

THE DISCHARGE REACTION MECHANISM OF THE MoO₃ ELECTRODE IN ORGANIC ELECTROLYTES

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Summary

Discharge and charge reactions of MoO₃ electrodes in organic Li⁺ electrolytes are shown to be reversible topotactic redox processes of layered molybdenum bronzes Li_x⁺[MoO₃]^{x-}. The kinetically accessible charge range amounts to 0.1 ≤ x < 1.5 with the lower limit of x depending on the precedent cathodic load. Complete re-oxidation to the binary oxide is kinetically hindered presumably as a result of small structural changes. The process is strongly affected by the size of the electrolyte cation, whereas no dependence on the anion species was observed. Reduction beyond x = 1.5 is at least partially associated with irreversible changes in the oxide structure. Similar reactions were found for non-stoichiometric molybdenum oxides e.g. Mo₁₈O₅₂ and Mo₈O₂₃.

Introduction

Molybdenum trioxide MoO₃ is known to be a suitable cathode material for organic electrolyte lithium batteries. Owing to the high degree of utilization of MoO₃ cathodes the practical energy density of the Li/MoO₃ couple exceeds that of the Li/CuS system [1]. Since the redox process of MoO₃ is reversible its application for secondary Li-batteries was proposed [2]. Although the phenomenological discharge behaviour of MoO₃ in organic solutions of Li⁺ salts is well known [1 - 4] neither the number of electrons involved nor the discharge products and reaction mechanism had been elucidated conclusively.

The formation of lower oxides of molybdenum [4,5] e.g. according to MoO₃ + 2 Li⁺ + 2 e⁻ ⇌ MoO₂ + Li₂O [4] as well as the formation of Mo-oxyhalides [2] and of ternary phases [6] were proposed for potential discharge reactions. By coulometric analysis of MoO₃ dissolved in γ-butyro-

lactone (BL) electrolytes the number of electrons involved in the reduction process has been reported to be two [7]. On the other hand, even low current density discharge of MoO_3 did not yield more than 1.5 F/mol MoO_3 [3] which is in agreement with the observations made by other workers [1,4] and with our own results.

In a previous paper on electrochemical reactions of the layered oxide MoO_3 in aqueous and non-aqueous electrolytes we were able to show that the reversible behaviour of MoO_3 electrodes is clearly to be interpreted on grounds of topotactic redox phenomena [8]. The transition metal oxide layers are being retained as two-dimensional matrix units in the course of the reversible redox reactions and cations are taken up from the electrolyte into the interlayer space (Figs. 1 and 2). In this paper results are presented

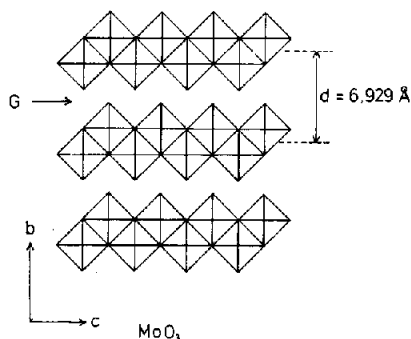


Fig. 1. Scheme of MoO_3 layer lattice; (100) face with MoO_6 octahedra sharing edges. d = distance between neighbouring layers; G = van der Waals gap.

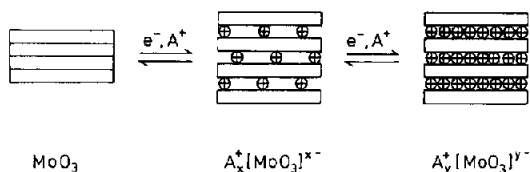


Fig. 2. Scheme of the reversible topotactic redox reaction of MoO_3 in organic electrolytes ($x < y$; negative charges on layers omitted). The range $[\text{MoO}_3]^{x-} \rightleftharpoons \text{MoO}_3 + xe^-$ is kinetically hindered on re-oxidation.

on electrochemical and structural investigations of the influence of cation size and of different anions and solvents on the discharge and re-oxidation behaviour of MoO_3 in organic electrolytes.

Experimental

Electrolytes

Dimethylsulphoxide (DMSO, AR grade) was purified by refluxing at reduced pressure over CaH_2 and subsequently fractionating in vacuum over

a 1.5 m packed column. Butyrolactone (BL, reagent grade) was fractionated in vacuum and stored over 4 Å molecular sieve. 1,2-Dimethoxyethane (DME, reagent grade) was refluxed over sodium and distilled at normal pressure. All solvents were saturated with purified argon. Solutes were vacuum-dried: LiClO_4 at 180 °C for 40 h, LiCl at 180 °C for 20 h, KClO_4 and AlCl_3 at 120 °C for 15 h.

