Research Article

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Rational synthesis of silicon into polyimide-derived hollow electrospun carbon nanofibers for enhanced lithium storage

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Abstract: Flexible energy devices with high energy density and long cycle life are considered to be promising applications in portable electronics. In this study, silicon/carbon nanofiber (Si@CNF) core–shell electrode has been prepared by the coaxial electrospinning method. The precursors of polyimide (PI) were for the first time used to form the core–shell structure of Si@CNF, which depicts outstanding flexibility and mechanical strength. The effect of doping concentrations of silicon (Si) nanoparticles embedded in the fiber is investigated as a binder-free anode for lithium-ion batteries. A 15 wt% doped composite electrode demonstrates superior performance, with an initial reversible capacity of 621 mA h g\(^{-1}\) at the current density of 100 mA g\(^{-1}\) and a high capacity retention up to 200 cycles. The excellent cycling performance is mainly due to the carbonized PI core–shell structure, which not only can compensate for the insulation property of Si but also has the ability to buffer the volume expansion during the repeated charge–discharge process.

Keywords: flexible electrode, polyimide, carbon nanofibers, core–shell structure, lithium storage

1 Introduction

With the development of portable electronics, such as wearable devices, implantable biomedical devices, electronic “skins” and so on, there is an increasing demand for flexible electrodes with high energy densities, long cycling life and low environmental pollution (1–5). Currently, commercial electrode materials need to be mixed with conductive additives and polymer binders, which are not flexible enough to adapt to some features of freestanding electrodes, including high conductivity, structural stability and fast ion transport. Electrospinning has been proved as a promising route for the preparation of flexible nanofiber membranes with unique three-dimensional (3D) network structure and good mechanical strength, which can efficiently avoid the tedious slurry-coating process of traditional electrodes (6–9). Especially, electrospun carbon nanofibers (CNFs) have been playing a leading role in lithium-ion batteries (LIBs) due to their high surface area, excellent electronic conductivity and simplicity of the preparation process (10,11).

At present, silicon (Si) has unprecedented theoretical specific capacity (4,200 mA h g\(^{-1}\)) compared with that of graphite (372 mA h g\(^{-1}\)), low working potential and abundant reserve in nature, which makes it a promising candidate as the LIB anode material in the future (12–15). However, most Si electrodes suffer from pulverization caused by the large volume change (400%) during the lithium alloying and dealloying processes (16,17). This huge volume change will lead to the collapse of electrodes, insulation of active material and large consumption of electrolyte, eventually resulting in a sharp decay of capacity.

A number of effective strategies have been proposed to overcome the aforementioned problems by controlling the morphology of Si materials, such as nanoparticles (NPs) (18–20), nanotubes (21), nanowires (22,23), nanoporous architecture (24,25) and carbon-incorporated composites (26–29). Among these materials, silicon/carbon composite fibers, synthesized via electrospinning, have received much attention because of their high...
specific surface area and facile preparation method (30,31). Actually, this improvement has inherent limitations if Si NPs are incorporated in carbon fibers simply, because drastic volume variation during the lithium ion insertion/delithiation process will destroy the electrode structure. Then, the cracks, resulting from the destruction of the electrode, could cause a new solid electrolyte interphase (SEI) formation by consuming electrolyte continuously. This in turn results in irreversible capacity fading. More importantly, although some researchers have developed carbon/silicon composite nanofiber mats via the combination of electrospinning and foaming processes, the mechanical flexibility and cycle stability cannot meet the demand for further applications (32,33).

In this study, we synthesized a silicon/carbon nanofiber (Si@CNF) core–shell electrode by encapsulating Si NPs in the interconnected hollow CNFs using polyimide (PI) as a precursor for the first time. The CNF derived from PI depicts good structural stability, and the fiber continuity is still well maintained even after high-temperature treatment. Three different silicon/carbon ratio composites (Si@CNF-10 wt%, 15 wt% and 20 wt%) were prepared separately, and the effect of doping concentration was studied. All the obtained Si@CNF composites were directly put into coin cells as flexible anodes without adding any carbon conductors and binders. The results indicate that the cycling performance of the Si@CNF-15 wt% composite anode is significantly greater than that of the other two Si-based electrodes.

