DEVELOPMENT OF PROMISING CATHODE MATERIALS BASED ON MODIFIED SPINELS FOR Li-ION BATTERIES

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Keywords: Iron-modified lithium manganese spinal, solid phase synthesis, X-ray structural determination.

An iron-modified lithium manganese spinel, $LiFe_xNi_{0.5-x}Mn_{1.5}O_4$, where $0 \leq x \leq 0.4$, has been developed as a promising cathode material for Li-ion batteries. Conditions for obtaining single-phase cubic spinels from Li_2CO_3, Mn_2O_3, Ni_2O_3 and Fe_2O_3 as starting materials have been optimized.

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INTRODUCTION

Modern development in the field of chemical energy and power sources is associated with elaboration of various new materials. Application of these allows to decrease weight and dimensions of power sources, increase their energy capacity, capability and resourcefulness. Lithium-ion batteries (LIB) are now ubiquitous. Recently they found application in electric and hybrid vehicles.[1]

Lithium rich compounds represent a promising cathode material of Li-ion accumulators due to their valuable electrochemical properties and represent cathode material of the next generation high-performance lithium-ion batteries.[2,3] These compounds are of great interest mostly because of the high capacity exceeding 250 mAh g^{-1}. However, a number of disadvantages, such as voltage drop caused by unwanted phase transformations during cycling, as well as low operational performances still limit their application. Improved cycling stability can be achieved by cathode materials doping (modification). Regarding costs and raw materials, Fe-Mn-based systems are economically attractive cathodes for LIB containing Fe as a cheap promising alternative to commercial $LiCoO_2$ and $LiMn_2O_4$.

The goal of the present work was to develop promising cathode material based on Fe modified Li-manganese spinel $LiMn_2O_4$, including optimalization of preparation conditions for $LiFe_xNi_{0.5-x}Mn_{1.5}O_4$ type single-phase, homogeneous, nanostructured cubic spinels as cathode materials for LIBs.

EXPERIMENTAL

The properties of the synthesized samples were studied using a Paulik-Paulik-Erdey type derivatograph (MOM, Hungary) with simultaneous recording of temperature (T) and weight loss (TG) curves, as well as the corresponding differential curves (DTG) and (DTA) at heating rate of 10° min^{-1}. X-ray diffraction patterns of the synthesized samples were recorded on DRON-3M type diffractometer with Cu-K_α radiation in the range 2θ = 10°- 60°. The detector speed was 2° min^{-1}. Chemical analyses of the samples were implemented by atomic absorption method with Perkin-Elmer AAnalyst 200 atomic absorption spectrometer. Three methods were tested to obtain single phase $LiFe_xNi_{0.5-x}Mn_{1.5}O_4$ ($0 \leq x \leq 0,4$) samples:

Method 1. Initially, the Li_2CO_3, Mn_2O_3, Ni_2O_3 and Fe_2O_3, were mixed in a corundum crucible in necessary amounts to obtain samples of given composition, and the mixture was placed in a cold electric furnace. After heating to 700 °C, the crucible was cooled, the heat-treated mixture was thoroughly mixed and again placed into the furnace for 1 h at 700 °C. The mixing process was repeated, and the mixture was placed again into the oven for 1 h at 700 °C. The $LiFe_{0.3}Ni_{0.2}Mn_{1.5}O_4$ (sample No. 3**)** and $LiFe_{0.4}Ni_{0.1}Mn_{1.5}O_4$ **(**sample No. 4) were prepared in this way.

Method 2. A crucible with carefully mixed starting components was placed into an electric furnace. The sample was heated for 5 h at 700 °C and then cooled in the open air to room temperature. As a result, samples No. 2 and No. 5 with composition $LiFe_{0.3}Ni_{0.2}Mn_{1.5}O_4$ and $LiFe_{0.4}Ni_{0.1}Mn_{1.5}O_4$, respectively, were obtained.

