



# Cycling strategies for optimizing silicon nanowires performance as negative electrode for lithium battery



Lucie Leveau<sup>a,\*</sup>, Barbara Laïk<sup>b</sup>, Jean-Pierre Pereira-Ramos<sup>b</sup>, Aurélien Gohier<sup>c</sup>,  
Pierre Tran-Van<sup>c</sup>, Costel-Sorin Cojocaru<sup>a</sup>

<sup>a</sup> Laboratoire de Physique des Interfaces et des Couches Minces, École Polytechnique, Route de Saclay, 91128 Palaiseau Cedex, France

<sup>b</sup> Institut de Chimie et des Matériaux Paris-Est ICMPE/GESMAT, UMR 7182CNRS-UPEC, 2 à 8 rue Henry Dunant, 94320 Thiais, France

<sup>c</sup> Renault SAS, DREAM/DETA/SEE, 1, Avenue du Golf, 78288 Guyancourt, France

## ARTICLE INFO

### Article history:

Received 28 July 2014

Received in revised form 24 December 2014

Accepted 9 January 2015

Available online 12 January 2015

### Keywords:

Silicon nanowires

Lithium batteries

Cycling strategy

Limited capacity

Cycle life improvement

## ABSTRACT

The cycling conditions of silicon nanowires anode are investigated and a set of conditions is proposed in order to improve the cycle life of these electrodes, without any structure or surface optimization. Limitation of lithiation or delithiation to an intermediate value of  $900 \text{ mAh g}^{-1}$  allows to perform up to 1850 cycles at C/5 rate, which represents a significant increase of the electrode cycle life compared to that observed for standard cycling. This behavior is still attractive at higher current rate. At 1 C rate, it is proved that combining the lithiation-limited cycling with an upper cut-off voltage of 0.8 V improves the capacity retention by a factor 2. When using these optimized conditions, combined with a simple adding of fluoroethylene carbonate or vinylene carbonate in the electrolyte, a compact solid electrolyte interphase is formed upon cycling and an exceptional capacity retention is observed, reaching respectively 1500 and more than 2000 cycles.

© 2015 Elsevier Ltd. All rights reserved.

## 1. Introduction

Lithium-ion batteries are currently one of the most efficient technologies for energy storage but efforts are still needed to improve their energy density. The ability of silicon to form Li-rich alloys (up to  $\text{Li}_{15}\text{Si}_4$  at room temperature, *i.e.* a specific capacity of  $3580 \text{ mAh g}^{-1}$  [1,2]) makes it one of the best candidates to replace commercial graphite anode and to reach higher energies. The huge volume variation ( $\sim 300\%$ ) following this alloy formation is however detrimental to the durability of silicon electrodes since it induces mechanical stress that can cause pulverization of the material and break of electrical conductivity [3]. 1D nanometric structures, like silicon nanowires (SiNWs), have been proposed to improve the battery cycle life thanks to better accommodation of volume expansion than bulk silicon [4,5]. Moreover, they have the advantage of being directly grown on the current collector, preventing the use of any binder or conducting additives that lower the specific capacity of the electrode.

A standard galvanostatic cycling of silicon nanowires anode, with conventional potential limitations (2 V upper voltage to ensure full delithiation of the electrode, and 20 mV lower voltage

