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Promising Cathode Material for Lithium Power Sources $LaFe_{0.5}Cr_{0.5}O_3$

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Nanoscale powders of $LaFe_{0.5}Cr_{0.5}O_3$ with perovskite structure were synthesized by sol-gel combustion method in this work. From X-rays phase analysis obtained material was consisted of one phase $LaFe_{0.5}Cr_{0.5}O_3$ (space group P m -3 m). The average size of RCS of test material is 21 nm. Specific surface area is 14 m^2/g. The average particle size is 63.7 nm by approximation that particles form is spherical. Nanoscale powders of $LaFe_{0.5}Cr_{0.5}O_3$ were tested as cathode material for lithium power sources. The cathode material demonstrates the specific power capacity of 571 A·h/kg when the discharge of the source is up to 0.5V.

Keywords: sol-gel method, galvanostatic discharge, impedance, specific capacity.

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Introduction

During the last decades, a number of electrode materials with different mechanisms of lithium insertion and extraction have been developed for lithium-ion batteries. Such materials own not only a high specific capacity, but also a drop in capacity throughout tens, hundreds, and even thousands of charge-discharge cycles. Nevertheless, in order to find more advanced electrode material, many research groups are searching for cheap, easy to obtain and environmentally friendly promising materials for lithium current sources [1, 2].

Structural type of perovskite with the general formula ABO_3 is one of the most widespread materials among inorganic substances, it realized in a large number of oxide systems. Perovskites have been widely used as heating element, interconnector of solid oxide fuel cell, catalyst, thermistor materials and for electrochemical repeat hydrogen charge and discharge in alkaline solutions [3].

Simple and cheap methods of obtaining, good reproducibility of synthesis of such materials with predefined properties and the high stability of these materials to external factors make perovskites promising materials for studying. And implementation perovskites in production of lithium power sources in the future [4].

The aim of this work is studying the mechanisms of synthesis nano-sized $LaFe_{0.5}Cr_{0.5}O_3$ perovskite-like structure by sol-gel method with auto-burning, and using as electrode material for lithium power sources.

I. Experiment technique

Sol-gel method with auto-burning was used to receive complex oxide compound. This method does not require complex and expensive equipment, or rare and expensive reagents for synthesis compared to other methods. The initial materials for the sol-gel synthesis were nitrates crystal hydrates $La(NO_3)_3 \cdot 6H_2O$, $Cr(NO_3)_3 \cdot 9H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$ and citric acid as complex formation. Reagents dissolved in distilled water and mixed. Then in the resulting solution was added 25 % ammonia solution to establish the level of PH to 7. Prepared solution dried with access to air in the oven during a day at 140°C. After that the resulting xerogels heated to a temperature of 230°C, at this temperature activated auto-combustion. After the auto-combustion process nano-sized complex oxide $LaFe_{0.5}Cr_{0.5}O_3$ was formed.

Phase composition was controlled by x-ray analysis on DRON-3 diffractometer with Cu (Kα) –radiation. The obtained diffractograms were analyzed by the Rietveld method with software «FullProf».

The dependences of the material's conductivity on the frequency were received by method of electron impedance spectroscopy with device Autolab PGSTAT/FRA2 in the frequency range 10^5-10^{-2} Hz.

