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*Катодним темплатним методом були синтезовані електрохромні плівки Ni(OH)<sub>2</sub> при різних температурах. Було визначено, що найбільш плавка поверхня – у плівки, отриманої при 30 °С, що свідчить про її високі оптичні характеристики. Також було показано, що найкращі електрохімічні і електрохромні характеристики має плівка гідроксиду нікелю, отримана при 30 °С*

*Ключові слова: гідроксид нікелю, Ni(OH)<sub>2</sub>, електрохромізм, електроосадження, катодний темплатний синтез, полівініловий спирт*

*Катодной темплатним методом были синтезированы электрохромные пленки Ni(OH)<sub>2</sub> при разных температурах. Было определено, что наиболее плоская поверхность – у пленки, полученной при 30 °С, что свидетельствует о её высоких оптических характеристиках. Также было показано, что лучшие электрохимические и электрохромные характеристики имеет пленка гидроксида никеля, полученная при 30 °С*

*Ключевые слова: гидроксид никеля, Ni(OH)<sub>2</sub>, электрохромизм, электроосаждение, катодный темплатный синтез, поливиниловый спирт*

# THE ELECTROCHEMICAL CATHODIC TEMPLATE SYNTHESIS OF NICKEL HYDROXIDE THIN FILMS FOR ELECTROCHROMIC DEVICES: ROLE OF TEMPERATURE

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## 1. Introduction

Nickel hydroxide is the main component of nickel oxide electrode (NOE), which is used in alkaline accumulators [1, 2] and hybrid supercapacitors [3, 4]. Ni(OH)<sub>2</sub> also finds its applications in other fields: oxidation of organic compounds [5], sensors for some compounds [6], and electrochromic films [7].

The electrochromic films are used in devices that can alter their optical properties based on polarity of applied voltage, the amount of electricity and its duration. Different types of electrochromic films alter different optical properties: color, transparency, opacity. Electrochromic devices under control of a computer are called "smart windows". The latter are used to create satisfactory light and temperature in rooms, cinemas, hospitals, advertisement industry [8].

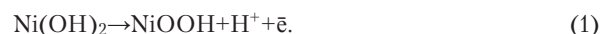
One of the main advantages of smart windows that change light transmittance is the possibility to save electric power. According to some sources, use of such windows allows reducing electric power used on room conditioning to 51 %, and reducing power consumption in peak hours to 15 % [9].

Amongst various systems that are used in electrochromic devices, the electrochemical systems stand out. These systems alter their optical states as a result of the reversible electrochemical reaction. As electrochromic systems, mainly

metal oxides (hydroxides) are used, and less commonly – some polymers and soluble redox pairs [10]. The advantages of electrochemical electrochromic systems are low cost, high color change efficiency. Unlike other electrochromic systems (liquid crystals, suspended particles), the current is required only for a color change.

All electrochemical electrochromic materials can be conventionally divided into two types: cathodic and anodic. Anodic-type materials are transparent in the initial state and during oxidation with anodic current transform into their colored state. In case of cathodic materials, transition into colored state occurs under the influence of cathodic current.

Nickel hydroxide is one of the anodic electrochromic materials. Deposited as a thin film, the nickel hydroxide is almost transparent and during anodic oxidation it transforms into the colored form – oxyhydroxide (NiOOH) according to the solid-state reaction (1):



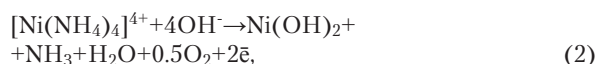
Nickel hydroxide (oxide) is viewed as an anodic electrochromic material to be paired with cathodic electrochromic materials (WO<sub>3</sub>, Nb<sub>2</sub>O<sub>5</sub>, Ir(OH)<sub>3</sub>) and produce grey color in the colored state. This material is also promising because of good reversibility, high specific coloration per unit of power and low power required to sustain the colored state. Thus,

deposition methods of Ni(OH)<sub>2</sub> (NiO) and their optimization raise a great interest.

