Development of Li Metal Anode with Modified Layer for All-Solid-State Batteries using Vacuum Deposition Process*

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All-solid-state batteries (ASSB) are composed entirely of solid materials and have an extremely low risk of ignition and better safety than conventional lithium-ion batteries.

In addition, all-solid-state lithium metal batteries, which use lithium metal as the anode material, are attracting attention as batteries that can achieve an energy density that surpasses that of conventional lithium-ion batteries.

In this study, a Li metal anode made by a vacuum deposition process to have a modified layer for a sulfide-based all-solid-state electrolyte was evaluated. Mg was selected for the modified layer, and the results show that a great ASSB performance was successfully achieved.

1. Introduction

In recent years, environmental issues have spurred various countries around the globe to implement policies aimed at promoting a shift from gasoline vehicles to electric vehicles. Batteries are one technology attracting attention from such initiatives. Lithium-ion batteries in particular are attracting attention due to their being compact, lightweight and having higher energy density than conventional batteries. However, the use of organic solvents as electrolyte materials has given rise to concerns about leakage, safety and reliability. Here is where all-solid-state batteries are expected to make a difference. Because all-solid-state batteries—including their electrolyte materials—are composed entirely of solid materials, they eliminate the above-mentioned issues and carry an extremely low risk of ignition. Furthermore, all-solid-state Li metal batteries that use lithium metal as the anode material are attracting attention for achieving higher energy densities than conventional lithium-ion batteries.

The authors have long been engaged in research and development of Li metal anodes using a vacuum deposition process. In this manuscript, they present their findings on Li metal anodes with modified layers for application in all-solid-state batteries that use sulfide solid electrolyte and that are attracting attention as next-generation batteries.

2. Li metal anode prepared using a vacuum deposition process

Here, we examine the characteristics of Li metal anodes prepared using a vacuum deposition process, along with the advantages of this manufacturing method over those using conventional anode materials.

2.1 Features[1]

A basic model of the vacuum deposition process is shown in Fig. 1. This manufacturing method is characterized by the ability to deposit thin films with excellent surface smoothness under high vacuum. It also enables the formation of high-purity films by controlling pressure and temperature on the basis of the unique vapor pressure curve of each material.

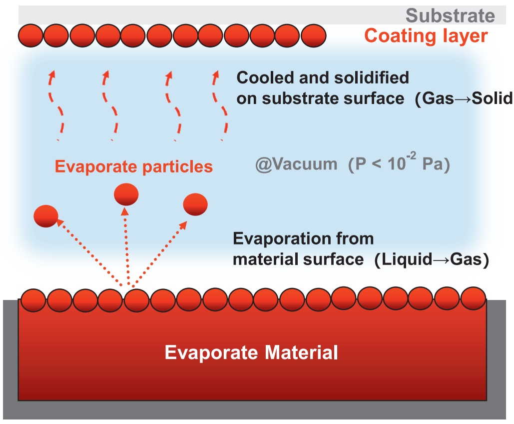

Fig. 1 Basic model of vacuum evaporation

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2.2 Advantages of this manufacturing method (differences between wet and dry coating)

Multiple processes are typically required to manufacture conventional lithium-ion battery electrode materials, including mixing and kneading active materials (such as graphite or silicon) with conductive additives and binders in an organic solvent (e.g., N-methyl-2-pyrrolidone), coating the mixture onto a current collector, drying to remove the solvent, and roll pressing to improve adhesion. Performing this many processes generally requires a wide range of manufacturing equipment. However, the vacuum deposition process can consolidate these steps into a single process (deposition), offering a possible advantage in terms of electrode formation. In particular, because an organic solvent drying process is no longer needed, we expect CO_2 emissions from manufacturing will be reduced, resulting in a lower environmental impact.

3. Preparation and characterization of Li metal anode

In this study, Li metal anodes were manufactured using a vacuum evaporation - sputtering composite system (Model: LX-200ES). A photograph of the system is shown in Fig. 2. This system features a load-lock chamber that enables multilayer film deposition in a continuous vacuum and supports deposition on substrates up to 200 mm square.

3.1 Preparation

Stainless steel foil (10 μm) was used as the substrate for the current collector. Prepared samples included both single-layer and multilayer Li films. In both cases, the Li film was deposited to 5 μm, Mg was selected for the modified layer, and the thickness was set to 50 nm, 200 nm, or 600 nm. In addition, deposition was carried out under a continuous vacuum, with Mg (deposited first by sputtering) being followed by Li (deposited by vacuum evaporation). As an example, a photograph showing the appearance of the single-layer Li film is shown in Fig. 3.

