

$(\text{Mo}_{0.3}\text{V}_{0.7})_2\text{O}_5$ AS A SOLID SOLUTION CATHODE FOR Li CELLS. PART I. ELECTROCHEMICAL BEHAVIOUR OF PRIMARY CELLS

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Summary

A new cathode material for Li cells has been prepared by using the Mo-rich limit of a range of solid solutions obtained by Mo substitution for V in V_2O_5 . $(\text{Mo}_{0.3}\text{V}_{0.7})_2\text{O}_5$ proves to possess two of the key requirements for cathodes to be used in Li cells, *i.e.*, high specific capacity and rate capability. At 1.0 mA/cm² and to 1.8 V cut-off it may incorporate 2.3 Li⁺/mole, thus giving capacities of ~0.3 A h/g. At current drains higher than 5 mA/cm², a substantial amount of this capacity may still be drawn. Low particle size (<10 μm) and high diffusion coefficients over the whole discharge range (>10⁻⁹ cm²/s) provide the basis for this rate capability. A comparison with the parent oxide, V_2O_5 , shows that a higher energy density is obtainable with $(\text{Mo}_{0.3}\text{V}_{0.7})_2\text{O}_5$.

Introduction

Transition metal oxides have so far received less attention than the corresponding chalcogenides as far as their capability to incorporate alkali ions in their structures is concerned [1]. However, the discovery of the excellent performance of oxides such as MnO_2 [2, 3] and V_2O_5 [4, 5] in Li cells has stimulated efforts aimed at understanding the mechanism of Li⁺ insertion in oxide-based matrices. As early as 1975, Ikeda [2] was able to demonstrate that MnO_2 could electrochemically form a ternary phase with Li and a similar reaction was then proposed for Li/ V_2O_5 cells [1].

Transition metal oxides may be based on both layered and tridimensional framework structures. A number of oxides of the latter kind has now been reported to accept Li⁺ in structural cavities with rates and/or capacities comparable or even higher than those shown by the layered structures [6 - 9]. Vanadium pentoxide and electrochemically active MnO_2 (such as the γ and γ - β phases) provide examples of framework structure oxides [10, 11] in which Li⁺ diffusion occurs through the paths provided by a network of channels.

Lithium/vanadium pentoxide cells, extensively investigated especially at Honeywell Laboratories, are of practical interest in both reserve and primary active configuration [5] due to their high and constant potential (~ 3 V) and high energy density. However, as pointed out by Murphy [10], the use of V_2O_5 may give rise to some drawbacks connected with: (a) low electronic conductivity; (b) irreversible reduction for Li^+ /mole uptake greater than 1; (c) solution decomposition on charging, and (d) low solubility in organic solutions. Such limitations have prompted investigation of cathodes based on shear structure oxides similar to V_2O_5 . V_6O_{13} provides an example of such compounds and is reported to be an efficient cathode material for both primary and secondary Li cells [7].

In this laboratory, a mixed Mo-V oxide, $(Mo_{0.3}V_{0.7})_2O_5$, was taken into consideration because of the similarity between its structure and that of V_2O_5 [12]. Preliminary electrochemical tests were satisfactory, showing that high capacities could be drawn from this material at high c.d.

Experimental

$(Mo_{0.3}V_{0.7})_2O_5$ was prepared by slightly modifying Kihlborg's technique [12]. Stoichiometric amounts of MoO_3 , V_2O_5 and Mo (instead of V_2O_3) were thoroughly mixed and then heated at $650^\circ C$ for 2 days in an evacuated quartz tube. The X-ray powder pattern of this compound matched the one reported by Kihlborg (in the latter, the intensity of the strong reflection of the 001 plane at 4.17 \AA was erroneously reported as weak). Samples prepared with a slight V_2O_5 defect showed the same X-ray pattern. This was also the case with a sample annealed at $350^\circ C$ for 1 day. Before the end of this work, we successfully prepared $(Mo_{0.3}V_{0.7})_2O_5$ at $500^\circ C$ by allowing higher reaction times. This enables one to use glass instead of quartz tubes and contributes to maintaining a low overall level of cost for this oxide, the starting materials being relatively inexpensive.

