



Alloys and Electrochemical Properties of Aluminum Foils for Current Collectors of Lithium-Ion Battery

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1. Introduction

There has been rapid development in the field of lithium-ion batteries (LIBs) since the 1990s, and they are now being used in a wide variety of products ranging from electronic equipment to automobiles. Al foil is used for the positive electrode current collector of LIBs. This started when Professor Yoshino, one of the co-inventors of LIB, adopted Al foil as the LIB cathode current collector for the first time. He applied for a basic patent on LIBs using LiCoO_2 at the positive electrode active material and carbon at the negative electrode active material and a patent on using Al foils as the current collectors^{1),2)}. In high-potential environments such as those encountered at the positive electrode in LIBs, metals are usually ionized and hence cannot be used as current collectors. He discovered by trial and error that Al foil can be used as a current collector for positive electrodes, which was a major step in the development of LIBs. The current collector must be mechanically strong because it receives a large

amount of stress during electrode manufacturing (Fig. 1). Further, since thin current collectors contribute high energy density by increasing the amount of active material, so it is desirable to minimize their thickness. In addition, suppression of side reactions, low cost, and homogeneity are also important. On the other hand, for electrochemical reasons, Cu foil is used for the negative electrode.

The UACJ Group manufactures both Al foil and rolled Cu foil for current collectors. In this report, Al foil alloy for the positive electrode current collector and its electrochemical properties are described.

2. Characteristics of Al foil alloy for current collector

Al foil that is generally used as the positive electrode current collector is not composed of purely Al; instead, it contains trace impurities and additives, such as Fe, Si, and Mn. There are aluminum alloys from 1000 series to 8000 series depending on the type and amount of additive elements. Blending with such

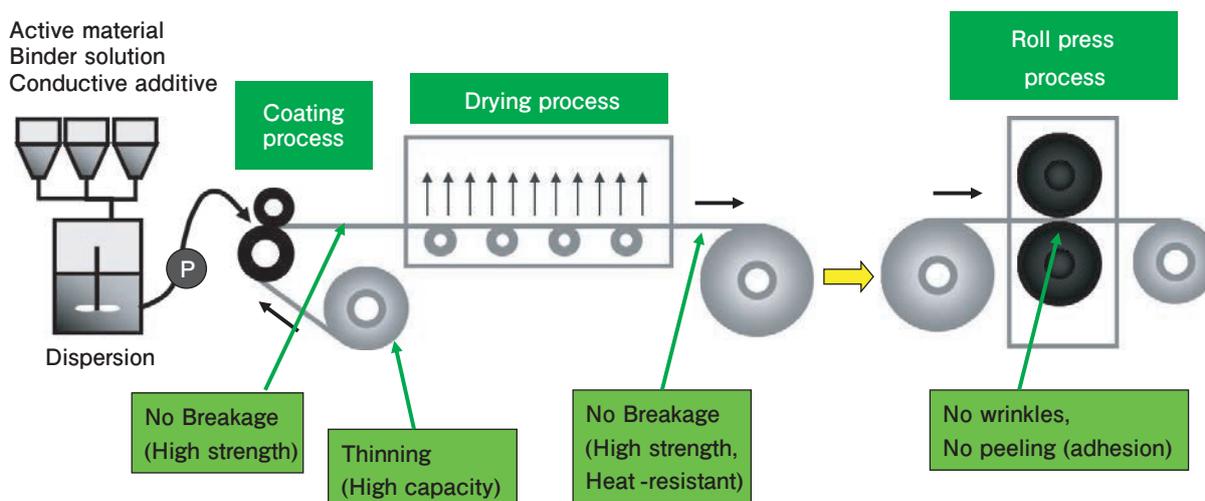


Fig. 1 Electrode manufacturing process and its properties required.

