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Structural originations of irreversible capacity loss from highly lithiated copper oxides

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ABSTRACT

We use electrochemistry, high-energy X-ray diffraction (XRD) with pair-distribution function analysis (PDF), and density functional theory (DFT) to study the instabilities of Li_2CuO_2 at varying state of charge. Rietveld refinement of XRD patterns revealed phase evolution from pure Li_2CuO_2 body-centered orthorhombic (*Immm*) space group to multiphase compositions after cycling. The PDF showed CuO_4 square chains with varying packing during electrochemical cycling. Peaks in the $G(r)$ at the Cu–O distance for delithiated, $LiCuO_2$, showed CuO_4 square chains with reduced ionic radius for Cu in the 3+ state. At full depth of discharge to 1.5 V, CuO was observed in fractions greater than the initial impurity level which strongly affects the reversibility of the lithiation reactions contributing to capacity loss. DFT calculations showed electron removal from Cu and O during delithiation of Li_2CuO_2.

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1. Introduction

Charge storage in secondary lithium-ion battery (LIB) cathode materials is a critical technology to the development of high-energy power sources for electric and hybrid vehicles; however there are relatively few practical materials. The range of commercially viable cathode compositions for LIBs must be broadened to market cost-competitive electric drive vehicles. To meet future performance requirements, cathodes must have high lithium capacity over thousands of charge and discharge cycles while being safe, inexpensive, and environmentally benign with the ability to be recycled. Lithiated copper oxides offer many environmental and cost-savings benefits over cobalt-based chemistries. Copper is an abundant relatively inexpensive transition metal with lower toxicity than cobalt and nickel [1]; however the over-lithiated copper oxides, Li_2CuO_2 and $Li_3Cu_2O_4$, are limited by poor capacity retention after a high initial charge cycle [1–4]. High initial charge capacity of Li_2CuO_2 is based upon an orthorhombic body-centered, *Immm*, structure which provides a large number of lithium sites [5]. Li_2CuO_2 can theoretically de-intercalate up to 2.0 Li^+ per unit formula, which far exceeds the practical limit of lithium ions intercalated per unit formula by commercial battery materials, 0.5 Li^+ for $LiCoO_2$ and 1.0 Li^+ for $LiFePO_4$. Poor capacity retention during the lithium extraction reaction limits the application of Li_2CuO_2 as active cathode materials, however Li_2CuO_2 has been successfully explored as a sacrificial additive to allow stable anode solid electrolyte interface (SEI) formation during an initial cycle at high states of charge [4].

While theoretical evaluation of Li_2CuO_2 indicates a high Li^+ capacity, its practical evaluation shows that the high specific capacity is only achieved upon the initial charge [6,7]. Several authors have commented on structural distortions associated with the lithiation and de-lithiation of Li_2CuO_2 [2–4]. The loss of capacity has been attributed to both structural transformations and chemical side reactions where the larger orthorhombic structure collapses into a denser-packed layered structure during delithiation [6]. First principles computational efforts were not able to identify a suitable 4-fold coordination transition metal (Cu, Pt, Fe) to stabilize iso-structural Li_2NiO_2 in the *Immm* structure upon delithiation [6]. Experimental work by Imanishi et al. showed the reversibility and capacity of Li_2CuO_2 is improved when nickel is substituted for copper, making a Li_2CuO_2–Li_2NiO_2 solid solution [5]. Calculation results indicated that the *Immm* structure might be stabilized by Al and Ga and other transition metal dopants, however an improvement could not be realized experimentally [7].

Lithium removal from copper oxide electrodes upon charging proceeds with irreversible decomposition according to [2,4]

$$Li_2CuO_2 \rightarrow LiCuO_2 + Li^+ + e^- \quad (1)$$

$$2LiCuO_2 \rightarrow 2Li^+ + 2e^- + 2CuO + O_2 \quad (2)$$

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The decomposition reaction scheme to produce CuO and oxygen is not complete, possibly by the formation of CuO on the surface of the particles [8]. Prakash et al. has reported that a two-step electrochemical oxidation process is involved in the removal of 1.0 Li^+ from Li_2CuO_2 [3] creating $Li_{1.5}CuO_2$ ($C2/m$) and $LiCuO_2$ ($C2/m$) phases. The $Li_2CuO_2 \leftrightarrow Li_{1.5}CuO_2$ transition had high initial capacity with poor capacity retention while the $Li_{1.5}CuO_2 \leftrightarrow LiCuO_2$ transition had lower initial capacity with good retention. Clearly the structural transformations associated with the $Li_{1.5}CuO_2 \leftrightarrow Li_{2-z}CuO_2$ transition are highly detrimental to electrochemical reversibility in this system [3], whereas $LiCuO_2 \leftrightarrow Li_{1.5}CuO_2$ transformation was found to be highly reversible. The structural stability in the highly lithiated copper oxide system is not fully understood, such as the lack of the reversibility of the *Immm* structure, the packing of the CuO_4 square chains, electron loss from oxygen bands in trivalent copper oxide compounds, high oxidation state of copper, and even the existence of a displacement type reactions.

