

The cost of electrochromic “smart” windows ranges from 200–800 USD/m². The high cost is determined by the small volume of production and the high cost of vacuum methods for applying device layers. The development of other methods could lead to lower costs and further mass use of “smart” windows.

The paper presents the work on improving the electrochemical method of deposition of electrochromic films based on Ni(OH)₂. Composite electrochromic films were deposited from Ni(NO₃)₂ solutions with the addition of water-soluble polymers – polyvinyl alcohol (PVA), polyvinylpyrrolidone (PVP), and mixtures thereof. Two PVA grades and one PVP grade were used in the experiments. As a result, six films were obtained from solutions of different compositions and concentrations of polymers.

An investigation of the optical properties of the films in the initial state showed that there is no intense absorption of light in the entire visible spectrum and the transmission corresponds to a glass substrate. Thus, the formed electrochromic films will not produce tints and visible light absorption in the finished electrochromic element.

The electrochemical and electrochromic characteristics of the films differed significantly depending on the amount and specific polymers used. The film obtained from a solution containing PVA grade 24–99 was the most electrochemically active, while the best electrochromic characteristics were in the film deposited from a solution of a mixture of PVP grade 24–99 and PVP. Moreover, the films obtained in solutions containing separately PVA grade 24–99 and PVP had worse electrochromic characteristics, and the electrochemical characteristics were the same or worse relative to the film obtained in a mixture of polymers.

The results of the method of electrochemical impedance spectroscopy showed compliance with the found electrochromic and electrochemical characteristics of the formed films

Keywords: electrochromism, nic-kel hydroxide, polyvinyl alcohol, polyvinylpyrrolidone, optical characteristics, electrochemical impedance spectroscopy

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CHARACTERISTICS INVESTIGATION OF COMPOSITE ELECTROCHROMIC FILMS BASED ON Ni(OH)₂, POLYVINYL ALCOHOL, AND POLYVINYLPIRROLIDONE

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1. Introduction

The synthesis of hydroxide compounds with certain properties is one of the main areas of applied research in

chemistry and materials science [1, 2]. Metal hydroxides have found wide application in various fields of creating new materials for electronics [3], medicine [4], new ways of synthesizing organic compounds [5], and other areas.

One of the most studied compounds is nickel (II) hydroxide [6]. This is due to a number of its unique properties, which allow it to be used in battery systems [7] and supercapacitor electrodes [8]. The basis of its use is the reversibility of the processes of electrochemical oxidation and reduction, as well as the semiconductor properties of the oxidized form, NiOOH [9].

In addition to the listed uses, nickel hydroxide is positioned as an electrochromic material. Thin films of Ni(OH)₂ deposited by certain methods are transparent in the initial state, oxidize during anodic polarization and acquire a dark brown color. Upon polarization by the cathode current, dark films restore their initial transparent state [10].

An important point is that films deposited on the cathode from Ni(NO₃)₂ solutions have weak adhesion to substrates (ITO, FTO). Low adhesion hinders their use as components of electrochromic devices. However, compared to other deposition methods, the electrochemical method of film formation is more attractive. The advantages of Ni(OH)₂ electrochemical deposition include low cost and ease of implementation, good controllability of deposit properties, low power consumption, and ease of automation [11].

2. Literature review and problem statement

The quality of nickel hydroxide as an electrochromic coating is determined by the high electrochemical and electrochromic characteristics of the deposit. Along with these qualities, the film should have high stability under increased illumination, sudden temperature changes, multiple reversible electrochemical oxidation-reduction, and good adhesion to the substrate. Different approaches are used to improve the performance of electrochromic nickel hydroxide films.

For example, to improve the stability, the authors of [10] proposed to obtain porous deposits of nickel hydroxide electrochemically from solutions of a mixture of NiCl₂, KCl, and H₂O₂. The deposits obtained had high stability and rate of switching between color states, which was determined by the high porosity of the deposits. This effect is obviously due to the high porosity leading to an increase in the specific surface area and, as a consequence, a decrease in the actual current density on the surface.