## 2. Literature review and problem statement

Many preparation methods of nickel hydroxide and oxide electrochromic materials are known. The following methods are commonly employed in experimental works: pulse laser deposition [11], vacuum sputtering [12], chemical bath deposition [13], sol-gel process [14], spray pyrolysis [15], etc. The main disadvantage of previously listed methods is the difficulty of implementation in the production process of electrochromic devices. The latter is related to the difficulty of automation, high power consumption, difficulties in controlling parameters of electrochromic films and technological issues related to manufacturing of large electrochromic devices.

Electrochemical deposition methods stand out among other methods for deposition of nickel hydroxide films. The anodic electrochemical deposition method involves deposition of nickel hydroxide film by decomposition of nickel ammine complexes at the anode [16] (reaction 2). The cathodic electrochemical method is realized by reduction of nickel nitrate with the formation of OH<sup>-</sup> ions (reaction 3). The formed OH<sup>-</sup> ions, in turn, react with Ni<sup>2+</sup> ions according to reaction 4 [17].



Electrochemical methods have a few advantages over other deposition methods. The first one is a simple control of process parameters by regulating the current density. The second is simple process automation in analogy to galvanic electrochemical productions.

One type of cathodic electrochemical deposition is a cathodic template method, which differs in that the process is conducted in nickel nitrate solution with the addition of polyvinyl alcohol [18]. PVA-Ni(OH)<sub>2</sub> composites deposited with this method have a structure different from those prepared from pure nitrate solutions. Ni(OH)<sub>2</sub> films prepared with PVA have a high coloration degree, reversibility during coloring-bleaching, and high adhesion to the substrate [19]. However, solutions containing polyvinyl alcohol have a significant viscosity, which can lower ion mobility and influence diffusion and electrochemical processes. Viscosity is determined by solution concentration and temperature. In previous studies, the optimal concentration of 5% has been chosen. Thus, the next step in the research related to the development of cathodic template synthesis is selection of the optimal temperature.

## 3. Aim and objectives

The aim of the work is to establish optimal deposition temperature for cathodic template synthesis and to determine the influence of deposition temperature on morphology and structure of PVA-Ni(OH)<sub>2</sub> composite films.

The aim has been achieved by setting and fulfilling the following objectives:

- to deposit electrochromic films using cathodic template synthesis at different temperatures of the electrolyte;
- to compare the morphology of prepared electrochromic films and also their optical and electrochemical properties based on deposition temperature;
- to evaluate the influence of temperature on properties of electrochromic nickel hydroxide films;
- to choose an optimal temperature for synthesis of nickel hydroxide films with high electrochemical and optical properties.

## 4. Research methods employed to evaluate the influence of temperature on the deposition process of PVA-Ni(OH)<sub>2</sub> films

Deposition regimes employed for deposition of electrochromic nickel hydroxide films are listed in Table 1. A cell with a low-permeability diaphragm separating the anodic and cathodic chamber have been used for deposition of nickel hydroxide films.

Table 1

Cathodic template synthesis regimes

Deposition time, min	Electrolyte composition		Current density, mA/cm <sup>2</sup>	Electrolyte temperature, °C
	Cathodic chamber	Anodic chamber		
80	1M Ni(NO <sub>3</sub> ) <sub>2</sub> 5% PVA	1M KNO <sub>3</sub>	0.625	10, 20, 30, 40, 50, 60

An electrochemically polished nickel foil has been used as a substrate for deposition of electrochromic films (Fig. 1, a). The working electrode area was 4 cm<sup>2</sup>. The polishing has been carried out directly before deposition of the electrochromic film. After electrochemical polishing, the electrode was washed with a large amount of distilled water.

