



Nanocrystalline silicon embedded in an alloy matrix as an anode material for high energy density lithium-ion batteries



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HIGHLIGHTS

- Si alloy comprising Si nanoparticles embedded in the inert matrix is synthesized.
- It delivers a high initial discharge capacity with good cycling stability.
- As compared to pure Si, the Si alloy material shows superior cycling performance.
- Si alloy can be a promising anode material for high performance lithium-ion battery.

ARTICLE INFO

Keywords:

Silicon alloy
Inactive matrix
Anode material
Lithium-ion battery
Cycling performance

ABSTRACT

The development of electrode materials with high capacity and good cycling stability is a challenging prerequisite for improving the energy density of lithium-ion batteries. In this work, we synthesize silicon nanoparticles embedded in the inactive Al_4Cu_9 , AlFe and TiFeSi_2 matrix phases, as an anode material. The silicon alloy material exhibits good high rate performance and delivers a high initial discharge capacity of $1459.3 \text{ mAh g}^{-1}$ with capacity retention of 85.7% after 200 cycles at a current density of 300 mA g^{-1} . The superior cycling performance of the silicon alloy compared to that of micro-sized pure silicon can be attributed to the unique structure of the alloy material. Here, the nano-sized silicon particles reduce the ionic diffusion path length and minimize volume expansion during lithiation, while the inactive matrix phases accommodate volume changes during repeated cycling and provide a continuous electronic conduction pathway to the silicon nanoparticles.

1. Introduction

The rapidly growing demand for portable electronic devices, electric vehicles and large-scale energy storage systems is driving further development of electrode materials for rechargeable lithium-ion batteries with high energy density and long cycle life [1–3]. For this application, silicon has been considered a promising anode material due to its high theoretical capacity, low reduction potential, environmental friendliness and low cost [4–9]. Despite its high potential as an anode material, the implementation of Si-based anodes has been challenging due to the detrimental electrode pulverization resulting from large volume changes and the instability of the solid electrolyte interphase (SEI) layer formed on the electrode surface during cycling, which results in rapid capacity fading upon cycling [10,11]. The mechanical stress induced by repetitive volume changes causes electrode cracking and pulverization, and thus results in poor electrical contact between the active materials,

electronic conductors and the current collector. Various approaches have been adopted to address these issues, including synthesis of nano-sized Si materials with various morphologies [12–15], alloying with inert metals [16–20], utilizing highly adhesive and self-healing polymer binder materials [21–25] and embedding silicon in conductive carbon [26–28]. In particular, considerable improvement in cycling performance could be achieved in silicon alloy materials comprised of active Si and inert metal matrix. The inert metal phases should be electronically conductive and be able to endure the mechanical stresses arising from the volume expansion of Si particles during lithiation. To meet the above requirements, soft materials have usually been employed as inert matrix materials. Hard materials can also withstand the stresses applied during lithiation of silicon nanoparticles [29,30]. Thus, we sought to employ both soft and hard materials as inert metal phases when embedding nanocrystalline Si particles in the matrix of the alloy.

In this work, we synthesized a silicon alloy material with an inert

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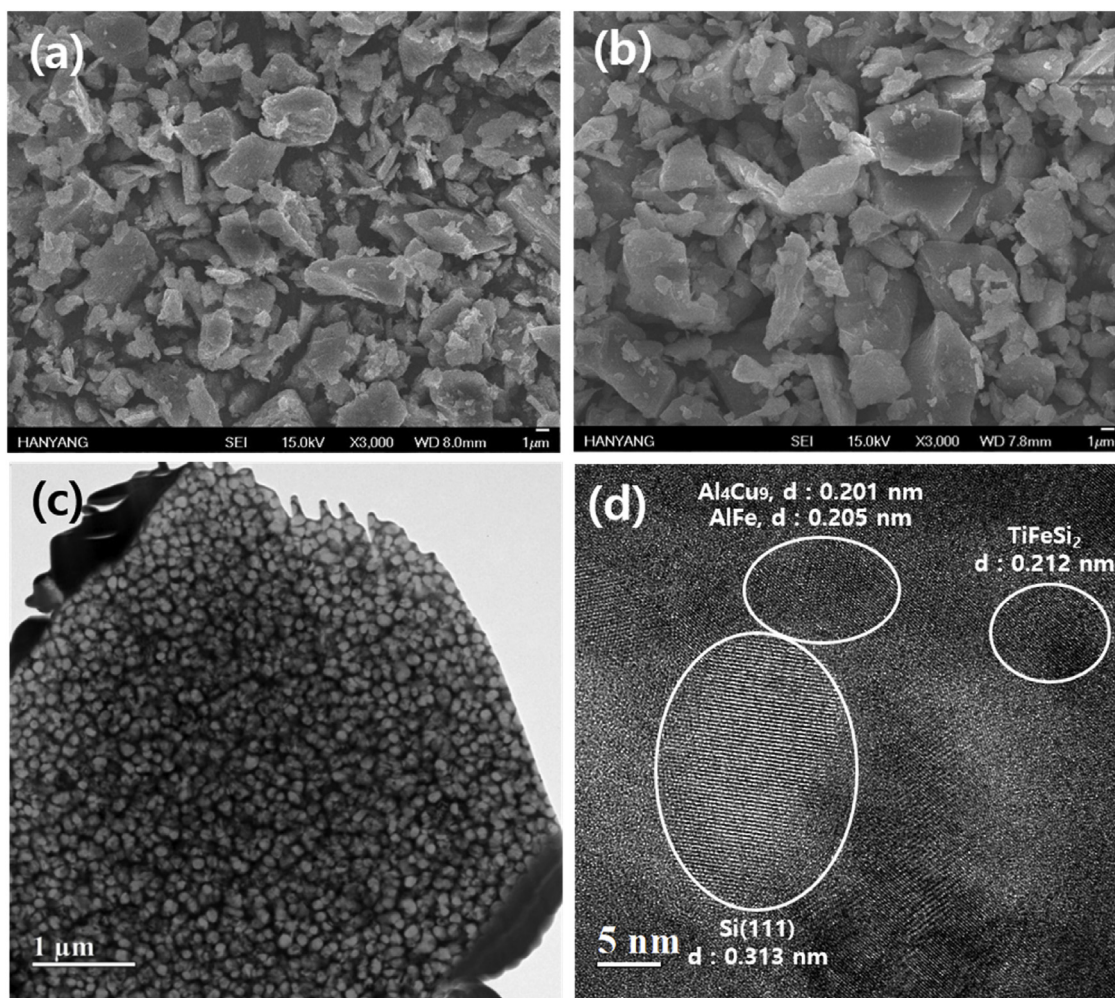


