

A COMPARATIVE ELECTROCHEMICAL STUDY OF MoO_3 , V_2O_5 AND MoV_2O_8 AS RECHARGEABLE CATHODES IN LITHIUM CELLS

A. TRANCHANT* and R. MESSINA

*Laboratoire d'Electrochimie, Catalyse et Synthèse Organique, CNRS,
2, rue Henri Dunant, 94320 Thiais (France)*

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Summary

The cathodic performances of V_2O_5 , MoO_3 and MoV_2O_8 were examined to find the best candidate for a rechargeable cathode for lithium cells: in this respect, MoV_2O_8 was found to be the most promising. Its main advantage as a cathodic material compared with V_2O_5 and MoO_3 is its good cycling behaviour over a wide voltage range, even when the discharge goes to completion. This good rechargeability may be due to the formation of an amorphous phase as soon as the discharge occurs.

Introduction

In the development of rechargeable lithium batteries, increasing attention has been focused on new, mixed oxide-based cathode materials exhibiting high energy density and reversible lithium incorporation. Recently, V_2O_5 - MoO_3 systems have been proposed as cathode materials in lithium batteries operating at room temperature [1]. They have been reported to be more promising than their parent oxides V_2O_5 and MoO_3 . Although V_2O_5 and MoO_3 undergo intercalation of lithium ions into their crystal lattice, they are not appropriate candidates for secondary lithium batteries because of their poor rechargeability after a deep discharge [2 - 6]. Extensive lithium insertion can induce irreversible structure reorganization resulting in poor reversible electrochemical performances. Most studies of substitute compounds to overcome this irreversibility have been made using either non-stoichiometric forms such as V_6O_{13} , $\text{Li}_{1+x}\text{V}_3\text{O}_8$, and molybdenum compounds intermediate between MoO_2 and MoO_3 [7 - 11], or amorphous compounds such as V_2O_5 - P_2O_5 glasses [12, 13]. Another potentially attractive group of materials for use as high energy lithium cell cathodes is mixed oxide-based systems such as MoV_2O_8 [1].

*Author to whom all correspondence should be addressed.

In this paper, the electrochemical behaviour of MoV_2O_8 is compared with that of V_2O_5 and MoO_3 in order to select the best candidate for secondary lithium batteries able to undergo deep discharge with the least reversibility loss.

Experimental

Electrochemical characterisation

Electrolyte

High purity propylene carbonate (PC) was used as-received, but the dimethoxyethane (DME) was dried prior to use by storage over molecular sieves, and the LiCF_3SO_3 was vacuum dried at 100°C for 12 h.

All the electrolytes, obtained from Fluka, were protected from moisture by keeping them in an argon-filled glove box.

Cathode materials

MoO_3 and V_2O_5 were supplied by Johnson Matthey Chemical, Ltd. The MoV_2O_8 was prepared according to the method reported by Lecerf[†]. An appropriate mixture of the analytically pure oxides MoO_3 and V_2O_5 (in a molecular ratio equal to 1) were melted in a silica crucible at 700°C followed by quenching to room temperature. The sample was then ground before X-ray and electrochemical measurements were taken. Its X-ray pattern closely matches that reported by other workers and especially Eick and Kilsborg [14]. According to our X-ray results, MoV_2O_8 is the major compound formed by the fusion of MoO_3 and V_2O_5 at 700°C but the presence of other intermediate phases cannot be excluded. (Table I)

TABLE 1

X-ray data of MoV_2O_8 obtained by fusion of V_2O_5 and MoO_3 at 700°C

Compound	$d_{\text{obs}}(h k l)$ (Å)								
MoV_2O_8	—	4.81	4.463	4.143	3.776	3.553	3.455	3.229	3.137
MoV_2O_8^*	9.67 (200)	4.843 (400)	—	4.118 (001)	3.772 (201)	3.565 (110)	—	3.235 (600)	3.120 (401)
MoV_2O_8	2.873	—	2.644	2.555	2.471	2.296	2.069	—	1.943
MoV_2O_8^*	—	2.698 (111)	2.650 (510)	—	—	—	2.060 (002)	2.011 (202)	1.941 (1000)

* MoV_2O_8 X-ray pattern according to ref. 14.

[†]Laboratoire de Chimie des Matériaux Inorganiques et de Cristallographie, INSA, Rennes, France.

The 99.999%-pure graphite used for the working electrode preparation was supplied by Koch-Light.

