

A thin film silicon anode for Li-ion batteries having a very large specific capacity and long cycle life

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Abstract

A thin film of Si was vacuum-deposited onto a 30 μm thick Ni foil from a source of n-type of Si, the film thickness examined being 200–1500 Å. Li insertion/extraction evaluation was performed mainly with cyclic voltammetry (CV) and constant current charge/discharge cycling in propylene carbonate (PC) containing 1 M LiClO₄ at ambient temperature. The cycleability and the Li accommodation capacity were found to depend on the film thickness. Thinner films gave larger accommodation capacity. A 500 Å thick Si film gave a charge capacity over 3500 mAh g⁻¹ being maintained during 200 cycles under 2 C charge/discharge rate, while a 1500 Å film revealed around 2200 mAh g⁻¹ during 200 cycles under 1 C rate. The initial charge loss could not be ignored but it could be reduced by controlling the deposition conditions.

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1. Introduction

Portable IT electronic appliances such as cellular phones, PCs and camcorders are now getting into third generation equipments, which require Li-ion batteries working as a power source to double the energy and power densities. In responding to this requirement the active materials now 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]. Trials to improve the performances have provided successful results to some extent. Lee and coworkers [3] and Yoshio and coworkers [4] succeeded in improving the cycleability, but the results still needed improvement for practical applications, and the high power capability appears to be insufficient. Yonezu and coworkers have provided an attractive method to obtain a high capacity and long cycle life with Si film by sputtering on a roughened Cu substrate but it appears to be required to prolong the cycle life [5].

We have found that a Si film, vacuum deposited on a Ni foil, revealed a specific energy density over 1000 mAh g⁻¹ with satisfactorily long cycle life [6], however, the power

capability was still insufficient for practical use. We thus challenged to improve the power capability of the Si film. By the use of carrier-doped conductive Si as the evaporating source, we could improve the high power capability to a great extent [7]. The remaining issues to be solved are to expand the film thickness and minimize the initial capacity loss. In this paper we would like to show the results obtained with a quantitative examination of the power capability together with the investigation of the origin of the initial capacity loss.

2. Experimental

About 0.5 g of crushed Si crystals were loaded on a tungsten boat, which was heated by applying electric power directly. A metallic Si film was prepared by evaporating in vacuum onto a 30 μm thick Ni foil to give several thicknesses in the range of 200 to 1500 Å. The film thickness was controlled by monitoring the deposited film thickness with a quartz vibrating microbalance mounted near the substrate in the vacuum chamber. As the source of the metallic Si, three kinds of Si were examined, i.e., intrinsic pure Si, negative carrier doped Si (5 Ωcm), and positive carrier doped Si. The deposition rate was controlled by changing the input power applied to the tungsten boat.

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The obtained film was cut into 10 mm × 10 mm squares, a Ni lead wire spot-welded on, and offered for the evaluation of Li insertion/extraction performance with CV and constant current charge/discharge cycle test in PC in the presence of dissolved 1 M LiClO₄. A Pyrex cylindrical cell with three electrodes was used for the electrochemical evaluation, whereby pure metallic Li foils were used as the reference and counter electrodes. All the measurements were conducted in a glove box filled with dried Ar at ambient temperature.

3. Results and discussion

At first we examined the constant current Li charge/discharge performance for the Si film vacuum deposited with an evaporation source of intrinsic Si. Fig. 1 shows the constant current charge/discharge curves of a 1000 Å thick deposited film.

The available discharge capacity during the cycle was as high as around 2000 mAh g⁻¹ which is five times of the ideal capacity of the graphite electrode, while the cycleability was not acceptable revealing a gradual decreasing of the capacity during cycles. In addition, the initial charge/discharge efficiency was as low as 75% giving a very large initial capacity loss of 750 mAh g⁻¹. For the purpose of finding out the cause of the poor performance we examined the effect of the film thickness. In Fig. 2 the discharge curves are shown for a 1500 Å thick Si film, where we see all the discharging properties are worse than that of the former.

