

Short communication

## Silicon nanoparticle and carbon nanotube loaded carbon nanofibers for use in lithium-ion battery anodes



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### ABSTRACT

In this report, we introduce electrospun silicon nanoparticle and carbon nanotube loaded carbon nanofibers (SCNFs) as anode materials in lithium-ion batteries (LIBs). The one-dimensional structure of electrospun nanofibers provides porosity for the anode material. Carbon nanotubes (CNTs) in the electrospun fibers reduce the volume expansion of silicon nanoparticles (SiNPs) and improve mechanical stability of the electrode. Both CNTs and carbon nanofibers enhance electronic conduction by connecting SiNPs in SCNFs for electrode reactions. These contribute to improved electrochemical performance of SCNF anode-based LIBs resulting in the enhancement of capacity and cycling ability.

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## 1. Introduction

Rechargeable lithium ion batteries (LIBs) have varied applications such as in electrical vehicles, mobile electronic devices, and grid-scale stationary energy storage systems [1,2]. Advanced LIBs grow higher energy densities, greater power performances, and safety [3–5]. As the most promising LIB anode candidate, Si has a theoretical capacity of  $4200 \text{ mA h g}^{-1}$ , which is about ten times higher than that of graphitic carbon ( $372 \text{ mA h g}^{-1}$ ) [5–7]. However, after several tens of cycles, severe pulverization triggered by volume changes (expansion and shrinkage) greater than 300% after lithium insertion and extraction cause Si electrode degradation [8–10]. The pulverization of the Si causes an electrical disconnect between the active material and the current collectors [11–13]. The volume change of the Si renders the solid electrolyte interphase (SEI) layers on the Si surfaces mechanically unstable [2,3].

The poor cyclability due to the large volume change in Si causes a severe drop in capacity during charge/discharge cycles, especially at high current density extraction [8].

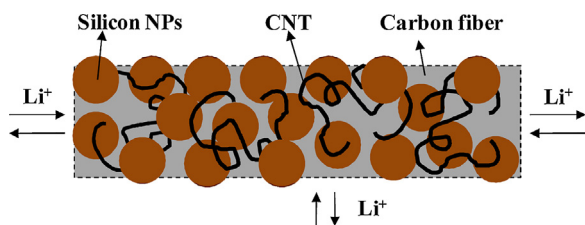
Nanostructured silicon nanoparticles (SiNPs) can overcome pulverization because nano-sized Si can stress relaxation during volume expansion [3]. In order to take advantage of nanostructured Si, many studies have fabricated active Si anodes in several nanostructures (such as nanowires [14–19], nanotubes [20,21], nanoparticles [22–25], and hollow Si nanostructures [26–30]) to enhance cycling performance. Previously we studied three-dimensional (3D) porous Si/Cu film-based and 3D porous Si@Ni inverse opal structure anodes with good stability and high rate performance for use in LIBs [31,32]. In this paper, we introduce a Si active material anode for LIBs, SiNP and carbon nanotube (CNT) loaded carbon nanofibers (SCNFs), fabricated using electrospinning and subsequent carbonization at  $1000^\circ\text{C}$  in nitrogen for 1 h.

The electrospinning process has been used for a variety of energy-related applications and devices because many one-dimensional (1D) nanostructures can be produced with fine morphology and composition control [33,34]. Many researchers have developed 1D electrospun structured silicon nanofibers for advanced anode materials [6,8–10,33,35–37]. With 1D structure, the SCNFs can provide high porosity for the anode. The SiNP–CNT composite in SCNFs not only improves the mechanical properties of the anode and reduces Si volume expansion, but it also

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**Fig. 1.** Schematic illustration of Si nanoparticle (SiNP) and carbon nanotube (CNT) loaded carbon nanofibers (SCNFs).

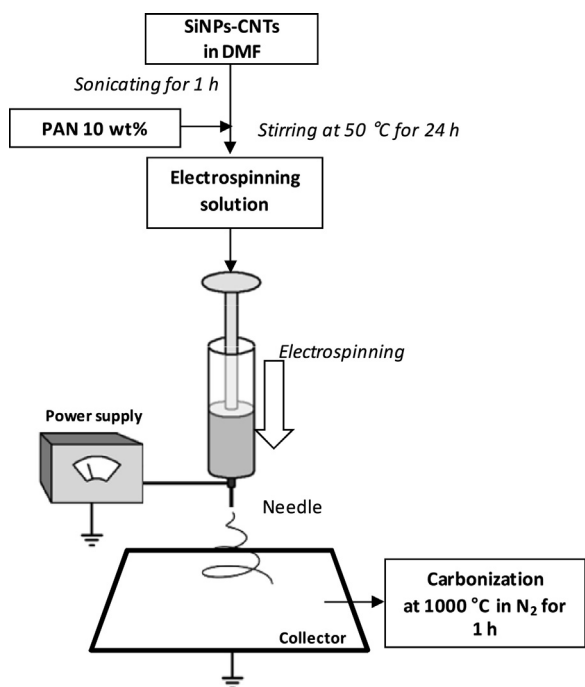
supports excellent electrical conductivity in the Si matrix [38–42]. The CNT conductive network can act as a pathway for electrical contact between SiNPs in the carbon fiber, as illustrated in Fig. 1. These advantages contribute to the increased electrochemical performance of SCNF anode-based LIBs.

