Preparation of an Amorphous $80\text{LiCoO}_2\cdot 20\text{Li}_2\text{SO}_4$ Thin Film Electrode by Pulsed Laser Deposition

Masaki NISHIMURA, Kenji NAGAO, Yusuke ITO, Minako DEGUCHI, Atsushi SAKUDA, Akitoshi HAYASHI,* and Masahiro TATSUMISAGO*

Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University, 1-1 Gakuen-cho, Naka-ku, Sakai, Osaka 599-8531, Japan

*Corresponding authors: hayashi@chem.osakafu-u.ac.jp, tatsu@chem.osakafu-u.ac.jp

ABSTRACT

An amorphous $80\text{LiCoO}_2\cdot 20\text{Li}_2\text{SO}_4$ (mol%; $\text{Li}_{1.2}\text{Co}_{0.8}\text{S}_{0.2}\text{O}_{2.4}$) thin film electrode is prepared by pulsed laser deposition (PLD). Although the $\text{Li}_{1.2}\text{Co}_{0.8}\text{S}_{0.2}\text{O}_{2.4}$ electrode material has been synthesized via mechanochemistry and includes a cubic LiCoO_2 crystalline phase, amorphous $\text{Li}_{1.2}\text{Co}_{0.8}\text{S}_{0.2}\text{O}_{2.4}$ (without the cubic phase active material) is successfully obtained using the PLD method. The atomic ratio of Li/Co in the obtained film as determined by ICP-AES is identical to that of the milled powder. X-ray photoelectron spectroscopy reveals that the thin film mainly contains Co^{3+} and SO_4^{2-} . The amorphous $\text{Li}_{1.2}\text{Co}_{0.8}\text{S}_{0.2}\text{O}_{2.4}$ thin film electrode is directly deposited on the $90\text{Li}_3\text{BO}_3\cdot 10\text{Li}_2\text{SO}_4$ (mol%) oxide electrolyte to form closely-attached electrode-electrolyte interface. The fabricated all-solid-state cells shows a higher discharge capacity than the cell fabricated using the electrode derived from the mechanochemically prepared $\text{Li}_{1.2}\text{Co}_{0.8}\text{S}_{0.2}\text{O}_{2.4}$, which partially includes electrochemically-inactive cubic LiCoO_2 nanoparticles. It is noted that complete amorphization of $\text{Li}_{1.2}\text{Co}_{0.8}\text{S}_{0.2}\text{O}_{2.4}$ is effective in increasing reversible capacities.

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Keywords : Pulsed Laser Deposition, Amorphous Thin Film, Positive Electrode Active Material, All-solid-state Battery

1. Introduction

Lithium ion batteries (LIBs) are widely used as a power source for various portable electronic devices. Improvements in the energy density of LIBs are required for their application in large-scale energy storage devices. The development of positive electrode active materials with a high capacity is key to enhancing energy density. Layered LiCoO_2 has been commonly used as a positive electrode active material in LIBs. However, the amount of lithium ions extracted during the charging process must be limited to maintain the layered structure, making it challenging to achieve a high capacity in conventional LIBs.^{1,2}

