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On the Preparation and Characterization of a New Polymorph of V_2O_5

J. M. COCCIANTELLI, P. GRAVEREAU, J. P. DOUMERC,* M. POUCHARD, AND P. HAGENMULLER

Laboratoire de Chimie du Solide du CNRS, 33405 Talence, France

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A new metastable γ' variety of V_2O_5 has been prepared by chemical or electrochemical deintercalation of lithium from a γ-LiV_2O_5 bronze. The structure of the new phase has been determined with a Rietveld method and compared to those of the normal V_2O_5 oxide and of γ-LiV_2O_5. γ'-V_2O_5 transforms into the normal form of V_2O_5 at 340°C.

Introduction

Cycling a Li//V_2O_5 battery in the 3.8- to 2-V range leads to the formation of a new polymorph of V_2O_5 which we have called γ'-V_2O_5. This material is obtained by the deintercalation of lithium from the γ-$Li_xV_2O_5$ bronze formed after the positive electrode is discharged beyond $x = 1$ (*1*, *2*). During the deintercalation process γ'-V_2O_5 is mixed with the normal form of V_2O_5. Pure γ'-V_2O_5 has also been obtained by charging a Li//γ-LiV_2O_5 battery (*3*).

The realization of a positive V_2O_5 or γ-LiV_2O_5 electrode requires the addition of some carbon for improving the conductivity and teflon as a binder. In order to obtain a pure product, we propose a chemical method for preparing γ'-V_2O_5 based on the oxidation of γ-LiV_2O_5 by a solution of bromine in acetonitrile. Such a mild synthesis method leading to a metastable phase at room temperature excludes single crystal growth. On the other hand, vanadium atoms cannot be precisely located by neutron diffraction. Therefore, the structure of this phase has been refined with a Rietveld treatment of the X-ray diffraction data.

Experimental Results

γ-LiV_2O_5 was synthesized at 650°C in an evacuated silica tube according to the reaction (*4*)

$$0.95\ LiVO_3 + 1.15/4\ V_2O_5 + 0.95/4\ V_2O_3 \rightarrow Li_{0.95}V_2O_5$$

Deinsertion of Li from γ-LiV_2O_5 was performed with a solution of bromine in acetonitrile (300 mg of the bronze reacts with 200 ml of a 10 *M* solution of bromine). After 2 weeks of stirring, we obtained an orange–yellow product which was then washed with pure acetonitrile.

The residual concentration of lithium determined by photoemission with a Per-

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* To whom correspondence should be addressed.

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TABLE I

DETAILS OF DATA COLLECTION AND OF RIETVELD REFINEMENT

Diffractometer	Philips PW 1050
Wavelength	λ Cu$K\alpha$ ($K\alpha_2/K\alpha_1$ = 0.50)
2ϑ range; step (°)	10–110; 0.02
Computer program	DBW.2S (*6*)
Space group	*Pnma*
Z	4
a (Å):	9.9461(3)
b (Å)	3.5852(1)
c (Å)	10.0423(4)
Number of reflections	268
Number of refined parameters	37
Scattering factors	V^{5+} and O^{2-} corrected for anomalous dispersion (*7*)
Profile function	Pseudo-Voigt ($PV = \eta L + (1 - \eta)G$) ($\eta = 0.682$) (*13*)
Background correction	Polynomial function (degree 5 in 2ϑ)
Full width at half maximum (H) function	$H^2 = U\,tg^2\vartheta + V\,tg\vartheta + W$ (*8*)
Maximal final value for shift/e.s.d.	0.03
$R_p = \Sigma\lvert y_i - y_{ci}\rvert/\Sigma y_i$	0.0812
$R_{wp} = \lvert\Sigma w_i(y_i - y_{ci})^2/\Sigma w_i y_i^2\rvert^{1/2}$	0.1108
$R_I = \Sigma\lvert``I_o" - I_c\rvert/\Sigma``I_o"$	0.0738
$R = \Sigma\lvert``F_o" - \lvert F_c\rvert\rvert/\Sigma``F_o"$	0.0702

kin–Elmer spectrophotometer was smaller than $x = 0.006$. The quasi-complete deintercalation of lithium was confirmed by the color of the compound, which is similar to that of normal V_2O_5.

Electrochemical preparation of γ'-V_2O_5 was performed in a coin cell. The anode was a lithium foil and the positive electrode a mixture of γ-LiV_2O_5 with teflon and graphite. The electrolyte was a solution of $LiAsF_6$ in PC/EC/DME.

