Films based on nickel (II) oxides and hydroxides are used in electrochromic cells as one of the active materials that change their optical characteristics under the action of an electric current. Electrochemical deposition, due to which composite films of Ni(OH)$_2$-polyvinyl alcohol (PVA) can be formed on the electrically conductive substrate, can become an alternative to expensive vacuum methods. The presented study is devoted to the study and improvement of the electrochemical method of deposition of Ni(OH)$_2$-PVA electrochromic composite films.

This study illustrates the influence of the grade of the used polyvinyl alcohol on the main qualitative characteristics of Ni(OH)$_2$-PVA electrochromic composites. Four PVA grades have been used for the study: 17−99, 24−99, 30−99, and 30−88, which differ in the viscosity of solutions and the degree of hydrolysis. The deposition has been carried out by the electrochemical method in the presence of the listed grades of polymers dissolved in the electrolyte.

As a result of the study, it has been shown that the properties of electrochromic films depend on the grade of PVA used. To a greater extent they depend on the degree of hydrolysis, and to a lesser extent – on the molecular weight of the polymer, expressed in terms of viscosity.

Analysis of the data obtained makes it possible to assert that the degree of PVA hydrolysis has a greater effect on the final characteristics of the films than the viscosity of solutions. However, viscosity also affects the properties. Moreover, it has been found that there is some optimum for this value. In this case, in terms of the characteristics of the films obtained, the optimal PVA has been the one with an average viscosity (PVA 24-99) among polyvinyl alcohols of three grades with the same degree of hydrolysis. The results obtained make it possible to recommend the use of PVA with an average viscosity and a degree of hydrolysis of less than 99 %. Based on the literature data, assumptions have been made that allow explaining the results obtained by the change in the hydrophobicity of the film and the properties of the transparent SnO$_2$:F layer on glass

Keywords: electrochromic device, electrochromism, electrochemical deposition, nickel hydroxide, polyvinyl alcohol, acetate group, hydrophilicity, hydrophobicity, adhesion, template

INFLUENCE OF USED POLYVINYL ALCOHOL GRADE ON THE ELECTROCHROMIC PROPERTIES OF Ni(OH)₂-PVA COMPOSITE FILMS

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1. Introduction

Electrochromism is a phenomenon associated with a change in the optical properties of systems when an electric current is passed through them [1, 2]. Optical properties that can be varied include color [3], transparency [4], haze [5], and reflectance [6]. Devices based on systems exhibiting electrochromism can be used in various fields – in the advertising industry, in the creation of multimedia devices, in the aviation, auto, and construction industries. In this case, electrochromic elements are mainly positioned as working elements of various displays and so-called "smart" windows. The latter can be used in buildings to reduce the brightness of sunlight, which saves the energy needed to cool the premises.

Different types of systems can be used as electrochromic elements in structures: liquid crystals [7, 8], suspended particles [9, 10] or systems, in which electrochemical reactions occur [11, 12].

Nickel (II) hydroxide is one of the promising materials that can be used in electrochromic devices [13]. This material belongs to those, in which a change in the optical state is achieved by an electrochemical reaction with the formation of NiOOH from Ni(OH)$_2$.

It was shown in [14] that a composite material based on Ni(OH)$_2$ and polyvinyl alcohol (PVA) had advantages over pure Ni(OH)$_2$. In this case, the synthesis of the specified material was carried out by an electrochemical method.

Considering that the deposition of nickel-containing electrochromic compounds for the commercially available

smart windows is carried out using vacuum methods, the latter leads to a significant increase in the cost of technology. For this reason, the cost of the smart windows with electrochromic elements reaches $200-400$ USD/m^2. This is the main reason that prevents the spread of this technology. In this case, the study and development of alternative methods of applying electrochromic coatings is an urgent task on the way to reduce the cost and, accordingly, the widespread introduction of electrochromic devices.

