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Note

THERMAL EVOLUTION OF THE LITHIATION PRODUCT OF Mn_3O_4

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The reactions induced by thermal treatment of lithium insertion compounds are of interest in order to have a detailed knowledge of the stability of these phases. In addition, these processes yield various ternary oxides under mild experimental conditions that differ markedly from the classical ceramic method. In this way, the thermal evolution of the lithiation products of various metal oxides has been recently examined [1–3].

In this paper, the thermal decomposition of the lithiation product of the tetragonal spinel phase Mn_3O_4 is studied under different experimental conditions.

EXPERIMENTAL

A high purity Mn_3O_4 sample was obtained by the thermal decomposition of commercial MnO_2 at 850 °C. The chemical lithiation of this solid was carried out with *n*-butyllithium working at 37 °C. The determination of total Li and Mn contents in the samples was effected by atomic absorption spectrometry.

The X-ray diffraction patterns were obtained with a Siemens D500 apparatus using Cu $K\alpha$ radiation, with a graphite monochromator and digital data handling. Differential scanning calorimetry (DSC) curves were obtained with a Mettler TA 3000 apparatus at heating rates of $8° \text{ min}^{-1}$. IR spectra were obtained with a Perkin–Elmer 599 spectrometer.

RESULTS AND DISCUSSION

Chemical lithiation at 37 °C for periods of time lower than 7 days yielded mixtures of the insertion compound $Li_xMn_3O_4$ [4] and unreacted Mn_3O_4. The chemical analysis of the sample obtained after 7 days of treatment showed the nominal composition $Li_{1.85}Mn_3O_4$. When lithiation was carried out for longer periods, the chemical and phase composition showed minor changes.

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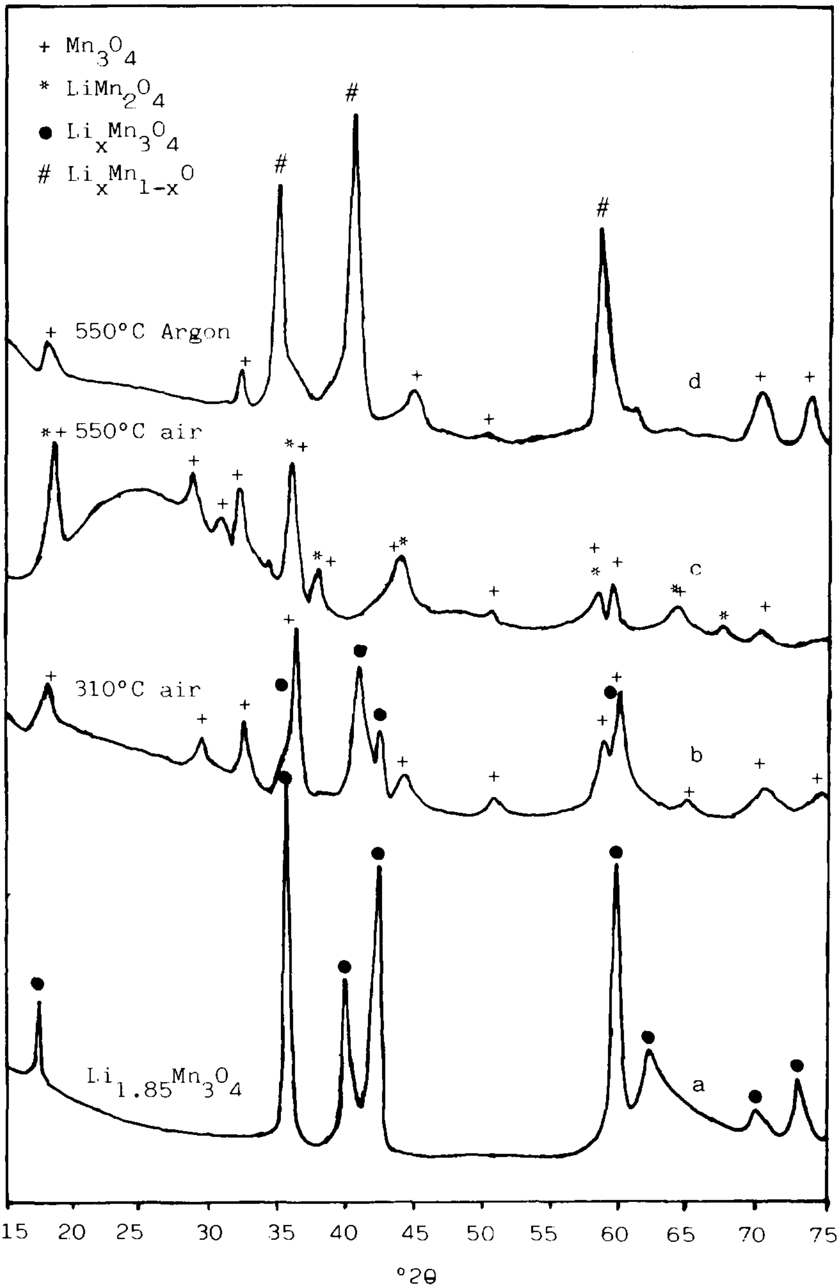

