Li insertion/extraction reaction at a Si film evaporated on a Ni foil

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Abstract

In an attempt to provide a Si material having a long cycle life as an anode of Li-ion batteries, we prepared a metallic Si film on a Ni foil by a vacuum evaporation method. Due to the presence of a naturally formed compact passivation film on the Ni foil, a homogeneous, compact amorphous-like Si film strongly adhering to the Ni substrate could be obtained very easily. The Si film thus obtained on a Ni foil was evaluated electrochemically with cyclic voltammetry (CV) and constant current charge/discharge cycle test (CT) in two types of solvents containing 1 M LiClO$_4$, i.e. propylene carbonate (PC), and a 1:1 (v/v) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC). Two strong peaks were observed on the anodic branch of the CV at 300 mV (versus Li/Li$^+$) and 500 mV and the constant current discharge curve of CT produced a wide plateau at around 400 mV in EC/DMC with a discharge capacity of 1700–2200 mAh/g at a discharge rate of 2C. Nearly the same performance was observed as well in PC, where no solvent decomposition was detected. The capacity depended on the preparation conditions and the film thickness. The cycleability at 2C charge/discharge rate was over 750 cycles. One of the important issues to solve is to reduce the large initial charge loss.
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1. Introduction

Due to the rapid progress of the IT technology, portable IT equipment including cellular phones and laptop PCs is expected to become more strongly powered, which demands the powering batteries to be highly improved in capacity and power. The required capacity is expected to double within a few years. One of the most promising candidates is the Li-ion battery.

In order to realize the doubled specific capacity, both of the active materials in the cathode and anode should be replaced by new materials. A number of studies have so far been conducted on the cathode materials involving Li–transition element oxide spinel, and Li–manganese oxide layered compounds. Among them, the high capacity materials having the specific capacity over 200 mAh/g are: LiMn$_{1/2}$Ni$_{1/2}$O$_2$ [1,2], Li[Ni$_x$Li$_{(1/3)-(2x/3)}$Mn$_{(2/3)-(x/3)}$]O$_2$ [3], surface-modified LiCoO$_2$ [4], mechanochemically synthesized Li–Mn–O spinels [5], ammonia- and lithia-doped manganese oxide [6], Li[Cr$_{1/6}$Li$_{5/18}$Mn$_{5/9}$] [7], xLiMO$_2$–(1 − x)Li$_2$RuO$_3$ (M = Co, Ni, Zr, Li) [8], and magnesium-substituted LiCoO$_2$ [9]. The specific capacity, however, is at most 250 mAh/g which corresponds to only 150% increase in the present capacity.

This means that an increase of over 300% of the anode capacity is needed to satisfy the demand. The presently used active anode material is graphite, whose maximum capacity of Li insertion is 372 mAh/g. The required capacity for the new active material should be over 1100 mAh/g. Among the attractive materials like Li$_{2.6}$Co$_{0.4}$N [10] and Li–metal alloys [11,12], the likeliest candidate is metallic Si whose maximum capacity of Li insertion is as high as 4200 mAh/g [13]. The discharge curve of Si during the electrochemical extraction of Li is sufficiently flat, very similar to that of graphite, making it very attractive. The cycleability of Si, however, is too poor to be utilized for the anode of actual Li-ion batteries.

Experiments to solve the cycleability problem has so far been performed. Yoshio and co-workers have succeeded to prolong the cycle life by coating the surface of a fine powder of Si with a CV-deposited carbon [14]. The specific capacity for guaranteeing the cycle life is insufficient (800–900 mAh/g) to meet the demand. Niu and Lee provided a novel method incorporating Si particles in a sol–gel graphite composite matrix and succeeded to keep the specific capacity over 2400 mAh/g [15]. But the cycle life is still too short to be accepted in the commercial batteries. Yonezu and co-workers [16] and Sayama et al. [17] proposed an elegant method to form an amorphous Si film on a specially roughened surface of a Cu current collector. They succeeded to

attain 3500 mAh/g with their amorphous film, fairly good cycleability.

