

Short communication

## Measurement of the diffusion rate of Li in silicon by the use of bipolar cells

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### Abstract

Due to the lack of diffusion data of Li in solid silicon at room temperature, we decided to determine the diffusion coefficient of Li in solid silicon by the use of a bipolar cell system where a sheet of silicon sample is sandwiched as the bipolar electrode between two facing bipolar cell compartments. In both of the cell compartments counter and reference electrodes were mounted. In one of the cell compartments (Cell A), an electrolyte containing Li<sup>+</sup> was filled, while the facing compartments (Cell B) was filled with an electrolyte containing Na<sup>+</sup> instead of Li<sup>+</sup>, and a needle-like W/WO<sub>x</sub> electrode, which can sense the Li<sup>+</sup> concentration, was mounted near the surface of the bipolar electrode.

At first the potential of the bipolar electrode in Cell A was set at the natural potential, and the potential in Cell B was polarized at a sufficiently positive potential, then the potential in Cell A was set at a definite cathodic potential and the signal–time curve of the W/WO<sub>x</sub> electrode in Cell B was recorded. During the cathodic polarization in Cell A Li<sup>+</sup> was incorporated in the bipolar electrode, migrating from the Cell A side to the Cell B side, and transferred to the electrolyte in Cell B compartment. As a result, the signal of the Li<sup>+</sup> sensing electrode began to increase after a time delay which corresponds to the time for Li to migrate in the bipolar electrode from the Cell A side to the Cell B side. From the value of time delay we could calculate the diffusion coefficient by the use of a diffusion equation where a parameter of the thickness of the bipolar electrode is involved.

The obtained value of the diffusion coefficient of the vacuum-deposited film was 10<sup>−9</sup> cm<sup>2</sup> s<sup>−1</sup> independent of the polarization potential. In contrast, the silicon single crystal sample obtained by thinning the silicon single crystal wafer gave about 2 × 10<sup>−11</sup> cm<sup>2</sup> s<sup>−1</sup>. The larger value obtained with the vacuum-deposited film is attributed to the loose structure of the deposited film.

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### 1. Introduction

Silicon is one of the most promising materials as the anode of the next generation of Li-ion batteries. Although a number of studies on the chemical diffusion coefficient of Li ( $D_{\text{chem}}$ ) in solid active materials of Li-ion batteries have been conducted [1–11], reliable data on the diffusion coefficient of Li in silicon at an ambient temperature appears not to have been published. Providing fundamental data on the diffusion of Li is very important for electrode designing. During the course of our study on the vacuum-deposited silicon film for the anode of Li-ion bat-

tery, we have recognized that the rate of Li insertion/extraction depends on the thickness of the deposited film, indicating that the thicker film gave lower rate value. The reason why the rate is dependent on the film thickness may be due to the lowering of the rate of diffusion on the thicker film whose physical properties may differ from those of thinner film, or to the poorer contact of the thicker film to the substrate. Thus, we tried to determine the Li diffusion coefficient in vacuum-deposited silicon film for different thicknesses. The method of determination was potential step chronoamperometry (PSCA) where the polarized potential of the sample silicon electrode in a Li<sup>+</sup> containing electrolyte was stepped to another definite potential and the obtained current–time curve was plotted based on a Cottrell Plot from which the diffusion coefficient was calculated. The obtained values were dependent on the film thickness and the  $D_{\text{chem}}$  value was larger for thicker films, which contradicts the

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observed tendency described above that the thicker film should give smaller values [12].

Provided that the process during potential stepping is not controlled by the Li diffusion process but by the charge transfer reaction, the diffusion data obtained by this method is meaningless. We supposed that the PSCA method corresponds to this situation and is not suitable for the present purpose, and accordingly, it was required that we use the other more reliable method. Since we succeeded obtaining reliable  $D_{\text{chem}}$  values in the case of Li diffusion in metal foils [13–15], we attempted to apply the same method to the case of a silicon sample. The method is based on the bipolar cell method where a sheet of silicon sample is used as a bipolar electrode and is sandwiched between two facing bipolar cell compartments. The bipolar cell method does not use the current–time curve during the Li insertion/extraction reaction but, instead, uses the breakthrough time, which is the time for Li to pass through the sample film, and accordingly, it is not influenced by the surface condition of the sample. Therefore, more reliable data on  $D_{\text{chem}}$  should be obtained.

