Evaluation of the Li insertion/extraction reaction rate at a vacuum-deposited silicon film anode

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Abstract

We have recognized that a vacuum-deposited silicon film shows very attractive Li insertion/extraction reaction performance, but the reaction rate in view of Li diffusion in the silicon film has not been determined yet.

In this study, we performed analysis of the reaction rate by the means of potential-step chronoamperometry (PSCA) method. Samples of the silicon films of several different thicknesses ranging from 500 to 14000 Å were prepared by depositing silicon in vacuum on an etched Ni foil. The current–time curves were recorded under PSCA condition and offered to evaluate the apparent diffusion coefficient D_{app} of Li in the silicon films. The obtained D_{app} values were as low as 10^{-10} to 10^{-13} cm^2 s^{-1}, which were dependent on the film thickness.
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1. Introduction

Highly graphitized carbons are now used widely as an anode material of practical Li-ion batteries. For responding to the strong desire of portable electronic appliances to double the battery capacity, we have to replace the anode material by some new material having far larger specific capacity than that of graphite. Among many candidates, silicon is believed to be a promising one, since it has the largest capacity having favorable discharge performance as the anode material. However, the greatest issue is its low cycleability.

A number of papers have so far been published to overcome the issue [3,4]. Sanyo Corporation has reported that a silicon film sputtered on a roughened copper substrate reveals very high cycleability [5].

We have found that a vacuum-deposited amorphous silicon film showed very stable Li insertion/extraction performance [1,2]. The important issue other than the cycleability, however, appears not to have been paid attention. That is the rate of Li insertion/extraction reaction at the silicon materials. This is very important, because if the rate is too slow we cannot use silicon for the practical application.

Since the reaction rate of Li insertion/extraction at a silicon film appears to have not been evaluated yet, we initiated to determine the rate of Li insertion/extraction reaction. There are several methods for the rate evaluation, i.e., electrochemical impedance spectroscopy (EIS), PSCA, etc. We examined the possibility of these methods for the evaluation in the preliminary experiment and found that the first one was unable to deliver reproducible data, which may be due to the complicated surface morphology of the deposited film. In this situation, we decided to utilize PSCA method, which gives current decay curve as the measure of the reaction rate. From the rate of decay, we could calculate apparent diffusion coefficient (D_{app}) by assuming that the rate is controlled by diffusion of Li in silicon. In case of slow electron transfer reaction rate, the calculated D_{app} values have no meaning in view of diffusion coefficient, but we preferred to use it for convenience in comparing the decay rates measured for many samples having different thicknesses.

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2. Experimental

2.1. Metallic silicon source and vacuum deposition

Silicon films of several different thicknesses ranging from 500 to 14000 Å were prepared by vacuum deposition method. N-type silicon wafer (Shin-Etsu Chemical Co., Ltd. 5×10^{-22} mol m^{-3} of phosphor doped, $5\,\Omega$ cm) was used as the evaporation source. The delivered silicon wafer was crushed to small pieces. The pieces were loaded in a tungsten heating boat, which was set in the vacuum chamber and evacuated to about 5×10^{-5} Torr. Then, electric power was applied directly to the tungsten boat for heating, resulting in deposition on a Ni foil substrate of 30 μm in thickness (Nilaco Co., Ltd.). Prior to the deposition of silicon, the Ni substrate was etched with an aqueous solution of FeCl$_3$ for obtaining sufficiently roughened surface. The vacuum deposition was conducted by the use of a vacuum evaporation equipment, VPC-260 (ULVAC Co., Ltd.) with a deposition rate of about 15 Å s^{-1}. The deposition rate and the film thickness were controlled by monitoring the deposited film weight with a quartz vibrating microbalance mounted near the substrate in the vacuum chamber.

2.2. Electrochemical evaluation

The electrochemical measurements were carried out with a Pyrex cylindrical three-electrode glass cell of 30 mm in diameter. A 1 cm × 1 cm square foil cut from the silicon-deposited Ni foil was used as the test electrode after spot-welding a Ni lead wire at the corner. Pure Li metal foils were used as the counter and reference electrodes. The electrolyte solution was propylene carbonate (PC) containing 1 M LiClO$_4$, where no additional solvent was mixed. The electrochemical evaluation of the silicon films was conducted by cyclic voltammetry (CV) and potential-step chronoamperometry (PSCA). CV was done at a potential sweep rate of 1 mV s^{-1}. For conducting the electrochemical evaluation of CV and PSCA, a Potentio-galvanostat HA-151 (Hokuto Denko Co., Ltd.) combined with a function generator HB-111 (Hokuto Denko Co., Ltd.) was used.

Li insertion/extraction rates were estimated as the apparent diffusion coefficient D_{app} of Li in silicon. The D_{app} values were evaluated by analyzing current–time (i–t) curves obtained with PSCA measurement. All the measurements were performed in a glove box filled with a flowing dry argon gas at room temperature.