In the present paper, we would like to provide an easier and more convenient method where the cycle life is as long as 700 cycles or more by keeping the capacity over 1500 mAh/g. The method is based on a simple vacuum deposition of Si film at an appropriate rate on a Ni foil that can be used as a current collector. The reason why Ni foil was used is that the surface of Ni is covered with a thin compact passivation oxide film which strongly adheres to the substrate metal [18]. Since the affinity of metallic Si to oxygen is strong [19], the vacuum-deposited Si film on the top of the passivation film is expected to be sticking tightly to the passivation film even after repetitions of Li insertion/ extraction which involves large expansion and shrinkage.

2. Experimental

2.1. Metallic Si sources and vacuum evaporation

Two kinds of Si were examined, i.e. 99.99% purity Si powder (200 mesh, Nilaco Metal Co.) and boron-doped n-type semiconducting Si (300 Ω cm) wafer. The latter was crushed to small pieces before evaporation.

About 0.5 g of the Si powder or crushed pieces of the wafer was put in a tungsten heating boat. A 30 mm thick, 10 cm × 5 cm rectangular Ni foil (Nilaco Metal Co., 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. An electric current was passed directly on the tungsten boat to heat the loaded Si to melting point. The evaporation was controlled by monitoring the deposited thickness with a quartz crystal microbalance mounted near the Ni foil. The deposition rate was controlled to be about 1 Å/min where a preferable film giving a long cycleability was obtained.

A photograph of vacuum-deposited Si film on a Ni foil is shown in Fig. 1 and a Ni foil before the deposition is shown for comparison. The blue color is indicative of the uniformity of the deposited film. To examine the sticking strength of the deposited film, we scratched the film surface with a needlepoint. The scanning electron microscope (SEM) images of the scratch are shown in Fig. 2, by which we can infer that the Si film is not brittle but soft and is adhering tightly to the Ni surface.
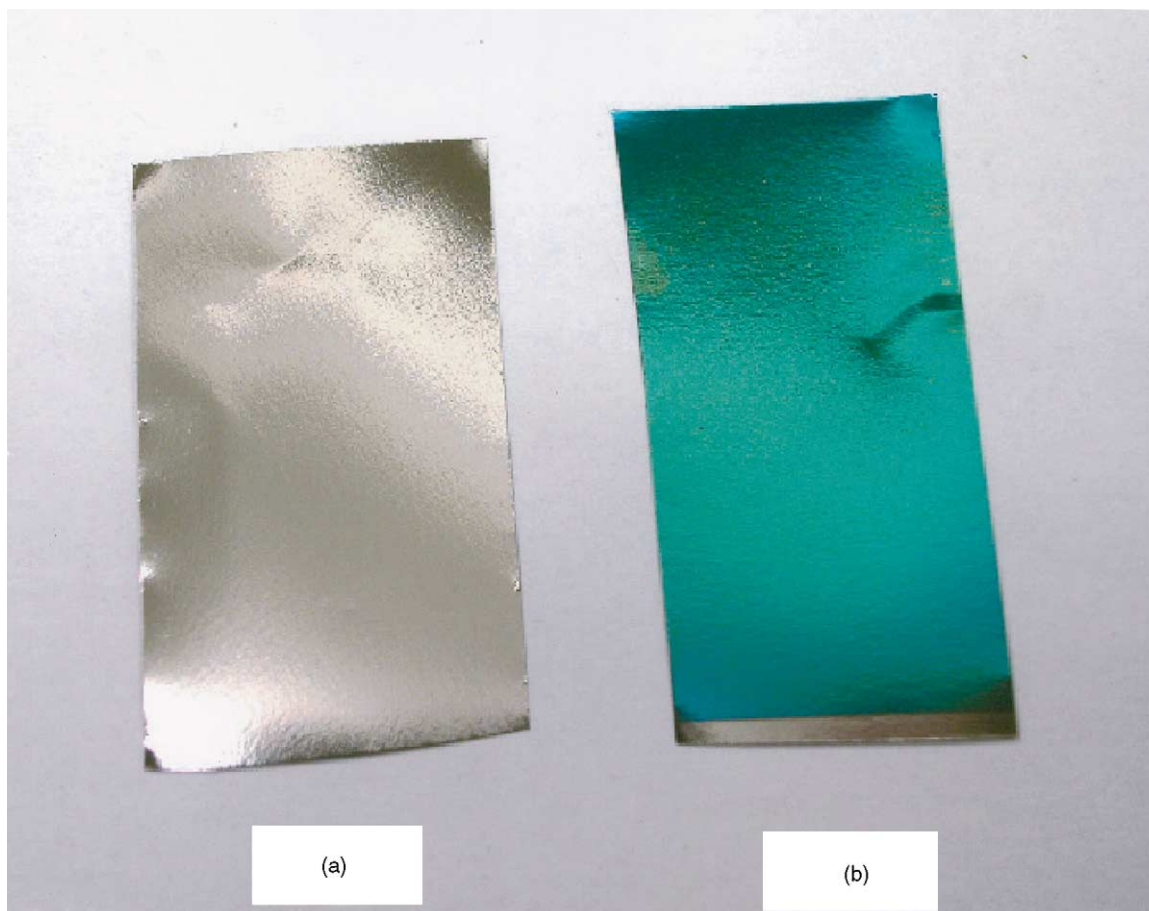

