Rhombohedral Form of $Li_3V_2(PO_4)_3$ as a Cathode in Li-Ion Batteries

J. Gaubicher,[†] C. Wurm,[‡] G. Goward,[†]
C. Masquelier,[‡,§] and L. Nazar*[,†,§]

Department of Chemistry, University of Waterloo,
ESC 131, Waterloo, Ontario N2L 3G1, Canada, and
Laboratoire de Physico-Chimie des Solides,
UMR CNRS # 8648, Université Paris-Sud,
91405 Orsay Cedex, France

Received April 26, 2000
Revised Manuscript Received June 29, 2000

Solid-state electrode materials for Li-ion batteries are of considerable interest worldwide. Along with the intensively studied transition-metal oxides Li_xMO_2 (M = Co, Ni, and Mn) and $Li_xV_2O_5$, polyanion structures built of corner-sharing MO_6 octahedra (M = Fe, Ti, V, and Nb) and $(XO_4)^{n-}$ tetrahedra (X = S, P, As, Mo, and W)[1−11] have garnered much attention. Seminal studies on these materials focused on $Fe_2(XO_4)_3$ (X = S,[1] Mo,[2] and W[3]). Materials such as Li_xFePO_4,[4] $Li_xMM'(XO_4)_3$,[5−10] $Li_xFeP_2O_7$,[11] and Li_xVOXO_4[12−14] were recently identified as good hosts for the extraction/intercalation of Li between 2.5 and 4 V vs Li/Li$^+$.[6,15] Because of the lower covalence of the M−O bonds in these polyanion structures, the Fe^{3+}/Fe^{2+} and V^{4+}/V^{3+} redox couples lie at more useful potentials than in the simple oxides.

The NASICON framework $[MM'(XO_4)_3]_\infty$,[16] which allows for extensive substitution on the octahedral (M and M′) and tetrahedral (X) sites, is particularly attractive because of its inherently high ionic conductivity. Up to a total of 5 Li ions can be accommodated in $Li_3Fe_2(PO_4)_3$.[8] The $Li_{3\pm x}V_2(PO_4)_3$ system has scarcely been studied, however. The stable modifications obtained through classical solid-state reactions at high temperature are monoclinic A−$Li_3V_2(PO_4)_3$, isotypic with the α form of monoclinic $Li_3Fe_2(PO_4)_3$,[17,18] and rhombohedral B−$Na_3V_2(PO_4)_3$ with the NASICON framework.[19,22] The B modification of $Li_3V_2(PO_4)_3$ investigated here differs from the A phase in the way the “lantern” units $[V_2(PO_4)_3]$ are interconnected.[8] Okada et al.[20] and Padhi[21] showed that extraction of 2 Li from A−$Li_3V_2(PO_4)_3$ occurs at 3.8 V vs Li/Li$^+$ (V^{3+}/V^{4+}). Deinsertion of Li from the mixed ion phase B−$Li_2NaV_2(PO_4)_3$ has been reported, although the electrochemical performance was not as good. Rhombohedral $Li_3V_2(PO_4)_3$ has been cited earlier in the literature, prepared by apparent oxidation of $Na_3V_2(PO_4)_3$ to $V_2(PO_4)_3$, followed by re-intercalation of Li;[22] however, this synthesis is not reproducible. Here we report on the first preparation of the rhombohedral B−$Li_3V_2(PO_4)_3$ by ion exchange from $Na_3V_2(PO_4)_3$ and on the first investigation of its electrochemical behavior upon Li extraction, coupled with ex situ X-ray diffraction (XRD) and solid-state ^{7}Li NMR studies.

Rhombohedral B−$Li_3V_2(PO_4)_3$ (B−LVP) was prepared by ion exchange from $Na_3V_2(PO_4)_3$ (B−NVP). B−NVP was obtained by solid-state reaction from a stoichiometric mixture of V_2O_3 and $3NaH_2PO_4$ reacted under a constant gas flow of 10% H_2 in N_2 for 3×20 h at 900 °C. Ion exchange of $Na^+ \leftrightarrow Li^+$ was effected by stirring the B−NVP powder in a concentrated aqueous solution of $LiNO_3$. After 24 h, the resulting green powder was filtered and washed with water. The procedure was repeated twice; chemical analysis (ICP) showed that the exchange was nearly complete and led to a composition of $Li_{2.82}Na_{0.12}V_2(PO_4)_3$.

