

# Lithium insertion in naturally surface-oxidized copper

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## Abstract

In order to investigate the effect of copper oxide naturally formed on copper as the common anode current collector and as an electrode additive, the electrochemical behavior of lithium insertion in three naturally surface-oxidized copper powders and one copper foil was studied. Powder X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), particle size distribution measurement, galvanostatic cell cycling and cyclic voltammetry were employed for structural and electrochemical characterization. Although the XRD analysis can only detect the presence of pure Cu phase, the XPS analysis reveals clearly the presence of a CuO layer on the copper powders or the copper foil. The thickness of this CuO layer is estimated as thick as 147 nm. The lithiation capacity associated with this CuO layer can reach 48 mAh/g for copper powders but only 1 mAh/g for the foil. This small capacity, or  $5.2 \times 10^{-3}$  mAh/cm<sup>2</sup> per unit area of copper foil, is fortunately negligible compared with that of a common anode material in a lithium-ion cell; while the capacity associated with this CuO layer must be taken into account when using a copper powder as an additive to improve the cycling stability.

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## 1. Introduction

In a lithium ion cell, except for the three main components namely a positive electrode, a negative electrode and an electrolyte, two current collectors are also very important for the cell performance but they are often ignored. A basic requirement for an eligible current collector is its electrochemical stability against the contacting electrode (either anode or cathode) material and electrolyte during charge–discharge process. In the state-of-the-art lithium-ion technology, foils or screens of aluminum and copper are most commonly used as the current collectors for positive and negative electrodes, respectively. The use of aluminum current collector is based on the fact that electro-polished aluminum is found stable in the potential range between 1 V and 5.5 V or higher versus Li/Li<sup>+</sup> in LiPF<sub>6</sub> electrolyte solution [1] although it has pitting corrosion problem in the electrolyte of other lithium salts such as Li(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>N [1–5]. To the contrary, copper is found electrochemically stable in the low potential range below 3.4 V versus Li/Li<sup>+</sup> except that it experiences environmental cracking under specific metallurgical conditions at or near the lithium potential [6]. It may be oxi-

dized above 3.4 V versus Li/Li<sup>+</sup>, especially at the presence of small amount of impurities HF and H<sub>2</sub>O [7]. Therefore, copper is regarded as an inert current collector material for anodes of lithium-ion cells.

On the other hand, copper has been found to be able to alloy with lithium to form Cu–18 at.% Li [8,9], suggesting the possibility of lithium insertion into copper. Furthermore, during the storage and transportation under ambient atmosphere, surface oxidation may take place on copper foils or screens, leaving a copper oxide (Cu<sub>x</sub>O) coating on the exposed parts. Tarascon and co-workers [10,11] reported that Cu<sub>x</sub>O electrode has a reversible capacity of about 400 mAh/g in the 3–0.02 V range, with a first lithiation capacity of 850 mAh/g for CuO and 600 mAh/g for Cu<sub>2</sub>O. Such significant irreversible capacity losses imply that, in addition to the formation of well-known solid-electrolyte-interface (SEI) layer on the carbonaceous particles, the first-cycle irreversible capacity loss of a lithium-ion cell should be partially attributed to the lithium insertion process in the surface CuO coating. Besides, since copper powder is sometimes used as an additive to improve the cycling stability of anode materials [12,13], the electrochemical capacity associated with this CuO layer should be taken into account.

This study is aimed at estimating the influence of copper oxide coating out of natural surface-oxidation on the copper current collector or copper additive and also examining

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the possibility of forming Cu–Li alloy under the conditions of lithium-ion cells. For these purposes, we purchased commercial high-purity copper powders to fabricate copper electrode laminate. Surprisingly, a copper oxide coating has been found to exist on the particle surface of the “high-purity” graded copper powders. With these copper powders and foil as electrode, we have investigated the lithium insertion and extraction processes in them.

## 2. Experimental aspects

Three commercial copper powders, graded 99.7% (2N), 99.99% (4N) and 99.999% (5N) were brought from Shanghai Reagent Co. Ltd, Guangfu Fine Chemical Institute (Tianjin, China), and Delan Fine Chemical Factory (Tianjin, China), respectively. Copper foil (99.99%, 22  $\mu\text{m}$  in thickness) was bought from Tongling Copper Foil Factory (Anhui, China). They were coded in this study as 2N-Cu, 4N-Cu, 5N-Cu and f-Cu, respectively. Three electrode laminates were prepared by casting slurries consisting of the copper powders (96 wt.%) and poly(vinylidene fluoride) (PVDF) (4 wt.%) dispersed in 1-methyl-2-pyrrolidinone (NMP) onto the copper foil. The electrodes were then dried at 80 °C for 2 h and calendared to obtain a laminate porosity between 60% and 70%.

