



# Electrochemical synthesis of 1D core-shell Si/TiO<sub>2</sub> nanotubes for lithium ion batteries



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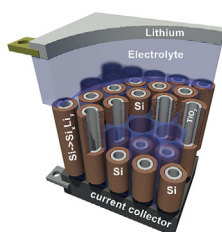
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## HIGHLIGHTS

- A new method for synthesis of 1D core-shell TiO<sub>2</sub>/Si nanotubes is developed.
- Continuous Si network without grain boundaries and Si-Si interfaces is designed.
- TiO<sub>2</sub>/Si has capability to release stress allowing Si to expand without fracture.
- Nanostructured Si anode shows good cycle stability.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 8 May 2017

Received in revised form

20 June 2017

Accepted 2 July 2017

### Keywords:

Silicon

Titania

Electrosynthesis

Nanotubes

Silicon anode

## ABSTRACT

Silicon negative electrode for lithium ion battery was designed in the form of self-organized 1D core-shell nanotubes to overcome shortcomings linked to silicon volume expansion upon lithiation/delithiation typically occurring with Si nanoparticles. The negative electrode was formed on TiO<sub>2</sub> nanotubes in two step electrochemical synthesis by means of anodizing of titanium and electrodeposition of silicon using ionic liquid electrolytes. Remarkably, it was found that the silicon grows perpendicularly to the z-axis of nanotube and therefore its thickness can be precisely controlled by the charge passed in the electrochemical protocol. Deposited silicon creates a continuous Si network on TiO<sub>2</sub> nanotubes without grain boundaries and particle-particle interfaces, defining its electrochemical characteristics under battery testing. In the core-shell system the titania nanotube play a role of volume expansion stabilizer framework holding the nanostructured silicon upon lithiation/delithiation. The nature of Si shell and presence of titania core determine stable performance as negative electrode tested in half cell of CR2032 coin cell battery.

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## 1. Introduction

Lithium ion batteries (LIBs) are one of the most important energy storage devices already commercialized for portable electronics in which the graphite negative electrode with its charge storage capacity of 372 mA h g<sup>-1</sup> is still used. To meet the

demands of higher energy density in applications, such as electric vehicles, the present focus is on the negative electrodes with high theoretical charge storage capacity. Silicon with its charge capacity of  $3590 \text{ mA h g}^{-1}$  corresponding to  $\text{Li}_{15}\text{Si}_4$  formation may be a good electrode alternative [1–3]. The main shortcoming of silicon in the form of micrometer in size particles is, however, its high volume expansion upon lithiation resulting in high mechanical stress, pulverization, and loss of electric contact with the particle leading to loss of charge capacity. Various approaches such as encapsulation [4] and self-healing strategies [5] have been applied to overcome the high volume expansion issues. The present paper is focusing on composite core-shell structure in which core material would act as a volume expansion stabilizer. By using the tools offered by electrochemistry, we aim to precisely manipulate with the nanosize of Si on the core material. In more fundamental terms, the main interests are: i) to create a core-shell structure in which the core material work as a volume expansion stabilizer, holding nanostructured Si upon lithiation/delithiation, ii) create a pure continuous Si network without adding of binders, conductive additives and alloying elements, which may be an issue for fundamental understanding of Si size effects, iii) facilitate electron transfer through formation of 1D geometry of the Si electrode as an alternative for electron-random-walk through particle-particle interfaces. One of the best composite candidates for this purpose is a  $\text{TiO}_2/\text{Si}$  hybrid. Recent reports have demonstrated the promising LIBs properties with  $\text{TiO}_2/\text{Si}$  electrodes without the need of adding binders and conductive additives [6,7]. However, in all of these studies, the used sputtering/evaporation methods for silicon synthesis (such as CVD, PVD) result in Si deposition at the top of  $\text{TiO}_2$  nanotubes, i.e. incomplete filling of the titania framework. The area capacity of  $0.02\text{--}0.12 \text{ mA h cm}^{-2}$  has been reported for Si modified  $\text{TiO}_2$  nanotubes and other systems based on  $\text{TiO}_2$  framework such as sulphated titania, tin oxide modified titania [7–12]. Herein we report fully electrochemical method of silicon synthesis using ionic liquid electrolytes which allows complete filling of  $\text{TiO}_2$  nanotubes with amorphous silicon from bottom to the top of nanostructure.

This synthesis process fill in the gap between the previous works on sputter deposited Si at the top-surface of titania nanotubes [6,7] and expectations for having cheap and nevertheless powerful Li ion battery electrodes. The composite nanostructure is formed in two electrochemical steps: anodic oxidation of titanium and cathodic reduction of  $\text{Si}^{4+}$  species in order to form 1D  $\text{TiO}_2/\text{Si}$  core-shell structure (Fig. 1a). In this work, we optimize the materials geometry to get a robust silicon shell on titania nanotube wall and we show the feasibility of our method for Li ion battery application. With its organized structure, titania nanotube array [13] serve a role of a framework holding the nanostructured silicon upon lithiation/delithiation. The battery testing shows an interest of our strategy to use the nanostructure as negative electrode in lithium ion battery technology.

