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Electrochemical lithium insertion in β -MoO₃: novel Li_xMoO₃ bronzes

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Abstract New lithium molybdenum bronzes have been synthesized by electrochemical lithium insertion. Through electrochemical spectroscopy techniques we have detected that lithium insertion proceeds at least in a two-step reduction process. The maximum amount of lithium inserted in β -MoO₃ leads to a high specific capacity of the cell of 370 Ah kg⁻¹. However, this capacity was lost after the first charge-discharge cycle, resulting in a total loss of 25%, due to structural transformations. The structural study of the insertion process showed that each step of the process can be associated with the formation of different single phases of variable composition, Li_xMoO₃.

Keywords Insertion reaction · Lithium molybdenum bronzes · Rechargeable lithium batteries

Introduction

In solid state chemistry the development of new chemical methods of synthesis has been very important to obtain new advanced inorganic materials with interesting chemical and physical properties and different structural features. With these characteristics, advanced inorganic materials have several commercial applications [1]. In this sense, transition metal oxides belong to one of the groups of inorganic materials with interesting properties that show several types of complex structures formed mainly by two-dimensional or three-dimensional frameworks of octahedra or tetrahedra. These oxides have been studied extensively owing to their potential in

technological applications as superconductors, catalysts, optical materials, chemical sensors, ionic conductors, and electrochemical devices [2].

One of the most common structures is the ReO₃ type, which is the base to describe many non-stoichiometric compounds within the extended family called “tungsten oxide bronzes” [3]. Its structural arrangement consists of WO₆ units which are repeated along the three directions through shared corners (see Fig. 1). The tunnels in their crystalline structure allow insertion of ions in order to form a great variety of compounds called perovskite-type bronzes (PTB). Therefore, owing to their interesting chemical, electrical, and optical properties, many bronzes A_xWO₃ (A = Li, Na, K, Mg, Zn, etc.) with the ReO₃-type structure have been extensively studied [4, 5, 6]. The formation of these bronzes is due to an insertion reaction, which is governed by topotactic aspects between pristine oxides and their corresponding bronzes.

In recent years, soft chemistry methods have been shown to be efficient to prepare new materials which are difficult to synthesize by classical methods. Such a situation has led to the preparation of many new polymorphs of transition metal oxides. Rao et al. [7] have reported the formation of a new peculiar polymorph of MoO₃ with a ReO₃-type structure by dehydration of MoO₃·H₂O. This new polymorph, later called β -MoO₃, additionally has been obtained by several workers through different soft chemistry methods [8, 9, 10, 11, 12].

Nevertheless, in all these methods the formation of β -MoO₃ was accompanied by the difficulty of obtaining it free from impurities of α -MoO₃, the thermodynamically stable polymorph at room temperature. This difficulty in the preparative methods has limited a deep study on the ability of this oxide to incorporate ions by an insertion reaction, and actually only hydrogen molybdenum bronzes have been synthesized by chemical methods [8, 13].

In this work we present a study of the formation of lithium molybdenum bronzes through electrochemical methods. The main advantage in using this technique is that the redox potential, rate of insertion, and

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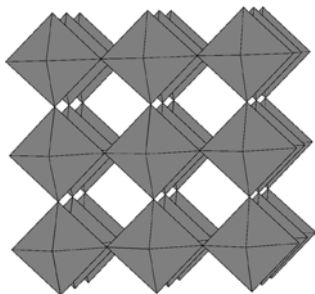


Fig. 1 ReO_3 -type structure adopted by some transition metal oxides

stoichiometry can all be controlled while discharging the appropriate cell, allowing preparation of intermediate phases, i.e. Li_xMoO_3 .

Experimental

$\beta\text{-MoO}_3$ was prepared by ion exchange of an aqueous solution of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ passed through a cation-exchange resin (Dowex 50WX8-200). As the product of this process, we obtained a solution with a pale green colour and a pH of about 2. This solution was placed in a 50 mL vessel that was connected to a vacuum pump for 36 h. By this time, all water was removed slowly and a green powder was obtained. The green powder crystallized as $\beta\text{-MoO}_3$ when it was heated at 250 °C for 2 h in a flowing oxygen atmosphere. Structural characterization of $\beta\text{-MoO}_3$ was carried out using diffraction and spectroscopic techniques, as described previously [14]. These studies revealed that $\beta\text{-MoO}_3$ was free of the most stable polymorph, $\alpha\text{-MoO}_3$.