2. Literature review and problem statement

In [14], an electrochemical method was proposed for the deposition of a composite electrochromic material Ni(OH)$_2$-PVA, which is simple, reliable, and does not require complex expensive equipment. Films obtained by this method have high adhesion to the surface of the electrically conductive glass, have good transparency [15], and can be stored in a dry state. In this case, the key component of the electrolyte is polyvinyl alcohol.

Polyvinyl alcohol is produced on an industrial scale and does not significantly increase the cost of the electrolyte to obtain [16]. At the same time, PVA is widely used in materials for electrochemical devices. For example, in [17], the researchers used PVA as part of a composite negative electrode of a supercapacitor based on an activated carbon material. In [18], a hydrogel based on PVA, polyethylene glycol, and glutaraldehyde was used as an electrolyte for a supercapacitor. Also, researchers in [19] used polyvinyl alcohol as part of an electrolyte for quasi-solid Zn-MnO$_2$ batteries. In turn, the work [20] showed the use of a PVA-based membrane in methanol fuel cells.

At the same time, PVA has found its application in the elements of electrochromic devices. Recently, researchers have proposed a method for forming a nanocomposite material based on polyaniline and polyvinyl alcohol for an electrochromic device [21]. In turn, the work [22] proposed the formation of a solid polymer electrolyte for an electrochromic device based on WO$_3$. In this case, the polymer electrolyte was prepared using polyvinyl alcohol followed by thermochemical crosslinking.

Since the films obtained from solutions of polyvinyl alcohol have considerable flexibility in the wet state this water-soluble polymer has found application in numerous applied studies. The special properties of PVA films and fibers containing water or solutions are characterized by significant elasticity and ability to repeatedly stretch (compress) with subsequent return to their original dimensions. This is the main reason for the use of materials based on the specified polymer in flexible electrochemical devices. At the same time, the largest number of works concerns a relatively new direction – flexible, stretchable (deformable) current sources. An example is the work [23], in which the authors proposed an electrolyte based on PVA for a flexible supercapacitor. At the same time, the authors emphasized that gel-polymer electrolytes based on polyvinyl alcohol (PVA) were widely known for their excellent mechanical strength, low cost, lack of toxicity, and chemical stability. In another work [24], the researchers proposed a flexible supercapacitor with a film electrode based on PVA, carbon nanotubes, and polyaniline. The specified supercapacitor had a simple manufacturing method, high flexibility, and electrochemical characteristics, in particular a specific capacity of 196.5 mF/cm^2. Moreover, after 5000 charge-discharge cycles, the capacity dropped only to 71.4 % of the original one.

However, there are a large number of polyvinyl alcohol grades that can vary significantly in their properties. It should be noted that the sources do not always indicate exact data for PVA of different grades used in experiments. There are two main differences between the grades. They are the degree of hydrolysis and molecular weight. The molecular weight, in turn, determines the viscosity of PVA solutions. According to [25] and [26], PVA grade is determined by a combination of two numbers "... the first number in the grade name indicates the viscosity of a 4 % aqueous solution at +20 °C, the second number is the degree of hydrolysis ...".

It should be mentioned that in some works there is a strong influence of PVA grade used. This is also seen as a result of compounds and composites obtained in their presence in biological research [27], for the manufacture of special-purpose paper [28], films used in optics [29].

It should be noted that the PVA effect on the properties of electrochromic Ni(OH)$_2$ films was partially evaluated in [30]. However, this work used only two grades of PVA with different degrees of hydrolysis. Besides, the deposition was carried out on nickel substrates for the use in electrochromic mirrors.

At the same time, glasses or polymers coated with a layer of transparent electrically conductive oxides with various additives are used in electrochromic windows. It is known that the adhesion forces strongly depend on the substrate material and the nature of the substance deposited on the substrate. Thus, the effect of different PVA grades during deposition on different substrates can be different.

3. The aim and objectives of the study

The study aimed to determine the effect of different PVA grades on the properties of electrochromic composite films of Ni(OH)$_2$-PVA when deposited on glass coated with an electrically conductive transparent oxide.

