

A STUDY OF ELECTROCHROMIC Ni(OH)₂ FILMS OBTAINED IN THE PRESENCE OF SMALL AMOUNTS OF ALUMINUM

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Дослідження відноситься до синтезу електрохромних плівок на основі гідроксиду нікелю з алюмінієм в якості допанта. Осадження велося катодним темплатним методом у присутності полівінілового спирту з розчинів, що містять 0,01 M Ni(NO₃)₂ і Al(NO₃)₃. Нітрат алюмінію вводився у різній кількості: 0,138, 0,257 і 0,550 мМ. При цьому необхідна концентрація алюмінію була розрахована з теоретичних обґрунтованих міркувань і з використанням рівняння, що виражає закон Фарадея. При цьому всі отримані плівки проявляли електрохімічну активність, а плівка, осаджена з розчину, який містив 0,01 M Ni(NO₃)₂ і 0,138 мМ Al(NO₃)₃ продемонструвала найкращі результати. При цьому, ця плівка працювала обернено і мала більш високе значення глибини затемнення в процесі циклування – 81 %. У свою чергу, плівка отримана при тих же умовах, але без допанта давала значення глибини затемнення – 75,8 %.

Всі плівки, отримані в присутності алюмінію в розчині електроосадження, при затемненні і особливо при освітленні, мали меншу швидкість процесу в порівнянні з еталонним зразком, отриманим без допанта.

Дослідження морфології отриманих плівок показало, що остання мало відрізняється. При цьому плівка, отримана в присутності 0,138 мМ Al(NO₃)₃, мала сферичні освіти на поверхні. Також було показано, що морфологія основи, в якості якої виступало скло з нанесеним покриттям SnO₂:F, значно відрізнялися від морфології плівок отриманих без і допантом.

Крім того, було показано, що плівка, отримана з розчину з 0,01 M Ni(NO₃)₂ і 0,138 мМ Al(NO₃)₃, мала в своєму складі алюміній. Масове відношення алюмінію до нікелю в межах поверхні плівки коливалось від 1:10,23 до 1:6,44

Ключові слова: Ni(OH)₂, гідроксид нікелю, електрохромізм, електроосадження, циклічна вольтамперометрія, алюміній, добуток розчинності

1. Introduction

Electrochromism is a phenomenon that is characterized by a change of material's optical properties under applied current and had been studied for over half a century [1, 2]. Films of oxide, hydroxide, some polymer and other compounds deposited on conductive transparent substrates can reversibly change their optical properties when polarized with electrical current and are called electrochromic compounds. Electrochromic compounds can change a wide range of optical characteristics: light absorption, color, reflectivity [3, 4]. Electrochromic "smart" windows are considered the most promising application for electrochromic materials. Nevertheless, this is not the only application for electrochromic materials. Other possible applications include interactive interior decoration, indicators, construction of meeting rooms, patient examination rooms, cinemas, car window shading, etc. A wide range of applications for electrochromic windows

leads to the development of new electrochromic materials and film deposition methods for new and classic materials. Deposition of electrochromic materials is being developed towards the formation of 0D, 1D, 2D and 3D nanosized materials [5, 6]. In addition, the introduction of some amounts of foreign cations into the crystal lattice of oxide and hydroxide materials alters crystal parameters which can result in significant changes in electrochemical and electrochromic behavior [7, 8].

Nevertheless, despite significant progress in the development of electrochromic materials, there is still now widespread use of electrochromic devices. This is mainly due to their high cost which varies from 100 to 800 US\$ for square meter [9, 10]. Such cost limits the benefits from using electrochromic devices and threatens their mass adoption. Therefore, the development and improvement of new and classic methods for deposition of electrochromic materials with improved characteristics is the number one priority of researchers in this field.

2. Literature review and problem statement

Doping of oxides and hydroxides is a common approach for improving their electrochemical and electrochromic characteristics. Doping by “foreign” cations during synthesis results in deformation of the crystal lattice, resulting in defects, due to different sizes of ions. Such defects improve the reactivity of the material, which alters electrochromic and other properties of materials.

For instance, the authors of [11] describe the WO₃ film doped with cobalt and nickel which showed high specific characteristics. The obtained film also consumed less power for coloring and had a higher switching speed.

Other authors [12] synthesized NiO doped with 1 % cobalt. Such insignificant amount of the dopant resulted in significant improvement of electrochromic properties. In comparison to undoped NiO, the cobalt doped film had lower switching time – 3.4 s (5.4 s undoped). The films also showed high reversibility, high coloration degree of up to 88.3 % and higher coloration efficiency of 47.7 cm²C⁻¹.

Titanium dioxide-doped WO₃ (13–38 %) deposited on FTO via spray pyrolysis showed good uniformity, transparency and adhesion to the substrate [13]. The TiO₂-doped film demonstrated high specific electrochromic characteristics, high reversibility of coloration-bleaching and double the coloration degree of pure TiO₂.

The paper [14] is another example of doping. Its authors propose several dopants – Zr, Sn, Li, Ti and Mo for electrochromic Nb₂O₅ films. It is described that depending on the dopant, its content and sintering temperature, the resulting films produced different colors on coloration (Li⁺ intercalation): gray, brown or blue.