Purification of solvents and preparation of solutions have been reported in a previous paper [13]. $LiAsF_6$, $LiBF_4/MF$ was prepared according to the technique described by Ebner and Walk [14], which is reported to give a stable solution for Li/V_2O_5 cells.

Three cell configurations were tested. Button cells have been made as already described [13]. Prismatic cells had the cathode material supported on a U-shaped expanded Ni net completely surrounded by a separator and a Li ribbon. Rolled-type cells, having the internal diameter of AA size cells, were made by spirally winding the Ni-supported cathode material, the separator and Li.

$(Mo_{0.3}V_{0.7})_2O_5$ is a semiconductor ($\rho = 4 \times 10^4 \text{ ohm cm}$). At low discharge rates ($\leq 0.5 \text{ mA/cm}^2$) it can be used without additives, but at higher c.d. Teflonized carbon black has to be added to limit polarization losses. A 2:1 carbon black-Teflon mixture, obtained by boiling an emulsion of the 2 components, was mostly used (30% where not otherwise indicated).

Handling of all the materials was done in an Ar filled dry box having an H₂O vapor content below 10 ppm as monitored by the device described by Manev [15].

Diffusion coefficients were obtained in a 2-electrode cell using the current pulse technique described by Worrell [16]. Preliminarily, it was ascertained that in the experimental conditions adopted Li polarization was negligible so it could act as both counter and reference electrode. In the formula used for D calculation:

$$\Delta E = mVi\tau/FA(\pi Dt)^{1/2}$$

the following quantities were used: m (slope of the E/x curve) = 0.44, V (molar volume) = 58.98 cm³, i (current pulse) = 0.003 A, τ (duration of the pulse) = 30 s, A (cathode area) = 1.26 cm².

The possibility of dissolution of (Mo_{0.3}V_{0.7})₂O₅ in LiClO₄/PC-THF was examined by differential pulse polarography after the salt had been in solution for several months.

X-ray analyses were obtained with a Philips diffractometer using Ni-filtered Cu K α radiation.

Results and discussion

(Mo_{0.3}V_{0.7})₂O₅ is the Mo-rich limit of a range of solid solutions starting from V₂O₅ and having the general formula (Mo _{x} V _{$1-x$})₂O₅. Its structure is isotypic with that of R-Nb₂O₅, with distorted MO₆ octahedra arranged as in V₂O₅ [12, 17] (Fig. 1) through the sharing of corners and edges. Basically, the structure can be described as built of edge sharing octahedra forming zig-zag chains in the c direction. Adjacent chains are connected by corner sharing between octahedra. Alternatively, the structure may be described as a shear structure formed by slabs of ReO₃-type, two octahedra thick, extending infinitely in the bc plane. These slabs are interconnected by edge sharing between octahedra.