Fig. 2 Appearance of LX-200ES

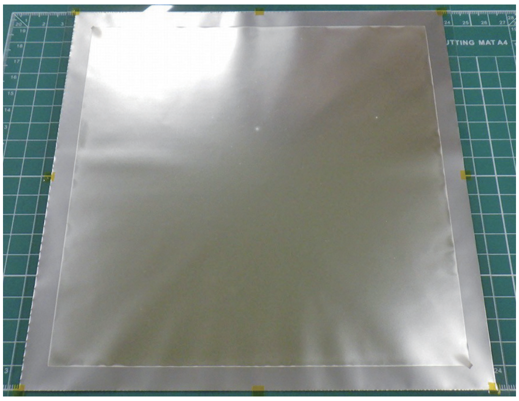

Fig. 3 Appearance of Li thin film (on SUS foil)

3.2 Thin film characterization

The thin film characterization was conducted via surface and cross-section observation. Processing for cross-section observation was performed using an IM4000II ion milling system (Hitachi High-Tech), which is equipped with a cooling mechanism and installed in a dry room. Microstructure observation of both the surface and cross-section was then conducted using an SU8220 field emission scanning electron microscope (also by Hitachi High-Tech), followed by elemental analysis of the cross-section.

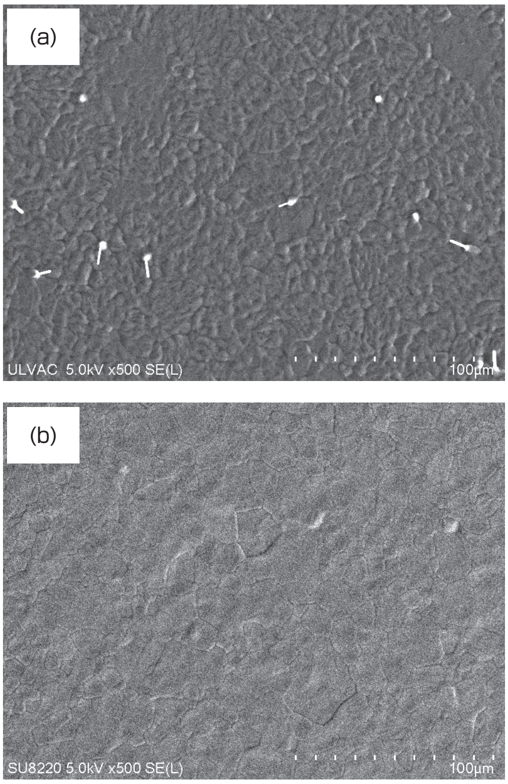

Fig. 4 Surface morphology of Li thin film
(a) Li 5 μm, (b) Li 5 μm/Mg 200 nm

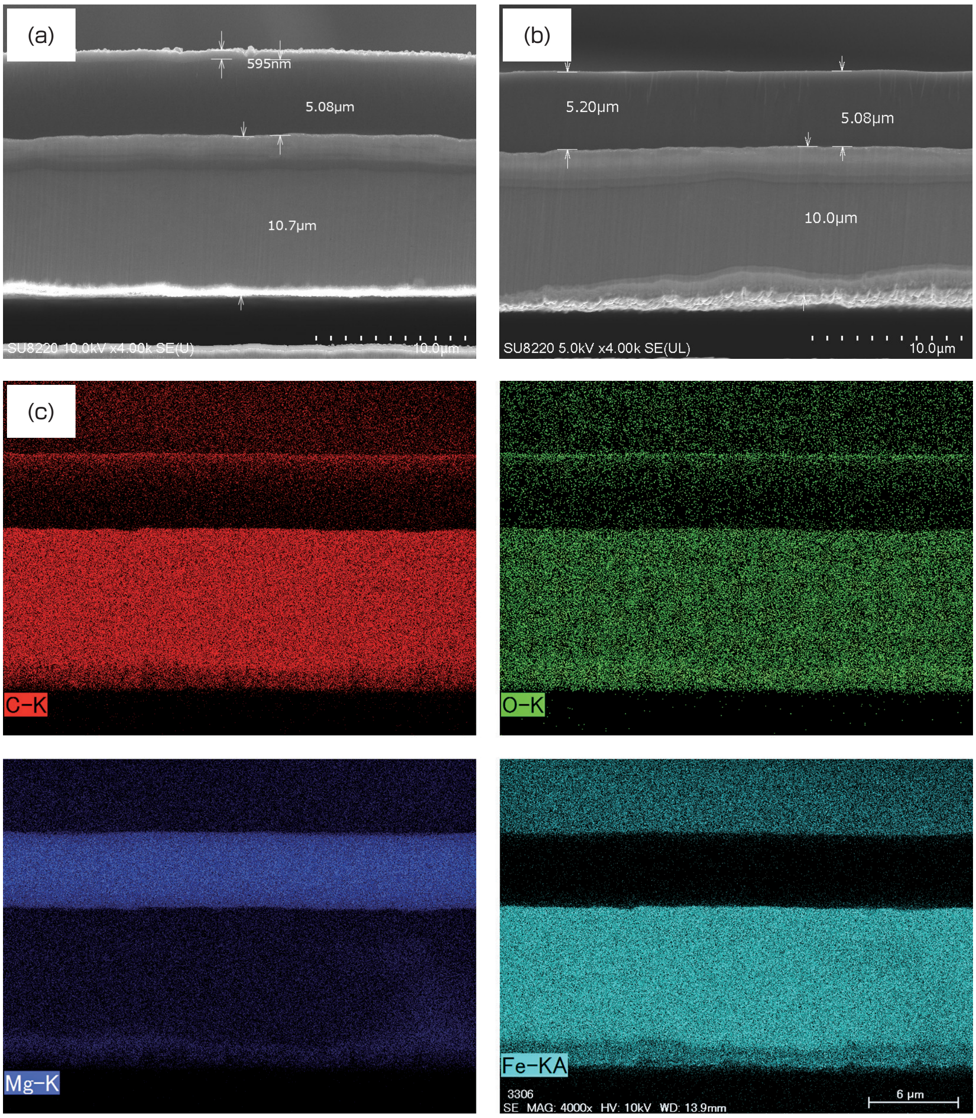

Fig. 5 Cross-section morphology of Li thin film
(a) Li 5 *μm*, (b) Li 5 *μm*/Mg 200 nm, (c) Elemental mapping images (C, O, Mg, Fe) ※Li 5 *μm*/Mg 200 nm

Observation results for the surface are shown in Fig. 4, and those for the cross-sections of the single-layer and multilayer Li films (with only the 200 nm Mg layer) are shown in Fig. 5.

