Journal of the European Ceramic Society **10** (1992) 123–128

Room-temperature Preparation of Li_2MoO_4 and its Sintering

Michio Inagaki
Faculty of Engineering, Hokkaido University, Kita-ku, Sapporo, 060 Japan

&

Yasuo Nishikawa, Mototsugu Sakai
Materials Science, Toyohashi University of Technology, Tempaku-cho, Toyohashi, 441 Japan

(Received 6 August 1991; revised version received 9 December 1991; accepted 18 December 1991)

Abstract

A powder of Li_2MoO_4, well-defined in crystalline structure and particle morphology, was prepared at room temperature and its sintering behavior was examined.

The Li_2MoO_4 powder was precipitated by dropping the starting solution, prepared from $(NH_4)_6Mo_7O_{24}$ and LiOH by dissolving into degassed water, into ethanol at room temperature with agitation by either mechanical stirring or high-frequency ultrasound. The preparation conditions in terms of the starting aqueous solution, the organic precipitator and the way of agitation were experimentally determined for obtaining the powder in a single-phase, well-crystallized state and with well-defined morphology. The powder thus obtained could be formed into disks with relative density of 85% using a pressure of 20 MPa; these could be sintered into pieces with relative density of 94% at 500°C.

Es wurde Li_2MoO_4-Pulver mit definierter kristalliner Struktur und Teilchenmorphologie bei Raumtemperatur hergestellt und das Sinterverhalten dieses Pulvers untersucht.

Das Li_2MoO_4-Pulver wurde ausgeschieden, indem eine Ausgangslösung, die aus in entgastem Wasser aufgelöstem $(NH_4)_6Mo_7O_{24}$ und LiOH bestand, in Ethanol bei Raumtemperatur und unter Erschütterung (Hochfrequenz-Ultraschall) getropft wurde. Um einphasiges Pulver in gut auskristallisiertem Zustand und mit definierter Morphologie herzustellen, wurden zunächst die Herstellungsbedingungen in Bezug auf die wässrige Ausgangslösung, das organische Ausscheidungsmittel und die Art der Bewegung während des Ausscheidungsvorganges experimentell untersucht. Die erhaltenen Pulver wurden bei einem Druck von 20 MPa zu scheibchenförmigen Proben mit einer relativen Dichte von 85% verpreßt. Diese Proben konnten bei 500°C zu einer Dichte von 94% gesintert werden.

Une poudre de Li_2MoO_4 avec une structure cristalline et une morphologie des particules bien définies a été préparée à température ambiante, et son comportement lors du frittage a été étudié.

La solution de départ (préparée à partir de $(NH_4)_6Mo_7O_{24}$ et de LiOH dissouts dans de l'eau dégazée et en évaporant l'ammoniac) a été ajoutée goutte à goutte à de l'éthanol à température ambiante en agitant par ultrasons haute fréquence pour donner un précipité de poudre de Li_2MoO_4. Les conditions opératoires en ce qui concerne la solution aqueuse de départ, l'agent organique de précipitation et la manière d'agiter ont été determinées expérimentalement pour obtenir une poudre monophasique et bien cristallisée, et avec une morphologie bien définie. La poudre ainsi obtenue a pu être préssée en forme de disque avec une densité relative de 85% en utilisant une pression de 20 MPa; ces disques ont pu être frittés en morceaux avec une densité relative de 94% à 500°C.

1 Introduction

Lithium compounds have applications in different fields, particularly in the energy-related sectors such as the secondary battery[1] and the nuclear fusion reactor.[2] For the synthesis of these lithium com-

Journal of the European Ceramic Society 0955-2219/92/$5.00

pounds, great care has to be taken because of problems with sublimation and the corrosive nature of lithium compounds.

