On-site fabrication and charge-discharge property of TiO₂ coated porous silicon electrode by the liquid phase deposition with anodic oxidation

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ABSTRACT

TiO₂/porous Si (PSi) nanocomposites were fabricated by liquid-phase deposition with anodization of PSi. Scanning electron microscopy-energy-dispersive X-ray spectroscopy showed that TiO₂ 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 TiO₂/PSi nanocomposites were fabricated by anodization of PSi in a H₂TiF₆ 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 TiO₂/PSi nanocomposites as Li-ion battery anodes were determined. Improvements in the charge/discharge capacity were achieved

by improving the PSi wettability by TiO₂ deposition and activation of Si on the surface of the anodized PSi fine pores. TiO₂/PSi fabricated by anodization maintained a high charge/discharge capacity without rapid degradation, because SiO₂, 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 HF₂⁻ 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 TiO₂ in fine pores in anodized PSi was performed using the LPD. In this process, both SiO₂, 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 TiO₂/PSi nanocomposites. In this study, various TiO₂/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 TiO₂/PSi nanocomposites prepared by the LPD will be useful for Li-ion battery (LIB) anodes. TiO₂ reacts with Li ions to form a Li composite metal oxide as follows:

When a TiO₂ 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 TiO₂ electrode is inferior to a graphite electrode (372 mA h g⁻¹) in terms of capacity and energy density. However, TiO₂ can absorb Li with slight volume expansion; therefore TiO₂ can be used as an anode material with a satisfactory cycling performance and safety [17,18]. In this work, we attempted to deposit TiO₂ on PSi, which has low resistivity, i.e., 3.0–4.0 mΩ cm, by the LPD to fabricate TiO₂/PSi nanocomposites. Fabricated TiO₂/PSi nanocomposites prepared the LPD in the presence of various F⁻ scavengers had fine pores derived from the PSi substrate, and TiO₂ coated part of the surfaces of the fine pores in PSi. The Si substrate provided the active material for a LIB anode when the fabricated TiO₂/PSi nanocomposites were used as electrodes:

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 TiO₂ on the surfaces of PSi fine pores is an effective method of overcoming this disadvantage; TiO₂ 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 TiO₂ 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 TiO₂/PSi nanocomposites. The TiO₂/PSi nanocomposites were used as LIB anodes, and the charge/discharge performances were evaluated using half-cell electrochemical measurements.

2. Experimental section

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 μm and $3.0\text{--}4.0$ $\text{m}\Omega\text{ cm}$, 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/H₂O/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 N₂ adsorption isotherms (Quantachrome Instruments Co., Ltd. (Florida, United States), NOVA 2200e).

2.2. *TiO₂ 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; H₂TiF₆/H₂O/EtOH solution was used as the electrolyte. The electrode-electrolyte contact area was about 1.65 cm². 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 TiO₂ 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 cm², rinsed with 1.0 mol L⁻¹ LiClO₄–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 cm² 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 $\text{HF}/\text{H}_2\text{O}/\text{EtOH}$ 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 $\text{m}^2\cdot\text{cm}^{-1}$ 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 $(\text{NH}_4)_2\text{TiF}_6/\text{H}_3\text{BO}_3$ or $\text{H}_2\text{TiF}_6/\text{H}_3\text{BO}_3$ 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 $(\text{NH}_4)_2\text{TiF}_6/\text{H}_3\text{BO}_3$ 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 deposited only outside the pores, with no deposition inside the pores. This is because the poor wettability of PSi inhibits permeation of the LPD solution into the nanopores on the surface of the PSi substrate[23]. In contrast, TiO_2 deposition on the PSi

Fig. 1. Cross-sectional SEM images and EDX line profiles of titanium(left) and top-view SEM images(right) for the as-prepared PSi after the LPD reaction. (A): $(\text{NH}_4)_2\text{TiF}_6\text{-H}_3\text{BO}_3$ mixed LPD reaction solution, (B): $\text{H}_2\text{TiF}_6\text{-H}_3\text{BO}_3$ mixed LPD reaction solution, LPD reaction time: 1 and 6 h.

substrates immersed in the $\text{H}_2\text{TiF}_6/\text{H}_3\text{BO}_3$ LPD solution was not observed. The pH of the $\text{H}_2\text{TiF}_6/\text{H}_3\text{BO}_3$ solution is much lower than that of the $(\text{NH}_4)_2\text{TiF}_6/\text{H}_3\text{BO}_3$ solution. Maki et al. previously reported that the pH of the LPD solution strongly affects the surface morphology and growth rate of the TiO_2 thin film [26]. At low pH, the degree of supersaturation decreases because hydrolysis of the titanium fluoride complex becomes harder [26], leading to a significant decrease in the nucleation density in the LPD solution. The amounts of TiO_2 deposited are therefore lower in the LPD solutions of low pH.

