



Short communication

Silicon on conductive self-organized TiO₂ nanotubes – A high capacity anode material for Li-ion batteries

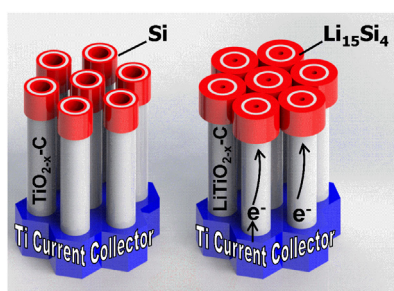
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HIGHLIGHTS

- Lithiation of Si coated self-organized, carburized TiO₂ nanotubes.
- Si coated nanotubes show both high cycling stability and specific capacity.
- High rate capability without losing capacity, due to the thin film character of Si.
- Advantages of both active materials can be accessed in a single cell.
- Direct 1D electron transport is enabled without binders or conductive additives.

GRAPHICAL ABSTRACT



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ABSTRACT

The study of high energy density electrode materials is central to the development of Li⁺-ion batteries. Si is among the most promising anode materials for next generation Li⁺-ion batteries. Model composite electrodes of self-organized, conductive titania (TiO_{2-x}-C) nanotubes coated with silicon (Si) via plasma enhanced chemical vapor deposition (PECVD) are produced and studied in terms of their lithiation/delithiation characteristics. The nanotube array provides direct one dimensional electron transport to the current collector, without the need of adding binders or conductive additives. Both components of the composite can be lithiated delivering 120 μAh cm⁻² total capacity for a film thickness of 1 μm and a Si loading of ~10 wt.%. 86% capacity retention upon 88 cycles at a rate of C/5 and 60 μAh cm⁻² total capacity at a rate of 10 C are achieved owing to the low lateral expansion and thus good adhesion of the thin Si coating to the TiO_{2-x}-C nanotubes, and due to the formation of a stable solid electrolyte interface (SEI) in ethylene-carbonate (EC), dimethyl-carbonate (DMC), vinylene-carbonate (VC) electrolyte with 1 M LiPF₆.

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1. Introduction

Due to its high specific capacity of 3580 mAh g⁻¹ (Li₁₅Si₄) [1] at room temperature and low lithiation/delithiation voltage of ~0.5 V vs. Li/Li⁺, both leading to high energy densities, Si is considered the most promising anode material for next generation Li⁺-ion batteries. Low Li⁺ and electronic conductivity however limit the

maximum power output of Si. The high volumetric expansion of Si of up to 280% upon lithiation [2,3], causes fast mechanical degradation of electrodes based on micrometer sized Si particles or films [4]. Additionally, the change in active surface area throughout lithiation/delithiation cycles leads to cracking of the SEI and to its re-formation on freshly exposed Si, which causes SEI thickening, consumption of Li and electrolyte, and consequently to a loss in capacity upon operation. Our approach to overcome these issues is to use a thin Si film of ~10 nm supported on a stable, electronically conducting high aspect ratio surface. Thin Si films are known to

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have a superior cycling stability compared to micro particles or films due to their expansion preferentially in direction normal to the film surface avoiding crack formation and delamination [5,6]. Additionally, they provide short diffusion paths for Li^+ -ions and electrons allowing for high lithiation/delithiation rates. A drawback of thin films is their low mass per unit area which we compensate by using a support material with a high surface to volume ratio. The use of anodically grown, self-organized TiO_2 nanotubes [7–10] supported on Ti, which directly serves as current collector, and annealed to carbon containing TiO_2 anatase under reducing conditions [11] provides direct one dimensional electron transport towards the current collector and eliminates the need for using conductive carbon to increase the electronic conductivity, which would decrease the electrode's gravimetric capacity. The anatase phase of TiO_2 itself is an active material towards lithium insertion, with a theoretical capacity of 335 mAh g^{-1} , the usually measured capacity of 168 mAh g^{-1} is however used in literature to derive the rate of 1C [12,13]. About 0.6 mol Li can be inserted per mole TiO_2 at 1.78 V vs. Li/Li^+ [14]. Nanotextured anatase TiO_2 can be fully lithiated forming LiTiO_2 [15–17].

