

# Hydrothermal synthesis of nanocrystal NiMoO<sub>4</sub> for hybrid capacitors application



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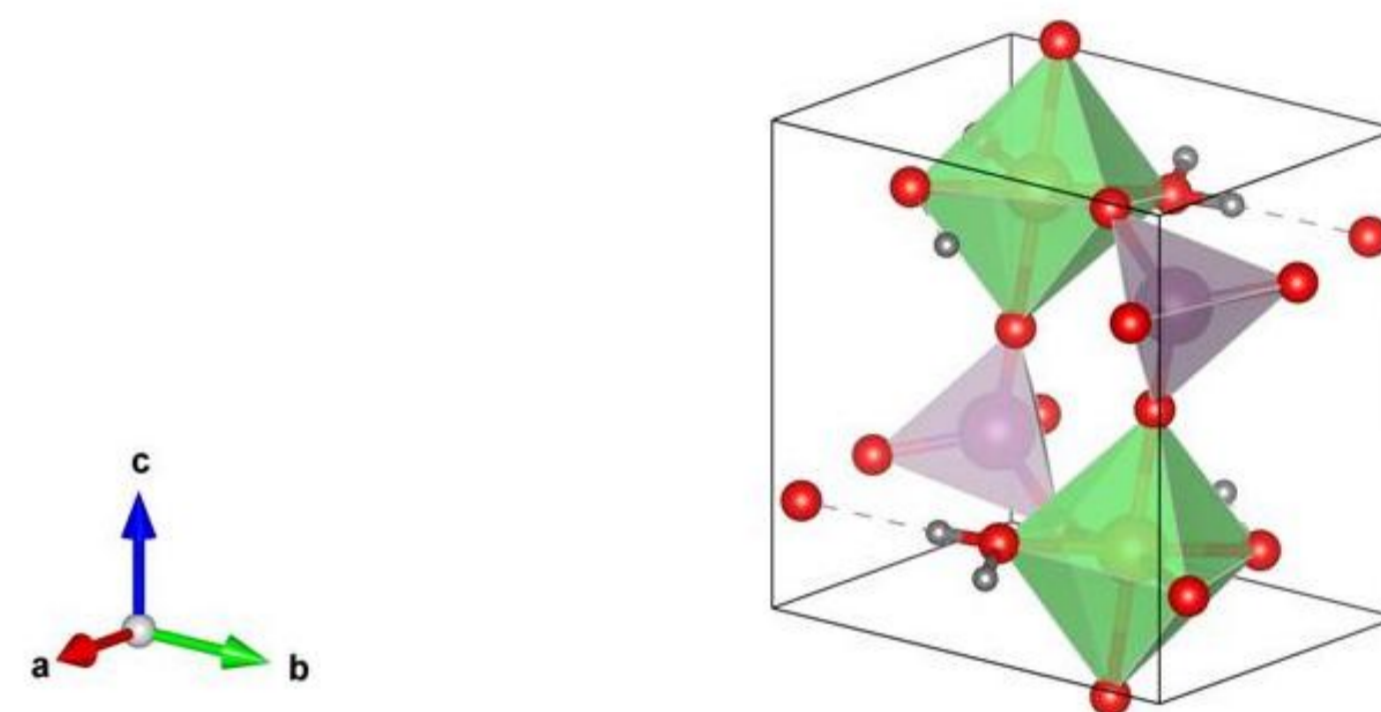
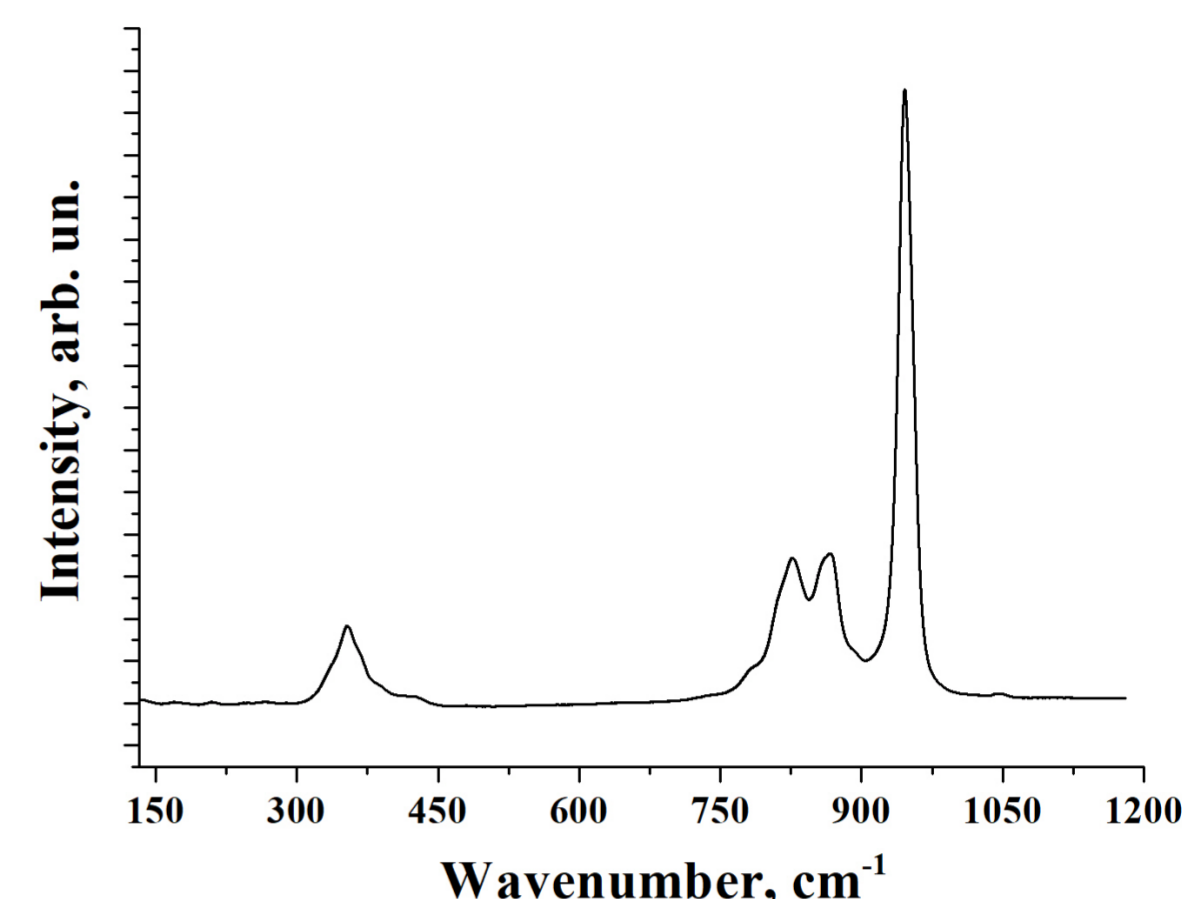
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Nanostructured materials deserve much of attention due to their unique electrochemical, optical, magnetic, electrical and photocatalytic properties [1]. Among them nickel molybdate (NiMoO<sub>4</sub>) is a promising electrode material due to its higher total capacity and higher electroconductivity. The object of research is the problem of obtaining nanomaterials based on nickel molybdate and the use of these materials as the basis of the electrode composition of electrochemical capacitors. The aim is to obtain nickel molybdate by hydrothermal method and study its structural and electrochemical properties.

