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BRIEF COMMUNICATION

Synthesis of Lithium–Manganese–Oxide Spinels: A Study by Thermal Analysis

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The synthesis of lithium–manganese–oxide spinels by reaction of Li_2CO_3 and $MnCO_3$ in air and under nitrogen to $T_{max} = 600°C$ has been investigated by thermogravimetric analysis and differential scanning calorimetry. When the reaction is conducted in air, the stoichiometric spinel $LiMn_2O_4$ is produced via a series of intermediate "oxygen-rich," defect spinel compounds $Li_{1-x}Mn_{2-2x}O_4$ $(0 \le x \le 0.11)$, whereas under nitrogen the reaction proceeds more directly to $LiMn_2O_4$. © 1994 Academic Press, Inc.

INTRODUCTION

Lithium–manganese–oxide compounds with a spinel-type structure are of interest as cathode materials for rechargeable lithium batteries (1–7). For example, the stoichiometric spinel $LiMn_2O_4$ is under investigation as a 4-V electrode (against lithium) for the compositional range $Li_yMn_2O_4$ $(0 < y \le 1)$ (2–6), whereas the "oxygen-rich," defect spinel $Li_2Mn_4O_9$ (alternatively, $LiMn_2O_{4.5}$ or $(Li_{0.89}\square_{0.11})[Mn_{1.78}\square_{0.22}]O_4$) is of interest as a 3-V electrode for the compositional range $Li_{2+z}Mn_4O_9$ $(0 < z \le 3)$ (7, 8). $LiMn_2O_4$ and $Li_2Mn_4O_9$ are the end-members of the solid solution system $Li_{1-x}Mn_{2-2x}O_4$ with $x = 0$ and 0.11, respectively. In this system the Li : Mn ratio is always 1 : 2. The synthesis of compounds that lie in this solid–solution range has been accomplished by the simultaneous decomposition of Li_2CO_3 and $MnCO_3$ in air; their composition is critically dependent on reaction conditions such as the oxygen partial pressure, reaction temperature, and time. Tight control of reaction parameters is therefore required to process spinel materials with a predetermined composition. In this communication we report differential scanning calorimetry (DSC) and thermogravimetric (TG) data that provide further information about the formation of $Li_{1-x}Mn_{2-2x}O_4$ spinel compounds and the dependence of composition on atmospheric conditions and temperature.

EXPERIMENTAL

For the DSC and TG experiments, powders of Li_2CO_3 and $MnCO_3$ were mixed in a 1 : 4 molar ratio and thoroughly ground in a mortar and pestle prior to firing. Approximately 10-mg samples were used for the thermal analyses. DSC and TG data were obtained on a Du Pont 1090 thermal analyzer at the University of Cape Town. A scanning rate of 20°C/min was used for both types of data collection. Standard $LiMn_2O_4$ and $Li_2Mn_4O_9$ samples were prepared for X-ray diffraction analysis according to the following procedures. $LiMn_2O_4$ was prepared from $LiOH \cdot H_2O$ and γ-MnO_2 (CMD) precursors, whereas $Li_2Mn_4O_9$ was prepared from Li_2CO_3 and $MnCO_3$. In both cases, the reagents were thoroughly mixed by ball-milling in hexane for 24 hr prior to firing. The $LiMn_2O_4$ sample was prefired in air at 450°C for 48 hr and thereafter at 650°C for 48 hr. $Li_2Mn_4O_9$ was synthesized by firing once at 400°C for 5 hr. Lattice constants were determined by an iterative least-squares refinement against an internal silicon standard. Powder X-ray diffraction patterns of the $LiMn_2O_4$ and $Li_2Mn_4O_9$ samples were recorded at a scan rate of $1.2°2\theta$/min on an automated Rigaku diffractometer with Cu$K\alpha$ radiation monochromated by a graphite single crystal.

