Journal of Solid State Chemistry **163,** 1–4 (2002)
doi:10.1006/jssc.2001.9403, available online at http://www.idealibrary.com on IDEAL®

RAPID COMMUNICATION

Synthesis of *o*-LiMnO$_2$ by Microwave Irradiation and Study Its Heat Treatment and Lithium Exchange

Ramesh Chitrakar,[1] Hirofumi Kanoh,* Yoshitaka Miyai, and Kenta Ooi[1]

*National Institute of Advanced Industrial Science & Technology, 2217-14 Hayashi-cho, Takamatsu 761-0395, Japan; and *Department of Chemistry, Faculty of Science, Chiba University, 1-33 Yayoi, Inage, Chiba 263-8522, Japan*

Received May 1, 2001; in revised form September 14, 2001; accepted September 21, 2001; published online November 27, 2001

Microwave irradiation of a suspension of γ-MnOOH in a 4 mol dm^{-3} LiOH solution brought about a rapid formation of semicrystalline orthorhombic LiMnO$_2$ (*o*-LiMnO$_2$) within 30 min at 120°C. Cubic Li$_{1.6}$Mn$_{1.6}$O$_4$ was obtained by heating *o*-LiMnO$_2$ at 400°C; lithium could be topotactically extracted from Li$_{1.6}$Mn$_{1.6}$O$_4$ with acid to form cubic H$_{1.6}$Mn$_{1.6}$O$_4$. © 2002 Elsevier Science

***Key Words:* *o*-LiMnO$_2$; Li$_{1.6}$Mn$_{1.6}$O$_4$; H$_{1.6}$Mn$_{1.6}$O$_4$; microwaves; ion-exchange.**

INTRODUCTION

Synthesis of spinel and layered types of lithium manganese oxides and their lithium extraction/insertion reactions have been studied for possible applications in extraction of lithium from seawater and as cathode materials for rechargeable batteries (1–8). LiMnO$_2$ exists in two ordered-rock salt polymorphs, orthorhombic (*o*-LiMnO$_2$, space group *Pmnm*) and monoclinic (*m*-LiMnO$_2$, space group C2/*m*). High-temperature and low-temperature type *o*-LiMnO$_2$ have been prepared by solid-state reaction at 700–800°C (7), and by a hydrothermal method at 120°C (3) or reflux method (4, 7), respectively.

Microwave methods have been used for synthesis of organic and inorganic materials (9–11). Microwave irradiation enhances the reaction speed significantly and reduces the reaction temperature in some processes. Energy transfer from the microwaves to the material is believed to occur through either resonance or relaxation, which results in rapid heating. Microwave irradiation of a gel obtained from potassium permanganate and maleic acid yielded cryptomelane type manganese dioxide at a lower temperature (320°C) and in a shorter time (40 min) with broad XRD peaks and low intensity, but the intensity of the XRD peaks increased with increase of calcination temperature (425°C) (11). In this paper, we report the synthesis of semicrystalline *o*-LiMnO$_2$ by microwave irradiation and study its heat treatment and lithium exchange.

EXPERIMENTAL

Two types of microwave equipment were used; an Advanced Microwave Model ETHOS 1600 labstation and a laboratory-made metal-lined microwave, both of which were operated at 2.45 GHz with a power supply of 600–800 W. Both the instruments were multimode and equipped with temperature and pressure monitoring device, the thermocouple being inserted into the Teflon container lined inside the quartz tube. A total of 2 or 15 g of γ-MnOOH (Toyo Soda Co., Japan) were mixed with 40 or 200 cm^3 of a 4 mol dm^{-3} LiOH solution in a Teflon container and covered with a cap which was kept tight by using a screw to avoid vapor leakage and exposed to microwave irradiation for 30 min, 1 h, and 2 h, at 120°C. The temperature was allowed to reach 120°C within 5 min. The process was a microwave assisted hydrothermal synthesis in closed and pressurized Teflon container. After cooling, the precipitate was filtered, washed with deionized water and dried at 60°C. The product was heated at 400°C for 4 h in air. The Li$^+$ extraction was carried out by stirring 1.0 g of heat-treated material with 1 dm^3 of a 0.5 mol dm^{-3} HCl solution for 1 day. The acid-treated materials were filtered and washed with deionized water and air-dried for 2 days.

RESULTS AND DISCUSSION

The equilibrium exchange between H$^+$ and Li$^+$ in γ-MnOOH was rapid; the formation of LiMnO$_2$ was

---

[1] To whom correspondence should be addressed. Fax: +81-87-869-3551. E-mail: k-ooi@aist.go.jp, chitrakar-ramesh@aist.go.jp.

