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Development of An Eco-friendly Surface Treatment Process for the Design of the Al Lead Tab in Lithium-ion Batteries

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ABSTRACT. With the recent popularity of mobile devices, the demand for lithium-ion batteries is increasing. In this study, the surface treatment process for the development of the Al (aluminum) lead tab for positive electrode, a key component of the pouch-type lithium-ion battery, was investigated. Anodizing and sealing processes were tested as surface treatment techniques. It was found that only a sealing process is needed to obtain sufficient adhesive strength. In the present study, an adhesive strength of 17 N/12 mm was achieved by degreasing and etching pretreatment, followed by a sealing process of 10 min duration. This adhesive strength was greater than that achievable using Cr (chromium) surface treatment. Using various surface analysis techniques, the shape and composition of the surface before and after being subjected to the surface treatment were compared and analyzed. The results of this study are expected to contribute to the development of an eco-friendly lead tab.

Key words: Al lead tab, Eco-friendly surface treatment, Sealing process, Lithium-ion battery

INTRODUCTION

Importance of the lithium-ion batteries

In modern society, mobile devices have become popular, leading to an increasing demand for rechargeable batteries. Lithium-ion batteries have largely replaced lead-acid batteries and nickel-cadmium secondary batteries, which were predominantly used in the past.[1,2] Lithium-ion batteries are classified into small, medium and large, according to their size. Small batteries are used in smartphones and notebooks, while medium and large batteries are typically used in electric vehicles and energy storage devices.[3] Lithium-ion batteries can be classified into cylindrical, rectangular, and pouch types, according to their shape.[4] Cylindrical lithium-ion batteries have standardized specifications and are mainly used in power tools and electric bicycles. The rectangular batteries are primarily used in smartphones with removable batteries. Pouch-type batteries are the thinnest of these types, and are used in smartphones in which the battery is built-in. It is easy to increase the capacity of a pouch-type lithium-ion battery by establishing a high energy density. Moreover, the pouch-type lithium-ion battery can be manufactured in various sizes.[4,5] Consequently, there is an increasing demand for pouch-type lithium-ion batteries, focusing on products which emphasize design. The pouch-type lithium-ion battery is composed of four elements: electrodes (anode, cathode), separators, packaging materials, and lead tabs.[4] In this paper, we focus our studies on the lead tab, which is an important component of the pouch-type lithium-ion battery.

Importance of lead tabs and trends in manufacturing techniques

The lead tab is a key component that determines the output performance and stability of a pouch-type lithium-ion battery. The lead tab is a part that protrudes from an electrode and is connected to an external terminal. It therefore serves to transfer the internal output of the pouch-type lithium-ion battery to the outside.[5,6] As shown in *Fig.* 1, the lead tab consists of a composite material in which a metal tab and a polymer film are bonded together. The lead tab is bonded to the film after the metal tab is subjected to surface treatment. The performance of the lead tab is determined by the magnitude of the adhesion between the metal tab and the polymer film. It is especially important to maintain the adhesion between the metal and the polymer film even in an electrolyte environment. In the early days of the lithium-ion battery industry, hexavalent Cr was widely used to treat the surface of lead tabs. Since hexavalent Cr is now known to be an environmental pollutant, which also adversely affects the human body, trivalent Cr surface treatment is currently used for the design of lead tabs in the industry.[7] However, there is a possibility that trivalent Cr may be oxidized to hexavalent Cr, so there is a

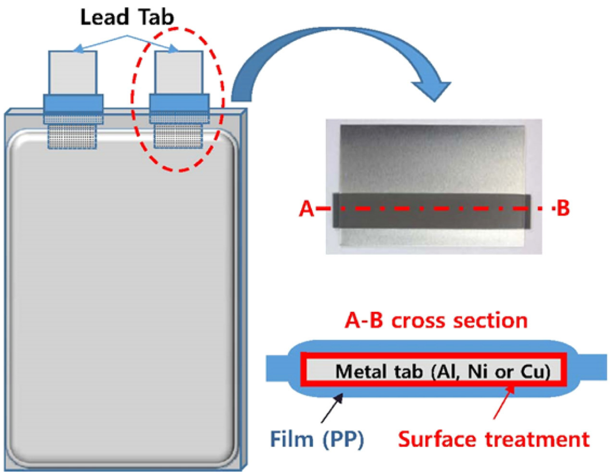


***Figure* 1.** Schematic diagram of pouch-type lithium-ion battery and the lead tabs present therein.

need to explore Cr-free surface treatments in the lithium-ion battery industry.[8]