As part of solving this goal, the following objectives were formulated:

– to deposit composite films of Ni(OH)$_2$-PVA from electrodeposition solutions containing different PVA grades;

– to compare the electrochromic and electrochemical properties of the films followed by an analysis of the results obtained.

4. Materials and research methods used to determine the effect of PVA grade on the properties of Ni(OH)$_2$-PVA films

The study used four grades of polyvinyl alcohol available for retail purchase. The grades are indicated in Table 1.

Table 1

PVA grades used in the study

PVA grade	17–99	24–99	30–88	30–99
Sample name	V17–H99	V24–H99	V30–H88	V30–H99
Electrolyte composition	4 % PVA, 0.1M Ni(NO$_3$)$_2$			

The same table shows the films and compositions of the deposition solutions. The PVA content was selected on the basis of the work [31], which showed the optimum concentration of PVA at 4 %.

Composite coatings were applied on pre-cleaned glass with an electrically conductive transparent coating. For this, a substrate with a conductive layer of SnO_2 doped with fluorine – FTO glass ($R<10$ Ohm/sq., Zhuhai Kaivo Optoelectronic Technology Co. Ltd., China) was used. The substrate was degreased by wiping with a paste of Na_2CO_3 soda and distilled water. Next, the substrate was washed with running and distilled water, and also treated in ultrasonic radiation in a container with 96 % ethanol for 10 minutes. The radiator power of the ultrasonic bath was 60 W, the radiation frequency was 41.5 kHz. Then, it was dried and, immediately before coating, it was wiped again with a lint-free cloth with 96 % C_2H_5OH. In this case, the dimensions of the working area of the FTO glass were 4 cm^2.

After cleaning the substrate by the cathodic template method, a $Ni(OH)_2$-PVA composite electrochromic coating was applied [32]. The deposition conditions were as follows: cathode current density – 0.1 mA/cm^2, deposition time – 10 minutes [33]. The resulting films were washed in distilled water for 10 minutes and dried at room temperature for one hour. After obtaining, the films were evaluated by a complex electrochemical method with the simultaneous determination of optical characteristics.

Electrochemical and optical measurements.

The electrochemical characteristics were evaluated by the method of cyclic voltammetry (CVA). The measurements were carried out using a three-electrode scheme. Cycling was performed in the [+201; +701 mV] mode relative to the normal hydrogen electrode (NHE) at a sweep rate of 1 mV/s. The reference electrode was a silver chloride electrode in a saturated KCl solution; the auxiliary electrode material was nickel foil. A saturated solution of 0.1 M KOH served as the electrolyte. The cell was made of transparent plastic – polymethyl methacrylate. During cycling, changes in the optical characteristics of the films were also recorded in parallel with the electrochemical characteristics. For the experiments, we used the installation shown in Fig. 1.
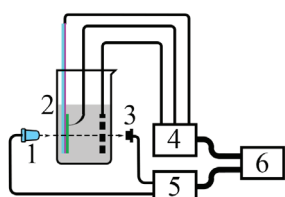

Fig. 1. Simplified diagram of the setup for studying the electrochemical and optical characteristics of electrochromic films: 1 — light source (5,500 K); 2 — cell with free electrolyte and tested film electrochromic electrode; 3 — photoresistor; 4 — electronic potentiostat (Elins P-8); 5 — ADC (E-154) and power supply unit of the light source; 6 — computer;
■ — glass; ■ — electrically conductive coating;
■ — composite electrochromic coating $Ni(OH)_2$-PVA

The setup used an ADC E-154 (Russia) and an Elins R-8 electronic potentiostat (Russia) together with control and registration programs supplied by manufacturers.

The optical system for recording the darkening-brightening curves worked as follows. The beam from the light source (1) passed through the transparent body of the cell (2) and the measured electrode as well as between the vertical parts of the П-shaped electrode (shown by the dotted line in Fig. 1). Further, after passing through the second wall of the cell body, the light beam hit the photoresistor.