Copper/Li coin-cells (2032 size) were made with 1 M  $\text{LiPF}_6$  in ethylene carbonate (EC):diethyl carbonate (DEC) (1:1 by volume) as the electrolyte. Galvanostatic cycling of these cells was performed under a constant current density of 0.06  $\text{mA}/\text{cm}^2$  between 0 and 3 V on a multi-channel battery cyclizer (Shenzhen Neware Co. Ltd). Cyclic voltammograms of the cells were measured on a CHI 604A Electrochemical Workstation at a scan rate of 0.2  $\text{mV}/\text{s}$  between 0 and 3 V. In addition to the cells of copper laminates against lithium, a cell of f-Cu foil against lithium was also similarly tested with cyclic voltammetry.

The crystal structure of the copper powders was analyzed using X-ray diffraction (Rigaku D/Max-rA,  $\text{Cu-K}\alpha$  radiation) with a two-theta scan from 30 to 90°. The surface composition of the copper particles component was studied using an X-ray Photoelectron Spectroscopy (ESCALAB MK II). The particle size distribution and specific surface area of the copper powders were measured with a sedimentation-type photo size analyzer (NSKC-1A).

## 3. Results and discussion

The X-ray diffraction (XRD) patterns of copper powders and foil are shown in Fig. 1. Obviously, all of the samples exhibit a pure phase of a cubic structure (space group  $Fm\bar{3}m$ , lattice parameter 3.607 Å). No peaks from copper oxide are detected by the X-ray diffraction although copper oxidation could take place in ambient atmosphere. Because copper is a relatively stable metal, when it is exposed in air, the pos-

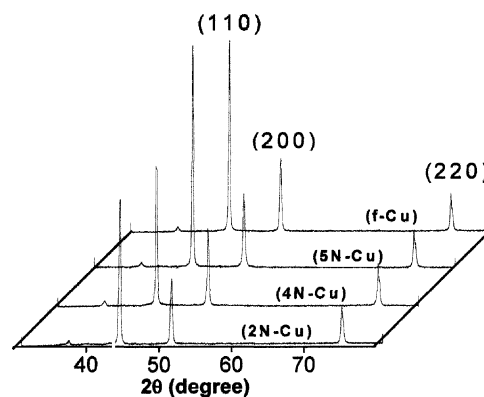


Fig. 1. XRD patterns of the samples: 2N-Cu, 4N-Cu, 5N-Cu, and f-Cu. The diffraction peaks for the Cu phase are indexed in the patterns.

sible oxidation likely only leads to the formation of a thin oxide layer on the surface. This thin layer could behave like a transparent medium to the diffraction X-rays. Therefore, means of surface analyses must be used to detect the possible oxide layer. As a powerful instrument of surface analysis, an X-ray photoelectron spectroscope (XPS) is used in this study. The Cu 2P spectra in the samples 2N-, 4N-, 5N-Cu and f-Cu are shown in Fig. 2. It is well established that two XPS peaks with binding energy at 933.6 and 953.6 eV are attributed to metallic copper ( $\text{Cu}^0$ ), while a peak around 942.6 eV can be attributed to  $\text{Cu}^{2+}$  in  $\text{CuO}$  [10]. It can be seen from Fig. 2a–c that  $\text{CuO}$  is present in the metal copper powders 2N-, 4N- and 5N-Cu. Considering the working principle of XPS technique, the detected  $\text{CuO}$  is most likely formed on the surface of copper particles out of natural oxidation in air. Consequently, all three powders are found to have a Cu/ $\text{CuO}$  core-shell structure.

For the copper foil (f-Cu), the binding energy peak around 942.6 eV is not distinct (Fig. 2d). Nevertheless, its Cu LVV Auger spectrum (Fig. 3) exhibits a peak at a kinetic energy of 919 eV. Since the sum of this kinetic energy and the binding energy of the strongest peak in Cu 2P spectrum, i.e. 933.6 eV, is 1852.6 eV, this relationship provides the evidence that  $\text{CuO}$  exists on the surface of copper foil [14]. Therefore, natural oxidation also takes place on the copper foil that is usually used as a current collector in lithium-ion batteries.

