

KEYWORDS: lithium-ion batteries, anodes, silicon, carbon nanotubes, nanohybrid materials

Because of their high energy and power density, lithium ion batteries (LIBs) are currently the most promising energy storage technology for mobile devices, electric vehicles, and large-scale energy storage. To further increase the energy density of LIBs, relentless research efforts have been invested in the development of new electrode materials and optimizing the electrode formulation.1–5 Commercial LIB anodes typically rely on Li-ion intercalation in graphite (372 mAh/g) or lithium titanate (175 mAh/g).5 However, much higher gravimetric energy densities have been achieved using anodes that react with lithium by alloying or conversion mechanisms (e.g., Si, Sn, GeO₂, SnO₂, Fe₃O₄, etc.).6–8 Unfortunately, these high capacity materials have disadvantages including poor cycling stability, large volume change during Li⁺ insertion/extraction, high voltage hysteresis, poor rate performance, poor Coulombic efficiencies (CE), and low electrical conductivity.9–12 To improve the ion and electron transport, as well as to alleviate mechanical stress, many researchers have looked into nanostructuring these active materials. However, nanostructuring often introduces problems of its own such as low tapped and electrode density as well as irreversible reactions taking place on the high surface area of the nanostructured materials. Ongoing research is developing strategies to alleviate some of these challenges.13–15

In particular, attractive strategies have been proposed to address the poor conductivity of high capacity materials by advanced carbon coating processes. For instance, a number of promising carbon cages have been proposed to buffer the volume change of active materials,16–18 but these further reduce the tapped density of the electrodes. Alternatively, flexible high-aspect conductive carbons, such as graphene and carbon nanotubes (CNTs), have been studied.19–21 However, these materials tend to phase segregate after slurry mixing. This is because most carbon additives with high conductivity disperse well in NMP, whereas metal or metal oxides materials tend to disperse water well, which makes it difficult to codisperse them with battery binders such as PVDF in NMP or CMC/SBR in water.22,23 This phase segregation during the
electrode coating and drying compromises electron conduction and results in poor material utilization and high ohmic losses. The phase segregation is particularly pronounced with high areal loading electrodes pursued in industry, which dry slower. Further, several researchers have shown that the interface between carbon additives and the active material can degrade over time, which further accentuates the above problems. Industrially, time-consuming kneading and high intensity mixing processes are used to reduce the agglomeration of carbon additives, and academically, methods are developed to anchor active battery materials on the surface of carbon additives (e.g., by synthesizing the active material in the presence of CNTs or graphene). However, to nucleate the active material on the carbon additives, the carbon surface typically requires oxidation or other chemical modifications, which in turn decreases their electronic conductivity and is poorly scalable.

In this work, we combine several of the above principles to fabricate advanced silicon/iron silicide anodes coated with CNTs. In particular, we focus on a continuous fabrication process that structures nanoparticles into secondary micrometer-sized particles on which CNTs are synthesized. Si is a promising active material because of its high theoretical capacity (>3500 mAh/g), low reaction potential (~0.35 V), and low cost. Here, we start from nanosized silicon particles (Si NPs) and react them with iron precursors to form iron silicide for three reasons: (i) to decrease the electrical resistance, which is $2.6 \times 10^4 \, \Omega \, \text{cm}$ in Fe$_x$Si$_y$ compared to $6.0 \times 10^3 \, \Omega \, \text{cm}$ in Si and (ii) to reduce the volume expansion during cycling. This comes at the cost of a lower capacity (iron silicides <100 mAh/g), but it should be noted that because of limitations in the capacity of current cathode materials (approximately 200 mAh/g), anode capacities in excess of 550 mAh/g do not substantially improve the overall battery performance. Here, we first optimize Si/FeSi cores with a capacity of 1200 mAh/g and then blend them with graphite to obtain 550 mAh/g anodes. (iii) CNTs can be synthesized from iron/iron silicide domains on Si nanoparticles. The latter results in a strong anchoring of the carbon additive on the active material and fosters a better electric network in the electrode. This approach inverts the classic approach where carbon additives such as CNTs or graphene are first oxidized followed by active material synthesis from surface defects, which compromises the electrical conductivity of the conductive material. These three properties address electron-transport challenges as well as problems related to phase segregation during the electrode mixing but do not solve problems related to the poor tapped density and poor electrode coating properties of nanomaterials. In commercial battery electrodes, small primary battery particles are often aggregated in larger secondary particles to alleviate electrode-coating challenges and increase the volumetric density. Here, we follow a similar strategy using spray drying to pack our Si nanoparticles into micrometer-sized spheres. The electrical resistance of micrometer-sized pure Si secondary particles would be too high for good battery operation, but this work shows that CNTs can be synthesized inside the crevices of the secondary particles hereby providing a good internal short-range electrical network. In addition, CNTs extending from the surface of the secondary particles can help with the interparticle long-range conductivity, which is particularly important as industry shifts to thicker electrode coatings.

