

# Amorphous silicon as a possible anode material for Li-ion batteries

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## Abstract

Silicon thin films have been deposited on porous nickel substrates by low pressure chemical vapor deposition using silane as the precursor gas. At 650°C, the substrates were covered by a 1.2 μm thick amorphous silicon layer. The films were electrochemically cycled vs. a lithium electrode. Despite high capacity up to 1000 mA h/g measured during the first three cycles, the films have shown poor cycling ability over 20 cycles. This fade of the specific capacity is assigned to mechanical disintegration of the electrode during cycling. © 1999 Elsevier Science S.A. All rights reserved.

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## 1. Introduction

Numerous studies currently aim at the improvement of the specific capacity of the anode material in Li-ion cells. Despite interesting performances of Sn based oxides [1–4], the irreversible capacity loss systematically observed on the first cycle for these compounds is a main drawback for their use as anode materials in lithium ion cells. For example, the irreversible capacity shown by SnO<sub>2</sub> is related to the reduction of the oxide material and the subsequent formation of Li<sub>2</sub>O and Sn [1–4] during the first cycle. The high specific capacity measured on the second and following cycles is due to the reversible formation and decomposition of lithium tin alloys which can accommodate up to 4.4 Li atoms per Sn atom. In order to avoid the irreversible capacity loss during the first cycle, several studies have aimed at the use of pure tin materials [5–7]. However, other problems associated with the tremendous volume change of the tin electrode during the cycling must be faced.

Not only tin is efficient in forming alloys with lithium. Silicon can also react with lithium to form alloys with a high Li/Si ratio, like Li<sub>22</sub>Si<sub>5</sub>. Despite the high theoretical capacity of silicon (4000 mA h/g), the alloying of lithium with well crystallized silicon can hardly occur at room temperature. However, the addition of Si atoms or poorly

crystallized silicon compounds can efficiently enhance the capacity of carbon based materials. For example, nanodispersed silicon [8–13] in carbon electrodes exhibit specific capacity up to 600 mA h/g. To determine the active role of amorphous silicon in such anodes, thin films have been prepared by low pressure chemical vapor deposition and their electrochemical performance has been characterized. In order to avoid mechanical disintegration of the silicon based electrodes (what usually occurs for tin electrodes [5–7]), the silicon material was deposited on porous nickel substrates. It was believed that the voids in the porous structure of the substrate can help the active silicon material to accommodate a volume change without pulverizing. Furthermore, the high specific area of the porous nickel can help to keep a good electrical contact between the current collector and the silicon layer during the electrochemical tests.

## 2. Experimental

Silicon thin films were prepared by chemical vapor deposition (CVD). Some 200 sccm flows of SiH<sub>4</sub> and 200 sccm flow of Ar/H<sub>2</sub> were mixed in the reactor. The pressure was maintained at 10 Torr during deposition. Thin films were deposited at 650°C onto porous nickel substrates for the structural characterization and electrochemical tests, and on quartz substrates in order to check the thickness. Scanning electron microscopy and X-ray diffrac-

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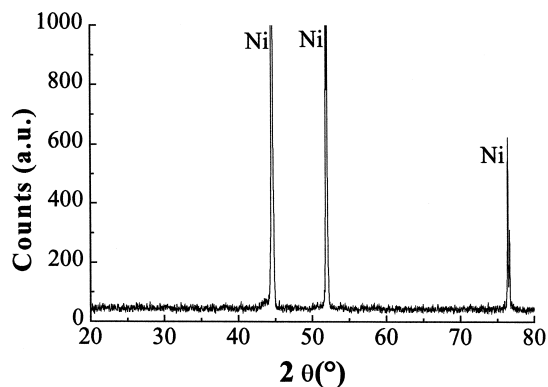


Fig. 1. Typical X-ray diffraction pattern of a silicon thin film (1  $\mu\text{m}$  thick) on a porous nickel substrate. Note that only the reflections of the substrate can be observed, thus indicating that the deposit is amorphous.

tion were used to characterize the materials. The amount of silicon deposited was estimated by weighting the quartz and porous nickel substrates before and after deposition. In addition, the thickness of the silicon thin film on quartz substrate was determined by examination of the film

