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Constructing High-Performance Carbon Nanofiber Anodes by the Hierarchical Porous Structure Regulation and Silicon/Nitrogen Co-Doping

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Abstract: Due to the rapid development of bendable electronic products, it is urgent to prepare flexible anode materials with excellent properties, which play a key role in flexible lithium-ion batteries. Although carbon fibers are excellent candidates for preparing flexible anode materials, the low discharge specific capacity prevents their further application. In this paper, a hierarchical porous and silicon (Si)/nitrogen (N) co-doped carbon nanofiber anode was successfully prepared, in which Si doping can improve specific capacity, N doping can improve conductivity, and a fabricated hierarchical porous structure can increase the reactive sites, improve the ion transport rate, and enable the electrolyte to penetrate the inner part of carbon nanofibers to improve the electrolyte/electrode contacting area during the charging–discharging processes. The hierarchical porous and Si/N co-doped carbon nanofiber anode does not require a binder, and is flexible and foldable. Moreover, it exhibits an ultrahigh initial reversible capacity of 1737.2 mAh g^{−1}, stable cycle ability and excellent rate of performance. This work provides a new avenue to develop flexible carbon nanofiber anode materials for lithium-ion batteries with high performance.

Keywords: lithium-ion battery; flexible anode; hierarchical porous structure; Si/N co-doping; high performances

1. Introduction

With the rapid development of bendable electronic products, such as flexible displays, wearable electronics and medical electronics, flexible energy storage systems with higher energy density have become an urgent demand [1,2]. Lithium-ion batteries, as energy storage devices, have attracted enormous attention due to their long cycle life, fast charge–discharge, high energy density, and no memory effect [3–6]. Flexible anode materials are a particularly important factor to obtain lithium-ion batteries with high electrochemical performance [7,8]. Therefore, the development of flexible anode materials with bendable function and excellent electrochemical performance has become one of the research hotspots.

Carbon fibers are one of the most widespread anode materials of flexible lithium-ion batteries [9,10]. However, untreated carbon fibers make it difficult to achieve the high performance demands of lithium-ion batteries due to their low reversible capacity. To obtain high electrochemical performance, it is common to fabricate holes of different sizes in carbon fibers [11–14]. Wang et al. reported that micropores can increase the number of active sites of lithium storage and the ability of ion adsorption [15]. Guo et al. reported that mesopores greatly enhance the capability rate and facilitate the transport of ions [16]. Chen et al. reported that abundant meso/macropores in carbon nanofibers can offer more active sites for Li storage and facilitate electrolyte penetration of the inner part of carbon nanofibers, improving the electrolyte/electrode contacting area [17]. In addition, element doping is another measure of modifying electrode materials. Silicon materials have been widely concerned because of their high theoretical capacity of 4200 mAh g^{-1} [18,19]. However, silicon materials undergo serious volume changes during the charging–discharging process, which leads to particle pulverization and rapid capacity decay [20,21]. Silicon–carbon composites can make use of the structural strength of carbon materials, so that the volume change in silicon materials can be alleviated during the charging–discharging process [22–25]. For example, Jang et al. prepared a pyrolytic carbon-coated silicon nanofiber anode, which has high capacity and excellent cycling performance [26]. Xu et al. reported a flexible 3D Si/C fiber paper anode with capacity of 1600 mAh g^{-1} , which was synthesized by simultaneously electro spraying nano-Si and polyacrylonitrile fibers, followed by carbonization [27]. Traditionally, carbon materials are used to modify silicon materials to obtain silicon-based anode materials with high electrochemical properties. Similarly, it may be effective to use silicon materials to dope carbon fibers to obtain high-capacity carbon fiber anodes. In addition, N doping was also used to improve the conductivity of carbon materials [28–30]. However, it is difficult to fully meet the requirements of high electrochemical properties using a single modification strategy. Therefore, the synergistic effect of various modification methods may be effective for the preparation of high-performance carbon nanofiber anodes.

Based on the above analysis results, we prepared a hierarchical porous and Si/N co-doped carbon nanofiber anode by novel gas–electric co-spinning technology in this work. Si doping can improve the specific capacity, N doping can improve the conductivity, and the fabricated micropores, mesopores and macropores can increase the number of reactive sites, improve the ion transport rate, and enable the electrolyte to penetrate the inner part of carbon nanofibers to improve the electrolyte/electrode contacting area during charging–discharging processes. This modified carbon nanofiber anode does not require a binder, and has the advantages of flexibility and foldability. Moreover, it exhibits a high initial reversible capacity of $1737.2 \text{ mAh g}^{-1}$, good capacity retention and outstanding rate ability. This work provides a new avenue for the development of flexible lithium-ion batteries.

2. Experiment

2.1. Materials

The reagents used in this paper included: polyacrylonitrile (PAN) (solid, molecular weight 150,000, Macklin), graphene (commercially available), N, N-dimethylformamide (DMF) (liquid, analytical purity, Macklin), nano silicon particles (Si) (50 nm) and polymethylmethacrylate (PMMA) (solid, Macklin). These reagents were analytically pure so could be used directly.

2.2. Preparation of Materials

The flow chart of preparation of the hierarchical porous and Si/N co-doped carbon nanofiber anode materials is shown in Figure 1. Firstly, 0.1 g graphene, 2 g polyacrylonitrile (PAN) and a certain amount of silicon were dissolved in 50 mL N,N-dimethylformamide (DMF) and vibrated with ultrasound for 20 min. Then, the pore-making agent polymethylmethacrylate (PMMA) was added to this solution, heated at 70°C using a water bath and stirred for 10 h. The obtained precursor solution was continuously spun on the flat plate

for about 1 h to obtain a fiber cloth by the gas–electric co-spinning method. The feed speed was 4 mL h^{-1} , the voltage was 5 kV, and the air flow was 10 Psi. Subsequently, the fiber cloth was placed in a blast drying oven for pre-oxidation, in which the temperature was raised from room temperature to 280°C with a heating rate of 2°C min^{-1} for 6 h. The purpose of pre-oxidation was to make PAN undergo three chemical reactions: cyclization, dehydrogenation and oxidation in this process, so as to make the carbon fiber cloth more stable before carbonization. Finally, the fiber cloth was calcined at 950°C under the protection of argon for 1 h, and then activated in ammonia for 30 min. High-temperature tubular furnace was used to increase the temperature from room temperature to 200°C with a heating rate of 2°C min^{-1} , and then the temperature was reduced to room temperature to obtain the hierarchical porous and Si/N co-doped carbon nanofiber anode materials.