Impressive results were achieved in previous reports where CNTs grown on the surface of Si particles for battery applications, however in these reports, CNTs were not structured in secondary particles. As a result, these batteries were only tested in low loading levels and show poor CE. In contrast, our CVD process on secondary particles reduces the BET surface area and therefore improves the CEs of the material. Further, we have performed blending
experiments of our electrodes with commercial graphite anodes to balance the electrode capacity, density and areal loading. Finally, we demonstrate a continuous flow synthesis method that allows to continuously synthesize these complex materials from simple precursors. As summarized in Figure 1, our approach enables a hierarchical design for battery electrodes where at the nanoscale the chemical composition of the primary particles and their interface with carbon additives is controlled while at the microscale the secondary particle size and carbon additives are controlling the ion and electron transport, and finally, flow synthesis allows for continuous material production.

RESULTS

Two synthesis routes were followed. In the first approach, a batch process is used where the secondary particles are first spray dried on a commercial tool (ESDT1 Lab Spray Dryer) and are then transferred to a batch CVD furnace for CNT synthesis. This process allows for efficient screening of different material parameters. In a second approach, the continuous flow process shown in Figure 1 is implemented. Both processes are described in detail in the Experimental Section. In the first approach, we spray dry an aqueous suspension of 50 nm Si nanoparticles (0.85 M, NPs) and iron nitrate (0.11 M). We selected this Si to Fe ratio in order to reach the capacity values of core materials between 1000 and 1500 mAh/g. In our calculation, if all Fe atoms form an FeSi2 phase, which has around 100 mAh/g, the resulting Si and Si$_x$Fe$_y$ core particles have a theoretical capacity of $\sim$1400 mAh/g. The dispersion was prepared by ultrasonication and mechanical stirring (500 rpm). The suspension was sprayed by a two-fluid atomizer to ensure narrow droplet size distribution and then dried with a flow of hot gas (220 °C) holding an outlet temperature of 90 °C. The process results in the formation of secondary clusters of iron nitrate and Si particles with an average diameter of $\sim$3 μm.

Figure 2a shows a scanning electron microscopy (SEM) image of these particles after the spray-drying process and heat treatment at 700 °C in H$_2$/He atmosphere to decompose the iron nitrate and form iron silicide. All particles have a spherical shape with diameters typically ranging between 1 and 5 μm. Next, CNTs are synthesized using CVD in a C$_2$H$_2$/H$_2$/He...
(50/50/400 sccm) atmosphere at temperatures ranging between 630 and 850 °C for 2−30 min depending on the targeted CNT loading of the electrode. As shown in Figure 2, these different CNT synthesis conditions result in varying CNT loadings, for instance, for 850 °C and 10 min growth (SiFeCNT-850-10), only few CNTs are observed on the surface of the spheres (length <3 μm, see Figure 2c), whereas for 30 min at 630 °C (SiFeCNT-630-30) much longer CNTs extend from the surface. Further, cross-section TEM analysis shows that CNTs are synthesized both inside and outside the pores of the secondary particle (see Figure 2g−i and S1 and S2). We anticipate that the CNTs inside the particles are critical for short-range electron transport because of the limited electrical conductivity of silicon/iron silicide in conjunction with the relatively large secondary particle size. This is important to achieve a high utilization of the active material as well as lower electrode impedance. This is verified electrochemically by reference experiments where the same spray-dried secondary particles are physically mixed with CNT powder instead of CVD grown (see further). In addition, the CVD process results in CNTs that are anchored on the particles and maintain good contact during cycling and therefore a better electrode stability.

In a second phase, the same materials are fabricated using a continuous flow CVD reactor (see Figure 1). The Si and iron nitrate solution was nebulized (Collison 1-jet nebulizer) in a N2 carrier gas (2000 sccm). The droplets are then passed through a silica gel drier and precipitated into the secondary solid particles. These particles are then carried by the N2 carrier gas into the CVD furnace where C2H2 and H2 gas is added (60/500 sccm) and CNTs are synthesized at 850 °C. As shown in Figure 2f, this continuous-flow synthesis process also results in spherical secondary particles decorated with CNTs (see SEM, XRD, and TGA data in Figures S3−S5).