In previous papers,[3,4] one of the authors has reported a new synthesis procedure for Li_2SnO_3, expected to have application as the solid blanket of a fusion reactor. The main process was the precipitation of a $Li_2Sn(OH)_6$ complex from an aqueous solution of lithium and stannic ions, followed by calcination at relatively low temperature (800°C). The grains of Li_2SnO_3 thus obtained were porous, consisting of small primary particles of about 0·2 μm size. The porosity of sintered pellets could be controlled by selecting the forming pressure and calcination temperature. Porosity control for the solid blanket of the fusion reactor was expected to be important for the recovery of tritium formed by nuclear reactions between lithium atoms and neutrons.

In the present work, a lithium double oxide Li_2MoO_4 was prepared at room temperature from aqueous solutions using ethanol as precipitating agent. Li_2MoO_4 was selected because molybdenum atoms were expected to act as neutron multipliers in the solid blanket of the fusion reactor. The morphological change caused by high-frequency ultrasonic agitation during precipitation and its effect on the sintering of the resultant powders were studied.

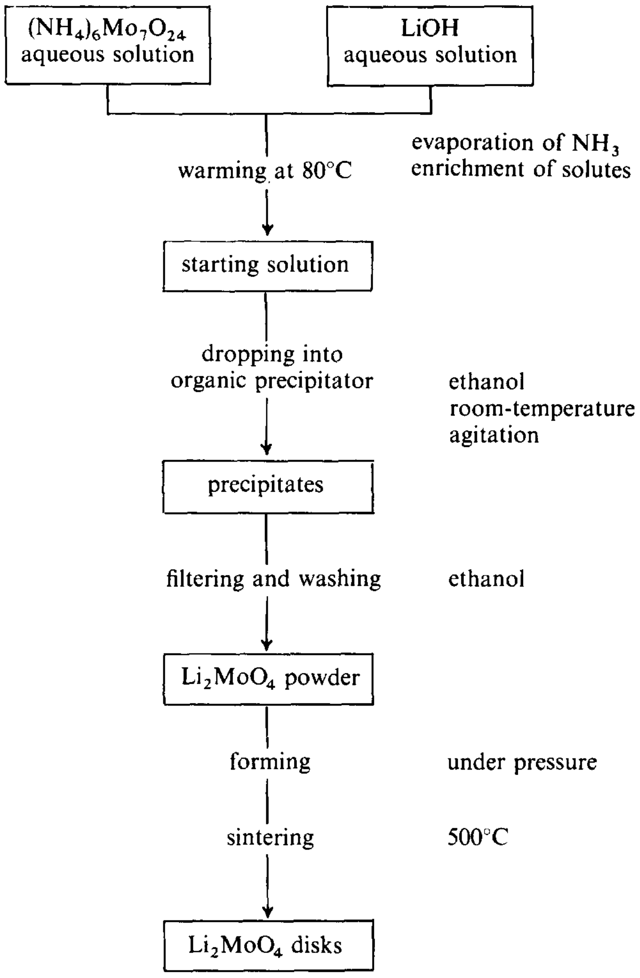

Fig. 1. Flow chart for the preparation of Li_2MoO_4 powder and its sintering.

2 Experimental and Results

2.1 Preparation of Li_2MoO_4 Powders

The general procedure for the preparation of Li_2MoO_4 powders at room temperature is shown as a flow chart in Fig. 1.

The hydrated p-ammonium molybdate $(NH_4)_6Mo_7O_{24}.4H_2O$ and hydrated lithium hydroxide $LiOH.H_2O$ were weighed in different ratios and then dissolved into distilled water which had been degassed by boiling in advance. The aqueous solutions thus prepared were warmed on a hot plate at about 100°C until the evaporation of ammonium was complete. It was essential for Li_2MoO_4 precipitation to remove ammonium ions from the solution and also desirable to enrich the solutes, as discussed later. The solutions containing lithium and molybdate ions were dropped into an organic precipitator, such as ethanol, with stirring either by magnetic stirrer or ultrasonic agitation. The precipitation occurred immediately after the addition of the aqueous solution to the precipitator. The precipitates thus obtained were filtered, washed by ethanol and then dried in an oven at 80°C. The resulting powders were characterized in terms of their crystalline structure by X-ray powder diffraction (CuK_α radiation) and in terms of their particle morphology by scanning electron microscopy (SEM). Some were sintered at different temperatures after forming into small pellets.

