Preparation of three-dimensional nanoporous Si using dealloying by metallic melt and application as a lithium-ion rechargeable battery negative electrode

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HIGHLIGHTS

- Nanoporous interconnected Si was prepared by dealloying in metallic melt.
- Nanoporous Si electrodes outperform in capacity and rate characteristics.
- Nanoporous Si has high electrical conductivity.
- Nanoporous Si-based electrodes accommodate expansion of Si upon lithiation.

GRAPHICAL ABSTRACT
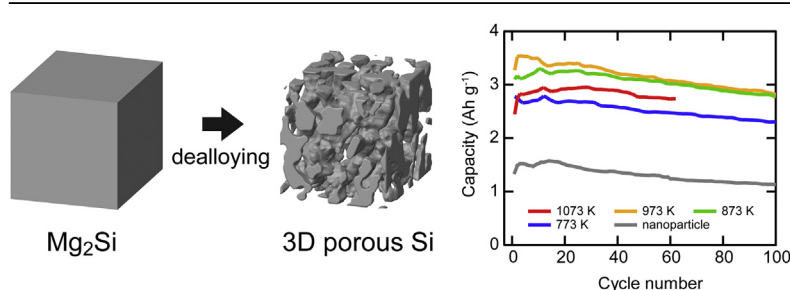
ABSTRACT

Silicon is a promising material for negative electrode in Li-ion batteries because of high gravimetric capacity. A Si nanomaterial that can accommodate volume expansion accompanied by lithiation is needed for practical application in Li-ion batteries. We prepare three-dimensional nanoporous interconnected silicon material with controlled pore and ligament sizes by dealloying using an Mg–Si precursor and Bi melt. The Mg atoms in the precursor selectively dissolve into Bi, and the remaining Si atoms self-organize into a nanoporous structure with characteristic length ranging from several ten to hundred nanometer. The Li-ion battery electrodes made from nanoporous silicon exhibit higher capacities, increased cycle lives, and improved rate performances compared with those made from commercial Si nanoparticles. Measurements on the electrical resistivity and electrode thickness change by lithiation/delithiation suggest that the superior performance of nanoporous Si electrode originates from the following: (1) The nanoporous Si has much lower electrical resistivity compared with that of the nanoparticle Si owing to the n-type dopant incorporated during dealloying. (2) The nanoporous Si-based electrode has higher porosity owing to the presence of intra-particle pores, which can accommodate Si expansion up to higher levels of lithiation.

1. Introduction

The development of Li-ion batteries (LIBs) with a high capacity, low capacity fade, and high operation rate is of great technological importance for application in portable electric devices and electrical vehicles [1]. Si is drawing increasing attention as an active

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material for the negative electrode of LIBs because it has a theoretical Li capacity of 3579 mAh g^{-1} at room temperature, which is about 10 times that of the currently used graphite electrode [2]. However, Si electrodes suffer from a volume expansion of 280% with Li insertion [3]. This large volume change pulverizes Si while the conductive network between the active material and the current collector is lost, rapidly degrading the cyclic performance [4]. To overcome these issues, researchers have reported applying nanostructured Si, including nanoparticle [5–7], thin film [8,9], nanowire [10–13], nanotube [14,15], hollow nanoparticle [16–18] and three dimensional (3D) nanoporous [19–28] structures, because they exhibit higher pulverization resistance than the large sized Si [29]. Among those nanostructured Si, the nanoporous Si (NP–Si) with interconnected pores is one of the most promising active materials because the many open channels in this structure act as ideal volume expansion buffers [19–28]. In addition, the large surface area in this structure is favorable for rapid Li insertion/extraction reactions. With regard to these advantages, the processing of NP–Si and its application as LIBs have been extensively studied. For example, Kim et al. reported the formation of 3D NP–Si by annealing and etching the mixture of Si gels and SiO$_2$ nanoparticles [19]. Magasinski and coworkers fabricated NP–Si composites by deposing Si nanoparticles onto an annealed carbon black template [20]. The preparation of nanoscale interconnected Si had also been attempted via a disproportionation reaction of SiO [21]. Recent research interests focus on the large-scale synthesis of NP–Si through a simple and low-cost route, e.g. etching Si with HF-based solutions [22–24], magnesiothermic reduction of silica [25], air-oxidation demagnesiation of Mg$_2$Si [26] and etching of Al–Si [27] or Fe–Si [28] dual phase alloys. These NP–Si materials have been demonstrated to exhibit excellent LIB performance in capacity and cycle life.