## 2. Experimental

### 2.1. Bipolar cell

The bipolar cell used in this study is shown in Fig. 1. Teflon made cylindrical cells whose inner diameter was 15 mm, each having a flange, were facing together and a sheet of the sample silicon electrode was sandwiched between the two facing cell compartments and fixed tightly by the use of bolts and nuts in the hole of the flanges. In one of the compartment (Cell A), an electrolyte comprised of a 1:1 (v/v) mixture of ethylene carbonate (EC) and dimethylcarbonate (DMC) containing 1 M LiClO<sub>4</sub> was used to fill it and, in the other compartment (Cell B) an electrolyte containing 1 M NaClO<sub>4</sub> instead of LiClO<sub>4</sub> was used to fill it. As shown in Fig. 1, Cell A worked as a three electrode system while Cell B worked as a two electrode system. In Cell B, a Li<sup>+</sup> sensing electrode, a W/WO<sub>x</sub> electrode, was mounted near the surface of bipolar electrode. The preparation and the performance of this electrode is described elsewhere [13–16].

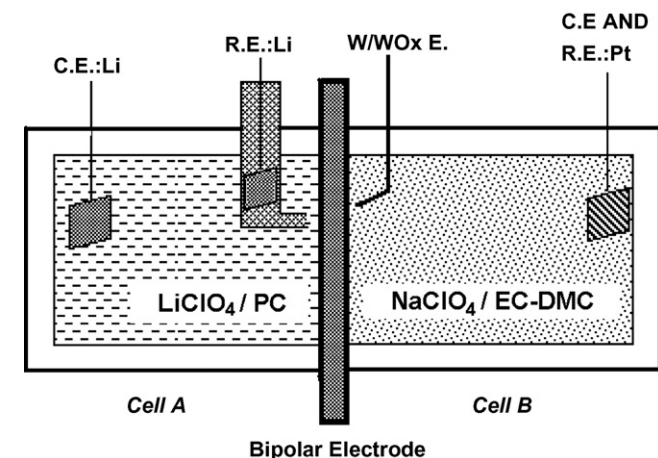


Fig. 1. Schematic figure of the bipolar cell used for the determination of the Li diffusion coefficient.

### 2.2. Bipolar electrode

The bipolar electrode was prepared by vacuum-depositing a silicon film on a 8- or 10- $\mu\text{m}$ -thick Ni substrate. The source of silicon was a phosphor doped 7  $\Omega\text{ cm}$  wafer for IC substrate which was provided by Shinnetsu Chemical Co. The wafer was crashed and filled on a tungsten boat which was put in a vacuum chamber. Electric power was supplied directly to the boat for heating the silicon sample at the melting point, resulting in the deposition of silicon on a Ni substrate that was mounted over the tungsten boat. The thickness of the deposited silicon was controlled by monitoring a quartz vibrating microbalance mounted near the substrate. The Ni sheet deposited with a silicon film was used as the bipolar electrode.

On the other hand, instead of a vacuum-deposited silicon film, thin silicon crystal sheets of 100 and 180  $\mu\text{m}$  thick were examined as another silicon sample, which was kindly provided by Shinnetsu Chemical Co.

### 2.3. Measurement

Prior to the measurement of the Li<sup>+</sup> concentration–time curve, the potential of the silicon film bipolar electrode, we measured the signal–time curve for the bare Ni substrate. An 8- $\mu\text{m}$ -thick Ni foil was examined as the bipolar electrode. At first, the potential of the Ni foil was set at a natural electrode potential in Cell A, and at a sufficiently positive potential as compared to the Pt counter electrode in Cell B. After such conditioning for one hour, the potential of the bipolar electrode in Cell A was stepped to a definite cathodic potential (say, 65 mV vs. Li|Li<sup>+</sup> electrode) and the Li<sup>+</sup> concentration signal of W/WO<sub>x</sub> electrode versus time curve was recorded during the polarization. An example of the signal–time curve thus obtained is shown in Fig. 2, where two signal–time curves are shown at different polarization potentials. Fig. 2 shows that the signal–time curve begins to rise up after a definite time delay (breakthrough time,  $t_b$ ) from the time zero where the electrode polarization was started.  $t_b$  is the time required for the Li inserted in Ni to migrate from the face of Cell A to that of Cell B. The diffusion coefficient of Li in Ni can be calculated as described in the following section.

All the measurements were performed in an Ar gas filled glove box and the temperature of the bipolar cell was maintained at 25  $^{\circ}\text{C}$ .

## 3. Results and discussion

The chemical diffusion coefficient of Li in a Ni foil can be calculated by the use of Eq. (1) [16]. The obtained value of  $D_{\text{chem}}$  was  $1 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$  and was invariable throughout the potential range between 50 and 500 mV versus Li|Li<sup>+</sup> [16].

$$t_b = \frac{l^2}{\pi^2 D_{\text{chem}}} \quad (1)$$

where  $l$  is the thickness of the Ni foil.

