

A vacuum deposited Si film having a Li extraction capacity over 2000 mAh/g with a long cycle life

Tsutomu Takamura^{a,*}, Shigeki Ohara^b, Makiko Uehara^b, Junji Suzuki^b, Kyoichi Sekine^b

^a Department of Applied Chemistry, Harbin Institute of Technology, West Dazhi Street, Harbin 150001, China

^b Department of Chemistry, Rikkyo University, Nishiikebukuro, Toshimaku, Tokyo 171-8501, Japan

Abstract

We have found that a Si film vacuum deposited on a Ni foil has a Li insertion capacity over 2000 mAh/g with cycleability over 1000 cycles, but a great issue was its difficulty to obtain a sufficiently thicker film capable of high current charge/discharge. In the present paper the examination of the high current charge/discharge performance of thicker Si film in relation to the film formation condition. The electrochemical evaluation was performed with cyclic voltammetry (CV) and constant current charge/discharge test with various loading currents in PC containing 1 M LiClO₄.

A Si film prepared with a rapid deposition rate gave a discharge capacity over 2000 mAh/g even with a very high charge/discharge rate over 10 C. In addition, the surface roughening of the substrate foil was found to play an important role to provide a thick film capable of high current performance. The constant discharge curve gave a wide plateau in the potential range between 200 and 500 mV versus Li/Li⁺. The XRD pattern of the deposited film gave no peaks due to Si, indicating the film to be amorphous. The SEM image of the deposited film was rather homogeneous, and after 500 cycles it still covered the entire surface of the Ni substrate though the surface became inhomogeneous. © 2003 Elsevier B.V. All rights reserved.

Keywords: Li-ion batteries; Ultrahigh capacity anode; Si film; Vacuum deposition; Surface roughening of substrate

1. Introduction

Strong demand of the third generation of portable electronic appliances, such as cellular phones, PCs, portable TVs, and camcorders is to double the energy and power densities of the power sources, since they will be mounted with highly advanced software capable of responding to a wide variety of social requirements. The most promising batteries are Li-ion batteries because of their largest discharging capacities and highest working potential. In responding to this requirement the active materials now practically used in the batteries should be replaced by novel high performance materials. Silicon is one of the best candidates for the anode material but the great issues are its very poor cycleability and the insufficient power capability [1,2].

Several trials to improve the cycleability have been performed. Yoshio and co-workers have succeeded to prolong the cycle life by coating the surface of a fine powder of Si by a CVD-deposited carbon [3]. The issue to be solved for guaranteeing the cycle life is how to keep the charging potential

limit exactly. Lee and coworkers succeeded to improve the cycleability, but it appears still insufficient for the practical use [4]. Niu and Lee provided a novel method to incorporate Si particles in a sol-gel graphite composite matrix and succeeded to keep the specific capacity over 2400 mAh/g [5]. The cycle life, however, is still short to be accepted in the commercial batteries. Yonezu and co-workers provided an attractive method where a sputtered Si film changes into an amorphous Si film on a specially roughened surface of Cu current collector. They succeeded to attain 3500 mAh/g with their amorphous film, the cycleability, however, is still required to be improved [6,7].

We have found that a vacuum deposited Si film on a Ni foil shows satisfied capability for energy density with satisfactorily long cycle life [8], but that was performed mainly with cyclic voltammetry (CV) and without examining the power capability with thicker films. Recently, Yazami and co-workers showed very similar to us with a vacuum deposited Si film [9]. Our challenge to obtain a thicker Si film having a good high power performance has lead to partial success [10,11]. The purpose of the present study is to examine the power capability with constant current charge/discharge method on a thicker vacuum deposited Si film, and to find an improving method if necessary. Bearing

* Corresponding author. Tel.: +81-45-902-4602; fax: +81-45-902-4658.
E-mail address: takamur@green.ocn.ne.jp (T. Takamura).

in mind that the electron conductivity plays an important role in the high rate electrochemical reaction, we tried to use a carrier doped conductive Si as the evaporating source. In the present paper we will show the results obtained with a thicker conductive film which can afford to give over 2000 mAh/g working over 1000 cycles with 10 C rate discharge.

2. Experimental

Three kinds of Si were examined; i.e. 99.99% purity Si powder (200 mesh through, Nilaco, Metal Co.), phosphor doped n-type semi-conducting Si ($7 \Omega \text{ cm}$), and p-type Si wafers (Shinetsu Chemicals Co.). The wafer was crushed to small pieces before evaporation.