2 Experimental

2.1 Materials

Si powder (80 nm in diameter; Shanghai Gexin Nano Technology Co., Ltd), pyromellitic dianhydride (PMDA), 4,4′-diaminodiphenyl ether (ODA), styrene–acrylonitrile copolymer (SAN; Sinopharm Chemical Reagent Co.) and N,N′-dimethylformamide (DMF) (Tianjin Fuyu Fine Chemical Co. Ltd) were used without further treatment.

2.2 Fabrication of Si@CNF composites

The electrospinning shell solution was prepared with 1.50 g of ODA and 1.64 g of PMDA in 15 ml of DMF. The solution was stirred at room temperature until the viscosity of the resulting polyamic acid (PAA) solution reached a maximum value. The electrospinning core solutions were prepared as follows. First, 2 g of SAN was dissolved in 6 ml of DMF, then 15 wt% of Si NPs were added into the SAN solution with continuous stirring at 60°C for at least 6 h. The other core solutions (10 and 20 wt%) were also prepared by the same way.

Figure 1a shows a schematic of the dual nozzle coaxial electrospinning setup. Three different components of SAN/Si NP solutions were used as the core solutions to form the hollow core embedded with Si NPs, while the PAA solution

![Figure 1](image-url)

Figure 1: (a) Schematic of dual nozzle coaxial electrospinning setup and (b) electrospun preparation process and structure of Si@CNF.
was utilized as the outer shell solution to form a compact carbon shell. The flow rates of core and shell were controlled by two syringe pumps. Parameters were set as follows: applied voltage was 20–25 kV, receiving distance was 18 cm and the feeding speed rates of the inner and outer solutions were 0.4 and 0.8 mL h⁻¹, respectively. The stabilization was performed at 300°C for 0.5 h under air atmosphere with a rate of 3°C min⁻¹. Then, the obtained Si/SAN@PI nanofibers with 10, 15 and 20 wt% Si were carbonized in a tube furnace in an Ar atmosphere at 800°C for 1 h at a heating rate of 10°C min⁻¹ to form the Si@CNF-10, 15 and 20 wt% composites, respectively. In addition, a PI-based CNF from the pure PAA precursor was also prepared using the same process (34,35).

2.3 Material characterization

The as-prepared Si@CNF core–shell fibers and bare Si NPs were characterized by X-ray diffraction (XRD; Bruker D8 ADVANCE) in a range of diffraction angle 2θ, from 10° to 90°. The morphologies of fibers were investigated using a field emission scanning electron microscope (SEM, JEOL JSM-6700F; JEOL, Tokyo, Japan) and a transmission electron microscope (TEM, JEOL JEM-2010F). The elemental analysis of the samples was performed using an energy-dispersive X-ray spectroscopy system. The weight content of Si in the Si@CNF composite was calculated based on the thermogravimetric analysis (TGA; Netzsch) at a heating rate of 10°C min⁻¹ in air.

2.4 Electrochemical characterization

Electrochemical performances were measured using CR2032-type coin half cells, and the obtained flexible Si@CNFs were directly employed as working electrodes without adding any binder or conductive materials. The areal loading of the flexible Si@CNF electrode is in the

![Figure 2:](image) (a and b) SEM images (the inset is an optical image of Si@CNF under bending), (c) TEM image, (d) HRTEM image of Si@CNF, (e) EDX elemental mappings of carbon, silicon and oxygen and (f) SAED pattern.
range of 2–3 mg cm\(^{-2}\). The assembly was performed in an Ar-filled glove box. Lithium metal was utilized as a counter electrode. A Celgard 2400 microporous polypropylene membrane was used as a separator. The electrolyte was 1 M LiPF\(_6\) dissolved in a mixture of ethylene carbonate/diethyl carbonate/ethyl methyl carbonate (1:1:1 volume ratio). The assembled cells were cycled at current rates ranging from 100 to 1,000 mA g\(^{-1}\) over potentials of 0.01–2 V (vs. Li/Li\(^+\)) using a NEWARE CT-4008 battery test system. The cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) tests were conducted on a CHI660E electrochemical workstation.

