DEVELOPMENT OF PROMISING CATHODE MATERIALS
BASED ON MODIFIED SPINELS FOR Li–ION ACCUMULATORS

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Abstract

Promising cathode materials based on iron-modified $LiMe_xNi_{0.5-x}Mn_{1.5}O_4$ (where Me = Fe and x = 0.1 – 0.4) type compounds have been developed. Conditions for phase pure nanostructured samples with cubic spinel structure obtaining based on $LiCO_3$, Mn_2O_3 and Ni_2O_3 initial reagents are optimized. For this purpose, a number of solid-state synthesis methods in the 180 – 700 °C interval are used. Cathode materials based on Fe–Mn are economically attractive due to the high abundance of Mn and Fe in nature. Cathode materials for lithium–ion batteries containing iron, nickel and manganese can be a promising alternative to commercial $LiCoO_2$ and $LiNiO_2$ samples.

Modern development of high technologies in the field of chemical power sources is associated with elaboration of new materials. Application of these allows decreasing weight and dimensions of power sources and increasing their energy capacity, capability and resourcefulness.

Nowadays batteries represent very important technological objects. The three major components of most batteries, including lead–acid, used for startup of car engines, as well as wildly used compact lithium cells that are flourishing in a wide range of different applications (e-books, watch, etc.) are electrodes (anode and cathode) and electrolyte. An intensive search for efficient, in terms of price and operational performances, of above mentioned components for new type batteries is carried out by all developed countries.

Lithium–ion batteries (LIB) are now ubiquitous. Recently they found application in electric and hybrid vehicles. There is an inevitable shift underway as the automotive industry transitions from traditional gasoline powered vehicles to more efficient, environmentally responsible modes of transport. Hybrid electric vehicles and electric vehicles are making inroads into the global marketplace, but the going is slow and the obstacles are many. As yet, these vehicles have not returned much profit for their manufacturers. However the problems can be solved with the improvement of batteries technology. There are prerequisites to increase the energy of lithium batteries and reduce their prices. Currently new fuel sources are in

development. Meanwhile, lithium-ion power sources continue to be the most preferable in the next 20 years.

It is known that LIBs are used in electric and hybrid cars. Besides, lithium-rich compounds represent a promising cathode material of Li–ion accumulators due to their high electrochemical properties. These properties are mainly determined (settled) by synthesis methods, firing process, and a number of other factors. Lithium-rich compounds represent cathode material of the next generation high-performance lithium–ion batteries [1, 2]. These compounds are of great interest mostly because of the high capacity exceeding 250 mA·h/g. 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). Lithium–ion batteries currently occupy a dominant position in the applied electronics due to their high energy density, efficient performance and non-polluting nature. Besides, as noted earlier, Li–ion batteries are considered promising for more complex areas of technology. Regarding costs and raw materials, Fe–Mn-based systems are economically attractive due to abundance of iron and manganese in nature. Therefore, LIB cathodes containing Fe and Ni can become a cheap promising alternative to commercial $LiCoO_2$ and $LiMn_2O_4$.

The goal of the preset work is development of promising cathode material based on Fe modified Li–manganese spinel $LiMn_2O_4$, currently used in practice, which includes:

1. Determining crystallization onset temperature of $LiMe_xNi_{0.5–x}Mn_{1.5}O_4$ (Me = Fe) type samples with spinel structure;

2. Optimizing conditions to obtain phase-pure, homogeneous, nanostructured cubic spinel samples; and

3. Investigating impact of used synthesis method over more morphology, phase composition and structure of the cathode material based on $LiMe_xNi_{0.5–x}Mn_{1.5}O_4$, where Me = Fe is doping metal.

Properties of the synthesized samples are studied using a MOM derivatograph (Hungary) with simultaneous recording of four curves: temperature (T) and weight (TG) curves, as well as the corresponding differential curves (DTG) and (DTA) at a furnace heating rate of 10°/min. X-ray diffraction patterns of the synthesized samples are recorded on DRON–3M-type diffractometer with Cu-K_α radiation in the range $2\theta = 10 – 60°$. The detector speed was 2°/min. d_α/n denotes the interplanar spacing (Å) and I/I_0 – the relative intensity. Chemical analysis of the samples are implemented by atomic absorption method, as well as traditional methods of chemical analysis.

