

Development of an Li Metal Anode Using a Vacuum Evaporation Process

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Because the market for lithium ion batteries is expected to grow rapidly, efforts are underway to develop an advanced rechargeable Li-ion battery. One approach for such a rechargeable battery that is attracting attention uses lithium metal as the anode, because the result would be a high-capacity, light-weight battery that is ideal in terms of energy density. However, in order to put a lithium metal anode into practical use, it is necessary to solve the problem of dendrites that occur during repeated cycles of charging and discharging. Other issues that need to be addressed include safety and battery life.

Compared to conventional roll-press Li foil, our vacuum evaporated Li film has shown excellent cycle performance. We were also able to stabilize the active Li surface after deposition by applying a “chemical-passivation” process that we developed.

1. Introduction

The market for lithium-ion batteries (LiBs) is expected to grow rapidly due to their use in a wide range of applications, such as smartphones, drones, and electric vehicles (EVs). In the automotive market, emissions regulations are being tightened in major countries, as exemplified by Euro 7 in Europe, the Zero-Emissions Vehicle (ZEV) regulations being strengthened in California, and China moving toward the New Energy Vehicle (NEV) regulations. It is becoming difficult for conventional engine technologies based on use of fossil fuels to comply with these regulations. For this reason, automakers are beginning to shift their focus toward popularizing EVs and plug-in hybrid (PHV or PHEV) vehicles¹⁾. According to a survey by a think tank, more than 60 million EVs and PHVs are expected to be sold globally in 2040²⁾, and the demand for battery capacity is also expected to surge. Consequently, there is a pressing need to enhance production facilities and develop large-capacity batteries, with battery makers competing furiously toward commercialization of the technology.

2. Anodes in LiBs

2.1 Current LiBs and next-generation LiBs using an Li metal anode

An LiB has a structure in which a cathode, an anode, and a separator are stacked and immersed in an electrolyte, as shown in Figure 1. As mentioned above, development efforts related to the materials and manufacturing methods of the various components are underway to increase battery capacity. Currently, a graphite-coated film is used for the anode, with a theoretical energy density of 370 mAh/g. Replacing this graphite anode with a material that has greater energy density would increase battery capacity³⁾. In particular, it is considered ideal to switch to an Li metal anode with a theoretical energy density of 3860 mAh/g, which is gaining attention as a likely next-generation anode.

2.2 Issues facing an anode using roll-press Li foil

Although Li metal is ideal for increasing capacity, it has issues in terms of safety and service life. These issues are presumed to be caused by dendrites, which are needle-shaped precipitations of Li metal that occur over the life of repeated charging/discharging cycles⁴⁾. As these dendrites grow, they cause short circuiting between the cathode and the anode, potentially causing a fire, etc. Additionally, as shown in Figure 2, Li that does not enable charging/discharging occurs, called “dead Li” because it falls off during the growth stage, posing an issue in terms of battery life⁵⁾. It is said that dendrites are caused by the current concentration that occurs on the anode during charging⁶⁾,

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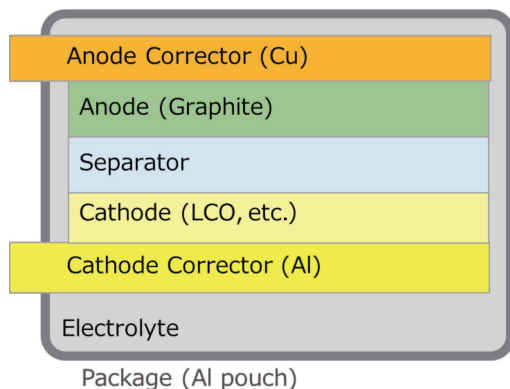


Fig. 1 Battery structure

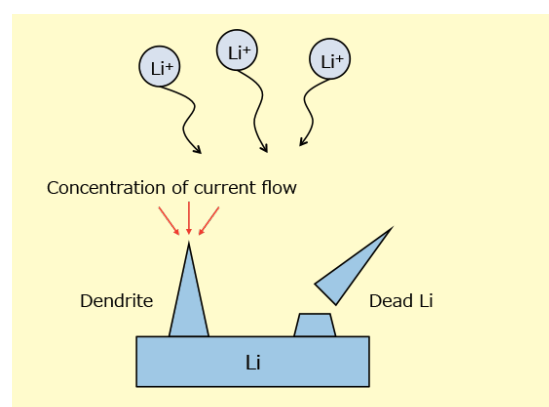


Fig. 2 Dead Li generated during charging and discharging

and it is considered that flattening the Li surface and forming a uniform passivation film at the same time could improve the current distribution, thereby suppressing the formation of dendrites. It is considered that Li foil manufactured using a roll-press process, which is currently being used widely as the Li metal anode, will not solve the aforementioned issues because of the surface roughness of the roll-press rollers and the process atmosphere. As a means of solving these issues, the authors focused on a vacuum evaporation process that provides excellent surface flatness and in which the processing atmosphere can be controlled. Furthermore, with an eye toward applying this process to an existing mass-production coating line, the authors have selected a roll-to-roll evaporation process and are carrying out development work toward mass production of Li metal anodes.