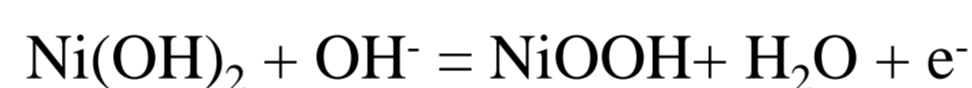
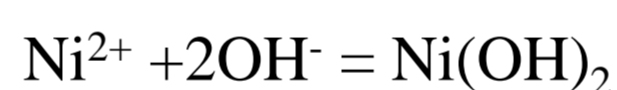
Nanocrystal nickel molybdate was obtained by hydrothermal method. With this purpose Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O were being dissolved in distilled water until transparent solution was obtained. The solution was kept in an autoclave at 180 °C during 2 hours. We used Raman spectroscopy and impedance spectroscopy to study the structure and electrochemical properties of obtained nickel molybdate.

The bands from nickel molybdate registered within the range of Raman spectroscopy (Figure 1) are well correlated with the modes typical for β-NiMoO<sub>4</sub> [2]. Relatively intensive bands with maximums 947, 870, 828, and 354 cm<sup>-1</sup> are typical for triclinic crystal system of NiMoO<sub>4</sub> with P1 space group. The crystalline structure of the hydrate is made up from NiO<sub>6</sub> and NiO<sub>5</sub>(H<sub>2</sub>O) pairs of octahedrons with common edges, joined by MoO<sub>4</sub> tetrahedrons (Figure 1). In Raman spectra of nickel molybdates hydrates the intensive peak at 947 cm<sup>-1</sup> corresponds to symmetrical stretching vibrations of molybdenum ions in tetrahedron coordination of oxygen atoms and is typical for a lot of molybdates. The bands with the maximums of 870 and 828 cm<sup>-1</sup> correlate with asymmetrical bending modes in O–Mo–O connections. The band with the maximums of 354 cm<sup>-1</sup> correlate with asymmetrical bending modes. In Raman spectra of hydrate we registered the weak intensity band at 1050 cm<sup>-1</sup>. The occurrence of this band in hydrates spectra can be justified by coordinated water bending fluctuation modes [3].