0022-4596/02 $35.00

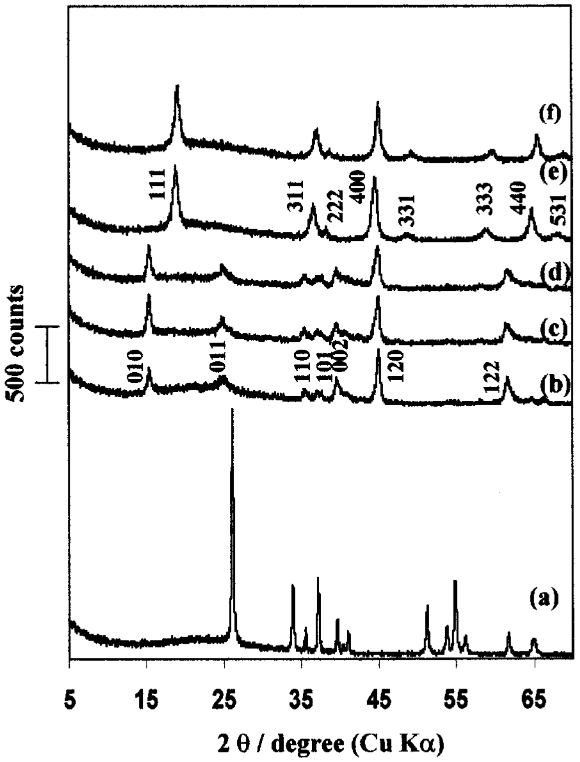

FIG. 1. XRD patterns of different materials: (a) γ-MnOOH, (b) o-$LiMnO_2$: microwaved for 30 min, (c) o-$LiMnO_2$: microwaved for 1 h, (d) o-$LiMnO_2$: microwaved for 2 h, (e) $Li_{1.6}Mn_{1.6}O_4$, (f) $H_{1.6}Mn_{1.6}O_4$.

completed within 30 min by microwave irradiation at 120°C. The XRD pattern for the 30-min irradiated sample could be indexed to orthorhombic cells of $LiMnO_2$ with lattice parameters ($Pmnm$, $a = 2.81$ Å, $b = 5.76$ Å, $c = 4.52$ Å), these lattice parameters being comparable with the literature values ($a = 2.80$ Å, $b = 5.75$ Å, $c = 4.57$ Å) (7). The peak intensities of the XRD pattern of the $LiMnO_2$ samples were broad and almost the same for different microwave irradiation times (30 min to 2 h) (Fig. 1). Croguennec *et al.* (12) have reported that the broad diffraction peaks of o-$LiMnO_2$ can be explained in terms of stacking faults. The fault occurrence is treated as a cation disorder. The (011) diffraction peak was known to correlate with the stacking faults (12, 13). A full width at half maximum (FWHM) in (011) peak is a good measure of fault occurrence. The FWHM of (011) peak at $2\theta = 24.8°$ in the present o-$LiMnO_2$ was 0.85°, which showed that the material has relatively disordered orthorhombic structure. In particular, smaller crystals correspond to higher fault concentrations. The Li/Mn mole ratio was nearly 1 in all $LiMnO_2$ samples prepared at different time intervals (Table 1). The formula of $LiMnO_2$ was confirmed from the chemical analysis of lithium and manganese and the mean oxidation number of manganese (Z_{Mn}). Slightly high values ($Z_{Mn} \approx 3.2$) for the mean oxidation number of manganese were observed. The SEM images of o-$LiMnO_2$ showed a smaller and less defined needle shape than the precursor γ-MnOOH (Fig. 2). The time for conversion from γ-MnOOH to o-$LiMnO_2$ in the microwave experiment was markedly reduced in comparison to the conventional hydrothermal synthesis, for which about 1 day was needed at 120°C. The acceleration of this conversion suggests a direct interaction between γ-MnOOH and the microwaves, in addition to the rapid heating of the LiOH solution.