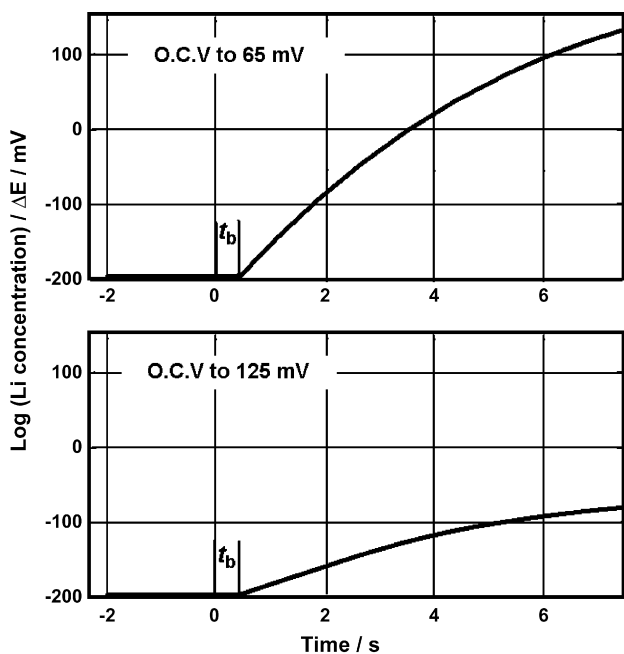


Fig. 2. Signal–time curves of a W/WOx Li<sup>+</sup> sensing electrode at 25 °C in Cell B for the case of an 8- $\mu\text{m}$ -thick Ni foil bipolar electrode. The stepping potentials are indicated in the figure.

The determination of  $D_{\text{chem}}$  of Li in a silicon film deposited on a Ni substrate was performed by the use of such a two-ply foil as a bipolar electrode, which was sandwiched between Cell A and Cell B. The procedure of the measurement was the same as that performed for a Ni single layer foil. The examples of the Li signal–time curves obtained at four different polarizing potentials for 1- $\mu\text{m}$ -thick silicon on an 8- $\mu\text{m}$ -thick Ni substrate

are shown in Fig. 3, where we see that the concentration of Li<sup>+</sup> in Cell B begins to increase after breakthrough time  $t_b$  which is longer than that in the single phase Ni substrate. The longer time required is the reason that the time required for Li to migrate from the Cell A side to Cell B side consists of two components,  $t_{\text{Ni}}$  and  $t_{\text{Si}}$ , where  $t_{\text{Ni}}$  is the breakthrough time for Li to migrate in the Ni phase, and  $t_{\text{Si}}$  is that for Li in the silicon phase, respectively. Overall breakthrough time,  $t_b$ , was found to be almost independent of the polarization potential, within the experimental error, as shown in Fig. 3.

The overall breakthrough time  $t_b$  in this case can be expressed by Eq. (2).

$$t_b = t_{\text{Si}} + t_{\text{Ni}} \quad (2)$$

The value of  $t_{\text{Si}}$  can be obtained by Eq. (2) with the measured value of  $t_b$  and the value of  $t_{\text{Ni}}$  which is reported in the previous paper [16]. The chemical diffusion coefficient of Li in the vacuum-deposited silicon film was obtained by the use of Eq. (1), where  $t_{\text{Si}}$  was used instead of  $t_b$ , and the thickness of silicon film used was  $l$ . The obtained values are plotted in Fig. 4, which shows that the observed  $D_{\text{chem}}$  value, which is about  $10^{-9} \text{ cm}^2 \text{ s}^{-1}$ , are not only independent of the polarization potential, but are also independent of the thickness of silicon film. The reliability of the value obtained in this study is supported by the fact that the  $D_{\text{chem}}$  obtained was independent of the sample thickness.