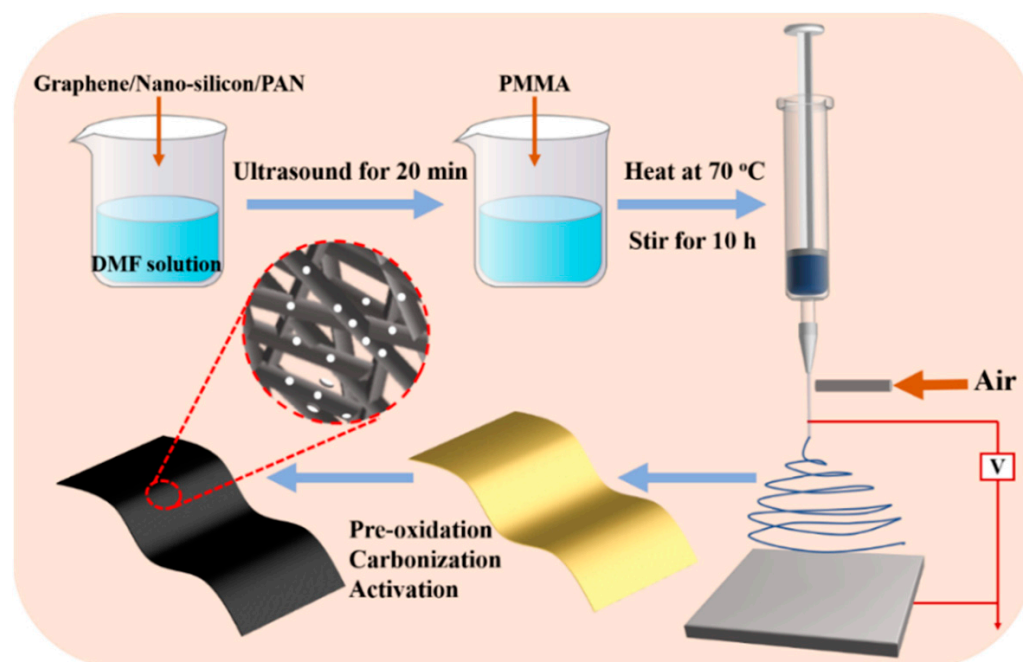


Figure 1. The flow chart of preparation of the hierarchical porous and Si/N co-doped carbon nanofiber anode materials.

In the process of preparing the materials above, by changing the mass ratio of PAN:PMMA = 2:1, 2:2, 2:3 and 2:4, carbon nanofibers with different proportions of PMMA were obtained (named CNFs-PMMA1, CNFs-PMMA2, CNFs-PMMA3 and CNFs-PMMA4, respectively, according to the added PMMA masses of 1 g, 2 g, 3 g and 4 g). After determining the optimal amount of PMMA, according to the added Si mass (0%, 5%, 10% and 15%, the mass ratio of Si/PAN), the hierarchical porous Si/N co-doped carbon nanofiber anode materials were named CNFs-Si0%, CNFs-Si5%, CNFs-Si10% and CNFs-Si15%, respectively.

2.3. Materials Characterization

Microscopic morphology of the samples was observed using scanning electron microscopy (SEM, HITACHI-SU8220, Tokyo, Japan), and the corresponding element mapping on the surface of materials was analyzed by an energy dispersive spectrometer (EDS). The hole size distribution of samples was measured using a nitrogen adsorption–desorption apparatus (BET, BELSORP-miniII, BEL Japan Inc., Osaka, Japan).

2.4. Electrochemical Measurements

The prepared anode sheet of lithium-ion batteries was a flexible carbon fiber, which did not require binders to be added and did not have to be coated on the copper foil, compared with traditional electrodes. The prepared hierarchical porous and Si/N co-doped

carbon fiber, after being sliced, can be used directly as a battery anode. The weight of the anode was ~ 0.76 mg, the diameter of the electrode was 9 mm, and the mass loading was ~ 1.2 mg cm $^{-2}$. A metal lithium sheet was used as the counter electrode, the electrolyte was added in the ratio EC:DEC:EMC = 1:1:1 (*v/v*) to the solvent containing 20% fluoroethylene carbonate (FEC) and lithium hexafluorophosphate (LiPF $_6$), and the separator was porous polypropylene. The electrochemical experiments were carried out by using commercial CR2032 cells at room temperature. The blue electric system (Land CT2001A, Blue Power Company) was set to maintain constant current charge–discharge, and the voltage range was from 0.01 to 3 V. The rate performance of batteries was tested at different current densities (0.05, 0.1, 0.2, 0.5 and 1 C, 1 C = 1000 mAh g $^{-1}$). Princeton (PMC1000A) electrochemical workstation was used to test the cyclic voltammetry (CV) in the voltage range of 0.01–3 V with a scanning rate of 0.01 mV s $^{-1}$. The electrochemical impedance spectroscopy (EIS) tests were carried out in a frequency range between 0.1 Hz and 100 kHz with an amplitude of 5 mV.

3. Results and Discussion

Figure 2a shows the digital photo of a hierarchical porous and Si/N co-doped carbon nanofiber cloth, which is flexible and foldable. It can be used directly as a flexible lithium-ion anode without the addition of binders. The microstructure of the carbon nanofiber cloth is further tested, and the SEM images of CNFs-PMMA1 and CNFs-PMMA3 are shown in Figure 2b,c. The diameter of the carbon nanofibers is about 400 nm and the fibers are cross-linked. With the increase in the PMMA content from CNFs-PMMA1 to CNFs-PMMA3, many macropores of different sizes emerge in the fibers. It is speculated that micropores and mesopores may also exist in the fibers. However, it is difficult to judge whether there are smaller holes through SEM images. Therefore, the pore size distribution is further explored by a nitrogen adsorption–desorption test in the follow-up study.

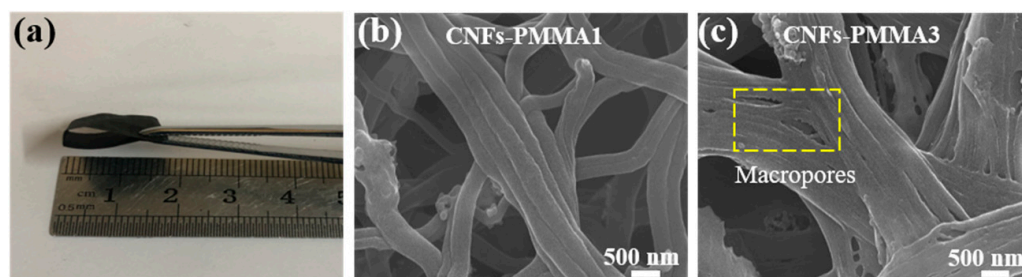


Figure 2. (a) A digital photo of the hierarchical porous and Si/N co-doped carbon nanofiber cloth, SEM images of (b) CNFs-PMMA1 and (c) CNFs-PMMA3.