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additives affects the electrical, thermal, and mechanical properties of Al foils; thus, the desired performance can be achieved by adjusting the composition of Al alloy foils. Al alloys that are commonly used as current collectors include three types of series, namely the 1000, 3000, and 8000 series alloys. The 2000, 5000, 6000, and 7000 series alloys represent high-strength Al alloys, which are not often used for electrode manufacturing, as they are extremely difficult to roll into foil thickness. In addition, the 4000 series alloys contains a large amount of Si, which can undergo oxidation at high potential when exposed to the surface and might be eluted into electrolyte; therefore, these series alloys are not suitable for use in LIBs. Generally, the 1000 series alloys have excellent conductivity, the 3000 series alloys have excellent strength, and the 8000 series alloys have excellent ductility and strength equivalent to the 1000 series alloys. The typical compositions of the alloys are shown in **Table 1**. The 1000 series alloys are called pure-Al as they contain Al with a purity of 99.00% or more. These alloys may contain mainly Fe and Si impurities; the name of the alloy changes depending on its purity. General-purpose alloys used in LIBs include 1085 (Al 99.85%), 1N30 (Al 99.30%), and 1100 (Al 99.00%). In general, although they are not as strong as other alloys, their strength can be improved by controlling the additive elements and metallic structure.

When high-strength current collectors are required, the 3000 series alloys, such as 3003, are used. In LIBs, there are cases where Mn in the positive electrode active material dissolves into the electrolyte and affects capacity loss³; however, practically, there is little such negative effect and 3003 has been widely used. As will be explained in the next chapter, Al forms a passivation film of AlF_3 on the electrode, so

the added component Mn does not elute.

The 8000 series alloys have other elements added that are not covered in the other series. The 8021 alloy, a prominent member of the 8000 series alloys, is obtained by adding Fe to the 1000 series alloys. It exhibits excellent ductility and corrosion resistance. Generally, the 8000 series alloys are used as an alloy for packaging, but its use as a current collector is also increasing.

3. Properties of the electrochemical stability

3.1 Formation of a passive film on the outermost surface

The potential at a positive electrode current collector is 3.0–4.5 V vs. Li, and hence the current collector must not undergo corrosion, participate in side reactions with the electrolyte, or undergo redox reactions in this potential range. The standard electrode potential of Al is 1.4 V vs. Li; hence, it is thermodynamically prone to redox reactions, is not suitable for current collectors. However, in a non-aqueous solvent containing fluoride electrolytes, such as LiPF_6 or LiBF_4 , a very thin passive and stable film, several nanometers thick, is formed on the Al foil. This passive film, formed by the reaction mechanism shown in Eq. (1) on the surface of the Al foil during the first charging, is stable in the battery and could

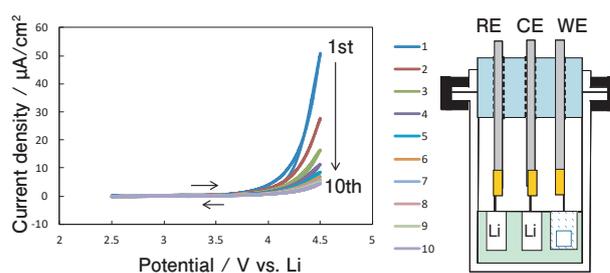


Fig. 2 CV measurement of 1085.

Table 1 Composition and its characteristics of Al foil for the positive electrode⁴⁾.

Alloy	Chemical composition (wt%)								Conductivity* (%IACS)	Characteristic
	Si	Fe	Cu	Mn	Mg	Zn	Ti	Al		
1085	≤ 0.10	≤ 0.12	≤ 0.03	≤ 0.02	≤ 0.02	≤ 0.03	≤ 0.02	≥ 99.85	60.1	High conductivity
1N30	≤ 0.7		0.10 ≤	0.05 ≤	≤ 0.05	≤ 0.05	–	≥ 99.30	58.4	Low cost
1100	≤ 1.0		0.05-0.20	≤ 0.05	–	≤ 0.05	–	≥ 99.00	58.0	High strength
3003 (Al-Mn)	≤ 0.6	≤ 0.7	0.05-0.20	1.0-1.5	–	≤ 0.1	–	bal.	47.2	High strength
8021 (Al-Fe)	≤ 0.15	1.2-1.7	≤ 0.05	≤ 0.05	≤ 0.05	≤ 0.05	–	bal.	57.8	Ductility

*: Equivalent value based on the resistivity measured at liquid nitrogen temperature.

suppress side reactions, such as corrosion during charging and discharging⁵).