Electrochemical lithium insertion was carried out in Swagelok-type cells using lithium as the negative electrode and a 1 mol/dm³ solution of LiPF_6 in ethylene carbonate (EC)/dimethyl carbonate (DMC) (50:50) as electrolyte. The positive electrode was formed as a pellet with a diameter of 7 mm, using a mixture of $\beta\text{-MoO}_3$, carbon black, and ethylene-propylene-diene-therpolymer (EPDT) in a 90:9:1 ratio. In order to avoid any contact with moisture, all cells were assembled in a glove box under an argon atmosphere. The electrochemical cells were charged-discharged by applying a

continuous current density of $\pm 80 \mu\text{A}/\text{cm}^2$ in galvanostatic mode and a sweep rate of $\pm 10 \text{ mV}/2 \text{ h}$ in potentiostatic mode, and cycled in the potential range of 3.2–1.0 V vs. Li^+/Li^0 . The electrochemical behavior of the insertion reaction was observed through a multichannel galvanostatic/potentiostatic system (MacPile II) [15].

Structural transformations in the matrix-host during the lithium insertion process were studied by X-ray diffraction (Siemens D-5000 with Cu K_α radiation).

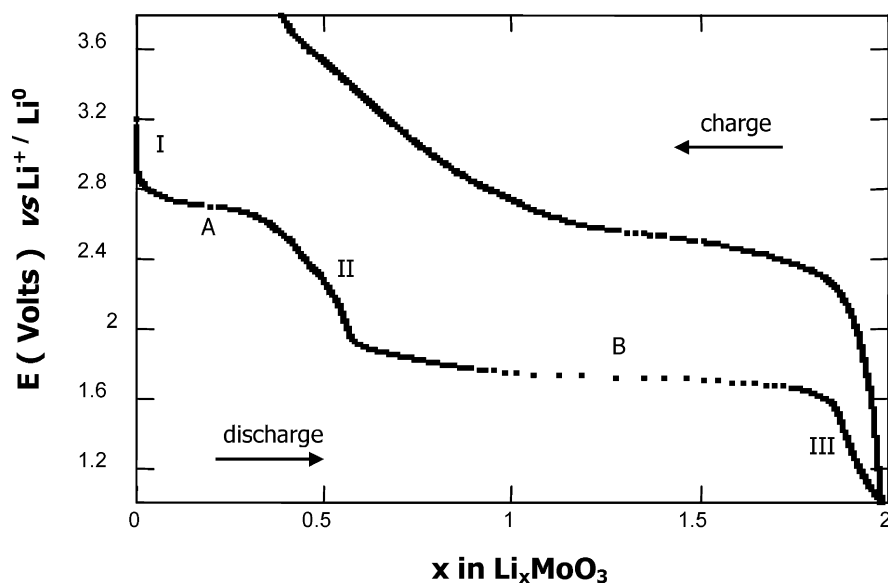
Results and discussion

The voltage-composition plot obtained from the first charge-discharge cycle for a cell containing $\beta\text{-MoO}_3$ as the active material is shown in Fig. 2. In the first instance we detected that electrochemical lithium insertion and deinsertion is feasible in this molybdenum oxide. The lithium insertion proceeds through different processes, as can be deduced from the evolution of the cell voltage with x in Li_xMoO_3 . This plot reveals the existence of three regions where a continuous variation of the potential with composition is observed (labeled as I, II, and III), and two voltage plateaus (~ 2.7 and ~ 1.7 V vs. Li^+/Li^0 , labeled as A and B). In a first approach, we assumed that the continuous voltage variation with composition corresponds to a single-phase region (I, II, and III), but that the voltage plateau was associated with a two-phase region (A and B).

The maximum lithium inserted in $\beta\text{-MoO}_3$, i.e. ~ 2 lithium per formula, leads to a specific capacity for the cell of about 370 Ah kg^{-1} . This value is better than the specific capacity developed by a cell using $\alpha\text{-MoO}_3$, the most stable polymorph at room temperature [16].

In order to check the ability of $\beta\text{-MoO}_3$ to insert-deinsert lithium without polarization effects, we carried out a complete charge-discharge cycle for several cells, using different current densities: 80, 150, and 400 $\mu\text{A}/\text{cm}^2$ (see Fig. 3). From these experiments we can observe the ability of $\beta\text{-MoO}_3$ to insert lithium reversibly

Fig. 2 Voltage vs. composition plot for a charge-discharge cycle of a cell with configuration $\text{Li}/\beta\text{-MoO}_3$ under galvanostatic conditions