To obtain the optimal addition content of PMMA, the cycle and rate performances of CNFs-PMMA1, CNFs-PMMA2, CNFs-PMMA3, and CNFs-PMMA4 anodes in lithium-ion batteries are tested, and the results are used as the basis for selecting the content of PMMA. Figure 3a shows cycle performance curves of the four anodes at a current density of 0.05 C, from 0.01 to 3 V. The CNFs-PMMA3 anode has the highest initial capacity of 1437.2 mAh g $^{-1}$ among the four anodes. After 100 cycles, the CNFs-PMMA3 anode can still reach 985.3 mAh g $^{-1}$. Figure 3b shows the rate performance curves of four anodes. Compared with CNFs-PMMA1, CNFs-PMMA2, and CNFs-PMMA4 anodes, the CNFs-PMMA3 anode shows excellent rate performance. The specific capacity of the CNFs-PMMA3 anode is 1469.9, 1307.6, 1213.1, 956.3 and 686.3 mAh g $^{-1}$ at the current density of 0.05, 0.1, 0.2, 0.5 and 1 C, respectively. Therefore, the amount of PMMA added in CNFs-PMMA3 is selected as the optimal result.

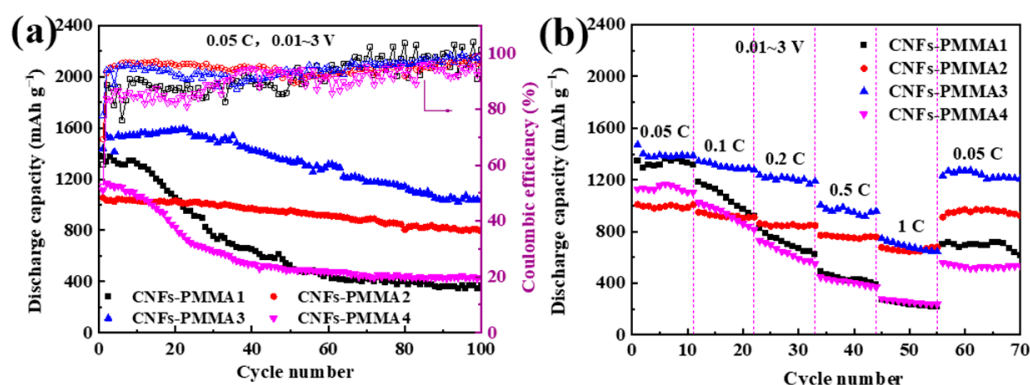


Figure 3. (a) Cycle performance and (b) rate performance curves of CNFs-PMMA1, CNFs-PMMA2, CNFs-PMMA3, and CNFs-PMMA4 anodes in lithium-ion batteries.

After determining the amount of PMMA, the effect of the silicon content on the hierarchical porous carbon nanofiber anode is further studied. The microscopic morphologies of CNFs-Si0%, CNFs-Si5%, CNFs-Si10% and CNFs-Si15% materials are shown in Figure 4a–d. These carbon nanofibers have a good fiber shape with a diameter of about 1 μm , which are randomly intertwined to form a fiber cloth. With the increase in the Si content from CNFs-Si0%, CNFs-Si5%, CNFs-Si10% to CNFs-Si15%, the white particles increase, due to the agglomeration of nano silicon particles. The SEM image of CNFs-Si10% and the corresponding EDS mapping of elements are shown in Figure 4e. Some holes exist in the fiber, and the nanofiber is cross-linked. In addition, Si, C and N elements are evenly distributed, indicating that Si and N are effectively doped in nanofibers. It is worth noting that the N element is doped through ammonia activation during the experiment. It was reported that N doping can improve the conductivity of carbon materials [28–30], which is not discussed further in this work.

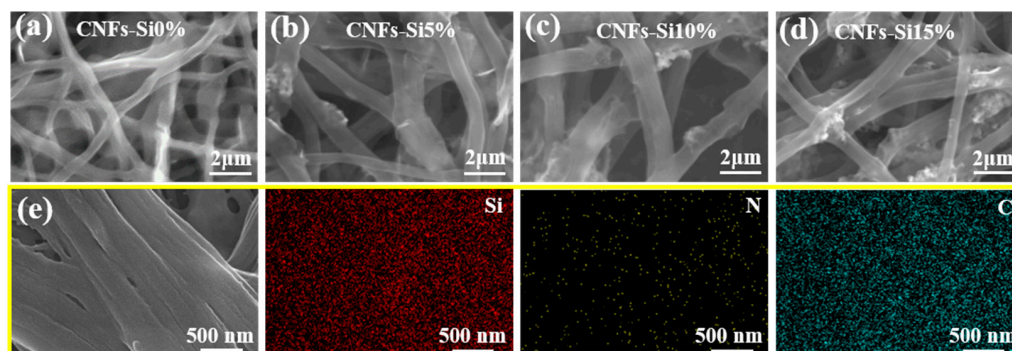


Figure 4. SEM images of (a) CNFs-Si0%, (b) CNFs-Si5%, (c) CNFs-Si10% and (d) CNFs-Si15%. (e) SEM image and the corresponding EDS mapping of Si, C, and N elements in partial CNFs-Si10%.

Nitrogen adsorption–desorption curves of CNFs-Si0%, CNFs-Si5%, CNFs-Si10% and CNFs-Si15% are shown in Figure 5a. When $P/P_0 > 0.4$, a hysteresis loop appears in the nitrogen adsorption–desorption curves of all samples, which belong to the IV isotherm. The corresponding pore size distribution curves are shown in Figure 5b, which show that all samples have micropores (pore size less than 2 nm) and mesopores (pore size between 2 and 50 nm), which aligns with the experimental expectation. Combined with the SEM images and EDS mapping in Figure 4, this result indicates that a Si/N co-doped carbon nanofiber anode with a hierarchical porous structure has been synthesized.