The specific surface of the samples was measured by

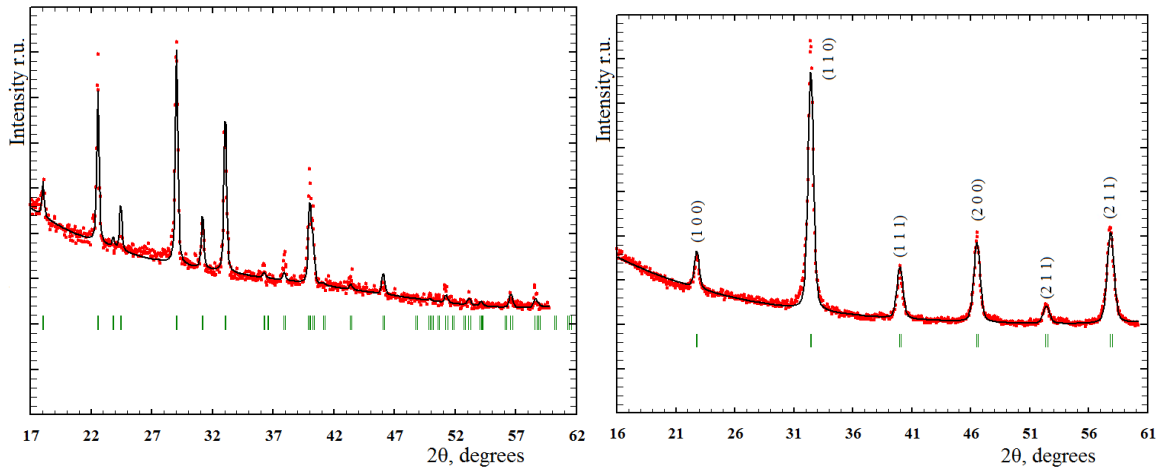


Fig 1. Diffractogram of dried xerogel (a), and synthesized nano-sized powder of perovskite-like structure $LaFe_{0.5}Cr_{0.5}O_3$(b).

chromatographic method in gas sorption analyzer NOVA Quantachrome 2200e. The method consists in determination of the volume of adsorbed (desorbed) nitrogen by the samples at a temperature of liquid nitrogen and further calculation of the specific surface by BET method.

Measuring of intercalation discharge characteristics $LaFe_{0.5}Cr_{0.5}O_3$ as cathode material for lithium power sources were made by two electrode scheme: cathode based on $LaFe_{0.5}Cr_{0.5}O_3$ /electrolyte/ metallic lithium. All technological operations for the production model of LDS were carried out in a glove-hermetic glass box with an argon atmosphere. The electrochemical cell contained a lithium anode and a cathode based on $LaFe_{0.5}Cr_{0.5}O_3$. The working mixture for the cathode was a homogenized pulp with $LaFe_{0.5}Cr_{0.5}O_3$ (85 % weight) with the addition of acetylene soot (10% weight) as a conductive additive and (5 % weight) of an acetylene suspension of Teflon as a binder. 1 M solution of $LiBF_4$ in γ-butyr-olactone was used as an electrolyte. After sealing, for reliable wetting of electrodes by electrolyte, LDS models were kept at room temperature for 24 hours. Parameters of discharge were selected using units C with a dimension A/ kg. The value of xC is the current density at which specific capacity of the source discharged by 1/x hours. The resulting cells were discharged in galvanostatic mode with different values of current in units of C. Galvanostatic charge-bit curves were automatically logged on to the computer by computerized multichannel installation for cycling current sources [5].

II. Results and Discussion

For synthesis of nano-sized powder of perovskite structure was used one of the varieties of the Pechini methods: sol-gel method with auto-burning. Complex oxide $LaFe_{0.5}Cr_{0.5}O_3$ of perovskite-like structure was formed as a result of the chemical reaction:

$$La(NO_3)_3 \cdot 6H_2O + Fe(NO_3)_3 \cdot 9H_2O + Cr(NO_3)_3 \cdot 9H_2O + C_6H_8O_7 \rightarrow$$
$$\rightarrow LaFe_{0.5}Cr_{0.5}O_3 + CO_2 + N_2 + H_2O + O_2$$

Methods and peculiarities of synthesis by this method were described in the paper [6]. Ammonium nitrate (IV) is formed in xerogel at an intermediate stage after drying the solution in drying box [7]. Experimental x-ray diffractogram of formed xerogel during synthesis by sol-gel method with auto-burning presented on Fig. 1, a.

The phase of ammonium nitrate is clearly visible on the diffractogram (IV), and also the absence of any other phases of metal oxides or already formed perovskite Fig. 1, a. The diffractogram of the resulting material after auto-burning is presented on Fig. 1, b. The reflexes present on this diffractogram belong to one phase $LaFe_{0.5}Cr_{0.5}O_3$. It means that the chosen synthesis method allows synthesizing a single-phase nano-sized powder of complex oxide perovskite-like structure $LaFe_{0.5}Cr_{0.5}O_3$.