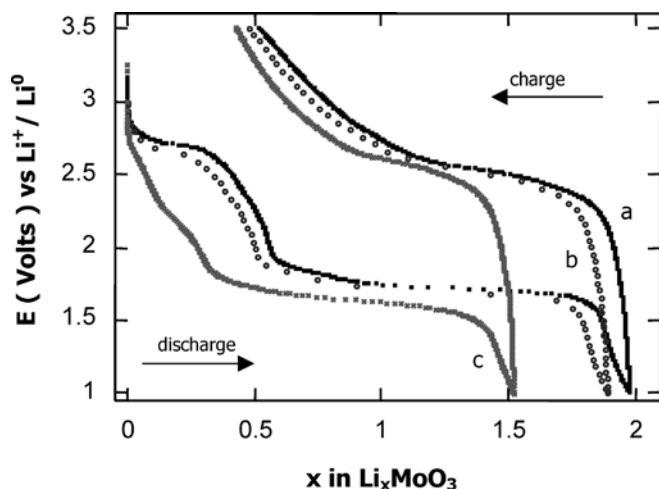


Fig. 3 Voltage vs. composition plot for a charge-discharge cycle of several $\text{Li}//\beta\text{-MoO}_3$ cells run at different current densities: (a) 80, (b) 150, and (c) $400 \mu\text{A}/\text{cm}^2$

without suffering considerable degradation during the lithium insertion-deinsertion process. Such a situation was confirmed when a cell was charged-discharged for 25 cycles under a current density of $400 \mu\text{A}/\text{cm}^2$ (see Fig. 4). During the first charge-discharge cycle the cell exhibited a capacity loss of 25%, probably due to a structural rearrangement. Nevertheless, after the first cycle the cell was able to maintain a specific capacity of about 280 Ah kg^{-1} .

All reduction processes detected during the electrochemical lithium insertion in the $E(x)$ plot were analysed in more detail, by determining the current relaxation with time at each voltage step in a potentiostatic experiment. Figure 5 shows the behaviour of the I vs. t curves along the discharge process. At high potential values, between 3.3 and 2.7 V vs. Li^+/Li^0 , only small currents are detected and the cell exhibits a low capacity. At low potential values, below 2.7 V, the maximum current in each step increased, reaching its maximum value at 2.5 V vs. Li^+/Li^0 . In this region (peak labelled as A), the behaviour of the current with time is far from the $t^{-1/2}$ law. Similar behaviour was observed when the relaxation curves around the peak labelled as B were analysed in detail. On the basis of these results, we deduced that diffusion of the lithium ions is not the process that rules the insertion reaction. We can conclude that in both cases the system is crossing a two-phase domain.

In order to know the nature of the transformations occurring in the matrix-host while lithium insertion proceeds, we carried out an X-ray diffraction study of some lithium molybdenum bronzes. We have synthesized by electrochemical methods and characterized by X-ray diffraction several samples with the composition Li_xMoO_3 , where x corresponds to compositions belonging to different regions of the E vs. x diagram (I, II, III, A, and B). Following the procedure described in the Experimental section, several cells with the configuration $\text{Li}/\text{electrolyte}/\beta\text{-MoO}_3$ were discharged at predetermined values of x .

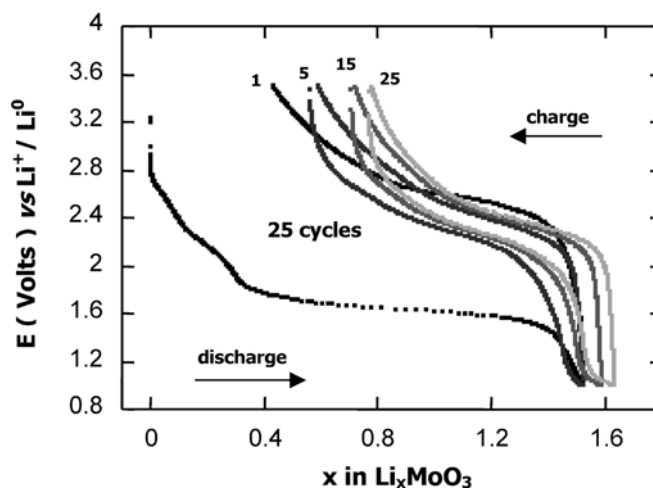


Fig. 4 Voltage vs. composition plots for several charge-discharge cycles of a cell with configuration $\text{Li}//\beta\text{-MoO}_3$ when it was cycled at $400 \mu\text{A}/\text{cm}^2$

We found that the corresponding diffraction patterns of the bronzes were not similar to the parent oxide. At low values of lithium insertion, e.g. $x=0.2$, a new phase with variable composition and cubic symmetry seems to be formed. It called our attention to the surprising formation of a cubic phase at low composition ($x \leq 0.3$); these results differ from those obtained in studies of WO_3 , where the ideal cubic phase is formed after the appearance of other phases with intermediate symmetry [6]. Different compositions were prepared in this composition range, but in all cases we had difficulties in obtaining the single phase and at least two phases were always detected: monoclinic and cubic (m+c).