Purpose of this study

The present study attempts to develop an optimal process for applying an eco-friendly surface treatment technology that does not involve the use of Cr on the Al lead tab (used for positive electrode in lithium-ion batteries and abbreviated as "Al tab" hereafter). Two different methods were tested for the surface treatment of Al tabs. The first surface treatment method investigated was the anodizing of the Al surface. During electrochemical anodic oxidation, the surface Al is oxidized and converted to porous Al_2O_3. After undergoing the anodization process, the corrosion resistance of the Al surface is improved, and effective dyeing is possible on the porous Al surface.[9,10] In this study, we have investigated the effect of the microporous structure of the Al oxide on the adhesion of polymer films. The second surface treatment method investigated here is the sealing process of Al. The sealing process involves the immersion of the Al surface in water vapor or in a high-temperature chemical solution. The Al_2O_3 present on the Al surface reacts with H_2O to form boehmite ($AlO(OH)$), and fills the pores in the Al_2O_3 matrix on the surface. The role of sealing is to prevent contamination of the coating and to improve corrosion resistance.[11,12] Since the metal adhesive layer of the lead tab polymer film is polar, it is expected that the adhesive strength will be improved if the Al tab surface is also polarized. Therefore, the effect of chemical change on the surface of Al tab due to the sealing process was also investigated.

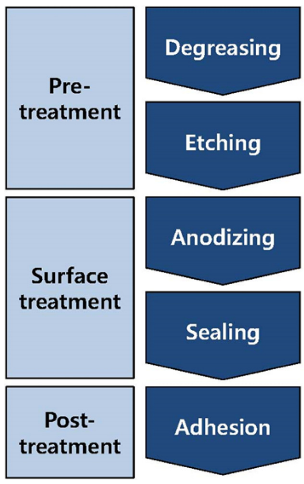
EXPERIMENTAL

Reagents and instruments

Industrial-grade reagents were used for all reagents, such as Na_2SiO_3, H_2SO_4, and oxalic acid dihydrate. The Al tab used was a grade A1050 material, produced by Novelis Korea Ltd. A three-layer polypropylene composite film was used as the lead tab adhesive film. An EX 2500 series programmable switched-mode power supply (SMPS) from ODA Technological Co., Ltd. was used as the anodizing power supply. A carbon rod purchased from Alfa Aesar was used as the counter electrode. The electrolyte used for the evaluation of the adhesive strength was one produced by Panax Etec Co., Ltd. The electrolyte solution consisted of 1: 1: 1 (vol%) solution of ethylene carbonate (EC), diethyl carbonate (DEC), and dimethyl carbonate (DMC) containing 1.0 M $LiPF_6$. Surface morphology was measured using an optical microscope (OLYMPUS BX51M) and Field Emission Scanning Electron Microscope (FESEM, Ultra Plus). Contact angles were measured using PHOENIX-300 TOUCH and X-ray photoelectron spectra (XPS) were recorded using the PHI Quantera II (Ulvac-PHI) system.

Experimental methods

Scheme 1 shows a schematic of the entire process for the fabrication of the lead tab. In the pretreatment process, degreasing and etching are performed. Degreasing is carried out at 45 °C with 5% Na_2SiO_3 for 30 s.[13] Etching is performed for 30 s at 24 °C using 1 M H_2SO_4. In the surface treatment process, sealing is carried out, either on its own, or after anodization. Anodizing is performed for 600 s by applying 40 V DC power to the Al tab in 0.3 M oxalic acid.[14,15] The sealing is carried out for 0 to 60 min in distilled water



