

Mechanical milling effect on structural and electrochemical properties of lithium-nickel-manganese-cobalt oxide cathode materials

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Electrode materials microstructure modification is one of the promising methods for improving Li-ion battery performance (e.g. power, cycle rates). In cathode materials (materials for positive electrode) based on lithium-nickel-manganese-cobalt oxide (NMC) maximum charge/discharge currents are limited both because of low Li-ion diffusion values inside the grains of the material and its low electronic conductivity [1, 2]. Theoretically, current values can be increased by reducing particle size of the material [3]. As a result, the smaller the particle size, the shorter the lithium diffusion paths and the larger the surface area of the active material being in contact with the conductive additives and electrolyte [4, 5]. It is known that particle size reduction correlates well with electrochemical properties improvement for lithium-iron phosphate (LiFePO₄) [6, 7], lithium-manganese phosphate (LiMnPO₄) [8] and spinel (LiMn₂O₄) [9] cathode materials. The particle size effect plays an important role in the electrochemical performance of layered cathodes NMC for lithium-ion batteries. In particular, for such materials as LiNi_{0.50}Mn_{0.50}O₂, LiNi_{0.33}Mn_{0.33}Co_{0.33}O₂ and LiNi_{0.40}Mn_{0.40}Co_{0.20}O₂, LiNi_{0.4}Mn_{0.4}Co_{0.18}Ti_{0.02}O₂ the above property is presented in works [10, 11]. The authors showed that due to ultra-small particle size the large surface area of the active material led to losses in the energy consumption of the cathodes with accelerated degradation of the working surface and various side electrochemical reactions as causes. It was found [12] that besides the reducing the initial particle size to nano-size, several things occur, namely, layered structure disordering, transition metals reduction, and impurity phases formation. The most balanced capacitive and charge/discharge characteristics for layered cathode materials seem to be obtained with particles not exceeding 100 nm in size, submicron particles [10, 11]. From this point of view, high-energy planetary milling is still considered to be a route to gain particles of a given size.

It is known that structural and electrochemical properties of NMC materials depend drastically on conditions that preparation and synthesis were held under. Furthermore, it is rather difficult to systematize the effects obtained in different works because of various before measurement sample preparation conditions and the final result can be significantly affected via those factors. Nowadays there are no researches for the effect on the properties of series NMC cathode materials synthesized under similar conditions and caused by mechanical milling. Moreover, in such works, an accurate approach to characterizing the microstructure is of a great importance. It is necessary to separate the size effects from the effects associated with the crystal structure microdeformations and, accordingly, to reveal interrelations between various microstructural defects and electrochemical properties in the materials under study.

In this report we represent preliminary results obtained from a research for the crystal structure and microstructure effects in commercial NMC electrode materials caused by high-energy milling. Milling was carried out for 0, 4.5, 12, 24 and 72 hours and the content of nickel, manganese and cobalt in the studied samples was taken in the proportions of 8:1:1, 5:2:3 and 1:1:1. Methods that were used to analyze the structure of mechanically synthesized materials are as follows: scanning electron microscopy and two complementary diffraction methods - X-ray diffraction and high-resolution neutron diffraction. Data analysis was held via Rietveld and Williamson-Hall methods. Nonlinear dependence of particle size reduction on the time of mechanical action in a planetary mill as well as anisotropic change in the morphology of NMC particles during milling was revealed. Within the gained errors the atomic crystal structure changes were not detected for all NMC samples used in the experiments. Coin-cells of standard size 2016 with electrodes based on modified NMC powders in proportions of 85% active substance, 5% carbon black (C45) and 10% PVDF were prepared and electrochemical measurements were carried out by chronopotentiometry method. Data from electrochemical experiments contain information about the first three cycles in the galvanostatic mode at rates of 0.1C and 1C as well as the total number of successfully completed cycles. It is also important to note that the degradation rate of the modified NMC is monitored. Preliminary results obtained from experiments with NMC111 show that in comparison to original, not milled electrode material, the milled samples do operate with less capacity. In comparison to the unmilled sample, the capacity drop of about 60% for the sample milled for 72 hours was detected when the material was cycled on a rate of 0.1C. When the cycling rate was changed from 0.1C to 1C the capacity reduced by several orders of magnitude: 85.4 mAh/g vs 6.4 mAh/g for not milled samples, 84.5 mAh/g vs 2.9 mAh/g for the samples milled during 12 hours and 50.7mAh/g vs 0.03 mAh/g for 72 hour-milled

samples. Explanation of these effects is being discussed. This work is carried out with the support of the Russian Science Foundation, pr. No. 21-12-00261.

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