3 Results and discussion

The preparation process of the Si@CNF sample is illustrated in Figure 1b. The coaxial electrospinning is conducted at room temperature (36,37). The collected Si/SAN@PAA core–shell polymer fibers were first stabilized in air at 300\(^\circ\)C for 30 min, during which the inner SAN becomes molten. Then, Si/SAN@PI nanofibers were further carbonized in an Ar atmosphere at 800\(^\circ\)C for 1 h. The molten SAN is completely decomposed and freestanding Si@CNF composite conductive membranes were finally synthesized after the carbonization process. The inset in Figure 2a shows that the as-prepared Si@CNF films have good mechanical strength, are flexible and can be easily bent or folded. In addition, compared with other common precursors, such as polycrylonitrile (35,38), the CNFs derived from PI have outstanding structural stability, and the fiber continuity can still be well maintained after high-temperature treatment (39–42). Thus, the Si@CNF films are feasible to be used as freestanding and binder-free anode materials for LIBs.

The overall morphology of the Si@CNF is shown in Figure 2a, and the core–shell composite fibers were successfully synthesized based on the coaxial electrospinning, with a very small amount of Si NPs forming clusters on the fiber surface. From Figure 2b, it can be observed that the diameters of fibers are in the range of 1–2 \(\mu\)m and that the Si NPs are well embedded in the core section. The TEM image of Si@CNF (Figure 2c) also shows the visible hierarchical silicon/carbon core–shell structure. It is expected that the 3D interconnected carbon web can be employed as a high conductive channel for electrons and Li ions during cycling, and the compact fiber shell can effectively block electrolyte contact with Si directly but endow fast transmission of Li ions (14). Additionally, as can be seen from the high-resolution transmission electron microscopy (HRTEM) image of Si@CNF (Figure 2d), the lattice fringe spacing is approximately 0.31 nm; this corresponds to the crystalline Si(111) plane. The distribution and elemental mapping of Si, C and O in the Si@CNF electrode were investigated by SEM and EDX (Figure 2e). From the C and Si element mappings, it can be seen that Si NPs are well-wrapped inside the core section along the fiber axis. Figure 2f shows the selected-area electron diffraction (SAED) pattern recorded on the core section; the diffraction rings match well with the (111), (220) and (311) planes of Si, indicating the presence of Si in the core.

Figure 3a shows the XRD patterns of raw Si NPs, Si@CNF composite and pure CNF. It can be seen that Si NPs present well-defined diffraction peaks at 2\(\theta\) of 28.4\(^\circ\), 47.3\(^\circ\), 56.1\(^\circ\), 69.2\(^\circ\), 76.3\(^\circ\) and 88\(^\circ\), which correspond to the (111), (220), (311), (400), (331) and (422) planes of crystallized Si (JCPDS No. 27-1402), respectively. After incorporating Si NPs into the carbon matrix, the resultant silicon/carbon composite fibers exhibit the same Si peaks, but intensities become lower. In addition, one

![Figure 3](image-url)
carbon peak at around 23° can be found in Si@CNF, which is due to the formation of carbon fiber matrix. However, the peak is weak and broad, indicating that the carbon matrix is mainly composed of disordered carbon (43,44). Figure 3b presents the Raman spectrum of Si@CNF, CNF and Si NPs. For the Si@CNF composite, a main peak at about 510 cm\(^{-1}\) is consistent with the spectrum of Si NPs. The characteristic peaks at 1,356 and 1,590 cm\(^{-1}\) are the D peak and G peak, respectively, revealing the presence of CNF (45,46). TGA profiles of the as-prepared Si@CNF composites with various silicon/carbon ratios are shown in Figure 4. Based on the TGA results, it can be seen that the contents of Si in the three samples are about 10 wt%, 15 wt% and 20 wt%, respectively.