The metallic substrate has been chosen because of two reasons:

- high electrical conductivity of nickel in comparison to indium-tin oxide coated glass which results in better distribution of current density along the electrode-height;
- better sensitivity during recording of the coloring process, because light beam passes two times through the Ni(OH)<sub>2</sub> film: light source → Ni(OH)<sub>2</sub> film → mirror nickel surface → Ni(OH)<sub>2</sub> film → photoresistor.

For evaluation of optical and electrochemical properties, cyclic voltamperometry (CVA) in parallel with the recording of the coloring-bleaching process have been used. A cell depicted in Fig. 1 b has been employed. A silver chloride in saturated KCl solution was used as a reference electrode. The auxiliary electrode was made out of nickel foil. In all experiments, a 0.1 M KOH solution was used as electrolyte. Optical characteristics were recorded using ADC E-154 (Russian Federation). Electrochemical characteristics were recorded using digital potentiostat-galvanostat Ellins P-8 (Russian Federation). The regime of electrochemical and optical measurements: potential range from +200 to +800 mV, scan rate 1mV/s, number of cycles – 5.

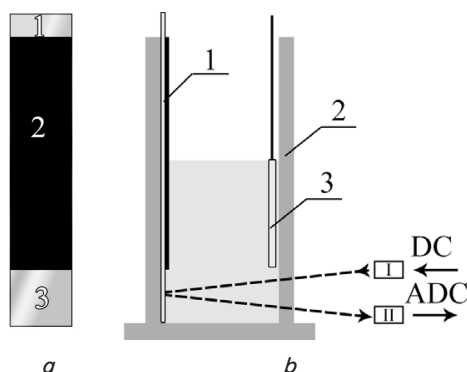


Fig. 1. Electrode and cell for electrochemical and optical tests: *a* – working electrode: 1 – region for connection of polarizing wire; 2 – black dielectric coated onto the surface of foil; 3 – mirror-like surface with electrochromic film; *b* – cell for recording of optical characteristics: 1 – working electrode; 2 – frame made out of transparent plastic; 3 – auxiliary electrode; I – source of white light (5500 K); II – photoresistor. DC – direct current source; ADC – analog to digital converter

In order to establish the structure of prepared electrochromic films, X-ray diffraction patterns were recorded in Co-K $\alpha$  monochromated radiation, without separating the film from the substrate. DRON-3 diffractometer (Russian Federation) was used for this.

In order to determine the morphology of prepared PVA-Ni(OH) $_2$  composite films, the Scanning Electron Microscope (SEM) JEOLJSM-6510LV (Japan) and Atomic-Force Microscope (AFM) NT-MTD “NTegra” (Russian Federation) were used in the experiments.

### 5. Experimental results of determining the deposition temperature influence on properties of nickel hydroxide films

#### 5. 1. Comparison of morphology of nickel hydroxide films deposited at different electrolyte temperatures

Fig. 2 shows SEM images of nickel hydroxide films deposited at different temperatures.

Image analysis revealed a dependency of film morphology on deposition temperature.

At 10 °C the film is thin, transparent and the substrate surface can be seen through it. Characteristic droplet-like regions of dissolution at the grain boundaries are observed.

At 20 °C the film is patchy and non-uniform. Lighter patches are most likely the regions where the film peeled off of the substrate. Incomplete cracking is observed in other regions. In the region where the film fell off, there is a thin layer of deposit through which metallic substrate can be seen.

At 30 °C, there are a few regions where the film is partially or completely absent. The film is covered in a net of cracks. Uneven film spottiness can be observed.

At 40 °C, two drastically different regions can be observed. The first one is covered with a net of cracks, the second is a region with parallel stripes. Such structure could've formed because the film in this region partially drifted off due to the low viscosity of the solution at a higher temperature.

The film deposited at 50 °C has a strongly pronounced morphology. The film is composed of severely cracked regions and regions with peeled off deposit, the surface of

which is quite large. It should be noted that in the region where the deposit has peeled off, no morphology characteristic of metallic samples is observed, meaning that there is a thin layer of hydroxide deposit in those regions.