Solutions of LiAlCl_4 were prepared by slowly adding a mixture of 1 mol AlCl_3 and 2 mol LiCl to the solvent with stirring in order to avoid an excess of AlCl_3 . Excess LiCl is only scarcely soluble in BL and DME and tends to precipitate.

Electrodes

MoO_3 powder (analytical grade) was pressed into Pt gauze at 5000 kg/cm^2 and sandwiched between porous glass. The samples were pretreated by heating to 150 °C for 15 h at 10^{-2} Torr. This changed the colour from yellow to green; the specific conductivity at 25 °C of pressed powder pellets of heat treated and untreated oxide was found to be $< 10^{-8} \text{ ohm}^{-1} \text{ cm}^{-1}$. The oxides $\text{Mo}_{18}\text{O}_{52}$ and Mo_8O_{23} were prepared according to the literature [9]. All current densities correspond to the geometrical surface and can only be approximate values.

Potentials were measured *vs.* the saturated aqueous calomel electrode (SCE) which was separated from the compartment of the working electrolyte by two fritted tubes filled with working electrolyte. The lower tube end terminated in a Luggin capillary.

The potentials Li/Li^+ *vs.* SCE are -3.05 V in 0.5 M LiClO_4/BL or 0.5 $\text{LiAlCl}_4/\text{BL}$ and -3.35 V in 0.5 M $\text{LiClO}_4/\text{DMSO}$ or 0.5 M LiCl/DMSO respectively and were determined by micropolarization of Li electrodes.

Cell

Galvanostatic and cyclovoltammetric measurements were carried out in cells of the double-H type fitted with an inlet for inert gas. The working electrode was faced by two Pt counter electrodes, separated by glass diaphragms.

Instrumentation

Constant current was controlled by potentiostats via a constant voltage decay at an external resistance. *X/t* recorders provided with a high impedance operational amplifier (Knick Diomod 73 W) served for the continuous recording of potentials.

X-ray investigations were performed by powder methods in sealed glass capillaries with $\text{CuK}\alpha$ radiation. Precautions were taken to exclude moisture and oxygen on transfer of the sample material to the capillaries.

Results and Discussion

In order to detect a potential participation of chloride ions Cl^- in the reduction and re-oxidation process of MoO_3 as proposed by Campanella and

Pistoia [2,7] the reduction and re-oxidation of MoO_3 was performed in LiClO_4/BL , $\text{LiAlCl}_4/\text{BL}$ and $\text{LiClO}_4/\text{DMSO}$, respectively. LiCl/DMSO was chosen in addition to BL since its outstanding anion solvating power [10] allows high concentrations of LiCl which is only scarcely soluble in other commonly used aprotic solvents such as BL, propylene carbonate (PC) and DME.

Typical discharge/charge characteristics are shown in Figs. 3 and 4.

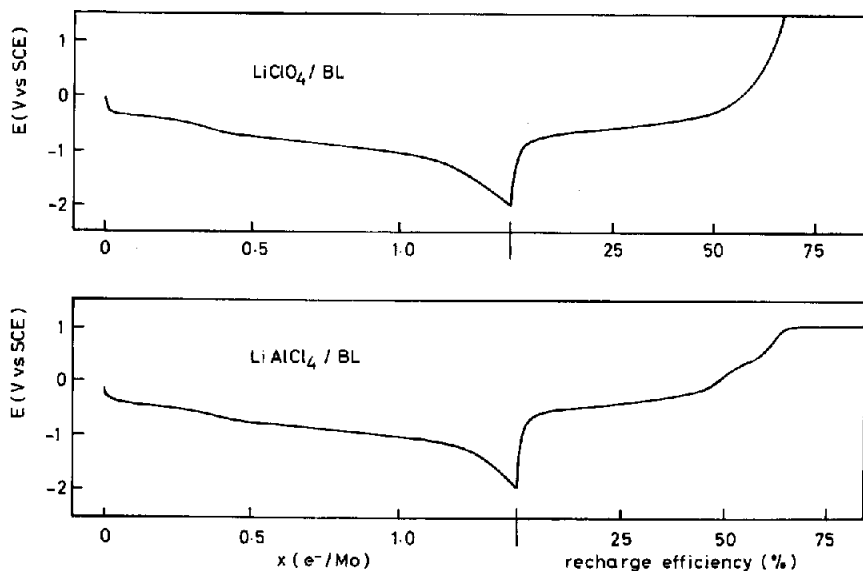


Fig. 3. Galvanostatic reduction/re-oxidation of MoO_3 pressed powder electrodes containing 3 wt % graphite powder in 0.5 M LiClO_4/BL and 0.5 M $\text{LiAlCl}_4/\text{BL}$. $i \approx 300 \mu\text{A}/\text{cm}^2$; 1st cycles.