In [12], the researchers grew nanorods consisting of semiconductor In₂O₃ on an electrically conductive transparent FTO glass substrate. Next, using the hydrothermal method, a nickel hydroxide film was formed on top of the formed nanorod substrate. The resulting film had high specific characteristics and stability. Obviously, the positive effect is the creation of a greater degree of contact between the electrochromic film and the current lead. At the same time, the researchers emphasized that nickel hydroxide most often has poor adhesion to the surface of electrically conductive substrates and, therefore, is used only as a precursor for the formation of electrochromic NiO by annealing.

By doping with copper, the characteristics of NiO films, which were formed chemically, were improved [13]. The obtained films changed their parameters depending on the amount of the dopant, the concentration of which reached 1%. As a result, the authors showed the best stability of the doped film with a copper concentration of 0.5% compared to the undoped one. The addition of Cu was used to change the morphology of the increase in specific surface area, which had a positive effect on the transport characteristics in the solid phase of the substance.

The paper [14] reported on the synthesis of stable electrochromic NiO deposits using metal vapor deposition using a hot filament. Nanostructured NiO films had high specific characteristics and high stability of characteristics.

The authors of [15] proposed to improve the characteristics of the Ni(OH)₂ film by treating the substrate surface to obtain a developed surface of the latter. It was shown that because of electrochemical treatment in an HCl solution, an additional increase in the surface area appeared due to the formation of microcavities. Ni(OH)₂ deposited on the substrate surface had a better color uniformity during coloring and higher specific electrochemical characteristics. At the same time, it was additionally shown in [16] that the electrochemical treatment proposed in [15] increased the adhesion of the nickel hydroxide deposit to the base.

This treatment increases the contact area between the electrochromic coating and the electrically conductive substrate, thereby improving the adhesion of the two layers and reducing the transition resistance.

In [17], the specific characteristics of nickel oxide were improved by forming an array consisting of ZnO nanorods on electrically conductive substrates. After modification of the substrate, NiO films were deposited onto the substrate by the electrochemical method from Ni(NO₃)₂ solutions. The resulting films had a high rate of switching between the optical states of the electrochromic film, high parameter stability, and good adhesion to the electrically conductive substrate.

The formation of titanium oxide nanostructures on the substrate surface followed by nickel oxide deposition was described in [18]. This approach to the formation of an electrochromic coating made it possible to increase the number of color change cycles, as well as other quality characteristics in general.

The same group of authors investigated the formation of a porous NiO coating on TiO₂ [19]. The films formed in this way had high electrochromic properties compared to pure NiO.

It should be noted that the authors of [12, 16–19] generally used the same approach to increasing the characteristics of electrochromic films, i.e., the creation of a developed substrate surface, on which an electrochromic film was subsequently deposited.

A fundamentally different approach in terms of characteristics is the production of polymer-based composite materials with new properties.

Thus, [20] shows that electrochemical coprecipitation of nickel hydroxide together with polyvinyl alcohol (PVA) led to the stabilization of the properties of the obtained electrochromic film. This improved the optical properties and adhesion of the film to the nickel base. In turn, other works showed the importance of choosing a PVA grade for the electrochemical, electrochromic [21], and adhesive [22] properties of a composite electrochromic film.

The electrochemical preparation of polymer-inorganic composites with polyvinylpyrrolidone (PVP) [23] also led to the formation of high-quality films with stable electrochromic properties. The work also found the optimal concentration of PVP, 0.5–1%.

Interestingly, the optimal concentration for PVA in the electrochemical deposition solution of Ni(OH)₂-PVA composite films was different compared to PVA and amounted to 4–5% [24].

Presumably, the use of polymers in the deposition of electrochromic composite films leads to their inclusion in the structure, which relieves the internal stresses of the deposit, and also gives them some flexibility. This is the difference

between the second approach to the modification of hydroxide-based films.

The third method for increasing film parameters is to increase the substrate microrelief using various methods [10, 13, 14]. An increase in morphological irregularities, as well as an increase in porosity, directly affects the transport and kinetic characteristics of sediments. The specific area and diffusion coefficient of the proton through the crystal lattice during electrochemical reactions play a key role in the rate of the entire process. However, these parameters most likely will not affect the adhesion and stability of the deposit parameters over time.