Experimental technique

The electrochemical cell has been described in detail elsewhere [15]. The working electrodes were prepared by pressing a mixture of cathode material (2 - 3 mg) and graphite (in a weight ratio of 10/90) onto a stainless steel grid. An aluminium rod was used as a counterelectrode and lithium as the reference electrode. All potentials are referred to the reference system Li/Li^+ .

Voltammetry and chronopotentiometry experiments were performed using a three electrode device (Tacussel). Cells were cycled automatically between appropriate upper and lower voltage limits.

X-ray analysis

X-ray analyses were carried out using an X-ray diffractometer with $\text{Cu K}\alpha$ radiation ($d = 1.5405 \text{ nm}$).

X-ray experiments were carried out on pure cathode materials pressed onto a stainless steel grid without graphite addition. Electrochemically-reduced samples were washed, under an argon flow, with dried and degassed, distilled tetrahydrofuran before the X-ray measurements were made.

Results and discussion

Comparative structural data of MoO_3 , V_2O_5 and MoV_2O_8

The structures of MoO_3 , V_2O_5 and MoV_2O_8 , constructed from MO_6 octahedra ($M = \text{metal atom}$, $\text{O} = \text{oxygen atom}$), are represented in Fig. 1. The MoO_3 structure consists of layers of infinite zig-zag chains of MO_6 octahedra, while that of V_2O_5 and MoV_2O_8 can be described as a shear structure composed of octahedra forming ReO_3 type slabs which are infinitely long in the a and c directions. The thickness of these slabs is the only difference between the structures of these vanadium compounds: three octahedra thick for MoV_2O_8 and two for V_2O_5 .

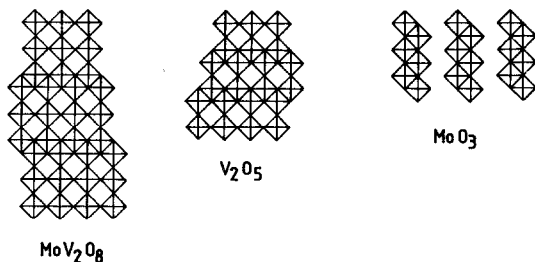


Fig. 1. The crystal structure of MoV_2O_8 , V_2O_5 and MoO_3 . (The structures are represented in terms of the MO_6 octahedra which are obtained by joining the centers of the oxygen atoms coordinated with each metal atom.)

Electrochemical study

The electrochemical behaviour of MoO_3 , V_2O_5 and MoV_2O_8 is compared in Figs. 2 and 3. As shown in these Figures, under our experimental conditions, MoV_2O_8 exhibits the highest rechargeable specific capacity.

The major drawback to the use of MoO_3 as a cathode material is the irreversible lithium insertion occurring at the beginning of the electroreduction. This insertion takes place in the MoO_3 layered structure, resulting both in a new distribution of the octahedra MO_6 groups and a trapping of the first intercalated Li^+ which then induces a loss in the recharge efficiency of this material [16]. On the other hand, in the distorted MoO_3 structure, the intercalation of further Li^+ ions is almost reversible, although the Faradaic capacity tends to decrease as cycling proceeds.

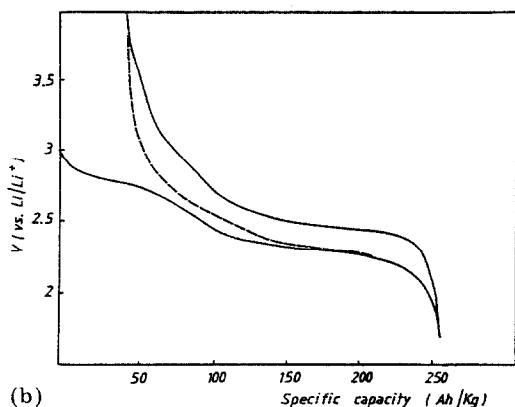
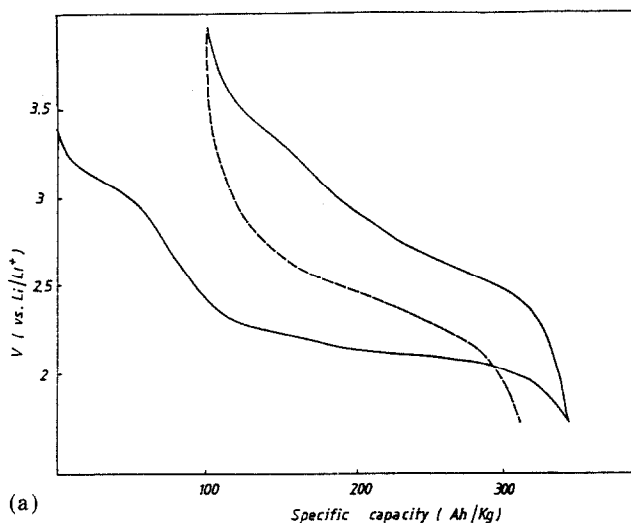


