

O.M. Popovych¹, I.M. Budzulyak¹, M.M. Khemii¹, R.V. Ilnytskyi¹, L.S. Yablon¹,
D.I. Popovych², I.I. Panko¹

Laser-modified nanocrystalline NiMoO₄ as an electrode material in hybrid supercapacitors

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

²Ya. S. Pidstryhach Institute for Applied Problems of Mechanics and Mathematics, Lviv, Ukraine

The nanocrystalline NiMoO₄ obtained as a result of hydrothermal synthesis was exposed to laser radiation with a pulse energy of 70 mJ/cm² for 5 minutes. The phase composition and size of crystallites of the triclinic structure of NiMoO₄ were determined by X-ray analysis. The average crystallite size was 18 nm for laser-irradiated nickel molybdate. Impedance analysis was used to analyze the temperature dependence of the electrical conductivity of laser-modified NiMoO₄. The frequency index of the power law, determined by the nonlinear approximation method, was 0.5-0.67, which corresponds to the hopping mechanism of charge carriers. The electrochemical behavior of NiMoO₄ was studied using cyclic voltammetry and galvanostatic charge/discharge testing. The laser-irradiated NiMoO₄ reaches a specific capacitance of 553 F/g at a scan rate of 1 mV/s. The hybrid electrochemical system based on electrodes of modified NiMoO₄ and carbon material provides high Coulomb efficiency (95%) for a significant number of charge/discharge cycles.

Keywords: hybrid supercapacitor, laser irradiation, nickel molybdate, electrical conductivity, specific capacitance.

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Introduction

In the last decades, research in the field of energy storage has significantly increased due to the rapid development of nanotechnology. Energy storage devices are based on electrochemical and electrostatic processes governed by electrons in electrode materials and provide more reliable and flexible power supply while reducing dependence on the fossil fuel industry [1, 2]. The development of hybrid supercapacitors (HSC) is of significant importance for energy accumulation and storage. HSC have several advantages over traditional batteries and supercapacitors [3]. They are capable of achieving higher energy density compared to symmetrical supercapacitors and higher power compared to lithium-ion batteries, making them ideal for applications that require high power output over a long period of time. In a hybrid supercapacitor, the energy storage mechanism is based on both electrochemical and electrostatic principles [4]. A

capacitive electrode stores energy by adsorbing ions, while a battery-type electrode stores energy through an electrochemical reaction. During discharge, both electrodes release the stored energy simultaneously, producing a powerful output current. However, hybrid supercapacitors are still in the early stages of development, and there are challenges that need to be overcome before they can find extensive use. Among them are the optimizations of electrode materials, increasing the energy efficiency of the device, and reducing production costs.

By choosing the optimal methods of obtaining and modifying nanostructure materials, it is possible to increase the energy and power density of accumulation and storage devices [5]. In particular, one of the factors of increasing the surface area, improving the chemical reactivity of the electrode and adsorption of active particles and, accordingly, increasing the performance of devices is the defective structure of electrode materials [6,

7]. However, traditional technologies for obtaining nanomaterials with predetermined structural properties require high temperatures and are energy-intensive. An alternative is laser irradiation of synthesized materials, which is characterized by a much faster and localized thermal effect, allowing for accurate control of the physicochemical properties of the material and its transformation into a more stable energy state [8, 9]. A perspective battery-type material for HSC is the nickel molybdate (NiMoO₄), which stores charge due to the redox reaction of Ni ions and has high electrical conductivity due to Mo ions [10, 11]. By varying the parameters of laser radiation (intensity, pulse duration, operating mode, and wavelength), the structural and morphological properties of nickel molybdate and, accordingly, the capacitive characteristics of electrodes based on it can be significantly improved.

I. Experiment

Nickel molybdate was obtained as a result of hydrothermal synthesis, the procedure of which is presented in [11]. The hydrothermally synthesized nickel molybdate was subjected to laser irradiation. The laser modification was carried out by emission of a Nd–yttrium–aluminum–garnet (Nd-YAG) laser in the near-infrared (1064 nm), which operates in the modulated Q-switched mode with a pulse duration of 10 ns and a pulse repetition rate of 28 Hz. The optimal laser energy in a pulse of 70 mJ/cm² has been experimentally determined, the effect of which does not damage the structure of the material and at the same time stabilizes the energy state. The irradiation duration was 5 minutes.