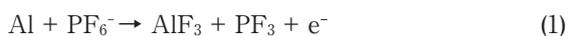


Fig. 2 shows the results of cyclic voltammetry (CV) measurements in which 1085 foil was cycled 10 times from 2.5 to 4.5 V. With an increase in potential above 4 V vs Li, the current density started to increase; moreover, the current density gradually decreased with each subsequent cycle. In the CV measurements, the reduction current was not observed; instead, only oxidation occurred. This suggests that either the Al was oxidized or the electrolyte underwent oxidative decomposition. Since the detected current decreases with each subsequent cycle, it is thought that Al reacts with the electrolyte, loses the active sites and is passivated. After the CV measurement, fluorine was detected when the outermost surface of the Al foil was analyzed by X-ray photoelectron spectroscopy (XPS). In the Al 2p spectrum, an Al³⁺ peak was observed at about 75 eV, revealing a shift to 76 eV after CV measurements. However, the peak of

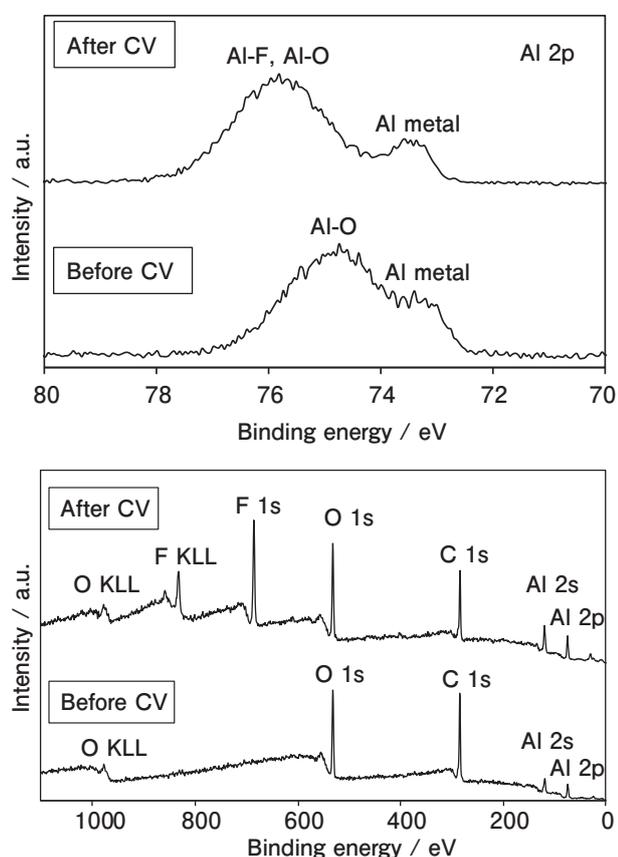


Fig. 3 XPS wide and Al-2p spectrum after CV.

AlF₃ itself is even higher at 77 eV, so it is considered to be a mixed peak of AlF and AlO (**Fig. 3**). Furthermore, as a result of analyzing the sample in the middle of the cycle, it was found that the formation of AlF₃ had already started at 4 V in the first cycle. There was almost no change in the XPS depth analysis results compared to the samples after 10 cycles (**Fig. 4**). It should be noted that fluorine is only present on the outermost surface and that the inside has a depth profile similar to that of a normal oxide film. Therefore, since the AlF₃ film is thinner than the natural oxide film (10 nm or less), it is estimated that there are few active sites for fluorination. Similarly, other Al alloys in the 1000, 3000, and 8000 series have also been found to reduce the current density with each subsequent cycle during the CV measurement.