Using these powders and foil, half-cells against lithium can be made for electrochemical characterization. Their typical charge–discharge curve and the specific capacity data are shown in Fig. 4. The measurement was performed at 0.06  $\text{mA}/\text{cm}^2$  between 0.02 and 3 V. Obviously, the voltage profile shown in Fig. 4a is similar to that for  $\text{CuO}/\text{Li}$  cells measured by Tarascon and co-workers [10]; the first discharge voltage profile consists of two sloping voltage ranges, i.e. 1.4–1 V, and 1–0 V. This result indicates again the existence of  $\text{CuO}$  in these copper samples. The first lithiation capacity for 2N-, 4N-, 5N- and f-Cu is 6, 48, 31 and 1  $\text{mAh}/\text{g}$ , respectively (Fig. 4b). A large irreversible capacity loss is observed for these samples; after 50 cycles, 2N-, 4N-, 5N- and f-Cu electrodes retain a reversible capacity of about 1,

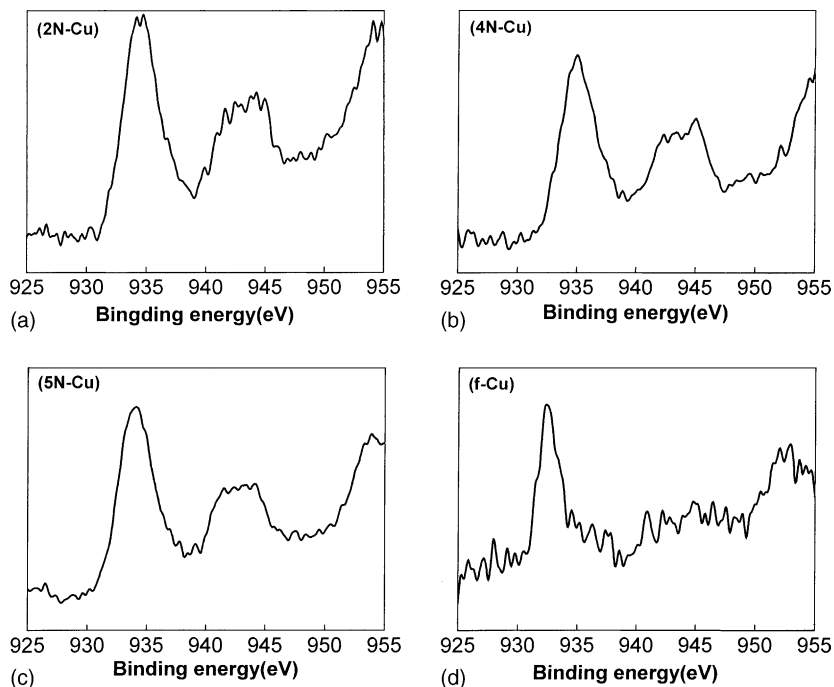


Fig. 2. XPS spectra (Cu 2P) of (a) 2N-Cu, (b) 4N-Cu, (c) 5N-Cu, and (d) f-Cu.

5.5, 5.5 and 0.1 mAh/g, respectively. If we assume that the first discharge capacity of the CuO shell is also 850 mAh/g [10], the CuO content in these copper samples can be calculated. In addition, the particle size distribution and specific surface area of these copper powders were measured in this study. With the assumptions that the copper particles are spherical and the CuO layer is fully dense on the powder particles or on the foil surface, the thickness of the CuO layer in each sample can be estimated. These results are summarized in Table 1. Hence, the CuO content in the “high purity” copper powders 4N-Cu and 5N-Cu are surprisingly high, being 5.6 wt.% and 3.6 wt.%, respectively. Only the 2N-Cu exhibits a relatively low CuO content (0.76 wt.%). Besides, the CuO layer thickness is calculated to range from 23 to 147 nm. It should be mentioned that the amount of interfacial copper oxide depends on rather the ambient conditions, e.g. humidity and temperature, than the purity of copper materials.

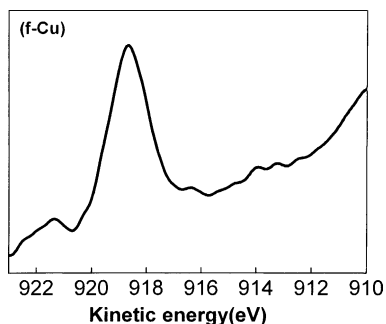


Fig. 3. The Cu LVV spectrum for the sample f-Cu.