To improve the wettabilities of the PSi surface and the SiO_2 layer formed by anodization, the as-prepared PSi was thermally oxidized at 300 °C for 4 min in air [25]. Fig. 2 shows the SEM images and EDX line profiles of Ti with oxidized PSi substrates after the LPD reaction in various solutions.

Fig. 2. Cross-sectional SEM images and EDX line profiles of titanium(left) and top-view SEM images (right) for the oxidized PSi as substrates after the LPD reaction. (A): $(\text{NH}_4)_2\text{TiF}_6\text{-H}_3\text{BO}_3$ mixed LPD reaction solution, (B): $(\text{NH}_4)_2\text{TiF}_6$ LPD reaction solution, (C): H_2TiF_6 LPD reaction solution, (D): $\text{H}_2\text{TiF}_6\text{-H}_3\text{BO}_3$ mixed LPD reaction solution, LPD reaction time: 1 and 6 h.

The cross-sectional EDX line profiles of Ti show that TiO_2 was deposited in the nanoporous layer on the surface of the PSi substrate. These results are different from those for the as-prepared PSi substrates, because of the presence of Si terminal groups, i.e., Si-H groups, on the surface of the as-prepared PSi. The as-prepared PSi surface with Si-H groups is relatively hydrophobic [27,28], and it has been reported that Si-H groups react easily with F^- scavengers [23,29]; therefore the LPD reaction becomes inactive. The substitution of Si-H groups by silanol groups by PSi oxidation at high temperature

activates the F^- scavengers in the LPD reaction and enables permeation of the LPD solution into the nanoporous layer. When the thermally oxidized PSi substrate was immersed in $(NH_4)_2TiF_6/H_3BO_3$ aqueous solution as the LPD solution, the deposited TiO_2 filled the nanopores and overflowed outside the porous layer (Fig. 2A), because rapid nucleation of TiO_2 occurred by hydrolysis in the bulk phase as a result of the high pH of the LPD solution. In contrast, the cross-sectional and top-view SEM images suggest that the PSi substrate structure is preserved after deposition of TiO_2 by the LPD reaction in the nanopores on the surface of the PSi substrate. SiO_2 on the PSi surface acts as a F^- scavenger in $(NH_4)_2TiF_6/H_3BO_3$ and H_2TiF_6/H_3BO_3 solutions [30],; this suggest that the mean free path of the TiO_2 crystal nucleus in the hydrolysis of titanium fluoride complexes is short, and therefore on-site deposition of TiO_2 can be achieved.

We also evaluated a novel nanocomposite fabrication process consisting of anodization of the Si wafer and PSi with the LPD reaction. Anisotropic etching is useful for the fabrication of fine-structured nanocomposites, and therefore anodization of Si wafers and PSi was performed at 0–500 mV vs. Ag/AgCl. The formation of nano-PSi structures, anisotropic etching, and nanocomposite fabrication can be achieved at this potential. The Si wafer was anodized in $H_2TiF_6/H_2O/EtOH$ solution at a potential of 100–500 mV vs. Ag/AgCl and then TiO_2 deposition on the anodized Si wafer was performed by the LPD for 30 min. Fig. 3 shows the narrow-scan XPS spectra in the binding-energy region of Ti 2p for the Si wafer samples. Peaks derived from Ti were observed for all samples; the peaks for the anodized Si wafers at 300 and 400 mV vs. Ag/AgCl shifted to lower binding energy, i.e., ca. 459.7 eV. This XPS peak shift suggests that Ti atoms are chemically bonded to the Si substrate after anodization; therefore the LPD with anodization of the Si substrate is a novel method for the fabrication of metal oxide/PSi nanocomposites. Fig. 4 shows the SEM images and EDX line profiles of Ti with PSi anodized at 400 mV vs. Ag/AgCl after the LPD reaction in $H_2TiF_6/H_2O/EtOH$ solution. The top-view SEM image indicates that fine pores of diameter about 10 nm remained even after

anodization and the LPD reaction. The cross-sectional EDX line profile of Ti clearly shows that TiO_2 was deposited

