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All electrochemical process for synthesis of Si coating on TiO_2 nanotubes as durable negative electrode material for lithium ion batteries

Abirdu Woreka Nemaga[a,b], Jeremy Mallet[a,*], Jean Michel[a], Claude Guery[b,c], Michael Molinari[a], Mathieu Morcrette[b,c,**]

[a] Laboratoire de Recherche en Nanosciences, LRN EA4682, Université de Reims Champagne-Ardenne, Campus Moulin de la Housse, BP 1039, 51687 Reims Cedex, France
[b] Laboratoire de Réactivité et Chimie des Solides, LRCS, CNRS UMR 7314, Université de Picardie Jules Verne, 33 Rue Saint-Leu, 80039 Amiens Cedex, France
[c] Reseau sur le Stockage Electrochimique de l'Energie (RS2E), CNRS FR3459, 33 Rue Saint Leu, 80039 Amiens Cedex, France

HIGHLIGHTS

- Electrochemical methods for the synthesis of Si/TiO_2 nanotubes.
- Si nanostructure coating on amorphous and on anatase TiO_2 nanotubes.
- Si/TiO_2 has ability to release stress to stabilize Si volume expansion.
- Fully amorphous Si/TiO_2 nanotube composite shows good cyclic stability.

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ABSTRACT

The development of high energy density Li-ion batteries requires to look for electrode materials with high capacity while keeping their stability upon cycling. In this study, amorphous silicon (a-Si) thin film deposited on self-organized TiO_2 nanotubes is investigated as negative electrode for Li-ion batteries. Nanostructured composite negative electrodes were fabricated by a two-step cost effective electrochemical process. Firstly, self-organized TiO_2 nanotube arrays were synthesised by anodizing of Ti foil. Subsequently, thanks to the use of room temperature ionic liquid, conformal Si layer was electrodeposited on the TiO_2 nanotubes to achieve the synthesis of nanostructured a-Si/TiO_2 nanotube composite negative electrodes. The influence of the Si loading as well as the crystallinity of the TiO_2 nanotubes have been studied in terms of capacity and cyclic stability. For an optimized a-Si loading, it is shown that the amorphous state for the TiO_2 nanotubes enables to get stable lithiation and delithiation with a total areal charge capacity of about 0.32 $mA\,h\,cm^{-2}$ with improved capacity retention of about 84% after 50 cycles, while a-Si on crystalline TiO_2 nanotubes shows poor cyclic stability independently from the Si loading.

1. Introduction

One of the requirements for the development of high energy density Li-ion batteries applications is to use electrode materials with high capacity. Silicon is one of the promising negative electrode materials for next generation Li-ion batteries due to its high theoretical specific capacity (3579 $mA\,h\,g^{-1}$ for $Li_{15}Si_4$) and low discharge/charge voltage (0.4 V vs. Li^+/Li) [1–4]. Nevertheless, Si suffers from drastic volumetric change up to 300% [2] during the lithiation/delithiation process. The large volume change generates stress within Si particles, leading to particle pulverization, loss of electrical contacts between particles and between particle and current collector, and eventually rapid capacity fading [5,6]. Moreover, the repeated volume changes upon cycling cause breaking of SEI layers and expose fresh Si surface to the electrolyte, resulting in SEI re-formation, loss of active lithium in Li-ion configuration, continuous consumption of electrolyte, increased impedance, and poor reversibility [7–9].

One effective approach to overcome the Si limitations is the use of amorphous silicon (a-Si). Due to the intrinsic disorder of the amorphous state, a-Si reduces the net effect of volume expansion through the homogenous distribution of cracks and avoids the phase change from crystalline to amorphous during the initial lithiation process [10]. a-Si

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[*] Corresponding author.
[**] Corresponding author. Laboratoire de Réactivité et Chimie des Solides, LRCS, CNRS UMR 7314, Université de Picardie Jules Verne, 33 Rue Saint-Leu, 80039 Amiens Cedex, France.
E-mail addresses: jeremy.mallet@univ-reims.fr (J. Mallet), mathieu.morcrette@u-picardie.fr (M. Morcrette).

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is used in the form of thin films or nanostructures as it enables to release stress, to shorten ion diffusion length so as to facilitate electronic/ionic transport, and to benefit from a large surface area of nanostructure so as to store more Li^+ [7,11–13]. Among several nanostructured silicon, a-Si thin film directly deposited on the current collector is the most interesting because of strong adhesion to the current collector and lack of need of adding inactive binder or conductive additives. Graetz et al. [14] have reported strong performances for 100 nm thick a-Si thin films over c-Si nanoparticles with 12 nm diameters. The thin films delivered a reversible specific capacity of about 2000 mA h g^{-1} for 50 cycles, while the nanoparticles delivered only 1100 mA h g^{-1} initial specific capacity with 50% capacity retention after 50 cycles.

Classical techniques such as Physical Vapor Deposition and Chemical Vapor Deposition used to grow a-Si thin films remain complex, constraining, and costly with the need of high vacuum, toxic precursors and precise temperature control. Thus, such techniques are limited to industrial transfer and process of Li-ion batteries. Among alternative techniques, electrodeposition is promising because of its comparably lower cost, its simplicity to technological scale-up and its easily controllable parameters [15–17]. For electrodeposition of a-Si, the main issue is that it cannot be deposited in aqueous solvent due to its high reactivity with water and large negative reduction potential. However, different solutions have been proposed to electrochemically deposit Si thin films using organic solvents [18], molten salts [19], and ionic liquid [20]. If molten salts and organic solvents still have important drawbacks such as requirements of high temperature or environmental and safety issues for industrial processing, the room temperature ionic liquids (RTILs) electrolytes seem to be suitable for Li-ion battery applications thanks to their unique properties such as a large potential window, low vapour pressure, non-flammability and good conductivity [21,22]. The interest of electrodeposition for growing a-Si thin films as negative electrode material for Li-ion battery was recently demonstrated with interesting performances in terms of gravimetric specific capacity and reversibility [23–25].