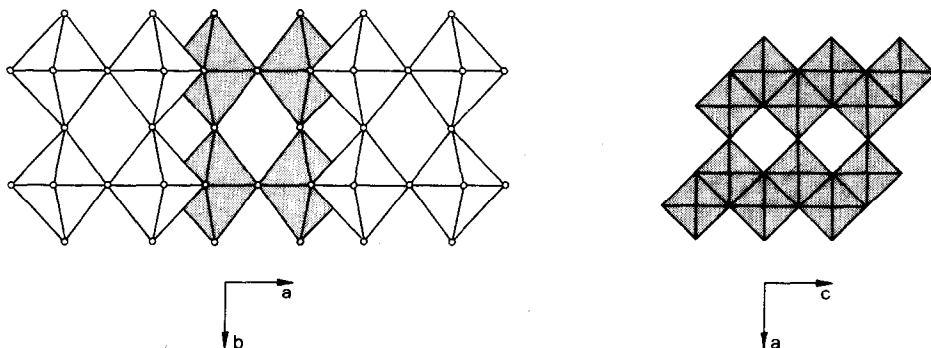
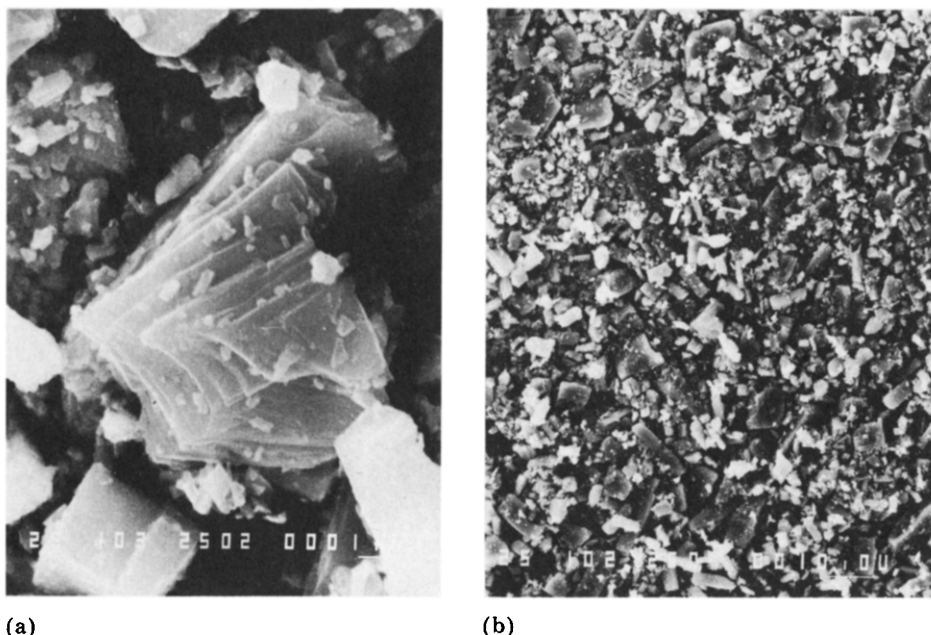


Fig. 1. The idealized structure of (Mo_{0.3}V_{0.7})₂O₅ based on MO₆ octahedra. Zig-zag chains along c , slabs in the bc plane.



(a) (b)
 Fig. 2. SEM pictures showing: (a) a typical crystal formed by slabs (1 cm = 1 μm); (b) particle size (1 cm = 10 μm).

The distortion of the metal atoms from the centres of these octahedra is different in the two oxides and, indeed, they have a different symmetry (V_2O_5 is orthorhombic, whereas $(Mo_{0.3}V_{0.7})_2O_5$ is monoclinic). This is also reflected in the M–O distances [12]. In particular, the unusually long V–O bond in V_2O_5 (2.81 Å), which allows the proposal of an alternative five-fold coordination for V [12, 17], is reduced to 2.54 Å in $(Mo_{0.3}V_{0.7})_2O_5$.

Murphy [10] has ascertained that V_2O_5 can incorporate Li^+ topochemically but not the larger cations Na^+ and Me_4N^+ . This had led the author to state that V_2O_5 has to be viewed as a framework host, rather than a van der Waals host, with weak chemical V–O bonding between layers still existing in LiV_2O_5 . This conclusion is even more applicable to $(Mo_{0.3}V_{0.7})_2O_5$ in which the length of the weak M–O bond is shorter, so that this compound may be considered as a tridimensional layered one. In the SEM picture of Fig. 2(a) a crystal with the typical interconnected slabs is represented.

Electrochemical reaction of $(Mo_{0.3}V_{0.7})_2O_5$ with Li also leads to the topochemical incorporation of Li^+ . We shall go into the structural details of this reaction in Part II of this work, whereas the relevant electrochemical features will be reported here.

