

MOLYBDIC OXIDES AS CATHODE ACTIVE MATERIALS IN SECONDARY LITHIUM BATTERIES

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Summary

Porous and amorphous molybdenum trioxides (MoO_3) have been prepared by thermal decomposition of the peroxide derived from the reaction of MoO_3 and H_2O_2 , and used as a cathode active material for secondary lithium batteries. These oxides showed excellent discharge capacities, corresponding to Li^+ -ion intercalation of up to ~ 3 and ~ 5 moles per mole of MoO_3 in a 1 M LiClO_4 solution of PC and PC-DME, respectively, and thus may be considered as useful for the cathodes of primary batteries as well as for secondary batteries.

Introduction

A variety of molybdenum oxides has been noted recently as cathode active materials in secondary lithium batteries [1 - 7]. Among these oxides, molybdenum trioxide (MoO_3) has a relatively high discharge capacity as the cathode, but the cell voltage is not as high compared with practical cathode active materials such as MnO_2 , V_2O_5 , etc. [7]. Also, cell voltage on charging should be reduced and the poor cycling behavior improved to facilitate the development of practical batteries.

It has been pointed out by several workers that amorphous cathode active materials are very useful for improvement of rechargeability [8 - 15]. A typical example developed by Sakurai *et al.*, and worth noting because of its simple method of preparation and cathode charge-discharge characteristics, is a V_2O_5 - P_2O_5 glassy material. On the other hand, an attempt to increase the discharge capacity has been made by the use of a porous thin film as the cathode rather than a bulk specimen, or a pressed copper-molybdenum sulfide powder [15].

Kurusu reported some interesting results of the reaction of MoO_3 or Mo powder with H_2O_2 [16]. On the basis of the results, these authors have

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prepared the porous and amorphous MoO_3 and evaluated it as a cathode active material. The preparation method of these oxides and their application as secondary lithium battery cathodes are described in this paper.

Experimental

Preparation of porous and amorphous MoO_3

The MoO_3 , obtained commercially, or by the thermal decomposition of ammonium paramolybdate, was added in limited amount to a 30% H_2O_2 solution at 60 °C. The result was a clear yellow solution which was treated as follows.

(i) After the filtration of unreacted MoO_3 , the solution was evaporated under reduced pressure by rotary evaporator to give a yellow solid (solid A). It was dried under vacuum at 20 °C, and then heated in air at a temperature above 170 °C to give porous MoO_3 .

(ii) Molybdenum powder was added to the above yellow solution, resulting in a blue solution which was evaporated by rotary evaporator, leaving a blue solid (solid B) behind. The solid was amorphous and used as the cathode after heating under vacuum below 150 °C.

Measurement of charge-discharge properties

The electrolyte was a 1 M LiClO_4 solution of propylene carbonate (PC) or a mixture (1:1 by volume) of PC and dimethoxyethane (DME). The solvent and electrolyte were purified and dried by the usual methods. A sheet electrode was used as the cathode and prepared as follows. The mixture of molybdenum oxide, acetylene black, and Teflon water dispersant was repeatedly rolled between two stainless steel rods to give a flexible sheet of thickness about 0.3 mm. The sheet was pressed on Ni mesh to establish an electrical terminal and fitted to the Teflon cell with gold electroplated on brass as an external electrical terminal. The effective cathode area was 1.33 cm^2 . An anode of Li foil was also fitted to the cell in a manner similar to that of the cathode. The two electrodes were set 15 mm apart and a reference electrode of Li on nickel wire was placed between them. The charge-discharge curve was measured by a microcomputer-controlled system developed by the authors [17].

Results and discussion

Characteristics of porous and amorphous MoO_3

The yellow solid, A, obtained by the reaction of MoO_3 and H_2O_2 , oxidized iodide ion. This could be considered as a kind of peroxide, the oxidizing ability of which corresponded to that of one active oxygen for one atom of Mo. The blue solid, B, showed no oxidizing properties for the iodide ion under the same conditions as that for solid A.

