

Characterization of $\text{Cu}_2\text{V}_2\text{O}_7$ as cathode material for lithium cells by X-ray and photoelectron spectroscopy

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Abstract

The oxidation state of vanadium and copper in $\text{Cu}_2\text{V}_2\text{O}_7$ after discharge to various depth-of-discharge in a lithium cell was measured by X-ray photoelectron spectroscopy. X-ray diffraction proves that the host lattice is destroyed by full discharge.

Introduction

Some transition metal compounds due to their favourable properties (high gravimetric energy density, conductivity, crystallographic open structure) are suitable as cathode materials for secondary lithium cells. Beside the well-known pure vanadium oxides (V_2O_5 , V_6O_{13} , V_4O_9) copper vanadates are now under investigation. In spite of the high energy density of $\text{Cu}_2\text{V}_2\text{O}_7$, little is known about this material. Sakurai [1] has proposed several phases ($\text{Cu}_2\text{V}_2\text{O}_6$, $\beta\text{-Cu}_2\text{V}_2\text{O}_7$). In this study, the oxidation state of vanadium and copper in $\text{Cu}_2\text{V}_2\text{O}_7$ is estimated by photoelectron spectroscopy.

Experimental

Pure phases of $\alpha\text{-Cu}_2\text{V}_2\text{O}_7$ were prepared from V_2O_5 and CuO according to methods cited in ref. 2. The lattice of $\alpha\text{-Cu}_2\text{V}_2\text{O}_7$ was identified as orthorhombic surface centered with lattice constants $a_0=0.838$ nm, $b_0=2.068$ nm and $c_0=0.644$ nm. The volume of the elementary cell is 1.1165 nm³.

Charge/discharge experiments were performed in 2025 size button cells with LiAl counter electrodes and 1.0 M $\text{LiAsF}_6/\text{PC-DME}$ solution (PC:DME 1:1).

The active mass contained polytetrafluoroethylene (PTFE) (6 wt.%) and graphite (4 wt.%). The cathodes were removed from the cells after discharge and subjected to X-ray photoelectron spectroscopy (XPS) and X-ray analysis.

Results and discussion

To determine the oxidation state and the degree of discharge, the V-2p, O-1s, Cu-2p and C-1s signals (from the graphite conduction material) were evaluated. The V-2p values (517.8 eV) for $\alpha\text{-Cu}_2\text{V}_2\text{O}_7$ tally with those for pure V_2O_5 [3]. The highly

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energetic O-1s structure (531.8 eV) corresponds to absorbed OH⁻ groups. The Cu-2p_{3/2} peak (935.4 eV) shows a Cu²⁺ state which, in addition to the energy value (942.7 eV), is also apparent due to the occurrence of a satellite structure (see Table 1).

The C-1s peak can be separated into three parts, which fit to that of the contaminating carbon ethoxy groups, respectively. The higher energetic structure at 293.6 eV can be explained by the interaction with electronegative atoms or loss structures.

In addition to the peaks of pure α -Cu₂V₂O₇, the spectra of sample 1 also have additional lines which can be allocated to the bonding agent: F-1s components of the PTFE and a C-F component (-293 eV). It is evident here that the energy of the peak of C-1s must be set at 285.5 eV, so as to reproduce the values for V-2p_{3/2} and Cu-2p_{3/2} in the original materials.

Sputtering of sample 1 has the following effect: the maximum energy of V-2p_{3/2} is reduced by about 1 eV with simultaneous broadening, i.e., there are noticeable concentrations present of vanadium (IV). At the same time, definite changes in the F-1s peak are detectable. An additional component occurs at 685 eV which can be assigned to the fragments of PTFE (the bonding energy is equivalent to the isolated fluorides). These parts increase with increasing depth-of-discharge.

The open-circuit voltage of LiAl/Cu₂V₂O₇ cells was 2.9 V with an internal impedance of about 30 Ω . The discharge curve is shown in Fig. 1 where two discharge voltage plateaus are clearly visible.

With progressive depth-of-discharge, vanadium is reduced, which results in a reduction of the bond energies (see Table 1 and Fig. 2). Initial significant differences

TABLE 1

Bonding energies (eV), the photoelectron spectra where taken with the VG ESCA 3 spectrometer under energization with Al K α

Sample	Phases	Cu-2p	V-2p	O-1s	Li-1s	C-1s	Cu-LVV
1	Initial material (Cu ₂ V ₂ O ₇)	935.4 942.7 ^a	517.8	530.8 531.8			916.9 ^b
2	The discharged cathode masses						
	End of plateau 1	932.6 935.3 944.5 ^a	517.6	530.6 532.9	54.5	285.5 287.3 288.7	915.7 ^b
3	Start of plateau 2	933.0 935.8	517.1	531.0 532.9	54.5	285.5 287.0 293.0	915.2 ^b
4	End of plateau 2	932.0	516.0	529.9 531.6	54.7	284.0 285.0 292.0	
5	Completely-discharged samples			531.8	55.4	284.0 285.5 289.5	
6	Same sample but sputtered	932.6	515.0 516.0	530.6	55.6	284.0 285.2 289.5	

^aSatellite structure. There is an additional energy level, indicating a change in oxidation state. This can also be concluded from the satellite structure.