Unlike other methods, electrochemical coprecipitation of organic substances together with a nickel hydroxide film [20–24] is simpler and cheaper. At the same time, given the positive effect of PVP and PVA, the joint use of two polymers can potentially improve the characteristics of the formed electrochromic films due to the synergistic effect.

3. The aim and objectives of the study

The aim of the work was to study the characteristics of composite electrochromic films based on $\text{Ni}(\text{OH})_2$, polyvinyl alcohol, and polyvinylpyrrolidone, which would make it possible to reveal the combined effect of PVP and PVA on the specific characteristics of electrochromic electrodes.

To achieve the aim, the following objectives were set:

- to compare the initial optical characteristics of $\text{Ni}(\text{OH})_2$ -polymer composite films (where the polymer is PVA, PVP, and mixtures of PVA with PVP);
- to compare the electrochemical and electrochromic properties of the obtained films.

4. Materials and methods

4.1. Materials used and technique for obtaining electrochromic films

All films were obtained on a glass substrate coated with fluorine-doped tin oxide (FTO glass, substrate resistivity $\rho_s \leq 10 \text{ Ohm/sq}$). (China, Zhuhai Kaivo Optoelectronic Technology Co. Ltd).

Prior to coating, the substrates were processed in several steps. First, the substrates were rubbed with Na_2SO_4 paste. This was followed by rinsing with running and distilled water, as well as treatment in 96 % ethanol at a temperature of 30 °C in ultrasound (60 W, 41,500 Hz).

The formation of $\text{Ni}(\text{OH})_2$ -polymer deposits was carried out with the polarization of the base by the cathode current in the following mode:

- deposition on the cathode with a current density of 0.1 mA/cm²;
- duration of the deposition was 10 min.

Different electrolytes were used to form different coatings. Further, the films obtained in the work are denoted according to Table 1. Each sample was obtained twice.

It should be noted separately that the deposition duration and current density were chosen based on the literature data for electrochemical deposition from 0.01 M $\text{Ni}(\text{NO}_3)_2$ without the addition of PVA and PVP [25], as well as according to the optimized values for cathodic template deposition from solutions of 0.01 M $\text{Ni}(\text{NO}_3)_2$ with PVA [26, 27].

Next, the samples were rinsed from water-soluble salts by keeping them in distilled water at 30 °C for 10 minutes

and dried for one day at room temperature. Before the experiments, the electrodes were stored in a dark closed box at room temperature.

Table 1

Electrolyte compositions and symbols of obtained samples

No.	Electrolyte composition	Sample symbol
1	0.01 M $\text{Ni}(\text{NO}_3)_2$, 4 % PVA (grade 24-99)	PVA 24-99
2	0.01 M $\text{Ni}(\text{NO}_3)_2$, 4 % PVA (grade 30-88)	PVA 30-88
3	0.01 M $\text{Ni}(\text{NO}_3)_2$, 1 % PVP ($M=12600 \pm 2700$ a.m.u.)	PVP 1 %
4	0.01 M $\text{Ni}(\text{NO}_3)_2$, 4 % PVA (grade 24-99), 1 % PVP ($M=12600 \pm 2700$ a.m.u.)	PVA24-99×PVP 1 %
5	0.01 M $\text{Ni}(\text{NO}_3)_2$, 4 % PVA (grade 30-88), 1 % PVP ($M=12600 \pm 2700$ a.m.u.)	PVA30-88×PVP 1 %
6	0.01 M $\text{Ni}(\text{NO}_3)_2$, 1 % PVP ($M=12600 \pm 2700$ a.m.u.)	PVP 0.5 %

4.2. Methods for investigating the characteristics of electrochromic films

Investigating methods of optical characteristics.

Optical parameters were recorded on a USB400-UV-VIS spectrometer (Ocean Optics, USA). A deuterium-tungsten halogen light source and P200-7-SR light guides were used in the measuring setup.

