Електрохромні плівки були отримані катодних теплатним методом в присутності двох типів полівінілового спирту: зі ступенем гідролізу 99 % і 85 %. В результаті отримані плівки показали відмінності в структурних, морфологічних, електрохромних і електрохімічних характеристиках. Обидві плівки були рентгеноаморфні і мали різну форму кривої на дифрактограмах в районі малих кутів 2θ, що відповідає відмінностям в напрямку площини 001. Порівняння морфології плівок, отриманих з розчинів, що містять ПВС з різним ступенем гідролізу, показали, що плівка, отримана в присутності ПВС зі ступенем гідролізу 99 %, має відносно плоский рельєф з малими розмірами неоднорідностей. З іншого боку, плівка, отримана в присутності ПВС зі ступенем гідролізу 85 %, виявилася більш нерівномірною. Її рельєф включав хвилясті лінії по всій поверхні, висота яких досягала 1,2 мкм. Циклічні вольтамперограми обох плівок також суттєво різнилися. ЦВА для плівки, отриманої в присутності ПВС зі ступенем гідролізу 85 %, мала гострі анодні і катодні піки близькі по висоті. При цьому потенціали піків становили +600 і +700 мВ. Навпаки, плівка, отримана в присутності ПВС зі ступенем гідролізу 99 %, мала більш розмиті піки і анодний пік струму, зсунутий в область більш позитивних потенціалів (+900 мВ). Електрохромні характеристики обох плівок також сильно різнилися. Плівка, отримана в присутності ПВС зі ступенем гідролізу 85 %, мала високу швидкість затемнення (60 с), але меншу абсолютну глибину затемнення (18 %). З іншого боку плівка, отримана в присутності ПВС зі ступенем гідролізу 99 %, мала в три рази меншу швидкість затемнення (200 с), але більшу абсолютну глибину затемнення (24 %). В результаті було запропоновано кілька механізмів, які пояснюють відмінності в поведінці плівок отриманих в присутності різних типів ПВС

Ключові слова: електрохромізм, електроосадження, тонкі плівки, Ni(OH)$_2$, нікель, полівініловий спирт, ступінь гідролізу, гідроксид нікелю

INVESTIGATION OF THE PROPERTIES OF Ni(OH)₂ ELECTROCHROME FILMS OBTAINED IN THE PRESENCE OF DIFFERENT TYPES OF POLYVINYL ALCOHOL

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1. Introduction

Modern stage of technological advance is the creation of so-called «smart technologies». These technologies integrate a computer, program and controlled device into a single object. The result of such merging is a «smart device», which optimizes working parameters, the main of which is energy and resource consumption, and also execution time [1].

«Smart windows» are one of such devices that incorporate the principles of «smart devices». Such windows enable the user to dynamically change various optical parameters based on the type of electrochromic element used. The list of controlled parameters includes color, reflectivity, transparency, glossiness. The application range of such devices is wide: glazing of buildings, meeting rooms, manipulation rooms, car windows, interior design, etc. However, the high price of 200–1000 USD/m² does not allow their widespread application [2, 3].

Thus, one of the new research problems is the development of cheaper electrochromic materials and reduction of manufacturing cost.

One of the promising electrochromic materials is nickel hydroxide, which possesses high specific parameters. According to the literature [4], its electrochromic efficiency is within 50–111 cm²/C. One of the methods for the deposition of Ni(OH)₂ is a cathodic template synthesis in the presence of polyvinyl alcohol (PVA) as a template [5, 6].

The simplicity of organizing the manufacturing process, the possibility of automation and easy control over parameters of the resulting electrochrome and power efficiency of such film deposition method make it distinguishable from the rest. Study on the parameter's influence on the properties of the resulting film can significantly affect the adaptation of this manufacturing method. This would also lead to reduced cost of one of the key components of the electrochromic element.