***Scheme* 1.** Schematic of the lead tab production process.

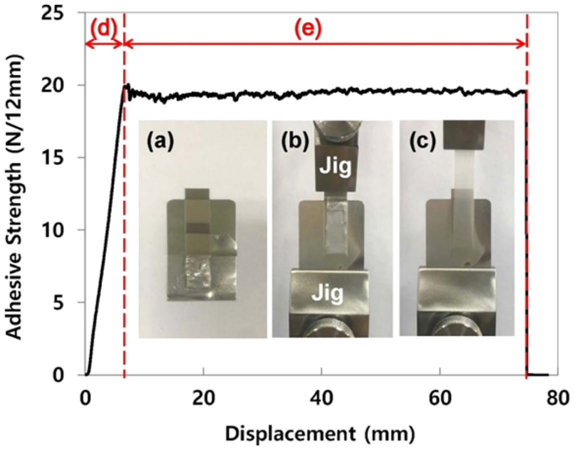


***Figure* 2.** (a-c) Adhesive strength measurement method (d, e) Adhesive strength as a function of displacement.

at 80 °C. In the post-treatment process, the surface-treated Al tab is bonded to the polymer film with heat to complete the fabricating the Al lead tab. Adhesion is carried out at 148 °C for 40 s at the tab jig, and at 145 °C for 9 s at the film jig.

Evaluation of the adhesive strength

A universal testing machine (UTM) is used to measure the adhesive strength between the Al tab and the film before and after its immersion in an electrolyte. The electrolyte immersion method consists of three steps. First, the Al tab is immersed in electrolyte and stored for 24 h at 85 °C. Next, the Al tab is taken out of the electrolyte and rinsed with water. Finally, the Al tab is dried for 15 min between 25 and 30 °C. The adhesive strength of the dried Al tab is then measured using a UTM. *Figs*. 2a, 2b and 2c depict the method used to measure adhesive strength. The polymer film of the Al tab is peeled off to the extent of about 1 cm. The Al tab is then fixed to the bottom jig of the UTM, while the peeled film is fixed to the top jig. At this stage, the angle between the Al tab and the film is expected to be 180°. As the top jig is pulled out, the adhesive strength between the Al tab and the film is measured. The variation of the adhesive strength with displacement is shown in *Figs*. 2d and 2e. It is clear that the film appears to be stretched initially, after which the adhesive strength appears to remain constant. This relatively constant value is assumed to correspond to the adhesive strength between the Al tab and the film.

RESULTS AND DISCUSSION

Effect of anodizing surface treatment on adhesive strength

Anodizing was first tested as a surface treatment method for the Al tab. Anodizing is known to form a fine porous

