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Synthesis and electrochemical characterization of anode material with titanium–silicon alloy solid core/nanoporous silicon shell structures for lithium rechargeable batteries

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HIGHLIGHTS

- A Ti–Si alloy is prepared by mechanically milling a mixture containing Si and TiH_2.
- The crystallite size of the Si and silicide phases is tuned by annealing temperature.
- Ti–Si alloy solid core/nanoporous Si shell structure composites are fabricated.
- Core/shell composites with graphite anode show good electrochemical performances.

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ABSTRACT

Composite materials composed of titanium–silicon alloy (Ti–Si alloy) core and porous Si shell (core–shell (C/S) composite) are prepared, and their electrochemical performance as anode materials for lithium-ion batteries is reported. The C/S composites are fabricated by selective etching of the titanium silicide phase in the surface region of a Ti–Si alloy that consists of titanium silicide and Si phases. The Ti–Si alloy is mechanically alloyed (MA) by ball-milling a mixture containing elemental Si and TiH_2. Prior to the etching treatment, some of the MA samples are annealed at temperatures ranging from 600 to 800 °C to further develop the crystalline structure; annealing leads to the increase in the crystallite size of the Si and silicide phases. Thereby, the core and shell structure of the C/S composites and their electrochemical behaviors are controlled. Electrodes prepared by blending the C/S composites with graphite show good cycle performance and rate capability.

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1. Introduction

Recently, much attention has been paid to the development of high-energy-density Li-ion batteries (LIBs) for use in electric vehicles and energy storage. To meet the demand for high energy density, it is necessary to find a suitable anode material to replace conventional graphite. Si and Si-based alloys are known to be promising candidates as anode materials owing to their high theoretical capacity. Despite many efforts over the last decades, their use in LIBs is still limited, due to the severe structural failure of the material caused by large volume changes during charge/

discharge (lithiation/delithiation) cycling. Various approaches for using Si and Si-based alloys, including various synthesis methods and material design strategies, and their current status have been discussed in detail in recently published review papers [1–8]. One approach to overcome the volume change and enhance the cycle life is to introduce a nanoporous structure [9–11]. Nanoporous structures are easily formed by the chemical etching process and the morphology can be controlled. However, although nano-structured electrodes with large surface-to-volume ratios offer a high rate capability, limiting the irreversible capacity caused by the formation of a solid electrolyte interface (SEI) layer and the potential for uncontrolled reaction with thermal runaway are challenges faced in the case of these electrodes [8]. Further, according to a previous report, the calculation of the specific capacity of a Li-ion

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cell as a function of the capacity of the anode material reveals that the maximum specific capacity of Si need not be utilized, and the total cell specific capacity noticeably increases as the anode specific capacity increases up to 1000 mAh g^{-1}, after which improvement becomes negligible [12]. Therefore, in the light of the above issues, a new Si-based anode material needs to be designed and synthesized.

It is suggested that the Si-transition metal alloys are attractive as anode materials because they form Si-nanocomposite structures which contain active Si phase and inactive binary silicides, and the Si-nanocomposites can be easily synthesized by mechanical milling [2]. In Ti–Si system, especially, TiSi$_2$ acts as inactive component to support Si and facilitate charge transport due to its highly conductive character [13].

In this work, we synthesize an anode material having Ti–Si alloy solid core and nanoporous Si shell structure (core–shell (C/S) composite) by etching the surface region of a Ti–Si alloy. The alloy consists of titanium silicide and Si phases, in which the titanium silicide phase is selectively etched to produce a composite particle with a nanoporous Si shell structure. The Ti–Si alloy solid core acts as the conductive skeleton of the composite particle and supports the porous Si shell. The structure, morphology, and electrochemical performance of the C/S composite are investigated.

2. Experimental

A Ti–Si alloy was prepared by mechanically milling a mixture containing elemental Si (325 mesh, 98%) and titanium hydride (TiH$_2$) for 3 h in an Ar atmosphere. Mechanical alloying was performed in a planetary-type mill with a water-cooling system using a vial and balls of hardened steel. The ball to powder weight ratio was 10:1. Several mechanically alloyed (MA) samples were annealed at temperatures ranging from 600 to 800 °C for 1 h under an Ar purge to further develop the crystalline structure. The MA and post-annealed powders were etched for 30 min with a 1 M hydrofluoric acid (HF) solution to obtain C/S composites; the depth of etching was controlled by changing the ratio of Ti–Si alloy weight to etching solution volume as illustrated in Table 1.

