

SYNTHESIS OF LiMn_2O_4 BY GLYCINE-NITRATE METHOD

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Glycine-nitrate method was used to synthesize lithium manganese oxides. For the molar ratio of lithium-to-manganese in precursor solution equal to 1:2 spinel LiMn_2O_4 was obtained. For molar ratio of 1:1 a mixture of Li_2MnO_3 and spinel phase different from LiMn_2O_4 was observed.

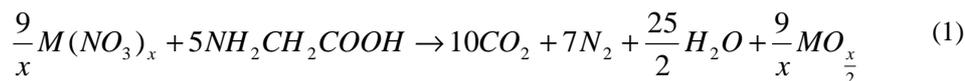
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1. Introduction

Li-Mn-O compounds belong to one of the most important groups of cathode materials for rocking chair batteries [1-13]. Acceptable environmental characteristics and low material cost make them an attractive concurrent to other cathode materials. Among lithium manganese oxides, LiMn_2O_4 is most extensively investigated [1, 7-13]. LiMn_2O_4 powders are traditionally made by a solid-state reaction: heating of the corresponding carbonates and/or oxides in the temperature range 700-900 °C [1, 8, 9, 13, 14]. Several successive heating (24-48 hours) and grinding procedures are required in this case, which are time and energy consuming. Other synthesis procedures have also been developed (Pechini process, spray pyrolysis method, etc) in which liquid state precursors enable to get better homogeneity and narrower particle size distribution [8, 9, 13]. These procedures are more or less complex, or require special experimental equipment.

Glycine-nitrate method was developed for simple and rapid synthesis of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramics [15]. For this purpose, precursor solution was prepared from the metal nitrates and glycine, which was then heated to the point of self-ignition. The role of glycine was to serve both as a fuel for combustion and as a complexant to prevent inhomogeneous precipitation of individual components prior to combustion. A stoichiometric mixture of oxidant and fuel is defined by [15]:



For high glycine-to-nitrate ratio the phases detected after self-ignition were mostly carbonates and oxides. Powder resulting from combustion was converted to ceramic material by calcinations, pressing and sintering. Glycine-nitrate method has also been applied for preparing orthorhombic Na_xMnO_2 , a potential cathode material for secondary sodium and lithium polymer batteries [16].

In this paper are reported the results related to the synthesis of lithium manganese oxides by the glycine-nitrate method.

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2. Experimental

1 M aqueous solutions of LiNO_3 and $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ were prepared from p.a. chemicals. They were mixed in 1 : 1 and 1 : 2 molar ratios so the total volume was 30-40 ml. Glycine was added in the mixture either as a solid or as a water solution. Amount of glycine was such to make glycine-to-nitrate molar ratio equal to 1:2. Precursor solution was placed in a glass beaker and heated in an oven at 200 °C until spontaneous ignition occurred. Ash resulting from combustion was pressed in pellets and heated at 800 °C for 4 hours. After grinding, obtained powders were examined by XRD. The XRD experiments were done with the $\text{CuK}\alpha_{1,2}$ radiation in 15-70° 2 θ range with the 0.05° step and 2 seconds exposition time.

Electrochemical experiments were performed in a three electrode cell filled with argon. Electrolyte was prepared by dissolving 1 M LiClO_4 in PC and EC mixture (1:1 mole ratio). Before dissolving p.a. LiClO_4 was dried under vacuum at 120-140 °C for at least 2 hours. PC and EC were distilled twice under vacuum, and the middle fraction was collected. Working electrode was made from synthesized material, "Vulcan" carbon black and PVDF mixed in 90:5:5 weight percent ratio and deposited on platinum foil from slurry prepared in N-Methyl-2-Pyrrolidone. Cathode material weighted 9.3 mg and was spread over 2.4 cm² of Pt-foil surface area. Both counter and reference electrode were lithium metal foils.

3. Results and discussion

In Fig. 1 the XRD patterns of powder samples A, B and C are shown. Sample A is prepared from precursor solution with Li : Mn molar ratio 1 : 2. In sample B, Li : Mn molar ratio is 1 : 1. Sample C, presented for the purpose of comparison, is LiMn_2O_4 prepared by solid state reaction of Li_2CO_3 and MnO_2 at 800 °C (3 × 24 hours of heating with successive grinding and pressing) [14]. From the XRD pattern of sample B two crystal phases are identified: the monoclinic Li_2MnO_3 [4,17], and the cubic defect spinel $\text{Li}_{1+x}\text{Mn}_{2-y}\text{O}_4$ [18]. The reflections belonging to defect spinel (Fig. 1b,) are slightly shifted to lower d-values if compared to normal spinel phase (Fig. 1c and Table 1).