RESULTS AND DISCUSSION

The TG and DSC plots for the reaction of Li_2CO_3 and $MnCO_3$ in air and under nitrogen are shown in Figs. 1 and 2, respectively. The TG plows show that both samples lose approximately 1% by mass during heating to 150°C; this mass loss was attributed predominantly to adsorbed water on the surface of the particles. The removal of the surface water was also manifest by the endothermic peaks

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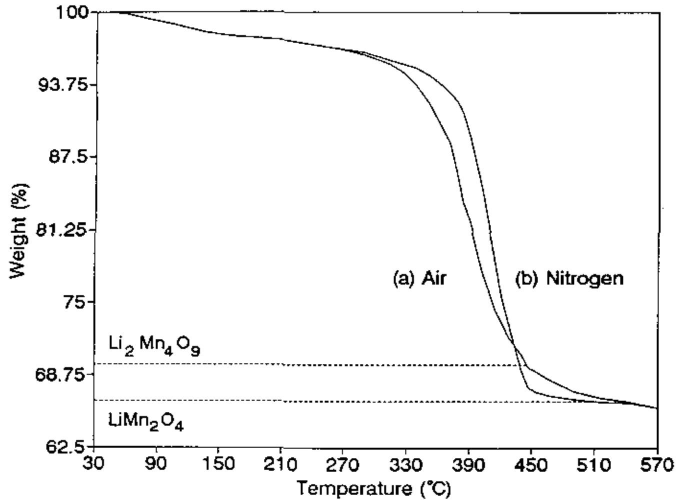

FIG. 1. Thermogravimetric data for the decomposition reaction Li_2CO_3 + $4MnCO_3$ (a) in air and (b) under nitrogen.

below 100°C in the DSC data in Fig. 2. Above 150°C the TG and DSC plots obtained in air and under nitrogen are distinctly different from one another and are indicative of different reaction processes.

Reaction in air. It has already been demonstrated that the reaction of Li_2CO_3 and $MnCO_3$ in air at 300–400°C results in the defect spinel $Li_2Mn_4O_9$ (8). The ideal reaction can be represented by

$$Li_2CO_3 + 4MnCO_3 + 2O_2(air) \rightarrow Li_2Mn_4O_9 + 5CO_2. \quad [1]$$

Reaction [1] necessitates the simultaneous decomposition of the two carbonate reagents and oxidation of the manganous ion (Mn^{2+}) to Mn^{4+}. In practice, however, it is difficult to control the stoichiometry of the final product; it is normally not fully oxidized and falls within the system $Li_{1-x}Mn_{2-2x}O_4$ ($0 < x < 0.11$). The TG curve indicates that the onset of the decomposition reaction occurs at approximately 270°C. The overall mass loss associated with the carbonate precursors in reaction [1] is 29.2%. The curve therefore shows that, under experimental conditions and allowing for the 1% mass loss due to surface water, the $Li_2Mn_4O_9$ composition is reached at approximately 450°C. On further heating, oxygen is lost from the spinel structure according to the reaction

$$Li_2Mn_4O_9 \rightarrow 2LiMn_2O_4 + \tfrac{1}{2}O_2. \quad [2]$$

The mass loss associated with the loss of oxygen from the spinel structure in reaction [2] is 3.0%. It can therefore be determined from the TG plot in Fig. 1a that the $LiMn_2O_4$ composition is reached at approximately 550°C.

The DSC plot obtained in air shows a broad exothermic peak between 260 and 520°C which is consistent with the formation of a wide range of spinel compositions in the system $Li_{1-x}Mn_{2-2x}O_4$ ($0 \leq x \leq 0.11$). Spinel phases within this system have very similar X-ray diffraction patterns as shown by the patterns of the standard $LiMn_2O_4$ and $Li_2Mn_4O_9$ samples that can be indexed to the face-centered unit cell of the prototype spinel space group *Fd3m* (Fig. 3a,b); the patterns can, in principle, be distinguished from one another by the lattice parameter value of the spinel phase which, from the X-ray diffraction analyses, varies from 8.232 Å in $LiMn_2O_4$ to 8.162 Å in $Li_2Mn_4O_9$. The lattice parameter of the $LiMn_2O_4$ product is in good agreement with that reported by Tarascon in a plot of lattice parameter against x in $Li_xMn_2O_4$ (8.234 Å) (9). The $Li_2Mn_4O_9$ product was similar to a sample that was analyzed by neutron-diffraction (8).

