Supplementary Information

Energy storage in *in-vivo* synthesizable biominerals

Sung-Wook Kim,[a,b] Kyu-Young Park,[c] Jungki Ryu,[d] Jong-Wan Ko,[e] Woosuk Cho,[f] Sang-Min Kim,[f] Chan Beum Park,[e] and Kisuk Kang[c,*]

[a] Sustainable Energy Technologies Department, Brookhaven National Laboratory, Upton, NY 11973, United States of America

[b] Department of Chemistry, State University of New York at Stony Brook, Stony Brook, NY11794, United States of America

[c] Department of Materials Science and Engineering, Seoul National University, Seoul 151-742, Republic of Korea

[d] Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 20139-4307, United States of America

[e] Department of Materials Science and Engineering, KAIST, Daejeon 305-701, Republic of Korea

[f] Advanced Batteries Research Center, Korea Electronics Technology Institute, Seongnam, Gyeonggi 463-816, Republic of Korea

[*] Corresponding author: Prof. K. Kang

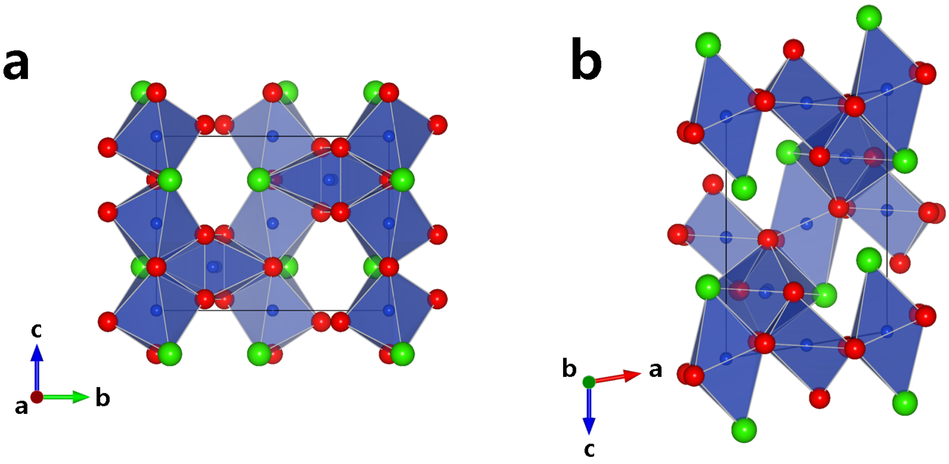
e-mail: matlgen1@snu.ac.kr, tel: 82-2-880-7088

Experimental Details

$Cu_2Cl(OH)_3$ was synthesized *via* a simple chemical route. $CaCO_3$ (1 g, Aldrich, 99%) was introduced into 1 L of 0.1M $CuCl_2{\cdot}2H_2O$ (Aldrich, 99%) aqueous solution. The mixed solution was stirred under ambient conditions, resulting in a green precipitate. The precipitate was washed several times with deionized water, gathered by vacuum filtration, and then dried.

The crystallinity of the synthesized powders was determined by X-ray diffraction (XRD) (Bruker, New D8 Advanced) with Cu-Kα radiation. Particle morphology was identified by scanning electron microscope (SEM) (Carl Zeiss, SUPRA 55VP) and transmission electron microscope (TEM) (Tecnai, F20). A homogeneous slurry composed of 70 wt% of $Cu_2Cl(OH)_3$, 20 wt% of carbon black (Super P), and 10 wt% of polyvinylidene fluoride binder on N-methylpyrrolidone was cast onto Cu foil to fabricate a test electrode. Test cells were assembled into CR2016-type coin cells in an Ar-filled glove box with the test electrode, a Li metal counter electrode, an organic electrolyte (1M $LiPF_6$ in a 1:1 (v/v) mixture of ethylene carbonate and dimethyl carbonate (DMC) (Techno Semichem)), and a polymer membrane separator (Celgard 2400). The test cells were operated by a battery cycler (WonA Tech, WBCS 3000) over a 0.01-3 V range at a current rate of 100 mA g^{-1}.

The crystal structure change during the electrochemical reaction was analyzed with *in-situ* XRD by using an Empyrean diffractometer (PANalytical) equipped with monochromated Cu Cu-Kα radiation. *In-situ* XRD was performed using a lab-made *in-situ* cell. The test electrode of the *in-situ* cell was prepared with the same composition, but on a Cu mesh. The galvanostatic method was used for electrochemical Li insertion and extraction. The cell was held at the each cut-off potential for 2 h to establish equilibrium before collecting diffraction patterns. The microstructures before and after the electrochemical reaction were compared using *ex-situ* TEM. The discharged and charged test cells were carefully disassembled in an Ar-filled glove box. The cycled electrodes were washed with DMC and dried. The cycled electrodes were then sonicated in ethanol. The sonicated cycled $Cu_2Cl(OH)_3$ particles were transferred to the TEM grid and then imaged.



c

	space group	a(Å)	b(Å)	c(Å)	α(°)	β(°)	γ(°)
atacamite	*Pnam*	6.030	9.122	6.868	90	90	90
clinoatacamite	$P2_1/n$	6.157	6.814	9.104	90	99.65	90

Figure S1. Crystal structures (a) atacamite and (b) clinoatacamite phases in $Cu_2Cl(OH)_3$ (blue: Cu, red: O, green: Cl). (c) Space groups and corresponding lattice parameters of both phases.