Recently, we have developed a novel dealloying method using a metallic melt for preparing NP–Si [30]. Dealloying is attracting attention because it provides 3D nanoporous metals by a simple route [31]. Dealloying, which commonly occurs in aqueous solution, is a selective leaching of less noble element(s) from a multicomponent precursor. The less noble element in the precursor is ionized (oxidized) and dissolved in aqueous solution, and the noble atoms left behind self-organize into a nanoporous structure by diffusion [32]. Dealloying has provided fine homogeneous 3D nanostructures in noble metals such as Au, Pt, and Cu [33–35]. However, it has not provided a nanoporous structure in less noble metals, including Si, because of their low stability against oxidation. Dealloying in metallic melt has overcome this limitation [36–39]. In metallic melt, selective dissolution can be induced using the miscibility of elements. For instance, A is immiscible in C, and B is miscible in C. By immersing an A–B solid in C melt, only B dissolves into the C melt and nanoporous A can be obtained. This phenomenon is physically equivalent to dealloying in aqueous solution, but is different because the dissolution of the element is not induced by the oxidization of metals. Therefore, this process is independent on the stability against oxidization (namely, the electrode potential of metal), and nanoporous structures can form. We have succeeded in preparing 3D NP–Si and showed that LIB electrodes exhibited improved capacity, cycle life, and rate properties compared with those made from commercial nanoparticle Si [30]. However, the mechanisms responsible for such improvements have not been fully understood yet.

In the present work, we discuss the preparation of NP–Si by dealloying in metallic melt. The effects of dealloying condition on porous structure and electrical properties of NP–Si are investigated. The capacity retention, cycle life, and rate properties of the different NP–Si-based LIB electrode are compared. In addition, the electrode volume change during lithiation/delithiation was measured *in-situ* to understand the relationship between volume accommodation by the pores and battery performance. The origin of high capacity, increased cycle life, and high rate operation in the dealloyed NP–Si based LIB electrodes is discussed.

2. Experimental

2.1. Nanoporous silicon preparation and characterization

NP–Si was prepared by immersing Mg–Si alloy compound precursor into a Bi melt. An ingot with the composition of Mg$_{72}$Si$_{28}$ (at.%) alloy was prepared by induction melting the pure Mg (99.9 mass %) and pure Si (99.99 mass %) in a boron nitride crucible under He gas atmosphere. The ingot was ground into a powder with a diameter less than 100 μm. Two gram of Mg$_{72}$Si$_{28}$ powder was immersed into a Bi melt of 150 g and held for 15 min at 773, 873, 973 and 1073 K, respectively. During immersion, the Bi melt was stirred by blowing He gas to enhance the interface reaction between precursor and melt. After immersion, the reaction product was collected and washed with 1 M nitric acid followed by drying at 393 K for 2 h in air. The phase of the product was identified by X-ray diffraction with Cu-Kα radiation (XRD; Bruker D8 Advance, Yokohama, Japan). Microstructures were observed by scanning electron microscopy (SEM; Zeiss Ultra55, Jena, Germany) and a focused ion beam system (FIB, SMI3050SE; SII, Chiba, Japan). The Porosity, average pore and ligament width, and surface area were calculated from a cross-sectional image using Image J. The electrical resistivity of a compressed NP–Si powder was measured by the four-probe method with an applied pressure up to 63 MPa (MCP-PD51; Mitsubishi Chemical Analytech, Kanagawa, Japan). The type of carrier in the Si was identified from the thermoelectric power measurement (hot-probe method) using the plate shape compressed NP–Si powder. One end of the sample was heated using a soldering iron, while the other end was kept room temperature. The thermoelectric voltage generated in the sample was measured by a standard voltmeter. The chemical composition was analyzed by the inductively coupled plasma optical emission spectrometry (ICP-OES, Thermo Fisher Scientific, IRIS Advantage DUO, Massachusetts, USA).

2.2. Electrochemical characterization

A strong PI binder is usually applied to suppress the volume change of Si-based electrode and improve its cyclic property [40]. In this work, a high strength type PI binder (U-Varnish-A, Ube industry, Tokyo, Japan) was used which needs annealing at 723 K for solidification. A slurry composed of NP–Si, acetylene black (AB; Denka, Tokyo, Japan) as the conductive additive, and polyamic acid as the precursor of PI binder was prepared by stirring at 500 rpm for 1 h with an appropriate amount of the N-methylpyrrolidone (NMP; Kishida Chemical, Osaka, Japan) addition. After a series of tentative experiments on the NP–Si electrodes with various compositions, the composition of NP–Si:AB:PI = 60:25:15 was found to be the optimum in achieving high capacity and retention rate, and thus being adopted in the present work. The slurry was then coated onto a Cu-foil current collector using a doctor blade coating machine. The electrode was pre-heated at 393 K for 10 min to evaporate NMP, followed by heating at 723 K for 1 h for the imidization of the binder. The resulting electrode has an active material layer with a mass loading from 0.5 to 0.6 mg cm^{-2}, and a thickness of approximately 10 μm. The electrode was punched into a circular shape with an area of 1.0 cm^2. For comparison, commercial nanoparticle Si with a diameter of about 100 nm (Alfa Aesar, Lancashire, UK) was used to prepare an electrode via the same procedure. A 2032-type coin cell was assembled in an argon filled glove box with a moisture content less than 1 ppm using the NP–Si as working