



Short communication

An amorphous Si film anode for all-solid-state lithium batteries



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H I G H L I G H T S

- Pure *a*-Si film anode exhibits excellent anode properties in all-solid-state batteries.
- The *a*-Si anode shows quite high rate capability and very low interfacial resistance.
- Charge/discharge cycles are stable with high coulombic efficiency over 99%.
- The high performance is achieved in *a*-Si films without any additives.

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This study reports an amorphous Si (*a*-Si) film as an anode material for all-solid-state lithium batteries. The film exhibits stable charge/discharge over 100 cycles and rapid charge transfer at the interface with a solid electrolyte. The potential performance of the *a*-Si film anode will become apparent in the present work.

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1. Introduction

Today, lithium-ion batteries (LIBs) are widely used as power supplies in many types of portable devices. Their much higher energy density compared to Ni–MH batteries has allowed remarkable downsizing and multifunction portable devices in recent decades. Recently, larger size batteries have become essential to apply LIBs as a power source for electric vehicles (EVs), where high energy density is crucial. However, graphite anodes, which are commonly used for commercial LIBs, have encountered their theoretical capacity limits. Therefore, alternative high capacity anode materials are strongly required.

Si is the most promising candidate for meeting the aforementioned demands. Its theoretical capacity for alloying to $\text{Li}_{4.4}\text{Si}$ is 4200 mAh g^{-1} , which is more than 10 times higher than that of graphite anodes [1]. However, at the expense of its exceptional lithium storage capacity, Si undergoes large volume changes during battery operation, which leads to drastic capacity fading due to the pulverisation of Si [2]. Vast efforts have been directed toward addressing volume expansion by forming Si into nano-sized or porous materials, as presented in review articles [3,4]. However, such approaches lower the loading of active materials and thus decrease the amount of active material included in the battery. On the other hand, Si anodes formed into thin films exhibit relatively good performance despite their dense structures. Amorphous Si (hereafter, *a*-Si) films prepared by vacuum deposition show rather stable cycle behaviors [5–7]. In addition, Si-based films fabricated by a pulsed laser deposition (PLD) method in our previous study exhibit excellent rate capabilities achieving 200 C as well [8].

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The rate capability is markedly higher than those having been reported for similar systems [9–12], as compared in Fig. 1, and even when they are compared on the basis of current density as shown in Fig. S1 of Supplementary information. Although it is quite important to identify the reason for the high rate capability, it is still unclear. Major differences from the other systems, which can be the reason for the high rate capability, are as follows: the Si-based films contain 10% FeS, and the rate capability is evaluated in a solid electrolyte. This study is aimed at the origin of the high rate capability.

In the previous study, FeS was used in the Si films because it was reported to effectively enhance the electrode properties of a conversion-type Si-based anode, Li_2SiS_3 , in which FeS was uniformly distributed in the Si-based material by PLD to provide high electronic conduction [13]. The FeS addition is effective, because Li_2SiS_3 is electronically insulating. On the other hand, Li–Si alloy formed in the electrode reaction boasts high electronic conductivity, and thus the FeS addition may not be necessary for the high rate capability. To clarify the effects of FeS on the rate capability, the electrode properties of *a*-Si without any additives must be investigated; however, thin-film fabrication of pure Si is not possible by PLD. In the present work, we adopted an r.f. magnetron sputtering technique to fabricate *a*-Si films. A $70\text{Li}_2\text{S}\cdot 30\text{P}_2\text{S}_5$ glass ceramic, which has been reported to show high Li^+ ion conductivity on the order of $10^{-3} \text{ S cm}^{-1}$, was selected as the solid electrolyte [14]. Here, we report the high rate and stable cycle performances of *a*-Si films in all-solid-state cells composed of $\text{InLi}|70 \text{Li}_2\text{S}\cdot 30\text{P}_2\text{S}_5|a\text{-Si}$ film.

2. Experimental

2.1. Sample preparation

a-Si films were deposited by r.f. magnetron sputtering using i-Miller CFS-4EP-LL, Shibaura Mechatronics Corp. The target material was 5N-pure Si purchased from Kojundo Chemical Laboratory Co., Ltd. Stainless-steel disks with 10 mm in diameter were used as substrates and were polished by 4000-grit sand paper and rinsed by ultrasonic cleaning in a mixture of acetone and 2-propanol in a volume ratio of 1:1 before the deposition. The base pressure in the sputtering chamber was approximately $1 \times 10^{-4} \text{ Pa}$ and was maintained at approximately 0.45 Pa during the deposition. The r.f.

power was 200 W, and the resulting deposition rate was approximately 3.6 nm min^{-1} . The film thickness and weight were measured by a surface profiler (Dektak 150, Veeco Instruments Inc.) and an electric microbalance (XP6U, Mettler-Toledo Inc.), respectively. Density of the Si film was calculated from these values measured for a thick film in order to avoid the inaccuracy. The obtained value was 2.3 g cm^{-3} , which indicates that the deposited films are quite dense, because it is almost comparable to the theoretical density of crystalline Si (2.33 g cm^{-3}). This density was used to calculate the film weight for evaluating the electrode performance. The obtained films were annealed with a lamp anneal furnace (MILA-3000, ULVAC, Inc.) under Ar atmosphere at $300 \text{ }^\circ\text{C}$ for 20 min. The local structure and surface morphologies of the obtained films were investigated by Raman spectroscopy (RAM-ANplus, Nanophoton) and scanning electron microscopy (SEM; VE-8800, Keyence Corp.), respectively.

