JOURNAL OF SOLID STATE CHEMISTRY 67, 285–290 (1987)

Structural Refinement of Delithiated $LiVO_2$ by Neutron Diffraction

M. M. THACKERAY* AND L. A. de PICCIOTTO

National Institute for Materials Research, CSIR, P.O. Box 395, Pretoria 0001, South Africa

W. I. F. DAVID

Rutherford Appleton Laboratory, Chilton, Didcot OX11 0QX United Kingdom

P. G. BRUCE

Department of Chemistry, Heriot-Watt University, Riccarton, Edinburgh EH14 5AS, United Kingdom

AND J. B. GOODENOUGH

Inorganic Chemistry Laboratory, South Parks Road, Oxford University, Oxford OX1 3QR, United Kingdom

Received January 8, 1986; in revised form June 30, 1986

Lithium has been extracted from the layered compound $LiVO_2$ by chemical oxidation with bromine. Previous X-ray data have shown that in $Li_{1-x}VO_2$ lithium extraction beyond $x \approx 0.33$ is accompanied by migration of one-third of the vanadium ions into the lithium-deficient layer to stabilize the structure; little information about the location of the lithium ions could be gathered from this data. The neutron diffraction data presented in this paper show that at a composition $Li_{0.22}VO_2$, determined by atomic absorption spectroscopy, the residual lithium ions are distributed over the octahedral sites of the original lithium layer; the possibility that a small fraction of the lithium ions partially occupy the tetrahedral sites in this layer cannot be discounted. No significant occupation by lithium of the tetrahedral or octahedral vacancies in the vanadium-rich layer could be detected. © 1987 Academic Press, Inc.

Introduction

Topochemical reactions of lithium with transition-metal oxides and sulfides at ambient temperature are of interest because they offer solid-solution electrodes for the lithium-battery industry (*1, 2*). In general, these reactions generate metastable compounds that transform or disproportionate with heat treatment into more stable phases.

Lithium extraction from the isomorphous layered oxides $LiMO_2$ (M = Co, Ni, V) has been demonstrated (*3–6*). These compounds have an ordered rocksalt structure in which the lithium and M cations reside in alternate layers in octahedral sites between a cubic-close-packed oxide-anion array.

---

* To whom correspondence should be addressed.

0022-4596/87 $3.00

Removal of lithium from $LiCoO_2$ does not perturb the MO_2 sublattice; in contrast, delithiation of $Li_{1-x}VO_2$ occurs in two stages. For the range $0 < x < 0.33$ lithium is removed from the structure without perturbing the VO_2 sublattice. At a critical concentration of lithium, $x \approx 0.33$, one-third of the vanadium ions migrate to the lithium-deficient layer. Further extraction of lithium, over the range $0.33 < x < 0.9$, is possible and results in the end member $Li_{0.1}V_{0.33}[V_{0.67}]O_2$, where $[V_{0.67}]$ refers to the cations in the original vanadium layer. Complete removal of lithium from the structure has not been possible. Heat treatment of the partially delithiated phase $Li_{0.5}VO_2$ to 300°C results in the stable spinel $Li[V_2]O_4$ (*7*) that may act as a host for both insertion and extraction of lithium (*8*). Lithium insertion yields the phase $Li_2[V_2]O_4$ in which the $[V_2]O_4$ spinel framework remains intact; this framework has a three-dimensional space that permits Li^+-ion transport (*9, 10*). Removal of lithium from $Li[V_2]O_4$ leaves a product ($Li_{0.27}V_2O_4$) that closely resembles extensively delithiated $LiVO_2$; transformation from the delithiated spinel to the delithiated layer structure necessitates a rearrangement of the vanadium ions in alternate layers between the cubic-close-packed oxygen anions from the 3 : 1 ratio in the $Li[V_2]O_4$ spinel to a 2 : 1 ratio as in $Li_{0.22}VO_2$.