In order to obtain single-phase Li_2MoO_4 powders which were well defined in crystalline structure and also in particle morphology, different conditions for the following experimental variables: atomic ratio of Li/Mo in the starting aqueous solution, pH value of the solution, type of organic precipitator, concentration of the aqueous solution after enrichment, and the method of agitation, were used.

2.1.1 Atomic ratio of Li/Mo in the starting aqueous solution

Into aqueous solutions of $(NH_4)_6Mo_7O_{24}.4H_2O$ with the concentration of 0·024 mol/liter different amounts of $LiOH.H_2O$ were added to produce atomic ratios of Li/Mo in the resulting solutions of 0·2, 1·5, 2·0 or 4·0. These starting solutions of 100 ml

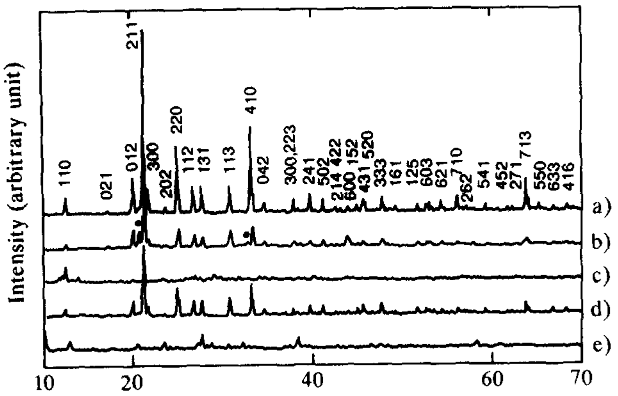

Fig. 2. X-ray powder patterns of Li_2MoO_4 precipitated from starting solutions with different Li/Mo ratios and pH values. (a) Li/Mo = 2·0, pH = 12·1; (b) Li/Mo = 4·0, pH = 12·1; (c) Li/Mo = 0·2, pH = 12·1; (d) Li/Mo = 2·0, pH = 6·4; (e) Li/Mo = 2·0, pH = 5·9.

were concentrated down to 15 ml on a hot plate and then added dropwise into ethanol (135 ml). The precipitates obtained were examined by X-ray diffraction.

As shown in Fig. 2(a), a single-phase crystalline Li_2MoO_4 was obtained from the solution with a Li/Mo ratio of 2·0 and a pH value of 12·1. All diffraction lines observed were indexed by using the crystal structure as reported in JCPDS Cards.[5] From the starting solution with a Li/Mo ratio of 4·0 (Fig. 2(b)), Li_2CO_3 was detected, in addition to crystalline Li_2MoO_4. By starting from the solutions with lower Li/Mo ratios than 2·0, precipitates were formed, but their structures could not be identified by X-ray (for example Li/Mo = 0·2, in Fig. 2(c)).

2.1.2 pH Value of the starting solution

The same solution with a Li/Mo ratio of 2·0 and a pH value of 12·1 was used as a starting solution. Into this solution 2N HCl was added to change the pH value to 5. The powder patterns of precipitates obtained from the solutions with different pH values are compared in Fig. 2.

The solutions with pH values above 6 gave a single-phase Li_2MoO_4 precipitate. Its crystallinity seemed to be better from solutions with a pH value of 12 than from those with lower pH values. The precipitates obtained from solutions with pH values below 6·0 could not be identified.

2.1.3 Organic precipitation medium

The same solution with a Li/Mo ratio of 2·0 and a pH value of 12·1 was added to different organic solvents: methanol, ethanol, propanol, butanol and acetone. Only ethanol was effective as a precipitation medium. Methanol mixed with the solution, but did not give any precipitate. The other solvents were not miscible with the aqueous solution and gave no precipitation.

The amount of ethanol relative to the starting aqueous solution was also important to produce a high yield of precipitate. The solution concentrated to 15 ml was added into ethanol volumes of 75, 135 and 225 ml; these represent 5, 9 and 15 times the volume of the starting solution, respectively. For a higher yield of precipitate, the larger amount of ethanol was more effective. By using 225 ml of ethanol and 15 ml of the enriched starting solution, a high yield of Li_2MoO_4 was obtained (up to 88% of the theoretical value).