Aluminum is often used as a dopant, including as a dopant for the subject of this paper. For instance, Chinese researchers describe a positive effect of aluminum as a dopant, when added to mixed nickel boron oxide (Al_xB_{0.15}NiO). The advantages of such films are their electrochemical characteristics and excellent transparency in the bleached state [15].

Electrochromic films containing aluminum can be activated under the ozone atmosphere [16]. The authors describe improved switching speed, transparency and reaction kinetics after ozone treatment.

Formation of Ni(OH)₂ films with high aluminum content was attempted in [17]. The authors describe that double Ni-Al hydroxide, resulted from electrochemical deposition from the solution containing nickel and aluminum salts, is inert. Their hypothesis is that film inertness is caused by poisoning of free Al³⁺ ions that were not incorporated into the precipitate.

Another example of aluminum used as a dopant in electrochromic materials is the work [18], in which the authors study the Al-doped ZnO film, which shows electrochromic properties in the near infrared spectrum.

The paper [19] is devoted to the study of WO₃ film modified with Al-doped ZnO. The authors note high electrochromic properties of the obtained nanocomposite material, which are, most likely, related to improved conductivity.

Doping is widely used in other scientific fields. For instance, the paper [20] describes graphene doped with boron and nitrogen showing a super high rate of charge and discharge when used as anodic material of lithium batteries. At the same time, another paper [21] describes lithium-doped three-dimensional covalent organic networks as a promising material for storing large amounts of hydrogen.

From the literature review, it follows that doping is a widespread method for the modification of a wide variety of materials. However, no studies devoted to electrochemical deposition of nickel hydroxide films with small amounts of aluminum have been found. Obviously, the use of small concentrations is generally not studied, as possible deposition chemism during doping is not studied in detail. Based on the literature review, the authors achieved positive results primarily by trial and error. Therefore, these questions became the basis for the conducted research.

3. The aim and objectives of the study

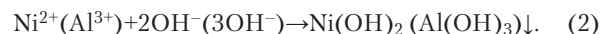
The aim of the study is the preparation and investigation of thin electrochromic Ni(OH)₂ films, doped with small amounts of aluminum. To achieve the set aim, the following objectives were formulated:

- electrochemical synthesis of nickel hydroxide films from solutions containing small amounts of the dopant;
- electrochemical and optical analysis of the obtained films;
- evaluation of the influence of the dopant on morphology and other characteristics.

4. Materials, methods and some theoretical bases for deposition of electrochromic Al-doped Ni(OH)₂ films

4.1. Theoretical basis for small dopant concentration in electrodeposition electrolyte

It is known; that the order of precipitation for insoluble compounds is determined by the solubility product (SP). In case when two different insoluble compounds can precipitate upon addition of the precipitant, the first compound to precipitate is the one with lower SP. If the difference between the SP of two insoluble compounds is low (lower than an order), then the rate at which the precipitant is added shouldn't have a major impact of the order at which precipitates are formed. In case when the difference in the SP is high (orders), the less soluble compounds would precipitate first when the precipitant is added. Further addition of the precipitant (after precipitation of less soluble compound) would result in precipitation of second compounds (more soluble, higher SP). Electrodeposition should be conducted at a very low current density (0.1 mA/cm² [22–25]). The electrodeposition occurs in two stages – electrochemical generation of OH⁻ ions at the cathode (1), followed by the chemical formation of Ni(OH)₂ (2).



Current density is such that the generation rate of OOH⁻ ions is small since they play the role of precipitant. For the solution containing Ni²⁺ and Al³⁺ ions, Al(OH)₃ would precipitate first (SP(Al(OH)₃)=1.0·10⁻²³–1.0·10⁻³²), followed by Ni(OH)₂ (SP(Ni(OH)₂)=2.0·10⁻¹⁵–6.3·10⁻¹⁸).

For aluminum to be incorporated into the nickel film, its concentration should be lowered significantly. Al(OH)₃ would precipitate initially, and after some time the concentration in the diffusion layer near the electrode would be low enough, which would allow for simultaneous precipitation

of both cations with the formation of a doped compound. Nevertheless, if the concentration of Al^{3+} ions is higher than some limit value, the entire current would be used for deposition of $\text{Al}(\text{OH})_3$, and no $\text{Ni}(\text{OH})_2$ deposition would occur. This limit concentration ($C_{\text{Al}^{3+}}^F$) can be calculated using formulas (3) and (4). It should be noted; that (3) is a modified expression of Faraday's law. The following constants and parameters were used in the calculation: δ_{DL} (assumed thickness of the diffusion layer)=0.075 cm, current density $i=0.1 \text{ mA/cm}^2$, electrode area $S=1 \text{ cm}^2$, $\tau=1/6 \text{ h}$ (10 min) [22–25].

$$v_{\text{OH}^-} = \frac{N_{\text{OH}^-}}{z \cdot F} \cdot i \cdot S \cdot \tau \cdot CE, \quad (3)$$

$$C_{\text{Al}^{3+}}^F = \frac{v_{\text{OH}^-}}{3 \cdot V} = \frac{v_{\text{OH}^-}}{3 \cdot \delta_{\text{DL}} \cdot S}, \quad (4)$$

where v_{OH^-} – number of OH^- moles which are produced during electrolysis, mole; N_{OH^-} – number of OH^- moles according to reaction (1), 2; z – number of electrons according to reaction (1), 2; F – Faraday constant, 26,8 A·h/g-eq.; CE – current yield according to equation (1) and (2), 1; V – volume of the diffusion layer near the electrode with the area of 1 cm^2 .