Figure 3 shows X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA), and nitrogen physisorption analysis of different SiFeCNT formulations (SiFeCNT-x-y with x the CNT synthesis temperature in °C and y the synthesis time in min). Parts a and b of Figure 3 show XRD patterns of hybrid iron silicide−CNT composite (SiFeCNT) samples prepared using different CVD temperatures and synthesis times. The Si precursor powder shows a cubic Si phase (JCPDS No. 27-1402). After a 30 min synthesis, a broad peak around 26° (002) originating from the CNTs is present for all temperatures, and this peak is less prominent as the temperature increases. Similarly, as temperature increases, the peak intensities from iron silicide phases, FeSi2 (JCPDS No. 35-0822) and FeSi (JCPDS No. 38-1397), increase. Therefore, we conclude that CNTs are synthesized efficiently at temperatures as low as 630 °C and iron silicide phases are formed more readily at higher CVD temperature. At 850 °C, the average crystalline size of the Si precursor calculated by the Scherrer equation is 52.8 nm (which corresponds well with the 50 nm particle listed by the provider), and this value decreases to 42.2 nm after CNT growth at the cost of a FeSi phase, which grows to 18.2 nm (SiFeCNT-850-30). At the same CVD temperature (850 °C), the iron silicide peaks increase with the reaction time from 3 to 20 min (see Figure 3b). Overall, this analysis shows that the CNT content and iron silicide to Si ratio can be controlled by changing reaction temperature and time. It is important to note that not all Si is converted to SiFe as this would reduce the capacity of the material too much. XPS (Figure 3c and S7) profiles confirm the formation of iron silicide phases. Si 2p spectra shows the peak at 99.5 eV shifts to higher binding energy at 99.8 eV after CNT growth. This is probably due to Si−Si bonds changing to Si−Fe bonds as shown in a previous study. The contribution at 101.5 eV in
SiFeCNT-850-30 is probably from the formation of a small amount of Si–C, as confirmed by the XRD results.

Several reports describe how CNTs can be synthesized from Fe catalyst rather than from iron silicides, which do not support CNT synthesis. Therefore, when the Si–Fe mixtures are heated in the CVD reactor, two competing reactions occur: the first is the synthesis of CNTs from iron and the second is the reaction of iron and silicon to form iron silicides. Our data suggest that at high temperature the silicide phase is formed rapidly, yielding fewer CNTs, whereas at lower temperature silicides are formed slowly, leaving more time for CNTs to grow from the iron particles. This is in agreement with previous studies on the synthesis of CNT forests on Si particle and Si wafers.

To investigate the mass loading of CNTs and their quality, we performed TGA of samples synthesized under different conditions (temperature and time) in synthetic air. Figure 3d shows that the CNTs grow more abundantly at low temperatures (630 °C). We believe this is due to the higher stability of the iron catalyst under these conditions as discussed above. As with all CNT-CVD synthesis processes, the CNT growth rate decreases with time because of catalyst poisoning and diffusion limits of carbon precursors and various other processes.

TGA analysis in air shows that SiFeCNTs synthesized at lower temperatures or short growth times increase in mass between temperatures of 200–400 °C (Figure S8a,b), which is likely due to iron oxidation. This increase in weight is missing at higher synthesis temperatures or times, suggesting that in those cases, almost all iron is converted to iron silicide. Further, as the synthesis temperature and time increase, the SiFeCNTs show an improved thermal stability. For example, the peak temperature in TGA decomposition shifts from approximately 550–650 °C when increasing the CVD temperature from 630 to 850 °C for 30 min growth (Figure 3e). This shift in TGA peak decomposition temperature indicates higher CNT quality. Finally, at 850 °C, the CNT decomposition peak position shifts to higher temperature as growth time increases (Figure S8c).

The BET surface area and pore volume of SiFeCNT-850-60 samples are 63 m²/g and 0.23 cm³/g, respectively (Figure 3f). In spite of the low density and high surface area of CNTs, the SiFeCNTs have a lower surface area and pore volume than SiFe clusters (77 m²/g and 0.44 cm³/g), which were synthesized from the same starting material but different atmosphere (H₂/He without C₂H₄ to suppress CNT growth). This lower surface area can reduce side reactions (formation of solid-electrolyte interphase, SEI), which is an important challenge when using nanomaterials in LIBs.