The  $D_{\text{chem}}$  value obtained with a silicon crystal was entirely different from those obtained with the vacuum-deposited film. Fig. 5 shows an example of the Li signal–time curve obtained with a 180  $\mu\text{m}$ -thick-silicon single crystal plate at the stepping potential of 50 mV. Since the thickness is very thick as compared with that of vacuum-deposited film, the time scale is quite

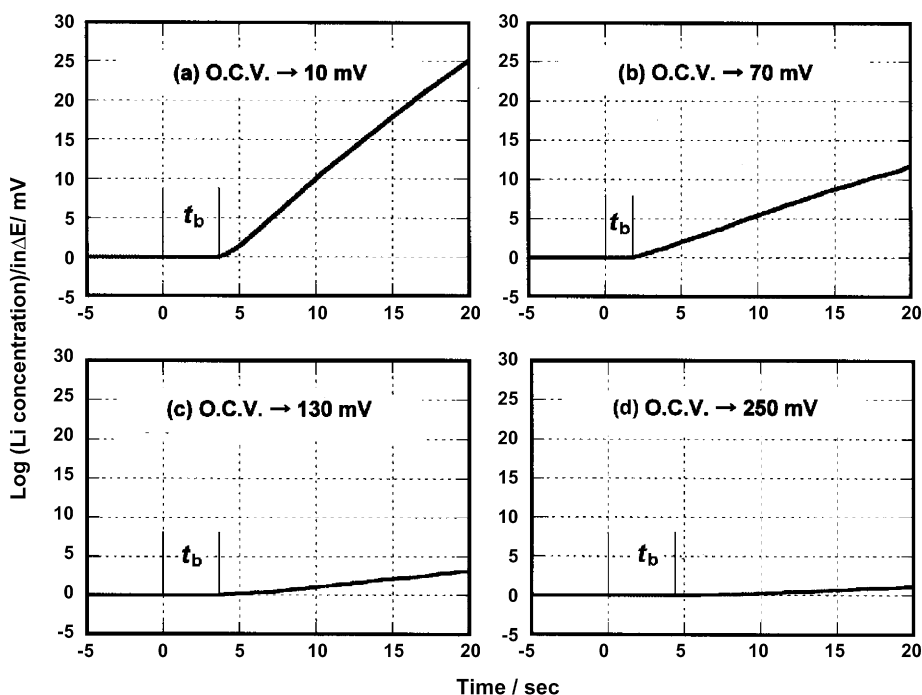


Fig. 3. Signal–time curves of a W/WOx Li<sup>+</sup> sensing electrode in Cell B at 25 °C for the case of two layered bipolar electrodes where an 8- $\mu\text{m}$ -thick Ni foil was vacuum-deposited with a 1- $\mu\text{m}$ -thick silicon film. The stepping potentials are indicated in the figure.

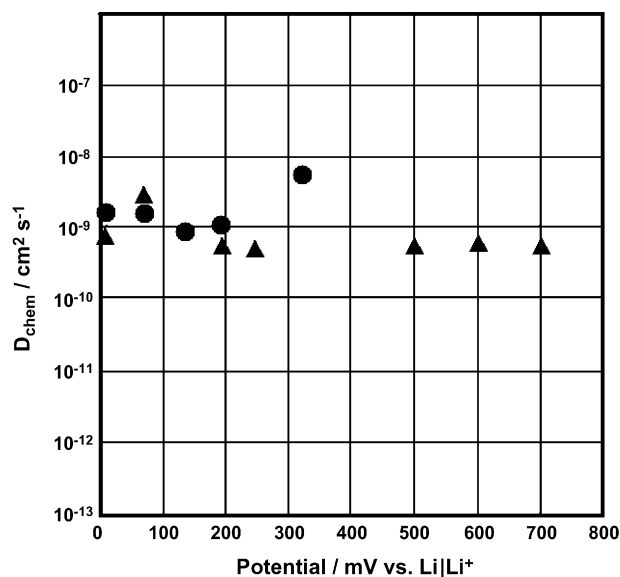


Fig. 4. The chemical diffusion coefficient of Li in vacuum-deposited silicon films at 25 °C plotted as a function of the stepping potential of the bipolar electrode. Circle: obtained with a 1- $\mu\text{m}$ -thick silicon film vacuum-deposited on an 8- $\mu\text{m}$ -thick Ni foil; triangle: obtained with a 2.4- $\mu\text{m}$ -thick silicon film vacuum-deposited on an 8- $\mu\text{m}$ -thick Ni foil.

a lot longer as compared with that obtained with the vacuum-deposited film. Although this prevented us from determining the precise  $D_{\text{chem}}$  value, we obtained the value of  $D_{\text{chem}}$  to be  $1.7 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$  for the 180  $\mu\text{m}$ -thick silicon crystal. In the case of the 100  $\mu\text{m}$ -thick-plate, the  $D_{\text{chem}}$  value obtained at 100 mV was  $1.9 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$ . Taking the experimental error into consideration, these results tell us that the  $D_{\text{chem}}$  value of Li in silicon crystal is  $2 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$ . This is about 1/50 of the value obtained for the vacuum-deposited film.

