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Si film electrodes containing surface-modified Cu current collectors prepared by a low temperature oxidation-reduction process

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ABSTRACT

A low-temperature oxidation-reduction process was used to modify the surface of a Cu current collector (foil) for a Si film electrode. The surfaces of the modified Cu foils were investigated under various oxidation-reduction conditions, and the electrochemical properties of Si film electrodes containing the surface modified foils were evaluated. Various nanostructures were found to have formed on the surface; for example, $Cu(OH)_2$ needles, CuO flowers, and CuO plates formed on Cu-foil surfaces oxidized at 313 K for 1, 10, and 30 min, respectively. Furthermore, these nanostructures were transformed to coral-like Cu_2O structures after reduction at 673 K. The amount of Cu_2O and the surface roughness decreased on increasing reduction time. The Si film electrode containing a Cu foil reduced for 6 h showed the best electrochemical performance (83.5% of the initial efficiency and 74.8% of capacity retention) due to the small amount of Cu_2O and the formation of coral-like structures.

1. Introduction

In recent years, increasing interest in flexible electronics has increased demand for flexible rechargeable lithium (ion) batteries that are suitable for use in products such as smart watches, flexible displays, and other wearable electronics [1]. Many efforts are underway to fabricate flexible power sources by using free-standing electrodes and the high-elastic current collectors such as metal alloys and carbons [2–4].

Meanwhile, the realization of thin batteries at micro or millimeter scale allows the development of more flexible batteries; however, thinner electrodes have lower capacities (due to the thinner cathode and anode). In addition, commercial carbon (graphite) anodes have relatively low capacities (372 mAh/g), limiting their applications in thin lithium batteries. To compensate for the decreased capacity caused by a thinner battery, new anode materials with high capacities are required to replace conventional carbon-based anodes.

Among the anode materials (Si, Sn, Al, and Ge), Si is an attractive material because of its high theoretical capacity (3579 mAh/g based on the formation of a $Li_{15}Si_4$ phase) at room temperature [5]. However, the formation-decomposition of the $Li_{15}Si_4$ phase during the charge-discharge process leads to a large volume changes (~300%), which result in a low initial efficiency and rapid capacity fade after several charge-discharge cycles.

Over the past decade, improved electrochemical properties of Si film electrodes have been reported by using surface-modified Cu current collectors (foils) prepared by various methods, including mechanical grinding, electrochemical etching, and the insertion of an intermediate layer [6–13]. A roughened surface fabricated by these methods improved adhesion between the Si film and the current collector, resulting in enhanced structural stability during electrochemical reactions. However, these approaches have a limited effect on the surface morphology at the micro scale; for example, the formation of scratches and grains.

Herein, an oxidation-reduction process was used to modify the surface morphology of the Cu current collector at the nanoscale. Oxidation processes led to the formation of various oxidized

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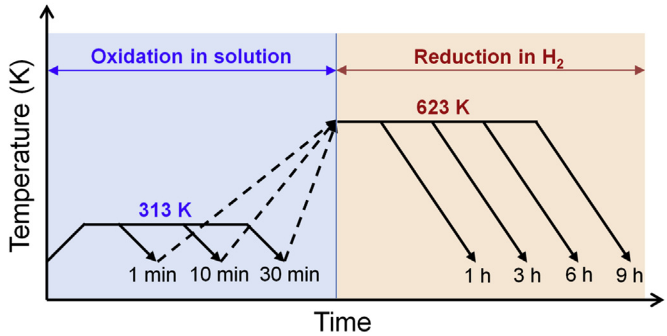

Fig. 1. Schematic diagram of oxidation-reduction process showing temperatures and holding times for modification of surface morphology of Cu current collector (foil).

nanostructures, such as nanoflowers, nanowires, and nanoplates [14,15], and the reduction process induced a deoxidized rough surface that could be controlled by altering the reduction temperature and the holding time. In our previous studies [16,17], Cu oxide nanostructures such as nanoflowers and nanoplates were found to form at high oxidation temperatures (373 K), and the electrochemical properties of Si films deposited on a Cu current collector reduced at 673 K were investigated. However, the surfaces of these foils were too smooth, and Cu oxide remained after reduction, leading to unsatisfactory electrochemical results, i.e., a high irreversible capacity during the initial cycle and a poor cycle performance.

In this work, we report the various nanostructures formed on Cu current collectors after low temperature oxidation-reduction process at 313 and 623 K, respectively, and the changes in surface morphology under different reduction conditions. In addition, the electrochemical properties of Si film electrodes with the surface-modified Cu current collectors were examined and analyzed on the basis of surface roughness and the quantity of remaining Cu oxide.