To test the electrochemical performance of the SiFeCNT secondary particles developed in this work, they were mixed with a carboxymethyl cellulose (CMC)–styrenebutadiene rubber (SBR) binder in DI water using a centrifugal planetary mixer. The electrodes were tested in half cells (2032 coin cells) using 1.3 M LiPF₆ in EC/DEC as an electrolyte with 10 wt % FEC electrolyte additive (see the Experimental Section). As control experiments, we spray dried pure Si secondary particles as well as SiFe particles without CNTs. These were then physically mixed with commercial CNT powders (Nanocyl NC7000) at the same loading to study the benefits of our in situ CVD synthesis of CNTs (see the Experimental Section). In what follows, we will refer to the physical mixtures of Si and SiFe with CNTs as Si+CNT and SiFe+CNT, respectively.
whereas particles with *in situ* CVD grown CNTs from SiFe clusters are denoted SiFeCNTs.

A first observation when coating the electrodes is that the material structured in secondary particles forms smooth battery slurries at standard solvent loading (see experimental section), whereas unstructured mixtures of Si nanoparticles and CNTs require a large amount of solvent and do not easily form good battery slurries. In addition, we observed some cracks in films using SiFe+CNT whereas our SiFeCNT electrodes did not show any cracks under the same conditions (see Figure S9). This may be due to the network of CNTs anchored on the SiFe clusters preventing cracks from forming.

Figure 4a shows the initial two cycles of our electrodes obtained in the 0.005–1.5 V range, which for the SiFeCNT electrode shows as expected a steep decrease in potential and a voltage plateau at ∼0.1 V. On the other hand, we found a sloped capacity contribution when using a SiFe + CNTs (same concentration of components), this is likely caused by excessive electrolyte decomposition and SEI formation on the exposed CNT surfaces when they are not structured in secondary particles (Figure S11).56,57 A main portion of the CNTs is positioned inside the secondary particles, which guarantees good internal electron transport and less SEI formation. This is reflected in the initial Coulombic efficiency (ICE), which is 74.2% for SiFeCNTs and only 56.5% for the reference sample where the CNTs are physically mixed.

After two formation cycles at 100 mA/g, the electrodes are at 1 A/g current density (1.0 to 0.005 V, 1 C-rates of SiFeCNT, SiFe-cluster, and Si-cluster are 1640, 1550, and 2275 mA/g, respectively) for 300 cycles (Figure 4b). Under constant current conditions, the SiFeCNT electrodes increase in capacity with cycles, reaching up to 1509 mAh/g at 50th cycle (0.6 C). The reversible capacities of SiFeCNT electrodes are 1495, 1336, and 1163 mAh/g at the 100th, 200th, and 300th cycle. In comparison, Si+CNT and SiFe+CNT clusters show much faster degradation. Note that the Si clusters achieve higher capacities in the first 18 cycles due to the higher capacity of Si compared to SiFe, but they degrade faster and their capacity is far off the theoretical capacity. The latter indicates a poor material utilization, as expected for micrometer sized secondary particles with low electric conductivity (no internal CNTs). CE values of SiFeCNT electrodes are noticeable higher than other formulations and already reach 99% at second cycle of 1 A/g, while SiFe+CNT electrodes only achieve 99% after 113 cycles and Si+CNT electrodes after 99 cycles.

As shown in Figure 4c, the SiFeCNT electrodes retain 43% of their capacity when increasing the C-rate from 0.25 to 5 C, while under the same rate conditions only 11% and 5% of the initial capacities are retained in SiFe+CNT and Si+CNT electrodes, respectively. This is probably due to the better electrical conductivity in the SiFeCNTs, for which we conducted galvanostatic intermittent titration technique (GITT) analysis and electrochemical impedance spectroscopy (EIS) measurements. Using GITT, the internal resistance can be estimated at different states of charge by calculating the voltage difference between closed-circuit-voltage (CCV) and quasi-open-circuit-voltage (QOCV, Figures 4d and S12).58,59 In the first cycle, SiFeCNT and SiFe+CNT electrodes show similar resistances, which decrease as lithiation proceeds. During delithiation, the difference in resistance between SiFeCNT and SiFe+CNT begins to increase above 0.7 V. In the second cycle, the SiFeCNT electrodes show lower internal resistance, indicating a lower ohmic and charge-transfer resistance. We suspect this is due to the (i) good interface between the CNTs and the Si particles on which they are
grown and (ii) good electron transport inside the micrometer-sized secondary clusters (Figures 2i and S13). In the physically mixed SiFe+CNT, the formation of SEI on the CNT surface may insulate them from the active material. Figure 4e shows the evolution of EIS data for SiFeCNT and SiFe+CNT electrodes over 300 cycles. In the Nyquist plot, semicircles (related to charge-transfer resistance) of the SiFeCNT electrode initially decrease and remain stable as cycling proceeds. Decreasing impedance values during the cycles indicate total resistance of the coin cell decreases, probably due to the improved contact between CNTs and Si after swelling of Si particles. On the other hand, the charge-transfer resistance of SiFe+CNT electrodes increases after the 50th cycle, which again indicates a degradation of the interface between the CNTs and the active material in physical CNT mixtures.

