

I.P. Yaremiy¹, M.L. Mokhnatskyi¹, P.I. Kolkovskiy¹, L.V. Mokhnatska¹,
S.I. Yaremiy², A.I. Kachmar¹, Kh.P. Cherkach

Promising Cathode Material for Supercapacitors LaFe_{0.5}Cr_{0.5}O₃ Perovskite Nanoparticles

¹Vasyl Stefanyk Precarpathian National University, Ivano-Frankivsk, Ukraine, mark351000@gmail.com

²Ivano-Frankivsk National Medical University, Ivano-Frankivsk, Ukraine

In this work, the Perovskite powders LaFe_{0.5}Cr_{0.5}O₃ with space group of P m - 3 m was obtained by sol-gel method. The nanoscale powders of LaFe_{0.5}Cr_{0.5}O₃ have been tested as a cathode material for electrochemical supercapacitors. The CVA and charge-discharge curves were obtained at 0.5 mV/s to 16 mV/s and 0.5 mA/s to 16 mA/s scan rates accordingly. It is established that the cathode material LaFe_{0.5}Cr_{0.5}O₃ demonstrates the specific capacity up to 16 F/g at discharge scan rate 0.5 mV/s. Additionally, the maximum of the specific capacity was calculated and it is determined that C is 29.26 F/g, and specific capacity of double electric layer C_{DEL} is 3.44 F/g. It was determined that, the contribution of the redox reactions in specific capacity is 88 %. The Nyquist plots and Mott-Schottky plots for LaFe_{0.5}Cr_{0.5}O₃ were obtained. They consist of two parts which correspond to different type of conductivity. Thus, it is established that LaFe_{0.5}Cr_{0.5}O₃ shows different types of conductivity depending on applied potential. The received values of flat band potential are -1.00 V and 0.16 V for n type and p type of conductivity accordingly.

Keywords: sol-gel method, perovskite structure, supercapacitor, impedance spectroscopy, specific capacity.

Received 16 November 2020; Accepted 15 December 2020.

Introduction

Due to the rapid development of electronics the number of personal gadgets such as mobile phones, smart watches, fitness bracelets, wireless headphones, mini cameras, smart glasses, etc. is increasing. Moreover, every year they become more complex and more functional, which leads to higher energy consumption. Consequently, against this background there is a need for development new energy storage devices with better capacity, less weight, cheaper, more reliable and environmentally friendly.

One of the alternative types of energy storage, which suits the conditions above, is supercapacitor [1, 2]. The advantages of supercapacitor's compare to classic batteries are low toxicity, high efficiency (more than 95 %), less weight, etc. All this makes supercapacitors very promising in the future. Therefore, researching new materials for supercapacitors with predefined properties is relevant today.

In recent years, the use of materials with a perovskite structure has been actively studied for supercapacitor applications [3, 4]. The perovskite is a complex oxide with the general formula ABO₃ which can be realized in a great number of oxide systems. Moreover, ABO₃ attract enormous interest of researchers due to their unique electrical and magnetic properties [5]. Additionally, the complex oxides with perovskite structure have been widely used in various fields, such as cathodes in solid oxide fuel cells, active oxidation catalysts, environmental monitoring films, active materials for chemical sensors for the detection of humidity, alcohols and gases, and so forth [6, 7, 8].

The aim of this work was to synthesize the nano-sized LaFe_{0.5}Cr_{0.5}O₃ with perovskite structure and apply it as a cathode material for an electrochemical supercapacitor.

