Fabrication of high-strength composite metal thin foil for future batteries using electroplating

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As the energy density of the secondary battery gets higher, the thickness of copper foil as an anode current collector material in the battery is dramatically decreasing. In consequence, many types of mechanical failures of copper foils or current collectors have been reported to take place during battery manufacturing processes or in use and have become a critical issue to be prevented. An electroplating technology is suggested to fabricate a copper-nickel or nickel-copper double-layered foil with excellent mechanical properties that can replace the conventional copper foil in the presentation. The electroplating processes were developed to control the microstructure of each metal layer and thereby minimize the degradation of mechanical strength and electrical resistivity after annealing at 190 °C for 10 min as a thermal load that is expected to be applied during manufacturing processes and in use of batteries. As a result, one copper and two nickel electroplating processes were selected. The copper electroplating led to a self-annealing phenomenon of copper by using the electroplating solution containing the additives as a suppressor and an accelerator, resulting in the microstructure of large grains after annealing. The nickel processes produced the foil with a columnar grain structure or a nano-crystalline structure by using two different kinds of electroplating solutions. By combining the copper process with either of two nickel processes and alternating the sequence, 4 kinds of 10 micrometer-thick copper-nickel or nickel-copper double-layered foils were fabricated. The mechanical and electrical properties and grain structures of the foils were characterized before and after annealing using the uniaxial tension test, the 4-point probe method, and an SEM-based and a TEM-based crystallographic orientation mapping technique. The results show that the nano-crystalline nickel is thermally stable and provides the double-layered foil with better mechanical and electrical properties after annealing than one with the columnar structure. The doubled-layered foil with the nano-crystalline nickel layer has about 3 times higher tensile strength than the copper single-layered foil and a moderate elongation and electrical resistivity after annealing. In addition, considering that various kinds of chemicals are being developed as an electrolyte for future batteries, our electroplating technology is expected to be a promising method to produce a current collector which is less reactive with a given electrolyte.

Keywords: *composite metal thin foil, mechanical strength, electroplating, annealing, microstructure*

1. Introduction

As the energy density of secondary battery rises, the thickness of the current collector in battery is rapidly decreasing. Since the anode and cathode current collectors mechanically support the battery structure that is composed of a liquid electrolyte and two porous electrode materials, decrease in thickness of current collector material is likely to cause mechanical failures during battery manufacturing processes or the use of battery.

Copper foils are the major anodic current collector material for lithium-ion batteries [1]. They are mainly produced through electroplating technique due to its low manufacturing cost and the ease to produce thinner foils. However, as the thickness of foil has decreased to less 10 μm, foils have become vulnerable to mechanical failures such as wrinkling and tearing during battery manufacturing the processes. Therefore, there are extensive efforts to improve the mechanical properties of copper foil for preventing failures.

In this study, we developed the electroplating techniques to control the microstructure of foil and to produce a high-strength composite foil. The foil consists of the copper and nickel layer and the two layers are intended to supplement the material properties of each layer. The copper layer was designed to have a grain structure for minimizing electrical resistivity and the nickel layer for maximizing mechanical strength. The grain structures of the fabricated composite foils were measured using an electron backscatter diffraction (EBSD) technique and were compared with the mechanical and electrical properties of the foils that were evaluated using the uniaxial tensile testing and the 4-poin probe method.

2. Experimental

2.1 Electroplating process conditions

A room-temperature Cu electroplating process was designed to maximize the grain size and to minimize the electrical resistivity after heat treatment [2]. The Cu electroplating electrolyte contains 0.5 M $CuSO_4 \cdot 5H_2O$, 1 M H_2SO_4, 1 mM HCl, 0.1 mM PEG (polyethylene glycol) as a suppressor and 50 μM SPS (bis- (3-sodiumsulfopropyl) disulfide) as an accelerator. Two Ni electroplating processes were developed to obtain different microstructures. One is the process using only SDS (sodium dodecyl sulfate) as an additive for a coarse grain structure, and the other the process using SDS and saccharin for a nano-crystalline structure. The Ni electroplating was conducted at 50 ℃. By combining the Cu electroplating process with the two Ni processes, 4 kinds of 10 μm-thick composite foils were fabricated.

The electroplating for both the single-material and composite foils was carried out on the 304 stainless steel plate as a substrate and the as-deposited films were detached from the substrate after electroplating. The detached foils were annealed at 190 ℃ for 10 minutes mimicking a thermal load that current collector material is expected to experience during the battery manufacturing processes in industry.

2.2 Measurement of microstructure

The cross-sectional microstructures of the as-electroplated and annealed foils were measured using an EBSD system where EDAX Pegasus with Hikari EBSD camera is attached to an FE-SEM (FEI Inspect F50). A

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transmission electron microscope (TEM) was used to observe the nanometer-sized grain structure that is barely measured using EBSD.