For a higher content lithium composition, i.e. $x > 0.3$, the diffraction patterns could not be indexed on the basis of any alkaline tungsten bronze known with the ReO_3 structure type. Nevertheless, the corresponding diffraction patterns for compositions $x=1$ and $x=1.6$ are in good agreement with two types of rhombohedral structures reported previously by Cava et al. [17, 18, 19], as can be seen in Fig. 6. In this process, each of the 12-coordinated cavities of the ReO_3 structure becomes two octahedral cavities occupied by lithium. Although we prepared several compositions over the whole range of insertion, we were able to obtain only the rhombohedral-1 phase pure ($x=1$). In the other cases, two phases were always detected: monoclinic and cubic ($x < 0.3$), cubic and rhombohedral-1 ($0.3 < x < 1$), and rhombohedral-1 and rhombohedral-2 ($x > 1$).

On the basis of these experiments we have concluded that, in order to know with precision the different phases formed in the $\text{Li}/\beta\text{-MoO}_3$ system, it is necessary to use another high-resolution characterization technique, i.e. neutron diffraction. Taking into account this result, it seems to be clear that there is a certain agreement between the different features detected in the

Fig. 5 Chronoamperogram obtained by discharging a Li// β -MoO₃ cell at a scan rate of -10 mV/2 h

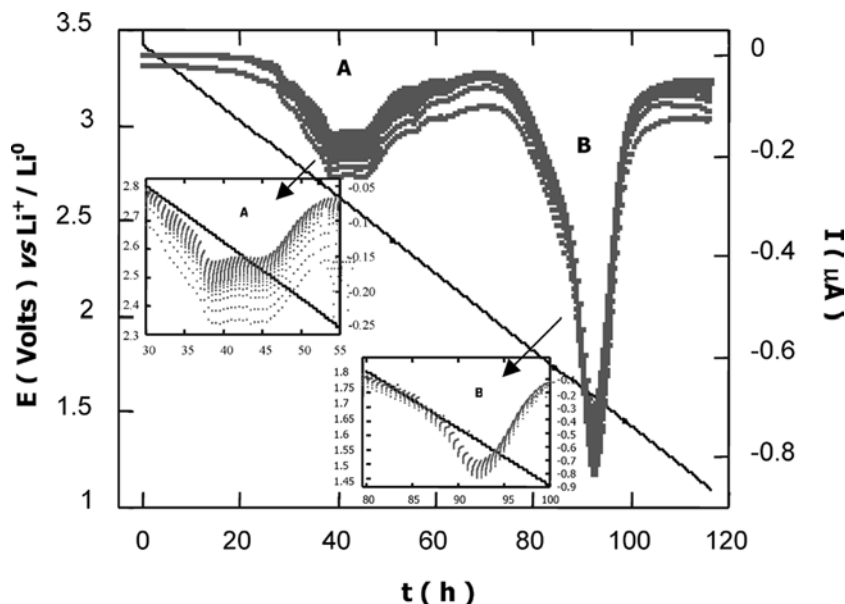
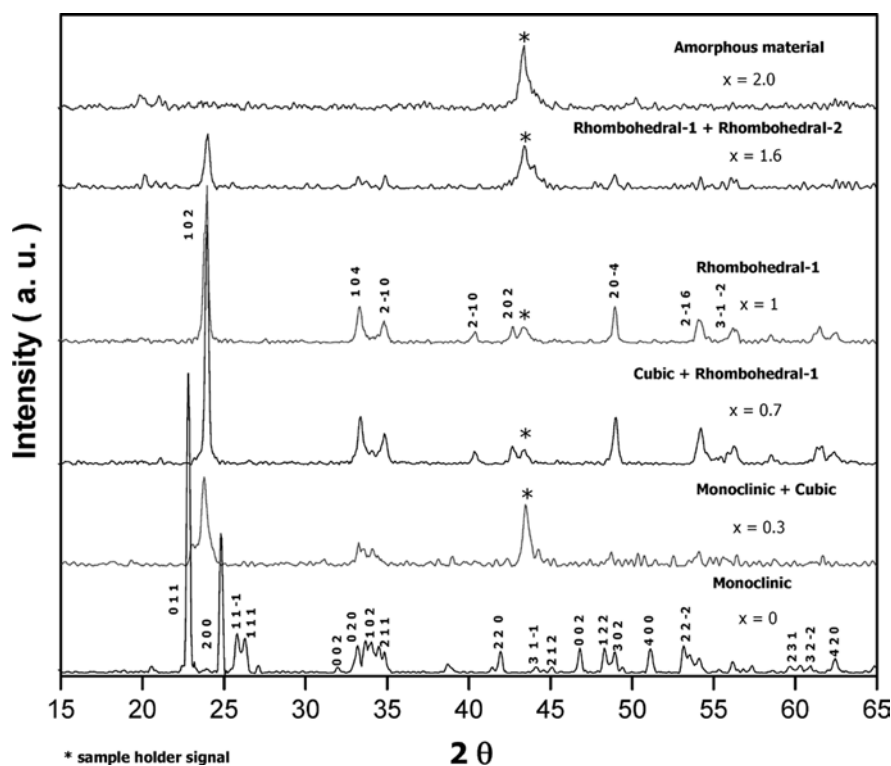


