Effect of Plasma Treatment on Copper Electrode to Enhance the Interfacial Stability for Anode – free Batteries Application

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Recently, various anode materials candidates have been proposed for Lithium (Li) secondary batteries. Among them, the use of Li metal as an anode material is being studied as a next-generation anode material. Li metal has the lowest oxidation/reduction potential of -3.04 V, a high theoretical capacity (3,860 mAh/g), and low density per unit which results in a reduction battery volume. However, Li metal has several issues; i) high reactivity electrolytes based on organic solvents, ii) growth of Li dendrites during charge and discharge, and iii) capacity loss due to the irreversible of Li-ions. Especially, an excessive amount of Li metal exacerbates these issues and leads to critical cause on Li metal batteries explosions. Therefore, it is essential to develop electrode improved the interface stability which plays an important role to promote the uniform Li-ion deposition and stripping. Meanwhile, anode-free batteries have considered as the spotlighted candidates alleviating the risk of Li metal battery explosion issues because it is possible to reduce the battery volume and operated by only Li-ion instead of Li metal. However, the use of a copper foil only still not ensure the interfacial stability due to Li dendrite growth. Therefore, researchers are investigating various chemical methods, such as structural modifications, artificial solid-electrolyte interphase (SEI) layer formation, and additive to add electrolyte, to address this challenge. In this study, we made use of low-temperature plasma treatment to stabilize the interfacial SEI thin film on the copper current collector through the control of process variables such as plasma power, pressure, and precursor gases. The electrochemical properties of the copper electrode with improved interfacial stability were analyzed by Cyclic Voltammetry (CV), Chronoamperometry (CA), and Impedance. Our modified copper interface with plasma treatment opens a new direction for implementing organic based batteries. This work provides a universal strategy to design for anode-free batteries application without a Li metal anode material.

Keywords: *Anode-free battery, Copper current collector, Solid-electrolyte interface thin film, Plasma treatment, Interfacial stability.*

1. Introduction

Lithium (Li) secondary batteries (LSB) are used in various fields such as portable devices, laptops, electric vehicles (EV), and energy storage devices (ESS). Particularly, the expansion of the EV market requires LSB to have improved capacity and power characteristics compared to conventional commercialized Li-ion batteries (LIB)[1,2)]. Therefore, research on next-generation secondary batteries that will satisfy high capacity and high-power properties by improving battery performance has been actively studied[3)].

Advantage of Li metal, which is currently attracting attention as an anode for next- generation secondary batteries such as Li-sulfur batteries or Li-air batteries, include high theoretical capacity (-3,680 mAh/g), lowest oxidation/reduction potential (-3.04 V vs SHE), and low material density (0.534 g/cm^3)[4)]. However, Li metal has not been generally considered as an anode because of Li dendritic growth resulting in various stability problems and degradation of battery performance[5, 6)]. Among the various methods to overcome inherent limitations, the adoption of the anode-free battery is a promising new advanced rechargeable battery, that has drawn attention with respect to high energy storage systems because of the complete removal of active anode (Li metal) material during assembly. Furthermore, the anode-free battery is easy to fabricate, can provide high energy density, is safer to handle during fabrication, and is low-cost[7)]. However, the electrolyte in anode-free battery is decomposed for the formation of the solid electrolyte interphase (SEI) layer during cycling due to the unstable copper anode surface, resulting in a rapid capacity decrease[8,9)].

In this study, we made use of low-temperature oxygen plasma treatment to form the copper oxide artificial SEI thin film on the copper current collector through the control of process variables such as plasma power, pressure, and precursor gases. The copper oxide formed on the copper anode was proposed as the current collector for the other anode due to their superior lithiophilicity for facilitating the Li nucleation. Moreover, the thin film produced via the plasma process exhibits significantly higher purity compared to that obtained through the liquid-phase chemical method. It also demonstrates a substantial difference in processing time and incurs significantly lower production costs[11, 12)].

