



Extensively interconnected silicon nanoparticles via carbon network derived from ultrathin cellulose nanofibers as high performance lithium ion battery anodes



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ABSTRACT

Silicon is a good alternative to conventional graphite anode but it has bad cycling and rate performance. To overcome these severe problems, extensively interconnected silicon nanoparticles using carbon network derived from ultrathin cellulose nanofibers were synthesized. Ultrathin cellulose nanofibers, an abundant and sustainable material, entangle each silicon nanoparticle and become extensively interconnected carbon network after pyrolysis. This wide range interconnection provides an efficient electron path by decreasing the likelihood that electrons experience contact resistivity and also suppresses the volume expansion of silicon during lithiation. In addition, Ultrathin cellulose nanofibers are carboxylated and therefore adhesive to silicon nanoparticles through hydrogen bonding. This property makes ultrathin cellulose the perfect carbon source when making silicon composites. As a consequence, it exhibits 808 mAh g⁻¹ of the reversible capacity after 500 cycles at high current density of 2 A g⁻¹ with a coulombic efficiency of 99.8%. Even at high current density of 8 A g⁻¹, it shows a high reversible discharge capacity of 464 mAh g⁻¹. Moreover, extensively interconnected carbon network prevents the formation of a brittle electrode with a water-based binder. Therefore, this remarkable material has a huge potential for LIBs applications.

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1. Introduction

Conventional lithium-ion batteries (LIBs) can provide relatively high capacity and power. But due to the velocity of technological developments such as high performance portable electronics and electronic vehicles, there is a huge demand for advanced lithium-ion batteries with higher energy and power density [1,2].

Silicon as an alternative of conventional graphite is a highly anticipated anode material because of its very high theoretical capacity of ~4200 mAh g⁻¹, low insertion voltage and natural

abundancy [3–6]. Even with such great advantages, silicon suffers from poor cycle stability and bad rate performance owing to the alloying mechanism and low intrinsic electric conductivity [7–9]. During cycling, the volume of silicon expands (up to 300%) and contracts, which generates serious stress on silicon particles and causes mechanical fracture [7,8]. The pulverized silicon particles lose their electric contacts, resulting in cycle stability degeneration. Throughout the last decade, many researchers have tried to solve these problems using nanotechnology [10–15]. By introducing nanostructures such as nanowire array [11,16], hollow nanospheres [14] and yolk-shell nano-structures [13] or by employing conductive materials like carbon [17–24], silicon as an anode material showed excellent cycle stability as well as good rate performance while maintaining its high capacity.

Especially, carbon materials such as graphene [17,22,23], carbon nanofibers [25] and carbon nanotubes [26,27] have been widely implemented in LIBs application. The common purpose of this

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implementation is to improve the electric conductivity. Carbon materials serve as the conductive platform so that the electrons travel through carbon rather than silicon nanoparticles which have high resistivity. Therefore, implementing an extensively and well-connected carbon network might result in good performance. If the electron travels through narrowly connected carbon network, it will experience contact resistance when it jumps to another carbon network. But if the carbon network is extensively connected, the chance of an electron experiencing contact resistance will decrease. However, to the best of our knowledge, most research adopting carbon materials haven't considered about the range of connectivity so far.

Herein, we synthesized extensively interconnected silicon nanoparticles via carbon network using ultrathin cellulose nanofibers as carbon sources. The range of connectivity is in tens of micrometers. Ultrathin cellulose nanofibers ($1.55 \text{ nm} \pm 0.532$) entangled with the silicon nanoparticles and then transformed into extensively well-connected graphitic carbon by pyrolysis. TEMPO-oxidized cellulose nanofibers were used as ultrathin 1-D nanomaterials because they have carboxylic groups and a high aspect ratio. It is well known that carboxylic groups can interact with the oxide layer of silicon nanoparticles through hydrogen bonding [28,29]. In addition, cellulose is naturally abundant and cost-effective, which makes a perfect candidate for battery application. We believe that an extensively connected carbon network can not only suppress the volume expansion of silicon nanoparticles but also provide the electrons to silicon nanoparticles efficiently. As a consequence, cycle stability is greatly increased and exhibits 72.2% (808 mAh g^{-1}) capacity retention after 500 cycles at high current density of 2 A g^{-1} and rate performance of 464 mAh g^{-1} at a current density of 8 A g^{-1} .

More significantly, an extensively connected carbon network holds silicon nanoparticles tightly together and prevents the formation of brittle electrodes when water-based binder is used. Water-based binders such as carboxymethylcellulose (CMC) and polyacrylic acid (PAA) improve cycle stability of silicon anode materials, but high stiffness of the binder resulted in brittle electrodes and thus inhibits practical use [30]. We show that the robust electrode is formed even at high thickness. We believe that this property as well as its excellent electrochemical performance can drag out the potential of silicon anode materials for LIBs applications.

