

*The surfaces of thin composite electrochromic Ni(OH)<sub>2</sub>-polyvinyl alcohol films, deposited by the cathodic template method on FTO glass substrates, were proposed to be processed using laser radiation. The processing of these films was carried out in a colored state with a laser beam of a semiconductor emitter with a wavelength of 650 nm (red) with a pulse duration of 3,000 μs, the beam diameter was about 40 μm. The energy at a single point was 37.5 J/cm<sup>2</sup>.*

*The result was a film with microholes of about 80 μm. The transparent areas of the surface did not exhibit electrochromic properties, which indicated the absence of the original electrochromic coating.*

*The study of the properties of the laser-processed film following a certain pattern showed that the characteristics of composite Ni(OH)<sub>2</sub>-polyvinyl alcohol coatings had changed significantly. On the one hand, the coloration depth of the films decreased by several percent, on the other hand, the specific electrochemical characteristics increased significantly.*

*The study also showed that laser processing did not lead to significant changes in the main properties of the transparent electrically conductive layer – color and resistance. Before and after laser processing, the surface resistance of FTO glasses was 12.1±0.9 and 14.4±1.2 Ohm/sq., respectively.*

*In addition, it was found that the processing of Ni(OH)<sub>2</sub>-polyvinyl alcohol films improved the adhesion of the latter to the surface of FTO glass. Based on the data obtained, a selective method was proposed for modifying thin colored films deposited on transparent conductive oxides (FTO, ITO, AZO) by visible laser radiation. This approach to changing the properties of films can be useful for areas related to the development of sensors, microelectronics, solar cells, small-sized current sources, electrodes with high efficiency, etc.*

**Keywords:** *laser processing, selective processing, electrochromism, electrochromic coating, deposition, nickel hydroxide, polyvinyl alcohol, adhesion*

UDC 544.653.2/3

DOI: 10.15587/1729-4061.2021.225355

# A STUDY OF THE POSSIBILITY OF CONDUCTING SELECTIVE LASER PROCESSING OF THIN COMPOSITE ELECTROCHROMIC Ni(OH)<sub>2</sub>-PVA FILMS

V. Kotok

PhD, Associate Professor

Department of Processes, Apparatus and General Chemical Technology\*

Senior Researcher

Competence center

«Ecological technologies and systems»\*\*

E-mail: valeriykotok@gmail.com

V. Kovalenko

PhD, Associate Professor

Department of Analytical Chemistry and Food Additives and Cosmetics\*

Senior Researcher

Competence center

«Ecological technologies and systems»\*\*

E-mail: vadimchem@gmail.com

\*Ukrainian State University of Chemical Technology

Gagarina ave., 8, Dnipro, Ukraine, 49005

\*\*Vyatka State University

Moskovskaya str., 36, Kirov,

Russian Federation, 610000

Received date 11.11.2020

Accepted date 22.01.2021

Published date 26.02.2021

Copyright © 2021, V. Kotok, V. Kovalenko

This is an open access article under the CC BY license

(http://creativecommons.org/licenses/by/4.0)

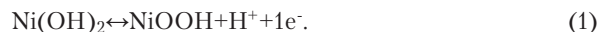
## 1. Introduction

Nickel hydroxide, as a component of various electrochemical devices, is one of the intensively studied substances [1]. The options for its obtaining and processing are varied since they allow varying its properties in a wide range [2]. This interest is primarily due to the wide range of its applications. The use of nickel hydroxide compounds is determined by the unique properties of the latter. The first of them is the possibility of carrying out a reversible electrochemical reaction between nickel hydroxide and nickel

oxyhydroxide (Ni(OH)<sub>2</sub> ↔ NiOOH). The second one indicates the different properties of each of the substances: color, conductivity, chemical behavior. For example, Ni(OH)<sub>2</sub> is light green but in thin films, it is a transparent substance. In turn, NiOOH is black with metallic luster though in thin films it is a dark brown substance. The color difference of the Ni(OH)<sub>2</sub> ↔ NiOOH pair has determined it as a promising electrochromic substance for the so-called Smart Windows with the ability to change light transmission [3, 4].

On the other hand, the high reversibility of the reaction (1) has predetermined the primary use of the substance

as a component of chemical current sources (CCS) – alkaline batteries:



Recently, this substance has also found application in the composition of the electrodes of asymmetric hybrid supercapacitors. These devices are a relatively new type of CCS and allow the discharge (charge) at high speeds [5, 6].

Since NiOOH is a strong oxidizing agent, a nickel oxide electrode is effective in deactivating a number of toxic organic substances [7, 8].

In addition, electrodes based on Ni(OH)<sub>2</sub> can act as sensors for some organic substances, such as glucose [9, 10], hydrogen peroxide [11, 12], when detecting microRNA [13], etc.

Thin films of nickel hydroxide have also found application in solar cells [14, 15]. This application is due to the fact that NiOOH (as well as NiO) can be easily obtained from Ni(OH)<sub>2</sub> and is a p-type semiconductor [16].

In several works devoted to the process of water decomposition [17, 18], Ni(OH)<sub>2</sub>-based composite materials have been proposed, which exhibit high catalytic properties. Moreover, it has been shown that Ni(OH)<sub>2</sub> with the addition of CaCO<sub>3</sub> during ball milling of polyethylene makes it possible to efficiently recycle the polymer to produce hydrogen [19].

In this way, new methods of obtaining, processing, and modifying nickel hydroxide will play a key role in the further improvement of materials used in various devices.

---

## 2. Literature review and problem statement

---

It should be noted that in modern applied areas there is not only controlled application of certain films but also their modification. Since the fields of application of oxide and hydroxide compounds of nickel are constantly expanding, it seems interesting to develop controlled methods of Ni(OH)<sub>2</sub> processing. One of such processing methods can be laser radiation processing with obtaining fine structures and patterns. In the case of composite and multilayer materials, the processing is also interesting, which allows you to selectively modify individual elements (layers) of materials. In other words, methods that allow you to modify the selected layers without destroying or changing the properties of the rest. These methods include, among other things, processing with laser radiation.

An example of such processing can be the work [20], in which the authors obtained the anodic active mass of a lithium-ion battery by sintering Co<sub>3</sub>O<sub>4</sub> particles into micron-sized particles. At the same time, cobalt nanoparticles were formed during sintering. Such material showed a significantly higher capacity efficiency.

Another work was also devoted to the modification of the electrodes of lithium-ion batteries by selective laser sintering [21]. As a result of using this processing method, the authors achieved the absence of the need to use a binder as well as to change the structure and morphology of the resulting active masses.

The successful use of laser processing for ultra-thick electrodes was demonstrated in [22]. It showed that perforation using laser radiation improved the characteristics of the electrodes five times, with a discharge capacity of 0.1 C. The researchers linked the increase in capacity with improved mass transfer and reduced internal resistance of the electrodes.

In [23], the positive effect of laser processing on the characteristics of the electrodes of lithium-ion batteries by laser annealing to obtain SiO<sub>0.76</sub> nanoparticles was noted.