Calculations show that the limit concentration of Al^{3+} is equal to 2.76 mM. However, the calculations do not account for migration and diffusion of aluminum ions due to the electric field and the difference between concentrations in volume and near the electrode. These two processes can partially compensate for the removal of aluminum ions. Thus, this theoretical concentration does not exclude the formation of $\text{Al}(\text{OH})_3$ alone. In order to approximately account for concentration increase due to diffusion and migration of Al^{3+} into the diffusion layer, the calculated concentration was divided by 5, resulting in 0.55 mM. This was taken as the base dopant (Al^{3+} ions) concentration in the electrolyte. Lower dopant concentrations were also tested.

4. 2. Materials and analysis methods for the study of films deposited from electrolytes containing different concentrations of Al^{3+}

Analytical grade reagents were used in the study. All solutions were prepared with distilled water. FTO glass $7.5 \Omega/\square$ (China, Zhuhai Kaivo Optoelectronic Technology Co.) was used as a substrate. Before the deposition, the FTO glass was treated as follows: washing with wet sodium bicarbonate, washing with distilled water, ultrasonic treatment in ethanol (50 W, 41.5 kHz), 400 s. Drying was conducted in the air atmosphere at room temperature.

Electrodeposition was conducted in a single compartment acrylic cell [26–28]. The working area of the FTO glass was $S=4 \text{ cm}^2$ ($2 \times 2 \text{ cm}$). All films were deposited cathodically at $i=0.1 \text{ mA/cm}^2$ for 10 min. $\text{Ni}(\text{NO}_3)_2$ 0.1 M with 5 % PVA, with the addition of aluminum nitrate (Table 1).

In all experiments, the electrode with freshly deposited films was washed by soaking in distilled water for 10 min.

Drying of the obtained films was conducted in air at room temperatures. Experimental data was recorded using the Elins P8 potentiostat and a custom cell for recording cyclic voltamperograms and bleaching-coloration curves [26–28].

The FTO glass with deposited nickel hydroxide film was used as a working electrode.

Nickel foil was used as a counter electrode and $\text{Ag}/\text{Ag}-\text{Cl}$ (KCl sat.) was used as a reference electrode.

All cyclic voltamperograms and coloration bleaching curves for $\text{Ni}(\text{OH})_2$ films were recorded under the same conditions: potential interval $E_1=201 \text{ mV}$ to $E_2=+751 \text{ mV}$, scan rate 1 mV/s , 5 cycles.

Additionally, after cyclic voltamperometry each film was colored potentiodynamically, starting at 201 mV to $+751 \text{ mV}$ at 1 mV/s , to evaluate their quality.

Morphology of composite PVA- $\text{Ni}(\text{OH})_2$ films was studied using the JEOL JSM-6510LV (Japan) scanning electron microscope (SEM) and NT-MTD “NTegra” (Russia) atomic-force microscope (AFM).

5. Analysis and comparison of optical and electrochemical properties of $\text{Ni}(\text{OH})_2$ films prepared with different amounts of Al^{3+}

For comparison, a reference sample was prepared from a solution of 0.01 M nickel nitrate with 5 % PVA. The solution did not contain any aluminum ions – Ni-Al-000.

Fig. 1 shows the cyclic voltamperometry (CVA) curve, coloration bleaching curve and the photograph of the colored film after cycling. Analysis of the cyclic voltamperogram allows to conclude that the film is fully operational starting from the second cycle, the peaks are rather well-defined, with the peak position and value being almost constant, after the second cycle. This indicated good cycling stability. The peak values are not equal, which indicated the incomplete reversibility of the electrode. It should be noted that peak height is a semi-quantitative parameter which determines the area under the CVA curve. The area between the X-axis and the curve characterizes the amount of electricity involved in the process. Thus, peak height can be used for semi-quantitative comparison of samples, in terms of electrochemical characteristics.

The coloration-bleaching curve of the reference film shows good reversibility of the electrochromic process and high coloration degree (Fig. 1, b). It is worth to note that the coloration degree is equal to the difference between transparency (T , %) in bleached and colored states. The average coloration degree is equal to 75.8 %. In each experiment, a photograph of the film in the colored state was taken for additional analysis. Fig. 1, c shows the photograph of the reference film in the colored state. The photograph shows that the film is colored uniformly and has no defects – spots, light regions, non-covered parts.

Table 1

Solutions used for film deposition and respective film labels

Solution No.	Composition	Film label
1	0.01 M $\text{Ni}(\text{NO}_3)_2$, 5 % PVA	Ni-Al-000
2	0.01 M $\text{Ni}(\text{NO}_3)_2$, 0.138 mM $\text{Al}(\text{NO}_3)_3$, 5 % PVA	Ni-Al-138
3	0.01 M $\text{Ni}(\text{NO}_3)_2$, 0.275 mM $\text{Al}(\text{NO}_3)_3$, 5 % PVA	Ni-Al-275
4	0.01 M $\text{Ni}(\text{NO}_3)_2$, 0.55 mM $\text{Al}(\text{NO}_3)_3$, 5 % PVA	Ni-Al-550