Depending on the transparency of the working electrode, the light incident on the photoresistor changed its intensity, which changed the resistance of the photoresistor. Changes in the voltage drop value on the photoresistor were registered with an ADC and recorded in digital form by the program.

5. Comparison of electrochemical and optical characteristics of film electrodes obtained with different PVA grades

Film electrodes were prepared from solutions with the same content of PVA and nickel nitrate. It should be noted that powders of different grades of PVA varied significantly in shape and particle size. There were also significant differences in the dissolution rate of different PVA grades.

As a result of deposition, four types of film electrodes were obtained from the obtained solutions. Each of the electrodes was subjected to cycling in a potentiodynamic mode with a parallel recording of the change in transparency (T, %). The plotted graphs are shown in Fig. 2–5.

The comparison of the graphs showed that electrochromic film composite electrodes had different characteristics. Since the electrochemical deposition of films differed by the grade of PVA used in the electrolyte, it was obvious that the type of polymer determined the difference in the obtained characteristics.
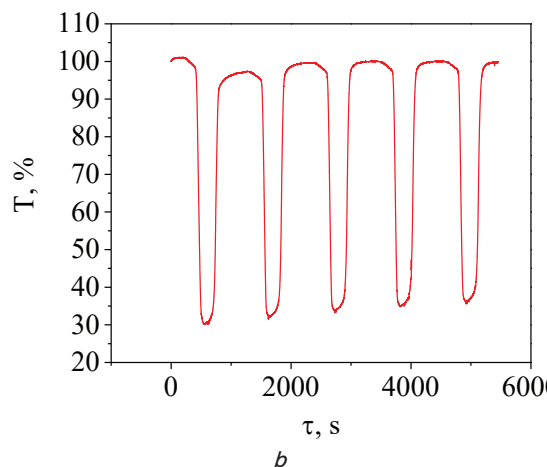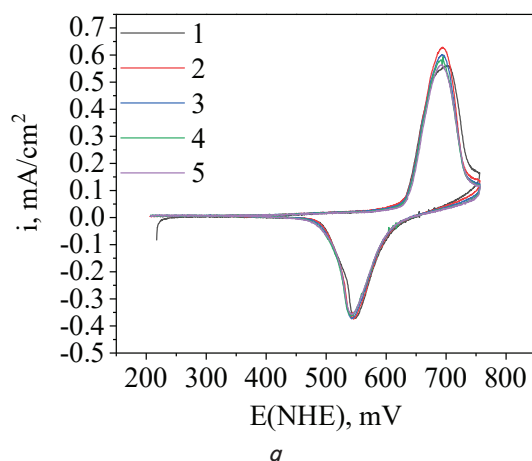

