

$(\text{Mo}_{0.3}\text{V}_{0.7})_2\text{O}_5$ AS A SOLID SOLUTION CATHODE FOR Li CELLS. PART II. STRUCTURAL CHARACTERISTICS AND SECONDARY CELLS

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Summary

It has been shown in Part I of this work that $(\text{Mo}_{0.3}\text{V}_{0.7})_2\text{O}_5$ has an electrochemical behaviour different from that of V_2O_5 . The two oxides have similar structures, with the MO_6 octahedra linked by corner and edge sharing to form interconnected zig-zag chains. These structures can incorporate Li^+ ions in bicapped cuboctahedron cavities of perovskite-type. This results, for V_2O_5 , in an elongation of the weak V—O bond along (010) and eventual bond breaking for $x > 1$ in $\text{Li}_x\text{V}_2\text{O}_5$. By contrast, $(\text{Mo}_{0.3}\text{V}_{0.7})_2\text{O}_5$ can incorporate more than 2 Li^+ /mole in its cavities without substantial structure reorganization and with only 10% expansion of the cell.

$\text{Li}/(\text{Mo}_{0.3}\text{V}_{0.7})_2\text{O}_5$ cells are rechargeable and more than 100 cycles were achieved at 0.5 - 1.0 mA/cm². After the 2nd cycle some structural alterations are produced which remain almost unchanged during further cycling.

Introduction

As shown in the first part of this work, $(\text{Mo}_{0.3}\text{V}_{0.7})_2\text{O}_5$ has discharge features quite at variance with those of the parent oxide V_2O_5 in spite of having a similar structure. Indeed, interconnections of MO_6 distorted octahedra are the same in both oxides [1], thus giving the same zig-zag chains linked by corner sharing. Therefore, the perovskite-like cavities formed by the octahedra have the same shape [2] and are expected to accommodate Li^+ with the same type of coordination.

However, the M—O bonds differ appreciably in the two oxides [1] and this was, in principle, assumed to be the cause of the different electrochemical pattern. A structural investigation was therefore undertaken along with the occurrence of discharge-charge processes.

We also considered the features of $(\text{Mo}_{0.3}\text{V}_{0.7})_2\text{O}_5$ as an electrode for secondary cells. Vanadium pentoxide in this respect suffers from two signi-

ficant limitations, *i.e.*, irreversible reduction below LiV_2O_5 [2] and electrolyte decomposition during charge due to the high potentials required. Such drawbacks were not shown by $(\text{Mo}_{0.3}\text{V}_{0.7})_2\text{O}_5$ during preliminary cycling experiments, thus prompting a deeper investigation in this respect also.

Experimental

All the relevant features of our electrochemical technique have been described in a previous paper [3] and in Part I of this work.

The samples to be X-rayed were prepared in a dry-box by the following technique. The cathode, after dismantling the cell, was housed in the specimen holder and then a few drops of a 4% collodion solution in ether were added. After evaporation of the ether, a thin layer of transparent collodion was left. In this way, undesirable reactions due to atmospheric moisture were prevented. The high degree of crystallinity of $(\text{Mo}_{0.3}\text{V}_{0.7})_2\text{O}_5$ allowed good diffraction patterns to be obtained even in the presence of this film.

Results and discussion

(i) Relationship between discharge and structural characteristics

The structure of V_2O_5 and $(\text{Mo}_{0.3}\text{V}_{0.7})_2\text{O}_5$, as reported in Fig. 1 of Part I, is composed of octahedra which form bicapped cuboctahedron cavities [2] of the type shown in Fig. 1. In these cavities two opposite square faces are capped with oxygen atoms so that Li^+ motion is only restricted to the (100) plane. Perovskite-like cavities provide square pyramidal sites for Li^+ accommodation; in the present oxides capping produces two additional such sites.