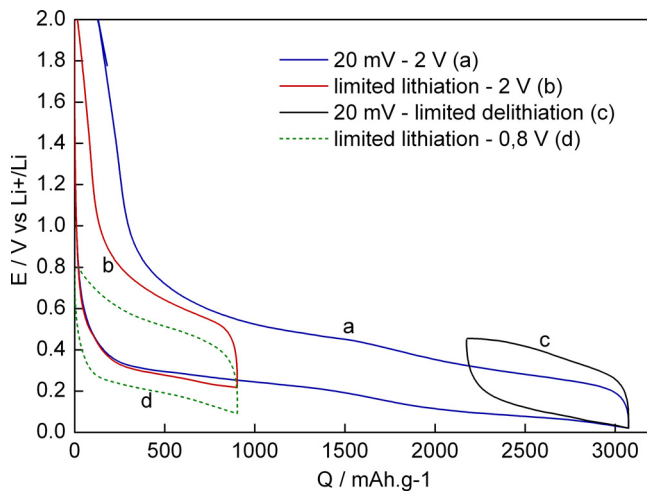
to prevent deposition of metallic lithium), allows reaching high reversible capacity, close to  $3000 \text{ mAh g}^{-1}$ . However, a fast decline of this capacity is observed after only one hundred cycles. Therefore, improvements of SiNWs electrode cycle life were proposed by surface coatings [6–9] or use of electrolyte additives [10–12]. However, only a few papers deal with the influence of the cycling conditions and provide some indications to enhance the capacity retention, for instance by increasing the lower cut-off voltage above 100 mV [13–16]. Chakrapani et al. [17] observed the promising effect of capacity limitation during delithiation process. In conventional carbonates mixture as electrolyte, they obtained up to 200 cycles at  $1000 \text{ mAh g}^{-1}$  with a slow rate of C/10. A greater cycle life was observed in ionic liquid electrolyte but with a much reduced capacity of  $320 \text{ mAh g}^{-1}$ .

This prompted us to propose here an extensive investigation of the influence of different cycling conditions. A comparative study of the cycling parameters is performed in order to improve the capacity retention of SiNWs electrode. The objective is to allow limited swelling of the silicon, by limiting either the depth of lithiation, or the depth of delithiation, or the delithiation cut-off voltage.

Extended optimized cycling experiments were performed leading to significant improvements of capacity retention at  $900 \text{ mAh g}^{-1}$ , with more than 1800 cycles at C/5 rate and more than 350 cycles at 1 C. Furthermore, we prove that combining these

\* Corresponding author: Tel.: +33169334359; fax: +33169334333.

E-mail address: [lucie.leveau@polytechnique.edu](mailto:lucie.leveau@polytechnique.edu) (L. Leveau).



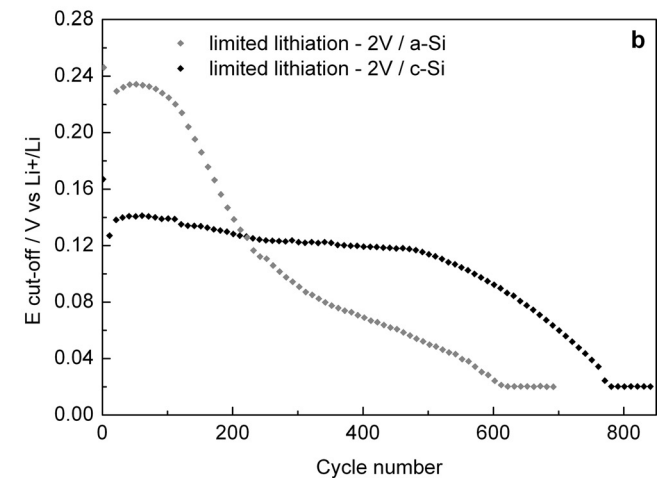
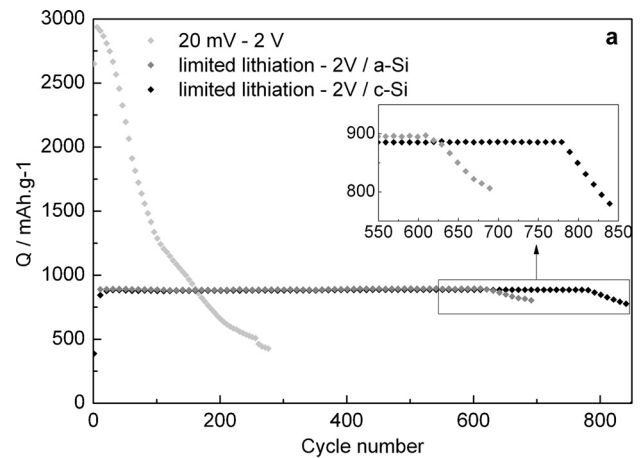
**Fig. 1.** Illustration of the adopted cycling strategies: a) standard cycling between 20 mV and 2 V; strategy b) lithiation-limited ( $900 \text{ mAh g}^{-1}$ ) cycling with delithiation to 2 V; strategy c) delithiation-limited ( $900 \text{ mAh g}^{-1}$ ) cycling with lithiation to 20 mV; and strategy d) lithiation-limited ( $900 \text{ mAh g}^{-1}$ ) cycling with reduced delithiation cut-off voltage of 0.8 V.

optimized cycling conditions with the use of an electrolyte additive can further enhance the capacity retention, with more than 2000 cycles at  $900 \text{ mAh g}^{-1}$  at 1 C rate.

