

Short communication

## High capacity and long cycle life silicon anode for Li-ion battery

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### Abstract

A silicon film was deposited on a Ni or Cu foil in vacuum up to a thickness of 4  $\mu\text{m}$  and the Li insertion/extraction behaviour was evaluated under constant current charge/discharge in an electrolyte solution of propylene carbonate containing 1 M  $\text{LiClO}_4$ . The surface of a 30  $\mu\text{m}$  thick Ni foil was roughened by etching with  $\text{FeCl}_3$ . The Li insertion/extraction performance was strongly dependent on the roughness factor. A thick silicon film is necessary for practical application. However, the cycle performance as well as the Li accommodation capacity was markedly depressed when the film thickness was increased. We found that the roughening of the substrate surface was a key factor for attaining good performance with a thick film. Surface roughening was found to be very effective, but the best performance was obtained by the use of an electrolytically deposited Cu foil on which a silicon film was vacuum-deposited rapidly.

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### 1. Introduction

Third generation 3C portable electronics appliances such as cellular phones, portable PC and cameras require to double the capacity and power of Li-ion batteries to power heavy hardware in them. Therefore, conventional battery materials presently used should be replaced by new materials having large specific capacity. The most commonly used anode material is graphite, whose theoretical capacity is limited to 372  $\text{mAh g}^{-1}$ .

Due to its very high theoretical Li accommodation capacity (9.81  $\text{Ah cm}^{-3}$ ) silicon has been studied extensively as an anode material for next generation Li-ion batteries [1–4]. A key issue is its short cycle life. Attempts are under way to solve the issue by using composites [5], nano-structured silicon [6,7], amorphous silicon [7,8], thin film [9] by vacuum deposition [10] or sputtering [11], or pillar structure [12]. Although remarkable improvements have been achieved by these studies, the cycle performance is still unacceptable for practical application.

Deposition of a silicon film by vacuum evaporation or sputtering on a metal foil substrate enabled us to prolong cycle life while maintaining high capacity [11,13]. We have examined a simple vacuum deposition method and succeeded in obtaining a

capacity of over 2000  $\text{mAh g}^{-1}$  with a cycle life as long as 1000 cycles with a 500  $\text{\AA}$  thick film [14]. The cycleability was shown to be poor for a thicker film [15]. This issue could be overcome by use of carrier-doped conductive silicon as the evaporation source on a surface-modified Ni foil [16]. But the thickness of the deposited silicon is still thin for providing enough capacity for practical use.

In an attempt to provide a sufficiently thick silicon film acceptable for practical use we have examined vacuum deposition conditions as well as surface roughening conditions. In the present paper, we present results obtained with a 3.6  $\mu\text{m}$  thick silicon film on a surface-modified Ni foil as well as those obtained on a Cu foil whose surface was electrolytically modified to form an agglomeration of tiny pyramid-like hill structures.

### 2. Experimental

The sources for vacuum deposition were phosphor-doped n-type semi-conducting silicon (30  $\Omega\text{ cm}$ ), and p-type silicon wafers prepared for IC technology (Shin-etsu Chemicals Co.). The wafer was crushed into small pieces for evaporation. As the metal foil substrate, a 30  $\mu\text{m}$  thick 8 cm  $\times$  4 cm rectangular nickel foil (Nilaco, 99.99% purity) and a 35  $\mu\text{m}$  thick 8 cm  $\times$  4 cm rectangular copper foil were used. The copper foil was specially made by Nippon Denkai Kogyo Co. The surface

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was modified by controlling the copper deposition conditions to form agglomerated pyramid-like tiny hills on the surface. Surface roughening of the nickel substrate was performed by etching with an aqueous solution of  $\text{FeCl}_3$  whose concentration was in the 0.2–3 M, the etching time being 1–10 min at an ambient temperature.

About 0.5 g of the silicon powder or crushed pieces of the wafer were loaded on a tungsten heating boat. Electric power was supplied directly through the tungsten boat to heat the loaded silicon to melt. The evaporation was controlled by monitoring the deposited weight with a quartz crystal microbalance mounted near the substrate metal foil. The deposition rate was adjusted to about  $1\text{--}15 \text{ \AA s}^{-1}$  for examining the effect of evaporation rate on electrochemical performance. The substrate foil thus loaded with the deposited silicon film was cut into a  $1 \text{ cm} \times 1 \text{ cm}$  square, spot-welded with a Ni lead wire, and subjected to Li insertion/extraction studies under constant current charge/discharge.