Fig. 3. XPS narrow scan spectra in the binding energy range of $\text{Ti}2p$ for the anodized silicon wafer at the potential of 100-500 mV vs. Ag/AgCl after the LPD reaction for 30 minutes in $\text{H}_2\text{TiF}_6/\text{H}_2\text{O}/\text{EtOH}$ mixture solution.

Fig. 4. Cross-sectional SEM image and EDX line profile of titanium(left) and top-view SEM image(right) for TiO₂ deposited into the fine pore in anodized PSi by the LPD reaction for 30 minutes in H₂TiF₆/H₂O/EtOH mixture solution. Applied potential for the anotization: 400 mV vs. Ag/AgCl reference electrode.

in the nanoporous layer on the surface of the anodized PSi substrate. These results strongly suggest that on-site deposition of TiO₂ was achieved by the LPD, using the Si surface as the F⁻ scavenger at the anodic potential. The pore size distributions of PSi anodized at various potentials were measured using N₂-desorption isotherms. The average pore diameter increased with increasing applied anodic potential, and the pore diameters of the TiO₂/PSi nanocomposites fabricated by anodization of PSi for 30 min at 200–500 mV vs. Ag/AgCl were about 9.5 nm, clearly showing that the mesopore walls in the PSi substrates are etched during the LPD reaction. Fig. 5 shows the FT-IR spectra for PSi anodized at

Fig. 5. FT-IR spectrum for TiO₂ deposited into the fine pore in anodized PSi by the LPD reaction for 30 minutes in H₂TiF₆/H₂O/EtOH mixture solution. Wavenumber range: (left) 1800-2300 cm⁻¹, (right) 700-1200 cm⁻¹.

300–500 mV vs. Ag/AgCl after the LPD reaction in H₂TiF₆/H₂O/EtOH solution. The three absorption bands at around 2100 cm⁻¹ observed for all the samples are assigned to the SiH₃ (2137 cm⁻¹), SiH₂ (2113 cm⁻¹), and SiH (2086 cm⁻¹) stretching modes, and the absorption band at 908 cm⁻¹ is assigned to the SiH₂ bending mode [31-33]. A weak ν_{SiO_2} absorption band at 1878 cm⁻¹ and stretching vibration of the Si–O–Ti⁴⁺ structure at 940 cm⁻¹ which were arrowed in Fig. 5 were also observed for the TiO₂/PSi nanocomposites [34], therefore it can be concluded that covalent bonds between Ti and the anodized PSi substrates were formed by the LPD reaction. Fig. 6(A) shows the narrow-scan XP spectra in the

Fig. 6. XPS narrow scan spectra in the binding energy range of (A)Ti2p and (B)Si2p. (i): anodized silicon wafer at the potential of 400 mV vs. Ag/AgCl after the LPD reaction for 30 minutes in $\text{H}_2\text{TiF}_6/\text{H}_2\text{O}/\text{EtOH}$ mixture solution, (ii): silicon wafer which was dipped into H_2TiF_6 aqueous solution, and (iii): as-prepared PSi.

binding-energy region of Ti 2p for PSi anodized at 400 mV vs. Ag/AgCl after the LPD reaction in $\text{H}_2\text{TiF}_6/\text{H}_2\text{O}/\text{EtOH}$ solution. H_2TiF_6 on a Si wafer was used as a reference for the Ti 2p signals. The peaks at 460.0 and 459.7 eV can be assigned to Ti $2p_{3/2}$ for the reference sample and for the TiO_2/PSi nanocomposite fabricated by the LPD reaction in $\text{H}_2\text{TiF}_6/\text{H}_2\text{O}/\text{EtOH}$ solution with anodization of the Si substrate, respectively. The position of the Ti $2p_{3/2}$ signal for the TiO_2/PSi nanocomposite shifts to lower binding energy, from 460.0 to 459.7 eV, as a result of anodization. It is worth noting that removal of F^- ions from the TiF_6^{2-} complex and coordination of oxygen atoms with Ti occurred in these systems; i.e., the LPD reaction occurs despite the absence of traditional F^- scavengers such boric acid and Al^{3+} ions. Fig. 6(B) shows the narrow-scan XP spectra in the Si 2p binding-energy region for the TiO_2/PSi nanocomposite and as-prepared PSi as a reference sample. A SiO_2 peak is observed at 103.3 eV for the TiO_2/PSi nanocomposite fabricated by thermal oxidation, but this peak is not observed for the nanocomposites fabricated by anodic oxidation. The SiO_2 surface formed by anodization is immediately dissolved by F^- ions, which are supplied by the TiF_6^- complex.