In addition, the same holds for the narrow potential plateau region on the discharge curve as well, viz. it extends to about 1000 mAh g⁻¹ in a 1000 Å thick film whereas it is reduced to 750 mAh g⁻¹ in the latter. Among several possible causes of the performance deterioration with the increase in the film thickness we paid attention on the electric conductivity and the looseness of the film structure.

At first we examined the effect of the electric conductivity of the deposited Si film. A conductive Si film was prepared

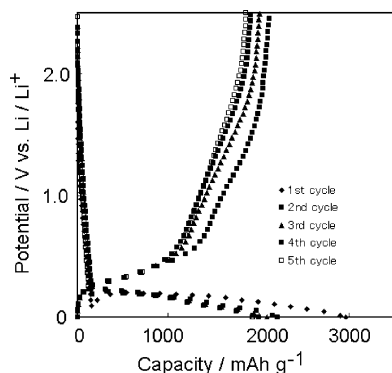


Fig. 1. Constant current charge/discharge curves of Li in PC containing 1 M LiClO₄ of a 1000 Å thick intrinsic Si film deposited on a 30 μm thick Ni film. The rate of charge and discharge is 1 C.

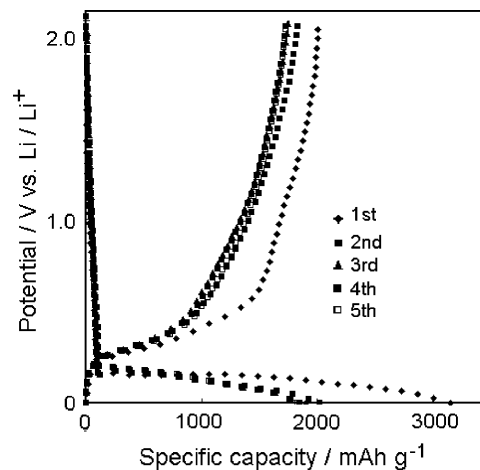


Fig. 2. Constant current charge/discharge curves of Li in PC containing 1 M LiClO₄ of a 1500 Å thick intrinsic Si film deposited on a 30 μm thick Ni film. The rate of charge and discharge is 1 C.

by using a carrier doped conductive Si as the evaporation source. Two types of n-type and p-type doped Si were examined where n-type film revealed better results. Fig. 3 shows the constant current charge/discharge curves for a 1500 Å thick deposited film.

As seen in the figure, not only the specific capacity but also the cycle performance are quite much improved as compared with those of intrinsic Si film (Fig. 2). The initial charge/discharge efficiency was much improved as well from 65 to 88%. Consequently, we can conclude that the electrical conductivity of the deposited film plays an important role in providing a favorable performance for the Li insertion/extraction reaction.

The cycle performance under 1 C rate of charge and discharge was examined with this film, the results being shown in Fig. 4, where we see that a very high specific capacity of over 2200 mAh g⁻¹ was kept during 200 cycles although a slight decrease in capacity is seen.

As seen in the case of an intrinsic Si film, the specific capacity was strongly dependent on the film thickness. To

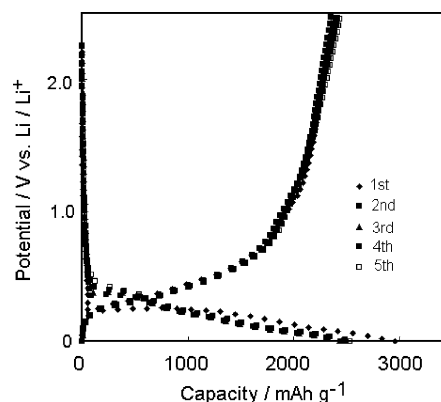


Fig. 3. Constant current charge/discharge curves of Li in PC containing 1 M LiClO₄ of a 1500 Å thick n-type conductive Si film deposited on a 30 μm thick Ni film. The rate of charge and discharge is 1 C.