Retention of the CoO_2 sublattice during lithium extraction from $LiCoO_2$ precludes the possibility of lithium entering the cobalt-filled layer. However, in the system $Li_{1-x}VO_2$ the migration of one-third of the vanadium ions into the lithium-deficient layer for $x > 0.33$ allows the possibility of lithium-ion diffusion into the tetrahedral and octahedral vacancies of the vanadium-rich layer over the range $0.33 < x < 0.9$. Previously reported X-ray data have provided information on the vanadium and oxygen-ion positions in delithiated $LiVO_2$ samples, but no information on the lithium-ion positions could be obtained on account of the weak X-ray scattering power of the lithium ions in the presence of vanadium. This paper presents neutron-diffraction data of $Li_{0.22}VO_2$ that provides information on the lithium-ion positions despite a degradation of peak resolution by sample broadening effects, such as particle-size reduction and stacking faults caused by the delithiation process. As vanadium is almost transparent to neutrons, having a scattering length of only -0.0390×10^{-12} cm, the neutron data are presented here in conjunction with the previously reported X-ray data.

Experimental

Lithium was extracted from $LiVO_2$ by chemical oxidation of the parent material with Br_2 in $CHCl_3$. A more detailed description of the preparative method is given elsewhere (*6*). Chemical analysis by atomic-absorption spectroscopy of the lithium content gave a stoichiometry $Li_{0.22}VO_2$.

Neutron-diffraction data were collected on the D1A powder diffractometer at the Institut Laue Langevin, Grenoble, France, at a wavelength of 1.384 Å. Structures were determined by the Rietveld method (*11*) based on the Cambridge Crystallographic Subroutine Library (*12*) with a program modified to incorporate a Voigt function as a peak-shape description (*13, 14*). This function, which is a convolution of Gaussian and Lorentzian components, allows the instrumental (Gaussian) and sample (Gaussian and Lorentzian) effects to be coded in a physically meaningful manner; the Lorentzian contribution is assumed to arise from particle-size effects.

The neutron-scattering lengths used in the structure refinement were $b(\mathrm{Li}) = -0.2030 \times 10^{-12}$ cm, $b(\mathrm{V}) = -0.0390 \times 10^{-12}$ cm, and $b(\mathrm{O}) = 0.5805 \times 10^{-12}$ cm (*15*). Initial unit-cell parameters were taken from previously reported X-ray data of

$Li_{0.22}VO_2$ (*6*). During the last cycles of refinement all structural and profile parameters were refined simultaneously.

Results and Discussion

$LiVO_2$ is characterized by the trigonal space group $R\bar{3}m$. With hexagonal axes and the origin of the unit cell at the centre of symmetry ($\bar{3}m$) the oxide anions are located at positions 6*c*, ideally at $(0,0,\frac{1}{4})$. The lithium and vanadium cations reside in alternate layers in octahedral sites between the cubic-close-packed oxygen planes. They are located at the special positions 3*a* and 3*b* at (0,0,0) and $(0,0,\frac{1}{2})$, respectively. There are two sets of crystallographically independent tetrahedra in the structure. Both sets are located at 6c positions, one in the lithium layer at an ideal position $(0,0,\frac{3}{8})$ and the second in the vanadium layer at $(0,0,\frac{1}{8})$. The *z* axis thus contains all possible tetrahedral, octahedral, and anion sites of this structure.

In cubic-close-packed structures the octahedra share edges with one another as do the tetrahedra; octahedra share faces with tetrahedra. Tetrahedra thus link octahedra in layers parallel to the (111) planes; they also link octahedra of adjacent layers. As ionic diffusion through a cubic-close-packed array is most likely to occur via shared faces and not shared edges, it is easy to visualize that diffusion could be either two dimensional, if the octahedral sites of alternate layers are filled with immobile cations, or three dimensional if octahedral and tetrahedral vacancies exist in alternate layers.

