



Highly conductive carbon nanotube micro-spherical network for high-rate silicon anode

Byung Hoon Park^a, Jun Hui Jeong^a, Geon-Woo Lee^a, Young-Hwan Kim^a, Kwang Chul Roh^{b,*}, Kwang-Bum Kim^{a,**}

^a Department of Materials Science and Engineering, Yonsei University, 50 Yonsei-ro, Seodaemun-gu, Seoul, 03722, Republic of Korea

^b Energy and Environmental Division, Korea Institute of Ceramic Engineering and Technology, 101 Soho-ro, Jinju-si, Gyeongsangnam-do, 52851, Republic of Korea

HIGHLIGHTS

- Si NPs are bound to CNT network through a very tiny amount of sucrose-derived carbon.
- The Si/CNT/C microsphere has an interconnected pore facilitating Li-ion transport.
- The Si/CNT/C microsphere exhibited superior rate capability with high capacity.

ARTICLE INFO

Keywords:

Lithium-ion batteries
Silicon/CNT microsphere
High-rate Si anode
Spray dry

ABSTRACT

We report on a highly conductive CNT micro-spherical network for high-rate silicon anode materials prepared by one-pot spray drying for lithium-ion batteries. The anode material contains silicon nanoparticles bound to CNTs through a small amount of sucrose-derived carbon. The first charge and discharge capacities of the Si/CNT/C microsphere electrode are measured to be 3152 and 2302 mA h g⁻¹ of the composite, respectively, at 0.1 A g⁻¹. The Si/CNT/C microsphere electrode exhibits an initial capacity of 1989 mA h g⁻¹ at current density of 1.0 A g⁻¹ and retains ~70% of the initial capacity after 100 cycles. Even at a high current density of 10 A g⁻¹, the Si/CNT/C microsphere electrode exhibits a capacity of 784 mA h g⁻¹ with a stable charge/discharge behavior. The superior rate capability of the Si/CNT/C microsphere composites can be attributable to the unhindered Li-ion transport through the highly conductive CNT buffer matrix, to which Si NPs are strongly bound by the sucrose-derived carbon. These salient results give further impetus to the study of CNTs for use as a buffer matrix to improve the rate capability of high-capacity electrode materials with large volume changes during charge storage.

1. Introduction

With rapidly increasing demands for high-performance portable electronics and electric vehicles, lithium-ion batteries (LIBs) with a high energy density and high power density have become the subject of intense study [1,2]. Silicon has long been considered a promising anode material for replacing graphite (specific capacity around ~372 mA h g⁻¹) in a LIB because of its superior theoretical capacity (~3587 mA h g⁻¹ for formed Li₁₅Si₄ at room temperature), practical operating voltage (~0.1 V vs. Li/Li⁺) and natural abundance (second-largest global resource) [3]. However, the practical application of Si has been hindered mainly due to the problems associated with its large volume changes (~300%) upon lithiation/de-lithiation. The large

volume changes cause a high internal stress, electrode pulverization, and an unstable solid electrolyte interphase (SEI), resulting in the loss of electrical contact and eventually rapid capacity fading, as well as poor rate capability [3,4].

Therefore, extensive efforts have been made to develop highly reversible Si-based anodes with extended cyclability [5–27]. One of the most effective approaches is the preparation of Si/carbon composites involve uniform distribution of silicon nanoparticles (Si NPs) in carbon matrix [11–14,17–25]. In these Si/carbon composites, the carbon acts as both a buffer for the Si volume changes during cycling and an electrical conducting pathway. Si/carbon composites can be categorized in terms of the carbon matrix as follows: (i) Si NPs/pyrolytic carbon microparticle composites [17–19], (ii) Si NPs/graphene

* Corresponding author.