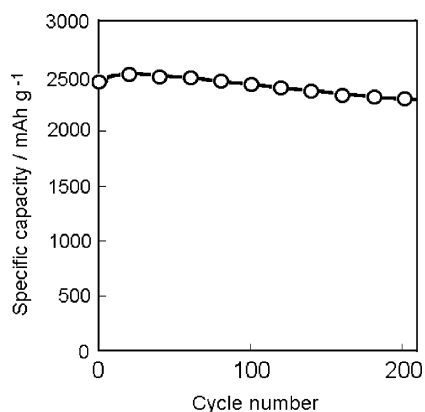


Fig. 4. Constant current charge/discharge cycle performance of Li in PC containing 1 M LiClO₄ of a 1500 Å thick n-type conductive Si film deposited on a 30 μm thick Ni film. The rate of charge and discharge is 1 C.

examine whether such a tendency is found also on the conductive film, a comparison with results of thinner film is required. A 500 Å thick film prepared from the n-type conductive Si was examined for two charge/discharge rates. Fig. 5 shows the results, indicating that the specific capacity for 1 and 2 C rates is much larger—over 3500 mAh g⁻¹, and shows that the capacity is dependent on the film thickness, also in case of n-type Si film.

Since the capacity in this case differs not so much between 1 and 2 C cases, we examined whether such a tendency holds for the thicker film.

In Fig. 6 the cycle performances are shown for the case of 1500 Å thick film of the n-type conductive Si under 10 C charge/discharge condition. It was strange that until near 40th cycle only a much restricted capacity was available but it suddenly jumped up to about 2500 mAh g⁻¹ which was not much changed thereafter. This may be elucidated by assuming that the film was too compact to accept a large amount of Li at a time at first but after repeating enforced Li

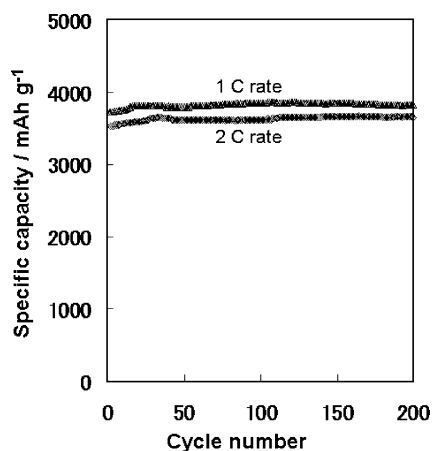


Fig. 5. Constant current charge/discharge curves of Li in PC containing 1 M LiClO₄ of a 500 Å thick n-type conductive Si film deposited on a 30 μm thick Ni film. The rates of charge and discharge are 1 and 2 C.

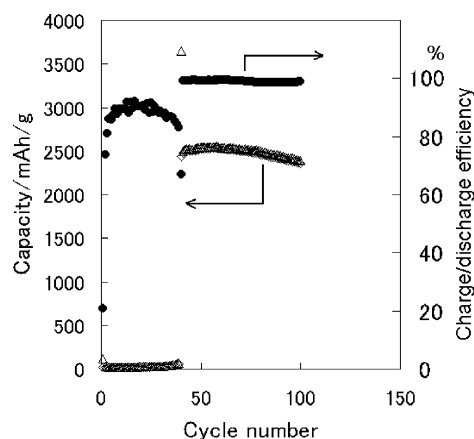


Fig. 6. Constant current cycle performance of a 1500 Å thick film of the n-type conductive Si under 10 C charge/discharge conditions in PC containing 1 M LiClO₄.

insertion/extraction the film structure was changed to accept a large amount of Li rapidly. It is interesting that the specific capacity was still as high as 2500 mAh g⁻¹ even under a heavy load of 10 C. Elucidation of this phenomenon remains to be studied in future.

The cycleability under a very heavy load of 12 C for charge/discharge was examined with a 500 Å thick film prepared from n-type Si. The results are shown in Fig. 7 where we see a similar situation of the initial suppression but afterwards the Li accommodation capacity rose to over 3000 mAh g⁻¹. This was maintained during 1000 cycles under the heavy load of 12 C.