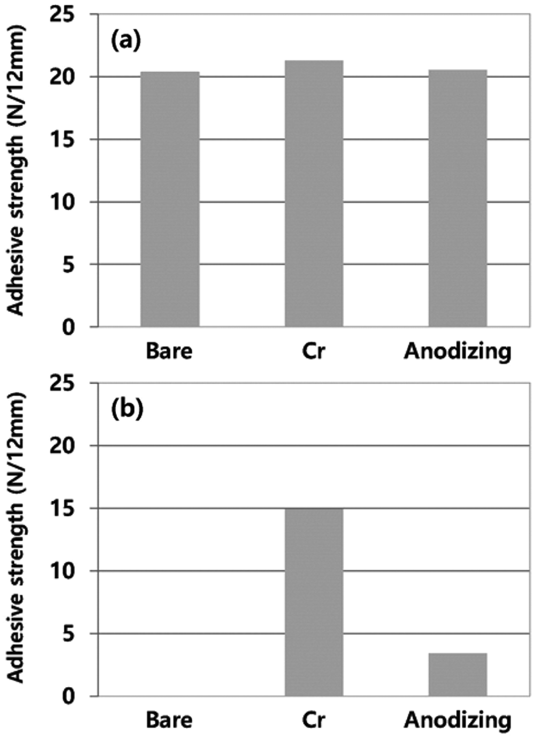


***Figure* 3.** Adhesive strength according to surface treatment type (a) before and (b) after immersion in electrolyte.

oxide film.[9,10] We wanted to investigate the effect of the formation of microporous structure of Al oxide on the adhesive strength of the film. The adhesive strength before immersion in electrolyte is about 20 N/12 mm, regardless of the type of surface treatment performed (see *Fig*. 3a). Adhesive strength after immersion in electrolyte is 0 N/12 mm on the bare Al surface, but increases to 15 N/12 mm after surface treatment with Cr (see *Fig*. 3b). The adhesive strength of the anodizing Al surface is about 3 N/12 mm, which is higher than that for the bare Al surface, but lower than that for an Al surface treated with Cr. This suggests that the anodizing surface treatment does not improve the adhesive strength of the Al tab to the same extent as surface treatment with Cr. Also, the adhesive strength before immersion in the electrolyte does not seem to depend on the type of surface treatment (see *Fig*. 3a). However, the adhesive strength after immersion in the electrolyte varies greatly depending on the type of surface treatment (see *Fig*. 3b). Therefore, it is suggested that the evaluation of the adhesive strength of the Al tab be done only after immersion in the electrolyte.

Effect of the sealing process on the adhesive strength

The metal adhesive layer of the film contains polar materials. If the Al surface is polarized, the chemical bonding between the Al tab and the film is expected to be enhanced.

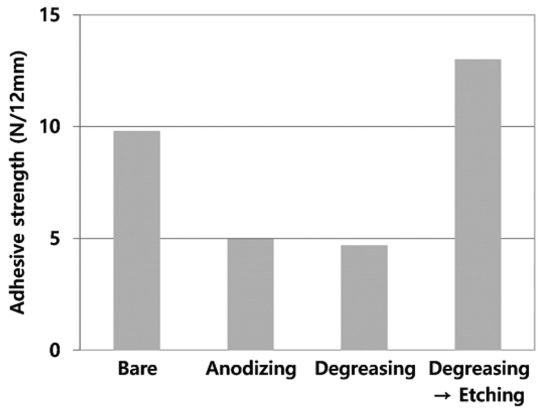


***Figure* 4.** Adhesive strength after immersion in the electrolyte, when the sealing process of Al is performed for 1 min. Different surface treatments were applied before the sealing process, as indicated.

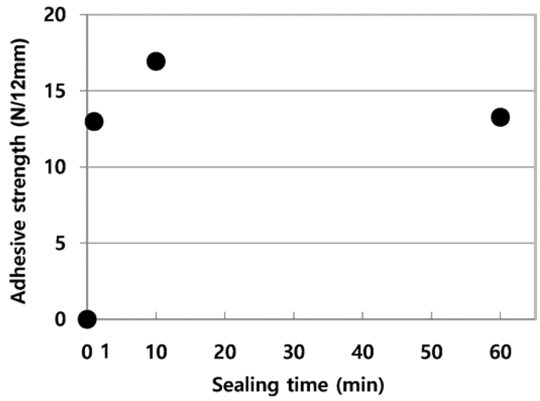


***Figure* 5.** Adhesive strength of Al tabs after immersion in electrolyte, as a function of sealing time. Degreasing and etching were applied as pretreatment steps in all cases.

In addition, the adhesive strength is expected to increase even in the presence of the electrolyte. We investigated the adhesive strength when the sealing process was performed after other processes such as degreasing, anodizing and etching. The adhesive strength after immersion in the electrolyte when the sealing process was performed for 1 min is shown in *Fig.* 4. After 1 min of sealing, the adhesive strength of bare Al without pretreatment increased to 10 N/12 mm, which was a significant improvement, as compared to the adhesive strength without sealing (0 N/12 mm; see *Fig.* 3b). When the surface was anodized followed by sealing after 1 min, the adhesive strength was measured to be 5 N/12 mm, which was slightly higher as compared to the case where sealing was not performed (about 3 N/12 mm). These results indicate that sealing improves the adhesive strength, regardless of the type of surface treatment. Therefore, the anodizing treatment may be excluded from the surface treatment process.

In fact, in the process of producing lead tabs industrially, the oil present on the Al surface of the raw material poses a problem. Therefore, it is necessary to remove the oil through pretreatment before the surface treatment process can be carried out. The adhesive strength of the Al tab, with only degreasing as a pretreatment, is about 5 N/12 mm, whereas the adhesive strength of the Al tab after degreasing and etching pretreatment is about 13 N/12 mm. The adhesive strength of the Al tab which has been degreased and etched is about three times higher than that of the Al tab which is degreased without etching. Therefore, it was decided to perform both degreasing and etching in the pretreatment process.