There is obviously no significant influence of Cl^- or AlCl_4^- on the discharge and recharge behaviour as compared to ClO_4^- electrolytes. This result is confirmed by cyclic voltammetry studies of MoO_3 in LiClO_4/BL , $\text{LiAlCl}_4/\text{BL}$ and $\text{LiClO}_4/\text{DMSO}$, LiCl/DMSO . The curves observed were very similar, in all cases; however, peak area and peak current of the re-oxidation reaction were clearly smaller than the corresponding values of the reduction process. The coulombic efficiencies calculated from peaks of cyclic voltammograms ($v = 1000 \text{ mV}/\text{min}$) also were lower than those of the low current density galvanostatic cycling, thus indicating a kinetic hindrance in the re-oxidation step.

Whereas an influence of the anion on the redox behaviour of MoO_3 in aprotic electrolytes could not be confirmed, we were able to show that the redox reaction is very sensitive to the type of cation present in the electrolyte phase.

Figure 5 shows the performance of MoO_3 cathodes in $\text{KClO}_4/\text{DMSO}$ and CsI/DMSO . The reduction in $\text{KClO}_4/\text{DMSO}$ starts at a potential very

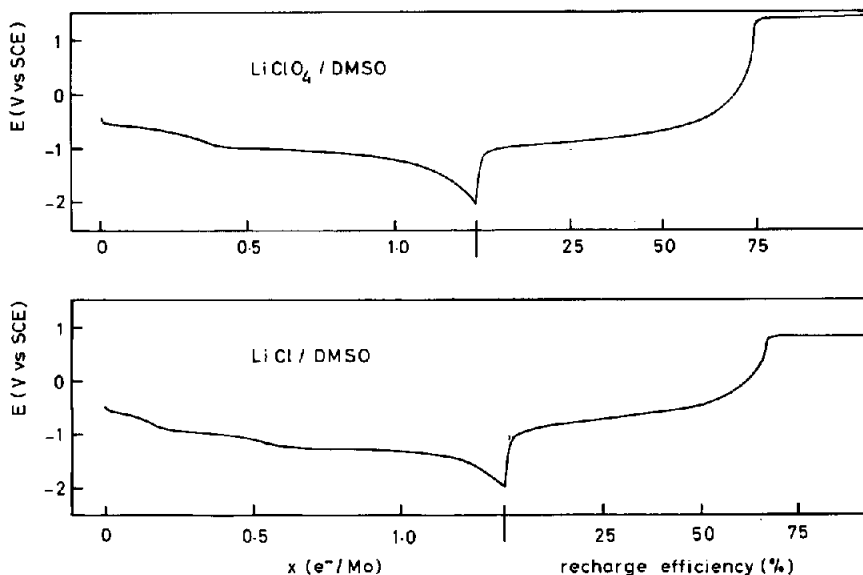


Fig. 4. Galvanostatic reduction/re-oxidation of MoO_3 pressed powder electrodes in 0.5 M $\text{LiClO}_4/\text{DMSO}$ and 0.5 M LiCl/DMSO , $i = 300 \mu\text{A}/\text{cm}^2$; 1st cycles.

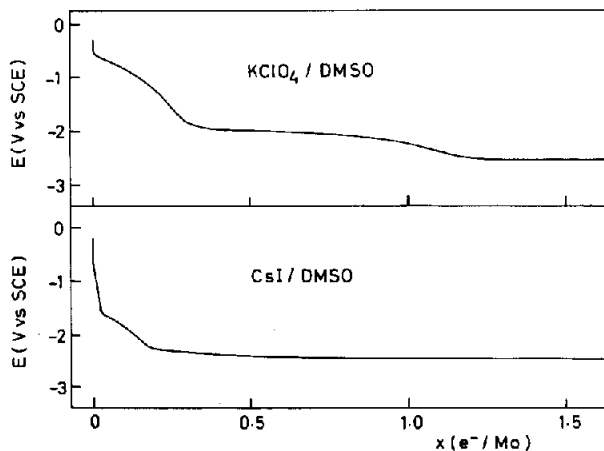


Fig. 5. Galvanostatic reduction of MoO_3 pressed powder electrodes in 0.5 M $\text{KClO}_4/\text{DMSO}$ and 0.5 M CsI/DMSO , $i \approx 300 \mu\text{A}/\text{cm}^2$.

