Lithium insertion into $Li_{1-x}V_2O_4$ $(0.7 \leqslant x \leqslant 0.9)$

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Abstract

Lithium insertion into defect rock salt phases of the system $Li_{1-x}V_2O_4$ $(0.7 \leqslant x \leqslant 0.9)$ has
been studied from a structural and an electrochemical point of view. The starting materials
were derived by lithium extraction from the spinel $Li[V_2]O_4$. The resulting defect rock
salt $Li_{1-x}V_2O_4$ compounds were relithiated chemically to a composition $Li_{1.8}V_2O_4$. Cyclic
voltammetry studies of the system show that the lithiation reaction is reversible. Gal-
vanostatic discharge curves, recorded at very low rates, indicate a single-phase lithiation
process up to a composition $Li_{\sim 2.3}V_2O_4$. Practical applications, however, are limited
because of the metastability of $Li_{1-x}V_2O_4$ $(x \geqslant 0.75)$, which decomposes slowly to form
VO_2.

Introduction

Over the past few years, many studies have focussed on the ambient
temperature topochemical reactions of lithium with oxide spinels in view of
their possible application in primary or secondary lithium cells [1–13]. Normal
cubic spinels, with prototypic symmetry $Fd3m$ (O^7_h) have the general formula
$A[B_2]X_4$, where the cubic-close-packed anions, X, occupy the 32e sites. The
cations, A and B, reside in one-eighth of the tetrahedral sites (8a) and one-
half of the octahedral sites (16d), respectively. Lithium ions can diffuse
through the interstitial space of the $[B_2]X_4$ sublattice, which constitutes a
three-dimensional network of channels comprising face-sharing 8a tetrahedra
and 16c octahedra. The isomorphous group of spinels $Li[M_2]O_4$, where M = Ti,
V, Mn, is of particular interest as electrodes for secondary systems, because
lithium can not only be inserted into, but also extracted from, these compounds,
thereby extending the electrode capacity. Furthermore, Li^+-ion diffusion has
been shown to be faster in spinels where the A site is occupied by lithium
cations rather than by relatively heavy metal cations [5].

A structural study of the topochemical reactions of lithium with the
spinel $Li[V_2]O_4$ showed that lithiation is possible up to at least a composition
$Li_2[V_2]O_4$ while maintaining the spinel $[B_2]X_4$ framework structure [9]. Recent

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electrochemical studies of the system $Li_{1+x}[V_2]O_4$ have confirmed its applicability in secondary lithium cells [6, 14].

Preliminary investigations have shown that delithiation of $Li[V_2]O_4$ can be carried out electrochemically in a lithium cell, and chemically, leading to a composition $Li_{0.27}V_2O_4$ [9]. The relative intensity distribution of the powder X-ray diffraction pattern of $Li_{0.27}V_2O_4$ was observed to be similar to that of $Li_{0.22}VO_2$. The latter compound was obtained by delithiating layered $LiVO_2$, and has a structure in which the vanadium cations occupy octahedral sites and are distributed in a 2:1 ratio in alternate layers in the cubic-close-packed anion lattice [15]. The powder X-ray diffraction patterns of delithiated spinel samples indicated that during delithiation a fraction of the vanadium cations migrates from the 16d to the 16c octahedral sites at $x \sim 0.3$ in $Li_{1-x}[V_2]O_4$ [9]. Cyclic voltammetry studies of the system $Li_{1\pm x}V_2O_4$, showed that the lithium extraction reaction beyond $x = 0.3$ was irreversible and provided further evidence of this mechanism [5]. However, re-lithiation was shown to be possible via a different mechanism.