2. Literature review and problem statement

Nickel (II) hydroxide is a compound with a wide range of applications. This compound was primarily used in electrodes of alkaline batteries [7, 8]. Today, the application range of Ni(OH)$_2$ is significantly wider. Nickel hydroxide finds its use as an active material in hybrid supercapacitors [9, 10], water decomposition electrodes [11] and oxidation of organic compounds [12]. Nickel hydroxide, as a component of the nickel oxide electrode, is also considered as an electrode for methanol fuel-cells [13] and even as an anti-corrosion coating [14]. However, one of the important research directions is the application of Ni(OH)$_2$ in electrochromic devices.

Cathodic template method for the deposition of transparent Ni(OH)$_2$ films is a simple, yet promising method. In this case, PVA serves as a template, which results in the formation of PVA-Ni(OH)$_2$ composite films with high qualitative characteristics after deposition [9, 15]. The paper [9] describes a comparative analysis of PVA, carboxymethylcellulose (CMC) and polytetrafluoroethylene (PTFE) as a template. It was discovered that the use of PVA as a template resulted in transparent electrochromic films with high adhesion. The papers [16, 17] also describe the use of PVA as a template for other compounds.

It is known that there are various types of polyvinyl alcohol with different degrees of hydrolysis, crystallinity, molecular weight and impurities [18, 19]. The type of PVA can define the properties of composites in which it is used. Properties of PVA are dictated by the synthesis method. The paper [20] describes that solubility, hydrophility and ability to form hydrogen bonds of PVA are primarily governed by the degree of hydrolysis. It is also described [21] that even the same grades of PVA can also differ in their properties. According to the authors, it is due to the structure, which depends on the synthesis method. In addition, the paper [22] describes significant changes in PVA-based fibers based on the type of the polymer used. The paper [23] describes that different grades of PVA as a stabilizer for membrane-bound and membrane-encapsulated ferments can significantly affect the activity of the latter. At the same time, the paper [24] describes that molecular weight and hydrolysis degree of PVA affect bioavailability and solubility of some poorly-soluble drugs. Using model itraconazole as a model drug, it was determined that the use of some grades of PVA is preferable for aqueous media. They came to the conclusion that PVAL 4-88 has the highest stability as a carrier for this drug.

The majority of authors use PVA in the template synthesis of nickel hydroxide [26, 27] and other compounds [28–30], omitting the characteristics of PVA, namely the degree of hydrolysis. However, the literature review allows concluding that the grade of PVA can significantly affect the properties of the resulting composites. The main question is how much the grade of PVA can affect the properties of the electrochromic PVA-Ni(OH)$_2$ composite film.

3. The aim and objectives of the study

The aim of the work was to determine the influence of the hydrolysis degree of PVA used on the properties of the resulting electrochromic Ni(OH)$_2$ film, in order to make a conscious choice of PVA for manufacturing of electrochromic devices.

Within the scope of the set aim, the following objectives were formulated:

– to prepare the electrochromic Ni(OH)$_2$ film from solutions containing PVA with different degrees of hydrolysis;

– to conduct a comparative analysis of morphology and structure of prepared films;

– to conduct a comparison of electrochemical and electrochromic properties of prepared films.

4. Materials and methods used in the research

Materials used in the research.

Electropolished nickel electrodes with the working area of 20×20 mm were used as substrates for film deposition. The electropolishing procedure is described in the literature [9].

The composition of electrolytes used for film deposition and deposition parameters are listed in Table 1.

Table 1

Synthesis conditions for deposition of the electrochromic film using the cathodic template method

Composition of the electrolyte in the cathodic chamber*	Electrolyte temperature, °C	Cathodic current density, mA/cm^2	Deposition time, min
Ni(NO$_3$)$_2$ – 1 mole/L ПВС – 50 g/L (J-Poval)	30	0.625	80

*Note: * – 1M KNO$_3$ solution was used in the anodic chamber*

Two electrolytes, the composition of which is listed in Table 2, were used in the research. Two types of polyvinyl alcohol were used.