The powder diffraction data were collected on a Philips PW 1050 powder diffractometer using a Bragg–Brentano geometry with a copper target and a takeoff angle of 6°. In order to minimize any preferential orientation of the crystallites, the upper layer of the sample was sifted. Actually 99% of the total energy is diffracted by a 4.6-μm thick and a 46-μm thick layer for 10° and 120° (2ϑ), respectively. The powder diffraction pattern was scanned by steps of 0.02° (2θ) from 10° to 110° (2θ) with a constant counting time of 40 sec.

The X-ray diffractograms of the new phase are quite different from that of normal V_2O_5 and reveal an orthorhombic cell close to that of γ-LiV_2O_5 (Table I). Therefore, we

TABLE II

POSITIONAL AND ISOTROPIC THERMAL PARAMETERS FOR γ'-V_2O_5 (SPACE GROUP *Pnma*)

Atom	Position	x	y	z	B_{iso} (Å^2)
V_1	4*c*	0.3758(30)	0.2500	0.5164(20)	1.24(7)
V_2	4*c*	0.0699(30)	0.2500	0.6015(20)	1.50(7)
O_1	4*c*	0.2521(90)	0.2500	0.6369(80)	3.1(3)
O_2	4*c*	0.4997(70)	0.2500	0.7571(80)	1.5(2)
O_3	4*c*	0.2934(90)	0.2500	0.3856(90)	4.4(3)
O_4	4*c*	0.5676(70)	0.2500	0.4616(80)	1.6(2)
O_5	4*c*	−0.0675(80)	0.2500	0.4600(70)	3.0(2)

TABLE III

INTERATOMIC DISTANCES AND ANGLES IN γ'-V_2O_5

V_1	O_1	O_3	O_4	O_4^i	O_4^{ii}	O_2
O_1	1.725(7)	2.55(1)	2.72(1)	2.72(1)	2.72(1)	2.74(1)
O_3	102°56	1.548(7)	2.83(1)	2.73(1)	2.73(1)	4.25(1)
O_4	151°66	105°77	1.985(6)	2.37(1)	2.37(1)	3.04(1)
O_4^i	97°46	104°97	75°30	1.891(6)	3.59(1)	2.91(1)
O_4^{ii}	97°46	104°97	75°30	142°54	1.891(6)	2.91(1)
O_2	72°49	175°05	79°18	76°05	76°05	2.713(6)
V_2	O_1	O_2^{iii}	O_5	O_5^{iv}	O_5^v	O_3
O_1	1.846(7)	2.72(1)	3.64(1)	2.74(1)	2.74(1)	2.55(1)
O_2^{iii}	105°08	1.581(6)	2.92(1)	2.79(1)	2.79(1)	4.62(1)
O_5	144°98	109°93	1.973(6)	2.38(1)	2.38(1)	3.66(1)
O_5^{iv}	94°30	106°66	75°90	1.896(7)	3.59(1)	3.26(1)
O_5^v	94°30	106°66	75°90	141°95	1.896(7)	3.26(1)
O_3	55°38	160°46	89°60	77°38	77°38	3.104(7)

Note. Symmetry code: (i) $1 - x, \frac{3}{4}, 1 - z$; (ii) $1 - x, -\frac{1}{4}, 1 - z$; (iii) $x - \frac{1}{2}, \frac{1}{4}, \frac{3}{2} - z$; (iv) $-x, \frac{3}{4}, 1 - z$; (v) $-x, -\frac{1}{4}, 1 - z$.

