



# Beyond theoretical capacity in Cu-based integrated anode: Insight into the structural evolution of CuO



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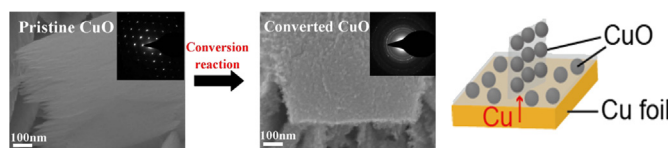
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## HIGHLIGHTS

- CuO/Cu integrated anodes were made with CuO nanoparticle-sheets on Cu collector.
- Integrated anodes showed higher capacity beyond the theoretical capacity of CuO.
- The oxidation of Cu current collector into CuO favors the higher capacity.
- Designed in situ chemical and electrochemical activating integrated electrode system.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 18 October 2014

Received in revised form

30 October 2014

Accepted 1 November 2014

Available online 3 November 2014

### Keywords:

Integrated electrode  
Lithium ion battery  
Copper current collector  
Oxidation reaction  
Additional capacity

## ABSTRACT

An excellent CuO/Cu integrated anode with CuO nanoparticle-aggregated microsheets on Cu current collector showed higher capacity beyond the theoretical capacity of CuO. The reoxidation of Cu including converted Cu nanoparticles and Cu current collector into CuO guaranteed the highly reversible conversion reaction and high capacity. The combined current ex-situ methods of XRD, SEM and TEM were used to find the origin of the additional capacity by examining the structural evolution and phase transformation of CuO/Cu integrated anode during electrochemical cycling. After 110 cycles, the discharge capacity of CuO/Cu integrated anode retained a large value of 706 mAh g<sup>-1</sup>, which is beyond the theoretical capacity of CuO materials (674 mAh g<sup>-1</sup>). The specific electrode configuration and the release of Cu from integrated Cu current collector made these CuO/Cu electrodes maintain high capacity and cycling stability. The present research demonstrates a protocol for the design of high-performance anode structure: in situ chemical and electrochemical activating integrated electrode system.

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## 1. Introduction

In advanced high-energy density battery systems, the fundamental mechanism for energy storage is the insertion of secondary species into solid electrodes, as opposed to the surface reactions occurring in many traditional electrochemical systems [1–3].

Anode materials that react with lithium through both alloying and conversion mechanisms often exhibit a much higher specific capacity than that of the present intercalation electrode materials [4–6]. Understanding how the lithium species interact with active materials and change the phase or structure of the original electrode materials is vital for enhancing the performances of lithium ion batteries [1]. For a better understanding of the reaction mechanism, all the components in a battery system, including both active materials, electrolyte and current collector, have to be monitored under real operating conditions. Copper foil is the most commonly used current collector, which holds active anode

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materials for lithium ion batteries [7–9]. The integrated active-materials/Cu-current-collector electrode can provide an available platform to study the actual reaction mechanism of anode system because the integrated anode has two main advantages: (1) the absence of both binders and carbon black is favorable for the direct study of their morphology and phase evolution upon electrochemical cycling (2) the integrated anode on Cu foil can effectively enhance the electronic conductivity, and shorten electron/ion transfer/diffusion length [10,11]. In order to utilize these advantages, the integrated CuO/Cu anode was designed as the model system to study the conversion mechanism of CuO electrode materials.

In recent years, much research interest has been focused on the investigation of conversion anode materials [4]. Among various metal oxides used as conversion anode materials, CuO is well known in the battery community because it acts as a positive electrode material in primary CuO/Li cells available in the market [12–15]. Many efforts have been made to the study of the conversion mechanism of CuO nanomaterials by various in-situ and ex-situ techniques, such as transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), X-ray absorption spectroscopy (XAS), and X-ray diffraction (XRD) [16–20]. The reduction reaction from CuO through the intermediate phases of  $\text{Li}_x\text{CuO}$  and  $\text{Cu}_2\text{O}$ , and finally to metal Cu, has been confirmed [21–23]. The new findings on the conversion reaction of CuO anodes are still progressing, for example, the existence of Cu long-range diffusion pathway within CuO anodes was reported, which is different from reported lithium diffusion pathway [24]. Recently, aging studies of lithium ion batteries have been given a lot of attention on their degradation using Cu as current collectors. The presence of lithium in the Cu current collector beyond the active materials has been confirmed by neutron depth profiling [25], and the lithium in current collector can lead to the degradation of its thermal and electrical behaviors. However, in our designed CuO/Cu integrated electrode, the involved conversion mechanism of CuO may warrant the conversion reaction occurring on Cu current collector, which further promotes the reversible reaction of  $\text{CuO} \leftrightarrow \text{Cu}$  at nanoscale in a more efficient way. In order to better understand the real conversion mechanism of CuO on Cu foil, the present integrated CuO/Cu anode, which was prepared through chemical and electrochemical oxidation of Cu current collector, was used to study the conversion reaction mechanism of CuO anode materials.