Amorphous materials have open and random structures, and it is possible to achieve higher capacities and a better cycle performance compared to crystalline electrodes.^{3,4} Recently, we reported the mechanochemical synthesis of amorphous $\text{LiCoO}_2\text{-Li}_2\text{SO}_4$ positive electrode active materials. The obtained $80\text{LiCoO}_2\cdot 20\text{Li}_2\text{SO}_4$ (mol%; $\text{Li}_{1.2}\text{Co}_{0.8}\text{S}_{0.2}\text{O}_{2.4}$) is a nanocomposite material with cubic LiCoO_2 nanocrystals embedded in the $\text{LiCoO}_2\text{-Li}_2\text{SO}_4$ amorphous matrix.⁵ Although Dahn et al. reported that cubic LiCoO_2 was electrochemically inactive,⁶ the all-solid-state cell fabricated using the $\text{Li}_{1.2}\text{Co}_{0.8}\text{S}_{0.2}\text{O}_{2.4}$ electrode showed a relatively high capacity of 163 mAh g^{-1} . The $\text{LiCoO}_2\text{-Li}_2\text{SO}_4$ amorphous matrix mainly functioned as an active material. Thus, it is expected that the capacity of the $\text{LiCoO}_2\text{-Li}_2\text{SO}_4$ active material could be improved by complete amorphization. However, it is difficult to prepare fully amorphous $\text{Li}_{1.2}\text{Co}_{0.8}\text{S}_{0.2}\text{O}_{2.4}$ via mechanochemistry. An alternative technique for amorphization of $\text{Li}_{1.2}\text{Co}_{0.8}\text{S}_{0.2}\text{O}_{2.4}$ is vapor phase preparation. In a previous study, we prepared amorphous solid electrolyte thin films using $\text{Li}_2\text{S-P}_2\text{S}_5$,⁷ $\text{Li}_2\text{S-GeS}_2$,⁸ and $\text{Li}_2\text{S-GeS}_2\text{-P}_2\text{S}_5$ ⁹ as well as amorphous transition metal sulfide electrode thin films such as TiS_x ^{10,11} by pulsed laser deposition (PLD). This technique can be used to prepare thin films by depositing plume species ablated from a target upon the irradiation of a high energy

pulsed laser. This technique allows for the preparation of thin films of high quality and density. The PLD method has also been used for the preparation of various crystalline electrode thin films using LiCoO_2 ,¹² LiMn_2O_4 ,^{12,13} and LiFePO_4 ¹⁴ which are used in LIBs. The properties of the crystalline thin films can be tuned by controlling the deposition temperature and post-annealing conditions.

In this study, a fully amorphous $\text{Li}_{1.2}\text{Co}_{0.8}\text{S}_{0.2}\text{O}_{2.4}$ thin film electrode is prepared by PLD, and its morphology, structure, and chemical composition are evaluated for the prepared film. Moreover, the amorphous $\text{Li}_{1.2}\text{Co}_{0.8}\text{S}_{0.2}\text{O}_{2.4}$ thin film electrode is directly deposited on a pelletized oxide electrolyte, and the electrochemical properties of the electrode are evaluated in all-solid-state cells.

2. Experimental

2.1 Preparation of the target for PLD

The chemicals LiCoO_2 (>99%, Nippon Chemical Industrial Co., Ltd.), $\text{Li}_2\text{SO}_4\cdot\text{H}_2\text{O}$ (99.9%, Wako Pure Chemical Industrial Co., Ltd.), and Li_2O (99.9%, Furuuchi Chemical Co., Ltd.) were used as the starting materials without further purification. First, the Li_2SO_4 crystal was obtained by the heat treatment of $\text{Li}_2\text{SO}_4\cdot\text{H}_2\text{O}$ at 300°C for 3 h under an Ar atmosphere. The target material at a nominal composition of $68.7\text{LiCoO}_2\cdot 17.2\text{Li}_2\text{SO}_4\cdot 14.1\text{Li}_2\text{O}$ (mol%; $\text{Li}_{1.5}\text{Co}_{0.8}\text{S}_{0.2}\text{O}_{2.6}$) was mechanochemically prepared. The target with a 25% lithium excess compared with that of $\text{Li}_{1.2}\text{Co}_{0.8}\text{S}_{0.2}\text{O}_{2.4}$ was used to compensate for lithium loss during the PLD process. A mixture of LiCoO_2 , Li_2SO_4 , and Li_2O was placed in a 45 mL zirconia pot with 160 balls (5 mm in diameter), and milled at 370 rpm for 50 h. The milled powder was pressed into a pellet (20 mm in diameter) at room temperature. All the processes were conducted under a dry Ar atmosphere.