The first is labeled as «partially hydrolyzed» with the hydrolysis degree of 85 %.

The second is labeled «fully hydrolyzed» with the hydrolysis degree of 99 %. The degree of hydrolysis was determined by the type and was calculated based on Fig. 1 and equation (1).
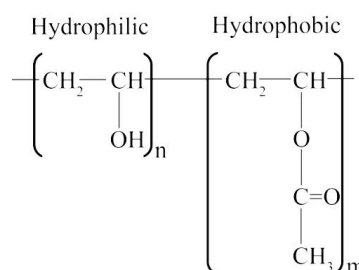
Fig. 1. A link of the polyvinyl alcohol chain: n — number of hydroxyl groups; m — number of acetate groups

$$D = n(n+m)\cdot100. \tag{1}$$

The deposition was conducted in a two-chamber cell separated by a low-permeability diaphragm, with a nickel anode.

As a result, two electrochromic films were obtained: from the electrolyte containing fully hydrolyzed polyvinyl alcohol and from the electrolyte containing partially hydrolyzed PVA.

The samples were labeled according to Table 2.

Table 2

Sample labeling

Descrip-tion	Ni(OH)$_2$ film deposited from the electrolyte with fully hydrolyzed PVA	Ni(OH)$_2$ film deposited from the electrolyte with partially hydrolyzed PVA
Label	FH	PH

Structural analysis.

The structure of the samples was determined by means of X-ray diffraction analysis, using the DRON-3 diffractometer (Cu-Kα radiation).

Morphology analysis.

The morphology of PVA-Ni(OH)$_2$ composite films was determined using the scanning electron microscope (SEM) JSM-7200F (Japan) and the atomic force microscope NT-MTD NTegra (Israel).

Evaluation of electrochemical and optical characteristics of deposited films. Optical and electrochemical characteristics were studied by means of cyclic voltammetry (CVA) with simultaneous recording of the coloration-bleaching process, using a cell depicted in Fig. 2.

Ag/AgCl (KCl sat.) was used as a reference electrode and nickel foil counter-electrode. 0.1 M KOH was used as an electrolyte for all experiments. Optical characteristics were recorded using the analog-to-digital converter E-154 (Russia), and electrochemical measurements were conducted using the digital potentiostat-galvanostat Ellins P-8 (Russia).
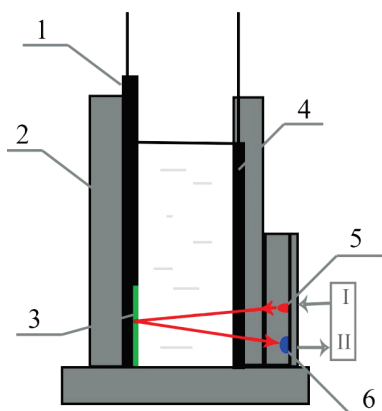

Fig. 2. Cell for electrochemical and optical tests: 1 — working electrode; 2 — frame made of transparent plastic; 3 — electrochromic film; 4 — counter-electrode; 5 — source of white light (5,500 K); 6 — photoresistor; I — input from stabilized power supply; II — output to the analog-to-digital converter

Testing regime: potential window +200 to +725 (+900) mV, scan rate 1 mA/s, number of cycles – 5.

5. 1. Structure and morphology analysis of samples prepared with different PVA

In order to evaluate the influence of PVA with different degrees of hydrolysis, it was decided to conduct X-ray diffraction analysis of prepared films. The obtained XRD patterns are shown in Fig. 3.