a

b

Fig. 2. Results for the V17–H99 film electrode: *a* — CVA; *b* — coloration-bleaching curve
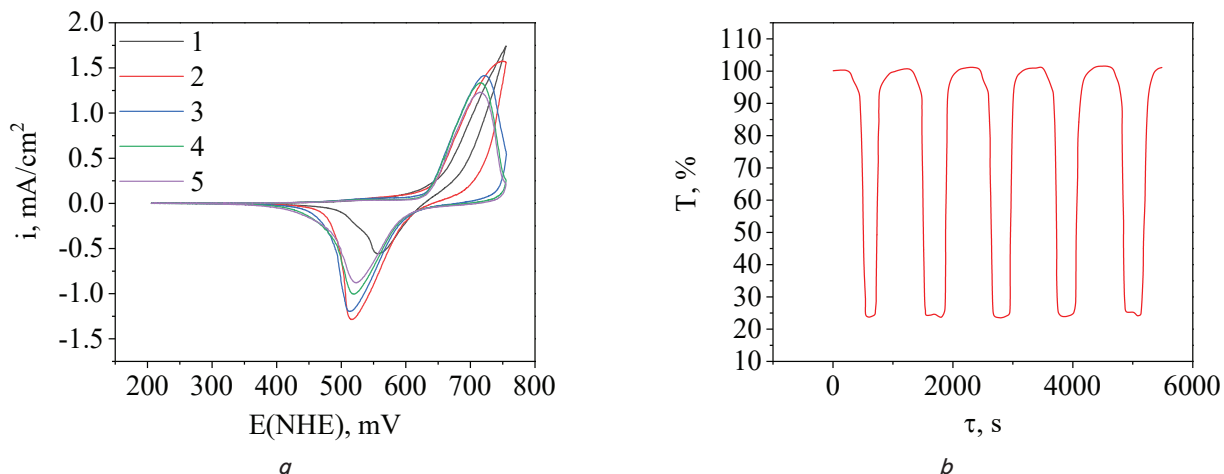
Fig. 3. Results for the V24–H99 film electrode: *a* – CVA; *b* – coloration-bleaching curve
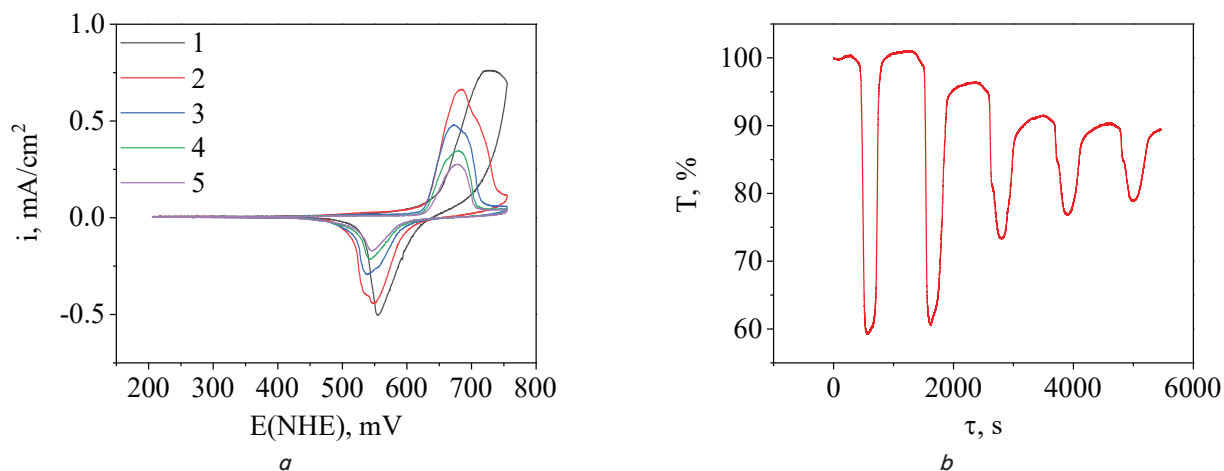

Fig. 4. Results for the V30–H99 film electrode: *a* – CVA; *b* – coloration-bleaching curve
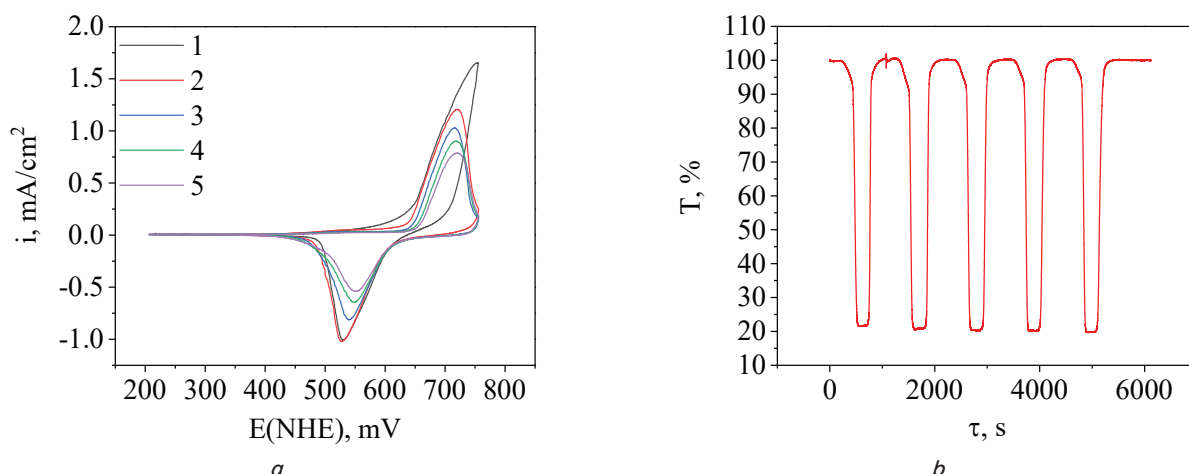