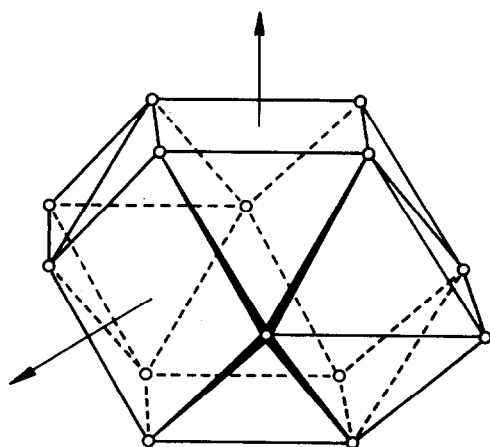


Fig. 1. Perovskite-like cuboctahedron cavity formed by MO_6 octahedra in $(\text{Mo}_{0.3}\text{V}_{0.7})_2\text{O}_5$. The arrows mark the directions of channels in the lattice for diffusion of Li^+ .

Murphy [2] has reported that in LiV_2O_5 the number of Li^+ equals the number of cavities, these being elongated compared with those present in V_2O_5 . More precisely, a predominantly uniaxial expansion occurs upon Li^+ uptake in the direction of the long and weak V—O bond (010). Incorporation of more than 1 Li^+ /mole leads to breakage of this bond, thus allowing mica-like cleavage parallel to the ac plane. In the voltage profile this results in the sharp knee marking the threshold for reversibility.

In a parallel investigation of chemical Li^+ incorporation by V_2O_5 , Murphy [4] has determined the variations of the parameters a , b and c of the fundamental cell. In $\delta\text{-V}_2\text{O}_5$, formed at room temperature by reaction of V_2O_5 with LiI in CH_3CN , b has passed from 4.38 to 4.97 Å. This consistent increase in b causes rupture of the V—O bond for Li^+ /mole greater than unity. A major structure reorganization ensues, preventing further reversibility.

To see whether the same situation applied to $(\text{Mo}_{0.3}\text{V}_{0.7})_2\text{O}_5$, X-ray experiments were performed at various stages of discharge down to the com-

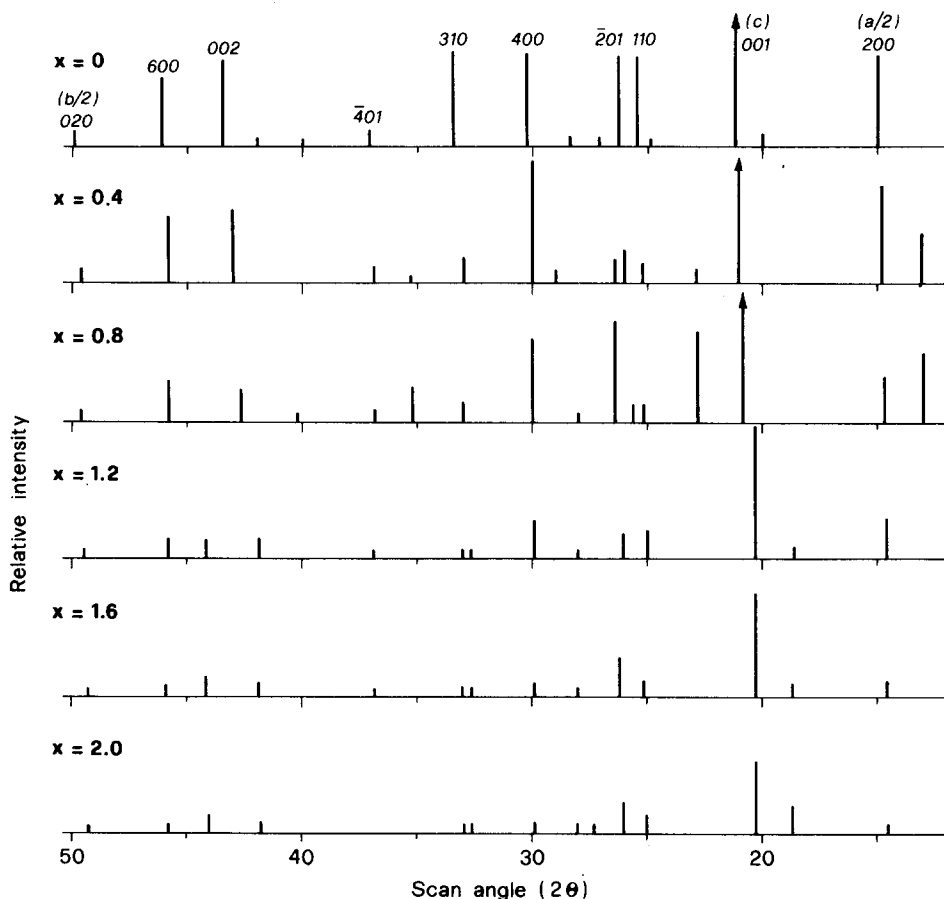


Fig. 2. X-ray diffractograms of $(\text{Mo}_{0.3}\text{V}_{0.7})_2\text{O}_5$ as a function of depth of discharge.