2.3 Evaluation of material properties

The mechanical properties of the foils were evaluated using a tensile testing system that was specially designed for thin-foil samples. The tensile strength and elongation of the foils were extracted from the stress-strain curve after tensile test. The electrical sheet resistances of the foils were measured using a 4-point probe system and the resistivity was calculated using the measured sheet resistance and the foil thickness.

3. Results and Discussion

3.1 *Grain structures and mechanical properties of single material foils*

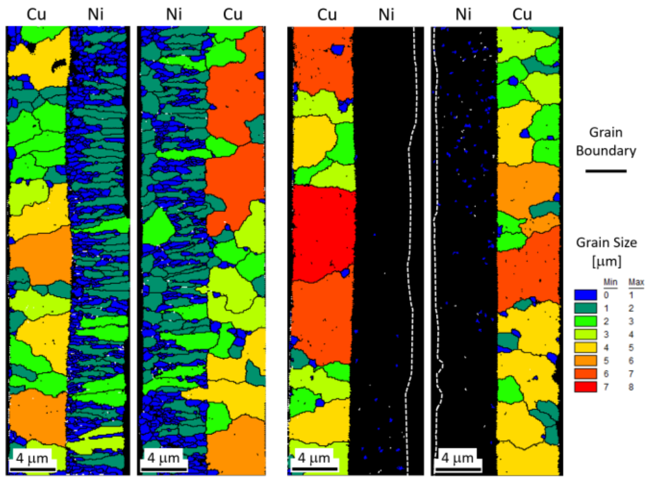
The EBSD measurement indicated that the as-deposited 10 μm-thick Cu foil consisted of the nanocrystalline grains and the recrystallized grains by self-annealing. Grain growth and abnormal grain growth during annealing led to large grains with a high fraction of twin boundaries. The tensile strength of the Cu foil dramatically decreases from 60.8 to 28.2 kgf/mm^2 after annealing, while the elongation increases from 3.0 to 7.1 % after annealing. The electrical resistivity after annealing is 1.9 μΩcm.

The microstructures of the Ni foils depended on the additive in the electroplating solution. SDS led to a columnar grain structure where the grains occupy almost the thickness of the foil, while SDS and saccharin a nanocrystalline structure where the grain size was about 70 nm. The changes in grain size and material properties of the Ni foils were inconsiderable after annealing, compared with those of the Cu foil. Notably, there was little change in grain size and material properties for the Ni foil electroplated using SDS and saccharin as additives.

3.2 *Grain structures and mechanical properties of composite foils*

Figure 1 and Table 1 shows the microstructures and material properties of the 10 μm-thick Cu-Ni or Ni-Cu composite foils after annealing. As shown in Fig.1, the Cu layers of all composite foils consist of huge grains occupying almost the entire thickness by grain growth and abnormal grain growth. On the other hand, there is a clear difference in microstructure between the Ni layers. In the composite foils where the Ni layer was deposited using only SDS, the large columnar grains are dominant. The use of SDS and saccharin resulted in the Ni foil with the nanocrystalline structure even after annealing. Although it caused an increase in electrical resistivity, the nanocrystalline Ni layer led to the highest tensile strength and moderate elongation (Table 1).

The annealed composite foil with the nanocrystalline Ni layer deposited using SDS and saccharin has 3 times higher strength than the annealed single copper foil. This result indicates that the composite foil with the nano-crystalline Ni layer is theoretically able to bear about three times higher mechanical load during battery manufacturing processes than the Cu foil. In addition, our composite foil is expected to have a high resistance to degradation of material properties or reaction with neighboring materials by thermal loads that current collect material goes through during battery manufacturing processes and in use.



(a) (b)

Fig. 1. Cross-sectional microstructures of 10 μm-thick composite foils in which the Ni layer has (a) columnar or (b) nanocrystalline grain structure, after annealing at 190 ℃ for 10 min. Black line and color inside foil indicate grain boundary (twin boundaries are excluded) and grain size, respectively. White dotted line in (b) denotes free surface of Ni layer. Black area in (b) indicates nanocrystalline Ni layer where EBSD intensity is too low to index the crystal orientation.

Table 1. Mechanical and electrical properties of 10 μm-thick composite foils after annealing.

Foil type	Tensile Strength [kgf/mm^2]	Elonga-tion [%]	Electrical Resistivity [μΩm]
Composite 1 : Cu - Ni (columnar)	52.1	3.6	2.6
Composite 2 : Ni (columnar) - Cu	57.3	2.7	2.8
Composite 3 : Cu - Ni (nanocrystalline)	87.8	3.3	3.0
Composite 4 : Ni (nanocrystalline) - Cu	82.4	3.4	3.1

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