Herein, we designed a high-performance CuO/Cu anode with CuO nanoparticle-aggregated microsheets on the Cu current collector via the chemical and electrochemical oxidation reactions on Cu foil at nanoscale. The specific electrode configuration and the oxidation of Cu from Cu current collector can maintain the high capacity and cycling stability of these CuO/Cu anodes. For the fabrication of this integrated anode system, a room temperature aqueous route was created to oxidize Cu foil surface with  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  to form electroactive CuO-microsheet thin films; CuO nanoparticle-aggregated microsheets on Cu foil were formed in-situ by the electrochemical redox reaction in battery system. Our current ex-situ observations indicated that in the first charge/discharge reaction, lithium conversion was followed by the transformation from single crystal CuO microsheets to CuO nanoparticles. The reoxidation of Cu including the converted Cu nanoparticles and Cu current collector into CuO has been proven, which favors the highly reversible conversion reaction and high capacity beyond the theoretical value of CuO anode. The superior cycling performances can be attributed to the structural stability of CuO nanoparticles aggregated into sheet-like structures and the oxidation of partial Cu current collector.

## 2. Experimental

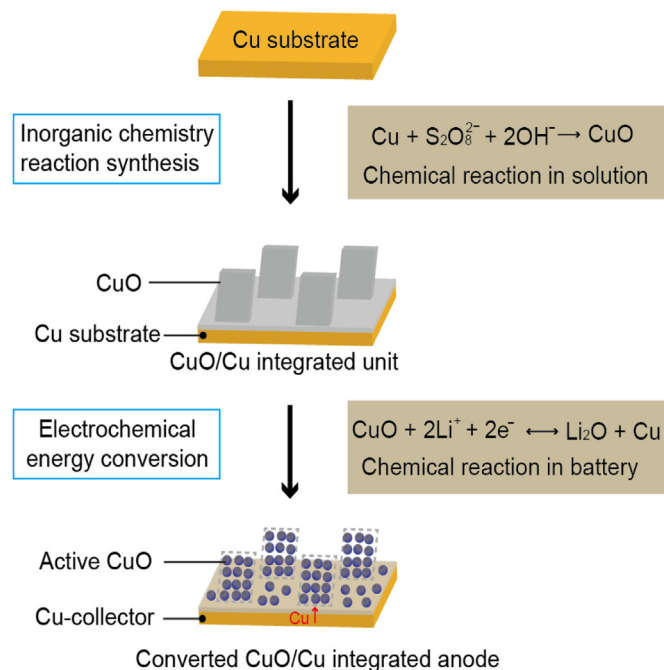
### 2.1. Synthesis of CuO microsheet array

Firstly, to remove surface impurities, Cu substrates were carefully cleaned with absolute alcohol and deionized water in an ultrasound bath. In our designed procedure, CuO grown on the surface of Cu substrate can be obtained by oxidizing Cu foil at room temperature in a mixture of aqueous solution of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  (0.15 M) and NaOH (2 M). After Cu foil was immersed into the clear colorless solution, the color of Cu foil rapidly turned to blue after seconds, indicating the growth of  $\text{Cu}(\text{OH})_2$  on the surface of Cu foil. After 40 h of reaction at room temperature, blue Cu foil was gradually transformed to black color. The presence of black color on Cu foil confirmed that CuO products were successfully grown on the Cu foil.

### 2.2. Electrochemical cell test

Cu foil with CuO grown on its surface was cut into discs, which were used directly as the working electrode without the use of binders and additives. Electrochemical tests were carried out by using coin type (CR2025) testing cells. Lithium metal disc served as the counter and reference electrode, a Celgard 2400 polypropylene membrane was used as separator, the electrolyte was 1 M  $\text{LiPF}_6$  in 1:1:1 mixture of ethylene carbonate, dimethyl carbonate, and diethyl carbonate. The CuO mass in each electrode was about 1 mg.

To determine the exact mass of CuO on Cu foil, the integrated electrodes were placed into 0.2 M  $\text{H}_2\text{SO}_4$  aqueous solution to remove the surface CuO. Subsequently, the copper foils were washed successively in water and ethanol, dried in a vacuum, and weighed. The mass of active CuO materials can be calculated



**Fig. 1.** Schematic representation of the synthesis of integrated CuO/Cu anode via chemical and electrochemical oxidation of the Cu current collector. The conversion reactions occurred within the limit of initial CuO microsheets, which include electrochemically driven nanocrystallization of CuO microsheets to CuO nanoparticles. During the discharge/charge process, the release of Cu from the current collector can maintain high capacity of CuO anode in the designed integrated anode system.

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