

Controlling Li_2CuO_2 single phase transition to preserve cathode capacity and cyclability in Li-ion batteries



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ABSTRACT

Li_2CuO_2 is synthesized via a solid-state reaction and its structure and microstructure is characterized using X-Ray Diffraction, Scanning Electron Microscopy and N_2 adsorption–desorption isotherms. The capacity of cathode material is evaluated at different preparation conditions to determine the factors affecting charge retention, cyclability, and assuring reproducibility during electrode fabrication. Progressing from previous reports, a maximum capacity retention of 140 mAh g^{-1} is attained in the potential window from 1.5 to 4.2 V (Li/Li^0) during ten cycles at C/15. The low capacity retention at extended cycling has been associated to the participation of irreversible oxygen redox process evaluated by theoretical calculations and cyclic voltammetry. These processes are minimized when the cycling potential window is confined from 2.0 to 3.8 V (Li/Li^0), thus, achieving a higher capacity retention up to 100 mAh g^{-1} during 60 cycles. Cycling at higher C/rates lowers the capacity down (60 mAh g^{-1} at C/5), but the maximum capacity is restored when returning to C/15. Thus, making Li_2CuO_2 an attractive material either as active compound or additive in cathodes for Li-ion batteries, as a result of its intrinsic properties such as environmental benign, abundance, cost and straightforward preparation process.

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1. Introduction

Li-ion batteries (LIB) are the most promising devices for energy storage, and particularly due to their high energy density have met commercial applications in mobile devices. In order to be extended for large-scale storage, one of the essential challenges is to envisage materials able to deliver higher energy densities and rate capabilities at low cost and long-term cycle life, without compromising safety [1–3]. To this concern, cathode material is of special interest since its properties considerably limit battery capacity, and on its turn overall energy density and performance. Desirable cathode properties have been directly connected to the following underlying physicochemical processes: high free energy reaction towards Li insertion and deinsertion, fast Li^+ kinetics in the electrode, high electronic conductivity, high Li^+ diffusivity across the solid phase, structural stability, low cost and green structure [4]. To date, no material has displayed all the aforementioned characteristics, whence a balance needs to be initially found throughout the rational modification of the pristine properties, in order to improve energy density and rate capability. For example, the extensive research on LiCoO_2 [5,6] and LiFePO_4 [7] have permitted the determination of

voltage limits and the addition of conducting coatings respectively in order to be used as cathodes in LIB.

Interestingly, the Li_2CuO_2 phase presents one of the highest theoretical capacities (490 mAh g^{-1}) among the transition metal oxides, and the possible deinsertion of up to two Li^+ per unit formula, which far surpasses the specific limits of 0.5 Li^+ for LiCoO_2 and 1 Li^+ for LiFePO_4 [8]. Additionally, copper is a low-cost and abundant metal in earth's crust (i.e. Mexico) with no environmental consequences, making their phases very attractive candidates as cathodes for LIB. Unlike LiFePO_4 , LiMnO_2 and LiCoO_2 , which have received much attention during the last decade, Li_2CuO_2 system has been seldom investigated because of preliminary reports indicating low stability and high capacity fade [4,9–11]. Presumably, this stems from the fact that high specific capacity is only attained in the first cycle, while capacity fade significantly acts for consecutive cycles due to chemical side reactions and structural transformations, particularly, the transition from an orthorhombic phase into a denser-packed layered structure during charging [12]. In this direction, previous analyses on the Li_2CuO_2 system have been focused on the elucidation of its crystal structure and phase transformations during cycling from a materials science standpoint [9–11], while fewer studies have been conducted to analyze changes in electronic structure more related to limitations in the electrochemical performance of this system [13].

