



# Uniform Si nanoparticle-embedded nitrogen-doped carbon nanofiber electrodes for lithium ion batteries



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## ABSTRACT

Preparing the homogeneous spinnable solutions with highly dispersed Li-electroactive nanoparticles has been of the crucial issues for electrospinning technique to develop nanocomposite with carbon nanofibers, because the particle aggregation can lead to a poor cyclic stability and formation of unstable solid electrolyte interface layers. Herein, we present that the commercial Si nanoparticles ( $\leq 50$  nm in diameter), with using polyethylene glycol (PEG), are embedded uniformly into nitrogen-doped carbon nanofibers (w-Si@N-CNFs) through a facile electrospinning route, followed by carbonization at 800 °C. The PEG played a critical role as dispersion agent to prevent the aggregation of Si nanoparticles during electrospinning, which successfully leads to the high dispersion and incorporation of Si nanoparticles without any agglomeration on N-CNFs. As anode materials for Li-ion batteries, the electrochemical properties of w-Si@N-CNFs was evaluated and compared to the non-uniform Si@N-CNFs (wo-Si@N-CNFs) that is prepared without PEG. The w-Si@N-CNFs anodes exhibit not only the enhanced Li-storage performances with a high capacity-retention of 66.0% without any drastic capacity fading after 150 cycles at a current density of 200 mA g<sup>-1</sup>, but also the notable rate performances with a reversible capacity of 1076.8 and 640.8 mA h g<sup>-1</sup> at current densities of 100 and 2000 mA g<sup>-1</sup>, respectively. These results demonstrate that the uniformly embedded Si nanoparticles enhance the electrochemical performances of the Si@carbon nanofibers, which is attributed to the well-dispersed Si nanoparticles surrounded by carbon layers without aggregation, resulted in leading to the formation of stable solid electrolyte interface layers and the alleviation of volume expansion of Si nanoparticles. This simple and cost-effective process is expected as a platform for development of anode materials based on nanoparticles-embedded CNFs nanocomposite along with electrospinning technique.

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## 1. Introduction

Lithium ion batteries (LIBs) are still considered as one of the power sources for portable electronic devices such as cell phones and laptops, owing to their stable cycling performance and operational safety. In recent years, with growing demands on battery performances, a higher energy and power density, and longer cycle lifetime have been increasingly issued in LIB market. However, the current commercial LIBs use the carbon materials as anodes (i.e., graphite), which has a low theoretical capacity of 372 mA h g<sup>-1</sup> (based on the reaction with Li<sup>+</sup>: 6C + Li  $\leftrightarrow$  LiC<sub>6</sub>) [1]. This limitation can make it difficult to improve the performance of LIBs. Hence, the

choice and design of anode materials can be key factors to improve the electrochemical performance for next generation LIBs. Silicon (Si) has been considered as a promising anode material because of its highest theoretical capacity of 4200 mA h g<sup>-1</sup> (based on the Li-alloying/de-alloying reaction: Si + 4.4Li  $\leftrightarrow$  Li<sub>4.4</sub>Si), low electrochemical potential (<0.5 V vs. Li/Li<sup>+</sup>) and abundance [2]. Nevertheless, its practical application in LIBs is still challenging due to the limitations such as a severe volume change (~400%) caused by the Li-alloying/de-alloying reaction, which leads to a crack and pulverization of electrodes, resulting in a formation of unstable solid electrolyte interface (SEI) layers and a rapid capacity fading [3]. To overcome these drawbacks, the various nanostructures such as Si nanoparticles [4], nanowires [5,6], nanotubes [7,8] and porous Si [9] has been proposed, which resulted in the enhanced electrochemical performances of Si anodes. However, the formation of unstable SEI layers and breaking of active materials from the current collector still occur in the electrodes owing to the unavoidable

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volume changes in Si during the charge/discharge process [10,11]. Thus, the formation of Si nanocomposites, along with coating the chemically stable and high electric conductive materials, can be an effective approach to alleviate the volume expansion and the side reaction with electrolytes [12].

Embedding the active materials in carbon nanofibers (CNFs) via an electrospinning technique is one of the attractive strategies to produce one-dimensional nanocomposite based on carbon nanofibers. Because CNFs as supporting materials can be effectively an electron-transfer pathway based on their one-dimensional structures with a high electric conductivity [13], and mitigate the volume change of active materials, when the active materials were incorporated within the carbon layers [14,15]. Furthermore, it is possible to turn out electrode materials on a mass production [16,17]. However, in case of development of Si-embedded carbon nanofibers (Si-CNFs), there is a critical problem. It is difficult to obtain a homogeneous suspension with well-dispersed Si nanoparticles in viscous spinnable solutions, and thereby causing the aggregation of Si nanoparticles in CNFs [18,19]. The formed Si agglomerates with several micrometers are not captured within the carbon matrix and are exposed to electrolyte directly, and consequently lead to a poor cyclic stability and formation of unstable SEI layers. To address these disadvantages, the carbon coatings on Si have been attempted previously. For examples, Xiangwu Zhang and coworkers reported the formation of carbon-coated Si-CNFs [20] and chamber-confined Si-CNFs [21] via a chemical vapor deposition with the thermal decomposition of acetylene ( $C_2H_2$ ). In addition, Xiuli Xing and coworkers reported the formation of pyrolytic carbon-coated Si-CNFs using sucrose coating [22]. Although these approaches resulted in an enhancement of electrochemical properties of Si-CNF anodes, the synthesis process is complicated and expensive, which can impede scalable production. These make the Si-CNFs nanocomposites difficult in the practical application of industrial fields.