position $\text{Li}_2(\text{Mo}_{0.3}\text{V}_{0.7})_2\text{O}_5$. In Fig. 2 a schematic arrangement of the diffraction patterns is reported. Soon after the incorporation of 0.4 Li^+ /mole, the main feature appears to be a shifting of all peaks to lower angles, this taking place over the whole composition range and indicating structure expansion. This behaviour reveals that in the $\text{Li}/(\text{Mo}_{0.3}\text{V}_{0.7})_2\text{O}_5$ cells the main cathodic reaction is topochemical Li^+ incorporation in the cuboctahedron cavities of the oxide structure.

In Table 1 the variation of the parameters a , b and c on discharge is summarized. For $x = 2$, a expands by 0.4 Å, b by 0.04 Å and c by 0.2 Å. The volume of the unit cell has changed from 179 Å³ in $(\text{Mo}_{0.3}\text{V}_{0.7})_2\text{O}_5$ to 197 Å³ in $\text{Li}_2(\text{Mo}_{0.3}\text{V}_{0.7})_2\text{O}_5$ with an increase of 10%. This limited increase after an uptake of 2 Li^+ /mole is a favourable characteristic of this compound and excludes cathode swelling during discharge. By contrast with V_2O_5 , b expansion in $(\text{Mo}_{0.3}\text{V}_{0.7})_2\text{O}_5$ is almost insignificant, thus excluding layer separation due to breaking of the long M—O bond. This result explains the high Li^+ incorporation in $(\text{Mo}_{0.3}\text{V}_{0.7})_2\text{O}_5$ without significant structural reorganization.

TABLE 1

Variation of the lattice parameters a , b and c of $(\text{Mo}_{0.3}\text{V}_{0.7})_2\text{O}_5$ as a function of Li^+ inserted per mole during discharge

x (Li^+ /mole)	$a/2$ (Å)	$b/2$ (Å)	c (Å)
0.0	5.89	1.828	4.17
0.4	5.99	1.838	4.23
0.8	6.03	1.844	4.28
1.2	6.06	1.845	4.34
1.6	6.07	1.848	4.36
2.0	6.09	1.850	4.37

However, as shown by the patterns of Fig. 2, 4 new peaks appear at the beginning of discharge ($2\theta = 13.1, 22.8, 26.5$ and 35.3° for $x = 0.4$). All these peaks are still present and higher at $x = 0.8$ and then disappear with the exception of the one at 26.5° . At $x = 1.2$, 2 new peaks are formed (18.7 and 44.2°). This pattern seems to be connected with minor structural alterations leading to the appearance/disappearance of new planes. In a tridimensional and distorted structure, such as that of $(\text{Mo}_{0.3}\text{V}_{0.7})_2\text{O}_5$, intercalation of a foreign ion is expected to produce such modifications.

The inequality of the sites available for Li^+ is also reflected in the peculiar voltage profile. We think that this oxide may be included in the class of pseudo two-phase compounds proposed by Armand [5]. As Li^+ is inserted, two adjacent phases are formed which correspond to two superstructures.

The two pseudo-phases are filled successively, according to their site energy, and this explains the sharp knee on the discharge curves.

As pointed out by Armand and confirmed by our experimental results, this kind of intercalation leads to a reversibility less smooth than that shown by perfectly non-stoichiometric compounds (such as TiS_2). However, we have ascertained that from both pseudo-phases Li^+ could be recovered upon recharge.

Following Murphy's conclusion on the equality between number of Li^+ ions and cavities in LiV_2O_5 [2], we are inclined to believe that in $\text{Li}_2(\text{Mo}_{0.3}\text{V}_{0.7})_2\text{O}_5$ there are 2 Li^+ per cavity. Quite possibly they reside in opposite square pyramidal sites (see Fig. 1), so being coordinated by 5 oxygen atoms.

