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On-site fabrication and charge–discharge property of TiO_2 coated porous silicon electrode by the liquid phase deposition with anodic oxidation

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ABSTRACT

TiO_2/porous Si (PSi) nanocomposites were fabricated by liquid-phase deposition with anodization of PSi. Scanning electron microscopy-energy-dispersive X-ray spectroscopy showed that TiO_2 was only deposited in the fine pores of anodized PSi (ca. 7.4 nm) when the PSi surface was anodized in the presence of Ti ions as F^- scavengers. The TiO_2/PSi nanocomposites were fabricated by anodization of PSi in a H_2TiF_6 electrolyte at a constant potential. The amount of Ti deposited was maximum at 300 mV vs. Ag/AgCl electrode, and the deposition process was controlled by varying the applied potential for PSi anodization. The charge/discharge capacities of the fabricated TiO_2/PSi nanocomposites as Li-ion battery anodes were determined. Improvements in the charge/discharge capacity were achieved by improving the PSi wettability by TiO_2 deposition and activation of Si on the surface of the anodized PSi fine pores. TiO_2/PSi fabricated by anodization maintained a high charge/discharge capacity without rapid degradation, because SiO_2, which causes rapid degradation of the charge/discharge capacity, was reduced by Li metal.

1. Introduction

Porous Si (PSi) can be fabricated by anodization of Si with etching solutions [1–3], and by stain etching [4,5] and metal-assisted chemical etching [6–8]. PSi can be also fabricated by anodization of Si wafers in HF aqueous solution. The fabrication of PSi by anodization is controllable by the current density [9,10] and changing the type and concentration of dopant in the Si wafer, the HF_2^- concentration in the etching solution, and the anodization current density, enabling the formation of nanopores and mesopores with various diameters. The liquid-phase deposition (LPD) method involves two types of reaction in solutions, based on the short mean-free-paths of the molecules [11–14]. The LPD is therefore very effective for the deposition of various metal oxides on the surfaces of substrates and in submicron pores. In this work, the deposition of TiO_2 in fine pores in anodized PSi was performed using the LPD. In this process, both SiO_2, which is generated by thermal oxidation of the PSi substrate, and the Si surface at the anodic potential, acted as F^- scavengers. The anodization of PSi with the LPD is expected to be a suitable approach for the fabrication of TiO_2/PSi nanocomposites. In this study, various TiO_2/PSi nanocomposites were fabricated by the LPD using various F^- scavengers, i.e., boric acid, the oxidized PSi surface, and the Si surface at the anodic potential. These TiO_2/PSi nanocomposites prepared by the LPD will be useful for Li-ion battery (LIB) anodes. TiO_2 reacts with Li ions to form a Li composite metal oxide as follows:

$$TiO_2 + xLi^+ + xe^- \leftrightarrow Li_xTiO_2 \qquad (1)$$

When a TiO_2 electrode is used as the LIB anode, the theoretical capacity is 170 mA h g^{-1} and the operating voltage is 1.75 V vs. Li/Li^+ [15,16], so the TiO_2 electrode is inferior to a graphite electrode (372 mA h g^{-1}) in terms of capacity and energy density. However, TiO_2 can absorb Li with slight volume expansion; therefore TiO_2 can be used as an anode material with a satisfactory cycling performance and safety [17,18]. In this work, we attempted to deposit TiO_2 on PSi, which has low resistivity, i.e., 3.0–4.0 mΩ cm, by the LPD to fabricate TiO_2/PSi nanocomposites. Fabricated TiO_2/PSi nanocomposites prepared the LPD in the presence of various F^- scavengers had fine pores derived from the PSi substrate, and TiO_2 coated part of the surfaces of the fine pores in PSi. The Si substrate

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provided the active material for a LIB anode when the fabricated TiO_2/PSi nanocomposites were used as electrodes:

$$Si + 4.4Li^{+} + 4.4e^{-} \leftrightarrow Li_{4.4}Si \quad (2)$$

One Si atom can theoretically absorb 4.4 Li atoms when Si is used as a LIB anode material; therefore the theoretical capacity of Si is very large (ca. 4200 mA h g^{-1}). Moreover, the operating voltage of Si is 0.0–0.4 V vs. Li/Li^{+} [19–22], which is relatively close to that of a Li electrode, and therefore a high energy density is expected. The use of PSi instead of a Si wafer should provide an electrode with superior high-speed charge/discharge characteristics and capacity, because of the large surface area of PSi. However, PSi has high hydrophobicity because of the lotus effect [23], derived from its fine structure and hydrophobic terminal groups. This suggests that Si in porous layers is not suitable as an active material and may cause a low initial charge/discharge capacity. The deposition of TiO_2 on the surfaces of PSi fine pores is an effective method of overcoming this disadvantage; TiO_2 is a superhydrophilic material [15–18,24] and a useful Li-storage material, and therefore the effective surface area of PSi for use as an electrode will be increased by TiO_2 deposition. In this work, a novel LPD method in which the F^{-} scavenger was not boric acid, but the oxidized PSi surface or Si surface at the anodic potential, was developed for the fabrication of TiO_2/PSi nanocomposites. The TiO_2/PSi nanocomposites were used as LIB anodes, and the charge/discharge performances were evaluated using half-cell electrochemical measurements.

