



# Nanosized Si/cellulose fiber/carbon composites as high capacity anodes for lithium-ion batteries: A galvanostatic and dilatometric study

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## ABSTRACT

Recently, we reported a simple method for obtaining nanosized silicon with promising electrochemical properties as an anode material for lithium-ion batteries; the method involves the formation of a composite electrode with cellulose fibers. It is demonstrated that the performance of these electrodes can be enhanced by the addition of conductive carbon black (CCB). This beneficial effect is not only a result of the improvement of electrical conductivity and inter-particle contacts, but also due to a reduction of the expansion and shrinkage undergone by the electrode when Li is inserted into Si or extracted from Li<sub>x</sub>Si, as revealed by *in situ* electrochemical dilatometry measurements. The best results were obtained with a CCB of high surface area and porosity. The Si/cellulose fiber/carbon electrodes obtained delivered charge capacities as high as 1800 mAh g<sup>-1</sup> and exhibited good capacity retention on cycling. These electrodes also exhibited lower expansion/shrinkage compared to carbon-free electrodes on discharging and charging the cell, respectively.

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## 1. Introduction

Attempts to replace graphite as standard anode material for lithium-ion batteries (LIBs) with other materials affording a greater lithium storage capacity have multiplied over the last decade. Recently, a new LIB using a tin-based anode material has been placed on the market [1]. Silicon, which is similarly reactive towards Li as Sn, but lighter, is an attractive alternative for further increasing the charge capacity of this new LIB generation [2]. Each Si atom can reversibly react with 3.75 Li atoms; this is equivalent to a charge capacity (specific charge) of 3579 mAh g<sup>-1</sup> [3], compared to only 372 mAh g<sup>-1</sup> and 993 mAh g<sup>-1</sup> from the reactions of Li with C [4] and Sn [5], respectively. The main shortcoming of silicon is the great volume change it undergoes during lithium alloying/dealloying [6], which causes alloy grains to fracture and electrical contact between them to be lost, ultimately leading to capacity fading on cycling.

This shortcoming has been addressed by preparing alternative electrodes of reduced particle size [7,8] or using thin films [9,10], among others. Our group has adopted a different strategy involving the deposition of nanoparticles onto cellulose fibers, a method which had previously been successful with Sn [11], Sb [12], and Si [13]. This latter electrode delivered an average charge capacity of 1400 mAh g<sup>-1</sup>, based on Si mass and after 50 cycles. This value exceeded substantially that of an electrode made from pure Si (ca.

400 mAh g<sup>-1</sup> after 50 cycles) but it is still far from the theoretical charge capacity cited above (3579 mAh g<sup>-1</sup>).

In this work, we improved the performance of this composite electrode with the addition of an appropriate conductive carbon black (CCB) during deposition of nanosized Si particles onto cellulose fibers. The electrochemical properties of the composites were characterized by charge/discharge cycling tests, and the electrode expansion and shrinkage effects by means of *in situ* electrochemical dilatometry analysis. The few studies so far reported utilizing this technique [14,15] have proved its suitability for the analysis of the dimensional changes of electrode materials, particularly alloy-based anodes, crucial for the new generation of Li-ion batteries.

## 2. Experimental

Nanosized Si (n-Si) was supplied by Aldrich, cellulose fibers by Arbocel<sup>®</sup>, and CCBs by TIMCAL (Super P) and Degussa (Printex XE2), respectively. Scanning electron microscopy (SEM) images were obtained with a JEOL 6400 scanning electron microscope. Specific surface areas and pore volumes were determined with a Micromeritics ASAP 2020 instrument, using N<sub>2</sub> gas as adsorbate at 77 K.

Cellulose fibers were added to a suspension of n-Si, or n-Si and carbon, in isopropanol and were then mildly heated (~363 K) to dryness. Three composites were prepared with the following composition in weight %: *composite A* (50 n-Si/50 cellulose fibers); *composite B* (50 n-Si/40 cellulose fibers/10 Printex XE2); *compos-*

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ite C (50 n-Si/40 cellulose fibers/10 Super P). All composites were dried at 353 K under vacuum for 1 h.

The electrodes were prepared by different procedures depending on the measurement type. For galvanostatic tests, the electrodes were simply prepared by pressing ca. 2 mg of composite on a stainless steel grid (diameter 7 mm) at 221.5 MPa. No other components (e.g., binders) were added during electrode preparation. Two-electrode Swagelok type electrochemical cells were assembled in an M-Braun 150 argon glove box using lithium metal as counter-electrode. The electrolyte was battery grade electrolyte ethylene carbonate/diethyl carbonate, EC:DEC 1:1 w/w, 1 M LiPF<sub>6</sub> with 2 wt.% of vinylene carbonate. Electrochemical measurements were recorded on a MacPile II potentiostat–galvanostat. Cycling tests were carried out in the potential window 1.5–0 V vs. the lithium counter electrode, using a specific current of 96 mA g<sup>-1</sup> (equivalent to C/10, C representing 1 Li<sup>+</sup> ion exchanged in 1 h, equivalent to 3579 mAh g<sup>-1</sup> for Li<sub>3.75</sub>Si).

For the electrochemical dilatometry measurements, electrodes (diameter 8 mm) were prepared by doctor blading the suspension onto a Cu substrate of 20 μm thickness prior to drying. The deposits of ca. 600 μm thickness were compacted at 37.7 MPa to a final thickness of 50–70 μm. A three-electrode cell was used with Li metal as counter and reference electrodes. The electrochemical dilatometer used in this work is a home-made apparatus described in detail elsewhere [16]. The electrolyte used was battery grade ethylene carbonate/dimethyl carbonate (EC:DMC) 1:1 w:w, 1 M LiPF<sub>6</sub> and was obtained from Ferro Corp. (USA). The cell was cycled with a combined galvanostatic–potentiostatic protocol. First, galvanostatic conditions (100 mA g<sup>-1</sup>) were used within the potential window between 0.01 and 1.2 V vs. Li/Li<sup>+</sup>. At the respective potential extremes, a potentiostatic step followed until the specific current decayed to a value of 50 mA g<sup>-1</sup>. The measurements were carried out with a standard battery cyler (Astrol Electronics AG, Switzerland).