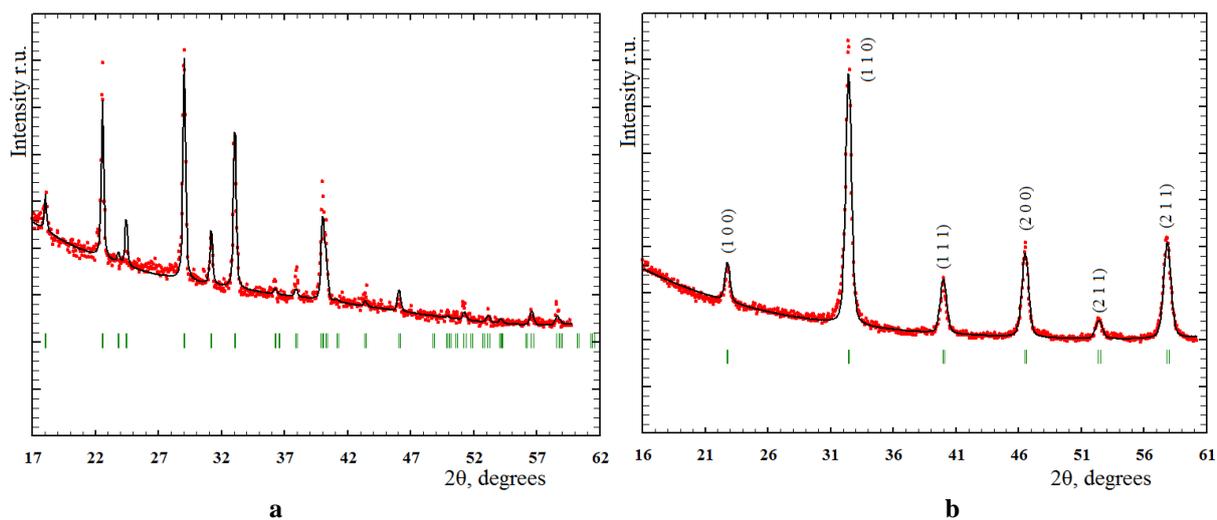


Fig. 1. Diffractogram of dried xerogel (a), and synthesized nano-sized powder of perovskite structure $\text{LaFe}_{0.5}\text{Cr}_{0.5}\text{O}_3$ (b).

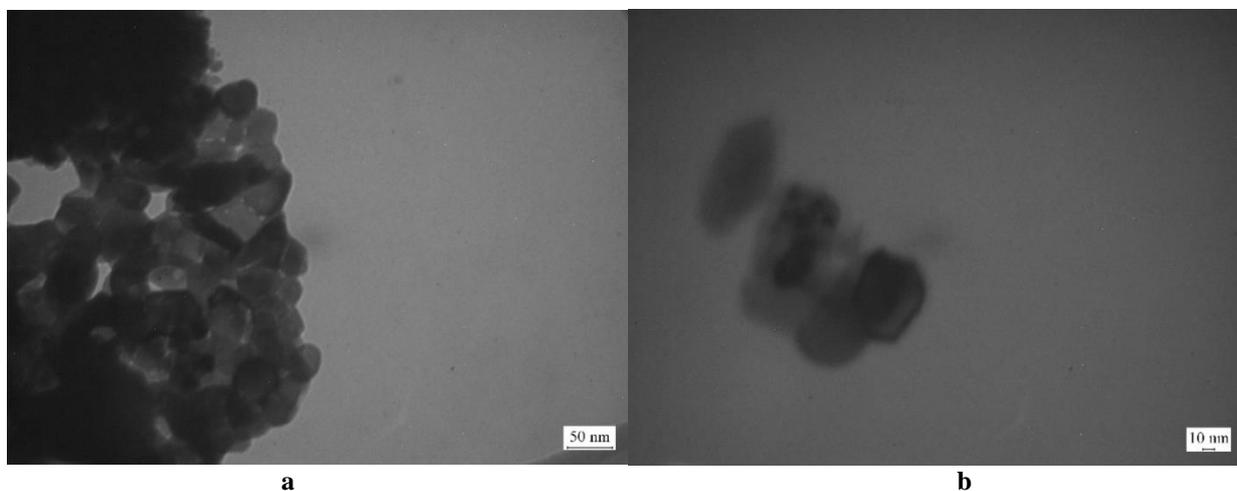


Fig. 2. TEM pictures of synthesized nano-sized powder of complex oxide perovskite structure $\text{LaFe}_{0.5}\text{Cr}_{0.5}\text{O}_3$ in scale 50 nm (a), and 10 nm (b).

I. Experiment technique

The nano-sized powder of perovskite structure $\text{LaFe}_{0.5}\text{Cr}_{0.5}\text{O}_3$ was obtained by sol-gel method. The nitrates crystal hydrates of corresponding metals and citric acid dissolved in distilled water were used for the synthesis. The level of $\text{pH} = 7$ was controlled by adding 25 % ammonia solution. After that, the obtained solution was dried with access to air until it became solid. Dried xerogel was heated to a temperature of 230°C to activate auto-burning [9].

Phase composition analysis and determination of crystal structure of obtained materials were performed by DRON-3 diffractometer with $\text{Cu}(\text{K}\alpha)$ radiation and X-rays focusing on the Bragg-Brentano. The experimental diffractograms were analyzed with the software “FullProf” using the method described in [10].