About 0.5 g of the Si powder or crushed pieces of the wafer was loaded in a tungsten heating boat. A $30 \mu\text{m}$ thick $8 \text{ cm} \times 4 \text{ cm}$ rectangular Ni foil (Nilaco, 99.99% purity) and the Si-loaded tungsten boat were mounted in a vacuum chamber and evacuated under the pressure of 10^{-7} Torr for 5 h at room temperature. Electric current was passed directly in the tungsten boat to heat the loaded Si to melt. The evaporation was controlled by monitoring the deposited weight with a quartz crystal microbalance mounted near the Ni foil. The deposition rate was changed to be about $1\text{--}15 \text{ \AA s}^{-1}$ for examining the effect of evaporation rate to the electrochemical performance. The obtained film was cut into $1 \text{ cm} \times 1 \text{ cm}$ square, spot-welded with a Ni lead wire, and offered for the evaluation of Li insertion/extraction performance with constant current charge/discharge.

The surface roughening of the substrate was performed by etching with an aqueous solution of FeCl_3 whose concentration examined was in the range of 0.2–2 M, the etching time being in the range of 1–10 min. at an ambient temperature.

The electrolyte solution examined was pure propylene carbonate (PC) containing 1 M LiClO_4 (Tomiya Chemicals, the contaminant water being less than 20 ppm). The constant current charge/discharge cycle test was conducted with various loading currents from 0.5 C to 30 C rates with the same rate for charge and discharge with a Hokuto-Denko HA-151 Potentio-galvanostat. The first charging was started at 2.0 V versus Li/Li^+ toward negative potential direction. All the measurements were performed in a glove box filled with a flowing dry argon gas at room temperature.

Scanning electron microscope (SEM) pictures were photographed with a JEOL JSM Type 5200 Scanning Electron Microscope. X-ray diffraction patterns of the films on the Ni foil were obtained with $\text{Cu/K}\alpha$ radiation by a Rigaku RINT-2000 Diffractometer before and after the electrochemical measurements.

3. Results and discussion

The Si film vacuum deposited from P-doped conductive Si (n-type Si) gave an excellent charge discharge capacity

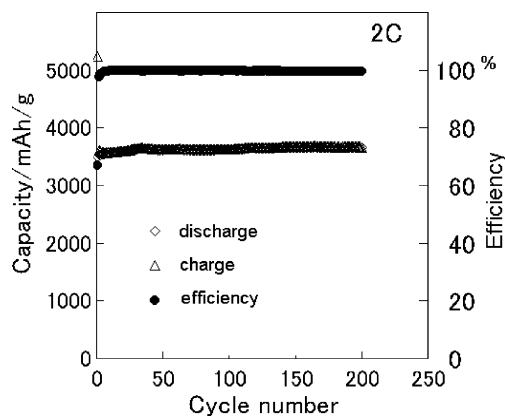


Fig. 1. Capacity retention and efficiency of 500 Å thick n-Si during charge/discharge cycling with 2C rate charge/discharge in PC containing 1 M LiClO_4 .

with long cycle life. The results obtained with a 500 Å thick film is shown in Fig. 1. The capacity is as high as 3600 mAh/g which was kept stable during 200 cycles. The charge/discharge efficiency was 100% after 15 cycles.

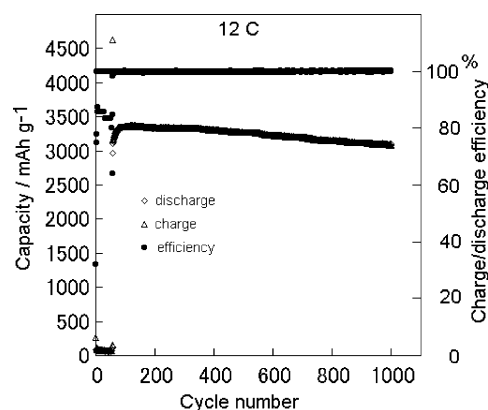


Fig. 2. Capacity retention and efficiency of 500 Å thick n-Si during charge/discharge cycling with 12C rate charge/discharge.