The electrolyte was 1 M  $\text{LiClO}_4$  in propylene carbonate (Tomiyama Chemicals), the contaminant water being less than 20 ppm. The constant current charge/discharge cycle test was conducted with various loading currents from 0.2 to 30 C rates, with the same rate for charge and discharge, with a Hokuto-Denko HA-151 Potentio-galvanostat. The initial charging was started at 2.0 V versus  $\text{Li/Li}^+$  toward negative potentials. All the measurements were performed in a glove box filled with flowing dry argon gas at room temperature.

SEM images were made by a JEOL JSM Type 5200 Scanning Electron Microscope. X-ray diffraction patterns of the films on the metal foils were obtained with  $\text{Cu K}\alpha$  radiation by a Rigaku RINT-2000 Diffractometer before and after the electrochemical measurements.

### 3. Results and discussion

A good cycle performance can be obtained with a simply deposited silicon film even on an untreated Ni substrate foil provided the film thickness is thin, as shown in Fig. 1. Thicker films, however, lead to capacity fading as shown in Fig. 2.

In a previous paper [17], we pointed out that surface roughening was an important factor for attaining a long cycle performance with thick silicon films deposited on Ni metal substrates, although no actual example was shown. We examined conditions for etching Ni with aqueous  $\text{FeCl}_3$ . A typical SEM image of a Ni surface thus etched is shown in Fig. 3, which was

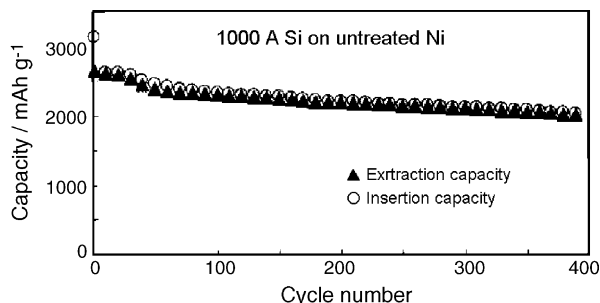


Fig. 1. Li insertion (charge)/extraction (discharge) cycle performance (1 C rate) of a 1000 Å thick silicon film deposited on an as-obtained Ni foil.

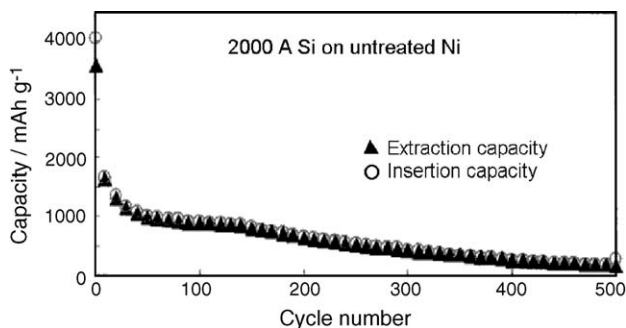


Fig. 2. Li insertion/extraction cycle performance (1 C rate) of a 2000 Å thick silicon film deposited on an as-obtained Ni foil.

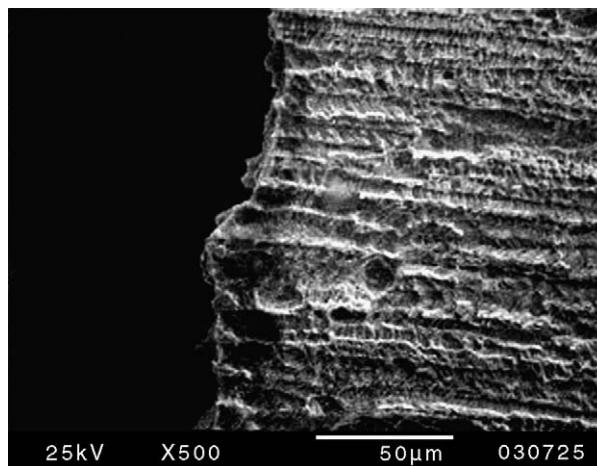


Fig. 3. SEM image of a 30 μm thick Ni foil whose surface was etched with 1 M  $\text{FeCl}_3$  for 1 min followed by etching with 0.3 M  $\text{FeCl}_3$  for 1 min.

selected among samples obtained by varying the etching solutions and etching times, a good roughening of the surface is evident.