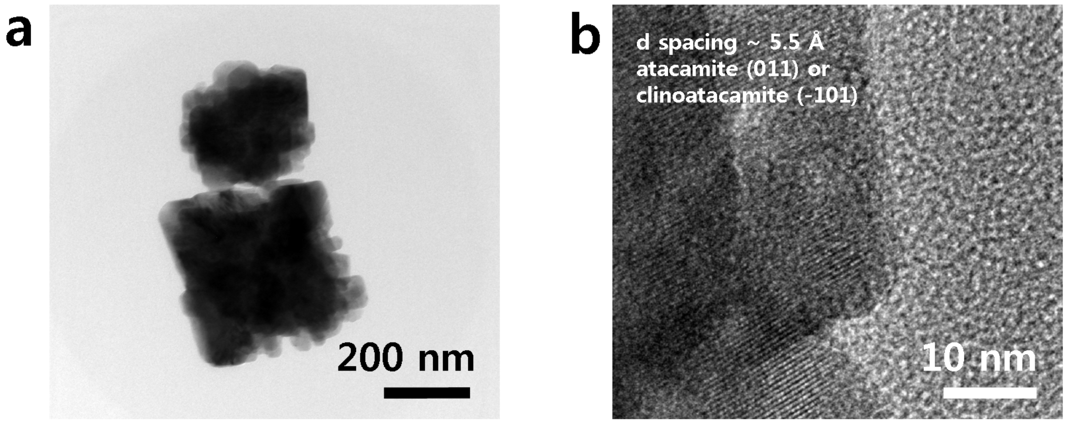


Figure S2. TEM images of synthesized $Cu_2Cl(OH)_3$ in (a) low and (b) high resolution. The measured d-spacing was approximately 5.5 Å, which is comparable to the inter-plane distance of atacamite (011) and clinoatacamite (-101).

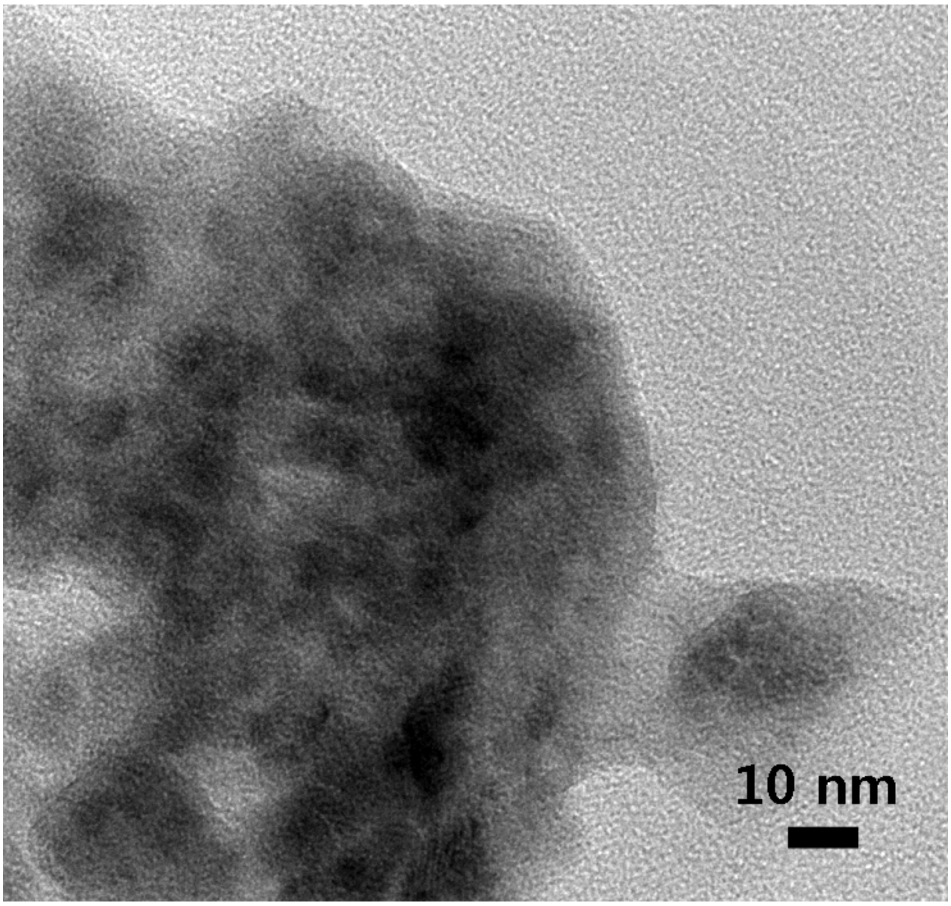


Figure S3. High resolution TEM image of $Cu_2Cl(OH)_3$ after discharge.