Fig. 1. Photographs of: (a) a 30 μm thick Ni foil; and (b) a 750 Å thick Si film vacuum-deposited onto it with a deposition rate of 1 Å/s.
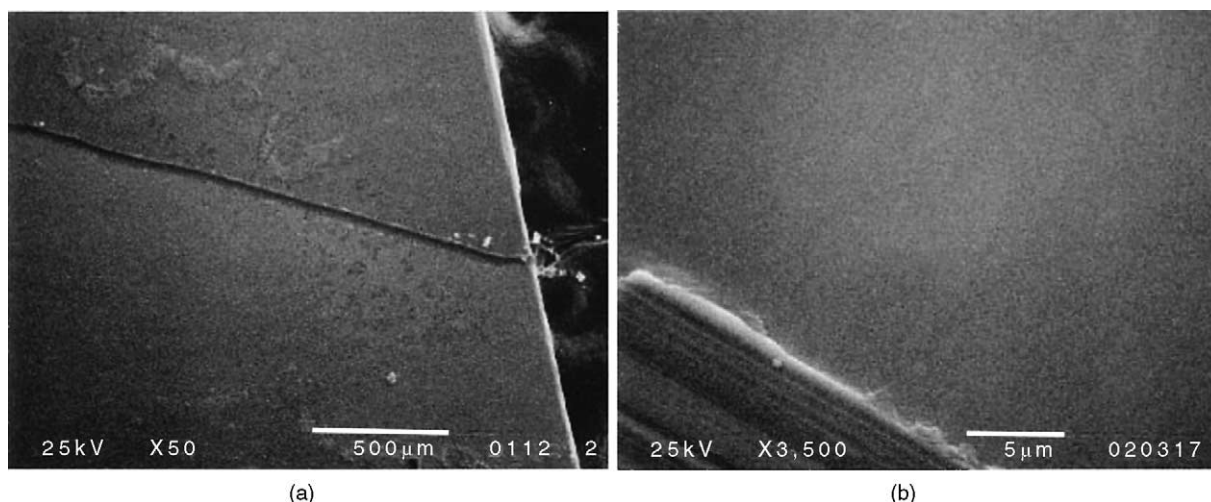
Fig. 2. SEM images of a 770 Å thick Si film vacuum-deposited onto a 30 μm thick Ni foil where we see a scratch line formed by scratching with a needlepoint: (a) low magnification; and (b) high magnification.