Investigating methods of electrochemical characteristics.

The electrochemical characteristics were evaluated by the potentiodynamic method. The electrode was connected according to the three-electrode scheme. The potential was turned from +210 mV to +760 mV relative to a normal hydrogen electrode at a rate of 1 mV/s. A silver chloride electrode in a 3 M KCl solution was used as a reference electrode. In parallel with the determination of the electrochemical characteristics of the electrodes, changes in the transparency of the film were also recorded. Cyclic voltammetry was carried out on a Gamry Interface 1010 potentiostat (USA).

Electrochemical impedance spectroscopy of the electrodes was carried out after cycling the electrodes in the mode described above on a Palmsens 4 potentiostat (Netherlands). Curve acquisition parameters – step 5 mV, interval 100,000–0.1 Hz. The curves were approximated using a specialized program PStace5, which came with a potentiostat.

Investigating methods of electrochromic characteristics.

The setup for determining the electrochromic characteristics consisted of a light source (5,500 K, China), a transparent cell with an electrolyte (0.1 M KOH), a recording photoresistor, an electronic potentiostat (Elins P-8), an ADC (E-154), and a stabilized power supply. The operating principle of the setup is considered in [24].

5. Results of investigations of $\text{Ni}(\text{OH})_2$ -polymer composite electrochromic electrodes

5.1. Results of optical measurements of $\text{Ni}(\text{OH})_2$ -polymer electrodes

Fig. 1 presents generalized data for the obtained films in the uncolored state. To compare the absorption spectra of the films, the graph also shows the dependence for a pure substrate, FTO glass. The experiment to determine

the absorption spectrum of the films in the uncolored state reflected significant differences between the films and the base when using different water-soluble polymers. In other words, such a measurement was dictated by the need to determine the relationship between the polymer used and the quality of the visible spectrum transmission of the films.

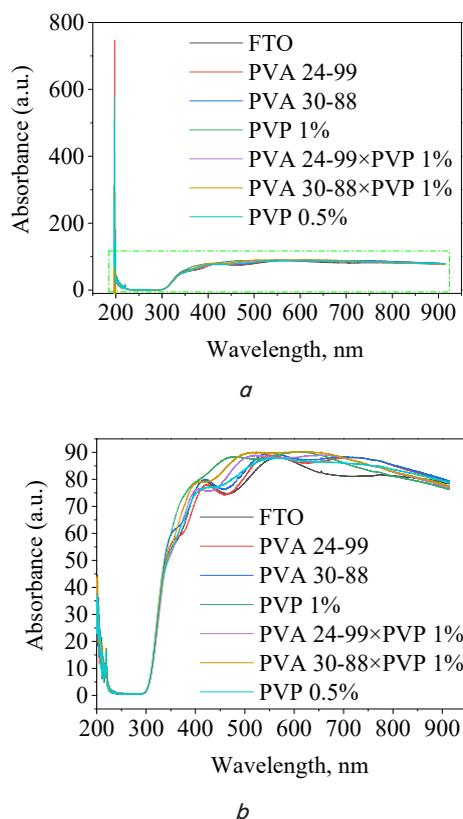


Fig. 1. Visible light absorption spectra for the synthesized $\text{Ni}(\text{OH})_2$ -polymer films: *a* – general view; *b* – an enlarged region marked with a green rectangle

The primary analysis is based on the overall absorption pattern in Fig. 1, *a*. Its analysis leads to the fact that the spectra of the films and the base were close. The general trend for all films is the following: complete absorption in the region of near-visible UV radiation, which is associated with absorption in the glass. There are also two regions – almost zero absorption in the violet region of the spectrum (up to 300 nm) and an increase in absorption starting from 300 nm with a maximum of about 550 nm (green). Zooming (Fig. 1, *b*) shows that all samples with films absorb slightly more light, starting in the region of 300–900 nm. In addition, all films absorb light more than the base in the range of yellow and red (550–800 nm). At the same time, when electrochromic films are deposited on the substrate, the peaks at 400 and 550 nm (pure FTO glass) are shifted to the short wavelength region of 380 and 500 nm, respectively. No other significant differences are found when comparing individual films with each other, or when comparing films with the base.

