Short communication

Electrochemical lithium insertion into amorphous MoO₃·2H₂O

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Abstract

Following the route of synthesis of β-MoO₃ through soft chemistry methods a new amorphous material with composition MoO₃·2H₂O has been detected. The hydrated molybdenum oxide showed the capacity for electrochemical lithium insertion. The maximum amount of lithium incorporated in this material ($\sim$3.3 Li/Mo) leads to a specific capacity of 490 Ah kg^{-1}. The charge–discharge curve showed a good reversibility in the potential range from 3.2 to 1.1 V versus Li$^+$/Li^0 where the cell voltage decreased monotonously as a function of the degree of lithium inserted. The electrochemical features of amorphous MoO₃·2H₂O suggest that it can be considered as a possible cathode candidate in rechargeable lithium batteries.
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1. Introduction

Several transition metal oxides has been investigated in the last decades as possible active materials in electrochemical cells for secondary lithium batteries [1–3]. Some candidates have been tested as positive electrodes based on cost, toxicity, and performance. Within this group of oxides studied, specifically the molybdenum oxides have received special attention due to their chemical and electrochemical properties [4–7].

In recent years, soft chemistry methods have shown to be efficient in preparing new materials which are difficult to synthesize by classical methods. This has led to the preparation of many new polymorphs of molybdenum oxide which usually are formed from selective intermediates [8,9]. In this way, following the route of synthesis of β-MoO₃ by vacuum drying technique we have detected the presence of its correspondence precursor, an amorphous hydrate molybdenum oxide MoO₃·2H₂O [9].

The electrochemical lithium insertion in some hydrated molybdenum oxides has been reported previously. Kumagai et al. [10,11] reported that more than 2.5 Li/Mo can be reversibly inserted into crystalline MoO₃·2H₂O when tested as a cathode material in non-aqueous lithium batteries. The amount of lithium inserted into this hydrated compound is higher than the 1.5 and 2 Li/Mo obtained for anhydrous α-MoO₃ and β-MoO₃ [4,12], respectively.

On the basis of previous studies, we have tested the amorphous MoO₃·2H₂O as an active material in an electrochemical lithium cell in order to find a correlation between the electrochemical data obtained for anhydrous and hydrated molybdenum oxides.

2. Experimental

The oxide-hydrate of molybdenum MoO₃·2H₂O was obtained during the synthesis of β-MoO₃ as was previously reported [9]. It was prepared by cation exchange of an aqueous solution of Na₂MoO₄·2H₂O passed through a cation exchange resin (Dowex 50WX8-200). As a product of this process, we obtained a solution with a pale green color and a pH of 2. This solution was placed in a 50 ml vessel that was connected to a vacuum pump for 36 h. In this time, all water was removed slowly and a green powder was obtained as a residue. The nature of the green powder was determined by different analysis techniques such as X-ray diffraction (Siemens D-5000 with Cu K$_\alpha$ radiation), TGA/DTA (STD-2960 TA Instruments), FTIR (Perkin Elmer) and electron spectroscopy (JEOL 5900 LV). The characterization of MoO₃·2H₂O was discussed in detail in a previous work [9].

The electrochemical lithium insertion was carried out through the charge–discharge of several *Swagelok* type cells in a multichannel galvanostat/potentiostat system

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(MacPile). Such cells were assembled inside a glove box under argon atmosphere (with less than 1 ppm of water and oxygen content) to avoid lithium decomposition. Electrochemical cells were prepared using a lithium pellet as negative electrode, a $1 \, \text{mol dm}^{-3}$ solution of LIPF_6 in ethylene carbonate (EC)/dimethyl carbonate (DMC) as electrolyte and a pellet made of the oxide-hydrate of molybdenum, carbon black, and ethylene-propylene-diene-therpolymer (EPDT) in a 90:9:1 ratio as the positive electrode. The cells were charged–discharged under potentiostatic conditions with scan rates of $\pm 10 \, \text{mV}/2 \, \text{h}$ and $\pm 10 \, \text{mV}/12 \, \text{h}$. Additionally, some cells were cycled under galvanostatic conditions with different densities of current between ± 80 and $\pm 400 \, \mu\text{A cm}^{-2}$.