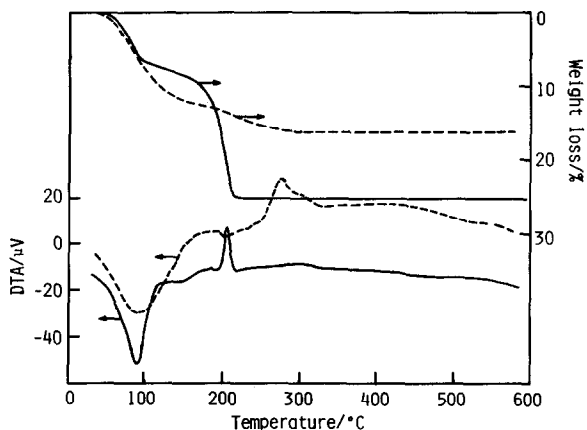
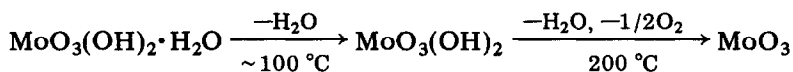


Fig. 1. TG and DTA curves of solids A (—) and B (---) in air at $10\text{ }^{\circ}\text{C min}^{-1}$.

The TG and DTA of solids A and B were carried out in air and the curves are shown in Fig. 1. In the case of solid A, two-stage decomposition was observed, and from the weight loss was assumed to conform to the equation:



The exothermic peak at $200\text{ }^{\circ}\text{C}$ in the DTA curve is supposed to correspond to the transformation of amorphous MoO_3 to the crystalline state. It was, however, difficult to obtain amorphous oxide by heat treatment below $200\text{ }^{\circ}\text{C}$ in air, because the resulting oxide would gradually crystallize under these operating conditions. The amorphous oxide was conveniently obtained by heating at $200\text{ }^{\circ}\text{C}$ under vacuum. Accordingly, the following oxides were prepared as cathode active materials: MoO_3 -a and -b by heating solid A in air at $170\text{ }^{\circ}\text{C}$ and $400\text{ }^{\circ}\text{C}$, respectively, and MoO_3 -c by heating solid A under vacuum at $200\text{ }^{\circ}\text{C}$.

On the other hand, the TGA curve of solid B showed a gradual decrease in weight based on the dehydration of combined and/or crystallized water, followed by the formation of MoO_3 as a final product at a temperature above $280\text{ }^{\circ}\text{C}$. Though the exothermic reaction from amorphous oxide to crystalline state was observed at around $270\text{ }^{\circ}\text{C}$, thermal treatments were carried out at $100\text{ }^{\circ}\text{C}$ and $150\text{ }^{\circ}\text{C}$ under vacuum to prepare amorphous MoO_3 use for as cathode active materials (MoO_3 -d and -e, respectively) and to prevent gradual crystallization of the resulting oxides, even below $270\text{ }^{\circ}\text{C}$.

The five kinds of MoO_3 , prepared as above, were characterized by XRD as shown in Fig. 2. The oxides (MoO_3 -a and -b) derived from solid A by heating in air were identified as a typical crystalline MoO_3 . The others (MoO_3 -c, -d and -e) were amorphous, but tiny diffraction peaks were observed in the MoO_3 -c derived from solid A because of slight crystallization.