By ESCA analysis we have determined the oxidation state of the metal atoms in $(\text{Mo}_{0.3}\text{V}_{0.7})_2\text{O}_5$. Molybdenum is present as Mo^{6+} only, whereas V is $\sim 70\%$ V^{5+} and $\sim 30\%$ V^{4+} . We have also attempted to see how these states are modified after electrochemical reduction. Unfortunately, the impossibility of making an *in situ* determination has led to reoxidation of the surface layers of the lithiated material, so that only Mo^{6+} and V^{5+} were detected.

(ii) Secondary cells

The efficiency of recharge during the first cycle was determined in prismatic cells at 0.5 mA/cm^2 (Fig. 3). It may be noticed that for $x = 0.4$ only 50% of capacity is recovered upon charge, thus indicating that 0.2 Li^+ /mole cannot be removed from the structure in normal charging conditions. The efficiency values at $x = 0.8$ and $x = 1.2$ are consistent with the impossibility of removing *ca.* 0.2 Li^+ /mole, this amounting to 25% at $x = 0.8$ and to 16% at $x = 1.2$.

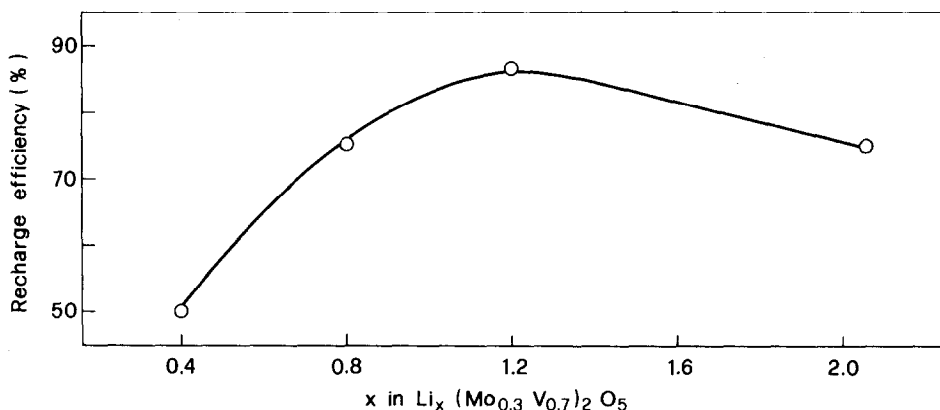


Fig. 3. Recharge efficiency (first cycle) as a function of Li^+ inserted per mole.

Low efficiencies at low d.o.d. have been frequently found in other Mo oxides [6, 7]. This is consistent with the hypothesis that a certain amount of Li^+ , when accommodated in these distorted structures, may occupy energy-

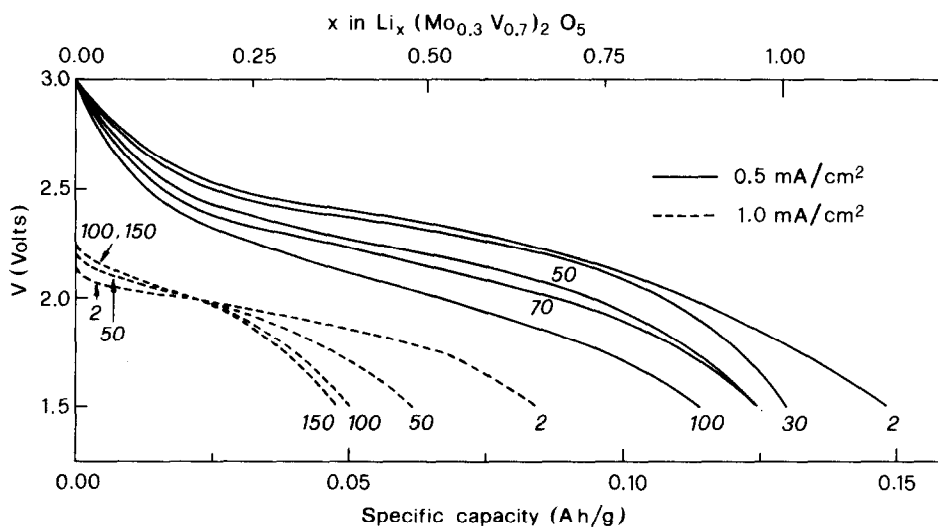


Fig. 5. Cycling behaviour of a prismatic cell (—) at 0.5 mA/cm^2 (55.7 mA/g) and of a rolled type cell (---) at 1.0 mA/cm^2 (122 mA/g). Depth of 2nd discharge, 58% at 0.5 mA/cm^2 and 33% at 1.0 mA/cm^2 .