2.2. Electrochemical evaluation

A 1 cm × 1 cm square foil cut from the Si-deposited Ni foil was used as the test electrode after spot-welding a Ni lead wire ($\phi = 0.3$ mm) at the corner. The test electrode was mounted in a cylindrical Pyrex glass cell (35 mm o.d., three-electrode system) where pure Li foils were used as counter and reference electrodes. Two kinds of electrolytes were examined: one is a 1:1 (v/v) mixture of ethylene carbonate (EC)/dimethyl carbonate (DMC) containing 1 M $LiClO_4$ (Tomiyama Chemicals, the contaminant water being less than 15 ppm) and the other, pure propylene carbonate (PC) containing 1 M $LiClO_4$ (Tomiyama Chemicals, the contaminant water being less than 20 ppm).

A linear sweep cyclic voltammetry (CV) with a sweep rate of 1 mV/s and a cycle test (CT) with $2C$ both for charge and discharge were conducted with a Hokuto-Denko HA-151 potentiogalvanostat. The CVs were recorded repeatedly with 20 cycles. The first scan 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.

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 Cu Kα radiation by a Rigaku RINT-2000 diffractometer before and after the electrochemical measurements.

3. Results and discussion

3.1. Li insertion/extraction performance in EC/DMC and PC

The overlapped CVs obtained in an electrolyte of EC/DMC containing 1 M $LiClO_4$ for the first 20 cycles of Li insertion/extraction reaction at the Si film vacuum-deposited on a Ni foil are shown in Fig. 3. Although the CV curve of the first cycle is much suppressed, the subsequent curves tend to settle rapidly to maintain a stationary curve where the charge/discharge efficiency is nearly 100%. The initial suppression may be due to the inactivated surface against the electrochemical reaction, but once exposed to the reaction, it becomes activated. Three peaks are recognized on both potential scanning branches toward negative potential, and positive potential. Upon repetition of charge/discharge cycles each peak became distinct and finally there were at least four peaks on both branches (Fig. 4). These peaks are attributed to the potential dependent formation and disappearance of Li–Si alloys of different compositions whose figure was given by Wen and Huggins [20]. The difference in the potential for each peak from that shown in the figure can be ascribed to the temperature difference and the kinetic
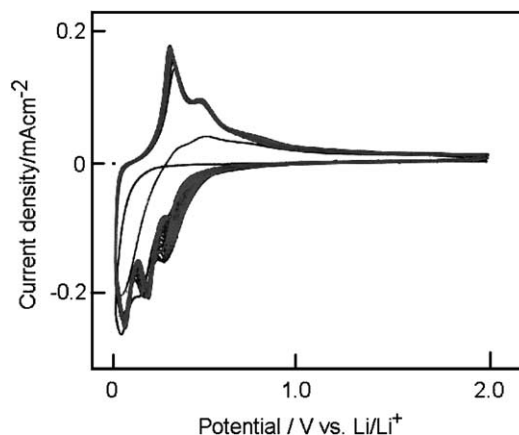