As mentioned in the Introduction, commercial anodes use Si only as an additive to graphite to create so-called blend electrodes. To investigate the viability of SiFeCNTs in such electrodes, we mixed SiFeCNT with commercial natural graphite (NG) powder and CMC-SBR binder (active material to binder ratio was 96:4 with no additional conductive additives). The blend ratio was adjusted to achieve a capacity of about 550 mAh/g since higher anode capacities would not provide significant overall improvement in cell performance due to the limited capacity of current cathodes. Both SiFeCNT and Si NP sample were mixed with graphite using a centrifugal mixer and were coated on Cu foil followed by calendaring to achieve industrial loading levels of active mass (6.5–7.0 mg/cm²) and high electrode density (1.5–1.6 g/cm³). To demonstrate the scalability of our material and electrode preparation, we used roll-to-roll coating to produce a 35 m long anode (Figure 5a,b). SEM images in Figure 5c show the SiFeCNT and Si NP particles are well distributed between the graphite particles. These electrodes were cycled under constant current and constant voltage mode between 0.005 and 1.5 V (formation cycles are shown in Figure S14). Both electrodes were designed to have a similar performance (SiFeCNT-graphite cells delivers 539 mAh/g and 3.75 mAh/cm² and the Si NP-graphite cells delivers 551 mAh/g and 3.72 mAh/cm²) to improve their packing density and reduce the amount of binder needed in the electrode formulation. Next, CNTs are grown directly from the surface of the Si particles using CVD, and we found that the nanotubes are formed both inside and outside of the secondary particles leading to better electron transport. In addition, the CVD-grown CNTs are strongly anchored on the secondary particles, and as a result, phase segregation challenges during mixing and coating are mitigated and the electric network is maintained during cycling. Pure SiFeCNT electrodes show a capacity of over 1150 mAh/g after 300 cycles at 1A/g and retain over 43% of their capacity at a rate of 5C. In addition, we present blend electrodes where SiFeCNT is mixed with graphite to obtain a 550 mAh/g anode. These were calibrated to obtain industrially relevant loading levels (>6.5 mg/cm² and >1.5 g/cm³) and show a CE of 99.5 from second cycle and capacity retention of 96.6% after 50th cycle. Finally, we demonstrate the scalability of our process by coating a 35 m long electrode on a roll-to-roll tool.

EXPERIMENTAL METHODS

Synthesis of SiFeCNT Using Continuous Flow Reactor. Initially, to synthesize nanoparticle (NP) clusters, 12 g of Si NPs (0.43 mol, SAT Nano) and 22 g of iron(III) nitrate nonahydrate (54 mmol, Fe(NO₃)₃·9H₂O, Sigma-Aldrich) were dispersed in DI water (500 mL) to yield a 6.8 w/v % precursor solution. This suspension was ultrasonicated for 30 min. Under continuous mechanical stirring (500 rpm), the suspension was atomized at 220 °C (inlet) with atomization pressure of 3 by using a two-fluid atomizer (0.8 mm orifice). The temperature of outlet was fixed at 90 °C. Particles were separated from the gas stream in a cyclone (69% yield) and collected in a glass bottle. After spray drying, the particles were transferred into a ceramic crucible in a horizontal tube furnace. Before the CVD process, the Si/Fe nano-clusters were purged with helium gas and reaction gases for 10 min, respectively. The powder was heat-treated with flows of 400/50/50 sccm He/C₂H₂/H₂ under different temperature ranges (630–850 °C). Heat-treatment time was controlled between 2 and 60 min, followed by rapid cooling and purging with He. The SiFe cluster was synthesized with the same spray-dried particles without C₂H₂ gas at 700 and 850 °C.