close to that in $\text{LiClO}_4/\text{DMSO}$; however, after a charge transfer of ~ 0.2 electrons per MoO_3 the potential decreases. The performance in $\text{NaClO}_4/\text{DMSO}$ is better than in $\text{KClO}_4/\text{DMSO}$ but is still inferior as compared to $\text{LiClO}_4/\text{DMSO}$. The reversibility of the MoO_3 reduction is very poor in $\text{KClO}_4/\text{DMSO}$ and limited to low x values. The results in CsI/DMSO are even more unsatisfactory. The structural investigations show that the distance d between the MoO_3 layer planes which amounts to 6.93 Å in the binary oxide

is increasing on cathodic reaction in Li^+ /DMSO and Li^+ /DME electrolytes to 7.89 Å for $x = 1.0$. From the magnitude of the lattice parameter enlargement perpendicular to the MoO_3 planes it is clear that non-solvated cations only are taken up into the interlayer space. This is in contrast with the results from the reduction of molybdenum trioxide in polar inorganic solvents *e.g.* H_2O and liquid ammonia, where solvent molecules are taken up along with the cations into the interlayer space [8]. Solvent uptake has also been found for the cathodic reduction of dichalcogenides *e.g.* MoS_2 in polar organic solvents [11]. In both cases changes of d values are considerable and account for the large dimensions of the solvent molecules.

For the reduction of MoO_3 in KClO_4 /DMSO a d value of 8.9 Å is observed which also is in agreement with the intercalation of non-solvated ions. In the case of Cs^+ several phases were found as reaction products which have not been identified.

The difference in reactivity of MoO_3 in organic Li^+ electrolytes as compared to K^+ and Cs^+ electrolytes has to be explained in terms of the topotactic reaction of the oxide crystallites at the electrode. It is known from studies of the intercalation mechanism of layered dichalcogenides that two-dimensional reactions at the phase boundary may be rate determining [12]. The growth of the new solid phase is correlated with strong elastic deformations of the chalcogenide and oxide layers and in addition depends on the ionic mobility of the cations inside the lattice. It is thus conceivable that the steric factor *i.e.* the cation radius may strongly influence kinetics and reversibility of the MoO_3 reduction.

The surprisingly negative potentials observed in the galvanostatic reduction of MoO_3 in solutions of large cations cannot be interpreted as poor thermodynamic stability of the resulting intercalation compounds. They are rather to be considered as the consequence of a large concentration polarization as was confirmed by current interruption in the course of a galvanostatic reduction of MoO_3 in 1 M KPF_6 /DME at low current density. The potential drop after current interruption was small at the start of the reduction but did increase with x , *i.e.* with the extent of the reaction. As the shape of the potential curves in Fig. 5 showed no marked dependence on cation concentration in the electrolyte, the increasing polarization is supposedly induced by slow diffusion in the solid phase.

The reduction of MoO_3 in Li^+ containing electrolytes was found to be affected by the presence of additional large size cations. In a 50 : 50 mixture of 0.5 M KClO_4 /DMSO and 0.5 M LiClO_4 /DMSO the utilization of MoO_3 decreases to about 50% of the value obtained in 0.25 M LiClO_4 /DMSO which confirms the strong influence of cation size on the reaction mechanism.

The coulombic efficiency of the re-oxidation reaction depends on the extent of the previous reduction. Bell-shaped curves of recharge efficiency *vs.* x , as shown in Fig. 6 for LiClO_4 /DMSO (1st cycles) are typical. The maximum recharge efficiency of about 75% agrees well with results from other laboratories in LiAsF_6 /BL [3], LiClO_4 /70% THF - 30% DME [1] and LiClO_4 /THF [4] electrolytes and with our previous studies. We found that

