

У дослідженні описана спроба стівосадження гідроксидів нікелю та марганцю для застосування в якості анодного матеріалу електрохромних пристроїв. Для цього використали катодний темплатний метод із полівиниловим спиртом. Осадження змішаного гідроксиду відбувалося в гальваностатичному режимі з розчину, у якому містився нітрат нікелю і марганцю в мольному співвідношенні 8 до 1.

В результаті проведеної роботи були отримані дві плівки, осаджені з чистого розчину, що містив тільки нітрат нікелю і змішаного розчину. Аналіз отриманих плівок показав кардинальні відмінності в їх структурі, морфології, електрохімічних і електрохромних властивостях. Плівка, отримана з чистого розчину, складалася з однієї фази переважно α -подібних форм $\text{Ni}(\text{OH})_2$. На відміну від цього, плівка, отримана в присутності марганцю, показала наявність двох фаз. Порівняння морфології показало, що плівка без допанта має відносно пласку морфологію з невеликими виступами, що не перевищують 160 нм. Плівка, отримана в присутності марганцю, мала на своїй поверхні безліч звищених виступів, висота яких доходила до 1200 нм.

Електрохімічні властивості плівки, отриманої в присутності Mn, були гірше, ніж у плівки, отриманої з чистого розчину. Це виражалося в менших висотах щільності струмів піків і менших питомих ємностях процесів окислення і відновлення. Електрохромні властивості у плівки, отриманої в присутності марганцю, також були децю гірше.

Було припущено можливий механізм погіршення питомих властивостей плівки, в разі використання такого методу отримання. Він полягає в осадженні другої фази, яка містить марганець. Ця фаза малоактивна і зменшує кількість електрохімічно активного $\text{Ni}(\text{OH})_2$ в плівці.

Також авторами запропоновані можливі варіанти використання отриманої структури

Ключові слова: електрохромізм, гідроксид нікелю, подвійний шаруватий гідроксид, допанта, марганець, полівиниловий спирт, електроосадження, циклування

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STUDY OF THE Mn^{2+} IONS INFLUENCE IN THE DEPOSITION ELECTROLYTE ON THE ELECTROCHROMIC PROPERTIES OF OBTAINED $\text{Ni}(\text{OH})_2$ FILMS

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1. Introduction

World's struggle for energy supplies, countries competing in the development of new power sources raise critically important questions of power consumption and saving [1, 2]. Many technologies are being developed aimed at reduction of resource consumption through rationalized utilization. These technologies are related to so-called «smart» devices, which are often connected to the Internet, combining into «Internet of things» [3, 4].

«Smart» devices are devices optimized in processing speed, power consumption, which operate with active user input and changing environmental conditions. Combination of «classic» device with computer, equipped with sensor,

control algorithms and internet connection is a key approach in the creation of a «smart» device.

«Smart» windows are one type of such «smart» devices. Their key feature is an active element deposited onto the glass. This element is able to reversibly change its optical properties, such as color, transparency, glossiness. Another device that is often bundled into «smart» windows is smart mirror, which can also alter its reflectivity coefficient [5, 6].

Smart windows can operate based on different systems: liquid crystals, liquid-state and solid-state electrochemistry, suspended particles [7].

Electrochemical systems have two major advantages – large spectrum of possible colors and power only consumed on switching the optical state. On the other hand, they are

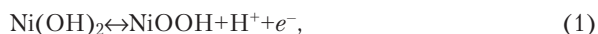
more difficult to manufacture, have long switching time and degrade over time.

Regardless of operating principle, the cost is high and currently ranges 200–800 US \$/m² [8, 9]. Therefore, the development of technologies aimed at reducing manufacturing cost is important for the widespread adoption of this technology.

One of the promising electrochromic materials is Ni(OH)₂ [10, 11]. Its films can be formed in different ways, including electrochemical method [12, 13]. Electrochemical method is the most cost-effective, easily automated, doesn't require complex equipment, in contrast to the most common method – vacuum sputtering. So, the development of this method, optimization and search for additives to Ni(OH)₂ film deposition electrolyte are one of the main problems for reducing the cost of electrochromic devices.