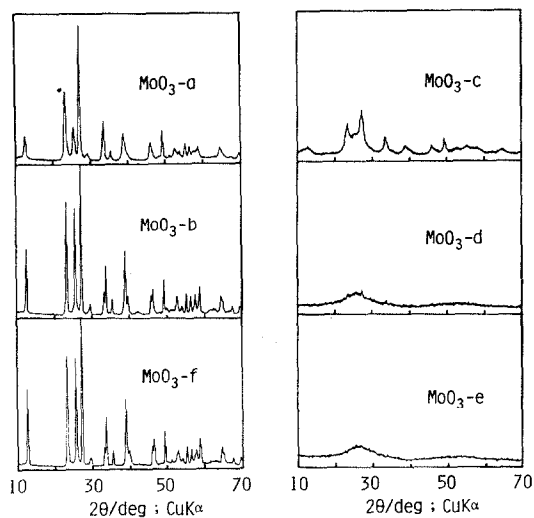


Fig. 2. XRD patterns of the MoO_3 prepared by thermal decomposition of solids A and B.

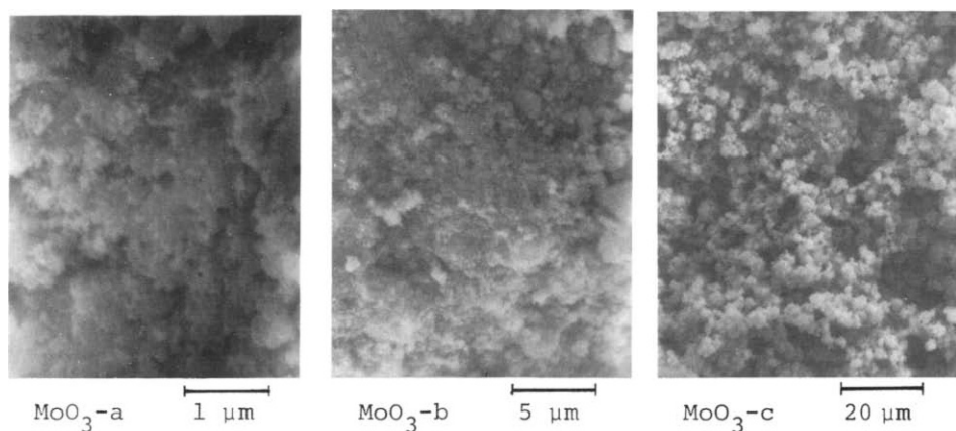


Fig. 3. SEM photographs of the MoO_3 prepared by thermal decomposition of solid A.

Furthermore, the scanning electron micrographs (SEM) of MoO_3 -a, -b, and -c showed porosity, Fig. 3. It is considered that the MoO_3 treated with H_2O_2 would intercalate oxygen in the layer, and the oxygen liberated on heating would give a porous oxide. This porous oxide preparation procedure is simple and may be applied to other materials.

Charge-discharge characteristics of MoO_3

The charge-discharge curves of crystalline and porous MoO_3 (MoO_3 -a and -b) were first measured in a 1 M LiClO_4 solution of PC, and are shown with the result of the preparation of MoO_3 (MoO_3 -f) by thermal decomposition of ammonium paramolybdate in Fig. 4. The oxides were discharged to

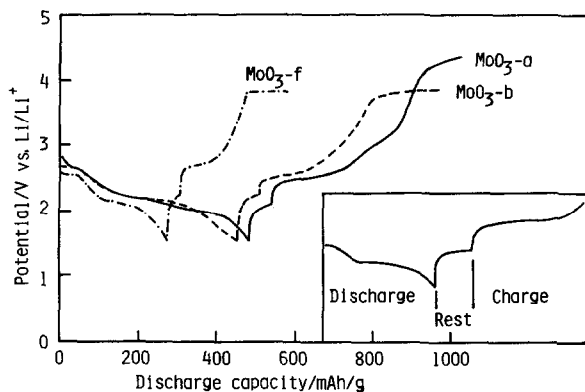


Fig. 4. Charge-discharge curves of MoO_3 -a, -b, and -f, at 1.0 mA cm^{-2} in a 1 M LiClO_4 solution of PC.