The XRD patterns obtained before and after the cycle test showed no evidence of the presence of Si crystals, implying that the deposited film had an amorphous like structure. This suggests that when the Si sample has an amorphous like structure, it is possible to realize a huge capacity anode having a long cycle life.

In regard to the size of the initial capacity loss, the amount of oxygen kept in the Si film structure is supposed to play

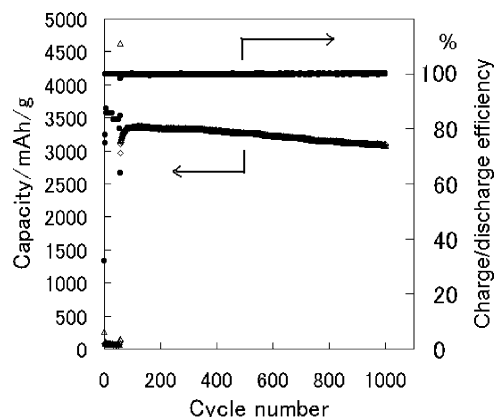


Fig. 7. Constant current cycle performances of a 500 Å thick film of the n-type conductive Si under 12 C charge/discharge conditions in PC containing 1 M LiClO₄.

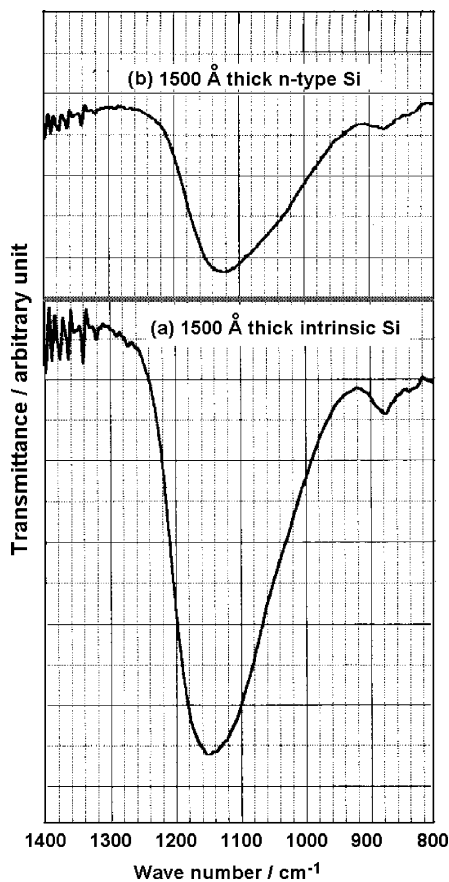


Fig. 8. IR spectra of 1500 Å thick vacuum deposited Si films on a Ni foil from the sources of intrinsic Si (a) and n-type conductive Si (b).

an important role, since during the first charge the oxygen is considered to be reduced by Li to form Li_2O which stays unchanged during the successive oxidation process. We evaluated the amount of oxygen by taking IR spectra of the film. Examples are shown in Fig. 8 where two spectra corresponding to the cases of Figs. 2 and 3, are shown, respectively.

The absorption band at around 1150 cm^{-1} is well attributed to the stretching vibration band of Si–O bond indicating the presence of oxygen atom bound with Si. The upper one (Fig. 8b) corresponding to the case of Fig. 3 is weaker than that of the lower case (Fig. 8a) corresponding to the case of Fig. 2.

Here, the lower strength of the Si–O band requires a lower amount of Li during the first charging process, resulting in a reduced initial charge loss. There is thus a good correlation between the strength of the absorption band and the size of the initial charge loss. This suggests that the initial charge loss will possibly be reduced by controlling the evaporation conditions.

4. Conclusions

We have been able to show that Si has a high potentiality for realizing a novel anode material for Li-ion batteries having a huge accommodation capacity for Li, a capability of high power performance, and keeping a very long cycle life. The conductivity of the electrode material and its amorphous nature are suggested to be key factors for the practical use. Several interesting phenomena shown in this paper remain to be investigated in detail in future.

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