Fig. 5 shows the cyclic voltammograms of copper powders and foil electrodes. For the copper powder electrodes (Fig. 5a–d), three cathodic peaks appear at 2.1, 0.9, and 0.6 V, respectively, in the first lithiation step. Similar peaks

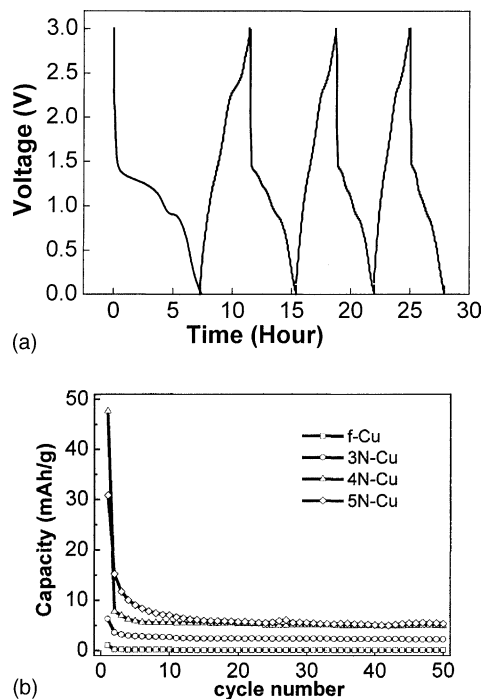


Fig. 4. Charge–discharge curve and the specific capacity data of copper powders and foil/Li cells: (a) the charge–discharge curve of 5N-Cu/Li cell (23.8 mg Cu, 1.54 cm<sup>2</sup>), and (b) the specific capacity data, under a current density of 0.06 mA/cm<sup>2</sup> between 0.02 V and 3 V.

Table 1  
Particle size distribution and the surface-oxidation results of copper powders

Samples	Particle size			Specific surface area (cm <sup>2</sup> /g)	CuO thickness (nm)	CuO content (wt.%)
	D10 (μm)	D50 (μm)	D90 (μm)			
2N-Cu	11	19	32	500	23	0.71
4N-CLi	7.3	20	36	590	147	5.6
5N-Cu	1.9	5.0	14	2000	83	3.6
f-Cu	—	—	—	—	580 <sup>a</sup>	0.11 <sup>a</sup>

<sup>a</sup> The values here are over-estimated (see Section 3 for details).

have been also observed by Tarascon and co-workers [11] in the differential capacity versus voltage of CuO/Li cells. Their transmission electron microscope (TEM) study suggests that these peaks correspond in turns to the formation of oxygen-vacant CuO-type structure, Cu<sub>2</sub>O and Cu nanograins embedded in Li<sub>2</sub>O matrix. Thus, the possibility of forming a Cu–Li alloy during electrochemical cycling can be excluded. In accordance with these three cathodic peaks, three somewhat broad anodic peaks at 2.7, 2.4 and 1.6 V are also ob-

served in Fig. 5a–d. In subsequent cycles, the anodic and, especially, the cathodic peaks become weaker compared with those appearing in the first cycle. This decrease in the peak intensity indicates an irreversible capacity loss in the first cycle. The results of the galvanostatic cycling (Fig. 4) have confirmed this capacity loss.

The typical cyclic voltammogram of an f-Cu/Li cell is shown in Fig. 5e. It is observed that cathodic and anodic peaks appear at the similar potentials as in the powder