The amounts of TiO_2 deposited and the weight losses of the PSi substrates were determined for the TiO_2/PSi nanocomposites fabricated by the LPD, with anodization of the Si substrate, in $\text{H}_2\text{TiF}_6/\text{H}_2\text{O}/\text{EtOH}$ solution; the results are shown in Fig. 7. Ti deposition showed a local maximum, i.e., $3.0 \times 10^{-6} \text{ mol m}^{-2}$, at an anodic potential of 300 mV vs. Ag/AgCl, and the PSi substrate weight loss showed a local constant value at an anodic potential of 250 mV vs. Ag/AgCl. This behavior is similar to that in the system in which SiO_2 formed on the surface of PSi by thermal oxidation acted as the F^- scavenger. It is therefore suggested that TiO_2 deposition involves competing reactions, namely TiF_6^{2-}

complex hydrolysis and dissolution of anodized PSi. The poor F^- -scavenging ability at a low anodic potential inactivates TiO_2 deposition by the LPD, and excessive substrate dissolution at a high anodic potential also inactivates TiO_2 deposition.

Fig. 7. Dependences of the deposition amount of TiO_2 and the weight loss of PSi substrates for the TiO_2 /PSi nanocomposites fabricated by the LPD reaction for 30 minutes in $H_2TiF_6/H_2O/EtOH$ mixture solution on the anodic potential against Ag/AgCl.

3.2. Electrochemical properties of TiO_2/PSi nanocomposites as anode for Li-ion battery

Fig. 8 shows the current–potential curves obtained by CV for the as-prepared PSi, and the TiO_2/PSi nanocomposites with thermally oxidized and anodized PSi substrates. The reduction current peak of a reduction wave of about 0.2 mA, caused by Li insertion in the as-prepared PSi, is observed in the potential region 0.0–0.8 V vs. Li/Li^+ . Higher reduction current peaks of other reduction waves

Fig. 8. Current-potential curve obtained by cyclic-voltammetry for several TiO_2/PSi nanocomposites as anodes for Li-ion battery obtained in the potential region of 0.0–3.0 V vs. Li/Li^+ at 0.5 $\text{mV}\cdot\text{s}^{-1}$ of the scan rate. (i) as-prepared PSi, (ii) TiO_2/PSi nanocomposite in the thermal oxidized PSi, and (iii) TiO_2/PSi nanocomposite in the anodized PSi.

derived from Li insertion are observed at 0.5 V vs. Li/Li^+ for the thermally oxidized PSi and in the potential region 1.2–2.5 V vs. Li/Li^+ for the nanocomposite with anodized PSi. These CV curves indicate that the reduction currents derived from Li insertion/extraction for the TiO_2/PSi nanocomposites are higher than that for as-prepared PSi, because of the significant improvement in the wettability and increase in the reaction field of redox reactions of the active material in the LIB anode. Furthermore, Li is inserted at a potential of 1.2 V vs. Li/Li^+ and extracted at 2.5 V vs. Li/Li^+ for the anodized TiO_2/PSi nanocomposite. This suggests that TiO_2 is in a favorable environment for electron acceptance in the nanocomposite with anodized PSi, i.e., the majority of the deposited TiO_2 is present not on the SiO_2 insulator but on the Si semiconductor. The anodized TiO_2/PSi nanocomposite shows a high reduction current in the potential region for lithium ion extraction, but the as-prepared PSi and the nanocomposite with thermally oxidized PSi show lower reduction currents in the potential region.