3. Experiment Method

For the experiment, we used the EWK-030 roll-to-roll evaporation system. Figure 3 shows an external view of

the EWK-030. This system can vapor-deposit Li on a Cu foil base that is 300 mm wide and 10 to 125 μm thick. Furthermore, because its structure allows the chamber to be docked to a dry room, the sample following film deposition can be handled without exposing it to a normal humidity environment. Using the system, a 20- μm Li film was deposited on Cu foil of 10 μm in thickness, and sample evaluation was performed.

4. Experiment Results

4.1 Surface flatness

Figure 4 shows images of roll-press Li foil and evaporated Li film obtained using an optical microscope. The surface of the roll-press Li foil shows what are presumed to be scars formed during processing. The surface roughness of roll-press Li foil, which is an existing technology, is presumed to be dependent on the rollers used for processing. On the other hand, the film obtained using



Fig. 3 “EWK-030” roll-to-roll Li evaporation system and dry room

ULVAC's vacuum evaporation process turned out to possess excellent flatness.

4.2 Surface stabilization of evaporated Li film

The outermost surface of an evaporated Li film is active. Consequently, when it is handled inside a dry room with a dew point of -50°C , the film reacts with the gas in the atmosphere, resulting in discoloration caused by the reaction product, as shown in Figure 5. In particular, Li_3N resulting from a reaction with nitrogen and LiOH resulting from a reaction with water are energetically unstable, and are presumed to adversely affect battery performance and safety⁷⁾. This means that passivation must be added in situ following the evaporation process. To address this, the authors developed a method of forming a stable coating film called "chemical passivation" on the Li surface. No discoloration occurred when an Li film formed using this method was handled inside a dry room (Figure 6). A sample processed using the new method and another sample not using the new method were exposed

to a normal environment (room temperature of 22°C and relative humidity of 44%), and color change over time was checked (Table 1). The unprocessed sample discolored after 10 seconds of exposure, while the processed sample showed no change in its external appearance, even after 60 seconds.

4.3 Symmetric cell charging/discharging test

The authors created CR2032-type symmetric cells that use roll-press Li foil and evaporated Li film as working electrodes and that have the configuration shown in Figure 7. In both cases, 100- μm roll-press Li foil was used for the counter electrode, 25- μm polypropylene was used for the separator, and 1M LiPF₆ (EC:DMC:DEC = 1:1:1 volume%) was used for the electrolyte. Figures 8 and 9 show the results of a 500-cycle charging/discharging test performed on these cells at a current density of 0.1 mA/ cm^2 . The charging/discharging behavior of the cells using the roll-press Li foil became unstable after 300 cycles. This is presumed to be because a resistance component was generated on the electrode surface as the Li melted

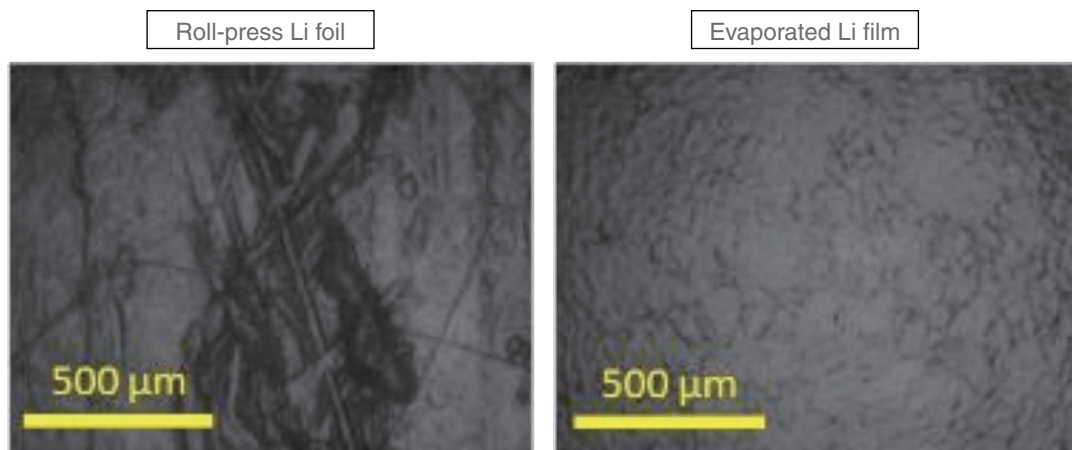


Fig. 4 Comparison of roll-press Li foil and evaporated Li film morphology



Fig. 5 Picture of untreated Li surface exposed to dry air

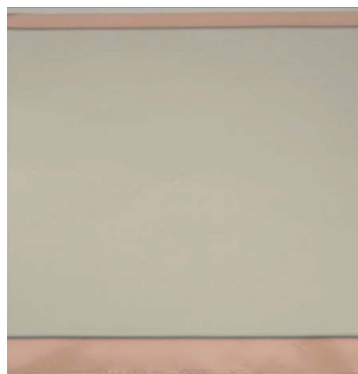


Fig. 6 Picture of treated Li surface not exposed to dry air

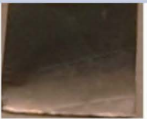
Time [sec.]	Initial	10	20	30	60	180
No Treatment						
With Treatment						