In this study, single-phase $Li_{0.28}V_2O_4$ and its lithiated product $Li_{1.8}V_2O_4$ were prepared and characterised; the lithiation reaction mechanism is presented, and the electrochemical performance of $Li/Li_{1-x}V_2O_4$ cells is examined. It has been assumed, however, that the structural data obtained from chemically-prepared samples are valid for the electrochemically-prepared materials. For convenience, samples will be described with an exact lithium content; it is stressed, however, that the structure and the reaction characteristics were found to be very similar for the range of defect phases $Li_{1-x}V_2O_4$ ($0.7 \leqslant x \leqslant 0.9$).

Experimental

The $Li[V_2]O_4$ spinel precursor was prepared by a method described previously [16]. It was delithiated chemically by reaction with a 0.125 M solution of bromine in chloroform. Prolonged treatment over several days at ambient temperature, in darkness and with constant stirring, was required to obtain a single-phase material, with stoichiometry $Li_{0.28}V_2O_4$, suitable for structure analysis. A lithiated phase of composition $Li_{1.8}V_2O_4$ was synthesised for structure analysis by reaction of $Li_{0.28}V_2O_4$ with n-butyllithium at 20 °C.

Electrochemical data were obtained from lithium cells of the type:

Li/LiClO$_4$ 1 M in propylene carbonate (PC): dimethoxyethane (DME) 1:1/

$$Li_{1-x}V_2O_4 \text{ (30 wt.% TAB)}.$$

In these experiments the $Li_{1-x}V_2O_4$ samples were prepared electrochemically, *in situ*, as this method gave a much tighter control of the initial stoichiometry and composition of the $Li_{1-x}V_2O_4$ electrode than was possible by chemical extraction of lithium.

The active material in the cathode, typically 30 mg, was mixed with a 30 wt.% blend of Teflon and acetylene black (TAB) in a 1:2 mass ratio. The

electrolyte components were dried and purified using standard methods; the cells were assembled and discharged under an argon atmosphere. Cycling tests were carried out in prismatic cells. Cyclic voltammetry experiments were carried out in three-electrode cells with the same electrolyte; lithium foil was used as both counter- and reference electrode.

Powder X-ray diffraction patterns were obtained on an automated Rigaku diffractometer equipped with a curved graphite single-crystal monochromator. The d-spacings were corrected with an internal Si standard. Structural characterisation of the parent compound $Li_{0.28}V_2O_4$ and of the chemically-lithiated material $Li_{1.80}V_2O_4$ was carried out by a least-squares refinement program developed by Wiseman [17], using integrated peak intensities. The goodness of fit is measured by the factor:

$$R = (\Sigma |I_{obs} - I_{calc}|)/\Sigma |I_{obs}|$$

The lithium content in various samples was determined by atomic absorption analysis.

Results

Structural characterisation of $Li_{0.28}V_2O_4$ and $Li_{1.80}V_2O_4$

Powder X-ray diffraction patterns of $Li_{0.28}V_2O_4$ and $Li_{1.8}V_2O_4$ are shown in Fig. 1. Both patterns can be indexed to a cubic cell with the space group $Fd3m$. Lithiation of $Li_{0.28}V_2O_4$ increases the cell constant from 8.151(3) Å in $Li_{0.28}V_2O_4$ to 8.250(3) Å in $Li_{1.8}V_2O_4$, which represents a volume expansion of 3.7% of the unit cell. The relative intensity distributions in $Li_{0.28}V_2O_4$ and $Li_{1.80}V_2O_4$ are very similar, but differ considerably from the spinel precursor
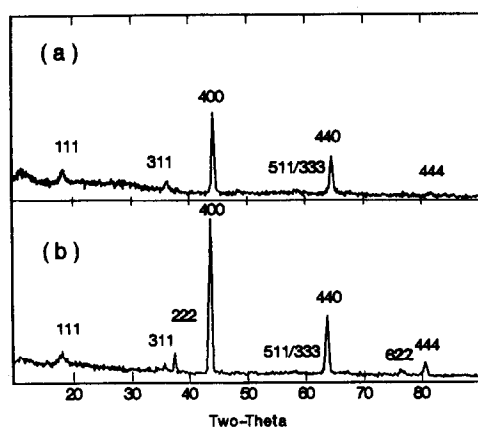
Fig. 1. Powder X-ray diffraction patterns of (a) $Li_{0.28}V_2O_4$ and (b) $Li_{1.8}V_2O_4$.