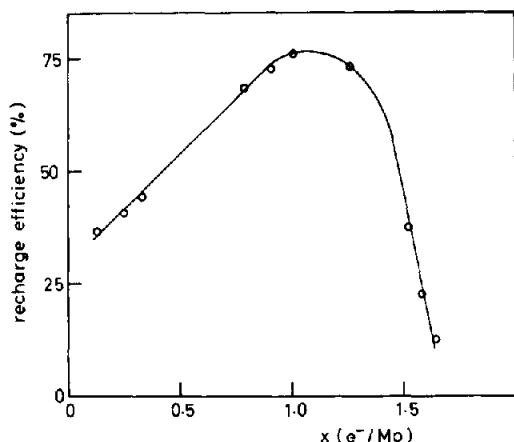


Fig. 6. Recharge efficiency of MoO_3 pressed powder electrodes in 0.5 M $\text{LiClO}_4/\text{DMSO}$ depending on x . $i \approx 300 \mu\text{A}/\text{cm}^2$; 1st cycles.

for the re-oxidized products only a slight decrease is observed for the inter-layer distance d as compared to the reduced state; on oxidation of *e.g.* $\text{Li}_{1.0}\text{MoO}_3$ to $\text{Li}_{0.23}\text{MoO}_3$ the d value decreases from 7.89 Å to 7.78 Å. The fact that on approaching the oxidation state of MoO_3 the electronic conductivity must decrease might serve as the base of a tentative explanation for the limited reversibility of the electrode reaction. Since MoO_3 itself is readily reduced although its electrical resistivity is rather high, this evidence is questionable. We found, however, that there is some effect of non-stoichiometry on the reactivity of MoO_3 . Slightly oxygen deficient "green" polycrystalline molybdenum trioxide prepared by heating of analytical grade MoO_3 at 10^{-2} Torr showed a better performance as compared to the faintly yellow stoichiometric phase.

Our studies in aqueous electrolyte phases demonstrated that the incomplete reversibility of the MoO_3 reduction is a result of kinetic effects, re-oxidation to the binary phase may be achieved on extended reaction times [8]. A more adequate explanation for this phenomenon seems to emerge from refined structural investigations. Preliminary studies on hydrated molybdenum bronzes obtained by cathodic reduction of MoO_3 indicate small changes in the structure of the oxide layers on reduction. These changes which are likely to be correlated with the distortion of the MoO_6 octahedra show a hysteresis effect, *i.e.* they are not reversible in the kinetically accessible redox range ($0.1 \leq x \leq 1.0$ for aqueous electrolytes) and may be responsible for the residual cations respectively negative charge in the solid [13]. On extended oxidation the original lattice is restored again with the formation of MoO_3 .

The breakdown of the coulombic efficiency at high x values seems at least in part to be due to irreversible non-topotactic structural changes of the host lattice as indicated by the occurrence of additional phases in the X-ray pattern of the products. Surface contamination resulting from solvent reduction may, however, also contribute to this reaction. Solvent decompo-

sition must be taken into account if the discharge is continued to a cut-off potential close to 0 V vs. Li. It is known from the behaviour of Li electrodes in aprotic electrolytes that the metal surface can be blocked by decomposition products of the solvent [14]. These blocking interfaces may result in a totally inactive electrode. There is some indication that properties of surface compounds depending on the electrolyte phase may be the key for an understanding of earlier observations [7, 15] on the influence of anions and solvents on the performance of MoO₃ electrodes. The recharge efficiencies of Li_xMoO₃ in different electrolytes were found in our experiments to be almost independent on the solvents for low *x* values (*x* < 0.25). The maximum recharge efficiency in LiClO₄/DME was, however, considerably lower than in LiCl, LiClO₄/DMSO and LiAlCl₄, LiClO₄/BL. A comparative examination of the re-oxidation efficiency of lithium electrodeposited on Cu from the above mentioned electrolytes containing different amounts of added water, showed an outstandingly poor result for the re-oxidation of lithium in H₂O contaminated LiClO₄/DME. As the solubilities of lithium salts in DME are considerably lower than those in DMSO or BL, blocking surface layers should be most stable in this solvent. Because of the more basic character of substances formed at the cathode (*e.g.* decomposition products of the solvent or inert lower oxides of Mo) the assumption of a beneficial effect of Lewis acids (*e.g.* AlCl₃ resulting from the equilibrium AlCl₄⁻ = AlCl₃ + Cl⁻) on the performance of the MoO₃ electrode seems reasonable. This concept was checked by addition of water and Lewis acids to BL and DMSO electrolytes (0.5 M LiClO₄ + 1.5 M H₂O/DMSO, 0.5 M LiClO₄ + 0.15 M B(CH₃COO)₃/DMSO, 0.5 M LiClO₄ + 0.5 M AlCl₃/BL). Whereas the addition of water resulted in an unfavourable effect on the utilization of MoO₃, the efficiency of the MoO₃ cathode was slightly improved by B(CH₃COO)₃ and considerably increased by addition of AlCl₃. There is, however, still the possibility that this increase might be due to small amounts of impurities and decomposition products introduced with the Lewis acids. A favourable influence of low viscosity solvents such as methyl formate on the performance of MoO₃ cathodes which has been reported [15] is not unexpected and should be interpreted in terms of availability of Li⁺ within the pores of the MoO₃ electrode.