The discharge profile of $Li/(Mo_{0.3}V_{0.7})_2O_5$ cells is quite different from that of Li/V_2O_5 cells, showing a short pseudo-plateau (less than 10% of total capacity) at 2.9 V, followed by a long pseudo-plateau at 2.2 V. The first plateau will often not be included in the calculations.

TABLE 1

Specific capacities and mean discharge voltages at 1.0 mA/cm² for button cells containing different electrolytes. Cathodes without additives. First plateau not included

Solution	Capacity (A h/g)	Mean voltage (V)
1M LiClO ₄ /PC	0.19	1.96*
1M LiAsF ₆ /PC	0.23	2.01*
2M LiAsF ₆ , 0.4M LiBF ₄ /MF	0.47	1.33**
1M LiAsF ₆ , 0.4M LiBF ₄ /PC	0.19	1.95***
2M LiClO ₄ /PC, THF(1:2)	0.22	2.08*

*1.8 V cut-off.

**1.0 V cut-off.

***1.5 V cut-off.

First of all, the influence of organic solutions on capacity and discharge voltage was investigated in button cells and the results are shown in Table 1. LiAsF₆, LiBF₄ in MF gives an exceedingly high capacity at low voltages so that we are inclined to believe that most of this capacity stems from electrolyte decomposition. LiAsF₆/PC and LiClO₄/PC-THF give satisfactory capacities and the latter was selected for further investigation due to the higher mean voltage. LiClO₄/PC-THF solutions are conveniently used in CuO-based 1.5 V Li cells [18].

Next, the influence of type and percentage of additives was investigated and the results are shown in Fig. 3. It will be noted that a 5% addition is

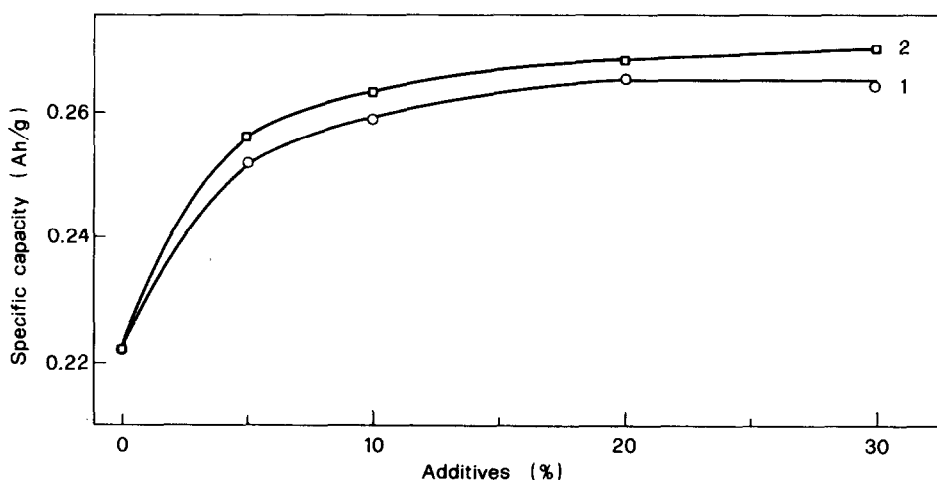


Fig. 3. Specific capacity as a function of % additives in the cathode. 1, graphite; 2, carbon black + Teflon (2:1). C.d., 1.0 mA/cm², first plateau not included.

sufficient to bring the capacity near to the maximum values. Indeed, the specific resistance, after addition of 5% Teflonized carbon black, decreased from 4.0×10^4 to 1.3×10^2 ohm cm. With 30% Teflonized carbon black ρ is lowered to 5 ohm cm, thus reducing to negligible values cathodic iR losses at high c.d.