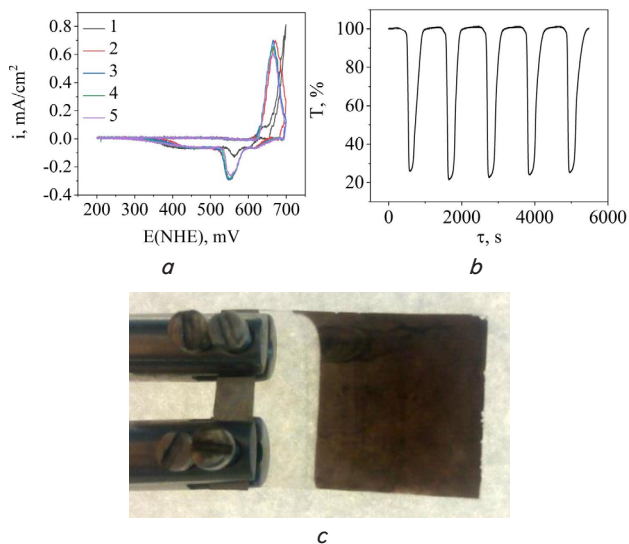


Fig. 1. Results for the Ni-Al-000 film:

a – cyclic voltamperometry curve, *b* – bleaching coloration curve, *c* – photograph of the electrode in the colored state

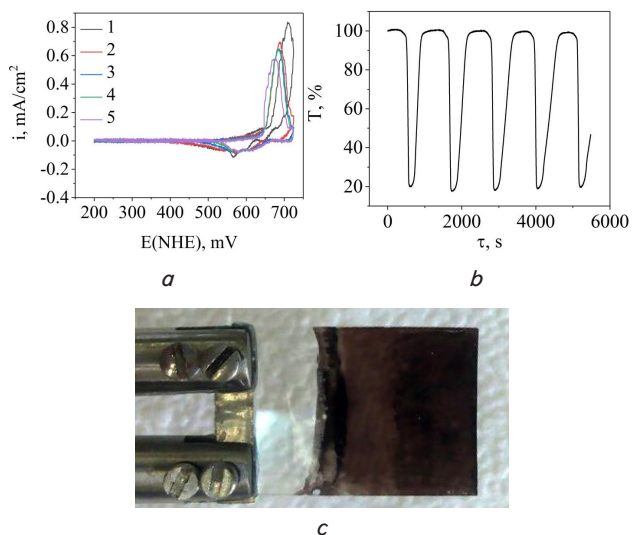


Fig. 2. Results for the Ni-Al-138 film:

a – cyclic voltamperometry curve, *b* – bleaching coloration curve, *c* – photograph of the electrode in the colored state

Cycling results of the film deposited from the solution with the lowest concentration of aluminum nitrate (0.138 mM $\text{Al}(\text{NO}_3)_3$) are shown in Fig. 2. Analysis of CVA allows to conclude about some degradation – anodic current densities are decreasing. This means that the capacity used for oxidation of $\text{Ni}(\text{OH})_2$ to NiOOH is also decreasing. The area under the cathodic part of the curve is rather small, which indicates the low release of current. On the other hand, the latter conclusion may not be entirely correct as the shape of the cathodic peak (capacity) is complex, and it may be greater. Nevertheless, this sample is clearly worse than the reference sample, as it has lower cathodic peak current density (i_k) and has roughly the same value of anodic peak current density (i_a) – Fig. 1.

The coloration-bleaching curve, Fig. 2, *b*, demonstrated a greater coloration degree than that of the reference sample – 81 %. The value of the coloration degree is almost constant. It should be noted that with lower anodic peak values the

bleaching time increases at a constant coloration degree. Film's peaks in the bleached state have no pronounced sharp angles which indicates longer bleaching and coloration times.

The photograph of this film is shown in Fig. 2, *c*. The film turned out to be rather uniform with the exception of a few dark regions.

The results for the film deposited in the presence of higher aluminum concentration (0.275 mM $\text{Al}(\text{NO}_3)_3$) are shown in Fig. 3. The electrochemical characteristics of this film indicate degradation as cathodic peaks are decreasing. However, in comparison to the CVA of Ni-Al-138, this film has constant anodic peaks. The values of peak currents (anodic and cathodic) are similar to the values of the reference film.

The coloration-bleaching curve is also similar to that of the reference sample. Coloration depth is almost constant, while switching times are increasing in comparison to the reference film. In comparison to the film deposited in the presence of 0.138 mM $\text{Al}(\text{NO}_3)_3$, the coloration degree decreased to 75 %.

The photograph of the film deposited in the presence of 0.138 mM $\text{Al}(\text{NO}_3)_3$ (Fig. 3, *c*) shows that the film is rather non-uniform. The film has a large number of transparent spots.

Data for the sample prepared in the presence of the highest aluminum nitrate concentration (0.55 mM) is shown in Fig. 4. The CVA shows a decrease of anodic peaks with each cycle (similar to the film deposited at 0.275 mM). Current values are lower than those of the reference sample. The increasing interval between peaks is also observed.

The coloration-bleaching curve shows that coloration and bleaching times are different. The coloration time is shorter, while more time is required for bleaching which increases with each cycle. Compared to the reference film, coloration degree is lower by ~10 %, it is also the lowest among all films prepared in the presence of aluminum.