As for the surface microstructure, it is observed in light of Fig. 4 that the Li multilayer film with an Mg underlayer had larger particle sizes than the single-layer Li film. This is presumed to be due to wettability with the substrate during Li deposition. Furthermore, for the cross-sectional microstructure, it is observed in light of Fig. 5 that the target film thickness of approximately 5 μm was achieved, and that Mg was uniformly diffused throughout the entire Li layer of the Li multilayer film. These results clearly show that Li-Mg alloys can be formed uniformly by performing lamination deposition in a consistent vacuum without any special treatment.

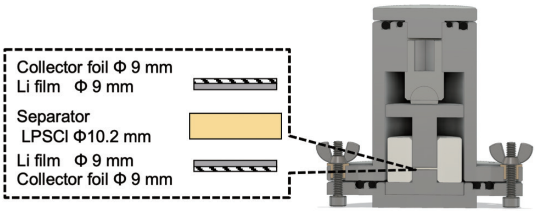

Fig. 6 Schematic diagram of all-solid-state battery

3.3 All-solid-state battery characterization

A schematic diagram of the all-solid-state battery characterization is shown in Fig. 6. In this study, a dedicated jig was used to assemble a symmetric cell using thin film as the working electrode, a piece of 100 *μm* rolled Li foil as the counter

