Si Microwire Anode with Enhanced Conductivity through Decoration with Cu Nanoparticles

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Original Research Article

ABSTRACT

The charging/discharging rate capability of Si anodes with record areal Li storage capacity has been improved by increasing their conductivity. The anodes consist of an array of Si microwires of about 1.2 µm in diameter, embedded in Cu at one end. The conductivity of the anodes has been enhanced by chemically depositing a thin layer of Cu particles on the walls of the Si wires. The enhancement of the conductivity has been evidenced by analyzing the curves of Li storage capacity versus cycle number.

Keywords: Si microwires, Si anode, Li ion battery, improvement of conductivity, cycling rate, high capacity.

1. INTRODUCTION

As a potential anodic material for Li ion batteries, Si has a theoretical capacity of 4200 mAh/g, which is more than ten times of graphite, the standard anodic material, with a nominal capacity of 370 mAh/g. Micro-structured Si in the form of wires overcomes problems caused by its 300 % volume expansion during its lithiation, allowing capacity stability over hundreds of cycles [1].

We have developed a new concept of Si microwire anodes that consists of an array of Si microwires embedded at one end in a Cu current collector [2]. The capacity of the anodes is very stable over 100 cycles [3], and breaks all the records when considering the capacity per area (mAh/cm^2) [4]. The mechanical stability of the wires is surprising, since their diameter (≈ 1.2 µm) is far larger than what was deemed reasonable (< 300 nm) for avoiding cracking. However, it has been observed that the resistance of the wires is large and may increase after tens of cycles. This effect could be due to a porosification process of the wires while lithiated/delithiated [5].

A number of reports can be found in the literature in the latest years, where it is intended to improve the conductivity of Si anodes by coating them with a conductive layer. Most of the works have used carbon as conductive additive [6-8]; nevertheless, the cycling stability of the anodes has been usually compromised due to no clear reasons. Cu has also been used, but the coating avoided reaching the maximum capacity of Si, even when the charging rate was slow, and large over-potentials were used [9]. A possible explanation is that the Cu coating constrained the dimensions of the Si wires, not allowing the volume expansion of the wires while being lithiated, as observed in [10].

In the present work, a film of Cu nanoparticles has been deposited on our anodes in order to increase their charging/discharging rate. The

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coating has been performed by an economical electroless chemical method. The coverage with the Cu film has been optimized to allow the wires to expand/contract while cycling, minimizing mechanical stress; in this way, the maximum possible capacity of Si can be reached.

2. EXPERIMENTAL DETAILS

The Si microwire anodes used for this study have been produced by a simple, and microelectronics compatible electrochemical-chemical method, which has been thoroughly described in [2]. The principal steps of the method are: a) Pre-structuring of Si wafers with a quadratic array of cavities; b) electrochemical etching of macropores; (c) chemical over-etching of macroporous Si to obtain a wire array; d) chemical deposition of a Cu seed layer at one end of the wires; e) electrochemical deposition of a Cu current collector on the seed layer; f) detachment of the anode from the (reusable) Si substrate.

The Si wires of the anodes were covered with a film of Cu nanoparticles, which were directly deposited by an electroless chemical method. The deposition method consists of immersing the anodes in a Cu-plating solution, controlling the immersion time. The temperature for the deposition was kept at 30 °C. The plating solution consists of 4 mL HF, 98 mL H_2O, 4 g $CuSO_4 \cdot 5H_2O$ and 4 g ethylenediaminetetraacetic acid (EDTA). The concentration of the different precursors was optimized in order to evenly cover the Si wires from the top to the bottom. EDTA is used as a complexer to retard the reaction rate on the surface of the wires, improving the homogeneity of the produced Cu films. The deposition method is a variation of the recipe used to deposit the seed layer at one end of the wires, to enable electrochemical deposition of the current collector of the anode afterwards [2]. It is based on some reports where Cu thin films were deposited on different substrates, but using Si as sacrificial material [11,12]. According to those reports, Si reacts with HF releasing 4 electrons, which are then accepted by Cu^{2+} ions, leading to the direct Cu deposition on the substrates. This redox process can be described by the half-cell reactions (1) and (2):

$$Si^0 + 6F^- \rightarrow SiF_6^{2-} + 4e^- \quad (1)$$

$$2Cu^{2+} + 4e^- \rightarrow 2Cu^0 \quad (2)$$

In the present work, Si wires were used as substrates and as sacrificial material. Just the surface of the wires is sacrificed, with a depth in the order of nanometers.