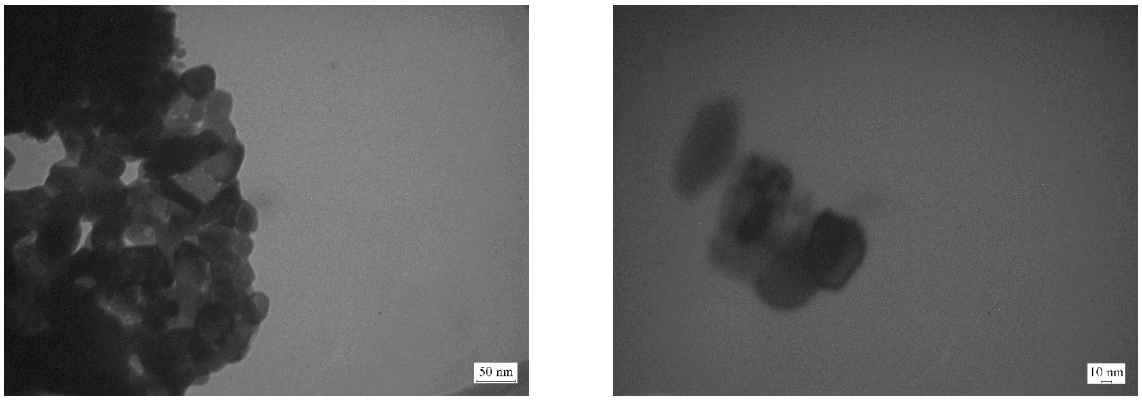
After simulation and decryption of diffractogram the following data were received: space group of perovskite powder P m -3 m, lattice size a = 3.904 Å, cell volume V = 59.5 $Å^3$, x-ray density ρ = 6.724 g/sm^3. The average size of the coherent scattering regions is 21 nm.

By the chromatographic method was measured specific surface area of the synthesized powder, which is 14 m^2/g. In the approximation that powder particles of nano-sized complex oxide perovskite-like structure $LaFe_{0.5}Cr_{0.5}O_3$ have a spherical shape, average particle diameter d_c and specific surface area S_n are related:

$$d_c = \frac{6}{rS_n},$$

where ρ – material density [7]. With the measured specific surface area by the chromatographic method and calculated x-ray density of the synthesized material established, that the average particle size is about 63.7 nm. We can be considered, that particles, on average in three times bigger than coherent scattering regions.

The images of the transmission electron microscope are represented on Fig 2. At detailed consideration of Fig. 2, a. it can be selected particles with size about 40 and 60 nm, it in two and three times bigger than coherent scattering regions. Fig. 2, b. shows a hexagonal particle. It consist of a few grains with close to the size of coherent scattering regions. All the above confirms the theoretical calculation of coherent scattering regions and the size of particles of the investigated material.



а **б**

Fig 2. TEM pictures of synthesized nano-sized powder of complex oxide perovskite-like structure $LaFe_{0.5}Cr_{0.5}O_3$ in scale 50 nm(a), and 10 nm(b).