2.1.4 Enrichment of the starting solution

The enrichment of the aqueous solution containing lithium and molybdate ions on a hot plate was performed for two purposes: to evaporate ammonium and to reduce the volume of the solution.

When the solution was added to ethanol before the completion of the ammonium evaporation, a crystalline $(NH_4)_6Mo_7O_{24}$ was detected in the precipitates obtained.

When the concentration of Li_2MoO_4 in the starting solutions after the enrichment was in the range 1·0–2·3 mol/liter, a single-phase Li_2MoO_4 precipitate was obtained. The crystallinity of the precipitate was as good as that shown in Fig. 2(a). With a concentration of 0·5 mol/liter, a large amount of ethanol was needed to yield a precipitate. When the concentration of the solution was less than 0·1 mol/liter, no precipitation was obtained.

The morphology was also affected by the concentration of the starting solution. The SEM micrographs in Fig. 3 show precipitates of Li_2MoO_4 obtained by dropping 15 ml solutions with different concentrations into 135 ml of ethanol with agitation using 45 kHz frequency ultrasound. From the solution with 1·0 mol/liter concentration, well-separated crystals of rather homogeneous size were obtained, as shown in Fig. 3(a); the yield was above 80%. With an increase in the concentration of the solution, the size distribution of the precipitated crystals becomes broad and the particles look to be bounded together, as shown for those from the 2·3 mol/liter solution in Fig. 3(b).

When the solution was enriched above a concentration of 2·5 mol/liter, spontaneous precipitation occurred during the process of enrichment, the product also being Li_2MoO_4. With complete evaporation of the water by heating, a crystalline powder of Li_2MoO_4 could be obtained. However, the morphology of the particles was irregular and could not be controlled.

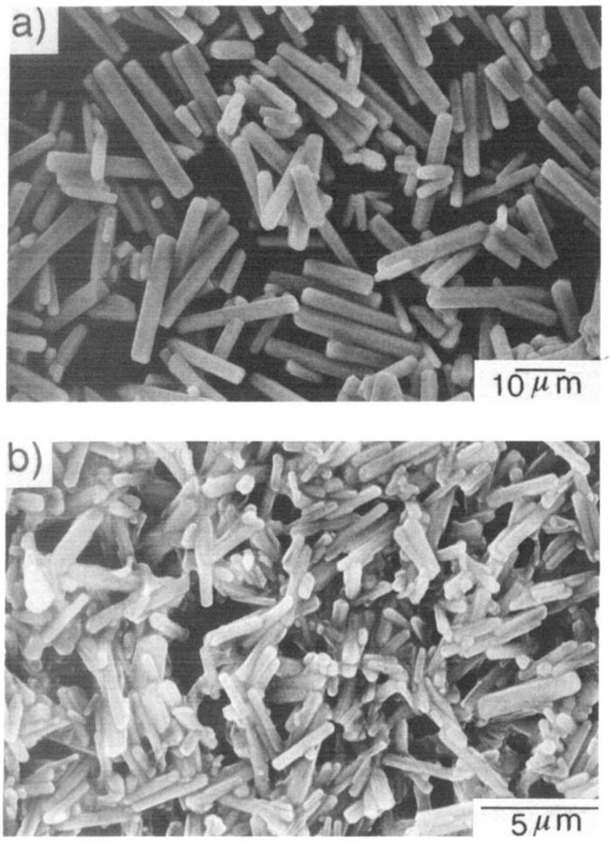

Fig. 3. SEM micrographs of Li_2MoO_4 precipitated from starting solutions with different concentrations. (a) 1·0 mol/liter; (b) 2·3 mol/liter.