2. Literature review and problem statement

Ni(OH)₂ is an anodic electrochrome [14, 15]. Anodic electrochromes change color when polarized with anodic current. In case of Ni(OH)₂, the color change is caused by a solid-state electrochemical reaction, which can be described by reaction (1) or full reaction (2) [16, 17]:



transparent dark-brown



Because this is a solid-state reaction, allotrope form, structure, presence of structural defects and admixtures affect the final properties of the film.

Modification of crystal lattice can be achieved with the introduction of relatively small quantities of dopant [18, 19]. Hydroxide materials can be modified by introducing significant amounts of metal ions [20, 21]. In the first case, the introduction of dopant results in the deformation of the crystal lattice, due to the mismatch of ionic radii of metals. In the second case, significant content of dopant metal leads to radical changes in the crystal lattice [22, 23]. Such changes in the crystal lattice lead to higher reactivity of the compound.

Manganese doping is used for materials of chemical power sources and electrochemical devices.

The paper [24] describes the use of Mn and Bi for doping of electrochromic V₂O₅ film. Substitution occurred according to the solid-state mechanism. Synthesized powders were studied using different methods – scanning electron microscopy, UV-vis spectroscopy and XRD analysis. It was found that manganese doping causes the absorption spectrum to shift towards the long-wave region. It is proposed that synthesized materials can be promising for use in optics and electrical devices.

The paper [25] is devoted to the study of electrochromic Co₃O₄ films doped with Mn, which were compared against undoped Co₃O₄. It was found that the introduction of 6 at. % Mn leads to the best effect on electrochromic properties – 35 % optical modulation and coloration efficiency of 29 cm²/C.

The paper [26] describes the synthesis of manganese oxide doped with 22.3–30.6 % nickel. The film was used as ion storage of the electrochromic device. The film was electrodeposited potentiodynamically, from the solution of

MnSO₄, NiSO₄ and NH₄OH. The electrochromic device composed of the NiO film and the proposed ion storage showed the best performance among the tested variants of electrochemical devices.

Chinese researchers potentiodynamically deposited NiO films with and without Mn doping [27]. The film was deposited from organic, (CH₃)₂NCH-based electrolyte onto FTO glass. Manganese-doped nickel oxide films demonstrated high specific characteristics – at 550 nm, light absorbance of 93 %, while for the undoped film this value was only 68 %. The Mn-doped film also showed a high coloration efficiency of 30.9 cm²/C and improved reversibility.

Thus, manganese doping of electrochromic materials, including those related to Ni(OH)₂, results in the improvement of their characteristics.

Cathodic template synthesis method, proposed by the authors [27, 28], can also be used for the synthesis of manganese-doped films. The key feature of the method is galvanostatic deposition regime, without organic solvents and in the presence of polyvinyl alcohol (PVA) and nickel nitrate. Galvanostatic deposition allows for easy control over film thickness and properties and addition of polyvinyl alcohol (4–5 % wt.) results in strong adhesion to the substrate [17]. So, the use of the proposed method could improve the characteristics of manganese-doped nickel hydroxides.

3. The aim and objectives of the study

The aim of the study is to prepare manganese-doped Ni(OH)₂ films using the cathodic template synthesis method and study their properties.

To achieve this set aim, the following objectives were set:

- using the cathodic template method, to deposit films from electrolytes with and without manganese;
- to study the morphology and structure of prepared films;
- to determine the influence of manganese as a dopant on the electrochromic and electrochemical properties of the film;
- to conduct a comparative analysis of the obtained data.

4. Materials and methods used in the synthesis and characterization of electrochromic films

Preparation of solution for the deposition of hydroxide without additives Ni(NO₃)₂·6H₂O (CP) and PVA (Japoval-24-99) were weighted assuming concentrations 1 M Ni(NO₃)₂ and 5 % PVA. PVA and crystalhydrate Ni(NO₃)₂·6H₂O were dissolved in distilled water, and the volume was adjusted. The solution was then used in the cathodic chamber of the electrolyzer.

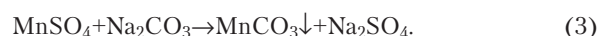
Preparation of solution for the deposition of double Ni-Mn hydroxide.

A solution containing nickel and manganese nitrate – 1 M and 0.125 M respectively (molar ratio Ni-Mn 8:1 [30]).

PVA was added to continuously stirred distilled water. After the dissolution of PVA, nickel nitrate powder was added, followed by the solution of Mn(NO₃)₂, and the volume was adjusted with distilled water.