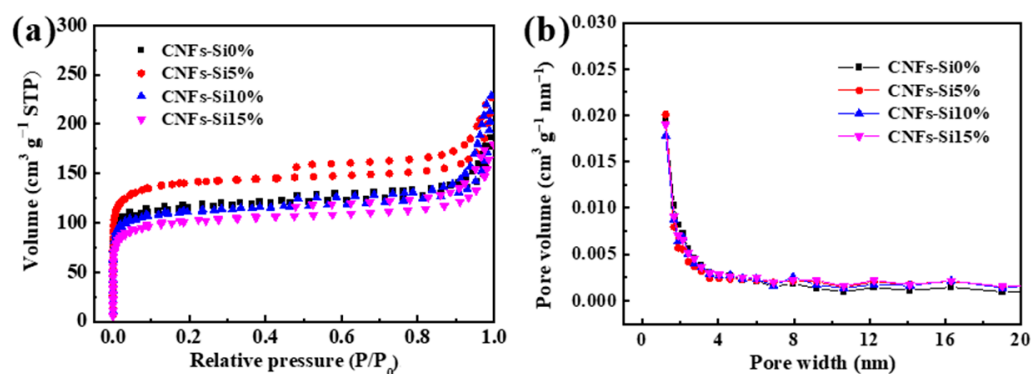


Figure 5. (a) Nitrogen adsorption–desorption curves, and (b) the corresponding pore size distribution curves of CNFs-Si0%, CNFs-Si5%, CNFs-Si10% and CNFs-Si15%.

Figure 6a shows cycle performance curves of CNFs-Si0%, CNFs-Si5%, CNFs-Si10% and CNFs-Si15% anodes at 0.05 C, from 0.01 to 3 V, in lithium-ion batteries. The initial capacity of CNFs-Si10% is 1737.2 mAh g⁻¹, and still maintains a high reversible capacity of 985.3 mAh g⁻¹ after 100 cycles, which is the highest capacity among the four anodes. CNFs-Si10% and CNFs-Si15% anodes have a high initial capacity, which can mainly be due to the addition of Si with high capacity, compared with CNFs-Si0%. The capacity of CNFs-Si15% anode decreases significantly after 20 cycles, because the nano-silicon in the materials experiences large volume expansion with the increase in silicon content, destroying its structure. The initial Coulombic efficiency of the CNFs-Si0%, CNFs-Si5%, CNFs-Si10% and CNFs-Si15% anodes is only 49.72%, 50.24%, 77.82% and 50.74%, respectively. The low initial coulombic efficiency is due to the fact that with the addition of the pore-forming agent PMMA, the number of micropores increases, providing many reactive sites, thus forming a high irreversible capacity with the formation of an SEI film with a large area during the first charge–discharge process. After the first charge–discharge, the Coulombic efficiency of each anode is close to stable, basically around 90%, which can be attributed to meso/macropores, which can offer more active sites for Li storage and enable the electrolyte to penetrate the inner part of carbon nanofibers, improving the electrolyte/electrode contacting area.

Figure 6b shows the rate performance curves of CNFs-Si0%, CNFs-Si5%, CNFs-Si10% and CNFs-Si15% anodes in lithium-ion batteries at different current densities. The CNFs-Si10% anode still exhibits excellent specific capacities of 1719.9, 1593.1, 1484.3, 1255.7 and 995.8 mAh g⁻¹ at 0.05, 0.1, 0.2, 0.5 and 1 C, respectively. It can be seen that when the current density changes to 0.05 C again, the specific capacity of the CNFs-Si10% anode is greater than 1518.1 mAh g⁻¹, indicating good rate performance. This is because the synergistic effect of N doping and the hierarchical porous structure can improve the conductivity, increase the reactive sites, and improve the Li-ion transport rate. The results of cycling and rate performances indicate that proper silicon/nitrogen co-doping and hierarchical porous structure regulation are important to improve the electrochemical performance of carbon nanofiber anodes. To the best of our knowledge, the outstanding electrochemical performances of the CNFs-Si10% anode are much higher than other reported flexible carbon fiber anodes for lithium-ion batteries (Table 1).

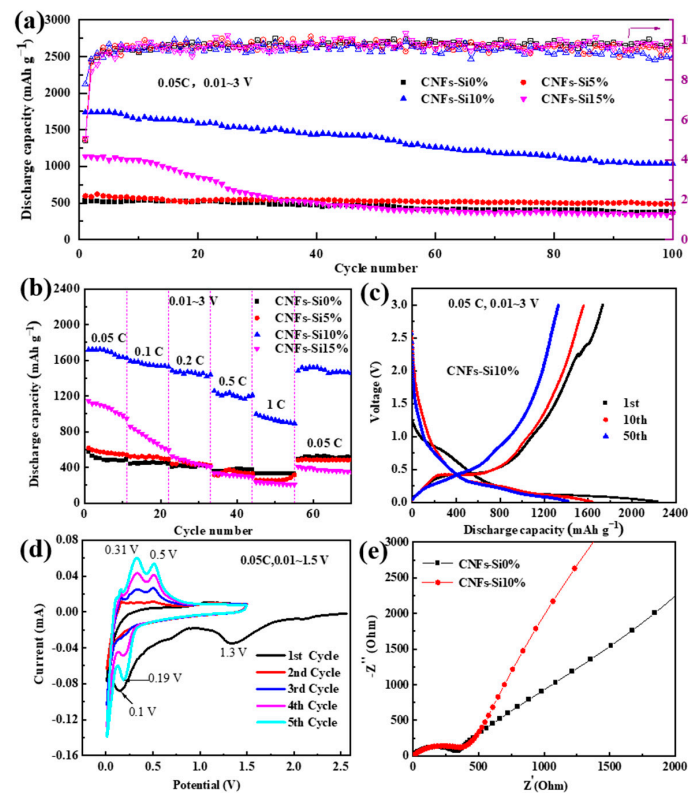


Figure 6. (a) Cycle performance and (b) rate performance curves of CNFs-Si0%, CNFs-Si5%, CNFs-Si10% and CNFs-Si15% anodes in lithium-ion batteries. (c) The charge–discharge curves of the CNFs-Si10% anode, (d) CV curves of the CNFs-Si10% anode, and (e) Nyquist plots of CNFs-Si0% and CNFs-Si10% anodes in lithium-ion batteries.

Table 1. Electrochemical performance of flexible carbon fiber anodes for lithium-ion batteries reported in this work.