The crystal structure of the laser-modified material was studied by X-ray diffraction method (DRON powder diffractometer, Cu K α radiation). The temperature behavior of the electrical conductivity of laser-modified nickel molybdate was studied using the AUTOLAB PGSTAT 12 measuring complex in the frequency range of 10⁻²–10⁵ Hz at a voltage of 0 V, in the temperature range of 25–200 °C. The sample was pressed into a cylindrical mold, 14 mm in diameter, with a material thickness of 1 mm. The real conductivity component was determined by the formula: $\sigma = h / (Z' \times S)$, where h is the thickness of the sample, Z' is the experimentally determined real part of the resistivity, S is the surface area of the sample under study. Electrochemical behavior was studied by potentiodynamic and galvanostatic methods using a Tionid charge/discharge stand. Electrochemical studies were carried out in a three-electrode cell using 6 M KOH electrolyte, in which a chlorine-silver electrode was used as a reference electrode, a platinum electrode as an auxiliary electrode, and a nickel molybdate electrode as a working electrode. The working electrode was formed from a mixture of nickel molybdate and acetylene black (80 to 20%) mixed in alcohol and pressed into a nickel mesh, 0.25 cm² in size. The mass of the active material in the electrode was 15 mg.

II. Results and discussions

Fig. 1 shows the X-ray diffraction patterns of the initial and laser-irradiated NiMoO₄ material. The XRD of both NiMoO₄ materials are in agreement with JCPDS 13-0128, which corresponds to a triclinic crystal structure with a P $\bar{1}$ space group [12, 13]. Average crystallite sizes calculated by the Scherer equation: $D = 0.9\lambda / \beta \cos\theta$, where $\lambda = 0.15405$ nm is the wavelength of Cu-K α radiation, β is the FWHM of the most intense maxima, and θ is the Bragg angle, were 17 nm for the initial and 18 nm for the laser-irradiated nickel molybdate. The lack of new bands in the Raman spectra [11] of the laser-irradiated material confirms the stability of the nickel molybdate structure to laser radiation. At the same time, there is a decrease in the integrated intensity and a slight broadening of the XRD bands of the modified material compared to the initial one, indicating the appearance of new structural defects due to laser irradiation.

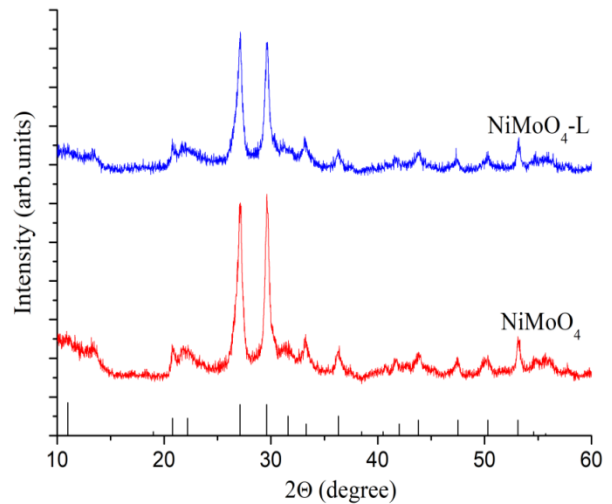


Fig. 1. X-ray diffraction patterns of the initial nickel molybdate (denoted as NiMoO₄) and laser-irradiated material (denoted as NiMoO₄-L).

To determine the effect of laser irradiation on the electrical properties of nickel molybdate, the temperature dependence of the conductivity was studied. The temperature dependence of the electrical conductivity at direct current for the initial and modified NiMoO₄ in the temperature range of 25–150 °C is typical for semiconductor materials (Fig. 2a). The DC electrical conductivity of the initial NiMoO₄ at room temperature is 4·10⁻⁵ S/m, while that of the laser-irradiated one is 3.7·10⁻⁵ S/m. For the initial NiMoO₄, the electrical conductivity increases up to a temperature of 175°C and decreases to 1.6·10⁻⁴ S/m at 200 °C. For laser-modified NiMoO₄, the electrical conductivity reaches its maximum value at 150 °C and decreases to 3.6·10⁻⁵ S/m at 200°C. The decrease in electrical conductivity at higher temperatures may be due to the scattering of charge carriers on lattice vibrations and point defects caused by the presence of higher oxidation states of Ni and Mo, as well as thermally activated defect generation.

The activation energy at DC can be calculated using the Arrhenius equation:

$$\sigma = \sigma_0 \exp(-E/kT),$$

where E is the activation energy, k is the Boltzmann constant, σ_0 is a constant, and T is the temperature. For this purpose, the dependences of $\ln\sigma_{dc}$ on $1/T$ were plotted, and their linear approximation was carried out in the temperature range of 25-150 °C (Fig. 2b). As a result, we obtained activation energy values of 0.13 eV for the initial NiMoO₄ and 0.03 eV in the range of 25-75 °C and 0.17 eV at 100-150 °C for the laser-irradiated NiMoO₄. For the modified material, there is an activation of defects with increasing temperature, which can act as traps for charge carriers, which leads to an increase in the activation energy.