Battery cycling tests were performed using half-cells, with Li as counter electrode. The separator was a glass fiber filter from Whatman, with pores of 1 µm. The electrolyte was LP-30, consisting of dimethyl carbonate and ethylene carbonate (1:1), plus 1 mol/L of $LiPF_6$. The tests were done with a battery charging system BatSMALL from Astrol Electronic AG. The anodes were cycled in a galvanostatic/potentiostatic mode, for which the voltage limits of 0.11 V for lithiation and 0.7 V for delithiation were set. This cycling mode consists of applying a constant current until a voltage limit is reached, and then applying a constant voltage either until the current decreases to 10 % of its initial value or when the capacity limit is reached.

SEM observations were performed with an Ultra Plus SEM from Zeiss.

3. RESULTS AND DISCUSSION

A curve of capacity versus cycle number of a Si microwire anode can be seen in Fig. 1. Just the capacity obtained during the lithiation process is shown. The anode has been cycled in a galvanostatic/potentiostatic mode, as described in the experimental details. The cycling rate was C/10 (lithiation or delithiation in 10 h, considering just the galvanostatic step) for the first 4 cycles, and C/2 (lithiation or delithiation in 2 h, considering just the galvanostatic step) for the following cycles. The capacity was limited to the 75 % of the maximum theoretic capacity of Si, to minimize mechanical stress and improve the performance of the anode [3]. As can be observed in the curve, the capacity is very stable upon cycling. Nevertheless, the portion of the lithiation capacity obtained galvanostatically, decreases with the cycle number, thus the time it takes for the lithiation process increases with the cycle number. This is an indication that the resistance of the wires increases with the cycle number, due to porosification [5] and amorphization [10] processes. As the resistance increases, the voltage limits of the anode (at which the galvanostatic charging/discharging is stopped) is reached faster and faster upon cycling.

With the objective of enhancing the conductivity of the wires, they were coated with Cu nanoparticles using the method described in the

experimental details section. Samples were produced with 20 and 30 s deposition time. SEM micrographs of the coated wires are shown in Fig. 2.

As can be observed in Fig. 2a, the sample coated for 20 s presents gaps between Cu particles, with particles of around 30 nm. Agglomerates of some particles are produced. When the wires are coated for longer times (30 s), the Cu particles merge, producing a porous Cu film (see Fig. 2b).

The cycling performance of the wires with and without Cu coating was tested. The curves of lithiation capacity versus cycle number of the different samples are shown in Fig. 3. For these tests, the cycling rate was also C/10 for the first 4 cycles and C/2 for the following cycles. As can be observed, the capacity of the sample with Cu deposited for 30 s presents the lowest capacity. On the other hand, the capacity of the 20 s sample is comparable with the sample without coating (3150 mAh/g).

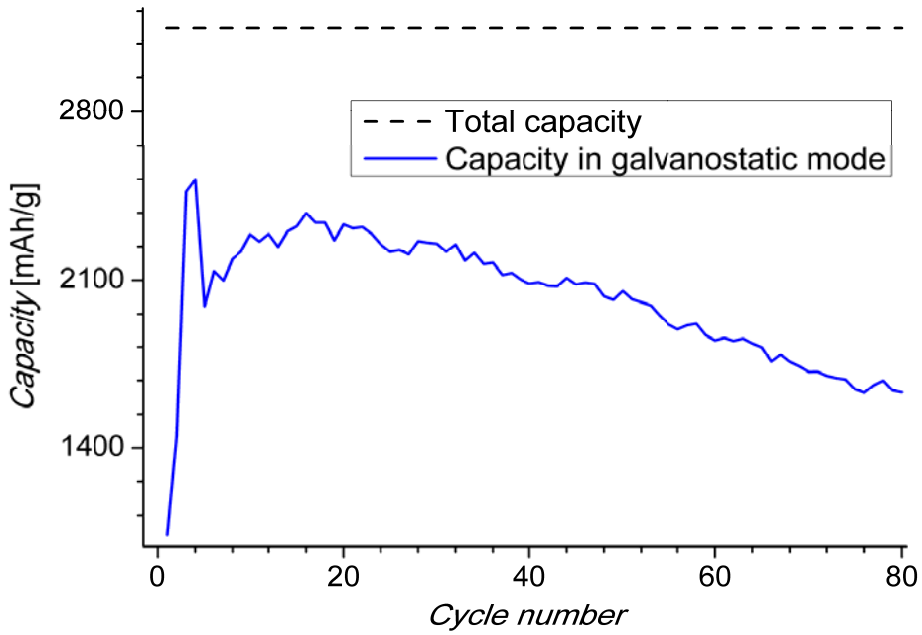

Fig. 1. Curve of capacity versus cycle number of Si microwire anode without any coating. The anode was cycled at C/10 for the first 4 cycles and at C/2 for the following cycles. The portion of the capacity obtained galvanostatically is also plotted