2. Experimental

2.1. Synthesis of ultrathin cellulose nanofibers

Cellulose pulp purchased from Domsjö Fabriker AB (Domsjö, Sweden). The pulp was previously washed with HCl solution (pH 2). Cellulose pulp (20 g in dry content) was suspended in sodium phosphate buffer (1800 ml, pH 6.8) and warmed up until $60 \text{ }^\circ\text{C}$. After 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) radical (0.1 mmol) (Alfa Aesar, 98%) was added to the suspension, sodium chlorite (0.2 mol) (Sigma Aldrich, 80%) was added. After they were dissolved, sodium hypochlorite (1 mol) (Sigma Aldrich, 10–15% available chlorine) was added. The resulting suspension was stirred for 140 min and subsequently washed with distilled water using vacuum filtration. A suspension of 1 wt% was prepared and homogenized at high pressure (1600 bars) in a Microfluidizer (M-110EH, Microfluidics). The suspension was diluted to $\approx 3 \text{ mg ml}^{-1}$ and sonicated with a probe sonicator (20 kHz, 80% total power, 250 ml max volume) for 8 min.

2.2. Synthesis of silicon-carbonized ultrathin cellulose nanofiber composites

Silicon nanoparticles (100 mg) (<100 nm, American Elements)

were added to ethanol (3 ml) for wetting. After sonication for 10 min, distilled water (10 ml) was added, followed by sonication for 30 min as-prepared TEMPO-oxidized cellulose nanofiber solution (14 ml) (0.27 wt%) was added and sonicated for another 30 min. The solution was rapidly frozen by liquid nitrogen and then freeze-dried for 2 days to remove water completely. The resulting spongy-like yellow aerogel was pyrolyzed at $900 \text{ }^\circ\text{C}$ in Ar atmosphere for 5 h with a ramp rate of $10 \text{ }^\circ\text{C min}^{-1}$. The spongy-like black aerogel was obtained.

2.3. Material characterizations

Atomic force microscopy (AFM) image was acquired with an atomic force microscope (Veeco Dimension 3100 SPM) using the tapping mode in air. The sample was deposited onto pretreated mica substrate with 3-aminopropyl triethoxysilane (Sigma Aldrich, 99%) in order to positively charge the surface of the substrate. Scanning electron microscopy in transmission mode (STEM) image was obtained with a scanning microscope in transmission mode (JEOL JSM-7401F, 20 kV). Fourier transform-infrared spectroscopy (FT-IR) spectra were acquired with a FT-IR spectrometer (Varian 610-IR) equipped with an attenuated total reflection (ATR) element from 400 cm^{-1} to 4000 cm^{-1} . The structural morphology of the sample was examined by field emission scanning electron microscopy (FE-SEM, Hitachi S-4800, 15 kV). For the detailed structure examination, high resolution-transmission electron microscopy (HR-TEM) (JEOL JEM-2100F, 200 keV) equipped with an energy-dispersive X-ray spectrometer (EDS) was utilized. The crystallinity of the sample was measured by XRD using X-ray diffractometer (Bruker New D8 Advance, 40 kV, 40 mA) with a Cu target. Raman analysis was done by Raman spectrometer (Horiba T64000) equipped with an Ar laser (514 nm). Thermal gravimetric analysis (TGA) measurement was conducted using a TGA/DSC 1 analyzer (Mettler Toledo) with a ramp rate of $10 \text{ }^\circ\text{C min}^{-1}$ in air. N_2 adsorption/desorption isotherm and BJH pore size distribution diagram were obtained through a BELSORP-mini (MicrotracBEL Corp) at 77 K.

2.4. Electrochemical measurement

The sample, conducting additive (Timcal Super P C60), and binder (sodium carboxymethylcellulose, Sigma Aldrich, average $M_w \sim 90,000$) were mixed by a weight ratio of 75:15:15 in distilled water using a Mini-Mill pulverisette 23 (FRITSCH) for 30 min. The homogenous slurry was casted on a copper foil using a Doctor blade and dried in vacuum at $60 \text{ }^\circ\text{C}$ for 30 min. The loading mass of active materials is $\sim 0.7 \text{ mg cm}^{-2}$ and the thickness of the electrode used for electrochemical measurements excluding the current collector is about 10–20 μm . Electrodes dried again in vacuum at $120 \text{ }^\circ\text{C}$ for 2 h. Coin-type cells (CR2016) were assembled in an Ar-filled glove box using lithium metal foils as counter/reference electrodes, Celgard 2450 as separators and 1.3 M LiPF_6 in a 3:7 (v/v) ethylene carbonate (EC) and diethyl carbonate (DEC) with 10% fluoroethylene carbonate (FEC) additive as electrolytes (PANAX). The half-cells were measured galvanostatically in the voltage range of 0.01–1.5 V (vs. Li/Li^+). Every electrochemical test was performed on a WBCS3000S cyler (Wonatech).

For the lithium cobalt oxide (LCO) half-cell test, lithium cobalt (III) oxide (Alfa Aesar, 99.5%), conducting additive (Timcal Super P C60), and binder (polyvinylidene difluoride, MTI Corporation, average $M_w \sim 600,000$) were mixed with a weight ratio of 80:10:10 in N-Methyl-2-pyrrolidone (NMP) solvent using the same equipment mentioned above for 30 min. The homogenous slurry was casted on an aluminum foil using a Doctor blade resulting in a loading of active material of $\sim 4.4 \text{ mg cm}^{-2}$. The electrodes were

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