** Corresponding author.

E-mail addresses: rkc@kicet.re.kr (K.C. Roh), kbkim@yonsei.ac.kr (K.-B. Kim).

microparticle composites [20–23], and (iii) Si NPs/carbon nanotube (CNT) microparticle composites [24,25]. For Si NPs/pyrolytic carbon microparticles, Si NPs are embedded in a pyrolytic carbon matrix or coated with a thin layer of pyrolytic carbon. However, since pyrolytic carbon has a dense structure that lacks the adequate porous structures necessary to accommodate the Si volume changes, Si NPs/pyrolytic carbon microparticles exhibit poor cyclability [3,28,29]. Furthermore, the transport of Li ions across pyrolytic carbon could be hindered, leading to an unsatisfactory rate capability [30]. Compared with Si NPs/pyrolytic carbon microparticles, Si NPs/graphene microparticles exhibit improved cyclability because Si NPs are closely wrapped with a highly conductive 2-D graphene, which can accommodate the volume changes during cycling [20,22,23]. However, there is growing concern that Li-ion transport across graphene could be hindered due to its 2-D structure in the graphene-wrapped electroactive particles, thereby limiting its rate capability [31].

In this context, Si NPs/CNT microparticle composite is expected to provide more efficient Li ion transport from the bulk electrolyte than Si NPs/pyrolytic carbon microparticles and Si NPs/graphene microparticle composites due to the CNT's 1-D cylindrical nanostructure. Therefore, combining the high capacity Si NPs and mechanically stable conductive CNT buffer network with efficient Li-ion transport would be a potentially advantageous strategy to the improvement of rate capability as well as the cyclability of Si. Interestingly, however, only a few reports have addressed the advantages of Si NPs/CNT microparticles relative to Si NPs/pyrolytic carbon microparticles and Si NPs/graphene microparticles. For example, Feng et al. reported on a composite of porous Si NPs, CNTs, and a carbon matrix prepared by the spray drying of porous Si NPs and CNTs (~5 wt.%), followed by CVD carbon (~20 wt.%) coating [24]. According to their discussion, Si/CNT/C composite showed a marginal improvement in cyclability over Si/C composite prepared without using CNTs. Therefore, it could be inferred that it was not CNTs but CVD carbon that was responsible for the improvement observed for Si/CNT/C composite. In another example, Bie et al. reported Si composite composed of Si NPs, CNTs (~10 wt.%), resin-derived carbon (~20 wt.%) and Cu (~5 wt.%), prepared by spray drying and carbonization heat treatment [25]. The Si-CNT-C-Cu composite showed improved cyclability over bare Si NPs, since the CNT network with resin-derived carbon could endure large volume changes of Si NPs. In these Si/CNT/C composites the amount of CVD carbon or resin-derived carbon was larger than that of CNTs, therefore, it is unclear whether the CNTs themselves could effectively buffer volume changes of Si NPs during cycling.

In this study, we report highly conductive CNT micro-spherical network for use as a buffer for high-rate silicon anode material for lithium-ion batteries, which was prepared by one-pot spray drying. Specifically, the Si/CNT/C microsphere features Si NPs bound to CNTs (30 wt.%) with a small amount of sucrose-derived carbon (~2 wt.%). The CNTs consisted of an electrically conductive buffer matrix with an interconnected pore structure that could not only accommodate the huge volume expansion of the Si during charge/discharge, but also favor Li-ion transport in the Si/CNT/C microsphere. The tiny amount of sucrose carbon acted as a structural support that facilitated the binding of the Si NPs to the CNTs while linking the neighboring CNTs together. As a result, the first charge and discharge capacity of the Si/CNT/C microsphere electrode was measured to be as high as 3152 and 2302 mA h g⁻¹ of the composite at 0.1 A g⁻¹, respectively. Further, the Si/CNT/C microsphere electrode exhibited an initial capacity of 1989 mA h g⁻¹ at 1.0 A g⁻¹ and maintained ~70% retention of its initial capacity after 100 cycles. Even at a high current density of 10 A g⁻¹, the Si/CNT/C microsphere electrode showed stable charge and discharge behavior with a capacity of 784 mA h g⁻¹. The superior rate capability of the Si/CNT/C microsphere over recently reported Si NPs/pyrolytic carbon microparticle and Si NPs/graphene microparticle composites could be attributable to the unhindered Li-ion transport through the highly conductive CNT buffer matrix, to which the Si NPs

were strongly bound by the sucrose-derived carbon. This novel approach to the Si/CNT/C microsphere, as presented herein, may be extended to improving the cyclability and rate capability of high-capacity electrode materials that exhibit large volume changes during electrochemical charge storage.