To obtain information on the dynamics of charge carriers and to establish the nature of charge transfer mechanisms in nickel molybdate after laser irradiation, the frequency dependence of conductivity on alternating current in the frequency range 10⁻²-10⁵ Hz was studied (Fig. 3a). The relationship between conductivity and frequency of the applied field is described by the

following equation [14]:

$$\sigma(\omega) = \sigma_{dc} + A\omega^s,$$

where σ_{dc} is the frequency-independent conductivity, A is a constant value, ω is the angular frequency, and s is the frequency index ($0 < s < 1$). At a value of $s < 1$, the electrical conductivity is governed by the hopping mechanism of charge carriers between localized states or defects in the material by tunneling through a potential barrier. Using this law, the conductivity plot was fitted using the method of nonlinear approximation of curves and is shown in Fig. 3a, and the dependence of the fitted parameters is shown in Fig. 3 b.

The numerical value of the frequency degree and its temperature behavior determine the dominant conduction mechanism in the material. Thus, for the laser-irradiated NiMoO₄, the frequency index was 0.5-0.67 and decreased with increasing temperature (Fig. 3b). At higher temperatures, thermal energy can cause a decrease in the density of localized states, as defects and impurities

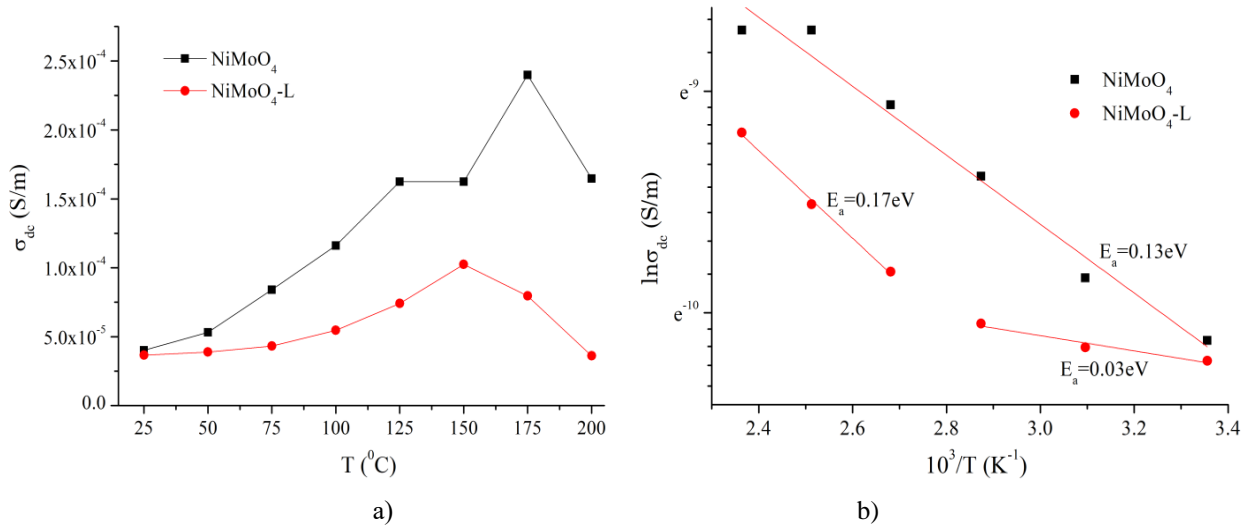


Fig. 2. The temperature dependence of the electrical conductivity (a) and the dependence of $\ln\sigma_{dc}$ on $1/T$ (b) at direct current of the initial and laser-irradiated NiMoO₄.