2.1.5 Stirring during precipitation

The solution which had been enriched up to a concentration of 1·0 mol/liter and which had a Li/Mo ratio of 2·0 and a pH value of 12·1 was dropped at a rate of 1·1 ml/min into ethanol of 135 ml volume (nine times the volume of the solution). Throughout the addition of the solution (about 15 min), the ethanol was stirred either mechanically by using a magnetic stirrer or with ultrasound at the high frequencies of 28, 45 and 100 kHz. After the addition, the stirring was continued for an additional 15 min. The mechanical stirring was performed by using a bar of about 10 mm diameter and 28 mm long, rotating with about 1000 rpm, in a 200 ml beaker. For ultrasonic stirring, a commercial ultrasonic cleaner with a power of 100 W was used.

The precipitates obtained, which were confirmed by X-ray to be a single phase of Li_2MoO_4, were observed under SEM. The SEM micrographs of the precipitates obtained for each stirring condition are shown in Figs 4 and 5.

The crystals in the Li_2MoO_4 precipitates were hexagonal pillars with a diameter of 1–5 μm and a length of 10–50 μm. The crystals obtained with mechanical stirring had relatively small sizes; intergrowths of crystals were also often observed, as can be seen in Fig. 4(a). The primary crystals seemed to grow from one nucleus in radial directions, probably being formed by dendritic growth. Such coagulation was already observed in the beginning of the precipitation, as shown in Fig. 4(b). Under the high frequency agitation, less dendritic growth was observed (Fig. 5), but the size distribution of the crystals was wide, large crystals (*c.* 5 μm in diameter and 50 μm in length) coexisting with small crystals (*c.* 1 and 10 μm). Under a stirring frequency of 45 kHz, rather homogeneous crystal particles were obtained, as shown in Fig. 5(b).

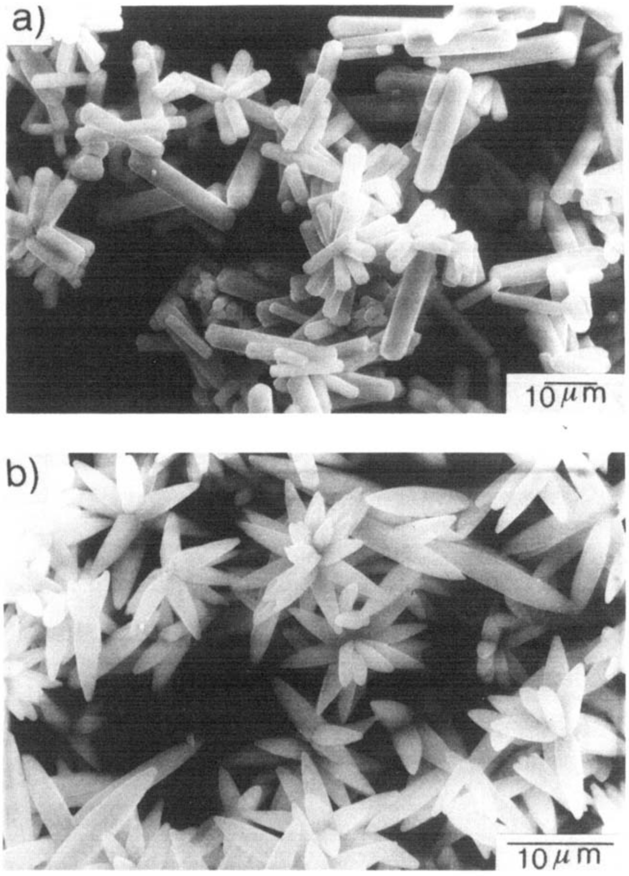

Fig. 4. SEM micrographs of Li_2MoO_4 precipitated using magnetic stirring. (a) Final product; (b) particles at the very beginning of precipitation.

2.2 Forming and sintering

The forming of the Li_2MoO_4 powders by compression and the sintering behavior of the resulting pellets were studied in relation to the preparation conditions already described.