2.2 Preparation of the thin film electrode

The thin film electrode was prepared by PLD with a KrF excimer

laser ($\lambda = 248$ nm, LPXPro, Lambda Physik). The laser energy was 300 mJ/pulse with a repeating frequency of 5 Hz. The deposition was performed under an O_2 atmosphere under a pressure of 1 Pa. The distance between the target and substrate was 7 cm. The thin film was deposited at 200°C on a Si substrate and a $90Li_3BO_3 \cdot 10Li_2SO_4$ (mol%) electrolyte pellet.^{15,16} The substrate temperature was chosen for improving characteristics of electrode-electrolyte interfaces based on a previous report.¹⁷ To avoid exposure of the deposited film to the atmosphere, a PLD vacuum chamber connected to an Ar-filled glove box was used.

2.3 Characterization

The morphology and thickness of the thin film were observed using field emission scanning electron microscopy (FE-SEM, SU8220; Hitachi High-Technologies Corp.). X-ray diffraction (XRD) measurements were performed using a diffractometer (SmartLab; Rigaku Corp.). The atomic ratio of Li/Co in the thin film was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES; SPS7800; Seiko Instruments). The structural units in the prepared film were investigated by X-ray photoelectron spectroscopy (XPS, K-Alpha; Thermo Fisher Scientific Inc.). The binding energies were calibrated with the adventitious C_{1s} peak at 284.7 eV. The sample was mounted on a sample stage in a dry Ar filled glove box. It was then transferred to an analysis chamber using an Ar filled transfer vessel.

The electrochemical properties of the prepared thin film electrode were evaluated by charge-discharge tests for the all-solid-state cells (Cu/Li-In/ $90Li_3BO_3 \cdot 10Li_2SO_4$ glass-ceramic/ $Li_{1.2}Co_{0.8}S_{0.2}O_{2.4}$ thin film electrode/Au). The $Li_{1.2}Co_{0.8}S_{0.2}O_{2.4}$ thin film prepared by PLD was used as a positive electrode and the $90Li_3BO_3 \cdot 10Li_2SO_4$ (mol%) glass-ceramic electrolyte^{15,16} was the separator. The thin film electrode was directly deposited on the $90Li_3BO_3 \cdot 10Li_2SO_4$ glass-ceramic pellet by PLD. Foils of indium (99.999%; 0.3 mm thickness; Furuuchi Chemical Corp.) and lithium (99.99%; 0.25 mm thickness; Furuuchi Chemical Corp.) were used to create a Li-In alloy negative electrode. A Cu foil was used as a negative electrode current collector and the indium, lithium, and copper foils were attached to the pellet and pressed at 120 MPa for 2 min. Au film as a positive electrode current collector was then deposited onto the $Li_{1.2}Co_{0.8}S_{0.2}O_{2.4}$ thin film electrode by vacuum evaporation. The charge-discharge tests for the all-solid-state cells were conducted at 100°C using a measuring device (Celltest system (1470E); Solartron Analytical). The loading weight of the thin film was approximately 0.1 mg cm^{-2} . The weight of the thin film electrode was calculated from the density of the $Li_{1.2}Co_{0.8}S_{0.2}O_{2.4}$ powder (3.958 g cm^{-3}), and the thickness of the thin film was determined from SEM. The density of the $Li_{1.2}Co_{0.8}S_{0.2}O_{2.4}$ powder was determined using a gas pycnometer (AccuPyc II 1340, Shimadzu).

3. Results and Discussion

A cross-sectional SEM image of the thin film deposited on a Si substrate by PLD is shown in Fig. 1. This SEM image indicates that a dense film without pores and cracks is obtained with a thickness of approximately 150 nm. Moreover, the thin film is attached firmly to a Si substrate. We also confirmed that the film deposited on the surface of the $90Li_3BO_3 \cdot 10Li_2SO_4$ (mol%) electrolyte pellet was relatively uniform.