The specific surface of the samples was measured by 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.

The electrochemical investigation of obtained material was carried out using a three-electrode system with 6M KOH electrolyte. The working electrode was prepared as a composition of active material and acetylene soot in a proportion of 9 to 1 wrapped in nickel mesh, for counter electrode was used platinum wire, and reference electrode (Ag/AgCl).

Galvanostatic charge-discharge curves, cyclic voltammetry performances, and electrical impedance spectroscopy in the frequency range $10^5 - 10^{-2}$ Hz were carried on *Autolab PGSTAT/FRA2* workstation with GPES and FRA-2 software.

II. Results and Discussion

The powders of complex oxide $\text{LaFe}_{0.5}\text{Cr}_{0.5}\text{O}_3$ with perovskite structure were obtained by sol-gel method with auto-burning. The detailed synthesis of this material was described in the previous article [11]. The Figure 1 shows the diffraction patterns of dried xerogel (Ammonium nitrate) (a), and synthesized nano-sized powder of the perovskite structure $\text{LaFe}_{0.5}\text{Cr}_{0.5}\text{O}_3$ (b). Also, Fig. 1 contains theoretical approximation by Rietveld method of experimental

diffraction patterns, calculated in software "FullProf".

The synthesized material has space group P m - 3 m with lattice size $a = 3.904 \text{ \AA}$ and cell volume $V = 59.5 \text{ \AA}^3$, calculated density $\rho = 6.724 \text{ g/cm}^3$. Figure 2 shows the transmission electron microscope images in scale 50 nm (a), and 10 nm (b). The average size of the particles is about 40 - 60 nm, calculated using the method described in [12].

The typical asymmetric CVA curves of LaFe_{0.5}Cr_{0.5}O₃ electrode in 6M KOH electrolyte in an enlarged potential range of 0.0 to 0.5 V under scan rate range of 0.5 to 16 mV/s, are showed in Fig. 3. The CVA curves of obtained LaFe_{0.5}Cr_{0.5}O₃ electrode are demonstrating the deviation from default electrochemical double layer behavior and redox peaks at $\approx 0.28 \text{ V}$ confirm the pseudocapacitive characteristics. There is a visible rise in peak current densities with linear increase of scan rates, which demonstrates the sufficient rate of ionic and electronic transportation during the redox reaction in electrolyte with good proficiency rate. Thus, in scan rate from 0.5 to 16 mV/s, there is not any observed redox peak-shift, and it once again shows the excellent stability and low internal resistance [3, 11]. The peaks near 0.35 V on the oxidation branch corresponds to the oxidation of Fe²⁺ to Fe³⁺ due to the intercalation of oxygen ions in an oxygen vacancy [3].

The Figure 4 shows the dependence of the specific capacity on the scan rate of the research material LaFe_{0.5}Cr_{0.5}O₃. We can see the non-linear decrease of specific capacity with increasing scan rate. The maximum of the

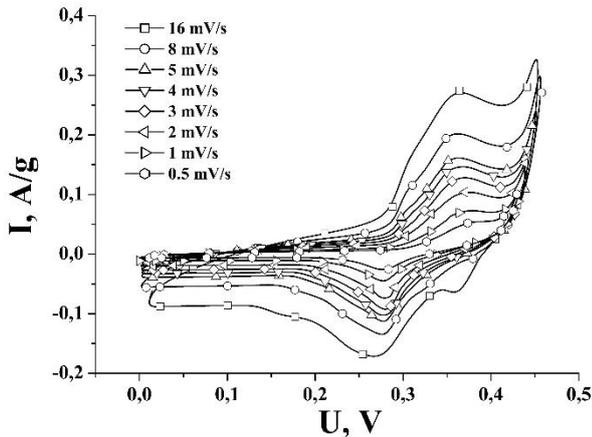


Fig. 3. CVA of the LaFe_{0.5}Cr_{0.5}O₃/KOH system for scan rates from 0.5 to 16 mV/s.