Reaction under nitrogen. When $MnCO_3$ is reacted with Li_2CO_3 under nitrogen, all the oxygen required for the formation of the spinel phase is derived from the carbonate precursors as shown in

$$Li_2CO_3 + 4MnCO_3 \xrightarrow{N_2} 2LiMn_2O_4 + CO_2 + 3CO. \quad [3]$$

In the absence of any free surrounding oxygen it is evident from the DSC plot that shows a sharp exothermic peak at T_{max} = 423°C (Fig. 2b), and the TG curve that shows a more abrupt change in mass with increasing temperature in air (Fig. b), that the formation of $LiMn_2O_4$ occurs within a temperature range under nitrogen narrower than that in air. These data therefore demonstrate that the formation of $LiMn_2O_4$ under nitrogen is more clearly defined and

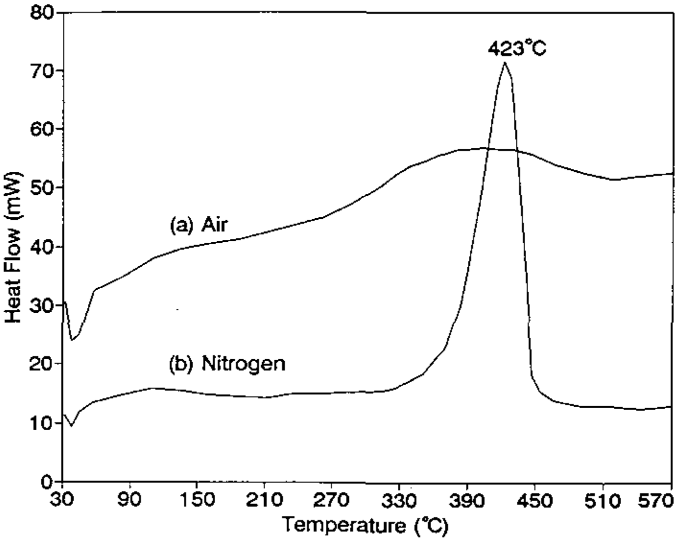

FIG. 2. Differential scanning calorimetry data for the decomposition reaction Li_2CO_3 + $4MnCO_3$ (a) in air and (b) under nitrogen.

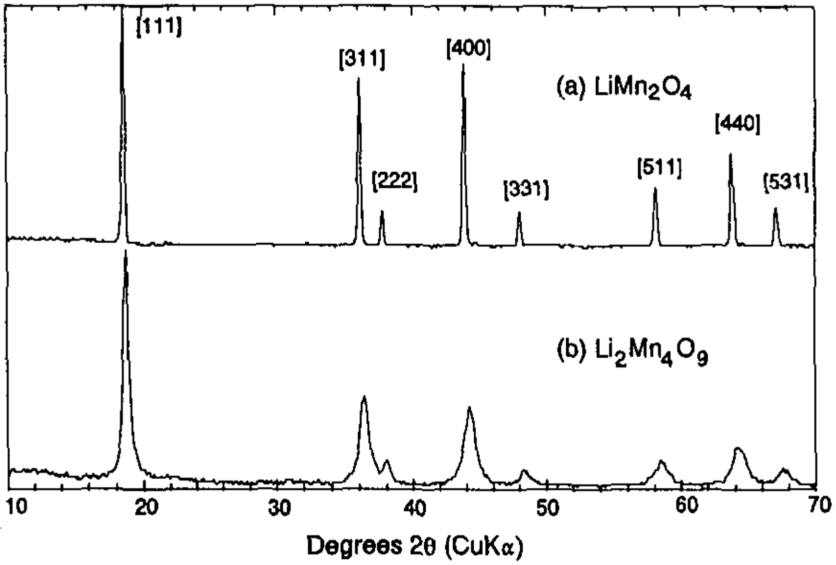

FIG. 3. Powder X-ray diffraction patterns of (a) $LiMn_2O_4$ and (b) $Li_2Mn_4O_9$.

that the stoichiometric spinel composition is reached at a temperature between 500 (TGA data, Fig. 1) and 450°C (DSC data, Fig. 2) which is significantly lower than that reached when the reaction is conducted in air.

Further work is being undertaken to characterize these spinel products in terms of the physical parameters that are important to the battery industry, for example, exact composition, particle size, surface area, density, and crystal morphology.

CONCLUSIONS

This study has demonstrated that lithium–manganese–oxide spinel compounds that fall within the solid solution range $Li_{1-x}Mn_{2-2x}O_4$ $(0 \leq x < 0.11)$ can be synthesized by reaction of $MnCO_3$ and Li_2CO_3 in air at moderate temperatures. It is difficult, however, to control the reaction parameters, for example, temperature and time, to produce a spinel compound with a predetermined stoichiometry. The study has, however, illustrated that the stoichiometric spinel $LiMn_2O_4$ can be produced at a moderately low temperature (less than 500°C) by performing the reaction under nitrogen. This result has commercial implications for the production of $LiMn_2O_4$ which, in the past, has been conventionally synthesized in air at higher temperatures, for example, 700–850°C.

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