3. Results and discussion

A 1000-Å-thick vacuum-deposited silicon film was at first prepared for the evaluation. The CVs are shown in Fig. 1. PSCA was performed successively for this 1000-Å-thick silicon film in each potential range indicated in Fig. 1, where Li insertion/extraction reaction takes place. The potential range
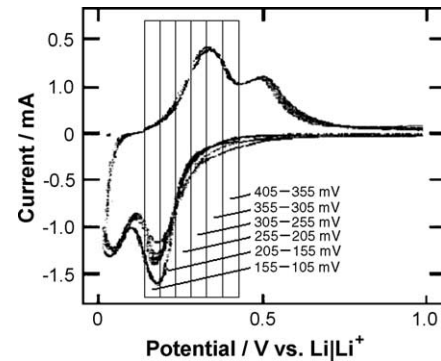

Fig. 1. Cyclic voltammograms (in PC containing 1 M LiClO$_4$) of a 1000-Å-thick silicon film deposited on a Ni foil. Sweep rate, 1 mV s^{-1}.

was selected by referring to the shape of CVs shown in Fig. 1. The current–time (i–t) curves were obtained at first by stepping the potential stepwise to descending (from positive to negative potential) to the negative extreme of 50 mV versus Li|Li$^+$. Then, the potential stepping direction was reversed toward the positive side for Li extraction and the stepwise potential stepping was performed to obtain the Li extraction (discharging) current–time curves.

A log i–t plot evaluated from the i–t curves in is shown in Fig. 2. From the slope of the straight line of log i–t plots, we evaluated the apparent diffusion coefficient D_{app} using the following equation:

$$\log i\, t^{-1} = -4\pi^2 D_{app} l^{-2},$$

where l is the thickness of the silicon film. The equation was derived from the equation (4.17) for a plane sheet in Ref. [6].

The D_{app} values obtained fall in the range of 1×10^{-12} to 3×10^{-12} cm^2 s^{-1} for this film. These values being quite lower than that in carbons [7] are not unlikely, when we refer to the literature value [8]. For the purpose of applying the silicon film to the anode of practical battery, it is necessary to look for a method to meet the requirement of high current charge/discharge.
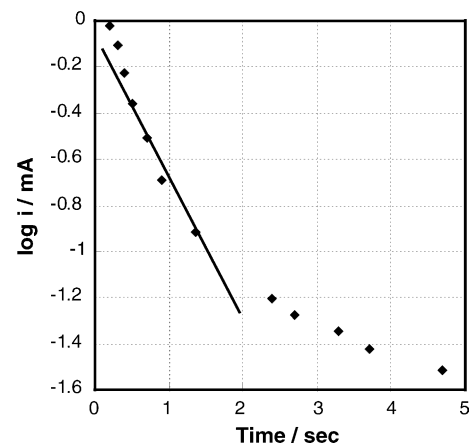

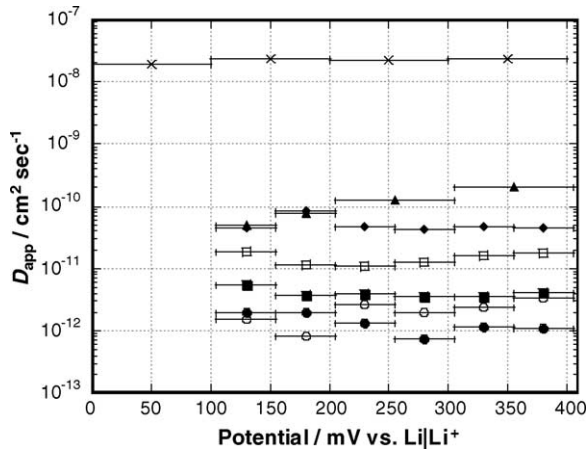Fig. 2. Log i–t plot of a 1000-Å-thick silicon film during delithiation (255 → 305 mV).

Fig. 3. The D_{app} values of Li in silicon films vacuum-deposited on Ni foils during delithiation: (●) 500 Å; (○) 1000 Å; (■) 2000 Å; (□) 4000 Å; (♦) 8000 Å; (▲) 14000 Å; (×) Melblon 3100 graphite fiber (pristine).
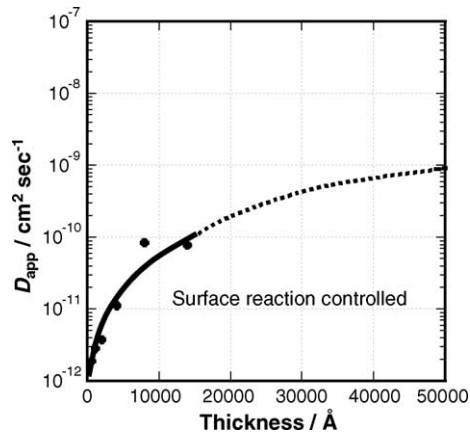

Fig. 4. Relationship between silicon film thickness and D_{app}.

The D_{app} values (10^{-10} to 10^{-13} cm^2 s^{-1}) obtained with silicon films of different thicknesses are shown in Fig. 3 together with the D_{app} values of Li in graphitized carbon fiber (Melblon 3100) [7]. The D_{app} values became larger with the increase in the silicon film thickness as shown in Fig. 4. If the rate-determining step is the diffusion process of Li in silicon, D_{app} values should be invariable regardless of the thicknesses. The present results suggest that the rate-determining step is not in the Li diffusion in the silicon film but possibly in the charge-transfer step on the surface. However, the contri-

bution of rate-determining process of surface reaction is expected to become less for the thicker film, resulting in that the D_{app} value approaches a meaningful value with the increase in the silicon film thickness as shown with a dotted line in figure.

4. Conclusions

The reaction rate of Li insertion/extraction of vacuum-deposited silicon film was determined by PSCA method, which implies the reaction is controlled by surface reaction. The evaluation of the D_{app} value for thicker film is required in order to clarify the rate determination step. We are now undertaking the evaluation of the D_{app} value for thicker silicon film.

If the D_{app} values of Li in silicon films were in the order of 10^{-10} to 10^{-13} cm^2 s^{-1}, the mass-transfer rate of Li being slower than that in carbon. It is desired to provide some advanced material design based on nano size material.

Acknowledgement

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