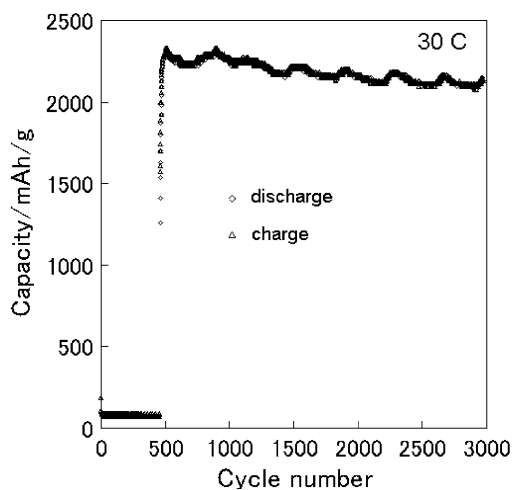


Fig. 3. Capacity retention of 500 Å thick n-Si during charge/discharge cycling with 30C rate charge/discharge in PC containing 1 M LiClO_4 .

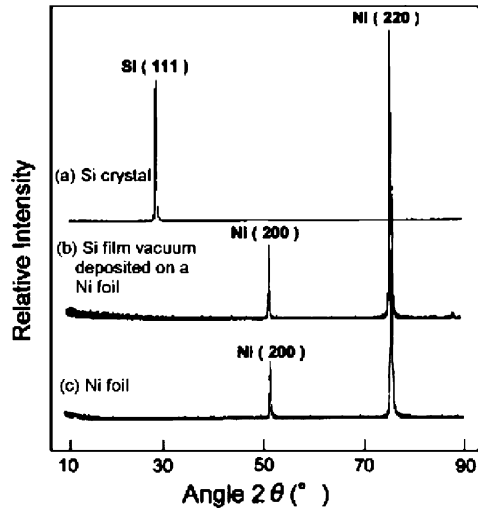


Fig. 4. XRD patterns of crystalline Si and a vacuum deposited Si film: (a) Si crystal; (b) 3000 Å thick vacuum deposited Si film on a 30 mm thick Ni foil; (c) 30 mm thick substrate Ni foil.

Two important factors should be maintained as a future high capacity anode material, i.e. cycle and power capabilities. Therefore, we examined the performance of our Si film by varying the charge/discharge rate from 2 to 30 C. Figs. 2 and 3 show the results obtained under the loading rates of 12 and 30 C charge/discharge. Surprisingly the film was durable even under such very heavy loadings as shown in Figs. 2 and 3. The capacity was as high as over 3000 mAh/g for the case of 12 C test, which could be kept during 1000 cycles. Also in the case of super heavy load of 30 C rate the charge/discharge capacity was still over 2000 mAh/g even after 3000th cycle although the capacity fluctuated during cycling. In the early stage of the cycle test at high rates, i.e. 12 and 30 C rates, however, only a very suppressed capacity was revealed, and after several tens or hundreds cycles the capacity suddenly jumped up to very high values. The mechanism is not clear at the moment. Anyhow, we have been able to prove that Si can afford to maintain very high capacity under very heavy load test for long cycles as far as we use

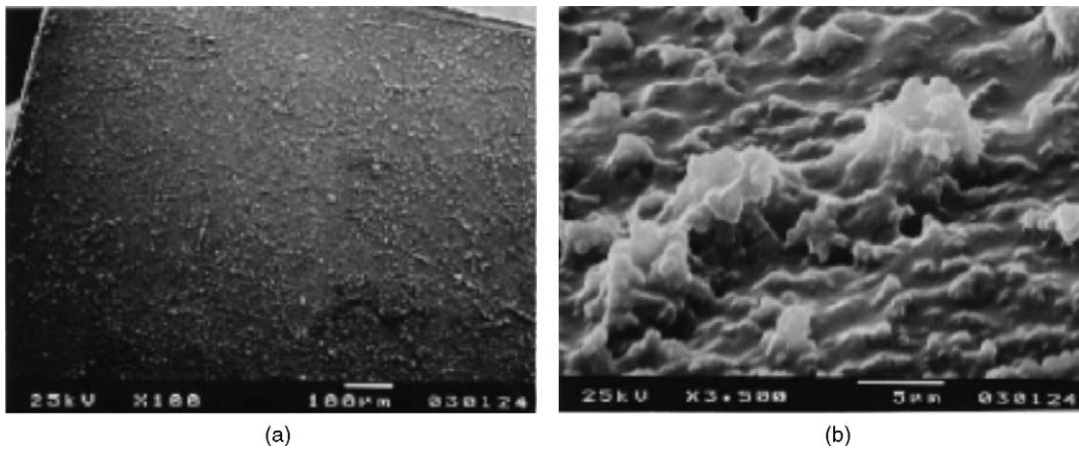


Fig. 5. SEM images of a 500 Å thick vacuum deposited Si film after 1000 cycles under 30 C constant current cycle test in PC containing 1 M LiClO₄, left: low magnification; right: high magnification.