able for discharge/charge current densities not greater than 1.0 and 0.5 mA/cm^2 , respectively [10]. Under these conditions 70 cycles were obtained at 40% d.o.d. and nearly 400 cycles at 25% d.o.d.

These results indicate a kinetically hindered charge process for V_2O_5 also, although this was not clearly stated in the literature. Kinetic hindrance to reoxidation has already been reported for other Mo oxides, *i.e.*, MoO_3 [6] and $\text{Mo}_{18}\text{O}_{52}$ [7].

The results of X-ray analysis after limited and extended cycling are shown in Fig. 6. Soon after the first cycle, some structural alteration was

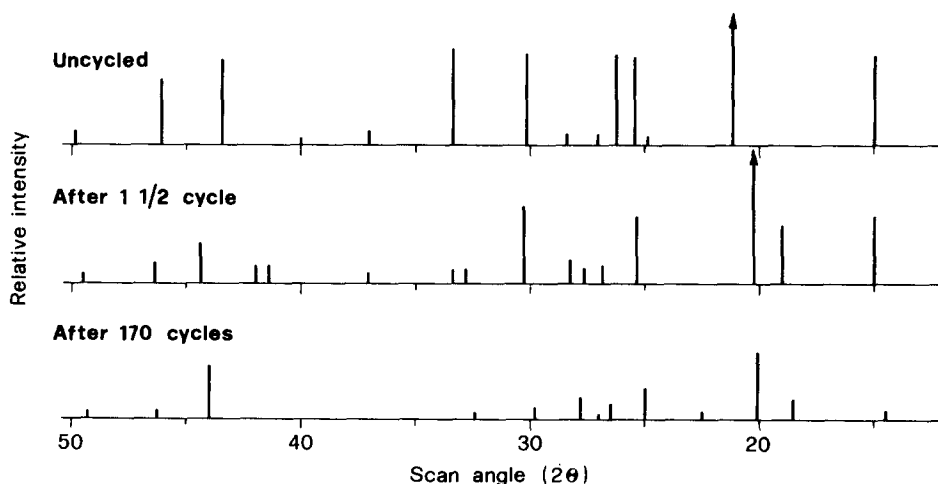


Fig. 6. X-ray diffractograms as a function of cycling.

evidenced by a somewhat different diffraction pattern. From the voltage profiles of Fig. 4 one could have anticipated such variations. On the same basis, limited variations should be expected on the following cycles. This is, indeed so, the diffraction pattern after 170 cycles being very similar to the one after one cycle.

In general, shifting of the peaks to lower angles in cycled cathodes tends to correspond to the shifting observed in $\text{Li}_x(\text{Mo}_{0.3}\text{V}_{0.7})_2\text{O}_5$ for $x > 1$. This would indicate that, upon cycling, substantial amounts of Li^+ are retained in the oxide structure. This could be the main reason for the decline in efficiency with number of cycles.

Conclusion

The possibility of accommodating more than 2 Li^+ /mole in the structural cavities of $(\text{Mo}_{0.3}\text{V}_{0.7})_2\text{O}_5$ gives high specific capacities to this material. Such incorporation takes place with minor structural alteration and cell volume increase, through paths allowing fast Li^+ motion.

Although a certain asymmetry exists between charge and discharge processes, the structural characteristics allow satisfactory rechargeability in practical cells. Unlike V_2O_5 , $(\text{Mo}_{0.3}\text{V}_{0.7})_2\text{O}_5$ can take more than 2 Li^+ /mole and still be rechargeable with high efficiencies as a result of the resistance of its structure to cleavage.

By adding these comments to the conclusions of Part I of this work, $(\text{Mo}_{0.3}\text{V}_{0.7})_2\text{O}_5$ may be included in the list of prospective cathode materials for practical Li^+ cells.

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