Anodes	Mass Loading (mg cm ⁻²)	First Reversible Capacity (mAh g ⁻¹)	Cycle Performance (mAh g ⁻¹)	Rate Performance (mAh g ⁻¹)	Reference
V ₂ O ₅ /MCCNFs	1.5–2.5	790.6 (0.1 A g ⁻¹)	487.7 (5 A g ⁻¹ , 5000 cycles)	456.8 (5 A g ⁻¹)	[31]
In ₂ O ₃ @CF	1.4	510 (0.1 A g ⁻¹)	435 (0.1 A g ⁻¹ , 500 cycles)	190 (1.5 A g ⁻¹)	[32]
γ-Fe ₂ O ₃ /C films	1	923.97 (0.2 A g ⁻¹)	1088 (0.2 A g ⁻¹ , 300 cycles)	380 (5 A g ⁻¹)	[33]
am-Fe ₂ O ₃ /rGO/CNFs	1.5–2.0	825 (0.1 A g ⁻¹)	739 (1 A g ⁻¹ , 400 cycles)	570 (2 A g ⁻¹)	[34]
FeCo@NCNFs-600	1.77–2.65	736.3 (0.1 A g ⁻¹)	566.5 (0.1 A g ⁻¹ , 100 cycles)	130 (2 A g ⁻¹)	[35]
Sn@C/CNF	2	891.2 (0.1 A g ⁻¹)	610.8 (0.2 A g ⁻¹ , 180 cycles)	305.1 (2 A g ⁻¹)	[36]
NCNFs	7.64	752.3 (0.05 A g ⁻¹)	411.9 (0.1 A g ⁻¹ , 160 cycles)	148.8 (2 A g ⁻¹)	[16]
γ-Fe ₂ O ₃ @CNFs	2.0	1065 (0.5 A g ⁻¹)	430 (6 A g ⁻¹ , 1000 cycles)	222 (60 A g ⁻¹)	[37]
G/Si@CFs	0.65–1	1036 (0.1 A g ⁻¹)	896.8 (0.1 A g ⁻¹ , 200 cycles)	543 (1 A g ⁻¹)	[38]
C/CuO/rGO	1.30–1.95	550 (0.1 A g ⁻¹)	400 (1 A g ⁻¹ , 600 cycles)	300 (2 A g ⁻¹)	[39]
CNF@SnO ₂	1.77–3.54	793 (0.5 A g ⁻¹)	485 (0.1 A g ⁻¹ , 850 cycles)	359 (4 A g ⁻¹)	[40]
Fe ₃ O ₄ /NCNFs	1.33	686 (0.1 A g ⁻¹)	522 (0.1 A g ⁻¹ , 200 cycles)	407 (5 A g ⁻¹)	[41]
MoO ₂ /C	85.7	752.5 (0.2 A g ⁻¹)	450 (2 A g ⁻¹ , 500 cycles)	432 (2 A g ⁻¹)	[42]
FCNF-3/4	1.0	775 (0.2 A g ⁻¹)	630 (0.2 A g ⁻¹ , 100 cycles)	250 (5 A g ⁻¹)	[43]
10-SnO ₂ @CNFs/CNT	1.5–2.5	500.9 (0.1 A g ⁻¹)	460.3 (0.1 A g ⁻¹ , 200 cycles)	222.2 (3.2 A g ⁻¹)	[44]
ZnSe@CNFs-2.5	0.8–1.2	737.5 (0.1 A g ⁻¹)	426.1 (5 A g ⁻¹ , 3000 cycles)	547.6 (5 A g ⁻¹)	[45]
CNFs/CNTs	1.27	1500.5 (0.05 A g ⁻¹)	545 (0.2 A g ⁻¹ , 400 cycles)	344.8 (2 A g ⁻¹)	[46]
SnO ₂ /TiO ₂ @CNFs	/	1061.2 (0.1 A g ⁻¹)	729.6 (0.1 A g ⁻¹ , 150 cycles)	206.2 (3 A g ⁻¹)	[47]
CNFs-Si10%	1.2	1737.2 (0.05 A g ⁻¹)	985.3 (0.05 A g ⁻¹ , 100 cycles)	995.8 (1 A g ⁻¹)	This work

Figure 6c shows galvanostatic charge–discharge curves of the CNFs-Si10% anode during the 1st, 10th and 50th cycle at 0.05 C in the voltage range of 0.01–3 V. During the first cycle, the charge–discharge capacity is 2232.5 and 1737.2 mAh g⁻¹, respectively, corresponding to an initial Coulombic efficiency of 77.82%. Irreversible capacity loss is mainly due to the formation of the SEI film and the decomposition of the electrolyte during the initial charge–discharge process [48]. From the 10th to 50th cycle, the discharge capacity dramatically reduces from 1640 to 1421.7 mAh g⁻¹, which may be due to the production of a residual irreversible side reactant after charging and discharging multiple times. It is

noteworthy that the Coulombic efficiency value increases to 95.7% and 96.6% during the 10th and 50th cycle, respectively.

To further appraise the lithium storage performance of the CNFs-Si10% anode, CV curves of five initial cycles were obtained from 0.01 to 1.5 V at a scan rate of 0.1 mV s^{-1} , as shown in Figure 6d. During the first lithiation, generation of the SEI film and the decomposition of the electrolyte could lead to a broad irreversible peak at 1.3 V, which disappears in the following cycles. Subsequently, a sharp anodic peak below 0.1 V corresponds to the phase transformation from Si to Li_xSi and lithium-ion insertion with carbon nanofiber materials in the CNFs-Si10% anode [48]. Upon delithiation, two cathodic peaks at around 0.31 and 0.5 V are attributed to the dealloying process of Li_xSi into Si, which is consistent with the reported results [49]. In the second cycle, a broad anodic peak located at around 0.19 V appears, which is associated with the lithiation of Si. In the following cycles, the cathodic and anodic peak positions are consistent, indicating good concurrency and reversibility. For the anodic peak at 0.19 V and the two cathodic peaks at 0.31 and 0.5 V, the current intensities gradually enlarge in subsequent cycles, corresponding to the activation process as a result of the reaction of more active sites with lithium-ion [50]. This phenomenon is typical for the Si-based anode for lithium-ion batteries [51,52]. The results show that the CNFs-Si10% anode has good stability.

To further explore the effect of Si doping on the performance of lithium-ion batteries, the EIS of CNFs-Si0% and CNFs-Si10% anodes were tested. Figure 6e shows the Nyquist plots of CNFs-Si0% and CNFs-Si10% anodes in lithium-ion batteries. The curve consists of an overlapping semicircle in the high-frequency region and an oblique line in the low-frequency region. The semicircle at high frequency refers to the diffusion and migration process of Li^+ in the SEI, and the oblique line at low frequency represents the migration impedance of Li^+ in the active substance [53]. The semicircle of the CNFs-Si0% anode is almost the same as that of the CNFs-Si10% anode, meaning that the small amount of silicon doping does not reduce the impedance of CNFs. Compared with the CNFs-Si0% anode, the CNFs-Si10% anode has a larger slope at low frequency. The larger the slope, the lower the Li-ion diffusion resistance. Therefore, the CNFs-Si10% anode has a higher capacity and lower lithium-ion diffusion resistance than the CNFs-Si0% anode. Meanwhile, the excellent cycle and rate capability results of the CNFs-Si10% anode also show that the nano silicon is dispersed in the porous of carbon fibers, and the porous structure can provide a buffer space for the Si volume change during the Li deintercalation process [53,54].