Preparation of Mn(NO₃)₂ solution.

Necessary amounts of MnSO₄·5H₂O and Na₂CO₃ were calculated from reaction (3):



The solution of $MnSO_4$ was drop-wise added to the Na_2CO_3 solution. This resulted in precipitation of manganese carbonate, which was filtered off. It was then dissolved in a measured volume of nitric acid with a known concentration. The solution was then filtered off from undissolved solids and evaporated to the required volume.

Cathodic template synthesis.

Films were deposited in the cathodic chamber of the cell shown in Fig. 1. Working electrode area – 2×2 cm. Before deposition, the working electrode was electrochemically polished to a mirror-like finish. Films were deposited at the following parameters: current density 0.625 mA/cm^2 , deposition time 80 min.

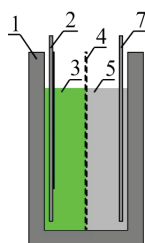


Fig. 1. Schematic of the cell with two chambers:
 1 – frame (PMMA); 2 – cathode (electropolished nickel foil (non-working area is coated with dielectric));
 3 – cathodic chamber with deposition electrolyte;
 4 – separator (Doramik®); 5 – anodic chamber with anolyte (1 M KNO_3); 7 – anode (nickel plate)

Methods used in the study.

Electrochemical and optical properties were studied using the setup shown in Fig. 2.

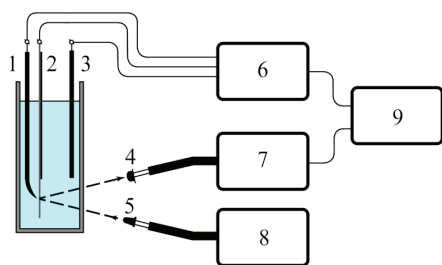


Fig. 2. Simplified schematic of the setup for studying electrochromic films: 1, 2, 3 – reference, working and counter electrodes respectively (shown in the measurement cell); 4 – photoresistor; 5 – source of white light (5,500 K); 6 – digital potentiostat; 7 – analog-to-digital converter (ADC); 8 – power supply; 9 – computer, dashed lines show light path

The setup uses ADC E-154 (Russia) and digital potentiostat Elins P-8 (Russia), along with standard software. $Ag/AgCl$ (KCl sat.) was used as a reference electrode. Nickel foil was used as a counter-electrode. The prepared films were cycled in the following regime: $E_{start} = +201 \text{ mV}$, $E_{end} = +751 \text{ mV}$ (NHE) at 1 mV/s .

To study the structure of the deposited films, XRD patterns of the prepared electrodes were recorded using the DRON-3 diffractometer (monochromated $Cu-K\alpha$, Russia).

Morphology of the samples was studied using the scanning electron microscope JEOL JSM-6510LV (Japan) and atomic-force microscope NT-MTD «NTegra» (Russia).

5. Analysis of prepared films and comparison of obtained data

5. 1. Film structure and morphology

Fig. 3 shows XRD patterns of the prepared films. Comparison of the obtained patterns revealed that both contain three intense peaks of nickel substrate. Patterns analysis with QUALX2.0 software [31] revealed the absence of peaks related to $Ni(OH)_2$ in the small-angle region and the rest of the patterns. This can be due to the X-ray amorphous nature of the deposit or small amounts of it.

The XRD pattern also shows a broad peak at $17^\circ 2\theta$. The presence of this peak indicates a significant structural difference of the films.

The morphology of the prepared films also differs – Fig. 4. The film prepared from the undoped solution is almost flat and doesn't have any non-uniform surface. The film deposited in the presence of manganese has ridges in the form of thin squiggly lines – Fig. 4, b.

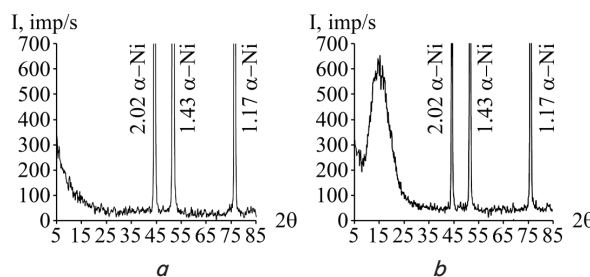


Fig. 3. XRD patterns:
 a – film deposited from undoped solution;
 b – film deposited from manganese-containing solution