Fig. 1. SEM images of (a) Si alloy and (b) pure Si particles. (c) FIB-TEM and (d) HR-TEM images of Si alloy particle.

matrix composed of a hard metal phase (TiFeSi_2) and soft metal phases (Al_4Cu_9 and AlFe). During repeated cycling, the inert matrix phase provided a continuous electronic conduction pathway and accommodated volume expansion during cycling, while the nano-sized silicon particles minimized mechanical stress generated during cycling and improved reaction kinetics due to the short diffusion pathway. As a result, the silicon alloy electrode exhibited a high initial discharge capacity with good cycling stability and significantly enhanced rate capability compared to pure silicon particles of a similar size and shape.

2. Experimental

2.1. Synthesis of Si alloy material

Silicon alloy was synthesized using arc melting followed by the single roll solidification method. The metal components used for the silicon alloy material were Si (60 at%), Cu (15 at%), Al (10 at%), Fe (7.5 at%) and Ti (7.5 at%). Copper, aluminum and iron metals were chosen as the inactive components due to their low cost and wide availability. Titanium was included for its high electronic conductivity and favorable alloy reaction with iron and silicon. An alloy button was obtained by arc melting in a Cu hearth using a non-consumable tungsten electrode under an argon atmosphere. The button was re-melted three times to ensure uniform distribution of all of the components in the alloy. Ribbons were produced by a graphite nozzle single-roll method under an inert atmosphere to prevent oxidation. The ribbons obtained were mechanically crushed into Si alloy powders in an

attrition mill at a rotating speed of 150 rpm with zirconia beads.

2.2. Electrode preparation and cell assembly

Si alloy electrode was prepared by coating an N-methyl-2-pyrrolidone (NMP)-based slurry containing Si alloy, Ketjen black, and poly (amine imide) (HV 4000 T, Solvay) binder at a weight ratio of 86.6:3.4:10 onto Cu foil using a doctor blade. The cast electrode was dried at 90 °C for 1 h to remove the NMP solvent. To thermally cure poly (amide imide) and achieve strong interfacial binding, the dried electrode was further thermally treated at 400 °C for 1 h under Ar atmosphere [24]. As a control sample, micro-sized pure Si particle purchased from Sigma-Aldrich (325 mesh, 99% trace metals basis) was used to prepare a Si electrode using the same procedure. A CR2032-type coin cell was assembled by sandwiching a polyethylene separator (Asahi ND420, 20 μm) between a lithium metal (Honjo Metal Co. Ltd., 200- μm -thick) and a Si alloy electrode. The cell was injected with liquid electrolyte comprised of 1.15 M LiPF_6 in ethylene carbonate (EC)/ethylmethyl carbonate (EMC)/diethyl carbonate (DEC) (3:5:2 by volume, battery grade, PANEX ETAC Co., Ltd.) containing 5 wt.% fluor-ethylene carbonate and 2 wt.% vinylene carbonate. All cells were assembled in an Ar-filled glove box.

2.3. Characterization and measurements

The surface and cross-sectional morphologies of the samples were characterized by field emission scanning electron microscopy (FE-SEM,

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