$Li_{1.6}Mn_{1.6}O_4$ was prepared by thermal treatment of o-$LiMnO_2$ at 400°C, the formula of $Li_{1.6}Mn_{1.6}O_4$ being confirmed from the chemical analysis and Z_{Mn} values (Table 1). The SEM image of $Li_{1.6}Mn_{1.6}O_4$ was the same as that of o-$LiMnO_2$ (Fig. 2). The DTA-TG curve of o-$LiMnO_2$ showed a sharp exothermic peak around 320°C with weight gain, which was due to the oxidation of trivalent manganese to tetravalent manganese (Fig. 3, bottom). When o-$LiMnO_2$ was heated at 400°C for 4 h, the weight gain was about 6%, which corresponded to the conversion from $LiMnO_{2.1}$ to $LiMnO_{2.5}$ ($Li_{1.6}Mn_{1.6}O_4$). The XRD pattern of $Li_{1.6}Mn_{1.6}O_4$ could be indexed to a cubic system ($Fd3m$) with lattice constant of 8.14 Å (Fig. 1). We carried out preliminary Rietveld analysis of $Li_{1.6}Mn_{1.6}O_4$ with three models: a model with excess lithium in the 16c site as $(Li)_{8a}[Li_{0.2}]_{16c}[Li_{0.4}Mn_{1.6}]_{16d}O_4$, a model with oxygen deficiency as $(Li)_{8a}[Li_{0.5}Mn_{1.5}]_{16d}O_{3.75}$ and a model of hexagonal lattice with cation deficiency as $(Li_{0.8}\square_{0.2})_{3b}(Mn_{0.8}\square_{0.2})_{3a}O_2$. The simulation results indicate that the first model traces the XRD peaks of $Li_{1.6}Mn_{1.6}O_4$. A structural refinement of $Li_{1.6}Mn_{1.6}O_4$ using Rietveld and TEM analyses is now in progress and will be reported elsewhere in near future. o-$LiMnO_2$ has a rock salt structure with a distorted cubic close-packed oxygen anion array in which zigzag layers of lithium and manganese cations alternate with one another. Recently Chiang *et al.* proposed that the structural transformation from orthorhombic to cubic spinel occurred via an intermediate structure (disordered rock salt), which had Li and Mn ions occupying both octahedral and tetrahedral sites in disordered distribution (8). The space group of the proposed intermediate structure is most likely $Fm3m$, since $Fd3m$ is a nonisomorphic k-sub group of $Fm3m$. We were able to construct the structural transformation of o-$LiMnO_2$ to cubic $Li_{1.6}Mn_{1.6}O_4$ (Fig. 4) in a manner similar to that proposed by Chiang *et al.* (8).

The extractability of lithium from $Li_{1.6}Mn_{1.6}O_4$ was investigated with a 0.5 mol dm^{-3} HCl solution; the Li^+ extractability reached 99%. The dissolution of manganese during the acid treatment was less than 2%. The Z_{Mn} values of manganese in the acid-treated samples were nearly equal to 4 (Table 1). This shows that the extraction