The above studies clearly demonstrate cuprate phases associated with capacity loss during first cycle. However, tractable applications have not been conducted with the Li_2CuO_2 system regardless of its multiple advantages, and its electrochemical behavior deserves a more

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profound discussion on the basis of the satisfactory structural characterization described in previous investigations. Additionally, it is overriding to have a baseline of maximum capacity for pure Li_2CuO_2 to appreciate further developments in terms of capacity and cyclability. Thus, this work firstly evaluates the relationship between cathode assembly and preparation conditions, establishing a maximum capacity under reproducible conditions. Subsequently, the electrochemical behavior of overall phase transition is discussed, and capacity retention is likewise analyzed when operation voltage is restricted. Density Functional Theory (DFT) calculations are employed to determine changes in electronic structure of phase transformations during cycling, in order to support experimental evidence of the underlying chemistry accounting for irreversible modifications during delithiation, and suggesting possible routes to seizing full theoretical capacity.

2. Materials and methods

2.1. Synthesis and cell assembly

The Li_2CuO_2 powder was synthesized via a conventional solid-state reaction using lithium oxide (Li_2O , 97%, Aldrich) and copper oxide (CuO , 99%, Meyer) as reagents in which lithium oxide excess with respect to the stoichiometric amount (10 wt%) was used to prevent lithium sublimation [14,15]. Reagents were ground in a mortar in order to obtain a homogeneous powder mixture. According to reaction (1), powders were thermally treated with a heating rate of $5\text{ }^\circ\text{C min}^{-1}$ up to $800\text{ }^\circ\text{C}$ for 6 h in air. Once the sample was synthesized, it was immediately placed in vacuum for their subsequent characterization.



Powder X-ray diffraction (XRD) measurements were conducted in a Bruker D8 Advanced diffractometer using $\text{Cu-K}\alpha$ radiation, $\lambda = 1.5406\text{ \AA}$, in steps of 0.02° over the 2θ range from 5 to 70° at room temperature. The diffractometer was operated at 40 kV and 35 mA . Li_2CuO_2 was identified using the corresponding Joint Committee Powder Diffraction Standards (JCPDS). The microstructural characteristics of the cuprate sample were determined via N_2 adsorption–desorption and scanning electron microscopy (SEM). Samples were degassed at $100\text{ }^\circ\text{C}$ for 12 h under vacuum prior to N_2 adsorption–desorption experiments, and subsequently, isotherms were acquired in a Quantachrome Autosorb-1 instrument at 77 K to determine BET surface area. SEM experiments were performed in a JEOL JMS-7600F using an accelerating voltage of 5.0 kV and a Low Angle Backscatter detector (LABe) and a Secondary Electron Imaging (SEI) detector.

Once the material was synthesized and characterized, the powder was stored in a dry globe box (M-Braun) with H_2O and O_2 concentration below 0.5 ppm . The active cathode powder was mixed with carbon Super-P (TIMCAL) and polyvinilidene fluoride (Sigma-Aldrich) in a relation 75:15:10 respectively in *N*-methyl, 2 pyrrolidone (Sigma-Aldrich). The resulting slurry was coated on a clean aluminum foil using a MSK-AFA-III compact Tape casting film coater (MTI) employing a $10\text{ }\mu\text{m}$ coating thickness, then, the electrode was dried either in a vacuum furnace during 12 h at $120\text{ }^\circ\text{C}$, or in vacuum during 36 h at room temperature, as described in brevity. Afterwards, the coated aluminum foil was hot pressed either on a calendaring machine at $4\text{ }\mu\text{m}$ separation and $90\text{ }^\circ\text{C}$, or by using a hydraulic press at 3.5 ton cm^{-2} at room temperature, as explained below. Cathodes were cut at 1.8 cm diameter and used in two electrode cells (EL-CELL), which were assembled in the dry globe box (M-Braun) along with a cleaned Li foil as anode. $150\text{ }\mu\text{L}$ of electrolyte (propylene carbonate, PC: ethylene carbonate, EC 1:1 + 1 M LiPF_6) were added to the glass fiber separator (Whatman 0.6 mm thickness) within the cell. A VMP-3 potentiostat/galvanostat (BIOLOGIC) was used to conduct all electrochemical experiments, consisting of galvanostatic charge/discharge experiments at multiple C-rates, for which C corresponds to the theoretical capacity of Li_2CuO_2 (490 mAh g^{-1})

assuming the removal of two lithium atoms from Li_2CuO_2 to during charging process. Further information (e.g. voltage limits, C-rates) is provided below.