Fig. 5. Results for the V30–H88 film electrode: *a* – CVA; *b* – coloration-bleaching curve

The comparison of the cyclic voltammogram (CVA) curves was carried out according to several parameters: the position and height of the peaks, the shape of the curve, the difference between the previous and the next cycle, the presence or absence of an anodic peak in the first cycle.

An analysis of the shapes of the curves showed that three main processes took place during the electrochemical cycling of films [36–38]. The first was the oxidation of uncolored $Ni(OH)_2$ into dark brown NiOOH, direct reaction (1):

$$\underset{\text{transparent}}{Ni(OH)_2} \leftrightarrow \underset{\text{dark brown}}{NiOOH} + H^+ + e^-. \qquad (1).$$
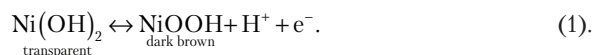
This process was characterized by an anodic peak. The second was the reduction of NiOOH to $Ni(OH)_2$ with a loss of color, the reverse reaction (1). The third was the evolution

of oxygen at the electrode, which was most pronounced on the CVA of sample V17−H99, reaction (2).

$$2OH \rightarrow \tfrac{1}{2}O_2 + H_2O + 2e^-. \tag{2}$$

This process was seen by a slight rise in the current in the curve to the left of the anodic peak.

It should be noted that the highest peak was in sample V24−H99. In this case, the anodic peak was not observed in the first cycle, and the height of the peaks first increased, and then decreased from the third cycle. In turn, sample V17−H99 had the most stable characteristics – the CVA curve repeated the shape and heights of the peaks from cycle to cycle. Nevertheless, the peak heights were the lowest in comparison with others and did not exceed 0.06 and 0.04 mA/cm^2, respectively, for the anodic and cathodic processes. In contrast to V24−H99, sample V17−H99 had a distinct anodic peak in the first cycle. The CVA curves of samples V30−H99 and V30−H88 also significantly differed both among themselves and in comparison with the previous samples. One of the important differences in the CVA curve of sample V30−H99 was the presence of an anodic peak in the first cycle, which was shifted towards positive potentials. The shape of the cyclic V30−H99 varied greatly from cycle to cycle, and the peak heights fell by more than two times by the end of the cycle.

Sample V30−H88 was characterized by an average height of the peaks, while there was no anodic peak in the first cycle. It is worth noting that the peaks of the cathodic and anodic processes fell during cycling, reaching about half the initial value for the anodic and cathodic processes, and were 0.065 and 0.05 mA/cm^2, respectively.

It is also worth noting that the differences in the films were manifested in the different potentials of the cathodic and anodic processes. Thus, for the V17−H99, V24−H99, V30−H99 and V30−H88 films, peaks of the anodic and cathodic potentials took place at +694, +546; +716, +522; +679, +545; +720, +551 mV (for the 5th cycle). The differences between the highest and lowest values of the anodic and cathodic peaks were 41 and 29 mV, respectively.

Based on the analysis made, it can be concluded that the use of a particular grade of PVA can significantly change the electrochemical properties of the samples.

In turn, a comparison of the coloration-bleaching curves also showed significant differences in the properties of the obtained films. Differences were observed both in the shape of the curves and in the difference between the darkened and lightened states, the so-called coloration depth (D, %). The latter was numerically equal to the difference ($T_{transp.} - T_{col.}$).