Fig. 2. Cyclic chronopotentiograms of MoV_2O_8 (a) and MoO_3 (b) (—, first cycle; ---, second discharge). Voltage limits: 1.7 - 4 V; 1 mA-PC / LiCF_3SO_3 1 M.

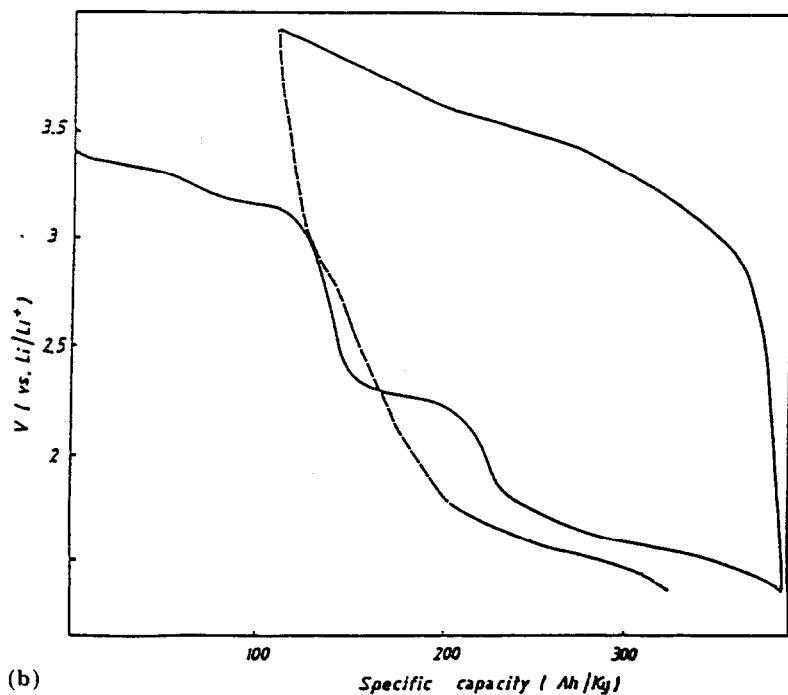
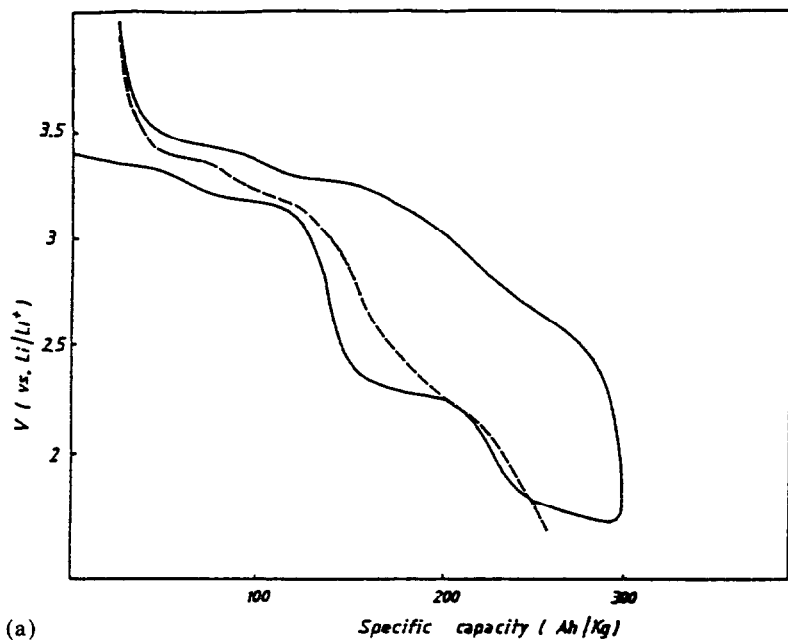
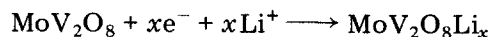


Fig. 3. Cyclic chronopotentiograms of V_2O_5 (—, first cycle; ---, second discharge). (a) Voltage limits: 1.7 - 4 V; (b) voltage limits: 1.4 - 4 V. 1 mA-PC/LiCF₃SO₃ 1 M.