4. Conclusions

In this work, we successfully synthesized hierarchical porous and Si/N co-doped carbon nanofiber anodes. SEM images and nitrogen adsorption–desorption tests confirm that a hierarchical porous structure exists in carbon nanofiber materials, and the EDS mapping confirms that Si and N elements are doped into carbon nanofiber materials. Compared with other anodes, the CNFs-Si10% anode obtained has a high initial reversible specific capacity, high capacity retention, and excellent rate performance in lithium-ion batteries. This excellent electrochemical performance is mainly due to the fact that Si doping can improve specific capacity, N doping can improve conductivity, and the fabricated hierarchical porous structure can increase the number of reactive sites, improve the ion transport rate, and enable the electrolyte to penetrate the inner part of carbon nanofibers to improve the electrolyte/electrode contacting area during charging–discharging processes. This work provides a new avenue for developing flexible anode materials for lithium-ion batteries with high performance.

Author Contributions: Y.C.: conceptualization, methodology, writing—original draft; J.W.: software, data curation; X.W.: cell fabrication and testing; X.L.: supervision, data interpretation, writing—review & editing; J.L. (Jun Liu): conceptualization; J.L. (Jingshun Liu): methodology; D.N. methodology; J.D.: supervision, data interpretation. All authors have read and agreed to the published version of the manuscript.

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References

- Wang, X.; Weng, Q.; Yang, Y.; Bando, Y.; Golberg, D. Hybrid two-dimensional materials in rechargeable battery applications and their microscopic mechanisms. *Chem. Soc. Rev.* **2016**, *45*, 4042–4073. [\[CrossRef\]](#) [\[PubMed\]](#)
- Zhou, Y.; Yang, Y.; Hou, G.; Yi, D.; Zhou, B.; Chen, S.; Lam, T.D.; Yuan, F.; Golberg, D.; Wang, X. Stress-relieving defects enable ultra-stable silicon anode for Li-ion storage. *Nano. Energy* **2020**, *70*, 104568. [\[CrossRef\]](#)
- Qi, W.; Shapter, J.G.; Wu, Q.; Yin, T.; Gao, G.; Cui, D. Nanostructured anode materials for lithium-ion batteries: Principle, recent progress and future perspectives. *J. Mater. Chem. A* **2017**, *5*, 19521–19540. [\[CrossRef\]](#)
- Zhou, C.; Liu, J.; Gong, X.; Wang, Z. Optimizing the function of SiO_x in the porous Si/SiO_x network via a controllable magnesiothermic reduction for enhanced lithium storage. *J. Alloys Compd.* **2021**, *874*, 159914. [\[CrossRef\]](#)
- Vernardou, D. Progress and challenges in industrially promising chemical vapour deposition processes for the synthesis of large-area metal oxide electrode materials designed for aqueous battery systems. *Materials* **2021**, *14*, 4177. [\[CrossRef\]](#)
- Valvo, M.; Floraki, C.; Paillard, E.; Edstrom, K.; Vernardou, D. Perspectives on iron oxide-based materials with carbon as anodes for Li- and K-ion batteries. *Nanomaterials* **2022**, *12*, 1436. [\[CrossRef\]](#)
- Fu, J.; Kang, W.; Guo, X.; Wen, H.; Zeng, T.; Yuan, R.; Zhang, C. 3D hierarchically porous NiO/graphene hybrid paper anode for long-life and high rate cycling flexible Li-ion batteries. *J. Energy Chem.* **2020**, *47*, 172–179. [\[CrossRef\]](#)
- Zeng, L.; Qiu, L.; Cheng, H.M. Towards the practical use of flexible lithium ion batteries. *Energy Storage Mater.* **2019**, *23*, 434–438. [\[CrossRef\]](#)
- Elizabeth, I.; Singh, B.P.; Gopukumar, S. Electrochemical performance of Sb₂S₃/CNT free-standing flexible anode for Li-ion batteries. *J. Mater. Sci.* **2019**, *54*, 7110–7118. [\[CrossRef\]](#)
- McCreery, R.L. Advanced carbon electrode materials for molecular electrochemistry. *Chem. Rev.* **2008**, *108*, 2646–2687. [\[CrossRef\]](#)
- Xu, Z.; Fan, L.; Ni, X.; Han, J.; Guo, R. Sn-encapsulated N-doped porous carbon fibers for enhancing lithium-ion battery performance. *RSC Adv.* **2019**, *9*, 8753–8758. [\[CrossRef\]](#)
- Nan, D.; Huang, Z.H.; Lv, R.; Yang, L.; Wang, J.G.; Shen, W.; Lin, Y.; Yu, X.; Ye, L.; Sun, H. Nitrogen-enriched electrospun porous carbon nanofiber networks as high-performance free-standing electrode materials. *J. Mater. Chem. A* **2014**, *2*, 19678–19684. [\[CrossRef\]](#)
- Miao, Y.E.; Huang, Y.; Zhang, L.; Fan, W.; Lai, F.; Liu, T. Electrospun porous carbon nanofiber@MoS₂ core/sheath fiber membranes as highly flexible and binder-free anodes for lithium-ion batteries. *Nanoscale* **2015**, *7*, 11093–11101. [\[CrossRef\]](#)
- Zhang, Q.; Zhou, K.; Lei, J.; Hu, W. Nitrogen dual-doped porous carbon fiber: A binder-free and high-performance flexible anode for lithium ion batteries. *Appl. Surf. Sci.* **2019**, *467*, 992–999. [\[CrossRef\]](#)
- Wang, X.; Sun, N.; Dong, X.; Huang, H.; Qi, M. The porous spongy nest structure compressible anode fabricated by gas forming technique toward high performance lithium ions batteries. *J. Colloid Interf. Sci.* **2022**, *623*, 584–594. [\[CrossRef\]](#)
- Guo, J.; Liu, J.; Dai, H.; Zhou, R.; Wang, T.; Zhang, C.; Ding, S.; Wang, H.G. Nitrogen doped carbon nanofiber derived from polypyrrole functionalized polyacrylonitrile for applications in lithium-ion batteries and oxygen reduction reaction. *J. Colloid Interf. Sci.* **2017**, *507*, 154–161. [\[CrossRef\]](#)
- Chen, X.; Gao, G.; Wu, Z.; Xiang, J.; Li, X.; Guan, G.; Zhang, K. Ultrafine MoO₂ nanoparticles encapsulated in a hierarchically porous carbon nanofiber film as a high-performance binder-free anode in lithium ion batteries. *RSC Adv.* **2019**, *9*, 37556–37561. [\[CrossRef\]](#)
- Yang, Z.; Wu, C.; Li, S.; Qiu, L.; Yang, Z.; Zhong, Y.; Zhong, B.; Song, Y.; Wang, G.; Liu, Y. A unique structure of highly stable interphase and self-consistent stress distribution radial-gradient porous for silicon anode. *Adv. Funct. Mater.* **2021**, *32*, 2107897. [\[CrossRef\]](#)