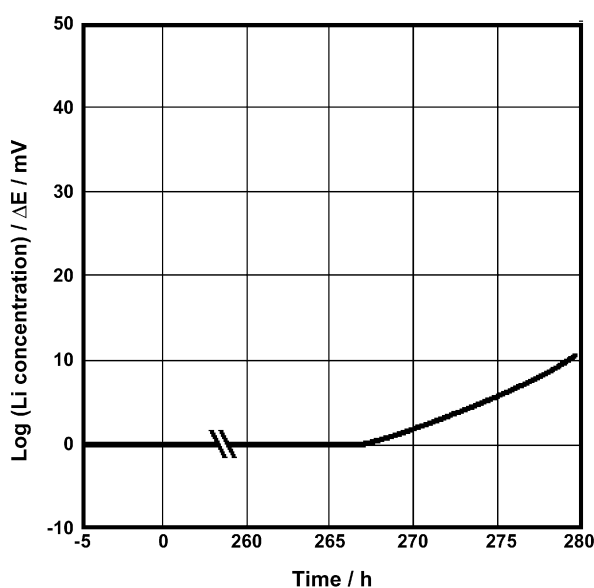


Fig. 5. Signal–time curves of a W/WO<sub>x</sub> Li<sup>+</sup> sensing electrode at 25 °C in Cell B for the case of a 180- $\mu\text{m}$ -thick single crystal silicon plate bipolar electrode. The stepping potential was from OCV to 50 mV vs. Li|Li<sup>+</sup> electrode.

We examined the reason why the  $D_{\text{chem}}$  value of the vacuum-deposited film is 50 times larger than that of silicon crystal. At first the density of the deposited film was evaluated. From the oblique view of the SEM image obtained for the vacuum-deposited film, we could estimate the thickness of the film whose weight/unit area was determined by the quartz crystal vibrating microbalance mounted near the sample in a vacuum chamber. The density of the film was calculated to be about  $1.2 \text{ g cm}^{-3}$ , which is roughly half of the silicon crystal density. This means that the vacuum-deposited film has a loose structure as compared with that of a single crystal, which allows Li migrate with a faster speed than in the single crystal.

Crystallographic evaluation for characterizing the deposited film was performed. While the low magnification SEM (viz.  $\times 3000$ ) of the vacuum-deposited silicon film on a roughened Ni substrate etched with a 1 M aqueous FeCl<sub>3</sub> solution showed an image having slick surfaces, implying an amorphous nature, high magnification SEM ( $\times 30000$ ) exhibited the silicon film to consist of the aggregate of a number of tiny particles (10–20 nm). Through TEM examination, we concluded that the tiny particles are randomly oriented silicon crystals [17]. Due to the random orientation, the inter-crystallite spacing is vacant, causing the formation of swelled film. This swelled nature of the deposited film is attributed to the fast motion of Li.

Silicon produces several alloys with Li [18]. The potential of the alloy formation is given in the paper by Wen and Huggins [18]. In the formation of the alloy, Li from the silicon matrix (wherein Li particles are dispersing) is captured, causing a retardation of the smooth motion of the Li. One may expect that, at the alloy formation potential, the value of  $D_{\text{chem}}$  should be lower than those at a potential of no alloy formation. However, no potential dependency is shown in Fig. 4, the reason for this is discussed in the following. The mechanism of alloy formation in the silicon matrix is a kind of phase nucleation in the matrix, where embryos of the alloy should be formed in the initial stage. If the concentration of Li is very low, the embryos cannot grow spontaneously and a Li particle near the embryo moves forward without being captured. Upon polarization of the bipolar electrode in Cell A, the concentration of Li in the electrode is too low to form the alloys, and incorporated Li can move forward to the Cell B side. During the polarization Li particles are enforced to be inserted in the bipolar electrode successively, resulting in an increased Li concentration near the Cell A side, and the alloy formation is allowed to take place. If we can detect the Li which have not been captured by alloy embryos, the diffusion coefficient determined in this way will be free from alloy formation. The measurement by the use of a W/WO<sub>x</sub> electrode mounted close to the Cell B face is considered to correspond to this situation.

#### 4. Conclusions

By the use of the bipolar cell method where the silicon sample was sandwiched between two facing compartments, we have been able to determine the chemical diffusion coefficient of Li in a silicon sample. The  $D_{\text{chem}}$  value at 25 °C obtained with a vacuum-deposited silicon film on a Ni substrate was

$10^{-9} \text{ cm}^2 \text{ s}^{-1}$ , while the value obtained with a single crystal silicon plate was  $2 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$ . The 50 times higher value for the vacuum-deposited film is elucidated based on the loose structure of the vacuum-deposited film.

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