Fig. 3. Overlapped CVs of a 770 Å thick Si film vacuum-deposited on a 30 μm thick Ni foil for the first 20 cycles in EC/DMC containing 1 M $LiClO_4$.
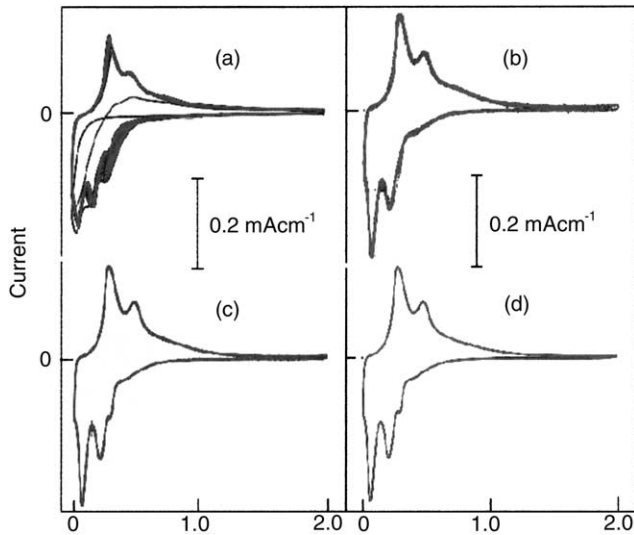
Fig. 4. Overlapped CVs of a 770 Å thick Si film vacuum-deposited on a 30 μm thick Ni foil at various cycles in EC/DMC containing 1 M LiClO$_4$: (a) initial 1–20th cycles; (b) 100–120th cycles; (c) 200–220th cycles; and (d) 300–320th cycles.

effect involved in the CV measurement. The shape of the CV curve was maintained for over 500 cycles.

The peaks appearing on the CV are similar to those obtained with graphite in shape and potential position, and attributed to the insertion and extraction of Li in the Si film formed on a Ni foil. This implies that the constant charge/discharge curves for Li insertion/extraction are similar to those obtained with graphite. In Fig. 5, constant current charge/discharge curves under 2C rate are shown for the case of the vacuum-deposited Si film. As expected, the curves are not so far from those of graphite, and show that about 80% of the total capacity can be withdrawn even under heavy duty charge and discharge in the potential range less than 1 V versus Li/Li$^+$, which is favorable for the commercial battery.
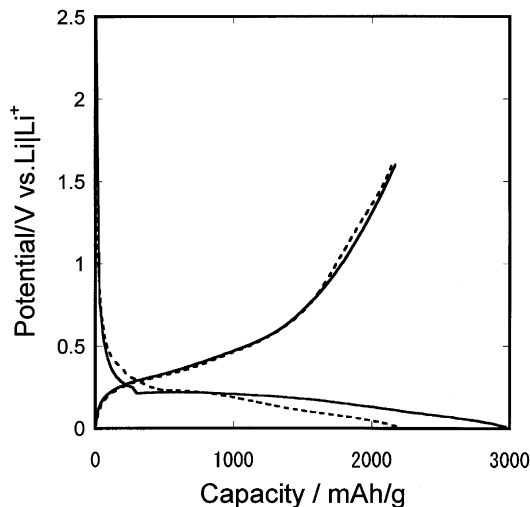

Fig. 5. Constant current charge/discharge curves (2C rate) of a 400 Å thick Si film vacuum-deposited on both sides of a 30 μm thick Ni foil, the initial two cycles in EC/DMC contain 1 M LiClO$_4$.
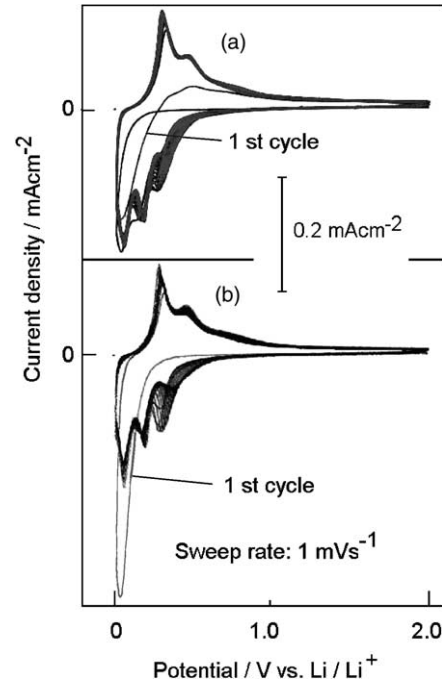

Fig. 6. Overlapped CVs of a 770 Å thick Si film vacuum-deposited on a 30 μm thick Ni foil for the initial 20 cycles in: (a) EC/DMC containing 1 M LiClO$_4$; and (b) PC containing 1 M LiClO$_4$.