3. Results and discussions

When lithium is electrochemically inserted into $\text{MoO}_3 \cdot 2\text{H}_2\text{O}$ the voltage of the cell Li/LiPF_6 $1 \, \text{mol dm}^{-3}$ in $\text{EC} + \text{DMC}(50:50)/\text{MoO}_3 \cdot 2\text{H}_2\text{O}$ varies with composition as shown in Fig. 1. In the first instance, the high open circuit voltage observed for the cell, 3.6 V versus Li^+/Li^0, is indicative that molybdenum exists predominantly as Mo(VI) within the structure. The maximum amount of lithium inserted (~3.3 Li/Mo) leads to a specific capacity of the cell of $490 \, \text{Ah kg}^{-1}$, when it is cycled in the range between 3.6 and 1.1 V versus Li^+/Li^0. This value exceeds by more than 20% the specific capacity developed by its homolog crystalline form, $(400 \, \text{Ah kg}^{-1})$ [10]. Such a situation is in agreement with other amorphous materials which present better specific capacities than their crystalline homologs [13–15]. Nevertheless, after the first cycle, the cell was unable to maintain this specific capacity for subsequent cycles and faded to near 55% of the initial value.

Another feature observed during the discharge of the cell is the monotonous fall of the voltage with respect the amount of lithium inserted. This continuous voltage drop is only
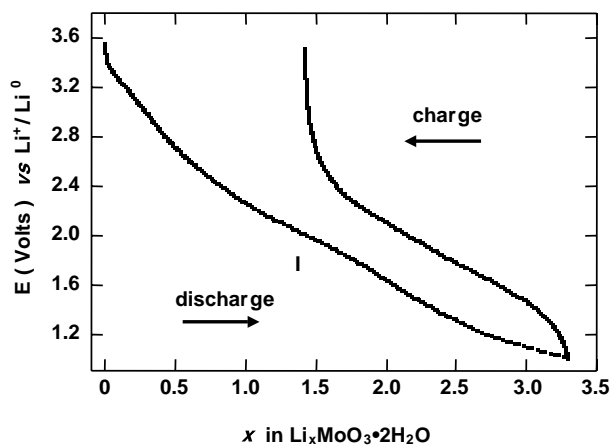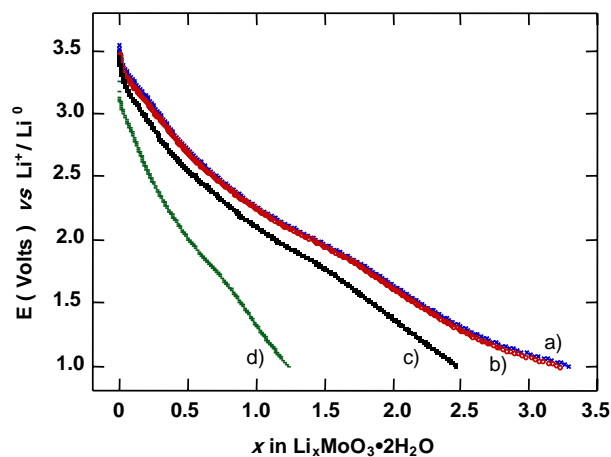

Fig. 2. Comparative curves E vs. x of four cells of configuration $\text{Li}//\text{MoO}_3 \cdot 2\text{H}_2\text{O}$ when it was cycled at (a) $\pm 80 \, \mu\text{A cm}^{-2}$, (b) $\pm 150 \, \mu\text{A cm}^{-2}$, (c) $\pm 240 \, \mu\text{A cm}^{-2}$ and (d) $\pm 400 \, \mu\text{A cm}^{-2}$.

interrupted by a slight slope change in the region labeled as I. This behavior is expected on the basis of the nature of amorphous hydrated oxide. Usually, during the lithium insertion process in a crystalline material, the active material of electrode may experience first order transition or continuous transitions which occur as a consequence of the filling of the different tunnels that are present in a regular pattern. The filled tunnel type involves a certain amount of energy, manifested through different slope changes in an potential–composition $(E–x)$ plot. These features are missing in our case due to the amorphous nature of the $\text{MoO}_3 \cdot 2\text{H}_2\text{O}$.