5.2. Investigation of electrochemical properties of $\text{Ni}(\text{OH})_2$ -polymer electrodes

Fig. 2 shows cyclic voltammograms (CV) for the formed electrodes.

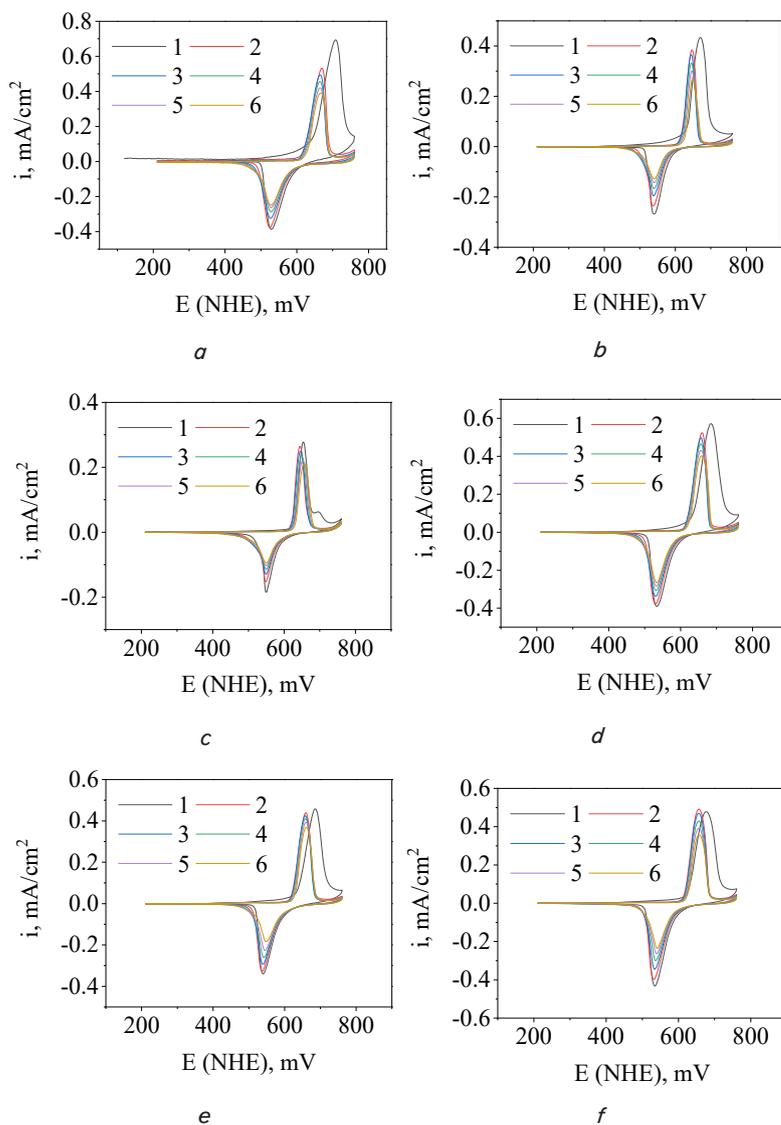


Fig. 2. Cyclic voltammograms (CV) obtained for films: *a* – PVA 24-99; *b* – PVA 30-88; *c* – PVP 1%; *d* – PVA24-99×PVP 1%; *e* – PVA30-88×PVP 1%; *f* – PVP 0.5 %

Comparison of the CVs of different electrodes allows us to conclude that the characteristics of the films differ significantly from each other. This is evidenced by numerous differences in the positions and heights of the peaks. The heights of the anodic peaks of the oxidation of $\text{Ni}(\text{OH})_2$ in NiOOH are higher for all films than in the reverse process, which is associated with the process efficiency being less than 100%. In this case, the PVP 1% film has the smallest peaks. The difference in the electrochemical behavior of the films also determines the differences in their electrochromic properties.