Herein, we design a fabric-like nanocomposite based on highly uniform Si nanoparticles-embedded nitrogen-doped carbon nanofibers (w-Si@N-CNFs) along with polyethylene glycol (PEG), which are synthesized via a facile single-nozzle electrospinning process followed by carbonization. We also report on the advantages of the uniformity of Si nanoparticles within N-CNFs, along with an evaluation of Li-storage performance of w-Si@N-CNFs nanocomposites as anode materials for LIBs. Furthermore, with comparison of the non-uniform Si@N-CNFs (wo-Si@N-CNFs), which are prepared using the same synthesis condition without PEG, the crucial role of PEG was discussed. The w-Si@N-CNFs nanocomposites exhibited a reversible capacity of  $1045 \text{ mA h g}^{-1}$  at a current density of  $200 \text{ mA g}^{-1}$  with an excellent capacity retention of 66.0% after 150 cycles and a high initial coulombic efficiency of 97% at the second cycle onward. The excellent electrochemical performance of the w-Si@N-CNFs nanocomposite anodes can be associated with not only the advantageous geometrical features of the uniformly encapsulated and highly dispersed Si nanoparticles in N-CNFs but also the network of nitrogen-doped carbon fabric structures, which offer a high electrical conductivity and soft buffer platform to prevent the huge volume expansion of Si nanoparticles.

## 2. Experimental

### 2.1. Synthesis of Si nanoparticles-embedded nitrogen-doped carbon nanofiber nanocomposites (w-Si@N-CNFs)

Urea (99.3+%, Alfa Aesar) and polyethylene glycol #6000 (PEG #6000, M.W.: 7400–9,000, Samchun chemical, Korea) were used as the nitrogen source and the dispersing agent, respectively, and were dissolved in dimethyl formamide (DMF, 99.5%, Samchun

chemical, Korea) with sonication for 10 min. Then the commercial Si nanopowder (average particle size:  $\leq 50 \text{ nm}$ , 98%, Alfa Aesar) was dispersed in as-prepared mixture solution under sonication for 60 min. The weight ratio of Si to PEG was 1:8. To prepare a spinnable solution, polyacrylonitrile (PAN, M.W.: 150,000, Sigma-Aldrich) and polyvinyl butyral (PVB, obtained from Institute for Advanced Engineering) were added in the homogeneous suspension with vigorous stirring at  $60^\circ\text{C}$ . The final solution was poured into a 15 mL plastic syringe and electrospinning was carried out by applying a voltage of 14 kV with a single-nozzle electrospinning system. The final products (w-Si@N-CNFs) were prepared through the stabilization of the as-spun w-Si@N-CNFs at  $280^\circ\text{C}$  for 2 h in air and subsequently, the carbonization process was performed at  $800^\circ\text{C}$  for 2 h in  $N_2$  atmosphere. For comparison, non-uniform Si@N-CNFs (wo-Si@N-CNFs) were prepared by a same condition without PEG.

### 2.2. Material characterization

The morphologies and microstructural features of all samples were examined using a field emission scanning electron microscope (FESEM, Hitachi, S-4300) and a transmission electron microscope equipped with an energy dispersive spectrometer (TEM and EDS, JEOL, JEM-2100F). The physicochemical properties of samples were characterized using an X-ray diffractometer (XRD; Rigaku, Ultima III) with Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) and a Raman FT-IR spectrometer (HORIBA Jobin Yvon, LabRAM ARAMIIS IR2). To calculate the mass ratio of Si to carbon in the samples, thermogravimetric analysis (TGA, METTLER TOLEDO, TGA/DSC 1) was carried out from 25 to  $1100^\circ\text{C}$  at a heating rate of  $10^\circ\text{C min}^{-1}$  in  $O_2$ .

### 2.3. Electrochemical measurement

To measure the electrochemical properties of the samples, working electrodes were fabricated using a slurry coating method on Cu foil. The slurry was composed of active materials, carbon blacks as a conductive material and sodium alginate as a binder in a weight ratio of 70:15:15. The prepared electrodes were cut into a disk of 1 cm in diameter, and Swagelok cells were assembled in an argon filled glove box with the working electrode, separator film (Celgard 2400), Li-foil as a counter electrode. The electrolyte was 1 M  $LiPF_6$  in ethylene carbonate (EC), propylene carbonate (PC) and diethyl carbonate (DEC) (volume ratio of 1:1:1) with 10 wt% of fluoroethylene carbonate (FEC). The galvanostatic charge/discharge tests of the cells were performed on an automatic battery cycler (WBCS 3000, WonA Tech, Korea) at different current densities in the voltage range of 0.001–2.0 V (vs.  $Li/Li^+$ ).

## 3. Results and discussion

Fig. 1 shows the schematic illustration of the formation of two types of nanocomposites synthesized with (w-Si@N-CNFs) and without (wo-Si@N-CNFs) PEG via facile electrospinning and subsequent pyrolysis processes, and the corresponding FESEM images are displayed respectively. As shown in Fig. 1b and c, the as-spun w-Si@N-CNFs and wo-Si@N-CNFs exhibit the fabric-like structures, which are observed commonly for polymer fibers by electrospinning [16,17]. However, in case of wo-Si@N-CNF, the aggregated Si particles were formed randomly as the droplet-like nanoclusters ( $>1 \mu\text{m}$ ) in the middle of nanofibers (Fig. 1c). After carbonization, the w-Si@N-CNFs exhibited a similar morphology to the as-spun w-Si@N-CNFs, in spite of a shrunken diameter of 300–400 nm, which can be caused by the decomposition of some elements (i.e., H and O) in CNFs during the carbonization at  $800^\circ\text{C}$  (Fig. 1d). The wo-Si@N-CNFs showed a similar fabric morphology to the w-Si@N-

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