About 0·4 g of Li_2MoO_4 powder was compressed in a mould under various pressures into disks with diameters of 13 mm and thicknesses of 1·5–2·0 mm. After compression, the bulk densities of the disks were calculated from the weights and sizes. These disks were sintered at 500°C in air and the change in

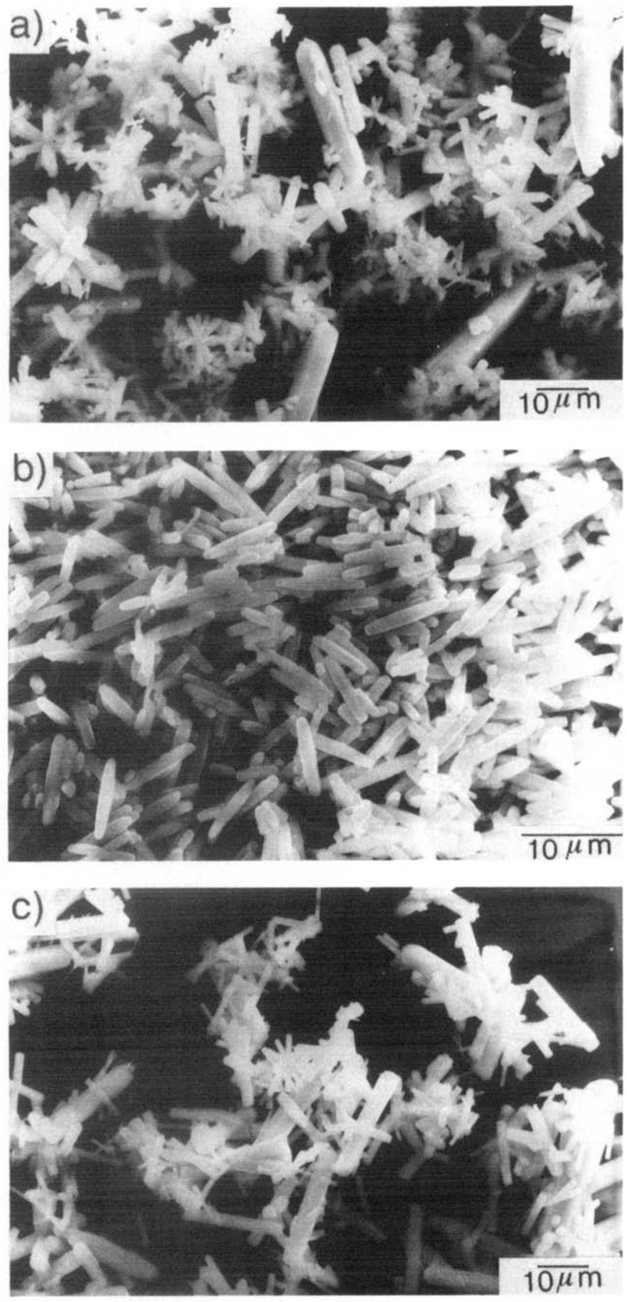

Fig. 5. SEM micrographs of Li_2MoO_4 precipitated using ultrasonic agitation at different frequencies. (a) 28 kHz; (b) 45 kHz; (c) 100 kHz.

bulk density was determined as a function of sintering time. The change in morphology of fracture surfaces with sintering was also followed by SEM.

2.2.1 Forming

The Li_2MoO_4 powder prepared with mechanical stirring could not be formed into disks, probably because of the dendritic morphology of the particles, as shown in Fig. 4.

The powder prepared from the starting solution with a concentration of 1·0 mol/liter and with agitation of 45 kHz, consisting of well-defined separated particles, could be formed into disks, the bulk density depending strongly on pressure. In Fig. 6, the bulk density of disks is plotted as a function of forming pressure. For each experimental point the density relative to the theoretical one is shown.

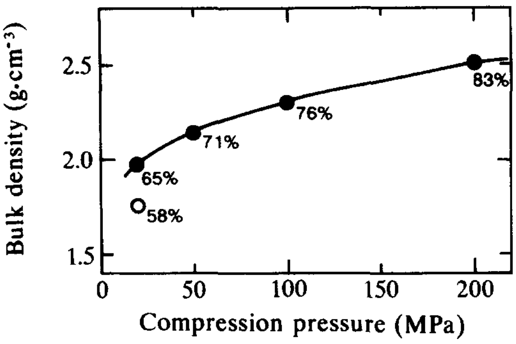

Fig. 6. Change of bulk density after pressing Li_2MoO_4 powder: ●, from the solution with a concentration of 1·0 mol/liter; ○, from that of 2·3 mol/liter.