The XRD patterns of the thin film and milled powder are shown in Fig. 2. Although the diffraction peak at approximately $2\theta = 45^\circ$ attributable to cubic $LiCoO_2$ is observed for the milled $Li_{1.2}Co_{0.8}S_{0.2}O_{2.4}$ powder,⁵ no diffraction peaks are observed for the thin film. These results indicate that the fully amorphous material is successfully obtained from the PLD method.

The atomic ratio of Li/Co in the amorphous thin film was determined by ICP-AES. The Li/Co ratio in the prepared film was

Figure 1. Cross-sectional SEM image of the $Li_{1.2}Co_{0.8}S_{0.2}O_{2.4}$ thin film prepared on a Si substrate by PLD.

Figure 2. XRD patterns of the $Li_{1.2}Co_{0.8}S_{0.2}O_{2.4}$ thin film prepared by PLD and the milled powder.

1.2 when the thin film was prepared using the stoichiometric $Li_{1.2}Co_{0.8}S_{0.2}O_{2.4}$ as a target. This indicates that lithium loss occurred during the deposition process. The Li/Co ratio of 1.5, which is consistent with the nominal composition of $Li_{1.2}Co_{0.8}S_{0.2}O_{2.4}$, was obtained using $Li_{1.5}Co_{0.8}S_{0.2}O_{2.6}$ as a target with a 25% lithium excess.

The XPS spectra of the film and milled powder are shown in Fig. 3. In the Co 2p spectrum of the thin film, the main peaks corresponding to Co 2p_{3/2} at 780 eV and a satellite peak at approximately 790 eV were observed; a main peak for Co 2p_{1/2} at 795 eV with a satellite peak at approximately 805 eV were also detected. In particular, the satellite peaks at 790 and 805 eV are characteristic of Co^{3+} .¹⁸ Thus, these satellite peaks indicate that the cobalt ions in the prepared film are mainly in the trivalent state. In the S 2p spectra of the amorphous thin film, the doublet peaks of S 2p_{3/2} and S 2p_{1/2} appear at approximately 168.5 and 169.7 eV respectively, and can be assigned to the SO_4^{2-} unit;¹⁹ these peaks are also detected in the case of the milled powder. In addition, doublet peaks at approximately 166.5 and 167.7 eV attributable to the SO_3^{2-} unit²⁰ are observed with a low intensity. These peaks are not observed in the milled powder, suggesting that the prepared thin film contained small amounts of SO_3^{2-} ions. The SO_3^{2-} ions are partially formed by the reduction of the SO_4^{2-} ions during PLD process.

Figure 4 shows that the initial charge-discharge curves of the all-solid-state cell fabricated with the amorphous $Li_{1.2}Co_{0.8}S_{0.2}O_{2.4}$ thin film as a positive electrode. The initial charge-discharge curves of the cell using the powder-compressed electrode with milled $Li_{1.2}Co_{0.8}S_{0.2}O_{2.4}$ ⁵ are also shown for comparison; the milled $Li_{1.2}Co_{0.8}S_{0.2}O_{2.4}$ powders deform plastically by a simple cold-pressing and a

Figure 3. XPS spectra of the $\text{Li}_{1.2}\text{Co}_{0.8}\text{S}_{0.2}\text{O}_{2.4}$ thin film prepared by PLD and the milled powder: (a) Co 2p spectra, (b) S 2p spectra.