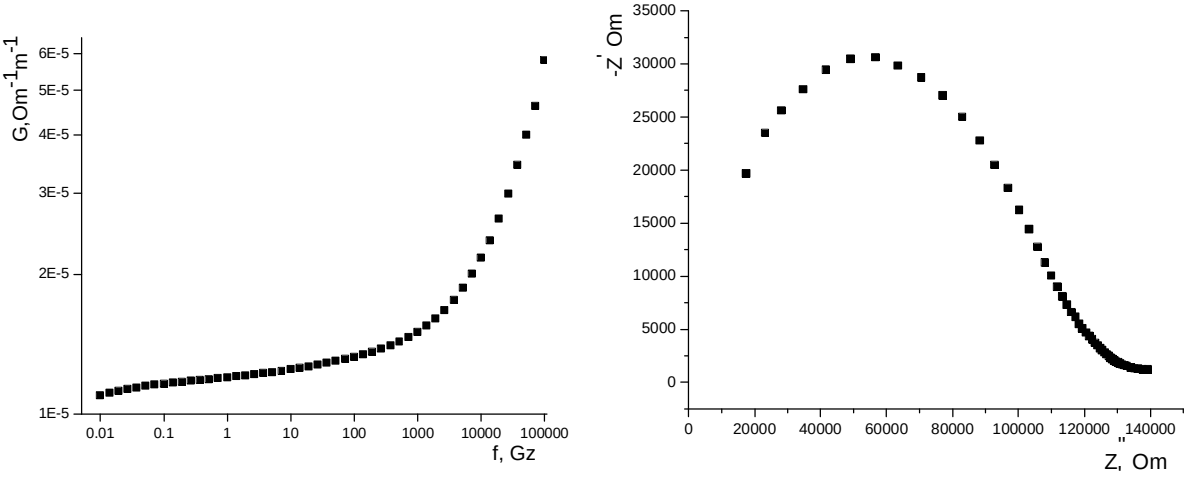


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Fig 3. Dependence of conductivity on the frequency of current (a), and experimental Nyquist curve for $LaFe_{0.5}Cr_{0.5}O_3$(b).

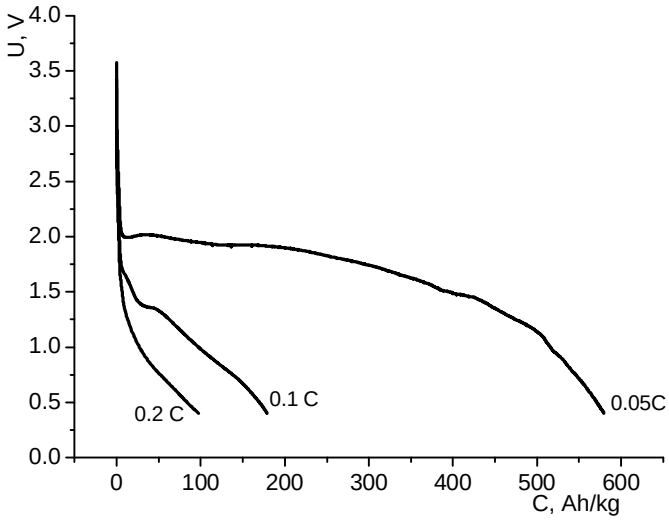

Fig 4. The discharge curves of cathodes based on $LaFe_{0.5}Cr_{0.5}O_3$ in galvanostatic mode.

To determine the electrical properties of the nano-sized complex oxide perovskite-like structure $LaFe_{0.5}Cr_{0.5}O_3$ were prepared pressed tablets of $LaFe_{0.5}Cr_{0.5}O_3$. Cells were formed with tablets, and measurements were made at room temperature.

Measurement by method of electron impedance spectroscopy were made in the frequency range 10^5-10^{-2} Hz, dependence of conductivity on the frequency of

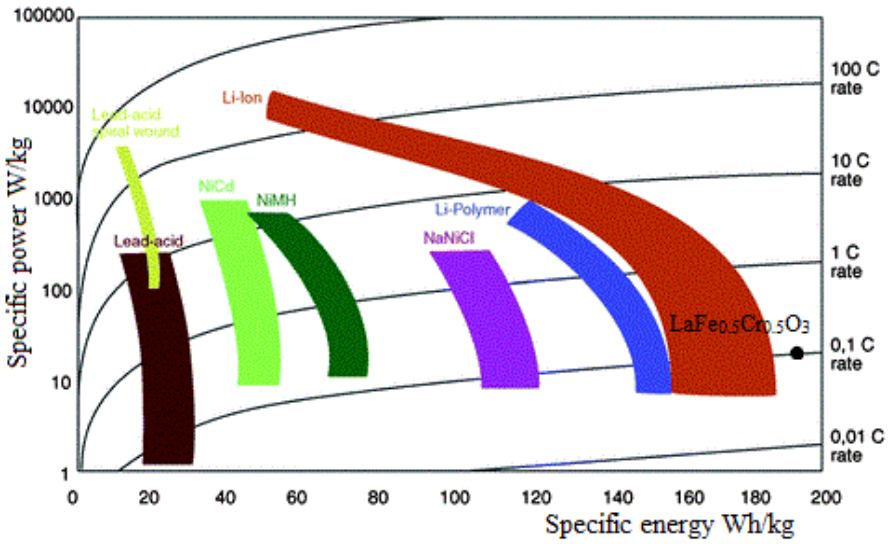

Fig. 5. Ragone plot with point of $LaFe_{0.5}Cr_{0.5}O_3$.

current (Fig. 3, a), and Nykvist curve (Fig. 3, b).