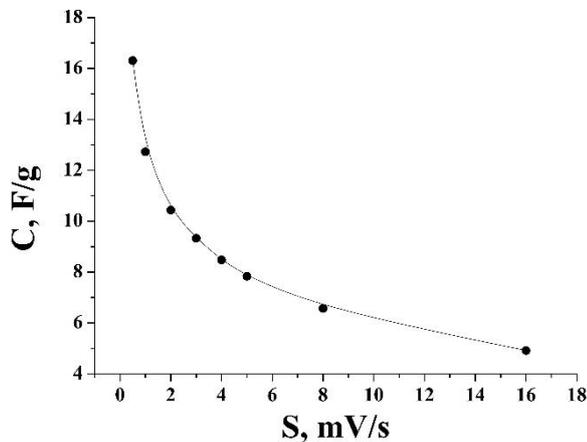


Fig. 4. Specific capacity of the LaFe_{0.5}Cr_{0.5}O₃/KOH system for scan rates from 0.5 to 16 mV/s.

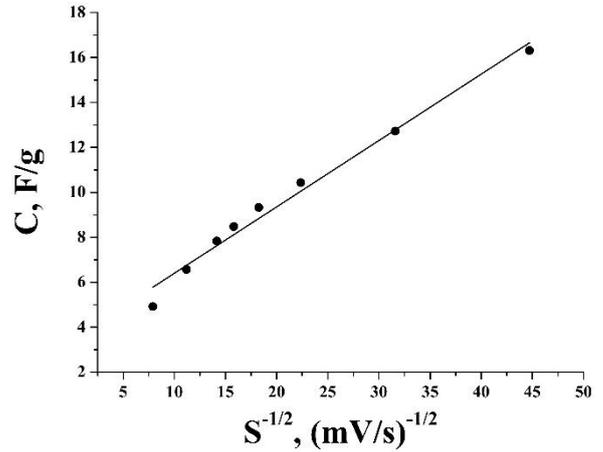


Fig. 5. Dependence of specific capacity on $s^{-1/2}$ for LaFe_{0.5}Cr_{0.5}O₃.

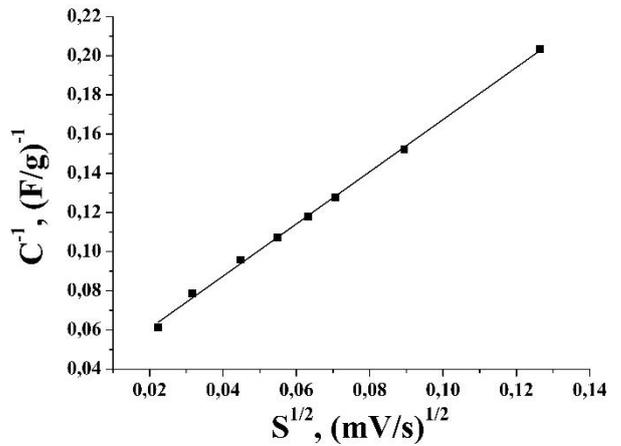


Fig. 6. Dependence of C^{-1} on $s^{1/2}$ for LaFe_{0.5}Cr_{0.5}O₃.

specific capacity is 16.3 F/g at scan rate of 0.5 mV/s. The specific capacity (C) consists of two parts, the first part is the capacity of the double electric layer (C_{DEL}) and the second is capacity of the redox reactions (C_F) [11]. From CVA curves view on the Fig 3,a we can make an assumption that the main part of LaFe_{0.5}Cr_{0.5}O₃ capacity contributes from the redox reactions.

From the kinetic model [13], diffuse component (C_F) depends on scan rate because it is a function of the reaction time, and scan rate is inverse to the time of diffusion. In case of linear diffusion, we can use the equation: $C = C_{s=\infty} + a\sqrt{s}$, where $C_{DEL} = C_{s=\infty}$ and a is a constant value. Figure 5 shows the linearly dependency of specific capacity (C) on $s^{-1/2}$, we can determine the C_{DEL} by the extrapolation of this line to the Y axis. Nevertheless, the capacity of the double electric layer C_{DEL} is 3.44 F/g. Additionally, we can extrapolate the dependency of the specific capacitance on the scan rate to the other side s is $0.1/C$ decrease linearly with $s^{1/2}$, so we can use such equation $\frac{1}{C} = \frac{1}{C_{x=0}} = b\sqrt{s}$, where b is a constant value [11]. The Figure 6 shows the dependency of C^{-1} on $s^{1/2}$ for obtained LaFe_{0.5}Cr_{0.5}O₃, extrapolation of this dependency to the Y axis made it possible to get the maximum of the specific capacity C is 29.26 F/g. The contribution of the redox reactions in specific capacity is 88 %, which confirms our assumption. Figure 7 shows the charge-discharge curves of the electrochemical system based on LaFe_{0.5}Cr_{0.5}O₃ electrode. There are linear sections on

discharge curves with different tilt angles, they indicate different mechanisms of electric energy storage. To calculate the amount of specific capacitance (C_m) we can use the formula: $C_m = \frac{C}{m} = \frac{I\Delta t}{\Delta U m}$, where I (mA) is the discharge current, Δt (s) is the discharge time, ΔU (V) is the potential during the discharge, and m (g) is the mass of the active material inside the electrode [11].