### 3. Results and discussion

The nano-silicon particles exhibited a flake-like morphology with a pseudo-circular shape and a diameter of 40–50 nm [13]. On mixing with cellulose fibers, the nanoparticles tended to adhere

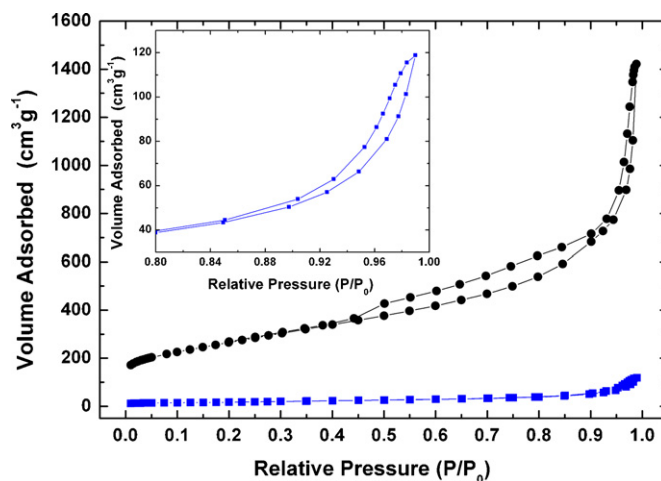


Fig. 1. N<sub>2</sub> adsorption/desorption curves for Printex XE2 (●) and Super P (■) carbon. Inset: detail of Super P adsorption/desorption curve at high pressures.

onto the fibers, thereby hindering agglomeration. The textural properties of the carbons obtained from N<sub>2</sub> adsorption measurements and SEM images showed some differences worth noting. Fig. 1 shows N<sub>2</sub> adsorption/desorption curves, the most salient features being the high adsorption amount and greater hysteresis loop observed for Printex XE2. The Brunauer–Emmet–Teller (BET) surface area as well as the total pore volume and mean pore size obtained from the adsorption branch by BJH method are included in Table 1. Printex XE2 had the highest specific surface area (950 m<sup>2</sup> g<sup>-1</sup>), 15 times greater than Super P (61 m<sup>2</sup> g<sup>-1</sup>), in agreement with the information provided by the suppliers (see Table 1). Also, the pore volume of Printex XE2 was significantly higher (1.7 cm<sup>3</sup> g<sup>-1</sup> vs. 0.2 cm<sup>3</sup> g<sup>-1</sup>), while differences in pore diameter were smaller (9.2 nm vs. 12.1 nm). SEM images of the two carbon blacks are shown in Fig. 2. The particles of Printex XE2 are submicronic in size with a tendency to form loosely bound agglomerates. By contrast, Super P carbon possesses bigger particles, with less tendency to agglomerate (based on manufacturer data, the particle size of Super P is 40 nm and hence larger than the 30 nm of

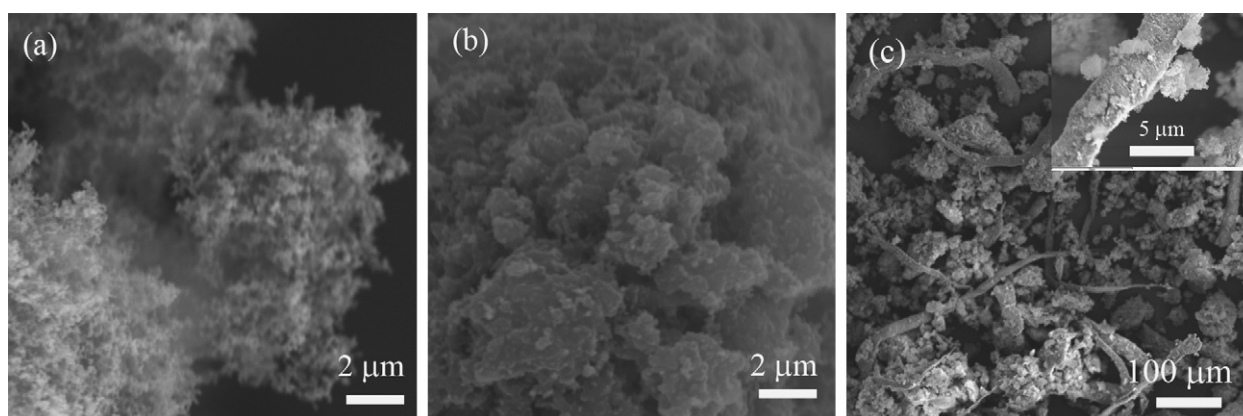


Fig. 2. SEM images of (a) Printex XE2 carbon, (b) Super P carbon, and (c) Si/cellulose fiber/XE2 composite electrode. Inset: detail of (c).

Table 1

S<sub>BET</sub>, pore volume, pore diameter and particle size of carbons.

Carbon	S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> )	Pore volume (cm <sup>3</sup> g <sup>-1</sup> )	Pore diameter (nm)	Particle size <sup>a</sup> (nm)
Super P	61 (62 <sup>a</sup> )	0.2	12.1	40
XE2	950 (910 <sup>a</sup> )	1.7	9.2	30

<sup>a</sup> Taken from the Timcal and Evonik Degussa catalogs.

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