The XRD pattern of B−$Na_3V_2(PO_4)_3$, from which B−$Li_3V_2(PO_4)_3$ was prepared by ion exchange, is shown in Figure 1a. The majority of the diffraction peaks can be indexed in an $R\bar{3}c$ cell previously proposed[19,22] with $a = 8.719(1)$ Å and $c = 21.789(1)$ Å, although high-resolution synchrotron XRD studies[23] show that the symmetry is actually monoclinic.[24] Additional low-intensity diffraction lines can be attributed to Na-ion ordering at room temperature that would give rise to a superstructure similar to but somewhat different from B−$Na_3Fe_2(PO_4)_3$.[17] The XRD pattern of B−$Li_3V_2(PO_4)_3$ obtained by ion exchange from the sodium phase is

---

[*] To whom correspondence should be addressed.

[†] University of Waterloo.

[‡] Université de Paris-Sud.

[§] Electrochemical Society active members. E-mail: Christian.Masquelier@chimsol.u-psud.fr and lfnazar@uwaterloo.ca.

(1) Nadiri, A.; Delmas, D.; Salmon, R.; Hagenmuller, P. *Rev. Chem. Minéral.* **1984**, *21*, 537.

(2) Manthiram, A.; Goodenough, J. B. *J. Solid State Chem.* **1987**, *71*, 349.

(3) Manthiram, A.; Goodenough, J. B. *J. Power Sources* **1989**, *26*, 403.

(4) Padhi, A. K.; Nanjundaswamy, K. S.; Goodenough, J. B. *J. Electrochem. Soc.* **1997**, *144*, 1188.

(5) Okada, S.; Nanjundaswamy, K. S.; Manthiram, A.; Goodenough, J. B. Proceedings of the 36th Power Sources Conference, Hyatt Cherry Hill, NJ, June 6−9, 1994.

(6) Nanjundaswamy, K. S.; Padhi, A. K.; Goodenough, J. B.; Okada, S.; Ohtsuka, H.; Arai, H.; Yamaki, J. *Solid State Ionics* **1996**, *92*, 1−10.

(7) Padhi, A. K.; Nanjundaswamy, K. S.; Masquelier, C.; Okada, S.; Goodenough, J. B. *J. Electrochem. Soc.* **1997**, *144*, 1609−1614.

(8) Masquelier, C.; Padhi, A. K.; Nanjundaswamy, K. S.; Goodenough, J. B. *J. Solid State Chem.* **1998**, *135*, 228−234.

(9) Padhi, A. K.; Manivannan, V.; Goodenough, J. B. *J. Electrochem. Soc.* **1997**, *145*, 1518−1520.

(10) Gaubicher, J.; Angenault, J.; Chabre, Y.; Le Mercier, T.; Quarton, M. *Mol. Cryst. Liq. Cryst.* **1998**, *311*, 45.

(11) Padhi, A. K.; Nanjundaswamy, K. S.; Masquelier, C.; Goodenough, J. B. *J. Electrochem. Soc.* **1997**, *144*, 2581−2588.

(12) Gaubicher, J.; Chabre, Y.; Angenault, J.; Lautié, A.; Quarton, M. *J. Alloys Compd.* **1997**, *262−263*, 34−38.

(13) Gaubicher, J.; Le Mercier, T.; Orsini, F.; Llorente, S.; Angenault, J.; Quarton, M. *J. Solid State Chem.* **2000**, *150* (2), 250−257.

(14) Gaubicher, J.; Le Mercier, T.; Chabre, Y.; Angenault, J.; Quarton, M. *J. Electrochem. Soc.* **1999**, *146* (12), 4375−4379.

(15) Goodenough, J. B.; Padhi, A. K.; Masquelier, C.; Nanjundaswamy, K. S.; Okada, S. 37th Battery Symposium, Tokyo Institute of Technology, Tokyo, Japan, Sept 25−27, 1996. Goodenough, J. B.; Padhi, A. K.; Masquelier, C.; Nanjundaswamy, K. S. U.S. Patent 08/840,523, 1997.

(16) Hong, H. Y. P. *Mater. Res. Bull.* **1976**, *11*, 173.

(17) D'Yvoire, F.; Pintard-Scrépel, M.; Bretey, E.; De la Rochère, M. *Solid State Ionics* **1983**, *9* & *10*, 851.

(18) Maksimov, B. A.; Muradyan, L. A.; Genkina, E. A.; Simonov, V. I. *Sov. Phys. Dokl.* **1986**, *31* (5), 370.

(19) Delmas, C.; Olazcuaga, R.; Cherkaoui, F.; Bochu, R.; Le Flem, G. *C. R. Acad. Sci. Paris* **1978**, *287*, 169.