Method 3. (Melting-saturation method) At the first stage of synthesis, the mixture of initial reagents was heated at 180 °C for 2.5 h, then the heating was followed at 700 °C for 5 h. In this case sample No.1, $LiFe_{0.3}Ni_{0.2}Mn_{1.5}O_4$, was obtained.

RESULTS

The results X-ray diffraction phase analysis studies are presented in Table 1.

The sample No. 1, $LiFe_{0.3}Ni_{0.2}Mn_{1.5}O_4$, obtained by melting-saturation method fits to the lithium manganese spinel $LiMn_2O_4$ (ASTM-736) card. Splitting of peaks 241 and 237 could be observed due to doping elements in the structure. $LiFe_{0.3}Ni_{0.2}Mn_{1.5}O_4$ (No. 2) and $LiFe_{0.3}Ni_{0.2}Mn_{1.5}O_4$ (No. 3) obtained by continuous and stepwise heat treatment at 700 °C (methods 2 and 1), respectively, are single phase spinels.

Table 1. Results of x-ray phase and x-ray structural studies of synthesized cathode materials of given composition for Li - ion batteries.

Sample 1 $LiFe_{0.3}Ni_{0.2}Mn_{1.5}O_4$		Sample 2 $LiFe_{0.3}Ni_{0.2}Mn_{1.5}O_4$		Sample 3 $LiFe_{0.3}Ni_{0.2}Mn_{1.5}O_4$		Sample 4 $LiFe_{0.4}Ni_{0.1}Mn_{1.5}O_4$		Sample 5 $LiFe_{0.4}Ni_{0.1}Mn_{1.5}O$	
d_α/n	I/I_0	d_α/n	I/I_0	d_α/n	I/I_0	d_α/n	I/I_0	d_α/n	I/I_0
4.73	36	4.73	53	4.73	38	4.67	55	4.64	92
-	-	-	-	-	-	2.71	5	-	-
-	-	-	-	-	-	2.59	30	-	-
2.48	100	2.48	100	2.48	100	2.46	92	2.46	89
2.41	10	-	-	-	-	-	-	-	-
2.37	18	2.37	20	2.37	21	2.35	18	2.35	24
-	-	-	-	-	-	2.08	26	-	-
2.06	77	2.06	67	2.06	74	2.04	100	2.04	100
1.88	11	1.88	9	1.88	9	1.87	18	1.87	16
-	-	1.60	18	-	-	-	-	-	-
1.58	23	1.58	22	1.58	19	1.56	26	1.56	32
a=0.824 nm		*a*=0.824 nm		*a*=0.824 nm		*a*=0.816 nm		*a*=0.816 nm	

$LiFe_{0.3}Ni_{0.2}Mn_{1.5}O_4$ (No. 2) and $LiFe_{0.3}Ni_{0.2}Mn_{1.5}O_4$ (No. 3) obtained by continuous and stepwise heat treatment at 700 °C (methods 2 and 1), respectively, are single phase spinels. Sample No. 4, $LiFe_{0.4}Ni_{0.1}Mn_{1.5}O_4$, obtained by method 1, mainly contains $LiMn_2O_4$, and in addition, the rudiments of $NiMn_2O_4$ (ASTM-1-1110) can also observed. Sample No. 5, $LiFe_{0.4}Ni_{0.1}Mn_{1.5}O_4$, obtained by method 2, is a single-phase spinel, other phases could not be detected.

CONCLUSION

Several $LiFe_xNi_{0.5-x}Mn_{1.5}O_4$, where $0 \leq x \leq 0.4$ composites as promising cathode materials for Li-ion batteries have been prepared via solid-phase synthesis methods.

The conditions to obtain single-phase samples of cubic spinels from Li_2CO_3, Mn_2O_3, Ni_2O_3 and Fe_2O_3 have been optimized.

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Received: 05.07.2020.
Accepted: 04.11.2020.