



Short communication

High-capacity thin film lithium batteries with sulfide solid electrolytes

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ABSTRACT

Thin film batteries with amorphous sulfide-based solid electrolytes were investigated. The interfacial resistance of the battery has been drastically reduced by inserting a very thin LiNbO_3 layer between the LiCoO_2 cathode and solid electrolyte. The cycle performance of the battery is affected by the composition of the $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ solid electrolyte. From XPS analysis, it is suggested that the electrochemical stability of the solid electrolyte changes as the composition of the solid electrolyte changes. Thin film batteries have shown both high capacity and good cycle performance with a solid electrolyte of suitable composition and silicon thin layer at the anode interface. Finally, a capacity of $400 \mu\text{Ah cm}^{-2}$ at 500 cycles has been achieved with a $9.1 \mu\text{m}$ -thick cathode.

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1. Introduction

Thin film lithium batteries are expected to be increasingly used as power sources of microdevices. Numerous studies have been done of thin film lithium batteries, especially using LiPON (lithium phosphorous oxynitride) film as the solid electrolyte [1–7]. LiPON has a wide electrochemical window and acceptable ionic conductivity of $2 \times 10^{-6} \text{ S cm}^{-1}$ at 25°C [8]. Meanwhile, few reports can be found about thin film batteries using a sulfide-based solid electrolyte [9,10] though they are widely used in bulk-type all-solid-state batteries (comprising electrolyte powders and electrode powders) because of its high ionic conductivity, as high as $10^{-3} \text{ S cm}^{-1}$ [11,12].

An amorphous $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ based solid electrolyte thin film was investigated in our laboratory. Since this sulfide solid electrolyte thin film has high ionic conductivity on the order of 10^{-4} – $10^{-5} \text{ S cm}^{-1}$, cell resistance and electrochemical performance of the thin film battery may be improved [13]. In this paper, we investigated thin film batteries using this sulfide solid electrolyte with a LiCoO_2 cathode/Li anode system.

LiCoO_2 cathodes have been widely used both in lithium-ion batteries and in all-solid-state batteries because LiCoO_2 has properties of high energy density, good cycle life, and easy preparation. In bulk-type solid lithium batteries using sulfide solid electrolytes, very high interfacial resistance of LiCoO_2 cathode/solid electrolyte

previously existed. Now such high interfacial resistance has been remarkably improved by inserting several types of nanometer oxide thin layers such as $\text{Li}_4\text{Ti}_5\text{O}_{12}$ or LiNbO_3 at the interface [14,15]. We have applied this structure to thin film batteries expecting reduced cell resistance.

Furthermore, we tried enhancing the capacity of the thin film battery by increasing the thickness of the LiCoO_2 cathode. The capacity of a thin film battery is mainly determined by the thickness of the cathodes in the lithium oxide cathode/Li anode system. However, the thickness of LiCoO_2 cathodes that have been reported is limited to about $6 \mu\text{m}$, resulting in the capacity of the thin film battery remaining at 250 – $280 \mu\text{Ah cm}^{-2}$ [6,7]. It has been reported that as cathode thickness increases, electrochemical performance of the thin film battery deteriorates, making it more difficult to fabricate the thin film battery. However, considering that these reports are generally based on LiPON film batteries, this tendency may not be equivalent to sulfide film batteries. The cathodes we examined had a maximum thickness of $9.1 \mu\text{m}$.

2. Experimental

Fig. 1 shows a schematic cross-sectional view of the thin film battery. All films except the lithium metal anode were deposited by pulsed laser deposition (PLD) at room temperature. A KrF excimer laser (248 nm) was focused onto a target with an incident angle of 45° at 10 Hz. The pulse energy was 400–1000 mJ. Thicknesses of films were measured using a surface profiler or cross-sectional SEM image. The compositions of the films were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES, iCAP6500 DUO, Thermo Fisher Scientific).