(20) Okada, S.; Arai, H.; Asakura, K.; Sakurai, Y.; Tamanaki, J.; Nanjundaswamy, K. S.; Padhi, A. K.; Masquelier, C.; Goodenough, J. B. The 37th Battery Symposium in Japan, 1996.

(21) Padhi, A. K. Ph.D. Thesis, The University of Texas at Austin.

(22) Gopalakrishnan, J.; Kasthuri-Rangan, K. *Chem. Mater.* **1992**, *4*, 745−747.

(23) Masquelier, C.; Wurm, C.; Elkaim, E.; Lauriat, J. P. In preparation.

(24) Most of the intense diffraction peaks split into two or three components that can be indexed in a monoclinic cell ($a = 15.124$ Å, $b = 8.733$ Å, $c = 8.847$ Å, and $\beta = 124.65°$).

10.1021/cm000345g CCC: $19.00

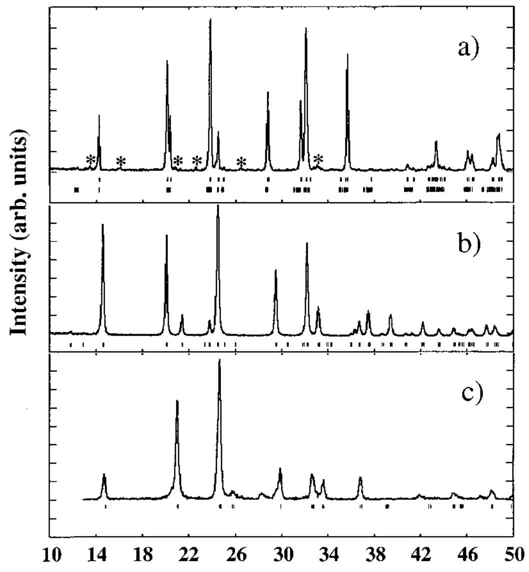

Figure 1. X-ray diffraction patterns (Cu Kα radiation) of (a) B−$Na_3V_2(PO_4)_3$ indexed in the rhombohedral (upper) and monoclinic (lower) cells. Asterisks denote superstructure reflections (see text), (b) B−$Li_3V_2(PO_4)_3$, and (c) B−$Li_3V_2(PO_4)_3$ oxidized to 4.1 V indexed in the $R\bar{3}$ cell.

shown in Figure 1b. All of the Na-superstructure reflections disappear as expected. The diffraction pattern was indexed in the space group $R\bar{3}$ with $a = 8.316(1)$ Å and $c = 22.484(1)$ Å, which is very similar to those of B−$Li_3Fe_2(PO_4)_3$ ($R\bar{3}$; $a = 8.3162(4)$ Å and $c = 22.459(1)$ Å).[8,25] There is thus a strong increase in the *c* axis along with a decrease in the *a* axis when Na^+ is substituted by Li^+. The origin of the expansion in *c* is probably the same as that suggested by Delmas[26] on reduction from $LiTi_2(PO_4)_3$ to $Li_3Ti_2(PO_4)_3$ and as that we have recently discovered for the corresponding $Li_3Fe_2(PO_4)_3$ NASICON structure:[25] namely, the M(1) crystallographic site of the NASICON structure, which is fully occupied in the sodium phase, is emptied in the lithium phase. This results in a strong repulsion between neighboring MO_6 octahedral faces along [001]. In B−$Li_3Fe_2(PO_4)_3$ ($R\bar{3}$), Li lies in a unique 4-fold-coordinated crystallographic site, shifted by approximately 0.8 Å along [001] from the M(2) site of the NASICON structure. We designate this as M(3) and propose that Li lies in a similar location in the B−LVP ($R\bar{3}$) structure.[27]

Electrochemical oxidation of B−$Li_3V_2(PO_4)_3$ under slow potentiodynamic conditions (10 mV/1.5 h) up to 4.1 V followed by equilibration shows that almost 2 Li can be extracted from the framework (Figure 2a).[28] Examination of the cyclic voltamogram and the corresponding chronoamperogram shows that oxidation of the V^{3+} to V^{4+}/Li deinsertion is a two-phase process with an equilibrium potential of 3.77 V. Significant deviation from diffusion-controlled kinetics occurs during this step, indicating that grain boundary migration dominates. In accordance, the transition is accompanied by structural change. Except for three minor reflections, the XRD pattern of the material oxidized to 4.1 V (Figure 1c) can be indexed in a rhombohedral unit cell ($R\bar{3}$) ($a = 8.430$ Å and $c = 20.764$ Å), showing that the *c* axis undergoes a large contraction compared to B−LVP (~8%). A better fit, where these three additional lines are indexed, can be achieved by refinement in a triclinic unit cell ($P\bar{1}$; $a = 14.441$ Å, $b = 8.916$ Å, $c = 9.043$ Å, $\alpha = 89.49°$, $\beta = 122.32°$, and $\gamma = 91.67°$) that represents a small distortion from $R\bar{3}$. Synchrotron XRD studies are underway that will allow us to distinguish between the rhombohedral and triclinic unit cells. Our parameters (in $R\bar{3}$) are very similar to those of $LiTi_2(PO_4)_3$ ($R\bar{3}c$; $a = 8.52$ Å and $c = 20.88$ Å)[26] and the related material, $Li_{1+x}Ti_{2-x}In_x(PO_4)_3$, where $x = 0.12$ ($R\bar{3}c$; $a = 8.5476$ Å and $c = 20.9512$ Å).[29] In both materials, the contraction can be explained, not by a major structural transformation of the lattice (vis-à-vis the more highly lithiated derivative), but by a shift away