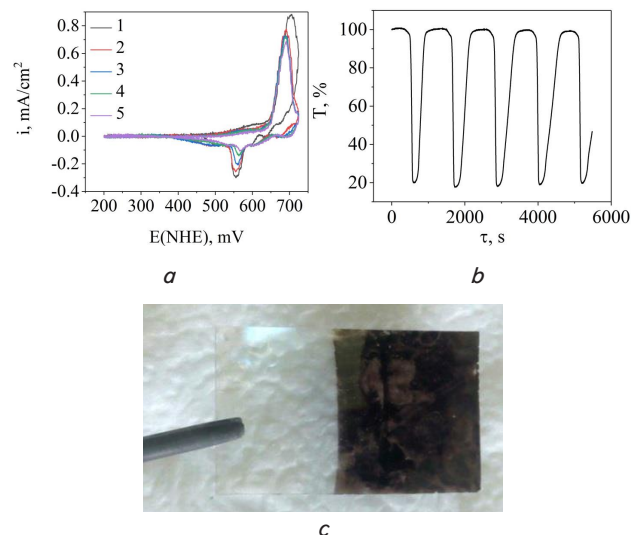


Fig. 3. Results for the Ni-Al-275 film:

a – cyclic voltamperometry curve, *b* – bleaching coloration curve, *c* – photograph of the electrode in the colored state

Fig. 4 shows the photograph of the Ni-Al-550 film. The film uniformity is low, there are transparent regions, which are likely uncolored parts of the film. Presumably, these can be aluminum compounds which is most likely $\text{Al}(\text{OH})_3$.

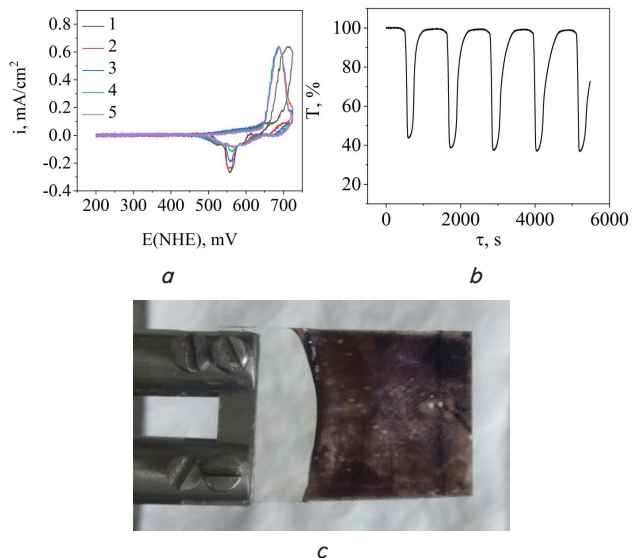


Fig. 4. Results for the Ni-Al-550 film: *a* – cyclic voltamperometry curve, *b* – bleaching coloration curve, *c* – photograph of the electrode in the colored state

5.1. Comparative analysis of morphology of Ni(OH)₂ prepared from solutions with different concentrations of Al³⁺

Scanning electron microscopy (SEM) analysis was conducted for the reference film and the film with the addition of 0.138 mM aluminum nitrate, which demonstrated the best electrochromic properties. SEM images for the reference sample and Ni-Al-138 are shown in Fig. 5, 6.

The SEM results allow to draw conclusions regarding sample morphology and size of irregularities. The sizes of irregularities for the first and second films are about 160 nm.

The films have similar morphology, however, the surface of the Ni-Al-138 film contains spherical inclusions.

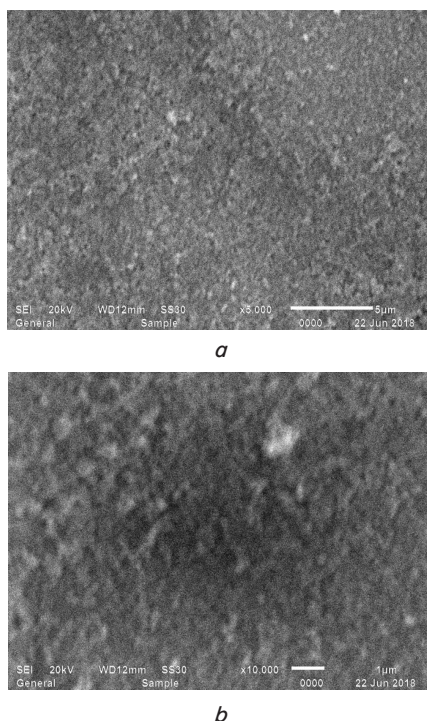


Fig. 5. Morphology of the Ni-Al-000 film: *a* – ×5000 magnification; *b* – ×10000 magnification

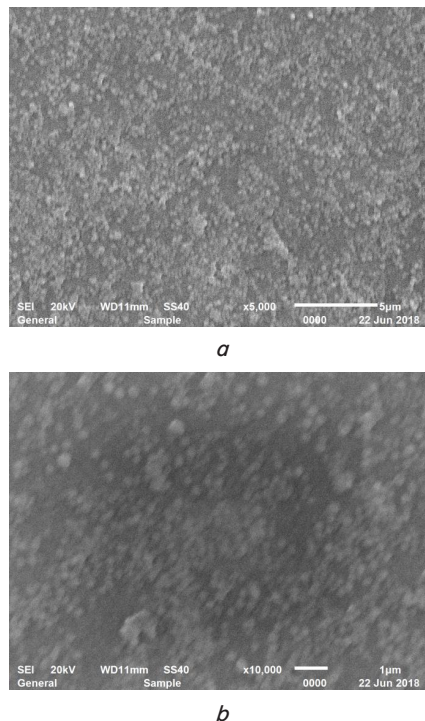


Fig. 6. Morphology of the Ni-Al-138 film: *a* – ×5000 magnification; *b* – ×10000 magnification