Fig. 6 X-ray diffraction patterns for Li_xMoO₃



electrochemical E - x plot (and I - t diagram) and the phases detected by X-ray diffraction.

Conclusions

Electrochemical lithium insertion in β -MoO₃ allows insertion of ~ 2 lithium atoms/formula, which leads to a specific capacity of 370 Ah kg⁻¹. Nevertheless, this value decreases by 25% after the first charge-discharge cycle. In the same way, we observe that electrochemical

lithium insertion in β -MoO₃ proceeds by at least two reduction steps (~ 2.7 and ~ 1.7 V vs. Li⁺/Li⁰). Such processes have been associated with the existence of new lithium molybdenum bronzes, Li_xMoO₃. Different compositions over the whole range of x have been studied by X-ray diffraction, and the corresponding results correlate well with the electrochemical characterization. The transformation of the first phase (cubic) to the second phase (rhombohedral-1), and the second phase to the third phase (rhombohedral-2), proceeds in both cases through a two-phase region. Nevertheless, we

had some difficulty in obtaining these bronzes in a pure form and only the rhombohedral-1 type was obtained successfully. Some further experiments are now in progress in order to obtain the different bronzes as single phases.

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References

1. Rao CNR, Raveau B (1998) Transition metal oxides: structure, properties, and synthesis of ceramic oxides. Wiley, New York
2. Interrante LV, Hampden-Smith MJ (1998) Chemistry of advanced materials: an overview. Wiley, New York
3. Hagenmuller P (1973) In: (eds) Comprehensive inorganic chemistry, vol. 4. Pergamon, Oxford
4. Brown BW, Banks E (1954) *J Am Chem Soc* 76:963
5. Whittingham MS (1982) In: Whittingham MS, Jacobson JA (eds) Intercalation chemistry. Academic Press, New York
6. Martínez-de la Cruz A, Torres-Martínez Leticia M, García Alvarado F, Morán E, Alario-Franco MA (1998) *J Mater Chem* 8:1805
7. Rao CNR, Gopalakrishnan J, Vidyasagar K, Ganguli AK, Ramanam A, Ganapathi L (1986) *J Mater Res* 1:280
8. McCarron EM III (1986) *J Chem Soc Chem Commun* 4:336
9. Parise JB, McCarron EM III, Von Dreele R, Goldstone JA (1991) *J Solid State Chem* 93:193
10. Harb F, Gerand B, Nowogrocki G, Figlarz M (1986) *CR Acad Sci Paris II* 303:349
11. Svensson G, Kihlberg L (1987) *React Solids* 3:33
12. Ferreira FF, Sousa Cruz TG, Fantini MCA, Tabacniks MH, de Castro SC, Morais J, de Siervo A, Landers R, Gorenstein A (2000) *Solid State Ionics* 136–137:357
13. Genin C, Driouiche A, Gerand B, Figlarz M (1992) *Solid State Ionics* 53–56:315
14. Juárez Ramírez I, Martínez-de la Cruz A (2002) *Mater Lett* (in press)
15. Mouget C, Chabre Y (1991) Multichannel potentiostatic and galvanostatic system “MacPile II”. Claix, France
16. Julien C, Nazri GA (1994) Solid state batteries: materials design and optimization. Kluwer, Boston
17. Cava RJ, Santoro A, Murphy DW, Zahurak S, Roth RS (1982) *J Solid State Chem* 42:251
18. Cava RJ, Santoro A, Murphy DW, Zahurak S, Roth RS (1983) *J Solid State Chem* 48:309
19. Cava RJ, Santoro A, Murphy DW, Zahurak S, Roth RS (1983) *J Solid State Chem* 50:121