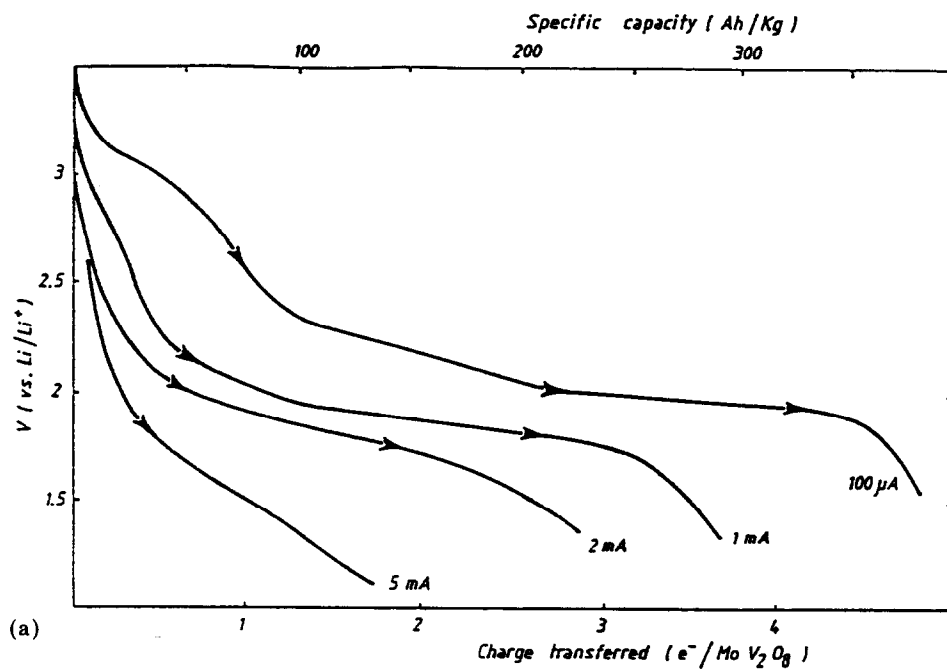
The significant difference between V_2O_5 and MoV_2O_8 is the absence of a large potential drop in the discharge of MoV_2O_8 . Furthermore, the complete Faradaic capacity of MoV_2O_8 can be obtained for a final potential 0.3/0.4 V superior to that of V_2O_5 . This must limit the reorganization of the MO_6 octahedra groups during MoV_2O_8 electroreduction. Supporting this view is the fact that the V_2O_5 recharge efficiency is considerably reduced when electroreduction is performed beyond a specific capacity of 300 A h kg^{-1} , up to the last discharge process at 1.5 V (Fig. 3). During such extended electroreduction, crystal lattice reorganisations are well known to occur, resulting in poor reversible electrochemical performance [17]. This suggests that the control of the lower voltage limit of cycling is of utmost importance to avoid irreversible reduction of this oxide. Such a dependence on electrochemical behaviour toward the depth of the discharge is never observed for MoV_2O_8 . A loss of 25 - 30% of the capacity, however, is obtained during the first recharge of MoV_2O_8 , no matter what the lower voltage limit of the first discharge.

Chronopotentiograms and a cyclic voltammogram of MoV_2O_8 are shown in Fig. 4. These experimental data show that nearly $5 e^-/MoV_2O_8$ specific capacity can be obtained at moderate discharge rates. With regard to the specific capacity found during the electroreduction of V_2O_5 (close to $2.5 e^-/V_2O_5$) and MoO_3 (close to $1.5 e^-/MoO_3$), it appears that the crystal structure of MoV_2O_8 allows a deeper reduction of molybdenum (VI) and vanadium (V). With regard to the crystallographical and electrochemical data reported on MoO_3 and V_2O_5 , the beginning of the MoV_2O_8 electroreduction (up to $1 e^-/MoV_2O_8$) may be regarded as an electronic transfer which mainly affects the vanadium (V) with the formation of a mixed valency compound containing vanadium (IV), just as observed for V_2O_5 [18]. On the other hand, during the main electroreduction process at 2.5 V to 2 V, the electronic transfer must occur simultaneously on both vanadium and molybdenum.