**Figure 4:** TG curves of Si@CNF with various ratios.

Figure 5a presents the CV profiles for the first three cycles of Si@CNF-15 wt% electrode at a scanning rate of 0.1 mV s\(^{-1}\) in a potential window from 0.01 to 2 V versus Li/Li\(^+\). In the first cycle, there is a reduction peak at 0.6 V, which resulted from the decomposition of the electrolyte and the formation of the SEI layer. The potential plateau of SEI formation disappears at the second cycle, indicating that the capacity is irreversible. From the second to third cycle, the new reduction peak at 0.16 V is due to the alloying process of Si to form Li\(_x\)Si, while two oxidation peaks at 0.38 and 0.52 V correspond to the delithiation reaction of Si. The peak current exhibits an enhanced intensity with increasing cycles, which is related to an activation process of the crystalline Si. Additionally, the shape of redox peaks has no apparent change after the first cycle, demonstrating that the Si@CNF anode has formed a stable SEI membrane in the first cycle.

Figure 5b shows the galvanostatic discharge/charge curves of the Si@CNF-15 wt% electrode for the first, fifth and tenth cycles in the potential ranging from 0.01 to 2 V at 100 mA g\(^{-1}\). As shown in Figure 3b, the first discharge curve shows a short slope plateau at 0.6 V, which is connected with the decomposition of the electrolyte to form an SEI film. After the first cycle, the charge/discharge profiles show the typical behavior of Li intercalating with amorphous Si (28). In addition, the first cycle delivered a discharge capacity of 1,078 mA h g\(^{-1}\) and a charge capacity of 628 mA h g\(^{-1}\), corresponding to an initial coulombic efficiency (CE) of 58.3%. The relatively low CE is mainly related to the formation of the SEI layer over the electrode surface at around 0.6 V. In the fifth cycle, charge/discharge specific capacities were approximately 636 and 622 mA h g\(^{-1}\), respectively. The CE quickly grew to 97.8%. Importantly, curves of the fifth and tenth cycles are much overlapped, which also indicated excellent reversibility of the Si@CNF-15 wt% composites as freestanding anodes for LIBs.

The cycling performances of Si@CNF-10 wt%, Si@CNF-15 wt%, Si@CNF-20 wt% and pure CNF electrodes at a current density of 100 mA g\(^{-1}\) in the voltage range from 0.01 to 2 V are depicted in Figure 5c. It can be easily observed that the Si@CNF-15 wt% anode demonstrated better cycle stability compared with other two Si-based electrodes. The reversible capacity of the Si@CNF-15 wt% electrode slowly changed from 621 mA h g\(^{-1}\) for the initial cycle to 483 mA h g\(^{-1}\) after 200 cycles, with a capacity retention of 77.8% and a high CE of 98.8%. However, the other two Si-based electrodes exhibit high reversible capacity in the first several cycles, but show very rapid fading with increasing cycles due to destruction of the electrode structure. For example, the capacity retention of Si@CNF-20 wt% is mere 13.8% after 200 cycles. The results indicate that the mass ratio of Si in composites has a great influence on the stability of silicon/carbon fiber electrodes. The Si@CNF-15 wt% electrode can obtain a better cycling stability because it has excellent structural buffering effect to absorb the mechanical stress induced by the volume changes of Si. When the content of Si is too high, the core–shell architecture will not be well maintained. Then, the SEI film would be fractured and formed repeatedly on the surface of electrode. Moreover, the repeated volume variation will lead to severe cracking and pulverization of electrode materials as well as the loss of electrical contact between Si NPs (47). If the proportion of Si in the carbon fiber is too low, there will exist an amount of dead Si NPs, these dead Si NPs will not be electrically connected to the carbon shell, which will cause the reduction of the capacity contribution of Si during cycling (10).

