



Silicon algae with carbon topping as thin-film anodes for lithium-ion microbatteries by a two-step facile method



E. Biserni ^{a,b}, M. Xie ^{c,*}, R. Brescia ^e, A. Scarpellini ^e, M. Hashempour ^f, P. Movahed ^f, S.M. George ^{c,d}, M. Bestetti ^f, A. Li Bassi ^{a,b}, P. Bruno ^a

^a Center for Nano Science and Technology @PoliMi, Istituto Italiano di Tecnologia, Via Pascoli 70/3, 20133 Milano, Italy

^b Department of Energy, Politecnico di Milano, Via Ponzio 34, 20133 Milano, Italy

^c Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309, United States

^d Department of Mechanical Engineering, University of Colorado, Boulder, CO 80309, United States

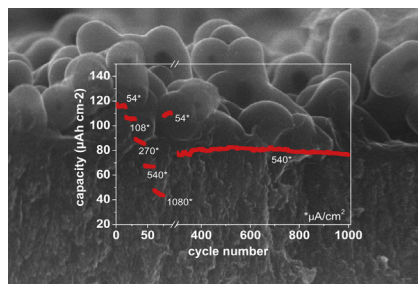
^e Department of Nanochemistry, Istituto Italiano di Tecnologia, Via Morego 30, 16163 Genova, Italy

^f Department of Chemistry, Materials and Chemical Engineering "Giulio Natta", Politecnico di Milano, Via Mancinelli 7, I-20131 Milano, Italy

HIGHLIGHTS

- We fabricate nanostructured porous Si algae covered by a carbonaceous capping layer.
- Nanoporosity of Si reduces mechanical stresses, while C forms a stable SEI layer.
- Nanoporous Si/C anodes show very good capacity retention up to at least 1000 cycles.
- Fabrication requires only two-steps with no need for harmful gases or chemicals.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 7 August 2014

Received in revised form

11 September 2014

Accepted 22 September 2014

Available online 7 October 2014

Keywords:

Lithium ion battery

Silicon anodes

Silicon nanostructures

Porous silicon

Cycle life

SEI layer

ABSTRACT

Silicon-based electrodes for Li-ion batteries (LIB) attract much attention because of their high theoretical capacity. However, their large volume change during lithiation results in poor cycling due to mechanical cracking. Moreover, silicon can hardly form a stable solid electrolyte interphase (SEI) layer with common electrolytes. We present a safe, innovative strategy to prepare nanostructured silicon–carbon anodes in a two-step process. The nanoporosity of Si films accommodates the volume expansion while a disordered graphitic C layer on top promotes the formation of a stable SEI. This approach shows its promises: carbon-coated porous silicon anodes perform in a very stable way, reaching the areal capacity of $\sim 175 \mu\text{Ah cm}^{-2}$, and showing no decay for at least 1000 cycles. With requiring only a two-step deposition process at moderate temperatures, this novel very simple cell concept introduces a promising way to possibly viable up-scaled production of next-generation nanostructured Si anodes for lithium-ion microbatteries.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

With rapid advances in the fields of microelectronic devices, microsensors, micromachines, RF-ID tags, MEMS, and drug delivery systems, the development of integrated power sources that enable the continued device operation is of great importance. To meet these demanding applications, microbatteries with high energy

* Corresponding author.

E-mail addresses: Xmdxx1182@hotmail.com, ming.xie@colorado.edu (M. Xie), bp4014iit@gmail.com (P. Bruno).

and power per unit area are urgently required and in this context lithium-ion technology is very promising. It is more important for microbatteries to achieve high capacity per footprint (mAh cm^{-2}) than per unit weight (mAh g^{-1}) or volume (mAh L^{-1}) [1,2]. In addition, the microbattery fabrication process should be compatible with state-of-the-art integrated circuit (IC) techniques, to lower the cost.

In order to further improve the areal capacity of microbatteries, three-dimensional (3D) nanostructured electrodes have been developed and investigated [3–8] which are generally realized by vacuum deposition or electroplating of active material onto a 3D metallic current collector, usually made of Ni or Ti, which are more expensive than conventional Al and Cu foils. In addition, 3D electrode fabrication usually involves wet chemistry, such as hydrothermal synthesis or etching, which is not compatible with the current IC technology. Therefore, when taking cost, complexity, and incompatibility into consideration, 3D nanostructured electrodes need more development to pitch into the microbattery market.

Besides the 3D concept, research is also heading for different materials with higher capacity. Silicon alloys with lithium up to $\text{Li}_{15}\text{Si}_4$ [9,10] at room temperature, this resulting in almost 10 times larger a capacity (3579 mAh g^{-1} for $\text{Li}_{15}\text{Si}_4$) than that of graphite (372 mAh g^{-1} [11]), which is the standard commercial material for negative electrodes. However, Slurry coating of Si-based anodes is mainly facing two drawbacks. First, they suffer from poor cycle life due to detrimental volume changes (i.e., theoretically up to 280% volume expansion [12]) of the host lattice upon alloying and de-alloying with Li. Extended fractures lead to a complete loss of electrical contact between active material and current collector and to pulverization. Second, the SEI layer formed by silicon in contact with common electrolytes is generally unstable and it detrimentally impacts the capacity retention [13,14].