Preliminary tests had shown that $(\text{Mo}_{0.3}\text{V}_{0.7})_2\text{O}_5$ could be discharged efficiently at high rates. Discharge curves at various c.d. were then obtained in both button and rolled type cells. The discharge profiles of the latter are shown in Fig. 4. The first short plateau disappears as the c.d. increases, whereas the potential of the second pseudoplateau declines slowly. The corresponding capacities as a function of c.d. are shown in Fig. 5. These results lead to two important observations. First, the specific capacity of $(\text{Mo}_{0.3}\text{V}_{0.7})_2\text{O}_5$ is much higher than that reported for V_2O_5 (theoretical value for 1 Li^+ /mole, 0.148 A h/g). At 1 mA/cm^2 it ranges from 0.27 to 0.30 A h/g, depending on the cell configuration and on the inclusion of the first plateau in the calculation. This corresponds to an uptake of 2.1 - 2.3 Li^+ per mole of $(\text{Mo}_{0.3}\text{V}_{0.7})_2\text{O}_5$ to a 1.8 V cut-off. Secondly, the capacity remains at high levels at high c.d. For instance, in rolled-type cells the capacity obtained at 5 mA/cm^2 (0.22 A h/g) is still 80% of the capacity obtained at 0.2 mA/cm^2 .

A high rate capability calls for a high velocity of diffusion of Li^+ in the solid matrix. Diffusion coefficients were determined for $\text{Li}_x(\text{Mo}_{0.3}\text{V}_{0.7})_2\text{O}_5$ in the range $0 < x < 2$. As pointed out by Worrell [16], the use of a polycrystalline material for such experiments instead of a single crystal leads to some degree of uncertainty in the results. First, the porosity of the pelletized material being different from zero, the real area will be somewhat greater

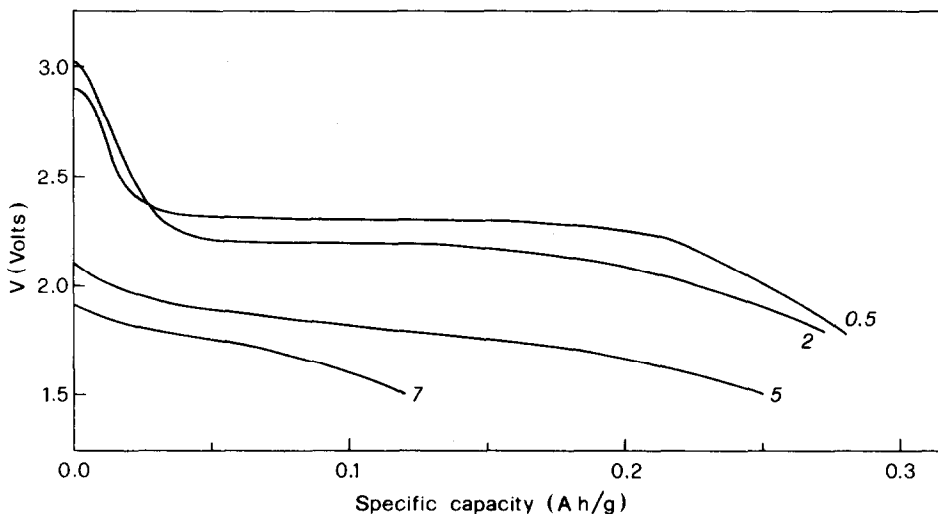


Fig. 4. Discharge curves of rolled-type cells at various c.d. (indicated on the curves as mA/cm^2).