Comparison of XRD-patterns (Fig. 3) reveals that the films have an X-ray amorphous structure, which is indicated by the almost complete absence of peaks corresponding to Ni(OH)$_2$. The insignificant difference between the samples is only noticeable in the range of small 2θ angles. The peaks characterize the 001 plane. Thus, there appears to be some structural difference in the film structure related to the 001 plane. The sharp peaks correspond to the nickel substrate.
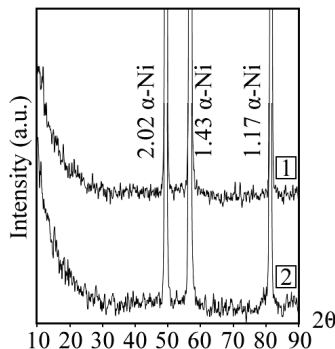

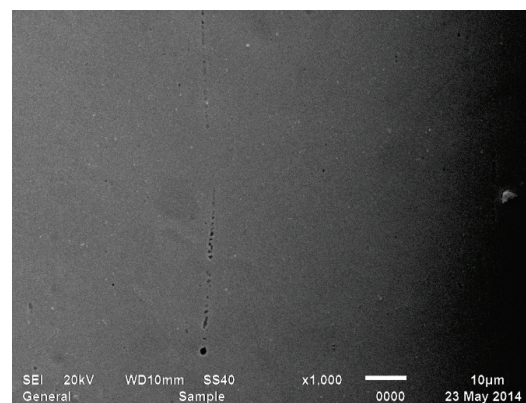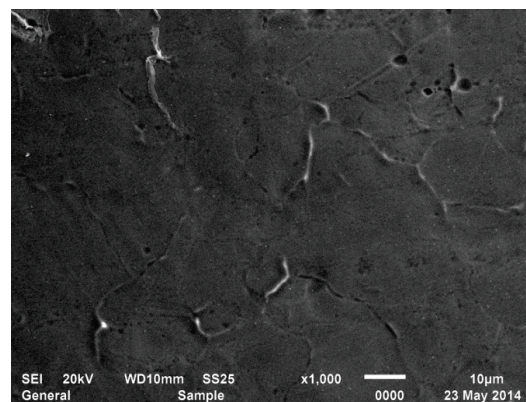Fig. 3. XRD patterns: 1 — sample PH, 2 — sample FH

a

b

Fig. 4. SEM images of the samples: *a* — sample PH, *b* — sample FH (×1000 magnification)

Sample morphology was analyzed by means of two types of microscopes. Fig. 4, 5 shows the images obtained for both samples. Analysis of the obtained images reveals that there are significant differences in surface morphology between two samples – Fig. 4, 5. Thus, the film obtained with 85 % hydrolyzed PVA shows some surface bumps.

The surface of this sample (Fig. 4, *a*, 5, *a*) is covered with bumps resembling wavy lines.
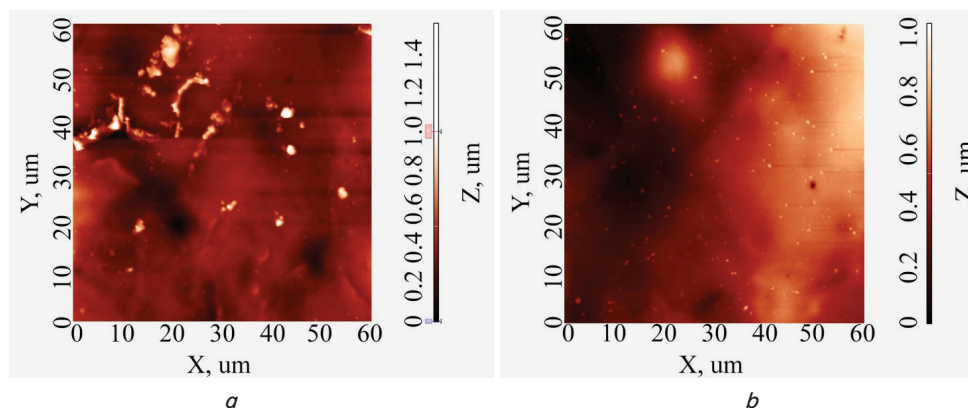
Fig. 5. AFM of the samples: *a* — sample PH, *b* — sample FH

The sample prepared in the presence of fully hydrolyzed PVA (degree of hydrolysis 99 %) is almost flat and does not show any large crevices or bumps. This can also be observed on AFM images. For the sample PH, the height of wavy lines reaches 1.2 µm. For the sample FH, the height of bumps barely reaches 0.7 µm and their diameter does not exceed 0.5 µm.