It should be noted that laser processing is also used in other areas. Thereby, [24] showed the use of laser engraving in the formation of supercapacitor microarrays for the power supply of stretched systems.

When forming the sensor system for glucose determination, the laser method of removing water from the composite material of the sensor was used [25]. It was shown that removing water from the sensor electrode materials in the oven resulted in materials with inferior performance compared to laser processing.

Femtosecond laser pulses were used in [26] to form soft and elastic microelectrodes. The resolution of drawings with a laser reached 3 μm. The authors positioned the proposed technology for creating biosensors.

Laser texturing was proposed by the authors of [27] as a processing method for increasing the anticorrosive properties of the Ti<sub>12</sub>Mo<sub>6</sub>Zr<sub>2</sub>Fe alloy. The increase in the corrosion resistance of the alloy occurred due to instant melting and solidification in an inert atmosphere as well as parallel chemical processes.

In the work devoted to a silicon-based antireflection coating, femtosecond laser processing was used with subsequent chemical modification [28]. The resulting coating had high antireflection and self-cleaning properties.

Using laser processing in [29], the characteristics of shape memory polymers with laser-deposited hierarchical micro/nanoscale elements were fabricated and studied. The structures under development were proposed for microfluidic devices and sensors with the ability to switch wettability.

As can be seen from the above examples, laser processing for creating patterns, surface modification, and application of fine structures can be successfully used in various applied directions. It should be noted that the most convenient is the use of laser processing for modifying flat films or surfaces. These include films based on Ni(OH)<sub>2</sub>-polyvinyl alcohol (PVA), which exhibit electrochromic properties [30, 31]. The use of laser processing in the case of thin Ni(OH)<sub>2</sub>-PVA films can significantly change their properties.

One of the methods of deposition of Ni(OH)<sub>2</sub>-PVA films is the cathodic template method [32, 33]. Since the cathodic template method is an electrochemical method, a conducting substrate is required for its implementation. In this case, it is interesting to implement selective processing with laser radiation that does not destroy the electrically conductive substrate.

The literature search for examples of modification of Ni(OH)<sub>2</sub>-PVA, Ni(OH)<sub>2</sub>, NiO films as well as other electrochromic materials by laser radiation did not give a positive result. Since modification by laser radiation can change and improve the characteristics of composite films, it was necessary to check this assumption. Therefore, the main issue of this study was to investigate the possibility of performing selective processing using laser radiation. The second issue was the search for parameters of the modification by laser radiation of Ni(OH)<sub>2</sub>-PVA films.

---

## 3. The aim and objectives of the study

---

The study aimed to test the possibility of performing selective laser processing of composite Ni(OH)<sub>2</sub>-PVA films on a glass substrate coated with a transparent electrically con-

ductive oxide. Carrying out such processing can, on the one hand, improve the characteristics of the selected composite, and, on the other hand, provide a powerful tool for the formation of microelectrodes based on colored film materials.

As part of the solution to this aim, the following objectives were formulated:

- to deposit  $\text{Ni(OH)}_2$ -PVA films by the cathodic template method;
- to determine the parameters of laser processing;
- to carry out laser processing of the obtained films and to compare the morphological, electrochemical, and optical characteristics of the processed and unprocessed films and substrates.

#### 4. Research methods used to determine the effect of temperature differences on the properties of $\text{Ni(OH)}_2$ -PVA films

##### *Obtaining composite $\text{Ni(OH)}_2$ -PVA films.*

All films were prepared on glass with a conductive transparent coating consisting of fluorine-doped tin oxide (FTO glass):  $R < 10 \text{ Ohm/sq.}$ , Zhuhai Kaivo Optoelectronic Technology Co. Ltd. (China).

FTO glass was degreased by wiping with a paste based on water and soda. Then, the substrate was rinsed with running and distilled water and also processed with ultrasound in an ultrasonic bath in 96 % ethyl alcohol (10 minutes, 60 W, 41.5 kHz). After that, they were dried immediately before the next operation and wiped again with a lint-free cloth with ethyl alcohol. In this case, the dimensions of the working area of the FTO glass were  $2 \times 2 \text{ cm}$ , the total dimensions were  $3 \times 2 \text{ cm}$ .

Before applying the composite coatings, “soft” etching was performed. This was necessary to ensure better adhesion of the film to the substrate as well as to improve the electrochemical and optical characteristics of the deposits [34]. In a series of experiments, “soft” etching was carried out in a gentle mode using low current densities so as not to significantly change the value of the surface electrical conductivity of substrates. The etching mode was chosen as follows:  $-0.25 \text{ mA/cm}^2$ , 10 s;  $+0.25 \text{ mA/cm}^2$ , 100 s;  $-0.25 \text{ mA/cm}^2$ , 40 s;  $+0.25 \text{ mA/cm}^2$ , 100 s;  $-0.25 \text{ mA/cm}^2$ , 40 s;  $+0.25 \text{ mA/cm}^2$ , 100 s. 1 M HCl was used as a solution for “soft” etching. After etching, the substrates were thoroughly washed in distilled water and an electrochromic coating was applied.

The preparation of electrochromic composite  $\text{Ni(OH)}_2$ -PVA coatings was carried out electrochemically using cathodic template deposition from a 0.01 M  $\text{Ni(NO}_3)_2$  solution with 4 % PVA at  $i = 0.1 \text{ mA/cm}^2$  for 600 s. The deposition regime was the same for all samples. All films were dried at room temperature for 1 day. One of the samples was subsequently not laser-processed and was used to compare the characteristics with the processed films.

##### *Laser processing of the resulting films.*

It should be noted that semiconductor laser emitters are both small-sized and powerful. The same emitters are relatively affordable, which can significantly reduce the cost of technology. There are laser semiconductor diodes on the market that emit in visible colors: red (650 nm), green (520 nm), and violet (405 nm). In this work, a 650 nm red laser diode with a power of 0.2 W was chosen. In order to process the  $\text{Ni(OH)}_2$ -PVA composite, the original film was tested in the modes described in the section *Electrochemical and optical tests*, and after testing, the film was colored. Col-

oration was performed by sweeping the potential of the film electrode from +201 to +701 mV (NHE) at a rate of 1 mV/s. The colored film was rinsed with distilled water and dried at room temperature for 1 hour. Then, the coated electrode was placed on the platform of the setup and processed with laser radiation by the specified pattern in the control program.

The setup consisted of three main parts:

- a laser diode attached to the carriage of a stepper motor that moved along the Y-axis;
- a platform attached to the second stepper motor, which moved along the X-axis;
- an electronic control unit with a power supply built on an Arduino Nano board and two A4988 stepper motor control drivers.

The Arduino Nano was controlled via a USB cable using a program installed on a PC. In turn, the Arduino Nano with the loaded sketch moved the platform, and the carriage with the laser along the X and Y axes, and also turned on and off the power to the laser diode. Thus, by loading the picture into the control program, it was possible to achieve processing by the required pattern on the colored film. The setup contained two X-Y liquid levels to adjust the position of the laser diode and platform. Two vertical fans created a constant flow of air parallel to the platform to carry away smoke and particles so that the laser beam was not scattered onto them. The optical system of the laser emitter made it also possible to adjust the focus of the laser point.

