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Nanoparticles of Complex Oxides $Li_{1+x}(Ni_yMn_zCo_{1-y-z})_{1-x}O_{2-\delta}$ $(0 \le x \le 0.2, 0.2 \le y \le 0.6, 0.2 \le z \le 0.4)$ Obtained by Thermal Destruction of Metal-Containing Compounds in Oil[1]

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Abstract—Cathode materials in the form of $Li_{1+x}(Ni_yMn_zCo_{1-y-z})_{1-x}O_{2-\delta}$ $(0 \le x \le 0.2, 0.2 \le y \le 0.6, 0.2 \le z \le 0.4)$ core–shell nanoparticles coated with a thin carbon shell were synthesized by thermal destruction of metal-containing compounds in oil and studied. The results of element analysis, X-ray diffraction analysis, scanning electron microscopy, X-ray photoelectron spectroscopy, and electrochemical tests of cathodes based on the obtained complex oxides in model cells were presented. The complex oxide $Li_{1.2}Ni_{0.2}Mn_{0.4}Co_{0.2}O_{1.9}$ was the most promising composition because the loss of capacity after 50 cycles was 4% at a current density C/2 and an operating potential of 3.0–4.4 V relative to E (Li/Li$^+$). When the current density in discharge increased sixfold (3 C), the loss of capacity was 14% relative to the value obtained at a discharge current C/2 at voltages 3.0 to 4.4 V.

Keywords: cathode materials, complex oxides, core–shell nanoparticles, thermal destruction of metal-containing compounds in oil, nanoreactor, lithium-ion battery

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INTRODUCTION

Complex oxides $Li_{1+x}(Ni_yMn_zCo_{1-y-z})_{1-x}O_{2-\delta}$ $(0 \le x \le 0.2, 0.2 \le y \le 0.6, 0.2 \le z \le 0.4)$ (below NMC) are the most promising cathode materials (CMs) for lithium-ion batteries (LIBs), which are of particular interest because of their ability to meet the ever-growing demand for energy storage devices. These multicomponent oxides have high specific capacity (more than 160 mA h/g at a charge of C/20), electric conductivity, and thermal stability, as well as high reliability in cycling and lower cost due to the synergistic effect of their nickel, manganese, and cobalt ions [1–6]. For these materials, however, cation disordering is a problem, i.e., cation mixing of lithium and divalent nickel ions due to the similarity of their ionic radii (0.069 and 0.076 nm, respectively), which leads to deterioration of the electrochemical parameters of CMs and a decrease in the specific capacity of the entire LIB [7].

On the other hand, in order to improve the basic electrochemical characteristics, many research groups synthesized nanostructured complex oxides by various methods [8–11]. These methods lead to an increase in the charge–discharge rate due to a sharp reduction in the diffusion length of lithium ions and the increase of electrode–electrolyte contact area. However, due to their nanosized nature, CMs more actively interact with the electrolyte, causing a large number of limiting stages, which eventually leads to serious safety problems not inherent in microsized materials, especially at high temperatures.

When reducing the size of primary crystallites, it is advisable to cover them with a stabilizing surface layer, which would prevent changes in the phase composition and crystallographic parameters. This coating should not lead to decreased diffusion rate of lithium ions, thus annihilating the advantages of the use of nanosized particles [12].

Our previous studies [13, 14] showed that dropwise introduction of a solution of metal-containing compounds in a melt solution of polyethylene formed nanoreactors, from which the volatile components that formed as a result of the thermal decomposition of the introduced salts evaporate together with the solvent. This forms nanoparticles whose composition is given by the molar ratio of salts in the initial solution. The use of this approach allowed us to perform the

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thermal decomposition of the introduced acetate solution in a polyethylene matrix and to obtain isolated nanoparticles consisting of a mixture of oxides of the same composition that was specified for the initial solution of the salts. The thermal treating of the obtained precursors gave the core–shell nanoparticles with an average size of 90 nm, whose shell was the nanometer layer of amorphous carbon. During the electric tests of CMs in model cells it was found that in the case of intercalation–deintercalation of lithium ions into/from the structure of CMs coated with an amorphous layer of carbon, the lithium ions diffuse into the shell; i.e., it can serve as an intermediate reservoir for storing the lithium ions and easily damp the inevitable "swelling" of the CM core [15].

The goal of this study was to prepare complex oxides $Li_{1+x}(Ni_yMn_zCo_{1-y-z})_{1-x}O_{2-\delta}$ ($0 \le x \le 0.2$, $0.2 \le y \le 0.6$, $0.2 \le z \le 0.4$) under different synthesis conditions and to perform comparative studies of the obtained oxides by modern physicochemical and electrochemical methods.