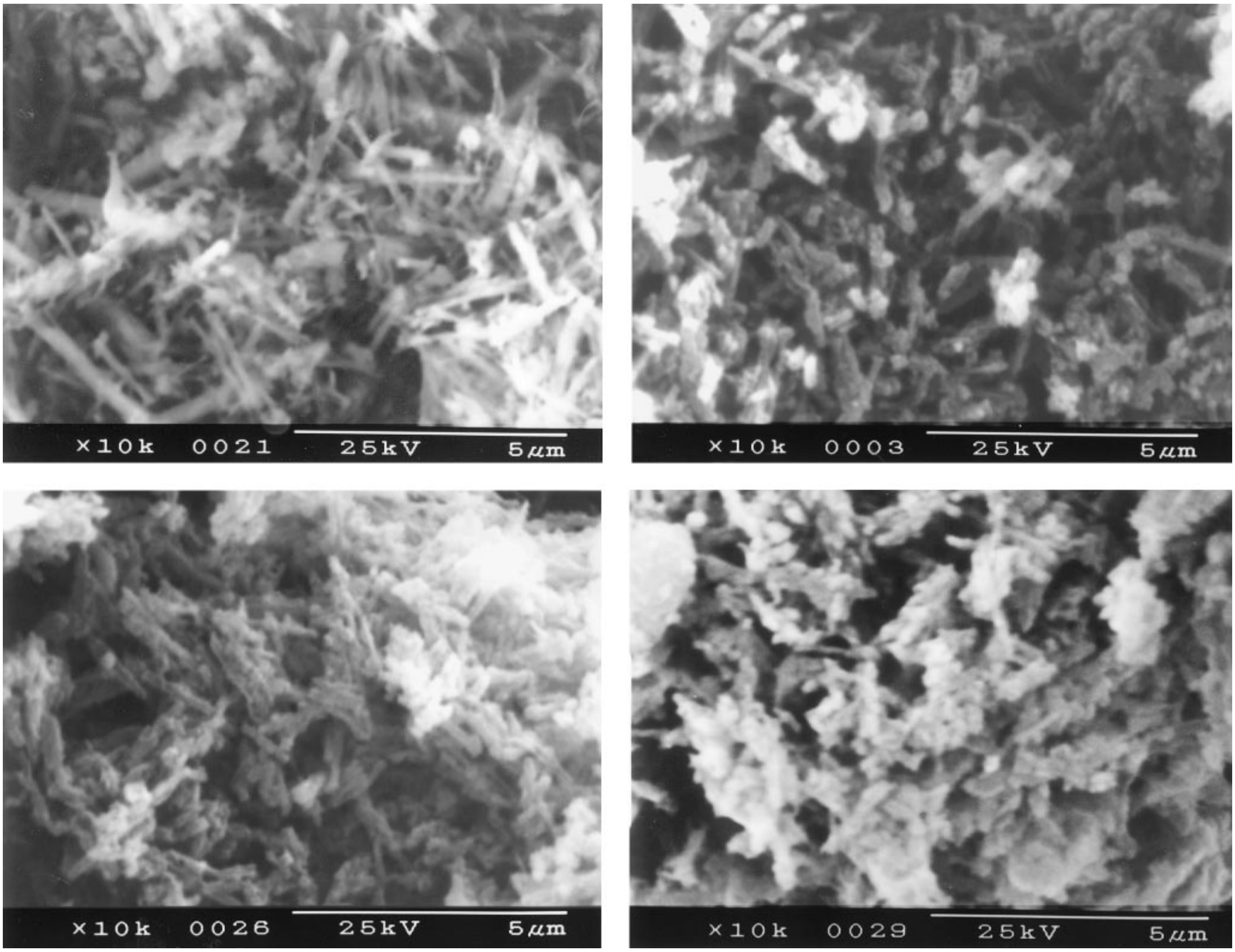

FIG. 2. SEM images of γ-MnOOH (top, left), o-$LiMnO_2$ (top, right), $Li_{1.6}Mn_{1.6}O_4$ (bottom, left), and $H_{1.6}Mn_{1.6}O_4$ (bottom, right).

progresses by the Li^+/H^+ ion exchange mechanism. The water content was determined by the weight loss from 100–400°C, assuming the product to be β–MnO_2. The H_2O/Mn ratios were close to 0.50. The formula of acid-treated material can be written as $H_{1.6}Mn_{1.6}O_4$. The SEM image of $H_{1.6}Mn_{1.6}O_4$ was almost same as that of $Li_{1.6}Mn_{1.6}O_4$ (Fig. 2). The XRD patterns of the $H_{1.6}Mn_{1.6}O_4$ preserved the cubic structure with only a slight decrease of the lattice constant, $a = 8.05$ Å (Fig. 1). The DTA-TG curves of $H_{1.6}Mn_{1.6}O_4$ showed an endothermic peak around 195°C with weight loss, which was due to the evaporation of hydroxyl groups (Fig. 3 top).

TABLE 1
Composition of o-$LiMnO_2$,[a] $Li_{1.6}Mn_{1.6}O_4$, and $H_{1.6}Mn_{1.6}O_4$

Sample	Li/Mn	H_2O/Mn	Z_{Mn}	Formula
o-$LiMnO_2$	0.99	—	3.24	$LiMnO_{2.12}$
$Li_{1.6}Mn_{1.6}O_4$	1.00	—	4.04	$Li_{1.58}Mn_{1.58}O_4$
$H_{1.6}Mn_{1.6}O_4$	< 0.01	0.51	4.00	$MnO_2 \cdot 0.51H_2O$

[a] Prepared via microwave irradiation for 30 min at 120°C.

Lithium uptake from LiCl-enriched seawater was studied by stirring 100 mg $H_{1.6}Mn_{1.6}O_4$ samples in 1 dm^3 of seawater (Li^+ concentration = 0.72 mmol dm^{-3}) for 6 days at room temperature. The lithium uptakes were in the range of 5.0–5.3 mmol/g (35–37 mg/g). Similar results have been reported for $H_{1.6}Mn_{1.6}O_4$ samples prepared via the hydrothermal route (3). The large lithium uptake of the present sample is due to the availability of strongly acidic sites in $H_{1.6}Mn_{1.6}O_4$, as evidenced by the pH titration curve towards lithium ions (3). The purpose of lithium uptake experiment from seawater was to investigate the applicability of $H_{1.6}Mn_{1.6}O_4$ for the extraction of lithium from seawater, because lithium has potential use in battery