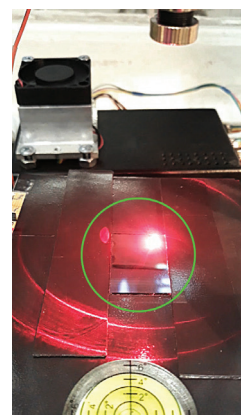


Fig. 1. Setup for laser processing in operation. The green circle marks the glass being processed in a colored state on the platform

The processing parameters were as follows: discrete step – 0.009375 mm (step), the delay between idle strokes – 500  $\mu\text{s}$ , and the burn-through time at a point – 3,000  $\mu\text{s}$ . The setup in operation is shown in Fig. 1. In total, two types of samples were obtained: without laser processing and with laser processing with one pattern. Hereinafter, the samples are referred to as “Original” and “Laser”, respectively.

##### *Electrochemical and optical tests.*

To evaluate the electrochemical and optical characteristics, we used the setup shown in Fig. 2.

The electrochemical characteristics were evaluated by the method of potentiodynamic cycling. The measurements were carried out using a three-electrode scheme [35]. Cycling was performed in the mode [+201; +701 mV] relative to the normal hydrogen electrode (NHE) at a sweep rate of 1 mV/s. A silver chloride electrode in a saturated KCl solution was used as a reference electrode. Nickel foil was used as an auxiliary electrode. The electrolyte was a 0.1 M KOH solution. The cell was

made of ABS+ plastic with transparent PMMA inserts and a built-in thermostat system. The temperature was maintained at  $+23\pm 2$  °C. During cycling, changes in the optical characteristics of the films were also recorded in parallel with the electrochemical data. After cycling, the electrode was colored in the previously described mode and processed with a laser. The next step was potentiostatic cycling with the recording of changes in optical characteristics. Potentiostatic cycling was performed based on the previously obtained results of potentiodynamic cycling. From the obtained cyclic voltammograms, the potentials of the anodic and cathodic peaks were taken, and each of them was injected alternately for 1 minute, each for 10 cycles.

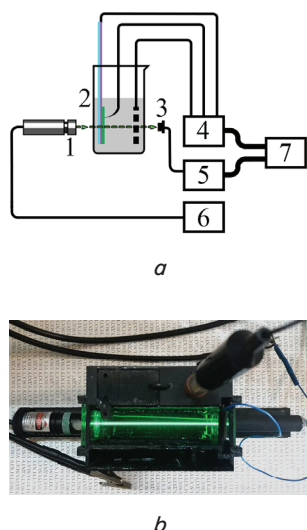
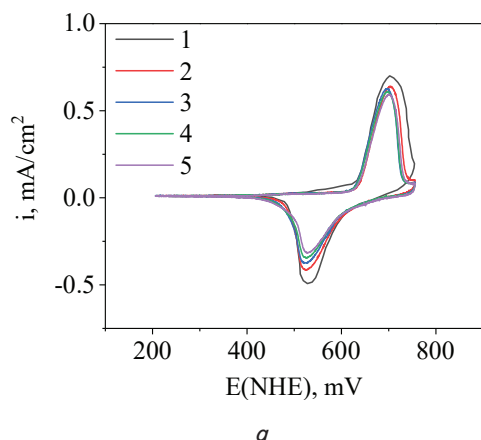


Fig. 2. Measuring setup and a cell as part of the setup: *a* – a simplified diagram of the setup for studying the electrochemical and optical characteristics of electrochromic films; 1 – semiconductor laser with a lens system (10 mW, 520 nm); 2 – a cell with a free electrolyte and an electrochromic electrode under test; 3 – silicon photodiode with built-in focusing lens; 4 – electronic potentiostat (Elins R-8); 5 – ADC (E-154) and power supply unit of the light source; 6 – laser power supply unit; 7 – computer; ■ – glass; ■ – conductive coating; ■ – composite electrochromic Ni(OH)<sub>2</sub>-PVA coating; *b* – photo of the cell (top view)

#### Surface resistance evaluation.

To assess the surface resistance of FTO glass before and after laser processing of electrodes, we used a UNI-T UT80B



(China) digital multimeter in the ohmmeter mode with a probe, which is shown in Fig. 3.

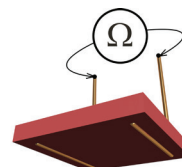


Fig. 3. Measuring probe for evaluating surface resistance with a connected multimeter

The probe consisted of copper electrodes ( $\varnothing=0.4$  mm) with a length of 1 cm and a distance of 1 cm between them. For measurements, the probe was applied to the sample being measured and pressed with the same force, while determining the average value of the resistance of the five measured.

#### Morphology and visual evaluation of electrodes.

To compare the quality of the films after all tests, the electrodes were colored by sweeping the potential of the film electrode from +201 to +701 mV (NHE) at a sweep rate of 1 mV/s. Then, the electrode surface was examined using scanning electron microscopy (REM-106I, Ukraine), and an optical microscope (Carl Zeiss, Germany). The photographs were taken without magnification as well.

## 5. Comparison of the obtained characteristics for film electrodes

In the experiments, one pattern was used to process the surface of an electrode coated with a composite coating. Subsequently, it was planned to conduct a separate study on the influence of the nature of the pattern on the characteristics of the electrodes.

During the research, it was necessary to answer two main questions. First, what would happen to the film under the action of a laser pulse, i.e. a sharp local rise in temperature. Second, to find out how the laser processing would affect the electrical characteristics of the electrically conductive oxide substrate (FTO layer).

### 5.1. Characteristics of a non-laser-processed film electrode

To determine the performance and electrochromic activity of the film electrodes, two electrodes obtained in the same mode were cycled. The results for one of them are shown in Fig. 4.

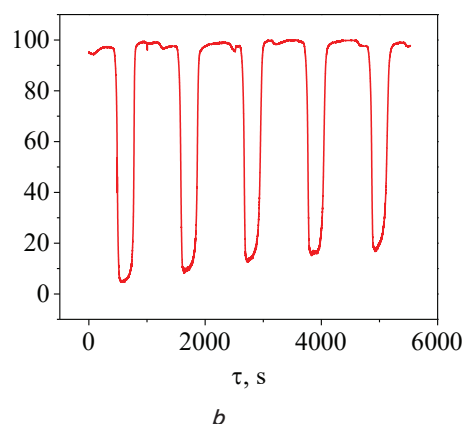


Fig. 4. Results for the non-laser-processed film: *a* – cyclic voltammogram (CVA); *b* – coloration-bleaching curve

Analysis of the characteristics shown in Fig. 4 allowed us to conclude that the film exhibits electrochemical and electrochromic activity. As evidence, there were clearly distinguishable anodic and cathodic peaks on the CVA, corresponding to the oxidation of Ni(OH)<sub>2</sub> in NiOOH (peak at +699 mV) as well as the opposite process (peak at +528 mV). In this case, the change in the nature of the curve (height, shape, and position of the peaks) during cycling was insignificant and decreased from cycle to cycle. Thus, the characteristics of the processes on the film electrode were stabilized over time.