The charge/discharge curves for the second cycles of several nanocomposites were recorded in the potential region 0.01–3.50 V vs. Li/Li^+ at 500 μA . The first charging capacity of the as-prepared PSi for charge/discharge at 500 μA was 550 $\mu\text{A}\cdot\text{h}$, and the capacity gradually decreased with the number of charge/discharge cycles; the charging capacity at the 15th cycle was 200 $\mu\text{A}\cdot\text{h}$. The thermally oxidized and anodized TiO_2/PSi nanocomposites showed first charging capacities of 850 and 1700 $\mu\text{A}\cdot\text{h}$, respectively. These values are clearly higher than that of the as-prepared PSi electrode, and it can be concluded that the increase in the first charging capacity is derived from the significant improvement in the wettability of the surface nanopores by TiO_2 deposition and the increased reactivity of Si in the nanopores in the LIB anode, as shown in Fig. S2. These results are in good agreement with the CV measurements shown in Fig. 8. However, rapid degradation of the charging capacity of the thermally oxidized TiO_2/PSi nanocomposite occurred after the first charge/discharge cycle, as can be seen in Fig. 9. This result is also supported by the CV measurements, in which the insertion current of Li increased however the extraction current did not. The reason for the degradation of the charging

capacity is therefore presumed to be deterioration of the structure of the thermally oxidized PSi substrate or an irreversible reaction of Li in the first charging process. In contrast, when the anodized TiO_2/PSi nanocomposite was used as an electrode, degradation of the charging capacity was not observed. However, the charging capacity of the anodized TiO_2/PSi nanocomposite gradually decreased with charge/discharge cycle number, and the final charging capacity at the 15th cycle was $200 \mu\text{A}\cdot\text{h}$. This

Fig. 9. Top-view (top) and cross-sectional SEM images(bottom) for several TiO_2/PSi nanocomposites as anodes for Li-ion battery after the charge/discharge of 15 cycles at $500 \mu\text{A}$. (A) as-prepared PSi, (B) TiO_2/PSi nanocomposite in the thermal oxidized PSi, and (C) TiO_2/PSi nanocomposite in the anodized PSi. Two kinds of images with different scale show for the top-view SEM images of the TiO_2/PSi nanocomposite in the thermal oxidized PSi.

degraded charging capacity value is similar to that of the as-prepared PSi, suggesting that one of the reasons for the degradation of the charging capacity is exfoliation of TiO_2 caused by repeated charging/discharging of the anodized TiO_2/PSi nanocomposite. This conclusion is supported by the decreased charging capacity in the potential region 1.0–1.5 V vs. Li/Li^+ , i.e., when Li is inserted into TiO_2 , and also shows that the distance between the layers of Si is expanded by Li insertion [35].

The as-prepared SiO_2/PSi nanocomposite, i.e., SiO_2/PSi nanocomposite without the TiO_2 deposition and the thermally oxidized TiO_2/PSi nanocomposite showed the rapid degradation of the first charging capacity after the first charging, i.e., from 1270 $\mu\text{A}\cdot\text{h}$ to 300 $\mu\text{A}\cdot\text{h}$ and from 850 $\mu\text{A}\cdot\text{h}$ to 160 $\mu\text{A}\cdot\text{h}$, respectively, as shown in Fig. S3. This fact strongly suggests that the rapid capacity degradation of the as-prepared SiO_2/PSi nanocomposite and the thermally oxidized TiO_2/PSi nanocomposite are caused by the presence of SiO_2 in the electrode. Fig. 9 shows the SEM images for the as-prepared PSi, and the thermally oxidized and anodized TiO_2/PSi nanocomposites after the 15th charge/discharge cycle. The surface morphology of the thermally oxidized TiO_2/PSi nanocomposite is quite different from those of the other samples. No cracks are observed on the nanoporous layer in the anodized TiO_2/PSi nanocomposite, even after the 15th charge/discharge cycle; it is therefore supposed that the pulverization of the TiO_2 anode active material by expansion and contraction during charging/discharging is one of the causes of the rapid capacity degradation. The surface oxidation states of the as-prepared PSi in the charge/discharge process were investigated using XPS; the spectra of PSi in several charging and discharging states were obtained, and are shown in Fig. S4. The insertion of Li into PSi is confirmed by the signal at 57.2 eV in the Li 1s region in the spectrum of the fully charged PSi. The same sample shows a signal at 104.4 eV and a signal from Si^0 at 99.6 eV in the Si 2p region. However, the peak at 104.4 eV is unclear in spite of our expectation which this peak is related to silicon affected by carbon [36]. Furthermore, the peak in the Li 1s region disappeared after the first discharge, which suggests that Li was removed from Si by discharging. Although a peak derived from a

Li–Si alloy in the Si 2p region cannot be detected, it can be confirmed by the peak from Li metal that ionized Li is present in the electrode.