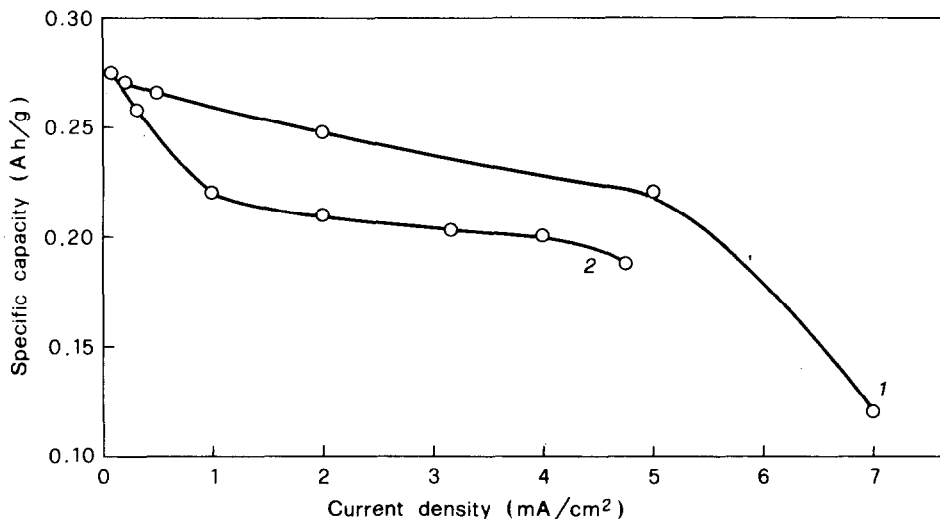


Fig. 5. Dependence of specific capacity on c.d. for rolled-type cells (curve 1) and button-type cells (curve 2). For both curves, first plateau not included. Button cells without additives. 1.8 V cut-off with the exception of discharges at 5 mA/cm² (1.6 V) and 7 mA/cm² (1.5 V) for rolled-type cells.

than its geometrical counterpart. Secondly, if there is electrolyte penetration into the pellet, diffusion of Li⁺ may also take place in the electrolyte channels.

Even with these limitations, the values obtained give a good indication of the diffusivity values*. We tried to reduce the source of errors by using a highly compacted cathode. The results are shown in Fig. 6. D values greater than 10^{-9} cm²/s were obtained over the whole composition range with a maximum of 6.0×10^{-9} cm²/s for $1.2 < x < 1.6$. The decline observed at high x values corresponds to the decreasing number of sites available for Li⁺ occupancy. These D values are among the highest measured for transition metal oxides and chalcogenides and explain the high rates observed.

Atlung [19] has pointed out that if a high D is coupled with a high cathode porosity, very efficient cathodes may be achieved on the basis of the relation: $Q = TD/r^2$, where Q is the efficiency, T the stoichiometric discharge time and r the radius of the particles. The SEM picture, Fig. 2(b), shows that most of the particles have linear dimensions well below 10 μm. With this value for r and with the above reported D values, cathode efficiencies above 90% may be obtained [19]. V₆O₁₃ has also been shown to be more efficient when particles in the range 1 - 5 μm are used, by comparison with 10 - 50 μm particles [7].

*Whittingham [1] reports 1×10^{-8} cm²/s for an LiTiS₂ single crystal and Worrell [16] 5.6×10^{-9} cm²/s for polycrystalline Li_xTiS₂ pellets.