In addition, the unprocessed sample changed its transparency (*T*, %) in a wide range – from 100 %, and in the colored state, it ranged from 5 to 16 %. Interestingly, the transparency in the colored state also stabilized over time. The difference in transparency in the colored state between the 2<sup>nd</sup> and 1<sup>st</sup> cycles was about 4 %, and the difference between the 5<sup>th</sup> and 4<sup>th</sup> cycles was already a smaller value of about 1 %.

The second sample, which was subsequently laser-processed, showed similar characteristics.

### 5. 2. Comparison of characteristics of laser-processed and unprocessed film electrodes

It should be noted that the colored layer of the Ni(OH)<sub>2</sub>-PVA composite was most likely removed completely during laser processing. In accordance with the pattern chosen for these experiments, Fig. 5, *a*, loaded into the program, a drawing was obtained on a colored film – Fig. 5, *b*. A micrograph of the pattern was obtained with magnification under an optical microscope in transmitted light. To estimate the real area of the remaining

coating, the photograph obtained by optical microscopy was processed in a graphic editor (Fig. 5, *c*). Next, the number of pixels for each of the colors was calculated, and, accordingly, the area occupied by the film and the area without coverage. If the initial area was taken as 100 %, then, the decrease in the film area in the case of laser processing occurred by about 7.3 % to 92.7 % of the initial value – Fig. 5, *d*. It should be noted here that with such a determination of the area, some error was possible.

In order to evaluate the effect of laser processing on the characteristics of the film, the coloration-bleaching curves were obtained in the potentiostatic mode – Fig. 5, *e*. On this graph, the value of (*T*) is the transparency of the film in percent. Comparison of the course of the two curves indicated that the processing unambiguously affected the optical characteristics of the film. As a result of film processing, the course of the curve changed as well as the values of transparency in the colored and bleached states. A quantitative comparison of the characteristics of the two films was realized by comparing the average coloration depth for each of the films when cycling in the potentiostatic mode. The average coloration depth (*D*) was calculated as the average value of the transparency differences (*T*) for the film in the most colored and bleached states during cycling. If the average coloration depth of the unprocessed film (Original) was taken as 100 %, then the average relative coloration depth of the processed film (Laser) would be 94.7 % – Fig. 5, *f*. The actual coloration depths of the Original and Laser samples were 63.44 % and 60.09 %, respectively. It should be emphasized that the obtained observations showed that after laser processing, the uncoated areas did not color with further cycling.

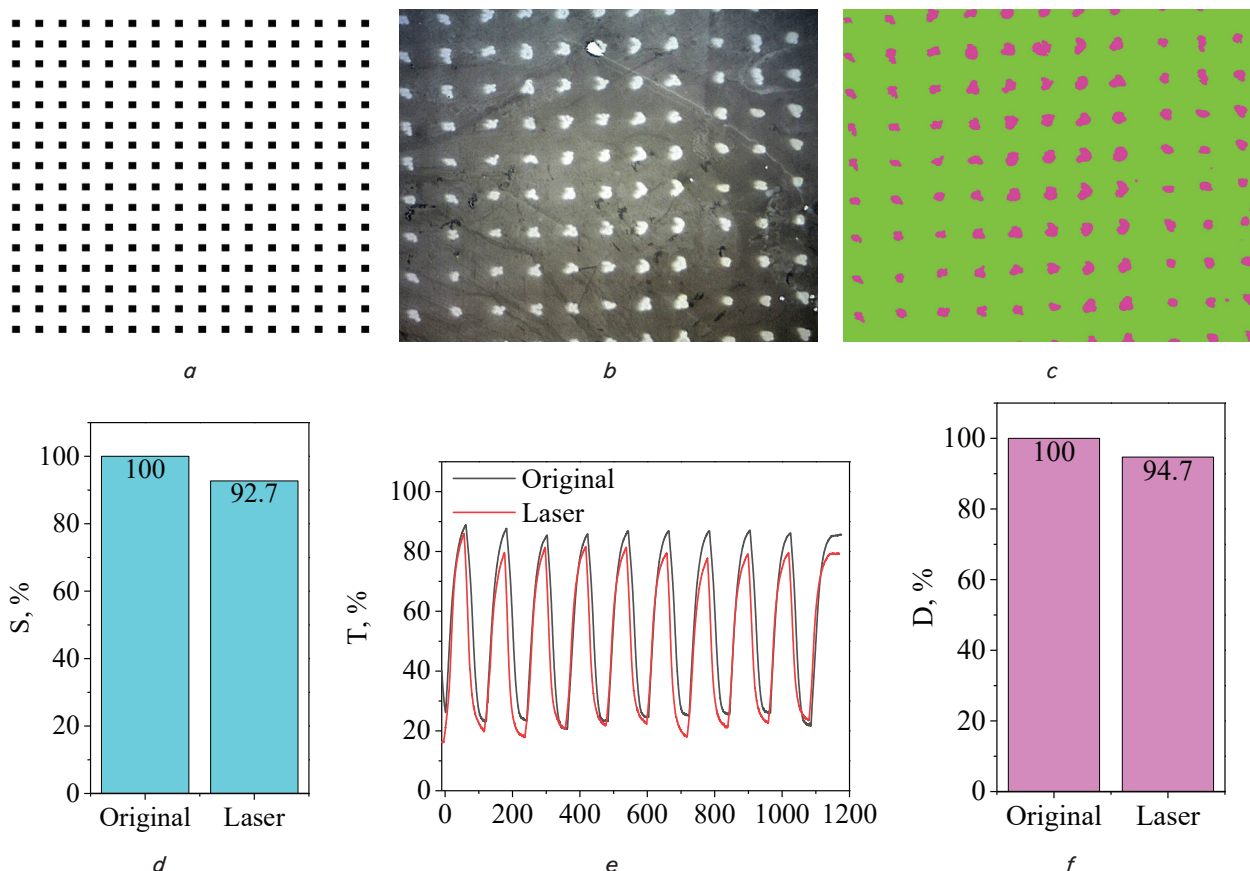


Fig. 5. Results for non-laser-processed (Original) and processed (Laser) samples: *a* – pattern according to which the film was processed; *b* – photomicrograph of the laser-processed film (magnification 80x); *c* – processed picture for the area calculation; *d* – comparison of the relative areas of the two electrodes coatings; *e* – coloration-bleaching curves of the samples; *f* – relative average coloration depths of the samples

It was also of interest to determine the amounts of electricity that went into the coloration and bleaching processes. Fig. 6 shows the average values of the amounts of the anodic process (coloration) and cathodic process (bleaching) electricity for the Original and Laser films.