2. Experimental procedure

Fig. 1 shows a schematic diagram of the oxidation and reduction processes that induce surface modification of the Cu current collectors. A 25-μm thick Cu foil was used as the current collector for a Si film electrode. For the surface oxidation of the Cu foil, a prepared solution of 5 M NaOH + 1 M $(NH_4)_2S_2O_8$ was poured into a steel autoclave containing a Cu foil disk (5 cm in diameter). The sealed autoclave was maintained at 313 K for 1, 10, and 30 min. Then, it was cooled slowly to room temperature, as shown in Fig. 1. The colors of the oxidized Cu foils were blue, dark blue, and black after oxidation at 1, 10, and 30 min, respectively. The expected oxidation reactions are as follows [18]:

$$Cu + 4OH^- + (NH_4)_2S_2O_8 \rightarrow Cu(OH)_2 + 2SO_4^{2-} + 2NH_3 \uparrow + 2H_2O \quad (1)$$

$$Cu(OH)_2 \rightarrow CuO + H_2O \quad (2)$$

After preoxidation, the foils were cleaned by sonication, removing any nanostructures weakly bound to the surface of the Cu foil. Subsequently, preoxidized Cu foils were placed in a furnace and annealed at 623 K for 1, 3, 6, and 9 h under a hydrogen atmosphere (50 SCCM). Prior to reduction, a preliminary experiment was conducted between 573 and 673 K for 30 min, to find the most suitable reduction temperature. The expected reduction reactions of the preoxidized Cu foils are as follows [19]:

$$2CuO + H_2 \rightarrow Cu_2O + H_2O \quad (3)$$

$$Cu_2O + H_2 \rightarrow 2Cu + H_2O \quad (4)$$

Si films were deposited using a DC magnetron sputtering system installed in a glove box, and the films were grown in the vacuum chamber under a pressure of 5×10^{-3} torr under an argon atmosphere. The thickness of the Si film was 560 nm, as measured by an Alpha Step profiler (Alphastep, KLA Tencor, USA). The

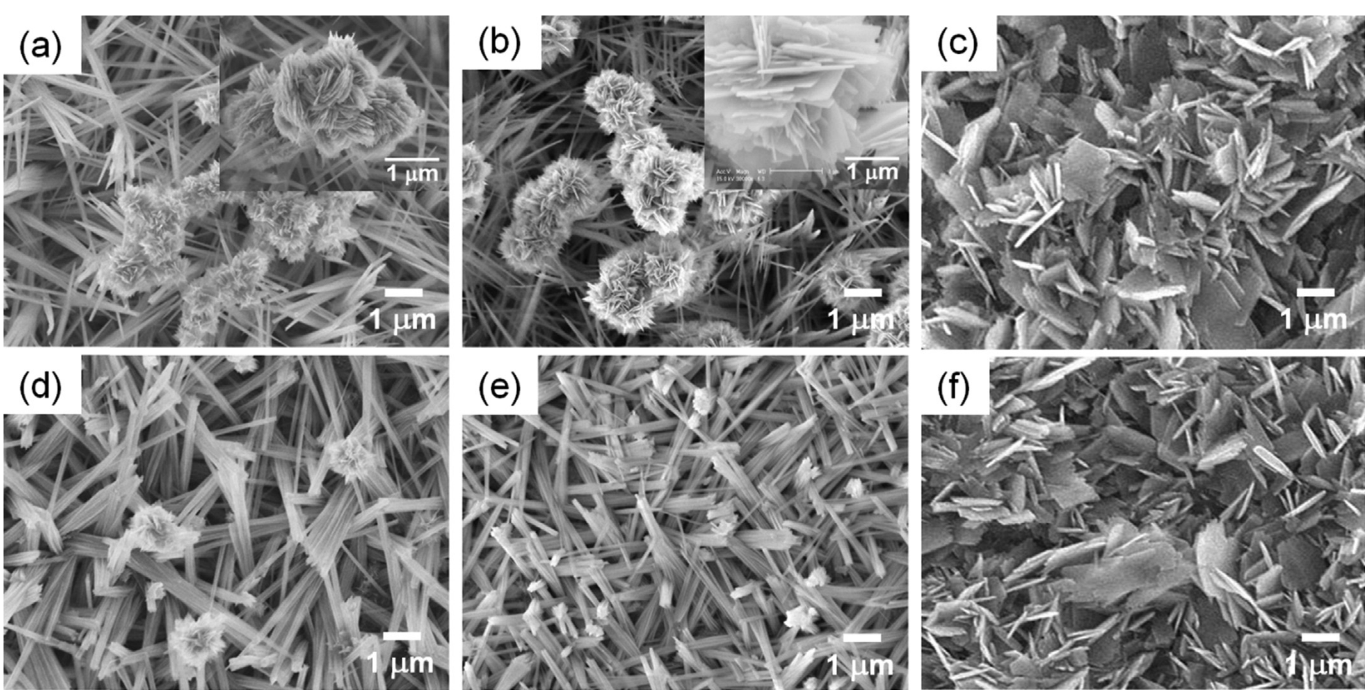

Fig. 2. FE-SEM images of oxidized Cu foils before and after sonication: (a), (d) 1, (b), (e) 10, and (c), (f) 30 min. Magnified images of nanoflower-like structures are shown in insets of subfigures (a) and (b).