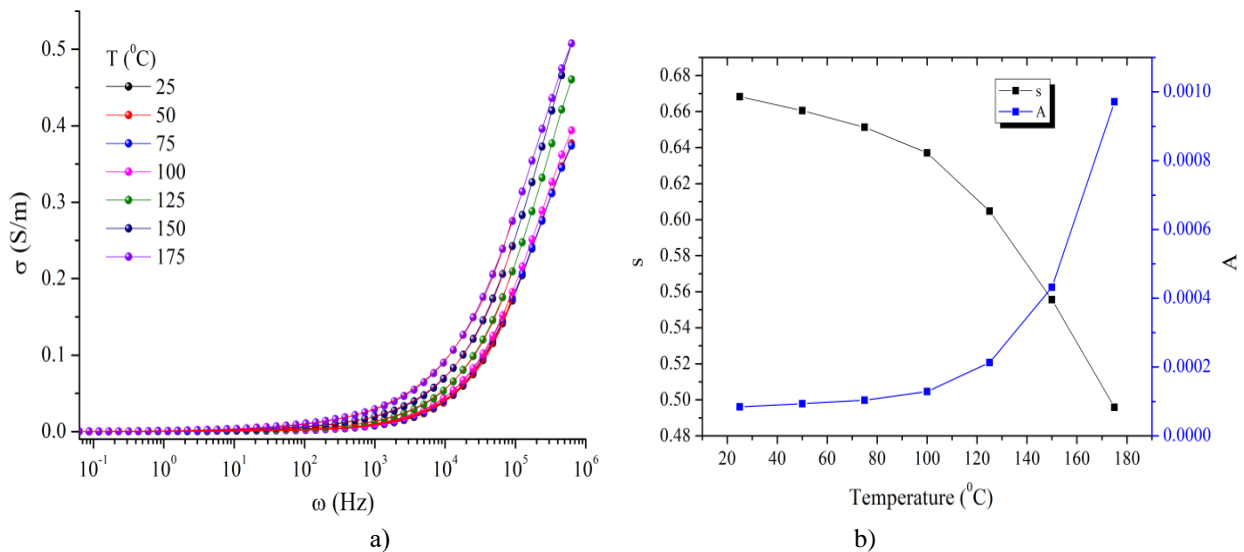


Fig. 3. Temperature dependence of the AC electrical conductivity of laser-irradiated NiMoO₄ (a). Dependence of s and A parameters on temperature (b).

become more mobile and the crystal structure of the material becomes more disordered. This can lead to a decrease in the number of available hopping sites and a corresponding decrease in the value of s . The Jonscher constant A depends on both the type of material and the temperature. The increase in A with increasing temperature (Fig. 3b) is characteristic of many materials with a hopping conduction mechanism and is associated with an increase in thermal energy available to promote the hopping process. At higher temperatures, thermal energy and laser irradiation can help overcome barriers to charge carrier movement by increasing the concentration of charge carriers that can participate in the hopping process, resulting in an increase in the overall electrical conductivity of the material.

The Arrhenius equation was used to determine the activation energy (ΔE_{ac}) of laser-irradiated NiMoO₄ at different frequencies [15]. Fig. 4 shows the linear dependence of $\ln\sigma$ on the inverse temperature. The figure shows that with increasing AC frequency, the activation energy decreases, indicating that at higher frequencies, the charge carriers in the material are subjected to more frequent and rapid changes in the direction of the electric field. This can facilitate the movement of charge carriers and make it easier to overcome the energy barrier. As a result, the activation energy required for the movement of charge carriers will decrease.

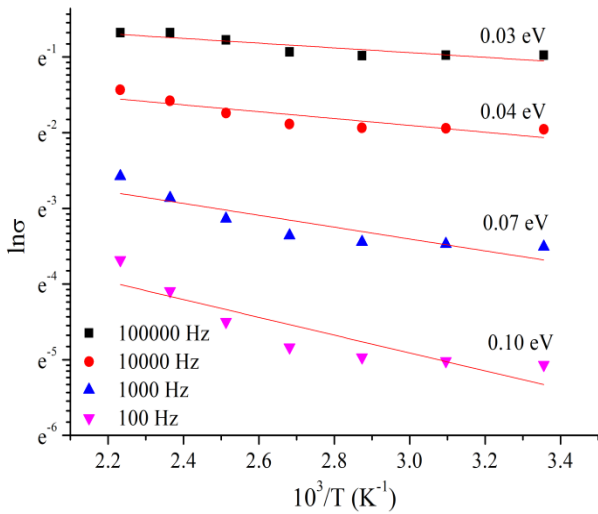
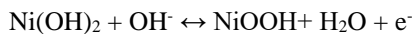
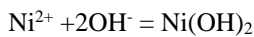


Fig. 4. The variation in σ as a function of inverse temperature (Arrhenius plot) of laser-irradiated NiMoO₄.

To determine the effect of laser irradiation on the capacitive characteristics of nickel molybdate, the electrochemical behavior of two systems was investigated: the initial NiMoO₄ and the laser-irradiated one. Cyclic voltammograms (CV) were recorded in the range of -0.2-0.4 V at a scan rate of 1, 2, 5 and 10 mV/s (Fig. 5a, b). Redox peaks on the CV arise from the interaction of nickel ions from the NiMoO₄ structure with OH⁻ groups from the electrolyte [16]:



One anodic and two cathodic peaks are observed on

the CV of both materials. The appearance of two cathodic peaks indicates that the reduction of NiMoO₄ forms a system with two phases existing at different potentials and is probably γ -NiOOH and β -NiOOH structures [17].

The specific capacitance was calculated using the formula $C=Q/m\Delta U$, where Q is the charge released by the system during cathodic scanning, ΔU is the voltage range, and m is the mass of the active material. The specific discharge capacitance at a scan rate of 1 mV/s was 575 F/g for the initial NiMoO₄ and 553 F/g for the laser-irradiated material and decreased to 242 F/g and 139 F/g at a scan rate of 10 mV/s for NiMoO₄ and NiMoO₄-L, respectively (Fig. 5c). For battery-type electrodes, such as nickel molybdate, the specific capacitance is mainly determined by the redox reactions of the active material and the diffusion of ions into and out of the electrode structure. As the scan rate increases, the time available for ion diffusion decreases, resulting in less efficient transportation of ions to the electrode. As a result, the capacitance decreases. In addition, at higher scan rates (10 mV/s), redox reactions on the electrode surface may not be able to keep up with the potential change, which leads to a decrease in the electrode area involved in the reaction, which also leads to a slight decrease in the capacitance. The laser-modified NiMoO₄ has a slightly lower capacitance compared to the initial material due to the reorganization of defects in the system, which stabilizes after laser irradiation.