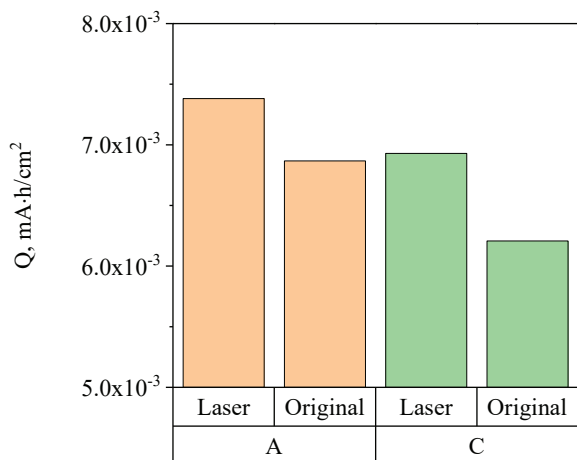


Fig. 6. Average specific values of the amount of electricity for the Laser and Original samples: A – anode (when colored); C – cathodic (when bleached)

Although the average coloration depth for the Laser sample decreased, the electrochemical performance, on the contrary, increased. The values of the amount of electricity for the anodic and cathodic processes were higher for the Laser sample than for the unprocessed sample.

**5. 3. Comparison of the surface resistance of substrates of laser-processed and unprocessed film electrodes**

As shown in the previous section, laser light removed the colored electrochromic composite coating. However, it remained unclear what was happening with the substrate. Considering that the transmission of the oxide coating was less than 100 %, there was a possibility of removing the coating or irreversible changes in the coating structure and, as a consequence, a significant change in the surface resistance. To evaluate the resistivity of the substrate, the Ni(OH)<sub>2</sub>-PVA films were carefully removed, and measurements were performed. The measurement results are shown in Fig. 7. The analysis of the obtained values showed that the resistivity for the substrate unprocessed by the laser was higher than the initial one ( $\Omega > 10 \text{ Ohm/sq.}$ ) since all the electrodes were subjected to a soft etching process. During the etching process, a part of the coating was removed and the resistance increased.

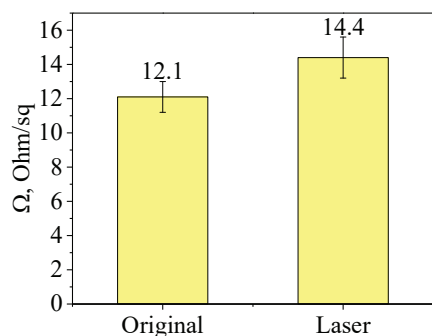


Fig. 7. Surface resistance values of the Original and Laser electrode substrates

The surface resistance slightly increased after laser processing. It should be noted that after laser processing, no visible color changes were found on the substrates.

**5. 4. Microscopy and comparison of film electrodes participating in the study**

To analyze the capabilities of the method, different patterns were applied to the colored electrodes – Fig. 8, 9.

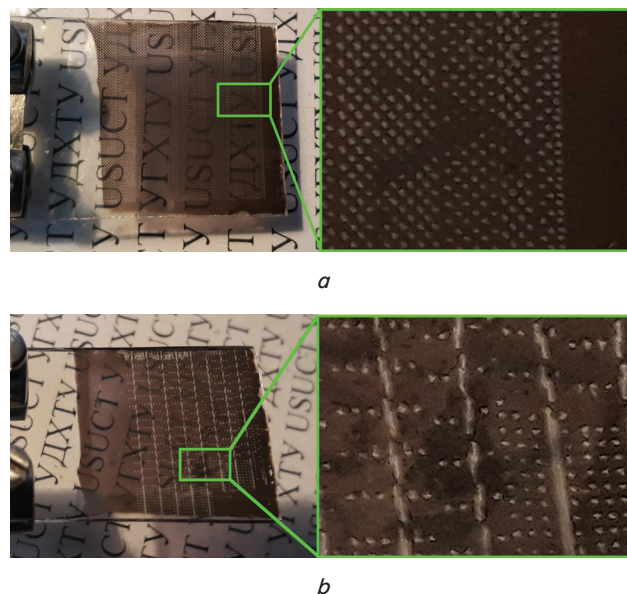


Fig. 8. Photographs of the electrodes of the laser-processed film with different patterns applied: a – pattern 1; b – pattern 2

Micrographs of film electrodes processed with laser radiation illustrated the possibility of obtaining patterns of varying complexity. In this case, the maximum resolution for drawing patterns corresponded to the beam diameter in our setup, i.e., 40 microns. In the photographs, you can also see that the drawing, consisting of small elements, is practically invisible without magnification. Thus, using laser processing, it is possible to make gradients, drawings, and inscriptions at the macro level. The average diameter of transparent spots in the experiments was determined using a micrometer ruler and was about 80–100 μm.

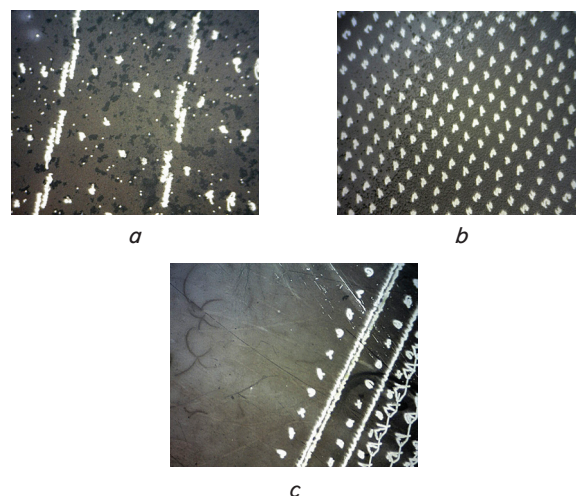


Fig. 9. Micrographs of the electrodes of the laser-processed film with different patterns applied (magnification 80x): a – pattern 1; b – pattern 2; c – pattern 3

To assess the morphology of the coatings processed with laser radiation, images of the electrode surface were obtained by electron microscopy Fig. 10.