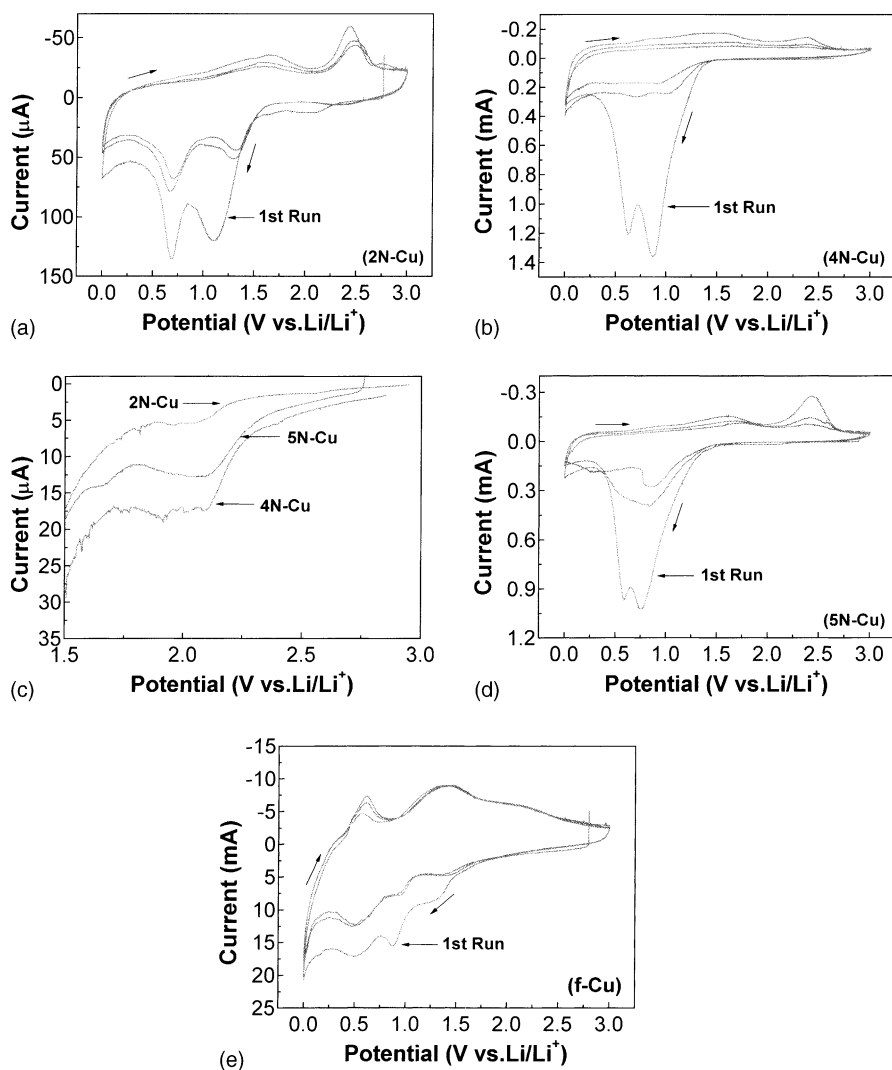


Fig. 5. Cyclic voltammograms of copper powders and foil electrodes with the electrolyte of 1 M LJPf6 dissolved in EC:DEC (1:1 by weight): (a) 2N-Cu, (b) 4N-Cu, (c) 5N-Cu, and (e) f-Cu; (d) is the amplified 1.5–3 V sections of (a)–(c). The scan rate was 0.2 mV/s in the range 0–3.

electrodes. Based on the first lithiation capacity of f-Cu/Li cell, that is about 1 mAh/g (Fig. 4b), the capacity per unit area of foil can be calculated to be  $5.2 \times 10^{-3}$  mAh/cm<sup>2</sup>. Usually, the load of active anode material, e.g. graphite, in a lithium-ion cell is in the order of 10 mg/cm<sup>2</sup>, corresponding to a capacity of about 3.4 mAh/cm<sup>2</sup>. Therefore, the irreversible capacity loss caused by the copper current collector is negligible. We may use this naturally oxidized copper foil as the current collector without fearing any reversible and irreversible capacity associated with the copper foil.

In addition, compared to the copper powder electrodes (Fig. 5a–d), a sharper cathodic peak is noticed near 0 V. This peak is believed to correspond to the lithium deposition on the foil. Correspondingly, a sharp anodic peak is followed on the reverse scan at 0.6 V, indicating the oxidation of deposited lithium [7]. Since the lithium deposition is not taken into consideration in the first discharge capacity value (850 mAh/g) measured for CuO electrodes, the real first discharge capacity of the CuO layer on the copper foil should be markedly higher than 850 mAh/g. Hence, the factual CuO thickness on f-Cu must be considerably thinner than 580 nm shown in Table 1. Similarly, the CuO content in f-Cu is less than 0.11 wt.%. On the other hand, if a copper powder is used as an additive to improve the cycling stability of anode materials [12,13], the electrochemical capacity associated with this CuO layer has to be taken into account.

#### 4. Conclusions

Three commercial copper powders and one copper foil have been analyzed in terms of the thickness and content of the copper oxide (CuO) naturally formed on their surfaces. We also evaluate the impact of this CuO layer on the electrochemical property of the copper current collector. It is found that these samples have been oxidized at different degrees. They correspond to a specific capacity as high as 48 mAh/g for the copper powder but only 1 mAh/g for the

foil. Therefore, its effect can be neglected when copper is used as a current collector; it cannot be neglected when a copper powder is used as an additive to improve the cycling stability.

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