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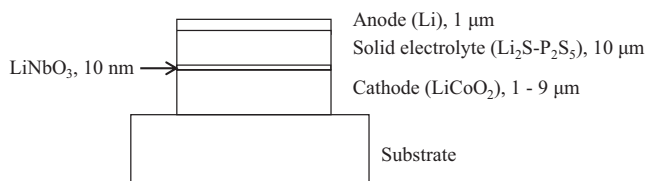


Fig. 1. Schematic cross-sectional view of the thin film battery.

First, LiCoO₂ cathode films were deposited on 0.5 mm-thick stainless steel substrates. A sintered LiCoO₂ pellet (Kojundo Chemical Laboratory Co., Ltd., 99%) was used as the target. The cathode thickness was then measured with the surface profiler. Cathode films were annealed after deposition at 500 °C for 1 h in air in order to crystallize. LiCoO₂ cathode films after annealing were identified by XRD (X'Pert PRO, PANalytical).

Thin films of 10 nm LiNbO₃ were deposited on the LiCoO₂ cathode films. A sintered LiNbO₃ pellet made from Li₂CO₃ powder (Kojundo Chemical Laboratory Co., Ltd., 99%) and Nb₂O₅ powder (Kojundo Chemical Laboratory Co., Ltd., 99.9%) was used as the target. LiNbO₃ films were then annealed at 400 °C for 30 min in air after deposition.

Subsequently, 10 μm-thick sulfide solid electrolytes were deposited. A pelletized mixture of Li₂S powder (Kishida Chem. Co., Ltd., 99.9%) and P₂S₅ powder (Aldrich Chemical Co. Inc., 99%) was used as the target without sintering. The atmosphere of the deposition chamber was 10⁻² Pa argon gas. XRD was used to characterize the crystallinity of the solid electrolyte thin film. Electrochemical impedance spectroscopy (EIS) was performed to measure the ionic conductivity at room temperature with blocking electrode cells at frequencies from 0.02 Hz to 100 kHz using an electrochemical analyzer (ALS model 6005C, BAS Inc.). The amplitude of the AC potential was 10 mV.

Some batteries have a 20 nm silicon thin film deposited on the solid electrolyte film in order to improve cycle performance of the batteries. A silicon wafer with 625 μm thickness (Yamanaka Semiconductor Co., Ltd.) was used as the target. Finally, 1 μm lithium anode films were deposited using thermal evaporation of lithium metal. The anode film area, or the electrode area, was 1.13 cm².

Battery performance was evaluated with a 2032-type coin cell fabricated in an argon-filled glove box. To adjust the thickness to the battery case, a 0.5 mm-thick lithium foil was stacked on the thin film battery in contact with the lithium film anode. Constant current charge–discharge measurements were performed between 3.0 V and 4.2 V using a BLS battery test system (Keisokuki Center Co., Ltd.).

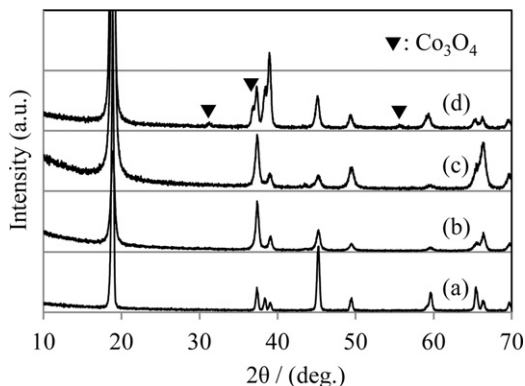


Fig. 2. XRD patterns of LiCoO₂ cathodes for several thicknesses and sintered PLD target: (a) target, (b) 0.9 μm, (c) 5.2 μm, and (d) 8.6 μm.