Table 1 Pictures of the difference across reaction times with “chemical-passivation”

Roll press Li foil : 20 μ m	Evaporated Li film : 20 μ m
PP Separator : 25 μ m	PP Separator : 25 μ m
Roll press Li foil : 100 μ m	Roll press Li foil : 100 μ m

Fig. 7 Half-cells structure of roll-press Li foil and evaporated Li film

and precipitated, causing large voltage fluctuations. On the other hand, the cells using the evaporated Li film showed little voltage fluctuation and exhibited stable charging/discharging over all 500 cycles, demonstrating that the evaporated Li film developed by the authors possesses characteristics superior to those of existing roll-press Li foil.

5. Reflections

As described in Section 4.2, it is presumed that products such as Li_3N and LiOH generated from reactions with the atmosphere during handling inside a dry room are formed non-uniformly on the surface of the evaporated Li film. These coating films are reduced and decomposed by reacting with the electrolyte during the initial charging operation, forming a new coating film called Solid Electrolyte Interface (SEI). Because SEI exhibits ion conductivity and also inhibits further decomposition of the electrolyte⁷⁾, a technology that could form a uniform and excellent SEI is considered key. It is presumed that the coating film obtained by the chemical passivation developed by ULVAC reacted with the HF present inside the LiPF₆ electrolyte during the initial charging operation, uniformly forming LiF. Inasmuch as LiF possesses ion conductivity and is stable inside the electrolyte, it is

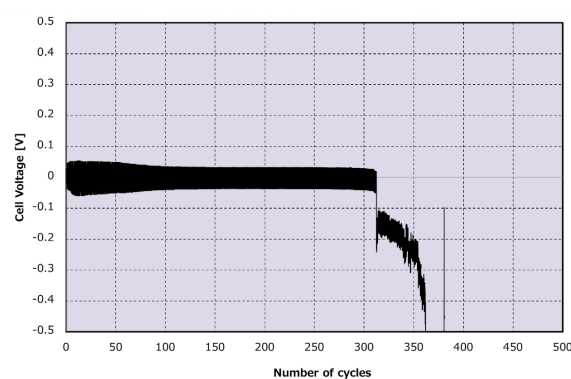


Fig. 8 Cycle performance of symmetric cell applied roll-press Li foil to working electrode

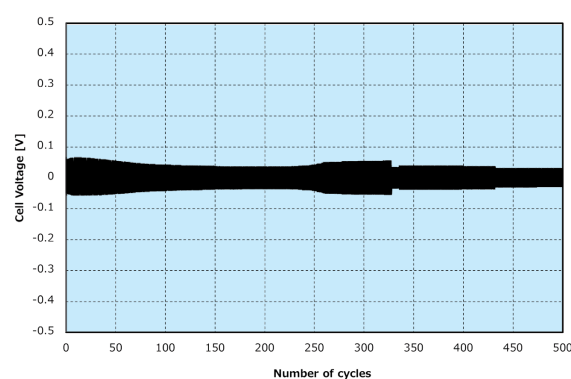


Fig. 9 Cycle performance of symmetric cell applied evaporated Li film to working electrode

presumed that the uniform formation of an excellent SEI produced the superior battery characteristics.

6. Conclusion

In symmetric cells, ULVAC's vacuum evaporated Li film demonstrated cycle characteristics superior to those of existing roll-press Li foil. Furthermore, we developed a "chemical passivation" process that stabilizes the active Li film surface following vacuum deposition. We plan in the future to deploy this technology to mass-production equipment, thus expanding next-generation battery anodes.

References

- 1) Mizuho Bank Industry Research Division: Mizuho Industry Focus 205, 11 (2018) (in Japanese).
- 2) New Energy and Industrial Technology Development Organization: Focus NEDO 69, 9 (2018).
- 3) New Energy and Industrial Technology Development Organization: NEDO Technology Roadmap for Stationary Battery 2013 (Battery RM2013), 10 (2013) (in Japanese).
- 4) Electrochemical Society of Japan, Committee of Battery Technology, Battery Handbook (Ohmsha, 2010), p. 58 (in Japanese).
- 5) Xin-Bing Cheng, Rui Zhang, Chen-Zi Zhao, and Qiang Zhang: Chemical Reviews, 117, 10406 (2017).
- 6) Kiyoshi Kanamura, Naohiro Kobori, and Hirokazu Munakata: BLIX, Symposium on Energy Storage, San Jose (2017), p. 6.
- 7) Electrochemical Society of Japan, Committee of Battery Technology, Battery Handbook (Ohmsha, 2010), p. 364 (in Japanese).