



## Si<sub>7</sub>Ti<sub>4</sub>Ni<sub>4</sub> as a buffer material for Si and its electrochemical study for lithium ion batteries



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### HIGHLIGHTS

- We report a facile method for synthesis of nano-Si embedded in Si<sub>7</sub>Ti<sub>4</sub>Ni<sub>4</sub> complex.
- Microstructure change of Si<sub>7</sub>Ti<sub>4</sub>Ni<sub>4</sub> relaxes volume expansion of Si.
- Si<sub>7</sub>Ti<sub>4</sub>Ni<sub>4</sub> inhibits further synthesis of SEI layer.
- Discharge capacity is maintained at almost 800 mAh g<sup>-1</sup> over 50 cycles.
- It retains 86% of capacity at 3200 mA g<sup>-1</sup> compared to that of 400 mA g<sup>-1</sup>.

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### ABSTRACT

Nano-Si embedded Si<sub>7</sub>Ti<sub>4</sub>Ni<sub>4</sub> is synthesized with the melt spinning method, which is facile, and applicable to mass-production. Si<sub>7</sub>Ti<sub>4</sub>Ni<sub>4</sub>, the buffer material, is electrochemically inactive toward lithium. Nevertheless, Si<sub>7</sub>Ti<sub>4</sub>Ni<sub>4</sub> has good electrical conductivity, in the order of 10<sup>5</sup> S m<sup>-1</sup>, which is more conductive than amorphous carbon that is usually used as a coating material for active material. Furthermore, the surrounding grain boundaries of Si<sub>7</sub>Ti<sub>4</sub>Ni<sub>4</sub> effectively relax volume expansion of Si. Therefore, it plays a critical role in maintaining the structure of electrode and the integrity of active materials. As a result, nano-Si embedded in Si<sub>7</sub>Ti<sub>4</sub>Ni<sub>4</sub> shows outstanding cycle performance over 50 cycles at 400 mA g<sup>-1</sup>, and it maintains 86% of its specific capacity at 3200 mA g<sup>-1</sup>, compared with that of 400 mA g<sup>-1</sup>. This indicates that nano-Si embedded in Si<sub>7</sub>Ti<sub>4</sub>Ni<sub>4</sub> can be a promising anode material for lithium ion batteries.

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### 1. Introduction

Lithium ion batteries (LIBs) have drawn considerable interest, due to the various possibilities of their application, such as cellular phones, laptop computers and small IT equipment. In contrast to conventional LIB, however, future LIBs will require high specific capacity and outstanding power performance. This is due to the fact that the new areas for LIBs to be applied to, such as electric vehicles and energy storage systems, require such properties. In reality,

conventional electric vehicles thus far suffer from lack of inferior mileage, and slow maximum speed, in contrast to vehicles with fossil fuel. In addition, the abundance of materials is also a critical issue, as LIBs are applied to expanded areas. Therefore, it is important to find a material with high capacity and power performance that is plentiful.

To find materials which fulfill such properties, many candidates have been researched for a long time, such as metal oxide, and alloy materials [1–4]. Among these possible candidates, Si is the most promising material for future LIBs, due to its high specific capacity of around 3580 mAh g<sup>-1</sup>, abundance, and low reacting voltage of around 0.2 V vs. Li/Li<sup>+</sup>, which is favorable for energy density [5–8]. Nevertheless, Si presents several problems, such as low electrical conductivity, large volume change during reaction with lithium, and the resulting pulverization of active material during cycling [9–11]. In more detail, Si reacts with 3.75 Li atoms at room

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temperature during lithiation, resulting in large volume expansion of around 300%. Si repeats the volume expansion and contraction during lithiation and de-lithiation, which leads to pulverization of the Si particles, finally resulting in loss of electric contact with the current collector, and so capacity fading occurs.

Many kinds of approaches have been attempted to overcome these problems, such as nano-sized structures [12–15], coatings [16–18], and matrix-buffered structures [19–21]. It was reported in many researches that nano-sized Si is more favorable to resist fracture [22,23], and coatings on Si could buffer critical volume expansion. These attempts were successful in improving cycle performances, and some products showed good performance, even at relatively high current density. These attempts, however, eventually met difficulties in real application to LIBs, due to the limitations in mass production, and low packing density of nano-materials.

In this work, nano-sized Si embedded in  $\text{Si}_7\text{Ti}_4\text{Ni}_4$  (the complex is abbreviated to STN) was synthesized using the melt-spinning method (Fig. S1), which is a promising technique for mass production. This method has already been used industrially for synthesizing polymer fibers such as nylon or polyester, and promising results for synthesizing amorphous metal fibers and metal alloy fibers have recently been shown [24–26]. The synthesized STN materials were pulverized to micron-sized particles, making it beneficial to the packing density. Research into SiTiNi alloys and its application to lithium ion batteries has already been done [27–30]. These results, however, largely focused on the microstructure dependence on the Si and the Ti content [27,28], and the possibility of SiTiNi alloys being applied to lithium ion batteries [29,30]. On the other hand, in this work, we focus on the investigation of buffer material,  $\text{Si}_7\text{Ti}_4\text{Ni}_4$ , and in depth analysis of the electrochemical performance of STN. The intrinsic properties were measured with various analytic methods, such as transmission electron microscopy (TEM), X-ray diffraction (XRD), and 4-point probe, and the electrochemical activity of the buffer material,  $\text{Si}_7\text{Ti}_4\text{Ni}_4$ , toward lithium was examined with X-ray absorption near-edge structure (XANES). Furthermore, electrochemical performances of STN with various current densities were carried out, and the reasons for STN to show outstanding electrochemical performance were investigated with TEM and electrochemical impedance spectroscopy (EIS), after cycles.