Fig. 5 d shows the galvanostatic charge/discharge curves of the initial NiMoO₄ and laser-irradiated at a current of 0.2 A/g in the range of -0.2 to 0.35 V. The asymmetry of the charge/discharge curves is caused by the irreversibility of the electrolyte in the structure of electrode materials due to the passage of Faraday reactions. Thus, the laser modification of NiMoO₄ leads to a decrease in the specific capacitance caused by the destruction of the crystallite surface and a decrease in the intercalation potential of the electrode.

To study the electrochemical parameters of electric energy devices, hybrid supercapacitor was formed with a cathode based on laser-irradiated NiMoO₄ and an anode made of carbon material placed in a 6 M KOH electrolyte. The presence of redox peaks on the CV of the hybrid electrochemical system (Fig. 6a) indicates the accumulation of charge due to Faraday reactions, which is typical for nickel molybdates, while flat areas on the CV correspond to the charge/discharge of the double electric layer of carbon material. As the scan rate increases, the shape of the CV becomes more rounded, which indicates an increase in resistance and a slowdown in the response time of electrochemical reactions.

The specific capacitance was determined from galvanostatic charge/discharge curves (Fig. 6b) at discharge currents of 0.2, 0.5, and 1 A/g by the formula: $C=It/m\Delta U$, where I is the discharge current, t is the discharge time, ΔU is the voltage range, and m is the sum of the masses of carbon material and NiMoO₄. The values of the specific capacitances of the hybrid electrochemical system are presented in Table I. The specific energy and power are calculated by: $E=1/7.2CAU^2$ and $P=E/t$, and the corresponding numerical values are presented in Table I.