The specific capacitance (C_m) values are presented at the Fig 8. We can see that the capacity decreases when discharge current increases. It can be explained by the fact that there is not enough time for ions to completely infiltrate into the electrode and enter vacancies. The maximum of specific capacity 10.1 F/g is obtained at the discharge current of 0.5 mA.

The electron impedance spectroscopy in the frequency range $10^5 - 10^{-2}$ Hz was made to determine the electrical properties of the nano-sized complex oxide perovskite structure $\text{LaFe}_{0.5}\text{Cr}_{0.5}\text{O}_3$. The Nyquist plots at different values of potential are shown in Fig. 9.

The Nyquist plot at the electrode potential -1 V consists of small semicircle on high frequencies structure and straight line on low frequencies. Semicircle is the result of energy consumption for ion transportation through perovskite structure and straight line corresponds to double electric layer capacity. The electrode potential changing from -1 V to

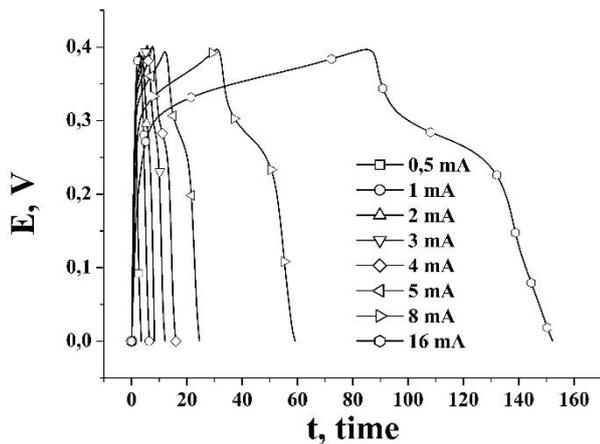


Fig. 7. The charge-discharge curves of $\text{LaFe}_{0.5}\text{Cr}_{0.5}\text{O}_3$ in the potential window from 0 to 0.4 V at various currents.

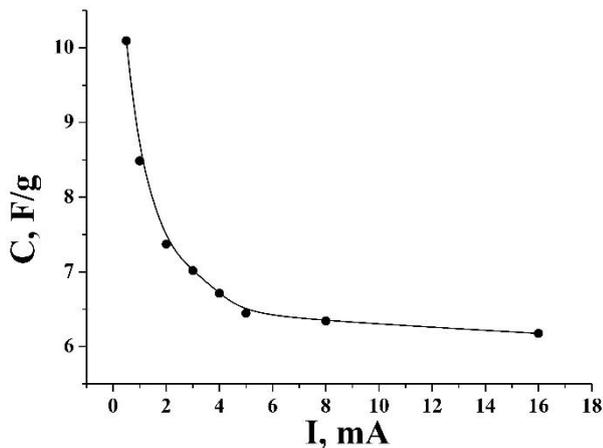


Fig. 8. The specific capacitance density of $\text{LaFe}_{0.5}\text{Cr}_{0.5}\text{O}_3$, measured from discharge part of the charge discharge curves.