## 2. Experimental

SiNWs were grown by Hot-Filament Chemical-Vapor Deposition (HF-CVD) according to the vapor-liquid-solid mechanism [18]. The substrate was a commercial stainless steel foil of  $50 \mu\text{m}$ -thickness covered by a 3 nm film of evaporated gold catalyst, as previously described [19]. CVD synthesis was carried out at  $540^\circ\text{C}$  and 7.5 mbar using  $\text{SiH}_4$  as a precursor and  $\text{H}_2$  as a carrier. A tungsten filament was heated to decompose  $\text{H}_2$  and prevent the formation of amorphous silicon between the nanowires. The prepared sample has  $5 \text{ cm} \times 5 \text{ cm}$  dimensions and the mass of SiNWs, determined by weighing of the uniform deposit, was  $0.25 \text{ mg cm}^{-2}$ .

Pieces of this electrode of approximately  $0.25 \text{ cm}^2$  were cut and assembled into coin-type 2032 cells, with lithium metal foil as counter electrode and a combination of propylene (Celgard, 2400) and glass fiber (Whatman, GF/C) as separators. The electrolyte for the first set of experiments at C/5 rate was a standard commercial solution of 1 M  $\text{LiPF}_6$  in 1:1:1 mixture of ethylene carbonate (EC), dimethyl carbonate (DMC) and diethyl carbonate (DEC). For the second set of experiments, at 1 C rate, a homemade solution of 1 M  $\text{LiPF}_6$  in EC/DMC (1:1) was used. These two similar electrolytes were compared beforehand, showing similar results, with slightly



**Fig. 2.** Cycling of SiNWselectrode in EC-DMC-DEC + 1 M  $\text{LiPF}_6$  with C/5 rate: influence of the cycling method used (complete cycling between 2 V and 20 mV, capacity-limited cycling, with or without a first complete cycle at C/20). Evolution of reversible capacity (a) and cut-off voltage (b) in function of the cycle number.

better rate capabilities for the homemade electrolyte. Current values were all expressed according to the theoretical capacity of silicon ( $1\text{C} = 3.58 \text{ A g}^{-1}$ ).

Electrochemical cycling was performed using a VMP3 battery tester (Bio-Logic), in galvanostatic mode. The error in cut-off capacity is estimated to be  $\pm 40 \text{ mAh.g}^{-1}$  because of the experimental mass error of Si. However, this doesn't lead to significant variation of the cycle life when testing different cells in parallel. Charged and discharged capacities are extracted at each cycle, as well as the cut-off voltage, but for better clarity of the graph, they are displayed only every ten cycles.

**Table 1**

Description of the applied cycling strategies with the corresponding cycle life

	End of lithiation	End of delithiation	C-rate	Cycle number at $900 \text{ mAh g}^{-1}$ or higher
Conventional cycling a	20 mV	2 V	C/5	160
Strategy b	$900 \text{ mAh g}^{-1}$	2 V	1 C	100
			C/5	780
Strategy b' (with complete 1st cycle)	$900 \text{ mAh g}^{-1}$	2 V	1 C	195
			C/5	610
Strategy c	20 mV	$900 \text{ mAh g}^{-1}$	1 C	260
			C/5	1850
Strategy d	$900 \text{ mAh g}^{-1}$	0.8 V	1 C	340
				365 without additive
				1450 with FEC
			1 C	> 2000 with VC

Download English Version:

<https://daneshyari.com/en/article/184634>

Download Persian Version:

<https://daneshyari.com/article/184634>

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