Nevertheless, whatever the techniques used to grow the a-Si thin films with thickness in the range of a few hundreds of nanometers and regardless of their excellent performance, thicker films are required to deliver sufficient capacity to satisfy the high energy demand of Li-ion batteries. Unfortunately, increasing the thickness of the film has negative impact on the electrochemical performance of the electrode [26–28] because it causes larger volume expansion and weak adhesion to current collector causing the film to peel off from the current collector. One effective way to overcome the challenge is to use nanostructured substrate which enables to increase the surface area and then the Si active mass and in the same time, to enhance the adhesion between the a-Si layer and the substrate. For instance, Tao et al. [29] have used nickel macro-nanocones hierarchical structure (Ni MHS) as a current collector to support electrodeposited Si film. The Ni MHS supported Si thin film composite negative electrode exhibited a capacity of around 0.2 mA h cm^{-2} with good capacity retention over 100 cycles. Even if this design improves the performance of the device compared to a-Si thin films, the Ni MHS in the composite is electrochemically inactive versus Li^+ which gives extra inactive mass to the electrode and therefore limits the interest of this nanostructured electrode.

It is a key to design a large surface area, electrochemically active template which can allow increasing Si active mass before reaching critical fractured thickness. Among various transition metal oxides nanostructure investigated as negative electrode for Li-ion batteries [30–32], TiO_2 is an attractive candidate to be used as negative electrode because of its miner structural change (less than 4%) in repeated lithiation/delithiation, a fast Li insertion/extraction, non-toxicity, cost effectiveness and safety, especially in its nanostructured form. Self-organized TiO_2 nanotubes supported on Ti, which serves as current collector, can easily be synthesised by anodizing Ti foil [33,34], which is not an easily task to be achieved for the other transition metal oxides. The anodically grown TiO_2 nanotubes can be a good support for electrodeposited Si film due to several advantages such as they are electrically conductive to be coated by electrodeposition, mechanically stable, and electrochemically active versus Li^+ to give extra capacity contribution in the Si/TiO_2 nanotube composite electrode. Moreover, they will provide a large surface area to enhance the Si active mass, and as they directly grown from the Ti current collector, they will provide facile 1D electron transport and avoids the need of adding conductive additives or inactive binder. Such strategy has already been studied by Brumbarov et al. [35] using composite electrodes of anatase titania (TiO_{2-X}-C) nanotubes coated with Si thin films grown by plasma enhanced chemical vapour deposition (PECVD) or by Ivanov et al. [36] who demonstrated the deposition of Si on TiO_2 nanotubes via magnetron sputtering for the fabrication of TiO_2-Si composite negative electrode. If interesting results were obtained, in the two studies, the areal capacity of the composite electrodes remained very low as the Si was only deposited at the top of TiO_2 nanotubes due to the high vacuum techniques growth mechanism which lead to a low loading of Si. The use of electrodeposition in ionic liquid to grow the a-Si layer could strongly improve the coating of the TiO_2 nanotubes from the bottom to the top as shown in our previous preliminary study [37].

In this work, the electrochemical synthesis of a-Si thin film conformally electrodeposited from bottom to top on TiO_2 nanotubes for the fabrication of Si/TiO_2 nanotube composite negative electrode for Li-ion battery has been investigated in detail. The composite nanostructure is formed in two electrochemical steps: i) anodic oxidation of Ti for the synthesis of TiO_2 nanotubes; ii) cathodic reduction of Si^{4+} in ionic liquid for the synthesis of Si/TiO_2 nanotubes nanostructured composite. It is shown that the amorphous or crystalline state of the TiO_2 nanotubes as well as the Si loading on the nanotubes play a role regarding the capacity and the cycling performance of the battery. By optimizing the Si loading within the nanotube framework, stable lithiation and delithiation as well as improved capacity retention have been demonstrated.

2. Experimental

2.1. Synthesis of TiO_2 nanotubes

Self-organized TiO_2 nanotube arrays were synthesised 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) according to a procedure described elsewhere [38]. The titanium foils were degreased by sonication in acetone, isopropanol and ethanol, followed by rinsed with deionized water and dried in an argon stream before use. The foils were anodized in diethylene glycol electrolyte containing 2 wt% HF (50% v/v) and 2 wt% H_2O. The anodization was conducted in a two electrode cell using the titanium foil as working electrode (1.0 cm^2) and platinum wire as counter electrode in applied voltage of 60 V for 17 h. Then the electrodes were cleaned with acetone for 30 min and dried with argon steam. To obtain crystalline TiO_2 nanotubes, the as-anodized TiO_2 nanotubes were annealed at 450 °C or 550 °C for 2 h using a thermal annealing furnace (Jetfirst, Jipelec) with argon flow. The morphology of the TiO_2 nanotubes before and after thermal treatment was examined using a scanning electron microscope (SEM, HITACHI S-3400N). Grazing incidence X-ray diffraction (XRD) with 3° incoming x-rays was performed to study the change in the crystallinity of the nanotubes after the thermal treatments.

2.2. Silicon electrodeposition on the TiO_2 nanotubes

Silicon was electrochemically deposited on as-anodized (amorphous) or anatase TiO_2 nanotubes using Voltalab (PGZ 100) from an electrolyte containing room temperature ionic liquid, 1-butyl-1-methylpyrrolidinium bis (trifluoromethanesulfonyl)imide ([$P_{1,4}$]TFSA) (Solvionic, 99.9%) and 0.1 M $SiCl_4$ (Aldrich, 99.99%). Prior to the