Figure 4. Initial charge-discharge curves of the all-solid-state cells (Cu/Li-In/ $90\text{Li}_3\text{BO}_3 \cdot 10\text{Li}_2\text{SO}_4$ glass-ceramic/ $\text{Li}_{1.2}\text{Co}_{0.8}\text{S}_{0.2}\text{O}_{2.4}$ /Au) at 0.013 and 0.13 mA cm^{-2} . A $\text{Li}_{1.2}\text{Co}_{0.8}\text{S}_{0.2}\text{O}_{2.4}$ thin film or powder-compressed electrode was used in the cell.

dense electrode layer is formed. The loading amount of the milled $\text{Li}_{1.2}\text{Co}_{0.8}\text{S}_{0.2}\text{O}_{2.4}$ powders was 38 mg cm^{-2} for the powder-compressed electrode with the thickness of ca. $150 \mu\text{m}$. The cells operated in the cut-off voltage of 1.0–4.0 V vs. Li-In (1.6–4.6 V vs. Li^+/Li) at a current density of 0.013 and 0.13 mA cm^{-2} at 100°C . The cell using the thin film electrode exhibits initial charge and discharge capacities of 321 mAh g^{-1} and 304 mAh g^{-1} at the current density of 0.013 mA cm^{-2} . Moreover, the initial reversible capacity of the cell with the thin film electrode at 0.13 mA cm^{-2} is 240 mAh g^{-1} , which is higher than the capacity of the cell with the powder-compressed electrode.⁵ Figure 5 shows the cycle performance of the cell with the thin film electrode operating at a current density of 0.13 mA cm^{-2} .

The initial charge capacity of the $\text{Li}_{1.2}\text{Co}_{0.8}\text{S}_{0.2}\text{O}_{2.4}$ (321 mAh g^{-1}) is higher than the theoretical capacity of the $\text{Co}^{3+}/\text{Co}^{4+}$ charge compensation (213 mAh g^{-1}). Therefore, there is another redox species in addition to the Co ions in the $\text{Li}_{1.2}\text{Co}_{0.8}\text{S}_{0.2}\text{O}_{2.4}$ thin film electrode. A possible redox species that could account for this additional capacity is oxygen, as is often observed in lithium-excess positive electrode active materials.^{21–25} Capacity fading is observed in the cycle tests involving a cell with the

Figure 5. Cycle performance of the all-solid-state cell (Cu/Li-In/ $90\text{Li}_3\text{BO}_3 \cdot 10\text{Li}_2\text{SO}_4$ glass-ceramic/ $\text{Li}_{1.2}\text{Co}_{0.8}\text{S}_{0.2}\text{O}_{2.4}$ thin film/Au) at 0.13 mA cm^{-2} .

powder-compressed electrode. It is likely that the degradation during cycling is caused by structural changes due to oxygen elimination or the formation of a resistive interfacial layer between the electrode and electrolyte.⁵ A detailed reaction mechanism has not yet been elucidated, and further structural analysis is necessary to understand the redox mechanism.

4. Conclusion

An amorphous $\text{Li}_{1.2}\text{Co}_{0.8}\text{S}_{0.2}\text{O}_{2.4}$ thin film electrode was prepared by PLD. Cross-sectional SEM images showed that the prepared film was dense without any pores or cracks. X-ray diffraction investigations revealed that the $\text{Li}_{1.2}\text{Co}_{0.8}\text{S}_{0.2}\text{O}_{2.4}$ active material prepared by PLD exhibited a halo pattern, while the active material prepared via mechanochemistry contained cubic LiCoO_2 crystals. The Li/Co atomic ratio of the thin film was the same as that of the milled powder, as determined by ICP-AES. The main structural units of the thin film, as determined by Co 2p and S 2p XPS, were the Co^{3+} and SO_4^{2-} ions. The reversible capacity of amorphous $\text{Li}_{1.2}\text{Co}_{0.8}\text{S}_{0.2}\text{O}_{2.4}$ thin films in the all-solid-state cells at 0.13 mA cm^{-2} was 240 mAh g^{-1} , which was higher than that of the mechanochemically prepared $\text{Li}_{1.2}\text{Co}_{0.8}\text{S}_{0.2}\text{O}_{2.4}$ containing cubic LiCoO_2 . It is clear that amorphous $\text{Li}_{1.2}\text{Co}_{0.8}\text{S}_{0.2}\text{O}_{2.4}$ functioned as an active material in the cell.

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