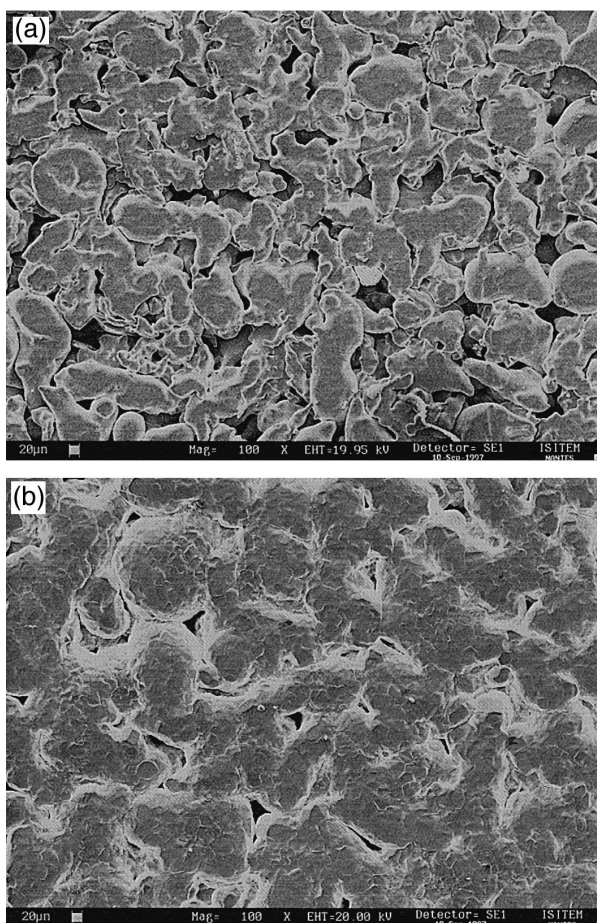


Fig. 2. Scanning electron micrograph of the (a) raw porous nickel substrate and (b) of the same sample covered by a 1.2  $\mu\text{m}$  thick Si film. The white bar on the left corner is 20  $\mu\text{m}$ .

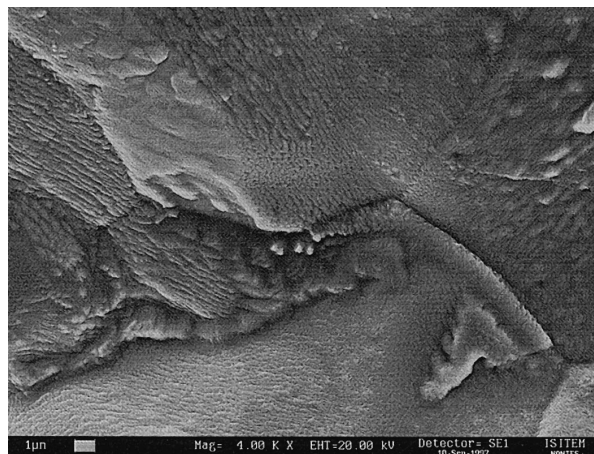


Fig. 3. Enlargement of Fig. 2b. The white bar on the left corner is 1  $\mu\text{m}$ .

crossed section by scanning electron microscopy. A second estimation of the amount of silicon deposited was calculated assuming a density of 2.33 for the silicon thin film. The discrepancy between the two values never exceeded 20% thus indicating dense films. Electrochemical tests were performed on as-deposited thin films on nickel substrates which were cycled between 1.10 and 0.05 V vs. a lithium reference electrode. The two electrodes were separated by a glass filter paper wetted with a standard  $\text{LiPF}_6$  electrolyte dissolved in a 1:1 mixture of ethylene carbonate and dimethyl carbonate (Merck). The electrochemical tests were performed in an argon filled glove box (less than 10 ppm  $\text{H}_2\text{O}$  and  $\text{O}_2$ ) using a Macpyle II.

### 3. Results and discussion

No reflections except those of the nickel substrate could be detected by X-ray diffraction on the compounds de-

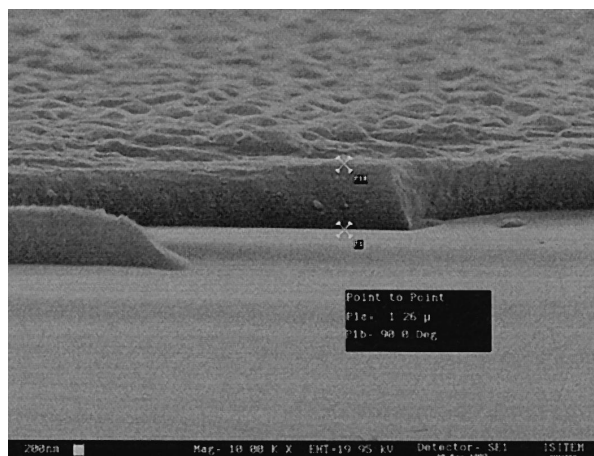


Fig. 4. Same Si deposit as in Fig. 2b but on a quartz substrate. The white bar on the left corner is 200 nm.

