Lithium Magnesium Manganese Oxides Prepared from Mg-Birnessite or Mg-Todorokite by a $LiNO_3$ Flux Method

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Layered and fibrous crystals of spinel-type lithium magnesium manganese oxide have been synthesized from Mg-containing birnessite and todorokite precursors respectively by a topotactic reaction in a $LiNO_3$ flux at 400 °C.

Spinels are of interest in the manganese oxide compounds used as selective adsorbents[1,2] and as insertion electrodes for lithium batteries.[3] Attempts are being made to improve the properties of spinels by substituting monovalent, divalent, trivalent cation, or penta-valent cations for some of the manganese ions in the spinel framework. A $LiNO_3$ flux[4] can yield two kinds of lithium manganese oxide crystals with tetra-valent manganese: Li_2MnO_3 at high temperatures, the same as lithium chloride[5] or other fluxes[6,7] with enough external oxygen; and $Li_{1.66}Mn_{1.67}O_4$ spinel at low temperatures (<500 °C). The spinel obtained by this method preserves the morphology of its manganese oxide precursor, which excludes other metal ions, such as γ-MnO_2 with [2 × 1] tunnels, H-type hollandite with [2 × 2] tunnels, and H-type birnessite with [2 × ∞] layers. Although the crystal system of the spinel is cubic, the adsorptivities of the spinels obtained from different precursors vary depending on the amount and distribution of spaces remaining after the precursors are transformed into the spinel.[8] In the present study, we used Mg-containing birnessite and todorokite manganese oxides (abbreviated as BirMO and TodoMO, respectively) as precursors, and paid attention to the morphology of crystals, Mg content and the oxidation state of manganese in the products.

Na-BirMO was prepared as reported in the literature.[9] To improve its crystallinity, the product was hydrothermally treated at 150 °C for 16 h in a 2 M NaOH solution. Na-BirMO was soaked in an aqueous solution of 0.5 M $MgCl_2$ and then stirred for 1 day. X-ray diffraction (XRD, RINT 2100 type of Rigaku) showed that Mg-buserite with a basal spacing of 9.67 Å was obtained. By drying Mg-buserite at 70 °C for 1 day, Mg-BirMO was obtained. Mg-TodoMO was produced after Mg-buserite was hydrothermally treated in a 0.5 M $MgCl_2$ solution at 150 °C for 2 days.

Mg-BirMO or Mg-TodoMO (1 g) was mixed with 20 g of $LiNO_3$ (Wako Pure Chemicals Industries, Ltd.), respectively, and then put into a pure alumina crucible (50 mL), and heated in a muffle furnace at 400 °C for different intervals of time. The products were washed with distilled water 3 times; filtered and dried at 70 °C. All the samples were subjected to XRD, chemical analysis, which included the metal elements analysis by atomic absorption spectrophotometry after dissolving samples in a mixture solution of HCl and H_2O_2 and the available oxygen analysis by the standard oxalic acid method.[10] TG–DTA was used to determine the content of water including water molecules and exchangeable H^+ ions and it indicated that Mg-BirMO and Mg-TodoMO lost water below 400 °C.

Table 1 summarizes the compositions of the precursors and the products after heating in the flux. Figure 1 shows that the products after 4–12 h heating are spinels (cf. JCPDS cards No. 32-0573) except for the long-term (e.g., (b)-72 h) heated samples with high d-value at 2θ = 19°. The photographs in Figure 2 illustrate the products retained the same plate and fiber morphologies as their precursors, respectively, at the scale of SEM. In the XRD pattern of the sample obtained from Mg-BirMO heated for 2 h (Figure 1 (a)-2 h), the peak of BirMO can be found at 6.98 Å (the

Table 1. Compositional data for the precursors and their products after heating in $LiNO_3$ flux at 400 °C