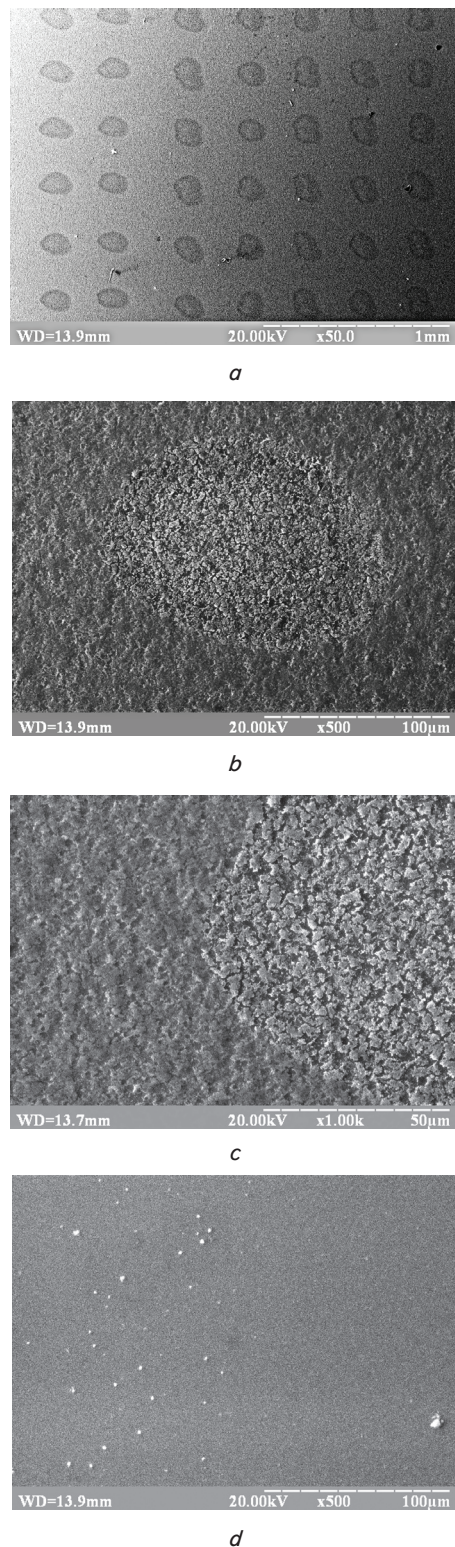


Fig. 10. Images of the surface morphology at different magnifications: *a*, *b*, *c* – the Laser sample; *d* – the Original sample

When analyzing the morphology, it can be seen that the places where the laser hit the film had a pronounced relief. In the figures, a clear boundary is determined between the

processed and unprocessed areas – Fig. 10, *c*. The place where the laser hit appeared to be composed of many scaly particles.

## 6. Discussion of the characteristics of processed and unprocessed film electrodes

Analysis of the data obtained in the study gives grounds to assert that in the case of using the described approach, it is possible to implement selective processing of  $\text{Ni}(\text{OH})_2$ -PVA films. This approach can be used in a variety of applications where nickel-based oxide-hydroxide compounds are used.

In addition, as can be seen from the measurements of the surface resistance, such processing either does not introduce or practically does not change this value – Fig. 7. In this case, such processing can be recommended as a selective modification of electrochromic and colored coatings deposited on electrically conductive transparent substrates such as FTO, ITO, AZO, etc. However, it is necessary to carry out extensive studies on the effect of laser radiation on conductive transparent oxide films.

Obviously, when processing with visible laser radiation, the  $\text{Ni}(\text{OH})_2$ -PVA layer is completely destroyed, since, after processing and cycling, the places processed with the laser do not change color and remain transparent. A possible mechanism for removing the film through the decomposition of nickel hydroxide and oxyhydroxide into oxide and water can also be proposed. According to the assumption put forward in this work, the laser beam causes instantaneous destruction of the film with the formation of water vapor. The latter, in turn, removes the film from the surface of the sample as a result of undermining the coating from the inside during a sharp expansion. It has also been noted that shorter laser exposure time (less than 3,000  $\mu\text{s}$ ) also leads to the removal of the  $\text{Ni}(\text{OH})_2$ -PVA coating. Given that the beam diameter is 40  $\mu\text{m}$ , it is easy to calculate the pulse energy equal to 37.5  $\text{J}/\text{cm}^2$ . This value is three orders of magnitude higher than the energy of lasers, which are used to perforate electrodes to improve their characteristics [36].

Despite some deterioration in optical characteristics associated with the removal of part of the electrochromic coating, the electrochemical characteristics are better for the electrode that has been processed with the laser. There can be several explanations for this behavior. The perforation of the electrode leads to an increase in the active surface through which ion exchange is carried out and, as a consequence, to an increase in the specific electrochemical characteristics.

On the other hand, the effect of increasing the adhesion of the electrochromic coating surface in the processed areas has been found – Fig. 11. In one of the experiments, only half of the electrode has been processed with laser radiation. During repeated cycling of this electrode in different modes, it has been noticed that a part of the film loses contact with the substrate and peels off (Fig. 11, *a*). After thorough rinsing with distilled water, only the part that has been processed with the laser remains on the surface (Fig. 11, *b*).

It is assumed that laser radiation removes a part of the coating, and the nearest layers to the point of the laser impact melt and increase adhesion to the substrate surface [37]. This is due to the fact that the coating contains polyvinyl alcohol with a glass transition temperature of about 85  $^{\circ}\text{C}$ . Thus, the second mechanism for improving the characteris-

tics may be associated with an increase in the adhesion of the hydroxide film to the FTO glass surface.

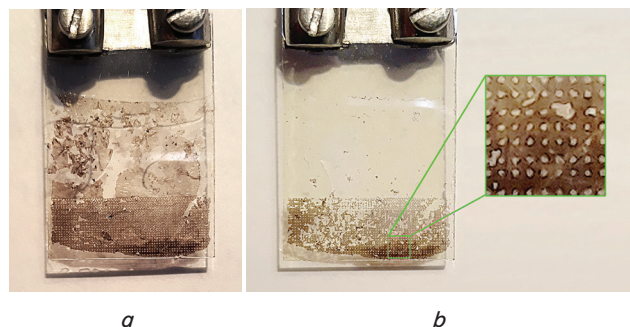


Fig. 11. Images of one of the laser-processed electrodes: *a* – after repeated cycling; *b* – followed by rinsing with water

In conclusion, it can be noted that by varying different processing parameters – the diameter of the laser beam, the applied pattern, the beam power, the duration of the processing, the wavelength of the laser radiation, when using a combination of lasers (visible, IR), it is possible to achieve the processing of multilayer multi-colored and transparent films. The use of laser power higher than those indicated in the study can negatively affect the selectivity of processing, since the electrically conductive layer, like glass, is not completely transparent and can also be heated. In this case, irreversible changes in their composition and structure can occur.

The boundary dimension of the accuracy of the patterns applied by the laser is determined by the laser wavelength. In the case of a red laser with a wavelength of 650 nm, the

maximum accuracy of the details of the drawings will not exceed approximately  $2\div 4$  of  $\lambda$ , i.e. 1.3–2.6  $\mu\text{m}$ . Thus, to increase the resolution, it is worth using shortwave radiation – a violet or ultraviolet laser. Considering that modern ultraviolet lasers have a wavelength of up to 160 nm, the approximate limiting resolution of the details of the applied drawings is 0.32–0.64  $\mu\text{m}$  (i.e., up to hundreds of nanometers).

Processing by this method can be organized on an industrial scale using high-power laser emitters and a system of mirrors that can turn the beam in the plane of the workpiece. In this case, processing will be much faster and quite cheap.

## 7. Conclusions

1. A selective method of laser radiation processing of the visible spectrum of thin colored films deposited on an electrically conductive substrate has been proposed. The processing parameters are as follows: the laser radiation wavelength – 650 nm, the pulse length – 3,000  $\mu\text{s}$ , and the pulse energy – 37.5 J/cm<sup>2</sup>.

2. It has been shown that a transparent electrically conductive layer is not destroyed by the laser irradiation and changes little in its characteristics. In this case, the surface resistance before and after processing is  $12.1\pm 0.9$  and  $14.4\pm 1.2$  Ohm/sq, respectively.