In this paper, we demonstrate that reversible lithiation takes place in both anatase TiO_2 and Si phases, when self-organized TiO_2 -C nanotubes coated with a Si thin film are used as negative electrode in a half-cell configuration.

2. Experimental

TiO_2 nanotubes were grown electrochemically on mechanically polished (4000P SiC grinding paper) Ti disks (99.6%, Advent) by exposing the polished surface (0.38 cm^2) to an electrolyte containing 50% ethylene glycol by volume (99.5%, Merck) in water (18.2 M Ω cm, Milli-Q, Millipore) and 1 wt.% NH_4F (99.99%, Merck) and by applying an anodic potential of 20 V for 1 h, after a voltage ramp of 1 V s^{-1} . After anodizing, the sample was thoroughly rinsed with deionized water (18.2 M Ω cm, Milli-Q, Millipore) to prevent further etching of the surface. In order to increase the electronic conductivity and to modify the Li insertion properties of the as grown amorphous TiO_2 nanotubes, carbo-thermal annealing was carried out in a horizontal tube furnace. The reactor tube was first purged with 750 sccm Ar for 2 h at room temperature (RT) to remove air. The Ar flow was then reduced to 200 sccm and kept constant until the end of the annealing procedure. Prior to increasing the temperature, 5 sccm acetylene were added to the Ar flow for 3 min. To avoid thermal stress during the temperature increase to 400°C , the ramping speed was gradually reduced from $10^\circ\text{C min}^{-1}$ until 200°C , to 5°C min^{-1} until 300°C , and finally 3°C min^{-1} until 400°C . After 20 min at 400°C , 0.1 sccm acetylene was added to the Ar flow for 1 h. The system was then kept for another 280 min at 400°C to allow for the complete transformation of the nanotubes and then cooled down to RT with 3°C min^{-1} . PECVD (Oxford Plasmalab 80+) with Ar diluted SiH_4 was used to coat the annealed nanotubes with silicon, at 1 Torr total pressure, with 465 sccm Ar and 35 sccm SiH_4 at 250°C for 1 min.

Scanning electron microscopy (SEM) (CrossBeam NVision 40, Zeiss) micrographs of TiO_2 -C nanotubes before and after Si deposition were used to determine the volume and therefore mass fraction of deposited Si. Energy Dispersive X-ray Spectroscopy (EDX) (JSM-7500F, JEOL) and X-ray Photoelectron Spectroscopy (XPS) (Specs Phoibos 100 hemispherical electron energy analyzer and a MCD-5 detector) were used ex-situ to qualitatively determine the chemical composition of the electrodes and the oxidation states of their components prior to cycling. The take off angle in XPS measurements was 0 relative to the surface normal and an Al K_α X-ray source (1486.6 eV) without monochromator was used. High resolution spectra were recorded for the Si 2p, Ti 2p, and C 1s

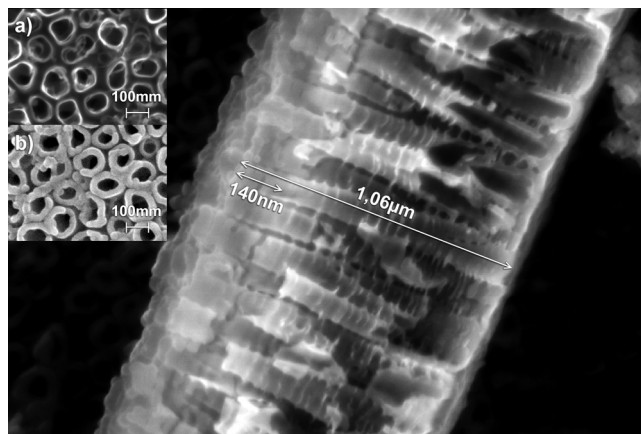


Fig. 1. SEM cross-section of TiO_2 -C nanotubes coated with Si; inset a): top view of non-coated TiO_2 -C nanotubes; inset b): top view of Si-coated TiO_2 -C nanotubes.

regions with a step size of 0.025 eV and a dwell time of 0.5 s. Quantitative analysis was performed using CasaXPS software (version 2.3.14dev38). All spectra were corrected for charging by shifting them to the position of the Ti 2p $_{3/2}$ peak of TiO_2 at 458.7 eV.