## 2. Experimental

### 2.1. Preparation of electrospun silicon nanoparticle (SiNP) and carbon nanotube (CNT) loaded carbon nanofibers (SCNFs)

Electrospun silicon nanoparticle (SiNP) and carbon nanotube (CNT) loaded carbon nanofibers (SCNFs) were prepared by single electrospinning of a SiNPs, CNTs, and polyacrylonitrile (PAN) mixture in *N,N*-dimethylformamide (DMF). The electrospinning process was performed as illustrated in Fig. 2. Multi-walled CNTs (20 nm diameter, 10  $\mu$ m length, ACN Co., Korea) were modified before employing a wet chemical oxidative process, using  $H_2SO_4/HNO_3$  mixture, to yield a good dispersion in the polymer solution [43]. Carboxylic acid groups ( $-COOH$ ) were attached to the CNT sidewalls, thereby increasing the surface accessibility of the metal precursors in the aqueous solution and resulting in increased metal deposition [43–45].

The SiNPs (0.3 g, <100 nm particle size, Sigma Aldrich Chemical, USA) and modified CNTs (6 mg,  $\sim 2$  wt% calculated by mass ratio of CNT:SiNP) were dispersed in DMF (9 g, Sigma Aldrich



**Fig. 2.** Schematic for the preparation of electrospun silicon nanoparticle (SiNP) and carbon nanotube (CNT) loaded carbon nanofibers (SCNFs).

Chemical, USA) using an ultrasonifer for 1 h. Then, PAN (1 g, Sigma Aldrich Chemical, USA) was completely dissolved in the dispersed SiNP/CNT mixture to obtain a 10 wt% PAN solution. The mixture was stirred for 24 h at 50  $^{\circ}C$ , and was subsequently loaded into 5 mL plastic syringes equipped with stainless steel needles. Electrospinning was carried out on an aluminum foil collector using an electrospinning system (ESR200R2, NanoNC, Ltd., Korea) with an electric voltage of 12 kV and a distance of 15 cm between the stainless steel needle and collector. The syringe flow rate was 1 mL h $^{-1}$ .

The only PAN nanofibers and SiNP-loaded PAN nanofibers (without CNTs) prepared were used as control samples.

### 2.2. Carbonization of the PAN shell

The as-electrospun SCNFs were thermally treated for the stabilization and carbonization of PAN. The stabilization of SCNFs was carried out at 200–300  $^{\circ}C$  for 1 h in air. The PAN's dense ladder-polymer structure begins forming by reacting with oxygen. This ladder-polymer structure prevented melting during the subsequent carbonization, which was carried out at 1000  $^{\circ}C$  for 1 h in a nitrogen atmosphere [46]. The temperature was increased at a slow rate of 3  $^{\circ}C$  min $^{-1}$ . The carbonization involved the heat treatment of the stabilized SCNFs to remove non-carbon elements. These elements were removed in the form of different gases ranging from 300 to 1000  $^{\circ}C$  in the nitrogen atmosphere. After carbonization at 800  $^{\circ}C$ , denitrogenation takes place. This resulted in the formation of a carbon network structure [46]. The carbonization mainly focused on the conversion of PAN into carbon, leaving the SiNP–CNT composite in carbon fibers.

The prepared control samples, including PAN nanofibers and SiNP-loaded PAN nanofibers, were carbonized with the same conditions to become carbon nanofibers and SiNP-loaded carbon nanofibers (SNFs), respectively.

## 3. Results and discussion

The morphologies of these fibers, including SCNFs, are characterized using scanning electron microscopy (SEM). Fig. 3 shows the SEM images of these fibers before and after carbonization at 1000  $^{\circ}C$  in nitrogen for 1 h. The as-electrospun polyacrylonitrile (PAN) fibers in Fig. 3(a) indicate smooth and unique shapes with average diameter of 400 nm. After carbonization, the fibers transformed into CNFs, as shown in Fig. 3(b). Although the CNFs shrink to having average diameters of 150 nm, their morphologies are still fibrous and continue to have a carbon mass of approximately 60 wt%, as demonstrated by thermogravimetric analysis (TGA) in Fig. 4(b). The carbonization of the PAN is investigated over the 25–600  $^{\circ}C$  temperature range in nitrogen. That reveals the PAN's dehydrogenation over the 300–500  $^{\circ}C$  temperature range. The remaining weight percent of the PAN is retained during denitrogenation in the carbonization process over the temperature range 500–1000  $^{\circ}C$ . PAN is a good candidate to be the substrate for SCNFs because of its good conductivity [46].

Fig. 3(c) and (e) represents the as-electrospun SNFs and SCNFs, respectively. Although the morphologies of these fibers seem to be similar, they have rough surfaces due to the presence of SiNPs. The carbonized SCNFs, seen in Fig. 3(f), with a moderate amount of CNTs (CNT:SiNP = 2 wt%) have an average diameter of 200 nm, smaller than that of the carbonized SNFs (400 nm) shown in Fig. 3(d). Known to be a good conductive material, CNTs are easily electrified under a high voltage. Thus, the electrospinning precursor containing CNTs can be spun to the collector faster than the other without CNTs, leading to a decrease in fiber diameter. Consequently, the porosity of SCNFs increases, creating a facile accommodation Li ions at the SEI for insertion and extraction.

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