^bKinetic energy of the Auger peak.

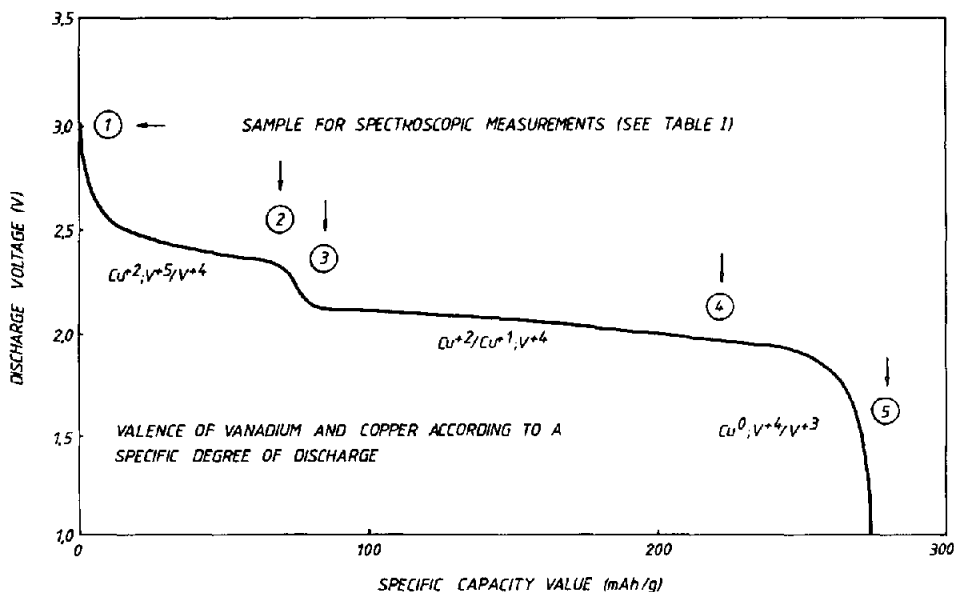


Fig. 1. The discharge ($I_E = 1 \text{ mA/cm}^2$) curve of $\text{LiAl}/\alpha\text{-Cu}_2\text{V}_2\text{O}_7$ system.

were detected by comparing non-discharged and discharged (end of the first discharge voltage plateau) samples. The low half-width of 2.1 eV, which is comparable with the spectra of the initial components, indicates the formation of a relatively uniform phase, which can be allocated to an oxidation state of 4.5. In addition to a main component allocated to Cu^{1+} , the $\text{Cu-}2p_{3/2}$ spectrum also has a noticeable Cu^{2+} component, which is also evident through the detectable satellite structure (see Fig. 2, the dotted line).

Significant changes were noted on the spectra of sample 3. The vanadium present is almost entirely tetravalent, although small amounts of Cu(II) are also detectable (see Fig. 2(a)). Noticeable are the considerable differences between the C-1s spectra of this sample.

The quantitative evaluation of the discharged samples 2 and 3 produced a total carbon concentration of around 52%, the vanadium concentrations were between 1.4 and 2.0% with oxygen concentrations of 12.5%. During discharge the expected lithium enrichment occurs, the content of oxygen also increases compared with sample 1. This produces the formation of lithium-copper-vanadium phases, which on average are equivalent to the compositions in the previous, initial discharge level.

Starting with sample 4, a re-specification of the energy reference point is again necessary. The C-1s peak can be split up in three components (Table 1). On the other hand, the higher energetic structure at 294 eV may be explained by the interaction with electronegative atoms or by structures emitting energy.

The low energetic carbon component must now be allocated an energy value of 284.0 eV (see Table 1). Indications of the former are not visible in the spectra.