At 60 °C, the film has an uneven net of cracks. There are regions of film exfoliation and peeling off. This structure is similar to the structure of the film deposited at 50 °C, however, the film is more intact with a lower number of peeled off regions. An assumption can be made about the two-layered structure of the film, because a deposit with holes in it can be seen in peeled off regions.

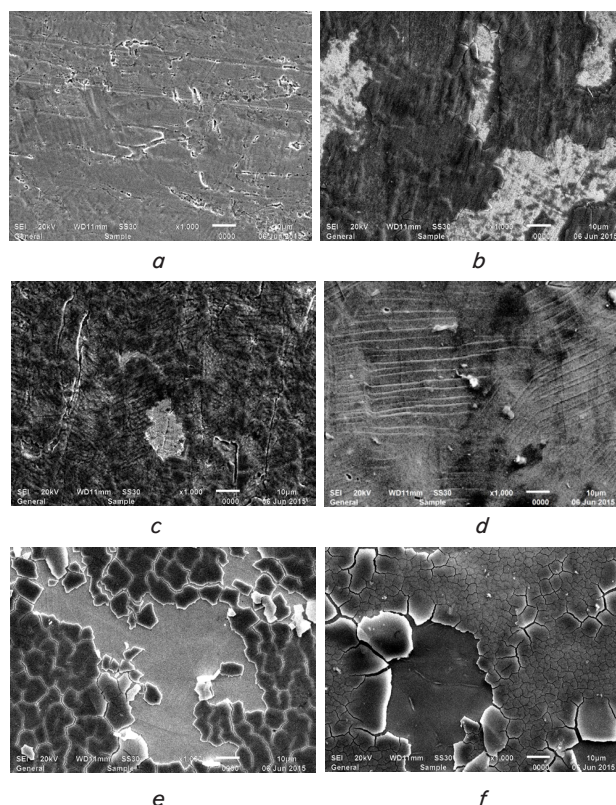


Fig. 2. SEM image of electrochromic films deposited at different electrolyte temperatures: *a* – 10 °C; *b* – 20 °C; *c* – 30 °C; *d* – 40 °C; *e* – 50 °C; *f* – 60 °C

To describe the surface microrelief of nickel hydroxide films deposited at different temperatures, the Atomic-Force Microscopy has been used (Fig. 3).

For the film deposited at 10 °C, the electrode surface is constituted by smooth bulges.

At a deposition temperature of 20 °C, many needle-like bulges are present on the film surface.

The film deposited at 30 °C has a surface with smooth bulges.

At a deposition temperature of 40 °C, the film surface reminds a folded structure.

The surface of the film that has been deposited at 50 °C has a number of smooth bulges.

At a deposition temperature of 60 °C, it can be seen that the film of nickel hydroxide is spread unevenly, because lines characteristic of the metal relief are clearly seen on the image. The surface also includes a number of small crevices.

Thus, it can be concluded that, according to SEM and AFM results, the films deposited at 30 °C are the most uniform. This leads to a preliminary conclusion that the films

deposited at 30 °C would have the best optical properties, i. e. minimal distortion of passing light.