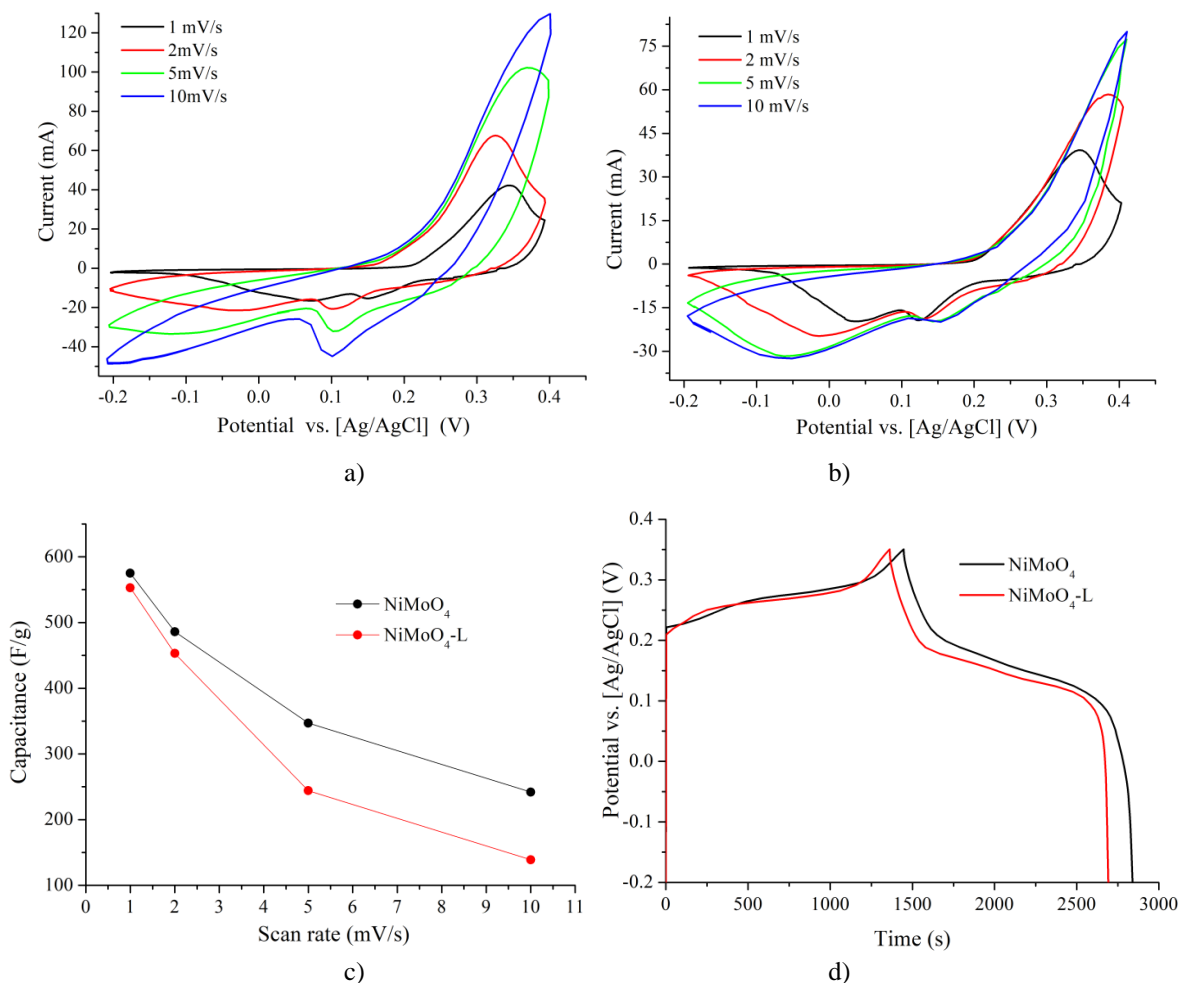


Fig. 5. Cyclic voltammograms of the initial (a) and laser-irradiated NiMoO₄ (b). Dependence of specific capacitances of NiMoO₄ and NiMoO₄-L on scan rate (c). Galvanostatic charge/discharge curves of the initial and laser-irradiated NiMoO₄ at a current of 0.2 A/g (d).

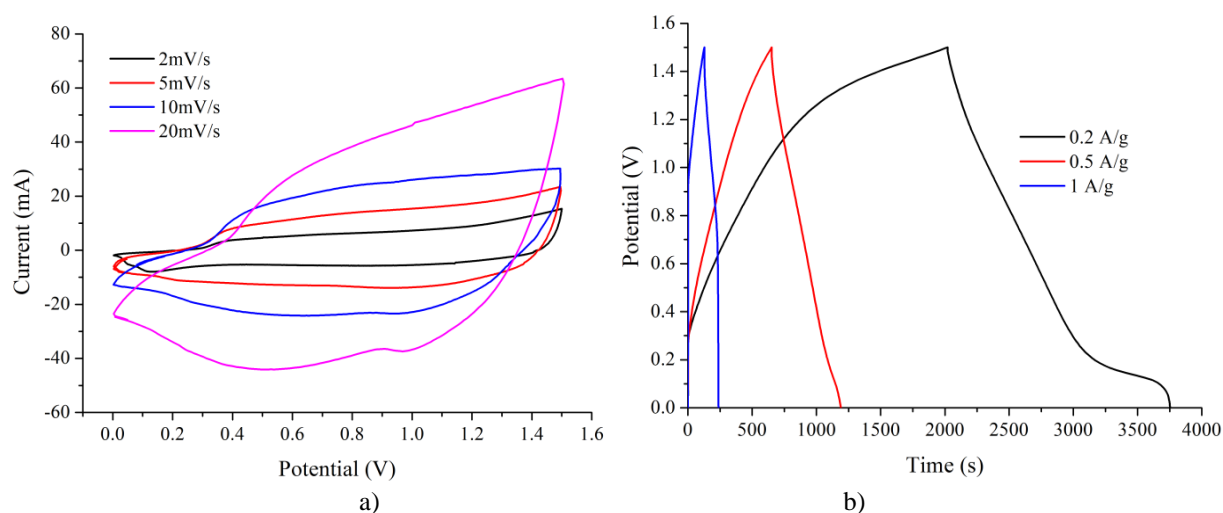


Fig. 6. Cyclic voltammograms (a) and galvanostatic charge/discharge curves (b) of a hybrid electrochemical system based on laser-irradiated NiMoO₄.

The increase in specific capacitance for HSC based on laser-modified material can be explained by the fact that at the initial stages of scanning, the active material is not completely involved in the intercalation of electrolyte ions. During repeated cycling of the hybrid electrochemical system based on NiMoO₄-L, more nickel

is converted to nickel oxyhydroxide, increasing the surface area involved in the redox reaction. This leads to an increase in the discharge time and, accordingly, an increase in the specific capacitance of the material and 95% Coulomb efficiency (Fig. 7).