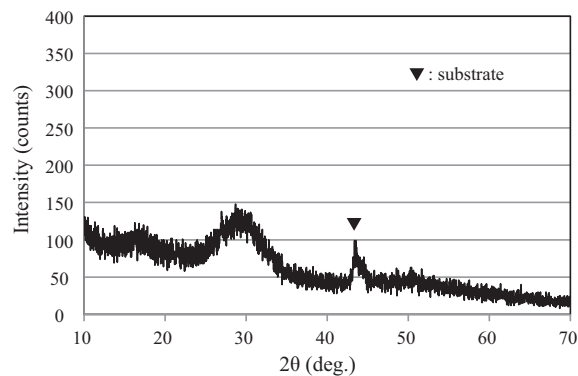


Fig. 3. XRD patterns of the solid electrolyte film on a stainless steel substrate.

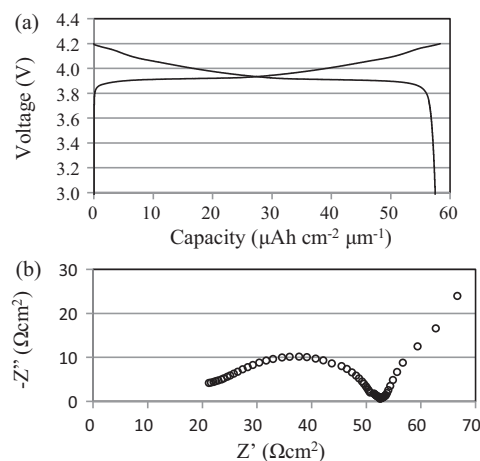


Fig. 4. (a) Charge/discharge curves of the thin film battery with 1 μm-thick cathode at a current density of 50 μA cm⁻². (b) AC impedance data at 3.95 V, the frequency range is 0.02 Hz to 100 kHz.

3. Results and discussion

Fig. 2 shows XRD patterns of the LiCoO₂ films after heat treatments. These patterns basically correspond to hexagonal LiCoO₂ phase and no apparent impurities were observed at thicknesses of 0.9 μm and 5.2 μm. Only with the 8.6 μm-thick LiCoO₂ film, additional slight peaks were observed. These are attributed to Co₃O₄ being generated. We deduce that the reason is that a lithium deficiency is generated in the target or the film during a long time deposition similarly as in the sputtering method [7].

Fig. 3 shows the XRD pattern of the Li₂S–P₂S₅ solid electrolyte film. The thickness of the film is about 10 μm. No apparent peaks

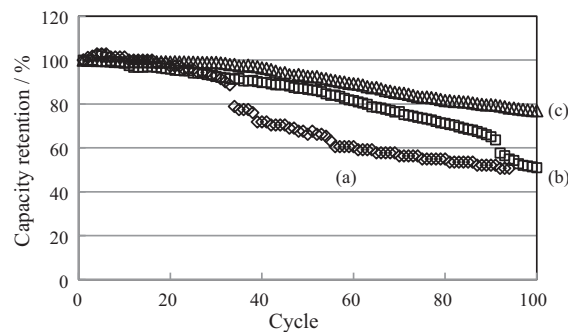


Fig. 5. Cycle performance of thin film batteries with cathode thickness of 1 μm for several compositions of the solid electrolyte at a current density of 100 μA cm⁻² between 3.0 V and 4.2 V. The atomic ratio of Li/(Li + P) is (a) 70%, (b) 75%, and (c) 82%.