Fig. 3 shows a summary histogram of the coloration depth values of the films in the last coloring-bleaching cycle. Coloration depth D , % means the maximum difference between the transparency in the bleached and colored initial

state. Therefore, this value reflects the maximum amount of light that a given film can block.

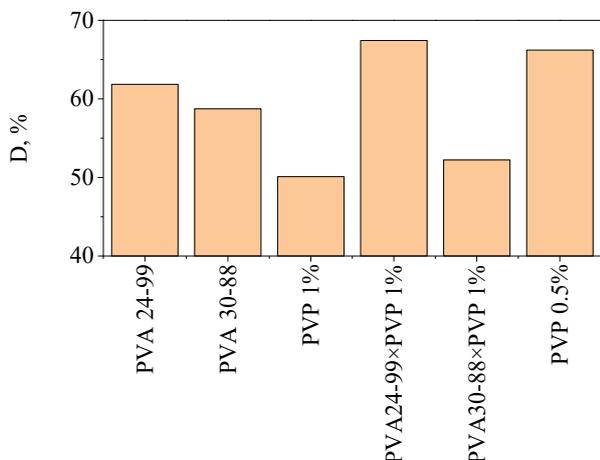


Fig. 3. Coloration depth D obtained for films in the last coloring-bleaching cycle: a – PVA 24-99; b – PVA 30-88; c – PVP 1 %; d – PVA24-99xPVP 1 %; e – PVA30-88xPVP 1 %; f – PVP 0.5 %

The analysis of the presented values of D , % shows that the results for two grades of PVA with PVP are significantly different. In the case of a mixture of PVA grade 24-99 and PVP, an increase in the D value is observed, and in the case of a mixture of PVA grade 30-88 and PVP, on the contrary, a decrease is observed. It should be noted that the worst result was obtained for the PVP 1 % film.

Fig. 4, a presents electrochemical impedance spectra for electrodes after cycling.

A comparison of the obtained impedance characteristics revealed that all electrodes differed significantly from each other in properties. To analyze the impedance characteristics of the electrodes, we chose an equivalent model used in studies related to the formation of oxide and hydroxide electrochromic films [25–27]. In the circuit, R_1 is the charge transfer resistance, R_2 is the uncompensated electrolyte resistance, W_1 is the Warburg impedance, and C_1 is the electric double layer capacitance. It should be noted that the simulation results according to the chosen model were in good agreement with the experimentally obtained dependences. As a result of processing the CV and impedance characteristics for the films, the cathode and anode average capacitances $C(a)$, $C(c)$, and the average total polarization $\eta(s)$ were obtained. The latter was calculated as the arithmetic mean of the difference in the position of the anode and cathode peaks on the CV. The values of the equivalent circuit elements R_1 , R_2 , W_1 , and C_1 were also calculated (Fig. 4, b), and summarized in Table 2.

Analysis of the values in Table 2 revealed significant differences between the deposited films.

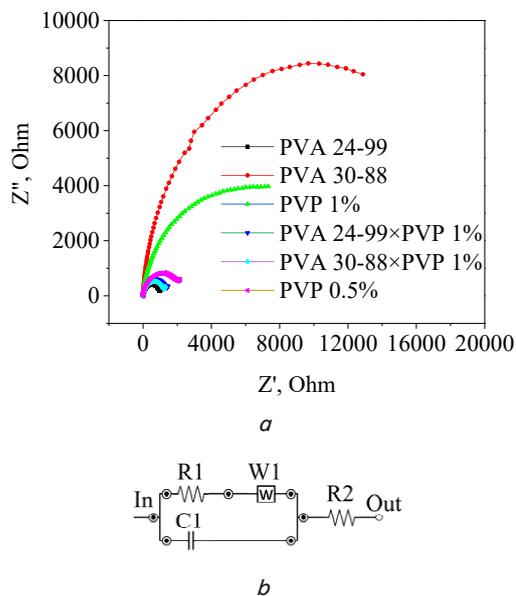


Fig. 4. Electrochemical impedance spectra: a – obtained for electrodes after cycling; b – equivalent circuit

In addition, the samples had significant differences in specific capacitances (Fig. 5) and charge transfer resistance (Fig. 6).