$Li[V_2]O_4$. The structure refinements were carried out using 9 intensities, corresponding to 10 reflections in the case of $Li_{0.28}V_2O_4$, and 13 intensities corresponding to 14 reflections in the case of $Li_{1.80}V_2O_4$.

(a) $Li_{0.28}V_2O_4$

Owing to the low number of measurable intensities on the X-ray diffraction pattern, the refinement was carried out on two independent sets of data. Only one data set is presented as the results obtained were in good agreement with one another. As very few reflections are clearly defined, the information that may be extracted is limited; nonetheless, good indications on the location of the vanadium ions could be obtained.

During the preliminary refinement cycles, the oxygen positional parameter (u) and the isotropic temperature factor (B_{iso}) were varied. This refinement yielded the values $u = 0.254(4)$ and $B_{iso} = 2.6(2.0)$ Å^2. In subsequent cycles, these parameters were fixed at $u = 0.254$ and $B_{iso} = 3.0$ Å^2; 0.28 Li$^+$ ions were placed in the 8a tetrahedral sites, as in the parent spinel structure. The V$^{3+/4+}$ cation occupancy was initially allowed to vary between the 16c and 16d octahedral sites but with the total number of vanadium cations being fixed at 2.0. A vanadium-ion distribution of 1.56(9) in the 16d sites and 0.44(9) in the 16c sites was obtained. In a subsequent unconstrained refinement, the vanadium cations were allowed to occupy the tetrahedral 8a positions as well as the octahedral 16c and 16d sites; this refinement led to a drop of the R factor from 21.4% to 14.4%. In this model, the vanadium-site occupancies refined to 0.13(5) in the 8a tetrahedra, 0.42(7) and 1.49(13) in the 16c and 16d octahedra, respectively, which amounts to a total of 2.04(25) vanadium cations per formula unit, in good agreement with the expected stoichiometry. The vanadium cations on the tetrahedral sites are probably pentavalent; this oxidation state is possible through the disproportionation reaction:

$$2V^{4+} \longrightarrow V^{3+} + V^{5+}$$
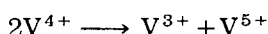
which is energetically favourable, as discussed elsewhere [15]. The full structural parameters are listed in Table 1(a), calculated and observed intensities in Table 1(b). Better fits could not be obtained due to the paucity and lack of high quality X-ray data.

(b) $Li_{1.80}V_2O_4$

In the course of the first few refinement cycles, the anion positional parameters and B_{iso} factor were refined; the vanadium cation occupancies were refined in subsequent cycles. The vanadium cations were constrained to a total of 2.0 and allowed to vary between the 16c and 16d octahedra. The best fits were obtained when the B_{iso} factors of the vanadium and lithium cations were fixed at 0.4 Å^2 and 0.8 Å^2, respectively. The vanadium occupancies refined to 0.50(2) and 1.50(2) in the 16c and 16d octahedra, respectively. The anion positional parameter refined to 0.251(2), which corresponds, within experimental error, to an ideal, undistorted cubic lattice. Finally, the lithium

TABLE 1

(a) Structural parameters of $Li_{0.28}V_2O_4$ ($R = 14.4\%$), space group: $Fd3m(O_h^7)$, $a = 8.151(3)$ Å.
(b) Observed and calculated intensities for $Li_{0.28}V_2O_4$