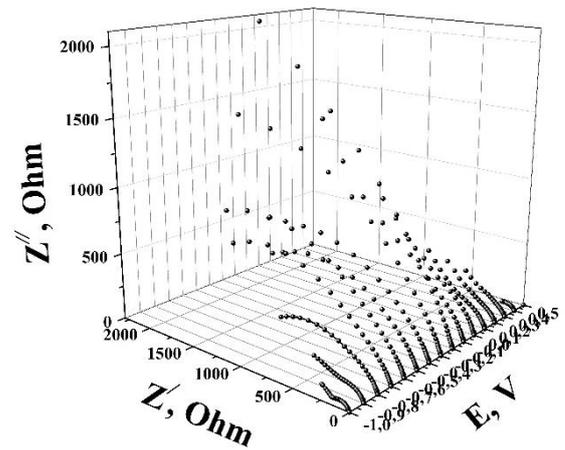


Fig. 9. Nyquist plots of $\text{LaFe}_{0.5}\text{Cr}_{0.5}\text{O}_3$

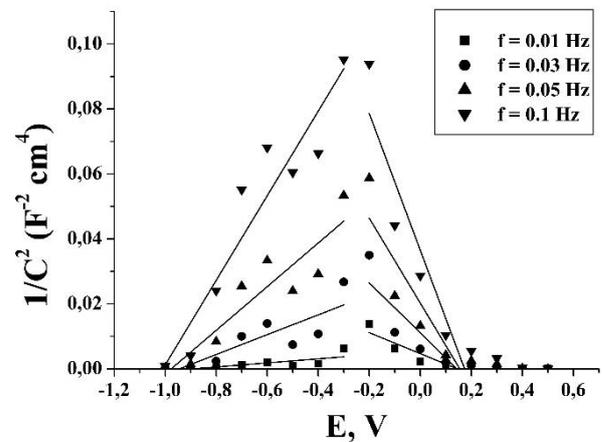


Fig. 10. Mott-Schottky plots of $\text{LaFe}_{0.5}\text{Cr}_{0.5}\text{O}_3$.

-0.3 V leads to semicircle straightening and resistance increasement. During further potential increasing from -0.3 V to 0.5 V resistance decreases and plots return to original view with two parts.

Therefore, the Poisson equation can be modified with Boltzmann distribution for electrons distribution in the region of space charge and Gauss's law for electric field on the border of charge to obtain Mott-Schottky equation [14]:

$$\frac{1}{C^2} = \frac{2}{\epsilon \epsilon_0 A^2 e N_D} \left(V - V_{fb} - \frac{k_B T}{e} \right),$$

where ϵ and ϵ_0 are dielectric constant and vacuum permittivity, e is an electron charge, A is BET surface area, N_D is a carrier concentration, E and E_{fb} are electrode potential and flat band potential values, T – an absolute temperature, k_B – Boltzmann constant. The linear fitting of the low-potential part allows calculating the flat band potential (E_{fb}), and the slope of the curve corresponds for the type of conductivity. The Mott-Schottky plots are presented in Fig. 10, they can be divided into two parts which correspond to different type of conductivity: from -1 V to -0.3 V and -0.2 V to 0.5 V with the same point of division as Nyquist plots. First area corresponds for n type of conductivity with $E_{fb} = -1.00$ V, and second area for p type the with $E_{fb} = 0.16$ V.

Conclusions

The powder with perovskite structure LaFe_{0.5}Cr_{0.5}O₃, obtained by sol-gel method, is nano-sized, which is confirmed by X-rays analysis and transmission electron microscope images.

The obtained nano-sized material LaFe_{0.5}Cr_{0.5}O₃ was used as cathode material and demonstrated the specific capacity up to 16 F/g at discharge scan rate 0.5 mV/s.

It was determined that, the calculated maximum of the specific capacity is 29.26 F/g, where 88 % is specific capacity of redox reactions.

It is established that LaFe_{0.5}Cr_{0.5}O₃ shows different types of conductivity depending on applied potential. The received values of flat band potential are -1.00 V and 0.16 V for *n* type and *p* type of conductivity accordingly.

Yaremiy I.P. – Doctor of Sciences, Professor, of the Department of Material Science and New Technology;
Mokhnatskyi M.L. – PhD student, of the Department of Material Science and New Technology;
Kolkovskiy P.I. – Doctoral student of the Department of Material Science and New Technology;
Mokhnatska L.V. – PhD student, of the Department of Material Science and New Technology;
Yaremiy S.I. – PhD, teacher of the Department of Medical Informatics, Medical and Biological Physics;
Kachmar A.I. – PhD of the Department of Material Science and New Technology;
Cherkach Kh. P. – student.