Table I.
Electrochemical parameters of a hybrid electrochemical system based on laser-irradiated NiMoO₄

Parameter	NiMoO ₄ -L		
Discharge current (A/g)	0,2	0,5	1
Specific capacitance (F/g)	233	185	78
Specific energy (Wh/kg)	73	58	24
Specific power (W/kg)	151	385	792

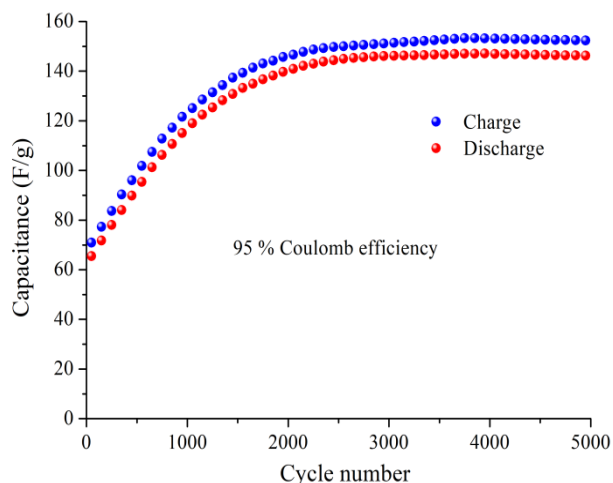


Fig. 7. Specific charge/discharge capacitance and Coulomb efficiency of a hybrid electrochemical system based on laser-irradiated NiMoO₄.

Conclusions

Laser modification of nanocrystalline NiMoO₄ by Nd-YAG laser radiation with a pulse energy of 70 mJ/cm² for 5 min stabilizes the defective nickel molybdate subsystem and leads to the appearance of new structural defects in the material that affect the change in electrical conductivity. It was found that the dc electrical conductivity of laser-irradiated NiMoO₄ decreases to $3.7 \cdot 10^{-5}$ S/m compared to the initial material ($4 \cdot 10^{-5}$ S/m). The study of the temperature dependence of the dc electrical conductivity of the modified material showed that in the range of 100–150°C, defects are activated, which leads to an increase in the activation energy. The mechanism of charge transfer in nickel molybdate after laser irradiation is governed by hopping of charge carriers between localized states or structural defects by stimulating their tunneling through a potential barrier. In addition, the electrode material based on laser-irradiated NiMoO₄ has a high specific capacitance and high Coulomb efficiency (up to 95%) for numerous charge/discharge cycles in a hybrid electrochemical system with a carbon-based electrode, which makes it promising for use in modern electrochemistry.

Popovych O.M. - PhD;

Budzulyak I.M. - Professor, Doctor of Physical and Mathematical Sciences;

Khemii M.M. – PhD student;

Ilnytskyi R.V. – Professor, Doctor of Physical and Mathematical Sciences;

Yablon L.S. – Professor, Doctor of Physical and Mathematical Sciences;

Popovych D.I. – Senior Researcher, Doctor of Physical and Mathematical Sciences;

Panko I.I. - Doctoral student.

- [1] J. Liu, J. Wang, C. Xu, H. Jiang, C. Li, L. Zhang, J. Lin, Z. X. Shen, *Advanced energy storage devices: basic principles, analytical methods, and rational materials design*, *Advanced science*, 5(1), 1700322 (2018); <https://doi.org/10.1002/advs.201700322>.
- [2] P. Simon, Y. Gogotsi, *Perspectives for electrochemical capacitors and related devices*, *Nature materials*, 19(11), 1151 (2020); <https://doi.org/10.1038/s41563-020-0747-z>.
- [3] A. Muzaffar, M. B. Ahamed, K. Deshmukh, J. Thirumalai, *A review on recent advances in hybrid supercapacitors: Design, fabrication and applications*, *Renewable and sustainable energy reviews*, 101, 123 (2019); <https://doi.org/10.1016/j.rser.2018.10.026>.
- [4] B. Rachiy, Yu. Starchuk, P. Kolkovskyy, I. Budzulyak, L. Yablon, V. Kotsyubynsky, O. Morushko, O. Khemiy, *Accumulation of Charge Mechanisms in Electrochemical Systems Based on Carbon and Nickel Tungstate*, *Surface Engineering and Applied Electrochemistry*, 56(6), 697 (2020); <https://doi.org/10.3103/S1068375520060149>.
- [5] H. Liu, X. Liu, S. Wang, H. K. Liu, L. Li, *Transition metal based battery-type electrodes in hybrid supercapacitors: A review*, *Energy Storage Materials*, 28, 122 (2020); <https://doi.org/10.1016/j.ensm.2020.03.003>.
- [6] Y. Zhang, L. Tao, C. Xie, D. Wang, Y. Zou, R. Chen, Y. Wang, C. Jia, S. Wang, *Defect Engineering on Electrode Materials for Rechargeable Batteries*, *Advanced Materials*, 32(7), 1905923 (2020); <https://doi.org/10.1002/adma.201905923>.
- [7] L.S. Yablon, I.M. Budzulyak, M.V. Karpets, V.V. Strelchuk, S.I. Budzulyak, I.P. Yaremiy, O.M. Hemiy, O.V. Morushko, *The structure and physical properties of composites formed from molybdenum sulfide*, *Journal of Nano- and Electronic Physics*, 8(2), 02029 (2016); [https://doi.org/10.21272/jnep.8\(2\).02029](https://doi.org/10.21272/jnep.8(2).02029).
- [8] H. Hu, Q. Li, L. Li, X. Teng, Z. Feng, Y. Zhang, M. Wu, J. Qiu, *Laser irradiation of electrode materials for energy storage and conversion*, *Matter*, 3(1), 95 (2020); <https://doi.org/10.1016/j.matt.2020.05.001>.
- [9] O. Khemii, I. Budzulyak, L. Yablon, D. Popovych, O. Morushko, R. Lisovskiy, *Structure and physical properties of modified β -Ni(OH)₂/C composites*, *Materials Today: Proceedings*, 35, 595(2021); <https://doi.org/10.1016/j.matpr.2019.11.207>.