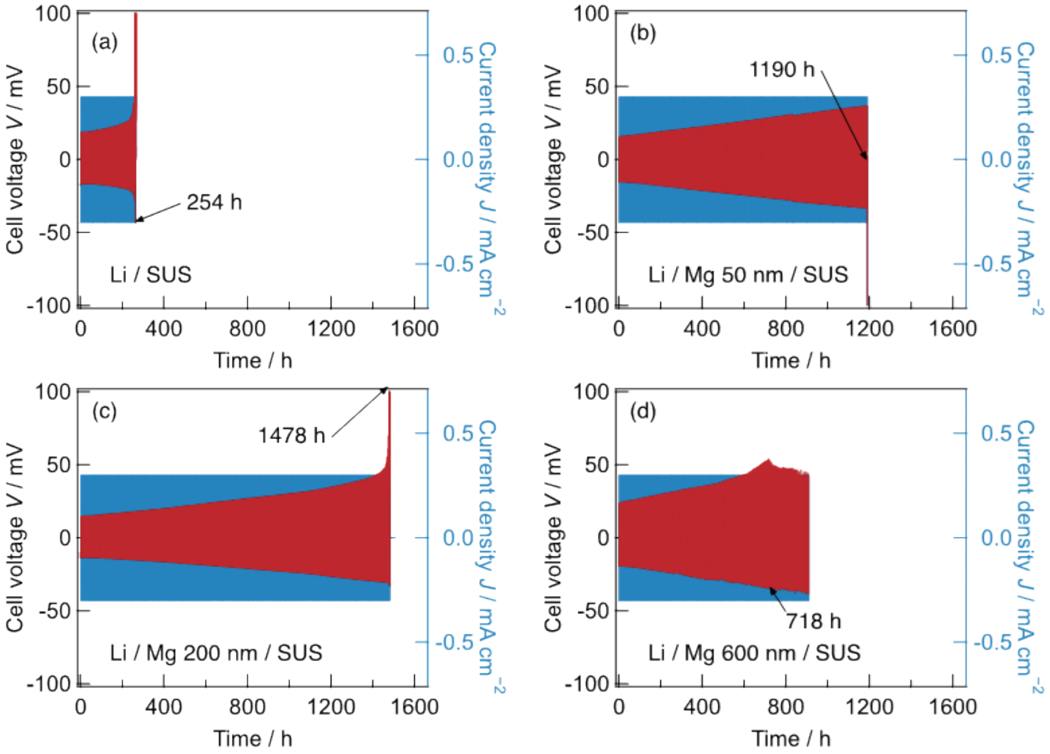

Fig. 7 Charge-discharge curves of symmetric cell
(a) Li 5 μm, (b) Li 5 μm/Mg 50 nm, (c) Li 5 μm/Mg 200 nm, (d) Li 5 μm/Mg 600 nm

electrode, and Li$_6$PS$_5$Cl (LPSCl) with an argyrodite-type structure as the solid electrolyte layer.

In terms of electrochemical characteristics, constant current charge–discharge testing was carried out at a current density of 0.3 mA/cm^2 and a cut-off capacity of 0.3 mAh/cm^2 using the VMP-300 high-performance electrochemical measurement system (BioLogic). Here, “durability” was defined as the time until either the upper or lower voltage limit of ±100 mV was reached, or until an internal short circuit occurred, resulting in an irreversible drop in operating voltage.

The results of the constant current charge-discharge testing are shown in Fig. 7(a) to (d), and the dependence of durability on Mg film thickness is shown in Fig. 8. While the durability of the single-layer Li film was 254 h, multilayering with Mg significantly improved lifespan, with the best performance (1,478 h) being observed around 200 nm.

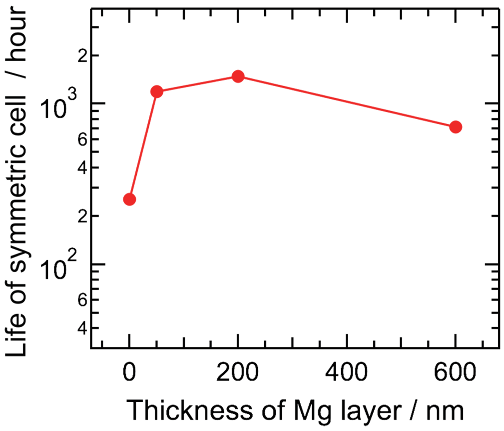

Fig. 8 Mg film thickness dependence in symmetric cell life

4. Discussion and future outlook

As described in the previous section, good battery performance was successfully achieved with Mg selected as the modified layer. One possible reason for this is that Li-Mg alloying suppresses the dendrite growth of Li deposited during charging by improving mechanical strength2) and wettability3). However, a specific mechanism has yet to be identified. As for the degradation mechanisms of all-solid-state batteries, various factors have been proposed, including dendrite growth, poor contact with solid electrolyte in void formation4) and volume changes due to Li deposition and dissolution5).

We consider uncovering the above mechanisms to be an important guideline for realizing thinner Li metal anodes with a longer service life in the future and plan on conducting instrumental analysis.

5. Summary

In this manuscript, we explained the effects and advantages of introducing a modified layer to Li metal anodes in all-solid-state batteries. Currently, the authors are working to develop a roll-to-roll vacuum deposition system that utilizes this technology. In the future, the aim is to develop equipment for the mass production of Li metal anodes, while contributing to the advancement of industry and science through the widespread adoption of next-generation batteries with high energy density.

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