19. Tian, H.; Tian, H.; Yang, W.; Zhang, F.; Yang, W.; Zhang, Q.; Wang, Y.; Liu, J.; Silva, S.R.P.; Liu, H. Stable hollow-structured silicon suboxide-based anodes toward high-performance lithium-ion batteries. *Adv. Funct. Mater.* **2021**, *31*, 2101796. [\[CrossRef\]](#)
20. Feng, K.; Li, M.; Liu, W.; Kashkooli, A.G.; Xiao, X.; Cai, M.; Chen, Z. Silicon-based anodes for lithium-ion batteries: From fundamentals to practical applications. *Small* **2018**, *14*, 1702737. [\[CrossRef\]](#)
21. Yu, C.; Du, Y.; He, R.; Ma, Y.; Liu, Z.; Li, X.; Luo, W.; Zhou, L.; Mai, L. Hollow SiO_x/C microspheres with semigraphitic carbon coating as the “lithium host” for dendrite-free lithium metal anodes. *ACS Appl. Energy Mater.* **2021**, *4*, 3905–3912. [\[CrossRef\]](#)
22. Terranova, M.L.; Orlanducci, S.; Tamburri, E.; Guglielmotti, V.; Rossi, M. Si/C hybrid nanostructures for Li-ion anodes: An overview. *J. Power Sources* **2014**, *246*, 167–177. [\[CrossRef\]](#)
23. Han, X.; Zhang, Z.; Chen, S.; Yang, Y. Low temperature growth of graphitic carbon on porous silicon for high-capacity lithium energy storage. *J. Power Sources* **2020**, *463*, 228245. [\[CrossRef\]](#)
24. Yang, J.; Wang, Y.X.; Chou, S.L.; Zhang, R.; Xu, Y.; Fan, J.; Zhang, W.X.; Liu, H.K.; Zhao, D.; Dou, S.X. Yolk-shell silicon-mesoporous carbon anode with compact solid electrolyte interphase film for superior lithium-ion batteries. *Nano Energy* **2015**, *18*, 133–142. [\[CrossRef\]](#)
25. Rehman, S.; Guo, S.; Hou, Y. Rational design of Si/SiO₂@ hierarchical porous carbon spheres as efficient polysulfide reservoirs for high-performance Li-S battery. *Adv. Mater.* **2016**, *28*, 3167–3172. [\[CrossRef\]](#)
26. Jang, S.M.; Miyawaki, J.; Tsuji, M.; Mochida, I.; Yoon, S.H. The preparation of a novel Si-CNF composite as an effective anodic material for lithium-ion batteries. *Carbon* **2009**, *47*, 3383–3391. [\[CrossRef\]](#)
27. Xu, Y.; Zhu, Y.; Han, F.; Luo, C.; Wang, C. 3D Si/C fiber paper electrodes fabricated using a combined electrospray/electrospinning technique for Li-ion batteries. *Adv. Energy Mater.* **2015**, *5*, 1400753. [\[CrossRef\]](#)
28. Peng, Y.T.; Lo, C.T. Electrospun porous carbon nanofibers as lithium ion battery anodes. *J. Solid State Electrochem.* **2015**, *19*, 3401–3410. [\[CrossRef\]](#)
29. Yuan, X.L.; Ma, Z.; Jian, S.F.; Ma, H.; Lai, Y.N.; Deng, S.L.; Tian, X.C.; Wong, C.P.; Xia, F.; Dong, Y.F. Mesoporous nitrogen-doped carbon MnO₂ multichannel nanotubes with high performance for Li-ion batteries. *Nano Energy* **2022**, *97*, 107235. [\[CrossRef\]](#)
30. Park, S.W.; Kim, J.C.; Dar, M.A.; Shim, H.W.; Kim, D.W. Superior lithium storage in nitrogen-doped carbon nanofibers with open-channels. *Chem. Eng. J.* **2017**, *315*, 1–9. [\[CrossRef\]](#)
31. Zhang, T.; Zhang, L.; Zhao, L.N.; Huang, X.X.; Li, W.; Li, T.; Shen, T.; Sun, S.N.; Hou, Y.L. Free-standing, foldable V₂O₃/multichannel carbon nanofibers electrode for flexible Li-ion batteries with ultralong lifespan. *Small* **2020**, *16*, 2005302. [\[CrossRef\]](#) [\[PubMed\]](#)
32. Zhao, H.; Yin, H.; Yu, X.X.; Zhang, W.; Li, C.; Zhu, M.Q. In₂O₃ nanoparticles/carbonfiber hybrid mat as free-standing anode for lithium-ion batteries with enhanced electrochemical performance. *J. Alloy. Compd.* **2018**, *735*, 319–326. [\[CrossRef\]](#)
33. Chen, Y.J.; Zhao, X.H.; Liu, Y.; Razzaq, A.A.; Haridas, A.K.; Cho, K.K.; Peng, Y.; Deng, Z.; Ahn, J.H. γ-Fe₂O₃ nanoparticles aligned in porous carbon nanofibers towards long life-span lithium ion batteries. *Electrochim. Acta* **2018**, *289*, 264–271. [\[CrossRef\]](#)
34. Zhao, Q.S.; Liu, J.L.; Li, X.X.; Xia, Z.Z.; Zhang, Q.X.; Zhou, M.; Tian, W.; Wang, M.; Hu, H.; Li, Z.T.; et al. Graphene oxide-induced synthesis of button-shaped amorphous Fe₂O₃/rGO/CNFs films as flexible anode for high-performance lithium-ion batteries. *Chem. Eng. J.* **2019**, *369*, 215–222. [\[CrossRef\]](#)
35. Li, X.Q.; Xiang, J.; Zhang, X.K.; Li, H.B.; Yang, J.N.; Zhang, Y.M.; Zhang, K.Y.; Chu, Y.Q. Electrospun FeCo nanoparticles encapsulated in N-doped carbon nanofibers as self-supporting flexible anodes for lithium-ion batteries. *J. Alloy. Compd.* **2021**, *873*, 159703. [\[CrossRef\]](#)
36. Zhu, S.Q.; Huang, A.M.; Wang, Q.; Xu, Y. MOF-derived porous carbon nanofibers wrapping Sn nanoparticles as flexible anodes for lithium/sodium ion batteries. *Nanotechnology* **2021**, *32*, 165401. [\[CrossRef\]](#)
37. Su, Y.; Fu, B.; Yuan, G.L.; Ma, M.; Jin, H.Y.; Xie, S.H.; Li, J.Y. Three-dimensional mesoporous γ-Fe₂O₃@carbon nanofiber network as high performance anode material for lithium- and sodium-ion batteries. *Nanotechnology* **2020**, *31*, 155401. [\[CrossRef\]](#)
38. Ma, X.X.; Hou, G.M.; Ai, Q.; Zhang, L.; Si, P.C.; Feng, J.K.; Ci, L.J. A heart-coronary arteries structure of carbon nanofibers/graphene/silicon composite anode for high performance lithium ion batteries. *Sci. Rep.* **2017**, *7*, 9642. [\[CrossRef\]](#)
39. Wu, S.H.; Han, Y.D.; Wen, K.C.; Wei, Z.H.; Chen, D.J.; Lv, W.Q.; Lei, T.Y.; Xiong, J.; Gu, M.; He, W.D. Composite nanofibers through in-situ reduction with abundant active sites as flexible and stable anode for lithium ion batteries. *Compos. Part B Eng.* **2019**, *161*, 369–375. [\[CrossRef\]](#)
40. Abe, J.; Takahashi, K.; Kawase, K.; Kobayashi, Y.; Shiratori, S. Self-standing carbon nanofiber and SnO₂ nanorod composite as a high-capacity and high-rate-capability anode for lithium-ion batteries. *ACS Appl. Nano Mater.* **2018**, *1*, 2982–2989. [\[CrossRef\]](#)
41. Guo, L.G.; Sun, H.; Qin, C.Q.; Li, W.; Wang, F.; Song, W.L.; Du, J.; Zhong, F.; Ding, Y. Flexible Fe₃O₄ nanoparticles/N-doped carbon nanofibers hybrid film as binder-free anode materials for lithium-ion batteries. *Appl. Surf. Sci.* **2018**, *459*, 263–270. [\[CrossRef\]](#)
42. Zhang, X.Y.; Gao, M.Z.; Wang, W.; Liu, B.; Li, X.B. Encapsulating MoO₂ nanocrystals into flexible carbon nanofibers via electrospinning for high-performance lithium storage. *Polymers* **2021**, *13*, 22. [\[CrossRef\]](#)
43. Chen, R.Z.; Hu, Y.; Shen, Z.; Pan, P.; He, X.; Wu, K.S.; Zhang, X.W.; Cheng, Z.L. Facile fabrication of foldable electrospun polyacrylonitrile-based carbon nanofibers for flexible lithium-ion batteries. *J. Mater. Chem. A* **2017**, *5*, 12914–12921. [\[CrossRef\]](#)
44. Zhang, S.G.; Yue, L.C.; Wang, M.; Feng, Y.; Li, Z.; Mi, J. SnO₂ nanoparticles confined by N-doped and CNTs-modified carbon fibers as superior anode material for sodium-ion battery. *Solid State Ionics* **2018**, *323*, 105–111. [\[CrossRef\]](#)