- [10] R. Xu, J. Lin, J. Wu, M. Huang, L. Fan, Z. Xu, Z. Song, *A high-performance pseudocapacitive electrode material for supercapacitors based on the unique NiMoO₄/NiO nanoflowers*, Applied Surface Science, 463, 721 (2019); <https://doi.org/10.1016/j.apsusc.2018.08.172>.
- [11] O. Popovych, I. Budzulyak, V. Yukhymchuk, S. Budzulyak, D. Popovych, *Raman spectroscopy of nickel molybdate and its modifications*, Fullerenes, Nanotubes and Carbon Nanostructures, 29(12), 1009 (2021); <https://doi.org/10.1080/1536383X.2021.1925253>.
- [12] W. Xiao, J. S. Chen, C. M. Li, R. Xu, X. W. Lou, *Synthesis, Characterization, and Lithium Storage Capability of AMoO₄ (A = Ni, Co) Nanorods*, Chemistry of Materials, 22, 746 (2010); <https://doi.org/10.1021/cm9012014>.
- [13] D. Ghosh, S. Giri, C. K. Das, *Synthesis, Characterization and Electrochemical Performance of Graphene Decorated with 1D NiMoO₄·nH₂O Nanorods*, Nanoscale, 5, 10428 (2013); <https://doi.org/10.1039/C3NR02444J>.
- [14] A.K. Jonscher, *The 'universal' dielectric response*, Nature, 267, 673 (1977); <https://doi.org/10.1038/267673a0>.
- [15] .F. Mott, *Conduction in non-crystalline materials*, Philos. Mag., 19(160), 835 (1969); <https://doi.org/10.1080/14786436908216338>.
- [16] A. Shameem, P. Devendran, V. Siva, R. Packiaraj, N. Nallamuthu, S. Asath Bahadur, *Electrochemical performance and optimization of α-NiMoO₄ by different facile synthetic approach for supercapacitor application*, Journal of Materials Science: Materials in Electronics, 30, 3305 (2019); <https://doi.org/10.1007/s10854-018-00603-3>.
- [17] S. Motupally, C.C. Streinz, J.W. Weidner, *Proton diffusion in nickel hydroxide films: measurement of the diffusion coefficient as a function of state of charge*, Journal of the Electrochemical Society, 142, 1401 (1995); <https://doi.org/10.1149/1.2048589>.

О.М. Попович¹, І.М. Будзуляк¹, М.М. Хемій¹, Р.В. Ільницький¹, Л.С. Яблонь¹,
Д.І. Попович², І.І. Панько¹

Лазерно-модифікований нанокристалічний NiMoO₄ як електродний матеріал в гібридних суперконденсаторах

¹Прикарпатський національний університет імені Василя Стефаника, Івано-Франківськ, Україна,
khemiiolha@gmail.com

²Інститут прикладних проблем механіки і математики ім. Я. С. Підстригача НАН України, Львів, Україна

Нанокристалічний NiMoO₄, отриманий в результаті гідротермального синтезу піддавали впливу лазерного випромінювання з енергією в імпульсі 70 мДж/см² протягом 5 хвилин. Фазовий склад і розміри кристалітів триклінної структури NiMoO₄ визначили методом X-променевого аналізу. Середній розмір кристалітів становив 18 нм для лазерно-опроміненого молібдату нікелю. Для аналізу температурної залежності електропровідності лазерно-опроміненого молібдату нікелю використовували імпедансний аналіз. Частотний показник степеня, визначений за допомогою методу нелінійної апроксимації, становив 0,5-0,67, що відповідає стрибковому механізму носіїв заряду. Електрохімічну поведінку NiMoO₄ досліджували з використанням циклічної вольтамперометрії та гальваностатичного зарядного/розрядного тестування. Лазерно-опромінений NiMoO₄ досягає питомої ємності 553 Ф/г при швидкості сканування 1 мВ/с. Гібридна електрохімічна система, сформована на онові електродів з модифікованого NiMoO₄ та вуглецевого матеріалу демонструє високу кулонівську ефективність (95%) для значної кількості циклів заряду/розряду.

Ключові слова: гібридний суперконденсатор, лазерне опромінення, молібдат нікелю, електропровідність, питома ємність.