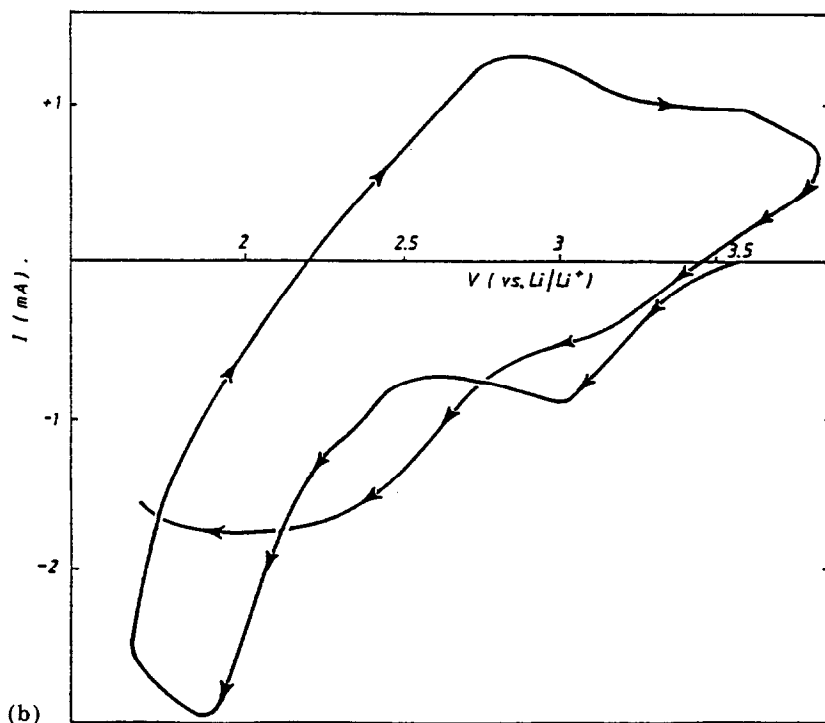
Examination of the shapes of the subsequent charge-discharge curves may lead one to assume that electroreduction of molybdenum and vanadium occurs simultaneously in a potential range of 1.7 V - 4 V in so far as no voltage drop is observed. Moreover, the limited decrease in potential during the charge-discharge processes agrees well with the assumption of an homogeneous single phase; that is, a lithium intercalation compound according to a reaction such as:



Evidence of such an insertion compound cannot be proved by X-ray analysis because of the formation of an amorphous state on discharge. Meanwhile, one can observe, during the beginning of MoV_2O_8 electroreduction, a significant shift of the (001) X-ray peak to lower angles, consistent with the formation of an intercalation compound. A simultaneous gradual increase in the widths of the diffraction peaks, and a decrease of



(a)



(b)

Fig. 4. (a) MoV_2O_8 chronopotentiograms at various current densities; (b) MoV_2O_8 cyclic voltammograms (10^{-3} V s^{-1}). $\text{PC}/\text{LiCF}_3\text{SO}_3$ 1 M.

their intensity, occurs as the electroreduction proceeds, and further X-ray observations become impossible, even during the recharge.

The cycling behaviour of MoV_2O_8 is reported in Fig.5. The specific capacity rapidly falls during the first few cycles and then remains fairly steady for subsequent cycles. From this, MoV_2O_8 is a promising candidate for use as active cathode in secondary lithium batteries over a wide potential range.

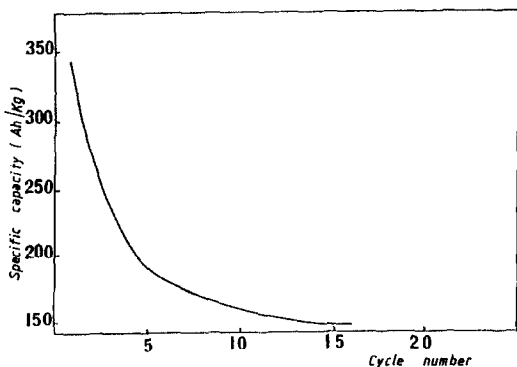


Fig. 5. Specific capacity of MoV_2O_8 as a function of the cycle number. Voltage limits: 1.7 - 4 V. PC/ LiCF_3SO_3 1 M - 100 μA .

Conclusion

This comparative electrochemical study of MoO_3 , V_2O_5 and MoV_2O_8 has shown that MoV_2O_8 is the best candidate cathode material of the three for secondary lithium batteries. The main advantages of this mixed oxide are:

- (i) a cycling efficiency of at least 150 A h kg^{-1} whatever the depth of discharge;
- (ii) a limited decrease of the potential during the charge-discharge.

Acknowledgements

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