## 2. Experimental

### 2.1. Preparation of materials

STN was synthesized by a melt spinning method from MK electronics. The procedure is as follows: 66 at. % Si, 17 at. % Ti and 17 at. % Ni were melted in a crucible, using an induction heating method. A thin stream of the molten metal was spun onto a rotating Cu wheel, and quenched rapidly ( $10^6 \text{ K s}^{-1}$ ), forming a ribbon. The as-prepared ribbon was pulverized to 8- $\mu\text{m}$  average particle size by ball-milling. Then, the powders were filtered using 325 mesh (Daihan Sci., Korea), to sort out particles above 45  $\mu\text{m}$ .  $\text{Si}_7\text{Ti}_4\text{Ni}_4$ -targeted material was synthesized using similar method: Stoichiometric amount of Si, Ti and Ni (atomic ratio of 7:4:4 respectively) were melted in a crucible by an induction heating method. The resulting molten metal was mixed well, slowly cooled in the crucible, and after cooling, the as-prepared material was pulverized by ball-milling. Nano-Si used was a commercial product from Sigma–Aldrich. Carbon coating on nano-Si was done with dopamine [31,32]. 0.2 g of nano-Si was mixed with 0.15 g of dopamine in 50 ml of Tris-buffer (pH 8.5), and stirred at 30 °C for 25 h. Then, polymer/nano-Si composite was separated by centrifugation, and washed with deionized water. The prepared composite was dried in a vacuum oven, and then carbonized at 400 °C for 2 h under Ar atmosphere. Finally, the material was heat treated at 800 °C for 3 h under Ar atmosphere.

### 2.2. Characterization

The composition and structure of STN were identified with XRD (Rigaku, D-MAX2500-PC) with Cu  $K\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) at 40 kV and 200 mA, and TEM (JEOL JEM-2100F). Before the TEM measurements, the prepared material was sliced to a few hundreds of nanometers thick using a focused-ion beam (FIB), and its microstructure was observed with TEM, and selected area electron diffraction (SAED) pattern.

$\text{Si}_7\text{Ti}_4\text{Ni}_4$ -targeted material with the same stoichiometric ratio as the buffer material was synthesized, and the properties, such as electrical resistivity and electrochemical activity toward lithium, were studied with a 4-point probe with pressure (LORESTA GP MCP T610), and X-ray absorption near-edge structure (XANES). Electrical resistivity of  $\text{Si}_7\text{Ti}_4\text{Ni}_4$ -targeted material was measured with a 4-point probe. The sample holder was filled with  $\text{Si}_7\text{Ti}_4\text{Ni}_4$ -targeted material powder and external pressure was applied to make a good physical connection. The intrinsic electrical resistivity was then measured. The TEM and SAED patterns were measured at the Korea Advanced Nano Fab Center (KANC), the 4-point probe measurements with pressure were performed at the Central Research Institute of Samsung SDI, and XANES was measured at the Pohang Accelerator Laboratory (PAL, 8C-line).

### 2.3. Cell fabrication and electrochemical measurement

82 wt. % STN, 6 wt. % Ketchen Black and 12 wt. % polyamide–imide (PAI) binder were mixed with *N*-methyl-2-pyrrolidone solvent, to form slurry. The prepared slurry was spread onto a copper foil, used as a current collector, using the doctor blade method. To activate the PAI binder, the as-prepared electrode was heat-treated at 350 °C under Ar atmosphere for 90 min, then vacuum-dried at 120 °C for 8 h. The prepared electrodes were transferred to an Ar-filled glove box, and cells were assembled. The electrolyte was 1.5 M  $\text{LiPF}_6$  with EC/DEC/FEC (5/70/25 volume ratio, Panatech Korea), and the separator was from SK Innovation. Lithium metal was used as a counter electrode, and the cell type was 2016.

Electrochemical properties, such as the charge/discharge process with various current densities, were measured with a WBCS3000 cyler (Won-A Tech, Korea). The voltage window for electrochemical measurements was 0.01–1.5 V vs.  $\text{Li/Li}^+$  (all the voltages below are vs.  $\text{Li/Li}^+$ ). Discharge was done in a current density of 400  $\text{mA g}^{-1}$  following a constant voltage of 0.01 V, until the current density had reached 9  $\text{mA g}^{-1}$ , and charge was done galvanostatic with the specified constant current densities. Before the practical cycles above, formation cycles were carried out; discharge with 100  $\text{mA g}^{-1}$  and constant voltage of 0.01 V, until the current density had reached 9  $\text{mA g}^{-1}$ , and charge with 100  $\text{mA g}^{-1}$ . The same process with a current density of 200  $\text{mA g}^{-1}$  was performed.

To measure EIS, a symmetric cell was used to separate the effects from the Lithium metal side; two cells, which were cycled to the same condition, were transferred into an Ar-filled glove box, disassembled, and re-assembled into a symmetric cell. EIS was conducted with open-circuit voltage in 5 mV amplitude, and the frequency range was from 100 kHz to 50 mHz (Zahner, Germany).

## 3. Results and discussion

### 3.1. Characterization of STN

The XRD patterns of STN in Fig. 1 show that STN is composed of Si and  $\text{Si}_7\text{Ti}_4\text{Ni}_4$ . Sharp peaks at  $2\theta = 28.47, 47.34$  and  $56.17^\circ$ , which are assigned to the (111), (220) and (311) of crystalline Si, respectively, reflect that the Si in STN is well crystallized (Si, JCPDS card

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