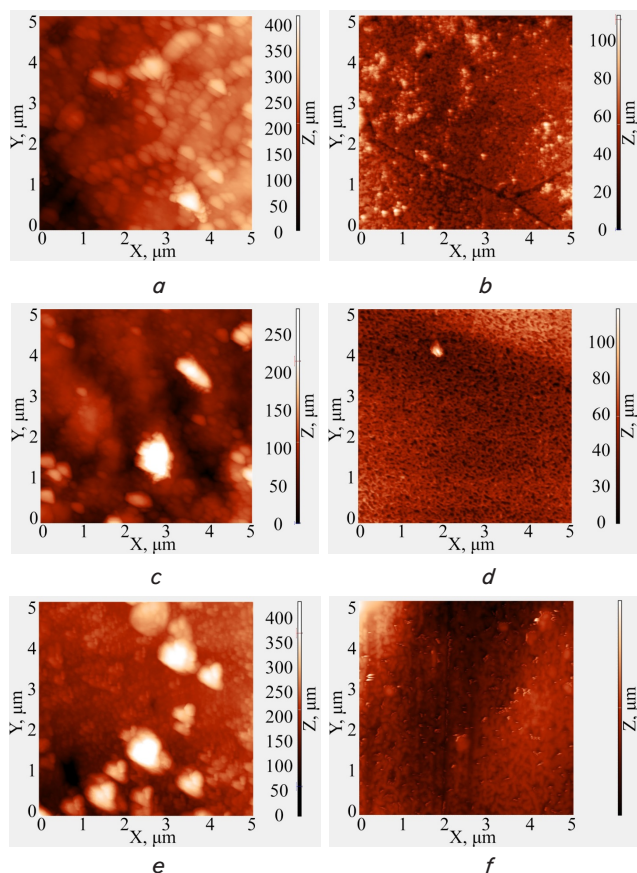


Fig. 3. AFM images of electrochromic films prepared at different deposition temperatures of electrolyte: *a* – 10 °C; *b* – 20 °C; *c* – 30 °C; *d* – 40 °C; *e* – 50 °C; *f* – 60 °C

### 5.2. Comparison of nickel hydroxide films prepared at different deposition temperatures

Fig. 4 shows X-ray diffraction patterns of films prepared at different deposition temperatures. The patterns were recorded without separating films from nickel foil, and so the substrate pattern is also presented for comparison. Intense peaks at 52 and 62° on Fig. 4 are reflexes of metallic nickel.

With the increase of deposition temperature and with the presence of electrochromic films, the intensity of reflexes in range the 10–30° increases, however, there are no well-defined reflexes, which indicated X-ray amorphous structure. The predominance of reflexes in a region of low angles indicates a structure that is similar to  $\alpha$ -Ni(OH)<sub>2</sub>. It should be noted that at deposition temperatures from 20 to 40 °C, a notable well-defined and sharp peak at 16° appears which corresponds to  $\alpha$ -Ni(OH)<sub>2</sub>. It is interesting to note that with increasing temperature, the intensity of the peak at 16° increases at first and decreases afterwards. The maximum peak intensity is for a deposition temperature of 30 °C. It should be noted that the patterns demonstrate the presence of phases with large interlayer distance between hexagonal planes in (100) direction.

Obviously, listed characteristics ( $\alpha$ -like structure, X-ray amorphously, the presence of a structure with interlayer distance in (100) direction that is larger than that of  $\alpha$ -Ni(OH)<sub>2</sub>) could indicate a large amount of structural wa-

ter, and the possible presence of other ions in the interlayer distance (100).

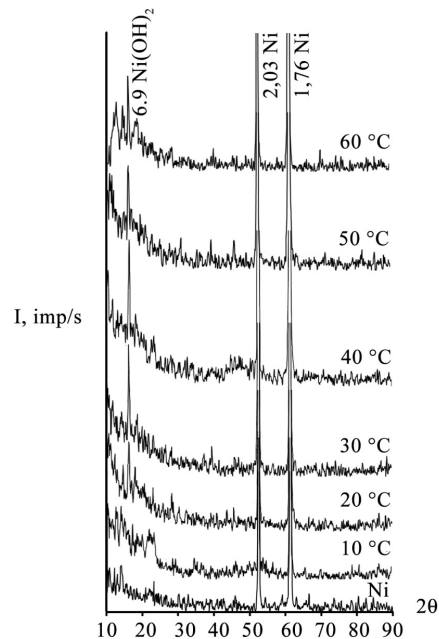


Fig. 4. X-ray diffraction patterns of nickel substrate and nickel hydroxide films deposited at different electrolytes

### 5.3. Comparison of optical and electrochemical properties of nickel hydroxide films prepared at different deposition temperatures

The conclusions regarding the electrochemical activity and influence of deposition on electrochromic properties have been drawn based on obtained cyclic voltamperograms and coloration-bleaching curves. Typical coloration-bleaching curve and CVA curve are shown in Fig. 5, *a*, *b* for the film prepared at 30 °C.