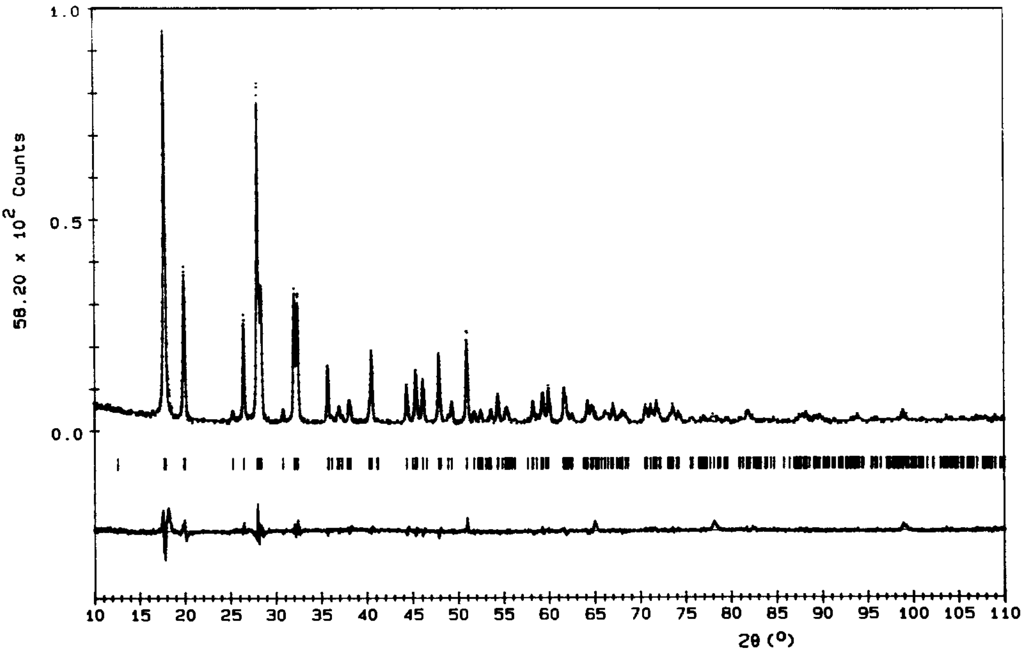

FIG. 1. Final Rietveld difference plots for γ'-V_2O_5. In the upper part, the observed data are shown by dots and the calculated pattern by a solid line.

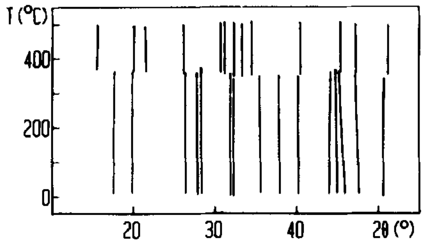

FIG. 2. Evolution of the X-ray diffractogram of γ'-V_2O_5 with temperature showing the transformation of γ'-V_2O_5 into the normal form.

took as starting positions for vanadium and oxygen atoms those of γ-LiV_2O_5. Experimental conditions and computation details are given in Table I, final atomic positions in Table II and selected bond distances and angles in Table III. The calculated and experimental spectra are compared in Fig. 1. These results correspond to satisfactory crystal structure model indicators (R_I = 0.074, R = 0.070) and profile factors (R_p = 0.081, R_{wp} = 0.111).

It was worthwhile to investigate the thermal behavior of γ'-V_2O_5 as a spontaneous transformation into the stable form of V_2O_5 may be expected. Figure 2 gives the thermal evolution of the X-ray diffraction pattern obtained with a Guinier–Simon camera using Cu*K*α radiation. It shows that γ'-V_2O_5 undergoes a transformation into the normal form of V_2O_5 near 340°C. The transformation gives rise to an exothermic peak at the same temperature in DTA experiments performed in dry oxygen athmosphere.

Discussion

The layer structure of γ'-V_2O_5 is based on VO_5 distorted pyramids sharing edges and forming infinite double ribbons parallel to the *b*-axis. These ribbons are linked by pyramid corners forming puckered layers perpendicular to the *c*-axis (Fig. 3b).

γ'-V_2O_5 is formed by chemical deintercalation of lithium from γ-LiV_2O_5 at room temperature. Under such conditions a solid-state reaction tends to proceed in the easiest way, i.e., by the route involving a minimum of structural change (*9*). Thus in the oxidation reaction of γ-LiV_2O_5 by bromine, lithium atoms which lie between the sheets are deintercalated without any major modification of the way in which VO_5 pyramids are linked to each other. However, interatomic distances undergo significant changes. As lithium is deintercalated, the sheets are slightly unfolded, leading to an increase of the *a* parameter while the interlayer dis-