The synthesized material has a mosaic microstructure, which explains the increase in conductivity with increasing frequency of current. Particles of material, formed by crystallites, have conductivity which far exceeds the conductivity of the intergranular boundaries.

Nyquist curve Fig. 3, b indicates double conduction mechanism of synthesized material. The high-frequency section is a pronounced arc of a semicircle, this is the electronic conductivity of the material, and the second part of the curve shows the ionic nature of the conductivity of this structure.

Cathodes for LDS modeling were prepared from synthesized material. The synthesized powder was mixed with acetylene soot to increase conductivity, and with acetylene suspension for binding in a proportion of 17:2:1. Then a suspension mixture was applied to etched aluminum films. The cathode was dried overnight. Models of LDS were made in a glove-hermetic glass box with an argon atmosphere. 1 M solution of $LiBF_4$ in γ-butyr-olactone was used as an electrolyte. Cathodic galvanostatic discharge curves Fig. 4.

LDS model shows specific bit capacity about 571 Ah/kg at discharge to 0.5 V and current density 0.05 C, which is a good result for a material with a high molar mass and a small specific surface area. The discharge curve has a characteristic appearance: a sharp decline in capacity from the initial value 3.5 V to 2 V, long plateau at around 2 V and the next slow decrease in potential to full discharge. The first section describes the processes of changing the charge of a double electric layer and slow recovery of electrolyte. On the second plot there is accumulation of lithium ions on the surface of the material and the third section corresponds to the intercalation of lithium ions into the perovskite structure.

Ragone plot is using to compare the performance of different generation and accumulation devices Fig 5. Area under the discharge curve is specific energy, and for current 0.1C equal 191 VAh/kg, discharge time 15.28 hours. Calculating the specific power, the point for $LaFe_{0.5}Cr_{0.5}O_3$ was delayed on the graph. This point shows that nano-sized powder of complex oxide perovskite-like structure $LaFe_{0.5}Cr_{0.5}O_3$ has better parameters then materials which are using in industry. It means that such material has a perspective of using in sources of accumulation and generation of electric energy in future.

Conclusions

The sol-gel method with auto-burning of synthesis is developed for synthesis nano-sized powder of complex oxide perovskite-like structure $LaFe_{0.5}Cr_{0.5}O_3$.

X-rays analysis shows: space group of perovskite powder P m -3 m, lattice size a = 3.904 Å, cell volume V = 59.5 $Å^3$, x-ray density ρ = 6.724 г/см^3. The average size of the coherent scattering regions is 21 nm.

Synthesized material $LaFe_{0.5}Cr_{0.5}O_3$ characterized by two mechanisms of conductivity, which is a consequence of the mosaic microstructure of the material.

LDS model with cathode based on nano-sized powder of complex oxide perovskite-like structure $LaFe_{0.5}Cr_{0.5}O_3$ shows specific bit capacity around 571 Ah/kg at discharge to 0.5V and current density 0.05C.

Ragone plot shows, that nano-sized $LaFe_{0.5}Cr_{0.5}O_3$ is promising material for lithium power sources.

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Перспективний катодний матеріал для літієвих джерел струму $LaFe_{0.5}Cr_{0.5}O_3$

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В даній роботі синтезовано порошки нанорозмірного $LaFe_{0.5}Cr_{0.5}O_3$ зі структурою перовскиту золь-гель методом за участі автогоріння. За даними Х-променевого фазового аналізу отриманий матеріал складається з однієї фази $LaFe_{0.5}Cr_{0.5}O_3$ (просторова група P m - 3 m). Середній розмір ОКР досліджуваного матеріалу 21 нм. Питома площа поверхні матеріалу складає 14 $м^2/г$. За наближенням, що частинки сферичної форми розрахований середній розмір частинки становить 63,7 нм. Здійснено елекрохімічні дослідження з використанням нанорозмірного порошку $LaFe_{0.5}Cr_{0.5}O_3$ у якості катодного матеріалу для літій іонних джерел струму. Катодний матеріал показує питому ємність 571 А·год/кг при розряді джерела до 0,5В.

Ключові слова: золь-гель метод, гальваностатичний розряд, імпеданс, питома ємність.