The XRD pattern of sample A (Fig. 1a) is the same as for sample C (Fig. 1c) pointing out that LiMn_2O_4 normal spinel was obtained by glycine-nitrate method. An additional reflection with $d = 2.03 \text{ \AA}$ value is due to the presence of a small amount of Li_2MnO_3 as concluded by comparing with sample B reflections. Li_2MnO_3 phase should appear during synthesis of LiMn_2O_4 at temperatures higher than 850 °C [19]. Thus, most probably, Li_2MnO_3 phase do appear in sample A on account of slightly different Li/Mn molar ratio, because the value 0.5 above mentioned is determined only by weighing chemicals before preparing precursor solutions.

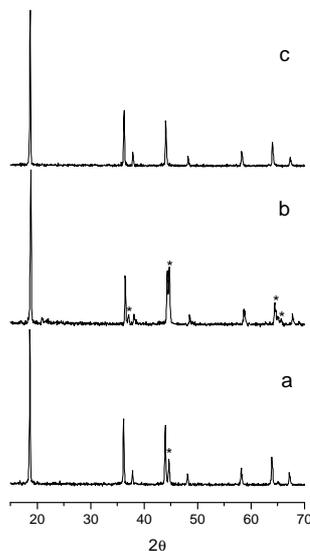


Fig. 1. XRD patterns of samples A and B synthesized by glycine-nitrate method, and of sample C prepared by solid state reaction. Characteristic reflections of Li_2MnO_3 phase are denoted by asterisk.

Table 1. The observed d values for A, B and C sample. The most intense reflections of Li_2MnO_3 phase (which do not overlap with spinel phase reflections) are marked with asterisk.

$d / \text{Å}$			
Cryst. plane	Sample A	Sample B	Sample C (LiMn_2O_4 – solid state reaction)
(111)	4.74	4.72	4.74
(311)	2.47	2.47	2.48
		2.42 *	-
(222)	2.37	2.36	2.37
(400)	2.05	2.04	2.06
	2.03 *	2.03 *	-
(331)	1.88	1.88	1.89
(511)	1.58	1.57	1.58
(440)	1.46	1.45 *	1.45
	-	1.43	-
	-	1.42 *	-
(531)	1.39	1.38	1.39

In order to test initial charging/discharging characteristics of sample A, two galvanostatic cycles were recorded, Fig. 2. Current density was $200 \mu\text{A}/\text{cm}^2$. Both charge and discharge curves show two distinct plateaus around 4 V, which are characteristic to well defined spinel structure of LiMn_2O_4 [7,9,11,13]. Significant loss of capacity between the first and the second cycle is also indicative for LiMn_2O_4 . The first charging capacity is around 115 mAh/g in the 3.3–4.35 V window. This is in accordance with the literature data, having in mind that sample A contains not only LiMn_2O_4 phase but also small amount of electrochemically inactive Li_2MnO_3 [1,11,13]. Deeper second discharging caused a short plateau around 2.75 V. It seems that lithium manganese oxide spinels, which have better capacity retention, are also more resistant in developing lower voltage plateau [20].

Sample B was not electrochemically tested because in addition to prevailing $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ phase it contains a large amount of Li_2MnO_3 . The possibility for obtaining $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ phase by glycine-nitrate method is important because these kinds of spinels are more resistive to capacity fading [19,20]. By changing experimental conditions in glycine-nitrate method it might be plausible to obtain pure $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ spinel and avoid complicated now-present preparation procedure.

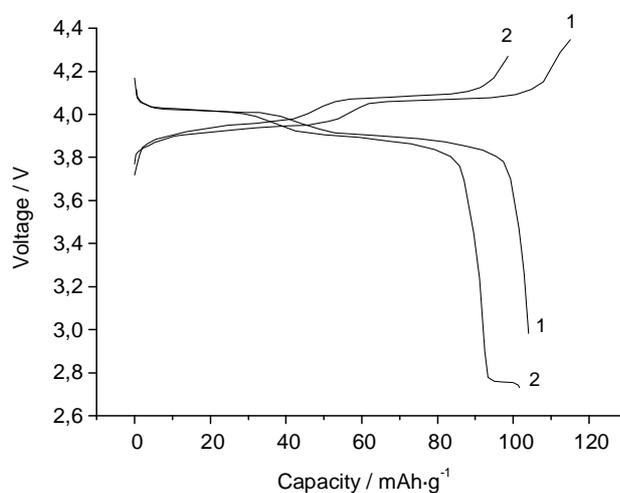


Fig. 2. Cycling behavior of sample A at room temperature during the first two cycles (1 and 2). Current density is $200 \text{ mA}/\text{cm}^2$.

4. Conclusions

The glycine-nitrate method is a very suitable rapid procedure for obtaining LiMn_2O_4 as useful cathode material for rechargeable lithium batteries. This method also offers the possibilities to investigate the synthesis procedures for obtaining pure $\text{Li}_{1+x}\text{Mn}_{2-y}\text{O}_4$ spinels with better cycling characteristics than LiMn_2O_4 .

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