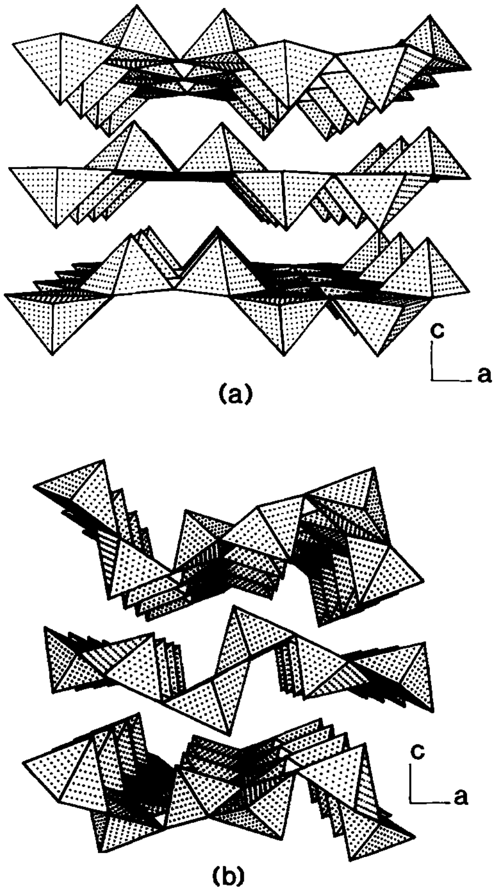

FIG. 3. Structure of the normal (a) and the γ' form (b) of V_2O_5.

TABLE IV

SOME CHARACTERISTIC V–O DISTANCES OF THE VO_5 PYRAMIDS IN SOME RELEVANT VANADIUM OXIDES

		Normal V_2O_5	γ'-V_2O_5	γ-LiV_2O_5[a]	δ-LiV_2O_5[b]
Average V–O distance in the VO_5 pyramid (Å)	V_2 site	1.838	1.84	1.820	1.850
	V_1 site		1.81	1.880	
Shortest V–O distance (Å)	V_2 site	1.577	1.58	1.608	1.610
	V_1 site		1.55	1.599	
Difference between the largest and the shortest distance in the pyramid base (Å)	V_2 site	0.24	0.13	0.23	0.08
	V_1 site		0.26	0.05	

[a] In the structure of γ, the V_1 sites are occupied by V^{4+} ions.

[b] V^{5+} and V^{4+} ions are randomly distributed in the structure of δ.

tances decrease. Double chains exist in both polymorphs, but VO_5 pyramids alternate up and down individually for γ'-V_2O_5, whereas they alternate by pairs for normal V_2O_5 (Fig. 3a).

The VO_5 pyramids have similar features in normal V_2O_5, δ-LiV_2O_5, γ-LiV_2O_5, and γ'-V_2O_5: (i) the shortest V–O distance remains between 1.55 and 1.61 Å for an oxidation state of vanadium between 5 and 4, (ii) the average V–O distance increases as the oxidation state of vanadium decreases from 5 to 4, and (iii) the pyramids tend to become more regular with reduction of the vanadium as shown in Table IV. Such an evolution is normally expected, and one may observe that for δ-LiV_2O_5 in which V^{5+} and V^{4+} are randomly distributed, the characteristic distances have values intermediate between those relative to the V_1 and V_2 sites in γ-LiV_2O_5.

An interesting feature of the structure of γ'-V_2O_5 is the existence of two different sites for the vanadium atoms, unlike what is observed in the normal form of V_2O_5 but like the situation in the γ-LiV_2O_5 bronze. However, the average V–O distance characteristic of the V_1 site strongly decreases on passing from the γ- to the γ'-phase to reach a value similar to that observed for VO_5 pyramids in other V^{5+} oxides (Table IV). Simultaneously, as shown in Table IV by the dispersion of the V–O distances in the pyramid base, the V_1 site is more distorted in the γ'-V_2O_5 oxide than the V^{4+} (V_2) site of the γ-LiV_2O_5 bronze, in agreement with the general tendency pointed out above. However, the difference between the longest and the shortest V–O distance in the pyramid base is smaller for the V_2 site of γ'-V_2O_5 than for the three other phases mentioned in Table IV, including the V_1 site of γ'-V_2O_5.

Conclusion

Preparation of γ'-V_2O_5 is a significant example of a topochemical deinsertion leading to a new metastable variety of V_2O_5 but keeping the memory of the original intercalated product. This new polymorph of V_2O_5 is kinetically stable up to ≃340°C, the temperature at which it transforms into the thermodynamically stable form of vanadium pentoxide. The electrochemical behavior of γ'-V_2O_5 is interesting as it explains the enhancement of the cell potential of $Li//V_2O_5$ batteries cycled in the 3.8- to 2-V range as reported elsewhere (*3*, *10*).

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