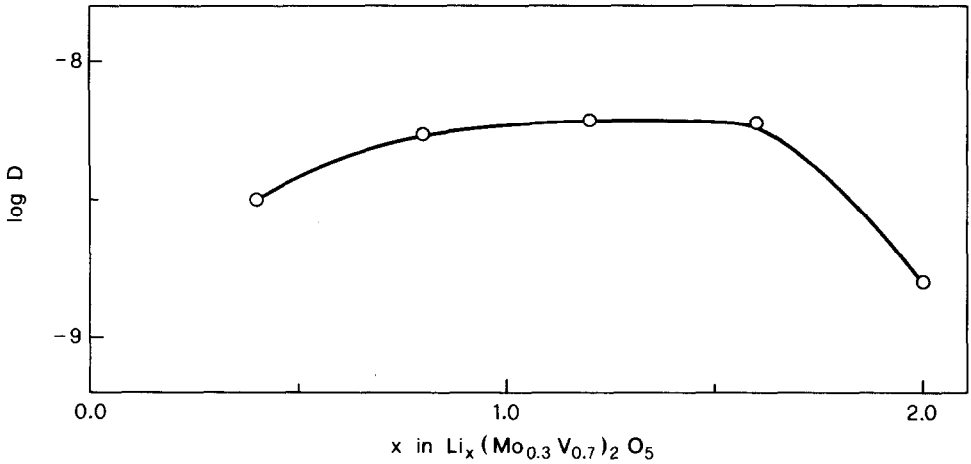


Fig. 6. Dependence of diffusion coefficients on the amount of Li^+ inserted.

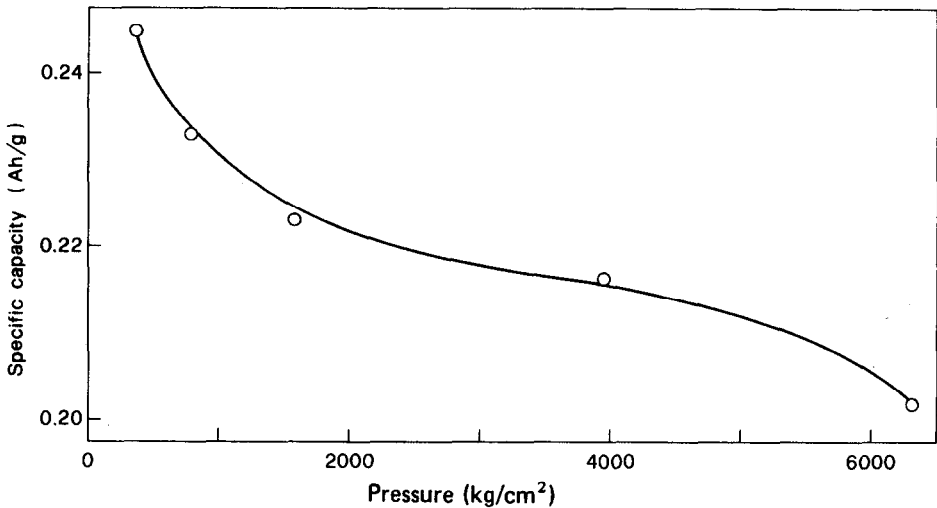


Fig. 7. Dependence of specific capacity on cathode compacting pressure in button cells. Cathodes without additives. First plateau not included. C.d., $1 \text{ mA}/\text{cm}^2$.

A high porosity ensures high electrolyte penetration and, in turn, ready availability of Li^+ ions which have to diffuse in the oxide structure. Therefore, a reduced compacting pressure is expected to be beneficial for the cathode efficiency as long as the mechanical integrity of the cathode is maintained.

Figure 7 shows that this is indeed the case for the present system, with specific capacities monotonically decreasing as a function of pellet density. Fortunately, at 39 MPa ($400 \text{ kg}/\text{cm}^2$) additive-free cathodes were still mech-

TABLE 2

Specific capacities and mean discharge voltages at various temperatures for button cells
C.d., 1 mA/cm². First plateau not included.

Temperature (°C)	Capacity (A h/g)	Mean voltage (V)
0	0.22	2.03
20	0.27	2.19
40	0.27	2.23
60	0.20	2.13

anically stable and this limit could be further lowered by using Teflon bonded electrodes.

The efficiency of Li/(Mo_{0.3}V_{0.7})₂O₅ cells remains fairly high even at low temperatures, as shown in Table 2, with acceptable decreases of capacity and mean voltage. At high temperatures the performance is also satisfactory, but some irregularities in the voltage profiles call for a better cell shape.