The fundamental understanding of the instabilities in high capacity Li_2CuO_2 is critical to enabling the design and discovery of future materials. We study the instabilities of Li_xCuO_2 at different states of charge, as obtained by electrochemical delithiation and lithiation during typical battery charging-discharging to formulate a broader understanding of the ties between structural transformation and capacity loss. The resulting Li_xCuO_2 materials are probed with high-energy X-ray diffraction (XRD) and analyzed using the pair-distribution function (PDF) and Rietveld refinement, to resolve the phase composition, and local and medium-range structure from 0.1 to 1.5 nm of the materials' various states of charge (lithiation). This approach provides information about the distribution of interatomic Cu–Cu, Cu–O and O–O distances, and reflects the local changes occurring during charging and discharging. The Li_2CuO_2 *Immm* structure is modeled with density functional theory (DFT) to gain fundamental understanding of the chemistry of this material, and provide insight into material stability.

2. Materials and methods

2.1. Materials preparation

Li_2CuO_2 was prepared by solid-state synthesis. Stoichiometric amounts of $LiOH \cdot H_2O$ (Alfa Aesar, 98%) and CuO (Alfa Aesar, 97%) were ground individually. Once ground, the powders were mixed together, pressed into pellets and calcined in static air at 800 °C for 15 h. A 3% mass excess of $LiOH \cdot H_2O$ was added to account for lithium loss at high temperature. The resulting pellets were ground in mortar and pestle in air and stored in an argon-filled glove box.

2.2. Electrode fabrication and electrochemical testing

Aluminum current collector foils were etched in 1M KOH, rinsed with DI H_2O, and wiped clean with acetone [9]. A slurry of the active material, Li_2CuO_2, was prepared consisting of: 83% Li_2CuO_2, 4% KS-6 graphite, 2% Super P Li-grade carbon, and 4% polyvinylidene fluoride. The PVDF binder was a 5% by weight solution in 1-methyl-2-pyrrolidone (NMP). After thorough mixing, the slurry was applied to the Al-foils and dried at 120 °C under vacuum for at least 12 h. The mass of active material was maintained between 30 and 40 mg Li_2CuO_2 over a 1 in^2 surface area. Negative electrodes were assembled from copper foils etched in 1 M HNO_3, rinsed with DI H_2O, and wiped clean with acetone. The electrodes were introduced into an Ar-filled glove box. A thin layer of lithium metal was rolled onto the copper foil surface in the glove box. The positive and negative electrodes were assembled into a "pouch" cell construction with a Celgard® porous polypropylene membrane. A small amount of 1 M $LiPF_6$ in 1:1 (v:v) ethylene carbonate/diethyl carbonate solvent electrolyte was wet onto the surface of both electrodes before packaging in a tri-foil pouch.

The batteries were charged and discharged using a Maccor 2300 battery tester over a voltage range of 1.5–4.2 V against the lithium metal anode at a $C/25$ rate (~9.8 mA) constant current. Batteries were taken off the charging or discharging cycles at the voltages given in Table 1. The positive electrode mixture Li_xCuO_2+electrode additive (Super P, K-6 graphite, PVDF) was then rinsed with diethyl carbonate to remove residual $LiPF_6$ electrolyte salt and scraped off of the aluminum current collector and dried under vacuum. The cathode mixtures were then heat-sealed in silica tubes before removal from the glove box for ex-situ high-energy XRD analysis.

2.3. Materials characterization

High-energy X-ray diffraction patterns were collected for the cycled Li_xCuO_2 materials at various states of charge (SOC) according to Table 1. Multiple cells were prepared and reproducibility was confirmed. Diffraction patterns were collected for as-prepared Li_2CuO_2 and cycled Li_xCuO_2 materials. Additional baseline measurements were performed on the electrode additives (Super P, K-6 graphite, PVDF) and an empty silica tube. The measurements were done at the 11-ID-C and 6-ID-C beamlines at the Advanced Photon Source (APS) with incident X-ray energy of 115 and 100 keV. The experiment was performed with the image plate detector (MAR-345) placed ~30 cm behind the sample. This setup allows the pair-distribution function analysis and Rietveld refinement to be carried out at the same time. In addition, several samples were measured with the detector ~100 cm behind the sample to carry out high resolution Rietveld. The main advantage of a 2D detector is its ability to cover a large portion of Q-space, thus increasing statistics and decreasing exposure time. Typically we accumulated about 6–8 exposures for each data set. The 2D detector pattern was integrated over the 360° azimuth angle to obtain the intensity as a function of the magnitude of the scattering vector Q. The detector calibration was done using CeO_2 and Si NIST powder standards. FIT2D program [10] was used to correct data for detector geometrical errors due to small angular misalignments, obliqueness, X-ray beam polarization, dark current and incident monitor counts, and for 2D image generation and file format conversion. The silica tube backgrounds were determined separately and subtracted during data analysis.

Table 1
Voltage and cycling parameters for electrochemically delithiated Li_2CuO_2.

Sample	Cut-off voltage		Current (mA)	Cycles #	Capacity (mA h/g)	Notes
	Charge	Discharge				
A	NA	NA	NA	NA	NA	As-prepared electrode
B	4.0	–	9.8	1	229	Charge only
C	4.2	–	9.8	1	255	Charge only
D	4.2	2.0	9.8	1	–	1 full cycle
E	4.2	1.5	9.8	1	–	1 full cycle
F	4.2	1.5	9.8	1+	–	Ending on 4.2 V charge
G	4.2	1.5	49.0	10	–	10 full cycles
H	4.2	1.5	49.0	10+	–	Ending on 4.2 V charge
I	3.3	–	9.8	1	100	Abbreviated charge