Fig. 1. X-ray diffractograms of Mn_3O_4 lithiated with *n*-butyllithium: a, room temperature; b, heated at 310 °C in air; c, heated at 550 °C in air; d, heated at 550 °C in argon.

The X-ray diffraction pattern of the lithiated phase is shown in Fig. 1a. This pattern is consistent with the presence of a tetragonal phase that maintains the ordering of manganese ions $[Mn_2]O_4$ as in Mn_3O_4. According

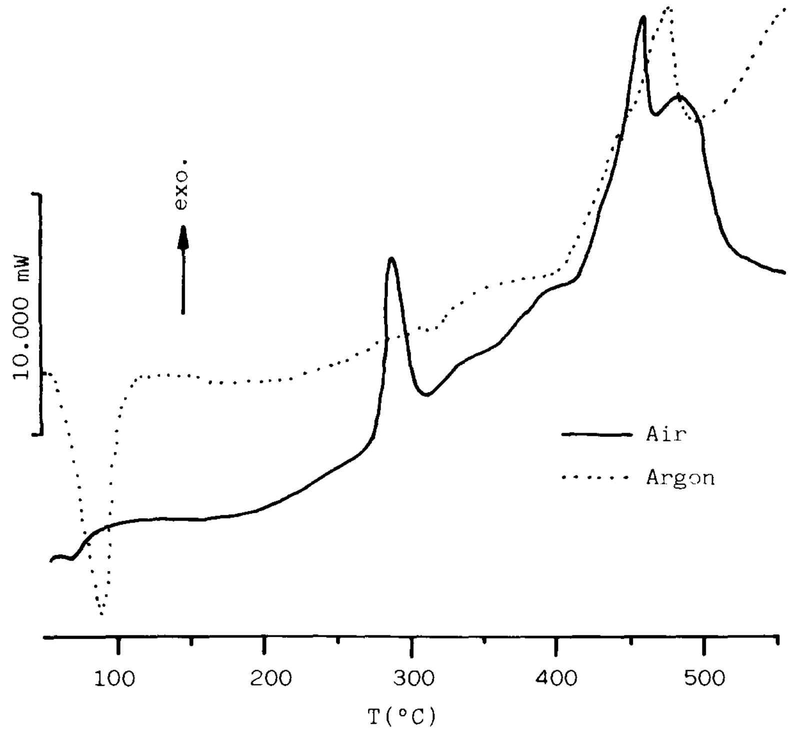

Fig. 2. DSC traces of lithiated $Li_xMn_3O_4$ samples.

to Thackeray et al. [4], this phase allows the insertion of one lithium ion per Mn_3O_4 formula, resulting in complete filling of the octahedral sites: $\{MnLi\}[Mn_2]O_4$. As the above-mentioned experimental formula has a higher Li content, it may be assumed that the sample contains other contaminant lithium compounds undetected by X-ray diffraction, such as Li_2CO_3 or Li_2O. The IR spectrum of this sample showed low intensity bands that could be ascribed to CO_3^{2-} ions. An alternative explanation could be based on the occupation of tetrahedral sites in the structure by lithium ions: $(Li_{0.85})\{MnLi\}[Mn_2]O_4$. However this possibility is not commonly accepted in the Mn–O–Li [4] or Fe–O–Li [1] systems, although due to the lack of experimental evidence because of the low X-ray scattering power of lithium, it cannot be ruled out.