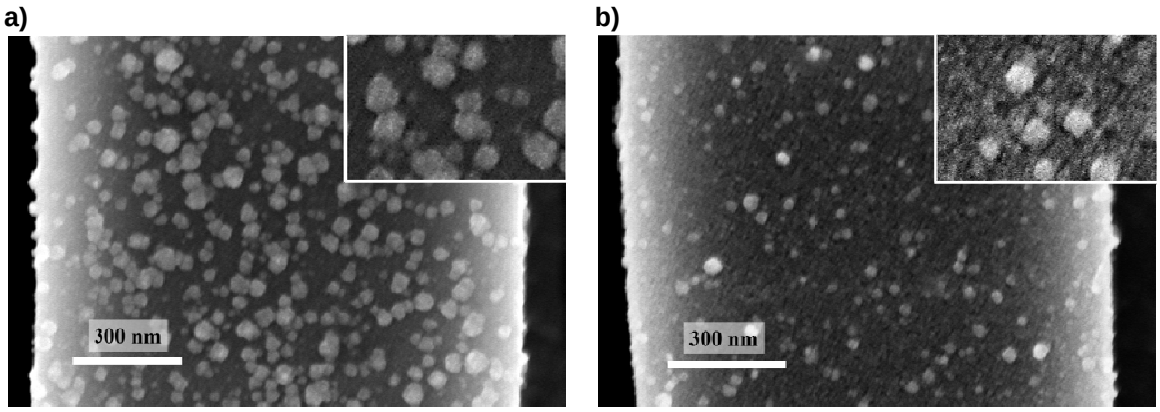

Fig. 2. SEM micrograph of Si microwires coated with Cu by electroless chemical deposition. a) Sample with Cu deposited for 20 s; b) sample with Cu deposited for 30 s. Cu particles are evident on the surface of the wires. The inset in the figures is a close up to observe details of the structure: the 30s sample is covered by a porous Cu film, instead of separated particles

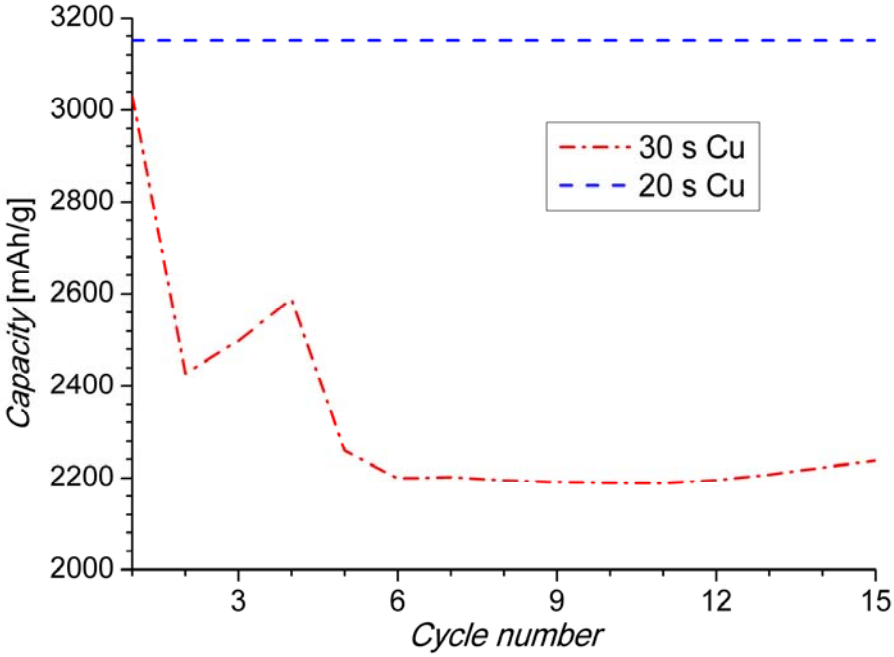

Fig. 3. Curve of the lithiation capacity versus cycle number of Si microwires with Cu deposited for 20 and 30 s. The anodes were cycled at C/10 for the first 4 cycles and at C/2 for the following cycles

To see if the lithiation rate capability of the wires was enhanced with the Cu coating, the percentage of the lithiation capacity obtained galvanostatically was calculated. Fig. 4 shows this percentage, obtained from the curves of Fig. 3. As can be observed, the sample with a Cu coating deposited for 20 s presents the highest percentages. This means that it takes less time for lithiating this sample (there is less capacity to be filled in the potentiostatic modus, which is a slower process). In this sample, the percentage of the capacity obtained in the galvanostatic modus is higher than in the other samples because it takes longer for the sample to reach the given potential limit (0.7 V). This is an indirect indication that the resistance of this sample is smaller than that of the sample with no coating.