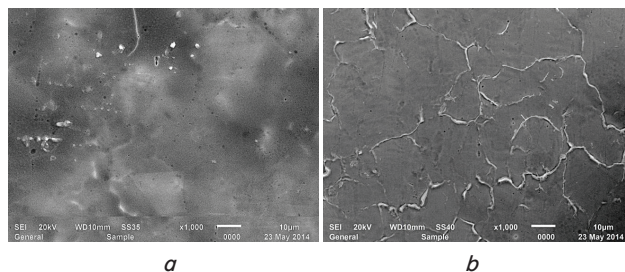


Fig. 4. SEM images:
 a – film deposited from undoped solution;
 b – film deposited from manganese-containing solution

Upon high magnification, AFM images show significant differences of the deposits – Fig. 5.

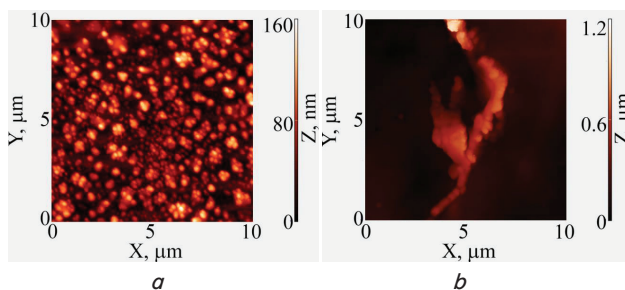


Fig. 5. AFM images:
 a – film deposited from undoped solution;
 b – film deposited from manganese-containing solution

The film deposited from the undoped solution shows round, small bumps, not higher than 160 nm (0.169 μm). Curved lines of the manganese-containing sample look different – Fig. 4, *b* and 5, *b*. These lines are composed of a single material and have spherical boundaries.

It is noted that the bumps of the sample deposited in the presence of Mn are higher by an order than that of the undoped sample – up to 1.2 μm (1200 nm).

In summary, it can be said that the films prepared under different conditions have significant structural and morphological differences.

5. 2. Electrochemical and electrochromic characteristics

To determine differences in electrochemical and electrochromic properties, the films were subjected to potentiodynamic cycling (Fig. 6), in conjunction with optical measurements – Fig. 7.

Comparative analysis of cyclic voltammograms (Fig. 7) allows concluding that the addition of manganese to the deposition electrolyte has a significant effect on film properties. The film deposited without manganese has more sloping peaks, but higher peak currents (+0.52 and -0.57 mA/cm^2), in comparison to the film with manganese (+0.26 and -0.28 mA/cm^2). It is interesting that the cyclic voltammogram of the manganese-doped sample has a rather high residual cathodic current (left of the cathodic peak) – Fig. 6, *b*. At the same time, the cathodic peak of cycles 2–4 appears to be split.

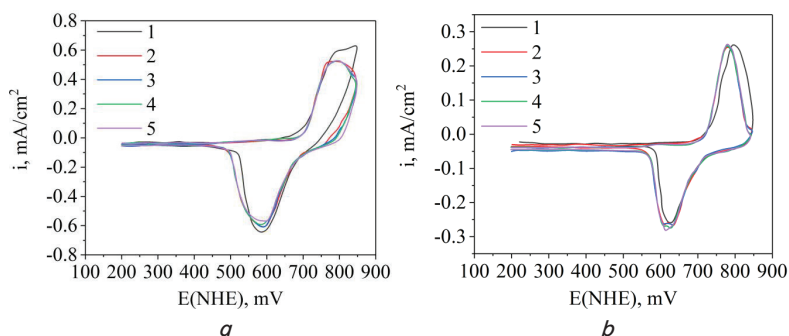


Fig. 6. Cyclic voltammograms: *a* – film deposited from undoped solution; *b* – film deposited from manganese-containing solution