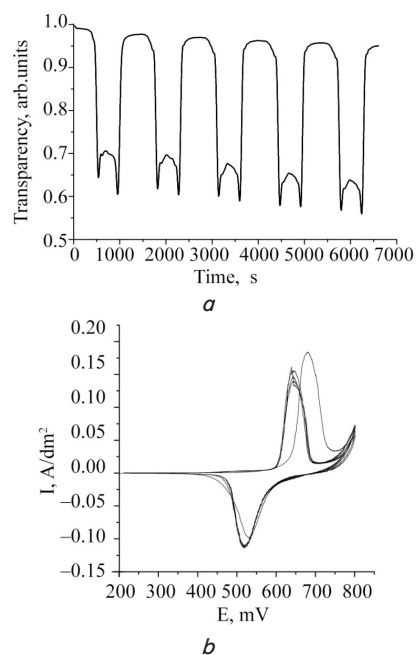


Fig. 5. Optical and electrochemical characteristics of the film prepared at 30 °C: *a* – Coloration-bleaching curve; *b* – cyclic voltamperogram

Fig. 6 shows optical properties histogram of nickel hydroxide films, on which the difference between the colored and bleached state of the film and also the difference between the bleached state of the first and fifth cycles for each temperature are presented.

The biggest difference between the colored and the bleached state corresponds to the film deposited at 30 °C. The latter indicates that deposition at 30 °C leads to the formation of films with the best electrochromic properties than at other temperatures.

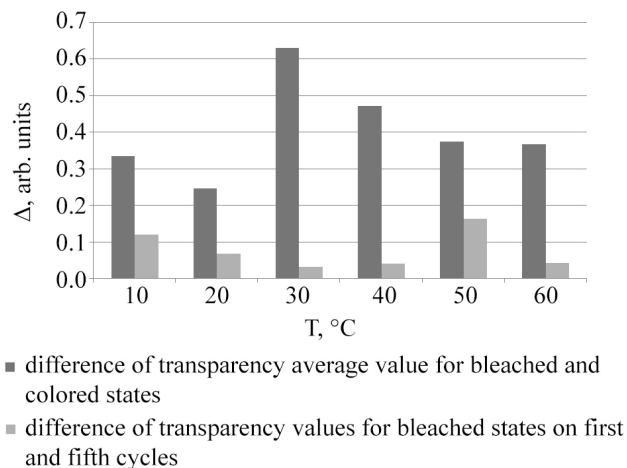


Fig. 6. Light transmittance change histogram for films deposited at different temperatures

In addition, the film deposited at 30 °C has demonstrated minimal deviation of light transmittance in the bleached state of the first and fifth cycle.

The best reversibility of the process has been demonstrated by nickel hydroxide films deposited at 30, 40 and 60 °C. However, it should be noted that the film prepared at 60 °C did not cover completely the surface of the electrode.

At a deposition temperature of 10 and 20 °C, the film bleaching occurred in spots.

For films deposited at 40 and 50 °C, good coloration and bleaching were characteristic of the first cycle and further bleaching was not uniform.

Evaluation of cathodic capacity during bleaching of nickel hydroxide films has allowed evaluating the electrochemical activity of electrochromic deposits. The results of calculating cathodic capacities are presented in Fig. 7.