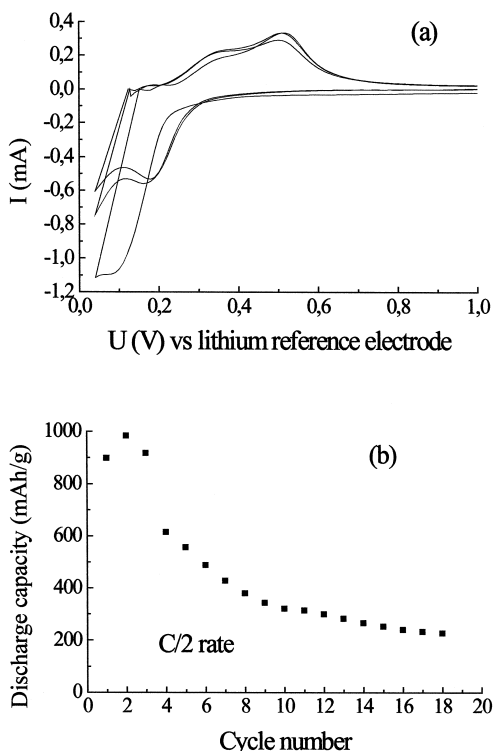


Fig. 5. (a) Slow scan cyclic voltamogram (10 mV/120 s) and (b) discharge capacity of a Si thin film (1.2  $\mu\text{m}$  thick) on a porous nickel substrate cycled versus a Li reference electrode in  $\text{LiPF}_6$  based electrolyte.

posited by LPCVD (Fig. 1). Therefore, we suppose that the film was amorphous.

Fig. 2a shows the surface of a porous nickel substrate. Pores 10 to 50  $\mu\text{m}$  wide can be observed. One can notice that the number and the width of pores have drastically decreased after CVD deposition (Fig. 2b). At higher magnification (Fig. 3), the scanning electron microscope (SEM) observations reveal the presence of very tiny grains covering the surface of nickel. The silicon seems to be organized into a columnar structure. However, the average size of the silicon particles is less than 100 nm in diameter.

Small amounts of oxygen and carbon were detected by energy dispersive X-ray analyze, in the range of a few atomic percent for each element compared to silicon.

The thickness of the film was checked on quartz substrates as shown in Fig. 4. According to the experimental conditions previously described, a 1.5 h deposition time is efficient for growing a 1.2  $\mu\text{m}$  thick silicon layer. This standard deposition time was used for the samples tested in this study.

The films deposited onto porous nickel substrates were then electrochemically tested. Although the cyclic voltammograms indicated a reduction peak around 0.2 V for all the cycles (Fig. 5a), the peak observed on the first cycle has a different shape than for the following cycles and seems bigger which suggests an irreversible capacity on the first charge cycle. After this first half-cycle, the reac-

tions occurring in the film seem to be reversible as can be seen on the oxidation peaks plotted at different cycles (Fig. 5a). In the case of our silicon thin films, without the addition of binders or conductive additives, the related capacity revealed that each silicon atom reacts with about one lithium atom instead of 4.4 as expected. However, other groups have mentioned that silicon electrodes (with acetylene black and PVDF) can reversibly react with lithium up to  $\text{Li}_4\text{Si}$  at room temperature [14].

In Fig. 5b, is plotted the discharge capacity, i.e., the when the  $\text{LiSi}$  alloy formed during the charge decomposes to silicon. The galvanostatic plot (Fig. 5b) shows a drastic fade in capacity after only four cycles. The capacity drops to 200 mA h/g after only 20 cycles. The cause of this capacity loss is still unclear up to now but it is probably related to mechanical disintegration of the electrodes since the porous current collector was not able to prevent severe active material loss during the electrochemical cycling. Unlike  $\text{SnO}_2$  electrodes, no inactive matrix of  $\text{Li}_2\text{O}$  is formed during the first cycle to accommodate the mechanical stress of the silicon layer.

#### 4. Conclusion

Amorphous silicon thin films react with lithium to reversibly form alloys. Specific capacity up to 1000 mA h/g can be obtained; however, a severe fade in capacity occurs after only a few cycles, probably due to the mechanical disintegration of the silicon electrode. As already observed for other 'new' anode materials ( $\text{SnO}_2$ ,  $\text{Sn}\dots$ ) the modifying of the microstructure seems to be the key factor for the improvement of the cycle life of this kind of electrode.

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