We evaporated a silicon film on to the surface-modified Ni foil thus obtained. Fig. 4 is an SEM image of a thick silicon film on etched Ni, in which we see an adherent silicon film on the

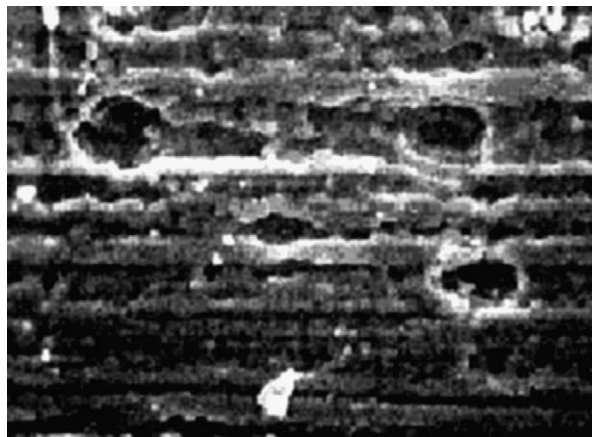


Fig. 4. SEM image of a 11,000 Å thick silicon film on deposited a 30 μm thick Ni foil, whose surface was etched with 1 M  $\text{FeCl}_3$  for 1 min followed by etching with 0.3 M  $\text{FeCl}_3$  for 1 min.

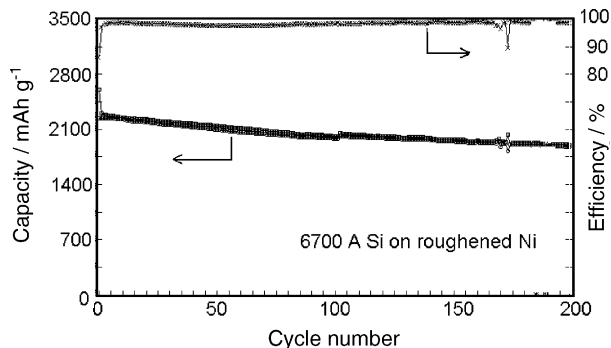


Fig. 5. Cycling performance (1 C rate) of a 6700 Å thick silicon film deposited on an etched Ni foil.

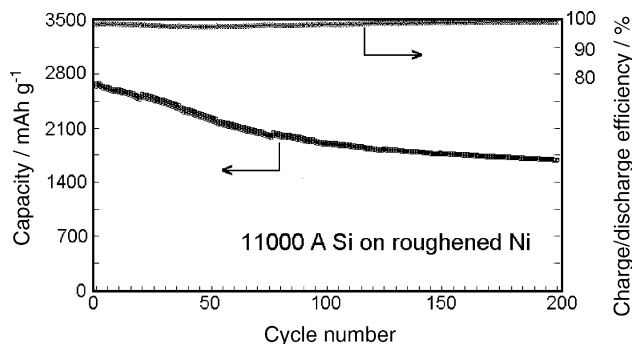


Fig. 6. Cycling performance (1 C rate) of a 11,000 Å thick silicon film deposited on an etched Ni foil.

roughened Ni surface. Fig. 5 shows the lithium cycling performance of a 6700 Å thick film deposited on a roughened Ni surface (30 μm thick). A stable cycle performance with a Li accommodation capacity of over 1700 mAh g<sup>-1</sup> even after 200 cycles can be seen. We increased the silicon film thickness to more than 10,000 Å and obtained an acceptable lithium accommodation capacity of over 1700 mAh g<sup>-1</sup> after 200 cycles even though the drop in capacity during the first 100 cycles is somewhat significant (Fig. 6).

The rate of silicon deposition had an influence on the cycle performance. The faster the deposition rate, the better the cycle performance. This may be due to the amorphous nature of the fast deposited films. A thicker 18,000 Å film was also studied, but no stable capacity could be realized (Fig. 7).