5. 2. Results of electrochemical and optical tests of prepared films

Prepared samples were tested by means of cyclic voltammetry with simultaneous recording of transparency (T, %) in time (τ, s). It should be noted; that because of internal factors that determine the operation parameters of the film, the potential window for the film prepared with fully hydrolyzed PVA was broadened to +900 mV. This is because coloration did not occur at the upper potential of +725 mV. This is likely because of a denser film structure, which could interfere with ion diffusion. Cyclic voltammograms for both films are presented in Fig. 6 and optical characteristics are presented in Fig. 7.

Comparative analysis of CVA curves of both films revealed significant differences in their behavior. Sample PH shows well-defined peaks with anodic and cathodic peaks laying at +700 and +600 mV. The nickel hydroxide film prepared in the presence of 99 % hydrolyzed PVA (sample FH) shows broader and less defined peaks. In addition, the peak current values are similar. The potential of the anodic peak is situated at a more positive value of +800 mV, and the cathodic peak potential is the same as sample PH (+600 mV).
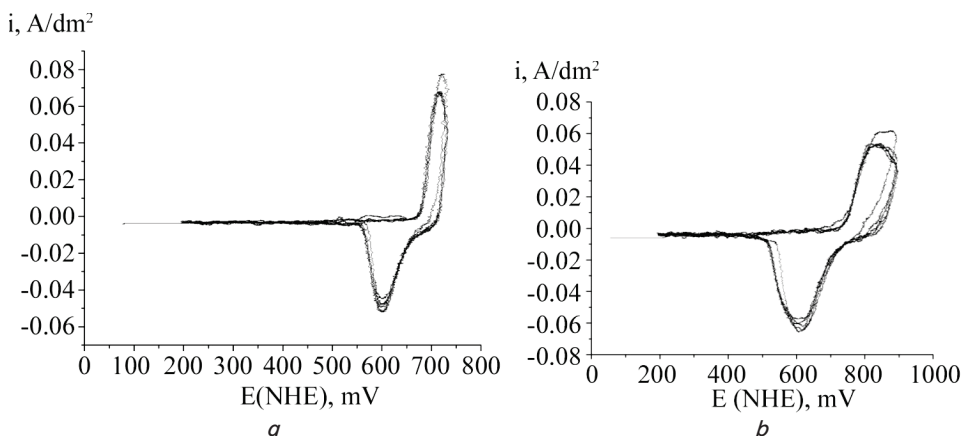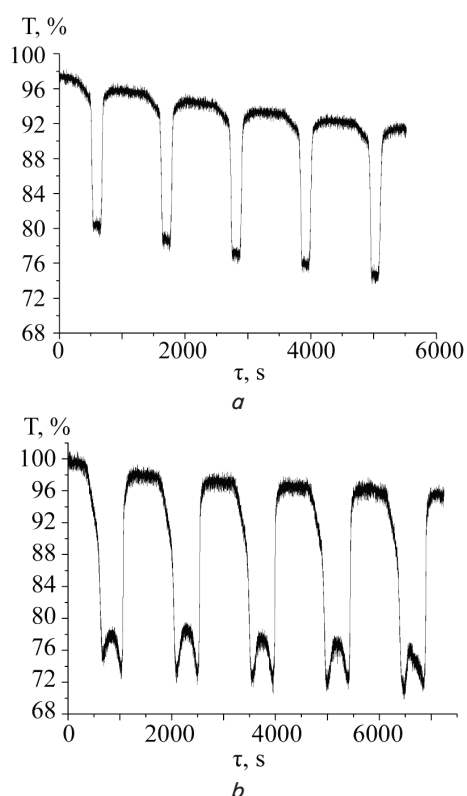

Fig. 7. Coloration-bleaching curves of the samples:
a — sample PH, *b* — sample FH

These observations indicate significant differences in the structure of the films.