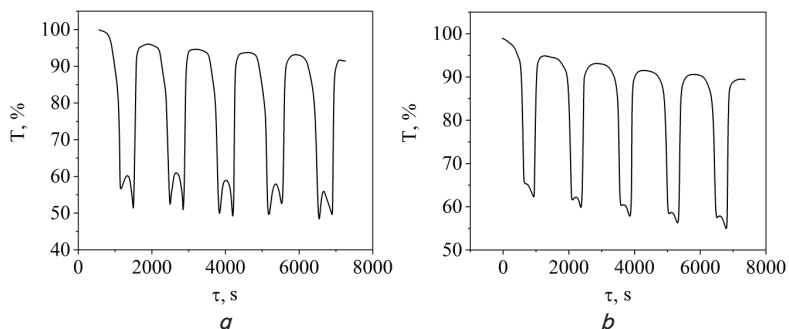


Fig. 7. Coloration-bleaching curves: *a* – film deposited from undoped solution; *b* – film deposited from manganese-containing solution

Coloration bleaching-curves revealed a significant difference in sample behavior. The sample deposited without manganese showed better performance – higher coloration degree and low irreversibility. For this sample, coloration degree reached 45 %. Coloration degree is calculated as differences between transparency (*T*) in bleached and colored states. At the same time, for the manganese-doped sample

coloration degree was about 35 %. Irreversibility (transparency difference between bleached state and 100 % for a given cycle) was higher for the Mn-containing sample.

Thus, the manganese-containing film showed worse characteristics than the undoped sample.

6. Discussion of data obtained for studied electrochromic films

The data obtained for the deposited films allows making a few important conclusions. Based on the results of XRD analysis, it appears that two separate phases are formed, instead of single-phase as previously assumed. It is possible that the second phase is manganese hydroxide $\text{Mn}(\text{OH})_2$ or MnOOH (groutite). Both phases can cause peaks at 2θ 19.80° and 16.56° based on the X-ray wavelength. Analysis of XRD patterns is also complicated by the presence of polyvinyl alcohol in the solution. This component can influence the formation of the crystal lattice and act as a surfactant and, for instance, affect the interlayer distance.

During cycling, these phases can also partake in the electrochemical reaction. A few transformations are possible: $\text{Mn}(\text{OH})_2[\text{chem.}] \rightarrow \text{MnOOH}[\text{el.-chem.}] \leftrightarrow \text{MnO}_2$ or $\text{MnOOH}[\text{el.-chem.}] \leftrightarrow \text{MnO}_2$. Reversibility of the reaction $\text{MnOOH}[\text{el.-chem.}] \rightarrow \text{MnO}_2$ is low. This is commonly known, as the transition from MnO_2 to MnOOH is widely used in zinc-manganese batteries, and can be described by reaction (4):



Because reverse transformation in reaction (4) is retarded, manganese oxyhydroxide would eventually transform into manganese dioxide and stop partaking in the reaction. This is likely observed on the cyclic voltammogram on cycles 2–3, where small peaks show up at the top of the cathodic peaks and disappear on the fifth cycle.

Fig. 4, 5, *b* show the grid of branching lines, which differentiates the manganese-containing sample. It is possible that this grid is a separate manganese-containing phase. In this case, this becomes a nanocomposite containing a mixture of oxide-hydroxide nickel and manganese material. Such material could be useful in other spheres, for instance, for water decomposition or sensor electrode.

Cyclic voltammetry curves of the doped films revealed a decrease in peak current density, meaning lower specific capacities. This was also accompanied by a decrease in electrochromic performance. Considering the deposition of two separate phases under the same conditions, the addition of manganese would mean less deposition of electrochemically active $\text{Ni}(\text{OH})_2$.

Assuming the previous assumption of separate phases, the following conclusion can be made. For the deposition of such films with two different phases, a noticeable positive effect on electrochromic properties would require significantly lower amounts of dopant. Dopant concentration should be such that the decrease of electrochemically active $\text{Ni}(\text{OH})_2$ would be counteracted via improved activity.

7. Conclusions

1. Cathodic template method was used to galvanostatically (0.625 mA/cm², 80 min.) deposit nickel hydroxide films without and with manganese doping (molar ratio of Ni to Mn 8:1). The synthesized films had significantly different structural, electrochemical and optical properties.

2. It was found that under experimental conditions, the films deposited from manganese-containing electrolyte had electrochromic characteristics inferior to those of undoped

films, due to the manganese-containing phase. The Mn-doped films had a coloration degree lower by about 10 % than undoped films.

3. The morphology of the Mn-doped films is composed of zig-zag-like ridges up to 1.2 μm high. The surface of the undoped film is rather flat with small bumps up to 0.16 μm.

4. It is proposed that lowering the dopant quantity to a few percents in the solution could lead to better electrochromic performance.

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