Atomic force microscopy (AFM) images were recorded for the substrate (FTO glass), reference sample and film deposited in the presence of 0.138 mM Al³⁺. Fig. 7–9 show AFM images of the substrate, Ni-Al-000, and Ni-Al-138 films. The surface of FTO is rough with peaks of up to 25 nm.

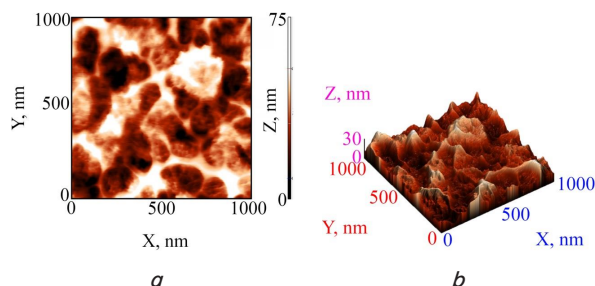


Fig. 7. Substrate (FTO glass) morphology: *a* – area 1000×1000 nm (250 nm maximum height); *b* – 3d model of the area

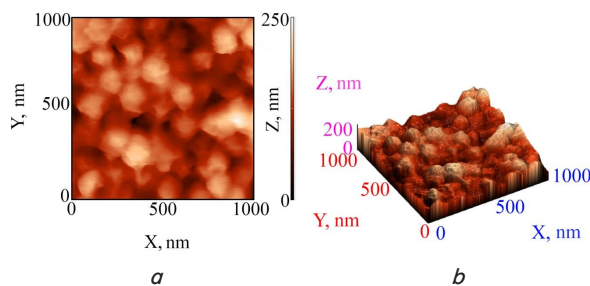


Fig. 8. Morphology of the Ni-Al-000 film: *a* – area 1000×1000 nm (250 nm maximum height); *b* – 3d model of the area

Comparison between morphologies of the reference sample (Ni-Al-000) and the film prepared in the presence

of 0.138 mM aluminum nitrate allows to conclude that both samples have similar surface relief. They both have less pronounced relief (compared to the bare substrate) with rounded shapes. The average size of protrusions for the reference sample is smaller than that for the sample with aluminum – 50 and 100 nm respectively. At the same time, the length of irregularities for the reference film and the film prepared in the presence aluminum is greater in comparison to the bare substrate – 120, 100 and 200 nm respectively.

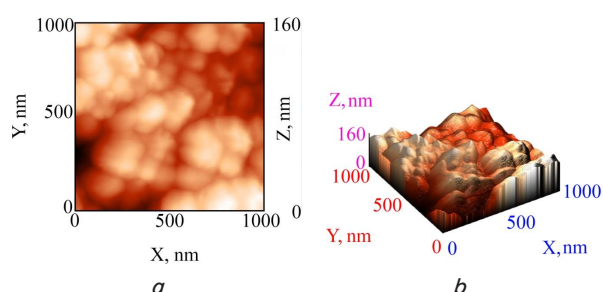


Fig. 9. Morphology of the Ni-Al-138 film:
 a – area 1000×1000 nm (250 nm maximum height);
 b – 3d model of the area

6. Discussion of data obtained for the studied films

The results of the conducted experiments confirm the hypothesis that dopants forming low-solubility compounds with the SP that is significantly different from the main precipitate should be introduced in small amounts. The previous work in a similar direction yielded a negative result – electrochemical activity and electrochemical properties were absent completely [17]. Additionally, it became possible to approximately evaluate and experimentally find the optimal concentration of Al^{3+} ions. Additionally, the results of energy-dispersive spectroscopy confirm the incorporation of aluminum ions into the film structure. The mass ratio of aluminum to nickel in the Ni–Al-138 film varied between 1:10.23 and 1:6.44.

It should be noted that this approach of introducing small amounts of dopants is applicable for cases when the precipitant is fed in small amounts at low rates. Otherwise (when the precipitant is fed in large amounts), coprecipitation is possible at high concentrations. An example of that is the chemical preparation of hydroxides (oxides). Such methods involve the addition of excess amounts of the concentrated precipitant into the actively stirred solution of mixed metal salts.

Obviously, the experimentally obtained concentration is related to the fact that aluminum is electrochemically inert,

and low concentrations of Al^{3+} in the electrolyte result in film activation, as described in paragraph 2. Further increase of dopant concentration in the electrolyte would result in even greater aluminum content in the film. However, in this case the number electrochemically active nickel ions would decrease, which would result in lower electrochemical and electrochromic characteristics of the film. On the other hand, specific characteristics relative to the mass of nickel would be higher. It should be noted that the studied system behaved predictably – in the presence of minimum aluminum concentration in the solution, an increase in specific film characteristics occurred. Further increase of $Al(NO_3)_3$ concentration in the electrolyte resulted in a gradual decrease of film's electrochromic properties.