At the state of the art, research works on strategies to cope with Si cracking, such as replacing bulk with porous materials [15], engineering the empty space [16], reducing amorphization-induced mechanical stresses by using non-crystalline silicon [9,17–19] or fabricating composite anodes where Si is mixed with other less-active materials that can buffer its volume expansion [20].

More in detail, nanoporous silicon has been investigated as a suitable material for enhancing LIB performances, for voids can effectively accommodate the volume expansion, as described by Wu and Cui [21]. Usually, porous silicon is obtained from bulk via electrochemical etching with hydrofluoric acid; the porous film is then used either as it is [15] or after ball-milling and mixing with other materials, such as C polymeric binders [22–26]. Recently, Liu et al. [27] adopted the strategy of covering Si nanoparticles with a thin C layer that acts as a stable interface towards the electrolyte; in addition, their pomegranate-inspired design aims to engineering some void space within the core–shell structure for Si to expand.

Combining Si with other less-lithium-active materials is introduced as an effective strategy [20]. Examples show that SiO_2 coating on Si improves capacity retention during cycling by buffering volume expansion and confining the detrimental activity of HF possibly evolving from electrolyte decomposition [28–30]. Even more promising is the route of composite anodes made of Si and C, whether they be in the form of mixed micrometrical-sized powders with C black and other additives [31–35], or in especially designed 3D nanostructures where C covers Si as a shell [21,36–40]. However, the sophisticated methodologies reported in these latter works generally require the use of expensive and extremely hazardous chemicals, such as HF or SiH_4 gas, and multistep treatments to tailor the anode nanostructure.

In alternative, physical vapour techniques are used to grow silicon nanostructures, as for example the Vapour–liquid–solid method for 1D-nanorods [38] or the Glancing Angle Deposition.

This latter allows to grow porous silicon in the form of columnar films to enhance its electronic transport [41], introducing, though, limitation in its thickness (300–500 nm).

So far, silicon planar thin-film anodes for microbatteries can only be realized within sub- μm thickness [41–45], leading to low areal capacity. Therefore, it is of importance to develop Si thin film anodes with enhanced areal capacity compared to 3D nanostructured electrodes, meanwhile offering a long and stable lifetime by managing mechanical instability due to volume changes.

In this work, we address the two main drawbacks of silicon anodes in lithium ion microbatteries by a two-layer architecture obtained by a facile two-step method. We fabricated novel nano-composite Si–C anodes by depositing nanostructured porous amorphous Si films by Pulsed Laser Deposition (PLD) at room temperature, followed by Chemical Vapour Deposition (CVD) of a thin carbon coating. The mesoporosity of the nanostructured Si films and its lack of crystallinity are expected to reduce the detrimental effects of volume variations and to avoid mechanical stressing due to amorphization in the first cycles. The thin CVD-grown carbon layer, then, is expected to promote the formation of a stable solid electrolyte interphase (SEI) layer and protect Si from direct contact with the electrolyte. Rather than covering the whole Si surface area with C, we propose an alternative anode structure where the formation of SEI is shifted away from the active silicon; this simple architecture allows for a straightforward two-step process that presents so far no upper limits to the obtainable film thickness.

2. Experimental

2.1. Film fabrication

In order to grow mesoporous hierarchical silicon films by PLD at room temperature, a rotating and translating monocrystalline $<100>n +$ doped silicon wafer target was ablated by a KrF laser beam ($\lambda = 248 \text{ nm}$, pulse energy 400 mJ, pulse duration 20 ns, repetition rate 20 Hz) with a fluence of $\sim 5 \text{ J cm}^{-2}$ and the ablated material was collected on copper discs (1.3 cm diameter).

As a background process gas, a mixture of Ar and H_2 ($<3 \text{ vol.}\%$) was inserted in the chamber while vacuum pumping, so to dynamically set the process gas pressure either at 60 Pa or 100 Pa, thus controlling the morphology of the grown film. The role of H_2 in the gas mixture is to passivate the Si surface.

Target-to-substrate distance was fixed to 50 mm and during deposition the substrate holder was rotated to widen uniformity over the deposition area. Deposition was carried out with the substrate at room temperature (see Table S11 in supporting information for a summary of the investigated samples and their deposition conditions).

For CVD, the samples were loaded into a quartz tubular furnace where a mixture of H_2 and N_2 gas (6 sccm and 100 sccm, respectively) was fluxed while ramping the temperature up to $825 \text{ }^\circ\text{C}$ at the rate of $10 \text{ }^\circ\text{C min}^{-1}$. After stabilization of the temperature (15 min), ethylene was added (20 sccm) during 5 min (or 7 min in the case of thicker sample) to the gas mixture, as a precursor for carbon deposition. After this time, the previous gas atmosphere of H_2 and N_2 was restored during the whole cooling down step. In addition to substrates previously covered by the Si film, some bare Cu substrates were also loaded into the furnace for the same coating process in the same conditions, so to get pure C(CVD) anodes to be used in reference cells.

Process temperature for the CVD was chosen to be right above the threshold for the ethylene decomposition but low enough to avoid any possible effect of recrystallization of the amorphous Si layer underneath. As for the reaction time, it was adjusted so to

Download English Version:

<https://daneshyari.com/en/article/7734825>

Download Persian Version:

<https://daneshyari.com/article/7734825>

[Daneshyari.com](https://daneshyari.com)