The DSC traces of the lithiated sample recorded under different experimental conditions are shown in Fig. 2. The curve obtained under static air atmosphere shows a sharp exotherm at around 290 °C and a more complex exothermal effect between 450 and 520 °C. The X-ray diffractogram of a sample prepared by interrupting the DSC experiment at 310 °C is shown in Fig. 1b. At this temperature, the diffraction lines corresponding to the tetragonal spinel Mn_3O_4 are present while the reflections of $Li_xMn_3O_4$

remain evident. This pattern shows that the exothermal effect at 290 ° C is responsible for a partial oxidation of $Li_1Mn_3O_4$ to Mn_3O_4 with the eviction of lithium from the structure that may remain in the samples as Li_2CO_3 and Li_2O. Again, the IR spectra show the presence of weak bands attributable to carbonate. The fact that the oxidation process is not completed at this temperature may be interpreted in terms of a kinetic inhibition of the reaction probably due to the formation of a Mn_3O_4 layer surrounding the particles of the lithiated product. A similar explanation has been suggested for other systems such as $Li_xCo_3O_4$ [3].

The X-ray diffractogram of a sample prepared at 550 ° C (Fig. 1c) shows that the $Li_xMn_3O_4$ oxidation is complete after the complex exotherm in the DSC diagram of Fig. 2a. The diffraction lines of the lithiated product are now absent and some of the reflections of Mn_3O_4 are highly broadened or show shoulders that could be ascribed to the ternary oxide $LiMn_2O_4$. The complex exotherm is then associated with the formation of this phase and with the simultaneous oxidation of the remaining $Li_xMn_3O_4$. A sample prepared at higher temperatures (700 ° C) showed a marked increase in the crystallinity of Mn_3O_4 and $LiMn_2O_4$. The formation of the ternary oxide may take place with the reaction of the lithium oxide and/or carbonate present in the sample.

The DSC curve obtained under dynamic argon atmosphere shows a single exotherm at around 460 ° C that corroborates the oxidative nature of the other effects shown in air atmosphere. The higher thermal stability of the lithiated phase in the inert atmosphere was demonstrated below the exotherm. The X-ray diffractogram of a sample heated and cooled under argon up to 550 ° C (Fig. 1d) is characteristic of a two-phase product containing a solid with a rock salt structure and a tetragonal spinel. The tetragonal phase can be identified as Mn_3O_4 while the rock salt phase has a unit cell parameter of $a = 4.424 \pm 0.003$ Å that differs slightly from that corresponding to MnO (4.445 Å). Johnston and Heikes [5] have shown that MnO can incorporate lithium in compositions $Li_xMn_{1-x}O$ with x up to 0.347, without changing the rocksalt structure of the monoxide. Using the data in ref. 5, the experimental a parameter found in our study can be converted to a value of $x = 0.053$. It should be noted that the preparation conditions of $Li_xMn_{1-x}O$ phases are critical in order to avoid higher Mn oxidation (Li_2O_2 and MnO in an inert atmosphere were the experimental conditions used in ref. 5). The thermal decomposition of $Li_xMn_3O_4$ in an inert atmosphere inhibits the formation of undesirable oxidation products.

In contrast, the Mn_3O_4 phase found in the decomposition product in argon does not allow significant Li to be admitted as it has been clearly stated that a minimum Li insertion in spinel structures displaces all Mn ions from tetrahedral to octahedral positions [4,6]. Thus, the spinel phase found in the X-ray diffractogram of Fig. 1d can be ascribed to a mixture of $Li_{0.05}Mn_{0.95}O$ and Mn_3O_4. From these results, the thermal evolution of

$LiMn_3O_4$ in an inert atmosphere can be summarized in terms of the eviction of Li from the octahedral sites with collapse of the $[Mn_2]O_4$ ordering and formation of the disordered rock salt phase. These processes reflect a redistribution of Mn oxidation states, according to the following equation

$$LiMn_3O_4 \rightarrow 0.489Li_{0.05}Mn_{0.95}O + 0.750Mn_3O_4 + 0.488Li_2O$$

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