The capacity of the 30 s sample is constrained to around 2200 mAh/g (see Fig. 3) due to the lack of space. Just a limited amount of Li is allowed into the Si structure due to the volume constraint. From Fig. 4 it can be seen that the galvanostatic capacity of this sample decreases with the cycle number. This is an indication that the resistance of the anode increases with the cycle number. This is not due to the coating loses conductivity; it is because the wires start cracking due to the lack of space for volume expansion of the wires. There is no direct evidence of cracking; however, it is a common effect happening when the volume expansion of materials is constrained, e.g. during thermal expansion [13]. In this way, one can conclude that it is positive that the Cu nanoparticles of the coating are separated, to allow that the Si wires expand when lithiated.

The coating enhances the electron transport on the surface of the anodes, even when the wires are not totally covered. A schematic of this is shown in Fig. 5. The electrons follow the path with the lowest resistance; in this way, the electrons “jump” from one Cu nanoparticle to another (path with less resistance), until they find a Li^+ ion to reduce to Li^0.

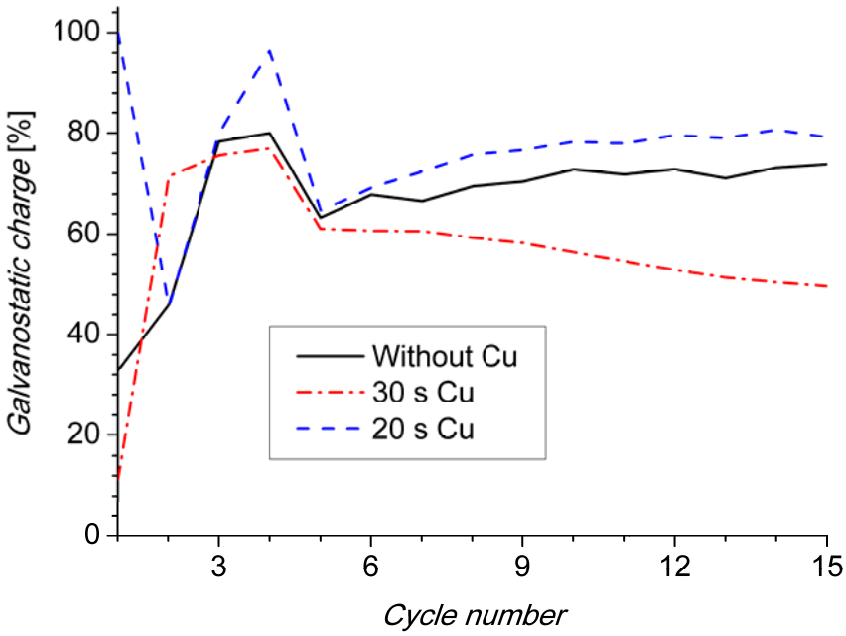

Fig. 4. Percentage of the lithiation capacity of Fig. 3 obtained galvanostatically

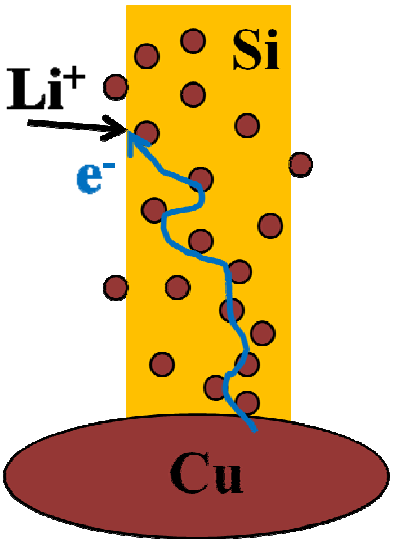

Fig. 5. Schematic of the electron transport in a Si wire coated with Cu particles (represented by circles). The Cu current collector is at the bottom

4. CONCLUSION

The lithiation rate capability of Si microwire array anodes has been enhanced by depositing a Cu-nanoparticle film on the wires. It has been found that the best performing anodes are the ones with separated Cu nanoparticles. If the wires are coated with a closed Cu film, they cannot expand while being lithiated, and the capacity is limited.

An optimized recipe for depositing Cu particles on the surface of Si wires, evenly from the top to the bottom, has been developed. The deposition is done by an economical electroless chemical method.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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