2. Experimental

2.1. Fabrication of porous Si

All chemicals used in this work were of analytical grade. A highly boron-doped p-type single-crystal (100) Si wafer, which was purchased from the Shin-Etsu Astech Co., Ltd. (Tokyo, Japan), was used as a working electrode. The thickness and resistivity of the Si wafer were 625 ± 25 mm and 3.0–4.0 mΩ cm, respectively. The Si wafer was cut into pieces of area 2×2 cm^2 with a diamond cutter, dipped in acetone and degreased ultrasonically for 15 min, removed from the acetone, and dried at room temperature. An electrochemical cell was prepared in a Teflon® vessel as follows. A Si wafer working electrode and platinum mesh counter electrode were fixed in the electrochemical cell. Then 5 wt% HF aqueous solution was poured into the cell, and removed after 5 min. A mixture of HF/H_2O/EtOH was then poured into the cell. The electrochemical cell filled with the electrolyte solution was left in a dark room at room temperature, and anodic oxidation of the Si electrode was performed under galvanostatic conditions of 60 mA cm^{-2} for 10 min. The electrolyte solution was removed after the anodic oxidation, and the anodized Si electrode was rinsed with deionized distilled water and methanol, and dried in an Ar atmosphere at room temperature. The surface morphology of the anodized PSi was observed using field-emission scanning electron microscopy (FE-SEM; JEOL Co., Ltd. (Tokyo, Japan), JEM6335F), and the surface area and the pore size distribution were determined from N_2 adsorption isotherms (Quantachrome Instruments Co., Ltd. (Florida, United States), NOVA 2200e).

2.2. TiO_2 deposition on Si wafer and PSi by the liquid-phase deposition, with anodized Si as F^{-} scavenger

The Si wafer or PSi working electrode, platinum mesh counter electrode, Ag/AgCl reference electrode, and a salt bridge were fixed in a three-electrode electrochemical cell; H_2TiF_6/H_2O/EtOH solution was used as the electrolyte. The electrode–electrolyte contact area was about 1.65 cm^2. The Si working electrode was anodized in the electrolyte at a constant potential from 0 to 550 mV vs. the Ag/AgCl electrode; anodization was performed for 30 min at room temperature. After anodization, the working electrode was removed from the electrolyte solution and rinsed with deionized distilled water and methanol, and dried in an Ar atmosphere at room temperature. The TiO_2 thin film on the Si wafer was characterized using FE-SEM, X-ray diffraction (Rigaku Co., Ltd. (Tokyo, Japan), RINT-TTR/S2), and Fourier-transform infrared (FT-IR) spectroscopy (Jasco Co., Ltd. (Tokyo, Japan), FT-IR 615R). The surface area was measured using the multipoint Brunauer–Emmett–Teller (BET) method (Quantachrome Instruments Co., Ltd. (Florida, United States), NOVA 2200e) and the amount of Ti deposited was quantified using inductively coupled plasma atomic emission spectroscopy (Horiba Co., Ltd. (Kyoto, Japan), Ultima 2000).

2.3. Evaluation of electrochemical properties as lithium-ion battery anode

Li ribbon immersed in hexane was purchased from the Sigma-Aldrich Co., LLC (Missouri, United States). The ribbon was cut into rectangles of area 1×2 cm^2, rinsed with 1.0 mol L^{-1} $LiClO_4$–EC/DEC (1:1) solution, and used as anodes for LIBs. The effective reaction area of electrode is equal to the electrode–electrolyte contact area, i.e., about 1.65 cm^2 as described in Section 2.2. The as-prepared PSi was thermally oxidized at 300 °C for 4 min in air [25] in a muffle furnace (Koyo Thermo Systems Co., Ltd. (Nara, Japan)), and was used as an electrode for reference measurements. Cyclic voltammetry (CV) was performed to confirm the potential response between the electrode and Li ions in the potential region 0–3.0 V vs. Li/Li^{+} at a sweep rate of 0.5 mV s^{-1}, using a CompactStat instrument (Ivium Technologies Co., Ltd. (Florida, United States)) The charge/discharge capacity of each anode was evaluated as follows. Charging and discharging were performed at 500 μA and repeated at most 15 times; the cutoff voltage was set at 0.01–3.50 V vs. Li/Li^{+}. The anode samples were removed at arbitrary charge/discharge cycle numbers, rinsed with methanol, and dried in an Ar atmosphere. The effects on the morphology and surface oxidation state of the fabricated TiO_2/PSi nanocomposites of repeated charging/discharging were observed using FE-SEM and X-ray photoelectron spectroscopy (XPS; JEOL Co., Ltd. (Tokyo, Japan), JPS-9010MC), respectively.

3. Results and discussion

3.1. Fabrication of TiO_2/PSi nanocomposites by the liquid-phase deposition method

Si wafers were successfully anodized in HF/H_2O/EtOH solution at a constant current of 60 mA cm^{-2} for 10 min, as shown in Fig. S1. The average depth and diameter of the formed pores were 27.7 μm and 7.3 nm, respectively, and the pore size distribution suggested that the diameters of the nanopores were almost uniform. The PSi surface area was determined to be 0.864 m^2 cm^{-1} using the multipoint BET method, showing that large numbers of nanopores were formed on the PSi surface by the etching process. The etched PSi samples were immersed in $(NH_4)_2TiF_6$/H_3BO_3 or H_2TiF_6/H_3BO_3 solutions for the LPD, with boric acid acting as the F^{-} scavenger; LPD was performed for 1 or 6 h. Fig. 1 shows the SEM images and EDX line profiles of Ti and the as-prepared PSi after the LPD reaction. The top-view SEM images show that the nanopores formed on the PSi substrate surfaces disappeared after the LPD by immersion in $(NH_4)_2TiF_6$/H_3BO_3 solution for 6 h. Furthermore, Ti was located on top of the porous layer, as can be observed from the cross-sectional EDX line profiles of Ti. These observations suggest that the nanopores disappear because the porous layer on the PSi substrate was covered by deposited TiO_2. In addition, TiO_2 was