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Characterizations and electrochemical behaviors of milled Si with a degree of amorphization and its composite for Li-ion batteries

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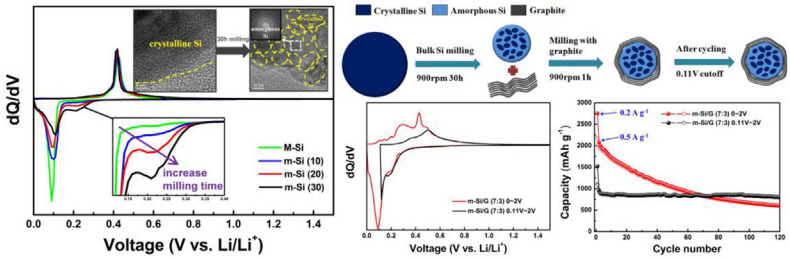
HIGHLIGHTS

- Electrochemical behaviors of milled Si are characterized with a degree of amorphization.
- Unlike crystallite Si, partially amorphous Si starts to react with Li near 0.32 V.
- Graphite is coated onto the milled Si using a simple milling process.
- The m-Si/graphite composite with 0.11 V cut-off shows a good cycle performance with 800 mAh g^{-1} over 120 cycles.

GRAPHICAL ABSTRACT



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ABSTRACT

Electrochemical behaviors of milled Si using high energy mechanical milling (HEMM) process are characterized with a degree of amorphization. The amount of amorphous Si increases with milling time, and Si crystallites are embedded in the amorphous Si matrix. Unlike crystallite Si, partially amorphous Si starts to react with Li near 0.32 V. An intermediate LiSi phase is identified at 0.17 V during the first discharge of amorphous Si with Li. The milled Si/graphite (m-Si/G) composite prepared by using the simple HEMM process shows excellent electrochemical performance with a reversible capacity of 800 mAh g^{-1} at a rate of 0.5 A g^{-1} when cycled between 0.11 and 2.0 V.

1. Introduction

Rechargeable Li batteries with high energy capacity and long cycle life have received much attention for use in portable electronic devices, electric vehicles and implantable medical devices [1–4]. Si is an attractive anode material for Li secondary batteries because it has a low discharge potential and the highest known theoretical charge capacity (~4200 mAh g^{-1}) [5]. However, a large volume change (>300%) during Li alloying and dealloying can pulverize Si particles and electrically disconnect from the current collector [6]. To overcome these problems, several approaches have been suggested, including the preparation of nano active materials [6–11], active/inactive composite materials [12–14] and Si-based carbon composites [14–19]. These approaches have improved the electrochemical performance of Si-based anodes.

Among the Si based materials, amorphous Si (a-Si) shows better cycling performance than crystalline Si (c-Si) because the stress intensification due to anisotropic volume expansion of c-Si results in significantly increased tensile stress values along the <110> direction compared to the isotropic expansion of a-Si case [20–24].

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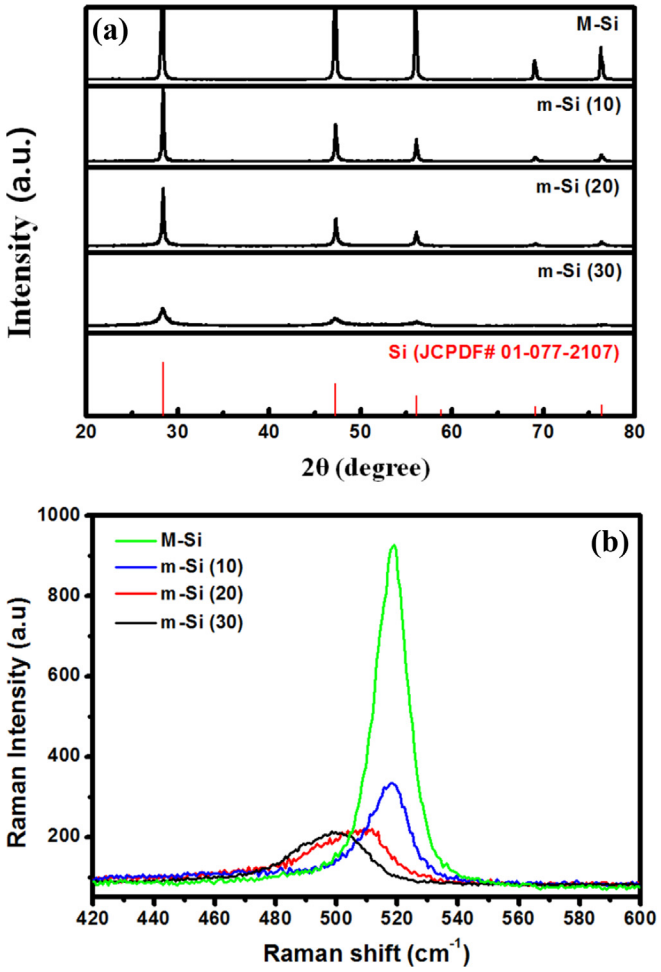

Fig. 1. (a) XRD patterns and (b) Raman spectra of M-Si, m-Si(10), m-Si(20) and m-Si(30) powders.

