



Nanocomposite Si/(NiTi) anode materials synthesized by high-energy mechanical milling for lithium-ion rechargeable batteries



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HIGHLIGHTS

- ▶ Silicon and Nitinol powder mixture was milled by high-energy mechanical milling.
- ▶ High-energy mechanical milling results formation of nanocomposite Silicon/Nitinol.
- ▶ Coin cell cross sectional microstructure presented after cycling.
- ▶ Prominent electrochemical properties obtained due to nanocomposite structure.
- ▶ 10-h milled nanocomposite exhibit stable capacity of 553 mAh g⁻¹ after 52nd cycle.

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ABSTRACT

Nanocrystalline Silicon (Si) embedded Ni–Ti composite anode materials are synthesized by using two-stage high-energy mechanical milling (HEMM). The overall composition of the Si and NiTi (Nitinol) powders are 65 at.% and 35 at.%. The effects of crystal size, crystal structure, and microstructure on the electrochemical properties of the nanocomposite powders are examined through X-ray diffraction, scanning electron microscopy, high-resolution transmission electron microscopy, electrochemical test and nano-indentation test. The capacities of the coin cells produced with the 6 and 10 h milled powders are 711 and 553 mAh g⁻¹, respectively, after the 52nd cycle. The efficiencies of the coin cells produced with the 6 and 10 h milled powders continue to maintain 97.2 and 97.5%, respectively, until 52nd cycle. Coin cells produced with 10 h milled powders show relatively low capacity fading, which are attributed to the nanocomposite structure comprised of Si nanocrystals embedded into amorphous Ni–Ti matrix phase. Coin cell of 10 h milled powders reveals the reduced number of voids. Therefore, it is believed that Si embedded Ni–Ti nanocomposite using a two-stage high energy mechanical milling can be a promising candidate for high performance Si based anode materials.

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1. Introduction

Lithium-ion rechargeable batteries have attracted more attention than other rechargeable batteries because of their superior performances such as higher energy density, higher operating voltages, and lower self-discharge, and because they are cost effective and safe [1–4]. Li-ion rechargeable batteries are widely used in the communications, electric vehicle (EV), and power storage sectors because these advantages can be readily exploited. Lithium easily reacts with several metals such as Sn, Sb, Al, Si, Pt, Ag, Zn, Cd, and Mg [5,6]. Among these metals, Si is the candidate with the most potential for application as an anode material

because of the high theoretical capacity of Si (Li_{4.4}Si: 4200 mAh g⁻¹) [4,7–11] and because it is inexpensive. Although Si is a potential candidate as an anode material, it unfortunately undergoes severe changes in volume (~400%) during lithiation and delithiation, which results in pulverization of Si anode materials and leads to loss of electrical contact between the active material and current collector; hence, its capacity fading is severe [12–14]. Several Si-composite materials have been developed to solve these problems [15–22]. It has been reported that mechanical milling is effective to the formation of Si-nanocomposite structures, exhibiting excellent cyclability without severe cracking [23–26]. In the case of silicon as an electrochemically active material, higher capacities can be achieved while affording the utilization of the inactive matrix. Such a nanocomposite could allow for more efficient cyclability in a composite anode. This technology concept has been realized in systems such as Si/TiN, Si/TiB₂, Si/SiC and Sn/C

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[27–29]. In particular, when the inactive phase was pre-milled and then again milled with Si, anodes made from the powder thus obtained showed better capacity retention than anodes containing a non-milled inactive phase [30], which was due to the smaller particle size of the inactive matrix, uniform distribution of stress throughout the electrode. However, in case that the matrix phase is exceedingly strong, Si crystals can be broken, which lead to the serious capacity fading. Therefore, it is necessary to find out the inactive matrix materials with ability to compensate the stress induced by Si volume expansion. Currently, some researchers has been tried to utilize super-elastic Nickel–Titanium (NiTi) alloy (nitinol) [31] as inactive matrix phase by using various methods such as melt-spinning and thin film deposition [32–34]. They expected that the super-elastic matrix could accommodate the stress driven by Si volume changes during charging and discharging. In present work, we investigate the possibility that Si embedded nanocomposite structure (Si/NiTi) can be synthesized by using high energy mechanical milling (HEMM) process, which is favorable to large scale production [23,24]. At first we prepared sub-micrometer sized Si powders from the first stage of mechanical milling and then the active Si is milled with NiTi alloy powders produced by gas atomization (in second stage-HEMM).

This study covers the crystal structure changes and Si distribution in Ni–Ti matrix and their electrochemical properties.