3. It has been shown that laser processing can improve the electrochemical and adhesive characteristics of composite Ni(OH)<sub>2</sub>-PVA films.

## References

1. Ash, B., Nalajala, V. S., Popuri, A. K., Subbaiah, T., Minakshi, M. (2020). Perspectives on Nickel Hydroxide Electrodes Suitable for Rechargeable Batteries: Electrolytic vs. Chemical Synthesis Routes. *Nanomaterials*, 10 (9), 1878. doi: <https://doi.org/10.3390/nano10091878>
2. Hall, D. S., Lockwood, D. J., Bock, C., MacDougall, B. R. (2015). Nickel hydroxides and related materials: a review of their structures, synthesis and properties. *Proceedings of the Royal Society A: Mathematical, Physical and Engineering Sciences*, 471 (2174), 20140792. doi: <https://doi.org/10.1098/rspa.2014.0792>
3. Firat, Y. E. (2020). Influence of current density on Al:NiO thin films via electrochemical deposition: Semiconducting and electrochromic properties. *Materials Science in Semiconductor Processing*, 109, 104958. doi: <http://doi.org/10.1016/j.mssp.2020.104958>
4. Kotok, V. A., Kovalenko, V. L., Zima, A. S., Kirillova, E. A., Burkov, A. A., Kobylinska, N. G. et. al. (2019). Optimization of electrolyte composition for the cathodic template deposition of Ni(OH)<sub>2</sub>-based electrochromic films on FTO glass. *ARPN Journal of Engineering and Applied Sciences*, 14 (2), 344–353. URL: [http://www.arpnjournals.org/jeas/research\\_papers/rp\\_2019/jeas\\_0119\\_7562.pdf](http://www.arpnjournals.org/jeas/research_papers/rp_2019/jeas_0119_7562.pdf)
5. Guo, Q., Yuan, J., Tang, Y., Song, C., Wang, D. (2021). Self-assembled PANI/CeO<sub>2</sub>/Ni(OH)<sub>2</sub> hierarchical hybrid spheres with improved energy storage capacity for high-performance supercapacitors. *Electrochimica Acta*, 367, 137525. doi: <http://doi.org/10.1016/j.electacta.2020.137525>
6. Kovalenko, V. L., Kotok, V. A., Sykchin, A., Ananchenko, B. A., Chernyad'ev, A. V., Burkov, A. A. et. al. (2020). Al<sup>3+</sup> Additive in the nickel hydroxide obtained by high-temperature two-step synthesis: Activator or poisoner for chemical power source application? *Journal of the Electrochemical Society*, 167 (10). doi: <http://doi.org/10.1149/1945-7111/ab9a2a>
7. Zeng, H., Zhang, W., Deng, L., Luo, J., Zhou, S., Liu, X. et. al. (2018). Degradation of dyes by peroxydisulfate activated by ternary CoFeNi-layered double hydroxide: Catalytic performance, mechanism and kinetic modeling. *Journal of Colloid and Interface Science*, 515, 92–100. doi: <http://doi.org/10.1016/j.jcis.2018.01.016>
8. Wang, Q., Wang, X., Tian, B. (2018). Catalytic performances of Ni/Fe layered double hydroxides fabricated via different methods in Fenton-like processes. *Water Science and Technology*, 77 (12), 2772–2780. doi: <https://doi.org/10.2166/wst.2018.265>
9. Zhao, Z., Sun, Y., Song, J., Li, Y., Xie, Y., Cui, H. et. al. (2021). Highly sensitive nonenzymatic glucose sensing based on multicomponent hierarchical NiCo-LDH/CCCH/CuF nanostructures. *Sensors and Actuators B: Chemical*, 326, 128811. doi: <https://doi.org/10.1016/j.snb.2020.128811>