- [1] H. Schraner F. Barzegar Q. Abbas. Current Opinion in Electrochemistry 21, 167 (2020) (<https://doi.org/10.1016/j.coelec.2020.02.010>).
- [2] R. Lisovsky, B. Ostafiychuk, I. Budzulyak, V. Kotsyubynsky, A. Boychuk, B. Rachiy, Acta Physica Polonica A 133(4), 876 (2018) (<https://doi.org/10.12693/APhysPolA.133.876>).
- [3] S. Hussain, M.S. Javed, N. Ullah, A. Shaheen, N. Aslam, I. Ashraf, Y. Abbas, M. Wang, G. Liu, and G. Qiao, Ceramics International 45(12), 15164 (2019). <https://doi.org/10.1016/j.ceramint.2019.04.258>
- [4] N. Arjun, G.-T. Pan, T. Yang Results in Physics 7, 920 (2017) (<https://doi.org/10.1016/j.rinp.2017.02.013>)
- [5] M. Coskun, O. Polat, F. Coskun and al. Journal of Alloys and Compounds 740, 1012 (2018) (<https://doi.org/10.1016/j.jallcom.2018.01.022>).
- [6] S. Hui, X. Jiayue, and W. Anhua, Journal of Rare earths 28(3), 416 (2010) ([https://doi.org/10.1016/S1002-0721\(09\)60124-1](https://doi.org/10.1016/S1002-0721(09)60124-1)).
- [7] S.M. Khetre, H.V. Jadhav, and S.R. Bamane, Rasayan Journal Chemistry 3(1), 82 (2010) ()
- [8] F. Deganello, G. Marci, and G. Deganello, Journal of the European Ceramic Society 29(3), 439 (2009) (<https://doi.org/10.1016/j.jeurceramsoc.2008.06.012>).
- [9] A. V. Kopaev, V. V. Mokljak, I. M. Gasyuk, I. P. Yaremiy, V. V. Kozub, Solid State Phenomena 230, 114 (2015). (<https://doi.org/10.4028/www.scientific.net/SSP.230.114>).
- [10] I. Yaremiy, S. Yaremiy, V. Fedoriv, O. Vlasii, A. Lucas, Eastern-European Journal of Enterprise Technologies. 5(5 (95)), 61 (2018) (<https://doi.org/10.15587/1729-4061.2018.142752>).
- [11] B.K. Ostafiychuk, H.M. Kolkovska, I.P. Yaremiy, B.I. Rachiy, P.I. Kolkovskiy, N.Y. Ivanichok, and S.I. Yaremiy, Physics and Chemistry of Solid State 21(2), 219 (2020). (<https://doi.org/10.15330/pcss.21.2.219-226>).
- [12] V. S. Bushkova, S. I. Mudry, I. P. Yaremiy, V. I. Kravets Journal of Physical Studies 20(1/2), 1702 (2016) (<https://doi.org/10.30970/jps.20.1702>).
- [13] M. Xu, L. Kong, W. Zhou, and H. Li, The Journal of Physical Chemistry C, 111(51), 19141 (2007) (<https://doi.org/10.1021/jp076730b>).
- [14] A.I. Kachmar, V.M. Boichuk, I.M. Budzulyak, V.O. Kotsyubynsky, B.I. Rachiy and R.P. Lisovskiy, Fullerenes, Nanotubes and Carbon Nanostructures 27(9), 669 (2019) (<https://doi.org/10.1080/1536383X.2019.1618840>).

I.П. Яремій¹, М.Л. Мохнацький¹, П.І. Колковський¹, Л.В. Мохнацька¹,
 С.І. Яремій², А.І. Качмар¹, Х.П. Черкач¹

Перспективний катодний матеріал для суперконденсаторів - наночастинки перовскіту LaFe_{0.5}Cr_{0.5}O₃

¹ДВНЗ «Прикарпатський національний університет імені Василя Стефаника», Івано-Франківськ, Україна
²Івано-Франківський національний медичний університет, Івано-Франківськ, Україна

Порошки перовскіту LaFe_{0.5}Cr_{0.5}O₃ з просторовою групою Р m -3 m отримувалися золь-гель методом. Дані порошки випробовувалися як катодний матеріал для електрохімічних суперконденсаторів. Встановлено, що катодний матеріал LaFe_{0.5}Cr_{0.5}O₃ демонструє питому ємність 16 Ф/г при швидкості розряду 0,5 мА/с. Було визначено, що вклад окисно-відновних реакцій у питому ємність складає 88 %. Отримано діаграми Найквіста та Мотта-Шотки, котрі складаються з двох частин з різним типом провідності.

Ключові слова: золь-гель метод, структура перовскіту, суперконденсатор, імпедансна спектроскопія, питома ємність.