Silicon nano-trees as high areal capacity anodes for lithium-ion batteries

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HIGHLIGHTS

- Silicon "nano-tree" structure for high surface capacities up to 7.1 mAh cm^{-2}.
- Remarkable rate capabilities compared to high loading Si electrodes in literature.
- Excellent rate capability performance during delithiation.
- Architecture ensuring combination of high energy and high power.

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ABSTRACT

Nanostructured silicon electrodes have attracted attention as a potential candidate for high capacity anode in lithium-ion batteries, thanks to their high specific capacity and their ability to accommodate silicon volume changes upon cycling. However, the silicon amount deposited on these nanostructured electrodes is generally low and leads to low surface capacities. Here, a new structure is proposed to increase the areal density of silicon on the electrode. A second growth of secondary nanowires on a silicon nanowires electrode leads to a "nano-tree" structure with surface capacities between 1.8 and 7.1 mAh cm^{-2}. These high loaded electrodes maintain very good rate capabilities and a rather stable cycling is observed for the intermediate loadings, with a capacity maintained above 2 mAh cm^{-2} after 100 cycles at C/5. This paper provides evidence of a successful synthesis of high loaded silicon electrodes for practical applications, of which the electrochemical performances outperform those of graphite commercial anodes.

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1. Introduction

Silicon has recently been studied as anode material for lithium-ion batteries. Indeed, it is an interesting alternative to replace commercial graphite due to its very high theoretical capacity, 3580 mAh g^{-1}, corresponding to the formation of Li$_{15}$Si$_4$ alloy [1,2]. However, a huge volume expansion occurs upon cycling [3,4] and

shortens the cycle life of the battery. Different strategies have led to significant improvement of the stability. In conventional composite electrodes, prepared as a slurry of silicon particles, carbon and binder, advances were mainly obtained by using other polymer binders that allow a better mechanical strength of the electrode during volume expansion [5–7]. Another solution consists in using nanostructured electrodes having a high surface/volume ratio to address the problem of volume change [8]. Various structures have been proposed, like silicon nanowires [9–11], silicon nanotubes [12,13] or hybrid structures [14–17]. Moreover, such nanostructures can be prepared with a bottom-up approach which leads to a direct contact of the active material with the current collector and therefore allows good electronic conductivity and good power performances, i.e. the ability to sustain high current rate without

any loss of capacity. On the contrary, in conventional composite electrodes, the use of a resistive polymer and the need of a good percolation between particles for electronic conductivity lead to poorer power performances, especially when increasing the electrode thickness.

A major drawback of nanostructured electrodes is that they present a huge porosity and therefore an increased reactivity with the electrolyte and a limited amount of silicon areal mass loading [8,11], generally below 0.3 mg cm^{-2}. As underlined by Zamfir et al. [11], one of the challenges for the future with nanostructured electrodes is to increase the amount of active material. To be competitive with commercial graphite anodes, an areal capacity above 2 mAh cm^{-2} would be required, which typically corresponds to silicon loading above 1 mg cm^{-2}. Although areal capacity is rarely specified for Si nanostructured electrodes, a few strategies have been reported to increase silicon amount on the electrode. First of all, the increase of nanowires diameter leads to a higher loading. But it remains below 1 mg cm^{-2} and it has a detrimental effect on the rate capability [18]. Other structures have been reported in the literature like Si nanoparticle-decorated Si nanowire networks leading to a 1.5 mg cm^{-2} loading and a capacity above 2 mAh cm^{-2} during 50 cycles [19]. A loading slightly below 1 mg cm^{-2} was also achieved with porous silicon nanowires [20,21]. Higher silicon loading of 5 mg cm^{-2} was reported by Liu et al. for three-dimensional network current collectors supported Si nanowires [22]. A 3D current collector was also used by Hu et al. [23] with deposition of a very high amount of amorphous silicon of 8 mg cm^{-2}. These electrodes showed stable cycling at respectively C/10 [22] and C/5 [23] for 50 cycles but their performances at higher current rate are not reported. More recently, Peled et al. [24] prepared electrodes with silicon nanowires on a carbon fiber current collector and presented a cycling with areal capacity above 3 mAh cm^{-2} for 30 cycles.