Based on this, only Cu(II) and V(IV) are detected. The low value for the binding energy of the lattice oxygen is typical for amorphously discharged vanadium pentaoxide electrodes. Whereas the vanadium ratio for sample 4 is again within the range of samples 2 and 3, the copper concentration is noticeably lower. A similar finding was made during the previous measurements for the second discharge plateau. Since the

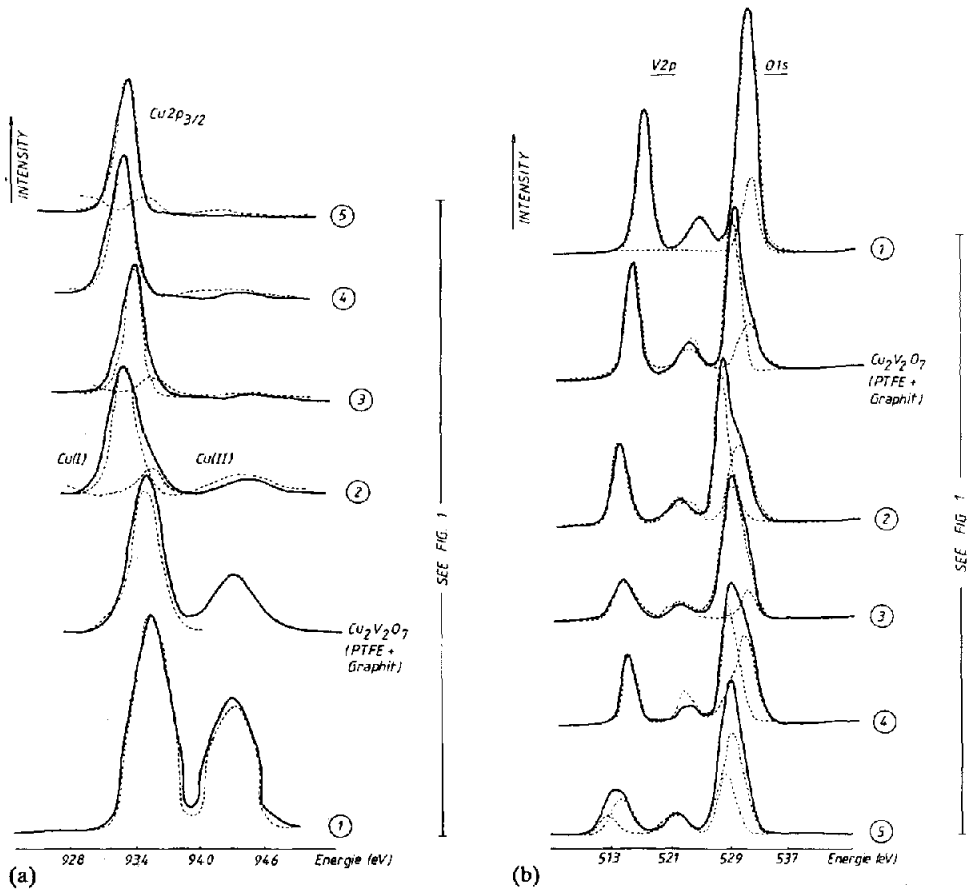


Fig. 2. The photoelectron spectra of: (a) Cu-2p_{3/2}, and (b) V-2p and O-1s. These figures show separated spectra (see ref. 4). Dotted lines indicate satellite structures.

relative lithium ratio has again been reduced, there appears to be a certain correlation to the copper ratio. The occurrence of a lithium maximum is thus confirmed for samples 2 and 3 at the end of the first discharge plateau.

Examination of the sample at the end of the discharge curve (sample 5) produced surprising results. Initially, an indication of Cu-2p lines is completely lacking in the spectra. V-2p occurs only at a very weak intensity. The fluorine concentration is roughly constant, however a Li-1s peak is immediately detectable.

This permits the conclusion, that this peak is to be assigned to absorbed LiO⁻ groups on the surface and the actual vanadates are masked by the binder, LiO⁻ and OH⁻ groups on the surface. The components of the binder can be detected by means of the F-1s peaks and the C-F structures.

Only after sputtering it is possible to clearly verify vanadium and copper peaks. Due to the expected reducing effects (see above), evaluation of the bonding energy (of Cu and V) for characterizing the oxidation condition is of relative value. Whereas the values for Cu-2p_{3/2} do not permit any differentiation between Cu(I) and Cu(O) (for intensity reasons it was not possible to detect the Cu LVV spectrum, which could clearly indicate this difference), the vanadium values are close to the V(III) compounds

[5]. An effect on the lithium bonding energies by the sputtering cannot be detected by comparison. The fluorine peaks are again strongly changed by the sputtering, which indicates decomposition of the PTFE.

Conclusions

Based on electrochemical and X-ray experiments, it was noted that the LiAl/ α - $\text{Cu}_2\text{V}_2\text{O}_7$ system shows a reversible behaviour and no significant, structural changes during cycling between 2.2 and 3.3 V. It was possible to cycle 80–90 mA h/g of active mass several times.

With progressive electrochemical reduction (end of the second discharge voltage plateau) it was no longer possible to deintercalate lithium ions through a charge process from the destroyed crystal lattice of the original material. Comparison of the discharge data, X-ray photoelectron spectra and X-ray diffractograms proof that after complete discharge ($C_p > 270$ mA h/g of active mass), the host lattice of the $\text{Cu}_2\text{V}_2\text{O}_7$ is destroyed.

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