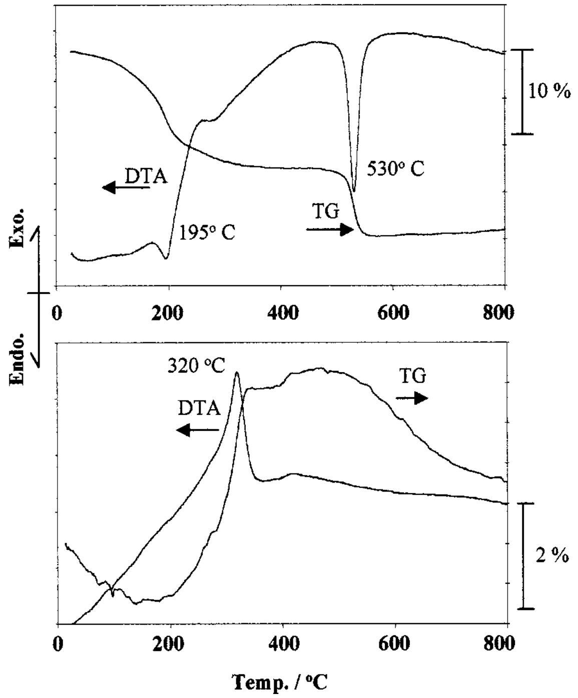

FIG. 3. DTA-TG curves of *o*-$LiMnO_2$ prepared by microwave irradiation for 30 min at 120°C (bottom) and of $H_{1.6}Mn_{1.6}O_4$ (top).

and furthermore $H_{1.6}Mn_{1.6}O_4$ can be used in removal of lithium from waste materials containing lithium generated in industries.

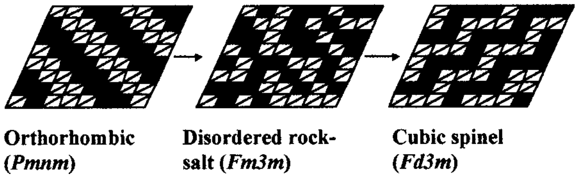

FIG. 4. Schematic representation of structural transformation of *o*-$LiMnO_2$ to cubic $Li_{1.6}Mn_{1.6}O_4$.

In conclusion, *o*-$LiMnO_2$ could be synthesized by different routes including hydrothermal, reflux, or microwave irradiation. The formation of semi-crystalline *o*-$LiMnO_2$ was achieved by the interaction of microwave irradiation with a suspension of γ-MnOOH in a 4 M LiOH solution in a very short time as compared to conventional methods.

ACKNOWLEDGMENTS

The authors thank Dr. K. Kunii of Shikoku Instrumentation Co., Ltd., Takamatsu, and Dr. J-H. Lee of the Research Institute for Solvothermal Technology, Takamatsu, for kindly providing facilities to carry out microwave experiments.

REFERENCES

1. J. C. Hunter, *J. Solid State Chem.* **39,** 142 (1981).
2. X. M. Shen and A. Clearfield, *J. Solid State Chem.* **64,** 270 (1986).
3. R. Chitrakar, H. Kanoh, Y. Miyai, and K. Ooi, *Chem. Mater.* **12,** 3151 (2000).
4. R. Chitrakar, H. Kanoh, Y. Miyai, and K. Ooi, *Ind. Eng. Chem. Res.* **40,** 2054 (2001).
5. A. R. Armstrong and P. G. Bruce, *Nature* **381,** 499 (1996).
6. R. Chitrakar, H. Kanoh, Y. Miyai, and K. Ooi, *J. Solid State Chem.* **160,** 69 (2001).
7. J. N. Reimers, E. W. Fuller, E. Rossen, and J. R. Dahn, *J. Electrochem. Soc.* **140,** 3396 (1993).
8. Y.-M. Chiang, H. Wang, and Y.-I. Jang, *Chem. Mater.* **13,** 53 (2001).
9. K. J. Rao, B. Vaidhyanathan, M. Ganguli, and P. A. Ramakrishnan, *Chem. Mater.* **11,** 882 (1999).
10. P. S. Whitfield and I. J. Davidson, *J. Electrochem. Soc.* **147,** 4476 (2000).
11. Q. Zhang, J. Luo, E. Vileno, and S. Suib, *Chem Mater.* **9,** 2090 (1997).
12. L. Croguennec, P. Deniard, R. Brec, and A. Lecerf, *J. Mater. Chem.* **7,** 511 (1997).
13. Y.-I. Jang, B. Huang, H. Wang, D. R. Sadoway, and Y.-M. Chiang, *J. Electrochem. Soc.* **146,** 3217 (1999).