With our experience in Chemical Vapor Deposition (CVD) synthesis, including silicon nanowires growth [10], we present here a new nanostructured electrode for lithium battery, with tree-like interconnected silicon nanowires. This structure was designed to increase the silicon loading, while keeping the advantages of nanowire-based electrodes: high surface/volume ratio allowing accommodation of volume changes, and bottom-up approach allowing mechanical strength of the electrode without any resistive additive (binder). A similar structure was already proposed by Thissandier et al. [25] for a supercapacitor electrode. In this paper, the synthesis of such structures is described, and the tuning of synthesis parameters is presented to reach different silicon loadings. Finally, electrochemical characterization is performed and a very high capacity, above 7 mAh cm^{-2}, is reached for the most loaded sample, with good capacity sustained at high current rate (over 60% capacity retention in lithiation at C/2 and close to 90% in delithiation at 1C). Moreover, a good cycling stability is observed for the intermediate loading, with a capacity maintained above 2 mAh cm^{-2} after 100 cycles at C/5.

2. Experimental section

2.1. Synthesis of silicon nanowires

At first, gold catalyst thin film is deposited on the stainless steel substrate (Goodfellow, 50 μm) by e-beam evaporation using a Plassys evaporator. Rate and thickness controls of the deposition are achieved through the use of a quartz crystal microbalance. Then, silicon nanowires growth is performed by Hot-Filament Chemical Vapor Deposition (HF-CVD) according to the Vapor-Liquid-Solid (VLS) mechanism [26], at 540 °C, 7.5 mbar and with SiH$_4$/H$_2$ (20/100 sccm) as gas precursor. Growth time varies

between 20 and 30 min. The prepared samples have 5 cm × 5 cm dimensions. The electrodes are cut in with a punch of 12 mm diameter and are used as is without any further preparation.

2.2. Electrochemical testing

The electrochemical tests are performed in two-electrode coin cells (CR 2032), with metallic lithium as counter electrode. The electrolyte is a homemade solution of 1 M LiPF$_6$ in a 1:1 (v/v) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) with a fluoroethylene carbonate (FEC) additive (+5 wt%) that already proved to enhance the cycling stability of SiNWs anodes [27]. Galvanostatic cycling was performed on a VMP3 battery tester (Bio-Logic). Current values were expressed as C/n where n indicates the number of hours required for a complete charge of the silicon electrode (1C = 3.58 A g^{-1}). Cycles were recorded between 20 mV and 0.8 V vs Li$^+$/Li.

2.3. Characterization

Images of the electrodes are made by Scanning Electron Microscope (SEM) (Hitachi S-4800). To observe cycled electrodes, coin cells are disassembled inside the Ar-filled glove box and the electrodes are rinsed with dimethyl carbonate (DMC) to remove any excess of electrolyte. After drying, the electrodes are transferred inside the SEM chamber.

3. Results and discussion

3.1. SiNW3D structure

The high mass loading structure described in this paper consists in tree-like interconnected silicon nanowires. Such structure is obtained thanks to a two-step CVD process schematized in Fig. 1a). First, standard nanowires are grown on the stainless steel current collector thanks to a gold-catalyzed VLS mechanism [26], as described in the experimental part. A SEM image of the nanowires obtained after this first step is displayed in Fig. 1b). Their diameters are governed by the thickness of catalyst layer and are typically between 10 and 250 nm for a catalyst layer thickness below 10 nm [18]. Their lengths are in the order of a few tens of micrometers and depend on the growth time. Silicon loading after this first step is still below 0.3 mg cm^{-2}. After this first growth, a new thin layer of gold catalyst is evaporated over this SiNW electrode and then a second growth is carried out using the same CVD process. As expected, a dewetting of the gold layer occurs and leads to the growth of secondary nanowires between and along the existing nanowires, as evidenced on the SEM image in Fig. 1c). It can be evidenced that during the second growth, the nanowires synthesized during the first growth keep growing in length.

The silicon loading of the final electrode is strongly influenced by the thickness of gold catalyst deposited at both steps and by the growth time. Hence several samples are prepared by changing these two parameters, their characteristics are summarized in Table 1. For sample 1, a 3 nm gold layer and a 20 min growth time are used for both steps. It leads to a silicon loading of 0.56 mg cm^{-2}. Higher loading is reached by increasing the thickness of gold layer to 10 nm and the growth time to 30 min for the first step (sample 2, 1.01 mg cm^{-2}). When a gold layer of 10 nm is also used for the second step, a high loading of 2.47 mg cm^{-2} is reached (sample 3).

SEM images of the prepared electrodes are displayed in Fig. 2. Nano-tree structures are clearly observed in the three samples, with branch nanowires emerging from trunk nanowires. A thickness difference is observed between the three samples. The lower thickness of sample 1 (~35 μm), evidenced on Fig. 2, can be