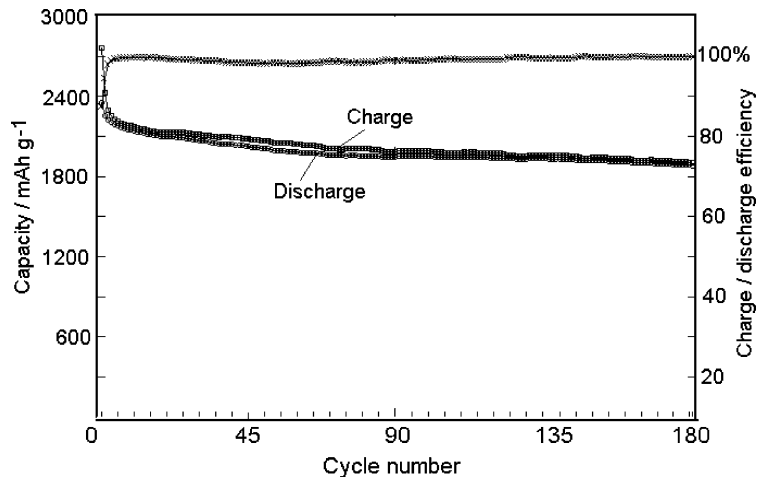


Fig. 6. 1 C rate Li charge/discharge cycle performance of a 3000 Å thick Si film in PC containing 1 M LiClO₄. The surface was filed with a fine sandpaper before the test.

a thin film vacuum-deposited on a Ni foil. The reason why the vacuum deposited Si film could be durable under heavy load charge/discharge should be examined. We supposed this could be realized by the amorphous nature of the deposited film.

In order to examine whether the vacuum deposited film is crystalline or amorphous structure, the XRD pattern was obtained for the vacuum deposited film on a Ni foil. Three patterns of Si crystal (a), deposited film on Ni (b), and Ni foil (c) are compared in Fig. 4. We cannot recognize any absorption peak on (b) near 28° where a strong absorption due to (111) of Si is expected to appear as seen on (a) if the sample is crystalline. The obtained results imply that the vacuum deposited Si film has amorphous like structure. As pointed out by Yonezu and co-workers [6,7] making Si amorphous is key technology to realize long cycle life with high capacity for Li insertion/extraction cycles. We suppose that the film obtained in this study to have an amorphous nature. The SEM image obtained with a 500 Å thick Si film after 1000 cycles charge/discharge test at 30 C rate is shown in Fig. 5. The chocolate-like image of the magnified photograph appears to be amorphous nature of the film.

The Si film revealing excellent performances in this study, however, is too thin to be applied to the practical batteries. It is important to examine whether thicker film exhibits also such an excellent performance. Recently we reported that a 1500 Å thick film revealed sufficient performances provided that we control the deposition condition for a carrier doped Si as the evaporating source for vacuum deposition [10,11]. We examined further for thicker film. We prepared a 3000 Å thick film but the available capacity was very poor. Bearing in mind the electrochemical reaction is surface reaction, we examined the surface properties of the thick film. Then we found that the inert nature of the thicker film was caused by the poor surface conductivity. The reason why the surface of the thicker film became poor conductive is unknown but removing the surface inert layer is expected to provide good results. We examined the thick film by removing the inert

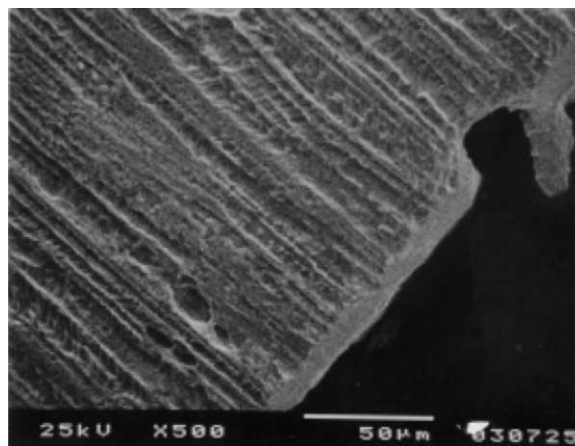


Fig. 7. SEM image of a Ni substrate foil after an appropriate etching by 1 M FeCl₃ aqueous solution for 5 min at an ambient temperature.