Atom	Position	x	y	z	B (Å^2)	n^a
(a) Structure						
Li^+	8a	0.125	0.125	0.125	1.0	0.28
V^{5+}	8a	0.125	0.125	0.125	0.5	0.13(5)
$V^{3+/4+}$	16c	0.000	0.000	0.000	0.5	0.42(7)
$V^{3+/4+}$	16d	0.500	0.500	0.500	0.5	1.49(13)
O^{2-}	32e	0.254(4)	0.254(4)	0.254(4)	3.0	4.0

hkl	I_{obs}	I_{calc}
(b) Intensities		
111	487	454
311	348	416
222	57	54
400	1312	1381
331	59	49
511 333	176	144
440	993	749
444	132	152
840	158	213

^{a}The occupancy, n, is given in terms of atoms in the site, per formula unit.

cation occupancies were allowed to vary in the 8a, 16d and 16c sites; an optimal distribution of the Li^+ ions was found when they occupied only the 8a and 16c sites with site occupancies of 0.4(2) and 1.4(2), respectively. This model gave an R factor of 7.6%. The final structural parameters and a list of calculated and observed intensities are given in Table 2. No improvement of the fit could be obtained by placing vanadium cations in the tetrahedral 8a sites or by allowing the lithium ions to reside in the 16d sites.

On the basis of this refinement, two observations can be made. Firstly, the vanadium cation distribution between the 16c and 16d octahedra remains practically unchanged during the lithium insertion process. The ratio of vanadium cations in alternate layers of octahedra in the oxide lattice is 5:3 in both the starting material, $Li_{0.28}V_2O_4$, and the lithiated compound, $Li_{1.80}V_2O_4$, which is close to the ratio observed in $Li_{0.22}VO_2$ [15]. Secondly, the inserted lithium cations fill the 16c sites in preference to the 16d octahedra. This implies that Li^+-ion diffusion still occurs through the 8a–16c–8a channels, as it does in the spinel $Li[V_2]O_4$.

TABLE 2

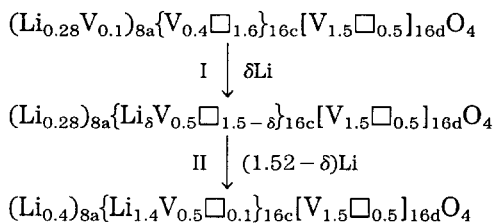(a) Structural parameters of $Li_{1.80}V_2O_4$ $(R = 7.6\%)$, space group: $Fd3m(O^7_h)$, $a = 8.250(3)$ Å.
(b) Observed and calculated intensities for $Li_{1.80}V_2O_4$

Atom	Position	x	y	z	B (Å^2)	n^a
(a) Structure						
Li^+	8a	0.125	0.125	0.125	0.8	0.4(2)
Li^+	16c	0.000	0.000	0.000	0.8	1.4(2)
$V^{3+/4+}$	16c	0.000	0.000	0.000	0.4	0.50(2)
$V^{3+/4+}$	16d	0.500	0.500	0.500	0.4	1.50(2)
O^{2-}	32e	0.251(2)	0.251(2)	0.251(2)	2.0(5)	4.0

hkl	I_{obs}	I_{calc}
(b) Intensities		
111	201	206
311	128	132
222	118	66
400	1112	1164
331	54	39
511 ⎫ 333 ⎭	72	41
440	566	573
531	37	29
622	73	70
444	136	146
800	75	67
662	50	51
840	227	209

^{a}The occupancy, n, is given in terms of atoms in the site, per formula unit.

Lithiation of $Li_{0.28}V_2O_4$ therefore occurs via a topochemical (single-phase) insertion reaction which can be expressed as follows:

$$(Li_{0.28}V_{0.1})_{8a}\{V_{0.4}\square_{1.6}\}_{16c}[V_{1.5}\square_{0.5}]_{16d}O_4$$

$$I \downarrow \delta Li$$

$$(Li_{0.28})_{8a}\{Li_\delta V_{0.5}\square_{1.5-\delta}\}_{16c}[V_{1.5}\square_{0.5}]_{16d}O_4$$

$$II \downarrow (1.52-\delta)Li$$

$$(Li_{0.4})_{8a}\{Li_{1.4}V_{0.5}\square_{0.1}\}_{16c}[V_{1.5}\square_{0.5}]_{16d}O_4$$