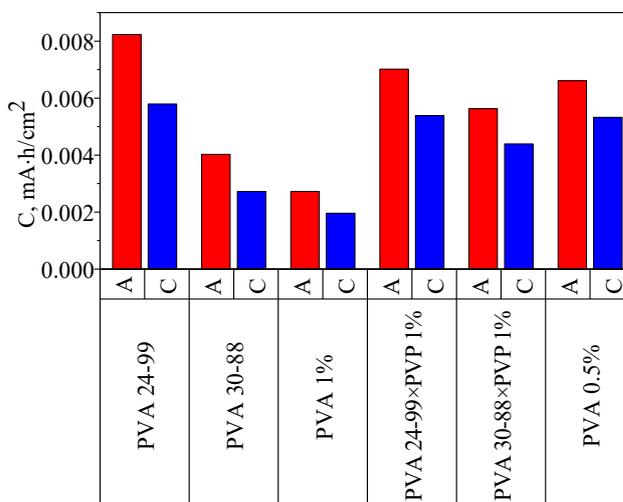


Fig. 5. Specific average capacitances of anodic (A) and cathodic (C) processes for the different samples

Table 2

Generalized electrochemical characteristics for the synthesized films

Sample	$C(a)$, mA·h/cm ²	$C(c)$, mA·h/cm ²	$\eta(s)$, mV	R_1 , Ohm	R_2 , Ohm	W_1 , Ohm	C_1 , F
PVA 24-99	0.008231	0.005795	144.9	775.5	19.1	230.3	$3.67 \cdot 10^{-5}$
PVA 30-88	0.004028	0.002723	110.5	10350	13.7	4927.0	$3.75 \cdot 10^{-5}$
PVA 1 %	0.002723	0.001962	99.8	3284	12.8	3708.0	$3.64 \cdot 10^{-5}$
PVA 24-99xPVP 1 %	0.007017	0.005394	129.7	1054	13.9	351.2	$4.6 \cdot 10^{-5}$
PVA 30-88xPVP 1 %	0.005629	0.004396	120.8	958.7	14.9	306.5	$4.6 \cdot 10^{-5}$
PVA 0.5 %	0.006610	0.005328	123.0	1339	12.7	631.2	$4.1 \cdot 10^{-5}$

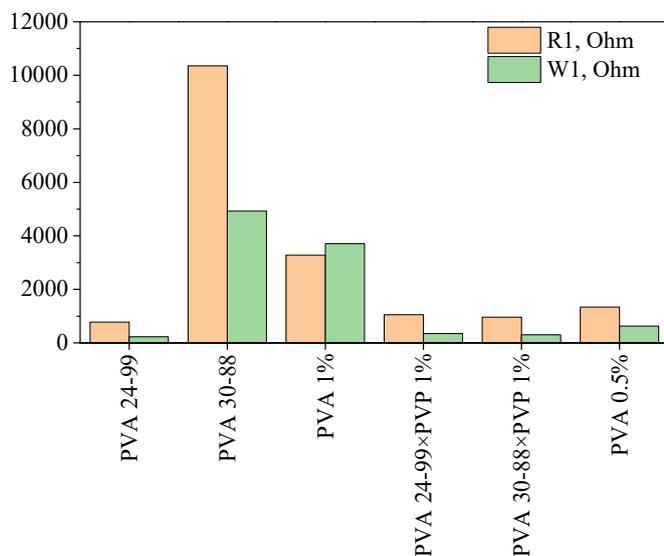


Fig. 6. Charge transfer resistance (R1) and Warburg impedance (W1) calculated by simulation based on experimental data of impedance spectroscopy

6. Discussion of the results of Ni(OH)₂-polymer composite electrochromic electrodes investigation

One of the important parameters of an electrochromic film is the initial transparency and light absorption of different wavelengths in the uncolored state. Poor light transmission characteristics, as well as their unevenness, will negatively affect the visual perception of the deposited films. Nevertheless, a comparison of the absorption spectra of the films shows that it is minimal and comparable with the glass used as a substrate (Fig. 1). Moreover, since there are no large absorption irregularities at all wavelengths, the films will not produce any tints in their original state.