With increase in forming pressure, the bulk density increased up to 83% of the theoretical value. It must be mentioned, however, that higher forming pressure led to a higher possibility of delamination in the disks.

The powder with a distribution in crystal size gave low bulk density. As an example, the bulk density of the disk formed from the powder prepared from the solution with the concentration of 2·3 mol/liter is plotted as an open circle in Fig. 6. Differences in bulk density after forming were found to affect strongly the following sintering behavior, as can be seen in Fig. 7.

2.2.2 Sintering

The changes in bulk density of two disks formed under a pressure of 20 MPa as a function of sintering time at 500°C are shown in Fig. 7. The SEM micrographs in Fig. 8 show fracture surfaces of disks of the high bulk density material as a function of sintering time.

The bulk density of disks increases with increase in sintering time and eventually approaches that for a single crystal. After five days, the relative density

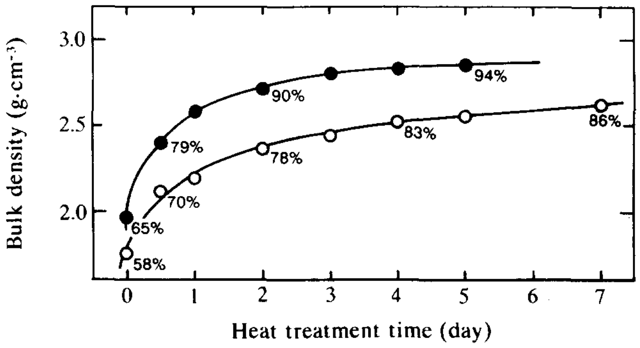

Fig. 7. Changes in bulk density of Li_2MoO_4 disks as a function of time (sintering at 500°C). ● and ○ as in Fig. 6.