Thus, it was found that the idea of doping nickel hydroxide films by introducing small concentrations of Al^{3+} into the electrolyte is correct. This approach can be used for a wide range of precipitation methods of low-solubility compounds with dopants, where precipitant feed (synthesis) rate is low. The limitation of the method is a low range of concentrations which can only be approximated. The exact determination can only be done experimentally under specific conditions. The theoretical basis allows to say that the film composition at the start and end of synthesis can differ significantly. This can be an interesting approach for preparing inhomogeneous materials, the composition of which varies across the depth.

7. Conclusions

A hypothesis on that dopants forming compounds with the SP lower than that of the main precipitate should be introduced in low amounts during electrodeposition, is confirmed.

The addition of aluminum nitrate to the electrodeposition electrolyte has a positive effect on the coloration degree of the resulting film. The coloration degree of the film prepared from the electrolyte with the addition of 0.138 mM $Al(NO_3)_3$ is 81 %. The reference sample without additives demonstrated a lower value of 75.8 %.

Increasing aluminum concentration from 0.275 to 0.550 mM $Al(NO_3)_3$ resulted in the worsening of electrochromic properties and appearance of the film.

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References

1. Deb S. K. A Novel Electrophotographic System // Applied Optics. 1969. Vol. 8, Issue S1. P. 192–195. doi: <https://doi.org/10.1364/ao.8.000192>
2. Hurditch R. Electrochromism in hydrated tungsten-oxide films // Electronics Letters. 1975. Vol. 11, Issue 7. P. 142. doi: <https://doi.org/10.1049/el:19750109>
3. Rosseinsky D. R., Mortimer R. J. Electrochromic Systems and the Prospects for Devices // Advanced Materials. 2001. Vol. 13, Issue 11. P. 783–793. doi: [https://doi.org/10.1002/1521-4095\(200106\)13:11<783::aid-adma783>3.0.co;2-d](https://doi.org/10.1002/1521-4095(200106)13:11<783::aid-adma783>3.0.co;2-d)
4. Livage J., Ganguli D. Sol–gel electrochromic coatings and devices: A review // Solar Energy Materials and Solar Cells. 2001. Vol. 68, Issue 3-4. P. 365–381. doi: [https://doi.org/10.1016/s0927-0248\(00\)00369-x](https://doi.org/10.1016/s0927-0248(00)00369-x)
5. Recent Advances in Electrochromic Smart Fenestration / Cai G., Eh A. L.-S., Ji L., Lee P. S. // Advanced Sustainable Systems. 2017. Vol. 1, Issue 12. P. 1700074. doi: <https://doi.org/10.1002/adsu.201700074>