It is believed that the best shape for a coloration-bleaching curve is close to a line that changes direction at right angles. Within the framework of the foregoing, it can be seen that samples V17-H99 and V30-H88 had the closest shapes to rectangular, and at the same time, they had little change in their characteristics during cycling. In contrast to those considered, sample V30-H99 decreased the amplitude of the change in transparency (T) and did not completely bleach (on the fifth cycle after bleaching the value of $T=90$ %).

Sample V24-H99, in turn, had relatively stable characteristics but slowly changed its transparency at the beginning and end of coloration.

As shown by the analysis of the graphs in Fig. 2–5, b, the grade of PVA used significantly affected the optical characteristics.

6. Discussion of the characteristics of film electrodes obtained in the presence of different PVA grades

In order to carry out a comparative analysis of the data obtained, the main characteristics were calculated for each of the films (Fig. 6, 7).

Generalized electrochemical characteristics are shown in Fig. 6. Fig. 6, a illustrates the averaged process capacities calculated by the method of numerical integration from CVA for the corresponding samples separately for positive and negative currents. Analysis of the data presented in Fig. 6, a indicates the presence of an explicit dependence of the process capacities on the grade of PVA used. It should also be noted that in all cases the anodic capacities significantly exceed the cathodic ones, which indicates the irreversibility of the processes. The analysis of the capacities depending on the viscosity of PVA solutions (samples V17−H99, V24−H99, V30−H99) indicates the possible presence of an optimum since a sample in the composition of PVA with an average viscosity of V24−H99 has the best characteristics in the series.
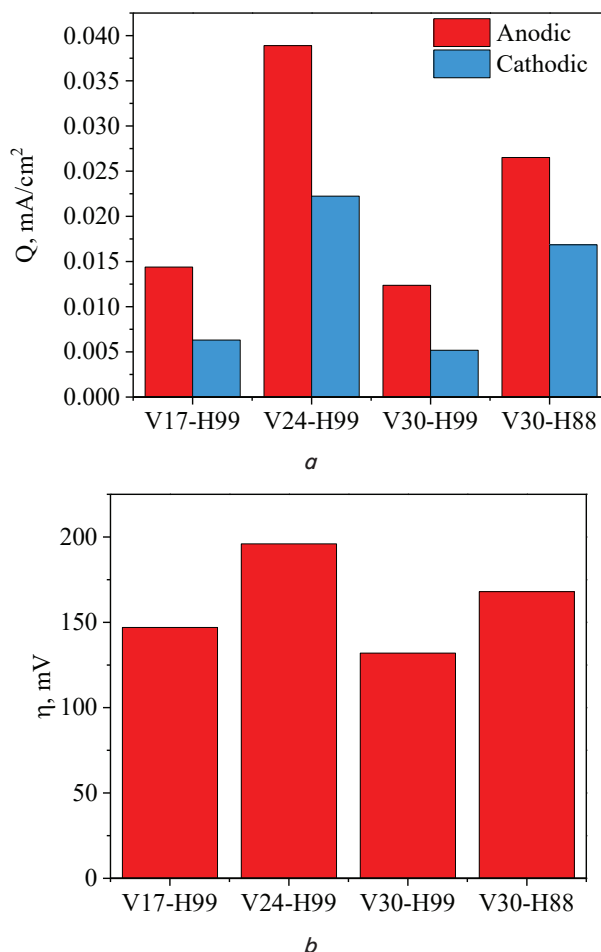

Fig. 6. Characteristics for film electrodes V17−H99, V24−H99, V30−H99, V30−H88: a — average specific capacities of anodic and cathodic processes for film electrodes; b — average total polarizations