The reversible capacity of the cell was determined by cycling several cells $\text{Li}//\text{MoO}_3 \cdot 2\text{H}_2\text{O}$ under different conditions. Fig. 2 shows the electrochemical behavior of the curve E versus x of different cells where is observed that an increase of current density leads to a lower amount of lithium inserted (i.e. 1.3 Li/Mo when applied current is $400 \, \mu\text{A cm}^{-2}$) causing a decrease in the specific capacity which is maintained near to $200 \, \text{Ah kg}^{-1}$. After 30 charge–discharge cycles the system was able to insert 1 Li/Mo reversibly, see Fig. 3. This situation probably occurs because lithium inserted reacts with the water molecules present in the material host causing a large incorporation of lithium during first charge–discharge cycle but a high decrease in the specific capacity in subsequent cycles. Note that specific capacity of the cell during the first discharge exceeds in 65% of the theoretical value. From these observation we conclude that the insertion process is not a unique process that takes place during the discharge of the cell $\text{Li}//\text{MoO}_3 \cdot 2\text{H}_2\text{O}$. A complete description of the processes that occurs during the discharge of the cell must include the reaction between Li and coordinated water and remaining water present in $\text{MoO}_3 \cdot 2\text{H}_2\text{O}$:
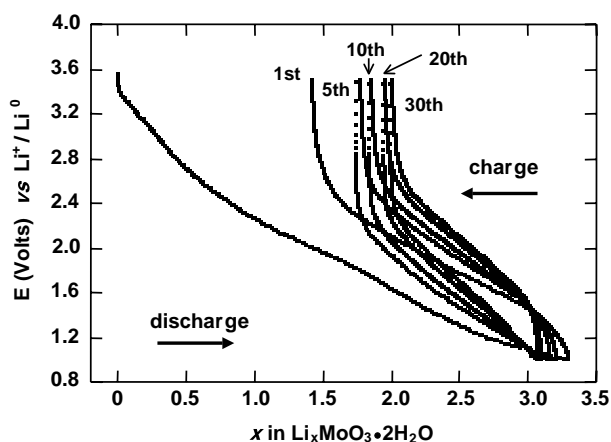
$$2\text{Li} + \text{MoO}_3 \rightarrow \text{Li}_2\text{MoO}_3 \tag{1}$$

$$1.3\text{Li} + 1.3\text{H}_2\text{O} \rightarrow 1.3\text{LiOH} + 0.65\text{H}_2 \tag{2}$$

Fig. 1. Typical curve E vs. x of a cell of configuration $\text{Li}//\text{MoO}_3 \cdot 2\text{H}_2\text{O}$ when it was cycled at $\pm 80 \, \mu\text{A cm}^{-2}$.

Fig. 3. Curve E vs. x that shows until 30 charge–discharge cycles of a cell of configuration Li//MoO$_3$·2H$_2$O when it was cycled at $\pm 80\,\mu\text{A cm}^{-2}$.

Fig. 4. Region of the chronoamperogram correspondent to the zone near to the reduction maximum I in the system Li//MoO$_3$·2H$_2$O.

The first reaction it is related to the insertion of lithium into the host network under the supposition that all Mo(VI) is reduced to Mo(IV). The remaining amount of lithium incorporated can be associated with the reaction between the water molecules and metallic Li. In fact, after the first charge–discharge cycle, about 1.4 Li atoms remain in the structure of MoO$_3$·2H$_2$O. This situation agrees with our reaction mechanics described by the chemical Eqs. (1) and (2). The reaction of lithium inserted with coordinated water molecules has been described previously by Kumagai et al. [13] in the course of the study of lithium insertion into a hydrated form of tungstic acid, H$_2$WO$_4$·2H$_2$O. Through X-ray diffraction and IR spectra analysis they detected the formation of LiOH as a product of the reaction between lithium and water. This situation cannot be confirmed in our study, due to the amorphous nature of the material and the deep blue color developed by the different bronzes synthesized that make it difficult to analyze by IR.

Nevertheless, kinetic electrochemical experiments can give us additional information about the discharge processes that take place in the insertion electrode. Through the analysis of the curve I–t we know more about the nature of the electrochemical lithium insertion process. Fig. 4 shows the kinetic data for the discharge curve around the process labeled as I. As is shown in the chronoamperogram, in every range of voltage, the current decays near to zero before the next voltage step is applied. On the other hand, the kinetic data obtained for the lower and upper voltage where I appears showed a similar behavior. On the basis of this data, we can conclude that the diffusion of lithium ions is the process that rules the insertion reaction in the whole range of composition. Taking this into account, we can conclude that lithium is inserted in MoO$_3$·2H$_2$O through a single phase solution. So, instead of the reaction of the lithium with water molecules, we observe a true solid solution electrode.

