Phase Composition and Structural Features of Li-Mn-Ni-O Cathode Materials Synthesized through Sol-Gel Method for Li-ion Accumulators

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Currently rechargeable lithium-ion batteries are in common use as a power sources for portable equipment. In most of these batteries $LiCoO_2$ or $LiNiO_2$ are used as cathode materials. In large-scale batteries it is preferable to use lithium-manganese spinel – $LiMn_2O_4$, because it is very cheap, less toxic, and has high energy density. However, commercial use of $LiMn_2O_4$ is limited, as its structural features and physical and chemical properties to much extent depend on the synthesis conditions. Drawback of the electrodes based on the lithium-manganese spinel is capacity loss on cycling, especially at high temperature that limits cycle-life of cathode. In its turn the cycle-life depends very much on the cathode material structure, on its structural integrity on cycling. During prolonged cycling of $LiMn_2O_4$ capacity fading takes place at the 4V plateau, which makes difficult to employ it in commercial production of lithium-ion batteries. One of the main reasons of the capacity fading is appearance of tetragonal distortion of cathode material due to John–Teller effect. Doping lithium-manganese spinel – partial substitution of manganese atoms with definite transition metal – is considered as promising method of stabilization of its structure. It may cause increasing of average oxidation state of manganese (>3,5) and hence, decreasing of degradation rate of cathode material during multiple cycling. Extensive research of effective dopent metals is being carried out. Comparison with $LiCoO_2$ and $LiNiO_2$, which are characterized by layered structure, reveals another considerable inferiority of cathode material based on cubic spinel. This is less mobility of lithium ions and related problem of decreasing of electrode material particle size. Solid-state technique does not allow obtaining fine dispersal materials because of the recrystallization due to prolonged influence of high temperature. The main efforts of elaborators of cathode materials are devoted to research of new and modification of existing materials by using a method of alternative synthesis. In this case low temperature sol-gel method seems to be promising. This method can provide for homogenous mixing at molecular level and can be used to control morphology, particle size and some other properties of obtained product.

As a follow up on the work carried out by the Institute of Inorganic Chemistry and Electrochemistry of the Academy of Sciences of Georgia in the field of promising cathode materials developing for lithium-ion accumulators, $LiMn_{2-x}Ni_xO_4$ compounds were synthesized through sol-gel process. The compounds were obtained through process involving the reaction between manganese, nickel and lithium acetate in the mixture of fumaric (or maleic) acid and ethylene glycol. The optimal temperature of gel heating for structuring pure-phase, homogeneous, fine dispersal samples of lithium-manganese spinels was 650-700°C, which is 200°C less, than temperature necessary for solid-state process.

The identification of synthesis products was carried out by using X-ray diffraction (DRON-3M, CuKα radiation), thermal, atomic absorption, and other analytical techniques. Analysis results testify to a formation of $LiMn_{2-x}NixO_4$ compounds with cubic spinel lattice, where $0 \leq x \leq 1$. Samples obtained through sol-gel method were compared with analogous samples obtained by solid-state technique. Comparison method was X-ray diffraction. It showed more homogenous picture of composition distribution and structural motive of crystalline lattice in samples obtained through sol-gel method. Samples synthesized through sol-gel method (850-900°C) within the range $0,5 \leq x \leq 1$ are characterized by two-phase X-ray patterns and represented mostly by cubic spinel with lattice parameter $a = 8.227 \div 8.182$Å and with nickel oxide – NiO as impurity. The single-phase system is represented only by samples for which $x < 5$. Compounds $LiMn_{2-x}Ni_xO_4$ obtained through sol-gel method in all range $0 \leq x \leq 1$ are characterized by cubic spinel with lattice parameter $a = 8.23 \div 8.174$Å. In samples obtained through optimal conditions no additional peaks were observed. One could conclude that within the range of $0 \leq x \leq 1$ normal spinel structure is maintained and dopent metal-nickel occupies 16(d) octahedral sites of manganese. When compared with high temperature method, application of sol-gel method nearly twice increases limit of isomorphic substitution of manganese atoms by nickel atoms in lithium-manganese spinel without disturbing its structural motive. Degree of dispersion of samples obtained through sol-gel method is considerably high than that of samples, synthesized through solid-state method. According to the testing data of part of samples (x=0.05-0.20), using of sol-gel method for obtaining cathode materials based on nickel-doped, pure-phase, homogenous, fine dispersal samples of lithium-manganese spinels promotes retention of their structure integrity on multiply cycling process and eventual improvement of electrochemical performance of cathode material.