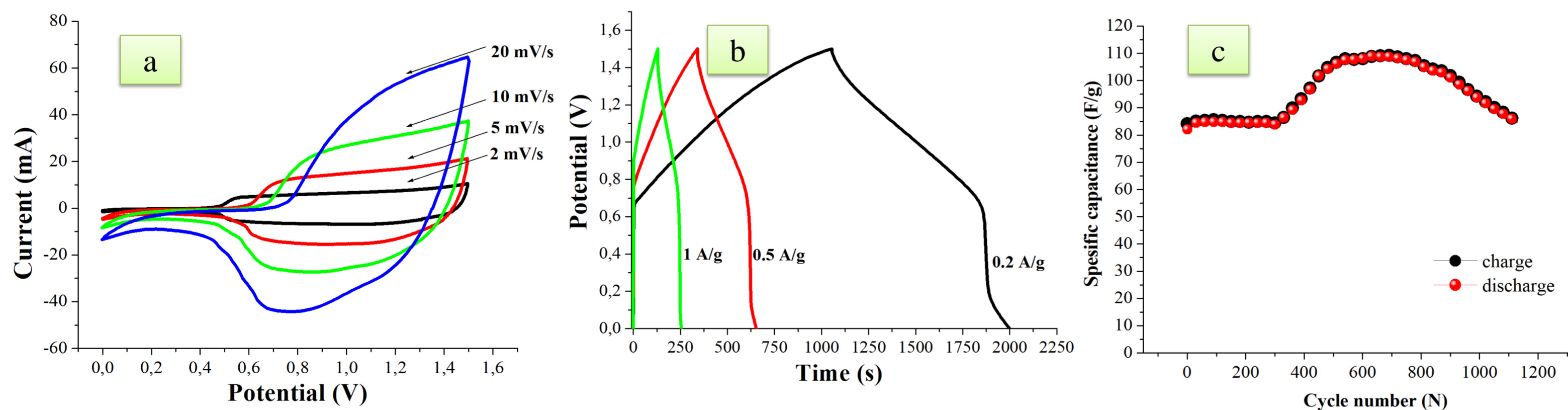


**Figure 1.** Raman spectra and crystal structure of NiMoO<sub>4</sub> hydrate. Purple balls indicate atoms of molybdenum, green – atoms of nickel, red – atoms of oxygen, gray – atoms of hydrogen

We have formed hybrid supercapacitor (HSC) to determine the practical application of electrode based on nickel molybdate. Cyclic voltammograms (CVs) of HSC NiMoO<sub>4</sub> / C in KOH electrolyte at scan rates of 2, 5, 10 and 20 mV/s are represented in Fig. 2 a. Hybrid supercapacitor in this potential range demonstrate quasi-rectangular shapes of cyclic voltammograms. Redox peaks on CVs are the result of the interaction of nickel ions from the structure of molybdate with hydroxyl ions from the electrolyte. This produces nickel hydroxide, which is converted into nickel oxyhydroxide:



Galvanostatic charge / discharge tests of HSC performed at specific currents of 0.2, 0.5 and 1 A/g are represented in Fig. 2 b. The nonlinearity of the curves confirms the pseudocapacitive behavior of the cathode material caused by electrochemical adsorption and redox reactions at the electrode / electrolyte interface. The specific capacitance of HSC based on NiMoO<sub>4</sub> was 256, 215 and 176 F/g at currents of 0.2, 0.5 and 1 A/g respectively. The dependences of the specific capacitance of the HSC on the cycle number are represented in Fig. 2 c. The specific capacitance of HSC NiMoO<sub>4</sub> / C in the initial 300 cycles is almost unchanged. Over the next 300 cycles the specific capacitance increases and reaches a maximum value of 110 F / g, then decreases linearly.



**Figure 2.** Cyclic voltammograms (a), galvanostatic charge / discharge curves (b), discharge specific capacitances vs. number of cycles (c) of hybrid supercapacitor NiMoO<sub>4</sub> / C.

Having analyzed Raman spectroscopy of nickel molybdate we established that as a result of hydrothermal synthesis we obtained nanocrystal NiMoO<sub>4</sub> hydrate with tetrahedral coordination of molybdenum ions. Nanocrystal nickel molybdate hydrate provides surface-active centers for redox reactions and promotes sufficient access of electrolyte ions in the internal structure of the material. This together provides higher electrochemical characteristics, namely longer cyclic stability, higher specific energy and specific capacitance of the hybrid supercapacitor based on hydrate.

1. Khemii O., Budzuliak I., Kotsyubynsky V., Yablon L., Ilnytskyi R., Boychuk V., Morushko O., Bandura K., Khemii M. Materials Science-Poland.- 2019.-37, N 4.-P.547.
2. Haetge J., Djerdj I., Brezesinski T. Chem. Commun. -2012. – 48. – P.6726-6728.
3. Isaac M., Santha N., Nayar V. J. Raman Spectrosc. – 1991. – 22. – P.237-239.