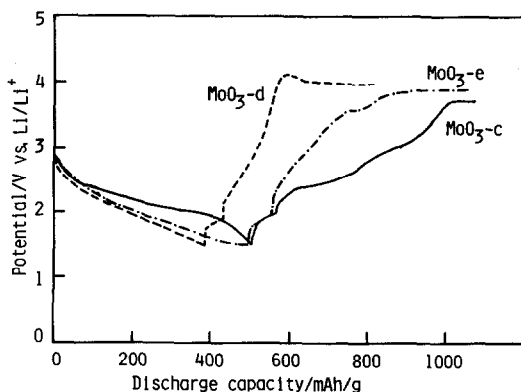


Fig. 5. Charge-discharge curves of MoO_3 -c, -d, and -e, at 1.0 mA cm^{-2} in a 1 M LiClO_4 solution of PC.

1.5 V at 1.0 mA cm^{-2} , and then charged for the same time as that of the discharge following a given rest time. The model to explain the charge-discharge curve is illustrated schematically at the corner of Fig. 4. An excellent discharge capacity was obtained in both cases, especially in MoO_3 -a. These capacities were about double those of the usual crystalline oxide (MoO_3 -f), and corresponded to Li^+ ion intercalation up to ~ 3 per MoO_3 . However, in the case of MoO_3 -a, the potential increased to over 4 V in the charging process beyond 80% of full charge. On the other hand, MoO_3 -b gave a good result without any increase in the potential, even in the final period of the charging process. The OH group would remain in the MoO_3 -a prepared at lower temperature and, hence, the potential would be expected to increase because of the interaction between the intercalated Li^+ ion and the OH in the MoO_3 layer.

The charge-discharge curves of amorphous oxides were measured in a manner similar to that above, and are shown in Fig. 5. The potential

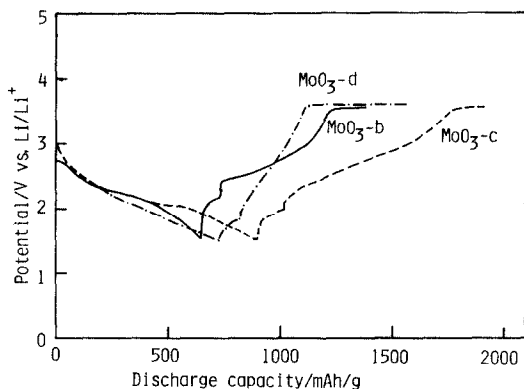


Fig. 6. Charge-discharge curves of MoO_3 -b, -c, and -e, at 1.0 mA cm^{-2} in a 1 M LiClO_4 solution of PC-DME.

decreased gradually as discharge progressed, as noted in the usual amorphous oxides. However, a potential plateau was observed at about 2 V in the case of MoO_3 -c, derived from solid A, the oxide that gave some small diffraction peaks in the XRD analysis. The discharge capacity of these amorphous oxides corresponded to Li^+ ion intercalation up to ~ 3 moles per MoO_3 in MoO_3 -c and -d. The potential in the charging process was below 4 V in these three oxides, which therefore could be used as cathodes for secondary batteries.

Finally the authors attempted to measure the charge-discharge curves using a 1 M LiClO_4 solution of PC-DME (1:1 by volume). The results for MoO_3 -b, -c, and -d, as typical examples, are shown in Fig. 6. The most striking characteristic of the results is the increase in discharge capacity, which corresponded to Li^+ ion intercalation of ~ 5 moles per MoO_3 in the discharge of MoO_3 -c. The potential in the final period of the charging process was suppressed below 3.5 V as an additional feature. This behavior would be considered as preferable in the application of MoO_3 cathodes to secondary batteries. Furthermore, these oxides could also be used as a cathode active material in primary batteries because of their high discharge capacities.

Though the improvement in capacity and the suppression of charging potential by using the PC-DME mixed electrolyte has been explained by other workers [18] as being due to an increase in electrolyte conductivity, our results will have to be discussed on the basis of electrode/electrolyte interface behavior.

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