Fig. 5 shows the effect of sealing time on the adhesive strength. The adhesive strength of the Al tab after 10 min of sealing process was about 17 N/12 mm and corresponded to the highest value attained. This figure is about 14% higher than the adhesive strength (15 N/12 mm; see *Fig.* 3b) of an Al tab whose surface was treated with Cr. Even if the sealing process is performed for a longer time, the adhesive strength does not increase significantly. Therefore, the pretreatment of the Al tab was performed by degreasing and etching, and surface treatment was performed by the sealing process for a duration of 10 min, so as to optimize the process.

Characterization of the optimized Al tab surfaces

We investigated the surface properties of Al tabs treated with optimized processes using various surface analysis methods. The images obtained by observing the surface of the Al tab using an optical microscope and SEM are shown in *Fig.* 6. After the pretreatment, but before the sealing process, the surface of the Al tab exhibits vertical grain structure (*Figs.* 6a, 6c, 6e). After the pretreatment and sealing processes, black spots are seen to appear on the surface of the Al tab (see *Fig.* 6b). Observing the enlarged surface structure using an SEM, it can be seen that a mesh-like structure is formed on the surface of the Al tab (see *Fig.* 6d).[16] When the surface is magnified, the mesh structure appears to be hollow, with pores sizes between 200 and 300 nm (see *Fig.* 6f). It is presumed that the formation of the mesh structure on the surface of the Al tab after the sealing process increases the adhesive strength between Al and the film.

The contact angle of the Al tab surface after the degreasing and etching pretreatments was measured to be 65.2° (see *Fig.* 7a). If the sealing is carried out after the pretreatment, the contact angle cannot be measured, which means that the surface of the Al tab becomes very hydro-

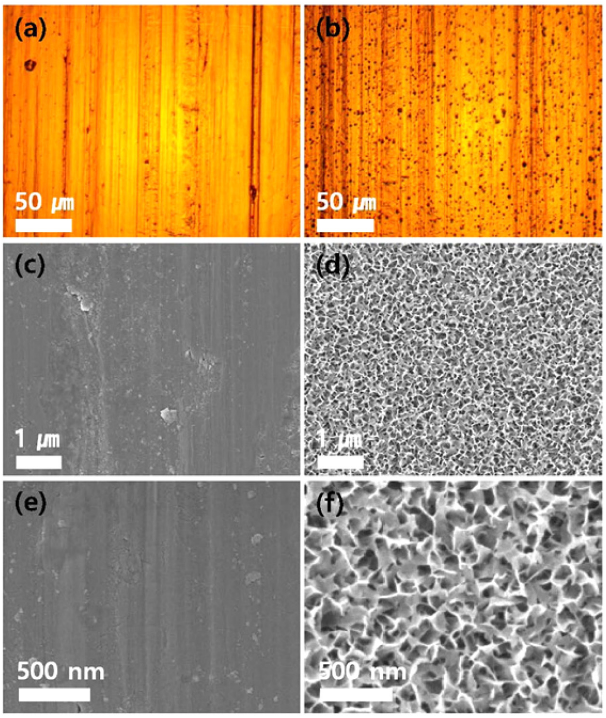


***Figure* 6.** (a, b) Optical microscope images (c-f) SEM images of Al tabs before (a, c, e) and after (b, d, f) the sealing process. Degreasing and etching were applied as pretreatment steps in all cases.

philic. In general, it is known that the contact angle increases when a pointed structure is formed on the surface.[17] However, the contact angle of the Al tab with the mesh surface decreased. It is presumed that the contact angle changes due to the change in the composition of the surface with the change in the surface structure. XPS analysis was performed to observe the change in the composition of the Al surface due to sealing.

XPS patterns before and after the Al2p sealing process are shown in *Fig*. 7b. After the sealing process, the XPS peaks appear to become sharper, with a decrease in the binding energy. The results of fitting curves to the Al2p spectra are shown in *Figs.* 7c and 7d.[18,19] *Table* 1 shows the atomic % calculation of Al2p after the sealing process. After the sealing process, the $Al(OH)_3$ content is seen to increase, with a corresponding decrease in Al_2O_3 content. AlOOH was expected to be formed on the Al surface due to the sealing process, but the XPS analysis revealed that more $Al(OH)_3$ was formed, rather than AlOOH. After sealing, there is a change in the chemical composition of the Al surface, and it is speculated that this change contributes to the improvement of the adhesive strength, along with the changes in physical shape.