Electrochemical characterisation

A cyclic voltammogram of an electrochemically-generated $Li_{1-x}V_2O_4$ sample shows an initial oxidation peak at 3.6 V that corresponds to lithium extraction from the tetrahedral A site of the $Li[V_2]O_4$ spinel precursor and to the simultaneous, but irreversible, migration of vanadium ions from the octahedral B sites to interstitial octahedral sites (Fig. 2) [5]. Thereafter, the cyclic voltammogram shows a very shallow and diffuse reduction peak at
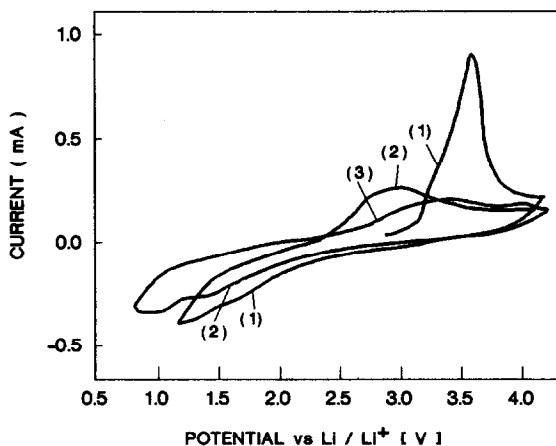
Fig. 2. Cyclic voltammogram of the system $Li_{1-x}V_2O_4$. Initial scan: anodic $(v = 1$ mV s$^{-1})$. The oxidation peak of the first cycle corresponds to the delithiation of $Li[V_2]O_4$.

~ 1.5 V with a corresponding, more distinct, oxidation peak at ~ 3.0 V. This reduction/oxidation process is attributed to reaction II suggested above, in which lithium is reversibly inserted into, and extracted from, a V_2O_4 defect rocksalt framework structure.

Cyclic voltammograms of chemically-prepared $Li_{1-x}V_2O_4$ samples were not always entirely reproducible, which highlighted the difficulties in controlling the stoichiometry and composition of the initial delithiated samples; these samples were often found to contain either partially delithiated spinel particles in which the $[V_2]O_4$ framework was still intact, or VO_2, the latter compound being formed by the decomposition, on standing, of small, extensively delithiated particles, even under inert conditions. Therefore, in an attempt to ensure the reproducibility of electrochemical data, galvanostatic discharge and cell cycling experiments were carried out with electrochemically-prepared $Li_{1-x}V_2O_4$ samples in which $0.7 \leqslant x \leqslant 0.9$. In these experiments lithium was extracted from $Li[V_2]O_4$ at a typical current density of 65 μA cm^{-2}; this process occurs at approximately 3.4 V versus Li/Li$^+$ until $x = 0.8$ in $Li_{1-x}V_2O_4$, beyond which the load voltage rises sharply (Fig. 3).

Previous electrochemical experiments have shown that at a very low current density (15 μA cm^{-2}) a sloping discharge curve extends to a voltage limit of 1.3 V, which is indicative of a single-phase lithium-insertion process in the defect rocksalt V_2O_4 framework structure. In practice, it was possible to discharge $Li_{0.13}V_2O_4$ on the first cycle to an overall composition $Li_{2.3}V_2O_4$; in this instance the specific electrode capacity is an attractive 0.349 A h g^{-1} based on the mass of the starting electrode material. However, in cell cycling tests that were carried out a higher current density (65 μA cm^{-2} during charge and discharge) with lower and upper voltage limits of 1.5 V and 4.2 V, respectively, the capacity utilisation of the electrode was severely reduced. For example, the capacity delivered by $Li_{0.13}V_2O_4$ after 8 cycles