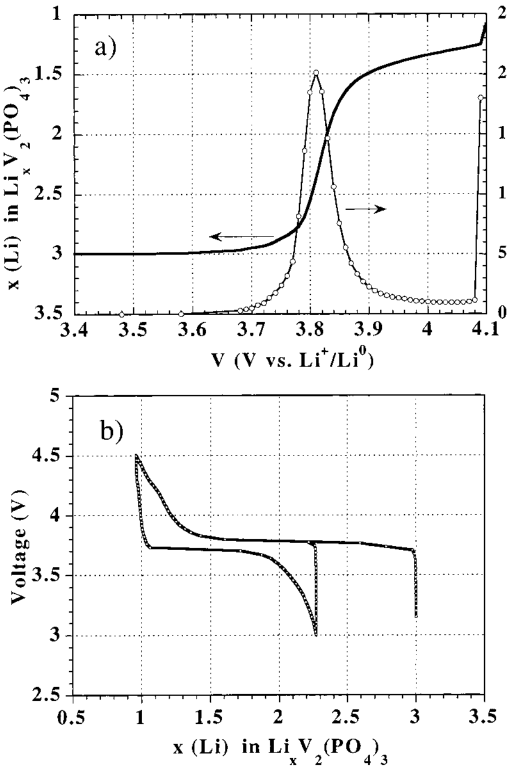

Figure 2. (a) Electrochemical oxidation (charge) of B−$Li_3V_2(PO_4)_3$, carried out at a potentiodynamic sweep rate of 10 mV/1.5 h up to 4.1 V. (b) Charge−discharge profile at a current density of *C*/10 (7 mA/g) for B−$Li_3V_2(PO_4)_3$. The latter was independent of the conductive carbon content in the electrode (up to 50% carbon).

---

(25) Masquelier, C.; Wurm, C.; Rodriguez-Carvajal, J.; Gaubicher, J.; Nazar, L. F. *Chem. Mater* **2000**, *12*, 522−532.

(26) Delmas, C.; Nadiri, A.; Soubeyroux, J. L. *Solid State Ionics* **1988**, *28−30*, 419.

(27) This has been confirmed by successful Rietveld fitting of the X-ray data starting with the model $Li_3Fe_2(PO_4)_3$ and replacing the Fe with V. Further studies on $Li_3V_2(PO_4)_3$ and $LiV_2(PO_4)_3$ using synchrotron and neutron diffraction data are in progress.

(28) $Li_3V_2(PO_4)_3$ was evaluated as a positive electrode material using a Mac-Pile controller, with lithium metal as the negative and reference electrode. The active material, acetylene black, and PVDF, in the weight proportion 75/20/5 were mixed in cyclopentanone and spread onto an aluminum disc. The electrodes had a surface area of 1 cm^2, contained ~2 mg (or 20 mg for XRD studies) of active material, and were heated at 80 °C for 1 h prior to assembly in Swagelok-type cells assembled using 1.0 M $LiPF_6$ in dimethyl carbonate (DMC; Aldrich)/ethylene carbonate (EC; Aldrich) (1:1) as the electrolyte. Extraction of the residual 0.12Na is assumed to occur on oxidation as well.

(29) Tran Qui, D.; Hamdoune, S.; Soubeyroux, J. L.; Prince, E. *J. Solid State Chem.* **1988**, *72*, 309.