The structural evolution of samples was characterized using X-ray diffraction (XRD) with Cu Kα radiation. The particle morphology and cross sectional image were observed using field emission scanning electron microscopy (FE-SEM). Elemental mapping was performed through energy-dispersive X-ray spectroscopy (EDX). The specific surface area of the porous samples was determined using the Brunauer–Emmett–Teller (BET) method.

For evaluating the electrochemical performance of the nanostructured composite, two types of electrodes were fabricated: The Type I electrode was composed of the C/S composite, a conductive additive, and a binder, while the Type II electrode was composed of the C/S composite and graphite as active material, a conductive additive, and a binder. An aqueous slurry containing 80 wt% active material, 5 wt% carbon black, and 15 wt% poly(acrylic acid) binder was pasted onto a 20 μm thick copper foil, dried under vacuum at 180 °C for 12 h, and subsequently pressed. Coin cells with a working electrode and Li foil counter electrode were assembled in an Ar-filled glove-box using 1 M solution of LiPF$_6$ in a mixture of ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 by volume)

Table 1
Etching conditions for preparation of C/S composites.

	Etching conditions
E1	2 g Ti–Si alloy/100 mL 1 M HF solution
E2	1.5 g Ti–Si alloy/100 mL 1 M HF solution

with 10% fluoroethylene carbonate (FEC). The cells were charged (lithiated) and discharged (delithiated) between 0.02 and 1.5 V at 30 °C. To determine the capacity and initial Coulombic efficiency, the cells were charged in a constant current–constant voltage (CC–CV) mode with a constant current of 100 mA g^{-1} and a constant voltage of 0.02 V, until the current tapered down to 10 mA g^{-1}, and then, the cells were discharged at a constant current of 100 mA g^{-1} for the first two cycles, and thereafter cycled in CC mode at 100 mA g^{-1}. The rate capability of the blended electrodes was investigated with various C-rates. The C-rate was estimated in terms of the reversible capacity measured in the CC–CV mode for the first two cycles.

3. Results and discussion

The MA sample consists of two phases: Si and the metastable silicide (U-phase). When annealed at 800 °C, the U-phase is transformed to the TiSi$_2$ phase, as previously reported [14]. Chemical etching of MA and post-annealed powder samples generates the porous Si shell with three-dimensional channels by removing the silicide phases; the etching is performed using the two different conditions listed in Table 1. The sample etched under condition E1 and E2 is denoted as MAE1 and MAE2, respectively. As the amount of the silicide phase removed from the MA sample using condition E2 is greater than that removed using E1, MAE2 exhibits a more intense diffraction peak of crystalline Si compared to MAE1. Cross-sectional SEM images (Fig. 1(a) and (b)) show that the silicide phase is selectively etched, resulting in a structure with the Ti–Si alloy solid core and porous Si shell, and the depth of the etching is controlled by adjusting the Ti–Si alloy mass for a given etching solution volume, as listed in Table 1. It appears that the depth of the etching is not affected by the size of MA powder particles (data not shown here). As expected, the sample shows more reversible capacity as an anode for LIBs with increased etching. The obtained reversible capacity values of MAE1 and MAE2 are 1032 mAh g^{-1} and 1447 mAh g^{-1}, respectively.

The structure of the porous Si plays a significant role in determining the transport behavior of Li ions and accommodates the volume change during charge/discharge cycling [9,11]. Annealing of the MA sample leads to the increase in crystallite size of the Si and silicide phases, allowing the structure of porous Si to be tuned. After annealing at 600, 700, and 800 °C, the MA sample was etched under condition E1; these samples are denoted as MAE600, MAE700, and MAE800, respectively. The cross-sectional SEM images of the etched samples are shown in Fig. 2; the porous structure becomes rough and the size of pores and Si phase increase as the annealing temperature increases. N$_2$ adsorption–desorption isotherms are employed to determine the surface area and porous structure of MAE1, MAE600, MAE700, and MAE800; all samples exhibit a type IV isotherm originating from the mesopores and macro-pores (Fig. 3a) [15]. Further, it can be observed that MAE1 has more meso- and macro-pores than the pre-annealed samples MAE600, MAE700, and MAE800. As the pre-annealing temperature increases, the meso- and macro-pores gradually diminish. Accordingly, the surface area measured by BET decreased with the increase in the pre-annealing temperature (Table 2). The pore size distribution, shown in Fig. 3b, reveals that the average pore size in the MA sample is 15 nm and that the pore size increases with increasing pre-annealing temperature, particularly in the case of annealing at 800 °C (MAE800) where almost no pores with sizes below 100 nm are observed.

The charge and discharge profiles are obtained to investigate the electrochemical behaviors of MAE1, MAE600, MAE700, and MAE800 (Fig. 4a–d). Annealing before etching treatment leads to an increase in the initial coulombic efficiency due to a declining BET