A first room temperature storage test has allowed us to ascertain that performance losses due to self-discharge processes are unlikely to happen in these cells. A rolled-type cell was kept for 70 days in a dry-box and then discharged at 1 mA/cm² with no decrease in either capacity or voltage. A parallel solubility test has revealed that (Mo_{0.3}V_{0.7})₂O₅ does not dissolve to any appreciable extent in LiClO₄/PC-THF. Differential pulse polarography experiments did not show any wave attributable to metal transition ions after leaving the oxide in contact with the solution for several months. These tests are satisfactory but, obviously, longer storage times are needed for a complete evaluation of the storage characteristics of these cells.

Finally, an intermittent discharge test was made at low rates. A button cell was discharged at the on-off regime of 4 h (typical of such devices as

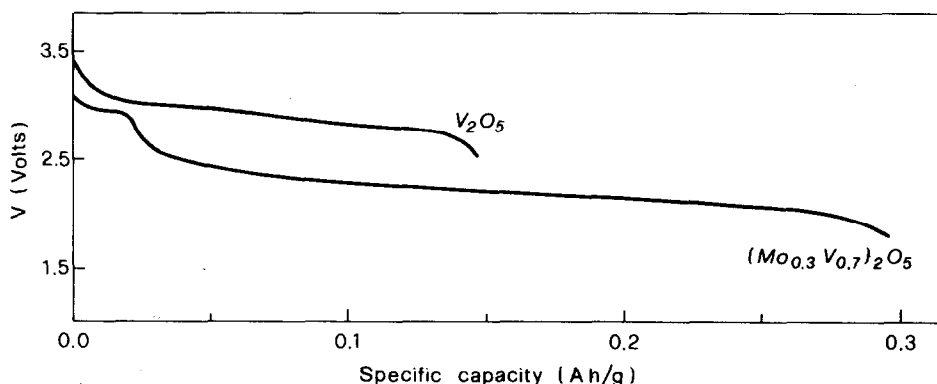


Fig. 8. Comparison of discharge characteristics of button-type cells containing (Mo_{0.3}-V_{0.7})₂O₅ and V₂O₅ (both with 30% Teflonized carbon black). C.d., 1.0 mA/cm².

radio transmitters) and showed the same performance as a continuously discharged cell.

To ascertain properly how this system compares with the one based on the parent oxide V_2O_5 , the two oxides were tested under identical conditions. Button cells were built with additive-containing cathodes and discharged at 1 mA/cm^2 . The discharge curves of Fig. 8 show that $\text{Li}/(\text{Mo}_{0.3}\text{V}_{0.7})_3\text{O}_5$ cells can offset their lower discharge voltage with a substantially higher capacity. Indeed, their specific energy (based on 1 mole of $(\text{Mo}_{0.3}\text{V}_{0.7})_2\text{O}_5$ and 2.3 moles of Li) is 606 W h/kg , whereas $\text{Li}/V_2\text{O}_5$ gives 409 W h/kg . From the above value for $\text{Li}/(\text{Mo}_{0.3}\text{V}_{0.7})_2\text{O}_5$ cells a volumetric energy density of 2.34 W h/cm^3 for the cathode can be calculated.

Conclusion

This new cathode material has proved to be highly efficient in primary Li cells both in terms of specific capacity and rate capability. No doubt, in this respect, it surpasses a well established cathode material such as V_2O_5 . However, it has two drawbacks, *i.e.*, the short initial plateau and a mean voltage (around 2.2 V) not compatible with devices working at 1.5 V or 3 V (watches, calculators, pacemakers, etc.).

The first drawback may be eliminated by current pulses of a few minutes until the potential of the second pseudo-plateau is reached. It has to be noted that during the latter portion of discharge and to a 2.0 V cut-off, $\Delta V/\Delta x$ is 0.25 , *i.e.*, the voltage regulation is fairly good. The second drawback is clearly unavoidable. However, due to its rate capability, this material seems to be more useful for medium and high power applications (radio transceivers, flashlights, tape recorders, etc.) requiring higher voltages. This would allow voltage compatibility through the use of a series of cells.

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