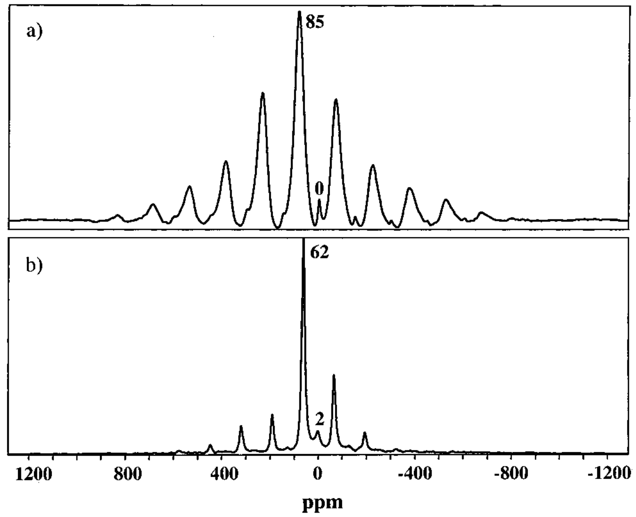

Figure 3. ^{7}Li MAS NMR spectra for (a) B−$Li_3V_2(PO_4)_3$ and (b) B−$LiV_2(PO_4)_3$ at 4.1 V after potentiostatic equilibration. The spectra were recorded on a Bruker DSX200 with a rotor-synchronized echo pulse sequence, using a pulse width of 1.2 μs, which corresponded to a 90° flip angle. Spectra are referenced externally to solid ^{7}LiCl at 0 ppm, and the isotropic resonances are marked on the spectra; all other peaks are spinning sidebands.

from the population of the M(2) sites, apparently toward preferential occupation of M(1)-related sites and by concomitant oxidation of V^{3+} ions to V^{4+}.

^{7}Li MAS NMR studies of the initial sample and of that equilibrated at 4.1 V support this proposal. The starting material, B−$Li_3V_2(PO_4)_3$, exhibits a single resonance at 85 ppm (Figure 3a) corresponding to Li in the 4-fold-coordinated M(3) site of the NASICON structure.[25] Extraction of up to 2 Li in the two-phase process results in the disappearance of the signal and the appearance of a single peak at 62 ppm (Figure 3b). We attribute the latter to a single M(1)-related site, as suggested by the large contraction of the *c* parameter in the oxidized sample. Occupation of the M(1) site in $LiTi_2(PO_4)_3$ has also been previously suggested on the basis of static NMR data.[30] This slight alteration in the site geometry, along with the difference in the Fermi contact term between V^{3+} ($Li_3V_2(PO_4)_3$) and V^{4+} ($LiV_2(PO_4)_3$), accounts for the shift from 88 to 60 ppm. Because the latter is a through-bond effect due to transfer of unpaired electron spin density onto the Li *s* orbital from the paramagnetic center, it is dependent on the spin density as well as the Li−O−M bond length and angle.[31] We note that reinsertion of Li is also possible: the NMR spectrum of the material after reduction to 3.0 V is identical with that of the starting material; furthermore, the unit cell parameters derived from full-profile refinement of the XRD pattern ($R\bar{3}$; a = 8.319 Å and c = 22.484 Å) are also the same as those in the starting material.

The charge−discharge profile of B−$Li_3V_2(PO_4)_3$ under galvanostatic control (Figure 2b) confirms that two alkali cations/electrons can be extracted under these conditions, which minimize possible parasitic electrolyte oxidation. On subsequent discharge, a polarization in the discharge curve at $x = 1$ is observed and only 1.3 Li are reinserted (Q_R = 90 mA·h/g), suggesting a kinetic limitation to the reinsertion of Li, which may be due to the structural changes incurred on extraction of 2 Li. This may be due to the localization of Li in the M(1) sites and/or the effective contraction along the *c* axis that also results or other structural effects that hinder displacement of Li from these sites.[32] Future work will focus on suppression of the transition by selective doping of the framework.

Acknowledgment. L.F.N. acknowledges the financial support of NSERC through the strategic and research grant programs. We thank Dr. Hiltrud Grondey (University of Toronto) for her invaluable assistance in acquiring the NMR data.

CM000345G

---

[30] Paris, M.; Martinez-Juarez, A.; Rojo, J.; Sanz, J. *J. Phys. Condens. Matter* **1996**, *8*, 5355.

[31] Lee, Y. L.; Wang, F.; Grey, C. P. *J. Am. Chem. Soc.* **1998**, *120*, 12601.

[32] The capacity loss may also be partly due to degradation of electrical contact between the current collector and the cathode material due to the strong anistropic contraction of the unit cell and/or partial dissolution of vanadium from the lattice on oxidation. Initial results from chemical analysis of the electrolyte following oxidation indicated only a very small V content in solution that would not account for the capacity loss; however, we cannot rule out the possibility of V entrapment in the binder or on the surface of the carbon particles.