10. Gualandi, I., Tessarolo, M., Mariani, F., Arcangeli, D., Possanzini, L., Tonelli, D. et. al. (2020). Layered double hydroxide-modified organic electrochemical transistor for glucose and lactate biosensing. *Sensors*, 20 (12), 3453. doi: <http://doi.org/10.3390/s20123453>
11. Zhao, J., Yang, H., Wu, W., Shui, Z., Dong, J., Wen, L. et. al. (2021). Flexible nickel–cobalt double hydroxides micro-nano arrays for cellular secreted hydrogen peroxide in-situ electrochemical detection. *Analytica Chimica Acta*, 1143, 135–143. doi: <http://doi.org/10.1016/j.aca.2020.11.047>
12. Zhou, J., Min, M., Liu, Y., Tang, J., Tang, W. (2018). Layered assembly of NiMn-layered double hydroxide on graphene oxide for enhanced non-enzymatic sugars and hydrogen peroxide detection. *Sensors and Actuators B: Chemical*, 260, 408–417. doi: <http://doi.org/10.1016/j.snb.2018.01.072>
13. Sun, J., Li, Y., Chen, C., Qi, T., Xia, D., Mao, W. et. al. (2018). Magnetic Ni/Fe layered double hydroxide nanosheets as enhancer for DNA hairpin sensitive detection of miRNA. *Talanta*, 187, 265–271. doi: <https://doi.org/10.1016/j.talanta.2018.05.037>
14. Koussi-Daoud, S., Planchat, A., Renaud, A., Pellegrin, Y., Odobel, F., Pauporté, T. (2017). Solvent-Templated Electrodeposition of Mesoporous Nickel Oxide Layers for Solar Cell Applications. *ChemElectroChem*, 4 (10), 2618–2625. doi: <https://doi.org/10.1002/celec.201700495>
15. Liu, X., He, Y., Zhang, G., Wang, R., Zhou, J., Zhang, L. et. al. (2020). Preparation and High Photocurrent Generation Enhancement of Self-Assembled Layered Double Hydroxide-Based Composite Dye Films. *Langmuir*, 36 (26), 7483–7493. doi: <https://doi.org/10.1021/acs.langmuir.0c01085>
16. Nie, Y., Yang, H., Pan, J., Li, W., Sun, Y., Niu, H. (2017). Synthesis of nano-Ni(OH)<sub>2</sub>/porous carbon composite as superior cathode materials for alkaline power batteries. *Electrochimica Acta*, 252, 558–567. doi: <https://doi.org/10.1016/j.electacta.2017.09.016>
17. Gonçalves, J. M., Martins, P. R., Araki, K., Angnes, L. (2021). Recent progress in water splitting and hybrid supercapacitors based on nickel-vanadium layered double hydroxides. *Journal of Energy Chemistry*, 57, 496–515. doi: <https://doi.org/10.1016/j.jechem.2020.08.047>
18. Sun, H., Zhang, W., Li, J.-G., Li, Z., Ao, X., Xue, K.-H. et. al. (2021). Rh-engineered ultrathin NiFe-LDH nanosheets enable highly-efficient overall water splitting and urea electrolysis. *Applied Catalysis B: Environmental*, 284, 119740. doi: <https://doi.org/10.1016/j.apcatb.2020.119740>
19. Cagnetta, G., Zhang, K., Zhang, Q., Huang, J., Yu, G. (2019). Augmented hydrogen production by gasification of ball milled polyethylene with Ca(OH)<sub>2</sub> and Ni(OH)<sub>2</sub>. *Frontiers of Environmental Science & Engineering*, 13 (1). doi: <https://doi.org/10.1007/s11783-019-1096-5>
20. Zhong, W., Huang, X., Lin, Y., Cao, Y., Wang, Z. (2021). Compact Co<sub>3</sub>O<sub>4</sub>/Co in-situ nanocomposites prepared by pulsed laser sintering as anode materials for lithium-ion batteries. *Journal of Energy Chemistry*, 58, 386–390. doi: <https://doi.org/10.1016/j.jechem.2020.10.013>
21. Acord, K. A., Dupuy, A. D., Scipioni Bertoli, U., Zheng, B., West, W. C., Chen, Q. N. et. al. (2021). Morphology, microstructure, and phase states in selective laser sintered lithium ion battery cathodes. *Journal of Materials Processing Technology*, 288, 116827. doi: <https://doi.org/10.1016/j.jmatprotec.2020.116827>
22. Park, J., Jeon, C., Kim, W., Bong, S.-J., Jeong, S., Kim, H.-J. (2021). Challenges, laser processing and electrochemical characteristics on application of ultra-thick electrode for high-energy lithium-ion battery. *Journal of Power Sources*, 482, 228948. doi: <https://doi.org/10.1016/j.jpowsour.2020.228948>
23. Li, Z., Jin, J., Yuan, Z., Yang, W. (2021). Surface modification of SiO<sub>x</sub> film anodes by laser annealing and improvement of cyclability for lithium-ion batteries. *Materials Science in Semiconductor Processing*, 121, 105300. doi: <https://doi.org/10.1016/j.mssp.2020.105300>
24. Zhang, C., Peng, Z., Huang, C., Zhang, B., Xing, C., Chen, H. et. al. (2021). High-energy all-in-one stretchable micro-supercapacitor arrays based on 3D laser-induced graphene foams decorated with mesoporous ZnP nanosheets for self-powered stretchable systems. *Nano Energy*, 81, 105609. doi: <https://doi.org/10.1016/j.nanoen.2020.105609>
25. Olejnik, A., Śliwiński, G., Karczewski, J., Ryl, J., Siuzdak, K., Grochowska, K. (2021). Laser-assisted approach for improved performance of Au-Ti based glucose sensing electrodes. *Applied Surface Science*, 543, 148788. doi: <https://doi.org/10.1016/j.apsusc.2020.148788>
26. Dotan, T., Berg, Y., Migliorini, L., Villa, S. M., Santaniello, T., Milani, P., Shacham-Diamand, Y. (2021). Soft and flexible gold microelectrodes by supersonic cluster beam deposition and femtosecond laser processing. *Microelectronic Engineering*, 237, 111478. doi: <https://doi.org/10.1016/j.mee.2020.111478>
27. Nagle Travessa, D., Vilas Boas Guedes, G., Capella de Oliveira, A., Regina Cardoso, K., Roche, V., Moreira Jorge Jr, A. (2021). The effect of surface laser texturing on the corrosion performance of the biocompatible β-Ti<sub>12</sub>Mo<sub>6</sub>Zr<sub>2</sub>Fe alloy. *Surface and Coatings Technology*, 405, 126628. doi: <https://doi.org/10.1016/j.surfcoat.2020.126628>
28. Chu, D., Yao, P., Huang, C. (2021). Anti-reflection silicon with self-cleaning processed by femtosecond laser. *Optics & Laser Technology*, 136, 106790. doi: <https://doi.org/10.1016/j.optlastec.2020.106790>

29. Kennedy-Hoyland, C., Aboud, D. G. K., Guermontprez, P., Kietzig, A.-M. (2021). Recovery behaviour of shape memory polymer with laser-inscribed hierarchical micro/nanoscale features. *Applied Surface Science*, 538, 147863. doi: <https://doi.org/10.1016/j.apsusc.2020.147863>
30. Kotok, V., Kovalenko, V. (2020). A study of the influence of polyvinyl pyrrolidone concentration in the deposition electrolyte on the properties of electrochromic Ni(OH)<sub>2</sub> films. *Eastern-European Journal of Enterprise Technologies*, 4 (6 (106)), 31–37. doi: <https://doi.org/10.15587/1729-4061.2020.210857>
31. Kotok, V., Kovalenko, V., Kirillova, E., Efimov, A., Sykchin, A., Kamalov, K. et. al. (2020). Study of the Ni(OH)<sub>2</sub> electrochromic properties of films deposited on fto glass with an additional conducting layer. *EUREKA: Physics and Engineering*, 4, 70–77. doi: <https://doi.org/10.21303/2461-4262.2020.001359>
32. Kotok, V., Kovalenko, V. (2020). Study of the Mn<sup>2+</sup> ions influence in the deposition electrolyte on the electrochromic properties of obtained Ni(OH)<sub>2</sub> films. *Eastern-European Journal of Enterprise Technologies*, 1 (6 (103)), 12–17. doi: <https://doi.org/10.15587/1729-4061.2020.194468>
33. Kotok, V., Kovalenko, V., Kovalenko, I., Stoliarenko, V., Vlasov, S., Ved, V. et. al. (2019). The study of activation impact during formation and testing of Ni(OH)<sub>2</sub> electrochromic films in the presence of Al<sup>3+</sup> and WO<sub>4</sub><sup>2-</sup> ions. *Eastern-European Journal of Enterprise Technologies*, 6 (5 (102)), 6–13. doi: <https://doi.org/10.15587/1729-4061.2019.185822>
34. Kotok, V. A., Malyshev, V. V., Solovov, V. A., Kovalenko, V. L. (2017). Soft Electrochemical Etching of FTO-Coated Glass for Use in Ni(OH)<sub>2</sub>-Based Electrochromic Devices. *ECS Journal of Solid State Science and Technology*, 6 (12), P772–P777. doi: <https://doi.org/10.1149/2.0071712jss>
35. Kotok, V., Kovalenko, V. (2018). A study of the effect of cycling modes on the electrochromic properties of Ni(OH)<sub>2</sub> films. *Eastern-European Journal of Enterprise Technologies*, 6 (5 (96)), 62–69. doi: <https://doi.org/10.15587/1729-4061.2018.150577>
36. Pröll, J., Kim, H., Piqué, A., Seifert, H. J., Pflöging, W. (2014). Laser-printing and femtosecond-laser structuring of LiMn<sub>2</sub>O<sub>4</sub> composite cathodes for Li-ion microbatteries. *Journal of Power Sources*, 255, 116–124. doi: <https://doi.org/10.1016/j.jpowsour.2013.12.132>
37. Kotok, V., Kovalenko, V. (2020). A study of the increased temperature influence on the electrochromic and electrochemical characteristics of Ni(OH)<sub>2</sub>-PVA composite films. *Eastern-European Journal of Enterprise Technologies*, 3 (6 (105)), 6–12. doi: <https://doi.org/10.15587/1729-4061.2020.205352>