Fig. 10 shows the XP spectra for the thermally oxidized TiO_2/PSi nanocomposite in several charging and discharging states. A new peak emerges in the low binding-energy region of Ti 2p, i.e., 456.0 eV, for the 300 $\mu\text{A}\cdot\text{h}$ charged sample, and this indicates that some of the tetravalent Ti in TiO_2 is reduced to trivalent Ti during the charging process. It is therefore suggested that in the charging process, Li is inserted into TiO_2 , as shown in reaction (1), until the potential reaches about 0.8 V vs.

Fig. 10. XPS narrow scan spectra in the binding energy range of (A)Ti2p, (B)Si2p, and (C) Li1s for the TiO_2/PSi nanocomposite in the thermal oxidized of the several charge and discharge status. (i): before the first charging, (ii): 300 $\mu\text{A}\cdot\text{h}$ charged, (iii) full-charged, and (iv) discharged.

Li/Li^+ . The trivalent Ti is oxidized to tetravalent Ti after discharging; therefore TiO_2 seems to react reversibly with Li. However, the intensities of the Ti signals for the thermally oxydized sample after the charge/discharge process are lower than those for the as-prepared sample. It is suggested that TiO_2 in the TiO_2/PSi nanocomposite is exfoliated by the expansion and shrinkage of the Si substrate caused

by Li insertion and extraction, and therefore the apparent amount of TiO_2 decreases. In addition, the XPS signal at 57.2 eV in the binding-energy region of Li 1s is observed after full charging, because of insertion of Li into the nanopores in the thermally oxidized samples. However, this signal remains even after discharging. This behavior is quite different from that of the as-prepared PSi, as shown in Fig. 9, and it is concluded that Li is not exfoliated from the Si substrate of the thermally oxidized sample by discharging. The probable reason for this phenomenon is residual SiO_2 in the thermally oxidized sample; i.e., Li is irreversibly inserted into the electrode and reacts with SiO_2 by the following reaction [37]:

SiO_2 remains after the nanocomposite fabrication process and causes rapid degradation of the charging capacity after the first charging cycle.

4. Conclusions

In this study, several TiO_2 /PSi composites were fabricated by the LPD. The hydrolysis of metal–fluoro complexes was promoted by various F^- scavengers, i.e., boric acid and SiO_2 generated by thermal oxidation or anodization of Si. On-site deposition of TiO_2 was observed in the fabrication of TiO_2 /PSi nanocomposites in the presence of solid F^- scavengers such as SiO_2 and anodized Si. These samples retained the large surface area derived from the nanopores in the PSi substrate; i.e., the novel LPD method without boric acid as a F^- scavenger was effective for on-site fabrication of TiO_2 /PSi nanocomposites. Furthermore, the electrochemical properties of a LIB anode based on the thermally oxidized and anodized TiO_2 /PSi nanocomposites fabricated by the LPD method were determined. The poor wettability of the surfaces of the mesopore walls in the anodized PSi substrates was significantly

improved by the deposition of TiO_2 on the surfaces of the mesopore walls. When the anodized TiO_2/PSi nanocomposites were used as an electrode, Si in the mesopores also worked as an active material, and the charge/discharge capacity increased as a result of the significantly improved wettability. However, in the case of SiO_2 prepared by the conventional LPD method, the SiO_2 in the as-prepared SiO_2/PSi nanocomposite and the irreversible reaction between SiO_2 and Li caused rapid capacity degradation when used as a LIB anode. The Si surface at the anodic potential was used as the F^- scavenger in the novel LPD method; this provides a new TiO_2/PSi nanocomposite fabrication method that does not use a SiO_2 insulator as the F^- scavenger. The anodized TiO_2/PSi nanocomposite fabricated by the novel LPD method showed a higher charge/discharge capacity and lower capacity deterioration than did electrodes with Si-based anodes.

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