To obtain $LiFe_xNi_{0.5–x}Mn_{1.5}O_4$ (Me = Fe and $0 \le x \le 0.4$) samples, the following methods are used:

Method 1. The initial reagents $LiCO_3$, Mn_2O_3, Ni_2O_3 and Fe_2O_3 in the amounts necessary to obtain samples of given composition are mixed in a corundum crucible and placed in a cold electric furnace and heated. Upon reaching 700°C in the furnace, the crucible is cooled, the heat-treated mixture is thoroughly mixed and again placed in the furnace ($\tau = 1$ h and T = 700°C). The mixing process is repeated and mixture again is placed in the oven (again $\tau = 1$ h and T = 700°C). In this case, $LiFe_{0.3}Ni_{0.2}Mn_{1.5}O_4$ (Sample 3) and $LiFe_{0.4}Ni_{0.1}Mn_{1.5}O_4$ (Sample 4) compositions are obtained.

Method 2. A crucible with carefully mixed starting components is placed in a cold electric furnace. Upon reaching 700°C, the sample is processed for τ = 5 h and then cooled in the open air to room temperature. As a result, Sample 2 – $LiFe_{0.3}Ni_{0.2}Mn_{1.5}O_4$ and Sample 5 – $LiFe_{0.4}Ni_{0.1}Mn_{1.5}O_4$ with a given composition are obtained.

Method 3. It is a melting-saturation method. At the first stage of synthesis mixture of initial reagents is treated at 180°C for 2.5 h and then at 700°C for 5 h. In this case Sample 1 – $LiFe_{0.3}Ni_{0.2}Mn_{1.5}O_4$ is obtained.

Table 1 presents the results of X-ray phase and diffraction studies. The structure of Sample 1 – $LiFe_{0.3}Ni_{0.2}Mn_{1.5}O_4$ obtained by melting–saturation method corresponds to lithium–manganese spinel $LiMn_2O_4$ (ASTM–736), but splitting of peaks 2.41 and 2.37 is observed. Sample 2 – $LiFe_{0.3}Ni_{0.2}Mn_{1.5}O_4$ obtained by continuous heat treatment at 700°C corresponds to phase-pure lithium–manganese spinel. Sample 3 – $LiFe_{0.3}Ni_{0.2}Mn_{1.5}O_4$ obtained by Method 1 also corresponds to pure lithium–manganese spinel. Sample 4 – $LiFe_{0.4}Ni_{0.1}Mn_{1.5}O_4$ obtained by Method 1 mainly represents spinel $LiMn_2O_4$. In addition, the rudiments of $NiMn_2O_4$ (ASTM–1–1110) are observed. Sample 5 – $LiFe_{0.4}Ni_{0.1}Mn_{1.5}O_4$ obtained by Method 2 is phase-pure spinel: other phases are not observed.

Table 1. Results of X-ray phase and structural studies of synthesized cathode materials of given compositions for Li–ion batteries.

Sample 1		Sample 2		Sample 3		Sample 4		Sample 5	
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	

In summary:

1. Based on iron-modified lithium–manganese spinel – $LiMe_xNi_{0.5-x}Mn_{1.5}O_4$, where Me = Fe and $0 \le x \le 0.4$ a promising cathode material is developed for Li–ion batteries;

2. Conditions for obtaining phase-pure nanostructured samples of cubic spinel based on initial $LiCO_3$, Mn_2O_3, Ni_2O_3 and Fe_2O_3 reagents are optimized;

3. Solid phase methods of synthesis are used:

a) High temperature (700°C) method with double mixing of the starting reagents during heat treatment;

b) High temperature (700°C) continuous method; and

c) Melting–saturation method (T_1 = 180°C and τ_1 = 2.5 h; T_2 = 700°C and τ_2 = 5 h);

4. As a result of X-ray phase and structural, as well as other analysis, it is established that phase-pure samples of the composition $LiFe_{0.3}Ni_{0.2}Mn_{1.5}O_4$ obtained by the continuous processing method at 700°C, as well as Method 1 correspond to phase-pure cubic spinel (ASTM–736);

5. Cathode material $LiFe_{0.1}Ni_{0.4}Mn_{1.5}O_4$ obtained by the Method 2 represents phase-pure spinel as other phases are not observed;

6. Cathode materials based on Fe–Mn are economically attractive due to abundance of iron and manganese in the nature; and

7. Cathode of lithium–ion batteries containing iron and nickel can become a cheap alternative to commercial $LiCoO_2$ and Li_2MnO_4.

References

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