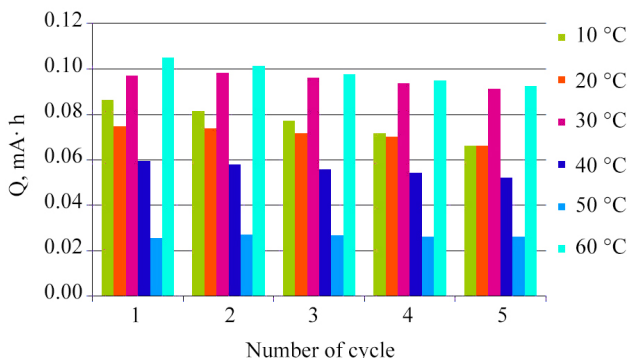


Fig. 7. Cathodic capacity histogram of Ni(OH)<sub>2</sub> films deposited at different temperatures

Upon increasing the temperature to 30 °C, an increase of capacity is observed, while upon increasing the tem-

perature above 30 °C, the decrease of capacity is observed. Thus, the film prepared at 30 °C is the most electrochemically active.

This result is supported by optical tests and visual assessment of the uniformity of the colored state.

The result acquired at 60 °C is likely related, on the one hand, to the high activity of hydroxide, and on the other, to non-uniform film deposition.

## 6. Discussion of morphology, structure, optical and electrochemical characteristics

### Surface morphology.

SEM images have shown a strong dependency of morphology on deposition temperature. Such dependency is determined by the viscosity of solution which changes with deposition temperature. Thus, electrolyte temperature would define the values of diffusion coefficients and ion mobility. The values of diffusion coefficients and ion mobility would in turn influence structure and morphological properties of deposited films. Non-uniformity of films can also be related to diminished convection in solution in the presence of high molecular compound – polyvinyl alcohol.

For some films, it has been demonstrated that they can consist of several layers. It also has been demonstrated that at elevated deposition temperatures (50–60 °C) films can peel off, showing its underlying layer.

High-resolution Atomic Microscopy has revealed non-uniformity at high magnification. Though it can be said that on the microlevel the films are sufficiently flat, as maximum relief shifts do not exceed 400 nM. The latter can indicate good optical characteristics of deposited electrochromic films.

The film prepared at 30 °C is the most uniform with maximum relief shift below 212 nM.

### Film structure.

All films deposited using cathodic template synthesis have a low degree of crystallinity, a large number of defects and, as a result, a large quantity of structural water and trapped ions. In addition, for films deposited at 20–60 °C, a sharp peak at  $2\theta=16^\circ$  appears on XRD pattern, the intensity of which is the highest for films deposited at 30 °C. Also, for all films, there is an elevation at  $2\theta=10-11^\circ$ , which indicates the presence of highly distorted  $\alpha\text{-Ni}(\text{OH})_2$ . The latter is in agreement with the literature on film deposition using electrochemical methods [20].

### Optical and electrochemical characteristics.

Based on optical properties, the best films are the ones prepared at a deposition temperature of 30–40 °C. The maximum coloration degree and minimal difference between the bleached state on the first and last coloration-bleaching cycle were for the film deposited at 30 °C.

The graph of cathodic reduction (bleaching) capacities has shown a partial correlation between optical and electrochemical characteristics. The highest capacity was found for the film deposited at 30 °C. A mismatch between high capacity and relatively low transmittance difference in the bleached and colored state for the film deposited at 60 °C is likely explained by non-uniform deposition. It should be noted that the sensor records the integral value of transmittance for the entire electrode surface, i.e. the obtained value is averaged.

## 7. Conclusions

1. Deposition of electrochromic thin films using template cathodic synthesis at different temperatures has been carried out and electrochemical and optical properties of the prepared films have been studied. It has been demonstrated that the optical characteristics of prepared films partially correlate with electrochemical characteristics.

2. It has been demonstrated that in the temperature range from 10 to 30 °C, the electrochemical characteristics and degree of uniformity are relatively high, however, bleaching and coloration of films deposited at 10 degrees is not uniform. Temperature increase above 30 degrees leads to an abrupt decrease of electrochemical and optical characteristics.