X-ray studies of the system $Li_{1-x}VO_2$ have established that for $x > 0.33$ one-third of the vanadium ions diffuse into the lithium-deficient layer to stabilize the structure (*6*). Structure refinement indicated a small concentration of vanadium in the tetrahedral sites of both layers with site occupancies <0.1. Since V^{5+} has a strong tetrahedral-site stability and the disproportionation reaction $2V^{4+} \rightarrow V^{5+} + V^{3+}$ requires little energy, it is believed that diffusion of vanadium from one layer to the next occurs via the two-step process:

$$\begin{array}{c} 2V_{3b}^{4+} + \square_{\text{tet}} \rightarrow V_{3b}^{3+} + V_{\text{tet}}^{5+} + \square_{3b} \\ \underline{V_{\text{tet}}^{5+} + V_{3b}^{3+} + \square_{3a} \rightarrow V_{3b}^{4+} + V_{3a}^{4+} + \square_{\text{tet}}} \\ 2V_{3b}^{4+} + \square_{3a} \rightarrow V_{3b}^{4+} + V_{3a}^{4+} + \square_{3b} \end{array}$$

where 3*a* and 3*b* refer to the octahedral sites of the lithium and vanadium layers, respectively.

The removal of lithium from the structure and the displacement of vanadium ions into the lithium-deficient layers necessarily leaves tetrahedral and octahedral vacancies in every layer of the structure. This raises the possibility of three-dimensional diffusion of lithium occurring in $Li_{1-x}VO_2$ over the range $0.33 < x < 0.9$.

Structure Refinement

The structure was refined in space group $R\bar{3}m$ initially with the structural parameters determined from previously reported X-ray data (*6*). As vanadium is virtually transparent to neutrons, the ratio of vanadium in adjacent layers was fixed at 2 : 1 during all stages of the refinement, and they were assumed to be randomly distributed over the octahedral sites within a layer.

Three models were used as starting points in the structure refinement.

Model I. Lithium placed only in octahedral sites, 3*a*, of the original lithium layer.

Model II. Lithium placed in the 3*a* octahedral sites and in the tetrahedral sites of the same layer.

Model III. Lithium placed as in Model II but also in the octahedral vacancies of the vanadium-rich layer.

During refinement of all three models the *z* parameter of the various ions, anisotropic temperature factors of the oxide ions, and site occupancy factors and isotropic tem-

TABLE I

STRUCTURAL AND HALF-WIDTH PARAMETERS FOR THE REFINEMENT OF TWO MODELS OF Li_xVO_2 BASED ON 54 REFLECTIONS

Model I: Lithium refined in octahedral sites of original lithium layer only.

$a = 2.878(1)$ Å; $c = 14.189(1)$ Å

	x	y	z	Occupancy	B_{11}	B_{33}
Li(1)	0	0	0	0.19(1)	3.1(6)	—
V(1)	0	0	0.5	0.67	2.0	—
V(2)	0	0	0	0.33	2.0	—
Ox	0	0	0.2464(2)	1.0	1.55(4)	2.43(11)

$U = 814(79)$; $V = -820(99)$; $W = 490(31)$; $t = 707(32)$

$R_N = 6.72\%$; $R_{WP} = 14.09\%$; $R_P = 19.92\%$; $R_E = 10.50\%$; $N - P + C = 2133$

Model II: Lithium refined in octahedral and tetrahedral sites of original lithium layer.