2. Experimental

2.1. Material preparation

Si/(NiTi) nanocomposite powder was prepared using a Simoloyr CM01 (Zoz GmbH, Germany) HEMM system, which was controlled using MALTOZ-software. The nanocomposite powder was prepared in two steps: (1) Commercially obtained Si powder (average particle size: $<40\ \mu\text{m}$, 98% purity) was milled for 12 h; (2) the milled Si powder from step (1) was mixed with NiTi alloy powder produced by gas atomization (average particle size: $<60\ \mu\text{m}$, 99% purity) in a ratio of 65 at.% Si and 35 at.% NiTi. This mixture is termed “as-mixed powder”. Samples of the as-mixed powder were milled for either 6 or 10 h to form two Si/(NiTi) nanocomposite phases. The entire milling process was performed at room temperature in a firmly sealed hardened vial and under a completely inert ambient atmosphere to eliminate oxidation. Yttrium-stabilized zirconia (YSZ) balls were used as the milling media, and the ball-to-powder weight ratio was maintained at 30:1. Stearic acid (5 wt%) was used as a process controlling agent (PCA), and the rotation speed of impeller was 800 rpm.

2.2. Characterization of materials

Phase analysis was performed using X-ray diffraction (XRD) with Cu- K_{α} radiation ($\lambda = 1.5418\ \text{\AA}$) operating at 8 kW and step size is 0.02° from 20 to 80° in the 2θ range. Field-emission scanning electron microscopy (FE-SEM) and high-resolution transmission electron microscopy (HR-TEM) were used to observe cross-sections of the milled powders and the coin cells produced with them. In particular, the cross-section of the coin cell was prepared by ion-milling after the extraction of Li-ion, and the anode plate was taken out in the glove box filled with Ar gas. To compare mechanical behavior between Si and Si/(Ni–Ti), nano-indentation test (Fischer, HM2000XYP) for obtaining hardness, elastic modulus and elastic strain were performed. Vickers diamond indenter was employed. The modulus and hardness was measured at load of 30 mN. All the obtained data were calibrated using a fused silica reference. For the preparation of test specimen, Si/(Ni–Ti) powders were mixed with acrylic powder and then pressed at $200\ ^{\circ}\text{C}$ and

then cooled to room temperature. The test specimen was shown in the schematic diagram Fig. 1.

2.3. Electrochemical tests

For the electrochemical evaluation, the milled Si/(NiTi) electrodes were prepared by coating Cu substrates with a slurry containing the following materials dissolved in *N*-methyl-2-pyrrolidinone (NMP): the active material (80 wt%), SFG6 graphite (10 wt%), Ketjenblack[®] (2 wt%) as a conductive agent, and polyamide-imide (PAI, 8 wt%) as a binder material. The electrodes were pressed and dried under vacuum at $350\ ^{\circ}\text{C}$ for 1 h. They were then cut into 14-mm-diameter discs. Coin-type electrochemical cells were assembled in an Ar-filled glove box. Celgard[®] 2400 was used as the separator, Li foil was used as both the counter and reference electrodes, and a 1-M solution of LiPF₆ (lithium hexafluorophosphate) dissolved in a mixture of ethylene carbonate (EC)/diethyl carbonate (DEC)/fluoroethylene carbonate (FEC) (5:70:25 by volume) was used as the electrolyte. Charge/discharge measurements (TOSCAT-3100, Toyo System Co., Ltd.) for the composite anodes were performed when constant current (CC) is applied over a voltage range of 0.01 and 1.5 V (constant current density of $2.5\ \text{mA cm}^{-2}$) at 0.1 and 0.2 C-rate for first and second cycles respectively, and 1.0 C-rate from third cycle.

3. Results and discussion

3.1. Evolution of composite structures

X-ray diffraction patterns for the pure Si, pure NiTi, and Si/(NiTi) composite powders are presented in Fig. 2. The intensities of the Si diffraction peaks (Fig. 2(a)) reduce with increasing milling time, which indicates pulverization of the Si powders during mechanical milling. The diffraction pattern for pure NiTi powder is presented in Fig. 2(b). The diffraction patterns for the Si/(NiTi) composite powders obtained after various milling times are shown in Fig. 2(c). In the 6 h milled composite powders, the peaks inside the rings indicate that the crystalline NiTi phase transforms into the nanocrystalline and amorphous phase. In particular, the 10 h milled composite powders, the amorphization is continued to proceed. Accordingly, the Si diffraction peaks are not changed significantly with increasing milling time and instead NiTi (Nitinol) peaks are abruptly broaden and their intensities are decreased, which indicates the phase transition from crystalline NiTi to (nanocrystalline + amorphous) Ni–Ti. From the XRD results, no significant contamination relevant peaks were observed due to YSZ balls (milling media) and PCA.

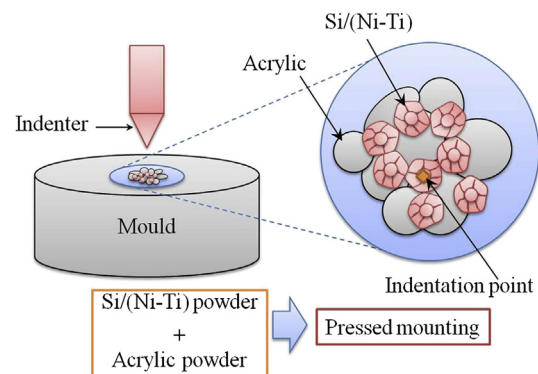


Fig. 1. Schematic illustration for preparation of Si/(Ni–Ti) nano-indentation test specimen.

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