It is presumed that this passive film also protects against the elution of Mn, an additive element of 3003, mentioned in the previous chapter. Cross sectional

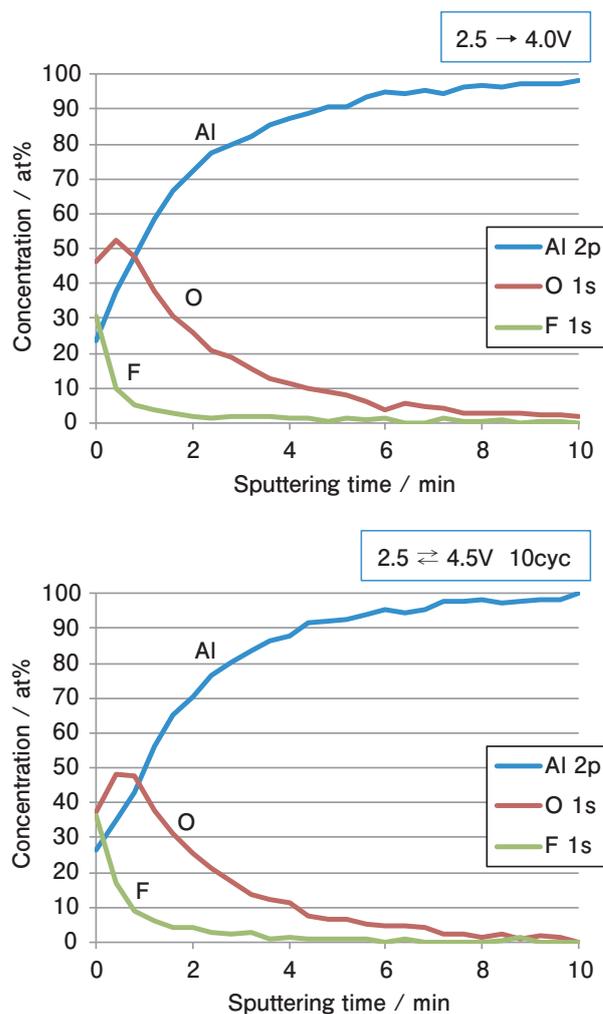


Fig. 4 Depth profile of XPS after CV.

transmission electron microscopy (TEM) and Energy dispersive X-ray spectroscopy (EDS) images of the 3003-alloy surface after CV measurement show that Mn particles in the vicinity of the surface remain intact (**Fig. 5**). In addition, we fabricated a LIB using $\text{Li}(\text{NiCoMn})\text{O}_2$ for the positive electrode and graphite for the negative electrode, and after 250 cycles at 45 degrees, we confirmed whether Mn was deposited on the negative electrode by ICP analysis (**Table 2**). This result also shows no difference in the amount of Mn detected between 1085 and 3003, indicating that they can be used as current collectors without any problems.

Thus, when a potential of ~ 4 V is applied to the current collector during the first charge, a passive film is instantly formed. Furthermore, by gradually losing the active site existing on the outermost surface, it can be stably used as a metal even in a high potential environment.

3.2 Using in imide salts and negative electrodes

As mentioned above, Al foil can be stably used as a positive electrode current collector depending on the film, but a stable film may not be formed depending on the electrolyte used. Salts such as lithium bis (trifluoromethanesulfonyl) imide (LiTFSI), are sometimes used instead of fluoride electrolytes. LiTFSI exhibits excellent heat, moisture, and chemical stability, and it might improve the properties of the cell (e.g. cycle life, high power). However, literature reports suggest that the positive electrode current collector may corrode when solely imide salts are used as electrolytes⁶. It is presumed that imide salts are very stable, fluorine is not desorbed, and an AlF_3 passive coating is not formed. Therefore, LiTFSI should be mixed with an electrolyte capable of forming a passive film (such as LiPF_6) or used at high concentrations.