$a = 2.878(1)$ Å; $c = 14.192(1)$ Å

	x	y	z	Occupancy	B_{11}	B_{33}
Li(1)	0	0	0	0.17(1)	2.2(5)	—
Li(2)	0	0	0.3618(30)	0.10(1)	2.2(5)	—
V(1)	0	0	0.5	0.67	2.0	—
V(2)	0	0	0	0.33	2.0	—
Ox	0	0	0.2463(2)	1.0	1.49(4)	2.55(12)

$U = 887(78)$; $V = -895(97)$; $W = 511(30)$; $t = 696(30)$

$R_N = 5.87\%$; $R_{WP} = 13.47\%$; $R_P = 18.96\%$; $R_E = 10.50\%$; $N - P + C = 2132$

where

$$R_N = \frac{\sum|I_{\text{obs}} - I_{\text{calc}}|}{\sum I_{\text{obs}}} \qquad R_{WP} = \left\{\frac{\sum w[Y_{\text{obs}} - Y_{\text{calc}}]^2}{\sum w[Y_{\text{obs}}]^2}\right\}^{1/2}$$

$$R_P = \frac{\sum|Y_{\text{obs}} - Y_{\text{calc}}|}{\sum Y_{\text{obs}}} \qquad R_E = \left\{\frac{N - P + C}{\sum w[Y_{\text{obs}}]^2}\right\}^{1/2}$$

I is the integrated Bragg intensity, Y is the number of counts at angle 2θ, w is the weight, and $N - P + C$ is the number of observations − number of variables + number of constraints.

perature factors of the lithium ions were varied. All three models showed a strong anisotropy of the oxide ions in the z direction as could be expected from delithiation of the lithium layers. Refinement of Model I with lithium located only on the octahedral sites of the original lithium layer yielded a stoichiometry $Li_{0.19}VO_2$ with R_N, R_P, R_{WP}, and R_E values (as defined in Table I) of 6.7, 19.9, 14.1, and 10.5%, respectively. A drop in R factors was observed when lithium was permitted to occupy both tetrahedral and octahedral sites of the original lithium layer (Model II). The occupancy of the octahedral (3a) sites and tetrahedral (6c) sites refined to 0.17(1) and 0.10(1), respectively, giving an overall stoichiometry $Li_{0.37}VO_2$ which has a lithium concentration somewhat higher than the 0.22 determined chemically. Refinement in Model III showed, within experimental error, an insignificant scattering from lithium in the va-

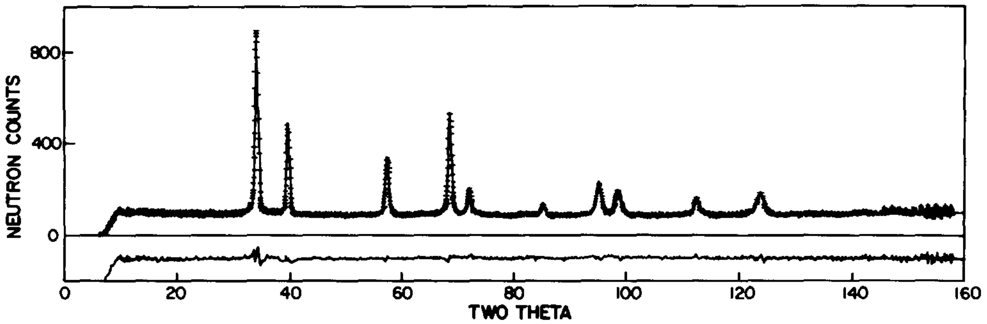

FIG. 1. The observed neutron-diffraction profile of $Li_{0.22}VO_2$ and calculated profile (Model II). The difference between the observed and calculated patterns is given below the profiles on the same scale.

nadium-rich layer. This refinement shows, despite the migration of vanadium to the lithium layer and the creation of octahedral-site vacancies in both layers, that lithium-ion diffusion in $Li_{1-x}VO_2$ is primarily restricted to the tetrahedra and octahedra within the original lithium layer. Any Li^+-ion occupancy of a vacancy in the vanadium layer must have a short residence time. The final stoichiometry of the delithiated product, as determined from Model I, is $(Li_{0.19}V_{0.33})[V_{0.67}]O_2$, where the round and square brackets refer to the cations in the original lithium and vanadium layers, respectively. This result is in good agreement with the stoichiometry $Li_{0.22}VO_2$ determined by chemical analysis. Model II shows that we cannot rule out the possibility of some tetrahedral-site lithium in the original lithium layers, which would be consistent with Li^+-ion motion within these layers. The final structural and half-width parameters of Models I and II are listed in Table I.