2.2. Computational details

Spin polarized DFT calculations of Li_2CuO_2 and LiCuO_2 structures were performed using the Vienna Ab-Initio Software Package [16–18]. PBE exchange correlation functional and the semiempirical DFT + U in the Dudarev's approach [19] were used with the aim of capturing the behavior of highly correlated systems, which otherwise lead to very delocalized valence electrons, the value of U_{eff} for Copper was set to 6 eV . Plane wave expansion and k-point sampling grids were set to 600 eV and $13 \times 13 \times 11$ respectively, a higher number of k-point grids ($17 \times 17 \times 15$) were utilized for the calculation of Density of States. Differently from previous reports, the antiferromagnetic behavior of Li_2CuO_2 was taken into account by imposing initial magnetic moments in copper atoms and the reported crystalline structure [20], which correctly calculates the electronic structure of the materials.

3. Results and discussion

3.1. Li_2CuO_2 characterization

Fig. 1 shows the XRD patterns of synthesized Li_2CuO_2 sample, along with its pure phase obtained from the Joint Committee on Powder Diffraction Standards database (JCPDS 00–084–1971). No secondary phases were observed considering the equipment resolution ($\leq 5\text{ wt}\%$). Li_2CuO_2 presents the orthorhombic structure of the space group *Immm*, with lattice parameters: $a = 3.659\text{ \AA}$, $b = 2.861\text{ \AA}$, $c = 9.39\text{ \AA}$. This structure consists of edge-sharing $[\text{CuO}_4]$ sheets [21,22].

Fig. 2 shows SEM images of morphological characteristics of Li_2CuO_2 material acquired with a LABe detector (Fig. 2a) and with a SEI, an upper detector (Fig. 2b). The inset shows the magnification of the SEI image. As observed, the Li_2CuO_2 displays aggregates with dense particles and different grain sizes (averaged particle size of $\sim 0.2\text{ }\mu\text{m}$) as expected in solid state synthesis. The image 2b acquired with LABe detector shows a homogeneous surface with high spatial resolution and uniform composition. Fig. 2b shows the SEI mode image, where the edges and contours of the particles are defined and the sample displays a dense, roughness

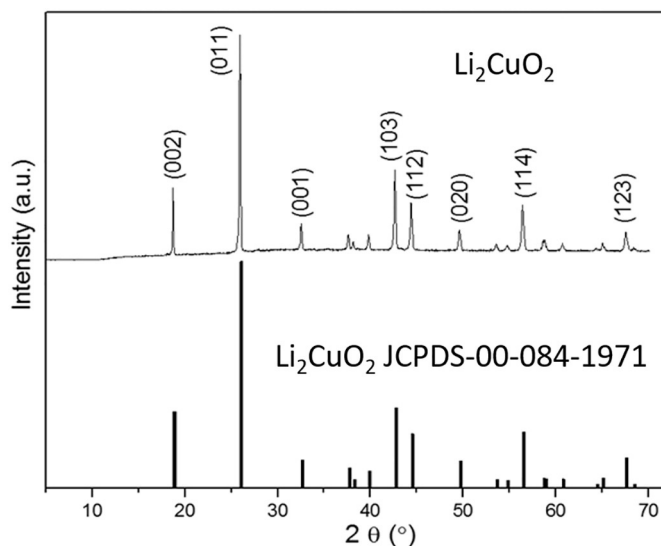


Fig. 1. X-ray diffraction patterns of synthesized Li_2CuO_2 powder (continuous line) and standard (bars) obtained from JCPDS database.

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