THERMAL ANALYSIS STUDY OF $LiMn_{2-x}Ni_xO_4$

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The spinel $LiMn_2O_4$ has been studied extensively because of its high possibility of being commercialised as a cathode material for secondary lithium batteries. In the present investigation substitution of a large amount of manganese with nickel ($LiMn_{2-x}Ni_xO_4$) ($0 < x < 0.5$) has been conducted using the solid state reactions of Li_2CO_3, MnO_2 and Ni_2O_3 at 1123 K. To understand the reaction mechanism, DTA and TG curves were taken. The variation of Ni content to manganese indicates high thermal stability of nickel substituted spinel.

Keywords: Spinel, solid state reactions, TGA/DTA, thermal stability.

INTRODUCTION

The spinel $LiMn_2O_4$ has been studied extensively because of its high possibility of being commercialised as a cathode material for secondary lithium batteries. Eventhough it has got a large theoretical capacity of 308 mAh/g, the potential drop from 4 V to 3 V vs Li/Li^+ offsets it. The average manganese ion valence falls below 3.5 and a strong Jahn-Teller distortion is introduced into the spinel structure. The configuration of the trivalent manganese ion in the spinel tends to be stabilised in the D4h symmetry rather than the octahedral symmetry. Hence, an elongation of the octahedra occurs in the spinel, resulting in a structural transition which increases the c/a ratio of the unit cell by 16%. To combat the onset of Jahn-Teller effect the substitutions of manganese with different valence metals (M = Ge, Fe, Co, Zn, Ni) has been tried [1-7]. In this paper, we report a successful preparation of low temperature $LiMn_{2-x}NixO_4$ ($0 < x < 0.5$) material by substitution of manganese with considerable amount of nickel using the solid state reaction route. This material has the additional advantage of intercalating a second lithium both chemically and electrochemically, leading to the formation of a potential 3 V $Li_2Mn_{1.5}Ni_{0.5}O_4$ compound with the same spinel structure as $LiMn_2O_4$. The kinetics of the reaction has been followed by DTA and TG.

EXPERIMENTAL

Stoichiometric quantity of Li_2CO_3, MnO_2 and Ni_2O_3 (all are AR grade) were ground well in agate mortar. The mixture was heated initially at 873 K for a period of 4 hours. The sample was then taken out, ground thoroughly and heated at 973 K for 4 hours. After grinding the mixture, a final heat treatment was made at 1073 K for 18-20 hours. The powders were then ground thoroughly and used for further investigations. Nickel content in the samples was varied from $0 < x < 0.5$ ($LiMn_{2-x}Ni_xO_4$). The powders were characterised by X-ray diffraction studies using model Jeol JDX 30 x-ray diffractometer. Differential analysis was made using PL thermal sciences STA 1500. Particle size analysis was made using Malvern Particle Sizer M3.0.

RESULTS AND DISCUSSION

X-ray diffraction (XRD) of the powders are shown in Fig. 1, wherein the region near the spinel (4 0 0) has been indicated. The lattice parameter estimated from the XRD data is $a = 8.17 + 0.05$ Å. In the materials prepared by solid state reactions method a shift of the XRD peaks toward high angles is observed with increase of nickel content in the spinel. A systematic variation of the lattice constant with increase of nickel content coupled with the single phase patterns indicate that a solid solution could be prepared. The results of thermal analysis data for following the reaction of decomposition of $Li_2CO_3 + MnO_2 + Ni_2O_3$ mixtures are
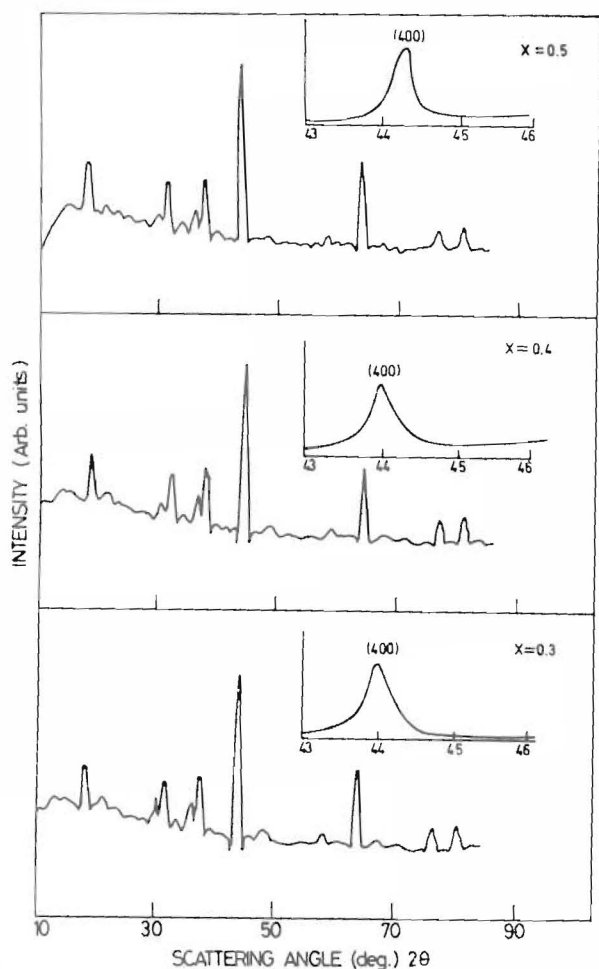
Fig. 1: XRD pattern of $LiNi_xMn_{2-x}O_4$ for $0.3 < x < 0.5$