The observation that slight oxygen deficiencies of MoO₃ did result in an improved electrode performance, which was also found to be true for addition of inert electronic conductors such as graphite, led us to a study of non-stoichiometric oxides Mo_{*m*}O_{*3m-n*}. Among these the metallic blue phase Mo₁₈O₅₂ has a close structural relationship to MoO₃. The triclinic oxide may be described as a shear structure consisting of MoO₃ type oxide layers which are separated by a van der Waals gap; the layers themselves are, however, regularly stepped (shear planes) [9]. The galvanostatic reduction of Mo₁₈O₅₂ in LiAlCl₄/DME which is shown in Fig. 7 yields 1.5 e⁻ per Mo; potentials and curve shapes as well as the re-oxidation efficiencies turned out to be closely related to those of MoO₃ electrodes. Thus it seems again that the electronic conductivity of the starting phase is of minor importance only with respect

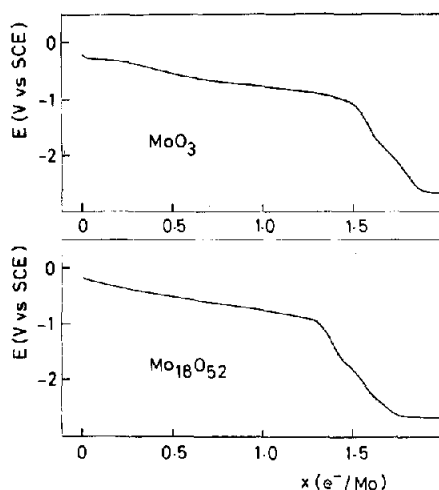
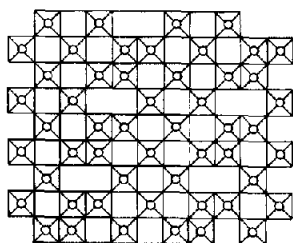


Fig. 7. Galvanostatic reduction of MoO_3 and $\text{Mo}_{18}\text{O}_{52}$ pressed powder electrodes in $0.35\text{ M LiAlCl}_4/\text{DME}$. $i \approx 300\ \mu\text{A}/\text{cm}^2$.

to the reversibility problem; ordered defect types such as shear planes obviously do not influence the reaction mechanism.

Besides the layer type structures in the Mo/O system a series of non-stoichiometric compounds is known among the $\text{Mo}_m\text{O}_{(3m-n)}$ oxides which are characterized by networks of MoO_6 octahedra connected in three dimensions. Preliminary studies showed that some of these phases also may take up small cations by cathodic reduction in organic electrolytes. Thus *e.g.* the oxide Mo_8O_{23} which has a metallic blue violet appearance and provides potential lattice sites for guest cations in the form of empty parallel channels (Fig. 8) does take up more than $1\ e^-$ per Mo in $0.35\text{ M LiAlCl}_4/\text{DME}$.



Mo_8O_{23}

Fig. 8. Scheme of Mo_8O_{23} crystal structure; empty channels are shown in cross-section.

Conclusions

The results obtained present a comprehensive picture of the behaviour of MoO_3 electrodes in organic electrolytes on the basis of a topotactic reac-

tion mechanism. Detailed studies on structure and electronic properties are still necessary in order to reach a thorough understanding of the origin of the kinetically hindered range in the re-oxidation step. Extended investigations by us revealed that the concept of topotactic redox reactions may be applied to electrode processes of a considerable number of additional transition metal oxides. Basic prerequisites for this type of reaction are (a) metal ions in higher oxidation states which easily undergo electron transfer, (b) considerable covalent bonding character in the solid matrix, (c) a suitable electronic band structure, (d) a system of interconnected *i.e.* well accessible empty lattice sites for guest cations, and (e) a high mobility of the latter inside the host lattice. Thermodynamically stable ternary phases with alkali metals may exhibit an analogous reactivity: we found for example that the layered vanadate $\text{Li}_{1.1}\text{V}_3\text{O}_8$ is able to take up reversibly ~ 0.5 electrons in organic lithium electrolytes.

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