Although Al foil is basically a current collector for positive electrodes, it can also be used as a current collector for negative electrodes when lithium titanate (LTO) is used as the active material. Al is not applied in graphite-based negative electrode current collectors, since the reaction potential of graphite-Li is close to that of Al-Li. The reaction potential of Al and Li is approximately 0.5 V vs Li; thus, when used as a

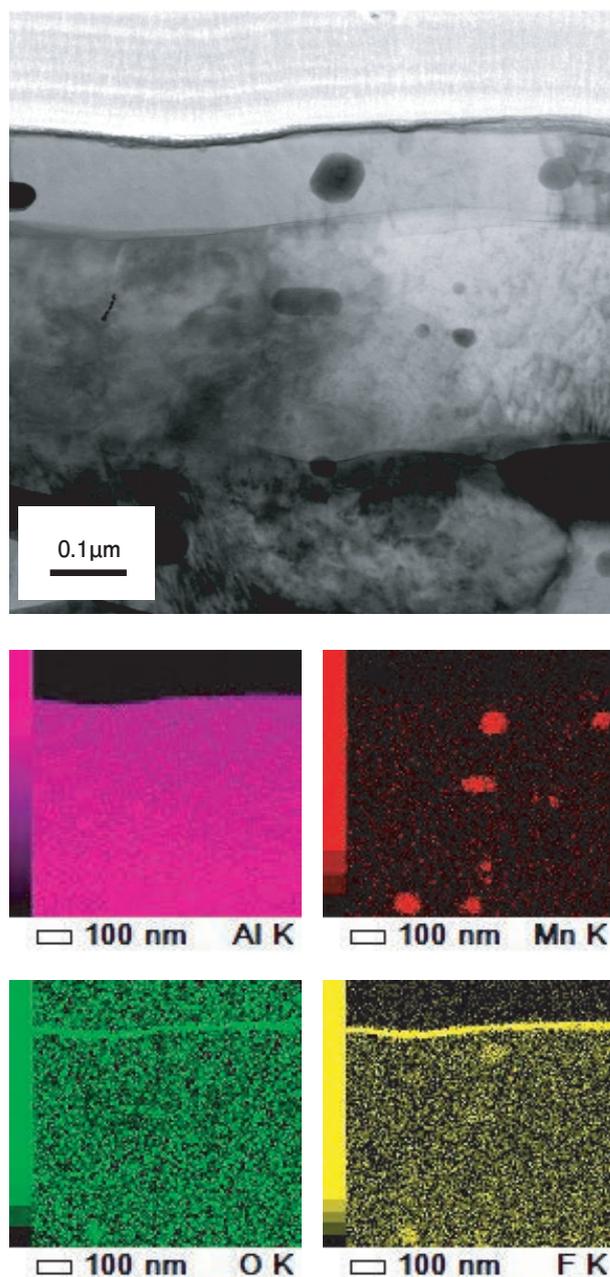


Fig. 5 Cross-sectional TEM image and EDS of 3003 after CV.

Table 2 ICP quantitative analysis result of negative electrode after 250 cycles at 45 degrees ($\mu\text{g}/\text{cm}^2$).

Alloy	Li	Mn	Fe
1085	75.6	0.24	0.14
3003	70.4	0.27	0.14

negative electrode, Al and Li are easily alloyed and lose their function as a current collector due to embrittlement. Since the redox potential of LTO is 1.5 V vs. Li, which is higher than the doping potential of Al, Al and Li are not alloyed at this potential and can be appropriately used as a current collector.

4. Conclusions

The composition and the characteristics of Al foils, which are used as current collectors at the electrodes in LIBs, are described. There are a wide variety of alloys and manufacturing methods, each with their respective characteristics. It is suggested that high-capacity and stable batteries can be produced by selecting an appropriate current collector with the desired mechanical and surface characteristics.

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