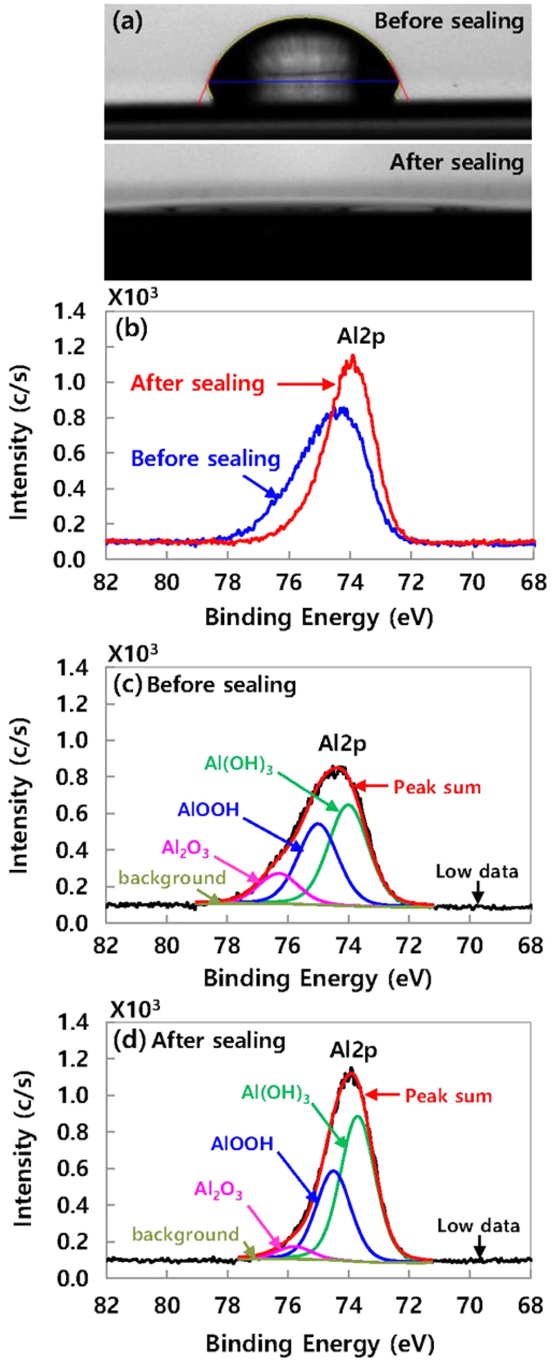


***Figure* 7.** (a) Contact angle and (b-d) Al2p XPS measurements of Al tabs before and after the sealing process. Degreasing and etching were applied as pretreatment steps in all cases.

CONCLUSION

In this study, we report the development of a Cr-free, eco-friendly surface treatment process. Anodizing and sealing were both tested as surface treatment processes, and it was concluded that only the sealing process could lead to

***Table* 1.** Al2p binding energy and atomic % of Al tabs before and after the sealing process

Compound	XPS fitting results of Al2p			
	Before sealing		After sealing	
	Binding energy (eV)	Atomic %	Binding energy (eV)	Atomic %
$Al(OH)_3$	74.0	48	73.7	59
AlOOH	75.0	38	74.5	36
Al_2O_3	76.3	14	75.8	5

Degreasing and etching were applied as pretreatment steps in all cases.

adequate adhesive strength. Degreasing and etching pretreatments were found to be essential, along with the sealing surface treatment. The optimal duration of the sealing process was found to be 10 min. The surface of the Al tab subjected to the sealing process formed a mesh-like structure, which also changed the surface composition. Physical and chemical changes of the Al tab improved the electrolyte resistance adhesive strength between the Al tab and the film. When the Al tab was treated via the optimal process outlined in this study, the adhesive strength was measured to be 17 N/12 mm, which is greater than the adhesive strength that can be obtained by treating the surface with Cr. The results of this study are expected to greatly contribute to formulating an eco-friendly and sustainable lead tab production technology.

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