At the same time, the analysis and comparison of optical characteristics revealed significant differences in electrochromic behavior. Both samples show different shapes of the coloration-bleaching curve. The coloration speed is also different – the time during which the transparency changes from maximum to minimum value. Additionally, the absolute coloration de-

Fig. 6. Cyclic voltammograms of prepared films: *a* — sample PH, *b* — sample FH

gree, which was calculated as a difference between maximum and minimum trenchancy in a single coloration-bleaching cycle also significantly changed. The calculated coloration speed for sample PH was about 60 s, while for sample HF it was 200 s. At the same time, the absolute coloration degree for samples PH and FH was 18 and 24 %, respectively.

6. Discussion of morphology, electrochemical and optical characteristics of electrochromic films

The obtained data indicated that the choice of suitable PVA type is of importance. It is evident, that the properties of PVA as a template significantly affect the properties of the resulting electrochromic film. It appears that the hydrolysis degree of PVA affects the structure and morphology of the film, which in turn affect their operation characteristics. The use of 99 % hydrolyzed PVA leads to the formation of flat homogeneous films, which results in improved optical characteristics, especially in the bleached state. The latter can be observed on the coloration-bleaching curve of FG samples, with the curve starting about 100 % transparency – Fig. 7, *b*. On the other hand, the use of 85 % hydrolyzed PVA resulted in the formation of non-uniform films, which negatively impacts the optical properties in the bleached state. This is likely related to light scattering on non-uniform surfaces, which is supported by the coloration-bleaching curve with the initial point being below 100 %. Gradual degradation and irreversibility upon bleaching are likely related to the nickel substrate, which has its own layer of oxides and hydroxides. The latter can also react with coloration and bleaching contributing to the curve, which was previously described in detail [5, 9, 15, 25]. It is notable that some structural differences appeared on the XRD patterns, which can be observed at small 2q angles. Nevertheless, both films are X-ray amorphous, which is likely related to the template synthesis method. The optical characteristics of two films were different, which highlights the in-fluence of PVA on electrochromic characteristics of prepared films. For sample FG, the surface of which was uniform and smooth, the coloration rate was slower, but the coloration degree was higher. For the sample prepared in the presence of partially hydrolyzed PVA (sample PH), the behavior is reverse – faster coloration but lower coloration degree. Thus, depending on the target application, the appropriate type of PVA, which would result in either faster coloration or deeper color, can be chosen.

These differences can be related to the different solubility of different PVA and also with the presence of hydrophobic acetate groups. The presence of an acetate group can affect the formation of $Ni(OH)_2$ due to the possible formation of a polymeric acetate complex with nickel ions. This can also be explained by partial hydrolysis of partially hydrolyzed PVA during deposition. This would result in the release of acetate ions that form weak complexes without an outer shell with Ni^{2+}. The formation of the complex affects the mechanism and formation rate of nickel hydroxide. Further research is required in order to clarify the formation mechanism.

7. Conclusions

1. By using PVA with different degrees of hydrolysis in the deposition of $Ni(OH)_2$, it was discovered that the type of polymer used has a significant effect on structural, morphological, electrochemical and electrochromic characteristics.

2. It has been discovered that using 85 % hydrolyzed PVA leads to the formation of films with significant bumps and lower transparency in the initial state.

3. The type of PVA template affects the main electrochromic characteristics. The film deposited in the presence 85 % hydrolyzed PVA had a high coloration rate (60 s), but lower coloration degree (18 %). On the other hand, the film deposited in the presence of 99 % hydrolyzed PVA had a coloration rate that is three times slower (200 s), but higher absolute coloration degree (24 %).

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