2. Experiment

To demonstrate Cu_xO_x structure, the oxygen plasma was discharged on Cu foil by inductively coupled plasma (ICP) process at room temperature for 30 s under the optimized condition with 20 sccm of O_2 gas flow and 200 W of plasma power. The surface morphology of Cu_xO_x structures were investigated via field emission-scanning electron microscope (FE-SEM). In addition, X-ray diffraction (XRD) analysis was conducted to define the crystallinity of Cu_xO_x structure

3. Results and discussion

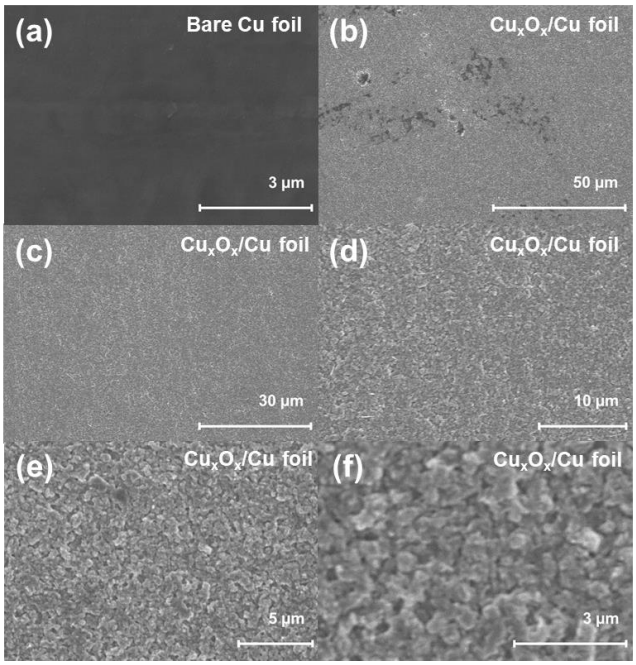

Figure 1. FE-SEM image of bare Cu and Cu_xO_x/Cu foil. (a) Bare Cu foil surface. (b-f) Cu_xO_x/Cu foil surface under the different magnification (x1.0 k ~ x15.0 k).

Copper oxide was manufactured on bare Cu foil using oxygen plasma and observed using FE-SEM. Bare Cu foil shows a relatively smooth surface (Figure 1a). Normally, these kinds of smooth surfaces have been reported which cannot serve as nuclei, results in uneven surface of Li deposition and the growth of Li dendrites during charge/discharge[10]. In contrast, the surface of copper foil treated with oxygen plasma was observed to be rough due to the formation of copper oxide (Cu_xO_x; CuO, Cu_2O, CuO_2). A color change from dark black (Figure 1a) to grey (Figures b-f) was noticed after the formation of copper oxide layer on the top of Cu foil. It means the oxygen plasma treatment have promising advantage to enhance the surface area of anode electrode materials which offer various nucleation site to be restrained the growth of Li dendrite.

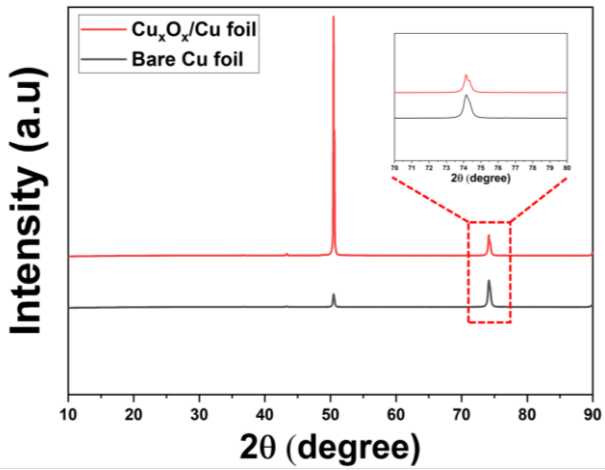

Figure 2. XRD patterns of Cu_xO_x/Cu foil at the 10 to 90 degrees.

The XRD patterns show the crystal phase composed of Cu, CuO, Cu_2O, and CuO_2 on oxygen plasma treated Cu foil. as shown in Figure 2. In particular, as copper oxide was formed, the intensity of the bare Cu foil increased rapidly, and two sharp peaks were observed. The absence of other impurity peaks indicates that the sample is very high purity.

4. Conclusions

In conclusion, oxygen plasma treatment of the copper electrode not only suppresses the growth of lithium dendrites through its roughened surface but also allows for rapid surface treatment, resulting in the formation of a high-purity copper oxide crystal thin film. Furthermore, the SEI layer, which tends to decompose during battery cycling and is challenging in anode-free batteries, can be transformed into a dense, continuous thin film through plasma treatment.

Acknowledgments

The authors gratefully acknowledge the extended support provided to this work by the Korea Institute of Industrial Technology (KITECH) internal project (EH230002)

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