Sample		Chemical Formula[a]	(Li+Mg)/Mn	Mg/Mn	Average oxidation state of Mn	Extractability[b]/%		
						Li	Mg	Mn
Mg-BirMO		$Na_{0.15}Mg_{2.26}Mn_{14}O_{28.62}\cdot 10.94H_2O$	0.16	0.16	3.75	-	71	10.8
Heated for	2h	$Na_{0.01}Li_{0.69}Mg_{0.27}Mn_{1.75}O_4$	0.55	0.15	3.87	63	32	8.4
	12h	$Li_{1.10}Mg_{0.25}Mn_{1.75}O_4$	0.83	0.15	3.96	90	21	5.8
	24h	$Li_{1.38}Mg_{0.25}Mn_{1.56}O_4$	1.04	0.16	3.94	92	17	4.3
	48h	$Li_{1.60}Mg_{0.22}Mn_{1.47}O_4$	1.24	0.15	4.04	100	49	2.6
	72h	$Li_{1.77}Mg_{0.23}Mn_{1.45}O_4$	1.37	0.16	3.98	89	25	2.1
Mg-TodoMO		$Na_{0.18}Mg_{3.77}Mn_{12}O_{25.88}\cdot 13.3H_2O$	0.31	0.31	3.67	-	78	9.4
Heated for	2h	$Li_{0.36}Mg_{0.51}Mn_{1.73}O_4$	0.50	0.30	3.82	71	14	5.7
	12h	$Li_{0.50}Mg_{0.51}Mn_{1.64}O_4$	0.61	0.31	3.95	56	13	3.9
	24h	$Li_{0.61}Mg_{0.49}Mn_{1.64}O_4$	0.67	0.30	3.90	58	14	4.7
	48h	$Li_{0.81}Mg_{0.48}Mn_{1.56}O_4$	0.83	0.31	4.00	56	13	3.8
	72h	$Li_{1.42}Mg_{0.45}Mn_{1.45}O_4$	1.29	0.31	3.91	56	22	2.1
	168h	$Li_{1.91}Mg_{0.38}Mn_{1.34}O_4$	1.71	0.28	3.96	50	50	1.2

[a] Na/Mn was less than 0.003 and 0.007 for samples from heated Mg-BirMO and Mg-TodoMO, respectively. [b] After stirring in 0.5 M HCl for 3 days, supernatants were analyzed.

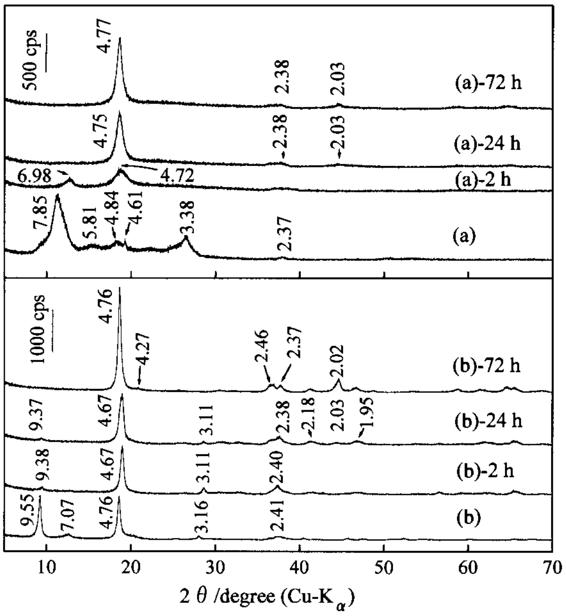

Figure 1. XRD patterns of (a) Mg-BirMO, (b) Mg-TodoMO and their corresponding products after heating in a $LiNO_3$ flux for different times. d-values in Å

basal spacing was less than that of Figure 1 (a) because of the water loss), showing the lithium insertion into the precursor, rather than a dissolution precipitation process. With an increase of heating time, the lithium content increased, accompanying the peak disappearance of the precursor. Meanwhile, during the transformation from each precursor to spinel, no other peak in XRD was detected. These results are the same as for other precursors we have reported;[8] namely, a topotactic reaction takes place between precursors and a $LiNO_3$ flux to form spinel.

The products had the same Mg/Mn molar ratio as the precursors, respectively (Table 1). This means during the lithium insertion there is no Li^+/Mg^{2+} ion exchange in the $LiNO_3$ flux. However, when Na-BirMO ($Na_{4.3}Mn_{14}O_{28.2}\cdot10.6H_2O$) was used as a precursor, we found Li^+/Na^+ ions exchanged rapidly. In Table 1, less Na^+ content in the products than in the precursors also shows the Na^+/Li^+ ion exchange.