The observed neutron-diffraction profile of $Li_{0.22}VO_2$ and calculated profile (Model II) are shown in Fig. 1. It is clearly evident from this figure that the peak shape, particularly at large 2θ values, is non-Gaussian, being characterized by distinct Lorentzian tail broadening as a result of particle-size effects. The apparent crystallite size, D, may be obtained from the half-width parameter, t, according to the expression

$$D = 36{,}000\lambda/(\pi^2 \sqrt{t}).$$

For Model I, $t = 707(32)$, which gives an average particle size of 190(5) Å. This is consistent with the significant reduction in particle size that occurs during delithiation of $LiVO_2$.

The presence of lithium in the tetrahedral and octahedral sites of the lithium layer (Model II) might appear unexpected, particularly on account of the very short intersite distance of only 1.71 Å; however, tetrahedral-site Li^+ ions may be stabilized adjacent to a vacancy in the vanadium layer, especially as mobile Li^+ ions in the mostly lithium layer would create octahedral-site vacancies adjacent to the tetrahedral-site Li^+ ions in that layer. This phenomenon can be expected in structures with partial interstitial site occupancy and equivalent or near-equivalent octahedral- and tetrahedral-site energies. This coexistence of lithium in face-shared tetrahedra and octahedra is already known; it has been observed in the lithiated spinel $Li_2[Mn_2]O_4$ in which lithium resides in both the tetrahedral *A* sites and interstitial octahedral sites of the spinel structure (*10*, *16*).

References

1. G. Pistoia, *J. Power Sources* **9**, 307 (1983).
2. M. S. Whittingham, *Prog. Solid State Chem.* **12**, 41 (1978).
3. K. Mizushima, P. C. Jones, P. J. Wiseman, and J. B. Goodenough, *Mater. Res. Bull.* **15**, 783 (1980).
4. M. G. S. R. Thomas, W. I. F. David, and J. B. Goodenough, *Mater. Res. Bull.* **20**, 1137 (1985).
5. K. Vidyasagar and J. Gopalakrishnan, *J. Solid State Chem.* **42**, 217 (1982).
6. L. A. de Picciotto, M. M. Thackeray, W. I. F. David, P. G. Bruce, and J. B. Goodenough, *Mater. Res. Bull.* **19**, 1497 (1984).
7. L. A. de Picciotto and M. M. Thackeray, *Mater. Res. Bull.* **20**, 187 (1985).
8. L. A. de Picciotto and M. M. Thackeray, *Mater. Res. Bull.* **20**, 1409 (1985).
9. M. M. Thackeray, W. I. F. David, and J. B. Goodenough, *Mater. Res. Bull.* **17**, 785 (1982).
10. M. M. Thackeray, W. I. F. David, P. G. Bruce, and J. B. Goodenough, *Mater. Res. Bull.* **18**, 461 (1983).
11. H. M. Rietveld, *J. Appl. Crystallogr.* **2**, 65 (1969).
12. J. C. Matthewman, P. Thompson, and P. J. Brown, *J. Appl. Crystallogr.* **15**, 167 (1982).
13. W. Voigt, *Münch. Ber.*, 603 (1912).
14. W. I. F. David and J. C. Matthewman, Rutherford Appelton Laboratory Report: RAL 84 064, SERC (1984).
15. G. Kostorz and S. W. Lovesey, *in* "Neutron Scattering in Materials Science, A Treatise on Materials Science and Technology" (G. Kostorz, Ed.), Vol. 15, p. 1 Academic Press, New York, 1979.
16. W. I. F. David, M. M. Thackeray, L. A. de Picciotto, and J. B. Goodenough, *J. Solid State Chem.* (1987), in press.