The specific capacity values are further calculated based on the mass of the Si only to better explain the impact of core–shell structure on the performance of the Si. According to the contents of Si and carbon in composite from TGA curves, the discharge specific capacity of Si in the
Si@CNF-15 wt% electrode is recalculated to be 3,837 mA h g\(^{-1}\) for the first cycle after deducting the contribution of CNF (∼200 mA h g\(^{-1}\) in Figure 5c) to the capacity of composite. The reversible capacity can be maintained at 2,214 mA h g\(^{-1}\) after 200 cycles (Figure 5d). This indicates that the hierarchical structure significantly improves the mechanical integrity of the electrode. Furthermore, the excellent electron conductivity of the carbon matrix can enhance the availability of Si.

Figure 5e presents the rate capabilities of the Si@CNF-15 wt% electrode with the current density increasing from 100 to 1,000 mA g\(^{-1}\). After carbonization, the Si@CNF-15 wt% can deliver reversible specific capacities of 658 and 354 mA h g\(^{-1}\) at the current densities of 100 and 1,000 mA g\(^{-1}\), respectively. In particular, when the current density is reduced back to 100 mA g\(^{-1}\), the capacity of 602 mA h g\(^{-1}\) could be recovered. The excellent rate capability confirms that the hierarchical fibrous structure can ensure structural robustness even at higher current densities. It is clearly noted that the void space in the core section can promote the effective transmission of Li ions into the electrode (48,49). This strongly suggests the superiority of using the novel structure-based silicon/carbon anode for high-performance LIBs.

Figure 6a displays the impedance spectra of the Si@CNF-15 wt% composite anode after the third and 200th cycles at 100 mA g\(^{-1}\). The semicircle in the high frequency region can be ascribed to a charge-transfer resistance (\(R_{ct}\)), which is related to the electrochemical reaction between the electrode and the electrolyte. The sloping line in the low frequency range represents the Warburg impedance, corresponding to the lithium-ion...
diFFusion process in the active material. The inset shows the corresponding equivalent circuit. Here, $R_s$ represents the electrolyte resistance of the cell and electrical contacts, and CPE of the electrode refers to capacitance. $R_{ct}$ of the Si@CNF-15 wt% at the third cycle is 169.8 $\Omega$ and reduces to 142.4 $\Omega$ after 200 cycles. The decrease in resistance with increasing cycle indicates an enhanced conductivity. Therefore, the hierarchical core–shell structure can not only maintain the integrity of the electrode but also provide channels for fast ion/electron transport, bringing about superior electrical conductivity of the overall electrode. Figure 6b shows the structural change during the cycling process for the Si@CNF electrode. The 3D interconnected carbon fiber network is able to alleviate the mechanical stress caused by volume variations during repeated charge/discharge reactions.

The structural robustness of the Si@CNF-15 wt% anode after cycling for 200 times is analyzed using SEM. As shown in Figure 6c, the overall fibrous morphology of the composite electrode is well-maintained after 200 cycles. From Figure 6d, it can be seen that the hierarchical core–shell structure of fibers as well as the encapsulation of Si NPs within the core is also visible after cycling. Additionally, it can be noted that even though the electrolyte may initially penetrate the interior through the space between the Si and the carbon network, most of the electrolyte is effectively blocked after a stable SEI is formed outside the transverse section, rather than in the internal space between the carbon skeleton and the Si. This helps to maintain good conductivity of the fiber, especially the electrical contact between the carbon skeleton and Si.

4 Conclusions

In summary, the Si@CNF core–shell electrode has been prepared by encapsulating Si NPs in the interconnected hollow CNFs, and the effects of different Si contents on the electrochemical performance of Si@CNF composite anodes were investigated. The flexible electrode has shown outstanding mechanical flexibility and cycle stability, and the Si@CNF-15 wt% composite electrode demonstrates a reversible capacity of 621 mA h g$^{-1}$ with a retention of 77.8% after 200 cycles under a current density of 100 mA g$^{-1}$. The superior electrochemical properties are attributed to the hierarchical core–shell structure, which can accommodate the volume expansion of Si and prevent electrolyte from entering into the core section during the process of charging and discharging. The scalable core–shell structure would be readily applied to other LIB electrodes that suffer from volume expansion.

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