A comparison of the anodic and cathodic capacities of the processes showed very serious fluctuations in values depending on the composition of the electrolyte used to form the electrochromic coating. The total polarization $\eta(s)$ of the electrodes also differed greatly. Among the characteristics obtained based on impedance measurements, the uncompensated electrolyte resistance R2 and the capacitance of the electrical double layer C1 were practically the same (Table 2). The latter fact is logical, since the structure of the electrodes, their dimensions, and the nature of the processes were similar. In the final case, the characteristics of the films were compared in terms of the specific capacitances of the anode and cathode processes and the R1 and W1 values.

It should be noted that the capacitance characteristics of the electrodes (Fig. 5) were minimal for the PVA 30-88 and PVA 1% samples. Sample PVA 24-99 demonstrated the largest capacitances. It was noteworthy that the nature of the change in the capacitance characteristics in Fig. 5 was similar to the nature of the change in the coloration depths D (Fig. 3) for the corresponding films, except for PVA 24-99xPVP 1%. Thus, we can conclude that the electrochemical characteristics partially correspond to the optical ones. Moreover, a comparison of the graphs in Fig. 3 and 5 leads to the conclusion that the combined use of two polymers PVA grade 24-99 and PVP does not lead to an

overall improvement in electrochemical characteristics. At the same time, this film has the best optical characteristics (Fig. 3).

Such a change may be due to the formation of a cross-linked polymer. Most likely, PVA grade 24-99 is more reactive and can interact with PVP to form a branched polymer. The latter can form a stronger bond with both the electrochromic nickel hydroxide and the substrate, thereby improving the characteristics of the composite as a whole. The possibility of forming cross-linked PVA-PVP polymers, for example, is shown in [28, 29]. The electrochemical cross-linking of polymers in the presence of certain ions is shown in [30].

Thus, during deposition, part of the current could be used to crosslink polymers and simultaneously form a composite. The latter can have better contact with the surface of the substrate. On the other hand, a certain amount of electric current is spent on the electrochemical crosslinking of two polymers, which reduces the Ni(OH)₂ current efficiency, thereby leading to a decrease in the average capacitances of the electrochromic film.

It is also interesting to analyze Fig. 5, and 6. A comparison of the data shows the highest resistances of R1 and W1 for PVA 30-88 and PVA 1% films. At the same time, these very films have the smallest specific capacitances among all samples (Fig. 5).

A comparison of the charge transfer resistance R1 and diffusion resistance W1 of the PVA 30-88 and PVA 1% films shows that both resistances are lower for the PVA 30-88 sample. In this case, its specific capacitance should be larger. However, the situation is the opposite. This dependence can be associated with a decrease in the simulation accuracy for these two films.

A limitation of the study is the absence of deposited films obtained at different current densities and deposition time intervals. It is also interesting to determine the effect of the presence of two polymers in the deposition electrolyte on the life of the formed electrochromic electrodes. Therefore, in further investigations of the effect of the addition of several polymers on electrochromic films, it is necessary to carry out their multiple cycling, as well as to study their preparation under different electrodeposition conditions.

The results of these studies can be used to further improve the characteristics of electrochromic films based not only on nickel hydroxide but also on other electrochromic oxides and hydroxides.

7. Conclusions

1. Films synthesized from Ni(NO₃)₂ solutions containing 4% polyvinyl alcohol, 0.5 and 1% polyvinylpyrrolidone, as well as mixtures thereof, are optically transparent and almost do not absorb light in the entire visible radiation spectrum, which indicates high transparency of the films in their original state.

2. A synergistic effect of increased electrochemical properties of the electrochromic film was obtained when using a solution containing a mixture of polyvinyl alcohol grade 24-99 and polyvinylpyrrolidone $M=12\ 600\pm 2\ 700$ a. m. u. This is most likely due to the cross-linking of polymers and, in turn, to the improvement in the functional properties of the composite.

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