2.2. Cell fabrication

Solid-state cells were assembled with an In–Li alloy showing a potential plateau at 0.62 V vs. Li^+/Li as the counter electrode. A $70\text{Li}_2\text{S}\cdot 30\text{P}_2\text{S}_5$ glass ceramic was used as the solid electrolyte. After the powder of the $70\text{Li}_2\text{S}\cdot 30\text{P}_2\text{S}_5$ glass ceramic (150 mg) was pressed into a pellet with 1 cm in diameter, the *a*-Si film was attached to one side of the electrolyte pellet as the working electrode. The counter electrode was formed on the other side by attaching a 10-mm-across Indium foil with a small piece of Li metal (ca. 1 mg). They were pressed together at 400 MPa into a three-layered pellet that acted as two-electrode cell. The cell was constructed in an Ar filled glove box, where the O_2 and water concentrations were kept under several ppm. The *a*-Si film electrode was cycled between 0.01 and 1.2 V vs. Li^+/Li at a constant current density of 0.1 mA cm^{-2} with 1 h rest periods to investigate the cycling performance. The cyclic voltammometry was also performed for the same cell at a sweep rate of 0.1 mV s^{-1} in the potential range between 0.01 and 1.2 V vs. Li^+/Li . The rate capability was evaluated at current densities from 0.1 to 10 mA cm^{-2} . The *a*-Si film was charged at a constant current density of $10 \text{ } \mu\text{A cm}^{-2}$ to 0.01 V vs. Li^+/Li and then kept at that potential until the current density decreased to $0.1 \text{ } \mu\text{A cm}^{-2}$ (CV mode) before discharging. These electrochemical measurements were made using PS-08 (Toho Technical Research) and VSP (Biologic) multichannel potentiogalvanostats at room temperature. The electrochemical impedance spectroscopy was performed after charging the *a*-Si film in the frequency range from 100 kHz to 1 Hz with the AC perturbation signal of 10 mV using a Solartron 1287 potentiogalvanostat connected with a 1260 impedance/gain-phase analyzer. The electrode properties were also investigated in a liquid electrolyte for comparison. The electrolyte was 1 M LiPF_6 dissolved in ethylene carbonate and diethyl carbonate mixed at 1:1 by volume (Ube Industries, Ltd.). Li metal was used as the counter electrode.

Note that the cell voltages of the solid-state cell are reported by adding the potential of the In–Li alloy (0.62 V vs. Li^+/Li) to the measured values in this paper to show the data as if lithium metal were used as the counter electrode. It must be also noted that electrochemical lithiation, or lithium insertion to Si, is expressed as charging in this paper, while discharging represents delithiation or lithium extraction, because this paper reports anode properties of Si.

3. Results and discussion

Fig. 2a shows a Raman spectrum of a sputtered Si film. The Raman modes at approximately 480 cm^{-1} and 300 cm^{-1} observed in the spectrum are typical signals for amorphous Si [15], indicating

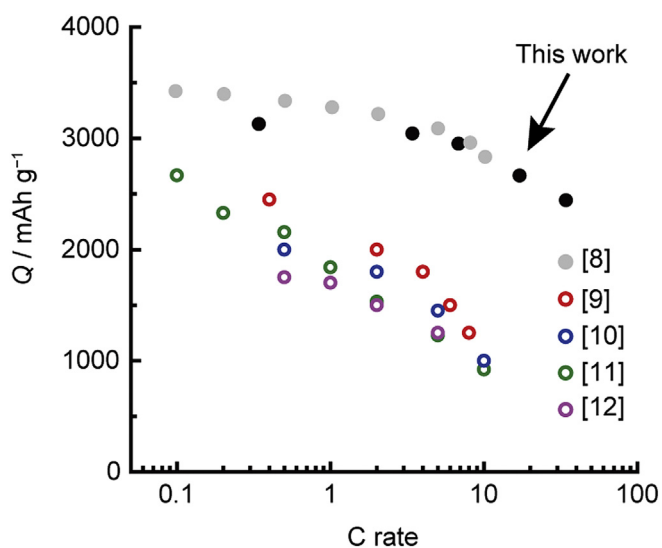


Fig. 1. Rate capability of Si films in the present and previous studies [8–12]. Observed discharge capacities (Q) are plotted against discharge C rates.

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