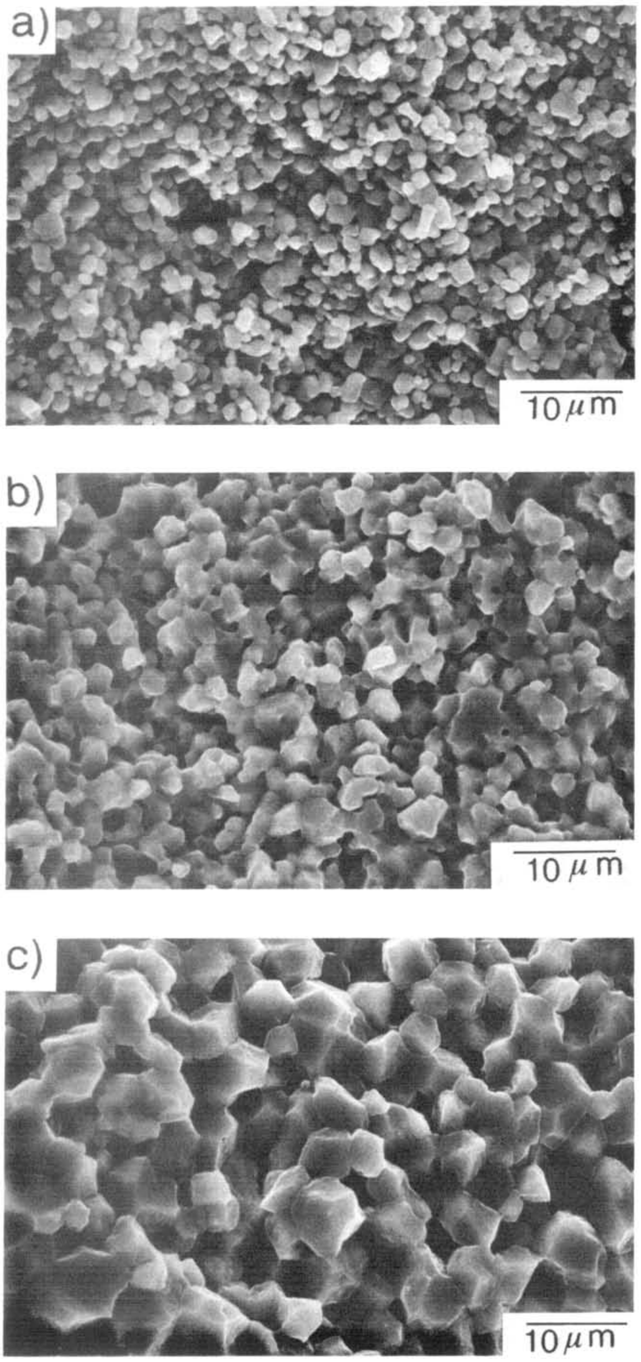

Fig. 8. SEM micrographs of Li_2MoO_4 disks sintered for different times at 500°C. The Li_2MoO_4 powder was prepared from a starting solution with a concentration of 1·0 mol/liter under 45 kHz agitation. (a) After 12 h; (b) after 2 days; (c) after 5 days.

reaches about 94% of the theoretical value. It is worth mentioning that the disk with the lower bulk density after forming never overtakes the one with higher as-formed density even after prolongation of the sintering time.

The morphology of the primary particles changes from hexagonal pillars to quasi-spherical after sintering for 12 h. These primary particles appeared to change to polyhedra and to sinter to each other after two days, and to grow up to about 5 μm after five days.

3 Discussion

Lithium molybdate (Li_2MoO_4) powders were obtained at room temperature from an aqueous solution containing lithium and molybdate ions by dropping it into ethanol. The conditions necessary to prepare single-phase Li_2MoO_4 with well-defined crystalline structure and particle morphology were: a starting aqueous solution with a Li/Mo ratio of 2·0, a pH value of 12, and no residual ammonium ions; a concentration of Li_2MoO_4 above 1·0 mol/liter; addition of the solution into a large amount of ethanol, more than nine times the volume of the starting solution.

The same compound could be obtained by the evaporation of the water in the starting solution. However, the present procedure (precipitation of the compound in ethanol) has the advantage of allowing control of the particle morphology. The same procedure could be applied to the preparation of alkali metal molybdates, such as K_2MoO_4,[6] and also Li_2SnO_3 (Inagaki, M., Nakai, T. & Nishikawa, Y., unpublished). The present procedure might be interesting for the synthesis of other compounds containing volatile components, such as lithium and molybdenum oxides.

The powder prepared by dropping the solution into ethanol with 45 kHz ultrasonic agitation had homogeneous particle size and gave a high bulk density in desks after sintering at 500°C. Mechanical stirring of the ethanol during precipitation gave a dendritic aggregation of the particles in the precipitates, which made it difficult to form disks by conventional pressing and to sinter to high density.

References

1. Abraham, K. M., Status of rechargeable positive electrodes for ambient temperature lithium batteries. *J. Power Sources*, **7** (1981/1982) 1–43.
2. Johnson, C. E. & Hollenberg, G. W., Recent advances in the development of solid breeder blanket materials. *J. Nucl. Mater.*, **122/123** (1984) 871–81.
3. Inagaki, M., Nakai, S. & Ikeda, T., Synthesis and sintering of Li_2SnO_3. *J. Nucl. Mater.*, **160** (1988) 224–8.
4. Inagaki, M., Nakai, S., Terai, T. & Takahashi, Y., Preparation of porous Li_2SnO_3 for blanket material of fusion reactor and its tritium release behavior. *Nippon Seramikkusu Kyokai Gakujutsu Ronbunshi*, **98** (1990) 469–75.
5. JCPDS Cards No. 12-763.
6. Inagaki, M., Nishikawa, Y. & Sakai, M., Synthesis and phase transitions of K_2MoO_4. *J. Mater. Chem.*, **3** (1992) 323–5.