## 2. Experimental

Titania nanotubes were formed by anodizing of titanium foils (Goodfellow, 99.6%) with 0.1 mm thickness using dc power supply (HP 6209B DC) coupled with dual display multimeter (FLUKE 45). Prior to use, the titanium foils were cleaned by sonication in acetone, isopropanol and ethanol, rinsed in deionized water and dried in an argon stream. The foils were anodized in an electrolyte composed of diethylene glycol, 2% HF (50% v/v) and 2%  $\text{H}_2\text{O}$ . The anodizing was performed in two electrode cell with the titanium as working electrode ( $1.00 \text{ cm}^2$ ) and platinum as counter electrode with the applied voltage of 60 V during 17 h. The distance between working and counter electrodes was kept constant at 14 mm. Then

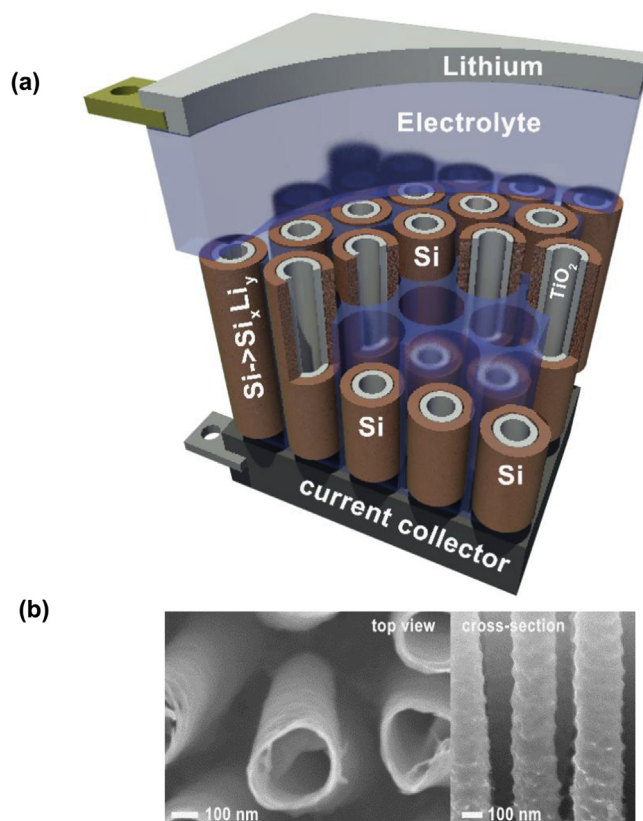


Fig. 1. (a) Scheme of silicon lithium ion battery half-cell used in the present study, (b) FE-SEM images of  $\text{TiO}_2$  nanotubes used as a framework for electrodeposition of silicon.

the electrodes were cleaned with acetone for 30 min and dried with argon steam.

Silicon was electrochemically deposited on  $\text{TiO}_2$  nanotubes (Votolab PGZ100) using ionic liquid, 1-Butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (Solvionic S.A.) electrolyte containing 0.1 M  $\text{SiCl}_4$  (Aldrich) in an argon filled glove box with  $\text{H}_2\text{O}$  and oxygen content less than 1 ppm. The deposition was carried out at  $50^\circ\text{C}$  in potentiostatic mode in three electrode cell with titania nanotubes as working electrode, platinum wire as quasi reference electrode (QRE) and platinum counter electrode at  $-2.8 \text{ V vs. Pt}$ . The amount of deposited silicon was controlled by charge passed in the electrochemical process. After deposition, the electrodes were immediately cleaned with acetonitrile, prior to characterization and electrochemical test in battery system.

The  $\text{Si}/\text{TiO}_2$  composites were tested as negative electrodes in half cell CR2032 coin cell in lithium ion battery. The coin cells were assembled in argon filled glove-box using lithium foil as counter/reference electrode and 1 M  $\text{LiPF}_6$  in ethylene carbonate/dimethyl carbonate, EC/DMC (1:1 v/v) electrolyte. Constant current charge/discharge at  $20 \mu\text{A cm}^{-2}$  was employed in a potential range of 3.00 to 0.05 V vs.  $\text{Li}/\text{Li}^+$  (based on the mass of deposited Si) to extract the capacity and cyclic stability of the material. Due to the low mass of the microelectrode formed on titania nanotubes and resulting large experimental error in determination of mass for calculation of gravimetric capacity, we rule out the possibility of capacity evaluation in  $\text{A.h.g}^{-1}$ . Therefore, the capacity was expressed in terms of areal capacity ( $\text{A.h.cm}^{-2}$ ) as demonstrated for other anodic  $\text{TiO}_2$  systems [7,8,10,11].

A field emission scanning electron microscope (FE-SEM, LEO GEMINI) was used for structural and morphological characterization of titania nanotubes and composites. Transmission electron

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