Synthesis of SiFeCNT Using Continuous Flow Reactor. Si and iron nitrate solution was prepared in the same way. An atomizer (Collison 1-jet nebulizer) was used to atomize the precursor solution in a flow of nitrogen gas (2000 sccm). A nebulized droplet was passed through a silica gel filled drier. After removal of moisture, the particles entered the furnace, where C₂H₂ (60 sccm) and H₂ (500 sccm) inlets were connected. At an 850 °C tube furnace, CNT formed from the surface of Si/Fe cluster. The resulting materials were collected on a 12 μm filter, connected in-line to the outlet of furnace.

Material Characterization. Morphologies of SiFeCNT materials were observed by scanning electron microscopy (SEM, a Leo Variable Pressure instrument with an acceleration voltage of 10 kV) and
transmission electron microscopy (TEM, TEM-1011, Jeol LTD). For TEM, the sample was sectioned at a thickness of 100 nm using a powertome XL. X-ray diffraction (XRD) patterns were obtained by using a Bruker D8 Advance (Cu Kα radiation, 6° min⁻¹ scan). Thermogravimetric analysis (TGA) analysis was performed using a PerkinElmer Pyris1 instrument machine under air atmosphere. After stabilizing the temperature at 30 °C for 30 min, samples were heated to 800 °C at a speed of 2 or 3 °C/min. Nitrogen physisorption was obtained by using a Micromeritics TriFlex porosimeter. X-ray photoelectron spectroscopy (XPS) was conducted using a PHI 5000 VersaProbe (Ulvac-PHI).

**Electrode Preparation.** The SiFeCNT samples were mixed with carboxymethyl cellulose (CMC, MTT Corp.) and styrene-butadiene rubber (SBR, MTT Corp) with a mass ratio of 10:1:5:1.5 in DI water solvent. For the SiFeCNT cluster and Si-cluster, each sample was mixed with CNT (Nanocyl NC7000), CMC, and SBR with a mass ratio of 7:3:1.5:1.5. The homogeneous slurry was casted on copper foil with 0.4−0.6 mg(Si or SiFe)/cm² active material and dried under 100 °C vacuum oven overnight. For the blending electrode experiments, SiFeCNT was mixed with commercial natural graphite (NG) in a 20:80 weight ratio. For the control experiment, a commercial Si NP blend electrode was prepared (Si NP/NG = 8:92). The blend powders were mixed with CMC and SBR with the mass ratio of 96:2:2 using DI water. The slurry was mixed using a centrifugal planetary mixer and casted on copper foil (active material: 6.5−7 mg/cm²). For roll-to-roll coating, we used Smartcoater 28 (Coatema Coating Machinery GmbH), and the drying temperature was 120 °C with film speed of 20 cm/min (unwinder and rewinder tensions are 10 and 20 N, respectively). After solvent evaporation in a fume hood, the electrode was pressed to increase the electrode density (1.5−1.6 g/cm³), followed by vacuum drying at 100 °C. For LiCoO₂ (LCO) electrodes (3.0−3.1 g/cm³), LCO was mixed with Super P and polyvinylidene fluoride (PVDF) with mass ratio of 94:3:3 using N-methyl-2-pyrrolidone (NMP), followed by calendaring and vacuum drying at 100 °C. To make a full cell, the SiFeCNT-graphite electrode was physically contacted with lithium chip in electrolyte for 10 min to decrease initial capacity loss by side reaction. SiFeCNT-graphite to LCO electrode mass ratio was 1:1.

**Electrochemical Characterization.** 2032-type coin cells were assembled inside the glovebox with metallic Li foil as a counter/reference electrode. Electrolyte was prepared by adding 1.3 M lithium hexafluorophosphate (LiPF₆) in ethylene carbonate (EC)/diethyl carbonate (DEC, Sigma-Aldrich) with 10 wt % fluoroethylene carbonate (FEC, Insight Biotechnology, Ltd.). The Si coin cells were tested at 25 °C under constant current mode (two formation cycles with 100 mA/g and 1 A/g for the cycling test) with a potential range of 0.005−1 V (or 1.5 V vs Li/Li⁺) using LAND cycler (Wuhan Biologic VMP3). Cyclic voltammetry (0.05 mV/s scan rate, 0.005−1.0 V), galvanostatic intermittent titration technique (GITT, 20 min reaction with 0.1 C and 40 min relaxation, 0.005−1.5 V), and electrochemical impedance spectroscopy (EIS, 1000−0.05 Hz, 5 mV amplitude) results were obtained using Biologic VMP3.

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