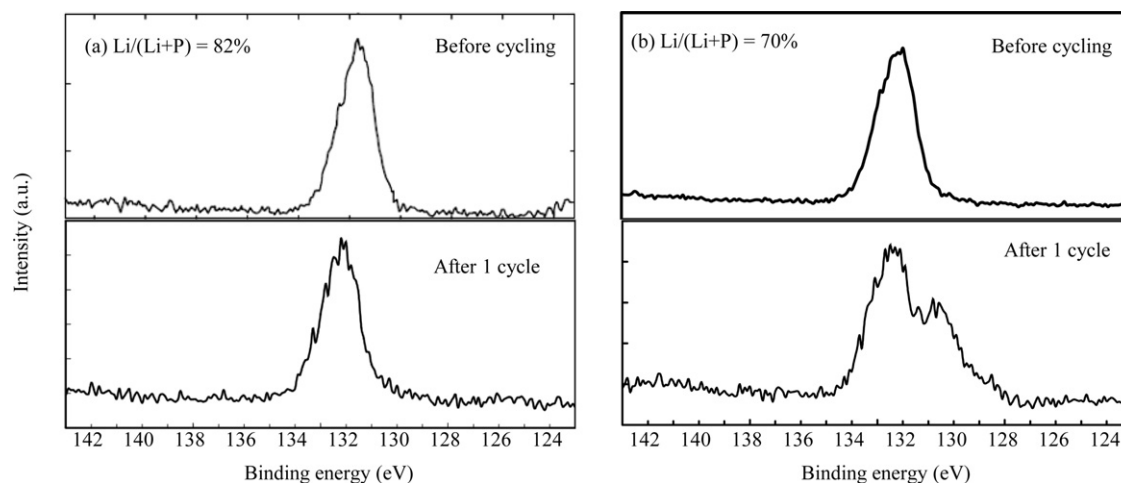


Fig. 6. P-2p XPS spectra of the solid electrolyte film on the anode side in thin film batteries before (upper) and after (lower) cycling. The atomic ratio of Li/(Li + P) in the solid electrolytes is (a) 82% and (b) 70%.

indicate that the solid electrolyte film is amorphous. The ionic conductivity of the solid electrolyte film is $4\text{--}8 \times 10^{-5} \text{ S cm}^{-1}$.

Remaining Figs. 4–8 show the electrochemical performance of the cell. Without the LiNbO_3 layer, cell resistance was over $3000 \Omega \text{ cm}^2$. Charge–discharge curves and AC impedance data of the cell with a 10 nm-thick LiNbO_3 interfacial layer are shown in Fig. 4. From the AC impedance data, cell resistance was only $70 \Omega \text{ cm}^2$, and the interfacial resistance was about $35 \Omega \text{ cm}^2$. This low value of $70 \Omega \text{ cm}^2$ is due to both bulk resistance, mainly contributed by the conductivity of the solid electrolyte, and low interfacial resistance. This is one of the advantages of sulfide thin film batteries.

Fig. 5 shows the cycle performance of batteries with several compositions of solid electrolyte, with atomic ratios of Li/(Li + P) of 70%, 75%, and 82%. Cycle performance improved as the atomic ratio of Li/(Li + P) increased. This suggests that some degradation in the solid electrolyte occurred, influenced by the composition. To investigate whether any changes occurred in the solid electrolyte during charging and discharging, XPS analysis (ESCA5400MC, ULVAC-PHI, Inc.) of the solid electrolyte was performed. Etching with Ar^+ from the anode side to the cathode side of the batteries, the XPS spectra of the solid electrolyte (Li-1s, P-2p, S-2p) was measured every 200 nm. As a result, a change was found before and after charge–discharge tests at the anode interface. Fig. 6 shows XPS P-2p spectra of solid electrolytes at the anode interface before and after charge–discharge tests. Besides a peak around 132.5 eV, which was observed in all data, another peak was observed at a lower energy of around 130.5 eV in the profile of P-rich (Li/(Li + P) = 70%) solid electrolyte after charge–discharge tests. This smaller peak suggests that

phosphorus in the solid electrolyte was electrochemically reduced. Meanwhile, no apparent differences were found in the XPS profile at the cathode side between the before and after charge–discharge tests. Considering the above results, it was presumed that cycle performance was affected by the electrochemical stability of the solid electrolyte, which corresponded to the composition of the solid electrolyte. Lithium being consumed by electrochemical reduction of the solid electrolyte is thought to be the reason for the deteriorating cycle performance.