We examined the present Si sample in PC electrolyte. In Fig. 6, the CVs are compared for those obtained in EC/DMC and PC for the first 20 cycles. As seen in the figure, there is no significant difference between the CVs obtained in EC/DMC and PC. Even in PC, a stable CV could be obtained without any initial irreversible charging peak current caused by the PC decomposition. As shown in Section 3.2, we succeeded in obtaining a cycle life over 700 cycles long in PC as well. Such a sufficient stability of the anode material against PC is very attractive since the battery assembled with an electrolyte based on PC can work very well even at low temperatures and the price is cheaper. Si is thus attractive as the anode of Li-ion batteries.

3.2. Cycleability

The poor cycleability is the critical issue in the conventional form of Si for the practical use in Li-ion batteries. We paid attention mostly to the cycleability performance of the present Si film sample. The cycleability test was conducted both by CV and CT under a high rate of charge/discharge.

In Fig. 4, the 20 times repeated CVs are compared for every 100 cycles for the test of a potential scan rate of 1 mV/s, which corresponds to about 1.8C rate based on the CT. As pointed out in Section 3.1, the shape of the CV pattern for the first cycle is much different from those of the subsequent cycles. After the second cycle, the CV pattern settled rapidly becoming a steady state pattern, i.e. the shape and the height of the CV peaks were unaltered for long-term repetition of cycles.
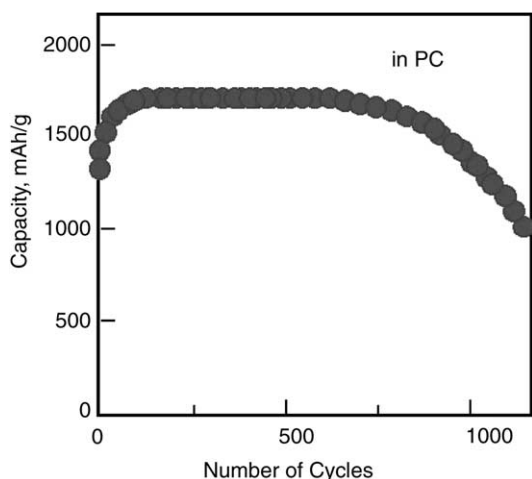
Fig. 7. Cycle number dependency of the Li extraction capacity of a 770 Å thick Si film. The capacity was evaluated from the extraction curves of CVs measured in PC containing 1 M LiClO₄.

The initial behavior was found to depend on the deposition condition. When the deposition was too fast, the film deteriorated very rapidly in cycleability, while a too slow deposition caused the film to be inert to the electrochemical reaction. In addition, the Li charge/discharge capacity was also dependent on the film deposition condition.

In the case of an appropriate formation condition, a long stability could be attained. An example of the cycle test by CV in PC is shown in Fig. 7. After 700 cycles, the CV peaks became deteriorated and diminished. The SEM image of the deteriorated sample at the 1250th cycle is shown in Fig. 8, exhibiting a roughened surface appearance. A constant current charge/discharge test by a 2C load revealed excellent stability within 100 cycles as well. These results are a strong indication of the possibility that Si can be used for the anode of practical batteries provided that the preparation process is appropriate. As suggested by Yonezu and
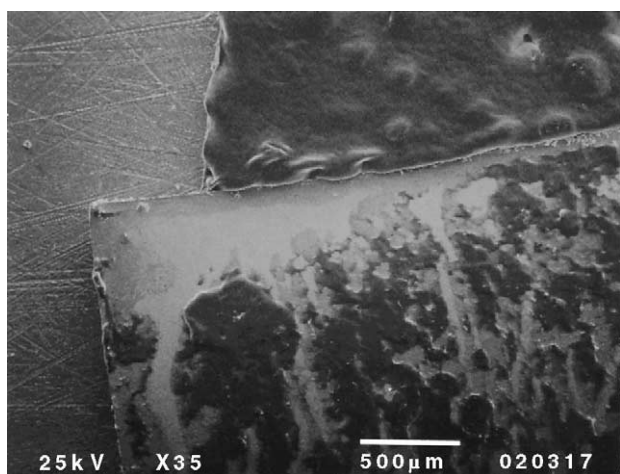