MoO$_3$·2H$_2$O is easily transformed to β-MoO$_3$ by a soft thermal treatment which is indicative that both oxides have structural elements in common. Since oxides with the well known stru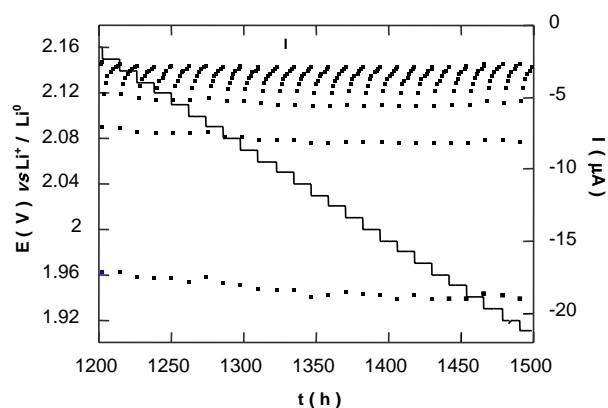cture type ReO$_3$, i.e. WO$_3$ and β-MoO$_3$, eliminate octahedra distortions as lithium insertion proceeds we carried out a structural study by X-ray diffraction of several samples with composition Li$_x$MoO$_3$·2H$_2$O ($x = 0.1$, 1 and 2). In our case, X-ray diffraction patterns of the samples analyzed revealed an amorphous material in each bronze eliminating the possibility of the formation of crystalline molybdenum lithium bronzes with low symmetry.

4. Conclusions

Electrochemical lithium insertion in MoO$_3$·2H$_2$O amorphous led to a specific capacity of the cell of 490 Ah kg^{-1}. This value exceeds notably the capacity developed by anhydrous β-MoO$_3$ (370 Ah kg^{-1}) and the different hydrated molybdenum oxides studied previously (400 Ah kg^{-1}). Nevertheless the capacity of the cell decreased by 45% after the first cycle due to a possible irreversible reaction between the lithium inserted and the coordinated water and remaining water present in MoO$_3$·2H$_2$O. In the same way, the specific capacity of the cell was affected by increases of the current density applied, showing a low diffusion of the lithium inserted into the amorphous material.

Although the cell was unable to maintain the high specific capacity developed during the first discharge, the system maintained a useful specific capacity (200 Ah kg^{-1}) after 30 charge–discharge cycles. This suggests that electrochemical lithium insertion in hydrated molybdenum oxides is a promising field in the search for active materials in new secondary lithium batteries.

References

[1] J. Desilvestro, O. Haas, J. Electrochem. Soc. 137 (1990) 5.

[2] R. Koksbang, J. Baker, H. Shi, M.Y. Saidi, Solid State Ionics 84 (1996) 1.

[3] C.G. Granqvist, Sol. Energy Mater. Sol. Cells 60 (3) (2000) 201.

[4] J. Haber, E. Serwicka, Polyhedron 5 (1986) 107.

[5] C. Julien, G.A. Nazri, Solid State Ionics 68 (1994) 111.

[6] C. Julien, A. Khelfa, J.P. Guesdon, A. Gorestein, Appl. Phys. A59 (1994) 173.

[7] E.M. McCarron III, J. Chem. Soc.: Chem. Commun. 4 (1986) 336.

[8] N.A. Caiger, S. Crouch-Baker, P.G. Dickens, G.S. James, J. Solid State Chem. 67 (1987) 369.

[9] I. Juárez-Ramírez, A. Martínez-de la Cruz, Mater. Lett. 57 (2003) 1034.

[10] N. Kumagai, K. Tanno, Electrochim. Acta 32 (1987) 1521.

[11] N. Kumagai, K. Tanno, J. Appl. Electrochem. 18 (1988) 857.

[12] I. Juárez-Ramírez, A. Martínez-de la Cruz, J. Solid State Electrochem. 7 (2003) 259.

[13] N. Kumagai, N. Kumagai, K. Tanno, Appl. Phys. A49 (1989) 83.

[14] J.J. Xu, A.J. Kinser, B.B. Owens, W.H. Smyrl, Electrochem. Solid State Lett. 1 (1998) 1.

[15] B. Yebka, C.G.A. Nazri, Mater. Res. Soc. Symp. Proc. 548 (1999) 229.