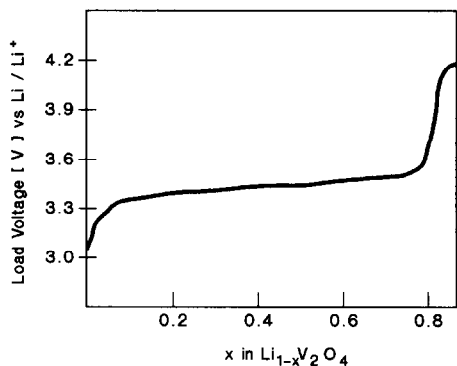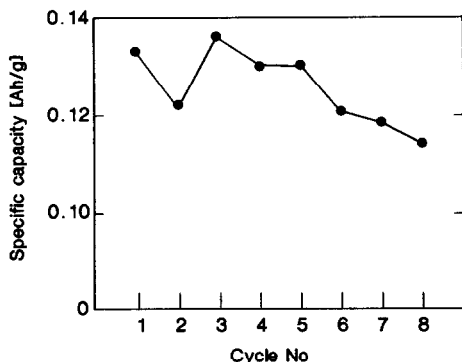Fig. 3. Initial charge profile of an $Li/Li[V_2]O_4$ cell (65 μA cm^{-2}).

Fig. 4. Specific capacity of an $Li_{1-x}V_2O_4$ electrode as a function of cycle number.
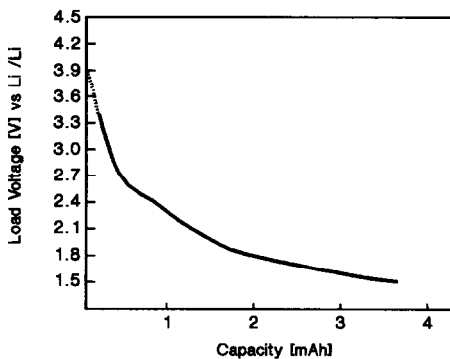
Fig. 5. A typical discharge profile of an $Li/Li_{1-x}V_2O_4$ cell at a current density of 65 μA cm^{-2}.

was 0.117 A h g^{-1}, which corresponds to the insertion of 0.73 Li$^+$ ions into $Li_{0.13}V_2O_4$ (Fig. 4). A typical discharge profile of an $Li/Li_{1-x}V_2O_4$ cell during the cycling experiments, that depicts the rapid drop in cell voltage at 65 μA cm^{-2}, is shown in Fig. 5.

Conclusions

Cyclic voltammetry studies of the system $Li_{1-x}V_2O_4$ in lithium cells have demonstrated a reversible lithium insertion reaction. From a structural point of view, it has been established that only a minor rearrangement of the vanadium cations occurs during the lithiation of $Li_{0.28}V_2O_4$ up to a composition $Li_{1.8}V_2O_4$ and that the reversible electrochemical process can be attributed to lithium insertion and extraction reactions with a defect rocksalt V_2O_4 framework structure. Preliminary galvanostatic cycling tests, however, have shown that electrodes with an initial composition $Li_{1-x}V_2O_4$ ($0.7 \leqslant x \leqslant 0.9$) present no advantages over the parent spinel $Li[V_2]O_4$, despite an anticipated

higher electrode capacity. Although at relatively low current densities (65 $\mu A \text{ cm}^{-2}$) the specific capacity of $\sim 0.12 \text{ A h g}^{-1}$ obtained from $Li_{1-x}V_2O_4$ electrodes is comparable with that obtained from the spinel electrode $Li[V_2]O_4$ [6], the energy density delivered by $Li/Li_{1-x}V_2O_4$ cells ($\sim 240 \text{ W h kg}^{-1}$) is inferior to that of $Li/Li[V_2]O_4$ cells (284 W h kg^{-1}) due to a lower average load-voltage. The structural instability of $Li_{1-x}V_2O_4$ and the relatively steep slope of the discharge curve, even at low current density, would appear to limit the utility of $Li/Li_{1-x}V_2O_4$ cells in practical applications.

Acknowledgement

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