Lithium metal has extremely strong reducing power. One method of suppressing the reducing power is by alloying lithium with another material. However, full alloying would induce a large volume change of the anode during charging and discharging, resulting in poor cycle performance. To alloy only the interface region of the solid electrolyte, a thin film of several materials that can be alloyed with lithium, such as Al, Si or Sn, was inserted between the anode and the solid electrolyte. Among these materials, Si was most effective in improving the cycle performance in our case. Fig. 7 shows the cycle performance of the $1 \mu\text{m}$ -thick cathode cell with and without a 20 nm Si layer between the solid electrolyte and Li metal anode. The cycle performance clearly improved with the Si layer. We believe that the Si layer reduced the reduction power of the lithium directly or kinetically. Though the reasons why Si gives better results than Al or Sn have not been clarified yet, reactivity with the solid electrolyte or the difference in the magnitude of the volume change might have some effect. Another reason might not be essential: Because we were not able to perform

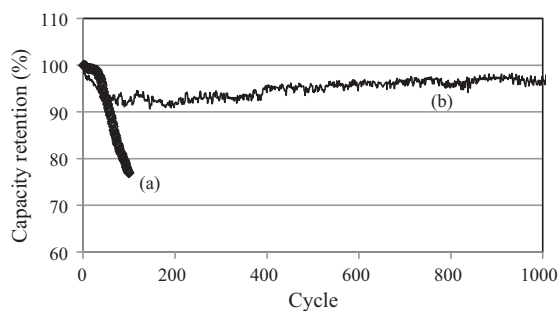


Fig. 7. Cycle performance of the thin film battery for $1 \mu\text{m}$ -thick cathode at a current density of $100 \mu\text{A cm}^{-2}$ between 3.0 V and 4.2 V (a) without Si thin layer, and (b) with a 20 nm Si layer between the solid electrolyte and Li metal anode.

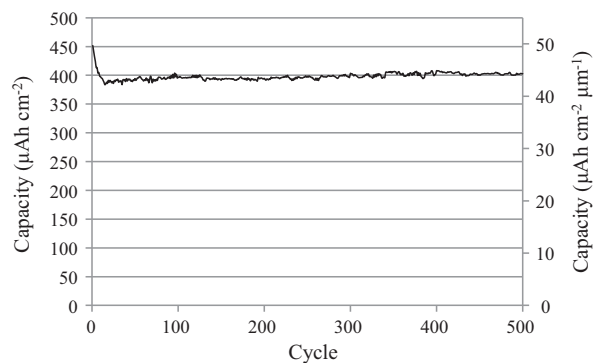


Fig. 8. Cycle performance of the thin film battery with $9.1 \mu\text{m}$ cathode at a current density of $100 \mu\text{A cm}^{-2}$. A 20 nm Si thin layer was inserted between the solid electrolyte and Li metal anode.

sufficient experiments, each deposition condition perhaps had not been optimized. So Si may fortunately bring the good results, or the battery may have been damaged during other deposition.

Fig. 8 shows the cycle performance of the 9.1 μm -thick cathode cell with a Si layer. Although the capacity decreases slightly in the early cycles, capacity degradation soon disappears and capacity retention stays at 80% at 500 cycles. Although the capacity of the cell is considerably lower than its theoretical value of $69 \mu\text{Ah cm}^{-2} \mu\text{m}^{-1}$, $400 \mu\text{Ah cm}^{-2}$ at 500 cycles is the highest value we have encountered in 4 V-class thin film batteries.

4. Conclusions

In this paper, a thin film battery with high capacity and good cycle performance was achieved. The interfacial resistance of the battery was drastically reduced by inserting a very thin LiNbO_3 layer between the LiCoO_2 cathode and sulfide solid electrolyte, similarly as in bulk-type sulfide solid-state batteries. Excellent cell resistance below $100 \Omega \text{cm}^2$ was observed, attributable to high ionic conductivity of the sulfide solid electrolyte and interfacial modification of the cathode.

Cycle performance of the battery was improved by adjusting the solid electrolytes and inserting a silicon thin layer between the lithium anode and solid electrolyte. Though the reasons for this are being investigated, we believe that the electrochemical stability of the solid electrolyte is very important for the battery's cycle

performance. Another reason could be that the sulfide solid electrolyte was able to match the volume change of the cathode or anode during charge–discharge cycling because it is a relatively soft material.

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