All electrochemical measurements were carried out in a three electrode t-cell with a stainless steel body (Union Tee Tube Fitting, Swagelok). Perfluoroalkoxy (PFA, Swagelok) sealing rings and stainless steel rods (1.4404 stainless steel, StahlRING GmbH) were used for contacting the working (WE), counter (CE) and reference (RE) electrodes. The steel rod current collectors for WE and CE were separated from the cell body by a cylinder made of high density polypropylene (HDPP). Lithium foil (99.9%, Alfa Aesar) was used as CE and RE. The electrolyte (SelectiLite battery electrolyte LP 30, Merck) used in all measurements was 1 M LiPF_6 in a 1:1 (w/w) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) with or without a 2 wt.% vinylene carbonate (VC) additive [18,19]. Two glass fiber (GF) separators (VWR Glass microfibers filter, 691) soaked with electrolyte were used to separate WE and CE at a pressure of 189 kPa. All cells were assembled in an Ar filled glove box (MBraun) with a water and oxygen content below 0.1 ppm. The assembled cells were connected to a potentiostat (VSP, BioLogic) outside the glove box and all experiments were performed at room temperature. All cyclic voltammetry (CV) measurements were performed with a scan rate of 0.05 mV s^{-1} in the potential window from 0.04 to 3.0 V vs. Li/Li^+ . Galvanostatic cycling with potential limitation (GCPL) was carried out in the potential window from 0.04 to 3.0 V vs. Li/Li^+ at a constant current of $j_0/10 = 11.2 \mu\text{A cm}^{-2}$ corresponding to a lithiation/delithiation rate of $\sim 0.093 \text{ C}$, where the C-rate of $1 \text{ C} = 120 \mu\text{A cm}^{-2}$ is derived from the maximal measured capacity of $120 \mu\text{Ah cm}^{-2}$. The rate capability of the composite was tested at currents $j_0/10, j_0/5, j_0/2, 1j_0, 2j_0$ and $10j_0$. Due to their different masses and specific capacities, the two components of the composite have different lithiation/delithiation C-rates, assuming that both active materials in the composite are lithiated and delithiated subsequently. The C-rates calculated from the measured maximal values of the specific capacities for a constant current density of $11.2 \mu\text{A cm}^{-2}$ ($=j_0/10$) are $51 \text{ mA g}_{\text{composite}}^{-1} = 0.09 \text{ C}_{\text{composite}}$, $57 \text{ mA g}_{\text{TiO}_2}^{-1} = 0.21 \text{ C}_{\text{TiO}_2}$ and $478 \text{ mA g}_{\text{Si}}^{-1} = 0.16 \text{ C}_{\text{Si}}$. The C-rates calculated from the theoretical maximum capacities for each component ($3580 \text{ mAh g}_{\text{Si}}^{-1}$, $168 \text{ mAh g}_{\text{TiO}_2}^{-1}$ and 534 mAh g^{-1} for the composite containing 10.7 wt.% Si) for the same current density ($11.2 \mu\text{A cm}^{-2}$) are $51 \text{ mA g}_{\text{composite}}^{-1} = 0.10 \text{ C}_{\text{composite}}$, $57 \text{ mA g}_{\text{TiO}_2}^{-1} = 0.34 \text{ C}_{\text{TiO}_2}$ and $478 \text{ mA g}_{\text{Si}}^{-1} = 0.13 \text{ C}_{\text{Si}}$. The mass of the composite and its components (TiO_2 -C and Si) was calculated

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