6. High performing smart electrochromic device based on honeycomb nanostructured h-WO₃ thin films: hydrothermal assisted synthesis / Kondalkar V. V., Mali S. S., Kharade R. R., Khot K. V., Patil P. B., Mane R. M. et. al. // Dalton Transactions. 2015. Vol. 44, Issue 6. P. 2788–2800. doi: <https://doi.org/10.1039/c4dt02953d>
7. Monk P. The effect of doping electrochromic molybdenum oxide with other metal oxides: Correlation of optical and kinetic properties // Solid State Ionics. 1995. Vol. 80, Issue 1-2. P. 75–85. doi: [https://doi.org/10.1016/0167-2738\(95\)00130-x](https://doi.org/10.1016/0167-2738(95)00130-x)
8. Özer N., Sabuncu S., Cronin J. Electrochromic properties of sol-gel deposited Ti-doped vanadium oxide film // Thin Solid Films. 1999. Vol. 338, Issue 1-2. P. 201–206. doi: [https://doi.org/10.1016/s0040-6090\(98\)00974-2](https://doi.org/10.1016/s0040-6090(98)00974-2)
9. Smart windows: electrochromic windows for building optimisation. URL: https://www.sageglass.com/sites/default/files/masdar_technology_journal_issue_5_september_2018_smart_windows.pdf
10. Azens A., Granqvist C. Electrochromic smart windows: energy efficiency and device aspects // Journal of Solid State Electrochemistry. 2003. Vol. 7, Issue 2. P. 64–68. doi: <https://doi.org/10.1007/s10008-002-0313-4>
11. Shen P. K. The Performance of Electrochromic Tungsten Trioxide Films Doped with Cobalt or Nickel // Journal of The Electrochemical Society. 1991. Vol. 138, Issue 9. P. 2778–2783. doi: <https://doi.org/10.1149/1.2086054>
12. Co-doped NiO nanoflake array films with enhanced electrochromic properties / Zhang J., Cai G., Zhou D., Tang H., Wang X., Gu C., Tu J. // Journal of Materials Chemistry C. 2014. Vol. 2, Issue 34. P. 7013–7021. doi: <https://doi.org/10.1039/c4tc01033g>
13. Electrochromic properties of spray deposited TiO₂-doped WO₃ thin films / Patil P. S., Mujawar S. H., Inamdar A. I., Sadale S. B. // Applied Surface Science. 2005. Vol. 250, Issue 1-4. P. 117–123. doi: <https://doi.org/10.1016/j.apsusc.2004.12.042>
14. Schmitt M., Aegerter M. A. Electrochromic properties of pure and doped Nb₂O₅ coatings and devices // Electrochimica Acta. 2001. Vol. 46, Issue 13-14. P. 2105–2111. doi: [https://doi.org/10.1016/s0013-4686\(01\)00380-2](https://doi.org/10.1016/s0013-4686(01)00380-2)
15. Electrochromic properties of Al doped B-substituted NiO films prepared by sol-gel / Lou X., Zhao X., Feng J., Zhou X. // Progress in Organic Coatings. 2009. Vol. 64, Issue 2-3. P. 300–303. doi: <https://doi.org/10.1016/j.porgcoat.2008.09.006>
16. Hole Doping in Al-Containing Nickel Oxide Materials To Improve Electrochromic Performance / Lin F., Nordlund D., Weng T.-C., Moore R. G., Gillaspie D. T., Dillon A. C. et. al. // ACS Applied Materials & Interfaces. 2013. Vol. 5, Issue 2. P. 301–309. doi: <https://doi.org/10.1021/am302097b>
17. Kotok V., Kovalenko V. Electrochromism of Ni(OH)₂ films obtained by cathode template method with addition of Al, Zn, Co ions // Eastern-European Journal of Enterprise Technologies. 2017. Vol. 3, Issue 12 (87). P. 38–43. doi: <https://doi.org/10.15587/1729-4061.2017.103010>
18. Near-Infrared Spectrally Selective Plasmonic Electrochromic Thin Films / Garcia G., Buonsanti R., Llordes A., Runnerstrom E. L., Bergerud A., Milliron D. J. // Advanced Optical Materials. 2013. Vol. 1, Issue 3. P. 215–220. doi: <https://doi.org/10.1002/adom.201200051>
19. A novel nanocomposite of WO₃ modified Al-doped ZnO nanowires with enhanced electrochromic performance / Bi Z., Zhang S., Xu X., Hu X., Li X., Gao X. // Materials Letters. 2015. Vol. 160. P. 186–189. doi: <https://doi.org/10.1016/j.matlet.2015.07.107>
20. Doped Graphene Sheets As Anode Materials with Superhigh Rate and Large Capacity for Lithium Ion Batteries / Wu Z.-S., Ren W., Xu L., Li F., Cheng H.-M. // ACS Nano. 2011. Vol. 5, Issue 7. P. 5463–5471. doi: <https://doi.org/10.1021/nn2006249>
21. Lithium-Doped 3D Covalent Organic Frameworks: High-Capacity Hydrogen Storage Materials / Cao D., Lan J., Wang W., Smit B. // Angewandte Chemie International Edition. 2009. Vol. 48, Issue 26. P. 4730–4733. doi: <https://doi.org/10.1002/anie.200900960>
22. Soft Electrochemical Etching of FTO-Coated Glass for Use in Ni(OH)₂-Based Electrochromic Devices / Kotok V. A., Malyshch V. V., Solovov V. A., Kovalenko V. L. // ECS Journal of Solid State Science and Technology. 2017. Vol. 6, Issue 12. P. P772–P777. doi: <https://doi.org/10.1149/2.0071712jss>
23. Optimization of electrolyte composition for the cathodic template deposition of Ni(OH)₂-based electrochromic films on FTO glass / Kotok V. A., Kovalenko V. L., Zima A. S., Kirillova E. A., Burkov A. A., Kobylinska N. G. et. al. // ARPN Journal of Engineering and Applied Sciences. 2019. Vol. 14, Issue 2. P. 344–353. URL: http://www.arpnjournals.org/jeas/research_papers/rp_2019/jeas_0119_7562.pdf
24. Kotok V., Kovalenko V. A study of the effect of cycling modes on the electrochromic properties of Ni(OH)₂ films // Eastern-European Journal of Enterprise Technologies. 2018. Vol. 6, Issue 5 (96). P. 62–69. doi: <https://doi.org/10.15587/1729-4061.2018.150577>
25. Kotok V., Kovalenko V. A study of the effect of tungstate ions on the electrochromic properties of Ni(OH)₂ films // Eastern-European Journal of Enterprise Technologies. 2018. Vol. 5, Issue 12 (95). P. 18–24. doi: <https://doi.org/10.15587/1729-4061.2018.145223>
26. Advanced electrochromic Ni(OH)₂/PVA films formed by electrochemical template synthesis / Kotok V. A., Kovalenko V. L., Kovalenko P. V., Solovov V. A., Deabate S., Mehdi A. et. al. // ARPN Journal of Engineering and Applied Sciences. 2017. Vol. 12, Issue 13. P. 3962–3977. URL: <https://pdfs.semanticscholar.org/5628/61836625c1b46d9daeb7bbe73e7d85338519.pdf>
27. Kotok V., Kovalenko V. The electrochemical cathodic template synthesis of nickel hydroxide thin films for electrochromic devices: role of temperature // Eastern-European Journal of Enterprise Technologies. 2017. Vol. 2, Issue 11 (89). P. 28–34. doi: <https://doi.org/10.15587/1729-4061.2017.97371>
28. Kotok V., Kovalenko V. The properties investigation of the faradaic supercapacitor electrode formed on foamed nickel substrate with polyvinyl alcohol using // Eastern-European Journal of Enterprise Technologies. 2017. Vol. 4, Issue 12 (88). P. 31–37. doi: <https://doi.org/10.15587/1729-4061.2017.108839>