shown in Figs. 2 and 3. Fig. 2 represents the TG and DTA of $LiMn_2O_4$ and Fig. 3 represents the TG and DTA of $LiMn_{1.6}Ni_{0.4}O_4$.

TG experiments

Implementation of McCarty and Green method has been followed for TG analysis. The initial equation for this technique is
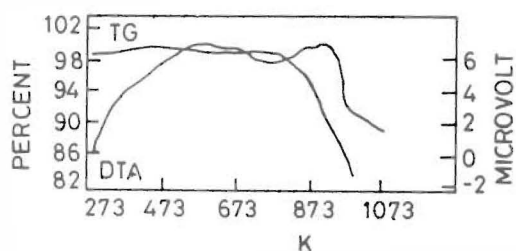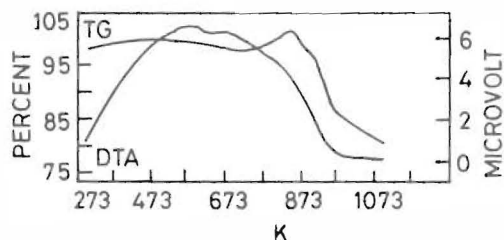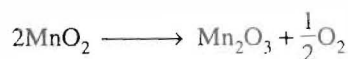

Fig. 2: TG & DTA of $LiMn_2O_4$

Fig. 3: $LiMn_{1.6}Ni_{0.4}O_4$

$$\frac{d\alpha}{dt} = \frac{z}{\beta \ e^{-E/RT\ (1-\alpha)}}$$

where α - percent conversion (reaction progress), z - pre-exponential factor (1/min), β - heating rate, E - activation energy, R - gas constant (1.987 cals/mole C), T - temperature (Kelvin) and a built in software was made use of to calculate activation energy, pre-exponential factor z and they are tabulated (Table I).

DTA experiments

Decomposition at 823 K may be attributed to the following transformation

$$2MnO_2 \longrightarrow Mn_2O_3 + \frac{1}{2}O_2$$

and weight loss of the dry samples starts even at 373 K and goes upto 973 K. Interaction between components takes place even at 373 K and when the temperature of heating is 573- 973 K, decomposition of Li_2CO_3 and MnO_2 may lead to the formation of $Li_2O . MnO_2$ phase to form a cubic spinel with lithium vacancies. The decomposition process for Li_2CO_3 is reported to occur as single step at 990 K. In the present investigation, it is not possible to distinguish individual components and this may be either due to non-predictability of the decomposition of individual components

TABLE I: Variation of activation energy and pre-exponential factor (TG), Temperature of inflection (DTA) with Ni content for the first order reaction

Mn	Ni	From TG curves		From DTA
		E_a Kcal/mole	lnz lit/min	K
2.0	0.0			887
1.9	0.1	40.43	21.27	943
1.8	0.2			969
1.7	0.3	30.38	14.39	980
1.6	0.4	29.58	13.31	*
1.5	0.5	21.98	9.59	*

in a mixture or combined effect of decomposition of the products in the mixture.

Variation of nickel content in the phase

Variation of activation energy and pre-exponential factor for the first order and variation of inflection temperature with nickel content are given in Table I. It is inferred from the values that energy of activation decreases as nickel content increases and the temperature of inflection steadily increases with increase in nickel content. This behaviour is understandable since thermal stability is better with higher nickel content because of its higher electronegativity. Decomposition temperature steadily but less significantly increases with nickel amount but the temperature range between the two processes is smaller when the nickel ratio increases. (The temperature of inflection is not able to be distinguished when Ni content ratio increases as indicated in Table I).

CONCLUSION

DTA and TG studies with variation of nickel content to manganese in the synthesis of $LiMn_{2-x}Ni_xO_4$ by solid reaction indicate higher thermal stability of nickel substituted spinel of $LiMn_2O_4$.

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