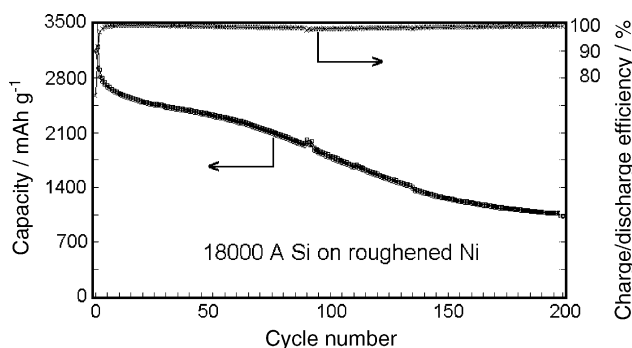


Fig. 7. Cycling performance (1 C rate) of a 18,000 Å thick silicon film deposited on an etched Ni foil.

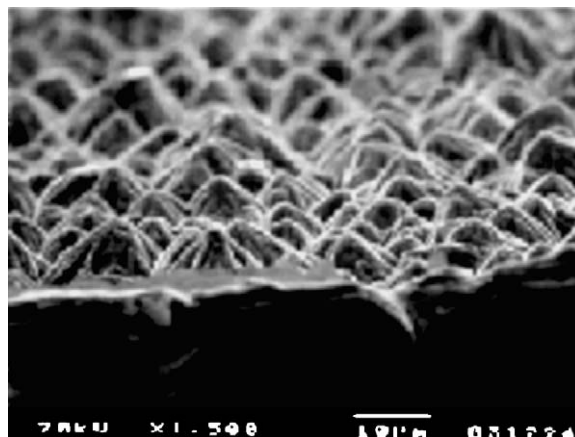


Fig. 8. SEM images of electrolytically deposited copper foil.

Since we found a limitation in the etching of Ni foil, we tried to examine another metal substrate for surface roughening. But among Cu, Ni and cupronickel alloy we could not find a better etching method. In the case of Cu, however, we found a roughening method other than etching. That involves the reverse process, i.e., electrolytic deposition. If Cu is deposited electrolytically on a large copper roll in an aqueous bath containing a high concentration of CuSO<sub>4</sub>, the roughness of the deposited Cu film can be controlled by the deposition conditions. Such a process has been established for mass production in Nihon Denkai Kogyo Co. This company provided the roughened Cu foil. The SEM image of the roughened Cu thus obtained is shown in Fig. 8. The surface area of the roughened surface evaluated by measuring the double layer capacity was the highest among the samples examined.

We deposited a 3.6 μm thick silicon film on the Cu foil and the cycle performance was obtained under 1 C rate constant current charge/discharge. The results are shown in Fig. 9, where the results obtained with a same thickness silicon film on a roughened Ni foil are shown for comparison. As seen in the figure, a capacity of around 2000 mAh g<sup>-1</sup> can be steadily sustained on the Cu foil whereas the capacity as well as the charge/discharge reversibility are very poor for the case with the roughened Ni foil. The thickness is in the range of practical application.

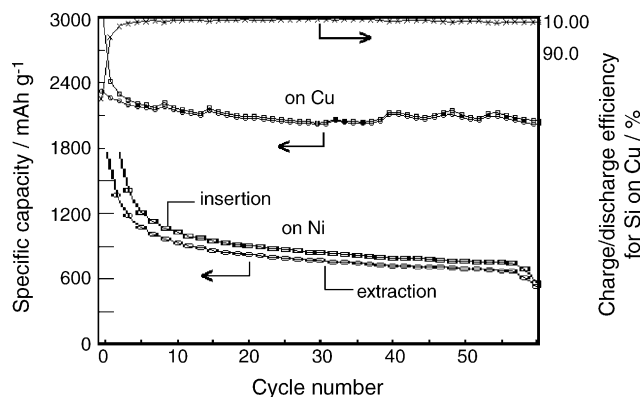


Fig. 9. Cycling performance (1 C rate) of a 3.6 μm thick silicon film deposited on a well-etched Ni foil and electrolytically deposited Cu foil.

#### 4. Conclusions

Surface roughening of the substrate was found to be a key factor for obtaining an excellent Li insertion/extraction performance of vacuum-deposited silicon films.

Etching with an appropriate etching solution did not give satisfactory results with thicker films. Use of a specially prepared copper foil whose surface was modified by controlled electrolysis in a  $\text{CuSO}_4$  solution was found to give an excellent performance. In addition, rapid deposition of the silicon film was also found to be a key factor for obtaining better cycle performance. We could attain steady capacities of about  $2000 \text{ mAh g}^{-1}$  over 50 cycles for a  $3.6 \mu\text{m}$  thick silicon film.

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