However, most of the methods for producing a-Si powder or film have relied upon a high cost synthesis process, namely chemical vapor deposition (CVD) [25–27]. a-Si can also be prepared by the high energy mechanical milling (HEMM) method, which decrease the particle size to produce a large amount of Si at one time [24,28]. Although Cui et al. showed that a-Si reacted with Li at a slightly higher potential than c-Si [29], electrochemical behaviors of a-Si using HEMM process have not been investigated fully. Such a comprehensive investigation would be important for designing Si based composites.

In this study, we investigate the degree of amorphization of milled Si for various milling times, and study the electrochemical behaviors of milled Si samples systematically. Based on the characteristics of milled Si, a milled-Si/graphite (m-Si/G) composite is prepared using simple HEMM, in which a few graphite layers are coated on the Si surface [30]. Since c-Si starts to react with Li below 0.11 V [31], the m-Si/G composite is tested as an anode between 2 and 0.11 V to investigate the electrochemical behavior of a-Si. Also previous studies have shown that the cycling life of a Si anode can be significantly improved by limiting the amount of Li that reacts with c-Si [29,32–34]. This approach, HEMM, would be attractive for practical applications because the starting materials and the synthetic processes are viable for large-scale production.

2. Experimental

2.1. Material preparation

Pure amorphous Si particles are not available commercially, and micron-size Si (M-Si) powder (Kosundo, 99%, 4 μm) was milled under Ar atmosphere using HEMM (Spex mill, 900 rpm) for various times (10, 20 and 30 h). Samples were referred to as m-Si (x), where (x) indicates the milling time. For the m-Si/G composite, m-Si (30) and graphite powders (MCMB, 10 μm) (7:3, by weight) were put into a 80 cm^3 hardened steel vial with stainless steel balls at a ball-to-powder ratio of 20:1. The HEMM process was conducted under Ar atmosphere for 1 h.

2.2. Materials characterization

All of the samples were examined using X-ray diffraction techniques (XRD, Rigaku, D-MAX2500) and Raman Spectrometer (HORIABA JobinYvon, T64000). A scanning electron microscope (SEM, JEOL, JSM-5600) was employed to observe the particle size of the milled Si samples, and high resolution transmission electron microscopy (HRTEM, JEOL, 3000F) analyses also were carried out to

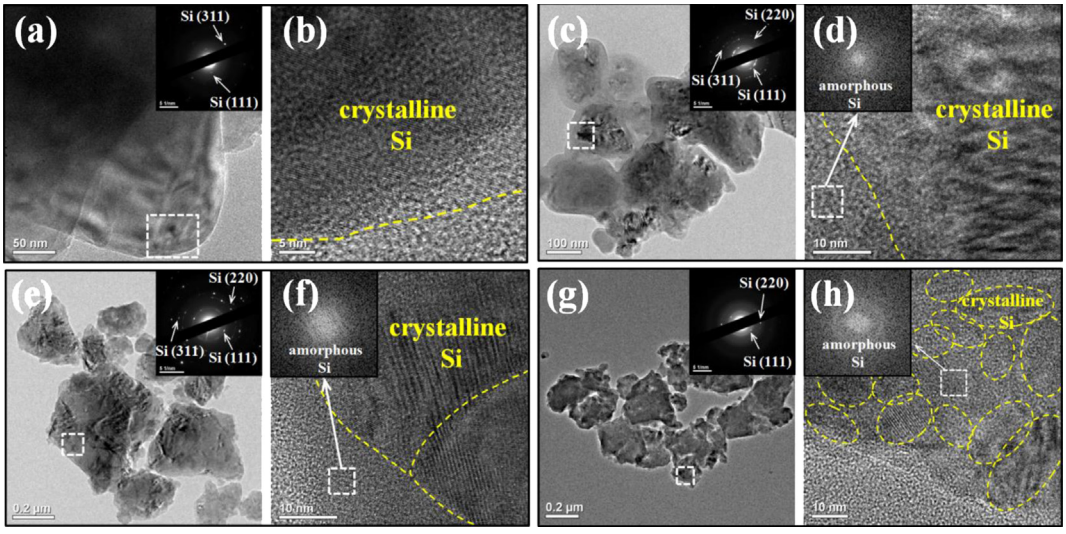

Fig. 2. Bright Field TEM image with SAED patterns and HRTEM images with FFT of (a,b): M-Si, (c,d): m-Si(10), (e,f): m-Si(20) and (g,h): m-Si (30).