3. The temperature influence on the characteristics of nickel hydroxide electrochromic films has been evaluated.

It has been demonstrated that temperature increase up to 30 °C improves the electrochemical and optical properties. However, with further increase of synthesis temperature, these properties degrade abruptly, especially uniformity of the coloration-bleaching process. Such character of dependency of electrochemical and optical properties on synthesis temperature is likely governed by two factors. This first one is the decrease of viscosity with increasing temperature, which eases the supply of nickel ions to the reaction region. The second – is the influence of temperature on the structure of hydroxide itself.

4. The optimal temperature for deposition of electrochromic films has been determined, which is 30 °C. At this temperature, the electrochromic film has a high degree of coloration and bleaching with the color transition being the most uniform among other films.

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**Описано закономірності впливу легування елементами втілення (O, N, H) на фізико-механічні властивості сплавів на основі цирконію. Наведено результати експериментальних досліджень щодо впливу обробки у контрольованому кисне- та азотовмісному середовищах на властивості зразків-кілець, вирізаних із цирконієвої оболонки тепловідляючого елемента марки Zr-1 % Nb. Показано особливості стану внутрішньої та зовнішньої поверхонь після обробок**

**Ключові слова:** цирконієві сплави, елементи втілення, приповерхневий шар, твердість, приріст маси, оболонка тепловідляючого елемента

**Описаны закономерности влияния легирования элементами внедрения (O, N, H) на физико-механические свойства сплавов на основе циркония. Приведены результаты экспериментальных исследований влияния обработки в контролируемом кислород- и азотсодержащих средах на свойства образцов-колец, вырезанных из циркониевой оболочки тепловыделяющего элемента марки Zr-1 % Nb. Показаны особенности состояния внутренней и внешней поверхностей после обработки**

**Ключевые слова:** циркониевые сплавы, элементы внедрения, приповерхностный слой, твердость, прирост массы, оболочка тепловыделяющего элемента

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# EFFECT OF OXIDATION AND NITRIDING ON THE PROPERTIES OF ZIRCONIUM ALLOYS

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## 1. Introduction

Due to the combination of unique physical and mechanical properties with the low cross section of absorption of thermal neutrons, zirconium and its alloys are widely used in nuclear technology. These properties make them non-alternative construction material for working in the active zone of thermal neutron reactors. However, some factors significantly reduce the possibility of their use. In particular, service properties of zirconium are essentially influenced by the interstitial elements – oxygen and nitrogen. Chemical-thermal treatment is one of the most effective methods of controlling the structure and characteristics of near-surface layers of metals, and as a result, they significantly affect functional properties of the material. Therefore, the expansion of ideas about the impact of the near-surface layer, enriched with interstitial elements, on properties of pipes made of Zr-1 % Nb alloy of heat generating elements (HGE), is quite appropriate.

It is known that the existence of oxygen or nitrogen in the lattice of zirconium inhibits absorption of the interstitial

elements (for example, hydrogen) and affect anticorrosive characteristics. However, the problem of peculiarities of saturation of internal and external shell surfaces of heat generating elements with interstitial elements has not been studied sufficiently enough. Therefore, one of the relevant problems at present in the area of zirconium alloys is the establishment of influence of oxidation and nitriding on the properties of shell surfaces of the heat generating elements.

## 2. Literature review and problem statement

Zirconium alloys are important structural material for products of an active zone and the HGE of nuclear power plants (including shells of the HGE) [1–3]. For the purpose of nuclear safety, the nuclear shell of elements of nuclear reactors should meet increased requirements. The most vulnerable element of the HGE is the wall of a pipe [4, 5]. The key to effective use of zirconium alloys is provision of their proper structural-phase state. The peculiarity of the zirconium alloy is high sensitivity of structural-phase state