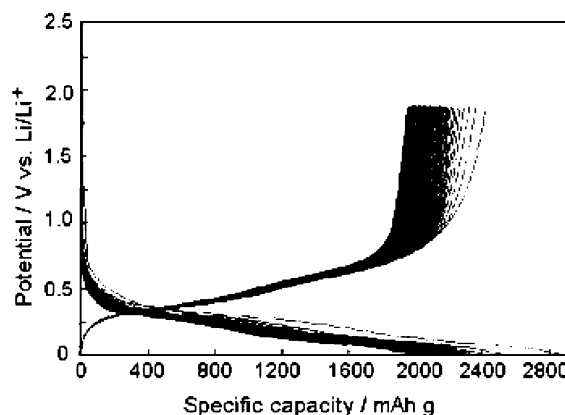


Fig. 8. 1 C rate constant current Li charge/discharge curves in PC (containing 1 M LiClO₄) obtained with a 4400 Å thick n-Si film vacuum deposited on an etched Ni foil shown in Fig. 7.

layer by paper grinding. The results obtained with the 3000 Å thick film after grinding are shown in Fig. 6, where we see over 1800 mAh/g is maintained during 180 cycles. This implies that the nature of the deposited Si film is influenced by

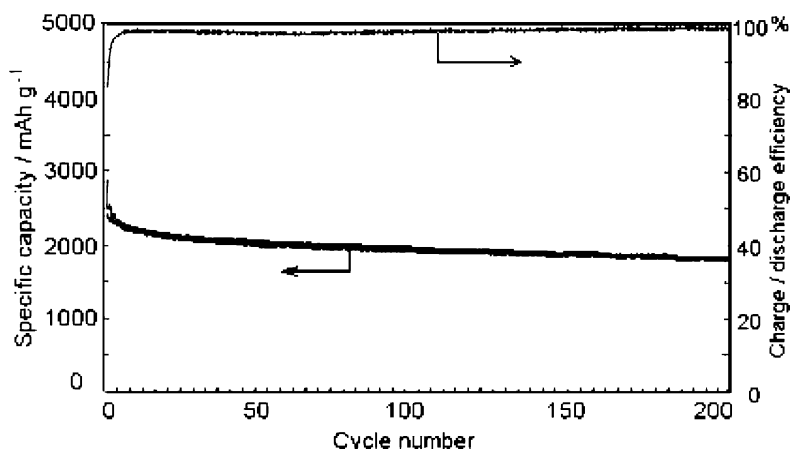


Fig. 9. 1 C rate constant current Li charge/discharge cycleability of a 4400 Å thick n-Si film vacuum deposited on an etched Ni foil shown in Fig. 7.

the surface condition of the substrate. A surface filed with sandpaper gave good results. Etching with FeCl_3 aqueous solution was found quite effective for obtaining high performance Si film.

A typical acceptable surface appearance of the substrate is shown in Fig. 7 for Ni foil. A 4400 Å thick Si film was deposited on the etched foil and the charge/discharge performance was examined. An example of constant current charge/discharge curves are shown in Fig. 8, where we see favourable discharge curves for 1 C rate test. Fairly good results of the cycle test were obtained as shown in Fig. 9. The next stage is to increase the deposition thickness over 10000 Å, i.e. 1 μm, where the specific capacity is kept over 2000 mAh g⁻¹ at 1 C rate charge/discharge during 500 cycles.

4. Conclusions

Vacuum deposited Si film revealed excellent Li charge/discharge performance especially when it was thin, while the high current performance was poor, especially under the heavy duty charge/discharge condition. Filing the surface of the deposited film with sandpaper, however, showed a remarkable improvement. Filing of the substrate gave preferable results as well. The effective way for attaining high performance with thicker film was to roughen by etching with FeCl_3 aqueous solution, implying that the surface condition of the substrate is a key factor for attaining acceptable performance with a thick deposited Si film.

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