A typical Mg-containing spinel characteristically has Mg^{2+} at the octahedral site, with a cation distribution of $(Li)[Mg_{0.5}Mn^{IV}_{1.5}]O_4$.[11] In the present study, since the oxidation state of manganese in the spinel was 4, as in $Li_{1.33}Mn_{1.67}O_4$, some Li^+ ions should be at the octahedral sites which had not been occupied by Mg^{2+}. The Mg and Li content in the octahedral sites may cause the spinel from Mg-BirMO to have a larger lattice constant (a_0 = 8.23 Å, calculated from [111] plane in Figure 1) than that from Mg-TodoMO (8.08 Å). The time-dependence of the (Li+Mg)/Mn ratio in Table 1 indicates that lithium insertion into Mg-BirMO is faster than that into Mg-TodoMO. This result on the one hand indicates that the initial interlayer space in BirMO is more convenient for lithium insertion than that of the [3 × 3] tunnels in TodoMO. On the other hand, since the Mg content in Mg-TodoMO is nearly equal to the amount needed for forming the $(Li)[Mg_{0.5}Mn^{IV}_{1.5}]O_4$ structure; the slow change of (Li+Mg)/Mn over a period of around 12–24 h may mean this structure is somewhat stable, and therefore further lithiation of this structure would be difficult.

The increase of oxidation state of manganese means that the reaction between precursors and the flux proceeds with oxygen-diffusion. Furthermore, O^{2-} ions are also needed to diffuse into the product to balance the positive charge of Li^+ ions. We have suggested[8] a "buffer space" model to explain the non-morphologic change after the increase of O^{2-} content in the transformation of hollandite, birnessite and γ-MnO_2 to spinel. The [3 × 3] tunnels in TodoMO provide spaces for the diffusion of O^{2-}.

The extractability of Li^+ and Mg^{2+} from the samples in Table 1 was investigated by stirring them in a 0.5 M HCl aqueous solution for 3 days. Almost all Li^+ ions were able to be extracted by acid-treatment from the spinel obtained from Mg-BirMO (Table 1). This differs from the spinel obtained from Mg-TodoMO. The Li^+ and Mg^{2+} extraction from $(Li)[Mg_{0.5}Mn^{IV}_{1.5}]O_4$ spinel proceeds by an ion-exchange-type mechanism.[12] Therefore, the difference in Li^+ extraction may be due not only to lattice size, but also the amount and distribution of the remaining buffer space after the structural transformation, which affect the H^+/Li^+ ion exchange.

The d-value of 4.76 Å in Figure 1 (b)-72 h and the peak which emerged at 4.27 Å show evidence of a small amount of the monoclinic phase (such as Li_2MnO_3) formed in addition to the spinel phase after long term heating in the flux.

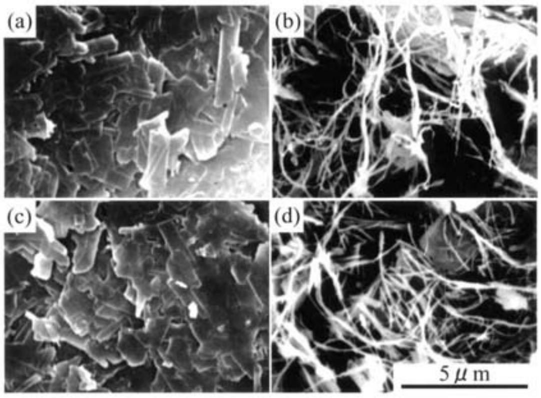

Figure 2. SEM Photographs of (a) Mg-BirMO, (b) Mg-TodoMO and (c), (d) their products, respectively, after heating for 72 h.

In conclusion, layered and fibrous Mg-containing spinel crystal can be synthesized by heating Mg-BirMO and Mg-TodoMO in a $LiNO_3$ flux at 400 °C via a topotactic reaction. The spinel obtained from Mg-BirMO shows good Li^+-extractability.

References and Notes

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