Fig. 8. SEM image of a 770 Å thick Si film vacuum-deposited on a 30 μm thick Ni foil photographed after the 1250th CV in PC containing 1 M LiClO₄. The SEM photograph was taken after being rinsed with water and dried.
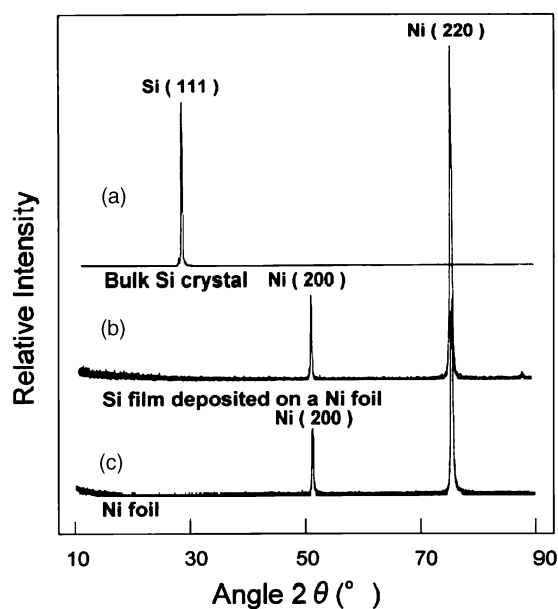

Fig. 9. XRD patterns of: (a) a Si crystal sample; (b) a 30 μm thick Ni foil having a 770 Å thick Si film vacuum-deposited on it; and (c) a 30 μm thick Ni foil.

co-workers [16], Sayama et al. [17], and Niu and Lee [15], the key factor for realizing a long cycle life with Si is its nano-structured phase material design. We examined XRD measurements for the Ni foil with a vacuum-deposited Si film before and after the cycle test but no indication of any peak due to crystalline Si could be ascertained (Fig. 9). This may imply that the deposited Si film is comprised of nano-sized phase or amorphous structure. Softness of the scratch shown in Fig. 2 may support this consideration.

3.3. Effect of the film formation condition

As indicated in Section 3.2, the Li charge/discharge capacity of the Si film was dependent on the film preparation condition. We examined the film thickness up to 1200 Å. A too thick film showed poor capacity though it was gradually improved after repetition of charge/discharge cycles. The film deposition rate was found to strongly influence the obtainable capacity. If the rate was too rapid, the homogeneity of the film could not be attained to give it an enhanced capacity. On the contrary, the film deposition with a too low rate resulted in an inert film for rapid insertion of Li.

We examined the source of the materials, i.e. pure Si powder and boron-doped conductive Si. The latter appeared to give better performances both in capacity and cycleability. The study, however, is still in too early stage to provide the most favorable condition of the film preparation.

The issue to be solved is the large initial capacity loss as shown in Fig. 5. The CV curves in the initial charge/discharge cycle reveal the irreversibility as well (Fig. 6). The cause of the initial irreversible charging capacity is

ascribed to oxidized Si formed by a reaction with residual air in the vacuum chamber, or oxidation at the time of exposure of the freshly prepared film to ambient air.

4. Conclusions

A vacuum-deposited Si thin film on a Ni foil has been shown to reveal an attractive performance as the anode material of Li-ion batteries. A long cycle life with sufficient capacity was exhibited even in a PC-based electrolyte solution. These results imply that Si has a potentiality to be used as the next active material having an extraordinarily high capacity and long cycle life. The key technology for realization is the nano- or amorphous-structured material design.

Acknowledgements

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