EXPERIMENTAL

The starting materials used were lithium $CH_3COOLi \cdot 2H_2O$ (99%, Aldrich), cobalt $Co(CH_3COO)_2 \cdot 4H_2O$ (99%, Aldrich), manganese $Mn(CH_3COO)_2 \cdot 4H_2O$ (99%, Aldrich), and nickel $Ni(CH_3COO)_2 \cdot 4H_2O$ (99%, Aldrich) acetates, acetic acid (99.9%), high-pressure polyethylene (HPPE) (Aldrich), and vacuum oil (VO) (State Standard (*GOST*) *38.01402-86*).

The synthesis of complex oxides $Li_{1+x}(Ni_yMn_zCo_{1-y-z})_{1-x}O_{2-\delta}$ ($0 \le x \le 0.2$, $0.2 \le y \le 0.6$, $0.2 \le z \le 0.4$) in the form of core–shell nanoparticles with a carbon coating consists of two stages: (1) preparation of nanoparticles of a mixture of metal oxides stabilized in the bulk of the polymer matrix and (2) high-temperature treatment.

At the first stage, the samples were synthesized by thermal decomposition of a solution of metal-containing compounds into a polyethylene–hydrocarbon oil (TMCC) solution melt [13, 14, 16] at 230–250°C. In a typical experiment, a solution of lithium, nickel, manganese, and cobalt acetates in a suitable molar ratio in acetic acid was introduced dropwise, while vigorously stirring, in the HPPE melt solution. In addition, an inert gas was fed to the reactor to ensure rapid and complete removal of volatile reaction products and to prevent the oxidation of metals. The amount of HPPE was calculated such that the concentration of the resulting nanoparticles relative to the matrix was 15–60 wt % [16]. The termination of gas formation indicated the end of reaction. After cooling, the liquid portion was separated from the precipitate. The second stage was the thermal treatment of the precipitate at 450–900°C for 8–24 h in an inert gas and air.

Methods of Investigation

The element analysis was performed by inductively coupled plasma atomic emission spectroscopy on an iCAP 6300 unit (Thermo Electron, United States). The phase composition was determined on a Bruker Advanced 8 (Germany) X-ray powder diffractometer. The operating mode: 40 kV, 40 mA, Cu radiation, nickel filter, $2\theta = 10°–80°$, scan step 0.01°. To interpret the diffraction patterns, the International Center for Diffraction Data database was used. The morphology and microstructure of the samples were studied with a Carl Zeiss Supra 40-30-87 scanning electron microscope (SEM) (Germany). The accelerating voltage for obtaining images in secondary and backscattered electrons was 1–10 kV. The chemical and electronic states of atoms were determined by X-ray photoelectron spectroscopy (XPS) on a PHI 5500 ESCA X-ray photoelectron spectrometer (Physical Electronic, United States).

The electric measurements were carried out in model cells according to two- and three-electrode schemes in galvanostatic and/or potentiostatic modes. The positive electrode was prepared by the following procedure. A homogenized mixture (80% cathode material, 10% acetylene black (Timcall), 10% polyvinylidene fluoride (PVdF) dissolved in N-methylpyrrolidone) was applied to aluminum foil and dried at 120°C for 12 h in a vacuum drying cabinet. The electrolyte was a 1 M solution of $LiPF_6$ in ethylene carbonate–dimethyl carbonate (1 : 1). Metallic lithium was a counterelectrode and reference electrode.

RESULTS AND DISCUSSION

In our previous studies [16, 17], we prepared complex oxides $Li_{1+x}(Ni_yMn_zCo_{1-y-z})_{1-x}O_{2-\delta}$ ($0 \le x \le 0.2$, $0.2 \le y \le 0.6$, $0.2 \le z \le 0.4$) and found that after the first stage of the process, nanoparticles of a mixture of metal oxides were obtained; they consisted of transition metal and lithium oxides uniformly distributed over the entire volume of the polymer matrix and had an ellipsoidal shape with an average size of 2.3 ± 0.4 nm.

$Li_{1.2}Ni_{0.2}Mn_{0.4}Co_{0.2}O_{1.9}$ (below LNMC) was used as an example to study the effect of the nanoparticle concentration in the polymer matrix at the first stage and the temperature mode of processing at the second stage on the basic physicochemical and electrochemical properties of the synthesized complex oxides.

During the heat treatment of the precursors obtained at the first stage of the process, the diffraction pattern showed reflections characteristic of a layered crystal structure of α-$NaFeO_2$ type already after annealing at 300°C due to their nanosized nature (space group $R\bar{3}m$, no. 166); further heat treatment (above 600°C) led to more intense reflections, which indicated the agglomeration of the primary crystallites (Fig. 1). According to [18], single-phase NMC forms at 500°C, but termination of crystallographic ordering