



Li₂CuVO₄: A high capacity positive electrode material for Li-ion batteries



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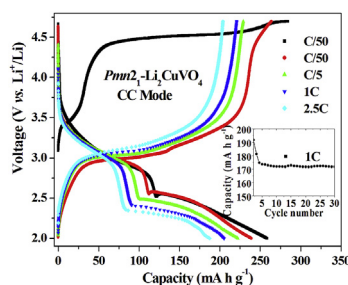
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HIGHLIGHTS

- We have been able to grow Li₂CuVO₄ single crystals.
- We solved the crystal structure using single crystal data.
- Li₂CuVO₄ is a good ionic conductor at temperatures above 100 °C.
- Interestingly, 2 lithium atoms can be reversibly extracted/inserted from/in Li₂CuVO₄.
- Li₂CuVO₄ shows high rate capability with a capacity of 175 mA h g⁻¹ at 1C rate.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 12 February 2016

Received in revised form

12 April 2016

Accepted 14 April 2016

Available online 22 April 2016

Keywords:

Single crystal structure

Vanadate

Positive electrode

Lithium cell

Ionic conductivity

ABSTRACT

The new compound Li₂CuVO₄ was synthesized by a solid state reaction route, and its crystal structure was determined from single crystal X-ray diffraction data. Li₂CuVO₄ was characterized by galvanometric cycling, cycle voltammetry, and electrochemical impedance spectroscopy. The structure of Li₂CuVO₄ is isotypic to Pmn2₁-Li₃VO₄. It can be described as a disordered wurtzite structure with rows of Li₁/Cu₁ atoms alternating with rows of (Li₂/Cu₂)-V-(Li₂/Cu₂) atoms along [100]. All cations are tetrahedrally coordinated. The lithium and copper atoms are statistically disordered over two crystallographic sites. The electrochemical cycling between 2.0 and 4.7 V indicates that almost two lithium atoms could be extracted and re-intercalated. This delivers a maximum discharge capacity of 257 mA h g⁻¹ at a C/50 rate (theoretical capacity = 139 mA h g⁻¹ for one lithium). Li₂CuVO₄ shows also high rate capability with a capacity of 175 mA h g⁻¹ at 1C rate. This demonstrates that Cu-based compounds can be very interesting as electrodes for Li-ion batteries if Cu-dissolution is avoided.

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1. Introduction

Polyanionic compounds have attracted much attention during the last decades because they have a potential for use as positive electrode in lithium or sodium-ion batteries. Several families of compounds [AMBO₃, AMPO₄, A₂MSiO₄, AMSO₄X, and A₂MPO₄X (A: Li, Na; M: Mn-Ni; X: F, OH)] have particularly been intensively investigated [1–11 and ref. therein]. The LiMPO₄ are perhaps the most interesting for practical applications. Indeed, the olivine

LiFePO₄ (theoretical capacity = 170 mA h g⁻¹) is a particularly promising example of positive electrode material, due to its advantages of being environmentally benign, inexpensive, and safe.

Compared to phosphates with the olivine-type structure, the homologous vanadates LiMVO₄ (M: Mn, Co, Ni, Cu) crystallize with different crystal structures at atmospheric pressure. LiMnVO₄ is isostructural with Na₂CrO₄ whereas LiCoVO₄, LiNiVO₄, and LiCuVO₄ crystallize with the spinel-type structure [12–15]. As in the spinel-type structure, the packing of the oxygen layers in the Na₂CrO₄ structure is ccp. The main structural difference is the distribution of the cations on the available sites. This is at the origin of the superior electrochemical performances of the spinel materials. Nevertheless, among these vanadates, only LiNiVO₄ thin films were successfully used as positive electrode in lithium-ion batteries [15].

The LiMVO₄ vanadates have been also tested as negative electrode materials [16–20]. The intercalation of *x* Li into LiCuVO₄ led to the formation of multiple phases (Li_{2.5}Cu_{0.5}VO₄ + Cu for *x* = 1.5, Li₃VO₄ + Cu for 1.5 < *x* < 2, and Li_{3+y}VO₄ + Cu for 2 < *x* < 5) [20]. Since in our previous studies related to LiMnVO₄, Li⁺ in tetrahedral sites was successfully replaced by Cu⁺ [21], we believe that the formation of these intermediate phases (Li_{2.5}Cu_{0.5}VO₄ and Li₃VO₄) is an indication of the existence of a solid solution Li_{3-x}Cu_xVO₄. Particularly, the composition *x* = 1 would be of great interest as positive electrode material for lithium-ion batteries since it would allow the deintercalation of two lithium atoms during the oxidation of Cu⁺ to Cu³⁺ delivering a theoretical capacity of 278 mA h g⁻¹. To confirm this hypothesis, we prepared the composition Li₂CuVO₄ by a solid state reaction route.

In the present work, we first describe the synthesis and the crystal structure of Li₂CuVO₄ determined by single-crystal X-ray diffraction. We then describe the electrochemical properties of Li₂CuVO₄ determined by electrochemical impedance spectroscopy, galvanometric cycling, and cycle voltammetry measurements.