45. Zhang, T.; Qiu, D.P.; Hou, Y.L. Free-standing and consecutive ZnSe@carbon nanofibers architectures as ultra-long lifespan anode for flexible lithium-ion batteries. *Nano Energy* **2022**, *94*, 106909. [[CrossRef](#)]
46. Huang, L.; Guan, Q.; Cheng, J.L.; Li, C.; Ni, W.; Wang, Z.P.; Zhang, Y.; Wang, B. Free-standing N-doped carbon nanofibers/carbon nanotubes hybrid film for flexible, robust half and full lithium-ion batteries. *Chem. Eng. J.* **2018**, *334*, 682–690. [[CrossRef](#)]
47. Mou, H.Y.; Chen, S.X.; Xiao, W.; Miao, C.; Li, R.; Xu, G.L.; Xin, Y.; Nie, S.Q. Encapsulating homogenous ultra-fine SnO₂/TiO₂ particles into carbon nanofibers through electrospinning as high-performance anodes for lithium-ion batteries. *Ceram. Int.* **2021**, *47*, 19945–19954. [[CrossRef](#)]
48. Nie, P.; Le, Z.; Chen, G.; Liu, D.; Liu, X.; Wu, H.B.; Xu, P.; Li, X.; Liu, F.; Chang, L. Graphene caging silicon particles for high-performance lithium-ion batteries. *Small* **2018**, *14*, 1800635. [[CrossRef](#)]
49. Zhang, J.; Zuo, S.; Wang, Y.; Yin, H.; Wang, Z.; Wang, J. Scalable synthesis of interconnected hollow Si/C nanospheres enabled by carbon dioxide in magnesiothermic reduction for high-performance lithium energy storage. *J. Power Sources* **2021**, *495*, 229803. [[CrossRef](#)]
50. Chan, C.K.; Peng, H.; Liu, G.; McIlwrath, K.; Zhang, X.F.; Huggins, R.A.; Cui, Y. High-performance lithium battery anodes using silicon nanowires. *Nat. Nanotechnol.* **2008**, *3*, 31–35. [[CrossRef](#)]
51. Zuo, X.; Wang, X.; Xia, Y.; Yin, S.; Ji, Q.; Yang, Z.; Wang, M.; Zheng, X.; Qiu, B.; Liu, Z. Silicon/carbon lithium-ion battery anode with 3D hierarchical macro-/mesoporous silicon network: Self-templating synthesis via magnesiothermic reduction of silica/carbon composite. *J. Power Sources* **2019**, *412*, 93–104. [[CrossRef](#)]
52. He, J.; Zhao, H.; Li, X.; Su, D.; Zhang, F.; Ji, H.; Liu, R. Superelastic and superhydrophobic bacterial cellulose/silica aerogels with hierarchical cellular structure for oil absorption and recovery. *J. Hazard. Mater.* **2018**, *346*, 199–207. [[CrossRef](#)] [[PubMed](#)]
53. Liu, H.; Meng, X.; Chen, Y.; Zhao, Y.; Guo, X.; Ma, T. Synthesis and surface engineering of composite anodes by coating thin-layer silicon on carbon cloth for lithium storage with high stability and performance. *ACS Appl. Energy Mater.* **2021**, *4*, 6982–6990. [[CrossRef](#)]
54. Li, Y.; Liu, X.; Zhang, J.; Yu, H.; Zhang, J. Carbon-coated Si/N-doped porous carbon nanofibre derived from metal-organic frameworks for Li-ion battery anodes. *J. Alloy. Compd.* **2022**, *902*, 163635. [[CrossRef](#)]