2. Experimental

2.1. Material synthesis

First, 600 mg of Si NPs (40–100 nm, GS Energy), 300 mg of CNTs (Carbon Nano-material Technology Co., Ltd.), and 112.5 mg of sucrose (Sigma Aldrich) were dispersed in 500 mL of deionized water. The aqueous mixture of Si NPs, CNTs and sucrose was stirred and sonicated with a tip sonicator for 2 h (VCX-750, Sonics & Materials, Inc.). Pristine CNTs were used without any surface modification in order to retain their high electrical conductivity. Then, the mixture was spray dried to fabricate micron-sized spherical Si/CNT/sucrose precursors by using a commercial spray dryer (B-290 mini spray dryer, Buchi). While passing through the heated zone, the solvent water in the microdroplets evaporated. Meanwhile, the Si NPs and CNTs were assembled, resulting in the formation of a spherical, micron-sized Si/CNT/sucrose precursor. The obtained precursor was further heated to 900 °C at a heating rate of 10 °C min⁻¹, and was maintained at 900 °C for 3 h in an N₂ atmosphere to prepare the Si/CNT/C microsphere. For comparison, the Si/CNT microsphere, which did not contain sucrose-derived carbon, was similarly prepared using the spray dry process.

2.2. Material characterization

The morphology and microstructure of the samples obtained at various stages of the synthesis process were investigated using SEM (JEOL-7800F, JEOL) and high-resolution TEM (JEM-ARM 200F, JEOL). The cross-sectional SEM image of the composite was investigated by focused ion-beam scanning electron microscopy (FIB-SEM, JIB-4601F, JEOL). The structural properties of these samples were also examined by X-ray diffraction analysis. Furthermore, X-ray photoelectron spectroscopy was used to investigate the elemental composition and oxidation/reduction states of the carbon materials using a K-alpha (Thermo, UK) source. The surface area of the samples was determined from the N₂ gas adsorption-desorption isotherms, which were obtained using the BET method (Autosorb-iQ 2ST/MP, Quantachrome). Raman spectroscopy (Jobin-Yvon LabRAM HR) was performed at room temperature using the conventional backscattering geometry. Thermogravimetric analysis (TGA) data were collected on a thermal analysis instrument (TGA/DSC 1, Mettler Toledo) at a heating rate of 10 °C min⁻¹ and an air flow rate of 50 mL min⁻¹. The electrical conductivity of pristine CNTs was determined by measuring *I-V* using the two-point probe method with a compressed-powder pellet in the cell (MPG2, Bio-logic) [32].

2.3. Electrochemical measurements

The electrochemical properties of the Si/CNT/C microsphere were investigated using 2032-type coin cells; a piece of lithium foil was used as the counter electrode, and 1-M LiPF₆ in ethyl carbonate (EC)/dimethyl carbonate (DMC)/diethyl carbonate (DEC) (2:2:1 v/v) with 10 wt.% fluoroethylene carbonate (FEC) additive was used as the electrolyte. The working Si/CNT/C microsphere electrode was prepared from a slurry of 80 wt.% Si/CNT/C, 10 wt.% carbon black, and 10 wt.% poly (acrylic acid) (PAA) binder; the mixture was applied to a Cu foil. Similarly, the Si/CNT microsphere electrode was prepared with the same electrode composition. Each working electrode had an area of 1.13 cm² (punched into discs with a diameter of 12 mm), and the amount of active material in the electrodes was approximately 1 mg cm⁻². The charge and discharge behaviors of the electrodes were

Download English Version:

<https://daneshyari.com/en/article/7724854>

Download Persian Version:

<https://daneshyari.com/article/7724854>

[Daneshyari.com](https://daneshyari.com)