2. Experimental section

2.1. Synthesis

Powder sample of Li₂CuVO₄ was first prepared by a direct solid state reaction from stoichiometric mixtures of Li₂O, CuO, and VO₂ (2CuO + 2VO₂ => Cu₂O + V₂O₅). The mixture was ground in an agate mortar, pelletized and heated at 600 °C for 12 h in a platinum crucible under argon or vacuum. The progress of the reaction was followed by powder XRD and a mixture of Li₂CuVO₄ and LiCuVO₄ was observed. Li₂CuVO₄ was then prepared from stoichiometric mixtures of Li₂CO₃, Cu₂O, and V₂O₅. The mixture was heated at 600 °C for 12 h in a platinum crucible under argon. This led to Li₂CuVO₄ as a major phase beside a little amount of unreacted Cu₂O. The resulting powder was then ground and fired at 600 °C for 12 h several times, however traces of Cu₂O were still observed. Since the DTA analysis (Fig. S1) indicated a partial decomposition around 500 °C, pure Li₂CuVO₄ could be obtained only by quenching the sample (fired at 600 °C) in liquid nitrogen.

It is well known that the particle size has an important impact on the electrochemical performances therefore, two samples were prepared. One was ground in mortar for 0.5 h (G-Li₂CuVO₄) and the other was ball milled for 12 h in ethanol (M-Li₂CuVO₄).

2.2. Electron microprobe analysis

Semiquantitative energy dispersive X-ray spectrometry (EDX) analyses of the powder and different single crystals including the one investigated on the diffractometer were carried out with a JSM-500LV (JEOL) scanning electron microscope (Fig. S2). The experimentally observed Cu/V molar ratios were close to one, as expected

for Li₂CuVO₄. The images of the hand mixed and ball milled powders were taken using a JSM-6700FV (JEOL) field emission scanning electron microscope (Fig. S3).

2.3. Powder X-Ray diffraction measurements

To ensure the purity of G-Li₂CuVO₄ powder, high precision powder XRD measurements were performed. The data were collected at room temperature over the 2θ angle range of 13° ≤ 2θ ≤ 93° with a step size of 0.015° using a RINT-TTR diffractometer (Rigaku) operating with Cu Kα radiations. Full pattern matching refinement was performed with the Jana2006 program package (Fig. 1) [22]. The background was estimated by a Legendre function, and the peak shapes were described by a pseudo-Voigt function. The refinement of peak asymmetry was performed using four Berar-Baldinozzi parameters. Evaluation of these data revealed the refined cell parameters *a* = 6.34323(6), *b* = 5.46621(6), *c* = 5.09767(5) Å, *V* = 176.754(3) Å³, in good agreement with the single crystal data listed in Table 1. Similar results were obtained for M-Li₂CuVO₄ powder.

2.4. Single crystal X-ray diffraction measurements

Single crystals of Li₂CuVO₄ suitable for XRD were selected on the basis of the size and the sharpness of the diffraction spots. The data collections were carried out on a Smart Apex diffractometer (Bruker AXS) using Mo Kα radiation. Data processing and all refinements were performed with the Jana2006 program package. A multi-scan-type absorption correction was applied using SADABS program [23]. For data collection details see Table 1.

2.5. Electrochemical cycling

Positive electrodes were made from mixtures of Li₂CuVO₄ powder, acetylene black (AB) and Polyvinylidene fluoride (PVDF) in a weight ratio of 62:30:8. The resulting electrode film was pressed with a twin roller, cut into a round plate (Φ = 14 mm) and dried at 130 °C for 12 h under vacuum. Li₂CuVO₄/LiPF₆+EC + DMC/Li coin-type cells (CR2032) were assembled in an argon-filled glove box,

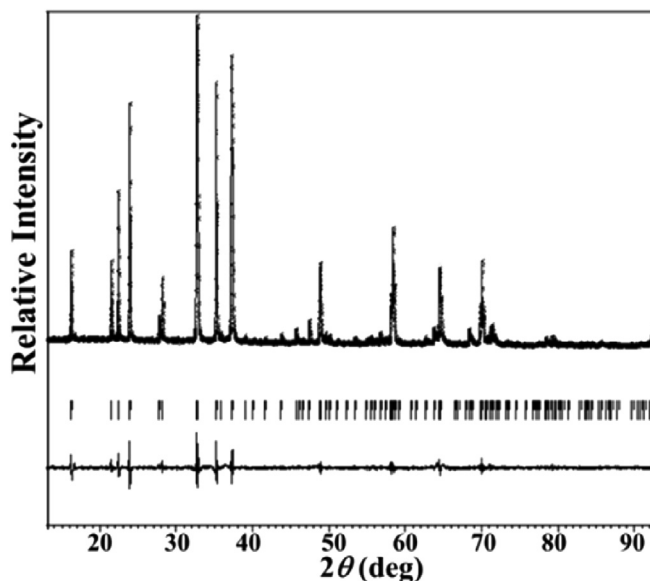


Fig. 1. Final observed, calculated and difference plots for powder XRD (Cu Kα radiation) refinement of G-Li₂CuVO₄.

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