No less interesting is the fact that the nature of the change in specific capacities and total polarization (h_S) for different samples is similar – Fig. 6, a, b. The latter has been calculated as the difference between the oxidation and

reduction peaks in CVA. On the one hand, an increase in capacity leads to a more complete operation of the electrochemically active component – $Ni(OH)_2$, on the other hand, an increase in polarization leads to a less reversible process. Therefore, such a change in these characteristics may seem strange. However, it should be noted that polarization can be caused by an ohmic voltage drop in the composite film since PVA is an insulator. On the one hand, the stronger the bond between the electrically conductive substrate-PVA-$Ni(OH)_2$ particles, determined by the PVA grade, the better the film will work, and the specific capacities of the processes will be higher. On the other hand, due to an increase in the interaction between the indicated phases, the ionic conductivity of the composite may decrease, which will lead to an increase in h_S. This can be indirectly confirmed by a detailed analysis of the characteristics of sample V30–H99 (Fig. 4). A sharp decrease in the currents on the CVA and a decrease in the amplitude on the coloration-bleaching curve indicate the loss of contact between the electrochromic $Ni(OH)_2$ particles in the composite and the conductive substrate. Moreover, this sample has the lowest total polarization among all, which indicates the weak forces of interaction of this PVA with the rest of the solid phases on the electrode.

The most important characteristic of electrochromic films is the coloration depth, which is shown in Fig. 7. The coloration depth is shown for the first cycle since the last cycles for sample V30–H99 are not representative. It should be noted that the nature of the D values is similar to the values shown in Fig. 6, which speaks in favor of the conclusions made earlier. It should be noted that both the PVA viscosity and the degree of hydrolysis affect the final characteristics of the formed electrodes. However, the viscosity of the solutions appears to be less significant among the two characteristics of PVA.

With a decrease in viscosity by 20 % (samples V30–H99, V24–H99), the difference between the D value is less than when the degree of hydrolysis is changed by 12.5 % (samples V30–H99, V30–H88).

In conclusion, we can say that the best characteristics have been shown by two PVA grades 24–99 and 30–88 with the D values of 80 % and 77 %, respectively. Based on the assumptions made, the next step in the study should be to test PVA with medium viscosities and with a degree of hydrolysis

less than 99 %. Another interesting direction is the use of mixtures of PVA grades to further increase the specific characteristics of electrochromic $Ni(OH)_2$-PVA films.

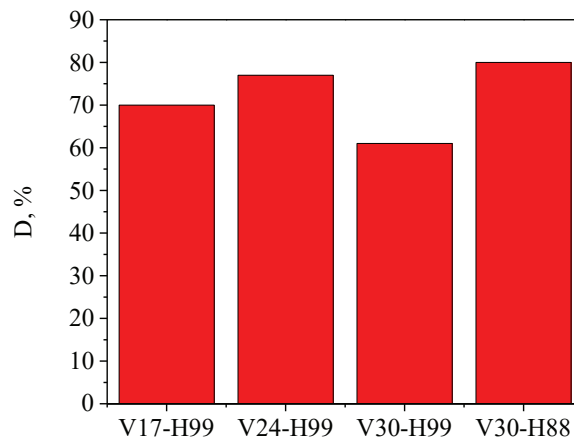Fig. 7. Coloration depths (D, %) on the first cycle V17−H99, V24−H99, V30−H99, V30−H88

7. Conclusions

1. Specific characteristics of $Ni(OH)_2$-PVA films deposited by the cathodic template method in the presence of different PVA grades on conductive glass substrates coated with SnO_2:F have been determined. For the corresponding PVA grades, the coloration depths of composite electrochromic $Ni(OH)_2$-PVA films are: for 17−99 grade the D value is 70 %, 24−99 grade the D value is 77 %, 30−99 rade the D value is 61 %, 30−88 grade the D value is 80 %.

2. The grade of PVA used in the electrolyte affects the electrochemical and optical characteristics. Moreover, the degree of hydrolysis is more important for the performance characteristics of electrochromic films than the PVA viscosity of a certain grade. With a decrease in viscosity by 20 % (V30−H99, V24−H99), the difference between the coloration depths of the samples is 16 %. This is less than the difference between the coloration depths (19 %) for the samples V30−H99, V30−H88, in which the degree of hydrolysis increases by 12.5 %.

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